

XII International Workshop on Sol-Gel Science and Technology



ABSTRACTS

SOLGEL
2003

International Conference • Sydney • Australia

XIIth INTERNATIONAL WORKSHOP ON SOL-GEL SCIENCE AND TECHNOLOGY



International Conference ◊ Sydney ◊ Australia

Table of Content

Foreword	3
Local Committee	4
International Advisory Board	4
Keynote Lecturers	4
Invited Speakers	5
Represented Companies and Speakers	6
Sponsors	6
Scientific Program	
Monday 25th August	8
Tuesday 26th August	9
Wednesday 27th August	11
Thursday 28th August	12
Friday 29th August	14
First Poster Session	16
Second Poster Session	24
Third Poster Session	33
Orals Sessions	
Keynote Lecturers	44
Invited Speakers	47
Monday Oral Session	61
Tuesday Oral Session	69
Wednesday Oral Session	88
Thursday Oral Session	97
Friday Oral Session	114
Posters Sessions	
Monday Poster Session	130
Tuesday Poster Session	204
Thursday Poster Session	283
Authors Index	353

Foreword

Since the inception of the highly successful International Sol-Gel Workshop series in Padova during 1981, sol-gel science and technology has evolved from its origins within traditional materials science to become an extraordinarily multidisciplinary area of research, spanning chemistry, physics, biology, materials science and nanotechnology. The 12th International workshop aims to celebrate and enhance this multidisciplinary character, with an exciting and diverse technical program. Keynote and invited speakers have been chosen to provide an overview of the directions in which sol-gel science and technology is heading. The rich oral and poster programs, which feature over 70 talks and 250 posters by delegates from 39 countries, will further highlight the basic research, technical/commercial developments and outstanding issues that make sol-gel science and technology such an exciting and rewarding field. To ensure that the poster sessions remain a key feature of the workshop, and to maximise their contribution as a forum for promoting discussions, three poster sessions will be run during an extended lunch on Monday, Tuesday and Thursday.

An important feature of the workshop will be the inaugural meeting of the new International Sol-Gel Society. The interim board for the new society has worked hard to ensure that it will become a reality during the Sydney Workshop, and we look forward to the unifying role that the ISGS will play within our community.

Special thanks are due to the Local Organising Committee, Conference Secretariat, and International Advisory Board, whose contributions, advice, and good humour have provided the rich plethora of ideas that have become embodied in the final Workshop program. We welcome you to Sydney, and hope that you enjoy an interesting and fruitful meeting.

Dr J. Bartlett,
Chair

Dr C. Barbé,
Co-Chair

Dr K. Finnie,
Co-Chair

Local Committee

Doctor Graham Atkins
Redfern Photonics, Australia

Doctor Christophe Barbé
Australian Nuclear Science and Technology, Australia

Doctor John Bartlett
Australian Nuclear Science and Technology, Australia

Mr John Blackley
Australian Nuclear Science and Technology, Australia

Doctor Gérard Calleja
Australian Nuclear Science and Technology, Australia

Doctor Kim Finnie
Australian Nuclear Science and Technology, Australia

International Advisory Board

Professor M. Aegerter (Germany)

Professor R. Almeida (Portugal)

Professor D. Avnir (Israel)

Doctor F. Babonneau (France)

Doctor J. Bartlett (Australia)

Professor J. Brinker (USA)

Professor A. Campero (Mexico)

Professor B. Dunn (USA)

Professor L. Esquivias (Spain)

Professor M. Guglielmi (Italy)

Professor B. MacCraith (Ireland)

Professor D. Mackenzie (USA)

Professor S. Sakka (Japan)

Keynote Lecturers

Professor Jeff Brinker
Sandia National Laboratories and The University of New Mexico, Albuquerque,
USA

Professor Bruce Dunn
University of California, Los Angeles, California, USA

Doctor Florence Babonneau
Université Pierre et Marie Curie, Paris, France

Invited Speakers

- Doctor Vadim Kessler
Swedish University of Agricultural Science, Sweden
- Professor Jarl Rosenholm
Department of Physical Chemistry, Åbo Akademi University, Finland
- Professor Ulrich Schubert
University of Technology, Austria
- Professor Plinio Innocenzi
Università di Sassari, Italy
- Doctor Michel Wong Chi Man
Ecole Nationale Supérieure de Chimie de Montpellier, France
- Professor Max Lu
FTSE, University of Queensland, Australia
- Doctor Philippe Belleville
Centre de l'Energie Atomique, France
- Professor Bakul Dave
University of Southern Illinois, USA
- Professor Byeong-Soo Bae
Korea Advanced Institute of Science and Technology, Korea
- Professor David Avnir
Hebrew University, Israel
- Professor Akiyoshi Osaka
University of Okayama, Japan
- Professor Brian MacCraith
National Centre for Sensor Research, Dublin City University, Ireland
- Professor Masayuki Nogami
Nagoya Institute of Technology, Japan

Represented Companies and Speakers

Sustainable Technologies International, Australia

Igor Skyrabin

Terahertz Photonics, UK

Zahoor Ahmad

Merck KgaA, Germany

Monika Kursawe

YTC America Inc., USA

Larry Meixner

National Institute for Materials Science, Japan

Kenjiro Fujimoto

Sponsors

The Australian Nuclear and Science Technology Organisation



Sustainable Technologies International



Scientific Program

Plenary Session

Fundamentals and Future Directions in a Multidisciplinary Community

Chairs: J.R. Bartlett and C.J. Barbé

- K-1** Sol-Gel Processing of Complex Functional Materials by **Jeff Brinker**

Plenary Session

Fundamentals and Future Directions in a Multidisciplinary Community

Chairs: J.R. Bartlett and C.J. Barbé

- K-2** The Integration of Sol-Gel Science in Nanobiotechnology by **Bruce Dunn**

- K-3** Advances in Characterisation Methods – Multiple length scales across multiple disciplines by **Florence Babonneau**

Sol-Gel Chemistry

Design and Reactivity of Functional Precursors

Chairs: C.J. Brinker and J.N. Hay

- I-1** Geometrical Molecular Structure Design Concept in Approach to Homo- and Heterometallic Precursors of Advanced Materials in Sol-Gel Technology
Vadim Kessler

- O-1** Electronic State and Photosensitivity of Metal Alkoxides Chemically Modified with β -Diketones
Y. Kowada, Hyogo Univ., Japan

- O-2** Mixed Oxide Materials Prepared from a Single Source Precursor: A Time Resolved SAXS Study of the Gelation and the Calcination Process
V. Torma, Institut für Materials chemistry, Technische Universität, Austria

- O-3** Cancelled

Routes to Colloids, Nanoparticles and Nanostructured Materials

Sol-Gel Chemistry in Confined Media and Control of Nanostructural Evolution

Chairs: F.O. Ribot and V. Kessler

- I-2** Monolithic silica and carbon exhibiting three-modal, hierarchical porosity
Jarl Rosenholm

- O-4** Wide-band acoustic characterization of a sol-gel matrix
M. Gindre, Univ. Paris VI, France

- O-5** All alkoxide sol-gel route to CoO-TiO₂ nano-powders
G. Westin, Department of Materials Chemistry, Ångström Laboratory, Sweden

- O-6** Synthesis of Organic-Inorganic Hybrid Particles by Sol-Gel Chemistry
J.N. Hay, Univ. Surrey and QinetiQ, UK
- O-7** Template Mediated Hybrid from Dendrimer
N.R. Choudhury, Ian Wark Research Institute, Univ. SA, Australia
- O-8** Formation of SiO₂ Nanoparticles in a NP-5 Water-in-Oil Microemulsion
K. S. Finnie, ANSTO, Australia

Tuesday 26th August

Organic-Inorganic Nanohybrids
Inorganic Nanoclusters in Polymeric Networks
Chairs: P. Innocenzi and G. Calleja

- I-3** Organofunctional Metal Oxide Clusters as Building Blocks for Inorganic-Organic Hybrid Materials
Ulrich Schubert
- O-9** Hybrid Organic-Inorganic Materials Based on Nanobuilding Blocks Assembled through Electrostatic Interactions
F.O. Ribot, Univ. Paris VI, France
- O-10** Formation, Self-Ordering and Structure of Organic-Inorganic Nanohybrid Networks
L. Matejka, Acad. Science, Czech Republic
- O-11** Control of the Morphology of Organic-Inorganic Hybrid Materials Elaborated by Reactive Processing without Solvent
V. Bounor-Legaré, Univ. Lyon 1, France
- O-12** Synthesis of Polymetallorganosiloxane Xerogels Using a Sol-Gel Method
Y.L. Zub, Nat. Acad. Science, Ukraine
- O-13** Sol-Gel Technology in the Control of Poss™ Functionality: A New Generation of Materials
J. Matisons, Flinders Univ., Australia
- O-14** Effects of pH on Gelation Time, Degree of Condensation and Porosity in Bridged Polysilsesquioxanes
D.A. Loy, Los Alamos, USA

Organic-Inorganic Nanohybrids
Interpenetrating Networks
Chairs: D.A. Loy and U. Schubert

- I-4** Hybrid Materials with Polymerisable Organic Functional Groups: a Structure-Property Outlook
Plinio Innocenzi

- O-15** Real time Study of UV Induced Photopolymerization in Hybrid Sol-Gel Glasses
C. Croutxé-Barghorn, Dep. Photochemistry, France
- O-16** cancelled
- O-17** Bridged Organic-Inorganic Hybrid Xerogels and Si/C/N-Ceramic Membranes:
New Non-oxide Materials Derived from Polysilsesquicarbodiimide Gels
E. Kroke, Fachbereich Materialwissenschaft, Fachgebiet Disperse F, Germany
- O-18** Preparation of Organic-Inorganic Hybrid Gel Films Based on Polyvinyl-polysilsesquioxane
Y. Abe, Tokyo Univ. Science, Japan
- O-19** C₆₀ Based Hybrid Nanocomposites Obtained in the Presence of Ultrasounds
M. Zaharescu, Institute of Physical Chemistry, "I.G. Murgulescu", Romania
- O-20** Layer-by-Layer Paving of Liposomal Organic-Inorganic Nanohybrid "Cerasome" on Substrates
K. Katagiri, Nara Institute of Science and Technology, Japan

**Mesostructured and Supramolecular Materials
Synthesis and Applications of Silicate Systems
with Periodic Structure and Engineered Porosity**

Chairs: M. Lu and R. Caruso

- I-5** New Approach for the Organisation and the shaping of Organo-Bridged Silicas
Michel Wong Chi Man
- O-21** Synthesis of Mesoporous Silica Nanoparticles using a Double Surfactant System
H. Imai, Keio Univ., Japan
- O-22** Templated Synthesis of Tailored Clays (based on sol-gel techniques) to Yield Increased Pore Volumes for Sorption and Exchange
K. M. Powell, Univ. Surrey, UK
- O-23** Core-shell Approach to Formation of Ordered Nanostructured Materials with MPEG-b-PDLLA
J.H. Chang, Korea Inst. Of Ceramic Engineering and Technology, Korea
- O-24** Cobalt Incorporation into Co-condensed Mesoporous Silicas
N.J. Coville, South Africa

**Mesostructured and Supramolecular Materials
Synthesis and Applications of Non-Silicate Systems
with Periodic Structure and Engineered Porosity**

Chairs: F. Babonneau and M. Wong chi Man

- I-6** Templated Synthesis of Non-Silicate Metal Oxides
G.Q. Max Lu

- O-25** Spongelike Macroporous TiO₂ Monoliths Prepared from Starch Gel Template
M. Iwasaki, Kinki Univ., Japan
- O-26** Surfactant Templated Mesoporous Titania Anion Exchanger
V. Luca, ANSTO, Sydney, Australia
- O-27** Template Synthesis of Metal Oxides
R.A. Caruso, Univ. Melbourne, Australia

Wednesday 27th August

Coatings and Membranes Structural Evolution and Characterisation

Chairs: P.A. Sermon and J.E. ten Elshof

- I-7** New Sol-Gel Routes for High-Permittivity Thin Film Preparation
P. Belleville
- O-28** Relationship Between Surface Skin and Defect Formation during Sol-Gel Spin-Coating
D.P. Birnie, Univ. Arizona, USA
- O-29** Preparation of Titania Nanosheets-Precipitated Coatings on Substrates by Treating SiO₂-TiO₂ Gel Films with hot water under vibrations
A. Matsuda, Toyohashi Univ., Japan
- O-30** A Microstructural Zone Model for the Morphology of Sol-Gel Coatings
M.A. Aegerter, Schott Glass Germany; INM, Germany
- O-31** Aluminophosphate Thin FilmsFilms
P.E. de Jongh, Philips, The Netherlands
- O-32** Radiative Striations of Spin-Coating Films: Surface Roughness Measurement and In-Situ Observation
H. Kozuka, Kansai University, Japan

Coatings and Membranes Properties and Novel Applications

Chairs: M.A. Aegerter and H. Kozuka

- I-8** Cancelled
- O-33** Sol-Gel Derived Inorganic Scintillators
J-M. Nedelec, Univ. Blaise Pascal & ENSCCF, France
- O-34** Nanostructured Ion-selective MCM-48 Membranes
J.E. ten Elshof, Univ. Twente, The Netherlands
- O-35** Sol-Gel Coating of Thin Display Glasses - Problems and Remedy
G. Guzman, Corning S.A., France

O-36 Sol-Gel Layers for Surface Modification of Non-Woven Textiles

A. Lobnik, Univ. Maribor, Slovenia

Thursday 28th August

Sol-Gel Optics Processing and Applications **Chairs:** R. Almeida and B-S. Bae

I-9 Sol-Gel Encapsulation of Molecules to Generate Functional Optical Materials
B.C. Dave

O-37 High Refractive-Index Microspheres of Optical Cavity Structure
Y. Arai, Tokyo Inst. Technol., Japan

O-38 Synthesis and Photoluminescence Features of Urea and Urethane Cross-Linked Siloxane Poly(Ethyleneoxide) Hybrids Derived from Carboxylic Acid Solvolysis
L. Fu, Univ. Aveiro, Portugal

O-39 Incorporation of Highly Luminescent Quantum Dots in Hybrid Organic-Inorganic Matrix
A. Martucci, Univ. Padova, Italy

O-40 Spectral Hole-Burning in Femtosecond Laser-Irradiated Eu³⁺-Doped Aluminosilicate Glasses
G.J. Park, Nagoya Inst. Technol., Japan

Sol-Gel Technology for Optoelectronics and Photonics Processing and Applications **Chairs:** B. Dave and A. Martucci

I-10 Self-Photopatterning of Photosensitive Sol-Gel Hybrid Materials for Fabrication of Micro-Optic Devices
Byeong-Soo Bae

O-41 Photoluminescence Stabilization in Erbium-Doped Silicate Sol-Gel Planar waveguides
R.M. Almeida, Instituto Superior Técnico, Portugal

O-42 Synthesis of Thermoplastic Organic-Inorganic Hybrid Polymers for Optical Fibre Fabrication
X. Luo, ANU, Australia

O-43 Narrow Band Polarized Light Emission from Organic Micro-Cavity Fabricated by Sol-Gel Technique
L. Xu, Fundan Univ., China

- O-44** Photo-Electrochemistry of Ormosil's Sandwiched Bacteriorhodopsin
P.C. Pandey, Banaras Hindu Univ., India
- O-45** Electrochemical and Electrochromic Properties of Ni Oxide/Hydroxide Film Deposited by Sol-Gel Technique
Y-E Sung, K-JIST, Korea
- Functional and Biologically Active Species in Sol-Gel Matrices**
Encapsulation and Function
- Chairs:** B. Dunn and A. Osaka
- I-11** Recent Advances in the Application of Sol-Gel Materials for Biochemical and Biomedical Applications
David Avnir
- O-46** Screening of Inhibitors Using Proteins Entrapped in Sol-Gel Derived Materials
J.D. Brennan, McMaster Univ., Canada
- O-47** Gelation of Hybrid Inorganic-Organic Silicates Monitored by NMR and Fluorescence Spectroscopy
G. M. Moran, UNSW, Australia
- O-48** Monitoring of Viability of Cells Immobilized by Sol-Gel Process
G. Kuncova, Institute of Chemical Process Fundamentals AS CR, Czech Republic
- O-49** **Sol-Gel Homogeneity: A Closer Look with Near-Infrared Imaging**
C.D. Tran, Marquette Univ. USA
- O-50** Sugar-Modified Silanes: Precursors for Silica Monoliths
M. A. Brook, McMaster Univ., Canada
- The Sol-Gel/Biology Interface**
Biomaterials and Biological-Inorganic Hybrids
- Chairs:** D. Avnir and K.S. Finnie
- I-12** Synthesis of Bioactive and Porous Organic-Inorganic Hybrids and their Biomedical Applications
Akiyoshi Osaka
- O-51** Sol-Gel films as substrates for tissue-cell culture growth
C. Zolkov, Israel Institute of Technology, Israel
- O-52** Sol-Gel Derived Hydroxyapatite Coatings on Anodized Titanium Substrates
R. Roest, UTS, Australia
- O-53** Antimicrobial Sol-Gel Coatings
B. Mahltig, GMBU, Germany

Functional Materials
Sensors, Molecular Recognition and Magnetism
Chairs: M. Mennig and M. Nogami

- I-13** Enhanced Optical Sensor Performance via the Sol-Gel Process
Brian MacCraith
- O-54** Sol-Gel Derived Imprinted Nanocomposites for Ba²⁺_(aq) Analysis
P.A. Sermon, Nano-Engineered Solids and Surface Reactivity Laboratory, UK
- O-55** Charge-Transfer Optical Sol-Gel Detectors for CW Contamination on Surfaces
C-T. Lin, Northern Illinois Univ., USA
- O-56** Optical Properties and Sensitivity of Xerogel Detection Layers for Fiber-Optic Hydrocarbon Sensors
V. Matejec, Institute of Radio Engineering, AS CR, 182 51 Prague, Czech Republic
- O-57** New Hybrid Organic-Inorganic Membranes Based on Molecular Recognition of Crown Compounds and Self-Assembled Urea Moieties Mediated by Sol-Gel Route
S.A. Cerneaux, Institut Européen des Membranes de Montpellier, France
- O-58** Novel Hybrid Sol-Gel Films for Multi-Analyte Sensing
C. McDonagh, Dublin City Univ., Ireland
- O-59** Influence of Preparation Conditions on Structure and Magnetic Properties of Sol-Gel Derived Iron-Doped Siloxane-Polyethyleneoxide Nanocomposites
S. H. Pulcinelli, Chemistry Institute, Sao Paulo St Univ., Brazil

Functional Materials
Electrochemistry, Catalysis and Durability
Chairs: C. MacDonagh and S. H. Pulcinelli

- I-14** Fast Proton Conduction in the Sol-Gel-derived Glasses and their Application to the Fuel Cell Electrolytes
Masayuki Nogami
- O-60** Porous Garnet Coatings Tailoring the Emissivity of Thermostructural Materials
A. Licciulli, Lecce Univ., Italy
- O-61** Preparation of Proton Conductive Inorganic-Organic Hybrid Films Using Epoxycyclohexylethyltrimethoxysilane and Orthophosphoric Acid.
K. Tadanaga, Toyohashi Univ., Japan
- O-62** Synthesis and Characterization of Optical Sol-Gel Adhesive for Military Protective Polycarbonate Resin
M.S. Keränen, VTT Electronics, Finland

- O-63** Silica with bimodal pores for solid catalysts prepared from water glass
R. Takahashi, Satoshi Sato, Toshiaki Sodesawa, Chiba University, Japan

From Research to Commercialisation
Industrial Applications of Sol-Gel Science and Technology
Chairs: B. MacCraith and G. Westin

- C-1** Sol-Gel route to cost-effective renewable energy
I. Skyrabin, *Sustainable Technologies International*, Australia
- C-2** Silica on Silicon Planar Lightwave Circuits Using a Novel Single Step Sol-Gel Process
A. Licciulli, *Terahertz Photonics*, UK
- C-3** Nanoparticles by Wet Chemical Processing in Commercial Applications
M. Kursawe, *Merck KgaA*, Germany
- C-4** Low-Pressure Drying of Large Porous Silica Monoliths
R. Ganguli, *YTC America Inc.*, USA
- C-5** Exploration of new and functional materials by combinatorial wet process
K. Fujimoto, *National Institute for Materials Science*, Japan

First Poster Session

"Fundamentals of Sol-Gel Chemistry and Nanohybrid Materials"

602 - Preparation of C₆₀-Siloxane Hybrids

Takahiro Gunji, Koji Arimitsu, Yoshimoto Abe, Tokyo University of Science, Japan
Robert West, University of Wisconsin-Madison, United States

603 - Hydrophobic Antireflective Silica Films via Sol-Gel Process

Yuhan Sun, Dong Wu, Yao Xu, Institute of Coal Chemistry, Chinese Academy of Science, China

604 - Thin Films and Nanoparticles of Spinels from new Classes of Single Source Molecular Precursors, MAI₂ (acac)₄(O*i*Pr)₄ and MAI₂ (acac)₃(O*i*Pr)₄(OAc), M= Mg, Mn, Co, Ni, Zn

Vadim G Kessler, Swedish University of Agricultural Sciences, Sweden
Gulaim A Seisenbaeva, SLU, Sweden
Stephane Parola, Universite Claude Bernard Lyon 1, France

605 - A novel sonochemical route to BaSO₄ nanocrystals with controlled morphologies

Sun Yuhan, Wu Dong, Li Junping, Chinese Academy of Science, China

606 - Importance of the Siloxane Network Formation on the Structural Stability of Cerasome, a Vesicular-Type Organic-Inorganic Nanohybrid

Mineo Hashizume, Hiroaki Inoue, Atsushi Ikeda, Jun-ichi Kikuchi, Nara Institute of Science and Technology, Japan

607 - Sub-micron silica/polymer composite particles prepared by a one step Sol-Gel process

Hanan Sertchook, David Avnir, The Hebrew University of Jerusalem, Israel

608 - Hybrid organic/inorganic Sol-Gel materials for proton conducting membranes

Mario Aparicio, Alicia Duran, Instituto de Ceramica y Vidrio (C.S.I.C.), Spain

609 - Tin Oxide Nanoparticles : Control of Size, Shape and Dispersion

Corinne Chaneac, Francois O Ribot, Sandra Da Costa, Elisabeth Tronc, Jean-Pierre Jolivet, Chimie de la Matiere Condensee (UMR 7574 / UPMC), France

610 - Preparation of Au-TiO₂ hybrid nanoparticles in silicate film made by Sol-Gel method

Mitsuhiko Kawazu, Masatoshi Nara, Toshifumi Tsujino, Nippon Sheet Glass Co.Ltd, Japan

611 - Sol-Gel Approach to Sr₂CeO₄ Phosphor from Single Alkoxide Precursors

Hong R Kim, Hankuk University of Foreign Studies, Korea

Hoseop Yun, Ajou University, Korea

612 - Phase composition and pore structure of yttria-stabilized zirconia nanopowders by Sol-Gel method

Ki-Chang Song, Chul-Won Cheong, Konyang University, Korea

Hae-Hyoung Lee, Dankook University, Korea

Sang-Chun Oh, Jin-Keun Dong, Yong-Youp Cha, Wonkwang University, Korea

613 - Preparation and Characterization of Peroxo Titanic Acid Solution using TiCl₃

Insoo Kim, KS Sohn, CK Lee, JH Sung, Dong-A University, Korea

KH Lee, Korea Institute of Machinery & Materials, Korea

614 - Adsorption of Pb (II), Ni(II), Cu(II), Co(II) and Zn(II) on organic-inorganic Sol-Gel derived amorphous silica-titania and hexagonal zirconia

Robson Fernandes de Farias, Universidade Federal de Roraima, Brazil

615 - Studies on new Ormosils derived from reactive alkoxysilane precursors as a function of hydrophobicity/hydrophilicity

Prem C Pandey, Banaras Hindu University, India

616 - Solvothermal synthesis of nanosize Zn₂SiO₄:Mn²⁺ phosphor from the precursor sol and its optical properties

Takuro Miki, Takumi Ogawa, Tetsuhiko Isobe, Keio University, Japan

617 - Synthesis and Reactivity of Titanium OXO-ALKOXO-Clusters

Stéphanie Le Calve, Bruno Alonso, Dominique Massiot, Centre de Recherche sur les Matériaux Haute Température, France

Laurence Rozes, François Ribot, Clement Sanchez, Chimie de la Matière Condensée, CNRS UMR 7574/UPMC; 4., France

Marie-Noelle Rager, ENSCP, CNRS UMR 7576, France

Michel Evain, Institut des Matériaux J. Rouxel, France

618 - Fabrication and Characteristics of Fluorinated Inorganic-Organic Hybrid Material Films

Dong Jun Kang, Jang-Ung Park, Sun Joo Kim, Byeong-Soo Bae, Korea Advanced Institute of Science and Technology, Korea

619 - Molecular structure and dissolved state of a heterobimetallic Ba-Ti alkoxide in a highly concentrated precursor solution

Hirokazu Shimooka, Shigemi Kohiki, Kyushu Institute of Technology, Japan

Makoto Kuwabara, The University of Tokyo, Japan

620 - Crystallisation of Titania Prepared via the Peroxo and Normal Sol-Gel Routes

Young Jun Hong, LG Chemical Ltd./ Research Park, Korea

Michael P Brungs, Rodney P Chaplin, University of New South Wales, Australia

Erden Sizgek, Australian Nuclear Science & Technology Organisation, Australia

621 - Super-hydrophilic Surface Modification of Mesoporous Silica by Sulfonation Route

Young Kwon Oh, Dong-Pyo Kim, Lan-Young Hong, Chungnam National University, Korea

622 - Preparation and Characterization of FeCo-Al₂O₃ and Al₂O₃ Aerogels

Anna Corrias, Maria F Casula, Andrea Falqui, Giorgio Paschina, Università di Cagliari, Italy

623 - Surface Modification of PTMS Particles with Organosilanes: TEOS-, VTMS-, and MTMS-Modified PTMS Particles

Hoe Jin Hah, Byung Jun Jeon, Sang Man Koo, Hanyang University, Korea

624 - Heat-Induced Precipitation and Light-Induced Dissolution of MetaNanoparticles in Hybrid Film

Shuichi Shibata, Keita Miyajima, Yusuke Kimura, Tetsuji Yano, Tokyo Institute of Technology, Japan

625 - Design and Characterization of a Metal-Organic Sol-Gel Precursor for the Formation of YBCO Thin Films

Lilian J Campbell, Andrea J Bubendorfer, Tim Kemmitt, Nick J Long, Industrial Research Limited, New Zealand

626 - Preparation of Hollow Ormosil Particles Containing Copper Nanoparticles

Jae In Um, Hoe Jin Hah, Jung Soo Kim, Sang Man Koo, Hanyang University, Korea

627 - Composite Silica Particles using a Mixture of Organosilane Monomers: Effect of Molar Ratio of Monomers

Dong Il Han, Hoe Jin Hah, Sang Man Koo, Hanyang University, Korea

628 - Synthesis of novel layered silica-organic nanocomposites by hydrolysis and polycondensation of alkoxytrichlorosilanes

Yasuhiro Fujimoto, Atsushi Shimojima, Kazuyuki Kuroda, Waseda University, Japan

629 - Room Temperature Synthesis and Characterisation of Hybrid Materials of Polymethylhydrosiloxane Modified by Hydroxide Organic Compounds

Faouzi Sediri, Noureddine Etteyeb, Néji Gharbi, Laboratoire de Chimie de la Matière Condensée, Université de Tunis-IPEIT, Tunisia

630 - Organically-Modified Silica Xerogels with Designer Elasticity and Hydrophobicity

Rita Badheka, Rebecca M A MacGibbon, Paul A Sermon, Nanoengineered Solids and Surface Reactivity Group, United Kingdom

631 - Controlled preparation of Pt/Al₂O₃ catalysts by Sol-Gel process

Leila Khelifi, Faculté des Sciences de Tunis, Tunisia

Abdelhamid Ghorbel, Université Tunis El Manar, Tunisia

632 - Synthesis of Nano Silica Particle for Polishing Prepared by Sol-Gel Method

Kazuaki Yoshida, Nippon Bunri University, Japan

Yasuhiko Arai, Hiroyo Segawa, Oita University, Japan

633 - Inorganic-Organic Hybrid Polymers by Polymerisation of Methacrylate

Substituted Oxotantalum Clusters with Methylmethacrylate: Thermomechanical and Morphological Properties

Angelika Basch, Namita Roy Choudhury, Ian Wark Research Institute, University of SA, Australia

Silvia Gross, University of Vienna, Austria

Ulrich Schubert, Vienna University of Technology, Austria

634 - Preparation of Tin Oxide-Based Metal Oxide Particles for Gas-Sensing

Application

Chan Yoon Jung, Hoe Jin Hah, Seung Hoon Han, Sang Man Koo, Hanyang University, Korea

635 - Sol-Gel synthesis of monodisperse SiO₂ nanoparticles through hydrolysis of tetramethoxysilane by organic amines

Nikolay N Khimich, Institute of Silicate Chemistry RAS, Russia

Anatoliy N Zhukov, Julia V Zviagilskaya, St. Petersburg State University, Russia

636 - Nanocomposites in the system of aromatic ester dendrimer - SiO₂. Synthesis and structure

Nikolay N Khimich, Institute of Silicate Chemistry RAS, Russia

Galina N Khimich, Institute of High Molecule Chemistry RAS, Russia

637 - Acetic acid as an effective reagent, solvent, and catalyst for the organic Sol-Gel processing

Nikolay N Khimich, Larisa A Koptelova, Irina A Drozdova, Institute of Silicate Chemistry RAS, Russia

638 - Preparation of self-organized nano-graded $\text{SiO}_2/\text{TiO}_2/\text{PMMA}$ thin film and its low-reflectivity

Kazuyuki Takami, Toshiya Watanabe, Kazuhito Hashimoto, RCAST The University of Tokyo, Japan

Akira Nakajima, Tokyo instituto of technology, Japan

639 - Preparation and properties of the transparent SiO_2/PMMA graded IPN thin film

Kazuyuki Takami, Toshiya Watanabe, Kazuhito Hashimoto, RCAST The University of Tokyo, Japan

Akira Nakajima, Tokyo instituto of technology, Japan

640 - Hybrid Sol-Gel Coatings Combined with Inorganic Inhibitors for Metal Corrosion Protection

Sang Il Seok, Advanced Materials Division, Korea Research Institute, Korea

Young Young Hwang, Korea Research Institute of Chemical Technology, Korea

Hae Hong Kim, Korea Research Institute, Korea

641 - Preparation and properties of aramid-silica hybrids with interphase bonding through 3-glycidoxypyropyl-trimethoxysilane

Hazrat Hussain, Martin-Luther University, Germany

Muhammad Ilyas Sarwar, Quaid-i-Azam University, Pakistan

Zahoor Ahmad, Kuwait University, Kuwait

642 - SAXS Study of Neodymium-Doped Poly(oxyethylene)/Siloxane Hybrids

Isabel C Correia Vilela, Maria C Gonçalves, Verónica De Zea Bermudez, Universidade de Trás-os-Montes, Portugal

Karim Dahmouche, Celso V Santilli, Instituto de Química, Universidade Estadual Paulista, Brazil

Nuno JO Silva, Luis D Carlos, Universidade de Aveiro, Portugal

Aldo F Craievich, Instituto de Física, Universidade de São Paulo, Brazil

643 - Improvement of the $\text{Mo}/\text{TiO}_2-\text{Al}_2\text{O}_3$ Catalyst by the Control of the Sol-Gel Synthesis

Andreia A Cecilio, Sandra H Pulcinelli, Celso V Santilli, IQ/UNESP, Brazil

Victor T Silva, IME, Brazil

644 - Structural Features of Phosphate Modified Zirconia Prepared by Sol-Gel Route

Carla A Kawaguti, Leila A Chiavacci, Sandra H Pulcinelli, Celso V Santilli, IQ/UNESP, Brazil

Valérie Briois, LURE, France

645 - Redispersable Titania Nanoparticles Obtained by Sol-Gel Route

Renata C Kaminski, Sandra H Pulcinelli, Celso V Santilli, IQ-UNESP, Brazil

647 - Synthesis, Structure and Properties of $\text{Na}_2\text{Zn}(\text{OEt})_4(\text{HOEt})_5$

Mikael Kritikos, Arrhenius Laboratory, Sweden

Åsa B Ekstrand, Uppsala University, Sweden

Michael Leideborg, Gunnar L Westin, Ångström Laboratory, Sweden

648 - Synthesis, Structure and Properties of $\text{ErNb}_2(\text{OPri})_{13}$

Mikael Kritikos, Arrhenius Laboratory, Sweden

Gunnar L Westin, Ångström Laboratory, Sweden

649 - Eduction of Sol-Gel Microspheres of Uranium Oxide from a Settling Vessel by Liquid Entrainment

Suryanarayana Saripalle, Radhakrishna Jayanti, Sapan K Mukerjee, Vijay N Vaidya, D

Sathiyamoorthy, Bhabha Atomic Research Center, India

650 - Study of the Pd-SiO₂ Obtained by Sol-Gel Process as Catalyst of the Limonene Oxidation

Edesia MB Sousa, Patricia AR Dutenhofner, Centro de Desenvolvimento da Tecnologia Nuclear - CDTN, Brazil

Helena V Gusevskaya, Universidade Federal de Minas Gerais, Brazil

651 - Sevidence of Heteroegenous Catalysis in Sol-Gel Process for PD/Al₂O₃ Catalysts Preparation

Shemseddine Fessi, Laboratoire de Chimie des Matériaux et Catalyse, Tunisia

652 - Insertion of substituted tetraphenylporphyrins in silica gels

Miguel A García-Sánchez, Antonio Campero, María de L Avilés C, Universidad Autónoma Metropolitana-Iztapalapa, Mexico

Martha P González-Arevalo, Mexico

654 - Organic-inorganic hybrid synthesis by reactive extrusion: fiction or reality

Alain Michel, CNRS, France

Laurent David, LMPB-University, France

Véronique Bounor-Legaré, Université Claude Bernard Lyon1, France

Sébastien Jiguet, France

655 - Gelation of Hybrid Inorganic-Organic Silicates Monitored by NMR and Fluorescence Spectroscopy

Eko S Kunarti, Graham E Ball, Grainne M Moran, UNSW, Sydney, Australia

656 - Low Temperature Sol-Gel Preparation of Hybrid Silica Nanotubes

Eko S Kunarti, Grainne M Moran, UNSW, Sydney, Australia

658 - Siloxane-Based Nano-Building Blocks by Reaction between Silanediol and Trifunctional Silicon Alkoxides

Plinio Innocenzi, Università di Sassari, Italy

Sandra Dirè, Petra Egger, Università di Trento, Italy

Giovanna Brusatin, Università di Padova, Italy

Maria L Di Vona, Silvia Licoccia, Universita' di Roma Tor Vergata, Italy

Maurizio Ferrari, CNR-IFN, Istituto di Fotonica e Nanotecnologie, via Som, Italy

Marcella Trombetta, Università Campus Bio-medico, Italy

659 - Sol-Gel Design of Some Hybrid Organic-Inorganic Carriers

Alina V Korobeinik, Yuriy L Zub, Institute of Surface Chemistry, NAS of Ukraine, Ukraine

Aleksej A Chuiko, NAS of Ukraine, Ukraine

B D Kabulov, AN of Uzbekistan, Uzbekistan

O G Ruzimuradov, K A Akhundzhanov, Institute of Chemistry and Physics of Polymers, Uzbekistan

S Sh Rashidova, AN of Uzbekistan, Uzbekistan

660 - Highly Porous Hybrid Silica/Latex Xerogels Dried at Ambient Pressure

Laura M Ilharco, Alexandra M Fidalgo, José M Martinho, José P Farinha, Maria E Rosa, Instituto Superior Técnico, Portugal

661 - Microstructure and Photocatalytic Property of $\text{SiO}_2\text{-TiO}_2$ under Various Process Conditions

Yong Kuk Kim, School of Materials Science and Engineering, Inha Unive, Korea

Jin Gyun Kim, Yoo Hang Kim, Wan In Lee, Inha University, Korea

662 - Immobilization of CdS particles in a hibrid Sol-Gel material

Victor I Boev, University of Minho, Bulgaria

Carlos J R Silva, M Jesus M Gomes, University of Minho, Portugal

663 - Influence of the Synthesis Method on the Properties of Ceria-Doped Alumina

Hugo Pérez-Pastenes, Gustavo Pérez, Jesús A Ochoa-Tapia, Tomás Viveros, Universidad Autónoma Metropolitana-Iztapalapa, Mexico

Noel Nava, Ascención Montoya, Instituto Mexicano del Petróleo, Mexico

664 - Preparation of “Green” Composites - In Situ Silica-filled Natural Rubber

Yuko Ikeda, Yoshihiro Kameda, Kyoto Institute of Technology, Japan

665 - Lamellar Organo-Bridged Silicones

Joël JE Moreau, Luc Vellutini, Catherine Bied, Michel Wong Chi Man, Ecole Nationale Supérieure de Chimie de Montpellier, France

667 - Non-Hydrolytic Route for the Synthesis of Al_2TiO_5 and $\text{Mg}_x\text{Al}_{2(1-x)}\text{Ti}_{(1+x)}\text{O}_5$ Powders

Silvia Licoccia, Enrico Traversa, Paolo Sebastianelli, Universita' di Roma Tor Vergata, Italy
Plinio Innocenzi, Università di Sassari, Italy
Alessandro Martucci, Università di Padova, Italy

668 - Synthesis and characterization of polyimide-silica hybrid materials; effect of matrix polarity on the mechanical and thermal properties of the resulting hybrids

Habibur Rehman, Helmut Schmidt, Institut fur Neue Materialien, Germany
Zahoor Ahmad, Kuwait University, Kuwait

670 - Preparation of Nano-crystalline ZnTiO_3 powders by the Sol-Gel Process

Lili Zhao, Fangqin Liu, Xuwen Wang, Northwest University, China

671 - Apatite Morphology and Phase Development in Sol-Gel Synthesis of Bone-Like Carbonated Apatite

Adriyan Milev, Kamali GS Kannangara, University of Western Sydney, Australia
Besim Ben-Nissan, University of Technology Sydney, Australia

672 - Chemical Reactions in Solution and Intermediate Solid State Transformations in Sol-Gel Synthesis of Bone-Like Carbonated Apatite

Kamali GS Kannangara, Adriyan Milev, University of Western Sydney, Australia
Besim Ben-Nissan, University of Technology, Sydney, Australia

673 -Mechanical properties of nano-hybrid films. Part 1: 3-glycidoxypolytrimethoxysilane

Gérard Calleja, Catherine Tartivel, Bruno Latella, David CASSIDY, Kim Finnie, Christophe Barbé, John Bartlett, Materials and Engineering Science, ANSTO

674 - Mechanical properties of nano-hybrid films. Part 2: influence of sol-gel chemistry

Gérard Calleja, Catherine Tartivel, Bruno Latella, David CASSIDY, John Bartlett, and Christophe Barbé , Materials and Engineering Science, ANSTO
Florence Babonneau, Université Pierre et Marie Curie, Paris, France

675 - Ceramic Micro-Particles for Controlled Release Synthesis using Combined Microemulsion and Sol-Gel Technology

Alexandra Bush, Linggen Kong, Rachael Trautman,
Christophe Barbé and John Bartlett
Materials and Engineering Science, ANSTO

676 - Preparation of dye doped silica nanoparticles via water-in-oil microemulsions

Lingga Kong¹, Christophe Barbé, John Bartlett, Kim S Finnie and Mark Blackford

Materials and Engineering Science, ANSTO

677- Titanium Oxoalkoxy Clusters as Precursors for Dense TiO₂ Coatings

Gérard Calleja, Christophe Barbé and John Bartlett, Materials and Engineering Science,

ANSTO

678 - Cracking And Decohesion Of Sol-Gel Hybrid Coatings On Metallic Substrates

B.A. Latella ¹, M. Ignat ², D.J. Cassidy ¹, C. Barbé ¹ and H. Li ¹

¹ Materials and Engineering Science, Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai, NSW, 2234. Australia.

² Laboratoire de Thermodynamique et de Physico-Chimie Métallurgique, associé au CNRS, E.N.S.E.E.G., BP 75, F-38402 Saint Martin d'Hères, France.

679 - Fluorinated copolymer/metal oxide hybrids: an interesting family of materials

Eric Bescher and J.D. Mackenzie

Department of Materials Science and Engineering

University of California Los Angeles

Los Angeles CA 90095

Second Poster Session

“Mesostructured Materials, Coatings, and Bio-materials”

701 - Sol-Gel Derived ZrO₂ Thin Films - Synthesis and Characterization

D T Senguttuvan, National Physical Laboratory New Delhi, India

K L Malhotra, Indian Institute of Technology New Delhi, India

702 - Sol-Gel Deposition of Zirconium Doped Tin Dioxide Thin Films by Non Alkoxide Precursors

D T Senguttuvan, National Physical Laboratory New Delhi, India

K L Malhotra, Indian Institute of Technology New Delhi, India

703 - TEM Observation of Crystallization of Barium-Strontium Titanate Film

P V Burmistrova, Russian Academy of Science, Russia

A S Sigov, K A Vorotilov, Moscow State Technical University of Radioengineering, Russia

D N Zacharov, O M Zhigalina, Institute of Crystallography, Russian Academy of Science, Russia

704 - Ferroelectrics Templated in Nanoporous Silicon and Alumina Membranes

E D Mishina, A S Sigov, V A Vasil'ev, K A Vorotilov, Moscow State Technical University of Radioengineering, Russia

705 - Effect of Annealing Temperature on the Properties of Methyl-Modified Silicate Films

A S Sigov, V A Vasil'ev, K A Vorotilov, Moscow State Technical University of Radioengineering, Russia

706 - Mixed cationic-nonionic surfactants route to synthesize high-quality MCM-48 under low surfactant/silicon molar ratio

YuHan Sun, Dong Wu, ShangRu Zhai, Chinese Academy of Sciences, China

707 - Fabrication of Nanostructured Metal Oxide Semiconductor Films Having Nest-Like Morphology through Pyrolytic Transformation of CBD-Processed Layered Hydroxide Metal Acetates

Shinobu Fujihara, Eiji Hosono, Toshio Kimura, Keio University, Japan

709 - Tailoring Electrical Properties of Modified SiO₂ Films

Thomas Huebert, Federal Institute for Materials Research and Testing, Germany

Andreas Klyszcz, Germany

Aki Shimamura, Japan

710 - Sol-Gel CaSiO₃ materials and calcium-containing inorganic compounds studied by natural abundance solid-state ⁴³Ca NMR

Zhongjie Lin, Mark E Smith, University of Warwick, United Kingdom

Frank E Sowrey, Robert J Newport, University of Kent, United Kingdom

711 - Multinuclear solid-state NMR study of Sol-Gel prepared CaSiO₃ materials

Zhongjie Lin, Mark E Smith, University of Warwick, United Kingdom

Frank E Sowrey, Robert J Newport, University of Kent, United Kingdom

712 - On the use of monolithic Sol-Gel derived mesoporous silica for the calibration of thermoporosimetry using various solvents

Jean-Marie Nedelec, Mohamed Baba, Université Blaise Pascal & ENSCCF, France

713 - Application of the Sol-Gel Method at the Fabrication of Microstructure Fibers

Jan Mrazek, Vlastimil Matejec, Milos Hayer, Ivan Kasik, Daniela Berkova, Institute of Radio Engineering, AS CR, Czech Republic, Czech Republic

714 - Preparation of New Photosensitive ZrO₂ Gel Films Using Hydroxyl substituted Aromatic Ketones as Chemical Modification Reagents and Their Patterning

Naoki Noma, Saori Yamazaki, Noboru Tohge, Kinki University, Japan

715 - Development of the photochromic coating on polycarbonate

Duck Kun Hwang, Yong Gun Shul, Hyun Jong Kim, Korea

716 - Sol-Gel derived anticorrosion coatings for metals and alloy surfaces

Bakul C Dave, Mukti S Rao, Xiankui Hu, Yogeeshwari Devaraj, Shirshak K Dhali, Southern Illinois University, Carbondale, United States

717 - Preparation of Composite Anatase TiO₂ Nanostructure by Precipitation from Hydrolyzed TiCl₄ Solution within Anodic Alumina Membrane

Kang-Jin Kim, Il-Su Park, Jong-Hyun Kim, Korea University, Korea

718 - Low Dielectric Hybrid Inorganic-Organic Mesoporous Silicate Thin Films

Ji-In Jung, Jae Young Bae, Byeong-Soo Bae, Korea Advanced Institute of Science and Technology, Korea

720 - Novel Route to the Synthesis of a Large Pore Mesoporous Titania with Full Anatase Nanocrystalline Domain

Indriana Kartini, The Nanomaterials Centre, Australia

Paul Meredith, Joao C Diniz da Costa, G Q Max Lu, The University of Queensland, Australia

722 - Sol-Gel Preparation and Mechanical Properties of Machinable Cellulose/Silica and Polyvinylpyrrolidone/Silica Composites

Kei Tanaka, Hiromitsu Kozuka, Kansai University, Japan

723 - Mesostructured silica monoliths via supercritical and ambient pressure drying

Christina K Raab, Viktoria Torma, Nicola Hüsing, Vienna University of Technology, Austria

724 - Oxide interphase with porosity gradient for SiC/SiC ceramic matrix composites

Stephane Parola, Universite Claude Bernard Lyon 1, France

Martine Verdenelli, Fernand Chassagneux, Catherine Sigala, Jean-Marie Letoffe, Sylvain Jacques, Henri Vincent, Jean-Pierre Scharff, Laboratoire des Multimateriaux et Interfaces UMR CNRS 5, France

725 - Development and Optimization of Protein Microarrays based on Pin-Printing of Sol-Gel Entrapped Biomolecules

Nicholas Rupcich, John D Brennan, McMaster University, Canada

726 - Entrapment of Functional Ligand-Gated-Ion Channel Receptors in Sol-Gel Derived Silica: Applications in Drug Screening

Travis R Besanger, John D Brennan, McMaster University, Canada

727 - Nanoporous Silicas from Cationic Polymer-Silica Hybrids

Graham M Gray, John N Hay, University of Surrey, United Kingdom

728 - Sol-Gel Biomaterial with Chemically Functionalized Surface for in Vitro Immunoassays

Herman S Mansur, Rodrigo L Orefice, Wander L Vasconcelos, Zelia P Lobato, Federal University of Minas Gerais, Brazil

730 - Preparation of hot water-resistant silica thin films from polysilazane solution at room temperature

Tomoko Kubo, Hiromitsu Kozuka, Kansai University, Japan

731 - Preparation and Characterization of Mesoporous Titania Gel Films

Hiroshi Hirashima, Hiroaki Imai, Miah Muhammed Yusuf, Keio University, Japan
Vladimir Balek, Nuclear Research Institute, Czech Republic

732 - The effects of SiO₂ barrier and N₂ annealing on Sb-doped SnO₂ transparent conducting film prepared by Sol-Gel dip coating

Tae-Young Lim, Chang-Yeoul Kim, Bum-Suk Kim, Korea Institute of Ceramic Engineering and Technology, Korea

Keum-Ho Auh, Hanyang University, Korea

734 - Combinatorial study for transparent conducting films in the Zn-Sn-O tie line

Alexander Kurz, Michel A Aegeerter, Institut fuer Neue Materialien, Germany

735 - Preparation and Characterization of Mesoporous Titania-Alumina Ceramics by Modified Sol-Gel Method

Silvester Tursiloadi, Research Center for Chemistry, Indonesia

Hiroaki Imai, Hiroshi Hirashima, Keio University, Japan

736 - Ordered mesostructured silica films: effect of pore surface properties on its sensing applications

Plinio Innocenzi, Università di Sassari, Italy

Paolo Falcaro, Università di Padova, Italy

Massimo Guglielmi, Italy

Lucrezia Palummo, Università "La Sapienza", Italy

Ruggero Caminiti, Italy

738 - Sol-Gel Derived SiO₂-TiO₂ Nanocomposite Membranes

Fred Getton, Paul A Sermon, Nanoengineered Solids and Surface Reactivity Group, United Kingdom

739 - Fluoride Sol-Gels and Nano-Coatings

Rita Badheka, Paul A Sermon, Nanoengineered Solids and Surface Reactivity Group, United Kingdom

740 - Corrosion Protection of Single Crystal Fluoride Windows by Sol-Gel Dip-Coated Tin Oxide Thin Films

Alessandro P Rizzato, Celso V Santilli, Sandra H Pulcinelli, IQ/UNESP, Brazil

Younes Messaddeq, UNESP, Araraquara, Brazil

741 - Investigations of MgF₂ Optical Thin Films Prepared from Autoclaved Sol

Tsuyoshi Murata, Hitoshi Ishizawa, Izumi Motoyama, Akira Tanaka, Nikon Corporation,

Japan

742 - Preparation of Calcium Phosphate Hybrids through Biomimetic Process

Maki Kishino, Mitsunobu Iwasaki, Seishiro Ito, Kinki University, Japan

743 - Synthesis of blood compatible PDMS-based organic-inorganic hybrid coatings

Takeshi Yabuta, Biomaterials Laboratory, Japan

Kanji Tsuru, Akiyoshi Osaka, Okayama University, Japan

Satoshi Hayakawa, Japan

744 - Encapsulation of Viable Aerobic Microorganisms in Silica Gels

Anthony P Taylor, Kim S Finnie, John R Bartlett, Peter J Holden, Australian Nuclear

Science and Technology Organisation, Australia

745 - Anti-Reflective Coatings of Flowerlike Alumina on Various Glass Substrates

Prepared by the Sol-Gel Process with Hot Water Treatment

Naoko Yamaguchi, Kiyoharu Tadanaga, Tsutomu Minami, Masahiro Tatsumisago,

Osaka Prefecture University, Japan

Atsunori Matsuda, Toyohashi University of Technology, Japan

746 - Sliding Properties on Flat Organic Polymer Coatings

Naoya Yoshida, Yuu Abe, Hisashi Ohsaki, Kazuhito Hashimoto, Toshiya Watanabe,

RCAST, The University of Tokyo, Japan

Akira Nakajima, Tokyo Institute of Technology, Japan

747 - Sol-Gel Synthesis of Nanocomposite Hybrid Biomaterials

Bisserka I Samunova, Elena D Kadiyska, Peter R Djambaski, Georgi E Chernev, University of Chemical Technology and Metallurgy, Bulgaria

Isabel M Miranda Salvado, Helena V Fernandes, University of Aveiro, Portugal

Elena P Dobreva, Liudmila V Kabaivanova, Institute of Microbiology, Bulgarian Academy of Science, Bulgaria

748 - Effect of different bidentate ligands on the micro-structure of zirconia sols for membrane application

Gerald I Spijksma, Nieck E Benes, Henk Kruidhof, University of Twente, The Netherlands

749 - Sol-Gel SiO₂ - ZrO₂ Coatings for Optical Applications

Maria Crisan, Mariuca Gartner, Luminita Predoana, Rares Scurtu, Maria Zaharescu,
Institute of Physical Chemistry "I.G. Murgulescu", Romania
Raluca Gavrilă, National Institute for Research & Development in Microtechnologie,
Romania

750 - Synthesis and characterization of microporous titania membranes

J Sekulic, JE ten Elshof, DHA Blank, University of Twente, The Netherlands
R Escobar Galindo, A Van Veen, Delft University of Technology, The Netherlands

751 - A new elaboration route by Sol-Gel process for cerium doped SrHfO₃ optical films and powders

Maricela Villanueva-Ibañez, Cécile LeLuyer, Jacques Mugnier, Laboratoire de Physico-Chimie des Matériaux Luminescent, France
Stéphane Parola, Université Claude Bernard Lyon 1, France
Olivier Marty, Laboratoire d'Electronique: Nanotechnologies, Capteurs J, France

754 - Preparation and studies of Bi₂O₃

Åsa B Ekstrand, Uppsala University, Sweden
Gunnar L Westin, Department of Materials Chemistry, Ångström Laboratory, Sweden

756 - Mesoporous silica supported sulfated zirconia prepared by a Sol-Gel process

R Akkari, Laboratoire de chimie des matériaux et catalyse, Tunisia
Abdelhamid Ghorbel, Université Tunis El Manar, Tunisia
N Essayem, F Figueras, Institut de recherches sur la catalyse, France

757 - Preparation and studies of ZnO:Al films and powders

Annika Pohl, Gunnar L Westin, Maria Wijk, Ångström Laboratory, Uppsala University, Sweden

758 - Nitrified and Denitrified Microbiological Mud Encapsulated by the Sol-Gel Method

G Aguirre, G Arriola, T Lopez, M Picquart, J Gomez, Universidad Autonoma Metropolitan, Mexico
D Aguilar, P Quintana, J Alvarado, Cinvestav-Merida, Mexico

759 - Study of Drug Delivery in Composites forming Interpenetrating Networks by Thermosensitive Poly(N-Isopropylacrylamide) Gels and Ceramic Matrix

Edesia MB Sousa, Centro de Desenvolvimento da Tecnologia Nuclear - CDTN, Brazil
Ricardo G Sousa, Universidade Federal de Minas Gerais, Brazil

760 - Mesostructured Silica Fibres Confinement of the Laser Dye. Host-Guest Interaction and Optical Properties

German M Telbiz, Institute of Physical Chemistry, Ukraine

Volodymyr L Vozny, Instityte of Physics, Ukraine

Vasily I Gerda, Volodymyr V Kovalenko, Volodymyr G Ilyin, Ukraine

762 - Size distribution evolution of Er_2O_3 sols used to grow high-density thin films

Giancarlo E S Brito, Institute of Physics -USP, São Paulo, Brazil

763 - Characterization and transport properties of surfactant templated silica layers for membrane applications

Tijana Radosevic, Nieck E Benes, Andre ten Elshof, University of Twente, The Netherlands

765 - Self-ordered nanoporous silica film fabricated by template Sol-Gel method for surface photovoltage gas sensor

Haoshen Zhou, AIST Umezono, Japan

Takeo Yamada, Itaru Honma, Energy Electronics Institute, Japan

766 - Making Methacryl and Urethane Polymerizable Composite Coatings Using POSS Building Blocks

Daniel Neumann, Elda Markovic, Kristina Constantopoulos, Rachel Pillar, Mark Fisher, Stephen Clarke, Janis Matsons, Flinders University, Australia

George Simon, Monash University, Australia

767 - Hybrid Silica Materials: Structural and Transport Properties

Haryadi Haryadi, Vicki Chen, UNSW, Australia

Grainne M Moran, Graham E Ball, Jim Hook, School of Chemical Sciences, UNSW, Australia

768 - Hybrid inorganic-organic Sol-Gel coatings in the $\text{SiO}_2\text{-TiO}_2$ system

Maria Zaharescu, Maria Crisan, Luminita Predoana, Mariuca Gartner, Institute of Physical Chemistry "I.G. Murgulescu", Romania

Dana Cristea, Stefania Degeratu, Elena Manea, National Institute for R&D in Microtechnologies, Romania

769 - Preparation and Characterization of Silica Aerogels Derived from Ambient Pressure

Jun Shen, Guangming Wu, Tongji University, China

Zhongsheng Deng, Bin Zhou, Yaodong Huang, Xingyuan Ni, Jue Wang, Pohl Institute of Solid State Physics, Tongji University, China

770 - Carbon Aerogel Films Synthesized at Ambient Conditions

Jun Shen, Guangming Wu, Tongji University, China

Jue Wang, Yanzhi Guo, Bin Zhou, Xingyuan Ni, Pohl Institute of Solid State Physics, Tongji University, China

771 - Electrochromism in Au-NiO Films

Fabio F Ferreira, Paula S Haddad, Márcia C A Fantini, Giancarlo E S Brito, Institute of Physics -USP, São Paulo, Brazil

772 - Compositional profiles in silica-based Sol-Gel films doped with erbium and silver

Ana C Marques, Rui M Almeida, Eduardo Alves, Ana Ramos, Instituto Superior Técnico, Portugal

773 - Effect of H₂ Annealing on the Properties of In₂O₃-SnO₂ Thin Films

Terho K Kololuoma, Arto Maaninen, VTT Electronics, Finland

Leena-Sisko Johansson, Joseph M Campbell, Helsinki University of Technology, Finland

Juha T Rantala, University of Oulu, Finland

774 - Nanostructured Sol-Gel thin films containing Coordinative Compounds

Anca Emandi, University of Bucharest, Faculty of Chemistry, Romania

Luminita Predoana, Maria M Zaharescu, Institute of Physical Chemistry, Romanian Academy, Romania

776 - Selective Deposition of Biocompatible Sol-Gel Materials

Todd M Harrell, Pamela M Norris, Robert Hull, Mary E Power, Bouvard Hosticka, University of Virginia, United States

779 - Incorporation of triphenylmethane dyes into Sol-Gel matrices deposited on textiles

Boris Mahltig, Horst Böttcher, GMBU-Dresden, Germany

Dierk Knittel, Eckard Schollmeyer, DTNW-Krefeld, Germany

780 - Characterisation of Sol-Gel process using sucrose as organic templates

Jimin Lim, Rachael M Catlin, Ngee Ann Polytechnic, Singapore

Joao C Diniz da Costa, G Q Max Lu, The University of Queensland, Australia

781 - Sol-Gel Derived Nano-Coated Coralline Hydroxyapatite

Besim Ben-Nissan, University of Technology, Sydney, Australia

Adriyan Milev, University of Western Sydney, Australia

Razi Vago, Israel

782 - Zirconia Sol-Gel Coatings on Anodized Titanium for Orthopaedic Applications

Richard Roest, Besim Ben-Nissan, UTS, Australia

Alan W Eberhardt, United States

783 - Syntesis of Organic-Inorganic Hybrid Membranes via Sol-Gel Process

Alessandra D'Epifanio, Debora Marani, Maria L Di Vona, Silvia Licoccia, Università di Roma Tor Vergata, Italy

784 - Influence of alkylene chain length on the morphology of chiral bridged silsesquioxanes

Qinghong Xu, Joël JE Moreau, Michel Wong Chi Man, Ecole Nationale Supérieure de Chimie de Montpellier, France

785 - Template-ordered mesoporous silica films thermally treated under inert, reducing or oxidising conditions

Tatiana I Levchenko, Institute of Surface Chemistry, Ukraine

Yuri V Plyuto, Aleksej A Chuiko, National Academy of Sciences of Ukraine, Ukraine

786 - Encapsulation of Ibuprofen in Mesoporous Silicas: Solid State NMR Characterization

Florence Babonneau, Nathalie Steunou, Lydie Camus, Chimie de la Matière Condensée, France

Ainhoa Ramila, Madrid, Spain

Maria Vallet-Regi, Departamento de Química Inorgánica y Bioinorgánica, Spain

787 - Thermal Stability of Periodic Mesoporous SICO Glasses

Raphaël Blum, Valérie Goletto, Bérangère Tourny, Florence Babonneau, Chimie de la Matière Condensée, France

788 - A glycerol-derived silica precursor for the encapsulation of protein in porous silica monoliths

Yang Chen, Zheng Zhang, John D Brennan, Michael A Brook, McMaster University, Canada

790 - Micropatterning of Sol-Gel Derived Thin Films Using Hydrophobic-Hydrophilic Patterned Surface

Tsutomo Minami, Takayuki Fujii, Kiyoharu Tadanaga, Masahiro Tatsumisago, Osaka Prefecture University, Japan

Atsunori Matsuda, Toyohashi University of Technology, Japan

792 - Marriage of Sol-Gel Processing with Imprinting Synthesis

Sheng Dai, Z.T Zhang, C.D Liang, M.C Burleigh, Oak Ridge National Laboratory, United States

793 - Effect of Sol-Gel Encapsulation on Lipase Structure and Function: A Small Angle Neutron Scattering Study

L.E. Rodgers^{1, 2}, P.J. Holden², R.B. Knott², K.S. Finnie², J.R. Bartlett² and L.J.R. Foster¹

¹ School of Biotechnology and Biomolecular Sciences, University of New South Wales, NSW, 2052, Australia.

² Australian Nuclear Science and Technology Organisation, PMB 1, Menai, NSW, 2234, Australia.

794 - Mesoporous Ceria and Pd/Ceria Nanophases: Preparation, Structure and Catalytic Application

Jin-An Wang, Li-Fang Chen, Yaminica Martinez, Instituto Politecnico Nacional, Mexico
Ascension Montoya, Juan Navarette, Salvador Castillo, Marina Moran-Pineda, Instituto Mexicano del Petróleo, Mexico

795 - Proton-conducting glass films for fuel-cell electrolyte

M. Nogami, H. Li, Nagoya Institute of Technology, Japan

Third Poster Session

“Sol-Gel Optics, Functional Materials and Industrial Applications of Sol-Gel Science and Technology”

901 - Processing of Alumina Rich Cordierite Porous Ceramics

D T Senguttuvan, S H Kalsi, K S Sharada, National Physical Laboratory New Delhi, India

902 - Optical Properties of Europium(III) Doped Nanocrystalline Films of TiO₂

Agnieszka Hreniak, Marcin Nyk, Krzysztof Maruszewski, Jan Misiewicz, Wroclaw University of Technology, Poland

Wieslaw Strek, Institute for Low Temperature and Structure Research, Poland

Dariusz Hreniak, Polish Academy of Sciences, Poland

903 - Influence of Grains Size on Luminescence Properties of Tb-doped Nanostructured Materials Prepared by the Sol-Gel Method

Dariusz Hreniak, Polish Academy of Sciences, Poland

Wieslaw Strek, Institute for Low Temperature and Structure Research, Poland

Robert Pazik, Piotr Mazur, Czestochowa University of Technology, Poland

Marcin Nyk, Jan Misiewicz, Institute of Physics, Wroclaw University of Technology, Poland

Maria Zabkowska-Waclawek, University of Opole, Poland

904 - Sol-Gel Synthesis of Vanadia - Silica for Photocatalytic Degradation of Cyanide

Adel A Ismail, Central Metallurgical R&D Institute, CMRDI, Egypt

905 - Multinuclear solid state NMR of the structural development of binary $\text{MO}_2\text{-SiO}_2$ -(M= Ti, Zr or Hf) gel materials

Philips N Gunawidjaja, Mark E Smith, University of Warwick, United Kingdom

David M Pickup, R J Newport, University of Kent at Canterbury, United Kingdom

906 - Preparation and electrical properties of $\text{Ln}_x(\text{SiO}_4)_6\text{O}_{(1.5x-12)}$ ($\text{Ln} : \text{Nd, La}$) with apatite structure

Keishi Nishio, Takashi Nakajima, Tadashi Ishigaki, Toshio Tsuchiya, Tokyo University of Science, Japan

907 - Polymerizable Organosols for Dental Materials

Simone Klapdohr, Norbert Moszner, Volker Rheinberger, Ivoclar Vivadent AG, Liechtenstein

909 - Crystallisation kinetics of -spodumene in lithium aluminosilicate Sol-Gel glasses

Maria R Moreira, Isabel M Miranda Salvado, University of Aveiro, Portugal

Rui F Silva, CICECO, University, Portugal

910 - The effect of preparation method and calcination temperature on the particle size and surface area of perovskites-type SrFeOX

Abdul Majid, Jim Tunney, Mike Post, Steve Argue, National Research Council of Canada, Canada

911 - Sol-Gel derived scintillating $\text{LuBO}_3 : \text{Ce}^{3+}$

Christelle Mansuy, Jean-Marie Nedelec, Rachid Mahiou, Université Blaise Pascal & ENSCCF, France

Christophe Dujardin, Université Claude Bernard Lyon 1, France

912 - From Research to Commercialisation: Monolithic HPLC-columns for fast separations

Karin Cabrera, Merck KGaA, A&R R&D Chromatography, Germany

Kazuki Nakanishi, Kyoto University, Japan

914 - Preparation of powder, film and fibre of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_3$ using $\text{La}(\text{MOE})_3$, $\text{Sr}(\text{MOE})_2$ and $\text{Ni}(\text{acac})_2$ precursors

Gunnar L Westin, Department of Materials Chemistry, Ångström Laboratory, Sweden

Kjell B Jansson, Arrhenius Laboratory, Sweden

Annika Pohl, Ångström Laboratory, Uppsala University, Sweden

917 - Polarization Holographic Gratings in Hybrid Sol-Gel Films

Pier Paolo Lottici, Raffaella Raschellà, Danilo Bersani, Iari-Gabriel Marino, Andrea Lorenzi, Angelo Montenero, University, Parma, Italy

918 - Porous SiO₂-BaMgF₄:Eu(II) Glass-Ceramic Thin Films and Their Strong Blue Photoluminescence

Seiki Kitta, Shinobu Fujihara, Toshio Kimura, Keio University, Japan

919 - Studies on the surface chemical modifications of TMOS based silica aerogels using various organosilane compounds

Venkateswara Rao Amiresetty, Shivaji university, India

Gérard Michael Pajonk, LACE ISM.UMR CNRS, Université Claude Bernard Lyon,43 Bd, France

920 - Functionalised Thiocalixarenes and Inclusion in Hybrid Materials for Optical Limiting

Stéphane Parola, Université Claude Bernard Lyon 1, France

Cédric Desroches, Marcus Örtenblad, Philippe Miele, Laboratoire des Multimateriaux et Interfaces UMR CNRS 5, France

Patrice Baldeck, Laboratoire de Spectrométrie Physique, Université Josep, France

Vadim G Kessler, Swedish University of Agricultural Sciences, Sweden

Cesar Lopes, Swedish Defence Research Agency, Sweden

921 - Low-Refractive-index Materials for producing Anti-Reflection film by Sol-Gel Process

Yurie Ota, Dai Nippon Printing Co.,Ltd, Japan

Toshio Yoshihara, Japan

922 - Characterization of Alumina Doped with Rare Earth (Ce, Eu, La) Oxides

Hugo Pérez-Pastenes, Gustavo Pérez, Jesús A Ochoa-Tapia, Tomás Viveros, Universidad Autónoma Metropolitana-Iztapalapa, Mexico

Noel Nava, Ascención Montoya, Instituto Mexicano del Petróleo, Mexico

923 - Preparation and properties of Rhodamine B derivative with ethoxy silano group and its application to suruface treatment film for display

Tomoji Ohishi, Shibaura Institute of Technology,Faculty of Engineering, Japan

924 - Gas sensing properties of nanocrystals oxide doped silica Sol-Gel film

Alessandro Martucci, Università di Padova, Italy

Dario Buso, Massimo Guglielmi, Carlo Cantalini, Italy

Mike Post, NRC of Canada, Canada

925 - Synthesis and Structures of Titanasiloxane Cage Compounds

Jeong Hyun Kim, Il Nam Jung, Korea

926 - Reduction of Eu³⁺ to Eu²⁺ in Al-codoped silica glasses fabricated by the Sol-Gel technique and CO₂-laser processing

Valerio Romano, University of Bern, Heinz P Weber, Switzerland

Bettina Wilhelm, Victoria University of Wellington, New Zealand

927 - Periodic structures of organic-inorganic hybrid material recorded by two-photon laser interference technique

Hiroyo Segawa, PREST, Japan

Shigeki Matsuo, Hiroaki Misawa, Tokushima University, Japan

928 - Molecular Design of Sol-Gel SiO₂-TiO₂ for Self-Cleaning Optics

Jason Leadley, Paul A Sermon, Nanoengineered Solids and Surface Reactivity Group, United Kingdom

930 - Photoluminescence Excitation Spectroscopy of Er³⁺/Yb³⁺ Co-Activated Silica-Alumina Monolithic Xerogels

Cristina Armellini, Maurizio Ferrari, CNR-IFN, Institute of Photonics and Nanotechnologies, Italy

Alessandro Chiasera, Sandra Dirè, Maurizio Mattarelli, Maurizio Montagna, L Zampedri, Università di Trento, Italy

Alessandro Martucci, G C Righini, Università di Padova, Italy

Stefano Pelli, CNR-IFAC, Institute of Applied Physics, Italy

931 - Application of chromium-containing silicas for synthesizing functional glasslike materials by the Sol-Gel method

Mykola Borysenko, Viktor Bogatyrov, Institute of Surface Chemistry of the National Academy, Ukraine

Aleksej A Chuiko, NAS of Ukraine, Ukraine

Evgenij Poddenezhny, Andrej Boiko, Gomel State Technical University, Belarus

933 - Textural and Structural Properties of Sol-Gel ZrO₂-CaO Mixed Oxides

Jaime Garcia, Tessy Lopez, Maximiliano Asomoza, Ricardo Gomez, Universidad Autonoma Metropolitana-Iztapalapa, Mexico

934 - Synthesis of TiO₂ nanoparticles with controlled size and phase for photo reduction of NOx"

Florencia M Moran-Pineda, Salvador Castillo, Instituto Mexicano del Petroleo, Mexico
Javier Hernandez, Mexico

935 - Physicochemical Characterization of Titania Gels Doped with Sodium and Cesium

Marcial Zamora, Tessy Lopez, Ricardo Gomez, Maximiliano Asomoza, Universidda Autonoma Metropolitana-Iztapalapa, Mexico

Xim Bokhimi, Universidad Nacional Autonoma de Mexico, Mexico

936 - Determination of Basic Sites by CO₂ Thermal Programmed Desorption on Sol-Gel CaO-SiO₂ Mixed Oxides

Tessy Lopez, Ricardo Gomez, Jaime Garcia, Maximiliano Azomosa, Universidad Autonoma Metropolitana-Iztapalapa, Mexico

937 - Zirconia and Cu/ZrO₂ Sol-Gel Materials. Spectroscopic Characterization

Tessy Lopez, Myrna Alvarez, Ricardo Gomez, Universidad Autonoma Metropolitana-Iztapalapa, Mexico

Juan Navarrete, Instituto Mexicano del Petroleo, Mexico

938 - Anhydrous Sol-Gel Synthesis of Titania-Doped Siloxane Polymer for Integrated Optics

Xinshi Luo, Congji Zha, Barry Luther-Davies, The Australian National University, Australia

939 - Characterization of spherical foamed silica

Sunuk Kim, Myungchul Jeon, Soonchul Hwang, RIST, Korea

942 - The Control of Hydroxyl Content in Sol-Gel Materials for Waveguide Optical Amplifier

Sang Il Seok, Advanced Materials Division, Korea Research Institute, Korea

Bok Yeop Ahn, Joo Hyun Kim, Korea

943 - Raman spectroscopic investigations of Ag⁺ and Ce³⁺ doping effects on the densification of nanoporous silica xerogels

Christophe Kinowski, Sylvia Turrell, Laboratoire de Spectrochimie Infrarouge et Raman, France

Mohamed Bouazaoui, Bruno Capoen, Laboratoire de Physique des Lasers Atomes et Molécules, France

Larry L Hench, Imperial College, United Kingdom

Jean-Marie Nedelec, Laboratoire des Matériaux Inorganiques, France

944 - Physicochemical and Acidic Properties of Sulfated Zirconia Supported by Alumina Prepared by Sol-Gel Process

Lassaad Ben Hammouda, Faculte des Sciences de Tunis- Campus Universitaire, Tunisia
Abdelhamid Ghorbel, Université Tunis El Manar, Tunisia

945 - Acidity of sulphated zirconia aerogels : Correlation between XPS studies, surface potential measurements and catalytic activity in isopropanol dehydration reaction

Mohamed Kadri Younes, Chemistry Dept. Faculty of Sciences Tunis, Tunisia

Abdelhamid Ghorbel, Université Tunis El Manar, Tunisia

Alain Rive, Robert Hubaut, Catalysis Lab. University of Sciences and Techn, France

946 - Salient Features of Synthesis and Structure of Surface of some Functionalized Polysiloxane Xerogels

Yuriy L Zub, Aleksej A Chuiko, Institute of Surface Chemistry, NAS of Ukraine, Ukraine
Daniele Cauzzi, Giovanni Predieri, Universita di Parma, Italy
Mark G White, Georgia Institute of Technology, Atlanta, United States

947 - Vanadia-Silica catalysts prepared by Sol-Gel method: application for epoxidation reaction

Noomen Moussa, Faculté des Sciences de Tunis, Tunisia
Abdelhamid Ghorbel, Université Tunis El Manar, Tunisia
Paul Grange, Université catholique de Louvain, Belgium

949 - Preparation and strengthening of nano-porous silica optical films with adjustable refractive index derived by Sol-Gel process

Guangming Wu, Jun Shen, Tongji University, China
Bin Zhou, Xingyuan Ni, Jue Wang, Pohl Institute of Solid State Physics, Tongji University, China

950 - Gel Entrapment Technique for Nd-YAG

Vijay N Vaidya, Bhabha Atomic Research Center, India
R V Kamat, BARC Trombay Mumbai, India

951 - Theoretical and Experimental Studies on Sol-Gel Zirconia doped with Alkaline Iones

Joel Alderete, Gina Pecchi, Antonio Buljan, Universidad de Concepción, Chile
Tessy López, Albino Moreno, Universidad Autónoma Metropolitana - Iztapalapa, Mexico

952 - Decomposition of a Sol-Gel precursor during the fabrication of YBCO films

Andrea J Bubendorfer, Lilian J Campbell, Tim Kemmitt, Nick J Long, Industrial Research Limited, New Zealand

953 - Photopatternable Hybrid Planar Waveguides Synthesized by Organically Modified Sol-Gel Method

Paolo Prospisito, Mauro Casalboni, Fabio De Matteis, Stefano Schutzmann, University of Rome Tor Vergata, Italy
Plinio Innocenzi, Università di Sassari, Italy
Giovanna Brusatin, Gioia Della Giustina, Università di Padova, Italy

954 - Sol-Gel Emulsions for Surface Base-Coat on Metal Alloys

Chhui-Tsu Lin, Charles A Sizemore, Northern Illinois University and ChemNova Technologies, United States
Sonic Fang, Green Products Inc., Taiwan, Province of China

955 - Nanostrucure and optical properties of $\text{Ln}_2\text{O}_3\text{-TiO}_2$ ($\text{Ln}=\text{La, Er}$) thin films

Giancarlo E S Brito, Thais G Amaral, Sérgio L Morelhão, Institute of Physics -USP, São Paulo, Brazil
Sidney J L Ribeiro, Rogéria R Gonsalves, Laboratory of Photonic Materials, Institute of Chemistry, Brazil
Younes Messaddeq, UNESP, Araraquara, Brazil

956 - Preparation of silicates using $\text{HSi(OC}_2\text{H}_5)_3$ and their NOx- adsorption behavior

Shingo Katayama, Synergy Ceramics Lab., FCRA, Japan
Noriko Yamada, Nippon Steel Corporation, Japan
Masanobu Awano, Synergy Materials R.C., AIST, Japan

959 - Sol-Gel Synthesis of $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ and $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ Glasses and Characterization by AFM, SNMS and NMR

Gundula Helsch, Technische Universität Clausthal, Germany
Lars P Hoyer, Günther H Frischat, Institut für Nichtmetallische Werkstoffe, Technische Un, Germany
Long Zhang, Institut für Physikalische Chemie, Westfälische Wilhelm, Germany
Jerry CC Chan, Hellmut Eckert, Westfälische Wilhelms-Universität Münster, Germany

960 - Optical Gain of Infrared Dyes in Hybrid Sol-Gel Based Channel Waveguides

Fabio De Matteis, Paolo Proposito, Mauro Casalboni, Vittorio Merlo, Roberto Russo, Stefano Schutzmann, University of Rome Tor Vergata, Italy

961 - Lifetime pH Sensor Based on Sol-Gel Doped New Luminescent Europium Chelate

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962 - Surface finishing of enamels by Sol-Gel coating

Marta Krzyzak, University, Germany
Günther H Frischat, Institut für Nichtmetallische Werkstoffe, Technische Un, Germany
Peter Hellmold, Germany

963 - Correlation between ionic conductivity and local dynamical behavior of cathions in lithium-doped Siloxane-Polyethers hybrids during gelation

Ana P Sacco, Karim Dahmouche, Celso V Santilli, Sandra H Pulcinelli, Instituto de Química-Universidade Estadual Paulista, Brazil

964 - Pneumatic Transport of Sol-Gel Microspheres of Uranium Oxide

Suryanarayana Saripalle, J Radhakrishna, Vinod R Ganatra, T V Vitalrao, N Kumar, Sapan K Mukerjee, Vijay N Vaidya, D Sathiyamoorthy, Bhabha Atomic Research Centre, India

966 - Effect of Synthesis Parameters on Sol-Gel Silica Modified by Zirconia

Gerardo R Rodriguez-Avendaño, Jose A de los Reyes, Tomas Viveros, Universidad Autónoma Metropolitana-Iztapalapa, Mexico

Jose A Montoya, Instituto Mexicano del Petroleo, Mexico

969 - Effect of concentration of diazoalcene molybdenum complex immobilized in hybrid matrix

Natercia P Nunes, A M Fonseca, Carlos J R Silva, Isabel C Neves, University of Minho, Portugal

970 - Mass spectroscopic characterization of MOD precursors of $\text{SrBi}_2\text{Ta}_2\text{O}_9$

Gerardo González Aguilar, M Elisabete V Costa, CICECO, DECV Universidade de Aveiro, Portugal

Isabel M Miranda Salvado, Universidade de Aveiro, Portugal

971 - Investigation of $x\text{Al}_2\text{O}_3 \cdot (100-x)\text{SiO}_2$ ($x=2,3,4,6$, and 8) samples structure

Maria Gracinda Ferreira da Silva, Portugal

972 - Progress towards Increasing the Laser Induced Damage Threshold (LIDT) of 'Pick off' Mirrors used in the Multipass Configuration of the Helen Laser at Awe by the Deposition of Sol-Gel Protective Layers

Nick J Bazin, AWE plc. Aldermaston, United Kingdom

J E Andrew, United States

J C Watson, United Kingdom

973 - Photoluminescence of Sol-Gel Hybrid Films Doped with Erbium Tris 8-Hydroxyquinoline

Oun-Ho Park, Jerome Pinot, Byeong-Soo Bae, Korea Advanced Institute of Science and Technology, Korea

974 - Sol-Gel Fabrication of High Quality Photomask Substrates

Rahul Ganguli, Larry Meixner, Steven Colbern, Matt Gleason, Mark Morris, YTC America Inc., United States

Satyabrata RayChaudhuri, United States

975 - Modification of Thermo-Optic Characteristics of Inorganic-Organic Hybrid Materials for Athermal Waveguide Application

Eun-Seok Kang, Woo Soo Kim, Kwang Soo Kim, Byeong-Soo Bae, Korea Advanced Institute of Science and Technology, Korea

976 - Sol-Gel Processed Functional Nanosized TiO₂ - Based Films for Photocatalysts and Other Applications

Aleksej A Chuiko, Anna M Eremenko, Natalie P Smirnova, Irina Petrik, Natalie Surovtseva, Vladimir Gayvoronskii, National Ukrainian Academy of Sciences, Ukraine

977 - The Effect of Copper Doping on Photo-induced Reaction of Titania Photocatalytic Film

Toshiya Watanabe, Hisashi Ohsaki, Naoya Yoshida, RCAST, The University of Tokyo, Japan

Yasuyuki Takada, Masataka Masuda, Kyushu University, Japan

978 - Conductive Sol-Gel Emulsion for Preparing Surface for Powder Coating

Chhiu-Tsu Lin, Northern Illinois University and ChemNova Technologies, United States
Sonic Fang, Green Products Inc., Taiwan, Province of China

979 - Upconverting Nanophosphors by Sol-Emulsion-Gel Technique

Amitava Patra, Sol-Gel Division, Central Glass & Ceramic Research Inst, India

980 - Sol-Gel Coatings of Metal Oxides on Nano TiO₂ electrodes in Dye-Sensitised Solar Cells

David Menzies, Raoul Cervini, Yi-Bing Cheng, George Simon, Leone Spiccia, Monash University, Australia

981 - Incorporation of Tris (di-phenyl-phenanthroline) Ruthenium (ii) Complex in Dense Silica Microspheres and their use in a Film-Membrane as a Carbon Dioxide Sensor.

Beatrice Launay, Philip Bowe, C Von Bultzingslowen, Aisling McEvoy, Brian D MacCraith, Dublin City University, Ireland

Colette McDonagh, National Centre for Sensor Research, Ireland

982 - The preparation and electrical properties of SrTiO₃-based Capacitor-varistor double function ceramics

Lili Zhao, Junsan Yang, Chunxue Zhai, Xuewen Wang, Zhiyong Zhang, Northwest University, China

983 - Sol-Gel Technology in Gas Chromatography

Jana Habsuda, SGE International Pty Ltd, Australia

Gerard Sharp, Angus Hibberd, Peter Dawes, Australia

Orals Abstracts

KEYNOTE LECTURERS

K1 - Sol-Gel Processing of Complex Functional Materials

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Nature combines hard and soft materials often in hierarchical architectures to get synergistic, optimized properties and combinations of properties with proven, complex functionalities. Emulating such natural material designs in robust engineering materials using efficient processing approaches represents a fundamental challenge to sol-gel chemists. We are investigating the combination of sol-gel processing with chemically- and mechanically-based self-assembly strategies to create nanocomposites in thin film and particulate forms. This presentation will first review our progress on evaporation-induced silica/surfactant self-assembly to prepare porous thin film nanostructures of interest for membranes and low K dielectrics. I will then describe new work where we use surfactant self-assembly to simultaneously organize hydrophilic and hydrophobic precursors into hybrid (organic/silica or metal/silica) nanocomposites that are optically or chemically polymerizable, patternable, or adjustable. For example, the co-self-assembly of amphiphilic photoacid generators with silica precursors results in photosensitive thin film mesophases in which the pore size, pore volume, surface area, and refractive index may be continuously varied over a range depending on the UV exposure time. Incorporation of switchable hydrogel or azobenze moieties provides a means to create nanostructures exhibiting chemo-, thermo- or opto-mechanical actuation. Biocompatible self-assembly allows us to immobilize cells in a robust self-contained, self-sustaining environment of interest for stand-alone cell-based sensors. As a new direction, we have exploited mechanically-based self-assembly to create superhydrophobic, fractal silica surfaces mimicking those of the Lotus leaf and desert beetle. These surfaces are self-cleaning and fundamentally affect flow, making them of general interest for fluidic-based microsystems.



K2 - The Integration of Sol-Gel Science in Nanobiotechnology

Bruce Dunn, University of California, Los Angeles, United States

One of the most dramatic themes in the emerging field of nanobiotechnology is the integration of engineered materials, structures and devices with biomolecular components, and their assembly into hybrid systems. This nanobiotechnology direction offers the promise of creating "cell mimetic" systems which consist of sensors, actuators and energy sources that are linked with information processing. These systems are designed to be autonomous, self-healing, functional over multiple length scales, and capable of feedback and control. Among the applications envisioned are health monitoring, sensor/transducer networks and chip level bio-analytical laboratories.

Sol-gel derived materials are likely to play a significant role in this nanobiotechnology effort. As a "bottom-up" fabrication strategy, sol-gel methods enable one to design materials to possess specific properties and microstructures at dimensions on the order of 1 to 100 nm. These materials provide the technological building blocks for the hybrid system. Sol-gel synthesis of nanoparticles is one significant direction as there is the ability to create materials with interesting optical, electronic and catalytic properties which couple to biomolecules. A second direction is the use of sol-gel methods to encapsulate a wide variety of biomolecules ranging from enzymes and other proteins, to antibodies, DNA and whole cells.

This presentation will review selected areas where sol-gel methods have demonstrated properties that can be utilized in nanobiotechnology applications. Some of these areas are at the individual component level; nanoscale power conversion and generation, energy harvesting, sensing and bio-amplification. Other results demonstrate the feasibility of using sol-gel methods to contribute to system architecture. These functions include bio-templating, supramolecular assembly and interconnects. Future directions for extending sol-gel methods in nanobiotechnology will be presented.

K3 - Advances in Characterisation Methods – Multiple Length Scales Across Multiple Disciplines.

Florence Babonneau, Chimie de la Matière Condensée, UPMC, Paris, France.

For many years, structural characterization of sol-gel oxide materials, was a real challenge because, of a lack in most cases, of long range order that prevents the use of X-ray diffraction techniques. Solid state Nuclear Magnetic Resonance (NMR) thus becomes more and more widely developed to probe the local environment of various network isotopes, among them ^{29}Si , ^{27}Al , ^{31}P , ^{11}B , ^{23}Na ... A first breakthrough occurred in this field with the first publications on ^{17}O solid state NMR. This isotope was for a long time a real challenge because of its low natural abundance and quadrupolar character. The possibility to prepare enriched samples and to use the newly developed sequence called MQ-MAS (Multi-Quanta Magic Angle Spinning) provided a route to resolved ^{17}O MAS-NMR spectra, and thus to a fine description of the various oxo-bridges present in the network, a first access to medium range order in sol-gel derived oxide-based materials.

Currently a large part of the sol-gel studies are devoted to the so-called hybrid materials with an increasing complexity in the structures. Here not only the two components, inorganic and organic, have to be characterized but also their respective spatial distribution and the possible interactions between them. The increasing number of high magnetic field spectrometers and the access to high spinning rate MAS probes make now possible the recording of high resolution ^1H MAS-NMR spectra. This opens the way to experiments that provide extremely precise information regarding spatial distribution of sites such as two-dimensional heteronuclear correlation experiments or double quantum ^1H experiments.

In the design of new hybrid structures, amphiphilic templating agents with various size, shape, charge density are now playing an increasing role. Their possibilities to self-organize in periodic assemblies provides a way to introduce long-range order in the final hybrid materials that can be characterized by small angle X-ray diffraction. Access to synchrotron radiation opens the way to time resolved experiments which are extremely useful in understanding the formation mechanism of these complex structures.

All along this presentation, examples will be given to illustrate which structural characterization techniques are currently available to characterize over various length scales the structure of a large variety of sol-gel derived materials.



I-1 - Geometrical Molecular Structure Design Concept in Approach to Homo- and Heterometallic Precursors of Advanced Materials in Sol-Gel Technology

Vadim G Kessler, Swedish University of Agricultural Sciences, Sweden

Gulaim A Seisenbaeva, Pia Werndrup, SLU, Sweden

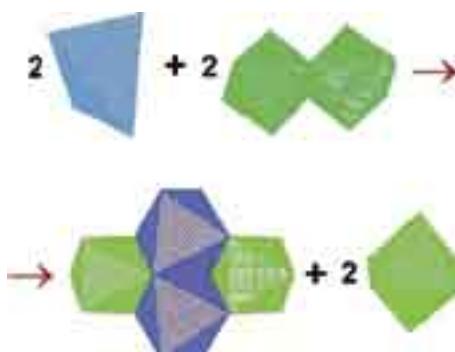
Stephane Parola, Universite Claude Bernard Lyon 1, France

General principles of formation and stability of the heterometallic alkoxides existing due to Lewis Acid-Base interaction, isomorphous substitution and heterometallic metal-metal bonds are discussed. The molecular structure design approach based on the choice of a proper molecular structure type and completing it with the ligands, providing both the necessary number of donor atoms and the sterical protection of the metal-oxygen core, is presented. Its applications in prediction of the composition and structure of single source precursors of inorganic materials are demonstrated for such classes of compounds as oxoalkoxides [1], alkoxide beta-diketonates [2], alkoxide carboxylates, derivatives of functional alcohols, metallatranes and metallasiloxanes [3]. Precursor role in preparation of fine powders and films of oxide materials such as spinels and late transition metal tantalates and niobates, metal materials such as rhenium-based alloys for high temperature resistant construction elements and sulfide materials for catalytical applications is discussed.

[1] Seisenbaeva G.A., Shevelkov A.V., Tegenfeldt J., Kloot L., Drobot D.V., Kessler V.G., Dalton Trans., 2001, 2762.

[2] Kessler V.G., Gohil S., Parola S., Dalton Trans., 2003, 544.

[3] Kessler V.G., Chem. Commun. (Feature Article), 2003, in press (DOI: 10.1039/b209168m)



I2 - Monolithic silica and carbon exhibiting three-modal, hierarchical porosity

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Monolithic silica exhibiting a trimodal, hierarchical pore structure has successfully been prepared via sol-gel-processing using a mixture of two structure-directing agents. Monolithic bodies with interconnected macropores in the micrometer range are a result of controlled phase separation and gelation kinetics, whereas textural mesopores in the 10-20 nm range originate from voids between particles. Furthermore, the particles exhibit internal mesoporosity with pore diameters in the 2-4 nm range originating from supramolecular templating by the surfactant. Poly(ethylene glycol) has been used together with alkylammonium or block-co-polymer surfactants to control the particle aggregation and internal structure, respectively. All three modes of porosity can be controlled independently from each other by adjusting the composition of the starting sol or the post-treatment conditions. The present work sheds light on the mechanism of formation of the complex framework architecture. Furthermore, the silica monoliths have been used as a mold for nano-casting of carbon, and carbon monoliths exhibiting interconnected, hierarchical macro-and mesopores with a controlled pore-size can be synthesized in a straightforward manner. These results open up the possibility to prepare inorganic, non-siliceous monoliths with a hierarchical pore-structure using the monolithic carbon as the mold for back-replication.



I3 - Organofunctional Metal Oxide Clusters as Building Blocks for Inorganic-Organic Hybrid Materials

Ulrich Schubert, University of Technology, Austria

Various (meth)acrylate-substituted metal oxide/alkoxide clusters of the general formula $M_xO_y(OH)_u(OR)_v(OOCR)_w$ ($M = Ti, Zr, Hf, Ta, Ti/Zr, Ti/Hf$) with various compositions, structures, diameters and shapes were obtained by reacting metal alkoxides with (meth)acrylic acid. The type of obtained cluster depends mainly on the metal alkoxide/carboxylic acid ratio and the kind of alkoxide groups of the parent metal alkoxide. The method is based on a self-limiting assembly of molecular building blocks and the in-situ generation of water by ester formation. The clusters differ by the mutual connection of the metal polyhedra. In each case, the metal oxide cluster core – with dimensions between 0.7 and 1.8 nm – is capped by the (meth)acrylate ligands, which are fully accessible for polymerization reactions.

Radical polymerization of small proportions of the clusters (0.5 – 2 mol%) with unsaturated organic co-monomers (methylmethacrylate, acrylic acid, styrene, etc.) results in inorganic-organic hybrid polymers in which the clusters crosslink the polymer chains. Glassy materials were typically obtained upon copolymerization of the clusters with MMA, while copolymerization with MA resulted in insoluble powders with high specific surface areas. EXAFS and SAXS measurement showed that the structural integrity of the clusters is preserved upon polymerization. Depending on the cluster type, either a statistical distribution of the clusters in the polymer or some aggregation was observed.

The swelling behavior in organic solvents, the thermal stability, the dielectric properties and the mechanical properties of the polymers are distinctly changed by incorporation of the functionalized clusters. The properties depend on the cluster portion in the polymer and also – to some extent – on the kind of cluster.

I4 - Hybrid materials with polymerisable organic functional groups: a structure-property outlook

Plinio Innocenzi, Università di Sassari, Italy
Giovanna Brusatin, Università di Padova, Italy

Hybrid organic-inorganic materials are an interesting example of materials where the importance of basic understanding of the detailed mechanisms of synthesis and structure is playing a crucial role in the development of the applications. A real homogeneity at molecular level is closely bounded to the performances of the final material and this is particularly true in photonics.

Different examples in the design of hybrid materials containing polymerizable functional groups will be presented and correlated with their mechanical and optical properties. The structure of the materials has been investigated by spectroscopic techniques (FTIR and FT-Raman) coupled with multinuclear magnetic resonance. New synthetic routes to hybrid materials containing epoxy functionalities will be presented, in particular the possibility to modulate the opening of the epoxy and the extension of the polymerisation will be shown.

Non-hydrolytic synthesis represents a possible option to control the opening of the epoxides, optical limiting applications of this specific material have shown a significant increasing of the performances. Many of the properties of the hybrid materials appear, in fact, controlled by the extent of the epoxy reactions and the formation of polyethylene chains of different length.

Another group of photopolymerizable hybrid materials is based on organically modified alkoxides of the type of 3-methacryloxypropyltrimethoxysilane and is one of the most popular precursors to synthesise hybrid material. Basic synthesis of these materials co-hydrolyzed with organically modified alkoxides bearing amine functionalities have shown specific features in the microstructure and at the same time become a tailored environment for organic guest molecules sensitive to acidic conditions.



I5 - New Approach for the Organisation and the Shaping of Organo-Bridged Silicas

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The Sol-Gel synthesis of bridged silsesquioxanes ($O_{1.5}-Si-R-SiO_{1.5}$; R = organic fragment) represents a fascinating bottom-up approach for the obtention of new hybrid materials. Owing to the mild reaction conditions of this process, interesting properties may be tuned to these hybrids according to the incorporated organic fragment. These materials are of high potentials and have already found application in many fields of interests such as heterogeneous catalytic systems, NLO materials and solid phase extraction or separation. These sought-after properties are mainly due to the intrinsic properties of the organic unit.

Numerous efforts are now being paid to prepare these materials with targeted morphologies, and also with high structuration in order to improve and to control their properties on different size scales. Periodic mesoporous bridged silsesquioxanes have been prepared using the surfactant-mediated method but until now these are limited to small organic bridging units and are exclusively synthesized in the presence of external surfactants.

A new and general route to shape-controlled hybrid silicas has been developed. The hydrolysis-condensation of multifunctional organobridged alkoxy silanes bearing urea groups has been studied. Through the hydrogen bonding of the urea units, these molecularly designed organosilanes tend to self-assemble into supramolecular architectures. By judicious hydrolysis of the self-organized molecular precursors, bridged silsesquioxanes with variable morphologies (fibers, spheres, tubes and sheets) have been obtained. The organic fragment directs the particular shape of these hybrids which can be amorphous but can also present a periodicity. The mechanistic formation of these self-assembled hybrid silicas has been elucidated and will be presented.

I6 - Templated Synthesis of Non-Silicate Metal Oxides

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This paper presents an overview of a new class of metal oxide crystallites in porous frameworks using block co-polymer as template. Two examples of such nanocrystalline particles – TiO_2 and ZrO_2 will be discussed. The synthesis of mesoporous TiO_2 involves a two-step sol-gel method. The first step of the process involves hydrolysis of titanium isopropoxide in a basic aqueous solution mediated by neutral surfactant. The solid product obtained from Step-1 was then treated in an acidified ethanol solution containing the same titanium precursor to thicker the pore walls. Low pH and higher loading of the Ti-precursor in Step-2 produced better mesoporosity and crystallinity of titanium dioxide polymorphs. The resultant powder exhibited a high surface area and large pore volume with uniform mesopores.

For ZrO_2 synthesis, a modified solid-state reaction method is used with polymer PEO as the template followed by hydrothermal treatment. The resultant nanocrystalline ZrO_2 exhibits strong diffraction peak at low 2-theta angle and their nitrogen adsorption/desorption isotherms are typical of IV type with H3 hysteresis loops. The tetragonal zirconia nanocrystals are uniform in size (around 1.5nm) and their mesopores focus on around 4.6nm. The zirconia nanocrystal growth is tentatively postulated as an aggregation mechanism. This study also reveals that the PEO template can interact with the Zr-O-Zr framework to reinforce the thermal stability of zirconia. The ratio of NaOH to ZrOCl_2 , crystallization and calcination temperature play an important role in the synthesis of mesoporous ZrO_2 . Cu-supported on such Zirconia was tested for methanol synthesis and was found very active and better than commercial methanol catalysts.



I7 - New Sol-Gel Routes for High-Permittivity Thin Film Preparation

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Delphine Veautier, Chimie de la Matiere Condensee (UMR 7574 / UPMC), France

Clément Sanchez, Universite P.M. CURIE PARIS, France

Meeting the further miniaturization in today's microelectronics industry requires development and control of reliable processes for making thin film capacitors. In this paper, results will be reported on the sol-gel development of new generation high-K dielectric materials. Development of high dielectric constant thin film capacitor based on ferroelectric lead-zirconate-titanate (PZT) has been previously reported in the former Sol-Gel conference held in Padova. Since that time, our work has been focused on the preparation of La-doped PZT (PLZT) solutions for performance optimization purpose. Same efforts have been devoted to synthesize a moisture non-sensitive, highly stable, long-term shelf life solution leading to reproducible coating properties. Ripening time of the sol highlighted using FTIR and viscosity measurements has been considered to be a sign for process repeatability. Ability to synthesize such a robust PLZT solution has allowed deposition of the same optimized film thickness per coating, and consequently has produced reproducible high dielectric property per film. Rapid annealing (2 min.) of PLZT final stack was performed at 700°C to achieve perovskite phase crystallization. The as-developed PLZT solution has achieved high-performance thin film capacitor (dielectric constant of 1000 and capacitance value of 50 nF/mm²) with film thickness as low as 0.2 µm. Nevertheless, although PZT or PLZT are considered to be the best perovskite materials for dielectric property, use of lead-based material will be short-term reproved in the microelectronics industry. That is why we also reported here preparation of $Ba_xSr_{1-x}TiO_3$ (BST) thin films by the sol-gel route. Barium, strontium and titanium best precursors have been selected regarding the formation of the pure perovskite crystalline phase after a 700°C densification step. Synthesis reproducibility and stability of the solution during a period of several months were checked. Structural characterizations (FTIR, XRD, TEM/SEM) and electrical properties were performed onto thin films deposited on Si/Pt 6 inches substrates. BST thin films with a capacitance of 20 nF/mm² have been thus obtained.

I8 - Development of interference multilayer systems on plastic foil by a wet-web coating technique

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A new continuous roll-to-roll coating technique for plastic foils has been developed for the preparation of dielectric interference multilayer systems. Such interference multilayer systems on plastic foil like anti-reflective coatings, near-infrared reflective or visible light reflective coatings have an interesting application potential in the field of displays and also as laminating foils for flat glass in the architectural or automotive sector.

The coating sols consist of SiO_2 - and TiO_2 nanoparticles respectively with polymerizable surface ligands like epoxysilanes or epoxide resins, disposed in isopropanol. The coatings are prepared using a 60 cm wide coating line, running with a line speed of about 1 m / min under clean-room conditions. As a coating technique, an offset-reverse coating setup using polished stainless steel rolls is investigated. The coatings are dried and cured within 2 min at 130° C. The homogeneity of the coating thickness is characterized by vis-reflectance spectroscopy. As examples, a 2-layer antireflective coating with a residual reflectance < 1 % and a 3-layer antireflective coating with a residual reflectance < 0.5 % on triacetate (TAC) foil is presented. Furthermore the preparation of a 3-layer green filter and the design of a NIR reflectance filter is shown. The durability of the multilayer system is investigated by steel-wool scratch tests and different climate tests.

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I9 - Sol-Gel Encapsulation of Molecules to Generate Functional Optical Materials

Bakul C Dave, Jenny Ottosson, Southern Illinois University, United States

Design of molecular materials for device applications depends on two factors: a) selection of molecules which exhibit well defined electronic or optical response, and b) assembly of these molecular components into a geometric structure that retains the rigidity, addressability, and stability necessary for practical applications. In this presentation, the strategy of sol-gel encapsulation of photo- and redox-active bio/molecules will be described for generating specific functional responses. The approach is based on using molecules as active species and sol-gel glass as structural matrix in which the molecules are selectively integrated. These materials are addressable by means of an applied stimulus. A designer approach that employs specific molecules for generating optical signals will be described. Model examples based on using these composite materials as prototype transient optical memory devices will be presented.

I10 - Self-Photopatterning of Photosensitive Sol-Gel Hybrid Materials for Fabrication of Micro-Optic Devices

Byeong-Soo Bae, Korea Advanced Institute of Science and Technology, Korea

Photosensitive materials making permanent refractive index change or surface modulation following by optical exposure is exploited in the fabrication of waveguides, gratings and holograms by producing microstructures on surfaces in many micro-optic applications. The sol-gel hybrid materials (HYBRIMER) in which the photosensitivity mechanisms in both of inorganic and organic materials can be applied can create high photosensitivity producing large light induced refractive index change accompanying with formation of surface microstructures. It will give the simpler technique of self-photopatterning to fabricate the micro-optic devices, which excludes the developing process. Recently, we reported various types of high photosensitive HYBRIMERS using different photosensitivity mechanisms of inorganic and organic groups in the HYBRIMER. The micro-optic devices were fabricated by the self-photopatterning using a photomask, a phasemask, and an interferometer.

Photochemical species like photoinitiators were locked or fixed inside the HYBRIMER molecular structure by light illumination. This resulted in higher refractive index and thickness of the photo-exposed region. Channel waveguide devices can be directly fabricated without using any developing process, which is called photochemical self-developing (PSD) process. Gratings were also imprinted directly by the laser interferometer.

Ge-doped HYBRIMER showed very large volume reduction as well as refractive index increase by light induced densification of silica structure. Combining photopolymerization of organics enhanced the photosensitivity. Surface relief micro-patterns with refractive index modulation were imprinted so that the fabrication of the micro-lens array was demonstrated.

Methacrylate in the HYBRIMER was photodecomposed to remove polar organics for the refractive index and the film thickness to be reduced. Self-photopatterning of low refractive index and dielectric constant film was made to fabricate the grating and the antireflective coatings by laser interferometer or phasemask.



I11 - Recent advances in the application of sol-gel materials for biochemical and biomedical applications

David Avnir, Jochanan Blum, Sharon Fireman-Shoresh, Hagit Frenkel, Faina Gelamn, Hebrew University, Israel
Sharon Marx, Institute of Biological Research, Israel

We continue to explore applications of sol-gel materials for biochemical and medical purposes. Recent advances from our laboratories in this area will be reviewed. Examples include:

I. The development of chirally imprinted sol-gel thin films for enantioselective recognition of bioactive molecules. Here we developed a general methodology for the chiral imprintability of submicron composite sol-gel films, and demonstrated their enantioselectivity under steady-state conditions. Several enantiomeric pairs were tested, with which two key analytical tools were used, namely fluorescence and radiolabeling. An example is the antihypertensive drug (S)-(-)-Propranol and its (R)-(+)-enantiomer, for which all four possible diastereomeric adsorption complexes (the (S)-drug with (S)- or (R)-imprinted surface; and the (R)-drug with these imprinted surface) were compared by the two analytical methods. In general, we showed that the sol-gel matrix is an excellent substance for tailoring specific film-adsorption and separation characteristics via molecular imprinting. The porosity, homogeneity and the ease of fabrication and stability are just some of its advantages. It was also found that molecular imprinting of sol-gel thin film is advantageous over the classical imprinting of acrylic polymers, not only because of its facile preparation, but also due to better kinetics, low non-specific adsorption and high association constants.

II. The application and development of sol-gel materials as protective matrices for enzymes under usually destructive conditions. An example for protection under such conditions is the demonstration of the ability to carry out enzymatic reactions in the presence of catalysts, which inhibit the activity of the enzymes under homogeneous conditions. Thus, sol-gel entrapped lipase remained active in the presence of the hydrogenating catalyst $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$, which itself was entrapped in another sol-gel matrix; both were used in the same reaction pot for the consecutive esterification and C-C double bond hydrogenation, leading to a variety of saturated esters.

I12 - Synthesis of Bioactive and Porous Organic-Inorganic Hybrids and their Biomedical Applications

Akiyoshi Osaka, Kanji Tsuru, Okayama University, Japan
Satoshi Hayakawa, Japan

Bioactivity has been exhibited by a number of ceramic materials since the invention of Bioglass®. Recently, some bioactive polymeric organic-inorganic hybrids have been introduced, including organically modified silicates (Ormosils). When porosity is introduced, the hybrids with biodegradability and tissue-bonding ability (bioactivity) are so useful and applicable for scaffolds for tissue regeneration. The hybrids involving gelatin, chitosan, polydimethylsilane, or some silane-coupling agents have been prepared. Their polymeric structures analyzed by Si NMR spectroscopy will be presented. Freeze-drying technique has been taken to introduce porosity to them. Another method of using sucrose or sodium chloride granules is applicable. Biodegradability in the Kokubo's simulated body fluid or lysozyme solution is controllable for the gelatin or chitosan porous hybrids. Some cells are adequately proliferated on the porous Ormosils. In vitro bioactivity or apatite deposition in the simulated body fluid will also be described for those solid and porous hybrids.



I13 - Enhanced Optical Sensor Performance via the Sol-Gel Process

Brian D MacCraith

National Centre for Sensor Research

Dublin City University

Ireland

This presentation will deal with recent advances in the optimisation sol-gel-derived materials for optical sensor applications. In particular, it will report on key developments in the area of printable, fluorescent sensor films for a range of applications including intelligent food packaging and biomedical monitoring. A novel formulation for carbon dioxide sensing, involving a MTEOS host matrix and doped sol-gel microspheres, will be described in detail. Data on Screen-printed, Inkjet-printed and spray-coated oxygen sensor films will also be presented. Recent developments in the area of ormosil host matrices with enhanced stability will be reported. Finally, the use of photopatternable hybrid sol-gels to produce novel platforms for sensor applications will be described together with performance data. Overall, the design flexibility inherent in the sol-gel process will be highlighted as an important feature in producing optimised sensor materials.

I14 - Fast proton conduction in the sol-gel-derived glasses and their application to the fuel cell electrolytes

Masayuki Nogami

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Japan

We have investigated the proton conductivity of the sol-gel-derived glasses. The glasses, prepared through the hydrolysis of the metal alkoxides, are porous, the pore surfaces of which are terminated with hydroxyl bonds and absorb water in a humid atmosphere. We found that the conductivity is proportional to the logarithm of the number of hydroxyl bonds and adsorbed water. The proton conduction is promoted by the dissociation of proton from hydroxyl bonds on the pore surfaces and the proton hopping between hydroxyl groups and water molecules. The effect of the pore-size and the glass constituents on the proton conduction was also investigated. In glasses having pores with size smaller than ~5 nm, the water molecules totally fill the pores, in which the motion of the water molecules is restricted in the pore, which result in the increase of conductivity. The incorporated phosphorous ions are concentrated on the pore surfaces, forming the POH bonds. The POH bonds are appreciated for increase the proton conduction, because that the proton in the POH group is strongly hydrogen bonded with the water molecules. The conductivities of these glasses follow the Arrhenius equation in the temperature range of -30°C to 150°C with the activation energy of ca 10kJ/mol. The conductivity at -25°C and 150°C was ca 10 and 170 mS/cm, respectively. These high proton-conducting glasses have potential for use in the field of fuel cells operating at temperature from -30 to 150°C.



O1 - Electronic State and Photosensitivity of Metal Alkoxides Chemically Modified with β -Diketones

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Naoki Noma, Kinki University, Japan

Electronic state and optical absorption spectra of metal alkoxides stabilized with β -diketones which had various substituents were calculated by the DV-X \leftrightarrow cluster methods. Fig. 1 shows a $\text{Ti}(\text{O}-\text{sec-Bu})_4$ model cluster of stabilized with 1-phenyl-1,3-butanedione, which is an example of model clusters. The origin of the optical absorption and the mechanism of the decomposition reaction of alkoxides with irradiation of light were discussed. The position of the first peak observed near UV region in the theoretical optical absorption spectra corresponded to that in the experimental ones. Energy gap between HOMO and LUMO in the alkoxides became smaller with longer conjugated system of the substituent in β -diketones. The main component of the first absorption peak observed in visible range was the transition to antibonding molecular orbitals mainly composed of the chelate ring. The results suggest that optical absorption of the gel film could be controlled by the length of the conjugated system of substituent in β -diketones, and the bonding nature of chelate rings should be important to understand the photosensitivity of the chemically modified titanium alkoxides.

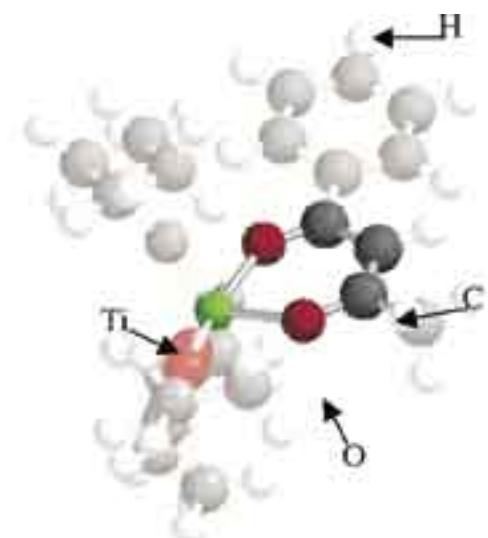


Fig. 1 Model of $\text{Ti}(\text{O}-\text{sec-Bu})_4$ cluster stabilized with 1-phenyl-1,3-butanedione

**O2 - Mixed oxide materials prepared from a single source precursor:
A time resolved SAXS study of the gelation and the calcination
process**

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Nicola Hüsing, Technische Universität, Austria

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Ulrich Schubert, Vienna University of Technology, Austria

Mixed metal oxide materials are of considerable importance for applications in catalysis and sensing. For many applications a controlled tailoring of the chemical and physical properties, and in addition a thorough understanding of their microstructure is needed. More precisely, a deliberate positioning of the different building blocks (metal oxides) already during the first synthesis steps is required. For purely silica based materials the evolution of the microstructure is well understood and a good control over the formation of the inorganic network can be achieved by an adequate choice of the precursor. However, when two or more different precursors are involved in the inorganic network formation, as in mixed metal oxide systems, the formation of the network becomes much more complex due to the different reaction rates of the various precursors, often resulting in a non-statistical arrangement of the different building blocks.

In the present work a novel way for the formation of mixed metal oxide gel networks is investigated by *in situ* SAXS measurements. A tailored bimetallic precursor is applied in sol-gel processing such as aluminum- and titanium-alkoxides chelated by acetylacetone-propyl-trimethoxysilane. This chelation has two consequences: a) the hydrolysis and the condensation rates of the transition metal alkoxide are reduced, and b) due to the coupling of the different components macroscopic phase separation cannot occur. Gel monoliths were prepared from this precursor and *in situ* SAXS spectra were recorded during the gelation process and during the calcination of the obtained aero- and xerogels up to 600°C.



O3 - Sol-Gel Single-Source Precursors to Functional Materials

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Smart nanocomposite materials merging different functionalities represent one of the most outstanding challenge for innovative applications. To develop nanostructured devices, the capability to control composition and microstructure of the nanocomponents is required. In the case of thin films embedding functional clusters, a homogeneous distribution of the doping particles inside the film is necessary to ensure the desired performances of the material. The design of suitable sol-gel precursors as nanosized “building block” represents an important task for the development of both composite materials consisting of nanoscopic semiconductor crystals embedded in dielectric host matrices, and of functional groups endowing the material with special functionality, such as fluorescence. The former materials find wide application in optics, the latter can be used as selective solid-state sensors for selected ions. Because of these considerations, we have developed five different single-source sol-gel precursors. To prepare metal sulfide-doped silica, suited single-source compounds bearing both silica and sulphide precursors are very advantageous. The thiourea moiety anchors the metal cations (i.e. Zn²⁺) directly to the forming silica network via M-S interactions and it is, in addition, the sulphur source. Consequently, the chosen precursor provides in principle a “molecule-to-nanocomposite” strategy to nanocomposite materials. Within the presented project we have synthesised and fully characterized through complementary methods (IR, NMR, X-Ray diffraction, ESI-MS, thermal analyses) three thiourea-functionalised silanes: (EtO)₃Si(CH₂)₃NHC(=S)NHPH, 1,4-[(EtO)₃Si(CH₂)₃NHC(=S)NH]2Ph and (MeO)₃Si(CH₂)₃N[C(S)NH(C₆H₅)](CH₂)₂NH[C(S)NH(C₆H₅)]. The embedding of fluorescent solid state sensors in silica was instead faced through the synthesis of two siloxanes: one bearing a fluorescent group, the dansylamide, (EtO)₃Si(CH₂)₃NHSO₂C₁₀H₆NMe₂ (Dns-APTES) the second having a pyridine group (EtO)₃Si(CH₂)₃NHCOC₅H₅N (2-Pic-APTES). Their coupling represents an efficient system for the sensing of metal ions and their embedding in a silica matrix enables the devise of a “molecule-to-material” route to solid-state sensors.



O4 - Wide-band acoustic characterization of a sol-gel matrix

C. Ould Ehssein, L Martinez, S Serfaty, K Melzak, P Griesmar, G Gouédard, Marcel Gindre, France

The sol-gel transition is monitored by five acoustic methods from the subsonic domain (0.1 Hz) to the high frequency domain (100 MHz). The sol-gel material studied is a silica based material elaborated under basic catalyst. Rheology is used to measure the viscoelastic constants G' and G'' in the subsonic range (0.1 Hz). In the audible frequency range (50 Hz-20 kHz), sound velocity through the gel matrix is recorded by a PC with a classical speaker/microphone system. In the 1MHz region, ultrasonic immersion transducers are used to measure Time Of Flight (TOF) through the material. A quartz crystal microbalance is used in the 1 to 30 MHz domain and the viscoelastic parameters G' and G'' are deduced from the equivalent impedance model. In the 100 MHz range, a Surface Acoustic Wave (SAW) sensor is used to measure the TOF of SAW propagating at the quartz/sol-gel interface. The viscoelastic constants or propagation speeds are deduced from these 5 methods. In all the cases the time evolution of the measured parameters gives the same gelation time. The G' and G'' time evolution measured at 0.1 Hz and 5 MHz are close and clearly exhibits the liquid to solid transition of the gel. The TOF compressional sound velocity measurement performed in the audible frequency range and in the 1MHz range exhibits two different speeds. In the 1MHz range, the gel has a compressional speed close to the speed of sound in the main fluid (1200 m/s) whereas in the audible frequency range, the compressional speed is close to 15 m/s. In the 100 MHz range, fast changes of the optical aspect of the gel like opacity or cluster growing are observed on the acoustic response. A special attention is given to link these five acoustic methods to the space scale investigated in the sol-gel matrix: macroscopic (0.1 Hz), mesoscopic (50 Hz-20 kHz or 1 MHz) and microscopic (5 MHz or 100 MHz).



05 - All alkoxide Sol-Gel route to CoO-TiO₂ nano-powders

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Kjell Jansson, Arrhenius Laboratory, Sweden

Co-TiO₂ materials as homogeneous and nano-composites of TiO₂ and Co metal or oxide has become of very high interest during the last year due to their potential in room temperature functioning spintronics. Very recent studies on Co-doped (<8 atom%) anatase thin films prepared by physical techniques have shown ferromagnetism magnetism in some cases, while in other cases no magnetism were observed. There is still much uncertainty of the origin and even of the detailed structures of these materials, such as if the doping is homogeneous or heterogeneous, which coordination and oxidation state the cobalt atoms possess. The observations made so far have been quite diverse ranging from homogeneous Co²⁺ doping in anatase to 50 nm sized Co-metal clusters in low doped anatase. Therefore, it is of importance to study these materials with processing routes that allows for detailed construction of e.g. homogeneous and different nano-structured oxides. One of the strongest candidates to this is sol-gel processing based on reactive alkoxides that allow for complete removal of all organic parts by hydrolysis at room temperature, and thereby give great possibilities to control the formation of phases and crystal sizes during heat-treatment.

We have prepared and studied Co-oxide doped TiO₂ nano-powders with 0-12 atom% Co, by an all alkoxide based route using Co-methoxy-ethoxide and Ti(OPr)₄. The amorphous precipitates or gels were heat-treated in air to yield the nano-particle anatase phase at temperatures below 500°C. It was found that complete removal of the organic parts was essential for the synthesis of phase pure anatase and that phase separation occurred within the ca 20 nm sized Co-TiO₂ particles into one more and one less Co-rich part at 600°C. The studies on the reactions taking place on heating and the phase contents of materials quenched from different temperatures were studied by; thermo-gravimetry, IR- and Raman spectroscopy, X-ray diffraction and in some cases with TEM-EDS and SEM. The magnetic properties will be briefly described compared with those of the corresponding films.

O6 - Synthesis of Organic-Inorganic Hybrid Particles by Sol-Gel Chemistry

John N Hay, Anna Arkhireeva, Miguel Manzano, University of Surrey, United Kingdom

Steve J Shaw, Helen J Masters, QinetiQ, United Kingdom

The sol-gel process provides a facile route to inorganic oxide nanoparticles. This presentation will describe work carried out in three areas to synthesise micron and sub-micron size organic-inorganic hybrid particles.

1. The synthesis of ORganically MOdified SILica (ORMOSIL) particles has been carried out using both the hydrolytic and non-hydrolytic sol-gel routes. The hybrid (nano)composites are organically modified with an alkyl or aryl group covalently bonded to silicon.

1.1 Hybrids have been synthesised in an aqueous sol-gel process by a modified Stöber route, producing spherical nanoparticles with diameters in the range 50 – 300 nm. While the size of the particles is fairly independent of the rate of addition of organically modified precursors, it decreases with decreasing reaction time and seed SiO_2 concentration. The results obtained over a wide range of experimental conditions suggest that the most plausible mechanism behind the formation and growth of the particles is the continuous nucleation and aggregation mechanism.

1.2 Ormosil particles have also been synthesised using the non-hydrolytic sol-gel route, which may lead to products of different morphologies because of the different polarity of the reaction system. Different reaction conditions were studied in order to optimise the size and shape of the particles:

- Choice of catalyst.
- Solvent selection.
- Degree of shear during reaction.
- Use of surfactants.
- Addition of polystyrene.

2. Hybrids have also been synthesised from hyperbranched polyesters by subsequent encapsulation in a silica matrix using the hydrolytic sol-gel route. Aggregation of the hyperbranched polymer occurs, although evidence suggests that the organic and inorganic components are associated on a nano scale. Optimisation of the reaction conditions allows the hybrids to be produced as isolated sub-micron spherical particles.

The results of all these studies will be reported in detail.



O7 - Template Mediated Hybrid from Dendrimer

Namita Roy Choudhury, Ian Wark Research Institute University of SA, Australia

Novel dendrimer-titania hybrids were prepared in this work from hydroky and amine terminated polyamidoamine dendrimer (PAMAM generation 4) and titanium alkoxide by an in-situ sol-gel process in presence of a ligand. Dendritic polymers are chosen because of their unique architectural features. They can be used as a template or, nanoreactor to synthesise nanoparticles to make dendrimer nanocomposite (DNC). Such DNC can then be used for optical, catalytic, biomedical applications. Dendrimers consist of a defined core, an interior branch and terminating groups. Depending on the generation, the molecular properties of a particular core dendrimer would vary. The concept of using them as precise nanoreactors (diameter between 1 to 15 nm) involves organization of small molecules or ions followed by their immobilization/stabilization as guest material. Such preorganisation can occur by acid-base interaction, salt formation complex formation through ligand-metal interaction. However, in any case, control of uniform particle size is extremely important. The hybrid material formed in situ is found to be transparent, brittle and yellow in colour. The transparent nature of the material confirms nanoscopic dispersion of the titania in the hybrid. The hybrids show higher thermal stability than their organic precursors. This is due to enhanced interaction of the inorganic material with the dendrimer as evidenced by PA-FTIR and XPS studies.

O8 - Powderless Fabrication of Nuclear Fuels - Sol-Gel Process

Vijay N Vaidya, Sapan K Mukerjee, Bhabha Atomic Research Center, India

Fabrication of UO_2 pellets using powder metallurgical process for the power reactors is a very well established route. Problems are associated with the fabrication of Pu or ^{233}U fuels using powder metallurgical route like handling of highly toxic radioactive powders, large number of mechanical steps in the fuel fabrication flow sheet, difficulties in remotisation of the process as a consequence, increase in the man-rem problems with the aging of the fabrication facility because of ^{241}Am built up etc. The sol-gel routes are designed to use the output of reprocessing plant in the form of solutions and convert them into consolidated gel particles thus eliminating the powder handling and the associated hazards. Vibro-compaction of multiple sizes of high density microspheres in fuel pin cladding has been used to fabricated VIPAC type fuel pins. A hybrid process involving the sol-gel process in the front end of fuel fabrication merged with the pellet making process called Sol-Gel Microsphere Pelletisation Process (SGMP) was developed to get the best of the two processes. Internal Gelation Process (IGP) is one of the well studied process in BARC for the preparation of gel microspheres of UO_2 , ThO_2 , $(\text{U},\text{Pu})\text{O}_2$, $(\text{Th},\text{U})\text{O}_2$ etc. The cooled ($\sim 0^\circ\text{C}$) nitrate solutions of U, Th and Pu is mixed with urea and HMTA solution in cooled condition ($\sim 0^\circ\text{C}$). The droplets of this mixture are contacted with hot oil (silicone oil $\sim 90^\circ\text{C}$) to make gel microspheres. Gel microspheres are washed first with CCl_4 , and then with NH_4OH solution, are dried at 150°C , calcined upto 500°C to remove ammonium nitrate. are then reduced in N_2+H_2 mixture at 600°C and are sintered at 1200°C for 3 hrs to produce >99% TD oxide microspheres of 70 to 700 μm dia. SGMP has been utilized to produce PHWR grade UO_2 , $(\text{U},\text{Pu})\text{O}_2$, $(\text{Th},\text{U})\text{O}_2$ pellets. Using two sizes of microspheres fuel pins have been vibro-compacted to give 80-82% smear density in the fuel pin. More than 800 kg of UO_2 microspheres have been prepared using this process at FCD on 10 kg/day scale demonstrating the possibility of industrial utilisation of the process at a later date.

CANCELED



09 - Hybrid Organic-Inorganic Materials Based on Nanobuilding Blocks Assembled through Electrostatic Interactions

Francois O Ribot, Delphine Veautier, Chimie de la Matiere Condensee (UMR 7574 / UPMC), France

Steve J Guillaudeau, Chimie de la Matiere Condensee, United States

Thierry Lalot, Synthese Macromoleculaire (UMR 7610 / UMPC), France

The assembling of nanobuilding blocks, such as functionalized oxo-clusters, is a possible route to hybrid organic inorganic materials where the nature and size of the inorganic component are perfectly defined. Moreover, if the interaction/reaction which promote the assembling is carefully controlled, tailored and model materials can be expected. Covalent or ionocovalent bonds are classically used to functionalize and assemble silicon or transition metals based nanobuilding blocks. Yet, much less attention has been paid to the electrostatic interaction for charged oxo-clusters.

Such an approach has been explored with the butyltin macrocation, $\{(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6\}^{2+}$, which exhibits a spherical oxo-core of about 10Å. This nanobuilding block was functionalized with polymerizable groups through the use of 2-acrylamido-2-methyl-1-propane sulfonate (AMPS) as charge compensating anions. Such an electrostatic interactions based functionalization is indeed efficient as 2D NOESY and ROESY ^1H - ^1H NMR, as well as ionic conductivity measurements, have shown that the anions remain attached to the butyltin oxo-core in solvents of low dielectric constant. However, in dissociating solvents the oxo-clusters and the polymerizable groups can be split.

The difunctional nanobuilding block was co-polymerized with methylacrylate (MA), in toluene under free radical initiation, and gels, the viscosity of which increases with the relative amount of nanobuilding blocks, were obtained. The dried systems have been characterized (^{119}Sn and ^{13}C solution and solid state NMR, thermal analysis) to quantify the polymerization and assess the full preservation of the nanobuilding blocks. These materials can be described as organic polymers cross-linked by inorganic nanobuilding blocks. However, because the cross-linking is based on electrostatic interactions, they can be swollen into gels or dissolved into solutions depending on the solvent used.

O10 - Formation, self-ordering and structure of organic-inorganic nanohybrid networks

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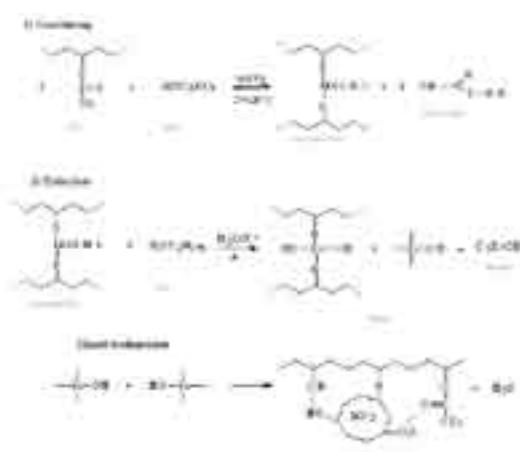
The organic-inorganic (O-I) network is a microphase-separated nanostructured system. Its structure, morphology and properties are remarkably determined by a character of network formation, which can be finely tuned. We have studied the O-I networks formed by different reaction mechanisms from two types of well-defined O-I precursors: (a) alkoxysilane-endcapped oligomers (ASO), crosslinked by sol-gel process, and (b) silsesquioxane (SSQO) clusters containing epoxy groups (EC), crosslinked by the reaction with an oligomeric diamine. In both cases, inorganic SSQO domains form junctions of the O-I network and the organic matrix consists of poly(oxypropylene). Structure evolution, gelation and structure ordering during polymerization were followed by NMR, chemorheology and SAXS. The inner structure of the SSQO domains, network structure, morphology and mechanical properties of the nanohybrids were determined by AFM, NMR, SAXS and DMA. The network build-up from ASO is sensitive to catalytic conditions of the sol-gel process. Acid catalysis results in production of loose siloxane/SSQO clusters whereas a basic catalyst promotes formation of compact cage-like structures of size 1-3 nm as network "crosslinks". The high content of the unreacted SiOH in the networks formed under acid catalysis leads to an interaction with organic matrix and chain immobilization, thus affecting glass transition. Crosslinking of EC with oligomeric diamines is governed mainly by the relative amount of the amine. At a stoichiometric composition, small 5-15 nm spherical Si-rich nanodomains are dispersed in the organic matrix. At amine deficiency, however, SSQO domains grow by sol-gel condensation leading to large cylinders 30-150 nm in diameter finally producing a continuous inorganic structure. Both hybrid types show structure self-organization during crosslinking and a regular arrangement of the cured networks. The experimental rubbery moduli of the networks were successfully predicted using the theory of rubber elasticity and taking into account the bi-continuous O-I structure or "filler effect" of hard dispersed nanodomains. The investigation proved that structure and properties can be tailored and predicted.



O11 - Control of the morphology of organic-inorganic hybrid materials elaborated by reactive processing without solvent

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Alain Michel, Laurent David, Bou-Huot Phe, LMPB, France

The present paper deals with the elaboration of organic-inorganic hybrids through a melt process without solvent by reactive processing and the control of the morphology of this heterogenous system. The synthesis is based upon ethylene vinyl acetate copolymer (EVA) crosslinking through an exchange reaction between the pendant ester groups from EVA and tetrapropoxysilane (TPOS) in presence of dibutyltin oxide (DBTO) as an indispensable catalyst. Then hydrolysis of alkoxy silane groups and silanol condensation results in silica network formation, which is cocrosslinked and interpenetrated with the organic network (figure 1). any parameters of elaboration are studied (temperature and time of crosslinking, temperature and time of hydrolysis, proportions of each reactant.....) and correlated with some properties. An important fundamental aspect was to understand the role of the main parameters which govern the size evolution of the silica particles such as crosslinking density before hydrolysis and the hydrolysis conditions and to be able to assess the distance between silica particles. In that way, an interesting approach was developed to correlate the kinetic of hydrolysis reaction by the assessment of propanol (Figure1) and the evolution of the morphology through SAXS measurement. All these informations are necessary to be able to control the mechanical and thermomechanical properties (creep resistance, shrinkage..) and transparency. his route of organic-inorganic hybrid synthesis opens future prospects to elaborate organic-inorganic materials in confined media.



O12 - Synthesis of Polymetallorganosiloxane Xerogels using a Sol-Gel Method

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Aleksej A Chuiko, NAS of Ukraine, Ukraine

Mietek Jaroniec, Kent State University, United States

Herbert W Roesky, Institut fur Anorganische Chemie der Universitat Gottin, Germany

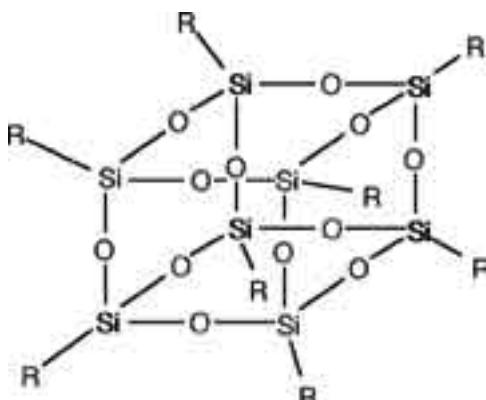
A new approach to the synthesis of polymetallorganosiloxane materials for sorption and catalytic applications is presented. The current work is focused on polyferromethyl- and vinylsiloxane, polychromomethylsiloxane, polyaluminomethylsiloxane, polytitanomethylsiloxane, and polyzirconiummethylsiloxane xerogels. The peculiarity of this approach is in the usage as a rule of highly concentrated solutions of the initial substances which include a highly alkalinized ($\text{pH} > 13$) solution of $\text{K}_3[\text{O}_3\text{SiCH}_3]$, with the salt being a source of organosilanol ligands. Formation of aqua- and hydroxocomplexes for such metals as Al, Fe, and Zr was studied by potentiometric titration and ^{13}C , ^{29}Si NMR spectroscopy. The gels formed from metal complexes in the presence of Na_2SiO_3 were transformed to color xerogels. The presence of metal complexes as ‘building blocks’ in these gels was corroborated by thermal analysis, IR and EPR spectroscopy. For instance, it was shown that polyferromethylsiloxane xerogels with a specific surface area greater than $450 \text{ m}^2 \text{ g}^{-1}$ are formed at $\text{pH} \sim 9$, while for gels formed at $\text{pH} \sim 2$ this area was much smaller. The pH dependence for the system studied differs from that observed for pure silica gels. A possible mechanism of this phenomenon is discussed.



O13 - Sol-Gel Technology in the Control of POSSTM Functionality: A New Generation of Materials

Jani G Matisons, Flinders University, Australia

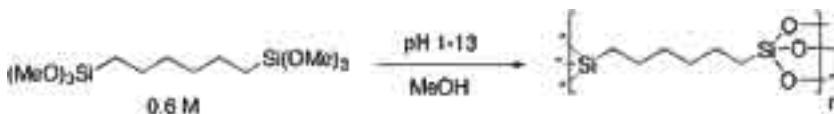
The 'bottom-up' approach to nanotechnology can be defined simply as one in which functional devices and systems are assembled from well defined nanoscale building blocks, much like the way nature uses proteins and other macromolecules to construct complex biological systems. Our approach uses 'bottom-up' synthetic methods to construct organic-inorganic hybrid materials and gels. Several years ago we developed methods for obtaining Si-H terminated silsesquioxanes, H8T8 (POSS), in much better yields. Such materials now provide us with versatile platforms for assembly into polymeric matrices. Furthermore, the sol-gel technology used in synthesis of these synthetic silica nanoparticles, can be applied to the 'in-situ' creation of hybrid silica domains in highly polar polymer materials. The 'bottom-up' approach has the potential to go far beyond the limits of 'top-down' technology by defining key nanometre-scale interactions, shapes and functionality through synthesis and subsequent assembly. Such synthetic methodology allows structures to be produced that have highly functionalised (dendrimers will be considered if time permits) and enhanced properties. It is now possible to combine materials with distinct chemical compositions, structures, sizes and morphology virtually at will.



O14 - Effects of pH on gelation time, degree of condensation and porosity in bridged polysilsesquioxanes

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The effects of pH on the gelation time, degree of condensation, and porosity of hexylene-bridged polysilsesquioxanes will be described. While the effects of pH on silica sol-gel systems are well known, the only comprehensive studies on the effects of pH on the formation of polysilsesquioxanes are associated with silane coupling agent chemistry. Because many polysilsesquioxanes do not readily form gels, it was necessary to use a hexylene-bridged polysilsesquioxane system to achieve gelation throughout the entire pH range. With excess water in methanolic solutions with constant ionic strength, the sol-gel polymerization of 1,6-bistrimethoxysilylhexane was studied from pH 1-13 at 0.5 pH unit intervals. In contrast with silica gels, the longest gelation times were observed at pH 4.5. Interestingly, this corresponds with the pH at which stable dispersions silane coupling agents have been reported. We used Si-29 NMR of the polymerizing sols, the alcogels and solid state NMR and porosimetry on the dried gels further illucidate the effects of pH on chemical structure of these materials before and after gelation. The gels forming at pH 4.5 displayed degrees of condensation only slightly less than those gels that formed in minutes or hours. The long gelation times appeared to be due to slow condensation kinetics at pH 4.5.



O15 - Real time study of UV induced photopolymerization in hybrid Sol-Gel glasses

Céline Croutxé-Barghorn, Olivier Soppera, Christiane Carré, Department of Photochemistry, ENSC Mulhouse, France

Hybrid organic-inorganic materials based on the sol-gel synthesis of an organically modified silicon alkoxide have demonstrated their great potential for applications in coatings, optics, catalysis... In a first step, hydrolysis and condensation reactions are led along the same way as in classical sol-gel glasses. Partial elaboration of the silicate backbone is thus achieved. Then, free-radical polymerization is proceeded by irradiating the sample under UV-light. Finally, the material consists of two crosslinked inorganic and organic networks that are interpenetrated. The relation between the organic and the inorganic part was investigated. Hydrolysis and condensation reactions were characterized by ^{29}Si NMR. Real Time Fourier Transformed Infra-Red spectroscopy was used to follow the photopolymerization of hybrid sol-gel under UV-irradiation. It was demonstrated that this reaction occurred efficiently in hybrid sol-gel although inhibition of free-radical polymerization by molecular oxygen is pronounced. Important structural modifications during irradiation were also pointed out. They concerned both inorganic and organic part of the hybrid material. It appeared that the condensation state of the silicate network was of crucial importance. Presence of the silicate backbone did not limit the final conversion ratio. On the contrary, it was found that photopolymerization occurred more efficiently for systems with the higher degree of condensation. Various photoinitiator systems were tested for their efficiency to induce the polymerization of pendant polymerizable moieties anchored on the partially condensed silicate network. The effects of photoinitiator concentration and light intensity were also studied. These results were confronted to classical kinetic models developed for all-organic photopolymers in order to point out the distinctive aspects related to the use of photochemical activation in hybrid sol-gel materials.

O16 - New polyimide-silica nano-composites from the Sol-Gel process using organically-modified silica network structure

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The polyimide (PI) matrix prepared by the reaction of pyromellitic dianhydride (PMDA) and oxydianiline (ODA) has been reinforced with organically-modified silica network structure using the sol-gel process. Aminophenyltriethoxysilane and PMDA were reacted in 2:1 molar ratio in dimethylacetamide (DMAc) as solvent to generate polyamic acid oligomeric species with alkoxy groups at the chain ends. Specific amounts of these were added to tetraethoxysilane (TEOS) solution in DMAc and then mixed with the high molecular weight polyamic acid solution. The reaction mixture was stirred after adding stoichiometric amount of water to carry out the sol-gel process. The hybrid films were cast by the solvent elution technique. Imidization was carried out by successive heating the films at 100°C, 200°C and 300°C for each one hour. Morphology, thermal and mechanical properties of these hybrids using PI-modified silica network were studied as a function of silica content and compared with the one in which reinforcement of the PI matrix was achieved using pure silica network generated from TEOS only. SEM studies show a drastic decrease in the silica particle size when PI oligomers were introduced in the silica network as spacer group. The diameter of the silica particles was in the range of 40 nm in the compatibilized system with no significant change observed on increasing silica content in the matrix. With the un-compatibilized system where silica network was generated directly from TEOS the particle diameter varied from 0.2 to 3 µm for 5 to 40% silica content respectively. The temperature dependence of loss modulus from DMTA shows a large increase in the glass transition temperature with increase in silica content for the compatibilized system in contrast to un-compatibilized one. Higher thermal stability and mechanical strength and improved transparency were observed in case of compatibilized hybrid system. The PI-active silica therefore was found to be a better reinforcement for PIs than the pure silica obtained from TEOS.



O17 - Bridged organic-inorganic hybrid xerogels and Si/C/N-ceramic membranes: New non-oxide materials derived from polysilsesqui-carbodiimide gels

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Hybrid xerogels consisting of a bridging organic group (R) covalently bonded to an inorganic silicon carbodiimide network of the type, $[(\text{NCN})_{1.5}\text{Si}-(\text{R})-\text{Si}(\text{NCN})_{1.5}]_n$ were prepared. Materials were formed by mild sol-gel reactions of bis(trimethylsilyl) carbodiimide, $\text{Me}_3\text{Si}-\text{N}=\text{C}=\text{N}-\text{SiMe}_3$, and organo-bis(trichlorosilanes), $\text{Cl}_3\text{Si}-\text{R}-\text{SiCl}_3$. Presently, we focus our efforts on starting materials containing flexible R groups, $-(\text{CH}_2)_x-$ (where, $x = 2, 6$, and 8), and the semi-rigid group $-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-$. The solid gels obtained are porous nanostructured materials. The chemical structure of the bridging organic group caused significant effects on the properties of the hybrid solids. Materials containing semi-rigid bridges showed higher specific surface areas than flexible structures. The thermal stability of the hybrid materials was also different. Besides, porosity and texture of the solids were highly influenced by the reaction parameters such as solvent, concentration, and temperature employed for the sol-gel polycondensations.

Polysilylcarbodiimide precursors have also been used to prepare Si/C/N ceramic membranes. The starting materials were spin-coated onto a porous Si_3N_4 substrate to form a preceramic layer followed by pyrolytic ceramization. Up to three coating-pyrolysis cycles were repeated to form amorphous membranes with different thicknesses. The products were investigated by FT-IR spectroscopy, XRD, SEM, porosimetry and gas permeation tests. SEM images show surfaces free of macroscopic cracks. The pore size of the membranes was determined to be 2-5 nm. Permeation experiments were carried out with a triply coated sample using a gas mixture of $\text{N}_2:\text{CO}_2:\text{H}_2:\text{CH}_4:\text{CO}$ with a concentration ratio of 65:15:10:5:5. Selectivities were measured to be 2-3 for H_2/CH_4 and ~4 for H_2/CO_2 . These values are in an interesting range for hydrogen gas separation. Most oxide ceramic membranes reported in literature are only stable up to 500°C, while the novel Si/C/N membranes presented here are stable up to ~1000°C.

O18 - Preparation of Organic-inorganic Hybrid Gel Films Based on Polyvinylpolysilsesquioxane

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The relationship between chemical structure and properties of polymer hybrids was investigated by evaluating mechanical and heat-resisting properties of the hybrids, which are prepared by the stepwise polymerization of vinyl groups and trimethoxysilyl groups of trimethoxy(vinyl)silane (VTS).

The chemical structure of the free-standing films was controlled by the following routes A and B. In Route A, poly(trimethoxy(vinyl)silane) (PVTS) with various degrees of polymerization (DPs) were obtained by the radical polymerization of VTS using di-t-butyl peroxide. The acid-catalyzed hydrolytic polycondensation of PVTSs gave rise to PVPSs with various DPs and degrees of condensation (DCs). Heat treatment of these polyvinylpolysiloxane (PVPS) provided transparent, homogeneous and flexible hybrid gel films. Tensile strength and Young's modulus of the gel films increased with an increase of DC while elongation decreased. On the other hand, tensile strength and Young's modulus of the gel films decreased with an increase of DP whereas elongation increased. In Route B, polyvinylsilsesquioxanes (PVS) with various DCs were prepared by the acid-catalyzed hydrolytic polycondensation of VTS. UV irradiation to the PVS led to transparent (or yellowish), homogeneous and tough PVPS hybrid gel films. Tensile strength and Young's modulus of the gel films increased with an increase of time of UV irradiation and DC of precursor polymer while elongation decreased. The gel films via Route B showed higher density, tensile strength and Young's modulus while elongation was smaller when compared with those via Route A. In addition, it was revealed that the heat-resisting properties of gel films markedly depend on DC.



O19 - C₆₀ based hybrid nanocomposites obtained in the presence of ultrasounds

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Maria Giubelan, Ion Peleanu, "Politehnica" University of Bucharest, Romania

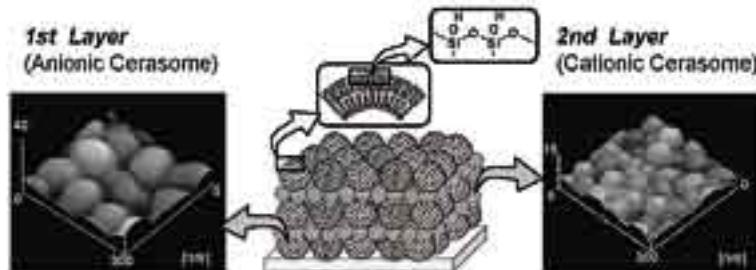
Aurelia Meghea, "Politehnica" University of Bucharest, Faculty of Indus, Romania

Since their discovery, fullerenes in general and buckminsterfullerene C₆₀ in particular, became a subject of great interest for studies. Being compatible with the sol-gel process, one of the promising approaches is to incorporate the fullerene molecules in sol-gel oxide matrices. Great part of studies deals with SiO₂ sol-gel oxide as the optimal matrix for entrapment of organic molecules. C₆₀ - doped silica matrices used through out present study have been prepared by sol-gel processing, using different alcoxide precursors, as a silicon oxide source: tetraethoxysilane (a), methyltriethoxysilane (b), phenyltriethoxysilane (c) and a mixture of phenyltriethoxysilane and tetraethoxysilane (d). C₆₀ - to - Si molar ratio was chosen to be 1.0 x 10⁻³ : 1 for all materials synthesized, final oxide composition remaining unchanged in all cases. The effects of ultrasounds on the gelation process was established by preparing two series of samples, either via sonication or in the absence of ultrasound processing. The properties of the resulted materials were also established. The prepared samples were characterized by XRD, IR, RPE and UV-VIS spectrometry. All methods have put in evidence the embedement of the fullerene into the silica matrix.

O20 - Layer-by-Layer Paving of Liposomal Organic-Inorganic Nanohybrid "Cerasome" on Substrates

Kiyofumi Katagiri, Ryo Hamasaki, Mineo Hashizume, Katsuhiko Ariga, Jun-ichi Kikuchi, Nara Institute of Science & Technology, Japan

Organic-inorganic nanohybrids have been attracting much attention in recent years, since they exhibit the characteristics properties of both organic and inorganic materials. Over a period of more than two decades they have become a well-established area in the field of the sol-gel method. Our major efforts have been devoted to creation of novel class of hybrids, which have more highly organized structures than those obtained from simple polymers. Recently, we have prepared a novel class of nanohybrid "Cerasome", which forms liposomal bilayer membrane with silicate frameworks on the surface by using of organoalkoxysilanes with lipid-like structure. Up to the present time, we have reported that the Cerasomes were obtained from proamphiphilic or amphiphilic type of organoalkoxysilanes bearing a triethoxysilyl head and a dialkyl tail by the conventional mixing or ethanolic sol injection method. It is confirmed that the Cerasomes provide more stable vesicular structures than the conventional liposomes due to formation of the siloxane networks on its surface. In the present work, three-dimensionally-packed vesicular assembling on substrates was successfully demonstrated by using of various types of the Cerasome. The assembling was achieved by employing an alternate layer-by-layer adsorption technique with an anionic and a cationic Cerasomes derived from the corresponding organoalkoxysilane lipids or surface modified ones with other organoalkoxysilane compounds, such as 3-aminopropyltriethoxysilane. Adsorption quantities of each Cerasome layers were evaluated by means of quartz crystal microbalance measurements. The surface structure of the Cerasome paving on a substrate obtained thus was observed by atomic force microscopy. The Cerasome particles closely packed like a stone pavement were clearly seen in both layers. In addition, difference in the particle size for each layer indicates the cationic and anionic Cerasomes undoubtedly formed the layer-by-layer assembly. The layered paving of the Cerasomes was observed in every layer at least up to 10th adsorption steps.



O21 - Synthesis of Mesoporous Silica Nanoparticles using a Double Surfactant System

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Since the synthesis of the M41S family by templating techniques using surfactants, mesoporous silica has much attention in diverse area, such as catalysis, adsorption, separation and chromatography. Controlling the ordered structure and apertures of mesopores has been investigated by changing the templates and preparation conditions. Recently, macroscopic forms of mesoporous silica have been noticeable for a variety of applications. Especially, small particles in nanometer-scales exhibit enormous potential as an easy-to-handle and accessible form. Here, we present a novel and simple method for the synthesis of mesoporous silica nanoparticles using a double surfactant system. Silica nanoparticles having well-ordered mesopores with an aperture of ca. 2.3 nm were prepared in an aqueous solution containing a cationic surfactant (CTAC) and non-ionic triblock copolymer (Pluronic F127). The particle diameter ranging in 30-50 nm was achieved through suppression of the grain growth by the coexistence of the block copolymer. The well-ordered hexagonal structure of mesopores in the silica particles was produced by previous hydrolysis of TEOS with hydrochloric acid and subsequent assembly of cationic surfactant micelles and anionic silicates at a basic condition.

O22 - Templat ed synthesis of tailored clays (based on sol-gel techniques) to yield increased pore volumes for sorption and exchange.

Katherine M Powell, University of Surrey, United Kingdom

Robert CT Slade, Neil I Ward, United Kingdom

Use of clays as adsorbents, catalysts and catalyst supports has increased markedly in recent years, and with it the need for porosity control has been identified. Liquid crystal templating with a variety of surfactants has been exploited, over the last decade, to great effect in the production of mesoporous silicates (e.g. MCMs). This research has recently expanded to include templated synthesis of modified clays with controllable layer/framework chemistry and high ion-exchange capacities; a strategic target is a significant increase in total pore volume per unit mass. We report the synthesis and modification of Laponite-related materials by liquid crystal templating, leading to increased pore volume and enhanced specific surface area. Materials produced using cationic and neutral surfactants, as well as those with varying tail length and head size were compared. A range of template removal methods has also been investigated. The characteristics of these tailored materials have been determined via nitrogen sorption porosimetry, X-ray diffraction, XRF analysis, FT-IR spectroscopy, atomic force microscopy, elemental microanalysis, and MAS-NMR.

Appropriate choice of surfactant, reagent concentrations, synthesis protocol and template removal strategy have led to markedly enhanced total pore volume and modified texture.

Sorption and ion exchange studies have been carried out to determine heavy metal uptake from effluent streams. ICP-MS, ion chromatography and atomic adsorption spectroscopy have been used to assess selectivity and efficiency of ion removal by Laponite-related materials.



O23 - Core-shell Approach to Formation of Ordered Nanostructured Materials with MPEG-b-PDLLA

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Work presented here describes an innovative approach for the preparation of ordered nanoporous ceramic materials that involves a self-assembly process at the molecular level based upon MPEG-b-PDLLA block copolymer templates. This approach provides for rapid self-assembly and structural reorganization at room temperature. Selected MPEG-b-PDLLA block copolymers have been synthesized with systematic variation of the chain lengths of the resident hydrophilic and hydrophobic blocks. The size and shape of the micelles that spontaneously form in solution are then controlled by the characteristics of the copolymer template. Formation of nanoporous silica at room temperature with short-preparation time is demonstrated and silica-containing materials evolve with uniform pore shape and wall structure. The formation mechanism of these nanoporous structures obtained by controlling the micelle size has been confirmed using both liquid and solid state ^{13}C and ^{29}Si NMR techniques. This work both proposes and verifies the formation mechanism of nanoporous structures in which the pore size and wall thickness are closely dependent on the size of hydrophobic cores and hydrophilic shells of the block copolymer templates. In this process, the silica precursor becomes bound to hydrophilic regions of the ordered copolymer after hydrolysis at the aqueous solution interface. The core-shell mechanism for nanoporous structure evolution is based upon the size and contrasting micellar packing arrangements that are dictated by the copolymer.

O24 - Cobalt incorporation into co-condensed mesoporous silicas

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For many years we have been investigating cobalt supported catalysts for use in the Fischer-Tropsch (FT) reaction (i.e. CO + H₂ to give fuels and chemicals). Herein we report the synthesis of Co supported mesoporous silica materials for use in the FT reaction.

Bifunctional periodic mesoporous organosilica materials were synthesized by co-condensation of 1,2-bistrimethoxysilyl ethane (BTME) with 3-glycidoxypropyltriethoxysilane (GPTS). Cetyltrimethylammonium bromide (CTAB) was used as the structure directing surfactant. Cobalt was incorporated into the organosilica materials by adding cobalt nitrate in the reaction mixture. Powder XRD, gas adsorption, TGA, DTA, Raman spectroscopy and SEM were used to characterize the materials. The effect of incorporating cobalt and varying the ratio of BTME:GPTS on the structural properties of these materials is examined.

Bifunctional periodic mesoporous organosilica materials consisting of ethane groups in the framework and glycidoxypropyl groups dangling in the channels were synthesized. Values of the lattice parameter, d(100), obtained for solvent extracted materials are higher than those of their as-synthesized counterparts. Cobalt incorporation leads to a collapse in the periodicity of the materials, as shown by the disappearance of the XRD peaks.

Increasing the amount of GPTS affects pore size, surface area and pore volume as well as shapes of the isotherms and hysteresis loops. The hysteresis loops of the Type IV isotherms obtained for GPTS-modified ethane silica materials change from type H3 to type H4. There is a tendency for pore sizes, determined from adsorption isotherms, to change from mesopore to micropore. Isotherms of cobalt incorporated GPTS-modified ethane silica materials change from Type IV, characteristic of mesoporous materials, to Type I, characteristic of microporous materials. The surface area, pore volume and pore diameter decrease with increasing loading of GPTS as well as after cobalt incorporation. TGA curves indicate that the organosilica materials have similar thermal stability and show that the surfactant is removed by solvent extraction. GPTS incorporation is confirmed by Raman spectroscopy.



O25 - Spongelike Macroporous TiO₂ Monoliths Prepared from Starch Gel Template

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Sean A Davis, Stephen Mann, University of Bristol, United Kingdom

TiO₂ materials with a hierarchical meso/macropore organization were fabricated by using titanium dioxide nanoparticles and starch gel templates. Starch sponges with high internal macroporosities were prepared by freezing and thawing of starch gels and were then infiltrated with colloidal suspensions of titania nanoparticles and air-dried to produce TiO₂-starch foams with pores up to 200 µm across depending on the starch concentration and the TiO₂ loading. The TiO₂ nanoparticles were deposited as coherent layers on the thin walls of the starch framework, which could be removed by calcination without significant disruption of the TiO₂ framework. The three dimensional macroporous structures of TiO₂-starch sponge composite and TiO₂ sponge induced the extremely high photocatalytic activity. The methods described are facile, low in cost, and environmentally benign and are extended to other inorganic(-organic) materials (organoclay, calcium phosphate, CaO-SiO₂ etc.) with macroporous architectures, provided that suitable nanoparticle building blocks are available.

O26 - Surfactant Templatated Mesoporous Titania Anion Exchanger

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The discovery that surfactant self-assembly could be exploited for the synthesis of ordered mesoporous silicates (OMS) with different structures [1,2] has inspired numerous attempts to replicate this chemistry with transition metal oxides [3,4]. Because of the tantalizing properties and wide application field of titanium oxide, our aim has been to develop convenient methods for the preparation of titanium oxide mesophase (TOM) materials using surfactant self-assembly methodologies. So far there have been a number of attempts to produce titanate materials in the form of powders, monoliths and thin films. However, we and others, have found that reported preparations, and the stability of mesostructured titanate materials templated using supra molecular assemblies based on surfactants and block copolymers, in many cases, lack reproducibility.

Here we report a method for the preparation of mesostructured titanium oxides using the Ti(III)-dodecylsulfate salt ($C_{12}H_{25}SO_4)_3Ti(III)$, titanium(IV) isopropoxide and ethanol solvent. In this method, hydrolysis condensation reactions are carried out in a controlled manner by the slow passage of water-saturated air over the precursor solution such that ethanol is gradually eliminated and water is introduced. Using this method we are able to prepare TOM materials having a worm hole mesoscopic texture similar to that found in silicate systems. It is not possible to easily create porosity in these materials through thermal decomposition of the surfactant without also inducing some framework breakdown. Instead, the surfactant can be readily eliminated by mild ion exchange reactions in which the surfactant is replaced by other oxo-anionic species such as VO^{2-} , WO_4^{2-} and CrO_4^{2-} even at high pHs. The resulting materials retain the mesoporous texture and are thermally stable to temperatures of around 300 to 400 °C. It will be demonstrated that the anion exchange properties of the titanate framework can be used for practical separations applications. In addition the ability to line the uniform tubular pores with a highly dispersed second transition metal oxide species, suggests that they may be useful for a variety of other applications including, selective catalytic reductions and oxidation reactions, photocatalysis, and as electrodes in lithium ion batteries.

The structure of the TOM materials has been studied by a variety of methods including FTIR, NMR and EXAFS and the mechanism of formation has been investigated using SAXS and SANS.

O27 - Template synthesis of metal oxides

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The ability to control the morphology of materials is highly desirable as structure plays an important role in the final properties of the material and hence its areas of application and performance efficiency. Template synthesis has shown how the outer morphology and inner porosity of materials can be tailored. Sol-gel chemistry can be combined with templates for the formation of a range of morphologies. This presentation will describe the use of organic templates including porous polymer gels, membranes and beads, and polymer fibres for the formation of monolithic, film, spherical, or tubular outer morphologies that contain porous inner structures. Examples of titanium dioxide materials obtained using the sol-gel template synthesis are shown in the figure. Metal alkoxide precursors are infiltrated into the template, where hydrolysis and condensation is conducted within the pores, leading to either a coating of the polymer material or a filling of the pores with an amorphous metal oxide. Heating results in removal of the organic template and generally crystallization of the metal oxide. Silica, titania, zirconia and mixed titania/zirconia structures are examples of materials that have been prepared. The properties of the final metal oxides are characterized by using electron microscopy, gas sorption and wide angle X-ray scattering. The photocatalytic properties of the porous materials containing titanium dioxide have been studied, and compared with Degussa P25 titania, by following the photodecomposition of 2-chlorophenol and salicylic acid.



O28 - Relationship between Surface Skin and Defect Formation during Sol-Gel Spin-Coating

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Spin coating is one of the standard methods for depositing sol-gel, nanocomposite, or polymer coatings onto flat substrates (silicon wafers, glass plates for displays, sensor substrates, etc.). It is a convenient technique and often produces quite uniform coatings with low defect counts. However, in some situations or for some compositions the defect counts can be quite high. Our recent research has been focused at understanding the defect formation mechanisms and looking for ways to prevent these defects. In particular, defects often arise as a result of rapid solvent removal because of the airflow over the wafer during the spin-coating process. Since solvent removal is happening at the top surface of the coating fluid then steep concentration gradients develop with depth inside the fluid. The top surface becomes more viscous, though the wafer spinning is subjecting the fluid to continual stretching. Simultaneously the depletion of solvent can cause surface tension changes that can instigate the Marangoni effect and allow lateral fluid motions and coating roughening.

The change in viscosity at the top surface can create a skin layer that impedes drying of the coating solution that lies below. Thus, different depths within the fluid may experience different drying conditions - and possible different final properties. The surface skin can also be the location where one kind of interesting defect initiates. The stretching caused by the radial fluid outflow exerts large forces on the top "skin" layer. If the skin forms early enough in coating then the forces may be large enough to actually rupture the skin at random locations. The surface ruptures create wispy locations of significantly thinner coating, but they do not result in complete penetration through the coating. The occurrence of these defects depends to a large degree on the volatility of key solvents used in the sol-gel process, with less volatile solvents being favored.



O29 - Preparation of Titania Nanosheets-Precipitated Coatings on Substrates by Treating $\text{SiO}_2\text{-TiO}_2$ Gel Films with Hot Water under Vibrations

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Tatsuo Matoda, Kiyoharu Tadanaga, Tsutomu Minami, Masahiro Tatsumisago, Osaka Prefecture University, Japan

Toshihiro Kogure, The University of Tokyo, Japan

Nanocrystals-dispersed materials have created an important field in science and technology because of their exceptional chemical and physical properties. We have shown that anatase nanocrystals were formed on sol-gel derived $\text{SiO}_2\text{-TiO}_2$ coatings with water vapor or hot water treatments [1,2]. The anatase nanocrystals are precipitated through hydrolysis of Si-O-Ti bonds, dissolution of SiO_2 component, migration of hydrolyzed titania species, and nucleation and growth of anatase nanocrystals. The hydrolysis, dissolution and recrystallization are influenced not only by the physico-chemical conditions like temperature, pressure and pH of the solution but also by external dynamic conditions such as vibrations of the materials and flow of the solution. Thus, these reactions of the gel materials with water under external dynamic conditions should influence the nucleation, growth and characteristics of the nanocrystals.

Here we report our success in preparation of titania nanosheets-precipitated coatings on glass substrates by treating the sol-gel derived $\text{SiO}_2\text{-TiO}_2$ films with hot water under vibrations. Nanosheets are characterized by a large surface-to-volume ratio, allowing the high reactivity at the nanosized level. The titania nanosheets in this study consist of several hydrated titania layers with a spacing of about 0.6 nm. The coatings of hydrated titania are superior to pure anatase coatings in the photocatalytic activities due to their large specific surface area and also show excellent antifogging properties due to their unique morphology. These phenomena are an exciting demonstration since anatase has been believed to be the best candidate as a photocatalyst and as a superhydrophilic material. The preparation of the titania nanosheets-precipitated coatings has been achieved by a finding that vibrations during hot water treatment affect significantly the nanostructure of the formed titania.

[1] Matsuda, Kogure, Matsuno, Katayama, Tsuno, Tohge, Minami, J. Am. Ceram. Soc., 76 2899 (1993).

[2] Matsuda, Kotani, Kogure, Tatsumisago, Minami, J. Am. Ceram. Soc., 13, 2144 (2001).

O30 - A microstructural zone model for the morphology of sol-gel coatings

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The thickness of dip-coated single sol-gel layers with good optical quality is easily controlled by varying the sol concentration and the withdrawal speed within a range from a few nanometers to about 200 nm and can be measured with high precision using a stylus profilometer. The coating's microstructure can be also well determined by X-ray diffraction, X-ray reflectometry and transmission electron microscopy (cross sections).

Using these techniques, a thorough study of the microstructure of transparent conducting ZnO:Al coatings deposited on fused silica substrates, as well as those reported in the literature for $\text{In}_2\text{O}_3:\text{Sn}$, $\text{SnO}_2:\text{Sb}$ and TiO_2 , shows that three different morphologies can be obtained: a grainy type, a layered type and a columnar type. The appearance of these structures in multilayer systems were found to depend essentially on the single layer thickness and an intrinsic crystallite size (ICS), determined from the data of thick films. All the so far obtained results are in very good agreement with a 3-zone model in which the intrinsic crystallite size is plotted against the single layer thickness (SLT) or in a more refined version if the ratio $q = \text{ICS}/\text{SLT}$ is plotted against the reduced temperature $T_{\text{sintering}}/T_{\text{melting}}$. Comparison with the Movchan-Demchishin and Polley-Carter models proposed for coatings obtained by PVD and CVD methods respectively will be presented.



O31 - Aluminophosphate Thin Films

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Paul JA van Tilborg, Organon, The Netherlands

Much research is done on porous aluminophosphate compounds. Their chemical composition is close to AlPO_4 . Analogue to zeolites, they are used as molecular sieve and, when modified, for catalytic applications. However, almost no work is done on non-porous aluminophosphate materials. It is known since a long time that thermally stable refractories can be prepared by mixing oxidic particles (for instance Al_2O_3 , TiO_2 , ZrO_2 , or MgO) with acidic metal-phosphate solutions or phosphoric acid. Heat treatment at 100-300 °C leads to hard and alkaline slag resistant refractories.

We will show that wet-chemically thin aluminophosphate films can be prepared using acidic aqueous solutions containing dissolved aluminium and phosphate. The various complexes in the solution were examined with ^{27}Al and ^{31}P NMR. When heating the samples, the solvent evaporates, and condensation takes place. Different aluminophosphate compounds can be formed, depending on the P/Al molar ratio, the temperature to which the sample is heated, and to a lesser extent the pH of the solution. The compounds were identified with a combination of XRD and ^{27}Al and ^{31}P solid state MAS NMR. We followed the condensation reaction using mass loss measurements and NMR, focussing on the formation of aluminiummetaphosphate, $\text{Al}(\text{PO}_3)_3$. In general, P/Al ratios ranging from 1.0 to 3.0 lead to stable films. These films are usually transparent. If the aluminophosphate films are filled with particles, fully inorganic coatings of at least 20 µm thick can be obtained. These films are hard and inert, and show a very good adhesion to glass substrates.

O32 - Radiative striations of spin-coating films: surface roughness measurement and in-situ observation

Hiromitsu Kozuka, Kansai University, Japan

Yuta Ishikawa, Naoki Ashibe, Japan

“Radiative striations,” i.e. radially extended ridges, are often observed on the surface of spin-coating films. In order to understand the mechanism of the evolution of striations, microscopic observation and surface roughness measurement were conducted on spin-coating films. Microscopic observation revealed that spin-on titania gel films prepared from an alkoxide-derived sol have radiative striations and cell-like patterns away from and near the spinning center, respectively. Similar morphologies were observed even when the film was prepared by placing a drop of sol on a stationary substrate. Surface roughness measurement indicated that the height (ten point height of irregularities, R_z) and the spacing (mean spacing of local peaks, S) of striations decrease with increasing spinning rate, and R_z and S of the film prepared on a stationary substrate were found on the R_z - and S-spinning rate curves extrapolated to 0 rpm.

These experimental facts strongly suggest that the mechanism of the evolution of striations should be the same between the films prepared on rotating and stationary substrates. Then, in situ observation was made on a titania sol layer dispensed on a stationary substrate using an optical microscope, where striation-like patterns and cell-like patterns away from and near the center, respectively, were found to be formed almost simultaneously on solvent evaporation.

Silicon powders of less than 0.1 micron in size were added in the sol so that the microscopic motion in the sol placed on a stationary substrate be visualized. Convections within the sol layer thickness were clearly observed on solvent evaporation, suggesting that the striations and cell-like patterns are formed via Benard or Marangoni convections. Smaller height and spacing of striations observed at higher spinning rates would be due to the smaller size of convections in thinner sol layers.



O33 - Sol-Gel derived Inorganic Scintillators

Christelle Mansuy, Rachid Mahiou, Jean-Marie Nedelec, Université Blaise Pascal & ENSCCF, France

Research directed towards scintillating materials is in constant development. The use of these materials in medical imaging equipment (X-rays, γ -rays, positron emission,...) requires improvement of their properties in particular their conversion yield. A major challenge is the control of the scintillator morphology and texture on a nanoscopic level. The sol-gel process is the best solution to achieve this control and also allows the low cost preparation of thin films of these materials. Examples representative of the work performed in our laboratory for the last three years will be given. This presentation will focuss on Lutecium based inorganic scintillators.

Specific sol gel routes have been developed to prepare rare earth doped LuBO_3 , LuPO_4 and Lu_2SiO_5 and will be presented. All materials are obtained as polycrystalline powders and borates and silicates are also obtained as optical quality thin films. Characterization of the obtained materials using various techniques (X-ray diffraction, SEM, TGA, EXAFS,...) will be presented.

In the case of thin films, specific characterization tools have been used (m-lines spectroscopy, waveguided excited luminescence, optical losses measurement).

Finally the optical properties have been studied and in particular the scintillation properties. Scintillation yields have been measured and demonstrate the interest of these materials.

This work was supported by the CNRS and MJER under "ACI Nanostructures 2001" project LuNaTIC and partially by the RNTS under project LuminiX.

O34 - Nanostructured Ion-Selective MCM-48 Membranes

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Sankhanilay Roy Chowdhury, Johan E ten Elshof, Albert Van den Berg, Dave HA Blank, University of Twente, The Netherlands

MCM-type oxides with ordered mesoporosity are promising materials for emerging applications in several fields such as catalysis, sensors and separation science. In view of their high porosity and well ordered geometries with narrow pore size distributions and low tortuosities, thin films of MCM-type materials are potential candidates for membrane applications. A disadvantage of thin films with the MCM-41 mesostructure for membrane applications is that the main transport paths tend to run in a direction parallel to the membrane surface. This results in a high tortuosity in the direction perpendicular to the substrate. MCM-48 on the other hand has a percolative 3D pore structure, so that a relatively low tortuosity in all directions is expected. Two types of supported silica membranes with MCM-48 mesostructure are demonstrated in the present study. The first type is an ion-selective MCM-48 layer deposited on a conventional macroporous α -alumina support for nanofiltration applications. The retention properties and liquid permeability of solvents are compared with that of a mesoporous γ -alumina membranes. The second type concerns the development of an ion-selective interconnect for micro-total analysis devices or micro-chemical systems. The support structure for the thin film is a 1 μm thick silicon-based microsieve with circular-shaped perforations of 0.5-1.2 μm diameter. The MCM-48 layer is deposited as a thin film covering the substrate and filling the pores, effectively resulting in a regular 2D array of micrometer-sized self-standing MCM-48 membranes. The transport of ions from aqueous solutions under the influence of an electrical potential difference is reported. It is demonstrated that the ion flux can be tuned by ionic strength and dc potential difference.



O35 - Sol-Gel Coating of Thin Display Glasses – Problems and Remedy

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Guillaume Guzman, Corning S.A., Centre Européen de Recherche de Fontainebleau, France

Modern display technology has generated an increasing demand for tailored functional coatings on thin glass substrates to reduce the weight. Though at present the corresponding coatings are mostly deposited by PVD techniques, sol-gel coatings offer promising alternatives for some forthcoming developments because of their lower deposition cost and superior surface properties. The suitability of such wet coating techniques for large area coatings has already been proven on an industrial scale for the dip coating technique e.g. in the fabrication of coatings for reflection reduction or contrast enhancement. If the same technique, however, is applied to thin substrates with a thickness less than 1 mm, the resulting coatings exhibit a deficient quality with a hazy appearance and an increased surface roughness. IR-thermographical monitoring during the deposition process revealed a severe local cooling due to solvent evaporation, which strongly impedes the process of film formation by condensation of atmospheric humidity and a deceleration of the further evaporation. The basic problem lies in the lower heat capacity of thin substrates, as most of the energy for the evaporation of the solvent has to be delivered by the substrate.

Several approaches to circumvent this intrinsic property of dip coating will be discussed regarding their practicability in an industrial process. A simple and very efficient remedy for the dip coating of substrates with a thickness down to only 0.1 to 0.2 mm will be introduced with a universal applicability to any sol-gel system. It will be shown that by this means the coating homogeneity and smoothness, as well as the reproducibility of the coating properties are improved significantly even for coatings on thicker substrates.

O36 - Sol-Gel layers for surface modification of non-woven textiles

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Karin Stana Kleinschek, Andreja Gutmaher, Slovenia

The goal of the proposed paper is to explain fundamental and practical approaches that will enable to create multifunctional responsive/adaptive textiles, which can change a number of specific properties in response to variation of environment or to application of some physical/chemical incentives. In order to obtain textile materials with desired performance, the textile surface is often modified with polymer layers before use.

There are several classes of polymer materials having adaptive or responsive properties. These materials are capable of reversible changes in their characteristics according to outside conditions or stimuli.

Sol-gel technology offers simple methods for manipulation of the structure, configuration and composition and chemical characteristics of organic matrices. This property and the ability to immobilize such a sol-gels covalently on textile support make this technology appealing in surface modification of textiles.

Tailored hybrid layer consisting of polymers having diverse natures will allow the combination of several antipodal properties in one thin polymer film. Therefore, the proposed paper focused on the fabrication of hybrid polymer layers on the surface of textiles, their characterization and understanding.

Non-woven textiles, made from PES and Nomex fibres were sol-gel doped. Several sol-gel precursors such as tetramethoxysilane (TMOS), methyltrimetoxysilane (Me-TriMOS), phenyltrimetoxysilane (Ph-TriMOS), diphenyldimethoxysilane (DiPh-DiMOS) and various ratios between TMOS and organically modified sol-gel precursors (ormosils) were used as surface modifier. Different instrumentation methods for doping purposes of non-woven textile materials were investigated and tested.

Sol-gel doped textile materials were characterized and defined by thickness, mass per unit area, mechanical properties, air permeability, pore volume, electrical resistance and resistance to surface wetting.

Best results in terms of mechanical properties, air permeability and resistance to surface wetting were obtained by using 100% methyltrimetoxysilane, irrespective to the type of polymer fibre used in non-woven textile.

O37 - High refractive-index microspheres of optical cavity structure

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Microspheres of refractive index of $n_D > 2.0$ have been investigated.

The organic-inorganic hybrid microspheres were prepared by the vibrating orifice technique using diphenyldimethoxysilane (DPhDMS), 3-glycidoxypropyltrimethoxysilane (GPTMS), and titanium tetra-n-butoxide (TTBu). For lasing demonstration, Eu³⁺-doped microspheres were prepared. Non-doped and Eu³⁺-doped microspheres were heated for increasing their refractive indices.

Refractive indices of hybrid microspheres increased with increasing the TTBu content, and $n_D = 1.72$ was achieved in the composition of 80TTBu-20DPhDMS. The optical microscopy photograph of microspheres of $n_D = 1.72$ is shown in Fig.1(a). The particles have good spherical shape and smooth surface and high optical transparency. The diameters of the particles was 5.2μm and could be controlled within 0.1μm. The refractive index of 80TTBu-20DPhDMS increased with increasing the heating temperature, and $n_D = 2.10$ and $n_D = 2.25$ were achieved by heating at 400°C and 450°C respectively. The heating evolved solvents, fired the organic groups from hybrid matrix, densified the matrix, and then resulted in the high refractive index microsphere of $n_D > 2.0$. The optical microscopy photograph of microspheres after 400°C heating is shown in Fig.1(b). The microspheres maintained their good shapes and high optical transparency. Eu³⁺-doped microsphere after heating was pumped by CW Ar-ion laser (466nm). Resonant emission from Eu³⁺-doped microsphere of $n_D = 2.10$ was performed.

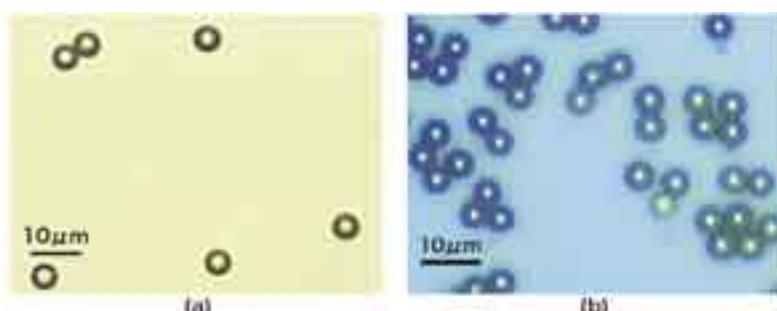


Fig.1 Optical microscopy photograph of microspheres
(a) before heating ($n_D = 1.72$), and (b) after 400°C heating ($n_D = 2.10$).

O38 - Synthesis and Photoluminescence Features of Urea and Urethane Cross-Linked Siloxane-Poly(Ethyleneoxide) Hybrids Derived from Carboxylic Acid Solvolysis

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The synthesis of a wide range of novel materials by “soft chemistry” methods has attracted considerable scientific interest in recent years. Sol-gel derived organic/inorganic hybrids are of increasing importance as constituents of multifunctional materials for a wide variety of applications, since they offer the prospect of combining the mechanical toughness and flexibility of the organic component with hardness and the thermal stability of the inorganic component. However, in materials derived from the conventional sol-gel process the high-energy vibrations associated essentially with OH groups result usually in quenching or lowering of the emission quantum yield. In order to overcome these shortcomings, a series of urea or urethane cross-linked hybrid materials have been synthesized here in the absence of water and oxygen using carboxylic acids (acetic or valeric acids) as the solvolysis agents of the di-ureasil or di-urethanesil precursors. The resulting hybrids are elastomeric monolithic films with excellent transparency. Di-ureasils exhibit a slightly yellowish hue, while di-urethanesils appear almost colorless. The solvolysis-derived hybrids and the corresponding ones obtained from the conventional sol-gel method have similar structure, as shown by X-ray diffraction, ^{29}Si and ^{13}C magic angle nuclear magnetic resonance, and Fourier transform infrared and photoluminescence (PL) spectroscopies. The PL properties have been recorded and the nature of the recombination process that dictates the light emission has also been studied. Compared to the hybrids prepared by means of the classical hydrolysis/condensation method, the xerogels proposed here have better PL efficiency, thus, showing promising potential applications in the fields of flat panel display systems and lighting technologies.



O39 - Incorporation of highly luminescent quantum dots in hybrid organic-inorganic matrix

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In the last 20 years different approaches have been developed to synthesize colloidal nanocrystals of controlled composition, size, shape and surface states. The organometallic approach is probably the most studied one and highly luminescent semiconductor nanoparticles can be prepared with controlled size, size distribution and surface states. Such colloids have many potential applications (photovoltaic, display, laser, etc.) but for many of these applications it is necessary to embed the colloids in solid matrix with controlled composition. In this paper we describe a method for transferring semiconductor quantum dots produced in non-polar solvents by organometallic approach in sol-gel matrix. ZrO_2 -ORMOSIL bulk and film have been homogeneously doped with different semiconductor quantum dots (CdSe , $\text{CdSe}@\text{ZnS}$, $\text{CdSe}@\text{CdS}$). Both the absorption and the emission properties of the semiconductor nanocrystals are slightly affected by the incorporation into the sol-gel matrix. The ZrO_2 content of the hybrids organic-inorganic films can be easily adjusted to get film with sufficiently high refractive index for the realization of semiconductor doped waveguides for optical integrated devices.

O40 - Spectral hole-burning in femtosecond laser-irradiated Eu³⁺-doped aluminosilicate glasses

Gil Jae Park, Masayuki Nogami, Nagoya Institute of Technology, Japan

Rare-earth ion-doped glasses have fascinating properties such as lasing, upconversion and spectral hole burning. We are interested in persistent spectral hole burning (PSHB) phenomenon of rare-ions for its potential application to high-density optical data storages. By using a sol-gel technique, we succeeded in the preparation of silicate glass doped with Eu³⁺ and Sm²⁺ ions exhibiting PSHB up to room temperature. More recently, we observed more faster and deeper hole formation in the sol-gel derived Sm²⁺ ion doped glasses that irradiated with x-ray. X-ray and laser irradiations have an advantage over the heating process of glass because of the possibility of space-selective modification of the glass. Local modification is easily created by moving the focused point of these lights. For instance, very recently, we successfully demonstrate the femtosecond (fs) laser induced valence manipulation of Sm ions in glasses and its PSHB properties. In present, we demonstrate photocontrol of the occurrence of PSHB in Eu³⁺ doped Al₂O₃-SiO₂ glasses by use of fs laser pulses. The exposure to fs laser causes both the reduction of Eu³⁺ to Eu²⁺ and the formation of intrinsic defects. Spectral hole burning experiment is performed on $^5D_0 \rightarrow ^7F_0$ transition of Eu³⁺ ion. The details including photoreduction mechanism and spectral hole burning properties will be discussed.



O41 - Photoluminescence stabilization in erbium-doped silicate sol-gel planar waveguides

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Er³⁺-doped silica-titania planar waveguides, prepared by sol-gel processing, have a tendency to exhibit a reversible photoluminescence (PL) quenching phenomenon at 1.5 μm, especially if they are not fully densified. In the present paper, the presence of porosity and OH species associated with such a simultaneous decrease in the Er³⁺ PL intensity and lifetime are followed in detail by infrared (FTIR) spectroscopy and ellipsometry. The relationship between the waveguide densification degree and the extent of phase separation in the silica-titania system is also investigated by FTIR spectroscopy. In order to prevent PL quenching, different chemical compositions and EtOH/precursor ratios, as well as optimized heat treatments, have been employed with the aim of obtaining fully densified waveguides with enhanced spectroscopic properties. Both the Er³⁺ PL spectra and the fluorescence lifetimes at 1.5 μm have been determined in these systems as a function of composition and Er³⁺ ion concentration. SiO₂-TiO₂-AlO_{1.5}-ErO_{1.5}, SiO₂-HfO₂-ErO_{1.5} and SiO₂-TiO₂-HfO₂-ErO_{1.5} waveguides, densified at 900 °C, appear to offer the best performance in terms of stability and strength of the PL signal.

O42 - Synthesis of Thermoplastic Organic-Inorganic Hybrid Polymers for Optical Fibre Fabrication

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Polymer optical fibre (POF) has attracted great interest in telecommunications due to its low temperature and low-cost processing. However, fabrication of single-mode polymer optical fibre is usually difficult because the properties of polymer are not isotropic, and the polymerisation process for preparing fibre preform with a designed refractive index profile is very complicated. Furthermore, few polymers are suitable for optical fibre fabrication (polymers having high glass-transition temperature and low optical losses at the infrared communication region are few). To meet the strong need for new materials in POF fabrication, we have investigated the possibility of synthesis of thermoplastic organic-inorganic hybrid polymers for POF application. The process for preparation of thermoplastic hybrid polymers consists of two steps: (1) hydrolysis of diphenyl dimethoxysilane (DPhDMS) with boric acid under anhydrous conditions, and (2) condensation of the hydrolysed product formed in step 1 with a second silicon alkoxide such as vinyl trimethoxysilane (VTMS). After removal of volatile components such as solvent and reaction by-product methyl borate, a transparent glassy polymer is obtained. The refractive index of the glassy polymer is tuneable by variation of the ratio between the two silicon alkoxides. The thermoplastic property of this glassy polymer is shown by its softening or melting behaviour occurred at from 80 °C to 100 °C. Substitution of VTMS with a UV cross-linkable monomer such as methacryloxypropyl trimethoxysilane (MPS) for increasing its glass transition temperature is also performed. In optical fibre fabrication, PMMA fibre preform with the thermoplastic hybrid polymer as a core is prepared by injection technique, and optical fibre fabrication and characterisations are performed.

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O43 - Narrow Band Polarized Light Emission from Organic Micro-Cavity Fabricated by Sol-Gel Technique

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Qinghai Song, Liying Liu, Wencheng Wang, China

We report the fabrication and optical properties of an organic light emitting micro-cavity. The cavity is a DCM doped PC film sandwiched between two Bragg reflectors, fabricated by alternately depositing TiO_2 and SiO_2 sol-gel thin films. Reflectivity up to 98% was achieved using the Bragg reflectors. To our knowledge, this is the first organic light emitting micro-cavity with two distributed Bragg reflectors (DBR). The cavity has a photonic band gap between 597–789 nm with a defect state inside the gap. A frequency-doubled output of a Q-switched Nd:YAG laser was used to optically pump the micro-cavity, narrow band optical pumped light emission from the cavity and its polarization-dependence were observed. Cavity quality factor $Q=\lambda/\Delta\lambda$ as high as 354 was achieved, this value is almost one order of magnitude higher than previous reports which had metal mirror/organic film/DBR configuration. Angular and polarization dependence of luminescence peak position were measured and agreed well with theoretical calculations based on matrix transfer method. TE and TM splitting as large as 16 nm was reached, which can lead to applications like polarized emission from an isotropic film.

O44 - Photo-electrochemistry of Ormosil's sandwiched bacteriorhodopsin

Prem C Pandey, Banaras Hindu University, India

The photoelectrochemistry of D96N Bacteriorhodopsin sandwiched between ITO electrode and a layer of ormosil is studied. The bacteriorhodopsin was dried over ITO electrode followed by formation of transparent ormosil layer. The transparent ormosil layer was made in aqueous acidic medium using phenyltrimethoxysilane and 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane. The ormosil sandwiched bacteriorhodopsin ormosils were characterized by microscopy. The photocurrent as a function of applied potential was recorded in the presence and absence of external light source. The photocurrent showed increasing magnitude at negative potential. The sensitivity of photo-electrochemical response of D96N bacteriorhodopsin was examined at varying pH and in the presence of proton donor and electron donor. A quantitative co-relation between concentrations of proton donor and electron donor and photocurrent was observed. The stability of ormosil sandwiched bacteriorhodopsin was examined to be more than a year for practical applications



O45 - Electrochemical and Electrochromic Properties of Ni Oxide/Hydroxide Film Deposited by Sol-Gel Coating

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An electrochromism (EC) is defined as a phenomenon in which a change in color (light transmittance) takes place in the presence of an applied voltage. Because of their low power consumption (<2 V), high coloration efficiency, and memory effects under open circuit conditions, EC devices have many potential applications in smart windows, mirrors, displays, and optical switching devices. EC device generally consists of a transparent electrically conducting layer, electrochromic cathodic and anodic coloring materials, and an ion conducting electrolyte. W oxide and Ni oxide/hydroxide are currently in widespread use as, respectively, cathodic and anodic coloring materials.

Ni oxide/hydroxide films could be prepared various techniques. Our group has previously reported on the EC properties of the EC layers deposited by the RF sputtering method [1,2]. This method has various advantages with respect to uniformity and reproducibility of the films, however, disadvantage of higher cost than the sol-gel coating method. Also, sol-gel method can provide more porous films. So, in this study, the Ni oxide/hydroxide films were prepared by a sol-gel method. The solution prepared by dissolving nickel hydroxide powder, which was synthesized in solvent, deposited on ITO substrate. Then EC properties of the Ni oxide/hydroxide deposited by sol-gel method were measured and compared with RF magnetron sputtering.

The electronic and micro-structural properties of nickel oxide/hydroxide films were investigated by X-ray diffraction, X-ray photoelectron spectroscopy, and scanning electron microscopy. Electrochromic properties of nickel oxide/hydroxide films were investigated by in-situ transmittance measurement when the potential cycling and potentiostatic pulse wave were performed. The sol-gel nickel oxide/hydroxide films could change reversibly during potential cycling and the films were stable in electrolytes with long cycling. The electrochemical properties, coloration efficiency, and electrochromic response were suitable for anodic electrochromic materials. The details on sol-gel synthesis/coating and the evaluation on EC application will be discussed in the conference.



O46 - Screening of Inhibitors using Proteins Entrapped in Sol-Gel Derived Materials

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In recent years a number of new methods have been reported that make use of immobilized enzymes or receptors, either on microarrays or in bioaffinity columns, for high throughput screening of compound libraries. A key question that arises in such methods is whether immobilization may alter the intrinsic catalytic and inhibition constants of the immobilized biomolecule. Herein, we examine how immobilization within sol-gel derived materials affects the catalytic constant (k_{cat}), Michaelis constant (K_m) and inhibition constant (K_i) of a series of enzymes, and the dissociation constant (K_d) of immobilized transmembrane receptors. These biomolecules were encapsulated into sol-gel derived glasses produced from either tetraethylorthosilicate (TEOS), glycerol-doped TEOS, or the newly developed silica precursor diglycetyl silane (DGS). It was found that the catalytic efficiency and long-term stability of all enzymes, and the stability and binding affinity of receptors, were improved upon entrapment into glycerol-doped TEOS or DGS derived materials relative to entrapment in TEOS based glasses, demonstrating the benefits of the biocompatible reagent glycerol. In general, the K_m values of enzymes entrapped in glycerol-loaded materials were typically higher than those in solution, while k_{cat} values were generally lowered upon entrapment relative to the value in solution, indicating that substrate turnover was limited by partitioning effects and/or diffusion through the silica matrix. Nonetheless, the apparent K_i values for entrapped enzymes and the K_d values for entrapped receptors were often in excellent agreement with the values obtained in solution, suggesting that such immobilized species may be suitable for high throughput screening studies.



O47 - Gelation of Hybrid Inorganic-Organic Silicates Monitored by NMR and Fluorescence Spectroscopy

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Transparent, inorganic-organic hybrid silica materials have been prepared via hydrolysis and condensation of tetraalkylorthosilicates and various organosiloxanes by sol-gel processing. These materials are being studied as matrices for the immobilization of biomolecules. Gel materials with favorable structures and properties can be obtained by controlling the chemistry of the process to suit the particular biomolecule dopant. Since gels are prepared under ambient conditions, the gelation step and the post-gelation drying processes are important factors in controlling the final structures and hence the immobilization of reagents. In these experiments, tetramethoxysilane (TMOS), methyltrimethoxysilane, (MTMOS) and hydroxy-terminated polydimethylsilane (PDMS) have been used as precursors to prepare gels. Non-ionic biocompatible templates such as polyethyleneglycol and D-glucose were used as pore-templates. Fluorescence and nuclear magnetic resonance methods have been developed for *in situ* monitoring of reaction processes during polymerization, gelation and aging of gels. The fluorescent dye pyranine is sensitive to the proton acceptor characteristics of the solvent and so is used as a photoprobe to observe changes in the solvent composition during these processes. Nuclear magnetic resonance spectroscopy using spin-lattice relaxation (T1) measurements are employed to monitor the mobility of water within the matrix, and spin-spin relaxation (T2) properties of the solvent are used to monitor the onset of gelation. Gelation occurs when the growing silicate aggregates form a network, and this results in a minimum value of the T2 for solvent molecules (water or alcohol) and hence gelation times can readily be determined for a range of reaction compositions. The gelation time is greatly influenced by the type of organosiloxane, mole ratio of organosiloxane to TMOS, template content, pH and the temperature at which the monoliths were formed.

O48 - Monitoring of viability of cells immobilized by Sol-Gel process

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Steven Ripp, Gary S Sayler, University of Tennessee, United States

Katerina Demnerova, Institute of Chemical Technology, Czech Republic

Radomira Vankova, Institute of Experimental Botany, Czech Republic

In this work we compared different optical method for determination of content of biomass and viability of immobilized cells, which can be used for evaluation of the influence of the most commonly used immobilization into alginate and also for entrapment into inorganic matrix prepared by sol-gel process. Concentrations of entrapped cells *Saccharomyces* species were determined by measurement of intensity of fluorescence of natural fluorophores (tryptophan, tyrosine, pyridoxine, and coenzyme NAD(P)H). The intensities of fluorescence at ex/em = 320/360 nm and ex/em = 330/440 nm were proportional to concentrations of immobilized biomass and living cells respectively, in the range 0-15 g/l. Determination of concentration of living cells was based on time scan of the intensity of fluorescence of NAD(P)H during aerobic/anaerobic switch. The advantage of this method is that the concentration of living cells can be determined from NAD(P)H fluorescence even if the peak of NAD(P)H interferes with fluorescence of substrate or product. To adjust the concentration of living cells in the whole volume of a reactor lag-time was measured as the interval between the switch of the circulation of aerated medium and the beginning of the changes of NAD(P)H fluorescence. The influence of immobilization into layers from prepolymerized tetramethoxysilane and alginate was monitored by the luminescence measurements of bioluminescent reporters with lux AB immobilized in alginate and silica layers. After 8 month from immobilization the bioluminescence of silica layers containing these cells were not substantially decreased in contrast to alginate layers that were erode. The viability of tobacco cells was estimated from the measurements of intensity of luminescence of artificial substrate fluorescein diacetate. That was made in one step together with determination of biomass content by measurement 2-D fluorescence spectra. This simple method that needs sampling showed sensitivity of plant cells on conditions during matrix formation.



O49 - Sol-Gel Homogeneity: A Closer Look with Near-Infrared Imaging

Chieu D Tran, Dora Ilieva, Santhosh Challa, Marquette University, United States

Recently developed near-infrared (NIR) spectroscopic imaging instrument was used to study kinetics of sol-gel formation and structure of proteins entrapped in sol-gels. This imaging spectrometer possesses all advantages of conventional spectrometers. It also has additional features which NIR spectrometers cannot offer, namely, its ability to provide kinetic information at different positions within a sample. The high spatial resolution and sensitivity of the InSb infrared camera make it possible for the imaging spectrometer to determine the kinetic and structural information from data recorded by a single pixel. Kinetics of sol-gel reactions, determined by this imaging instrument, show that the initial hydrolysis of the TEOS, MTES or mixture of these two alkoxy silanes is relatively inhomogeneous. The inhomogeneity is dependent on the number of pixels used to calculate the spectrum for each spot. Single pixel provide the largest inhomogeneity while no inhomogeneity was observed when an average of a large number of pixels (e.g., 10 X 10) is used. The inhomogeneities observed for TEOS-sol-gels are different from those for the MTES sol-gels, and those for sol-gels prepared from a mixture of TEOS and MTES are relatively larger and more similar to those of the MTES sol-gels.

The imaging spectrometer also enable determination of structure of proteins including bovine serum albumin (BSA), trypsin and lysozyme entrapped in sol-gels. Spectra of entrapped proteins were found to be dependent on the location (i.e., spectra are different at different locations within a sol-gel sample) and the number of pixels used to calculate the spectra (at the same location, spectra calculated from 1 X 1, 5 X 5, 7 X 7 and 15 X 15 square of pixels are also different). It seems that the entrapped proteins distributed inhomogeneously within the sol-gel sample. Conformation of entrapped proteins are different. Interestingly, the inhomogeneity in the concentration and conformation of entrapped proteins was found to change concomitantly with the sol-gel formation processes.

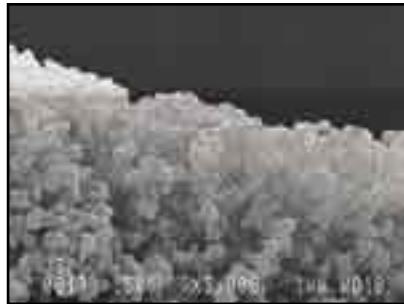
O50 - Sugar-Modified Silanes: Precursors for Silica Monoliths

Michael A Brook, Yang Chen, Kui Guo, Zheng Zhang, John D Brennan, McMaster University, Canada

The objective of our research in this area is the development of precursors for protein-doped silicas that are not only biocompatible, but provide improved cure characteristics, lower degrees of monolith shrinkage, and the possibility of pore templating, such that the flow of materials through the resulting silica monolith can be controlled. We set out to develop precursors that could be reproducibly prepared through a straightforward and scaleable route and that were uncontaminated by catalysts or byproducts, with the exception of byproducts that are protein stabilizing.

The preparation of alkoxy silanes derived from sugars and sugar alcohols including glycerol, sorbitol, maltose and dextran by direct transesterification with TEOS is described. These sugarsilanes were hydrolyzed to prepare monolithic, mesoporous silica. The sol-gel hydrolysis and cure rates are very sensitive to ionic strength, but not to pH: comparable rates of gelation were observed for any specific compound at constant ionic strength over a pH range of about 5.5-11. Pore sizes in the silica monoliths (~2-3 nm diameter) were marginally increased by the addition of non-functional polyethylene oxide (PEO) (pore sizes: no PEO, 3.1 nm; PEO MW 2000, 10000, 3.3 and 3.6 nm, respectively): protein dopants such as Human Serum Albumin did not act as porogens. PEO terminated with Si(OEt)₃ groups (TES-PEO) was very efficient at increasing pore size (TES-PEO MW 200 and 10000, led to pores of average diameter 3.8 and 6.1 nm, respectively). The addition of a multivalent metal such as Mg²⁺ to the sol increased pore sizes of glycerol-derived silica, but lead to decreased sizes in silica prepared from Si(OEt)₄. Residual sugars in the silica monolith reduced the magnitude of shrinking. Further reduction in shrinkage was achieved by the addition of sugar-derived trifunctional coupling agents to the sol. Proteins such as Factor Xa entrapped in the mesopores were found to remain native and enzymatically active over many months.

These precursors offer significant advantages over TEOS for the preparation silica monoliths containing proteins.



O51 - Sol-Gels Films as Substrates for Tissue-Cell Culture Growth

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Tissue-derived cells are anchorage dependent cells and require therefore attachment to a solid surface for viability, growth and spread over. The chemical characteristics of the substrate determine the behavior, function and shape of the attached cells.

Motivated by the demonstrated advantages of sol-gel materials for many bioapplications, we have been developing a new family of films for tissue culture growth, based on these special materials. A major advantage of sol-gel films is that they can be tailored to the specific growth-conditions requirements of various cells. Here we report the investigation results of the influence of substrate surface hydrophobicity and of film positive charge density on Buffalo Green Monkey (BGM) cell line adhesion, growth and shape. The films were prepared from various ratios of methyltrimethoxysilane (MTMOS)/tetraethoxysilane, to achieve different hydrophobicities; and from various ratios of MTMOS/polyamine-poly-L-lysine (PLL), to achieve variability in the surface cationic site concentrations. Various film preparation protocols were tested and optimized. Enumeration of the attached cells to sol-gel films was determined daily for 1-7 days. The results revealed that PLL promotes cell growth and that intermediate hydrophilicity is optimal for that purpose. Generalization of this novel methodology towards other cells and other cell-growth applications is in progress.

O52 - Sol-Gel Derived Hydroxyapatite Coatings on Anodized Titanium Substrates

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Hala Zreiqat, Australia

The anodization of titanium involves the formation of a thin, dense and compact, oxide layer. In this process the rutile structure of the original titanium oxide is converted into an anodic oxide film containing Anatase crystalline structure. It is this Anatase structure and how it influences the bonding properties of the sol gel coating of hydroxyapatite (HAp) was the main aim of this research project.

Method and Materials

The titanium samples were anodized in a phosphoric/sulphuric acid with differing phosphoric acid concentrations. The samples were also anodised at 3 different voltages, 25V, 50V and 75V. Both anodized and unanodized samples were spin coated with patented sol-gel alkoxide-derived hydroxyapatite and examined with x-ray diffraction, NMR and scanning electron microscopy.

Calcium precursor solution was prepared by using Ben-Nissan et al. [1] method by dispersing calcium diethoxide in absolute ethanol followed by dissolving the calcium diethoxide with ethylene glycol while stirring vigorously. Stoichiometric amount of phosphorus precursor solution was prepared by diluting, of either $\text{P}(\text{OEt})_3$ or $\text{HOP}(\text{OEt})_2$, in absolute EtOH while stirring. After complete dissolution of the $\text{Ca}(\text{OEt})_2$, the stoichiometric quantity of phosphorus precursor solution was added drop-wise to the calcium precursor solution.

The samples anodized using a mixture of phosphoric acid (H_3PO_4)/ sulphuric acid (H_2SO_4) solution was found to produce a more adherent and homogenous HAp coated surface.

It is envisaged that this improved technique could help to produce new generation of more efficient bioactive HAp coatings on titanium and titanium alloys for orthopaedic and dental implant applications.

[1] B. Ben-Nissan, D.D. Green, G.S.K. Kannangara, C.S. Chai and A. Milev, 31P NMR Studies of Phosphate Derived Nanocrystalline Hydroxyapatite, J. Sol-Gel Sci. & Tech., 21, 27-37, (2001).



O53 - Antimicrobial Sol-Gel Coatings

Boris Mahltig, Dirk Fiedler, Horst Böttcher, GMBU, Germany

The embedding and immobilization of various antimicrobial substances in sol-gel coatings is a rewarding technique to prepare new biocidal materials. By chemical modification of these coatings a controlled release of the antimicrobial substances can be obtained. The embedding of silver or its compounds enables the preparation of simple and environmental friendly biocidal materials. The rate and the amount of the liberated silver ions which determines the antimicrobial efficiency can be controlled by the kind of the modified silica matrix, by additives like polyol compounds and by the annealing conditions. The co-immobilization of organic biocides extends the range of application concerning different types of microorganisms and avoids the adaptation of microorganisms. Different applications of the antimicrobial protection of coated wood and textiles are proved. Also medical equipment like catheters can be protected against microbial contamination.

O54 - Sol-Gel derived imprinted nanocomposites for $\text{Ba}^{2+}_{(\text{aq})}$ analysis

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It is clear that there is a whole raft of ion sensing technologies (including ion-selective electrodes) but by and large these will not meet the analytical requirements of those running oil wells. Optical fibers are cheap and can be used in a discrete or a distributed context. They are already used in temperature analysis in oil wells but to make them able to sense ions they must become chemically smart by the application of a chemically-active coating that responds to strain induced by an ion-active phase. Presented here is work on a rugged Ba^{2+} sensitive and selective optical fiber for use in oil wells via the immobilisation of Ba^{2+} chelating species (L) on solid silica (S) supports, using bi-functional silanes, and sol-gel techniques. The authors report sol-gel routes to bulk S, molecularly imprinted S, L/S nanocomposites and characterization data for each of these, from FT-IR, NMR, BET, DSC and BET analyses. These sol-gel nanocomposites have been evaluated in terms of selectivity to $\text{Ba}^{2+}_{(\text{aq})}$ and the most promising have been dip coated as thin films that have been evaluated as $\text{Ba}^{2+}_{(\text{aq})}$ sensors. The potential of this approach for environmental and medical diagnostics is considered.

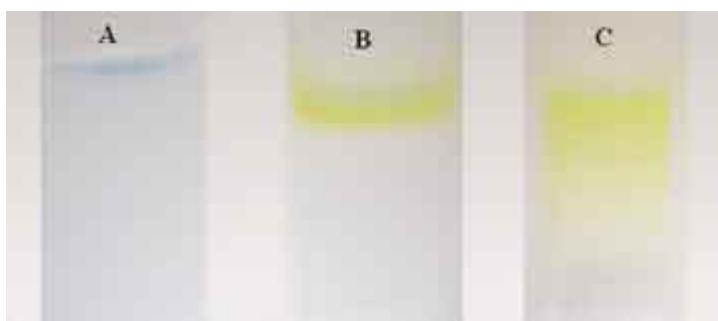


055 - Charge-Transfer Optical Sol-Gel Detectors for CW Contamination on Surfaces

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A colorimetric sensor encapsulated in a sol-gel strip or aerosol is designed for detecting chemical warfare agents (CWAs) contamination on surfaces. This innovative sensor is based on a reactive charge-transfer (CT) mechanism that gives a sharp color change of sensors in the presence of CWAs. For a direct CT colorimetric monitor for mustard gas (HD), the reactive material is a metal-organic ligand (such as Cu(II) acetate) which acts as an electron acceptor (or Lewis acid). HD is a good Lewis base (or electron donor) due to its non-bonding electrons on the sulfur atom of HD. Upon contact with HD, the sensor will respond a fast (in a few seconds) and sharp color change from the sky blue to a canary yellow color. Figure 1 shows a color change of Cu(II)-doped sol-gel sensor: (A) initial sky blue of sensor, (B) 10 min after HD analogue added, noting that a color change to canary yellow is seen immediately in seconds, and (C) 5 h after HD analogue added. The colorimetric sensor is selective and specific only responding positively to the chlorinated sulfide (i.e., HD). The detection limit of HD analogue is calibrated at 0.03 μ L per 1.5 mL sensor volume.

The current detector used in monitoring CWAs contamination on surfaces is a M8/ M9 paper indicator and a CAM - chemical agent monitor. The paper type of chemical detector generally shows a light color change upon interactions with CWAs, and a reasonable amount of reactive chemical agents (in free liquid form) is needed to promote an observable color change. In this presentation, an indirect, but reactive CT colorimetric detector for nerve agents (G-series) and a reverse CT colorimetric detector for VX will also be described. An integrated optical sensing system that combines colorimetric sol-gel concentrator-indicators with laser-induced breakdown spectroscopy (LIBS) will also be illustrated.



O56 - Optical Properties and Sensitivity of Xerogel Detection Layers for Fiber-Optic Hydrocarbon Sensors

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Materials prepared by the sol-gel method have shown their great potential for the development of detection parts of optical chemical sensors. In these sensors the detection of chemicals is based on changes of optical properties of the detection part induced by the chemicals penetrating in it. These changes depend on optical and physico-chemical properties of the detection part. This paper deals with the *in situ* determination of these properties for doped silica xerogel layers coated on optical fibers.

The xerogel layers were applied on silica fibers and microscopic slides by the dip-coating method from input sols. Tetraethoxysilane, methyltriethoxysilane and phenyltriethoxysilane, ethanol, hydrochloric acid and water were used at the preparation of the input sols. The contents of methyl and phenyl groups in the sols were varied with the aim of preparing xerogels with different hydrophobicity and refractive index. The gels were dried at temperatures below 110 °C.

The thickness and complex refractive index of the xerogel layers prepared on slides were evaluated by profilometry and spectral ellipsometry. The sensitivity and physico-chemical properties of the layers applied on fibers were determined from angular and temporal changes of the output power from the fiber measured in ranges of 600-700 and 1500-1700 nm. In these experiments the xerogel layers were exposed to gaseous mixtures of aromatic and aliphatic hydrocarbons and the fiber was excited by an inclined collimated beam. Theoretical models were used for the determination of the complex refractive index of the layers as well as of the parameters of the interaction kinetics of the layers and hydrocarbons.

The results show correlation between the parameters of the layers applied on the slides and determined on the fibers. It was found that the sensitivity of the layers to hydrocarbons can be expressed through the refractive indexes of the layer and liquid hydrocarbon, light absorption coefficient of the layer and partition coefficient of the hydrocarbon. So far a maximum sensitivity of about 0.01 vol.% has been achieved.

This work was supported by the Grant Agency of the CR (contract No. 102/02/0780)



O57 - New hybrid organic-inorganic membranes based on molecular recognition of crown compounds and self-assembled urea moieties mediated by Sol-Gel route

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Nadine Hovnanian, France

Towards the objective of mimicking biological transport, artificial systems functioning as carriers or as channel-forming superstructures have recently been developed. A promising field is the study of hybrid dense membranes containing well organized receptors covalently linked to a polymeric matrix, obtained by sol-gel process. In that goal, specific alkoxy silane precursors were synthesized containing crown ether, urea functions and aromatic rings based on three encoded features: the molecular recognition sites for anions and cations are covalently bonded; the supramolecular guiding interaction is the urea head-to-tail hydrogen bond association, assisted by pi-pi stacking interactions; the covalently bonded alkoxy sil groups allow by hydrolysis-condensation to transcribe the solution self-organized structures in a solid heteropolysiloxane material. Urea functions have been used for their ability to self-assemble either in solution or in solid state by hydrogen bonding able to form organized channel for anion transport. Aromatic rings enhance by pi-pi stacking this organization and permit orientation of crown ethers for the cation transport. The resulting self-organized hybrid materials revealed to be of great interest for the facilitated transport of biological molecules as zwitterionic phenylalanine or ATP ions in aqueous media. We will describe the synthesis and characterization of such self-organized hybrid systems and we will present their interesting and potentially useful functions as separation devices.

O58 - Novel hybrid Sol-Gel films for multi-analyte sensing

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Frank V Bright, University of Buffalo, United States

Multianalyte optical chemical sensor systems are of increasing importance, especially in the context of microsystem applications. A key element of such systems is the development of printable sensor materials with stable calibration functions on a common instrumentation platform. We have developed novel hybrid films based on doped n-octyltriethoxysilane (Octyl-triEOS)/tetraethoxysilane(TEOS) composites which have been patterned onto a variety of substrates for multi-analyte optical sensing applications. Optical oxygen and carbon dioxide sensors have been realised using these films. Oxygen sensing is based on the luminescence quenching of the lifetime of the oxygen-sensitive ruthenium complex, ruthenium(II)tris(4,7-diphenyl-1,10-phenanthroline) while carbon dioxide sensing techniques based on a variety of pH-sensitive luminescence complexes have been used. All luminophores have been chosen to be spectrally compatible, enabling single wavelength, LED excitation and photodiode or CCD detection for the dual sensor. A phase-based detection system is employed which enhances sensor performance compared with intensity-based techniques. The oxygen sensor response is characterised by linear Stern-Volmer behaviour, enabling single point sensor calibration, as well as enhanced luminescence lifetime and excellent long term stability. Both the sensitivity and the degree of linearity of the response can be tuned by varying the proportion of precursor. A variety of coating techniques have been used including dip and spin-coating as well as ink-jet and pin-printing. In particular, this study investigates the relative merits of ink-jet and pin-printing techniques for multi-analyte sensor chips.



059 - Influence of preparation conditions on structure and magnetic properties of Sol-Gel derived Iron-doped Siloxane-Polyethyleneoxide Nanocomposites

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Brazil

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Leila A Chiavacci, Karim Dahmouche, Celso V Santilli, Instituto de Quimica-Universidade Estadual Paulista, Brazil

Valérie Briois, LURE Centre Universitaire Paris-Sud, France

Aldo F Craievich, Instituto de Fisica-Universidade de Sao Paulo, Brazil

Materials containing magnetic nanoparticles have attracted attention due to their application in many fields like magnetic storage devices, smart materials and biomedicine. By the other side, organic-inorganic hybrid materials such Siloxane-Polyethyleneoxyde (POE) systems have been used as host material for many dopants such as Lithium, Europium and more recently Iron to induce ionic conduction, luminescent and magnetic properties, respectively. These nanocomposites have extraordinary implications that derive from the possibility of both mixing at nanosized level and bonding covalently the organic and inorganic components. In this work we investigate the influence of preparation conditions such as pH of the precursor sol, nature of Iron salt and Iron doping level on structure and magnetic properties of Iron-doped siloxane-POE hybrids prepared by sol-gel process. For Fe(II)-doped samples prepared in neutral pH, SAXS results suggest the existence of a two-level hierarchical structure. The primary level is composed of spatially correlated siloxane clusters embedded in the polymeric matrix and the secondary, coarser, level consists of domains where the siloxane clusters are segregated. The structure of Fe(III)-doped hybrids prepared in the same conditions is different, revealing the existence of iron oxide-based nanoclusters (identified as ferrihydrite with wide-angle X-ray diffraction (XRD)) dispersed in the polymer matrix. The different magnetic features between Fe(II) and Fe(III)-doped samples are consistent with the structural differences revealed by SAXS. While Fe(II)-doped composites exhibit a paramagnetic Curie-type behaviour, hybrids containing Fe(III) ions show thermal and field irreversibilities. The use of an acid catalyst (HCl) during the synthesis process modifies the hybrid structure and properties: in such conditions EXAFS results show the formation of two iron species (FeCl_4^- and FeO_x) in Fe(III)-doped hybrids, whose respective proportions depend on Iron doping level. The 60 Å sized FeO_x domains were also detected by SAXS. The structural differences induced by distinct preparation conditions have been associated to the variations on the magnetic and thermomechanical properties of the samples.

O60 - Porous garnet coatings tailoring the emissivity of thermostructural materials

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Daniela Diso, Massimo Mazzer, Giovanni Torsello, Alfonso Maffezzoli, Italy

The power radiated by a surface influences the energy transfer processes following a T4 slope law. It is therefore clear that, at high temperature, the study and control of spectral emissivity of materials play a key role in many important technologies: reentry vehicle thermal protection shields, high temperature radiators, selective emitters in thermophotovoltaic generators. We have developed a class of thick porous garnet coatings that may rise or lower the spectral emissivity of thermostructural materials in the VIS, NIR, IR regions. The porosity of the coating, nearly cancel any emission contribution from the underlying materials due to the scattering in the inhomogeneous system: pore/high refraction garnet. The yttrium aluminium garnet polycrystals vary their emissivity as a function of the doping rare earth elements they contain. We achieved an emission control capability in the range 700-3000nm. Porous coatings have been prepared from ceramic slips containing a reactive colloidal phase and rare earth garnet powders prepared drying and calcining mixed oxide aqueous gels. The general formula for the garnet was: $\text{Er}_x\text{Y}_{3-x}\text{Al}_5\text{O}_{10}$, the thickness of the coatings ranges between 50 and 400 microns. The coatings have been investigated by morphological and microstructural studies. A dedicated experimental set up has been developed to measure the spectral emissivity up to 1600°C in different heating conditions.



061 - Preparation of Proton Conductive Inorganic-Organic Hybrid Films Using Epoxyhexylethyltrimethoxysilane and Orthophosphoric Acid

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Atsunori Matsuda, Toyohashi University of Technology, Japan

Solid materials with high proton conductivity have attracted much attention for the application to a variety of electrochemical devices. Among these electrochemical devices, polymer electrolyte-type fuel cells (PEFCs) are extensively studied as a new energy conversion device. The PEFCs are at present used at temperatures lower than 100 °C because the proton conductive membranes used for the fuel cells lose their conductivity at temperatures higher than 100 °C. To improve energy conversion efficiency and to avoid CO poisoning of catalysts, PEFCs which can operate at temperatures higher than 100 °C are strongly desired.

We have reported the preparation of proton conductive solid electrolytes by the sol-gel method, and very recently we have prepared proton conductive inorganic-organic hybrid membranes, which showed high proton conductivity even at temperatures higher than 100 °C with low relative humidity, from 3-glycidoxypropytrimethoxysilane (GPTMS), tetramethoxysilane (TMOS) and orthophosphoric acid (H_3PO_4) [1]. It was found that the epoxy group in GPTMS plays an important role in keeping H_3PO_4 in the hybrid films.

In the present study, we have prepared proton conductive inorganic-organic hybrid films, which show high proton conductivity at temperatures higher than 100 °C under low relative humidity, from epoxyhexylethyltrimethoxysilane (EHTMS), which has a longer organic chain compared with GPTMS, and H_3PO_4 by the sol-gel method.

Self-supporting, flexible films with a thickness of about 150 to 300 μm were obtained. Addition of EHTMS to GPTMS- H_3PO_4 hybrid films led to the increase in the tensile strength of the film and to the formation of hybrid films with larger P/Si ratio. DTA-TG measurements revealed that the films were stable up to about 200 °C. The ionic conductivity of the films increased with an increase in the content of H_3PO_4 in the films. The ionic conductivity of the films increased with an increase in the relative humidity and was about $1 \times 10^{-2} S cm^{-1}$ under 20 % relative humidity at 130 °C.

This work was supported by the project "Research and Development of Polymer Electrolyte Fuel Cell" of NEDO, Japan.

[1] K. Tadanaga et al., Chem. Mater. (2003), in press.

O62 - Synthesis and Characterization of Optical Sol-gel Adhesive for Military Protective Polycarbonate Resin

Mikko S Keränen, Terho K Kololuoma, Juha T Rantala, VTT Electronics, Finland
Marcin Gnyba, Gdańsk University of Technology, Poland
Paavo Raerinne, Defence Forces Technical Research Centre, Finland

Sol-gel adhesive material for isostatic i.e. hotpressing lamination process was synthesized using 3-aminopropyltrimethoxysilane (APTES), 3-glycidyloxypropyltrimethoxysilane (GPTS) and methacryloxypropyltrimethoxysilane (MPTS) as precursors. Reaction dynamics between APTES and GPTS was followed on-line with Raman spectroscopic technique. Lamination process was optimized varying hotpressing times (20-60 min.) and pressures (500-3000 psi) at constant temperature (+70°C). Mechanical peel-off properties were found to be excellent for studied composition, 25-30 kg/cm² (180° peel test) at its best. One possible application of laminated structure is a visor of soldier's helmet. The ballistic protection properties were tested by shooting with 1.1 gram standard fragment, and determining the v_{50} velocity value, which corresponds 50 % perforation. The laminated structure gave 5.7 % better protection compared with solid polycarbonate. Laminated components have high transparency (over 90%) at visible light range as well as high environmental stability. Keywords: Sol-gel, adhesive, lamination, Raman spectroscopy, ballistic protection.



063 - Silica with bimodal pores for solid catalysts prepared from water glass

Ryoji Takahashi, Satoshi Sato, Toshiaki Sodesawa, Chiba University, Japan

A bimodal porosity with macropores and mesopores is attractive in the fields such as catalysis, adsorption and separation. In the past decade, Nakanishi et al. have reported the preparation of bimodal porous silica gel based on sol-gel method with an organic polymer [1], where macropores are formed by fixing a transitional structure of spinodal decomposition. Although the bimodal porous silica is attractive, its application is restricted because of high cost of silicon alkoxide. Recently, we reported the preparation of bimodal porous silica from water glass. In the present work, we describe the detail in the structure of the obtained material

The bimodal porous silica was prepared by adding water glass into aqueous solution of polyacrylic acid with stirring. Thus prepared sol was held for 1 day for gelation at room temperature. The obtained wet gel was dried after washing and aging in an appropriate solution. Finally, the dried gel was calcined at prescribed temperature.

The size of interconnected macropores can be sequentially controlled from 1 to 20 micrometers by changing starting composition, and it is suggested that the macropores are formed by phase separation. The mesopore size can be also controlled from 2 to 20 nanometers by changing aging condition. Thus, macroporous silica can be prepared also from water glass. We can prepare monolithic silica with various shapes, such as rod, plate and sphere. The gas flow resistance in the macropores was also measured to ensure the effectiveness of macropores. A monolith formed in the rod was used for the measurement, and pressure difference between the both ends of the rod was measured as a function of gas flow rate. Because of the smoothness of macropores, the pressure loss in the macroporous silica is much smaller than the columns packed with powder, and can be approximated with simple straight pipe model.

INDUSTRIAL APPLICATIONS

C1 - Sol-Gel route to cost effective renewable energy

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Sustainable Technologies International (STI) (and its predecessor -STA) has been involved at the forefront of so-gel technology since 1987. Our initial work built on research in Victoria on cadmium stannate¹ for transparent conductor and infra-red applications. In spite of the success (and patents) this was replaced by other transparent conductors such as tin oxide and indium tin oxide due to the environmental concerns with cadmium. The ITO work and subsequent optical films utilising titania were a basis for our extended involvement in electrochromic materials^{2,3}.

In 1994, we recognized that sol-gel was the basis for imminent renewable energy technologies that are based on nano-oxides and electrochemical interaction. We leveraged our sol-gel and electrochromic expertise in developing photoanodes for dye solar cells (DSC) and for hydrogen generation, becoming world's first to productionise DSC technological solutions.

STI's unique manufacturing process will be presented with emphasis on sol-gel based routines, in particular, for creation of nano-structured oxide layers and their subsequent modifications.

Additionally, tandem and multifunctional solutions for energy efficiency⁴ and direct generation of hydrogen by water splitting will be discussed.

¹ Coating Solutions, US Patent 4,960,466

² Preparation of metal alkoxides, US Patent 6,355,821

³ Preparation of peroxy and peroxyester tungsten derivatives European Patent 1163216

⁴ Electrophotochromic smart window and methods, US Patent 6,297,900



C2 - Silica on Silicon Planar Lightwave Circuits using a Novel Single Step Sol-Gel Process

Zahoor Ahmad, Avin Suyal, Habibur Rehman, Xu Li, Simone Cappelli, Duan Li Ou, Terahertz Photonics, United Kingdom

Development of a novel, low cost, single-step sol-gel process: SOLICA™, for high volume production of silica on silicon planar lightwave circuits (PLC's) is reported here for the first time. Optical components with performance better or similar to those produced by vapour based processes such as flame-hydrolysis (FHD) and chemical vapour deposition (CVD) can be produced using this process.

Fully densified glass layers as thick as 10 microns can be produced on 150 mm diameter Si wafers using a single spinning, drying and heating operation after densifying at temperatures ranging between 1000 and 1200°C (depending upon the composition) repeatably. A unique sol synthesis and subsequent modification process have been the key to avoid cracking of such thick films during drying and densification.

Densified glass layers with a thickness uniformity of < 1 % and a birefringence of $(2.4 \pm 0.5) \times 10^{-4}$ have been produced using a simple laboratory spinner. Dopants such as Ti (up to 5 mole%), Ge (up to 25 mole%), P (up to 8 mole%), B (up to 10 mole%) and Al (up to 5 mole%) were successfully incorporated to enhance the refractive index or to reduce the densification temperature.

Propagation losses between 0.05 - 0.1 dB/cm (depending upon the index contrast Δ defined as $[n_{\text{core}} - n_{\text{clad}}] / n_{\text{core}}$) have been measured on single mode straight waveguides and 36 cm long spirals for a Δ of upto 1.5%. Another important aspect of Solica is that it allows production of waveguides with Δ of up to 3%. Cladding layers densified at 1000°C shows excellent conformal filling of the narrow gaps down to sub-micron. We believe that SOLICA™ is capable of producing high performance silica on Silicon PLC's with added functionality at a cost 5 – 10 times cheaper as compared to the vapour-based processes.

C3 - Nanoparticles by Wet Chemical Processing in Commercial Applications

Monika Kursawe, Volker Hilarius, Ralf Anselmann, Gerhard Pfaff, Merck KGaA, Germany

Products of materials with at least one dimension in nanometer scale like carbon black and silica powders are well known in industry. The majority of these materials is made by solid state chemistry.

However, nanoparticulaire materials produced by wet chemical processing have a wide range of fascinating applications.

A sol of monodisperse SiO_2 -particles is developed for antireflex coatings on glass. With this sol, a porous, single-layer $\lambda/4$ coating which gives an antireflex effect over a wide range of the wavelength of light can be achieved. Although being porous, these antireflex coatings exhibit a good mechanic stability, sufficient for commercial applications. The antireflex coating sols are used to produce antireflex glass cover sheets for photovoltaic modules.

In this paper, an insight in the development of Merck's antireflective coating sols from the idea to commercial production is given.

Nanoparticulaire materials made by wet chemical processing are not limited to niche applications. Inorganic metal oxide coatings on thin mica platelets lead to a broad product range of pearlescent pigments. These inorganic layers, consisting of titanium dioxide or iron oxides, are manufactured by a wet chemical procedure. The well-defined layer thickness, varying from 50 to 300 nm, determines the optical effect of the pearlescent pigment.

By using synthetic SiO_2 -platelets instead of natural mica, impressive angle-dependant effect colours can be achieved. These synthetic SiO_2 -platelets are also produced by a sol-gel technique.

Spherical silica particles made by wet chemical processing are used in cosmetic formulations. The size distribution determines the skin feeling of the product. Also, certain colour or anti-wrinkle-effects can be achieved by coating the spherical particles.



C4 - Low Pressure Drying of Large Porous Silica Monoliths

Rahul Ganguli, Larry Meixner, De-Yin Jeng, Ray Chaudhuri, YTC America Inc., United States

Repeatable crack-free drying has been a long-standing and persistent problem in the sol-gel fabrication of large monoliths. Drying at ambient conditions can induce large stresses and crack the monolith. Supercritical drying can reduce drying stresses, but the related high-pressure processing steps can increase cost and raise safety issues. A novel low-pressure process with precise control of drying rate has been shown to economically dry gels as large as eighteen inches in diameter. Differences in microstructure between gels dried at low pressure and at near-critical pressure influence the properties of the resulting sintered glasses. The drying process may be scaled up to even larger sizes, providing an economical method to fabricate glass of sizes previously considered unfeasible using sol-gel technology.

C5 - Exploration of new and functional materials by combinatorial wet process

Kenjiro Fujimoto, Kazunori Takada, Takayoshi Sasaki, Mamoru Watanabe, National Institute for Materials Science, Japan

Combinatorial method has been developed as a process to prepare a lot of samples and examine their properties in a short time. We have hitherto developed a full-automatic robot system for preparation of ceramic powder by using wet synthesis process, and developed a powder X-ray diffractometer for the characterization of prepared compounds. In this study, we will show the results obtained by use of this system as a demonstration of its performance and how the combinatorial method is effective for preparation and characterization of pseudo-ternary compounds.

Starting materials used were aqueous solutions and slurries of nano-sized particles suspended in water or alcohol. The calcined products were characterized by powder X-ray diffraction. Powder X-ray diffraction was carried out using a combinatorial X-ray diffractometer developed for the high throughput characterization of the products by our laboratory and Rigaku Denki Corporation. This diffractometer is equipped with a position-sensitive proportional counter. Consequently, the diffraction pattern is obtained without scanning a detector, and it takes only 2 minutes to obtain one pattern.

We studied phase relation of $X\text{-ZnO-FeO}_{1.5}$ (X : NiO, CoO, ...) system by the combinatorial method. As an example, it was found that the single phase of Ni-Zn ferrite was obtained at a composition of $\text{NiO: ZnO: FeO}_{1.5} = 0.2: 0.2: 0.6$ at 1173K.

This full automatic combinatorial robot system spent about 8 hours from preparation and XRD measurement of 66 samples. As a result, this system can prepare and characterize about 200 samples in one day. When the ternary compounds are prepared with compositions varying every 0.1, three ternary phase diagrams can be obtained. From above result, it was found that the combinatorial approach is much more effective method for exploration of materials than conventional one.

Posters Abstracts

MONDAY POSTER SESSION

602 - Preparation of C₆₀-Siloxane Hybrids

Takahiro Gunji, Koji Arimitsu, Yoshimoto Abe, Tokyo University of Science, Japan
Robert West, University of Wisconsin-Madison, United States

A convenient hydrosilylation of C₆₀ With sila-functional silanes by using platinum catalyst to obtain C₆₀-silica hybrids with the aim to develop a new approach for the fabrication of C₆₀ containing novel materials.

Into the anhydrous hydrogen hexachloroplatinate (IV) toluene solution, C₆₀ and triethoxysilane were added and then stirred at room temperature for four days. Solid material was filtered and toluene was evaporated under vacuum. The residue was added into diethyl ether and then the insoluble solid was filtered off. Silylated C₆₀ was obtained by evaporating diethyl ether from the filtrate. Into a mixture of C₆₀-TES, polymethylsiloxane, and solvent, hydrochloric acid was added and then stirred for 2 h. The hydrolyzate was poured into a polypropylene beaker wrapped with polyethylene film with five pinholes and aged at room temperature for about three weeks. The other C₆₀-siloxane hybrid was also prepared by the same procedure by using silanol terminated polydimethylsiloxane instead of polymethylsiloxane.

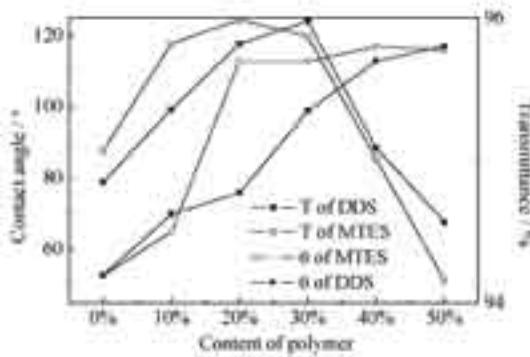
C₆₀-TES was isolated as a brown pasty liquid at the yield of ca. 40%. The average composition was estimated to be C₆₀[Si(OEt)₃]₃H₃ from the proton ratio of ¹H NMR spectrum using 1,4-dioxane as an internal standard. On the preparation of C₆₀-siloxane hybrid, the progress of the synthetic reaction was monitored by the color and state of the solution: At the beginning of this process, the solution was colored in yellow or brown and the viscosity was increased. The C₆₀-siloxane hybrids were homogeneous and transparent. The color of the C₆₀-siloxane hybrid varied from light yellow to deep brown with an increasing amount of C₆₀-TES. The UV-VIS spectrum of the hybrid was similar to that of C₆₀-TES, indicating that C₆₀-TES was incorporated into the siloxane network. Finally, a C₆₀-siloxane hybrid containing C₆₀ in the molar ratio of Si/C₆₀=500/1 and 1000/1 were prepared by this process.

Yuhan Sun, Dong Wu, Yao Xu, Institute of Coal Chemistry, Chinese Academy of Science, China

A sol-gel process was utilized to prepare hydrophobic antireflective silica films. Silica sol was synthesized by the hydrolysis of TEOS ($\text{SiO}(\text{C}_2\text{H}_5)_4$) under base catalysis. Polymeric solution of MTES ($\text{CH}_3\text{SiO}(\text{C}_2\text{H}_5)_3$) or DDS ($(\text{CH}_3)_2\text{SiO}(\text{C}_2\text{H}_5)_2$) was synthesized under acid catalysis, by which the hydrolyzed MTES or DDS was polymerized into ladder-like polymer or spiral line-like polymer. With the mixing of silica sol and polymeric solution, methyl-modified silica sols were prepared. Then spin-coating films were deposited on glass substrates. The change of particle size was investigated by photon correlation spectrum (PCS), SAXS and TEM. The transmittance of film was measured by UV-VIS. The hydrophobic property of film was characterized by its static contact angle for water.

From the result of SAXS, the average particle dimension d_{SAXS} varied very limitedly. But from the result of PCS, the mean particle diameter d_{PCS} increased, but didn't varied visibly, with the increase of polymer in the case of MTES and DDS. By TEM observation, MTES polymer connected silica particles into large and irregular clusters, meanwhile, DDS polymer into short worm-like clusters.

The hydrophobic property was not identical for the films from different methyl-modified silica sols. When deposited from silica-MTES sols, the contact angle for water increased firstly sharply from 52° to 113° and then presented a flat trend with the increase of MTES polymer. But the contact angle increased slowly with the increase of DDS polymer till the maximum of 119° (Figure). The transmittance of film has similar trend when using the two kinds of methyl-modified silica sols. It increased firstly and then decreased with the increase of polymer. The highest value reached 96.0%, which meant no reflection. The best antireflection was obtained in a componential range of polymeric solution in mixture between 20% and 30% (Figure). As a result, silica-MTES sol was more suitable to prepare hydrophobic antireflective film.



604 - Thin Films and Nanoparticles of Spinel from new Classes of Single Source Molecular Precursors, $\text{MAI}_2(\text{acac})_4(\text{O}i\text{Pr})_4$ and $\text{MAI}_2(\text{acac})_3(\text{O}i\text{Pr})_4(\text{OAc})$, M= Mg, Mn, Co, Ni, Zn

Vadim G Kessler, Swedish University of Agricultural Sciences, Sweden

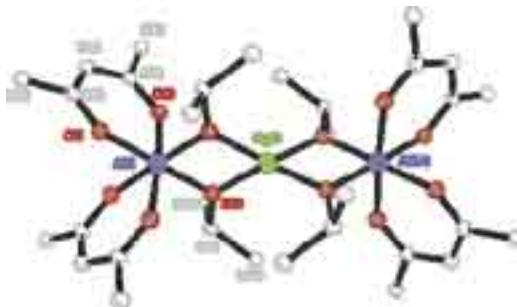
Gulaim A Seisenbaeva, SLU, Sweden

Stephane Parola, Universite Claude Bernard Lyon 1, France

Two new classes of single source precursors, $\text{MAI}_2(\text{acac})_4(\text{O}i\text{Pr})_4$ (1), M = Mg, Co, Ni [1] and $\text{MAI}_2(\text{acac})_3(\text{O}i\text{Pr})_4(\text{OAc})$ (2), M= Mn, Co, Zn [2] have been obtained by cost efficient single-batch techniques, based on interaction of divalent metal acetylacetonates with aluminium isopropoxide on reflux in hydrocarbon media with subsequent modification with additional quantities of acetylacetone or acetylacetone and acetic acid. The obtained compounds have been characterized by X-ray single crystal studies, IR, NMR and mass-spectrometry. Compounds of the 1 series are stable in solutions in hydrocarbons at temperatures below 25°C, but decompose on heating providing $\text{M}_2\text{Al}_2(\text{O}i\text{Pr})_6(\text{acac})_4$, along with $\text{Al}(\text{acac})_3$. Compounds of the 2 series are thermally stable in solutions and even sublime in vacuum with only minor decomposition according to mass-spectral data. Hydrolysis of 1 and 2 with subsequent thermal treatment provides access to nanoparticles of spinels at low temperature (400°C). Extremely uniform thin films of NiAl_2O_4 have been obtained by dip-coating technique from 0.15 M solutions of $\text{NiAl}_2(\text{acac})_4(\text{O}i\text{Pr})_4$ in toluene with subsequent thermal treatment at 400°C. They have been characterized by X-ray diffraction and SEM-EDS techniques. The thickness of films could be controlled by varying the elevation speeds and the number of deposited layers.

[1] Kessler V.G., Gohil S., Parola S., Dalton Trans., 2003, 544.

[2] Seisenbaeva G.A., Suslova E.V., Gohil S., Kessler V.G., Dalton Trans., 2003, in press.



605 - A novel sonochemical route to BaSO₄ nanocrystals with controlled morphologies

Sun Yuhan, Wu Dong, Li Junping, Chinese Academy of Science, China

Barium sulfate has received considerable attention for its applications in ceramics, pigments and fillers for polymers. The performance of BaSO₄ in its various applications depends on its crystalline phase state, dimensions and morphology. Therefore, many efforts have been made to control the size and morphology of BaSO₄ including the addition of organic additives and reverse micelles.

In this paper, we report a novel sonochemical method for the preparation of BaSO₄ nanocrystals with controlled morphologies in the presence of EDTA. The samples were characterized by XRD, XPS, SAED and TEM. It was found that the morphologies of the so-produced BaSO₄ exhibited spherical, spindly and petal-like by adjusting the pH of the system while just spherical nanoparticles were obtained under a similar reaction without ultrasound irradiation. Moreover, the formation mechanism was discussed in detail.

The XRD patterns indicated the produced ZnS were orthorhombic crystal structure.

Fig. 1 showed the TEM image of BaSO₄ obtained with different pH under ultrasound irradiation. Within the lower ranges of pH, the morphologies of BaSO₄ are spherical with the size of about 20nm. However, with the increase of pH, the morphologies of BaSO₄ changed from spherical to spindly (shown in Fig.1b). As the pH was increased to 12.5, petal-like morphologies appeared (shown in Fig. 1c).

In summary, a novel and convenient sonochemical technique has been successfully developed for the synthesis of BaSO₄ nanocrystals, where the variations of pH and other conditions allow us to control the morphologies of the products. This method may extend to synthesize other inorganic nanocrystals such as CaCO₃, BaCrO₄, CaSO₄, BaCO₃.

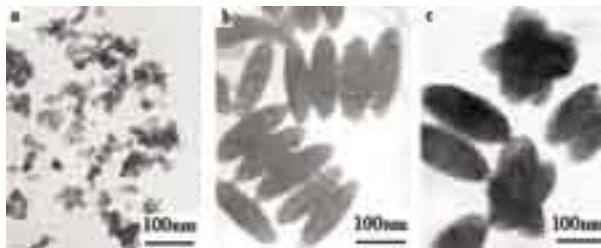


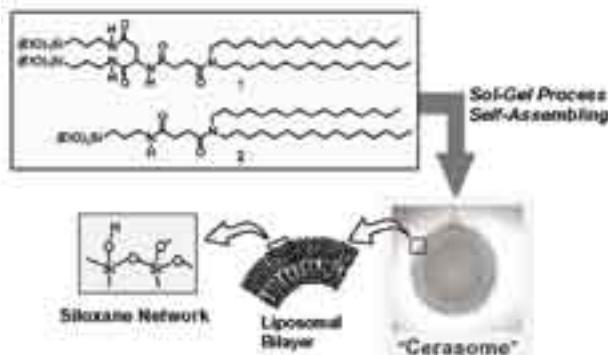
Fig.1 TEM images of: (a) pH=8; (b) pH=11.5; pH=12.5

606 - Importance of the Siloxane Network Formation on the Structural Stability of Cerasome, a Vesicular-Type Organic-Inorganic Nanohybrid

Mineo Hashizume, Hiroaki Inoue, Atsushi Ikeda, Jun-ichi Kikuchi, Nara Institute of Science and Technology, Japan

Cerasome, a lipid bilayer vesicle having silica frameworks on the surface, has recently developed by our group as a novel organic-inorganic nanohybrid material [1-3]. The Cerasome is prepared from an organoalkoxysilane lipid through hydrolysis, self-assembling, and polycondensation under appropriate conditions. In this work, the correlation between the development of the siloxane network and the structural stability of Cerasome was investigated. A novel Cerasome-forming lipid having two triethoxysilyl head groups (1) was designed and synthesized. The Cerasome prepared from the lipid 1 possesses high structural stability against a nonionic surfactant Triton X-100 (TX-100), similar with the case for the Cerasome formed with a single-head Cerasome-forming lipid (2). It was confirmed by the results of light scattering measurements and scanning electron microscopic observations. pH-Dependence of the Zeta-potential for the Cerasome showed that the isoelectric point of the Cerasome 1 was much closer to that of silica nanoparticles than that of the Cerasome 2. The results indicate that the surface of Cerasome 1 is much more silica-like than that of Cerasome 2. The time required to get sufficient structural stability of the Cerasome 2 against TX-100 was dependent on the medium pH, which affected on the hydrolysis and polycondensation of the alkoxy-silyl groups of the Cerasome-forming lipids. Thus the structural stability of the Cerasome is significantly dependent on the development of the siloxane networks on the vesicular surface.

- [1] K. Katagiri, K. Ariga, and J. Kikuchi, Chem. Lett., 1999, 661-662.
- [2] K. Katagiri, R. Hamasaki, K. Ariga, and J. Kikuchi, J. Am. Chem. Soc., 124, 7892-7893 (2002).
- [3] K. Katagiri, R. Hamasaki, K. Ariga, J. Kikuchi, J. Sol-Gel Sci. Technol., 26, 393-396 (2003).



607 - Sub-micron silica/polymer composite particles prepared by a one step Sol-Gel process

Hanan Sertchook, David Avnir, The Hebrew University of Jerusalem, Israel

We describe a convenient, one-step route to composite particles based on sol-gel chemistry. The simple one-stage synthesis we developed is based on performing the sol-gel polycondensation within a surfactant-stabilized emulsion of polystyrene (PS) or polydimethylsiloxane (PDMS) of various molecular weights and of tetraethoxysilane, all dispersed in a basic ethanolic medium. The parameters that dictate the formation of the composite particles were explored and characterized by several methods including TEM, BET surface area measurement, high resolution XPS, UV and FT-IR spectroscopies and thermal analysis by TGA and DSC. The particles were obtained in a monomodal distribution with diameters in the range of 200 – 500 nm, depending on the preparation conditions. The PS or PDMS phases are extractable, and when this extraction is carried out, porous silica particles are obtained in both cases. Likewise, partial extraction leads to core-shell architecture. The composite particles of PS/silica were also found to be good carriers for entrapped dye-molecules with no leaching. Because of the composite nature of the particles, both hydrophobic dyes - Sudan III and IV and hydrophilic dyes - the cationic Nile blue A- can be entrapped, utilizing the hydrophobic/hydrophilic nanophases of this composite material, respectfully.

608 - Hybrid organic/inorganic Sol-Gel materials for proton conducting membranes

Mario Aparicio, Alicia Duran, Instituto de Ceramica y Vidrio (C.S.I.C.), Spain

Hybrid organic-inorganic materials with nano-sized interfaces offer good opportunities to promote unique properties. One important application of these hybrid materials is the preparation of membranes for Proton Exchange Membrane Fuel Cell (PEMFC) operating at temperatures between 150 and 200°C. The increase of the PEMFC operation temperature would lead to better reaction kinetics, lower susceptibility to CO poisoning and the use of other fuels as methanol and gas. Poly(styrene-co-methacrylate) – silica covalent hybrid membranes have been synthesised by copolymerization of monomers (styrene –STY- and 2-hydroxyethyl methacrylate –HEMA-), with formation of covalent bonds between hydroxyl group of HEMA and pre-hydrolysed tetraethoxysilane (TEOS). Different molar organic/inorganic ratios were analysed in order to obtain homogeneous, stable and transparent membranes with tailored properties. Finally, two processes were studied to endow the membranes of proton conductivity: sulfonation of benzyl groups and incorporation of 12-phosphotungstic acid (PWA).

609 - Tin Oxide Nanoparticles : Control of Size, Shape and Dispersion

Corinne Chaneac, Francois O Ribot, Sandra Da Costa, Elisabeth Tronc, Jean-Pierre Jolivet, Chimie de la Matiere Condensee (UMR 7574 / UPMC), France

Crystalline tin oxide is a wide band gap semiconductor which is commonly used as active layer in gas sensing devices, for which the measure of the electrical conductivity allows to monitor the concentration of inflammable and/or toxic gas. In such an application, reducing the size of the particles, down to few nanometers, is interesting as it can highly increase the sensitivity of the devices because of the associated increase of the active surface where oxygen adsorption/desorption can take place.

Chimie douce has been confirmed as a convenient and versatile way to tailor the size and the shape of metal oxide particles in the nanometric range. We report the synthesis of crystalline tin oxide nanoparticles by thermolysis at 95°C of SnCl_4 in water or in HCl-water mixtures. Under such conditions, the precipitation of tin oxide is slow due to a weak nucleation and a large solubility. When no acid is added, spherical particles of about to 2 nm are obtained while acicular particles are formed when HCl is added. As shown by HR-TEM, the growth of the particles takes place in a specific crystallographic direction.

In order to process these particles as films or mesostructured materials, their dispersibility has been evaluated upon changing the surface charge density or the nature of the adsorbed layer. The thermal behavior of the particles was also investigated as a too easy sintering can be dramatic in gas sensing applications.

610 - Preparation of Au-TiO₂ hybrid nano particles in silicate film made by Sol-Gel method

Mitsuhiro Kawazu, Masatoshi Nara, Toshifumi Tsujino, Nippon Sheet Glass Co.Ltd, Japan

We have developed SiO₂ film doped with hybrid particles composed of Au and TiO₂ nano particles. TiO₂ nano particles with photo catalytic property were mixed with silica alkoxides coating solution with HAuCl₄,4H₂O. STS02 (purchased from ISHIHARA SANGYO KAISHA, Ltd) was used as TiO₂ nano particles with photo catalytic property. The average size of TiO₂ nano particles was 7 nm in diameter. The gel film coated on glass substrate was heated and then HAuCl₄,4H₂O were thermally reduced at 390°C. The film was finally sintered at 630 degree. The coated silica gel film doped with HAuCl₄,4H₂O and TiO₂ nano particles was turned into light blue from colorless gel film after heat treatment. The optical absorption spectrum showed the absorption peak of the film heated at 390°C shifted to 656 nm compare to SiO₂ film doped with Au nano particles without TiO₂ nano particles which had absorption peak at 542 nm. On the other hand, the film formed from coating solution incorporated TiAA (titanium tetraisopropoxide chelated by acetyl acetone) as TiO₂ source instead of TiO₂ nano particles had absorption peak at 550 nm. That means there was no effect on formation of Au nano particles when TiAA was incorporated. The average size of the particles was found to be about 23 nm in diameter by TEM observation. Furthermore EDX (Energy Dispersive X-ray Fluorescence Spectrometer) spectrum of nano particles in the film indicated that Au and TiO₂ nano hybrid particles were formed. Simulation results also supported that the size in diameter of Au nano particles had little influence on the absorption peak of the silica film doped with Au nano particles. These results would enable us to fabricate various colored glass with low reflectance using Au nano particles.

611 - Sol-Gel Approach to Sr₂CeO₄ Phosphor from Single Alkoxide Precursors

Hong R Kim, Hankuk University of Foreign Studies, Korea
Hoseop Yun, Ajou University, Korea

Preparation and characterization of sol-gel precursors of a blue emission phosphor Sr₂CeO₄ have been carried out. Each molecular precursor, [Sr₂Ce(O*i*Pr)₈] (1) and [Sr₂Ce₂O₄(O*i*Pr)₄(PrOH)₈] (2) was prepared from the mixtures of Sr chips and Ce(O*i*Pr)₄, respectively. X-ray single crystal and powder diffraction patterns, ICP emission, ¹H and ¹³C NMR were used to determine the evolution of structures from the precursor molecules to the ceramic oxides. The luminescent strontium cerium oxides were derived at mild reaction conditions such as 700°C for 1 h, and completely obtained at 1000°C for 1 h from these precursors. Comparing the spectra of these oxides derived from 1 and 2 with each other, the emission intensity ($\lambda_{\text{max}} = \sim 475$ nm) of the oxide derived from 1 is much stronger. The preliminary results suggest that the luminescent mechanism of Sr₂CeO₄ is based on a ligand-to-metal Ce⁴⁺ charge-transfer.

612 - Phase composition and pore structure of yttria-stabilized zirconia nanopowders by Sol-Gel method

Ki-Chang Song, Chul-Won Cheong, Konyang University, Korea

Hae-Hyoung Lee, Dankook University, Korea

Sang-Chun Oh, Jin-Keun Dong, Yong-Youp Cha, Wonkwang University, Korea

Yttria-stabilized zirconia (YSZ) nanopowders were prepared by sol-gel method using zirconium-n-butoxide (ZNB) and yttrium nitrate as precursors. The effect of water content added during the hydrolysis reaction of ZNB was investigated on the phase composition and pore structure of the product powders. The phase composition of YSZ nanopowders with calcination temperatures showed the same trend, irrespective of H_2O amounts added during the hydrolysis reaction of ZNB. All powders dried at 100°C were amorphous and transformed to cubic phase at 400°C, which converted to tetragonal phase at 1000°C. The powders showed the mixture of tetragonal and monoclinic phases from 1000°C to 1400°C. The pore size distributions of the dried powders prepared with small amounts of water (less than or equal to $\text{H}_2\text{O}/\text{ZNB}$ 20) showed mesopores, while those prepared with large amounts of water (greater than or equal to $\text{H}_2\text{O}/\text{ZNB}$ 50) exhibited micropores. In addition, the effect of yttria content added during hydrolysis reaction of ZNB was investigated on the crystalline phase composition and pore structure of the product powders. Crystalline phase of the powders made without yttria changed from the cubic to a phase in which monoclinic and tetragonal crystals coexist at 800°C and then transformed to a pure monoclinic phase above 1200°C. In contrast, the powders made with adequate content of yttria showed only the tetragonal phase above 1000°C. The pore size distributions of the powders prepared with yttria and calcined at 800°C showed mesopores, while those prepared without yttria and calcined at the same temperature exhibited macropores.

613 - Preparation and Characterization of Peroxo Titanic Acid Solution using $TiCl_3$

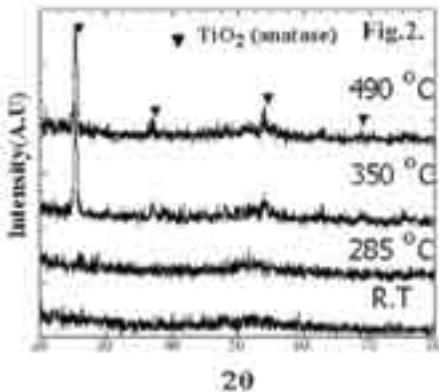
Insoo Kim, KS Sohn, CK Lee, JH Sung, Dong-A University, Korea
KH Lee, Korea Institute of Machinery & Materials, Korea

Titanium dioxide has attracted much attention because of its wide range of industrial applications. Many coating solutions have been developed. Among these, peroxy titanic acid solution (PTA), which has neutral pH and low material cost, is of great interest because most of coating solution based on metal alkoxide is acidic, which limited a use of metal as substrate. It has been reported that the PTA solution was prepared using $TiCl_4$, but no study about the preparation of the PTA using $TiCl_3$. In this study, the PTA solution was successfully prepared using $TiCl_3$ as a precursor. The TiO_2 film was dip-coated on quartz, slide glass and Si wafer using a PTA solution. The properties of the film with respect to annealing temperatures (up to 1000°C) were investigated in view of phase change, band gap energy, morphology etc. using a XPS, FESEM, AFM, TG/DTA, XRD and UV-VIS Spectrometer. Figure 1 is a typical SEM micrograph showing the surface morphology of TiO_2 film annealed at 500°C. A particle size was found to be less than ~10 nm as shown in Fig.1. Figure 2 shows the phase change in accordance with annealing temperatures. The amorphous-anatase phase transformation occurs in temperature between 285 and 350°C. This fact is well consistent with the result of TG/DTA. The crystalline size of TiO_2 films annealed in various temperatures was estimated from the Scherrer's formula and correlated with the band gap energy, based on the quantum size effect.

Fig.1



Fig.2



614 - Adsorption of Pb (II), Ni(II), Cu(II), Co(II) and Zn(II) on organic-inorganic Sol-Gel derived amorphous silica-titania and hexagonal zirconia

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The adsorption of Pb (II), Ni(II), Cu(II), Co(II) and Zn(II) from aqueous solutions on organofunctionalized sol-gel derived amorphous silica-titania and hexagonal zirconia is studied.

An inorganic-organic hybrid matrix of the type Si-Ti-(CH₂)₃-NH-(CH₂)₂-NH₂ is synthesized through sol-gel process and used as a water insoluble substrate for the adsorption of Pb(II), Ni(II) and Cu(II) cations from aqueous solutions. Five different values of cation concentrations are employed: 8, 16, 24, 32 and 40 ppm, and the final concentrations were measured by using atomic absorption spectrometry, after three different time intervals, 30, 60 and 120 minutes. Taking into account the obtained experimental results, the following adsorption affinity sequence can be established: Pb (II) > Cu (II) >> Ni (II). Furthermore, is verified that the affinity of the hybrid matrix towards nickel and copper is a function of time, whereas lead adsorption is time independent.

By using zirconium tetrabutoxide, diaminedecane and diamineoctane as precursors, a templated hexagonal zirconia sample is synthesized and characterized by X-ray diffractometry and scanning electron microscopy. The adsorption capacity of a such matrix towards Zn (II), Co (II), Ni(II) and Cu(II) is studied. The adsorption affinity of the synthesized hexagonal templated zirconia towards Zn (II), Co(II), Ni(II) and Cu(II) follows the sequence Zn (II) > Cu (II) > Ni (II) > Co(II). Is also verified that the adsorption of the considered cations follows the Langmuir and not Freundlich isotherm. All obtained isotherm are of type I according to the IUPAC classification. The adsorption affinity of the hexagonal zirconia matrix towards Ni (II) and Cu(II) is opposite of those previously observed for templated lamellar silica samples: Ni(II) > Cu(II). Such fact strongly suggests that the nanostrucure of the templated substrate can exert remarkable effects not only on the total amount of adsorbed cations, but also on the selectivity of the adsorption process.

615 - Studies on new Ormosils derived from reactive alkoxy silane precursors as a function of hydrophobicity/hydrophilicity

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We report here in the development of four different types of ormosil derived from two reactive ormosil's precursors namely 3-glycidoxypropyltrimetoxysilane and 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane followed by controlling hydrophobicity/hydrophilicity of the gelating systems. The ormosil-1 was made using reaction product of palladium chloride and 3-glycidoxypropyltrimethoxysilane followed by the ormosil formation in acidic medium in the presence of optimum amount of 3-aminopropyltrimethoxysilane and 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane. The ormosil-2 was made in acidic medium using 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane and trimethoxysilane. The ormosil-3 was made using reaction product of palladium chloride and 3-glycidoxypropyltrimethoxy silane followed by the ormosil formation in acidic medium in the presence of trimethoxysilane. Whereas ormosil-4 was made in aqueous acidic medium using phenyltrimethoxysilane and 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane. The ormosil-1 was applied to study the redox electrochemistry. It was found that:

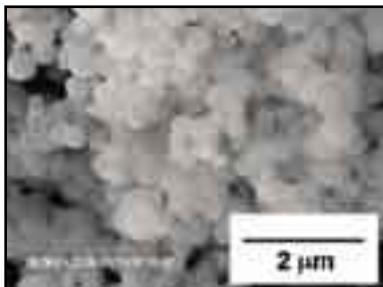
- (1) the palladium content affected the redox electrochemistry of potassium ferricyanide/ferrocene monocarboxylic acid, and
- (2) the kinetics of charge-transport was greatly altered while studying the electrochemistry of surface confined mediator-modified electrode derived from ormosil-1.

Ormosil-2 was found to be highly reactive and undergo self-assembly in the presence Lewis acid like palladium chloride. Ormosil-3 was used again to study the electrochemistry of surface confined redox material however the properties of the ormosil film was found significantly different as compared to ormosil-1. The reactivity of trimethoxysilane was examined to form ormosil network. The chemistry of trimethoxysilane for the formation of ormosil-2 and ormosil-3 is also examined. Ormosil-4 was found to be transparent even better than glass and used to study opto-electrochemistry. The opto-electrochemistry of Bacteriorhodopsin/Rhodamine sandwiched between ITO electrode and ormosil-4 has been studied. The ormosil sandwiched Bacteriorhodopsin showed high stability for practical applications without any loss of photoelectrochemical response after 1 year of continuous use.

616 - Solvothermal synthesis of nanosize $Zn_2SiO_4:Mn^{2+}$ phosphor from the precursor sol and its optical properties

Takuro Miki, Takumi Ogawa, Tetsuhiko Isobe, Keio University, Japan

The ethanol solution containing tetraethoxysilane was mixed with the aqueous solution containing zinc acetate, manganese (II) acetate and HNO_3 to obtain the precursor sol. Nanosize crystalline $Zn_2SiO_4:Mn^{2+}$ phosphor (the sample SC) was produced from this sol by solvothermal reaction in the supercritical ethanol at 265°C and 8MPa. In contrast, when the sol-derived gel was heated at less than 700°C, the phase separation between ZnO and SiO_2 occurs to form crystalline ZnO , as confirmed by in situ high-temperature X-ray diffractometry. For comparison with the nanosize sample, the bulk sample of Zn_2SiO_4 was produced from the mixture ZnO , $MnCO_3$ and SiO_2 by the conventional solid-state reaction at 700°C for 30min, followed by at 1200°C for 2h. The sample SC is uniform and spherical in shape, and its particle diameter is ~100nm (see Figure). According to ^{29}Si MAS NMR spectra, the bulk sample contains unreacted SiO_2 , but the sample SC does not contain any SiO_2 in spite of the lower reaction temperature. The optical absorption spectrum corresponding to charge transfer from O^{2-} to Zn^{2+} shifts toward shorter wavelength by 50nm, as compared with bulk sample. The excitation spectrum for the green emission due to d-d transition of Mn^{2+} also exhibits blue-shift in comparison with those of bulk. The hyperfine coupling constant obtained from the electron paramagnetic resonance of Mn^{2+} was larger for SC than that of bulk, showing that the larger ionisity of Mn-O bond for the former. Since the Mn^{2+} ion is incorporated into the Zn^{2+} site, the change in the nature of Mn-O bond reflects that of Zn-O bond. Therefore, as a result of the increase in the ionisity, more energy is needed for charge transfer from O^{2-} to Zn^{2+} , resulting in the blue shift of its absorption band for SC. We also found that the intensity of green emission of the sample SC for the excitation of charge transfer band increases with increasing the aging time in the supercritical ethanol. The factor for controlling the emission intensity will be discussed from the aspects of bond properties, the crystallinity, the incorporating process of Mn^{2+} into Zn_2SiO_4 matrix and so on.



617 - Synthesis and Reactivity of Titanium OXO-ALKOXO-Clusters

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Nano-building blocks, NBBs, defined as perfectly calibrated nanometric species, are good models for spectroscopies studies and good candidates for elaboration, by soft chemistry processes, of hybrid organic-inorganic materials.

The variety found in the NBBs (nature, structure, and functionality) associated to different assembling strategies, allows to build an amazing range of different architectures leading to different kinds of organic-inorganic interfaces (covalent bonding, complexation, electrostatic interactions...).

Titanium oxo-clusters are usually prepared in solution through the controlled stoichiometric hydrolysis of the metallic alkoxides $M(OR)_n$, or the corresponding complexed alkoxides, $M(OR)_{n-x}(LZ)_x$, (where LZ is a complexing ligand). These clusters combine a metallic oxo-core and labile alkoxo groups at the surface, which can be exchanged by nucleophilic species leading to the formation of functional NBBs. After these transalcoholysis reactions, the modified clusters keep the integrity of the oxo-core. For elaboration of hybrid materials, these clusters can be capped with polymerizable ligands or connected through organic spacers, like telechelic molecules or polymers, or functional dendrimers.

We focus our works on the cluster $Ti_{16}O_{16}(OEt)_{32}$, Ti16. Reactions with nucleophilic species as propyl or butyl alcohols were done. A better understanding of the surface reactivity of the cluster allows to optimize elaboration of hybrid materials by a better control of the hybrid interface. Nevertheless, localization of each surface alcoxo group is not easy by spectroscopies techniques. Association of crystallographic data and NMR spectra allowing attribution of the alkoxo group will be discussed. Analytical techniques used, diversified and complementary, are: X-ray diffraction and high resolution NMR spectroscopies [liquid NMR (COSY, HMQC, ROESY...), solid state NMR (Cross Polarization, homonuclear decoupling Lee-Goldburg, High speed MAS...)].

618 - Fabrication and Characteristics of Fluorinated Inorganic-Organic Hybrid Material Films

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Fluorinated materials have been widely utilized as packaging material and dielectric layers for the electronic and microelectronic industry due to their unique characteristics such as a low dielectric constant and hydrophobicity. In this study, fluorinated inorganic-organic hybrid materials (HYBRIMER) were successfully prepared from the fluoroalkylsilane (FAS) containing perfluoro-alkyl group and methacryloxypropyl-trimethoxysilane (MPTMS) by a sol-gel process. Optical and electrical characteristics of the fluorinated HYBRIMER films were made depending on the content and the fluoro-alkyl chain length of the FAS. Large fluorine content lowers the refractive index as well as the dielectric constant since fluorine has the lower electronic polarizability and creates higher free volume. The ranges of lowering the refractive index and the dielectric constant are very depending on the fluoro-alkyl chain length of the FAS. Thermo-optic coefficients (TOC), temperature dependence of the refractive index, of the fluorinated HYBRIMER were also investigated. TOC has negative values and the values increase with growing the fluorine content and the fluoro-alkyl chain length. On the other hand, the fluorinated HYBRIMER with the highest fluorine content and longest fluoro-alkyl chain is the most thermally stable. Thus, the thermally stable fluorinated HYBRIMER with unique characteristics (low refractive index and dielectric constant, high TOC, and good hydrophobicity etc) can be fabricated. It is also found that the fluorinated hybrid films have the gradient fluorine content creating the gradient characteristics in depth.

619 - Molecular structure and dissolved state of a heterobimetallic Ba-Ti alkoxide in a highly concentrated precursor solution

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Xerogels from a highly concentrated Ba-Ti alkoxide precursor solution using the methanol/2-methoxyethanol mixed solvent system are known to be suitable for preparation of translucent barium titanate ceramics and nanostructured freestanding films by direct sintering of the gels. In this study, the molecular structure of a heterobimetallic Ba-Ti alkoxide formed in a highly concentrated (1.2mol/l) Ba-Ti alkoxide precursor solution have been investigated using FT-IR, ¹H NMR, XANES and ICP-AES. Data from the analyses indicate that the reaction between barium ethoxide and titanium isopropoxide, which were used as the starting alkoxides, formed the heterobimetallic alkoxide BaTi(OMe)₄(OEt)(OEtOMe) that had a Ba/Ti ratio of 1 in the highly concentrated precursor solution. Complex impedance analysis was also carried out to investigate the effect of precursor concentration on the dissolved state of the Ba-Ti alkoxide. The molar electric conductivity decreased drastically in the concentration range of 0.6 to 1.2mol/l, which shows there are few ionic species resulting from dissociation of bimetallic alkoxide molecules in the highly concentrated precursor solution.

620 - Crystallisation of Titania Prepared via the Peroxo and Normal Sol-Gel Routes

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There have been several works to investigate the effect of sol preparation conditions on the crystal phase of titania. According to previous studies, higher acid concentration and lower reaction temperature during sol preparation accelerated rutile phase formation. This would be caused by a smaller seed particle size due to higher peptization (higher acid concentration) and lower speed of particle growth (lower reaction temperature). Therefore, it can be concluded that smaller precursor size prepared with a low condensation rate increases the formation of rutile phase. However, it was not clear which factor is more dominant factor. In this study, the dependency of resultant crystal phase on condensation rate and particle size has been investigated using the peroxy titania (PT) and normal titania (NT).

A titania sol was made by following procedure ; 53.42g of titanium tetrakisopropoxide and 20.93g of isopropanol were added to the round bottom flask. A mixture of 21g of isopropanol and 1.69g of water was added dropwise to the above solution during 4hrs at 25°C and the reaction mixture was refluxed for 24hrs. The above sol was dried at ambient temperature for 24hrs and amorphous titania powder could be obtained. The NT sol was prepared by peptizing the powder using HCl for 24hrs at room temperature(NT powder : HCl (37%) = 1:2 in wt). This NT sol was treated by H₂O₂ to produce a PT sol (NT powder : HCl (37%) : H₂O₂ (30%)= 1:2:2 in wt)and was continuously stirred for 24hrs. The resultant PT sol was clear with deep red colour. Particle size of each sol was measured by GPC and condensation rate was compared using crystallization temperature from DSC. The crystal phase was analyzed by XRD and Raman.

Titania prepared via the peroxy route (PT) was found to have a higher condensation rate (lower crystallisation temperature) and smaller particle size than that produced via the normal sol gel route (NT). The PT showed anatase phase while the NT showed rutile phase after heat treatment for 30mins at 450°C. Therefore it was found that condensation rate is the most important parameter in determining the crystal phase of the titania formed.

621 - Super-hydrophilic Surface Modification of Mesoporous Silica by Sulfonation Route

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Mesoporous silica having two or three dimensional open pore network was modified into super-hydrophilicity by wet chemical treatment methods. Mercapto functionalized mesoporous silica have been prepared by simple reaction of a mixture of tetraethoxysilane (TEOS) and mercaptotripropyltrimethoxysilane (MPTMS) in the presence of block copolymers (P123), under acid-catalyzed sol-gel reaction. The immobilized mercaptotripropyl groups in the open pore network were oxidized to sulfonic acid with H_2O_2 , followed by ionization with sodium sulfonate to result in hydrophilic property. Moreover, additional functionalization of surface hydroxide groups significantly led to super-hydrophilicity. The prepared silica retained SBA-15 pore structure with $\sim 60\text{\AA}$ average pore diameter when MPTMS was loaded up to 20%, as investigated by XRD and BET. And FT-IR signal at range 2550~2600cm⁻¹ and TGA/DTA peak at 340°C indicated presence of mercapto functional groups on the surface. Surface modification chemistry of the mesoporous silica was widely investigated by acid-base titration, zeta potential, ICP-AES, contact angle, solid-state ²⁹Si and ¹³C MAS NMR at various stages.

622 - Preparation and Characterization of FeCo-Al₂O₃ and Al₂O₃ Aerogels

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Nanocomposite materials constituted of FeCo nanoparticles dispersed into insulating matrices are of interest because of their magnetic and catalytic properties which are influenced by the size, volume fraction and composition of the nanoparticles. In particular, since two metals are present, the properties of the nanocomposite can vary depending on the formation of mixed composition nanoparticles or alloy nanoparticles.

FeCo-Al₂O₃ samples were prepared by the sol-gel method using aluminum tri-sec-butoxide, iron nitrate and cobalt nitrates as precursors; pure Al₂O₃ samples were also prepared for comparison. The obtained sols transform into gels in a few hours at room temperature in ordinary atmosphere. Aerogels are obtained by high temperature supercritical drying in an autoclave, followed by a treatment in air at 450 °C to remove organics. The samples are submitted to further treatments either in air up to 1000 °C or in hydrogen up to 800 °C.

The textural, morphological and structural characterization of the samples was performed by N₂ Physisorption at 77K, Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA), X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM).

Mesoporous aerogels are obtained with surface areas ranging from 250 to 500 m²/g depending on thermal treatment.

XRD and TEM show that the thermal treatments in air lead to the formation of a cubic nanocrystalline phase with a γ-Al₂O₃ like structure where Fe and Co are located in the vacancies of the spinel structure.

The thermal treatments in H₂ give rise to the formation of FeCo-Al₂O₃ nanocomposites constituted by FeCo alloy nanoparticles dispersed in γ-Al₂O₃. The average particle size of the FeCo nanoparticles can be modulated as a function of the temperature of the thermal treatment ranging from around 5 to 15 nm.

623 - Surface Modification of PTMS Particles with Organosilanes: TEOS-, VTMS-, and MTMS-Modified PTMS Particles

Hoe Jin Hah, Byung Jun Jeon, Sang Man Koo, Hanyang University, Korea

Phenyltrimethoxysilane (PTMS) hollow particles were prepared in an aqueous solution by two-step process that separates hydrolysis and condensation with controlling the pH of the medium. PTMS monomers were mainly hydrolyzed in acidic condition and condensed to form particles in basic condition. The obtained particles have a peculiar feature as of solubility in organic solvents such as acetone, benzene, chloroform, etc.

The surface modification of PTMS particles was performed in an alcoholic solution with tetraethyl orthosilicate (TEOS) and in an aqueous solution with other organoalkoxysilane monomers such as vinyltrimethoxysilane (VTMS) and methyltrimethoxysilane (MTMS). The surface-modified PTMS particles were prepared with the variation of silane monomer concentration, ammonium hydroxide concentration, reaction temperature, and reaction time. Among the obtained particles, VTMS- and MTMS-modified PTMS particles could be changed into channeled hollow particles with the treatment of acetone.

The changes in size and morphology of resultant PTMS particles and surface-modified PTMS particles were determined by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The composition of surface-modified particles was characterized with infrared spectroscopic analysis (IR), solid-state nuclear magnetic resonance spectroscopy (NMR), and thermogravimetric analysis (TGA). The changes in isoelectric point (IEP) of the modified particles were observed with zeta potential analyzer.

624 - Heat-Induced Precipitation and Light-Induced Dissolution of Metananoparticles in Hybrid Film

Shuichi Shibata, Keita Miyajima, Yusuke Kimura, Tetsuji Yano, Tokyo Institute of Technology, Japan

Starting sol was prepared from hybrid materials containing noble metal ions (Ag or Au) with a stabilizer N-(2-aminoethyl)-3-aminopropyltriethoxysilane. Noble-metal-ion-doped hybrid films were made on silica glass substrates by the sol-gel dip-coating technique. The films of 1mm in thickness were heated from 120°C to 1000°C under various atmospheres. After 120°C-500°C heating, Ag nanoparticles of wide range of radius were formed in the films and their sizes changed drastically with increasing temperature. Above 500°C, organic groups were completely evacuated and subsequently at 800°C, mono-dispersed Ag nanoparticles of 2- 4nm radius were precipitated in the resultant SiO₂ film on the substrate. On the other hand Au nanoparticles, which precipitated at 120°C, did not change their size distribution during the heating.

Photo-stability of the Ag-containing films was investigated by exposing them under Xenon lamp light. Under UV light irradiation, the Ag-containing sample heated at 800°C showed no decrease in the plasma absorption band, but the band of the films heated from 120°C to 500°C decreased noticeably. Comparison of calculated and measured plasma absorption bands along with FE-SEM observation were carried out to make clear the light-induced dissolution. Photo-induced dissolution of Ag-nanoparticles was closely related to the cluster-like silver involved in the films heated at relatively low temperatures.

625 - Design and Characterization of a Metal-Organic Sol-Gel Precursor for the Formation of YBCO Thin Films

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Keywords: YBCO films; chemical solution deposition

High temperature superconducting (HTS) film technology can be used in a number of applications such as microwave devices and long length power cables. Chemical solution deposition methods for making these films, such as spincoating or dipcoating a sol-gel precursor give advantages of speed, low cost and ease of fabrication. An ideal precursor requires homogeneity within the sol, good wetting and spinning properties and stability during manufacture, storage and processing. Here we describe a metal-organic precursor for the HTS compound $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) that exemplifies these properties. Our precursor uses only readily available, inexpensive reagents and can be prepared within hours.

The precursor has been adapted from a polymerized complex method analogous to the Peccini method for producing barium titanate powders. In this case, malic acid complexes of yttrium, barium and copper were employed, using glycerol as a cross-linking agent to polyesteryfy the malate forming a stable YBCO sol. The metal malate complex solutions were prepared by ligand exchange from the acetates. Water is used as the solvent, together with excess glycerol to control the viscosity for optimal spin coating conditions. The effect of metal : ligand ratio on the sol characteristics was investigated, as the malic acid concentration influences the growth rate, size, and stability of the metal oxide sol particles. Partial co-polymerization with the glycerol can restrict the number of acid groups available to perform this function, making the size and homogeneity of the particles, and thus the resulting sol, sensitive to its thermal history. These properties affect the nucleation and crystallization of YBCO and are important in controlling film quality.

626 - Preparation of Hollow Ormosil Particles Containing Copper Nanoparticles

Jae In Um, Hoe Jin Hah, Jung Soo Kim, Sang Man Koo, Hanyang University, Korea

Monodisperse hollow ORMOSIL particles were produced by two-step (acid-base) process in an aqueous solution with phenyltrimethoxysilane (PTMS). Particle size and hollow size can be controlled by changing monomer concentration, hydrolysis time and reaction temperature. Compared to emulsion/phase separation technique, the two-step method produces hollow particles without a template, including advantages such as high purity, high solid content, and easy process.

Using the hollow ORMOSIL particles in size of ca. 400 nm, Cu-containing particles were prepared by chemical reduction in an alcoholic solution. The hollow particles were dispersed to an alcoholic solution containing Cu(II) salt, and then a reducing agent was added to the solution. The mixture solution was stirred for 2 h in refluxing condition. The Cu-containing ORMOSIL particles were obtained through centrifugation and filtration. To find out optimum condition for the preparation of the particles, the reaction was performed with the variation of the anion of Cu(II) salt, reducing agent, solvent, and so on. The size of copper in resultant particles was in the range of 40-50 nm, and increased to ca. 250 nm by repeating reduction procedure.

In addition, using the resultant Cu-containing particles, Ag-containing ORMOSIL particles were also obtained by spontaneous redox reaction due to the difference of reduction potential.

The composition and crystallinity of metal particles in the resultant particles were determined by X-ray diffractometer (XRD). The size and morphology of the particles were observed with field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). And the resultant particles were also characterized by thermogravimetric analysis (TGA).

627 - Composite Silica Particles using a Mixture of Organosilane Monomers: Effect of Molar Ratio of Monomers

Dong Il Han, Hoe Jin Hah, Sang Man Koo, Hanyang University, Korea

Composite silica particles were synthesized by two-step (acid-base) process in an aqueous solution with a mixture of organoalkoxysilane monomers. The two-step process separates the hydrolysis and condensation procedures to easily control condensation rate. In this study, as silane monomers were used phenyltrimethoxysilane (PTMS), vinyltrimethoxysilane (VTMS), methyltrimethoxysilane (MTMS), and tetraethyl orthosilicate (TEOS). The reaction was performed in the variation of reaction temperature, hydrolysis time, and the molar ratio of silane monomers. The physical properties of resultant particles in combination of silane monomers were investigated with the change in the molar ratio of monomers. In particular, the hollow particles were obtained when the molar ratio of PTMS to VTMS was higher than 8.0 in the case of PTMS-VTMS combination. The hollow size of the resultant particles increased with increasing the molar ratio of PTMS to VTMS.

The size and morphology of the resulting particles were analyzed by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The change of zeta potential in the surface of particles in variation of the molar ratio of silane monomers was determined by zeta potential analyzer. In addition, the characterization of the obtained particles was preformed by infrared spectroscopic analysis (IR), solid-state nuclear magnetic resonance spectroscopy (NMR) and thermogravimetric analysis (TGA).

628 - Synthesis of novel layered silica-organic nanocomposites by hydrolysis and polycondensation of alkoxytrichlorosilanes

Yasuhiro Fujimoto, Atsushi Shimojima, Kazuyuki Kuroda, Waseda University, Japan

Self-organization of amphiphilic molecules has recently been utilized to prepare a variety of nanostructured materials. We have already demonstrated the self-assembling ability of hydrolyzed alkyltrialkoxysilanes to form layered inorganic-organic nanohybrids. In this study, alkoxytrichlorosilanes with long alkyl chains ($C_nH_{2n+1}OSiCl_3$, C_nOTCS , $n = 12, 14, 16, 18$ and 20) were prepared as the precursors, and silica-based nanocomposites with ordered nanostructures were synthesized. This method utilizes the difference in the reactivities between Si-Cl groups and Si-OR groups, and formed amphiphilic alkoxytrihydroxysilanes ($C_nH_{2n+1}OSi(OH)_3$) can self-organize to form layered structures.

Alkoxytrichlorosilanes (C_nOTCS) were synthesized by the reaction of n-alcohols ($C_nH_{2n+1}OH$) and tetrachlorosilane ($SiCl_4$). Partial hydrolysis of C_nOTCS was performed in the presence of aniline. In the cases of $n = 16, 18$, and 20 , precipitation occurred on cooling the hydrolyzed solutions. Although precipitation did not occur in the cases of $n = 12$ and 14 on cooling the solutions, precipitates were obtained by adding hexane. The precipitates were filtered and air-dried for 1 day.

The products exhibited the XRD patterns indicative of layered structures, and the d spacings varied in the range of ca. 4 - 6 nm, depending on the alkyl chain lengths. In addition, the SEM images of the products showed plate-like morphologies with the size of several micrometers. The layered structures consist of bimolecular layers of alcohol molecules and thin silica layers, which was revealed by ^{29}Si MAS NMR, ^{13}C CP/MAS NMR, and FT-IR. The formation of such nanostructures involves the self-assembly of $C_nH_{2n+1}OSi(OH)_3$ generated by the preferential hydrolysis of Si-Cl groups in C_nOTCS , followed by the solid-state polycondensation during the drying process. The ^{29}Si MAS NMR spectra of all the products showed the presence of Q⁴ signals, indicating that the alkoxy groups were eliminated at least partly to form siloxane networks. This is the first example of the self-assembly of alkoxyLATED derivative of monosilicic acid, providing a novel approach for the construction of ordered silica-based materials.

629 - Room Temperature Synthesis and Characterisation of Hybrid Materials of Polymethylhydrosiloxane Modified by Hydroxide Organic Compounds

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Abstract. Monolithic and transparent hybrid gels were obtained by reaction at room temperature, of polymethylhydrosiloxane (PMHS) with 1,3,5-trihydroxybenzene (DO1,3,5) 1,4-dihydroxybenzene (DO1,4) and 2-hydroxybenzoic acid (DO₂), in tetrahydrofuran, using hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) as catalyst. The products have been characterized by Infrared and ²⁹Si MAS-NMR Spectroscopy. The results show that the organic compounds have reacted with the PMHS leading to the monolithic and transparent gels in which both organic-inorganic bridges are formed. The thermal treatment procedure was determined by TGA and DTA curves recorded on the hybrid gel powder after drying at 70°C. The structure of the obtained materials, were studied by X-ray powder diffraction (XRD). A tetragonal silicon dioxide (SiO_2) phase is formed at 1500°C in the case of the three organic precursors.

Keywords: hybrid materials, polymethylhydrosiloxane, hydroxide, silicon dioxide.

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630 - Organically-Modified Silica Xerogels with Designer Elasticity and Hydrophobicity

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x moles of 1,6-bis(trimethoxysilyl)hexane (BIS) was used as an organic tether in silica sol gels produced by acid (SA00-SA10; HNO₃) or base (SB00-SB10; NH₄OH) catalysed hydrolysis-condensation of 1-x moles of tetraethoxysilane (TEOS). Each BIS unit provided two Si and 2 x leads us to the % Si that is BIS-derived in a gel. The total surface areas after heating to 423K increased and gelation times decreased as x increased. Acid catalysed gels were microporous, while the based catalysed ones mesoporous. All lost weight in air at high x at 600K exothermically. These gels were characterised in the bulk and as λ/4 optical coatings by UV-vis, ¹H NMR, ²⁹Si NMR, Raman and FTIR, AFM, laser-induced damage thresholds (LIDT), water and CH₄ adsorption. It is demonstrated in this paper that these xerogels have potential as coatings on chemically smart optical fibres.

	2x	%SiBIS	S (m ² /g)423K
SB00 (or SA00)	0.000	0.0	433 (203)
SB01 (or SA01)	0.010	1.0	519 (317*)
SB05 (or SA05)	0.050	5.0	696

631 - Controlled preparation of Pt/Al₂O₃ catalysts by Sol-Gel process

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In recent years, sol-gel process appears as an interesting way to better control the catalysts performances. However, in the case of metallic catalysts, the essential aim for the most reported investigations was the final product and its application without interest to the preparation conditions and chemistry involved to obtain the gel. For this reason, in this study, the preparation of the alumina supported platinum catalysts controlled by the sol-gel method, in order to inhibit the metal sintering effect observed on the supported metal catalysts treated at high temperature.

For the purpose reactions involved in a precursors mixture of aluminium sec-butoxide, platinum acetylacetone and sec-butanol as function of time and the amount of acetic acid used as gelation agent was followed by FTIR, UV-vis and ²⁷Al NMR spectroscopy.

Furthermore, relation between the gelation time, the polymerisation process and the textural and the structural properties of the obtained catalysts was investigated and compared to the properties of the catalyst prepared by impregnation method using the same metal precursor.

The obtained results show that BET surface area, alumina porosity, crystallographic alumina phase and platinum dispersion are strongly dependent on the ageing time and the amount of acetic acid. In fact, when using a prolonged time, exceeding 20 hours a poor metal dispersion is obtained due to the platinum acetylacetone reduction by sec- butanol. However, this dispersion is significantly improved when an adequate ageing time are selected. Furthermore, compared to the catalysts prepared by the impregnation of a sol-gel alumina by platinum acetylacetone, the catalyst prepared by the introduction of the same metal precursor during alumina preparation by sol-gel method shows better platinum dispersion. This seems to be related to the relative strength of the metal support-interactions. In addition, a better resistance to sintering is obtained when alumina textural properties are controlled by an adequate selection of the acetic acid amount.

632 - Synthesis of Nano Silica Particle for Polishing Prepared by Sol-Gel Method

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Monodispersed colloidal particles have wide applications in industries including catalysts, chromatography, polish, the spacer of liquid crystal and so on.

Stöber et al. reported a simple method for producing spherical silica particles in the micron size range. The method involves reacting alkyl silicates with water in alcohol solvent using dissolved ammonia as a catalyst. Since the publication of this pioneering work, silica particles made by the Stöber method have been used as model colloids in a large number of experimental investigations.

Nano silica particles are used for polishing of silicone wafers and magnetic disk substrates. For polishing, it is desirable that the powder is with monodispersion for the size and with smooth on its surface. But it is known that particles with large aspect ratio are more efficient for polishing than spherical particles.

In this study, we investigate a fabrication method for the nano silica particles with large aspect ratio, which are called as "cocoon shaped particles" and their generation mechanism. And, we also investigate relations between fabrication conditions and its polishing efficiency.

The particles are prepared from silicon alkoxide, water, ammonia and alcohol by a sol-gel method. We report effects of various reaction conditions on the diameters and shapes of the particle. And, the mechanism of forming the cocoon shaped particle is also discussed on basis of experimental results obtained by changing the reaction parameters such as temperatures, times, concentrations and so on.

The experimental results indicate that the concentration of primary particles at beginning stage of reaction is important and that the reaction temperature most influences its concentration. And, we propose that combined primary particles grow into the cocoon shaped particle. Combination of primary particles depends on concentration of primary particle at the beginning stage of reaction, so the aspect ratio is higher with increasing temperature. The effects of preparing conditions and polishing conditions are also investigated on polishing efficiency.

633 - Inorganic-Organic Hybrid Polymers by Polymerisation of Methacrylate Substituted Oxotantalum Clusters with Methylmethacrylate: Thermomechanical and Morphological Properties

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New inorganic-organic hybrid materials are prepared by free-radical polymerization and the properties evaluated. Methacrylate-substituted tetranuclear tantalum oxide clusters $[\text{Ta}_4\text{O}_4(\text{OEt})_8(\text{OMc})_4]$ were prepared by Sol-Gel reaction of the alkoxides with methacrylic acid. Samples of the hybrid materials were produced with Ta-cluster to methyl methacrylate ratios of 1:50 and 1:100 and were characterized by thermal and mechanical techniques and by surface analysis.

The glass transitions temperature of the hybrid materials are shifted to higher temperatures than pure PMMA as a result of cross-linking between the oxotantalum clusters and the polymer.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) results prove that thermal stability of the hybrid materials are significantly higher than in pure PMMA. The increase in T_g is also observed from dynamic mechanical analysis (DMA).

Evidence for cross-linking between the Ta-cluster and PMMA is obtained from IR analysis. Vibrations of Ta-O were found at 571 and 1072 cm^{-1} for Ta-oxide and at 1079, 635, 615, 591 and 561 cm^{-1} in the hybrid materials.

Surface studies performed by X-Ray photoelectron spectroscopy (XPS) indicate tantalum bonded to oxygen, which is in agreement with X-Ray structure analysis, and provide information about the atomic concentrations of the surface.

634 - Preparation of Tin Oxide-Based Metal Oxide Particles for Gas-Sensing Application

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Tin oxide-based metal oxide particles for gas-sensing application were prepared by wet process with organic-inorganic hybrid particles in an alcoholic solution. An aqueous solution of Tin(II) chloride, a precursor for tin oxide particles, was added to the dispersion of organic-inorganic hybrid particles. The reaction was performed in the variation of metal salt concentration, reaction temperature, and reaction time. The resulting tin oxide-deposited particles were filtered, washed, and then dried at 120°C for 12h in a vacuum oven. In various conditions, the change in size, morphology, and thickness of tin oxide deposited on the hybrid particles was investigated in this study. Moreover, the changes in physical property and structure of the obtained particles were also studied after calcination at different temperatures.

The size and morphology of the resultant particles were observed with field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The different characterization of the obtained particles was preformed by infrared spectroscopic analysis (IR), and thermogravimetric analysis (TGA). The changes in crystallinity and structure of resultant materials were confirmed by X-ray diffraction (XRD) patterns.

635 - Sol-Gel synthesis of monodisperse SiO₂ nanoparticles through hydrolysis of tetramethoxysilane by organic amines

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Suspensions of monodisperse SiO₂ nanoparticles produced by hydrolysis of tetraalkoxysilanes in the presence of ammonia are commercial products of varied application [1]. In order to improve the reproducibility researchers varied the conditions of the sol-gel processing, namely the chemical origin of the initial alkoxy silane and alcohol that was used as a solvent, temperature of the sol-gel processing, alkoxy silane concentration, alkoxy silane/water content ratio, concentration of ammonia, alkoxy silane addition rate, etc. Though all authors used ammonia as a catalyst for the sol-gel processing. The goal of the present work was to study the influence of the basicity and nucleophilicity of the base added to the sol-gel system as a catalyst on the monodispersity and size of the produced SiO₂ particles.

To do this we selected a series of stable aromatic amines, namely pyridine, 4-methylpyridine, 3-ethyl-4-methylpyridine, 2,6-dimethylpyridine, and 4-(dimethyl-amino)pyridine, as well as saturated amines, namely N-methylmorpholine, piperidine, N-methylpiperidine, and ethyldiisopropylamine. The amines show different basicity ($pK_a = 5-11$) and nucleophilicity. We used a standard technique to synthesize nanoparticles [1].

As a result we worked out a preparative technique to synthesize monodisperse SiO₂ particles of various nanoscale sizes. The method displays a good reproducibility and requires an uncomplicated apparatus. The use of weak bases ($pK_a = 5-7$) as catalysts was shown to result in the formation of ensembles of particles having rather small diameters (=10 -15 nm.) The ensembles tend to form gels. When the amine used as a catalyst is a strong base ($pK_a > 9$), then the increase of its concentration results in the increase of particle sizes along an almost straight-line size/concentration dependence. In this case the particles form almost instantly and their size doesn't change with subsequent mixing the sol-gel system being determined by the initial concentration of the base only. Thus, with 4-(dimethylamino)pyridine we observed the growth of particle sizes from ~10 nm (at 0.35 equiv of amine per 1 equiv TMOS) up to 220 nm (at 7 equiv of amine).

We proved that the catalytic activity of amines in the TMOS hydrolysis and condensation of the products resulting in the formation of nanodisperse SiO₂ particles is determined not only by the concentration of hydroxyls in the solution, i.e. the basicity of the amine. More to the point, this activity is determined by the nucleophilicity of amines. For example, in the case of diisopropylamine the particle size is much smaller than in the case of a weaker base but stronger nucleophilic catalyst like morpholine.

[1] - Sung Kyoo Park, Ki Do Kim, Hee Taik Kim, Colloids and Surfaces A: Physico-chemical and Engineering Aspects. 2002. V. 197. p. 7-17

636 - Nanocomposites in the system of aromatic ester dendrimer - SiO₂. Synthesis and structure

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The goal of our research is to investigate the possibility to produce nanocomposites in polar (SiO₂) and non-polar (aromatic ester dendrimers with terminal benzyl groups) systems without chemical bonding between components. In this case the structure of nanocomposites should be determined by van der Waals and hydrophobic-hydrophilic interactions.

We used the 2nd and 3rd generation aromatic ester dendrimers with oxybenzyl groups in the outer shell. These compounds were synthesized by the divergent method from phloroglucinol and 3,5-dioxybenzoic acid (the picture shows the 2nd generation of aromatic ester dendrimer):

These compounds were used as organic components of nanohybrids. Monolithic silica gel obtained by the organic sol-gel synthesis was taken as the inorganic component of the nanohybrids (SiO₂).

The formation of nanohybrids occurred as a result of a sol-gel process in the lack of water under the conditions of acid-catalyzed hydrolysis of tetramethoxysilane.

The structure of the synthesized compounds was confirmed by NMR data. Thermogravimetry and electron microscopy were used to investigate the synthesized nanohybrid samples (monolithic transparent or cracked opalescent cylinders depending on the size of the organic component molecule and its content in the composites). The microstructures were obtained from the curves of adsorption-desorption of ethanol. In general, when the sizes of dendrimer molecules are comparable with the size of micropores (1.5-2.5 nm), the introduction of dendrimers into the silica matrix toughens the matrix (in the case of 2nd generation aromatic ester dendrimers). On the contrary, the size of the 3rd generation aromatic ester dendrimers is much larger (> 3 nm) and the effect of the matrix toughening is absent.



637 - Acetic acid as an effective reagent, solvent, and catalyst for the organic Sol-Gel processing

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The aim of this work was to optimize the process of tetramethoxysilane (TMOS) hydrolysis and condensation used to prepare the monolithic silica gel from organic precursors in the presence of both water and a nonaqueous medium.

It was shown that the traditional sol-gel processing in the TMOS-solvent-catalyst-water system may be performed with the use of acetic acid (AcOH) as a solvent and catalyst. In fact AcOH is not an effective catalyst for the TMOS hydrolysis as compared to the traditionally used strong inorganic acids. Though this fact is compensated for by the reaction of AcOH with methyl alcohol that appears among the products in the sol-gel system. The product of this reaction is the volatile methyl ester of acetic acid. It is easily removed from the reaction medium, which suppresses the alcoholysis of the Si – OH bond and promotes for the condensation reactions. Monolithic gels that appear as a result of the condensation never crack in the course of drying and display increased density and hardness as compared to the gels synthesized in the presence of trifluoroacetic acid. Sol-gel processing in the AcOH-TMOS-water system enables one to synthesize nanohybrids using organic components that are unstable in a strong acidic medium or that react with acids.

We suggest an essentially new method of sol-gel processing that doesn't require introducing water or polar solvents (alcohols) in the system. Acetic acid is a solvent, catalyst, and reagent for the sol-gel process. The first stage of the process is the condensation of tetraalkoxysilane with acetic acid. Methyl alcohol that appears among the products of this stage can then either interact with acetoxy silane or esterify acetic acid. Opposite to formic acid that was proposed in the literature, AcOH is absolutely stable under the conditions of the sol-gel process. The monolithic samples that appear as a result of the process are almost colorless, which means that the content of carbon in their matrix doesn't exceed 2%. Sol-gel processing in the binary AcOH-TMOS system provides for the significant simplification of the sol-gel system and enables one to produce organic-inorganic hybrids from the components that are insoluble in polar systems.

638 - Preparation of self-organized nano-graded $\text{SiO}_2/\text{TiO}_2/\text{PMMA}$ thin film and its low-reflectivity

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Akira Nakajima, Tokyo instituto of technology, Japan

Anti or low reflective coatings by multi-layer structure with high and low refractive index materials has been applied to various industrial items such as monitors and show windows. Because of the easiness of the control of layer thickness and homogeneity in large area, dry process was initially utilized for the preparation of these coatings. However, recently, the number of wet-coating for this application is also gradually increasing.

Very recently, we have successfully developed an inorganic/organic nano-graded thin film utilizing the adsorption onto plastics of methyl methacrylate methacryloxy-propyl trimethoxysilan co-polymer. In this method, inorganic layer was formed by hydrolyzing metal alkoxide, and various inorganic materials can be applicable to its surface layer. Moreover, by mixing and controlling hydrolyzing rate of two different metal alkoxides, we have succeeded in preparing a laminated structure of two metal oxides in this inorganic layer by only one coating process.

In the present study, we demonstrate the preparation and property of the film prepared from this process utilizing titanium tetraisopropoxide and TEOS. The reflectivity of the PET film is decreased from 5% to less than 2% in the visible- wavelength range by this coating. This process may provide a new possibility to low-cost AR-coating by sol-gel method.

639 - Preparation and properties of the transparent SiO₂/PMMA graded IPN thin film

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The coating of inorganic material is one of the important technologies for providing a new function to polymer material. However, due to the large difference of thermal and mechanical properties between these two materials, peeling or cracking at the interface is a common problem during practical use. One of the ideal solutions for this problem is the graded interface, at which physical properties continuously change with respect to thickness. Additionally, industry has a growing need for transparent coatings that can impart new functions without loss of transparency or compromises in the design of industrial items.

Very recently, we have successfully developed a transparent inorganic/organic nano-graded thin film utilizing the adsorption onto plastics of methyl methacrylate methacryloxypropyl trimethoxysilan co-polymer. In this method, however, the size of the graded structure was limited to less than 50 nm due to the size of polymer molecule. On the other hand, graded structure is commonly prepared by using phase separation, and its size of the graded structure is generally more than a few micron.

In this paper, we demonstrate the processing of the inorganic/organic graded coating utilizing the Interpenetration Polymer Network (IPN), whose domain size is in the intermediate range between molecular size and phase separation structure. Methylmethacrylate and TEOS were employed as starting materials. The prepared film was transparent in the visible wavelength range and the size of the graded structure was almost 100nm. Detailed processing flow and film properties will be presented.

640 - Hybrid Sol-Gel Coatings Combined with Inorganic Inhibitors for Metal Corrosion Protection

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Hae Hong Kim, Korea Research Institute, Korea

The urgent need to replace chromate is being faced in the iron steel industry by environmental problems. Organic-inorganic hybrid protective coatings with inorganic inhibitors were formed on galvanized steel, and corrosion resistance was evaluated by salt spray test and potentiodynamic scans. The new hybrid sols for coatings were synthesized by mixing aqueous nano-sized AlOOH sols, different amounts of GPS (3-glycidyloxypropyltrimethoxysilane), and zirconium oxychloride hydrate and/or ceric nitrate hydrate as corrosion inhibitors. Particulate Boehmite(AlOOH) sols were prepared at 90°C by peptizing Al(OH)3 that is precipitates of acidic aqueous aluminum chloride solution neutralized by NaOH. The interaction between AlOOH and GPS and a local chemical structure was characterized by measuring the variation of ionic conductivity with time, FT-IR, NMR etc. The thickness and microstructure of the coated layer on metal were investigated by means of scanning electron microscopy. The hybrid sol coating on the galvanized steel showed good adhesion as well as effective corrosion protection layer without chemical pretreatment. The combined effects of sol-gel coatings with inorganic inhibitors will be discussed.

641 - Preparation and properties of aramid-silica hybrids with interphase bonding through 3-glycidoxypropyl-trimethoxysilane

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Nano-composites from aramid-silica system have been prepared via sol-gel process. Poly (phenyleneterephthalamide) copolymer chains were prepared by reacting a mixture of p- and m-phenylenediamines with terephthaloyl chloride in dimethylacetamide used as solvent. The sol-gel process in the polymer matrix was carried out through hydrolysis and condensation of a mixture of tetraethoxysilane and (3-glycidoxypropyl)trimethoxysilane. The later was used to develop linkage on one hand with silica network structure using alkoxy groups and on other with aramid chains at its secondary amine groups through glycidal groups of silane. Mutual interaction between the two disparate phases, aramid and silica network was thus created. Thin films of the composites containing different proportions of silica ranging from 5.0 to 25.0-wt.% were cast by the solvent elution technique. The alpha-relaxation temperature associated with the glass transition was measured by dynamic mechanical thermal analysis. The results showed an increase in the glass transition temperature from 328°C for the pure aramid to 352°C for the hybrid materials containing 25-wt.% silica, an indicative of the increased interfacial interaction between the two phases. Films having relatively low silica content were flexible and transparent, but those with high silica content were opaque and brittle. These films were tested for their tensile strength, modulus and toughness. The mechanical strength of the composites as compared to the pure aramid increased initially but with further addition of silica the strength decreased. The initial increase can be explained due to increased interfacial interaction between the two phases, however agglomeration of silica particles was responsible for decreasing strength at higher silica contents.

642 - SAXS Study of Neodymium-Doped Poly(oxyethylene)/Siloxane Hybrids

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The structural features of two families of sol-gel derived poly(oxyethylene)/siloxane hybrids doped with neodymium triflate, Nd(CF₃SO₃)₃, were investigated by Small-Angle X-ray Scattering (SAXS). Their organic/inorganic matrix is a siliceous network to which short oligopolyether chains are covalently bonded to both ends by means of urea and urethane linkages, respectively. Transparent, flexible, monolithic xerogels with $\chi^3 n^3 40$ (where n, so-called composition, represents the number of ether oxygen atoms per Nd³⁺ ion) were prepared. The SAXS patterns of the undoped di-ureasils exhibit a strong interference peak located at medium q-range which reveals the existence of a spatial correlation between the siloxane nanoclusters grafted to the polymer segments. The introduction of Nd³⁺ ions in such hybrids leads to the appearance in SAXS patterns of an additional scattered decreasing intensity at low q-range which reveals the existence of a two-level hierarchical structure: the primary level consists of small and spatially correlated siloxane nanoclusters and the secondary level corresponds to large domains, in which the siloxane clusters are located, surrounded by a depleted polymeric phase. A theoretical function was used to fit the experimental scattering curves and to determine the structural parameters corresponding to each level. The di-urethanesils hybrids exhibit quite different behavior since the two-level hierarchical structure already exists in the undoped sample. In both families, the increase of Nd³⁺ content leads to a decrease of the correlation peak intensity, suggesting that the cations interact mainly with the ether-type oxygen atoms of polymer chains. The determination of the structure of both type of composites allowed us to get a better understanding of their luminescent, ionic conduction and thermomechanical properties.

643 - Improvement of the Mo/TiO₂-Al₂O₃ Catalyst by the Control of the Sol-Gel Synthesis

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Traditional hydrotreating catalysts are constituted by molybdenum deposited in Al₂O₃ promoted by nickel and phosphorous. The increase in severity of the environmental regulations has started a search for new and more active catalysts. Several studies have shown that TiO₂-Al₂O₃ mixed oxides are an excellent support for the active phases. Results concerning the preparation, characterization and testing of molybdenum catalyst supported on titania-alumina are presented. The support was prepared by sol-gel route using titanium and aluminum isopropoxides, the titanium one chelated with acetylacetone (acac) to promote similar hydrolysis ratio for both the alcoxides. The effect of nominal molar ratio [Ti]/[Ti+Al] and complexing ratio [acac]/[Ti] on the microstructural features of nanometric particles was analyzed by X-Ray diffraction and N₂ adsorption isotherm measurements. The diffraction patterns of samples fired above 973 K show that the crystalline structure of the support remained unaltered after molybdenum impregnation. The catalytic activity of Mo impregnated supports was evaluated using the thiophene hydrodesulfurization at different temperatures and atmospheric pressure. Xerogel texture presents porous characterized by a monomodal pore size distribution centered around 5 nm. Maximal (218m².g⁻¹) and minimal (113m².g⁻¹) surface area were found for samples containing [Ti]/[Ti+Al] ratio equal to 0.1 and 1, respectively. These characteristics of porous texture are preserved after firing at 673 K.

644 - Structural Features of Phosphate Modified Zirconia Prepared by Sol-Gel Route

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The chemistry of sol-gel processes from aqueous solution of inorganic salts is complex due to the spontaneous occurrence of hydrolysis and condensation reactions. Aiming to control these reactions, anionic ligands can be added to the solution to favor the formation of new molecular precursors. Precursors sols were prepared by the admixture of zirconyl chloride aqueous solution to aqueous solution of different acids (sulfuric, phosphoric, nitric or acetic) at different molar ratios zirconium/acid. The largest interval of stability of the tetragonal zirconia during firing was observed for the phosphoric acid modified one. In this work the structural features of phosphate modified zirconia were analysed by ^{31}P NMR/MAS, EXAFS and PXRD. Results show that phosphate groups control the formation of gel network and the formation and stability of ZrO_2 tetragonal phase.

645 - Redispersable Titania Nanoparticles Obtained by Sol-Gel Route

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Sol-gel derived nanoparticles with controlled particle size and showing adjustable surface charge were prepared by chemical modification of titanium iso propoxide precursor with acetilacetone and para-toluene-sulfonic acid. It was shown that the size of nanoparticles can be finely adjusted by controlling the complexing ratio Acac/Ti. The presence of para-toluene-sulfonic acid complexed at the particles surface change their surface charge and limit the aggregation growth. As a consequence, the dried gel can be fully redispersed in water or in alcoholic solution. The role of the synthesis parameters (acidity, complexing ratio and hydrolysis ratio) on the mesoporous structure of titania gel is discussed to understand their influence on the mesostructure.

646 - Zirconium oxoclusters as molecular building blocks for highly dispersed ZrO₂ nanoprarticles in silica matrix

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Oxide nanoparticles embedded in dielectric matrices represent a class of nanocomposite systems endowed with outstanding optical, mechanical, electronic and thermal properties. To ensure the desired performances of the final material, a uniform distribution of the doping clusters inside the host matrix and the absence of grain agglomeration are necessary requirements. To this aim, a novel synthetic route to synthesize ZrO₂ doped-SiO₂ films was developed. It is based on the copolymerisation of an organically modified oxozirconium cluster Zr₄O₂(OMc)₁₂ (OMc = methacrylate), prepared via the sol-gel route by reaction of zirconium butoxide with methacrylic acid, with (methacryloxyethyl)triethoxysilane (McTES). This copolymerization of the cluster with the methacrylate-bearing siloxane represents a valuable route to yield a very homogeneous dispersion of the ZrO₂ precursor inside the silica network. The polymerization kinetics of McTES as well as the hydrolysis and condensation of the ethoxy groups were investigated through ¹H and ¹³C NMR. To the optimised solution, Irgacure 184 was added as photoinitiator. The solution was then cast into films by spin-coating and UV cured. Films about 400 nm thick were obtained after annealing at 450°C in air. The surface and in-depth composition of the thin films were investigated through X-Ray Photoelectron Spectroscopy. The depth profile evidences a homogenous distribution of the zirconium oxide within the films. The surface morphology of the coatings was investigated through Atomic Force Microscopy (AFM), which showed smooth, homogeneous and crack-free samples.

647 - Synthesis, Structure and Properties of $\text{Na}_2\text{Zn}(\text{OEt})_4(\text{HOEt})_5$

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Alkoxides are the most versatile and effective precursors in the sol-gel processing of advanced ceramic materials and glasses. It is known that if the lowest preparation temperatures and purest products are normally obtained when the heterometallic alkoxide precursor has the stoichiometry of the target oxide, but the present knowledge of precursor design does not allow for easy design of a certain structure and composition of a precursor alkoxide. Therefore it is worthwhile to systematically investigate the structures and properties of heterometallic alkoxide to obtain desired structures, but also to increase the fundamental knowledge to a state where the composition and preferably the structure can be designed by choice of synthesis route, solvent, added reagents like water and type of OR group. Relatively little attention has been paid to low valent 3d-element alkoxides with is much due to problems with the synthesis and handling of these compounds. In this work the synthesis and structure of a heterometallic Na-Zn -ethoxide, $\text{Na}_2\text{Zn}(\text{OEt})_4(\text{HOEt})_5$ used for preparation of the ceramic sodium ion conductor $\text{Na}_{1.8}\text{ZnSiO}_4$ is described. The compound was quite sensitive to decomposition when taken out of the solution phase which is probably due to the very high ratio of HOEt adducts per zinc atom. It was synthesised by reaction of ZnCl_2 and NaOEt in ethanol and the polymeric structure was determined by single-crystal X-ray diffraction techniques. Characterisation was made by its IR- and Raman-spectra.

648 - Synthesis, Structure and Properties of $\text{ErNb}_2(\text{OPr})_{13}$

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Alkoxides are the most versatile and effective precursors in the sol-gel processing of advanced ceramic materials and glasses. The molecular structure of the precursor is greatly affecting homogeneity and structure of the oxide particles and films produced by solution processing, which makes it interesting to make systematic and detailed studies of the structures and properties of alkoxides. An interesting feature of heterometallic alkoxides is the promise of low temperature processing of heterometallic glasses from heterometallic precursors with atomic scale control of the structure in e.g. a silica glass. One example where an atomic scale mixing is of great importance is in the Er-doped silica fibre and flat wave-guide NIR signal amplifiers, where high levels of Er-doping is desired, but if the Er-ions come in close proximity the optical gain is quenched. We have shown that with the isolated Er-ion precursor, $\text{ErAl}_3(\text{OPr})_{12}$ (1) very high non-quenching levels of Er doping can be achieved (2). The molecular alkoxide, $\text{ErNb}_2(\text{OPr})_{13}$ was prepared by metathesis with $2\text{KNb}(\text{OPr})_6$, KOPr^i and ErCl_3 and structurally determined by single-crystal X-ray diffraction. Each molecule contains an Er^{3+} ion sided by Nb^{5+} -ions, one via a double alkoxo-bridge and one via a triple alkoxo-bridge. It is isostructural with $\text{LaNb}_2(\text{OPr})_{13}$ (3), in spite of the large difference in ionic radius between Er^{3+} and La^{3+} . The compound was characterised by its IR- and UV-Vis-NIR- spectroscopic fine structure, and found to be structurally intact in solution.

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649 - Eduction of Sol-Gel Microspheres of Uranium Oxide from a Settling Vessel by Liquid Entrainment

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Continuous and choke-free transfer of sol-gel microspheres of uranium oxide, settling in a transfer vessel, onto a continuous drying equipment at an optimum solid loading, is of paramount significance in the sol-gel plant for the production of ceramic microspheres for nuclear fuel fabrication. An eduction technique, where spheres settling down, by gravity, countercurrent to a stream of a drive fluid, was adopted to effect the transfer of the microspheres from the transfer vessel, to the belt drier. A transport model based on the principles of two-phase fluidization and transport for eductive carriage of spherical particles by the drive-liquid, is proposed for predicting the optimum flow parameters, for the transfer of the microspheres at a controlled rate.

Sol-gel microspheres of uranium oxide of 2 to 2.5 mm size, prepared by hydrolysis of uranyl nitrate by internal gelation process, are wet, and are prone to easy distortion, prior to drying. In a remotized and automated plant, operating on a continuous basis, these wet microspheres have to be transported onto a traveling belt drier, which is designed to handle a monolayer of wet microspheres spreading over the width of the belt moving at an optimized linear speed. Hence, it is essential to optimise the solid loading rate onto the drier. Optimisation of the settling velocity of the microspheres, the upward flow of the liquid in the transfer vessel section above the eduction point and the flow rate of drive fluid, is accomplished with the help of a single recirculation pump and by regulating the overflow of transfer vessel.

A detailed analysis of the particle-transport mechanism adopting the eduction system from a settling bed of solids by liquid entrainment, has been carried out and a model based on Richardson-Zaki equation, is proposed and the same has been evaluated in the light of the experimental observations during the plant operations.

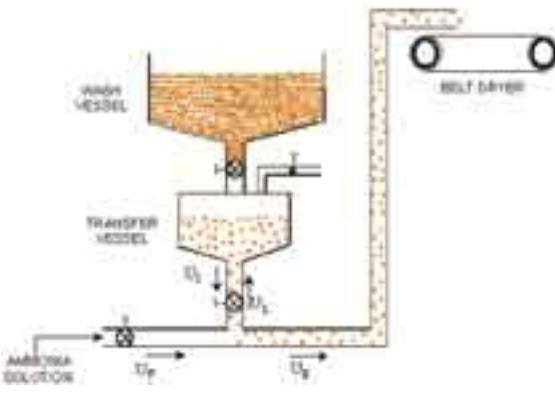


Fig. 1: Liquid Jet Transport System in Sol-Gel Process

650 - Study of the Pd-SiO₂ Obtained by Sol-Gel Process as Catalyst of the Limonene Oxidation

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Composites of SiO₂ doped with palladium were prepared by a sol-gel method. The materials were characterized by a powder X-Ray diffraction, nitrogen adsorption and scanning electronic microscopy. Catalytic behavior of the gels was investigated in the oxidation of limonene with dioxygen, in acetic acid solutions containing CuCl₂. All the catalysts studied showed an activity in the formation of carvyl acetate. No significant palladium leaching was observed which allows easy catalyst recovering and reusing.

651 - Evidence of Heteroegenous Catalysis in Sol-Gel Process for PD/ AL₂O₃ Catalysts Preparation

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The sol-gel process has developed a variety of chemical techniques to control the solution chemistry and the gelation reaction during the preparation of solid materials. However, the high reactivity of some metal alkoxides with water, remains a problem to control the final properties of solids. Many approaches have been devoted in this field. The chemical modification of metal alkoxides by complexing agents and the optimisation of many mixing techniques were tried. The aim of this work is to add to these researches a new process which could improve the reactivity control of some metal alkoxides during the gelation step.

The investigation by FTIR, UV-VIS and ²⁷Al NMR spectroscopy of the organic precursors mixture of aluminium-sec-butoxide (AsB), sec-butanol (sB) and palladium acetylacetonate (Pd(acac)₂) refluxed at 80°C, shows that a complexing step between Pd(acac)₂ and AsB occurs first, then a reduction of Pd(acac)₂ by sB to metallic palladium takes place. This is illustrated by the formation of butanone detected by IRTF spectroscopy and by the deposition of palladium particles identified by XRD. Finally, the condensation of the aluminium alkoxide occurs as indicated by the formed Al-O-Al bonds and the increase of the aluminium coordination. The heterogeneous catalysis of the sol-gel process was then evidenced when a gel is formed after adding metallic palladium to a stirred solution of AsB and sB. In order to improve the efficiency of the heterogeneous catalysed gelation, Pd/Al₂O₃ is used as a catalyst. In turn, to avoid the palladium reduction, the ageing temperature is lowered and the Pd(acac)₂ is added prior to an appropriate time of the AsB condensation. The obtained gel is dried in oven and calcined at different temperature. The characterisation of the resulting Pd/Al₂O₃ catalyst shows that the textural and the structural properties of the solid prepared by the catalysed sol-gel route is modified by the ageing temperature and the catalyst amount. Compared to the catalysts prepared by impregnation method, better BET surface area, higher thermal stability and improved catalytic activity for methane combustion are obtained.

652 - Insertion of substituted tetraphenylporphyrins in silica gels

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Phophyrins and metallic porphyrins feature a wide range of important electrical, optical and catalytic properties. In order to take advantage of them, a useful approach is frequently used, consisting in their appropriate fixation in a variety of solid supports. By using the so-called sol-gel method it has generally been possible to fasten important organic and biological molecules into inorganic networks, for example in silicon, titanium and aluminum oxides. The key to the appropriate fixation of these free or metal-substituted porphyrins in the gels is the setting of the appropriate functional group in the periphery of the macrocycle, which thus becomes more soluble in water or alcohols. The substituents more frequently employed have been the sulpho, carboxyl and pyridinium groups. These groups can in most cases be present in the plane of the porphyrin. We have tried to enlarge the number, type, and spatial disposition of such substituents, in order to evaluate the influence of these changes in the properties of the final materials. In this work we report the results obtained with the meso-5,10,15,20-tetraphenylporphyrin macrocycle in which hydroxyl, amino and other substituents have been placed in different positions of the phenyl groups. In the same way we were probed the use of different solvents mixtures, like dimethylformamide, methanol, ethanol and pyridine, to obtain monolithic xerogels with unaltered porphyrins embedded.

654 - Organic-inorganic hybrid synthesis by reactive extrusion : fiction or reality

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Two main routes are described in the literature to synthesize organic-inorganic hybrid polymer through the sol-gel process including hydrolysis-condensation of alkoxy silane. The first one consists in doing to react tetraalkoxysilane with either reactive end-capped organic polymers or oligomers or copolymers containing pendant alkoxide groups in solution. The second one consists in doing to react monomers containing trialkoxysilane groups in solution through hydrolysis-condensation reactions and then to initiate polymerization of monomer grafted onto inorganic phase. In these two routes, there is always the presence of solvent and water which limits the applications to coatings of glass, metal and polymer substrata and the morphology of the material is governed by phase separation. The original route that we develop is based upon three successive reactions. At first the cross-linking of ethylene covinylacetate copolymer (organic network synthesis) is carried out through ester-alkoxysilane interchange reaction. After cross-linking the hydrolysis of alkoxy silane groups confined in the polymer network leading to silica network grafted onto organic network is carried out by water diffusion. This procedure, step by step, presents three main advantages with respect to the conventional sol-gel processes. The first one is the control of the size of the silica particles through the cross-linking density before hydrolysis. The second one is the synthesis of organic-inorganic hybrids in absence of solvent and in thermomechanical conditions of polymer processing. The third one is the possibility to elaborate articles made in hybrid materials in mass and to expand their applications. An example of organic-inorganic hybrid synthesis integrated into a continuous process such as extrusion is described. The shape of the article is created at the die of a double screw extruder through extrusion of a dormant formulation (EVA, tetraalkoxysilane, catalyst) and it is cross-linked with the help of a microwave oven in line with the extruder. The kinetic aspects of the chemical reactions will be discussed to optimise the thermo-mechanical properties and the process of elaboration.



655 - Gelation of Hybrid Inorganic-Organic Silicates Monitored by NMR and Fluorescence Spectroscopy

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Transparent, inorganic-organic hybrid silica materials have been prepared via hydrolysis and condensation of tetraalkylorthosilicates and various organosiloxanes by sol-gel processing. These materials are being studied as matrices for the immobilization of biomolecules. Gel materials with favorable structures and properties can be obtained by controlling the chemistry of the process to suit the particular biomolecule dopant. Since gels are prepared under ambient conditions, the gelation step and the post-gelation drying processes are important factors in controlling the final structures and hence the immobilization of reagents. In these experiments, tetramethoxysilane (TMOS), methyltrimethoxysilane, (MTMOS) and hydroxy-terminated polydimethylsilane (PDMS) have been used as precursors to prepare gels. Non-ionic biocompatible templates such as polyethyleneglycol and D-glucose were used as pore-templates. Fluorescence and nuclear magnetic resonance methods have been developed for *in situ* monitoring of reaction processes during polymerization, gelation and aging of gels. The fluorescent dye pyranine is sensitive to the proton acceptor characteristics of the solvent and so is used as a photoprobe to observe changes in the solvent composition during these processes. Nuclear magnetic resonance spectroscopy using spin-lattice relaxation (T₁) measurements are employed to monitor the mobility of water within the matrix, and spin-spin relaxation (T₂) properties of the solvent are used to monitor the onset of gelation. Gelation occurs when the growing silicate aggregates form a network, and this results in a minimum value of the T₂ for solvent molecules (water or alcohol) and hence gelation times can readily be determined for a range of reaction compositions. The gelation time is greatly influenced by the type of organosiloxane, mole ratio of organosiloxane to TMOS, template content, pH and the temperature at which the monoliths were formed.

656 - Low Temperature Sol-Gel Preparation of Hybrid Silica Nanotubes

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Silica nanotubes have been prepared by employing DL-tartaric acid [1] as a structural modifier in the controlled hydrolysis of tetraalkyl orthosilicates at room temperature. Various alkoxy silanes including tetraethyl orthosilicate (TEOS), methyltriethoxysilane (MTES), polydimethylsiloxane (PDMS) and 3-aminopropyl triethoxysilane (APTES) have been used as precursors to prepare the nanotubes. The synthetic conditions have been systematically studied and a range of hybrid organosilicate tubes prepared. The physical characteristics of the materials were examined by scanning electron microscopy (SEM). SEM images show that the reaction products consist of hollow tubes along with some small spherical particles and aggregates. The tubes have rectangular cross-sections of 0.5-0.8 µm in diameter and lengths in the range 20-80 µm. The morphology of the nanotubes changes when organosiloxanes are incorporated as precursors. The adsorption of enzyme proteins on nanotube walls is readily observed by SEM. We are currently developing methods for the incorporation of proteins into the nanotube structures. Option for doping or labeling of these nanotubes with fluorescent markers are also under investigation.

[1] Kukovecz, A., Konya, Z., Palinko, I., Monter, D., Reschetilowski, W. and Kiricsi, I., Chem. Mater., 2001, 13, 345-349

658 - Siloxane-Based Nano-Building Blocks by Reaction between Silanediol and Trifunctional Silicon Alkoxides

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The most promising route for the preparation of nanostructured organic-inorganic materials is the assembling of nano-building blocks. This synthetic approach allows controlling the extent of phase interaction, which in its turn governs the structure-properties relationships. We present here the synthesis of siloxane-based nano-building blocks prepared by reacting diphenylsilanediol with vinyltriethoxysilane or triethoxysilane. The reaction products have been obtained by condensation between silanediol and ethoxide groups in inert atmosphere, by a non-hydrolytic process and using triethylamine, pyridine or butyl lithium as catalyst. Different solvents and different reaction temperature have been employed with changing reagents and catalysts. According to different synthesis conditions, colorless to white crystals can be obtained. The ATR-FTIR study of the reaction mixtures shows the complete disappearance of the ethoxide groups and the formation of siloxane bonds. In the case of triethoxysilane, the Si-H bond is preserved in the final product. The presence of the base appears to strongly influence the hydrolytic stability of Si-O-Si bonds. The catalyst has to be removed after the reaction completion in order to avoid Si-O-Si cleavage and obtain a stable product even under air. The results of the spectroscopic characterization by FTIR, Raman and multinuclear NMR will be presented and the structures of different condensation products will be proposed. The first results on the film formation by assembling of vinyltriethoxysilane/diphenylsilanediol-derived product will also be discussed, using FTIR results and basic optical properties.

659 - Sol-Gel Design of Some Hybrid Organic-Inorganic Carriers

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With an aim to joint the best properties of organic (aqua-soluble) and inorganic (polysiloxane) polymers the carriers were synthesized using sol-gel technique. Such synthetic method gives ample opportunities of design both carriers and their surface layer. It is very important for modern liquid chromatography which requires carriers having high stability in relation to temperature and mechanical influences, and also having a surface layer with significant chemical and hydrolytic stability.

Here, we report the one-stage synthesis and structure-adsorption characteristics of hybrid organic-inorganic carriers prepared using three approaches: (i) synthesis of polysiloxane xerogels with bifunctionalized surface layer; (ii) synthesis of hybrid carriers by realization of hydrolytic and polycondensation reactions of alkoxy silanes in a solution already had formed of (oligo)polymer (for example, sodium oligo-n-styrenesulphonate, polycaproamide, chitocane, etc.); (iii) obtaining of hybrid sorbents in a course of simultaneously proceeding polymerization reactions of oligomers of an organic origin (for example, acrilonitrile). Variation of the synthesis conditions allows to obtain hybrid materials with different structure-adsorption characteristics. Synthesized hybrid materials were investigated by numerous physical methods (thermal analysis; SEM and TEM; IR and Raman spectroscopy; solid-state ^{13}C and ^{29}Si NMR spectroscopy, etc.) with the purpose of an establishment of dependences such as "composition - structure - properties". At last stage was carried out chromatography testing of the received carriers in HPLC and HLTPC and significant potential of the offered approaches is shown.

660 - Highly Porous Hybrid Silica/Latex Xerogels Dried at Ambient Pressure

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It is the purpose of the present work to describe a novel, low-cost, sol-gel route for the preparation of highly porous monolithic xerogels, stable under atmospheric conditions and suitable for machining. Recent work proved the possibility of obtaining pure silica aerogels by subcritical drying of aged alcogels that meet all these requirements, except in the mechanical properties. To improve this aspect, the process followed here consists in incorporating an organic phase since the first stages of the sol-gel process. The hybrid alcogels were prepared by acid catalyzed co-hydrolysis of tetraethoxysilane and poly(butyl-metacrylate) latex particles containing trimethoxysilane groups at the surface, followed by base catalyzed condensation. After convenient aging, the gels were washed with isopropanol and left to dry under atmospheric pressure. It is shown, by uniaxial compression tests, that the inclusion of the latex increases the deformability of the material, without loss of the typical aerogel-like properties of the inorganic xerogel. The hybrid xerogels are hydrophobic materials, with an envelope density as low as 0.35 g cm^{-3} , corresponding to a porosity of 83%, distributed in a bimodal pore structure of interconnected macropores and mesopores. The chemical and physical properties of the dry gels have been analyzed by volume shrinkage upon drying, envelope density determinations, scanning electron microscopy (SEM), nitrogen sorption isotherms and diffuse reflectance infrared spectroscopy (DRIFT).

661 - Microstructure and Photocatalytic Property of SiO₂-TiO₂ under Various Process Conditions

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The purpose of this study is to synthesize TiO₂ photocatalyst which is highly effective in decomposing volatile organic compounds. In this work, the crystallinity, rutile/anatase ratio, particle size of TiO₂, and reactive surface area is controlled by varying the SiO₂ content, calcination temperature and different synthetic procedure. XRD, SEM, BET and UV-Visible Spectroscopy studies probe the microstructure and photocatalytic characteristics of the synthesized SiO₂-TiO₂ powders, and the optimum conditions to get the most active powders are determined. Titanium isopropoxide and tetraethylorthosilicate are used as precursors of titania and silica, respectively. Isopropanol and ethanol are employed as solvents, and nitric acid is used as a catalyst. $x\text{SiO}_2-(1-x)\text{TiO}_2$ ($x=0.1, 0.2, 0.3, 0.4$), powder is prepared with various sintering temperature with sol-gel and hydrothermal process. It is confirmed that the silica-titania mixture has high thermal stability, which results in the suppression of phase transformation of titania from anatase to rutile. As the silica content increases from 0.1 to 0.4 mole ratio, the crystallite size decreases from 11.23 to 7.29 nm. This result confirms that embedding amorphous SiO₂ into titania inhibits the growth of anatase crystal of titania particles to a certain extent. All the XRD patterns of titania powders synthesized at 250°C by hydrothermal process can be assigned to anatase, and the decrease in crystallite size from 12.36nm to 9.44 nm with the increase in surface area is observed. The dichlorobenzene (DCB) decomposition rate for sol-gel derived SiO₂-TiO₂ powders prepared at 750°C increases as silica content increases. The photoactivity of powder with 30mole% silica is higher than Degussa-P25, and however, the powders prepared at 250°C by hydrothermal process have lower DCB decomposition rate than Degussa-P25 due to the low surface area and low crystallinity.

662 - Immobilization of CdS particles in a hibrid Sol-Gel material

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The hybrid organic-inorganic materials prepared by sol-gel procedure gives an opportunity to obtain solid state monoliths filled with in situ generated inorganic particles. It is an interested area of research because the filling fraction of the inorganic components influences the optical and mechanical properties of the final material. Our investigations were focused on the preparation and characterization of CdS particles immobilized in the hybrid UREASILICATE matrix. They were synthesized by a simple homogeneous precipitation via rapid inorganic reaction between aqueous solutions of $\text{Cd}(\text{NO}_3)_2$ and CH_3CSNH_2 in the ureasilicate sol at the appropriate pH of the media.

The matrix (host media) has been prepared by sol-gel technique through covalent linkage between isocianate group of organically modified silicon alkoxide (3-isocyanatepropyltriethoxysilane) and the terminal amine groups of double functional oligopolyoxyethylene (Jeffamine, ED-600). The subsequent hydrolysis and condensation of silicon alkoxide terminal groups allows the formation of 3-D inorganic network.

The obtained materials were characterized by spectroscopic (UV-visible, photoluminescence and FTIR), thermal (DSC), mechanical (DMA) and structural (XRD) measurements.

663 - Influence of the Synthesis Method on the Properties of Ceria-Doped Alumina

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Alumina sol-gel has been widely employed as catalytic support because of the purity and controlled properties of solids obtained. On the other hand, ceria is a fundamental component in automotive catalytic converters due to its capability to store and release oxygen. In this work, we have prepared ceria-doped aluminas using two preparation methods, varying the synthesis conditions. The materials were characterized to observe the differences in thermal stability and textural properties.

Ceria-doped aluminas were prepared at low concentrations (0, 2 and 5 % wt CeO_2) as described (Method A): i) aluminum tri-sec-butoxide was dissolved in excess of 2-propanol at 5°C ii) HNO_3 solution was added slowly together with a solution of $\text{Ce}(\text{NO}_3)_3$ in 2-propanol, and iii) gels obtained were aged 24 h, dried in vacuum at room temperature and calcined at 700 and 1000°C in air flow. In addition, Al_2O_3 - CeO_2 samples were prepared with the following variations (Method B): $\text{Ce}(\text{NO}_3)_3$ was dissolved together with aluminum alkoxide (part i) and the synthesis catalysts was NH_4OH instead of HNO_3 . The solids were characterized by N_2 physisorption, DTA, TGA, XRD and 2-propanol reaction test.

The effects on structural and surface properties as well as thermal behavior were determined on ceria-doped alumina. The materials obtained by Method B present similar textural properties than alumina (i.e., specific areas, pore volumes and acidity), but marked differences in structural and thermal behavior; the XRD analyses of these samples calcined at 1000°C show the presence of segregated CeO_2 and present differences in DTA and TGA behavior. We also found that in materials obtained by Method A, the ceria addition shows the following: i) a diminution of surface area and pore volume, ii) decrease acidity, determined by 2-propanol dehydration, and iii) similar thermal behavior to that of undoped alumina, as observed by DTA and TGA. In all samples, alumina and ceria-doped aluminas calcined up to 1000°C present γ -alumina phase with a pore volume ca. 1 g/cm³.

In summary, ceria appears to be well incorporated in alumina when solids are obtained by Method A, whereas these obtained by Method B present segregation of CeO_2 .

664 - Preparation of “Green” Composites -- In Situ Silica-filled Natural Rubber

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In order to prepare a “green” (eco-friendly) composite composed of natural rubber (NR) and in situ silica, the reaction condition of in situ generated silica in the NR matrix was investigated in detail, especially from the viewpoint of increase of the in situ silica content in NR. The effect of in situ silica content on the mechanical properties was also discussed. NR was subjected to tight milling to prepare the NR sheet and the sheet was immersed in tetraethoxysilane (TEOS). The swollen NR sheet was then immersed in the aqueous solution of n-butylamine at 40°C to follow the sol-gel reaction of TEOS. The amount of n-butylamine was 1/20 mol against the amount of swollen TEOS. The immersing time, temperature and the amount of water were varied. The samples were dried under vacuum at 40°C. The amount of in situ silica was determined by a thermogravimetry. The morphology of in situ silica in the NR matrix was investigated by a transmission microscopy. The in situ silica-filled NR vulcanizates were mechanically prepared by the conventional mixing on a two-roll mill and were subjected to the uniaxial tensile measurement and dynamic mechanical analysis.

The swelling degree of NR in TEOS was important to control the in situ silica content in NR. Additionally, the concentration of catalyst affected the amount of in situ silica in NR. The particle size of in situ silica became larger with the increase of silica content from ca. 10 nm to ca. 40 nm for 10phr ~ 40phr loadings in the NR matrix, respectively. The dispersion of in situ silica particle was more homogeneous than that of commercial silica (VN-3), which was mechanically mixed with NR. The better reinforcement effect of in situ silica for NR was observed with increasing the silica content. The in situ silica filling in NR is a good method to prepare the rubbery nano-composites with unique characteristics.

665 - Lamellar Organo-Bridged Silicones

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The acid-hydrolysis of an organo-bridged bisdiethoxysilylated molecular precursor bearing urea groups, $(EtO)_2MeSi(CH_2)_3NHCONH(CH_2)_{12}NHCONHCH_2SiMe(OEt)_2$, has been performed in pure aqueous medium. The scanning electron microscopy (SEM) analysis revealed plate-like forms for the resulting bridged siloxane hybrid with a lamellar structure as determined by powder X-ray diffraction (PXRD) studies with a sharp peak at 28.5 angströms. The solid state ^{29}Si MAS-NMR spectrum exhibits a moderately condensed material with complete preservation of the Si-C bonds throughout the hybrid network. In comparison, the classical sol-gel hydrolysis-condensation of the molecular precursor in ethanol with stoichiometric amount of water and fluoride anion as catalyst produced an amorphous featureless solid.

667 - Non-Hydrolytic Route for the Synthesis of Al_2TiO_5 and $\text{Mg}_x\text{Al}_{2(1-x)}\text{Ti}_{(1+x)}\text{O}_5$ Powders

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Interest in aluminum titanate spans a wide range of technologies due to its unique thermal and chemical properties. The use of an appropriate oxide dopant, such as MgO, allows to stabilize the Al_2TiO_5 phase as well as to control the grain grown effects. Among the numerous studies on the synthesis of aluminum titanate, those based on sol-gel methods indicated the possibility of decreasing the processing temperature hence achieving more effective microstructural control. Conventional sol-gels routes, however, do not avoid the lack of homogeneity due to the different hydrolysis rates of aluminum and titanium alkoxides. A different approach might be the non-hydrolytic sol-gel route which involves the direct condensation of the precursors in aprotic solvents. Different procedures have been considered changing the precursors and varying the reaction solvent $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$). The most promising results were obtained using the following reagents: $\text{AlCl}_3 + \text{Ti(OiPr)}_4 + \text{Mg}(\text{NO}_3)_2$ or $\text{TiCl}_4 + \text{Al(OsBu)}_3 + \text{MgSO}_4$. The reactions were monitored using ^{13}C NMR spectroscopy and gas mass spectrometry. Al_2TiO_5 and $\text{Mg}_x\text{Al}_{2(1-x)}\text{Ti}_{(1+x)}\text{O}_5$ powders were prepared by heating the gels at various temperatures ranging from 600-1200°C. The formation of the different phases was studied by X-ray diffraction analysis. The magnesium-containing materials showed a very high thermal stability. No decomposition of aluminium and magnesium titanate phase was in fact observed even after 120 hours of firing at 1200°C.

668 - Synthesis and characterization of polyimide-silica hybrid materials; effect of matrix polarity on the mechanical and thermal properties of the resulting hybrids

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Polyimide-silica hybrid materials have been prepared through the sol-gel process by mixing various proportions of tetraethoxysilane(TEOS) with polyamic acids. Two types of polyamic acids were employed. The first was obtained by reacting an equimolar mixture of oxydianiline (ODA) and pyromellitic dianhydride (PMDA) in dipolar aprotic solvent (DMAc). The second was prepared using a mixture of ODA and 2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane, 6F-OHDA in molar ratio 9:1 respectively and reacting with stoichiometric amount of PMDA in DMAc. Hybrid films were cast by evaporating the solvent at 70°C. Curing was carried out by successive heating of these films at 100°C, 200°C and 300°C for each one hour. During the heating polyamic acids were converted to polyimides and sol-gel reaction, which consists of hydrolysis and condensation of TEOS proceeded simultaneously. FTIR was used to monitor the reactions. Only the 10 mol % addition of 6F-OHDA in the polyimide chain resulted in drastically different microstructure for the resulting hybrids. The hydroxyl groups from 6F-OHDA allows the secondary bonding between the polyimide and growing silica phase and thus retard the gross phase separation. SEM, stress-strain analysis and temperature variation of storage and loss modulus were used to characterize the hybrid materials. Thermal and mechanical characteristics for both types of hybrids have been compared and related to the two different types of structures of polyimide, one containing pendant hydroxyl groups and other no such groups on the chain.

670 - Preparation of Nano--crystalline ZnTiO₃ powders by the Sol-Gel Process

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ZnTiO₃ powders were prepared with [Zn(Ac)₂·2H₂O] and Ti(OC₄H₉)₄ materials by the Sol-Gel process. The effects of (), PH value and gel temperature on the gel quality was investigated in detail. In addition, the effect of calcining temperature on the qualities of ZnTiO₃ powders was studied. The thermogravimetry analysis and the differential thermal analysis (TG-DTA) were used to simulate the behaviors of dry gel burnout. The crystal structure and purity of the powders were studied with X-ray diffraction (XRD) spectrometer. The experimental results show that the higher quality gel can be prepared when the gel conditions is, and the gel temperature keep low and unchangeable. The ZnTiO₃ powders of higher purity can be obtained if the calcining temperature is 900°C.

671 - Apatite Morphology and Phase Development in Sol-Gel Synthesis of Bone-Like Carbonated Apatite

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Synthetic prosthetic materials are at present broadly used in the orthopaedic surgery. However, new highly organized substitute materials that resemble chemical, morphological and biological properties of living bone are needed in order to improve bone tissue integration. We have produced apatite that mimics the plate-like morphology of bone mineral. The methodology emulates biominerization, where topotactic transition from octacalcium phosphate to hydroxyapatite is believed to occur *in vivo*. In the second part of this work apatite phase evolution, carbonate content and morphology are considered as a function of temperature during heat treatment. The importance of the chemical reactions that occur in solution, and the influence of the morphology of the intermediate phase on the crystalline sizes and shapes of the ultimate apatite phase have been considered. The overall carbonate content varies from 6.4 to 2 wt%, within the temperature range of 500 - 900°C. This carbonate content corresponds well with the amount found in mammalian hard tissues. Although, apatite crystals in comparison to the natural bone are relatively large (1.5 to 2 micron and 0.1micron thick) the similarities to bone crystal morphology suggests that this novel method is very promising for the production of range of new generation bone-graft materials.

672 - Chemical Reactions in Solution and Intermediate Solid State Transformations in Sol-Gel Synthesis of Bone-Like Carbonated Apatite

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A novel method has been developed to produce monophasic, plate-like, mixed A-B type carbonate containing apatite (CAp) similar to bone apatite. The method involves formation of plate-like calcium phosphonate salts as intermediates which act as templates for the formation of apatite phase. This work reports the identification of chemical reactions in solution and the formation of intermediate compounds that lead to production of plate-like carbonated apatite. During thermal ageing of the starting solution a number of consecutive reactions have been monitored that resulted in crystalline calcium hydrogen-phosphonates with plate-like morphology. The increased stability of these calcium phosphonate salts (up to 250°C) is attributed to the association of calcium ions with both phosphoryl and carbonyl functional groups in the newly formed hydrogen-phosphonate species. The plate-like morphology of the calcium phosphonate precursor had substantial influence on the morphology of the subsequent amorphous calcium phosphate phase at 300°C. The chemical reactions have been studied by one- and two-dimensional nuclear magnetic resonance (NMR) and infrared (IR) spectroscopic techniques, which allow elucidating chemical structures of most molecular units in the solution and in the solid state prior to apatite formation.

673 - Mechanical properties of nano-hybrid films
Part 1: 3-glycidoxypolytrimethoxysilane

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Sol-gel hybrid coatings are used in many optical applications, due to their good optical response and the improved scratch resistance that they provide for polymeric surfaces. By introducing organic moieties in the coating, the mechanical properties of the resulting coatings can be readily modulated to achieve optimum adhesion and hardness required to provide good scratch resistance properties.

In this study, the relationship between film nanostructure and mechanical response is investigated. The nanohybrid solutions used for coating were composed of a 1:1 molar ratio of 3-glycidoxypolytrimethoxysilane (GTMS) and tetraethoxysilane (TEOS), prehydrolysed under acidic conditions (pH2). GTMS was selected because of its ability to undergo both inorganic polycondensation and organic epoxy polymerisation, and the use of GTMS as a polymer precursor in hybrids is widely described in the literature. It was combined with TEOS to increase the overall mechanical resistance of the resulting hybrid films. The mechanical properties of the corresponding coatings were characterised by measuring their Young's Moduli, hardness and adhesion using nano-indentation and tensile testing.

The effect of epoxy ring opening during sol-gel processing on the evolution of mechanical properties will be discussed, and compared to that of coatings produced from pure organic epoxides. The relationship between hydrolysis-polycondensation conditions and mechanical response will also be presented.

674 - Mechanical properties of nano-hybrid films

Part 2: influence of sol-gel chemistry

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The influence of organic chain length and chemical functionality on the structural evolution and mechanical properties of nanohybrid films was investigated by spin-coating mixtures of TEOS and selected alkyltrialkoxy silanes (methyltrimethoxysilane (MTMS), vinyltrimethoxysilane (VTMS), phenyltrimethoxysilane (PhTMS), and n-octyltriethoxysilane (OTES)). The mixtures were prehydrolysed at pH2 prior to deposition. The connectivity of the inorganic and organic networks during processing was investigated by ^{13}C - and ^{29}Si -NMR, SAXS, FT-IR and Raman spectroscopy, while the corresponding mechanical properties of the coatings (Young's modulus, hardness and adhesion) were probed via nano-indentation and in-situ tensile testing.

The mechanical properties of the coatings were found to be strongly modulated by the size of the organic modifier, with increasing size leading to a corresponding decrease in the Young's modulus. In contrast, only small differences were observed between the mechanical response of films obtained from precursors with similar chain lengths but different chemical functionality. This effect is attributed to nanosegregation of the organic and inorganic domains during the structural evolution of the coatings, which leads to a significant decrease in the long-range connectivity of the network. Increasing the size of the organic substituent promotes nanosegregation. The relationship between the connectivity of the inorganic network, the volume fraction and size of the organic modifier, and the mechanical response will be discussed.

In our investigation in GTMS/TEOS sols for hybrid coatings, the impact of the organic group on the sol morphology and its relationship with the mechanical response of the corresponding film was investigated. GTMS/TEOS sols were compared with a series of equivalent sols produced from different organotrialkoxysilanes.

The Young's Modulus and hardness of films produced from pre-hydrolysed solutions at pH2 of equimolar mixtures of RSi(OR)_3 and tetraethoxysilane (TEOS), where R= Me, Vinyl, Phenyl, and Octyl, were measured. The values obtained could be compared to those of previously studied films from GTMS/TEOS sols prepared in the same conditions.

A relationship between chain length and mechanical properties was outlined. The assumption of a segregation of the silica nano-domains in the presence of long-armed organotrialkoxysilane was considered. Small Angle X-ray Scattering and ^{29}Si NMR Spectroscopy analyses were performed in order to emphasise the possible presence of nanosegregation in such systems and will be discussed.

675 - Ceramic Micro-Particles for Controlled Release Synthesis using Combined Microemulsion and Sol-Gel Technology

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Controlled release technologies have many applications in such diverse fields as the pharmaceutical, agricultural, cosmetic and food industries, where tailored release rates and protection of the active molecule for delivery at a specific site or time are advantageous. Micro-encapsulation can also be beneficial for protecting the active materials from potentially aggressive environments or to prevent reactive mixing of substances until a specific target site is reached. We have developed a process combining water-in-oil microemulsion chemistry with sol-gel technology, to produce spherical SiO_2 micro-particles (approximately 10-50 μm in diameter) for encapsulating and releasing active chemical compounds. The average particle size is controlled by the microemulsion parameters, including the surfactant and solvent concentrations, and by the sol-gel parameters, particularly water-to-silicon alkoxide ratio, pH, temperature, ageing and mixing conditions. Physical properties of the SiO_2 micro-particles, which affect the release rates of the encapsulated molecule, include pore size and tortuosity.

The effect of synthesis parameters, including surfactant concentration and sol-gel solution ageing time, on the morphology of the SiO_2 micro-particles produced will be discussed in detail. Preliminary results showing the corresponding rate of release will also be presented.

676 - Preparation of dye doped silica nanoparticles via water-in-oil microemulsions

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Sol-gel technology has been developed over the past decade to encapsulate organic or biological species within inorganic matrices at ambient temperature. Combining such techniques with microemulsion-mediated alkoxide sol-gel processes provides a unique technique, by which spherical ceramic particles containing encapsulated species can be formed with a narrow size distribution, and the particle size and nanostructure independently controlled.

In this work, nanosized silica particles with diameters of ~16 and ~30 nm containing encapsulated rhodamine dyes were formed using microemulsion systems based on Brij-30/cyclohexane and Triton X-114/toluene, respectively. Under the acid-catalysed conditions used, the encapsulation efficiency increased gradually with increasing addition of dye, to a maximum of ~ 60 %. The selection of solvent for washing the freshly prepared nanoparticles had a significant impact on the apparent encapsulation efficiency. In particular, more dye was lost when washing with dichloromethane than with toluene for nanoparticles produced in the Triton X-114/toluene system. The effect of key process parameters on particle size, porosity, and encapsulation efficiency will be addressed.

Keywords: Silica nanoparticles; Microemulsion; Encapsulation; Rhodamine.

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Titanium oxoalkoxy clusters are structured intermediates in the hydrolysis and polycondensation reactions of titanium alkoxides, making them potentially valuable nano-building blocks for the preparation of titania coatings. However, controlling the structure and chemical functionality of such clusters to direct their sol-gel chemistry in a predicted way remains a challenge today. Although a large number of titanium oxoalkoxy clusters have now been described in the literature, methods for predicting the structural evolution of products produced during their reaction with water or other strong nucleophiles are still to be defined.

In this work, the reaction between a well defined titanium oxoalkoxy cluster (i.e. $\text{Ti}_6\text{O}_4(\text{O}i\text{Pr})_8(\text{OAc})_8$), and methanol (MeOH) was investigated. MeOH is a strong nucleophile, whose reactivity towards $\text{Ti}_6\text{O}_4(\text{O}i\text{Pr})_8(\text{OAc})_8$ is expected to provide us with a better understanding of the reactivity and structural evolution of such clusters during hydrolysis. The cluster was reacted with selected quantities of MeOH in a neutral solvent and the reaction products were analysed by ¹H and ¹³C NMR. Thin films were deposited on Si wafers by the spin-coating method. The density of the films was estimated from their relative refractive indices (measured using ellipsometry), while their smoothness and homogeneity were investigated by atomic force microscopy.

The reaction between MeOH and $\text{Ti}_6\text{O}_4(\text{O}i\text{Pr})_8(\text{OAc})_8$ led to the formation of a new cluster, at a rate dependent on the MeOH-to- $\text{Ti}_6\text{O}_4(\text{O}i\text{Pr})_8(\text{OAc})_8$ mole ratio, and no isolated substitution of the isopropoxy or acetyl groups was evident (even at low mole ratios). When MeOH was used in excess, the new cluster was isolated as the single product of the reaction, together with the expected release of isopropanol. Ellipsometric data revealed that the density of titania films obtained from the methanolysis product was significantly higher than that obtained from the parent cluster. The properties of the new cluster and the optical properties of the corresponding films will be discussed.

678 - Cracking And Decohesion Of Sol-Gel Hybrid Coatings On Metallic Substrates

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Thin film coatings based on organically modified silanes were synthesized using sol-gel technology. Various mixtures of tetraethoxysilane and glycidoxypipyltrime thoxysilane precursors were used to produce sol-gel coatings on as-received and thermally oxidised copper, aluminium and titanium substrates. The mechanical properties and adhesion behaviour of the coatings were assessed using nano-indentation and microtensile testing, respectively. The relationship between the film structure and its mechanical response is examined. It is shown that the mechanical properties (hardness and Young's modulus) of the coatings is influenced dramatically by the organic substituent and the presence of an oxide layer thermally grown on the substrate material prior to deposition plays an important role on the film/substrate adhesion behaviour.

679 - Fluorinated copolymer/metal oxide hybrids: an interesting family of materials

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Some fluoropolymers exhibit unique properties such as high thermal stability, "nonstick" characteristics, high UV resistance, etc. Lumiflon® is one such polymer that has found many uses as a protective coating for a number of applications. Because of the reactive hydroxyl groups the structure of the copolymer, it appeared natural to attempt to cross-link the polymer with metal alkoxides such as TEOS in order to modify or improve its properties.

When TEOS is refluxed with the co-polymer in the presence of various catalysts, the resulting material is an organic-inorganic hybrid that exhibits a continuous variation in properties between that of the pure co-polymer and sol-gel derived silica. Under some conditions, the fluoropolymer-silica nanocomposite remains transparent throughout the entire TEOS/SiO₂ compositional range. The hybrids are either rubbery or transparent depending on the TEOS content. Hardness, thermal decomposition temperature, contact angle, abrasion resistance have been measured. Solid state NMR shows that SiO₂ clusters are present in the hybrid. By replacing TEOS with an optically active precursor, such a neodymium methoxyethoxide, a Nd³⁺-doped fluoropolymer is obtained. In all cases, we theorize that crosslinking between the fluorinated co-polymer and the metal alkoxide occurs, which makes these new hybrids particularly interesting for their mechanical and optical properties.

TUESDAY POSTER SESSION

701 - Sol-Gel Derived ZrO₂ Thin Films - Synthesis and Characterization

D T Senguttuvan, National Physical Laboratory New Delhi, India

K L Malhotra, Indian Institute of Technology New Delhi, India

Thin films of ZrO₂(Zirconia) have been deposited on various substrates using sol gel dip coating method. Different polymorphs i.e cubic, tetragonal and monoclinic have been obtained, without stabilization agents, by control of the sintering temperatures. The atomic percent of zirconium and oxygen in the films has been determined from core level ESCA spectrum and for typical 800°C sintered films; these are 48% and 52% respectively. The refractive index n, the extinction coefficient k, and the band gap have been calculated from measurements of reflectance and transmittance and are found to be different from those deposited by other techniques. The observed positions of the imaginary part of dielectric function (ϵ_2) have been used in conjunction with theoretically reported data in literature, to infer the electronic structure of these films

702 - Sol-Gel Deposition of Zirconium Doped Tin Dioxide Thin Films by Non Alkoxide Precursors

D T Senguttuvan, National Physical Laboratory New Delhi, India

K L Malhotra, Indian Institute of Technology New Delhi, India

Zirconium doped tin oxide films have been deposited by alcoholic sol gel method using non alkoxide precursor $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and zirconium iso propoxide. Using dip coating method , thin films of thickness up to $0.18\mu\text{m}$ have been uniformly deposited on corning 7059, KBr and silicon substrates. Influence of various processing parameters such as pulling speed and sintering temperature on their microstructure electrical and optical properties have been investigated. Infra red transmission spectra, ESCA and Xray analysis have been carried out to monitor various stages of processing.

703 - TEM Observation of Crystallization of Barium-Strontium Titanate Film

P V Burmistrova, Russian Academy of Science, Russia

A S Sigov, K A Vorotilov, Moscow State Technical University of Radioengineering, Russia

D N Zacharov, O M Zhigalina, Institute of Crystallography, Russian Academy of Science, Russia

BST films ($\text{Ba/Sr} = 70/30$) were prepared by chemical solution deposition (CSD) from alkoxides solution modified by 2-ethylhexanoic acid. The films were deposited on $\text{Si}-\text{SiO}_2-\text{Ti-Pt}$ substrates and annealed at $550-800^\circ\text{C}$.

The microstructure of BST thin films at different crystallization temperature (T_c) was investigated by transmission electron microscopy (TEM).

Different types of perovskite grains were discovered: type I – perfect grains of 10-60 nm in size without defects, and type II – porous grains of the size of 80-300 nm with large surface area. The size of type I grains is slowly increased with the increase of crystallization temperature, whereas the size of type II grains is rapidly decreased, and at $T_c=800^\circ\text{C}$ they are completely disappeared. Formation of type II porous grains is caused by crystallization process behaviour. Transformation from amorphous to crystalline state in BST occurs at the temperature lower than the temperature of liquid synthesis.

The value of dielectric constant of BST films is strongly depend from crystalline structure of the films: the decrease of the volume part of type II porous grains accompanies by the increase of dielectric constant.

The study is supported by RFBR Grant N 01-02-16620, INTAS 75-2002, U.S. CRDF-R.F. Ministry of Education Award VZ-010-0.

704 - Ferroelectrics Templated in Nanoporous Silicon and Alumina Membranes

E D Mishina, A S Sigov, V A Vasil'ev, K A Vorotilov, Moscow State Technical University of Radioengineering, Russia

Ultra-small (10-50 nm) ferroelectric nanostructures are prepared by dipping or capillary wetting of porous matrix into a PZT sol-gel precursor followed by crystallization during annealing at 700°C. Porous silicon and porous alumina were used as the templates. The structure of porous substrates as well as PZT nanostructure were studied by AFM and TEM. It was found that on top of porous Si nanostructure a PZT layer is formed after dipping. In order to remove the PZT film, the surface was either etched by argon beam (for silicon substrate) or cleaned by the solvent rinsing prior to annealing (alumina substrate). The presence of ferroelectric phase was checked optically by second harmonic generation (SHG) technique: ferroelectric phase is noncentrocymmetric and produces an intensive second harmonic radiation while for centrosymmetric pyrochlor phase the SHG intensity equals zero in dipole approximation. In this way, the SHG gives a remote noncontact probing of polarization state. Increasing the annealing temperature up to 600°C does not change the SHG intensity of the structure in comparison with pure porous silicon membrane. Nanostructures annealed at 700°C reveal strong SHG radiation pointing to the crystallization of nanoparticles in ferroelectric phase.

705 - Effect of Annealing Temperature on the Properties of Methyl-Modified Silicate Films

A S Sigov, V A Vasil'ev, K A Vorotilov, Moscow State Technical University of Radio-engineering, Russia

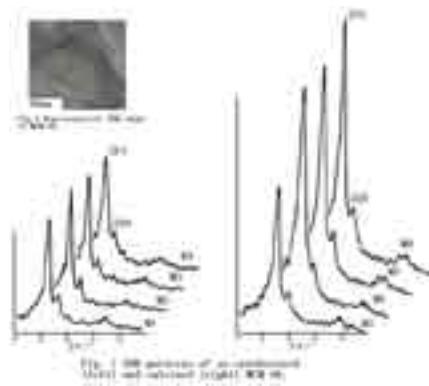
Methyl-modified silicate films with different content of methyl groups ($\text{Me/Si} = 0.25, 0.5, 0.75, 1.0$) are prepared by sol-gel route on silicon substrates. Film structure and its evolution during heat treatment were studied by ellipsometry (refractive index and shrinkage) and IR spectroscopy. In the range of annealing temperature from 200 to 400°C the films have a low shrinkage (1-3 % depending on Me content) and refractive index near 1.38. Thermodestruction of methyl groups starts at 450-500°C depending on methyl content and is accompanied by decrease of refractive index indicating formation of nanoporous structure (near 550°C). Further increase of annealing temperature (near 600°C) leads to high shrinkage and increase of refractive index due to disappearance of nanopores within silicate matrix. This thermal reconstruction process is sufficiently governed by Me content in the films (before pyrolysis), occurring easier in the case of high Me content and less branching structure. Full densification of silicate structure is observed near 700°C.

706 - Mixed cationic-nonionic surfactants route to synthesize high-quality MCM-48 under low surfactant/silicon molar ratio

YuHan Sun, Dong Wu, ShangRu Zhai, Chinese Academy of Sciences, China

Siliceous MCM-48 materials have been efficiently synthesized using a mixture of cetyltrimethylammonium bromide (CTAB) and p-Octyl polyethylene glycol phenyl ether (OP-10) as templates with low molar ratio of CTAB to silica (0.139:1) and low concentration of mixed surfactants (ca.5%) and within a wide range of CTAB/OP-10 ratio (0.08~0.25). Powder X-ray diffraction (XRD), N₂ adsorption, ²⁹Si magic-angle-spinning (MAS) NMR spectroscopy, high resolution transmission electron microscopy (HRTEM) and thermogravimetric and differential scanning calorimetry studies (TG-DSC) have been employed to characterize the cubic mesoporous MCM-48 molecular sieves. XRD and ²⁹Si MAS NMR data indicate that the use of mixed surfactants allowing higher ordering and better condensation and thicker wall of the cubic mesostructures. TEM and N₂ adsorption results show well-defined three-dimensional channels for the cubic mesophase. Furthermore, the effect of OP-10/CTAB ratio on the physical properties of MCM-48 materials and the reaction mechanism is discussed in detail.

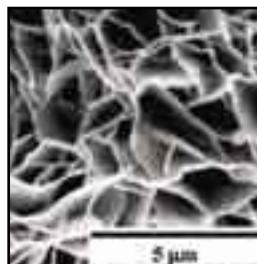
A typical synthesis is performed at 383 K for 72h using tetraethyl orthosilicate (TEOS) as the silica source and CTAB and OP-10 as the structure-directing agent with molar composition of TEOS/CTAB/OP-10/Na₂O/H₂O = 1.0/0.139/x/0.234/55.7, x=0.006~0.035. For comparison, MCM-48 is also synthesized by using single CTAB as template and the molar composition of the gel is 1.0 TEOS/0.234 Na₂O/0.166 CTAB/55.7 H₂O. Fig.1 shows XRD patterns of as-synthesized and calcined MCM-48 materials obtained with various OP-10/CTAB ratios. All these samples are typical of the cubic crystallographic space Ia3d, which are consistent with previously reported MCM-48 silica. A representative TEM image of calcined MCM-48 as shown in Fig.2 which proves the pore structure is highly ordered.



707 - Fabrication of Nanostructured Metal Oxide Semiconductor Films Having Nest-Like Morphology through Pyrolytic Transformation of CBD-Processed Layered Hydroxide Metal Acetates

Shinobu Fujihara, Eiji Hosono, Toshio Kimura, Keio University, Japan

Nanoscale porous structures of metal oxide semiconductor films having high specific surface areas have been required in electrochemical fields including chemical sensors, photocatalysts and dye-sensitized solar cells. We prepared nanostructured porous metal oxide (Co_3O_4 , NiO and ZnO) films with a nest-like morphology by pyrolytic transformation of layered hydroxide metal acetates (LHMAs). Such the morphology was originally formed as interlaced nanoflake assemblies on glass substrates during hydrolysis-controlled chemical bath deposition (CBD) in methanolic solutions of metal acetate hydrates. The deposition process was as simple as immersing the substrates in the solutions and keeping them at low temperatures, typically 333 K. It was a key to induce heterogeneous nucleation of LHMAs through control of a degree of supersaturation, which was generated by the progress of hydrolysis and polymerization of the metal acetate complexes. Nucleation, crystal growth and morphology of the deposited LHMA films were found to depend on the nature of the metal ions as well as the content of water. Hydration water contained by starting zinc acetate dihydrate was quantitatively enough to evolve the nanoflake assemblies while additional water was necessary for cobalt or nickel acetate tetrahydrate. The LHMA nanoflakes were transformed into thinner nanoflakes consisting individually of pertinent metal oxide nanocrystallites by heating at low temperatures, typically 423 K, in air. This pyrolytic transformation was achieved without morphological deformation and hence the nanostructured metal oxide films were successfully obtained. The figure shows the structure of the resultant ZnO film.



709 - Tailoring Electrical Properties of Modified SiO₂ Films

Thomas Huebert, Federal Institute for Materials Research and Testing, Germany
Andreas Klyszcz, Germany
Aki Shimamura, Japan

The use of the favourable mechanical properties of SiO₂-based films prepared via a low cost technology for electronic components like sensors and resistors demands a reduction of electric resistance. This can be achieved by adding nano-scaled conductive fillers to the dielectric matrix. We prepared organic modified silica films filled with carbon black or Ruthenium oxide and investigated the electric properties in dependence on film composition and structure. Precursor solutions were obtained from an usual acid hydrolysis of a mixture of TEOS, MTES, water and alcohol. For thick films further organic modified silanes were added. Then alcoholic solutions of Ruthenium chloride or carbon black were allocated to obtain up to 60vol% filler in the films. Solutions were characterised by particle size and viscosity measurements. Films were precipitated on silicon, glass and ceramic sheets by dip coating and screen printing. The heat-treated films were characterised by SEM, EDX and XRD. The film resistance was estimated by an I-V measurement system using a mercury electrode. The films prepared by dip coating have a thickness of 30 to 1000nm; screen printed films a thickness of 10 to 30μm. The nano-structured morphology consists of 35 to 180nm RuO₂ or 200 to 800nm carbon black particles in an amorphous matrix. The electric resistance R of the films changes from 10¹⁴ to 10⁻²Ω/sq in dependence on composition x. This non-linear behaviour can be discussed in the frame of percolation theory using the relation $R=R_c(x-x_c)^{-\beta}$ (see Fig. 1). A critical concentration x_c of 6vol% for RuO₂ and 50vol% for carbon black, at which the resistance drastically decreases, were yielded. The relative large x_c for carbon black due to the secondary particle size can be drastic reduced to <5 vol% by the use of carbon nano fibres. A further decrease of carbon filler amount can be achieved by an anisotropic orientation of the carbon nano fibres in an electric field before gelation. The obtained results show that electric properties of sol-gel based films can be tailored for specific technical applications by the kind of the conductive fillers, particle size, composition and orientation in the isolating matrix.

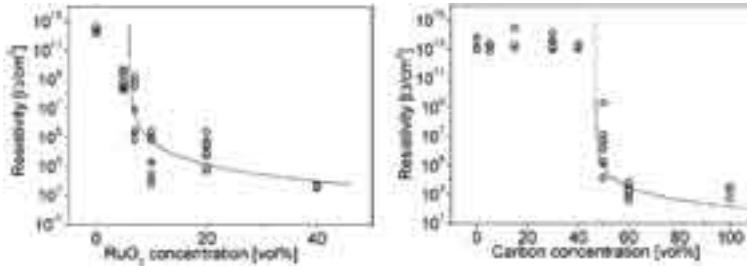


Fig. 1: The dependence of sheet resistance on conductive particle concentration

710 - Sol-Gel CaSiO₃ materials and calcium-containing inorganic compounds studied by natural abundance solid-state ⁴³Ca NMR

Zhongjie Lin, Mark E Smith, University of Warwick, United Kingdom
Frank E Sowrey, Robert J Newport, University of Kent, United Kingdom

Solid-state ⁴³Ca NMR data is still relatively scarce despite its importance in many materials ranging from glasses, cements, ceramics, minerals, superconductors to sol-gel and bioactive materials. This is mainly due to its low natural abundance of 0.135%, but additionally, its low gyromagnetic moment and significant quadrupole moment.

In this report, new natural abundance ⁴³Ca MAS NMR data measured at high magnetic field at 14.1T has been presented for a range of sol-gel prepared bioactive materials (for the first time at natural abundance), and for calcium-containing binary and ternary inorganic compounds. These data show a chemical shift range of more than 250 ppm and good signal to noise ratio. In some cases, the quadrupolar interaction parameters can be extracted from simulation of the spectra when they display a characteristic quadrupolar lineshape. The ⁴³Ca NMR results for sol-gel prepared CaSiO₃ materials indicate that Ca species attach to the surface of sol-gel silicate network at lower temperature (120 °C) before migrating into the silicate part of the materials at higher temperature (500 °C), which is confirmed by ¹⁷O NMR data. In binary compounds where Ca is coordinated by halogens and other typical non-metal elements or oxygen, the isotropic chemical shift is found to linearly correlate with the product of ΔX (the electronegativity difference) and mean Ca-X bond length. In ternary compounds where Ca is coordinated by oxygen, the isotropic shift is correlated with mean Ca-O distance, which is consistent with previous study.

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711 - Multinuclear solid-state NMR study of Sol-Gel prepared CaSiO₃ materials

Zhongjie Lin, Mark E Smith, University of Warwick, United Kingdom
Frank E Sowrey, Robert J Newport, University of Kent, United Kingdom

A multinuclear solid-state NMR study with emphasis on ¹⁷O NMR has been conducted to investigate the structure of a range of sol-gel prepared bioactive CaSiO₃ materials and their changes during heat treatment. The materials were prepared by two-stage hydrolysis with TEOS hydrolysed first and then the calcium source, with three different (CaO)_x(SiO₂)_{1-x} compositions (x = 0.2, 0.3 and 0.5) studied.

The ¹⁷O NMR results reveal that at low temperature (120 °C), the network structure is dominated by bridging oxygens (Si-O-Si) with contributions from Si-OH. This indicates that the Ca species are attached to the surface of the silicate network. The ¹⁷O NMR result is supported by ⁴³Ca NMR data showing the chemical shift of these materials are quite close to the starting calcium material, which indicates a similar local environment. After moderate heat treatment (up to 350 °C) the silicate network further condenses through loss of OH groups, and at the same time a weak non-bridging ¹⁷O signal begins to appear. At higher temperatures (≥ 500 °C), non-bridging oxygens (nbo) become increasingly important; hence the metal now plays a central role and begins to dominate the change of the structure. The calcium which was initially not part of the silicate network (probably on the surface) migrates into the silicate part of the materials, acts as a network modifier and gradually breaking down the silicate network by forming nbo. The intensity of nbo resonance increases with increasing CaO molar ratio in the materials as well as the temperature. This is confirmed by ²⁹Si NMR data showing increasing Q² and Q³ resonances associated with increasing CaO content after heating at 500 °C. ¹H and ⁴³Ca NMR results are also consistent with this conclusion. ¹⁷O solid-state NMR proved to be a very sensitive probe of bridging and non-bridging oxygens, with the MAS spectra giving direct resolution of these species, showing structural changes with calcium concentration and temperature of these sol-gel prepared silicate materials.

References

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712 - On the use of monolithic Sol-Gel derived mesoporous silica for the calibration of thermoporosimetry using various solvents

Jean-Marie Nedelec, Mohamed Baba, Université Blaise Pascal & ENSCCF, France

Thermoporosimetry is based upon the experimental shift of the temperature of transition of a given solvent when this solvent is trapped in a confined environment.

The authors have shown recently that such a technique is very useful to study cross linking level in elastomers and allows the determination of mesh size distribution and swelling ratio precisely. The more severe drawback is that this technique requires a precise calibration and thermo dynamical data related to the solvent used.

We have proposed to use sol-gel derived silica monoliths to perform such calibration. The precise control of the ageing procedure of the gels result in a control of the texture of the materials. Silica gels with narrow pore size distributions have been used with different solvents. The use of gels with pore size varying between 25 and 270 Å allowed to derive the following equations (a) and (b) for n-heptane and cyclohexane respectively.

$$Rp(\text{\AA}) = 587.4 / \Delta T + 2.4 \text{ with } -40 < \Delta T < 0^\circ\text{C} \quad (\text{a})$$

$$Rp(\text{\AA}) = 16.93 + 125.43 * \exp(-(1/\Delta T + 0.0756)/0.0205) \text{ with } 0 > \Delta T > -55^\circ\text{C} \quad (\text{b})$$

Where Rp is the radius of the pore and ΔT is the shift in the transition temperature.

For cyclohexane, the solid to solid phase transition occurring at $\sim -90^\circ\text{C}$ for free cyclohexane was used instead of the liquid to solid transition. This is very original and demonstrates that the theoretical concept of thermoporosimetry can be extended to any kind of transition.

Finally this technique has been applied to visualize the cross linking profiles inside a polyisoprene sample filled with carbon black, confirming the great potential of this technique to study polymeric samples provided that a precise calibration is available.

713 - Application of the Sol-Gel Method at the Fabrication of Microstructure Fibers

Jan Mrazek, Vlastimil Matejec, Milos Hayer, Ivan Kasik, Daniela Berkova, Institute of Radio Engineering, AS CR, Czech Republic, Czech Republic

The sol-gel method has shown its potential for the fabrication of photonic devices optical fibers, included. Microstructure fibers (MSFs) represent a novel type of optical fibers composed of a pure silica core surrounded by a grid of air holes. Usually, these fibers are fabricated in several steps by drawing an input stack from silica tubes or/and silica rods. The preservation of the arrangement of the stack during drawing is important for fabricating MSFs with regularly arranged air holes. This paper presents results of an approach for the preparation of MSFs which is based on the employment of thermally treated gels for fixing parts of the input stack.

The gels used for the formation of bridges between silica parts of a stack were prepared from sols mixed of TEOS, phosphorous oxychloride, boron tribromide, ethanol, HCl and water. Alkoxide sols as well as sols containing colloidal particles of the gels heat-treated up to 500 °C were employed. The sols were applied on stacks composed from a ring of six silica tubes arranged around the central silica rod. The gels formed in gaps between the tubes were slowly dried at the ambient temperature and then heat-treated at temperatures up to 1000 °C by using a programmed increase of temperature. Repeated preparation of gel bridges was also tested. A preform for drawing the MSFs was prepared by inserting the stack into a silica tube. The fibers were drawn at a temperature of about 2000 °C.

The regularity of air holes was evaluated on polished samples of the prepared stacks and of MSFs by using transmission optical microscopy. The refractive-index profiles, concentration profiles, spectral attenuation and waveguiding parameters of the fibers were measured.

The results show that doping of the gels with phosphorous or boron oxide enables more complete densification of the gel parts of the stack and thus better fixation than the gels prepared without these dopants. However, also incompletely densified parts of the stack are fully sintered at fiber drawing. The dopants modify the refractive-index profile of the fiber and therefore their waveguiding properties.

This work was supported by the Grant Agency of the CR (contract No. 102/02/0779)

714 - Preparation of New Photosensitive ZrO₂ Gel Films Using Hydroxyl-substituted Aromatic Ketones as Chemical Modification Reagents and Their Patterning

Naoki Noma, Saori Yamazaki, Noboru Tohge, Kinki University, Japan

We have been studying a novel patterning process using gel films. We have found that gel films which derived from metal alkoxides with chemical modification reagents such as β -diketones are photosensitive and leaching in organic solvents of the gel films irradiated with UV-light results in fine patterns. As the properties of the gel films are changed depending on the combination of metal-alkoxides and chemical modification reagents, it is important to elucidate relationship between the properties and the structures of reagents. In the present study, photosensitive ZrO₂ gel films containing hydroxyl-substituted aromatic ketones as a new group of chemical modification reagents have been prepared and their properties such as photosensitivity and patterning properties investigated. ZrO₂ gel films were prepared from zirconium butoxide chemically modified with hydroxyl-substituted aromatic ketones by the sol-gel method. The gel films obtained showed absorption bands, characteristic of the π - π^* transition of chelate rings, at around 400nm. The bands were shifted to longer wavelength regions than those for the gel films using β -diketones. The reason is thought that the hydroxyl-substituted aromatic ketones have π -electron systems to form condensed chelate rings. The absorptions bands associated with the chelate rings gradually decreased in intensity with UV-irradiation using a high pressure mercury lamp. This indicates that the chelate rings dissociate by the UV-irradiation and that the gel films exhibit photosensitivities. Utilizing the photosensitivities, fine patterns (about 1 μ m) could be fabricated by UV-irradiation through a mask and leaching.

715 - Development of the photochromic coating on polycarbonate

Duck Kun Hwang, Yong Gun Shul, Hyun Jong Kim, Korea

Photochromic materials are a well-known class of compounds which change their color upon irradiation with light. This interesting effect can be used for optical waveguides, light modulators, delay generators and optical storage media. Properties of photochromic compounds introduced in polymer matrix are of great interest because of the possibilities of their practical use. The photochromism of the transition metal oxides has received considerable attention due to the high potential of large area optical switching devices switching between a transparent and a strong absorptive state. In this study, heteropolyoxometallates as transition metal oxides are coated with hybrid organic-inorganic binder on the polycarbonate (PC) substrate. The hybrid binder is formed as a result of the controlled hydrolysis and condensation of the 3-glycidoxypipropyl-trimethoxysilane (GPTMS) and tetraethylorthosilicate (TEOS) by the sol-gel technique. Photochromic inorganic-organic hybrid films were obtained by dip-coating of sol on PC substrates and it was formed the colorless and transparent film for optical measurement. In the Fig. 1, photochromic coatings on PC substrate show the reversible transmittance change before and after UV irradiation. It should be efficient light protector under UV irradiation.

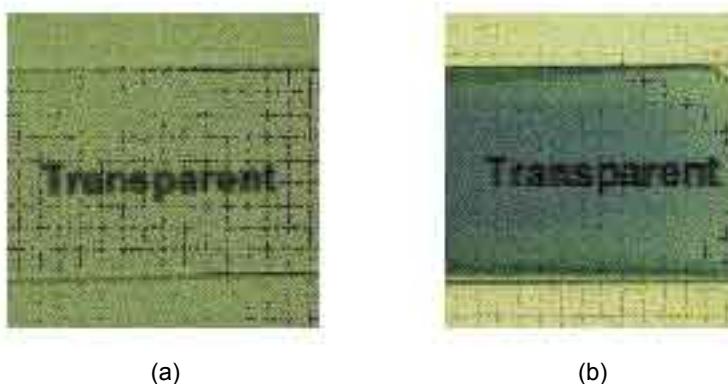


Fig. 1: Surface appearance of the photochromic coating on PC:
(a) before and (b) after UV irradiation

716 - Sol-Gel derived anticorrosion coatings for metals and alloy surfaces

Bakul C Dave, Mukti S Rao, Xiankui Hu, Yogeeshwari Devaraj, Shirshak K Dhali, Southern Illinois University, Carbondale, United States

There is a current need for alternative coatings that provide corrosion resistance to metals or alloy surfaces due to the environmental hazards posed by conventional coatings. This presentation will focus on novel organically-modified sol-gel anticorrosion coatings for metal and alloy surfaces. The basic concept of chemical conversion of alloy surface is based on activation of surface by pretreatment with plasma followed by deposition of a hydrophobic, nonporous sol-gel barrier layer for surface protection and corrosion prevention. The properties of these silica based coatings can be tuned by varying the composition of precursors. The evaluation of hydrophobicity, adhesive strength, and anticorrosion properties of organically-modified sol-gel derived coatings will be discussed. The prospects of sol-gel derived coatings as potential alternatives for chromate coatings will be elaborated.

717 - Preparation of Composite Anatase TiO₂ Nanostructure by Precipitation from Hydrolyzed TiCl₄ Solution within Anodic Alumina Membrane

Kang-Jin Kim, Il-Su Park, Jong-Hyun Kim, Korea University, Korea

Ramamurthy Vittal, Central Electrochemical Research Institute, India

Hydrolysis of TiCl₄ is the process commonly used for obtaining rutile TiO₂ film for dye sensitized solar cells. In the past decade, there has been considerable interest in using anodized alumina membrane (AAM) to prepare nanofibrils and TiO₂ nanowire arrays by sol-gel chemistry(1,2). Here we report the use of AAM to produce for the first time a unique TiO₂ nanostructure, composed of tubules and rods, and propose its formation mechanism.

The TiO₂ nanostructure was grown on the AAM inner surface by precipitation from hydrolyzed TiCl₄. Clear solution of 0.2 M TiCl₄ was loaded on top of AAM. The soaked membrane was heated for 2 h at 50°C, followed by dissolving the membrane with 3 M NaOH. The resulting material was annealed for 2 h.

A SEM image of TiO₂ nanostructures below shows that the material consists of rods encompassed by cylindrical tubules. Typically the tubules consist of 50-80 nm particles in diameter, whereas the rods are made up of about 20 nm particles. Tubule diameters exceed the AAM pore size. Raman data show the nanostructure crystallizes as anatase. The diameters of the tubules and rods are essentially independent of annealing temperature.



AAM surface provides initial nucleation sites, which is analogous to the formation of a rutile TiO₂ on SnO₂ from hydrolyzed TiCl₄ (3). The enlargement of the tubule diameter is explained by assuming that TiO₂ particles continue attaching themselves onto the inner wall during its dissolution in acidic TiCl₄ through bond formation. However, rods grow in the AAM channel. As TiCl₄ solution becomes saturated with time at 50°C, nucleation of TiO₂ begins in the solution, leading to formation of particles in the AAM pore center.

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718 - Low Dielectric Hybrid Inorganic-Organic Mesoporous Silicate Thin Films

Ji-In Jung, Jae Young Bae, Byeong-Soo Bae, Korea Advanced Institute of Science and Technology, Korea

The mesoporous silicate thin films are promising materials in such applications as sensor arrays, nanoreactors, electronic and photonic function devices, low-dielectric constant films, and hosts for large organic species. Organic functional groups can be incorporated in the inorganic network by grafting methods or by co-condensation, yielding specific pore surface properties such as hydrophobicity, optical and electronic activity. The co-condensation method allows a higher organic content and a more homogeneous organic distribution. We fabricated the hexagonal and cubic mesoporous silicate thin films with changing the ratio of amphiphilic alkylhalide surfactant ($(C_nH_{2n+1}N(CH_3)_3)X$, n=6-16, X=Cl or Br) and tetraalkoxysilane. Using different alkylhalide surfactant with different alkyl chain length and TMB (1,3,5-trimethylbenzene, $C_6H_3(CH_3)_3$) as an auxiliary organic additive, we fabricated mesoporous silicate thin films with different pore size and mesostructure. We also fabricated PFAS (perfluoroalkylsilane, $CF_3(CF_2)_x-(CH_2)_2-Si(OCH_3)_3$) hybrid inorganic-organic mesoporous silicate films with different perfluoroalkyl chain length (x=0-7). We have studied characteristics of mesoporous structure with XRD, TEM, isothermal N_2 -sorption measurements, FT-IR, TGA, SEM, and AFM. We characterized the dielectric constant of hybrid organic-inorganic mesoporous silicate thin films depending on mesoporous structure, pore size and perfluoroalkyl chain length.

720 - Novel Route to the Synthesis of a Large Pore Mesoporous Titania with Full Anatase Nanocrystalline Domain

Indriana Kartini, The Nanomaterials Centre, Australia

Paul Meredith, Joao C Diniz da Costa, G Q Max Lu, The University of Queensland, Australia

Titanium dioxide is one of the most commonly used wide-bandgap semiconductors and has potential for use in photovoltaic, photocatalysis and other photonic applications. A porous, high surface area TiO_2 with anatase or rutile crystalline domains is advantageous for high efficiency devices. Therefore, much attention has so far been paid to developing synthesis routes to obtain such properties. Molecular self-assembly pathways are of great interest to nanotechnologists. Nanostructures with mesoporosity can be tailored by varying the synthesis conditions and compositions. However, there are significant challenges related to obtaining mesoporous titania with full anatase crystalline domains. To date, several researchers have obtained mesoporous titania with a wide range of mesophases. In general, the crystalline domains of anatase in the pore walls were obtained by heat treatment. The heat treatment is a significant issue with respect to device fabrication. Additionally, excessive heating causes mesopore collapse, leading to the formation of dense materials which will decrease device efficiency as well. Here we report a new route to the synthesis of mesoporous titania with full anatase crystalline domains. This route involves anatase nanocrystalline seeds as the titania precursor and a block copolymer surfactant, Pluronic P123 as the template for the hydrothermal self-assembly process. A large pore (7-12 nm) mesoporous titania with a high surface area of 106 – 130 m^2/g after calcination at 400°C for 4h in air is achieved. Higher surface areas are expected by applying solvent extraction to remove the block-copolymer template. Characteristics of the seed precursors as well as the resultant mesoporous titania powder were studied using XRD analysis, N_2 -adsorption/desorption analysis, FTIR and TEM. We expect these materials will be especially useful for photoelectrochemical solar cell and photocatalytic applications.

722 - Sol-Gel Preparation and Mechanical Properties of Machinable Cellulose/Silica and Polyvinylpyrrolidone/Silica Composites

Kei Tanaka, Hiromitsu Kozuka, Kansai University, Japan

Acetyl cellulose (AC)/silica and polyvinylpyrrolidone (PVP)/silica composites were prepared by the sol-gel method in order to achieve organic/inorganic composites with strength and Young's modulus similar to those of cortical bones.

AC/silica composites were prepared from solutions of mole ratios, $\text{Si}(\text{OCH}_3)_4 : \text{AC} : \text{H}_2\text{O} : \text{HNO}_3 : \text{tetrahydrofuran} : \text{CH}_3\text{OC}_2\text{H}_4\text{OH} = 1 : x : 10 : 0.01 : y : 2.53$, where x was defined for the monomer, and $(x, y) = (0.5, 26.4), (1.0, 26.4)$ or $(2.0, 32.0)$, via gelation at 30°C and drying at 30 - 70°C. The dried gels were biphasic in SEM scale with submicron or micron silica-rich particles in AC-rich matrices. The dried gels were machinable, and specimens $44 \times 5 \times 2 \text{ mm}^3$ in size were served for the three-point bending test. The increase in AC/silica ratio allowed plastic deformation, and decreased the strength and Young's modulus. Higher drying temperatures resulted in increase in strength and modulus. AC/silica composites thus obtained had bending strengths of 48 - 100 MPa and Young's moduli of 2 - 4 GPa.

PVP/silica composites were prepared from solutions of mole ratios, $\text{Si}(\text{OCH}_3)_4 : \text{PVP} : \text{H}_2\text{O} : (\text{HNO}_3, \text{HCl}, \text{H}_2\text{SO}_4, \text{CH}_3\text{COOH} \text{ or } \text{NH}_3) : \text{CH}_3\text{OH} : \text{CH}_3\text{OC}_2\text{H}_4\text{OH} = 1 : 1 : 4 : z : 20 : 0.93$, where $x = 0.001$ for NH_3 and 0.01 for the acids, via gelation and drying at 40°C. The dried composites were homogeneous in SEM scale. CH_3COOH and NH_3 as the catalysts gave more porous gels with lower strengths and moduli, which increased when the gels were further dried at a higher temperature, 50°C. PVP/silica composites thus obtained had bending strengths of 17 - 80 MPa and Young's moduli of 1 - 4 GPa, exhibiting less plastic deformation than AC/silica composites.

723 - Mesostructured silica monoliths via supercritical and ambient pressure drying

Christina K Raab, Viktoria Torma, Nicola Hüsing, Vienna University of Technology, Austria

Lyotropic liquid crystalline phases of surfactants in water are widely used as structure directing agents for mesostructured materials. The conventional inorganic precursors for Si-based materials, TEOS or TMOS, are insoluble in surfactant/water phases without addition of co-solvents and furthermore form alcohol during sol-gel processing which is often detrimental for the supramolecular aggregates of surfactants. Tetrakis(2-hydroxyethyl)orthosilicate, a water-soluble diol-modified silane, shows a very good compatibility with lyotropic phases of surfactant molecules since the ethylene glycol released during hydrolysis affects the liquid crystal arrays only to a minor extent. Non-ionic polyethylene glycol containing amphiphilic molecules such as Brij56 and the block copolymer Pluronic P123 were employed as structure-directing templates in various concentrations with tetrakis(2-hydroxyethyl)orthosilicate for supercritically-dried and ambient pressure-dried mesoporous silica monoliths.

The surfactant-templated monolithic aerogels and aerogel-like materials were structurally (SAXS, TEM, SEM, N₂-sorption measurements) and chemically (elemental and thermal analysis) investigated. For certain concentrations of Brij56 and P123 the final structures show Bragg reflections in SAXS measurements indicative of a regular arrangement of mesopores which could also be confirmed by microscopic methods. Wormlike structures and a periodic hexagonal build-up of the network were observed even more distinct in the case of the monoliths dried at ambient pressure.

724 - Oxide interphase with porosity gradient for SiC/SiC ceramic matrix composites

Stephane Parola, Universite Claude Bernard Lyon 1, France

Martine Verdenelli, Fernand Chassagneux, Catherine Sigala, Jean-Marie Letoffe, Sylvain Jacques, Henri Vincent, Jean-Pierre Scharff, Laboratoire des Multimateriaux et Interfaces UMR CNRS 5, France

Ceramics are promising materials for high-temperature applications. However, their use is limited because of their low fracture toughness. Extensive work has been developed on ceramic matrix composites (CMC) reinforced with ceramic fibres in order to increase fracture toughness, and has focused on the fibre/matrix interface. In order to improve CMC mechanical behavior, it is necessary to elaborate an interphase between fibre and matrix. The interphase must allow fiber debonding and pull-out and must be compatible with the fiber and the matrix at high temperature. We have investigated the concept of porous interphase. The porous layer allows cracks deviation whereas the dense one avoid the gaseous infiltration during the SiC CVD matrix process and act as a diffusion barrier for oxygen. The concept of porous oxide interphase was explored for SiC/SiC composites. Elaboration of oxides on SiC Hi-Nicalon fibres was previously reported as well as investigations on the protective role of the coating towards oxidation reactions (1-3). The coatings did not degrade the fibre strength and allowed the preservation of mechanical properties after a thermal treatment in an oxidative environment. These coatings were therefore potential interphases for CMCs and porous/dense coatings (Al_2O_3 - SiO_2) were elaborated on Hi-Nicalon fibres by dip-coating. The SiC matrix was performed using CVD techniques. The porosity was created by the formation of micellar phases using surfactants and their subsequent thermal decomposition. The so-called microcomposites were characterized by SEM, TEM, XRD, EDS and tensile tests. Tensile tests have shown brittle behaviour (fracture) despite a high tensile strength and no fibre debonding was observed.

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725 - Development and Optimization of Protein Microarrays based on Pin-Printing of Sol-Gel Entrapped Biomolecules

Nicholas Rupcich, John D Brennan, McMaster University, Canada

Protein microarrays have been emerging as an important new tool for multianalyte detection and proteomics studies. To date, most protein microarrays have been formed either by covalently immobilizing proteins onto activated surfaces, or via affinity interactions (avidin-biotin, His6-Ni(NTA)) between proteins and appropriately derivatized surfaces. Recently, both our group and Bright's group have demonstrated that pin-printing of biological species entrapped within a sol-gel matrix can lead to the production of viable protein microarrays. The physical entrapment method overcomes many of the problems associated with other immobilization techniques, such as poor control over protein orientation and activity. In this presentation, we will discuss methods used to optimize sol-gel based protein microarrays, including the choice of sol-gel precursor and the use of chemical modification of the glass slide surface. We also discuss extensions of this technology, which demonstrate its ability to move beyond conventional immobilization methods. These include the co-entrapment of multiple components within a single array element and the ability to immobilize different types of biomolecules within a single array element. As an example, the microarraying of a coupled two enzyme reaction involving glucose oxidase and horseradish peroxidase along with the fluorogenic reagent Amplex Red allowed for "reagentless" fluorimetric detection of glucose. A second system involving the detection of urea using co-immobilized urease and fluorescein dextran, which derives a signal based on the use of a pH induced change in fluorescein emission intensity upon production of ammonium carbonate owing to hydrolysis of urea. The immobilization protein-protein interactions and other protein-based interactions onto microarrays will also be described.

726 - Entrapment of Functional Ligand-Gated-Ion Channel Receptors in Sol-Gel Derived Silica: Applications in Drug Screening

Travis R Besanger, John D Brennan, McMaster University, Canada

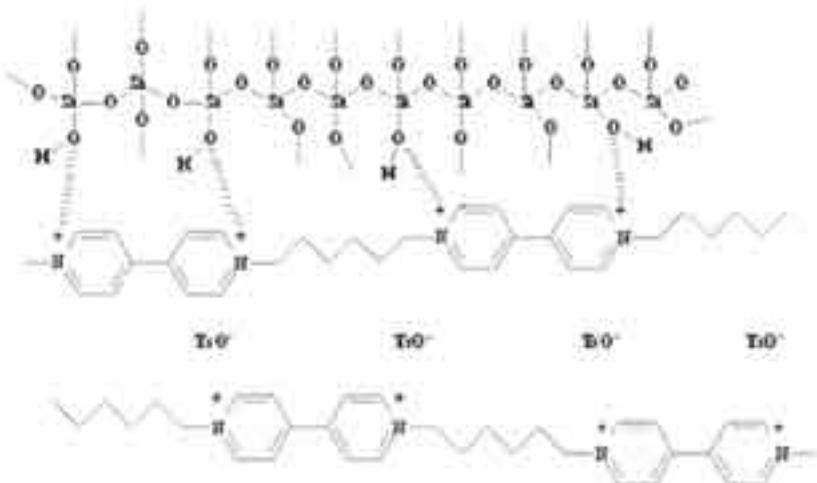
The entrapment of soluble proteins (enzymes, antibodies, regulatory proteins) within sol-gel derived silica has been extensively studied as a route for biomolecule immobilization. However, only a handful of reports have described the successful entrapment of membrane-bound proteins, such as bacteriorhodopsin, within sol-gel derived materials and to date, the immobilization of membrane bound receptors, such as ligand-gated ion channels, has not been reported. In this presentation, a highly biocompatible sol-gel based entrapment method has been developed and successfully utilized for the entrapment of ligand-gated ion channels such as the nicotinic acetylcholine receptor (nAChR). Early investigations indicated that the use of TEOS and TMOS as sol-gel precursors led to the production of a large amount of alcohol, which denatured the membrane receptors and solubilized the phospholipid membrane structure needed to support and maintain proper folding of the protein. However, the use of a novel diglycerylsilane (DGS) precursor made immobilization of liposomes and transmembrane ionophores possible. Steady-state and time-resolved fluorescence measurements reveal that phospholipid vesicles composed of phosphatidylcholine remain intact, and are able to undergo phase transitions, characteristic of normal bilayer structures, in DGS but not in TEOS derived silica. Furthermore, through the development of a unique fluorescence assay, it was possible to monitor transmembrane ion-flux across liposomes containing the transmembrane ionophore Gramicidin A. This presentation will focus on our recent efforts to monitor transmembrane ion fluxes from entrapped nAChR, and the results of our studies on the binding of agonists and antagonists to the immobilized receptor will be described. The implications of our findings with regard to the use of immobilized receptors for high-throughput drug screening will be discussed.

Graham M Gray, John N Hay, University of Surrey, United Kingdom

In recent years the use of small molecules or polymers as templates to synthesise silica with controlled porosity has been subject to much attention.

The possibility of polyviologens (bipyridinium polymers) acting as non bonding templates during the hydrolytic sol-gel process has been reported. A possible mechanism for this interaction involving electrostatic interactions was proposed (figure 1, below).

Investigations into possible templating effects under different conditions have revealed a strong correlation between the alkyl spacer length in the polymer and the pore size distribution when base catalysed.



728 - Sol-Gel Biomaterial with Chemically Functionalized Surface for in Vitro Immunoassays

Herman S Mansur, Rodrigo L Orefice, Wander L Vasconcelos, Zelia P Lobato, Federal University of Minas Gerais, Brazil

The research of silicate glasses obtained by sol-gel method has experienced important growth in the last 2 to 3 decades mainly in the biomedical field. They can provide a suitable host matrix for immobilization of biomolecules, such as enzymes, proteins and lipids, retaining their bioactivity. This fact is based on the low-temperature involved in the sol-gel process of hydrolysis and condensation, when compared to traditional extreme temperature processes of glass manufacturing. It is important to note that the term immobilization can refer either to a temporary or to a permanent localization of the biomolecule on or within a support. In the present work, silica gels were prepared by sol-gel polymerization of tetraethoxysilane (TEOS). The hydrolysis occurred when TEOS was mixed with deionized water in PBS solution, at $\text{pH} = 7.40 \pm 0.05$. The surface modifying reagents with different chemical groups, such as 3-aminopropyltriethoxysilane (APTES), 3-mercaptopropyltrimethoxysilane (MPTMS), 3-glycidoxypolytrimethoxysilane (GPTMS) and 3-isocyanatopropyltriethoxysilane (ICPES) were added to the solution during the reaction. FTIR spectroscopy was used to characterize the presence of specific chemical groups in the materials and also to detect the immobilization of protein in the porous gel network (bands of amide-I and amide-II). FTIR spectra have clearly shown the presence of the chemical groups incorporated to the gel network. The bioactivity of the produced solid-phase substrates was tested through Enzyme Linked ImmunoSorbent Assay (ELISA). The sols were cast into 96-well-plate polystyrene molds, where gelation occurred. The results have shown that glasses with chemically functionalized surfaces regulate the extent of bioimmobilization of proteins. The amine, thiol and hydroxyl terminated porous gels have tailored the interaction with the antibody-antigen, during the coupling process. We believe that it is due to hydrogen-bonds, Van der Waals and ionic forces, hydrophobic and hydrophilic interactions, sulfide bonds and steric hindrance acting at the silica gel functionalized surface. Therefore, such novel biomaterial system could be advantageously used in immunoassays of diagnostic kits.

730 - Preparation of hot water-resistant silica thin films from polysilazane solution at room temperature

Tomoko Kubo, Hiromitsu Kozuka, Kansai University, Japan

Polysilazane films of about 0.2 micron in thickness were prepared on single crystal silicon substrates by spin-coating using a xylene solution of polysilazane (5 mass%) as the coating solution. The polysilazane films were then suspended on aqueous solutions of various acids and bases at room temperature, and the changes in infrared absorption spectra and in durability in hot water were studied. The polysilazane films were found to be converted effectively to hot water-resistant silica films when exposed to basic vapors, for example, from aqueous solutions of ammonia and triethylamine.

The polysilazane films were suspended on ammonia water of various concentrations for various periods of time at room temperature. Higher ammonia concentration and longer exposure resulted in higher rates of polysilazane-to-silica conversion and higher durability of the resultant films in hot water. When the polysilazane films were suspended on 1 mol/L ammonia water for 6 h at room temperature, infrared absorption peaks attributed to Si-H and N-H vibrations almost completely disappeared and instead Si-O-Si peaks appeared. The resultant silica film showed reduction in thickness only by 2% when soaked in 80°C water for 24 h. Durability in hot water was also studied for $\text{Si}(\text{OC}_2\text{H}_5)_4$ -derived silica gel films by soaking in 80°C water for 24 h. Alkoxide-derived gel films that were kept standing at room temperature for 18 h and those suspended on 1 mol/L ammonia water for 18 h showed reduction in thickness in 80°C water by 65 and 98%, respectively. After being heated at 500°C for 10 min, on the other hand, the alkoxide-derived film showed reduction in thickness in 80°C water only by 4%. These indicate that silica films as durable in hot water as alkoxide-derived, fired silica films can be obtained just by exposing polysilazane films to basic vapors at room temperature.

731 - Preparation and Characterization of Mesoporous Titania Gel Films

Hiroshi Hirashima, Hiroaki Imai, Miah Muhammed Yusuf, Keio University, Japan
Vladimir Balek, Nuclear Research Institute, Czech Republic

Mesoporous TiO_2 (anatase) with large surface area is attractive due to its potential applications. The sol-gel method is one of the most appropriate technologies to prepare thin films. In this study, sol-gel derived TiO_2 films with mesopores were prepared by surfactant templating, and characterized by the emanation thermal analysis (ETA).

TiO_2 sols were obtained by hydrolysis of titaniumtetra-n-butoxide in ethanol solution. The gel films were prepared by spin coating on glass substrates. The wet gel films were dried at 90°C under an atmospheric pressure after immersion in a cetyltrimethylammonium chloride (CTAC) or benzyltrimethylammonium chloride (BTAC) solution for 1h (CTAC- or BTAC-modified films). The dried gel films were annealed at temperatures up to 500°C. The xerogel films were characterized by XRD, ellipsometry, SEM, AFM and ETA.

The annealed xerogel films, about 100nm in thickness, were transparent. The refractive indices of the films immersed in the CTAC or BTAC solution were more than 10% lower than those of the films without immersion, and they depended on the surfactant species. The low refractive index of surfactant-modified films may be attributed to their high porosity. The average pore size increased more than 2 times with surfactant immersion. The pore size and shape obviously depended on the size and shape of the surfactant micelles. The ETA results clearly showed the differences in the surface area and the thermal stability of the surfactant-modified films. The evaluated ETA results and structural changes in the films during heating were discussed. The surface morphology of films can be controlled with changing surfactant species.

732 - The effects of SiO₂ barrier and N₂ annealing on Sb-doped SnO₂ transparent conducting film prepared by Sol-Gel dip coating

Tae-Young Lim, Chang-Yeoul Kim, Bum-Suk Kim, Korea Institute of Ceramic Engineering and Technology, Korea
Keum-Ho Auh, Hanyang University, Korea

Transparent conducting film is very important in the area of displays such as liquid crystal display, plasma display panel, and electroluminescence display. It is also applied to solar cell, infrared-reflection window glass, antireflection coating, anti-frost coating and antenna. Indium-tin-oxide (ITO) film fabricated by sputtering method has been widely used for displays because it has a good electrical property, but it has drawbacks of its high cost and weak chemical durability. Tin oxide is a good transparent conducting film of which merits are a good chemical durability and a low-cost material.

In this study, the transparent conducting thin film of ATO (antimony-doped tin oxide) was successfully fabricated by sol-gel dip coating method. Tin chloride (SnCl₂) was dissolved into 99.9% pure ethanol of which concentration was 0.5M. 10mole% of SbCl₃ to SnCl₂ was added and stirred at 60°C for 1hr. Citric acid and ethylene glycol were added as chelating agents. The molar ratio of citric acid, ethylene glycol, and ethanol was 1:4:8. ATO thin film was fabricated by sol-gel dip coating method. The glass substrate was firstly cleaned by acetone, ethanol, and distilled water. It was dipped in ATO sol-contained bath and withdrawn with varying speed of 50-200mm/min. The coated film was dried at 150°C for 10min and heat-treated at 550°C for 2hrs.

The crystal phase of the ATO thin film was identified as SnO₂ by XRD (X-ray diffraction) analysis. The film thickness was observed as 100nm/layer by FE-SEM (field emission scanning electron microscopy). The optical transmittance and the electrical resistivity for 400nm thick ATO thin film on SiO₂-coated glass were 84% and 5.0×10⁻³ Ωcm when it was annealed in nitrogen atmosphere. XPS (X-ray photoelectron spectroscopy) analysis showed that SiO₂ layer inhibited Na ion diffusion and the formation of impurities like Na₂SnO₃ and increased the contents of Sb and the composition ratio of Sb⁵⁺ to Sb³⁺. N₂ annealing showed the result of reducing Sn⁴⁺ as well as Sb⁵⁺ so that the resistivity was decreased.

734 - Combinatorial study for transparent conducting films in the Zn-Sn-O tie line

Alexander Kurz, Michel A Aegeerter, Institut fuer Neue Materialien, Germany

Transparent conducting oxides play today a key role in many optoelectronic devices. These applications rely on the established n-type transparent conducting oxides (TCOs) such as $\text{SnO}_2:\text{F}$ or Sb , $\text{ZnO}:\text{Al}$, $\text{In}_2\text{O}_3:\text{Sn}$. New binary, ternary and even more complex TCOs materials are presently developed to get improved properties (resistivity, work function, transparency, etc.), and coatings based on these new materials have been produced by sputtering and pulse laser deposition (PLD).

The presentation focuses on a search for new sol-gel TCOs on the $\text{ZnO}-\text{SnO}_2$ tie line. More than 200 sols have been prepared with six different Sn precursors and two Zn precursors dissolved in eight organic solvents with Zn:Sn ratio 1:1, 2:1, and 3:1. Various additives have also been used to obtain optical quality transparent coatings on borosilicate and fused quartz substrates by the spin or dip coating techniques. Single or multilayer coatings have been sintered in air up to 1000°C. Most of the coatings showed a mixed phase structure made of crystalline SnO_2 and an X-ray amorphous Zn compound. Using Sn alkoxides and ZnCl_2 as precursors with a Zn:Sn ratio of 2:1 a crystalline mixed phase of Zn_2SnO_4 and SnO_2 was however obtained. The presence of a crystalline ZnSnO_3 phase expected for the coatings made with sols having a ratio Zn:Sn = 1:1 is difficult to ascertain because of the poor crystallinity. This phase has been however obtained during the calcination of ZnSn(OH)_6 powder between 400 and 700°C. Contrary to the results obtained by sputtering and PLD none of the sol-gel coatings is really conducting, even after a forming gas treatment (specific resistivity $\rho_{\min} > 10 \Omega\text{cm}$). Moreover a p mapping of the coating's surface shows large inhomogeneities probably due to the presence of regions with different structural phases. The adjustment of the precursor concentration (Zn/Sn ratio) is therefore important to obtain pure Zn_2SnO_4 and ZnSnO_3 crystalline phases. Also an adequate doping has to be found to increase the electron carrier concentration.

735 - Preparation and Characterization of Mesoporous Titania-Alumina Ceramics by Modified Sol-Gel Method

Silvester Tursiloadi, Research Center for Chemistry, Indonesia
Hiroaki Imai, Hiroshi Hirashima, Keio University, Japan

Titania-alumina ceramics with mesopores are interesting materials as catalysts and catalyst supports. In this study, mesoporous titania-alumina has been prepared by supercritical extraction and surfactant-modification.

Monolithic wet gels of $0.2\text{TiO}_2\text{-}0.8\text{Al}_2\text{O}_3$ were prepared by hydrolysis of aluminum-sec-butoxide and titanium-iso-propoxide in an n-propanol solution with acid catalyst. The wet gel was dried at 90°C for 24h (Xerogel), or immersed in an n-propanol solution of surfactant, benzyltrimethylammonium chloride (BTAC) or cetyltrimethylammonium chloride (CTAC), at room temperature for 24h, and then decanted and dried at 90°C for 24h (Surfactant-modified gel). The solvent in the wet gel was supercritically extracted in CO_2 at 333K and 24MPa for 2h (Supercritically extracted gel). Changes in the microstructure of the gels during heating were evaluated by TGA-DTA, N_2 adsorption, SEM and XRD.

After calcination at 500°C , the specific surface area of the gels was about $400\text{m}^2\text{ g}^{-1}$. The average pore radius for the supercritically extracted gel, about 8nm, was about 50% of the alumina aerogel, but about 4 times larger than that of the xerogel and the surfactant-modified gels. The aerogel-like mesoporous ceramics are obtained by the supercritical extraction with CO_2 . For the surfactant-modified gels and the supercritically extracted gel, the specific surface area was larger than $200\text{m}^2\text{ g}^{-1}$ after calcination at 800°C . The pore size and pore volume of these gels hardly decreased after calcination at 800°C , although diffraction peaks of rutile were found. On the contrary, the pore size, pore volume and surface area of the xerogel remarkably decreased after heating up to 800°C . The thermal stability of the microstructure of mesoporous titania-alumina is improved by the surfactant immersion or the supercritical extraction.

736 - Ordered mesostructured silica films: effect of pore surface properties on its sensing applications

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Mesostructured thin films have been fabricated via dip-coating using self-assembling processing in presence of block-copolymers acting as templating agents. The films have been thermally calcined at different temperatures to remove the templates. The mesophase has shown a high degree of thermal stability up to 950°C, before the collapse of the porous phase in silica films. Titania and germania films have shown to be stable up to 600°C.

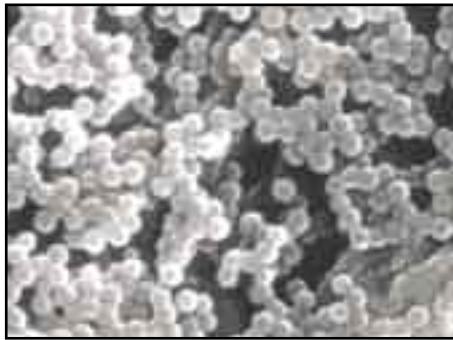
Energy Dispersion X-Ray Diffraction has been used to characterize the films in different conditions of synthesis and annealing. This method is particularly effective to analyse mesostructured films because of the set-up that is employed and the fast acquisition times [1]. An incident polychromatic X-ray radiation is used and the diffracted beam is energy resolved by a solid state detector located at a suitable scattering angle. The diffractometer operates in vertical $q/\text{geometry}$ and is equipped with an X-ray generator (W target), a collimating system, step motors and a solid-state detector connected via an electronic chain to a multichannel analyzer. Both the X-ray tube and the detector can rotate around their common centre where a cell is placed.

[1] R. Caminiti, V. Rossi Alberini, Int. Rev. Phys. Chem. 18(2), 263-299 (1999).00

738 - Sol-Gel Derived $\text{SiO}_2\text{-TiO}_2$ Nanocomposite Membranes

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A porous borosilicate substrate has been coated with a base-catalyzed SiO_2 sol-gel. Onto this was reacted titanium isopropoxide, where it reacted with surface OH to give a TiO_2 overcoat. This nanocomposite membrane is shown to have excellent permeability and activity in the isomerisation of butenes. The potential of these sol-gel membranes for selective hydrocarbon conversion is described.



739 - Fluoride Sol-Gels and Nano-Coatings

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MgF_2 is transparent from 115 nm through to the IR. It is also of low refractive index (n). n increases as the MgF_2 porosity decreases (e.g. is 1.25 when the porosity is 33% but is 1.31 when the porosity is 19%). MgF_2 is thus extensively used in optical coatings. Its protective and anti-reflective coatings have been conventionally produced by ion-beam sputtering or CVD.

The literature contains four sol-gel routes to MgF_2 . Here MgF_2 was prepared in a N_2 glove-box in which a solution of magnesium methoxide $\text{Mg}(\text{OMe})_2$ in methanol (9.5%, Aldrich) was added dropwise to a stirred HF (48.8% Aldrich) solution in methanol. Water from the aqueous HF was present in a $\text{Mg:H}_2\text{O}$ molar ratio of 1:2.1. MFALE and MFALM were prepared using ethanol and methanol solvents at an alkoxide:HF:ROH mole ratio of 1:2:200. All sols were stable for over a year.

MFALM and MFALE had average particle sizes (d_{TEM} (nm)) that were small (see Fig.1)(i.e. 5.0 and 7.0). Therefore not surprisingly the total surface area of MFALE deduced from its type IV N_2 isotherms at 77K with their N_2 hysteresis loop was high, but then decreased (as did its pore volume and porosity P) on heating (see Table) as F was lost (see Fig.2).

Hence, initially the MgF_2 sol-gel was of very high area (see Fig.3) and porosity. XPS after drying at 333K suggested Mg:F ratios in MFALM and MFALE that were higher than expected (i.e. 1:1.4 and 1:1.4 respectively). XRD confirmed (see Fig.4) MgF_2 at ambient temperature.

MFALE was coated onto fused SiO_2 (FS) to a thickness of 88nm and was then compared to CVD MgF_2 . Uv-visible profiles confirmed the thickness of the coatings and AFM their roughness (i.e. less than that of the substrate). 3w laser-induced damage thresholds (N/1) were better for MFALE ($>12.5\text{J/cm}^2$) than MFALM sol-gel fluoride coatings. This means that they have good potential for optical coatings in laser systems. However they do adsorb water (as revealed by FTIR) and this needs to be controlled. For the moment we report the highest area and highest porosity sol-gel MgF_2 whose potential is now reported in full.

Temp. (K)	S(m^2/g)	Pore Vol. (cm^3/g)
423	821	1.00
673	212	0.84
773	178	0.84



Fig. 1 TEM of MFALE

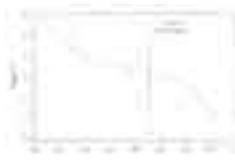


Fig. 2 DSC of MFALM versus T_p . The absence of an endotherm suggests MgF₂ formation at 700K.

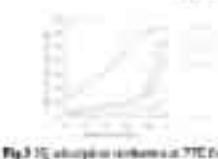


Fig. 3 XRD of MFALE after RTTE



Fig. 4 XRD of MFALM after RTTE

740 - Corrosion Protection of Single Crystal Fluoride Windows by Sol-Gel Dip-Coated Tin Oxide Thin Films

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Younes Messaddeq, UNESP, Araraquara, Brazil

Single crystal is used for optical windows, lenses and prisms particularly when optical transmission into the ultraviolet and infrared is desired. Unfortunately this single crystal has a poor chemical durability in aqueous environments due to hydrolytic surface attack. The chemical durability of such crystal can be improved by recovering the surface with transparent films that have good chemical resistance in acid and basic environments. In this work, we compare the corrosion resistance in water of uncoated and SnO_2 -coated single crystal samples during different times of exposure in water. The evolution of surface nanostructure during etching of coated and uncoated samples were characterized by Grazing-Incidence Small Angle X-ray Scattering (GISAXS) and X-Ray Reflectometry (XRR). The changes in the optical properties were accompanied by Infrared Spectroscopy (FTIR). The set of results shows that the transparent tin oxide films could be used for improve the chemical durability of single crystal fluoride windows.

741 - Investigations of MgF₂ Optical Thin Films Prepared from Autoclaved Sol

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An ultra-low refractive index is very advantageous when one designs antireflection coating. We have successfully obtained high quality MgF₂ thin films with ultra-low refractive indices by sol-gel method using sols which were prepared from magnesium acetate and hydrofluoric acid. The sols were autoclaved in a Teflon cell at 120-180°C for 24 h. After autoclaving, methyl acetate was detected by gas chromatography from the disperse medium. It was proven that autoclaving produces methyl acetate from acetic acid in the dispersed medium. The autoclaving also reduced the viscosity of the sol, enabling the condensation of the sol to be up to 10wt%. The sols were coated on SiO₂ glass or CaF₂ crystal substrates by spin coating. Subsequently the samples were baked at 100-200°C for 1 h. We measured the hardness and elasticity of the thin films by nano-indentation. The hardness of films increased below 150°C, and in the range of 150°C-200°C, the hardness became constant. The optical properties of the thin film, such as refractive index and transmittance, were investigated in an UV range, especially in a deep UV range of below 250 nm. The refractive index was affected by autoclaving temperature and baking temperature. The refractive index was 1.18 at 190 nm when the sol was autoclaved at 140°C. The ultra low refractive index resulted from the porous structure of the film, consisting of the nanosize grains (10-15 nm). The thickness of the film could be controlled by changing the concentration of sol, and good linearity existed between the concentration of sol and the film thickness. The SiO₂ glass substrate with thin films which consisted of single layers on both sides showed high transmittance over a very wide range of wavelength, the value was higher than 98.5% in the range of 250 nm-190 nm.

742 - Preparation of Calcium Phosphate Hybrids through Biomimetic Process

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Starch sponge was obtained by freeze-drying starch sol at -20 °C after the sol was prepared by mixing starch powder (3-10 g) with water (50 mL) at 95 °C. Then the starch sponges were soaked in SBF solution with various organic acids for 1-10days, and were dried at room temperature for a week. SEM micrographs showed that starch sponges had bicontinuous macropore network with 10-50 um in diameter. From the results of FE-SEM micrographs, characteristic X-ray image of Ca and P and XRD pattern for starch sponges soaked in SBF solution, their surface was covered with amorphous calcium phosphate. TG-DTA curves demonstrated that 2.5wt% of calcium phosphate was coated on the starch sponge. After starch sponge with calcium phosphate was calcined at 700 °C, all starch was burn out and amorphous calcium phosphate was crystallized to hexagonal hydroxyapatite

743 - Synthesis of blood compatible PDMS-based organic-inorganic hybrid coatings

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Silicone rubber involves polydimethylsiloxane (PDMS) is one of the synthetic polymers that have been used for in vivo and ex vivo medical devices. It is not biodegradable in the human body fluid. Moreover, it is only biotolerant, hence silicone has no potential to bond to human tissue directly as the surface is encapsulated by a fibrous tissue. In contrast, the titanium dioxide (TiO_2) layers formed on titanium and titanium alloys have been reported to form an inorganic layer such as calcium phosphate and subsequently adsorb proteoglycan on the inorganic layer under our body environment: thus, the fibrous tissue does not encapsulate the implants. Moreover, those TiO_2 layers have good blood compatibility. Therefore, one may expect that the organic-inorganic hybrid materials consisting of PDMS and a TiO_2 component are bioinert and blood compatible. On the other hand, stainless steel (SUS316L) has been used for clinical devices such as stent to open up choked blood vessels. However, it is still insufficient in blood compatibility and many efforts have been attempted to obtain blood compatibility.

We thus synthesized PDMS- TiO_2 hybrids and coated SUS316L with the hybrids using sol-gel process. Furthermore, we evaluated the blood compatibility of the hybrid-coated SUS316L substrates in terms of blood coagulation time (PT and PTT), the amount of fibrinogen and platelet adhesion property. We found that the PDMS- TiO_2 hybrid coating little affects the blood clotting system. The platelet adhesion was far suppressed on the PDMS- TiO_2 hybrid coating compared with the coating-free SUS316L substrates. We therefore concluded that the PDMS- TiO_2 hybrid coating has good blood compatibility, and is applicable to other substrates.

744 - Encapsulation of Viable Aerobic Microorganisms in Silica Gels

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There have been numerous reports of bioencapsulation of microorganisms in a variety of host matrices, including sol-gel derived materials. There has, however, been a notable absence of procedures to ensure that the data acquired was only from cells encapsulated within the gel, and not cells growing on the surface or in the surrounding broth. The aim of this study, was to develop techniques to sterilise the surface of gels and the liquid broth they were immersed in, so that the metabolic activities could be accurately assigned to fully encapsulated cells only. Gel surfaces were sterilized by daily UV-irradiation. The surfaces of the gels and the overlaying broth remained sterile for the duration of the experiments, as demonstrated by the lack of visible surface growth and viable cells in the broth. We report the encapsulation of a viable, metabolically active, aerobic fungus *Penicillium chrysogenum* and the aerobic Gram-positive bacterium *Streptomyces rimosus* in gels derived from aqueous silica colloid. Carbohydrate consumption (catabolism) and antibiotic biosynthesis (penicillin or oxytetracycline) (anabolism) were recorded in both, demonstrating that the encapsulated cells remained viable within the gel matrix. This demonstrates that the silica gels used are sufficiently porous to sustain metabolic activities of aerobic cells, which require the diffusion of oxygen as well as other substrates. The certainty that the metabolic activities recorded were only due to cells living in the gel ensures the significance of the data and further enhances the technique as a useful scientific tool.

745 - Anti-Reflective Coatings of Flowerlike Alumina on Various Glass Substrates Prepared by the Sol-Gel Process with Hot Water Treatment

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Anti-reflective coatings play an important role in a wide variety of optical technologies by reducing reflection losses at interfaces between two media. A reduction in surface reflection is typically accomplished by the application of a porous anti-reflective single-layer coating of quarter-wavelength in optical thickness. The sol-gel method is a well-known process to produce such porous films. On the other hand, it has been reported that surfaces possessing a gradual change of refractive index (n) to sufficient depth, such as a cornea of moth's eye, minimize reflection over a broad range of wavelengths and angles of the light incidence. A periodic microstructure, so-called "Moth-Eye" structure, brings about a gradual change of the refractive index between a substrate and air; refractive index of the coating (n_c) close to the interface matches that of the substrate (n_s), and the average refractive index at a certain depth decreases to lower values further away from the interface to the surface of the coating. We have already reported that Al_2O_3 thin films with a roughness of less than 100 nm are formed through immersion of the porous Al_2O_3 gel films in boiling water after a heat treatment at 400 °C [1]. We call this structure the "flowerlike structure." This structure becomes dense from the surface to the substrate and the refractive index should gradually change.

In the present study, we have succeeded in preparing anti-reflective coating films on various glass substrates through the sol-gel method by the formation of Al_2O_3 thin films with small roughness. On soda-lime-silica glass substrates ($n_s=1.52$), the reflectance was less than 0.5% in a wavelength region from 220 to 620 nm. On silica glass substrates ($n_s=1.46$), the reflectance was less than 0.5% in a much wider wavelength region from 220 to 780 nm.

[1] K.Tadanaga, N.Katata, and T.Minami, J. Am. Ceram. Soc., 80, 1040 (1997).

746 - Sliding Properties on Flat Organic Polymer Coatings

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Recently a variety of hydrophobic coatings have been reported, and now higher hydrophobicity and functions are required of the coating. Concerning the advanced hydrophobicity, sliding properties such as sliding angle and velocity should also be considered in addition to water contact angle. Several groups reported the sliding properties in terms of surface energy, droplet size and contact angle hysteresis, however, we have less information to prepare the hydrophobic surface with nice sliding properties. Therefore we systematically prepared a lot of organic copolymers, and studied the sliding properties of their coatings.

Mixtures of several ratios (0-100%) of methyl methacrylate (MMA) and fluoroalkyl methacrylate (FMA) were radically copolymerized. 2,2,2-trifluoroethyl methacrylate (FMA-F3), 2-(perfluorobutyl)ethyl methacrylate (FMA-F9), 2-(perfluorohexyl)ethyl methacrylate (FMA-F13), 2-(perfluoroctyl)ethyl methacrylate (FMA-F17), and 2-(perfluoro-7-methyloctyl)ethyl methacrylate (FMA-F19) were used as FMA. Copolymers were coated on glass substrates by spin coating method, and then the samples were heated at 120°C for 1h. With these samples, hydrophobic properties were evaluated. The contact angle and sliding angles were measured with 7 mg and 30 mg droplet, respectively. The sliding velocity was measured with 30 mg droplet on 35° inclined surface.

The obtained copolymer coatings showed highly flat and smooth surfaces by AFM and laser microscope. The water contact angles were systematically changed with changing ratio and length of FMA, which were simply depended on F atom concentration by XPS. The sliding angles showed complicated relation to hydrophobicity or F atom concentration, as shown in Figure 1. These sliding angles can be interpreted with contact angle hysteresis as Furmidge reported (J. Colloid Sci., 1962, 17, 309), and the hysteresis depends on fluoroalkyl chain length. It may be caused from the freedom and mobility of surface chemical structure. In contrast, the sliding velocity can be interpreted with surface energy (Figure 2). It is noteworthy that the sliding mode was changed from sliding with constant velocity to that with constant acceleration with decrease of surface energy.

747 - Sol-Gel Synthesis of Nanocomposite Hybrid Biomaterials

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Recently a significant attention has been paid to the sol-gel synthesis of composites due to the possibility of obtaining new hybrid materials with nanoscaled structure, which can be successfully applied in medicine, dentistry and biotechnology. These materials are excellent matrices for immobilization of organic compounds and various types of biochemical, such as enzymes, whole cells, antibodies and other proteins.

In the present article the research results on the sol-gel synthesis and structure of the nanocomposite biomaterials for whole cell immobilization are described and discussed.

Nanocomposite hybrid materials have been prepared by the sol-gel method at room temperature as matrices for immobilization of thermophilic bacterial cells. Two different type of silica precursors have been used - tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS). The hybrids have been prepared by replacing different quantity of the SiO₂ precursor with different type of organic components - polyethylene glycol (PEG), polyvinyl alcohol (PVA), combination of PEG and PVA, polyacrylic amid gel (PAAG) and combination of acrylic amid (AA) and PVA.

The structure of the matrices was studied by IR and Raman Spectroscopy, XRD, NMR, AFM, EDS, BET and SEM. The results proved that all the studied samples are amorphous and with pores with average diameter about 2 nm. From the SEM and AFM it has been established that the structure of the amorphous hybrids is built up of an inorganic - organic network consisting of self-organized nanobuilding blocks. We suggest a probable model of network formation for the studied nanocomposite hybrids.

Whole cells of thermophilic bacillus sp. UG 5 strain with benzonitrile degradation activity have been immobilized by entrapment within the sol-gel network or by adsorption on the surface. It was proved that the obtained materials can be successfully used as matrices for immobilization of thermophilic bacteria with nitrilase activity.

748 - Effect of different bidentate ligands on the micro-structure of zirconia sols for membrane application

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Zirconia and hafnia membranes have a great potential, due to their chemical and thermal stability. However, the sol-gel preparation of these membranes is rather complicated due to the high reactivity towards water of the alkoxide transition metal precursors. To moderate their sensitivity towards hydrolysis commercially available precursors can be stabilized by exchanging one or more alkoxide groups for a bidentate (bridging or chelating) ligand.

In the present study the effect of different complexing ligands, e.g., acidic acid, acetyl acetone, triethanolamine and diaminepentane, on the hydrolysis rate of zirconium propoxide and zirconium butoxide precursors is examined. The stabilization effect of the ligands on the hydrolyze rate is monitored via changes in temperature and viscosity during reaction. The oligomer size, measured using a zeta-size device, and refractive index are studied as functions of the aging time. Dried sols are characterized with XRD in order to assure that non-crystalline structures can be formed. All stabilization and sol formation experiments are performed in a helium glove-box to avoid hydrolysis.

749 - Sol-Gel SiO₂ - ZrO₂ Coatings for Optical Applications

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SiO₂ - ZrO₂ films have many applications being materials with interesting optical and photonics properties (waveguides, micromirrors, transducing layers for waveguide-based gas sensors). SiO₂ - ZrO₂ based nanostructured multilayers films have been prepared by sol-gel method from metallorganic precursors by low temperature polymerization reactions. Simultaneous gelation of both cations was realized. Homogeneous and transparent films were obtained at room temperature by dipping and spinning procedure on glass and silicon wafer substrates. Samples with successive deposited layers (1-3 layers) and successive thermal treatments have been also studied. Each deposited layer was thermal treated 1h at 300°C. The coatings were characterized by XRD, spectroellipsometry (SE), UV-VIS spectroscopy and AFM methods. The influence of substrates, number of coatings and number of thermal treatments on the optical and structural proprieties of the films was established. The thickness of three deposited SiO₂ - ZrO₂ layers is about 496 nm on glass substrate and 413 nm on the silicon wafer substrate. The films deposited on the glass are more porous than those deposited on the silicon. Optical waveguide on silicon substrate were prepared using these materials.

750 - Synthesis and characterization of microporous titania membranes

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Microporous ceramic membranes have a high application potential due to their chemical, mechanical and thermal stability. Ceramic membranes with a pore size smaller than 2 nm can be prepared by the polymeric sol-gel technique. Many research groups have studied microporous membranes made of amorphous silica with pore sizes of 0.3-0.5 nm. Although this type of membrane shows good properties in gas separation and pervaporation, its hydrothermal and chemical stability are limited. Amorphous titania is expected to exhibit better performance in that respect. However, it is well established that transition metal alkoxides are much more reactive towards nucleophilic reagents such as water than silicon alkoxides. This leads to difficulties in controlling the relative rates of hydrolysis and condensation and control of polymeric network formation.

In this study a procedure for the preparation of microporous titania membranes by a polymeric sol-gel technique is reported. Several titanium alkoxides were used as precursor, and nitric acid was employed as acid catalyst to promote the formation of a polymeric sol. The influence of the acid/titanium ratio, water/titanium ratio, method of mixing components and refluxing time on particle size and sol stability were investigated. The pore properties and phase evolution of the unsupported material was characterised by nitrogen adsorption at 77 K, positron beam analysis and high temperature X-ray diffraction. The thickness and quality of the layers was checked with HR-SEM, permporometry and gas and liquid permeation experiments.

Highly reproducible microporous titania layers with pore size ≤ 0.8 nm were obtained on mesoporous γ -alumina substrates. Moreover, a high chemical stability is achieved. The upper limit of thermal stability of the amorphous phase is $\sim 300^\circ\text{C}$. Higher calcination temperatures led to the crystallisation of the material into anatase, which is accompanied by a collapse of the microstructure.

751 - A new elaboration route by Sol-Gel process for cerium doped SrHfO₃ optical films and powders

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Classically, materials type ABO₃ exhibit different properties depending on the A metal alkaline and B transition metal used. The alkaline hafnates are dielectric compounds. In this work we present for the first time the elaboration of optical thin films and powders from strontium hafnate doped cerium. In our case the interest resides onto the potentiality like scintillation materials for X-ray or γ-ray optical detection. In this first attempt, a stable sol-gel solution has been obtained with success and we present the elaboration and characterization of films and powders. The sol is elaborated with hafnium ethoxide and strontium ethoxide like precursors and cerium nitrate like dopant. The synthesis was made in atmosphere controlled to avoid precipitation. The solution is deposited on carefully cleaned silica substrates followed by annealing up to 1000 °C to form crystalline films. Powders of this material were prepared by drying the sol before heat treatment to different temperatures. The films and powders were characterized by different methods: X-ray diffraction, transmission electron microscopy, Fourier transform infrared spectroscopy and Raman spectroscopy to obtain information of nanostructural composition of products. When the annealing temperature is lower than 650 °C the film is amorphous and has good waveguide performance. The optogeometric properties of film were obtained by m-line spectroscopy ($\lambda=543.5$ nm) giving a refractive index higher than 1.78 for a thickness about 460 nm. The optical losses are determined at 632.8 nm. The spectroscopic properties is measured and strongly depend on structure of material and the thermal treatment.

754 - Preparation and studies of Bi₂O₃

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Sol-gel processing Bi₂O₃ films and powders has received little interest, but a recent increased interest stems from the increased interest in oxygen ionic conductors for applications in fuel-cells where the δ-Bi₂O₃ has shown a high oxygen conductivity. Sol-gel processing is a very promising technique for practical manufacture of fuel-cell elements due to its low cost and low requirements of substrate geometry and properties. We have started an investigation of the preparation and stabilisation of different bismuth oxide phases using different bismuth-alkoxide and modified alkoxide precursors. In this work the formation of Bi₂O₃ oxide films and powders from Bi(OC₂H₄OC₂H₄OCH₃)₃ and Bi(OC₂H₄OCH₃)₃ is studied. The precursors were prepared by ligand exchange from Bi(OEt)₃, synthesized by metathesis of BiCl₃ and NaOEt and purified re-crystallisation of the crude powder. Films and powders were obtained from the toluene solutions and converted to oxide at 400-650°C. Different heat-treatments were made to study the formation of different Bi-oxide phases. The techniques used were: thermo-gravimetric analysis, differential scanning calorimetry, IR and Raman spectroscopy, SEM-EDS, TEM-EDS and X-ray diffraction.

756 - Mesoporous silica supported sulfated zirconia prepared by a Sol-Gel process

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A great interest has been renewed for zirconia materials owing to their acidic properties induced by sulfation. Sulfated zirconia solids are able to catalyse alkane isomerization reactions under mild conditions. However, the number of active sites of sulfated zirconia is limited by the available surface area, and it appears useful to design catalysts which would combine the acidic properties of sulfated zirconia with a high surface area and an enhanced thermal stability of a support such as silica. Moreover, the catalytic performances of a catalyst are highly related to its porosity. The classical methods of preparation may overcome the difficulties mentioned above, but could not allow the control of porosity.

Inorganic oxide aerogels exhibit high surface area and large porosity. Moreover, their rigid and porous framework prevents from sintering upon heating treatment. These properties make aerogel oxides very interesting both as supports and as catalysts.

The aim of this work is to study in a first step, the effect of preparation conditions on gelation time and on textural properties of the silica support. Thus, mesoporous silica supports were prepared with high surface areas($900\text{ m}^2/\text{g}$) and an excellent thermal stability.

In a second step, we investigated the effects of zirconium and sulfate addition on the gelation process and on the resulting properties of the silica supported sulfated zirconia samples.

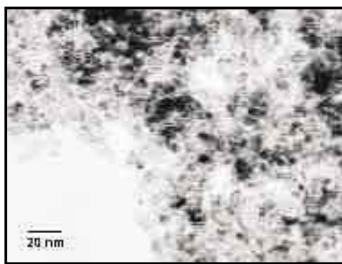
Preparation of the mesoporous silica supported sulfated zirconia was realised by using TEOS and $\text{Zr}(\text{acac})_4$ as precursors, sulfation was done *in situ* (with different SO_4/Zr ratios) and drying was performed under supercritical conditions of the solvent.

Catalyst characterizations were done by means of N_2 physisorption, DRX, DTG/MS, chemical analysis and ^{29}Si NMR MAS. This method leads to samples with a large pore size diameter (80 \AA), high surface area ($700\text{ m}^2/\text{g}$) and remarkable acidic properties. Textural and structural properties were correlated to the catalytic behaviour of the different solids. Catalytic performances of the different samples were studied in the reaction of n-Hexane isomerization .

757 - Preparation and studies of ZnO:Al films and powders

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Al-doped ZnO films are of interest as transparent electrodes on e.g. photo-voltaic cells and much attention has been devoted to the preparation of such films. Most studies have concerned physical techniques, but there have also been made a considerable amount of studies on solution-based techniques, due to their cost effectiveness and simple equipment, but it has proven rather difficult to produce homogeneous Al-doping the ZnO in this way. We have investigated a route to ZnO: Al (0.5, 1, 3%) films using acac modified Zn-alkoxides with methoxy-ethoxo and dimethoxy-ethoxo ligands. Films were obtained by spin-coating on quartz and window glass and powders by deposition of the solution on aluminium foil. Studies of the conversion from gel to oxide were made with thermo-gravimetric analysis, infrared spectroscopy, X-ray diffraction, scanning electron microscopy and transmission electron microscopy. It was found that heat-treatment to 400°C converted the amorphous gel to the ZnO. Studies with TEM-EDS showed that the films and powders consisted of 3-5 nm sized ZnO particles and that the Al was homogeneously distributed within the large areas with no Al clusters found even for the 3% sample. SEM-EDS studies showed that the highly transparent films were very smooth and up to 500 nm thick. Post heat-treatment with reducing atmosphere was used to improve the conductivity.



758 - Nitrified and Denitrified Microbiological Mud Encapsulated by the Sol-Gel Method

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The aquatic underground mantle in Yucatan represents the only one source of water supply to the domestic consumer. Nevertheless this mantle is extremely vulnerable to infiltration of pollutants as nitrates due to the karstic layer. Nitrates are inorganic pollutants, which mobility and stability make them highly dangerous in aerobic systems as underground water. This contaminant has been found up to 223mg/L in artesian wells, whereas the maxima limit permitted by the Wealth World Organization is 45 mg/L. Innovative biomaterials which come from the nitrified and denitrified microbiological mud encapsulated in inert matrix using the sol-gel technique are presented; it developed represents an available alternative to make the water drinkable in situ of the underground water of Merida in the state of Yucatan. Sol-gel method has been extensively used for the preparation of such kind of materials permitting a higher stability and viability of useful organisms.

In this work the thermal characterization of nitrified and denitrified mud coealed in tetraethoxilane is presented. The characterization was performed by a photopyroelectric technique, whose detector was made with a 110mm PVDF. The cell was constructed in such a way that the sample was inside the cell, and the bottom of the cell was closed by the PVDF foil.

Thermal effusivity as a function of temperature was obtained illuminating the PVDF directly by a modulated 1W Tungsten lamp. The sample is enclosed inside of a chamber, using a Peltier cell that controls temperature in a range from 15°C to 70°C. The sample is on top of the PVDF, which is illuminated by a modulated tungsten lamp. Optical properties of the system were also analyzed by infrared and in-situ Raman spectroscopy.

759 - Study of Drug Delivery in Composites forming Interpenetrating Networks by Thermosensitive Poly(N-Isopropylacrylamide) Gels and Ceramic Matrix

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Hydrogels are polymeric networks compatible with water and used in products of commercial value in order of billions of dollars, such as super-absorbents, materials for chemical separation or purification, biomedical dispositivo for controlled drug delivery, contact lens, etc. The objective of this work is to investigate the synthesis of composite materials based on thermosensitive poly(N-isopropylacrylamide) gels and silica matrix obtained by sol-gel method, resulting in a polymeric interpenetrating network to be used in dispositives for controlled drug release. The samples were obtained from two solutions: one containing N-isopropylacrylamide monomer, N,N'-methylenebisacrylamide cross-linker and the initiators, ammonium persulfate and sodium metabisulfite, and the other from tetraethoxysilane, ethanol, water and HCl and HF as catalyst, and phosphate disodium of betametasone as model drug. The effects of various parameters were investigated on the release rate of the drug, and were studied in vitro. In this work it has been observed that they affect positively or negatively in final result, but the hybrid materials were shown to be suitable for controlled delivery of drug substances.

760 - Mesostructured Silica Fibers Confinement of the Laser Dye. Host-Guest Interaction and Optical Properties

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Mesoporous and mesostructured materials derived by templating sol-gel chemistry are attractive candidates for optical applications such as lasers, optical sensors and host for quantum confined structures and are very efficient for dye doping. Dyes can be incorporated at high concentrations while still having isolated dye molecules in the final solids, a property that is useful in creating low-threshold laser materials and fast response photochromic composites with a large change in absorption. Here we report about peculiarities of preparation of the mesostructured silica fibers and composite materials - mesostructured silica fibers confinement of the laser dye such as Rhodamine 6G, Coumarine 120, Oxazine 1 and Phenalenone and optical properties this systems. The samples were characterized by XRD, IR-, Raman spectra, optical microscope, atomic absorption microscopy and TGA. The peculiarities of a forming in field pH below 0.1 mesoporous silica, template by cylindrical surfactant micelles are investigated. Is shown, that depending on acidity of reactionary medium the spontaneous growth of particles of silica on a phases boundary results in a formation of fibers, gyroids, spheres and other shapes, the overwhelming majority which one is represented by axially symmetrical bodies. It was show that fluorescence properties of composite materials and resource of resonant for composite laser materials is depending from energy of the exciting pulse and impulse frequency, nature of laser dyes embedded in fibers. Most likely, that strong "guest - guest" and "the host-guest" interaction figure a significant role in the described phenomena.

762 - Size distribution evolution of Er₂O₃ sols used to grow high-density thin films

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The present work reports on preparations of erbium oxide/hydroxide pristine and nanoparticulate sols. These sols are suitable to deposit thin films by the dip - coating method and result in a denser film.

The gel precursor was prepared by an alcoholic suspension of erbium oxi-hydroxide. Controlled amounts of 2,4-pentanedione (AcAc) were added to the erbium oxi-hydroxide suspension and lead to the formation of an erbium complex. The results showed that the particle size distribution shifts towards low values with the increase in the AcAc concentration. The complex, obtained by excess of the AcAc ligand added, [Er(AcAc)₂], was identified by FTIR spectroscopy and X-ray diffraction. The erbium complex decomposes at low temperature giving the denser erbium oxi-hydroxide film.

The dependence of the particle size with AcAc titration was followed by Small Angle X- Ray Scattering technique. Nanoparticles with controlled size can support dopants or additives on their surface, such that their optical properties can be tailored in the visible region.

Taking these data into account we were able to propose the better conditions to produce erbium oxide thin films, by sol-gel and dip coating methods. For example, erbium oxide films intercalated with titanium oxide films present the property of X-rays guidance. The study of these films is of great interest due to their use in different applications of optical X-rays devices.

763 - Characterization and transport properties of surfactant templated silica layers for membrane applications

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Ceramic membranes commonly consist of a stack of different layers. In general, the selective (mass transport) properties of such a stack are determined by the layers with the smallest pores. For meso- and microporous layers prepared via a sol-gel route, control and architecture of desired pore morphology on a nano-scale can be achieved via the use of surfactants. The resulting membrane layers can show remarkable performance. For example, very thin surfactant templated silica (STS) layer applied as selective layer with pores in the range of 1 nm shows high salt retention, combined with a very high water flux. For gas separation applications, the STS layer applied as an intermediate layer does not itself offer significant resistance to gas transport, but it provides a smooth defect free surface for an amorphous gas selective silica layer and helps to avoid infiltration of the amorphous material into the membrane support. Consequently, the presence of the extra STS layer results in improved gas separation performance of microporous silica membranes.

This study aims at the synthesis and characterization of surfactant templated layers with gradually decreasing pore sizes (ranging from large mesopores to micropores) onto porous supporting structures. Membrane applications require adequate connectivity of the pores in the direction of transport and thus certain structures, such as the cubic MCM48 with 3D interconnected pore network, are preferred. Techniques used for characterization of the well-defined thin STS layers include optical methods (e.g., ellipsometry), transport (gas and liquid permeation), XRD, permporometry, and IR.

765 - Self-ordered nanoporous silica film fabricated by template Sol-Gel method for surface photovoltaic gas sensor

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The large surface area created by nanosize pores in self-order nanoporous materials enables improvement in the gas adsorption properties of surface photo voltage (SPV) devices. This paper reports possible application of the self-ordered hexagonal and cubic-like nanoporous silica films to SPV type NO_x gas sensor, the film being synthesized by the spin coating method and by use of nonionictype triblock copolymer surfactant as a template. The self-ordered nanoporous silica film is assembled as a gas adsorption insulator layer of the Metal-Insulator-Semiconductor (MIS) structure based on the SPV characterization system. The sensing properties of each SPV device were estimated under NO and NO₂ gas exposure conditions. These SPV samples exhibit clear bias shift by NO or NO₂ gas adsorption in self-order nanoporous films and also indicate the gas accessibility dependence on nano-structures.

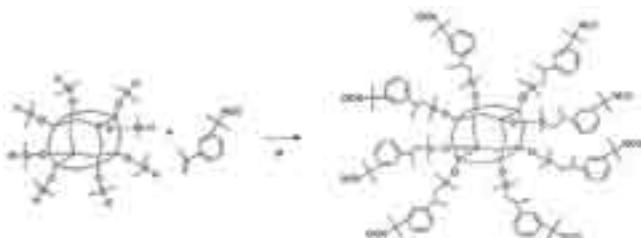
766 - Making Methacryl and Urethane Polymerizable Composite Coatings Using POSS Building Blocks

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The inorganic nature and multiple reactive functionalities of POSS (polyhedral oligomeric silsesquioxanes) make these compounds ideal for use in the construction of organic-inorganic hybrid nanomaterials. The focus of our research is in forming new crosslinked polymer structures by designing POSS molecules containing multiple reactive groups which can be further polymerized. The incorporation of these multiple reactive groups will allow each POSS cage to be dispersed with greater solubility and covalently linked to the organic network at a number of points.

We report here the synthesis of a new type of POSS macromer with eight reactive isocyanate groups suitable for the synthesis of hybrid organic-inorganic urethane nanomaterials (Scheme 1). This macromer has also been used to synthesize the first cross-linked polyurethane with discrete POSS molecules dispersed within the polymer matrix.

Whilst a number of groups(1) have recently shown that multi-reactive POSS cages and other inorganic clusters can indeed be synthesized and polymerized, to date, very little has appeared about their reactivity, structure and resultant physical properties. Future work will be to further functionalize the POSS-isocyanate macromer by incorporating photochromic groups and subsequent polymerization. It is therefore anticipated that this new concept will provide improved mechanical/thermal/physical properties of the POSS component as well as an additional functionality conferred by the incorporated photochromic group.



Scheme 1. Synthesis of octakis[m-isopropenyl- α - α' -dimethylbenzyl] isocyanatodimethyl-siloxyoctasilsesquioxane $Q_8M_8^{TM}$

(1) Zhang, C., Laine, R.M. *J Organomet. Chem.*, 29, 2327 (1996);); Zhang, C., Laine, R.M., *JACS*, 122, 6979 (2000); Sellinger, A., Laine, R.M., *J. Organomet. Chem.*, 521, 199 (1996); Provatas, A., Luft, M., Mu, J., White, A.H., Matisons, J.G., Skelton, B.W., *J. Organomet. Chem.*, 565, 159 (1998); Choi, J., Hracup, J., Yee, A.F., Zhu, Q., Laine, R.M., *JACS*, 123, 11420 (2001); Laine, R.M., Choi, J., Lee, I., *Adv. Mater.*, 13, 800 (2001)

767 - Hybrid Silica Materials: Structural and Transport Properties

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Hybrid organic-inorganic silica materials have been prepared from TEOS ($\text{Si}(\text{OC}_2\text{H}_5)_4$) and MTES ($\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$) by sol gel processes using HCl as a catalyst. A template molecule namely glycerol has been introduced in order to control pore character of the materials. The preparation is aimed at producing the unsupported silica membranes for separation applications. The interaction between the template and the silica networks has been examined by ^{29}Si CPMAS NMR through variable contact time experiments to derive the cross polarization transfer rate between silicon and adjacent protons (TSiH) as well as the proton mobility (T1p). The results show that protons from the template molecules are in close contact with the surface of the hybrid materials. ^{29}Si MAS NMR (Single Pulse Excitation) has been used to quantify the proportion of various silicon groups in the silica membranes. The results show that the hydrophobic character of the material can be controlled during the sol gel process and the incorporation of the hybrid groups is shown to be quantitative. In addition, physiorption measurements indicate that pore character can be adjusted by controlling the glycerol concentration. Pulse Field Gradient (PFG) NMR has been used to study transport phenomena within the materials as well as providing information on the structural of the pore space. Diffusion of water, studied by PFG, reveals that hydrophobic character strongly determines the transport properties of water in addition to the pore size of the hybrid silica membranes.

768 - Hybrid inorganic-organic Sol-Gel coatings in the SiO₂ - TiO₂ system

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It is well known that the sol-gel films in the SiO₂ - TiO₂ system are suitable for several optical applications due to the high refractive index of TiO₂ that allows to obtain coatings with desired refractive index depending on the TiO₂ amount in the composition.

As compared with the similar pure oxide compositions, in the case of the sol-gel hybrid inorganic-organic compositions, monolayer films with suitable thickness could be obtained.

In the present work the influence of the substituted Si-alkoxides and the method of deposition on the structural and optical properties of the films obtained in the SiO₂ - TiO₂ system was studied. Methyltriethoxysilane (MTEOS) and 3-(trimethoxysilyl)propyl methacrylate (TSPM) were used as SiO₂ sources and Ti(OBu)₄ was used as TiO₂ source. Acetylacetone was added as chelating agent and the synthesis was carried out in acid medium. The films were deposited on glass and oxidized Si-wafers by dipping and spinning. The films were characterized by XRD, spectro-ellipsometry (SE), IR and UV-VIS spectroscopy and Atomic Force Microscopy (AFM).

The results obtained have shown that in the case of hybrid films desired thickness could be obtained by one layer deposition. The thickness of the films and the optical properties depend on the bulkiness of the organic substituent bound to Si and on the method of deposition. Among other optical applications such films were experienced as optical waveguides.

769 - Preparation and Characterization of Silica Aerogels Derived from Ambient Pressure

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Silica aerogels, due to their nanoporous structure, high porosity, large surface area and very low bulk density, possess excellent thermal, acoustic, optical, adsorbing and catalytic properties and thus are potentially important to be used as thermal or sound insulation materials, catalysts, adsorbents, and sensors. However, aerogels are usually obtained via supercritical drying, their high production costs due to the use of expensive autoclaves restrict industrial applications. In order to be successful in the market, it must be possible to make the aerogel material in large commercial volumes and at low cost. Therefore it is of great interest to decrease operation pressures and temperatures.

In this paper, silica aerogels were made by sol-gel techniques using industrial silicon derivatives, followed by silylation of the alcogels and drying in the atmosphere. Trimethylchlorosilane and dimethyldimethoxysilane were used as the silylation agents. Although cracks occurred, the aerogel granules obtained were low density (about 140kg/m^3) and translucent. The specific surface area, scanning electron microscopy, transmission electron microscopy and the pore size distribution of the silica aerogels were investigated. It shows that the diameter of the silica particles is about 6nm and the average pore size is about 14.5nm. The specific surface area is about $700\text{m}^2/\text{g}$. Fourier-transformation infrared spectroscopy and ^{29}Si magic angle spinning nuclear magnetic resonance techniques were used to detect the organic groups on the internal surface of the silica aerogels which showed the existence of the methyl groups. The thermal conductivity of the silica aerogels was determined by transient hot-wire technique in which a platinum hot wire was squeezed inside the samples. The thermal conductivity of the silica aerogels derived from E40 is about $0.014\text{wm}^{-1}\text{K}^{-1}$ at room temperature and 1 atm. It was a little larger than the thermal conductivity of bulk silica aerogels derived from supercritical drying. It was assumed that the air in the gaps between the granules contributed a lot to the total thermal conductivity.

770 - Carbon Aerogel Films Synthesized at Ambient Conditions

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Carbon aerogels derived from organic sol-gel process and supercritical drying are novel porous materials with interconnect structures and higher electrical conductivity, which are considered to be ideal electrode materials for supercapacitors and rechargeable batteries. The objective of the research was to synthesize carbon aerogel films at ambient conditions. Resorcinol formaldehyde (RF) and carbon aerogel films have been produced with extremely high RC ratio (molar ratio of resorcinol to catalyst) followed by subcritical drying. The structure of the porous films was investigated using electron scanning microscope. The specific surface area was measured by using nitrogen adsorption (BET) and electrical conductivity was measured with four-probe method. It was found that with extremely high RC ratio, the porous structure of RF and carbon aerogel films can be controlled from micro to macro porous at ambient conditions. With respect to the application as electrodes for full cells, carbon aerogel films with different porous structures on the two surfaces have been also obtained through optimizing the sol-gel process.

771 - Electrochromism in Au-NiO Films

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Electrochromic materials exhibit significant, reversible optical absorption at visible wavelengths when controlled electrochemically.

Among the electrochromic materials, nickel oxide is one of the best for applications in display devices, smart windows, batteries and gas sensors due to its high stability under cycling. Nickel oxide is an anodic coloring material that changes color from light gray to dark brown.

Different methods of deposition are used to deposit composite films. Among them, sputtering, sol-gel, dip coating and spin coating are the most utilized.

The aim of this work is to characterize electrochemically composite gold-nickel oxide films obtained by the sol-gel and dip coating methods. The Au-NiO films were grown in a multi-layered form.

The films were deposited on $\text{In}_2\text{O}_3:\text{Sn}$ conducting glass plates at $12 \text{ cm} \cdot \text{min}^{-1}$ and at 40°C . The films were annealed in air at 250°C for 5 minutes.

The simultaneous measurements of the I vs. V plot and spectral transmission of the films, cycled in a 0.1M KOH solution, were recorded with an optical fiber spectrometer.

The charge capacity of the NiO_x film deposited by the sol-gel method is much larger than that presented by the NiO_x film deposited by sputtering. This difference can be associated to the larger porosity and crystalline structure of the material deposited by the sol-gel method.

Fig. 1 shows the in situ spectral transmittance of the NiO_x films deposited by sputtering and sol-gel plus dip coating methods. The difference between the bleached and colored states is much larger for the NiO_x film grown by sol-gel. The addition of gold in the oxide matrices gives rise to different reflected/transmitted colors (blue and red). These colors depend on the Au particle's size and the matrix in which the particles were added, especially in the case of Au and NiO_x deposited by the sol-gel method. The particle sizes were estimated by SAXS measurements and confirmed by TEM experiments.

Therefore, the color of Au-NiO_x films can be tailored by the use of pre-determined growth conditions.

772 - Compositional profiles in silica-based Sol-Gel films doped with erbium and silver

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The photoluminescence (PL) efficiency of Er-doped silica-titania planar waveguides, prepared by sol-gel processing, may be enhanced through the incorporation of Ag⁰ metal particles. On the other hand, the presence of residual Si-OH groups limits the optical activity of the Er³⁺ ions. In this work, we have used Rutherford Backscattering Spectroscopy (RBS), combined with Elastic Recoil Detection Analysis (ERDA), in order to study the incorporation behaviour of Ag and H species during the heat treatments used to densify the films. The presence of OH species, as well as the structure of the films and their degree of densification, have also been investigated by FTIR spectroscopy. The RBS results indicate a homogeneous distribution of Er in the as-deposited films. On the contrary, Ag displays a bimodal in-depth profile centred at the film surface and at the film/substrate interface. Annealing at up to 700°C eventually leads to in-diffusion and concentration of all the Ag species at the latter interface. The hydrogen concentration reaches minimum values for annealing at 500 °C and 900 °C, with apparently larger values for temperatures in between. During the heat treatments, the Er profile remains stable. The high mobility of silver ions and the presence of residual concentration of H in the films could explain the differences in the PL behaviour of planar waveguides, concerning in particular a PL quenching effect, with and without Ag, or with different OH contents.

773 - Effect of H₂ Annealing on the Properties of In₂O₃-SnO₂ Thin Films

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Transparent and conductive In₂O₃-SnO₂ thin films, with a Sn content of 55-25 at.-%, are alternative materials for commonly used ITO (Sn 5-10 at.-%). Their advantage over ITO is their reduced cost due to lower In content. During this work In₂O₃-SnO₂ coatings were fabricated by spin-coating method using the coating solutions prepared from tin(IV) and indium(III) 2-isopropoxyethoxides. Electric conductivity of the air and H₂ annealed samples were analyzed. The maximum conductivity for air annealed samples was obtained with the smallest SnO₂ content, being 24 S/cm for single layered coating. For samples having Sn content from 30 to 40 at.-%, annealing at hydrogen containing atmosphere increased the conductivity of the films. On the other hand, with other Sn contents conductivity was decreased. The biggest relative conductivity increase for single-layered, H₂ annealed coating was 7600 % (1 S/cm → 76 S/cm). The effect of the H₂ annealing on the chemical composition and crystal structure of the fabricated films was investigated using XPS and XRD, respectively. There are clear differences in crystal structures and chemical compositions of the films, which are attributed to the observed irreversible changes on the electrical conductivities.

774 - Nanostructured Sol-Gel thin films containing Coordinative Compounds

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Multi-photon absorption is one option for blocking high intensity beams from reaching sensitive detectors. To date two-photon absorption has been investigated, as well as multiple sequential one-photon absorption events, usually called excited state absorption. For example, in semiconductors three-photon absorption has been studied in which the last absorption step has been assigned to free carrier absorption. Instantaneous three and four-photon absorption have proven to be difficult to observe since the three and four photon coefficients are usually very small. This is not the case for the nanostructured coordinative compounds embedded in sol-gel thin films as will be discussed here. The films were prepared from oxide and hybrid inorganic-organic silica matrices and metal complexes of the transition metals of the series "d"/"f" of the general formula [MnL₁L₂] where M is the metallic cation, n=1-2, L₁ a β -diketone, L₂ an azoderivative or a Schiff base generally bi or three dentate ligands. The metal-ligand bond is a donor - acceptor one and produces a push - pull effect toward the π -delocalized electrons of the complex like a small device. This phenomenon is enhanced in the whole thin film by the interaction of the complex with the sol-gel support. For the complexes that exhibit a strong line emission a laser effect was observed in the thin films.

776 - Selective Deposition of Biocompatible Sol-Gel Materials

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An aqueous sol-gel route has been developed for electrochemically controlled deposition onto micro and nanofabricated electrodes. TEOS and MeTEOS were hydrolyzed under acidic conditions, and alcohol products were removed by distillation. The resulting clear sol has a hydrolysis ratio between 40 and 45. Following hydrolysis, pH was raised to 5.0 with addition of potassium hydroxide. At room temperature, this sol is stable for approximately 30 minutes. Gelation can be electrochemically induced at cathodic surfaces by locally increasing pH. Films of significant thickness and durability have been formed within seconds of deposition at -1.0V. Selective deposition has been demonstrated on platinum microelectrodes. Furthermore, proteins and other biological species can be incorporated into this aqueous route due to mild pH, ionic, and temperature conditions. Proteins such as bovine serum albumin have been successfully entrapped in electrodeposited gel, while smaller molecules such as fluorescein have been observed to diffuse through the pores. This sol-gel electrodeposition process is ideal for device fabrication, particularly in the field of electrochemical biosensors.

779 - Incorporation of triphenylmethane dyes into Sol-Gel matrices deposited on textiles

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The incorporation of triphenylmethane dyes into sol-gel layers formed from silica was used for coating of textile materials. These incorporations were performed with four different triphenylmethane dyes differ in electrical net charge and structural abilities. The investigation concerns the both cationic dyes malachite green (MG) and crystal violet (CV), the anionic guinea green (GG) and pigment blue 61 (PB) without any electrical net charge. All coating procedures were performed using an acidic sol-gel process starting from a solution of tetraethoxysilane and the dye in a mixture of water and ethanol. Three different types of textile polyester, polyamide and cotton were used. The prepared samples and their leaching and bleaching abilities were investigated using UV/VIS-spectroscopy. The leaching and bleaching fastness of the dye containing sol-gel coated textiles were compared to the abilities of the same dyed materials without any sol-gel coating. Both fastness abilities were also investigated as function of dye concentration and as function of concentration of epoxysilane in the silica matrix. The fastness abilities of all investigated dyes could be significantly improved by incorporation into the silica layer but high leaching fastness is only reached in case of cationic dyes due to the direct electrostatic attraction to the negatively charged silica matrix. Also small amounts of epoxysilane added to the sol-gel process lead to a drastic enhancement of leaching and bleaching fastness.

780 - Characterisation of Sol-Gel process using sucrose as organic templates

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This work presents the results of the characterisation of the effect of sucrose as a template added to a sol derived from a tetraethoxysilane (TEOS) acid catalysed process. The sucrose templated sols were gelled and dried at 50°C and calcined at 400°C under atmospheric conditions. Spectroscopy and structural characterisation techniques such as TGA, FTIR, and N₂ adsorption were employed to analyse the samples. Thermogravimetric analysis (TGA) showed that the mass loss increased with the template concentration and the templates started burning off at 275°C. However, the sucrose template was not completely burnt off at 400°C as the FTIR results showed rugged spectra due to carbon functional groups, in particular as the template concentration increased. Silica functional groups were also observed at the IR spectra at 800 and 1080 cm⁻¹ (Si-O-Si) and 960cm⁻¹ (Si-OH).

The N₂ adsorption isotherms for samples with small silica sol to sucrose template solution (x:y) ratios 10:1 and 10:2 resulted in isotherms of type I, characteristic of microporous materials. As the concentration of template increased (i.e. sample 8:4), the isotherm slightly changed, indicating the formation of mesopore materials, as saturation occurred for P/P₀ > 0.2. Samples 6:6 and 4:8 showed hysteresis (capillary condensation), clearly indicating the formation of mesoporous structures. Structural parameters (surface area, pore volume and pore radius) increased with increasing the sucrose template solution ratio, particularly pore volume. These results strongly suggest that the sucrose re-arranged the silica structure leading to mesopore materials.

781 - Sol-Gel Derived Nano-Coated Coralline Hydroxyapatite

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Current bone graft materials are mainly produced from coralline hydroxyapatite (HAp). Due to the nature of conversion process, coralline HAp has retained Calcium carbonate residue and the structure possesses micro and nanopores within the inter pore trabeculae resulting in high dissolution rates. Under certain conditions these features reduce durability and strength respectively and hence influence longevity and are not utilised where high structural strength are required.

To overcome these limitations, a new double-conversion technique has been developed.

This patented technique involves two-stage application route where in the first stage complete conversion of coral to pure HAp is achieved. In the second stage a sol-gel derived HAp (100nm) coating is directly applied to cover the micro and nano-pores within the intra pore trabeculae material, whilst maintaining the useful large pores. In preliminary studies, biaxial strength was improved by 120% due to this unique double treatment.

This application is expected to results in high purity, enhanced durability and strength in the physiological environment through vastly reduced dissolution rates and elimination of intra-trabecular nano and micro-pores.

It is anticipated that this new material can be applied to load bearing bone graft applications where high strength requirements are pertinent.

782 - Zirconia Sol-Gel Coatings on Anodized Titanium for Orthopaedic Applications

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The morphology and the tribological properties of the zirconia sol-gel coatings on both anodized and un-anodized titanium surfaces were investigated. The anodization of titanium involves the formation of a thin, dense, compact, oxide layer, which improves wettability for further coating. This process involves the conversion of the rutile structure of the original titanium oxide into a mostly crystalline anatase structure.

The Titanium samples were anodized in sulphuric and phosphoric acid at varying concentrations. The samples were anodized at differing currents and differing time periods ranging from 10 mins to 90mins.

These samples then were coated with zirconia, utilizing spin coating method. These coatings were prepared by alkoxide sol-gel chemistry and coating methods, using techniques and protocols developed in an earlier work [1] and were examined with x-ray diffraction, scanning electron microscopy and atomic force microscopy.

The tribological properties were investigated using an Orthopod machine, with six pins (3/8 inch diameter) that can articulate in number of different combinations against opposing coated and control specimens. Polyethylene pins were used in a bovine serum environment to simulate an articulating joint at room temperature. The amount of the wear and wear products was measured by profilometry and SEM analysis.

[1] M. J. Paterson, P.J.K. Paterson and B. Ben-Nissan, "The Dependence of Structural and Mechanical Properties on Film Thickness in Sol-Gel Zirconia Films", *J. Mater.Res.*, 13, 2 , 388 (1998).

783 - Syntesis of Organic-Inorganic Hybrid Membranes via Sol-Gel Process

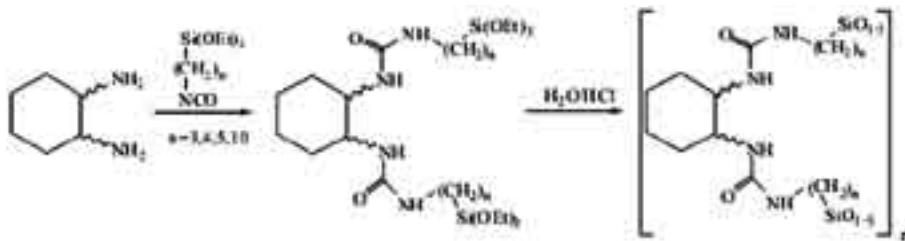
Alessandra D'Epifanio, Debora Marani, Maria L Di Vona, Silvia Licoccia, Università di Roma Tor Vergata, Italy

Direct methanol fuel cells (DMFC) are widely studied for their possible application in the automotive industry or in portable devices because of the simple fuel cell setup. The proton-conducting membrane is one of the key components of a fuel cell system. Because of their importance in the fuel cell field, polymeric electrolytes have received considerable attention over the last few years. Recently, it has been shown that membranes based on polyetheretherketone (PEEK) are very promising as their low cost, high thermal stability, good mechanical properties, and good conductivity when sulfonated. The conductivity of PEEK is directly related to the extent of sulfonation, in fact sulfonated cation-exchange membranes must have ion-exchange capacities with a minimum range of 1.4 to 1.7 meq/g to meet the requirements needed for DMFC. However the mechanical properties of PEEK tend to progressively deteriorate with sulfonation. Different strategies are available to improve PEEK properties. In this presentation we will report the synthesis of an organic-inorganic hybrid polymer. The sulfonated PEEK was covalently bound to $-\text{Si}(\text{OR})_3$ groups, then hydrolytic sol-gel process with 5% and 10% $\text{Si}(\text{OR})_4$ or $\text{Ti}(\text{OR})_4$ was performed to obtain a composite membrane.

784 - Influence of alkylene chain length on the morphology of chiral bridged silsesquioxanes

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The syntheses of four diureido derivatives of chiral *trans*-(1R,2R)-diaminocyclohexanes with different chain lengths between the urea groups and the silicon atoms have been achieved by the reaction of the isocyanato-alkyltriethoxysilanes with *trans*-(1R,2R)diaminocyclohexane. The acid-hydrolysis of these compounds have been examined. An odd-even effect is observed for short chain lengths ($n=3,4$) with the formation of chiral helices. With long carbon chain ($n=5, 10$) the lipophilic nature of the latter predominates over the chiral property of the diureido-cyclohexyl moiety. For $n=10$, a lamellar hybrid silica is obtained instead of the helical form. The crystalline nature of this layered material was confirmed by transmission electronic microscopy measurement (TEM) and by powder X-ray diffraction (PXRD) studies.



785 - Template-ordered mesoporous silica films thermally treated under inert, reducing or oxidising conditions

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The work aims at evaluation of the parameters that govern the synthesis of the template-ordered mesoporous silica films. We have examined how the conditions of thermal treatment of the as-synthesised silica films affect their final mesophase structure.

The transparent template-ordered silica films have been dip-coated on glass slides from a precursor solution prepared in accordance with the published procedure (C. J. Brinker et al., 1997) by adding CTAB template to a silica sol. The as-prepared films were subjected to thermal treatment either in a flow of Ar or H₂, or underwent calcination in air. The thermal treatment initiated the final cross-condensation of silicate oligomers and the removal of the template that resulted in the formation of the hexagonal mesoporous structure with the channels predominantly running parallel to the surface of glass support. The films thermally treated in a flow of H₂ and Ar reveal the unit cell parameters of 36.4 and 37.1 Å, respectively, which exceed the value of 35.2 Å found for the calcined samples.

It has been found out by the comparing the intensity and broadness of the diffraction peaks of the synthesised mesoporous silica films that the materials which passed calcination are less ordered as compared to those thermally treated in a flow of Ar or H₂. We have assumed that such difference is connected with the influence of the conditions of thermal treatment on the removal of the template molecules that accompanies condensation of silicate oligomers.

In order to confirm this, IR transmittance spectroscopy has been used to monitor the process of the template removal. The intensity of the CTAB characteristic absorption bands (C-H stretching vibration of the CH₂ group at 2935 and 2853 cm⁻¹) in the spectra of the as-synthesised films treated at different temperatures exhibits a degree of the removal of the template molecules. It has been observed that elimination of the template from the as-synthesised films upon calcination in air is complete by 250°C. A complete removal of the template upon the thermal treatment of the as-synthesised films in a flow of H₂ or Ar occurs around 300 and 350°C, respectively.

786 - Encapsulation of Ibuprofen in Mesoporous Silicas: Solid State NMR Characterization

Florence Babonneau, Nathalie Steunou, Lydie Camus, Chimie de la Matière Condensée, France

Ainhoa Ramila, Madrid, Spain

Maria Vallet-Regi, Departamento de Química Inorgánica y Bioinorgánica, Spain

Mesporous silicas have a capability for accepting and delivering organic compounds and thus to act as drug delivery system. It has already been shown that ibuprofen molecules can be encapsulated with loading as high as 30 wt% in MCM-41 silicas, functionalized or not by amino groups. Interactions between the guest molecules and the host matrix have been investigated by solid state NMR. The ^{13}C MAS-NMR single pulse or cross polarization spectra, as well as the ^1H MAS NMR spectra demonstrate an extremely high mobility of the ibuprofen molecules when the matrix is not functionalized, despite the presence of a carboxylic function on the ibuprofen molecules. It suggests that the molecules are certainly present as hydrophobic dimers in the pore channels. On the contrary when the silica surface is functionalized with amino groups, the ^{13}C NMR response shows a strong restriction in mobility suggesting the existence of interactions between the amino groups and the carboxylic groups. In order to demonstrate this hypothesis, benzoic acid, which exhibits a similar behavior when encapsulated, has been used as a model compound. The availability of benzoic acid with a ^{13}C -fully enriched carboxylic groups makes possible the use of ^{29}Si - ^{13}C double resonance techniques, whose preliminary results will also be discussed.



787 - Thermal Stability of Periodic Mesoporous SiCO Glasses

Raphaël Blum, Valérie Goletto, Bérangère Toury, Florence Babonneau, Chimie de la Matière Condensée, France

The use of bis(silylated) precursors, $(RO)_3Si-X-Si(OR)_3$, in conjunction with surfactants allows the preparation of periodic mesoporous organosilicas (PMOs). A large variety of PMOs has already been investigated. The presence of Si-O and Si-C bonds in the framework makes them very suitable as precursors for porous oxycarbide glasses. Previous studies on sol-gel derived SiCO glasses have demonstrated the unique high temperature properties of these materials in terms of mechanical strength and chemical durability. Additionally, if these materials can exhibit a periodic porous network, then they can find applications as filters, catalysts or membranes for severe operating conditions. The challenge will thus be to convert PMOs in SiCO glasses without a total collapse of the porous network during the pyrolysis treatment under inert atmosphere.

PMOs with 2D-hexagonal and cubic Pm3n structures have been prepared from bis(trialkoxysilyl)ethane and cetyltriethylammonium bromide. The two samples have been pyrolyzed under Argon up to 1000°C, and the pyrolysis intermediates analyzed by X-ray diffraction using synchrotron radiation, multinuclear solid state NMR (^{29}Si , ^{13}C and 1H) and N_2 adsorption-desorption experiments. While the 2D-hexagonal structure collapses after pyrolysis at 800°C, with a total cleavage of the Si-C bonds, the cubic Pm3n structure is retained after pyrolysis at 1000°C. The sample is a SiCO glass with mixed SiC_xO_{4-x} units ($x=0,1,2$) and a very large surface area of 730 m²/g. The mechanism for the organosilica-to-glass transformation will be discussed as well as the high temperature behavior of these glasses.

788 - A glycerol-derived silica precursor for the encapsulation of protein in porous silica monoliths

Yang Chen, Zheng Zhang, John D Brennan, Michael A Brook, McMaster University, Canada

Silanes derived from glycerol, particularly diglycerylsilane DGS, are useful precursors for protein-doped silica monoliths. DGS undergoes rapid and complete hydrolysis at room temperature in water, or in a suitable buffer solution that optionally contains enzymes or other proteins. The resulting silica monoliths exhibit lower degrees of shrinkage compared to silica prepared in a sol-gel process with conventional TEOS or TMOS starting materials. It was also found that the stability of the encapsulated enzymes such as Factor Xa, as measured by enzymatic activity, in DGS-derived monoliths were dramatically improved, even after long-term storage (8 months). This was most likely due to the sol-gel by-product glycerol, which remains in the silica to provide a biocompatible internal environment. The porosity of these gels is low. However, macroporous gels can be produced by introducing poly(ethylene oxide)(PEO), or poly(ethylene oxide) terminated with Si(OEt)₃ groups, respectively, into the sol. The encapsulated enzymes also exhibit excellent biological activity in these porous monoliths. These results make DGS an attractive candidate for applications in the areas of biosensors, column chromatography and capillary electrophoresis.

790 - Micropatterning of Sol-Gel Derived Thin Films Using Hydrophobic-Hydrophilic Patterned Surface

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Osaka Prefecture University, Japan
Atsunori Matsuda, Toyohashi University of Technology, Japan

Micropatterning techniques of sol-gel derived films have attracted much attention for the practical applications of these films to devices like integrated optical circuits and micro-electronic memories. One approach to generate finely patterned oxide thin films is irradiation of UV light on photosensitive precursor gel films. As another approach, micropatterning of oxide thin films using patterned self-assembled monolayers has also been reported. Very recently, we have proposed a new approach to form convexly shaped SiO_2 micropattern by using superhydrophobic-superhydrophilic patterned surface [1].

In the present study, the formation process of convexly shaped oxide micropattern using hydrophobic-hydrophilic micropatterned surface has been examined, and this technique was applied to several oxide thin films such as SnO_2 , ZrO_2 and Al_2O_3 . Firstly, hydrophobic-hydrophilic patterned surfaces were prepared on glass substrates by selective UV irradiation through a photomask on double-layered films of a very thin TiO_2 gel film as underlayer and a hydrolyzed fluoroalkyltrimethoxysilane layer as the top layer. Precursor solutions were then spin-coated on the hydrophobic-hydrophilic patterns, and the coated substrates were dried at room temperature. It was found that the micropatterns of oxides were very difficult to be formed on the hydrophobic-hydrophilic patterned surfaces from metal-alkoxides as a precursor solution, but convexly shaped micropatterns were formed on the hydrophilic region of the pattern when metal chlorides or oxychlorides were used as starting materials. This patterning technique must have a wide variety of applications such as fabrication of micro-optical components and finely patterned transparent electrodes.

[1] K. Tadanaga, J. Morinaga, T. Fujii, A. Matsuda and T. Minami, Glass Tech., 43C, 275-277 (2002).

792 - Marriage of Sol-Gel Processing with Imprinting Synthesis

Sheng Dai, Z.T Zhang, C.D Liang, M.C Burleigh, Oak Ridge National Laboratory, United States

Molecular imprinting involves arranging monomers of polymerization synthesis around a template molecule so that complexes are formed between the monomer and template molecules. Subsequent polymerization of the monomer molecules results in the trapping of template molecules in a highly cross-linked amorphous polymer matrix. Extraction of the imprint molecules leaves a predetermined arrangement of ligands and a tailored binding pocket. Thus far, the organization of precursor monomers has been achieved mainly in inhomogeneous organic polymer matrices, with little control over structural parameters such as pore sizes and surface areas. We have recently introduced a facile approach to the simultaneous production of hierarchical microstructures and mesostructures. The essence of our new methodology is the combination of two powerful imprinting techniques at different scales: (1) molecular imprinting and (2) micelle templating synthesis. The resulting porous hybrid materials exhibit favorable arrangement of not only the first coordination shell but also the tailored second coordination shell. The motivation for synthesizing hierarchical materials with microscopic and mesoscopic forms centers on the synergistic importance of stereochemistry, pore size, and surface area in determining such properties as flow and transport phenomena, capacity, and selectivity in separation efficiency. The simplicity of this technique should lead to a wide variety of new, highly selective sorbents, the properties of which can be optimized for many metal ions with the proviso that they form stable coordination complexes with a suitable bifunctional ligand containing a silane group.

793 - Effect of Sol-Gel Encapsulation on Lipase Structure and Function: A Small Angle Neutron Scattering Study.

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The successful development of sol-gel immobilised biocatalysts depends upon the characterisation of the relationship between gel structure, maintenance of the active state of catalysts, such as proteins and whole cells, and the optimisation of activity. The application of small angle neutron scattering (SANS) techniques to the characterisation of sol-gel hosts containing biocatalysts offers the opportunity to explore this relationship and is the focus of the investigations reported here.

Lipases, such as *Candida antarctica* lipase B (CALB) have been found to have dramatically increased activities when immobilised in sol-gel hosts and are applied to a variety of industrial processes, making them appropriate for structure/activity studies using SANS. Such scattering techniques permit analysis in solution at low concentrations which are relevant to both physiological interpretation and industrial application. SANS also facilitates analysis of enzymes in the immobilised state. Contrast variation studies enable the structures of the sol-gel bioencapsulates and the host material to be explored independently, giving information about the interaction between them. Characterising both the solution state and the immobilised form of a protein, as well as their respective activities, enables the effects of sol-gel encapsulation to be more fully assessed, as well as adding to information regarding the structure-function relationships of lipases.

We report here the determination of the activities of the encapsulated and free forms of CALB and its conformation in dilute solution. Gels were produced by fluoride-catalysed hydrolysis of fixed ratios of tetramethylorthosilicate (TMOS) and methyltrimethoxysilane (MTMS). Phase separation between the enzyme and the evolving sol-gel matrix was minimised by incorporating glycerol into the sol-gel precursor solution. Incorporation of glycerol appeared to enhance the stability and bioactivity of the encapsulated enzyme. The potential stabilising effect upon the enzyme of the sodium fluoride catalyst was also investigated. The deduction of structure/property correlations and a more rigorous understanding of the effects of sol-gel encapsulation upon biological entities are currently being developed. The application of neutron scattering techniques and activity studies to elucidating the effects of sol-gel bioencapsulation on bioactivity will be discussed.

794 - Mesoporous Ceria and Pd/Ceria Nanophases: Preparation, Structure and Catalytic Application

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Ascension Montoya, Juan Navarette, Salvador Castillo, Marina Moran-Pieda, Instituto Mexicano del Petróleo, Mexico

Mesostructured nanophase of ceria was prepared in a base condition by using surfactant (CTAB) as template. Textural properties, crystalline structure, reduction behaviour and surface morphology of ceria and Pd/ceria were studied by various techniques such as BET, TG, XRD, TPR, SEM-EDS, TEM and FTIR-CO chemisorption. Finally, NO reduction by CO was tested over ceria and Pd/ceria under both conditions of oxygen presence and absence.

Both XRD analysis and TEM observations, together with SEM-EDS confirm that nanosized ceria crystals has cubic structure with homogeneous chemical composition in the temperature between 400 and 800°C. CO chemisorption on Pd/ceria forms multiple bonds of CO-metal complex and CO₂ resulting from both CO oxidation and CO disproportionation catalysed by metallic palladium. Ceria and PdO/ceria have significant different reduction behaviours: two reduction peaks were observed in TPR profile of ceria that correspond to reduction of surface and bulk oxygen, respectively; however, the TPR of PdO/ceria shows a very sharp, negative peak at about 80 °C. It is postulated that the negative peak relates to hydrogen generation due to decomposition of a palladium hydride phase formed by molecular hydrogen dissociative adsorption/absorption on metallic Pd during the H₂-TPR procedure. In both conditions of oxygen presence and absence, ceria and Pd/ceria are active for CO oxidation and NO reduction with high selectivity to N₂.

795 - Proton-conducting glass films for fuel-cell electrolyte

Masayuki Nogami, Haibin Li, Nagoya Institute of Technology, Japan

Protonic-conducting materials have attracted much attention, because of their potential use in clean-energy fields such as fuel cell and chemical sensors. Here, we first report the preparation of sol-gel-derived glass films exhibiting high proton conductivity. The primary object of this strategy involves the control of the pore structure in the film using an interfacial silica-surfactant self-assembly technique. The conductivity of silica film with pore channels parallel to the substrate surface was low and independent of environment humidity. On the contrary, the film prepared using $C_{16}EO_{10}$ had cubic-type structural pores smaller than ~ 2.5 nm in diameter, the conductivity of which increases with increasing the water content in the pore. Furthermore, the motion of adsorbed water molecules was restricted in the small pores, so that the waters were retained under low humidity, resulting in high conductivity. We also confirmed that our high proton-conducting glass films are used for the electrolyte of the thin film fuel cell.

901 - Processing of Alumina Rich Cordierite Porous Ceramics

D T Senguttuvan, S H Kalsi, K S Sharada, National Physical Laboratory New Delhi, India

Porous ceramics are increasingly becoming important in particulate gas filtration. They are an effective alternative to the honeycombed structure in the case of diesel engine. Porous ceramics has been made by infiltrating ceramic slurry into a polymeric sponge followed by drying and heating to burn out the polymeric sponge and obtain a ceramic sponge with large open porosity. In this paper we report the addition of SiO_2 in the gel form increases the strength of high alumina cordierite (0.47, 0.23 & 0.30 mol fraction of SiO_2 , MgO and Al_2O_3) ceramics. The microwave drying reported to take around 5-10 min depending on the power and the amount of loading the shapes of the object is maintained in most of the structures. Sintering Temperature was optimized around 1380°C for conventional processing and that for composite sol gel process it was around 1200°C. The results were analyzed using XRD data and SEM micrographs.

**902 - Optical Properties of Europium(III) Doped Nanocrystalline Films of
 TiO_2**

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Wieslaw Strek, Institute for Low Temperature and Structure Research, Poland

Dariusz Hreniak, Polish Academy of Sciences, Poland

Synthesis of europium(III) doped nanocrystalline TiO_2 films without and with Ag nanoparticles are described. Preparation of thin films by deposition and spin-coating of sols on silicon, quartz and ITO-glass substrates has been presented. The films morphology and structure were determined by the TEM, SEM and XRD techniques. The emission spectra and luminescence decays have been measured. Results of the preliminary measurements of the cathodoluminescence and electroluminescence are presented also. Influence of the metallic silver particles on the optical properties of $\text{Eu}^{3+}:\text{TiO}_2$ has been investigated.

903 - Influence of Grains Size on Luminescence Properties of Tb-doped Nanostructured Materials Prepared by the Sol-Gel Method

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Wieslaw Strek, Institute for Low Temperature and Structure Research, Poland

Robert Pazik, Piotr Mazur, Czestochowa University of Technology, Poland

Marcin Nyk, Jan Misiewicz, Institute of Physics, Wroclaw University of Technology, Poland

Maria Zabkowska-Waclawek, University of Opole, Poland

Synthesis of nanosized powders of lanthanide silicates and yttrium-aluminium garnet doped with Tb^{3+} -ions via the sol-gel method has been presented. The luminescence spectra and decay profiles of luminescence have been measured. The influence of grains size on structure and luminescence properties of the obtained materials has been investigated. Stronger quenching of emission from the 5D_3 level as compared to the 5D_4 emission as grains size decrease has been observed. The influence of incorporating of nanocrystals into sol-gel silica glasses on their physicochemical properties has been shown and discussed.

904 - Sol-Gel Synthesis of Vanadia - Silica for Photocatalytic Degradation of Cyanide

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Cyanides used in some chemical synthesis and metallurgical processes are highly toxic and must be destroyed or removed from wastewaters prior to discharge. Vanadia – silica xerogel as photocatalyst has been prepared via sol-gel technique by dissolving ammonium metavanadate (AMV) and tetraethylorthosilicate (TEOS) and applied for photodegradation of cyanide from solution. The optimum conditions for preparation of V_2O_5 - SiO_2 gel is 1:1 of V: Si molar ratio and TEOS: H₂O: C₂H₅OH is 1: 8: 4 mole ratios at 30 °C for 10 minute, at these conditions the photoactivity of V_2O_5 - SiO_2 was 98.5% at surface area 310 m²/g . The calculated activation energy of the reaction between AMV and TEOS was found to be -10.81 k cal/g. The optimum loading of vanadia – silica xerogel was 0.166 wt % that give 98.5 % cyanide removal efficiency after 3 hrs. The overall kinetics of photodegradation of cyanide using vanadia – silica photocatalyst was found to be first order.

**905 - Multinuclear solid state NMR of the structural development of binary
MO₂-SiO₂-(M= Ti, Zr or Hf) gel materials**

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David M Pickup, R J Newport, University of Kent at Canterbury, United Kingdom

The addition of metal oxides into the silica network, can give materials with useful optical, electronic or catalytic properties. For example, (ZrO₂)_x(SiO₂)_{1-x} and (HfO₂)_x(SiO₂)_{1-x} materials are of interest due to their high dielectric constant and (TiO₂)_x(SiO₂)_{1-x} because of its catalytic properties. These properties depend on how the added metal enters the silica structure and its distribution, e.g. is it homogeneous or phase separated. A fully multinuclear approach has been adopted but the combination of ²⁹Si and ¹⁷O NMR is particularly useful to study the atomic structure of (MO₂)_x(SiO₂)_{1-x} (M= Ti, Zr, Hf) xerogels, with x up to 0.4 and heat treatments up to 750° C. Results from ¹⁷O NMR are very important for revealing whether or not the oxides are atomically mixed or if there is evidence of any phase separation. At x = 0.1, ¹⁷O NMR suggests that for Zr, Hf and Ti all the metal is in the silica phase which then allows the ²⁹Si data to be much more unambiguously interpreted. Results from the ²⁹Si NMR show interesting properties of how each metal has a different effect on the silica network. The differing effects of Zr and Hf on the Q speciation are rather surprising. A new NMR approach is to study titanium which has become possible through the advent of high magnetic fields. A novel development is to use samples enriched in ⁴⁹Ti making the spectra easier to interpret. The static ⁴⁹Ti spectra reveal clear changes in the titanium environment with processing.

906 - Preparation and electrical properties of $\text{Ln}_x(\text{SiO}_4)_6\text{O}_{(1.5x-12)}$ ($\text{Ln} : \text{Nd}, \text{La}$) with apatite structure

Keishi Nishio, Takashi Nakajima, Tadashi Ishigaki, Toshio Tsuchiya, Tokyo University of Science, Japan

In this study, $\text{Ln}_x(\text{SiO}_4)_6\text{O}_{(1.5x-12)}$ ($\text{Ln} : \text{Nd}, \text{La}$) for the electrolyte of the Solid Oxide Fuel Cell (SOFC) were prepared by the sol-gel process. It has been reported that the apatite structure of $\text{Ln}_x(\text{SiO}_4)_6\text{O}_{(1.5x-12)}$ shows higher ionic conductivity than yttrium-stabilized zirconium oxide at the working temperature of the SOFC. $\text{Ln}_{10}(\text{SiO}_4)_6\text{O}_3$ is a major component of the $\text{Ln}_x(\text{SiO}_4)_6\text{O}_{(1.5x-12)}$ system. $\text{Ln}_{10}(\text{SiO}_4)_6\text{O}_3$ consists of $\text{Ln}_{9.33}(\text{SiO}_4)_6\text{O}_2$ and a small amount of Ln_2SiO_5 . It is said that the ionic conductivity of $\text{Ln}_x(\text{SiO}_4)_6\text{O}_{(1.5x-12)}$ decreases with increases in the amount of Ln_2SiO_5 with nonapatite structure. The object of the present study was to bring about this decrease by generating Ln_2SiO_5 in the system.

The solution for preparing the powder was prepared using tetraethoxysilane ($\text{Si}(\text{OC}_2\text{H}_5)_4$) and neodymium acetate 6 hydrate ($(\text{CH}_3\text{COO})_3\text{Nd} \cdot 6\text{H}_2\text{O}$) or lanthanum acetate 6 hydrate ($(\text{CH}_3\text{COO})_3\text{La} \cdot 6\text{H}_2\text{O}$) as raw materials and acetic acid (CH_3COOH), 2-methoxyethanol ($\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OH}$), and tri-ethanolamine ($\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$) as solvents. To obtain the powder, the solution was heat-treated at 600°C for 2 h. The disks made from the powder were heat-treated at temperatures between 1100 and 1500°C for 10 h. The results of the XRD investigation indicate that almost all diffraction peaks of these samples could be assigned to the diffraction of $\text{Ln}_{9.33}(\text{SiO}_4)_6\text{O}_2$. The sample $x=10.00$ included a small amount of Ln_2SiO_5 . The ionic conductivity of the sample $x=10$ was higher than that of other samples ($x = 9.33$ and 10.67).

907 - Polymerizable Organosols for Dental Materials

Simone Klapdohr, Norbert Moszner, Volker Rheinberger, Ivoclar Vivadent AG, Liechtenstein

In dental filling materials a high strength as well as a low polymerization shrinkage can be achieved by a high degree of filling of the matrix system with inorganic fillers. Conventional fillers consist of macrofillers like grinded glasses and /or microfillers e.g. pyrogenic silica with average particle sizes between 0.04 and 1.0 µm. The use of non-agglomerated silica nanoparticles especially below 40 nm provides novel dental materials with several advantageous properties, particularly high transparency and high filler loading of the monomer resin while the viscosity remains relatively low. Besides for dental composites this is also very promising for dental adhesives or coatings. We prepared polymerizable organosols with non-agglomerated nanoparticles and investigated the influence of the particle size and different surface modification agents on the viscosity and the mechanical properties of the nanofilled monomer resins. Surface modification was performed by silanisation with different methacrylate-group containing silanes under acidic conditions. Visible light curable monomers showing different functionality, hydrophilicity and viscosity were evaluated for their loading capacity and compatibility with the functionalized silica nanoparticles. Their mechanical properties were discussed. We found, that the polarity of the polymerizable monomers as well as the viscosity play an important role in the filler loading capacity and the transparency of the composite. The consistency of the organosols can be varied to some extent by the choice of the silane used for the surface functionalization of the nanoparticles.

909 - Crystallisation kinetics of β-spodumene in lithium aluminosilicate Sol-Gel glasses

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Rui F Silva, CICECO, University, Portugal

The lithium aluminosilicate silicate (LAS) glass-ceramics are technologically very important due to their low thermal expansion coefficient and consequent high resistance to thermal shock. These properties are related with the formation of crystalline phases in the LAS system, namely β -spodumene ($\text{LiAlSi}_2\text{O}_6$; $\alpha = -6.3 \times 10^{-7} \text{C}^{-1}$ at RT-1100°C). The preparation of these materials by the conventional melting process leads to lithium oxide losses by volatilisation and to the formation of undesired crystalline phases during the cooling process. The sol-gel process is here an alternative route that avoids such features due to the low processing temperatures involved. It is very important to understand the crystallisation kinetics of these materials in order to assess the amount of the different crystalline phases formed for a given thermal cycle. The present study reports on two distinct approaches for such investigation: (i) non-isothermal and (ii) isothermal methods. Stoichiometric compositions of β -spodumene are prepared using tetraethylorthosilicate (TEOS), aluminium nitrate nonahydrated and lithium nitrate as raw materials. Ethanol absolute is used to dissolve the nitrates (molar ratio EtOH/TEOS=35). Water is added until a molar ratio $\text{H}_2\text{O}/\text{TEOS}=12$ and ammonia is used as catalyst (molar ratio $\text{NH}_3/\text{TEOS}=0.4$). The obtained sols are put on Petri dishes at 60°C until gelification and the obtained gels are dried for 48 hours at 120°C after ageing for two weeks at 60°C. All samples are kept 4 hours at 400°C to burn the residual organics. The non-isothermal method is based on differential thermal analysis (DTA) experiments under constant heating rates (10, 12, 15 and 20°Cmin⁻¹) up to 1000°C, while the isothermal method is based on the analysis of X-ray diffraction (XRD) spectra of crystallised samples submitted to heat treatments at the temperature range 600-1350°C. β -spodumene crystallization kinetics is investigated on the basis of the Johnson-Mehl-Avrami (JMA) theory with several distinct approaches leading to Avrami coefficients, n , in the range of 2.11-2.38 and activation energies, E_a , within 345-362 kJ.mol⁻¹.

910 - The effect of preparation method and calcination temperature on the particle size and surface area of perovskites-type SrFeOX

Abdul Majid, Jim Tunney, Mike Post, Steve Argue, National Research Council of Canada, Canada

We have investigated the synthesis of perovskite-type SrFeO_x using three preparative methods: sol-gel, mechanochemical processing and solid state reactions at high temperature of the corresponding oxides. The sample obtained after calcination of the gel from sol-gel method, contained the least amount of strontium carbonate impurity. The amount of strontium carbonate impurity decreased with the increase in calcination temperature. Perovskites obtained have been characterized by X-ray diffraction (XRD), nitrogen adsorption isotherms and scanning electron microscopy (SEM). Samples obtained from three methods have been compared with respect to calcination temperature, crystallite size and specific surface area. The averaged crystallite size of the obtained perovskites was evaluated by Pawley method from the XRD data using Topaz software. SEM revealed a high microstructural uniformity.

911 - Sol-Gel derived scintillating LuBO₃:Ce³⁺

Christelle Mansuy, Jean-Marie Nedelec, Rachid Mahiou, Université Blaise Pascal & ENSCCF, France
Christophe Dujardin, Université Claude Bernard Lyon 1, France

Research directed towards scintillating materials is in constant development. The use of these materials in medical imaging equipment (X-rays, γ -rays, positron emission,...) requires improvement of their properties in particular their conversion yield.

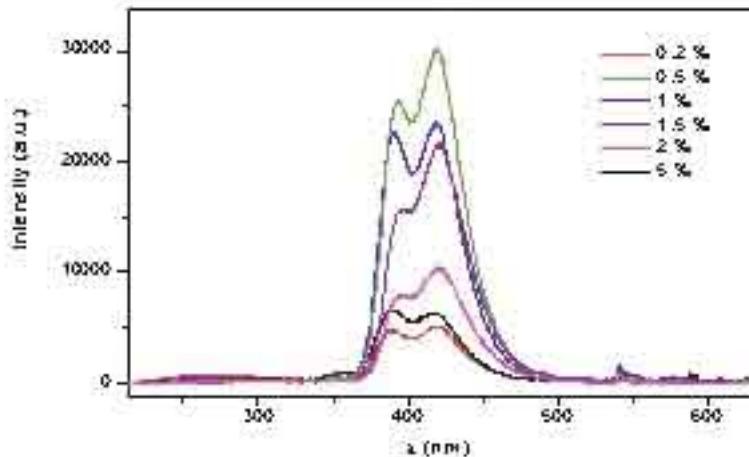
Among the various possible materials, rare earth activated lutetium orthoborate appear to be a good scintillator candidate¹. The objective of this work is to prepare LuBO₃:Ce³⁺ via a sol-gel route. In effect, this soft chemistry route allows the control of the morphology and the texture of the materials² and also to prepare directly the material as a thin film.

Powders and thin films of LuBO₃ containing various amount of Ce³⁺ doping ions have been prepared. Very pure materials are obtained and their morphology is presented. The scintillation properties have been studied and in particular the effect of the Ce³⁺ concentration on the conversion yields. Optimum is found around 0.5 % molar (cf figure).

The authors would like to thank the Réseau National des Technologies pour la Santé for funding under project LuminiX

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912 - From Research to Commercialisation: Monolithic HPLC-columns for fast separations

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Monolithic HPLC-columns with tailor-made bimodal pore structures have been prepared according to a sol-gel process based on the hydrolysis and polycondensation of tetraalkoxysilanes in the presence of water soluble polymers used as precursors. Occurrence of a phase separation during the polycondensation step leads to monolithic materials with co-continuous silica structures having defined macro- and mesopores. As a result the total porosity of monolithic HPLC columns is about 15% higher compared to conventional particulate ones. Consequently, they show a much higher permeability and respectively much lower column back pressure which allows the operation of those columns with higher flow rates. Therefore, monolithic HPLC columns (Chromolith-columns) can be used for fast separations which will be demonstrated with various applications.

914 - Preparation of powder, film and fibre of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_3$ using $\text{La}(\text{MOE})_3$, $\text{Sr}(\text{MOE})_2$ and $\text{Ni}(\text{acac})_2$ precursors

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Lanthanum nickel oxide based materials have received much interest as key materials in different applications, e.g. fuel cells, gas sensors and catalysts. In these applications, it is important that the materials can be built up on surfaces and made in different shapes and sizes and with great degree of structural and compositional control. In the homologous series $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$, a number of phases are observed in between the end points LaNiO_3 and La_2NiO_4 . By Sr substitution at the La site, it is possible to adjust the electric and catalytic properties of these materials. In the La_2NiO_4 phase it is possible to substitute up to 50% of the La atoms with Sr without reconstruction of the structure leading to the LaSrNiO_4 composition. The dominating synthesis routes to these materials are based on solid-state reactions at high temperature and in the case of thin films, vapour based techniques as CVD and PLD have been used. Solution routes based on metal salts as oxalate, nitrates and micro-emulsion technique have also been used in attempt to reduce the synthesis temperature and cost.

In this study we describe a route based on precursor solutions of lanthanum and strontium alkoxides and nickel acetylacetone, to powders, films and fibres of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ with $x = 0.00; 0.25; 0.50; 0.75$ and 1.00 . Lanthanum and strontium alkoxides were prepared by dissolving metal chips in methoxy-ethanol and the $\text{Ni}(\text{acac})_2$ was dried by heating under vacuum. The precursor solutions were mixed to 1M metal concentration and heated at 60°C , 8h prior to use.

The decomposition process investigated by TGA up to 1000°C contained several steps. The phase development was investigated on quenched materials from different temperatures, by studies with FT-IR and Raman spectroscopy, X-ray diffraction, SEM-EDS and TEM-EDS. Powders, films and fibres of compounds in the series $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ with $x = 0.00; 0.25; 0.50; 0.75$ and 1.00 were obtained at temperatures in the range $750^\circ\text{C} - 1000^\circ\text{C}$.

917 - Polarization Holographic Gratings in Hybrid Sol-Gel Films

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Polarization holographic gratings have been written in organic-inorganic films prepared by a sol-gel technique based on tetraethoxysilane (TEOS), diethoxydimethylsilane (DMDEOS), 3-(triethoxysilyl)-propyl-isocyanate (ICPTEOS) and containing Disperse Red 1 (DR1). The gratings have been produced through the photoinduced birefringence effect and characterized through their diffraction efficiency. Different configurations of polarization of the writing and reading beams have investigated and pure polarization gratings in sp polarization geometry with high diffraction efficiencies have been observed. These gratings act as half-wave plates for the diffracted beam and the diffraction efficiency is independent on the polarization of the probe. Different concentrations of the dye and of the precursors are investigated.

918 - Porous $\text{SiO}_2\text{-BaMgF}_4\text{:Eu(II)}$ Glass-Ceramic Thin Films and Their Strong Blue Photoluminescence

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Recent advances and challenges in ultraviolet (UV) light emitting diode (LED) based on wide-gap semiconductors have opened possibilities for new designs of optoelectronic devices such as full-color UV-LED display and solid-state white lighting. Red, green or blue thin film phosphors are highly attractive for these applications. Eu(II)-doped oxide or fluoride materials have been intensively investigated for applications to blue phosphors. The Eu(II) ion has a $4f^7$ electronic configuration and shows broad absorption band in the long-wavelength UV region due to an allowed $4f\text{-}5d$ transition. $\text{BaMgF}_4\text{:Eu(II)}$ is known to be a violet-blue emitting material and has been studied in the form of powders, single crystals or thin films [1]. While thin film phosphors are expected to be successfully integrated in the devices, their brightness and efficiency are generally inferior to powder phosphors.

Our strategy to improve performance of the thin film phosphors is based on fabrication of porous oxyfluoride glass-ceramics that can scatter excitation UV light well. In this study, porous $\text{SiO}_2\text{-BaMgF}_4\text{:Eu(II)}$ thin films have been prepared by a trifluoroacetate-based sol-gel method [2]. Silicon alkoxide solutions were mixed with trifluoroacetate solutions containing barium, magnesium and europium(III). N,N-dimethylformamide was also added. The solutions were spin-coated on silica glass substrates and were heated at temperatures 773 - 1073K. During the heat-treatment, Eu(III) was easily reduced to Eu(II) and was incorporated preferentially into BaMgF_4 crystals. The resultant glass-ceramic films exhibited high and low transmittance in the visible and UV region, respectively. The photoluminescence measurement evidenced the improved blue emission efficiency due to effective scattering of the excitation UV light in the films.

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[2] S. Fujihara, Recent. Res. Dev. Mater. Sci., 3 (2002) 619.

919 - Studies on the surface chemical modifications of TMOS based silica aerogels using various organosilane compounds

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Silica aerogels are transparent nanostructured porous materials consisting of more than 95% air and less than 5% silica in the form of a highly cross linked network. Although the aerogels have several technological applications such as Cerenkov radiation detectors, acoustic and thermal superinsulators, containers for micrometeorites and liquid rocket propellents, but the main problems are : (1) the aerogels are very brittle and (2) they adsorb moisture from the humid surroundings and hence get deteriorated with time. Therefore, in the present paper, the experimental results on the surface chemical modification of the tetramethoxysilane (TMOS) based silica aerogels using various organosilane compounds of the type R_nSiX(4-n), n=1 to 3, R= alkyl or aryl, X = chloro or alkoxy), are reported. The surface chemical modification during silica sol formation resulted in hydrophobic and flexible silica aerogels. Silica alcogels produced by mixing TMOS, organosilane compound, methanol (MeOH), water and ammoniumhydroxide (NH₄OH), in the molar ratio of 1:0.5:12:4:5.7x10⁻³ respectively, were supercritically dried to obtain the aerogels. In all, ten organosilane compounds having zero to three functional groups have been used. The optical transimission of the organically modified (O.M) silica aerogels decreases with increase in the O.S amount which is due to larger pore and cluster sizes. The contact angle has been found to be around 120 degrees for monoalkyl O.S. compounds (e.g., methyltrimethoxysilane) and for trialkyl O.S. compounds (e.g., hexamethyl disilazene) it is as high as 135 degrees. The alkylchlorosilane compounds resulted in cracked and shrunk (>10%) aerogels and the alkylalkoxysilane compounds gave monolithic and low shrinkage (< 5%) aerogels. The attachment of aryl (e.g.,phenyl) functional groups to the aerogels showed the highest thermal stability of 550°C compared from the alkyl functionalised aerogels (300°C). The aerogels have been characterized by differential thermal and thermogravimetric analyses (DTA and TGA), Fourier Transform Infrared Spectroscopy, FTIR) and optical transimission measurements.

920 - Functionalised Thiocalixarenes and Inclusion in Hybrid Materials for Optical Limiting

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Optical Power Limiting (OPL) materials were developed for the protection of optical sensors toward intense laser aggressions. Thiocalixarenes were investigated for optical limiting on the basis that they display delocalised electrons, they can be selectively functionalised either on the upper rims or the lower rims and are interesting species for the formation of metal complexes. Moreover, the presence of electron donating sulphur bridges can play an important role regarding non-linear optical properties. The chemistry of these macrocycles was thus previously reported and they showed very interesting optical properties.¹ The macrocycles were incorporated into an inorganic matrix using the sol-gel process. It is well known that the sol-gel route allows easy inclusion of organic dyes into an oxide network because of the low temperature of the process. Both Class I and Class II hybrids were considered. A second functionalisation (lower rims) with metal alkoxide groups was therefore investigated in order to prepare the class II hybrid materials incorporating the optically active molecule. The same macrocycle core was thus selectively functionalised on both sides, and used for its optical properties on one side and as a precursor suitable for the sol-gel process on the other side. Optical characterizations were performed both on the molecules and the materials. The alkynylthiocalixarenes appeared to be the most interesting species because of low clamping and high linear transmission. The formation of sol-gel hybrids incorporating functionalised thiocalixarenes is thus an appropriate and promising way to produce efficient optical limiters.

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921 - Low-Refractive-index Materials for producing Anti-Reflection film by Sol-Gel Process

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Toshio Yoshihara, Japan

Low-refractive-index materials are prepared by using sol-gel process and used to make anti-reflective film which is coated on plastic mirrors, goggles, windows, and various displays, such as television, liquid crystal display(LCD), electroluminescence display(EL), plasma display. Recently, the preparation of anti-reflection film via widespread coating is required. This sol-gel process is advantageous to accomplish easily of the mass-production of thin film and also the plant cost is inexpensive. Generally, sol-gel process is used for the preparation of inorganic metal oxide under mild condition starting from metal alkoxide. The reaction includes hydrolysis of this starting material and followed polycondensation of hydrolyzed intermediates, which are de-ethoxylated compounds. In order to accomplish the sol-gel reaction, the high reaction temperature more over 500 degrees is needed. Accordingly, wet coating on the plastic thin film has never been applied in the sol-gel process due to the high reaction temperature. In this study, the low-refractive-index materials are formed from SiO_2 sol prepared by hydrolyzing Methyltriethoxysilane($\text{CH}_3\text{Si}(\text{OR})_3$) and followed polycondensation under the acidic condition below 100 degrees. After the reaction, a buffer solution in which consists of $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$, was added into this solution. The SiO_2 sol is coated onto the transparent plastic thin film. The coated layer is thermally treated at a temperature lower than the heat distortion temperature of the transparent plastic thin film. In this reaction condition, quality of low-refractive-index layer is almost equal to that of low-refractive-index layer obtained by a gas phase method.

922 - Characterization of Alumina Doped with Rare Earth (Ce, Eu, La) Oxides

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Noel Nava, Ascención Montoya, Instituto Mexicano del Petróleo, Mexico

The importance of Rare Earth Oxides (REO) as catalytic promoters is due to the generation of reactive sites, vacancy types and improvement of thermal stability and catalytic properties toward NO_x reduction, oxidation of CO as well as TWC. Alumina-based mixed oxides have been widely studied with different types of elements, forming solid solutions at certain concentrations. In the case of REO-promoted oxides prepared by impregnation method, the solids obtained results in poorly dispersed REO over the surface. In this work, we have prepared well-dispersed alumina-REO materials (RE = Ce, Eu or La) by the sol-gel method and characterized by several techniques.

Alumina-REO mixed oxides were prepared with 5 and 10 % wt of CeO_2 , La_2O_3 and Eu_2O_3 as described: i) aluminum tri-sec-butoxide was dissolved in excess of 2-propanol at 5°C, ii) HNO_3 solution was added slowly together with a solution of RE salt in 2-propanol, and iii) the gels obtained were aged 24 h, dried in vacuum at room temperature and calcined at 700°C.

Dried materials were characterized by DTA and TGA. The samples calcined at 700°C were analyzed by N_2 physisorption, XRD, NMR and TEM.

Supports containing REO present lower specific areas, pore volumes and average pore diameters than pure alumina; this is attributed that in general REO posses lower values of textural properties than Al_2O_3 .

REO-containing materials show the same behavior in thermal analyses for each composition (0, 5 or 10 %). While in 5 % REO materials only three thermal processes are present corresponding to physical desorption of water and hydrocarbons, hydrocarbons combustion, boehmite dehydroxylation and structural conformation toward γ -alumina; samples with 10 % also show an exothermic process after 900°C attributed to phase segregation.

X-ray diffraction analyses present microcrystalline γ -alumina in all samples calcined at 700°C. NMR experiments show an increment of pentahedral coordination, even though size of RE is larger than other dopants (e.g. Ti or Zr). The different characterization techniques demonstrate that rare earth elements show good incorporation and are well dispersed in the alumina matrix.

923 - Preparation and properties of Rhodamine B derivative with ethoxy silano group and its application to surface treatment film for display

Tomoji Ohishi, Shibaura Institute of Technology, Faculty of Engineering, Japan

Rhodamine B derivative with ethoxy silano group has been prepared from a reaction of Rhodamine B sulfonyl chloride with aminopropyltriethoxysilane in dry pyridine. This new Rhodamine B derivative reacts with SiO₂ sol to connect directly with a network of silica matrix. Wavelength selective absorption film for display was prepared by use of SiO₂ sol solution containing the new organic dye derivative. This sol solution was coated on PET film, followed by heat-treatment(100 degrees centigrade) to form a thin film. The PET film with the thin film containing organic dye has flexibility. The organic dye did not ooze in water or alcohol since the organic dye bonds to inorganic skeleton. This film has a good performance (contrast enhancing performance) since the organic dye is heavily incorporated with high concentration in the film. This film can be used to surface treatment film for displays, such as CRTs and PDPs.

924 - Gas sensing properties of nanocrystals oxide doped silica Sol-Gel film

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Dario Buso, Massimo Guglielmi, Carlo Cantalini, Italy

Mike Post, NRC of Canada, Canada

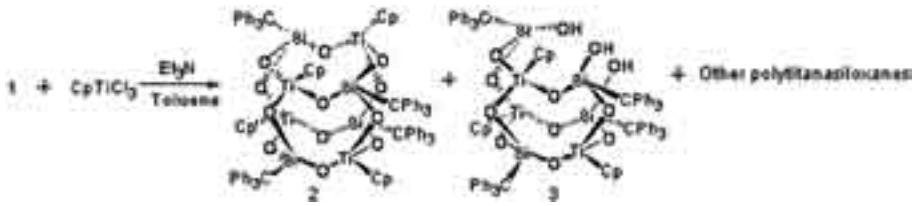
Nanoporous silica films doped with different functional oxide nanoparticles (NiO , Co_3O_4 and SnO_2) have been synthesized by sol-gel method. The nanoporosity of the sol-gel matrix provides a path for the gas molecules to reach the functional ultrafine particles embedded in the glass matrix, which reacts with the gas species generating a variation both in optical and electrical properties of the nanocomposite films.

The nanocomposites were obtained mixing a matrix solution of tetraethyl orthosilicate (TEOS) and methyltriethoxysilane (MTES) as SiO_2 precursors, with a doping solution containing metal chlorides as precursor for the functional metal oxide particles. 3-Aminopropyltriethoxysilane (APTES) or 3-(2-aminoethylamino)propyltrimethoxysilane (AEAPTMS) bearing either amine groups capable of coordinating the metal ions and a hydrolyzable silyl group for anchoring the metal complex moiety to the silicate matrix was used as bifunctional ligand. Thin films of composition $60\text{SiO}_2\text{-}40\text{NiO}$, $60\text{SiO}_2\text{-}40\text{SnO}_2$ and $85\text{SiO}_2\text{-}15\text{Co}_3\text{O}_4$ were deposited on Si or SiO_2 glass substrates and heated at different temperatures. Microstructure development of the nanocomposite has been studied by X-Ray diffraction (XRD), transmission electron microscopy (TEM) and Fourier transform infrared (FT-IR) spectroscopy. Nanocrystals precipitate at $400\text{-}500^\circ\text{C}$ grow with heat treatments. The variation of OH content and porosity have been monitored by FT-IR measurements. The film composition evaluated from Rutherford backscattering spectrometry (RBS) was in good agreement with the nominal one. The nanocomposite films showed a reversible change in the optical transmittance in the VIS-NIR range when exposed to CO and also a reversible change of the resistivity when exposed to CO and H_2 . The effect upon optical transmittance and resistivity of the residual porosity, testing temperature and gas concentration have been studied.

925 - Synthesis and Structures of Titanasiloxane Cage Compounds

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The presence of metal in the siloxane framework often can be improved for catalytic activity, thermal stability, and conducting property. In particular, transition metal-incorporated silica and zeolite have been shown to catalyze a variety of organic transformations. In such reactions, discrete cage-type polymetallasiloxanes can be excellent model compounds for the study on silica supported metal catalyst systems. In order to get discrete cage-type polymetallasiloxanes, silanetriol was synthesized and reacted with metal compounds. (Triphenylmethyl)silanetriol $[(\text{Ph}_3\text{C})\text{Si}(\text{OH})_3]$, 1] was prepared in high yield (98%) by the hydrolysis of (triphenylmethyl)trichlorosilane in excess water and used as precursor for synthesis of polymetallasiloxanes. Compound 1 reacted with MX_n ($\text{M} = \text{Si, Al, Ti}$; $\text{X} = \text{alkyl, halide etc.}$) to afford cage-type polymetallasiloxanes as major products. Such cage-type compounds were characterized by the analysis of ^1H , ^{13}C , ^{29}Si NMR, IR, Mass spectra, and X-ray diffraction data. As an example among these reactions, the reaction of 1 with CpTiCl_3 in the presence of triethylamine as a HCl scavenger in toluene solvent gave both compounds of cage type 2 and open-cage type 3. The sum yields of both compounds 2 and 3 were 54% (with the ratio of 2 to 3) and 81% (only compound 2) in 1: 1 and 1: 1.5 reactions of compound 1 and CpTiCl_3 , respectively. The crystalline solid structures of compounds 1 and 3 were disclosed by X-ray diffraction studies. Compound 2 was shown to be effective as a catalyst for the oxidation of olefin such as cyclooctene and norbornene with tert-butylhydroperoxide. In this presentation we will discuss the results obtained from these reactions in details.



926 - Reduction of Eu³⁺ to Eu²⁺ in Al-codoped silica glasses fabricated by the Sol-Gel technique and CO₂-laser processing

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Silica glasses doped with europium and, in some cases, aluminium have been produced from a precursor solution of tetraethoxysilane (TEOS) and additives by the sol-gel technique. Dotation has been in the range of 0.1-10% at. relative to silica for both dopants, and has been achieved by dissolving the appropriate amount of europium nitrate and, where applicable, aluminium nitrate in the precursor solution. After gelation the samples were heat treated at 950°C for several hours.

Following this treatment the bright red fluorescence characteristic for the trivalent europium ions (Eu³⁺) has been observed. The lifetime of the main line at 613 nm (FWHM ~10 nm) was measured to be 0.5-2 ms depending on the dopant concentration.

Subsequent CO₂-laser processing in air of the samples containing europium as well as aluminium gave rise, after excitation around 370 nm, to a bright blue fluorescence consisting of two broad bands (FWHM ~100 nm) centred at 450 and 490 nm, respectively. The fluorescence lifetimes were found to be shorter than 1 µs. This fluorescence is attributed to the divalent europium ion (Eu²⁺), leading to the conclusion, that the CO₂-laser processing resulted in the reduction of the trivalent to the divalent europium ion.

It has also been found that this reduction is not complete, a small fraction of the europium ions remains in the trivalent state as indicated by the observation of a weak red fluorescence. Our experiments showed that the reduction of Eu³⁺ to Eu²⁺ is activated by the addition of aluminium. Measurements carried out with laser processed samples containing europium but no aluminium did not revealed any blue fluorescence.

The use of europium and aluminium nitrate and subsequent CO₂-laser processing in air could therefore offer an alternative route to glasses containing divalent europium ions.

927 - Periodic structures of organic-inorganic hybrid material recorded by two-photon laser interference technique

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Shigeki Matsuo, Hiroaki Misawa, Tokushima University, Japan

Photonic crystals (PhCs) are materials, which have a periodic structure of the refractive index on a scale of the wavelength of light. PhCs are prospective for applications in various fields of photonics. Recently, a multi-beam laser interference (MLI) was proposed as one of the techniques for PhCs fabrication. A distinctive feature of this technique is the flexibility and ease in producing a periodically-modulated optical intensity field with a micrometer-order. In MLI, the material is exposed to the light interference pattern; then, wet etched in an appropriate solvent, resulting in the periodic structures of PhC or their templates.

We reported here on the preparation of the PhC structure in the sol-gel derived organic-inorganic films by using the MLI technique. In organic-inorganic materials, it is easy to add C=C bonding, which is achieved via a laser-induced photopolymerization in a interference field. We had prepared a gel film containing Si- and Zr-alkoxide as the inorganic constituent and the methacrylic group as the organic component. The film was exposed to the interference pattern at 380 nm wavelength and, then, wet etched in propanol. Two-dimensional (2D) periodic structures, which were composed of pillars of the composite material, were thus fabricated. Also, we report on the periodic structures which were produced by femtosecond pulses at 800 nm wavelength. 2D PhC recorded this way corresponded to the two-photon absorption induced photopolymerization. Their optical properties were investigated. When the adequate conditions of the laser power and exposed time were selected, the 2D PhC structures, which were similar to those recorded at 380 nm wavelength were fabricated. Fabricated structures were sensitive to the condition of laser exposure. Namely, when the exposure time is shorter or the laser power is weaker than the critical exposure dosage, the upper parts of some adjacent pillars are colliding with each other forming a pattern of periodically arranged islands. Optical properties in those novel periodic structures should depend on the vertical position of the incident light. Optical characterization will be carried out and compared with the properties of 2D PhC formed of vertical pillars.

928 - Molecular Design of Sol-Gel SiO₂-TiO₂ for Self-Cleaning Optics

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The sol-gel chemistry of SiO_{2(1-X)}TiO_{2(X)} prepared using the hydrolysis of tetraethoxysilane (TEOS) and titanium isopropoxide has been explored with regard to the formation of coatings that are useful in photocatalysis and self-cleaning optics. As X increases so the total surface area of these phases unexpectedly passes through a maximum:

The UV-vis cut-off, EPR, FTIR, DLS, TEM, TPR, XPS, acidity measurements all suggest that we are controlling the nature and number of the Si-O-Ti linkages formed. This sol-gel chemistry is described in detail.

X	SBET (m ² /g)	cut-off (nm)
0	795	288
0.05	977	320
0.15	903	332

930 - Photoluminescence Excitation Spectroscopy of Er³⁺/Yb³⁺ Co-Activated Silica-Alumina Monolithic Xerogels

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Alessandro Chiasera, Sandra Dirè, Maurizio Mattarelli, Maurizio Montagna, L Zampedri, Università di Trento, Italy

Alessandro Martucci, G C Righini, Università di Padova, Italy

Stefano Pelli, CNR-IFAC, Institute of Applied Physics, Italy

The development of an Er-doped glass integrated optical amplifier generally requires co-doping of glass with Yb. The pumping scheme at 980 nm, otherwise, would not be quite efficient, since the Er³⁺ absorption cross-section at this wavelength is not very high. The addition of Yb³⁺ as a sensitizing ion largely overcomes the problem because the absorption cross section of the Yb³⁺ $^2F_{7/2} \rightarrow ^2F_{5/2}$ transition is roughly tenfold higher than that of Er³⁺ $^4I_{15/2} \rightarrow ^4I_{11/2}$. Some deleterious processes, however, as the back energy transfer from Er³⁺ to Yb³⁺ ions, can also occur and should be considered.

In a previous work we paid attention to the effect of alumina on the emission of Er³⁺ ions at 1.53 μ m in Er₂O₃-Yb₂O₃-Al₂O₃-SiO₂ xerogels [1]. In this work we present photoluminescence (PL) excitation measurements on similar monolithic xerogels, with the aim of assessing the effect of Yb³⁺ co-doping on the fluorescence intensity at 1.53 μ m and of clarifying the Yb-Er energy transfer processes in this host glass. Monolithic silica xerogels doped with different concentrations of Er³⁺, Yb³⁺ and Al³⁺ were prepared by sol gel route with the procedure reported in Ref. [1]. The samples were thermally treated in air, and Raman spectroscopy was used to monitor the degree of densification of the glasses and the residual OH- content. The spectroscopic properties of the Er₂O₃-Yb₂O₃-Al₂O₃-SiO₂ xerogels were investigated by several techniques: absorption spectra in the UV-visible-NIR range; selective excitation of Er³⁺ and Yb³⁺ ions both upon CW and pulsed regime; photoluminescence excitation spectra over the wavelength 890 - 1010 nm range, spanning the energy range of the Yb³⁺ - $^2F_{5/2}$ and Er³⁺ - $^4I_{11/2}$ excited states.

[1] A. Chiasera, M. Montagna, R. Rolli, S. Ronchin, S. Pelli, G.C. Righini, R.R. Gonçalves, Y. Messaddeq, S.J.L. Ribeiro, C. Armellini, M. Ferrari, and L. Zampedri, J. Sol-Gel Sci. Tech. 26, 943 (2003).

931 - Application of chromium-containing silicas for synthesizing functional glasslike materials by the Sol-Gel method

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Aleksej A Chuiko, NAS of Ukraine, Ukraine

Evgenij Poddenezhny, Andrej Boiko, Gomel State Technical University, Belarus

A new variant of the sol-gel method for synthesizing optical silica glasses has been designed. The present paper is concerned with the possibility of application of chromium-containing silica (Cr/SiO_2) as a filler and source of doping ions. Highly disperse Cr/SiO_2 samples were synthesized through a step-by-step controlled adsorption of vapors of chromium oxochloride and hexane on the surface of fumed silicas. The composition of the prepared dark-brown Etard complex is $3\text{CrO}_2\text{Cl}_2\text{-C}_6\text{H}_{14}$. The complex is firmly sorbed to the surface. When heated in air, it decomposes to form oxide groups of trivalent chromium. In the IR spectra of the modified silicas there are absorption bands at 635 and 575 cm^{-1} which are related to valence vibrations of Cr-O bonds. Our studies of Cr/SiO_2 by the XRD technique makes it possible to identify the applied phase as Cr_2O_3 nanoclusters. With increasing chromium concentration in samples from 0.9 to 5.1%, the size of chromium oxide nanoclusters increases from 10 to 46 nm.

The procedure employed for synthesizing chromium-containing sol-gel glasses involved the following subsequent stages: hydrolysis of TEOS in a triple-component system $\text{Si}(\text{OC}_2\text{H}_5)_4\text{-H}_2\text{O-HCl}$ of starting compounds with their molar ratio of 1:16:0.01; addition of Cr/SiO_2 ; thorough dispersion in an ultrasonic bath; neutralization of the reaction mixture to $\text{pH} = 5.5\text{-}6.5$ using a solution of hexamethylenetetramine; gelation; drying of the gel; sintering in a furnace and holding at a temperature of $1140\text{-}1200^\circ\text{C}$ for 1.5-2.0 hours in various atmospheres (air, helium, hydrogen).

Unlike the samples obtained by the conventional method, the samples that were synthesized using aerosols modified with chromium oxide possess a higher optical homogeneity and, in addition, exhibit an increase in their refraction index (= 633 nm) in comparison with a pure silica glass. This seems to be attributed to the fact that the new glasses contain nanodimensional crystals of chromium oxide.

933 - Textural and Structural Properties of Sol-Gel ZrO₂-CaO Mixed Oxides

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ZrO₂-CaO sol-gel materials were obtained from zirconium n-butoxide and calcium sulfate. The references were prepared using calcium methoxide and zirconium n-butoxide as precursors. The gelation reactions were made at pH3 with H₂SO₄ as hydrolysis catalyst. The samples were annealed at 200, 400, 600 and 800°C during four hours. The relationship were varied from ZrO₂/CaO=10/90 to 90/10. The resultant solids were characterized by FTIR, DRX and BET specific surface area. An important IR band appears at 3650 cm⁻¹, in the CaO-H₂SO₄-pH3 sample, characteristic of stretching vibration of terminal hydroxyl groups. This band is due to the basic properties of the solids. Nevertheless in the samples ZrO₂-CaO-90/10-T the band disappears and only is observed a wide band at 3400 cm⁻¹. The band at high energy appears again in the samples ZrO₂-CaO-10/90-pH3. Amorphous samples were obtained until 400°C, and tetragonal zirconium oxide was stabilized in presence of Ca ions. Crystallite size, phase identification and its relative abundance in function of the CaO content was obtained using the Rietveld refinement. Specific surface area depends on the calcium content and thermal treatment in the mixed oxides. The ZrO₂ has 17.24 m²/g and CaO-H₂SO₄ has 64.12 m²/g. An positive effect of CaO in the specific surface area of ZrO₂ was observed. CaO develops basicity in ZrO₂. Using CO₂ as prove molecule to determine basic sites a maximum in the amount of CO₂ adsorbed on the mixed oxides is obtained in sample having ZrO₂-CaO-80/20 composition.

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934 - Synthesis of TiO₂ nanoparticles with controlled size and phase for photo reduction of NO_x

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Nanoparticles of titanium dioxide (TiO₂), predominantly in the anatase phase, were prepared by the sol-gel method and characterized by XRD, TEM, DSC, TG and BET. The particle size determined by TEM were between 20 and 50 nm. The analysis BET showed that the surface area of TiO₂ was between 6 and 80 m²/g; the poro distribution possessed monodispersity, the pores volume was between 0.020 and 0.1800 cm³/g and the mean pore size was between 10 and 50 nm. The X-ray diffraction pattern of the as-prepared sample confirmed the pure anatase phase of the material. These results will be very useful for the lately photocatalytic study of these materials for photo reduction of NO_x.

935 - Physicochemical Characterization of Titania Gels Doped with Sodium and Cesium

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The effect on titania by doping with lithium and rubidium titania gels has been studied in samples prepared by from titanium tetra-n-butoxide co-gelling with alkaline metals precursors (Li and Rb). Characterization by X-Ray diffraction of the samples shown that the doped titania is nanostructured, the particle size calculated from Rietveld refinement show that the particle size were estimated between 7.8 to 78 nm in Li/TiO₂ and between 10 to 38 nm for Rb/TiO₂ samples when they were annealed at 200°C or 600°C respectively. In the other hand in samples annealed at 600°C it was found that rutile phase is the main one in Li/TiO₂ while anatase is stabilized on Rb/TiO₂ sample. Using UV-Vis spectroscopy the effect of alkaline metals in the titania band gap was also observed. In general for both samples the band gap diminishes with thermal treatments. The low values correspond to the samples treated at 800°C.

Additional effects on textural properties were also observed. The specific surface area of doped samples is lower for Li/TiO₂ than for Rb/TiO₂.

Since titania is recognized as a promising basic catalyst when doped with alkaline metals, evaluation of their basic activity in the acetone condensation has been carried in the doped samples. It has been found that activity and selectivity to the different products depending of the titania phase, particle size, and of the semiconductor properties. These results will be discussed in the large version of the present communication.

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936 - Determination of Basic Sites by CO₂ Thermal Programmed Desorption on Sol-Gel CaO-SiO₂ Mixed Oxides

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Temperature-programmed desorption (TPD) of acid molecules is a popular method for the determination of basic amount of solid catalysts as well as basic strength because it is an easy and reproducible method. CO₂ is frequently used as a probe molecule, because of its small molecular size, stability and its acid character. Sol-Gel synthesis is an alternative method for obtaining solid catalysts with interesting textural and structural properties, the synthesis step comprise the hydrolysis and condensation of metal alcoxides these steps are followed by an annealing process, which lead to the formation of crystallographic phases in the solids obtained.

The sample synthesis were accomplish using HCl or HNO₃ as hydrolysis catalysts, Ca(OMe)₂, TEOS and water as the precursors. The samples prepared were CaO-HCl, CaOHNO₃, CaO-SiO₂-HCl and CaO-SiO₂-HNO₃.

The evolution of the samples was followed by FTIR as a function of temperature treatment. Samples were heated at 200, 400, 600, and 800 °C, the signal bands appears at 3600 cm⁻¹, 3400 cm⁻¹, 1650 cm⁻¹ and 400-1000 cm⁻¹. The intensity of the bands is reduced by the sample thermal treatment increase, nevertheless, hydroxylation remains even in samples treated at 800 °C. The crystalline structure of the samples was followed by XRD. Calcite (CaCO₃), calcium hydroxychloride (Ca-CIOH) and calcium oxide (CaO) phases were observed and refined by the Rietveld method, this technique gives information of the lattice, composition and crystal size for all the phases present. Defects in the network of the crystalline phases produce basic sites detected by thermal desorption of CO₂.

The synthesized mixed oxides show a great capacity for retention of OH groups. This property allowed to stabilized the oxygen vacancies of the structural defects, formed during the annealing process. The evolution of the different crystalline phases and its quantitative evaluation in function of the annealing temperature will be discussed in extend version.

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937 - Zirconia and Cu/ZrO₂ Sol-Gel Materials. Spectroscopic Characterization

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Zirconia and copper zirconia sol-gel materials were prepared using zirconium n-Butoxide and Cu(NO₃)₂ as precursors. The gelling reaction was made at pH 3 (HNO₃) with ter-butanol as solvent. The samples were dried and annealed at 200, 400, 600 and 800°C during 4 hours in air. The samples were characterized by FTIR, UV-Vis spectroscopy and nitrogen adsorption isotherms. The samples were studied by FTIR pyridine adsorption spectroscopy to determine the presence of Brönsted and Lewis acid sites. The spectra of pyridine adsorbed on the solids present 1610 and 1442 cm⁻¹ bands who were assigned to different vibration of the pyridinium species adsorbed and are characteristic of strong Lewis acid sites. Lower intensity bands at 1488, 1590 and 1577 cm⁻¹ were also observed and they were assigned to weak Lewis sites. These bands are shifted toward high energy of the spectra on function of the copper content. Zirconia calcined at 400°C has an specific surface area of 157 m²/g and mean pore diameter of 60 Å. The addition of copper into the network has only small effect on the specific surface area. The UV-Vis results shows E_g values between 3.4-4.5 eV for pure zirconia thermally treated at different temperatures. Nevertheless when copper is present the E_g values considerably diminishes, and Cu/ZrO₂ materials have E_g values from 2.9 to 3.2 eV.

The effect of Cu in the E_g band seems to be due to its incorporation into the ZrO₂ producing important effects in the semiconductivity properties.



938 - Anhydrous Sol-Gel Synthesis of Titania-Doped Siloxane Polymer for Integrated Optics

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Sol-gel synthesis of organic-inorganic hybrid materials for planar waveguides and devices has received growing interest due to its low-cost processing and good suitability for doping. Titania is an important optical dopant, and is normally incorporated into silica network at nano-particle forms by aqueous sol-gel process. In this paper, we report an anhydrous sol-gel process for synthesis of titania-doped siloxane polymer. The process consists of a hydrolysis of 3-methacryloxypropyltrimethoxysilane (MPS) with boric acid under anhydrous conditions, followed by a condensation with dimethyldimethoxysilane (DMDMS) and titanium ethoxide (TEO). The produced titania-doped polymer was coated onto silica and silicon substrates for optical characterisations. IR spectra show that TEO doping is useful in reducing the OH concentration in the polymer, while DMDMS doping is found effective in reducing the birefringence of the material. The methacryl groups of MPS are UV-polymerizable, and a direct UV writing process was applied to test the material's waveguide forming ability. The homogeneity and the environmental stability for titania in the hybrid matrix are examined by XRD, SEM and IR techniques, and results show that the anhydrous sol-gel process is useful for preparation of homogeneous and stable titania-doped siloxane polymers.

939 - Characterization of spherical foamed silica

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Spherical foamed silica was fabricated and characterized for the application of light thermal insulation. The foamed silica has density ranging from 0.18 to 0.25 in apparent packing density. The foamed silica has open pores but closed inside of individual silica sphere. They float on the water as far as the silica bubble is not broken completely. The pores formed in the silica ranges from 0.03 to 0.2 millimeter. The thermal behavior was tested by preparing silica foam board up to 1200 degree C.

942 - The Control of Hydroxyl Content in Sol-Gel Materials for Waveguide Optical Amplifier

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The fabrication of waveguide amplifier for integrated optics using sol-gel process has received an increasing attention. Potential advantage of lower cost by less capital equipment and easy processing makes this process an attractive alternatives to conventional technologies like flame hydrolysis deposition, ion exchange and chemical vapor deposition, etc. In addition, sol-gel process has been found to be extremely suitable for the control of composition as a host of Er ions. However, non-radiative quenching due to the vibration of residual OH groups restricted the use of a conventional sol-gel in optical amplifiers. Therefore, the sol-gel process has to be carefully controlled in order to minimize the residual OH content. In this work, a novel synthesis of the OH-controlled coating matrices by a hydrolytic/nonhydrolytic sol-gel reaction was presented. Silicon(IV) chloride (Aldrich), tetraethyl orthosilicate (Acros) were used as received. All of the preparation was carried out under N₂. The preparation of the coating matrices involved two steps of reaction: (1) Hydrolysis and condensation of tetraethyl orthosilicate by hydrolytic reaction to form $(\text{Si-O-Si})_x(\text{OH})_4-x-y(\text{OR})_y$, (2) Nonhydrolytic sol-gel reaction of SiCl₄ with $(\text{Si-O-Si})_x(\text{OH})_4-x-y(\text{OR})_y$ as an oxygen donor under nonaqueous conditions. The reaction between SiCl₄ and $(\text{Si-O-Si})_x(\text{OH})_4-x-y(\text{OR})_y$ was monitored as a function of OH content by means of reactor FT-IR, viscosity, GPC and NMR etc. Luminescence spectra after doping Er ions will be also compared with OH content

943 - Raman spectroscopic investigations of Ag⁺ and Ce³⁺ doping effects on the densification of nanoporous silica xerogels

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Silica xerogels with controlled pore size can be used as a host for organic polymers, metallic ions and nanoparticles. These post-doping facilities allow these materials, when densified, to have interesting properties for optical applications. The present work is devoted to the study of the doping effects with Ag⁺ and Ce³⁺ on the densification processes of nanoporous silica xerogels.

Doped and undoped porous silica gels with pore sizes of 50 Å and 75 Å containing doping ions were heat-treated at various annealing temperatures ranging from 800°C to 1150°C. The heat-treatment was performed in air for 1 hour at each temperature. Raman spectroscopy was used to follow the structural changes occurring at various stages of the gel-to-glass transformation. The effects of doping with Ag⁺ and Ce³⁺ ions on the structure of nanoporous silica gels and gel-derived silica glasses were also investigated. This structural study was based on the analysis of the evolution of the frequencies, intensities, and profiles of certain characteristic Raman bands of vitreous silica systems.

Raman spectroscopy showed that doping with Ag⁺ ions, even in small amount (less than 500 ppm), leads to a complete densification of xerogels at an annealing temperature lower than that of undoped ones. As an example, for 50 Å undoped xerogels, the densification is completely achieved at 1050°C while it occurs at 950°C for Ag⁺-doped samples. On the contrary, Ce³⁺ doping was found to slow down the densification process. In fact, the complete densification occurs at 1100°C in this case. Similar behaviors have been observed for 75 Å nanoporous samples. Moreover, it is worthy to note that when the densification temperature (temperature at which the densification is complete) is taken as a normalization parameter, then all the structural processes (for example evolution of defects D1 and D2 as a function of annealing temperature) related to the gel-to-glass transition seems to follow universal laws.

944 - Physicochemical and Acidic Properties of Sulfated Zirconia Supported by Alumina Prepared by Sol-Gel Process

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The isomerisation of light n-paraffins in the petroleum industry has become more important in recent years due to environmental legislation. Several catalytic systems have been considered for these reactions and among them sulfated zirconia (SZ) has attracted extensive attention because of its strong acidity and high activity at relatively low temperatures. Much work has been devoted to the preparation, the characterization and the applications of this catalytic material. However owing to its sensitivity to the preparation and activation conditions, a number of them found that the acidic and catalytic properties of sulfated zirconia system are strongly related to the preparation conditions. Other research groups consider that supporting SZ over alumina enhances significantly the activity and the stability of these catalysts.

The objective of this work is to clarify the effect of preparation parameters on the physicochemical and acidic properties of sulfated zirconia supported by alumina (SZA) catalysts prepared by sol-gel process. In fact, a series of SZA catalysts having a relative composition of 5%, 10%, 20% and 50% of ZrO_2 and different S/Zr atomic ratios were prepared using zirconium propoxide or zirconium acetylacetone and aluminium butoxide as precursors. The study of the physico chemical properties was carried out using IR, ^{27}Al NMR, XRD, N_2 adsorption at 77K, FTIR analysis of adsorbed C_6H_6 , ^{27}Al NMR-MAS, XPS and TPD-NH₃. Catalytic performances have been evaluated by means of n-hexane isomerisation reaction.

Results obtained show that the symmetry of Al undergoes an increase from tetrahedral to octahedral coordination, which may be assigned to the modification of the polymeric properties of aluminium alkoxide in presence of $Zr(Opr)_4$ and to the fixation of the acetylacetone bidentate ligands on Al atoms in the case of the $Zr(acac)_4$. Furthermore, the sequence of the addition of the different precursors during the preparation step by sol-gel method seems to be a crucial factor. On the other hand the increase of Zr and sulphate loading affect considerably the stability and the acidity of the sulfated zirconia supported by alumina and as consequence its catalytic behaviour.

945 - Acidity of sulphated zirconia aerogels : Correlation between XPS studies, surface potential measurements and catalytic activity in isopropanol dehydration reaction

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In our previous work, we showed that the hydration and sulphatation steps are determinant in the control of surface properties, mainly the acidity of the aerogel sulphated zirconia catalysts. In the present work we study qualitatively and quantitatively Lewis and Brönsted acidity of aerogel sulphated zirconia aerogel involving XPS spectroscopy, potential surface measurements and isopropanol dehydration reaction.

Qualitative and quantitative XPS results and surface potential measurements show that the surface of solid becomes more acidic in term of Lewis acidity and the oxygen species exist in three types, created by the introduction of sulphur in the bulk of solids, which one is responsible of Brönsted acidity. This type of oxygen species, in hydroxyl group, is different from the oxygen species of zirconia network and the oxygen sulphate group. Consequently, acidity of sulphated zirconia is mainly due to a strong Lewis nature of the surface, which can give a strong Brönsted acidity by water or reactant chemisorption.

Pure zirconia is inactive in the isopropanol dehydration in the temperature range 373K-423K but all aerogels containing sulphate ions produce mainly propene. Furthermore the activities change with the sulphate content and catalysts with nS/nZr atomic ratio below than 0.5 exhibit the highest activities at 413 K. The lower activity observed with the aerogel containing the highest sulphate content is probably due to the low surface area observed for this sample.

An interesting relationship between the change of surface potential for sulphated zirconia and their intrinsic activities in dehydration reaction of isopropanol is obtained. Furthermore we observe the same correlation between the oxygen species, responsible of Brönsted acidity, and the change of surface potential of these catalysts. Then, we can assume that the hydroxyl groups are responsible, directly or not, of the increase in the activity of the sulphated zirconia catalysts.

Considering the characterisation and catalytic results on these solids, it is possible to suggest that the active site in the dehydration of isopropanol on sulphated zirconia is a strong Brönsted site generated by adsorption of water on a strong Lewis site.

946 - Salient Features of Synthesis and Structure of Surface of some Functionalized Polysiloxane Xerogels

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On the basis of the authors' works a consideration is given to salient features of synthesis of a new class of sorbents and supports (namely polysiloxane xerogels with N-, O-, and S-containing functional groups) which are produced by the sol-gel method. The major advantage of sol-gel method consists in the possibility of using multiconstituent systems. In principle, one can vary both the nature and ratio of structure-forming agents [E(OR)_n, E = Si, Al, etc.] and composition and ratio of alkoxy silanes of the (RO)₃SiR' type. In the latter case an appropriate one-stage process enables one to produce polysiloxane xerogels with a complex surface layer that contains several functional groups R' varying in their nature. From the obtained experimental material it is possible to draw the following inferences. In most cases the advanced procedures enable us to synthesize readily polysiloxane xerogels with reproducible characteristics and surface layers that contain such functional species as amine, thiol, carboxyl, calixarene and (thio)urea groups. The structure-adsorption properties of the produced xerogels with a monofunctional surface layer are strongly affected by character of functional groups and conditions of synthesis. Further, we designed simple synthetic procedures which allow one to produce polysiloxane xerogels with a bifunctional surface layer. In this case the ratio of reacting alkoxy silanes and nature of an 'additional' functional group exert a profound effect both on degree of hydrophobicity of the surface of such materials and on their porosity; at certain ratios of reacting components it is possible to produce mesoporous materials with a biporous structure. The data collected with the help of a number of physical methods give evidence for the fact that, on the one hand, on the surface of functionalized polysiloxane xerogels there are present structural units of an identical nature and, on the other hand, the surface structures of these materials are similar in their character. This research was partially sponsored by NATO's Scientific Affairs Division in the framework of the Science for Peace Programme (Grant SfP 978006).

947 - Vanadia-Silica catalysts prepared by Sol-Gel method: application for epoxidation reaction

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The preparation by sol-gel route, finds a wide utility for the synthesis of catalysts. V-Silica mixed oxides are prepared using this method, and tested in the epoxidation reaction of an allylic alcohol. The reactivity of the catalyst depends on the operating preparation parameters (V/Si ratio, mode of drying, temperature of calcination, etc...).

A series of V-Silica catalysts with various molar ratios V/Si = (0.05, 0.1, 0.2) are prepared using TEOS and vanadium acetylacetone V (acac)₃ as precursors and the propan-1-ol as solvent. A mixture of H₂O and HNO₃ is used for TEOS hydrolysis. The preparation parameters chosen are : [TEOS] = 2 mol L⁻¹, molar ratio TEOS: H₂O: HNO₃ = 1: 4: 0.4, and temperature of 70°C. In this condition, it is found that the gelation time increases with V/Si ratio. This result could be explained by the complexation of the hydrolized TEOS with acetylacetone ligands which retards the polycondensation of silica.

Obtained gels are dried in oven at 120°C during 24 hours to get xerogels, or in the autoclave in the supercritical conditions of the solvent to get aerogels. Finally the solids are calcined in flowing air at 500°C.

Textural and structural properties of the catalysts are studied by nitrogen physisorption, XPS, Raman spectroscopy, TG / MS and XRD. These characterisations show that the drying in autoclave produces mesoporous solids with an important average pore diameter and high specific surface areas. Characterisation by XRD illustrate that both xerogels and aerogels are amorphous.

For the calcined xerogels, Raman spectroscopy shows two types of vanadia species on SiO₂ support; monomeric vanadyl groups and V₂O₅ crystallites. But, for the aerogels, no vanadia species are detected.

The epoxidation of the trans-2-hexen-1-ol has been investigated. In the case of xerogels, the epoxide yields are around 50% at 65°C for a molar ratio TBHP/alcohol of 4/7. This good activity is realized with no leaching of vanadium species in the solution. Nevertheless, the activity of the aerogels is partly due to the dissolution of the vanadium in the liquid medium. This difference in the catalytic behaviour is explained in terms of vanadia dispersion and metal oxide support interaction strength.

949 - Preparation and strengthening of nano-porous silica optical films with adjustable refractive index derived by Sol-Gel process

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Sol-gel derived nano-porous silica films have many good properties such as continuously adjustable refractive index, high porosity, and high laser damage threshold; therefore, they have much potential to be used as anti-glare and anti-reflectance for cathode ray tubes (CRT), color monitor tubes (CMT), solar energy use, lens in high power laser systems and others. Poor mechanical strength of the films, however, greatly confines themselves to commercial viability. In this paper, a scratch-resistant improvement of sol-gel derived nano-porous silica films with an adjustable refractive index by a base/acid two-step catalysis is reported. The silica films were prepared with the two-step catalytic sol-gel process and a dip-coating method, and then post annealed in air and a mixed gas atmosphere. The films were characterized with FE-SEM, AFM, TEM, FTIR, spectrophotometer, an ellipsometer, and the abrasion test, respectively. Ellipsometer analyses give that the nano-porous silica films have an adjustable refractive index ranging from 1.14 to 1.42 with an increase in the ratio of SiO₂ to TEOS in the two step catalysis. FTIR measurements have shown that the frequency shift of FTIR absorption w₄ (TO₃) peak of the films to a lower wave number results from a decrease in the average Si-O-Si bridging angle with the post annealing. An increase of FWHM of the w₄ peak is ascribed to a wide distribution of the bridging angle because of formation of strained Si-O-Si bonds caused by the post annealing. The abrasion and adhesion tests present that the two-step catalysis obviously improves the scratch-resistance and adhesion of the films, and the mixed gas treatment further strengthens the silica network. The increase in strength is attributed to more Si-O-Si bond cross-linkages between silica particles formed by the two-step catalysis and the mixed gas treatment.

Keywords: Sol-Gel Process; Optical Films; Silica; Nano-Porous Structure

950 - Gel Entrapment Technique for Nd-YAG

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YAG doped with Nd³⁺ has proved to be an outstanding solid-state laser material with room temperature operation and the choice of either continuous wave or pulsed emission at 1064 nm. Synthesis of Nd-YAG powders is carried out by using conventional powder metallurgy route. In this process the respective oxides of aluminum, yttrium and niobium are heated above 1500°C and above the mixtures are repeatedly cooled re-powdered and reheated. In this process all intermediate phases are produced also the dispersion of Nd is not uniform. To overcome these problems novel sol-gel routes have been investigated. Gel entrapment technique is one of such routes. The gel entrapment technique is a novel technique which is simple and inexpensive. We have demonstrated the use of gel entrapment the production of phase-pure YAG powder of high specific surface area and controlled morphology. The technique was subsequently used for the production of high purity neodymium-doped YAG powder with excellent microhomogeneity on an increased batch size of 1kg. Neodymium nitrate was dissolved in the beginning to have molecular level mixing with a solution of yttrium and aluminum nitrate. By gradual addition of a solution of hexamethylene tetramine (HMTA), the Al³⁺ ions formed a gel at pH 4, entrapping all the liquid containing Y³⁺ & Nd³⁺ ions. These ions were subsequently precipitated within the gel matrix at a higher pH by addition of ammonia. The gel was then washed, dried and heat-treated. The process conditions were seen to be conducive to retention of the homogeneity. Characterisation was done by thermogravimetry, differential thermal analysis, X-ray diffraction and scanning electron microscopy to ascertain the high quality of the product. The gel entrapment technique has been extended to variety of other oxide materials.

951 - Theoretical and Experimental Studies on Sol-Gel Zirconia doped with Alkaline Ions

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Sol-gel zirconia materials were prepared from zirconium n-butoxide and doped with alkaline ions. The concentration of lithium, sodium and potassium ions was 1 wt% and 15 wt%. The gelation was made at pH 7 using ethanol as solvent. M^+/ZrO_2 compounds were characterized by FTIR, UV-Vis and XRD. Dehydroxylation grade diminishes on function of the annealed treatment. This phenomenon induces a great amount of puntual and structural defects. It is well known that zirconia conventional solids are isolator materials. In our sol-gel materials, the band gap values change from 5.0 eV (isolator) to 3.1 eV (semiconductor) with the addition of alkaline ions. The existence of free electrons and vacancies of oxygen generates a electronic desequilibrium. Inclusion of Li, Na, and K ions stabilize the monoclinic phase because of the density charge effects.

The effect of alkalinus ions on band gap and vibrational frequencies could be explained using ab initio cluster models and periodic extended Hückel calculation. We have used the cluster model approximation to calculate the absorption bands of surface hydroxyl groups of ZrO_2 . All calculations have been performed at the Ab Initio Hartree Fock (HF) and Density Functional Theory (DFT), at B3LYP levels. Geometry optimizations were restricted to the acidic site, while the rest of the cluster was maintained fixed to simulate de solid environment. The electronic properties has been investigated by using semiempirical band structure calculations of the Extended Hückel type.

952 - Decomposition of a Sol-Gel precursor during the fabrication of YBCO films

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Chemical solution deposition is a fast inexpensive method for manufacturing high temperature superconducting (HTS) films. We present an environmentally friendly metal-organic precursor for depositing $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) films. The precursor is deposited by spin-coating onto lattice-matched substrates. The polymer film then undergoes a range of thermal treatments during the transformation to the ceramic YBCO phase. Careful thermal breakdown is required to provide a dense, impurity free crystalline film. We have characterized the film at each stage of thermal processing to examine the species present and determine the reaction path for the precursor decomposition and formation of YBCO. FTIR, Raman and nuclear reaction analysis techniques have been used to profile the quantities of carbon containing impurities. Using this approach to assist in the optimization of the thermal processing, YBCO films can now be prepared with short firing times, 1-2 hrs, producing final films containing less than 0.1 percent residual carbon, an impurity that has a detrimental effect on film performance.

953 - Photopatternable Hybrid Planar Waveguides Synthesized by Organically Modified Sol-Gel Method

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We report on the fabrication and characterization of planar hybrid organic-inorganic waveguides by ultraviolet (UV) light exposure. Optical transparent films were synthesized via sol-gel processing, 3 μ m thick films were deposited by a single-step spin-coating on glass and silicon substrates.

Precursor sols were prepared by tetramethylorthosilicate (TMOS) and 3-glycidoxypropyltrimethoxysilane (GPMTS), a iodonium salt was added as photoinitiator. After exposition to UV light for few minutes a consistent increase in the refractive index was found due to the photopolymerization of the epoxy groups. We reported and compared the refractive indexes measured with a standard ellipsometer method, with Abeles-Brewster angle and m-line techniques. A refractive index increase of about 0.02 at 633 nm has been observed between the UV-light exposed and unexposed regions. A variable angle spectroscopic ellipsometer (VASE) was used to analyze the refractive index dispersion in the spectral range 300-1500 nm and surface roughness. An increase of surface roughness, from 3.9 to 6.2 nm was observed upon photopolymerization of the films. The increase of the refractive index was obtained only via the opening of the epoxy in the guiding layer, whilst the buffer layer was prepared by thermal treatment of film synthesized without addition of the photoinitiator.

The reported results are very interesting and promising for application due to the easy and low-cost fabrication of channel hybrid waveguides using photolithographic masks directly in contact with the guiding layer and exposing to UV-light.

954 - Sol-Gel Emulsions for Surface Base-Coat on Metal Alloys

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A chrome-free, water-based, and hazardous air pollutant (HAPs)-free sol-gel emulsion is formulated for a metal surface pretreatment coating and an anti-fingerprint coating. The coating can be applied before any primers and topcoats are applied to a surface. These surface pretreatment coatings have excellent protective performance for galvanized steel (or galvalume), magnesium alloys (such as AZ31, AM20), titanium alloys (such as Ti-6Al-4V), and aluminum alloys (such as 2024-T3, 7075-T6), and other similar alloys. The coating is able to meet all quality control standards with regard to fingerprint resistance and earthing properties, electrical conductivity, corrosion resistance, abrasion resistance, and adhesion to metal surface and topcoat (liquid and powder paints).

The current practice in surface base-coat for metal alloys is a chromate conversion coating or a dispersion of hexavalent chromium compounds in paint as corrosion inhibitors. However, hexavalent chromium is toxic and carcinogenic. An environmentally friendly (chrome-free) sol-gel emulsion will be presented for surface base-coat of metal alloys that contains organofunctional silanes, metal chelating agents, non-toxic corrosion inhibitors, copolymer resins, HAPs-free co-solvents, and water. Figure 1 show two anti-fingerprint coated galvanized steel panels using a sol-gel emulsion. Both panels passed a 120 hours salt (fog) spray test (ASTM B117), where panel 1A was tested without alkaline solution washing and panel 1B was tested after 2 minutes of a 2% tri-sodium phosphate solution washing at 65 °C. Figure 2 displays two aluminum alloy panels of 2024-T3 treated with Alodine 1200 (panel 2A) and 2024-T3 treated with sol-gel emulsion (panel 2B) coated with an epoxy primer after a 1000 hours salt spray test. The results indicate that surface pretreatment on Al alloys done by sol-gel emulsion gives an equal or better performance than that done by the chromated Alodine 1200. Other results on formulations, applications, protective verifications, and finishing products will also be illustrated.

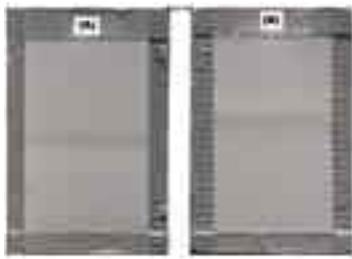


Figure 1



Figure 2

955 - Nanostrucure and optical properties of $\text{Ln}_2\text{O}_3\text{-TiO}_2$ ($\text{Ln}=\text{La, Er}$) thin films

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The present work reports on preparations of thin film erbium/lanthanum doped titanium oxide from sol-gel technique. The sols are suitable to deposit thin films by the dip - coating method and result in a dense film. The gel precursor was prepared by an alcoholic suspension of erbium/lanthanum oxi-hydroxide. Controlled amounts of 2,4-pentanedione (Acac) were added to this oxi-hydroxide suspension and then mixed with titanium butoxide and lead to the formation of a stable titanium/erbium/lanthanum sol. Films containing 10 mol% in lanthanides oxide [$(\text{Er}_{x}\text{La}_{0.1-x})\text{Ti}_{0.9}\text{O}_2$] were grown. Thin films have been dip-coated on glass substrates for $x = 0.01, 0.05$ and 1 . The nanostructure of the films was investigated by X-rays reflectometry. Optical properties were evaluated by photoluminescence and the prism coupling technique which allowed to access guided modes, thickness and refractive index as a function of the composition.

956 - Preparation of silicates using HSi(OC₂H₅)₃ and their NOx-adsorption behavior

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Preparation of Li, Ca and Ba silicates using HSi(OC₂H₅)₃ was investigated aiming at the application to a NOx absorbent. Li silicate was prepared by reaction of HSi(OC₂H₅)₃ with aqueous lithium silicate solution. Si-H bonds of HSi(OC₂H₅)₃ were hydrolyzed with the evolution of hydrogen gas, providing a silicate foam. Ca and Ba silicates were prepared from gels obtained using RSi(OC₂H₅)₃, HSi(OC₂H₅)₃ and alkaline-earth alkoxides. Alkaline-earth metal was reacted with an alcohol solution of partially hydrolyzed RSi(OC₂H₅)₃ to give a homogenous solution. HSi(OC₂H₅)₃, which was used as a gelation acceleration agent, was added to the solution. The solution was further hydrolyzed and allowed to gel at room temperature. These silicate foam and gels were heat-treated at 600 °C. The surface of these heat-treated silicates indicated the solid-basic property of H0 = 9 and adsorbed the acidic gases of NO. The silicates were placed in 500-1000 ppm NO diluted by Ar, followed by analyzing adsorbed NO. FT-IR spectrum of the NO-treated samples showed an absorption peak at 1385 cm⁻¹ in the Li silicate, absorption peaks around 1385 and 1455 cm⁻¹ in the Ba silicate and absorption peaks around 1385, 1440 and 1500 cm⁻¹ in the Ca silicate, corresponding to nitrate NO₃⁻ and/or nitrite NO₂⁻ ions. After heating the NO-treated samples at various temperatures in air, these FT-IR peaks were found to disappear above 500°C in the Li silicate and above 700°C in the Ba and Ca silicates.

Research supported by NEDO, under the Synergy Ceramics Project promoted by METI, Japan.



959 - Sol-Gel Synthesis of Na₂O-Al₂O₃-P₂O₅ and Na₂O-Al₂O₃-B₂O₃ Glasses and Characterization by AFM, SNMS and NMR

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The systems Na₂O-Al₂O₃-P₂O₅ and Na₂O-Al₂O₃-B₂O₃ are interesting because of their high chemical and mechanical stability, their permittivity and their catalytic functions. In this work we present different procedures and different precursors like inorganic and organic salts, alkoxides and acids for the sol-gel preparation of these glass systems. A novel Al-precursor, aluminum lactate, was used for the first time in the preparation of homogeneous and transparent sodium alumophosphate gels and glasses with the composition 43.8Na₂O-12.5Al₂O₃-43.8P₂O₅. The structure of the gels and the resulting glasses was investigated by liquid and solid state NMR and compared to these of glasses prepared by a traditional melting process. In the case of Al-lactate processing identical structures were identified.

In addition to bulk materials thin films were deposited by dip coating on various substrates, preferentially on silica glass to avoid any ion diffusion processes from the substrate into the coating. The coatings were characterized by atomic force microscopy (AFM) and secondary neutral mass spectrometry (SNMS). In the AFM the surfaces of the coatings were studied, the glass pattern, crystal growth, and porosity are differentiated. With the SNMS the expected elements and residual carbon were identified and diffusion profiles could be obtained. These data indicate that the amount of carbon can be removed oxidatively upon heating by using HClO₄ rather than HCl as the proton source in the sol-gel solutions.

The authors wish to thank the DFG, Bonn, Germany, for financial support.

960 - Optical Gain of Infrared Dyes in Hybrid Sol-Gel Based Channel Waveguides

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We report on the synthesis of dye-doped hybrid sol-gel based channel waveguides on glass and silicon substrates. Optical characterization by absorption, steady-state emission and light amplification measurements have been performed.

All the layers (buffer, guiding and cladding) have been grown by one step spin-coating process using hybrid organic/inorganic sol-gel route. Doped films have been obtained by incorporation of organic dyes emitting in the 1.0 - 1.3 μm spectral region. Channel waveguides have been synthesized by photolithographic and ion milling techniques. Profile quality of channel waveguides was estimated using optical and scanning electron microscopy (SEM).

Optical characterization of undoped layers has been accomplished by insertion loss measurements and refractive index characterization (using m-line and Abeles-Brewster techniques).

We investigated laser-excited emission of organic dye incorporated in channel waveguides. Measurements were performed in two different geometrical configurations (frontal and side) in order to characterize both spontaneous and guided emission. Amplified spontaneous emission (ASE) has been observed. An estimation of the optical gain coefficient, using the variable length strip method (VLS), has been obtained.

The high value of optical gain provides a very attractive possibility to exploit these materials as integrated solid-state laser sources in the infrared spectral region.

961 - Lifetime pH Sensor Based on Sol-Gel Doped New Luminescent Europium Chelate

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Luminescent lanthanide chelates have many applications, being useful alternatives to standard fluorescent dyes especially when there is significant autofluorescence. They are also useful donors for use in energy transfer experiments to determine static inter-molecular distances. These applications arise because of the chelates' excellent solubility and unusual spectral characteristics, including narrow ($< 10 \text{ nm}$) spectral emission, large Stokes shifts ($> 150 \text{ nm}$), potentially high quantum yields. Selvin et al. have synthesized several lanthanide chelates but all show inconvenient excitation maxima around 340 nm.

In contrast, our novel long-wave luminescent dye, based on europium luminescence initiated by a covalently-bonded antenna fluorophor (Fig. 1), shows excitation maxima at 370 nm where low cost LEDs are now available.

To design sensors of high stability and long lifetime, the sensor matrix and sensor technology are of prime interest. Sol-gel technology enables the production of proton-permeable glassy layers at room temperature and offers simple methods for manipulation of the basic composition, molecular structure, and hence the chemical characteristics of organic matrices.

Time-resolved fluorometry is preferable to conventional fluorometry, since there are no intensity related problems due to turbid samples, self-filter effect, and cuvette geometry. Also, the fluorescence decay time is usually independent of the concentration of the indicator, even when it has been partially modified by leaching out, by decomposition, or by photo bleaching.

In the current work, the Eu^{+3} -complex has been successfully entrapped into tetramethoxysilane (TMOS)-based sol-gel matrices. It was initially found that a Eu^{+3} -complex, which showed useful pH sensitivity in aqueous solution, lost this sensitivity when immobilized in sol-gel matrices. In order to recover this property, the pH indicator bromothymol blue (BTB) was added to the starting sol-gel components and it was found that the useful pH response that was present in water was not only restored, but was actually improved upon.

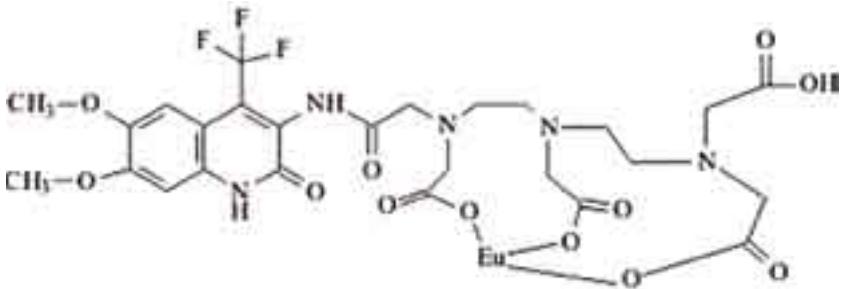


Figure 1: Synthesized Europium Complex

Fluorescence decay profiles from the Eu^{3+} -complex-impregnated coating (made from 2ml TMOS, 2.5 ml EtOH+ Eu^{3+} -complex (2mg) and 1ml HCl 10^{-3}) were examined whilst the coatings were immersed in various pH buffers. The pH of the buffer solutions was verified with a commercial electrode-type pH meter before each experiment.

Fluorescence decay times were taken at different pH values. Fig. 2 shows that the fluorescence decay lifetime varies strongly with pH and ionic strength.

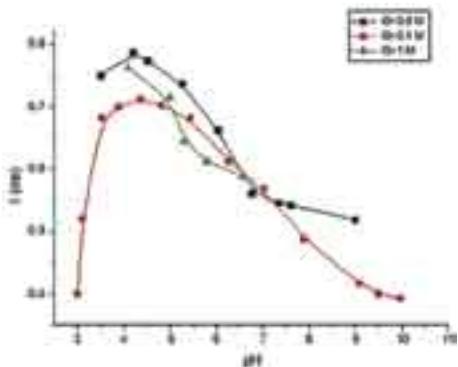


Figure 2: Effect of ionic strength on the titration plot of Eu^{3+} complex\ and BTB when doped in poly-TMOS. Excitation 370 nm; observed wavelength: 615 nm.

962 - Surface finishing of enamels by Sol-Gel coating

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Currently, sol-gel coating is a mature technology to improve surface properties of a wide spectrum of substrate materials, including glasses, ceramics, plastics and metals. However, the development of sol-gel coatings on enamels is challenging, because enamels are considered to be heterogeneous systems which possess more complex compositions than other materials.

The aim of this work was to enhance the chemical resistance of the enamels through an additional coating with components that are resistant to acids and alkalis. It was also aimed, as a side effect of these coatings, an enhancement of the mechanical resistance and an improvement of the anti-adhesive properties of enamels.

Tetraethoxysilane, methyltriethoxysilane, titanium alkoxides, zirconium alkoxides and silica sol were used as precursors for preparing the solutions. The coatings were prepared by dipping and spraying on different enamels. The thickness of these coatings varied from approximately 80 nm to 10 µm. Finally, the coatings were thermally treated at different temperatures and times.

The chemical resistance of the coated enamels was proved to be compliant with the DIN ISO standards. SiO_2 coatings of about 90 nm thickness, which are crack-free, can increase the chemical resistance of the coated substrates against acidic environment, which are independent of the composition of the enamels. The measured mass loss of the coated enamels, in comparison to the uncoated enamels, decreases approximetly by 60 to 95 percent. Coatings, such as $\text{SiO}_2/\text{TiO}_2/\text{ZrO}_2$, lead to no significant improvement in the chemical resistance against acids.

The alkali resistance of the coated substrates strongly depends on the composition of the enamels in the following cases:

- in case of chemically resistant enamels, no improvement of alkali resistance through coatings can be obtained,
- in case of chemically nonresistant enamels, a significant advance of alkali resistance through the $\text{SiO}_2\text{-ZrO}_2$ coatings is obtained.

The authors wish to thank the AiF, Köln, Germany, for financial support.

963 - Correlation between ionic conductivity and local dynamical behavior of cathions in lithium-doped Siloxane-Polyethers hybrids during gelation

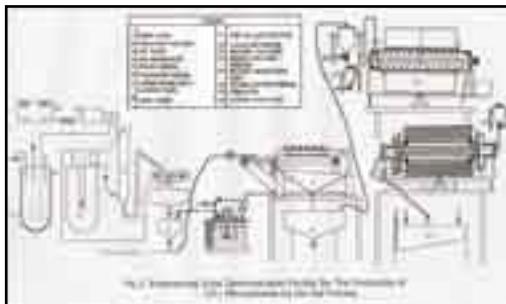
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Hybrids from the siloxane-polyether family prepared by sol-gel process are transparent, flexible and present better mechanical properties than pure polyethers. Moreover, as doped with lithium salts, they present ionic conductivity up to 10^{-4} ohm $^{-1}.$ cm $^{-1}$ which allow their use as electrolytes in electrochromic devices and batteries. In this work the evolution of ionic conductivity of lithium-doped siloxane-poly(oxyethylene) (POE) was followed during gelation by in-situ Complex Impedance Spectroscopy measurements. The electrical properties were correlated with the local dynamical behavior of the lithium ions obtained by ^{7}Li Nuclear Magnetic Resonance (NMR) such as the spin-spin relaxation time T2 and the fraction of mobile cathions in the gelling sol. Irrespective to the polymer molecular weight (500 and 1900 g.mol $^{-1}$), to the lithium doping level and to the lithium salt nature, all hybrids present two sites in NMR spectra which can be attributed to lithium ions interacting with solvent (water or ethanol) molecules present in the sol or ether-type oxygens of polymer chains, respectively. During the gelation process ionic conductivity is essentially due to lithium species surrounded by solvent molecules, as illustrated by the observed decrease of ionic conductivity in all samples, attributed to the progressive formation of the solid hybrid network in the sol resulting on the confinement of solvent in the pores. The strong increase of ionic conductivity near the gel point was well described by the percolation model. In this stage ionic conductivity is promoted by motions of lithium cathions interacting with ether-type oxygens of polymer chains. The ionic conductivity continues to increase during the gel aging, which is consistent with the expected increasing connectivity of POE chains during this process.

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Efficient movement of particles at the desired rate, eliminating saltation and dust generation by particle attrition, is vital to the success of sol-gel based nuclear fuel fabrication plant. Safety considerations in glove box operations necessitate vacuum transfers in preference to pneumatic transfers under positive pressure, though the free flowing microspheres are amenable to both types of transport. Nevertheless, pneumatic transfer under pressure pulses, is more suitable, wherever graduated weighing transfers over shorter distances into complex heat treatment equipments, is involved. Vacuum transfer is the obvious choice for bulk movement of particles from open storage vessels to closed silos separated by large distances. The choice of mode of transport is dictated by the nature and complexity of the processing unit both at the sending and receiving side. Based on these conditions of operational ease and controllability, the modes of transport are selected and the pneumatic parameters were optimised after several experiments in the commissioning trials for the following transfer operations : i) Transportation of UO_3 microspheres from the belt drier to the feeder vessel of the rotary calciner by vacuum transfer, through single piece $\frac{1}{2}$ inch size flexible nylon braided tube enclosed in 1" size nylon braided tube ii) Transportation of UO_3 microspheres from the feeder vessel to the rotary calciner under pressure, through $\frac{1}{2}$ inch SS tube iii) Transportation of calined U_3O_8 microspheres from the collector vessel to the feeder vessel of the reduction unit by vacuum transfer through $\frac{1}{2}$ inch SS tube iv)Transportation of U_3O_8 microspheres from the feeder vessel of the reduction unit to reduction unit under pressure and v) Transportation of the stabilised $\text{UO}_{2.06}$ microspheres from the stabilizer under pressure for bottling and storage through $\frac{1}{2}$ inch SS tube by tapping compressed air through timer based solenoid operations.

Pressure drops and air flow requirements for erosion free transport in different pneumatic loops are also estimated from theoretical correlations.



966 - Effect of Synthesis Parameters on Sol-Gel Silica Modified by Zirconia

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Silica has been studied by several authors extensively and its applications are very wide. Also, combinations of silica with a large number of other oxides have been undertaken. More particularly, previous work has been published on the silica-zirconia system as synthesized by the sol-gel method. However, it is necessary to shed light on several issues concerning the synthesis and characterization of this system by using the sol-gel method. Therefore the aim of this work was to investigate the synthesis of mixed $\text{SiO}_2\text{-ZrO}_2$ materials. The influence of the Zr source (zirconium oxichloride or nitrate), the ZrO_2 content, the synthesis pressure on the solids properties were studied and further modification of this type of procedure. The materials were synthesized by a sol-gel method using tetraethylorthosilicate (TEOS) as Si source and an inorganic Zr-containing salt. In a typical preparation, the Zr salt dissolved on water is added dropwise to a TEOS solution at 85°C. Nitric acid was used as hydrolysis catalysts. After condensation, two procedures were followed: one part of the gel was dried at atmospheric pressure as obtained and the other fraction was put into an autoclave and heated to 150°C. ZrO_2 weight contents of 10, 20 and 40% were used. Afterwards, the precursors were dried and calcined at 500°C. The solids were characterized by nitrogen physisorption, pyridine chemisorption followed by FTIR, ^{29}Si Nuclear Magnetic Resonance and scanning electron microscopy. Characterization of the solids revealed that mesoporous materials with very narrow pore diameter distribution were obtained when using the autoclave procedure from both nitrate and oxichloride zirconium salts. Differences in acidity as determined by pyridine adsorption were observed depending on the synthesis parameters.

969 - Effect of concentration of diazoalcene molybdenum complex immobilized in hybrid matrix

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The development of so-called fine chemistry requires the development of new catalysts with sophisticated molecular architectures in order to selectively transform reactants with specific structures. Due to this fact, the encapsulation of metal complexes in solid supports hosts has attracted much interest. The encapsulation of metal complexes in matrix by sol-gel can yield catalytic materials that combine some characteristics of the support with the electronic and stereochemical properties of the complex and could lead to the highly selective formation of certain products with a precise structure.

Sol-gel derived poly(oxyethylene), POE/siloxane hybrids produced by the versatile sol-gel process incorporating metal complexes have been investigated. The hybrid matrix host matrix used, U(600), is a di-ureasil type structure composed of a siliceous framework bonded to short POE segments via urea groups. The resulting materials exhibit a wide mechanical, thermal and mechanical stability range and started to be identified as potential and suitable media where catalytically and other chemical reactive species could be hosted or immobilized.

In this work, we describe the effect of concentration of the diazoalcene molybdenum complex, $\text{trans-[FMo(NNCHCHCH}_2\text{CH}_3\text{)(Ph}_2\text{PCH}_2\text{CH}_2\text{PPH}_2\text{)}_2\text{][BPh}_4]$, immobilized in the hybrid matrix. The host matrix was obtained by the reaction of an amino substituted polyethyleneglycol (Jeffamine, ED-600) and a substituted siloxane 1-[3-(trimethoxysilyl)propyl]urea.

The characterization of the complex and the final materials by spectroscopic (FTIR, UV/Vis, NMR), surface analysis (DRX, XPS) and thermal (DSC) techniques shows the evidence of immobilization of molybdenum complex in the hybrid matrix.

**970 - Mass spectroscopic characterization of MOD precursors of
 $\text{SrBi}_2\text{Ta}_2\text{O}_9$**

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$\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) is a well studied ferroelectric compound due to its excellent properties, namely high fatigue endurance and low leakage current, that allow it potential application as thin film for memory devices, namely Non Volatile Ferroelectric Random Access Memories (NVFRAMs). The Metalorganic Decomposition (MOD) of alkoxides and/or carboxilates is a widely used technique for the synthesis of several complex oxides including the above-mentioned compound. Despite the enormous importance of this synthetic method for these perovskite oxides, there are a few studies on the characterization of the chemical species formed at different steps of the reaction of the starting reagents. This work reports a mass spectroscopic study of the equilibrium at different stages of the reaction of bismuth ethylhexanoate, strontium ethoxide, tantalum ethoxide, acetic acid and/or ethylhexanoic acid. The results obtained in this study will be used to discuss the existing correlations between these chemical intermediate species and the properties of the obtained SBT thin film, namely the existing crystalline phases and its microstructure.

971 - Investigation of $x\text{Al}_2\text{O}_3\cdot(100-x)\text{SiO}_2$ ($x=2,3,4,6$, and 8) samples structure

Maria Gracinda Ferreira da Silva, Portugal

^{27}Al magic angle spinning nuclear magnetic resonance (^{27}Al MAS NMR), X-diffraction (XRD) and scanning electron microscopy (SEM) were used to characterise the structural evolution, with the heat-treatment temperature, of aluminosilicate samples prepared by the sol-gel method. Samples of the binary composition $x\text{Al}_2\text{O}_3\cdot(100-x)\text{SiO}_2$ ($x=2,3,4,6$, and 8) were prepared. At 120°C a great amount of aluminium is in tetrahedral sites, but with the increasing of the samples heat-treatment the amount of aluminium in octahedral sites increases. However, the samples at 800°C show crystallization and the NMR spectra suffer a notable change.

972 - Progress towards Increasing the Laser Induced Damage Threshold (LIDT) of 'Pick off' Mirrors used in the Multipass Configuration of the Helen Laser at Awe by the Deposition of Sol-Gel Protective Layers

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J E Andrew, United States

J C Watson, United Kingdom

Pick off mirrors are small hard coated dielectric mirrors situated in the spatial filters of the HELEN laser. They are essential components as they allow the multipassing of the laser beam through the amplifiers. Currently due to locally induced turbulence in the amplifiers to prevent stratification of the cooling gas the laser is restricted to a fluence of 15J/cm^2 as this turbulence induces localised focusing of the laser beam. At higher intensities the mirror begins to damage. This paper reports on attempts to overcoat these mirrors with a number of different sol-gel thin film coatings. The coatings individually have higher laser damage thresholds than the bare mirror and thus depositing them on the mirror could at best act as a protective layer or at worst act as a sacrificial layer thus protecting the more expensive mirror underneath. Alternating high/low refractive index materials derived from sol-gel processing deposited at the $\frac{1}{4}$ wave optical thickness were selected as potential candidates along with multilayers of single materials. The main low index component of the sol-gel coatings was base catalysed silica and a number of different high index transition metal oxides were used as the high index components. Results are presented for the suitability of these different materials from stability and coating uniformity aspect. Issues associated with coating such a small operational mirror, the subsequent vacuum conditioning and the overall LIDT of the coated mirror are also addressed.

973 - Photoluminescence of Sol-Gel Hybrid Films Doped with Erbium Tris 8-Hydroxyquinoline

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Development of planar-type optical amplifier is required for the complete building of the ultra-high speed network. Although the planar waveguide amplifier has been studied in many ways, the high concentration of Er^{3+} ions restricts the performance of planar optical waveguide due to concentration quenching in silica-based planar optical amplifiers. Recently, there are many studies on polymer materials doped with Er^{3+} ions in the forms of complex, which can prevent clustering of Er^{3+} ions and change the pumping wavelength. However, the polymer materials doped with Er complex shows poor optical and thermal properties. The sol-gel hybrid materials are composed of inorganic and organic components, which enables the incorporation of both inorganic and organic dopants with relatively high thermal stability. Therefore, the sol-gel hybrid material can be a potential candidate for planar optical amplifiers. In this work, the sol-gel hybrid material which has low loss near $1.5\mu\text{m}$ wavelength was prepared. Erbium tris 8-hydroxyquinoline (ErQ) was selected to incorporate into the hybrid matrix because the aromatic ligand of ErQ can be expected to absorb the pump energy and transfer to adjacent Er^{3+} ions. The sol-gel hybrid films doped with ErQ shows a clear photoluminescence at $1.5\mu\text{m}$ when they are pumped by 477nm light of Ar^+ laser which is not a resonant wavelength of Er^{3+} ions. Excitation mechanism is investigated by photoluminescence excitation measurement using the different wavelengths of Ar^+ laser to determine an effective wavelength for optical pumping. Photoluminescence and microstructural changes are also examined with UV illumination. The prepared sol-gel hybrid films doped with ErQ show no temperature quenching and very wide bandwidth of 73nm . Such a broad spectrum enables a wide gain bandwidth for optical amplification with WDM technology.

974 - Sol-Gel Fabrication of High Quality Photomask Substrates

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Satyabrata RayChaudhuri, United States

Synthetic silica photomask substrates are currently manufactured by cutting, grinding, and polishing glass boules prepared using a flame hydrolysis process. YTC America is developing an alternative technique, based on sol-gel processing, to fabricate high quality substrates. This new technology allows near net shape fabrication of synthetic silica monoliths, thus eliminating the need for cutting and grinding. The complex relationship between glass properties and process parameters in the formulation, drying, and sintering steps has been determined, and a repeatable process has been established. These substrates meet all SEMI specifications for ULTE hard surface photomask substrates for 248 nm lithography. The technology may also be extended to 193 nm and 157 nm photomask substrates. This sol-gel-based process may represent a unique and cost-effective alternative for manufacturing photomask substrates for deep UV lithography.

975 - Modification of Thermo-Optic Characteristics of Inorganic-Organic Hybrid Materials for Athermal Waveguide Application

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Thermo-optic effect is defined as the temperature dependence of a material's refractive index (dn/dT). In the design of the optical waveguide devices, the thermo-optic properties of the waveguide material are of considerable importance for modulating the light and the ability to control the values of dn/dT over a wide range is attractive for attempting to produce an effective thermo-optic waveguide device. However, current major waveguide materials, silica and an optical polymer, have so limited variable range of the dn/dT that the applications in thermo-optic waveguide are restricted. Recently, a sol-gel derived inorganic-organic hybrid material (HYBRIMER) composed of silica and an organic material is receiving attention as a promising candidate for a waveguide material that might be used to replace silica and polymer.

In this study, the effect of structural change in the HYBRIMER on the variation of dn/dT has been investigated and manipulation of the structure is proposed as a method for controlling the dn/dT in the HYBRIMER films. The value of dn/dT negatively increases with increasing molecular weight of the organic modifier or with an increase in the proportion of modifier in the sample. On the other hand, the dn/dT decreases with an increase in the degree of organic photo-polymerization. In addition, the value of dn/dT dramatically decreases as several kinds of the heterometallic oxide network were added in the HYBRIMER films. From these results, it can be seen that the value of dn/dT in these films can be varied over a wide range (the order of between $10^{-5}/^{\circ}\text{C}$ and $10^{-4}/^{\circ}\text{C}$) by changing the structure in the HYBRIMER films. Finally, athermal waveguide devices, where the optical path is unaffected by ambient temperature variations, was fabricated using a hybrid waveguide structure consisting of a HYBRIMER overladding layer (with specific values of refractive index and dn/dT) exhibiting specific properties that compensate for any temperature induced refractive index changes of the silica core.

976 - Sol-Gel Processed Functional Nanosized TiO₂ - Based Films for Photocatalysts and Other Applications

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Titania sol-gel layers are widely studied for optical applications, solar cell and photocatalysts. The main goal of this work is to synthesize the stable transparent, mechanically resistant functional TiO₂-based coatings perspective for ecological photocatalysis, non-linear optics as well as for abrasive-resistant decorative coatings. We synthesized porous titania and titania-based films by sol-gel route in presence CTAB and PEG. The photocatalytic characteristics of nanostructured titania, iron-titania and zirconium-titania films were compared with commercial P-25 TiO₂ in the film form. These sol-gel materials were characterized by UV-Vis, XRD, ellipsometry and photocatalytic methods.

1. Titania and iron/titania coatings. Wet chemical synthesis and photocatalytic characteristics of titania and Fe(III)-containing TiO₂ layers have been studied for the goal of environmental photocatalysis of mineralisation of chloro-organic compounds. Films with thickness from 200 nm to 600 nm were prepared using titanium alcooxide and dry FeCl₃ by dip-coating method.

2. Zirconia-titania coatings. Crack-free abrasion-resistant ZrO₂/TiO₂ transparent films with thickness of up to 600 nm on the glass substrates were prepared by the sol-gel process from the Zr and Ti alcoxides by using a chelating agent such as acetylacetone. The films are stable in 4N KOH and concentrated H₂SO₄. The films with ZrO₂/TiO₂ ratio 30%:70% are high active in the photoreduction of toxic Cr(VI) ions to non-toxic Cr(III) ions. 3. Titania porous films for non-linear optic (NLO) application. Reversible photoinduced variation of absorption and refraction have been studied with subbandgap excitation in picosecond range. Efficient cubic NLO susceptibility is 10⁻⁵ - 10⁻⁷ esu and it is sensitive to preparation technique. The efficient NLO response can be explained due to the resonant excitation of the deep defect states in the gap and it correlates with photocatalytic activity of the films.

977 - The Effect of Copper Doping on Photo-induced Reaction of Titania Photocatalytic Film

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Effect of transition metal doping on photocatalytic activity of titania has been studied by many researchers. Most of these experimental results show that the doped transition metal acts as a recombination center which traps generated electron-hole pairs. Due to it, the transition metal doping usually deteriorates photocatalytic activity. However several reports show the increased photocatalytic activity with transition metal doping. We also have reported that the Cu doping to porous titania increased photocatalytic decomposition rate of CH_3SH . The different effects reported suggest unknown mechanism to control photocatalytic process besides acting as recombination center.

In this paper, we examined the effect of the heat treatment on photo-induced reaction of titania thin film doped with Cu. Ti-isopropoxide solution was coated on the soda-lime glass with SiO_2 pre-coat layer. The first heat treatment at 500°C was conducted on coated samples to obtain the crystallized titania film. Solution of Cu ion has been coated on prepared titania and heat treated again at various temperatures. Although, the decomposability of oleic acid was increased with Cu coating, the second heat treatment decreased the photocatalytic decomposability. On the other hands, Cu doping decreases hydrophilic conversion rate in the both cases with and without the second heat treatment. The comparison of the photocatalytic activity and photo-induced hydrophilicity of Cu doped samples suggests that the existence of Cu on the titania surface has increased electron transfer resulting in the increase of oxidation rate, however when Cu is introduced into titania lattice, it acts as electron-hole trapping center.

We have also fabricated samples with thin Cu doping layer inside titania film by multiple coating procedure. Utilizing these fabricated samples, we examined the relation between the effect of the location of Cu layer and the effect of thickness of pure titania film on the photocatalytic reaction rate. The result of the comparison suggests that even when the concentration of Cu doping is dilute, the trapping efficiency is high enough to recombine all electron and hole pairs which pass through it.

978 - Conductive Sol-Gel Emulsion for Preparing Surface for Powder Coating

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A conductive sol-gel emulsion is formulated for surface treatment of low-conductive objects, such as MDF wood and ABS plastics. This sol-gel coating renders the object amenable to powder coating or other treatments that require the surface of the object to be conductive. The sol-gel coating generates a high abrasion resistant silicate film on a relative soft substrate (wood or plastics) via hydrolysis and polycondensation reactions. The hard xerogel layer can be polished to prepare a mirror-finish flat surface for a high quality powder coating.

The powder coating method is generally performed on objects having good heat resistance and a conductive surface. However, where the surface of an object is non-conductive, implying that object cannot be grounded or supplied with a charge of an opposite polarity to the charge of the powder, difficulties arise with enabling the powder to adhere to the surface of the object during the time between spraying and heating the powder to the melting temperature. The current practice uses a conductive vanish or creates a conductive moisture layer on the non-conductive surface for a powder coating application, with numerous disadvantages.

A solvent-free conductive sol-gel emulsion for surface treatment of low-conductivity surfaces is a formulation of an emulsified organofunctional silane solution. The solution forms a stable and compatible emulsion with water dispersion of electrical conducting particles. The sol-gel emulsion creates a thin, uniform, and dense film that adheres extremely well to the surface of the object being treated. The film provides a uniformly conductive surface for attracting powder particles evenly to the part, and a thermally stable sol-gel (a flame retardant barrier) that seals a thermal sensitive surface (such as MDF or ABS) while limiting the moisture loss of the object during subsequent powder coating applications. The results on formulations, applications, and finishing products will be illustrated.

979 - Upconverting Nanophosphors by Sol-Emulsion-Gel Technique

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Towards the end of the 20th century and into new millennium, there has been a renaissance in the study of rare-earth doped materials for photonic applications. Chemical synthesis through the sol-emulsion-gel method is an excellent route for the preparation of upconverting nanophosphors for photonic applications. The effects of the erbium concentration, crystal hosts and co dopant on the up converted emission of Er³⁺ in oxide nanocrystals are reported. The presence of co-dopant (Yb³⁺) also increases the overall intensity of the up converted emission. A cw diode laser at 975 nm was used as a pump source for resonant sequential excitation of the 4I11/2 and 4F7/2 levels. Green and red up conversion emission at 550 nm and 670 nm were observed from these oxide nanocrystals with 975 nm excitation. The overall intensity decreases with an increasing concentration of erbium in different hosts. In up conversion emission intensity for the same concentration of Er ions, BaTiO₃ host showed a highest up conversion emission intensity than that of ZrO₂ and TiO₂ host. We observed the overall up conversion luminescence intensity depends on crystal structure and particles size. The emission spectra and the pump intensity dependence of the luminescence intensities confirm that up converted emission in these materials is due to two-photon excited-state absorption (ESA) process

980 - Sol-Gel Coatings of Metal Oxides on Nano TiO₂ electrodes in Dye-Sensitised Solar Cells

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A sol-gel process has been used to deposit a thin film of ZrO₂ was coated on TiO₂ electrodes, for applications in dye-sensitised solar cells (DSSCs). The performance of the cells was improved when the thin layer of ZrO₂ had been deposited on the commercial nanocrystalline TiO₂ used to fabricate the electrodes. The overall conversion efficiency increased up to 2.3%. The thin ZrO₂ film forms a barrier for charge recombination without significantly affecting electron injection into the semiconductor. It was also found that, after a certain ZrO₂ thickness was reached, the efficiency dropped with further increase in thickness. This could either be due to a poorer ability of ZrO₂ to accept electrons from the dye compared to TiO₂, resulting in a decrease in the photojected electron density, or the electrons were not able to cascade into the TiO₂ and relied on surface transport to permeate thereby increasing back-electron transfer to the dye or electroactive species in the electrolyte. To further investigate this barrier layer effect, a conductive layer of ZnO was also coated onto the TiO₂ electrode. Again thick coats of ZnO were found to severely diminish the cells performance, but in this case this may be due to a lower conduction band energy of ZnO compared to that of TiO₂. However, with a thin ZnO coating on the surface of the TiO₂ electrode the conversion efficiency increased. This correlated with an increase in the amount of dye that was chemisorbed on the ZnO film.

981 - Incorporation of Tris (di-phenyl-phenanthroline) Ruthenium (II) Complex in Dense Silica Microspheres and their use in a Film-Membrane as a Carbon Dioxide Sensor.

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Colette McDonagh, National Centre for Sensor Research, Ireland

The preparation of monodisperse spherical silica particles, via the hydrolysis and condensation of tetraethoxysilane (TEOS), has attracted much research interest in recent years due to their application in ceramics, semiconductors, supporters for catalysers, chromatographics absorbents, etc. Even though applications of these materials are currently being extensively explored, their potential application was increased by the introduction of inorganic complex with functional properties. Silica glasses doped with photosensitive fluorophores have been prepared by the traditional sol-gel method for such applications as optical sensors, photocatalysts, dye lasers and photoelectrodes for solar cells. In this paper we report the incorporation tris(diphenyl-phenanthroline) ruthenium (II) complex in dense silica microspheres. Two synthetic methods were used to prepare inorganic doped silica sol-gels and compared. Method I involved a hydrolysis-condensation reaction of TEOS in the presence of the analyte sensitive reagent containing Ru(dpp)₃²⁺ under acidic condition. Method II involved the encapsulation of the tris(diphenyl-phenanthroline) ruthenium (II) complex and the immobilisation of the functional molecule in the pores of calcined silica spheres. Both methods were used to prepare silica and silica doped with tris(diphenyl-phenanthroline) ruthenium (II).

The doped particles were characterized by different spectroscopic techniques, nitrogen sorption and scanning electron microscopy (SEM). The final particles were also used in the preparation of a carbon dioxide sensing membrane.

982 - The preparation and electrical properties of SrTiO₃-based Capacitor-varistor double function ceramics

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The SrTiO₃ powders were prepared in the Sol-Gel process and solid-state reaction method. The effect of gel conditions on the quality of gels was investigated in detail; the effect of calcining temperature and the mole ratio of Ti/Sr on the SrTiO₃ powders were investigated by the X-ray diffraction (XRD) analysis too. The electrical properties and the micrographs of SrTiO₃-based ceramics prepared by the Sol-Gel process were compared with that of ceramics made from the solid-state reaction method. The experimental results show that the effect of the purity of SrTiO₃ powders on the electrical properties of ceramics is very notable. The properties of ceramics prepared by the Sol-Gel process is prior to all others from the solid-state reaction.

983 - Sol-Gel Technology in Gas Chromatography

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Gas chromatography (GC) is a powerful analytical separation technique for volatile organic compounds. The volatilised sample is introduced into a capillary column and is swept by a stream of inert gas, typically helium, hydrogen or nitrogen. Sample components separate as the sample passes through the column by boiling point or by the degree of specific interactions between the sample and the functional groups of the polymeric stationary phase which is coated on the inner walls of capillary columns.

In the past, a variety of stationary phase materials have been used to perform GC separations. Polysiloxane based stationary phases have been widely used in capillary GC columns due to their excellent coating properties and ability to separate a variety of organic substances. Lately, a number of stationary phases based on sol-gel materials were developed at SGE to produce capillary columns that are inherently inert, thermally stable with very low bleed levels and having excellent partitioning capabilities of either non-polar or polar columns. Also, due to the chemical nature of the sol-gel material that is covalently bonded to the surface of the fused silica, the maximum operating temperatures have been significantly increased.

In this paper, the benefits of the use of sol-gel materials over conventional stationary phases will be demonstrated on a number of chromatograms. Data will be presented showing comparison of bleed levels as well as a wide range of analyses normally not able to be achieved on conventional columns due to their lesser thermal stability and thus, maximum operating temperatures.

AUTHORS INDEX

A

- Abe, Yoshimoto 78, 130
Abe, Yuu 243
Aegerter, Michel A 90, 95, 232
Aguilar, D 252
Aguilar, Gerardo González 339
Aguirre, G 252
Ahmad, Zahoor 76, 125, 169, 193
Ahn, Bok Yeop 316
Ahn, Kwang-Soon 105
Akhundzhanov, KA 185
Akkari, R 250
Al-Kandari, Shaikhah 76
Alderete, Joel 324
Ali, A M 76
Almeida, Rui M 101, 264
Alonso, Bruno 145
Alvarado, J 252
Alvarez, Myrna 313
Alves, Eduardo 264
Aly, Z. 86
Amaral, Thais G 328
Amaral, Victor 119
Amiresetty, Venkateswara Rao 297
Andrew, J E 341
Anschütz, D. 54
Anselmann, Ralf 126
Aparicio, Mario 136
Arai, Yasuhiko 160
Arai, Yusuke 97
Argue, Steve 291
Ariga, Katsuhiko 80
Arimitsu, Koji 78, 130
Arkhireeva, Anna 66
Armelao, Lidia 174
Armellini, Cristina 307
Arriola, G 252
Ashibe, Naoki 92
Asomoza, Maximiliano 309, 311
Auh, Keum-Ho 231
Avilés C, María de L 180
Avnir, David 57, 111, 135
Awano, Masanobu 329

354

Azomosa, Maximiliano 312**B**

- Baba, Mohamed 214
Babonneau, Florence 46, 275, 276
Badheka, Rita 158, 236
Bae, Byeong-Soo 56, 146, 220, 342, 344
Bae, Jae Young 220
Baldeck, Patrice 298
Balek, Vladimir 230
Ball, Graham E 107, 182, 259
Barbé, Christophe 197, 198, 199, 200, 201, 202
Bartlett, John 197, 198, 199, 200, 201, 241, 280
Basch, Angelika 161
Bazin, Nick J 341
Belleville, Philippe 53
Ben-Nissan, Besim 195, 196, 270, 271
Benes, Nieck E 245, 256
Berkova, Daniela 215
Berni, A. 54
Bernstorff, Sigrid 62
Bersani, Danilo 295
Besanger, Travis R 226
Bescher, Eric 203
Bied, Catherine 191
Birnie, Dunbar P 88
Bizzari, A. 332
Blackford, Mark 200
Blank, Dave HA 94, 247
Blum, Jochanan 57
Blum, Raphaël 276
Boev, Victor I 188
Bogatyrov, Viktor 308
Boiko, Andrej 308
Bokhimi, Xim 311
Borysenko, Mykola 308
Böttcher, Horst 113, 268
Bouazaoui, Mohamed 317
Bounor-Legaré, Véronique 71, 181
Boury, Bruno 77

Bowe, Philip 118, 350
Boy, Philippe 53
Brennan, John D 106, 110, 225, 226, 277
Bright, Frank V 118
Brinker, C. Jeffrey 44
Brinkley, Jason F 115
Briois, Valérie 119, 172
Brito, Giancarlo E S 255, 263, 328
Brook, Michael A 110, 277
Brungs, Michael P 148
Brusatin, Giovanna 50, 184, 326
Bubendorfer, Andrea J 153, 325
Buljan, Antonio 324
Bullen, Craig 99
Bultzingslowen, C Von 350
Burleigh, M.C 279
Burmistrova, P V 206
Bush, Alexandra J 199
Buso, Dario 302

C

Cabrera, Karin 293
Calleja, Gérard 197, 198, 201
Caminiti, Ruggero 234
Campbell, Joseph M 265
Campbell, Lilian J 153, 325
Campero, Antonio 180
Camus, Lydie 275
Cantalini, Carlo 302
Capecchi, imone 125
Capoen, Bruno 317
Carlos, Luis D 98, 119, 170
Carré, Christiane 75
Caruso, Rachel A 87
Casalboni, Mauro 326, 331
Cassidy, David J 197, 198, 202
Castillo, Salvador 281, 310
Casula, Maria F 150
Catlin, Rachael M 269
Cauzzi, Daniele 320
Cecilio, Andreia A 171
Cerneaux, Sophie A 117

Cervini, Raoul 349
Cha, Yong-Youp 140
Challa, Santhosh 109
Chan, Jerry CC 330
Chaneac, Corinne 137
Chang, Jeong Ho 83
Chaplin, Rodney P 148
Chassagneux, Fernand 224
Chaudhuri, Ray 127
Chen, Li-Fang 281
Chen, Vicki 259
Chen, Yang 110, 277
Cheng, Yi-Bing 349
Cheong, Chul-Won 140
Chernev, Georgi E 244
Chiasera, Alessandro 101, 307
Chiavacci, Leila A 119, 172
Chomat, Miroslav 116
Choudhury, Namita Roy 67, 161
Chowdhury, Sankhanilay Roy 94
Chuiko, Aleksej A 72, 185, 274, 308, 320, 345
Clarke, Stephen 258
Colbern, Steven 343
Collins, Ian R 114
Constantopoulos, Kristina 258
Correia Vilela, Isabel C 170
Corrias, Anna 150
Corriu, Robert J. P. 77
Costa, M Elisabete V 339
Courtney, Lee 114
Coville, Neil J 84
Craievich, Aldo F 119, 170
Crisan, Maria 246, 260
Cristea, Dana 260
Croutxé-Barghorn, Céline 75

D

D'Epifanio, Alessandra 272
Dahmouche, Karim 119, 170, 335
Dai, Sheng 279
Dave, Bakul C 55, 218
David, Laurent 71, 181

Davis, Sean A 85
Da Costa, Sandra 137
Degeratu, Stefania 260
Demnerova, Katerina 108
Deng, Zhongsheng 261
Deshpande, Atul S 87
Desroches, Cédric 298
Devaraj, Yogeeshwari 218
De Matteis, Fabio 331
de Jongh, Petra E 91
de los Reyes, Jose A 337
De Matteis, Fabio 326
de Namor, Angela F D 114
De Zea Bermudez, Verónica 98, 170
Dhali, Shirshak K 218
Diniz da Costa, Joao C 221, 269
Dirè, Sandra 184, 307
Diso, Daniela 120
Di Vona, Maria L 184, 272
Djambaski, Peter R 244
Dobreva, Elena P 244
Dong, Jin-Keun 140
Dong, Wu 133
Drabarek, E. 86
Drozdova, Irina A 165
Dujardin, Christophe 292
Dunn, Bruce 45
Duran, Alicia 136
Dutenhefner, Patricia AR 178

E

Eberhardt, Alan W 271
Eckert, Hellmut 330
Ekstrand, Åsa B 175, 249
Emandi, Anca 266
Eremenko, Anna M 345
Escobar Galindo, R 247
Essayem, N 250
Etteyeb, Noureddine 157
Evain, Michel 145

F

Falcaro, Paolo 234

356

Falqui, Andrea 150
Fang, Sonic 327, 347
Fantini, Márcia C A 263
Farinha, José P 186
Fernandes, Helena V 244
Fernandes de Farias, Robson 142
Ferrari, Maurizio 101, 184, 307
Ferreira, Fabio F 263
Ferreira, Rute A Sá 98
Ferreira da Silva, Maria Gracinda 340
Fessi, Shemseddine 179
Fidalgo, Alexandra M 186
Fiedler, Dirk 113
Finnie, Kim S 197, 200, 241, 280
Fireman-Shoresh, Sharon 57
Fisher, Mark 258
Fonseca, A M 338
Foster, L.J.R. 280
Frenkel, Hagit 57
Frischat, Günther H 330, 334
Fu, Lianshe 98
Fujihara, Shinobu 210, 296
Fujii, akayuki 278
Fujimoto, Kenjiro 128
Fujimoto, Yasuhiro 156

G

Ganatra, Vinod R 336
Ganguli, Rahul 127, 343
Garcia, Jaime 309, 312
García-Sánchez, Miguel A 180
Gartner, Mariuca 246, 260
Gavrila, Raluca 246
Gayvoronskii, Vladimir 345
Gelamn, Faina 57
Gerda, Vasily I 254
Getton, Fred 235
Gharbi, Néji 157
Ghorbel, Abdelhamid 159, 250, 318, 319, 321
Gindre, Marcel 64
Giubelan, Maria 79
Gleason, Matt 343

Gnyba, Marcin 122
Goletto, Valérie 276
Gomes, Jesus M 188
Gomez, J 252
Gomez, Ricardo 309, 311, 312, 313
Gonçalves, Maria C 170
Gonsalves, Rogéria R 328
González-Arevalo, Martha P 180
Gouédard, G 64
Grange, Paul 321
Gray, Graham M 227
Griesmar, P 64
Griffith, C.S. 86
Gross, Silvia 161, 174
Guglielmi, Massimo 234, 302
Guillaudeu, Steve J 69
Gunawidjaja, Philips N 287
Gunji, Takahiro 78, 130
Guo, Kui 110
Guo, Yanzhi 262
Gusevskaya, Helena V 178
Gutmaher, Andreja 96
Guzman, Guillaume 95

H

Habsuda, Jana 352
Haddad, Paula S 263
Hah, Hoe Jin 151, 154, 155, 162
Hamasaki, Ryo 80
Hammouda, Lassaad Ben 318
Han, Dong Il 155
Han, Seung Hoon 162
Harrell, Todd M 267
Haryadi, Haryadi 259
Hashimoto, Kazuhito 166, 167, 243
Hashizume, Mineo 80, 134
Hay, John N 66, 227
Hayakawa, Satoshi 58, 240
Hayer, Milos 215
Hellmold, Peter 334
Helsch, Gundula 330
Hench, Larry L 317
Hernandez, Javier 310

Higgins, Clare 118
Hilarius, Volker 126
Hirashima, Hiroshi 230, 233
Holden, Peter J 241, 280
Hong, Lan-Young 149
Hong, Young Jun 148
Honma, Itaru 257
Hook, Jim 259
Hosono, Eiji 210
Hovnanian, Nadine 117
Hoyer, Lars P 330
Hreniak, Agnieszka 284
Hreniak, Dariusz 284, 285
Hu, Xiankui 218
Huang, Yaodong 261
Hubaut, Robert 319
Huebert, Thomas 211
Hull, Robert 267
Hüsing, Nicola 62, 223
Hussain, Hazrat 169
Hwang, Duck Kun 217
Hwang, Soonchul 315
Hwang, Young Young 168

I

Ignat, M. 202
Ikari, Ken-ichi 81
Ikeda, Atsushi 134
Ikeda, Yuko 190
Ilharco, Laura M 186
Ilieva, Dora 109
Ilyin, Volodymyr G 254
Imai, Hiroaki 81, 230, 233
Innocenzi, Plinio 50, 184, 192, 234, 326
Inoue, Hiroaki 134
Ishigaki, Tadashi 288
Ishikawa, Yuta 92
Ishizawa, Hitoshi 238
Ismail, Adel A 286
Isobe, Tetsuhiko 144
Ito, Seishiro 239
Iwamoto, Yuji 77
Iwasaki, Mitsunobu 85, 239

J

Jacques, Sylvain 224
Jansson, Kjell 65
Jansson, Kjell B 294
Jaroniec, Mietek 72
Jayanti, Radhakrishna 177
Jeng, De-Yin 127
Jeon, Byung Jun 151
Jeon, Myungchul 315
Jiguet, Sébastien 181
Jilavi, M. 54
Jitianu, Andrei 79
Johansson, Leena-Sisko 265
Jolivet, Jean-Pierre 137
Jung, Chan Yoon 162
Jung, Il Nam 303
Jung, Ji-In 220
Junping, Li 133

K

Kabaivanova, Liudmila V 244
Kabulov, B D 185
Kadiyska, Elena D 244
Kalsi, S H 283
Kamat, R V 323
Kameda, Yoshihiro 190
Kaminski, Renata C 173
Kang, Dong Jun 146
Kang, Eun-Seok 344
Kannangara, Kamali GS 195, 196
Kartini, Indriana 221
Kasik, Ivan 116, 215
Katagiri, Kiyofumi 80
Katayama, Shingo 329
Kawaguti, Carla A 172
Kawazu, Mitsuhiro 138
Kemmitt, Tim 153, 325
Keränen, Mikko S 122
Kessler, Vadim G 47, 132, 298
Khelifi, Leila 159
Khimich, Galina N 164
Khimich, Nikolay N 163, 164, 165
Kikuchi, Jun-ichi 80, 134

358

Kim, Bum-Suk 231
Kim, Chang-Yeoul 105, 231
Kim, Dong-Pyo 149
Kim, Hae Hong 168
Kim, Hong R 139
Kim, Hyun Jong 217
Kim, Insoo 141
Kim, Jeong Hyun 303
Kim, Jin Gyun 187
Kim, Jong-Hyun 219
Kim, Joo Hyun 316
Kim, Jung Soo 154
Kim, Kang-Jin 219
Kim, Kwang Soo 344
Kim, Kyung Ja 83
Kim, Sunuk 315
Kim, Sun Joo 146
Kim, Taesam 115
Kim, Woo Soo 344
Kim, Yong Kuk 187
Kim, Yoo Hang 187
Kimura, Toshio 210, 296
Kimura, Yusuke 152
Kinowski, Christophe 317
Kishino, Maki 239
Kitta, Seiki 296
Klapdohr, Simone 289
Kleinschek, Karin Stana 96
Klyszcz, Andreas 211
Knittel, Dierk 268
Knott, R B 280
Kogure, Toshihiro 89
Kohiki, Shigemi 147
Kololuoma, Terho K 122, 265
Kong, Linggen 199, 200
Koo, Sang Man 151, 154, 155, 162
Koplick, Andrew 124
Koptelova, Larisa A 165
Korobeinik, Alina V 185
Kovalenko, Volodymyr V 254
Kowada, Yoshiyuki 61
Kozuka, Hiromitsu 92, 222, 229
Kritikos, Mikael 175, 176
Kroke, Edwin 77

Kruidhof, Henk 245
Krzyzak, Marta 334
Kubo, Tomoko 229
Kumar, N 336
Kunarti, Eko S 107, 182, 183
Kuncova, Gabriela 108
Kuroda, Kazuyuki 156
Kursawe, Monika 126
Kurz, Alexander 232
Kuwabara, Makoto 147

L

Lalot, Thierry 69
Latella, Bruno A 197, 198, 202
Launay, Beatrice 118, 350
Layh, Marcus 84
Leadley, Jason 306
Lee, CK 141
Lee, Hae-Hyoung 140
Lee, KH 141
Lee, Wan In 187
Leideborg, Michael 65, 175
LeLuyer, Cécile 248
Letoffe, Jean-Marie 224
Levchenko, Tatiana I 274
Le Calve, Stéphanie 145
Li, H. 202
Li, Haibin 282
Li, Xu 125
Liang, C.D 279
Licciulli, Antonio 120
Licoccia, Silvia 184, 192, 272
Lim, Jimin 269
Lim, Tae-Young 105, 231
Lin, Chhiu-Tsu 115, 327, 347
Lin, Zhongjie 212, 213
Lindén, Mika 48
Liu, Fangqin 194
Liu, Liying 103
Lobato, Zelia P 228
Lobnik, Aleksandra 96, 332
Long, Nick J 153, 325
Lopes, Cesar 298

Lopez, Tessy 252, 309, 311, 312, 313, 324
Lorenzi, Andrea 295
Lottici, Pier Paolo 295
Loy, Douglas A 74
Lu, G Q Max 52, 221, 269
Luca, V. 86
Luo, Xinshi 102, 314
Luther-Davies, Barry 102, 314

M

Maaninen, Arto 265
MacCraith, Brian D 59, 118, 350
MacGibbon, Rebecca M A 158
Mackenzie, J.D. 203
Maffezzoli, Alfonso 120
Mahiou, Rachid 93, 292
Mahltig, Boris 113, 268
Majid, Abdul 291
Malhotra, K L 204, 205
Manea, Elena 260
Mann, Stephen 85
Mansur, Herman S 228
Mansuy, Christelle 93, 292
Manzano, Miguel 66
Marani, Debora 272
Marino, Iari-Gabriel 295
Markovic, Elda 258
Marques, Ana C 101, 264
Martinez, L 64
Martinez, Yaminica 281
Martinho, José M 186
Martucci, Alessandro 99, 192, 302, 307
Marty, Olivier 248
Maruszewski, Krzysztof 284
Marx, Sharon 57
Massiot, Dominique 145
Masters, Helen J 66
Masuda, Masataka 346
Matejec, Vlastimil 116, 215
Matejka, Libor 70
Matisons, Jani G 73, 258

Matkovskii, Olexander K 72
Matoda, Tatsuo 89
Matsuda, Atsunori 89, 121, 242, 278
Matsuo, Shigeki 305
Mattarelli, Maurizio 307
Mazur, Piotr 285
Mazzer, Massimo 120
McDonagh, Colette 118, 350
McEvoy, Aisling 118, 350
Meghea, Aurelia 79
Meixner, Larry 127, 343
Melzak, K 64
Mennig, M. 54
Menzies, David 349
Meredith, Paul 221
Merlo, Vittorio 331
Messaddeq, Younes 237, 328
Michel, Alain 71, 181
Miele, Philippe 298
Miki, Takuro 144
Milev, Adriyan 195, 196, 270
Minami, Tsutomu 89, 121, 242, 278
Miranda Salvado, Isabel M 244, 290, 339
Misawa, Hiroaki 305
Mishina, E D 207
Misiewicz, Jan 284, 285
Mitchell, D.R.G. 86
Miyajima, Keita 152
Montagna, Maurizio 307
Montenero, Angelo 295
Montouillout, Yves 53
Montoya, Ascención 300
Montoya, Ascensión 281
Montoya, Jose A 337
Moran, Grainne M 107, 182, 183, 259
Moran-Piedra, Marina 281
Moran-Pineda, Florencia M 310
Moreau, Joël JE 51, 191, 273
Moreira, aria R 290
Morelhão, Sérgio L 328
Moreno, Albino 324
Morris, Mark 343
Moszner, Norbert 289

Motoyama, Izumi 238
Moussa, Noomen 321
Mrazek, Jan 116, 215
Mugnier, Jacques 248
Mukerjee, Sapan K 68, 177, 336
Mulvaney, Paul 99
Murata, Tsuyoshi 238

N

Nah, Yoon-Chae 105
Nahar-Borchert, Saifun 77
Nakajima, Akira 166, 167, 243
Nakajima, Takashi 288
Nakanishi, Kazuki 293
Nara, Masatoshi 138
Nava, Noel 189, 300
Navarrete, Juan 281, 313
Nedelec, Jean-Marie 93, 214, 292, 317
Neumann, Daniel 258
Neves, Isabel C 338
Newport, Robert J 212, 213, 287
Ni, Xingyuan 261, 262, 322
Nishio, Keishi 288
Nogami, Masayuki 60, 100, 282
Noma, Naoki 61, 216
Norris, Pamela M 267
Nunes, Natercia P 338
Nyk, Marcin 284, 285

O

Ochoa-Tapia, Jesús A 189, 300
Ogawa, Takumi 144
Oh, Sang-Chun 140
Oh, Young Kwon 149
Ohishi, Tomoji 301
Ohsaki, Hisashi 243, 346
Oliveira, P.W. 54
Orefice, Rodrigo L 228
Örtenblad, Marcus 298
Osaka, Akiyoshi 58, 240
Ota, Yurie 299
Ottosson, Jenny 55
Ou, Duan Li 125

Ould Ehssein, C. 64

P

- Pajonk, Gérard Michael 297
Palummo, Lucrezia 234
Pandey, Prem C 104, 143
Park, Gil Jae 100
Park, Il-Su 219
Park, Jang-Ung 146
Park, Jin-Young 105
Park, No-Hyung 105
Park, Oun-Ho 342
Parola, Stéphane 47, 132, 224, 248, 298
Paschina, Giorgio 150
Patra, Amitava 348
Pazik, Robert 285
Pecchi, Gina 324
Peleanu, Ion 79
Pelli, Stefano 307
Pérez, Gustavo 189, 300
Pérez-Pastenes, Hugo 189, 300
Peterlik, Herwig 62
Petrik, Irina 345
Pfaff, Gerhard 126
Phe, Bou-Huot 71
Pickup, David M 287
Picquart, M 252
Pillar, Rachel 258
Pinot, Jerome 342
Plyuto, Yuri V 274
Poddenezhny, Evgenij 308
Podrazky, Ondrej 108
Pohl, Annika 65, 251, 294
Post, Mike 291, 302
Powell, Katherine M 82
Power, Mary E 267
Predieri, Giovanni 320
Predoana, Luminita 246, 260, 266
Prosposito, Paolo 326, 331
Puetz, Joerg 95
Pulcinelli, Sandra H 171, 172, 173, 237, 335

Q

- Quintana, P 252

R

- Raab, Christina K 223
Radhakrishna, J 336
Radosevic, Tijana 256
Raerinne, Paavo 122
Rager, Marie-Noelle 145
Raileanu, Malina 79
Ramila, Ainhoa 275
Ramos, Ana 264
Rantala, Juha T 122, 265
Rao, Mukti S 218
Raschellà, Raffaella 295
Rashidova, S Sh 185
RayChaudhuri, Satyabrata 343
Rehman, Habibur 125, 193
Rheinberger, Volker 289
Ribeiro, Sidney J L 328
Ribot, François O 69, 137, 145
Riedel, Ralf 77
Righini, G C 307
Ripp, Steven 108
Rive, Alain 319
Rizzato, Alessandro P 237
Rodgers, L.E. 280
Rodriguez-Avendaño, Gerardo R 337
Roesky, Herbert W 72
Roest, Richard 112, 271
Romano, Valerio 304
Rosa, Maria E 186
Rosenholm, Jarl B. 48
Rozes, Laurence 145
Rupcich, Nicholas 225
Rushena, M. 86
Russo, Roberto 331
Ruzimuradov, O G 185

S

- Sacco, Ana P 335
Samec, N. 332

Samuneva, Bisserka I 244
Sanchez, Clément 53, 145
Santilli, Celso V 119, 170, 171, 172, 173, 237, 335
Saripalle, Suryanarayana 177, 336
Sarwar, Muhammad Ilyas 169
Sasaki, Takayoshi 128
Sathiyamoorthy, D 177, 336
Sato, Satoshi 123
Sayler, Gary S 108
Scharff, Jean-Pierre 224
Schattka, Jan H 87
Schmidt, H. 54
Schmidt, Helmut 193
Schmuhl, Riaan 94
Schollmeyer, Eckard 268
Schubert, Ulrich 49, 62, 161
Schuler, Thomas 90
Schutzmänn, Stefano 326, 331
Scurtu, Rares 246
Sebastianelli, Paolo 192
Sediri, Faouzi 157
Segawa, Hiroyo 160, 305
Seisenbaeva, Gulaim A 47, 132
Sekulic, J 247
Senguttuvan, D T 204, 205, 283
Seok, Sang Il 168, 316
Serfaty, S 64
Sermon, Paul A 114, 158, 235, 236, 306
Sertchook, Hanan 135
Sharada, K S 283
Sharp, Gerard 352
Shaw, Steve J 66
Shchukin, Dmitry G 87
Shen, Jun 261, 262, 322
Shibata, Shuichi 97, 152
Shimamura, Aki 211
Shimojima, Atsushi 156
Shimooka, Hirokazu 147
Shul, Yong Gun 217
Sigala, Catherine 224
Sigov, A S 206, 207, 208
Silva, Carlos J R 188, 338

362

Silva, Nuno JO 119, 170
Silva, Rui F 290
Silva, Victor T 171
Simon, George 258, 349
Sizemore, Charles A 327
Sizgek, Erden 148
Skokanova, Jana 116
Skyrabin, Igor 124
Slade, Robert CT 82
Smått, Jan-Henrik 48
Smirnova, Natalie P 345
Smith, Mark E 212, 213, 287
Sodesawa, Toshiaki 123
Sohn, KS 141
Song, Ki-Chang 140
Song, Qinghai 103
Soppera, Olivier 75
Sousa, Edesia MB 178, 253
Sousa, Ricardo G 253
Sowrey, Frank E 212, 213
Spiccia, Leone 349
Spijksma, Gerald I 245
Steunou, Nathalie 275
Strek, Wieslaw 284, 285
Sun, YuHan 209
Sun, Yuhan 131
Sung, JH 141
Sung, Yung-Eun 105
Surovtseva, Natalie 345
Suyal, Navin 125
Suzuki, Keisei 81

T

Tadanaga, Kiyoharu 89, 121, 242, 278
Taguchi, Akira 48
Takada, Kazunori 128
Takada, Yasuyuki 346
Takahashi, Ryoji 123
Takami, Kazuyuki 166, 167
Tanaka, Akira 238
Tanaka, Kei 222
Tartivel, Catherine 197, 198
Tatsumisago, Masahiro 89, 121, 242,

278

- Taylor, Anthony P 241
Telbiz, German M 254
ten Elshof, Andre 256
ten Elshof, JE 247
ten Elshof, Johan E 94
Thomson, S.J. 86
Tohge, Noboru 216
Tondello, Eugenio 174
Torma, Viktoria 62, 223
Torsello, Giovanni 120
Toury, Bérangère 276
Tran, Chieu D 109
Trautman, Rachael 199
Traversa, Enrico 192
Trettnak, W. 332
Trogl, Josef 108
Trombetta, Marcella 184
Tronc, Elisabeth 137
Tshavhungwe, Alufelwi M 84
Tsuchiya, Toshio 288
Tsujino, Toshifumi 138
Tsuru, Kanji 58, 240
Tulloc, Gavin 124
Tunney, Jim 291
Turrell, Sylvia 317
Tursiloadi, Silvester 233

U

- Um, Jae In 154
University, Ajou 139
Uray, G. 332

V

- Vago, Razi 270
Vaidya, Vijay N 68, 177, 323, 336
Vallet-Regi, Maria 275
Vankova, Radomira 108
Van den Berg, Albert 94
van Tilborg, Paul JA 91
Van Veen, A 247
Vasconcelos, Wander L 228
Vasil'ev, V A 207, 208

Veautier, Delphine 53

- Vellutini, Luc 191
Venzo, Alfonso 174
Verdenelli, Martine 224
Villanueva-Ibañez, Maricela 248
Vincent, Henri 224
Vittalrao, T V 336
Viveros, Tomas 337
Viveros, Tomás 189, 300
Völger, Wolfgang 77
Vorotilov, K A 206, 207, 208
Vozny, Volodymyr L 254

W

- Wang, Jin-An 281
Wang, Jue 261, 262, 322
Wang, Wencheng 103
Wang, Xuewen 194, 351
Ward, Neil I 82
Watanabe, Mamoru 128
Watanabe, Toshiya 166, 167, 243, 346
Watson, J C 341
Werndrup, Pia 47
West, Robert 130
Westin, Gunnar L 65, 175, 176, 249,
251, 294
White, Mark G 320
Wijk, Maria 251
Wilhelm, Bettina 304
Wondergem, Harry J 91
Wong Chi Man, Michel 51, 191, 273
Wu, Dong 131, 209
Wu, Guangming 261, 262, 322

X

- Xu, Lei 103
Xu, Qinghong 273
Xu, Yao 131

Y

- Yabuta, Takeshi 240
Yamada, Noriko 329

- Yamada, Takeo 257
Yamaguchi, Naoko 242
Yamazaki, Saori 216
Yang, Junsan 351
Yano, Tetsuji 97, 152
Yoshida, Hiroshi 121
Yoshida, Kazuaki 160
Yoshida, Naoya 243, 346
Yoshihara, Toshio 299
Younes, Mohamed Kadri 319
Yuhan, Sun 133
Yun, Hoseop 139
Yurchenko, Gabriel R 72
Yusuf, Miah Muhammed 230

Z

- Zabkowska-Waclawek, Maria 285
Zacharov, D N 206
Zaharescu, Maria M 79, 246, 260, 266
Zamora, Marcial 311
Zha, Congji 102, 314
Zhai, Chunxue 351
Zhai, ShangRu 209
Zhang, Long 330
Zhang, Z.T 279
Zhang, Zheng 110, 277
Zhang, Zhiyong 351
Zhao, Lili 194, 351
Zhigalina, O M 206
Zhou, Bin 261, 262, 322
Zhou, Haoshen 257
Zhukov, Anatoliy N 163
Zolkov, Chen 111
Zreiqat, Hala 112
Zub, Yuriy L 72, 185, 320
Zviagilskaya, Julia V 163





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