French-German Adsorption Conference

October 24 – 26th 2023

ECPM - Strasbourg

Program

Tuesday October 24th

13:30   *Welcome coffee break*

14:00 – 14:15   Opening remarks

14:15 : Liquid adsorption session [Chair: Andreas Seidel-Morgenstern]

14:15 – 15:00   **Gabriele Iffland (BASF SE)**
Industrial Applications of Liquid Phase Adsorption

15:00 – 15:20   **S. Gravelle**, Separation of water and ethanol mixtures by nanoporous organosilica; a molecular dynamics study

15:20 – 15:40   **J.W. Lee**, Double-Layer Simulated Moving Bed Chromatography for Ternary Separations: Langmuir Isotherms

15:40 – 16:00   **M. Fiedler,** A molecular dynamics approach to calculate protein adsorption data

16:00 – 16:20   *Coffee break*

16:20 : Characterization Science session [Chair: Vanessa Fierro]

16:20 – 16:40   **A. Galarneau,** Characterization of carbon monolith for wastewater treatment under flow

16:40 – 17:00   **C. Cuadrado Collados,** Quantitative Assessment of Hydrophilicity/Hydrophobicity in Mesoporous Silica by Combining Adsorption, Liquid Intrusion and Solid-State NMR spectroscopy

17:00 – 17:20   **O. Osta,** The impact of the pore wall hydrophobicity on the density of confined water: A combined nitrogen and water sorption study.

17:20 – 17:40   **M. Benamar,** Understanding the evolution of microporosity during hierarchization treatments of side pocket containing zeolites

17:40 – 18:00   **A. Kahlal,** Towards a DFT approach to Mechanical Properties in Nanoporous Materials

18:00 – 20:00   **Poster session**

Wednesday October 25th

08:40 – 09:25 **Carlos Nieto-Draghi (IFP Energies Nouvelles)**
A new class of descriptors for nanoporous materials and its applications to Classification and CO2 gas adsorption into zeolites

09:25 TSA – processes session [Chair: Christian Voss]

09:25 – 09:45 **B. Claessens,** Cation-exchanged LTA Zeolites for the Separation of Propane and Propylene

09:45 – 10:05 **M. Roehnert,** Binary adsorption of light hydrocarbons on zeolites at low temperatures

10:05 – 10:25 **I. Bezverkhy,** D_2/H_2 separation by adsorption in zeolites under cryogenic conditions: understanding the mechanism from experiment and molecular simulation

10:25 – 10:45 **N. Braunschweig,** Adsorption Chiller for Industrial Application

10:45 – 11:00 *Coffee break*

11:00 : Gas adsorption session [Chair: Igor Bezverkhyy]

11:00 - 11:20 **G. Salazar Duarte,** Hidden Adsorption – TSA in industrial gas processing plants

11:20 - 11:40 **M.T. Rozaini,** Shaping of HKUST-1 for CO_2 capture from biogas

11:40 - 12:00 **Y. Xiong,** Transition metal-exchanged GIS zeolites for CO_2/CH_4 separation

12:00 - 12:20 **N. Kofmann,** Direct Air Capture with solid amine sorbents: understanding the effect of water on process performance

12:20 – 13:20 *buffet*

13:20 - 14:40 *poster session*

14:40: CO_2 adsorption session [Chair: Frieder Dreisbach]

14:40 - 15:00 **R. Morales Ospino,** Chitosan-based activated carbons for CO_2 capture and biogas upgrading

15:00 - 15:20 **V. Selmert,** Electrospun Carbon Nanofibers as Selective Adsorbent for the Separation of CO_2

15:20 - 15:40 **R. Pinto,** Effective microwave-assisted regeneration of MOF/graphene oxide composites for post-combustion CO_2 capture

15:40 - 16:00 **D. Chakraborty,** MOFs as sustainable sorbents for CO_2 capture solutions

16:00 – 16:15 Coffee break

16:15 : Transport and kinetics session [Chair: Pascaline Pré]

16:15 -17:   **Christian Bläker (University of Duisburg-Essen)**
                  Methods for Characterization of Activated Carbons, Zeolites and Silica Gels"

17:00 – 17:20   **S. Dutta,** Mediation of water vapour transport in nanopores via salt solutions: thermodynamic and kinetic study

17:20 – 17:40   **R. Denoyel,** Impact of tortuosity and surface diffusion on transport through porous media

17:40 – 18:00   H.O. **Rubiera Landa,** An Efficient Implementation of Maxwell-Stefan Theory for Modeling Gas Separation Processes

18:00 – 18:20   A . **Grim,** Improvement of axial dispersion estimation in porous media for gases under pressure: Experimental and modelling methods

18:20 : End of the day

20:00 : Dinner

Thursday october 26th

09:00 : Industial characterization of adsorbents [Chair: Kristin Gleichmann]

09:00 – 09:45   **Cécile Lutz (Arkema)**
                          Zeolithes for sustainable development

09:45 – 10:05   **S. Ehrling (3P),** The limits of surface and pore volume characterization

10:05 – 10:25   **K. Peikert,** Unraveling Hierarchical Pore Networks Using Differential High-Resolution Mercury Intrusion

10:25 – 10:45   **V. Razafindramanana (SM),** Vapour Adsorption Studies of Porous Materials

10:45 – 11:00 *Coffee break*

11:00 : Liquid adsorption and recycling session [Chair: Renaud Denoyel]

11:00 - 11:20   **A. Seidel - Morgenstern,** Frontal analysis method for determining adsorption isotherms

11:20 – 11:40   **S. Asad,** New Carbamoyl Surface-modified ZrO2 Nanohybrids for selective Au Extraction from E-Waste

11:40 - 12:00   **C. Plait,** Mesoporous adsorbent for palladium recovery: synthesis, characterization and adsorption properties

12:00 – 12:10   **Closing remarks**

12:10 : lunch box and departure

Poster presentations

1. Partially Mg-exchanged GIS for optimized CO2/CH4 and CO2/N2 separations, J. Al Atrach, Y. Xiong, I. Golub, E. B. Clatworthy, R. Guillet-Nicolas, V. Valtchev

2. Evaluation of CO_2-CH_4 separation performances by clay-based adsorbent materials for biogas up-grading, A. El. Azrak, D. Grekov, L. Truche, P. Pré

3. Efficiency of metal-loaded zeolite Y in dye degradation, H. Benaouda, N. Bouchiba

4. Preparation and Characterization of ion-exchanged offretite zeolites with cooper, silver and zinc for antibacterial applications, I. Bouledjouad, D. Dari, F. Djafri, F. Bennabi

5. Immersion Microcalorimetry to study the sulfur-carbon interaction, M-V Coulet, L. Gourmelen, R. Denoyel

6. Hydrogen isotopes separation by selective adsorption on FAU zeolites: influence of Si/Al ratio and cationic composition, C. Coutier, C. Cabaud, J-P. Bellat, I. Bezverkhyy

7. Quantification of Water and Silanol Species on Various Silicas by IR Spectroscopy, J.P. Debs, A. Travert, F. Thibault-Starzyk, P. Ghesquière, N. Malicki

8. Radon adsorption in purely siliceous zeolites: Grand Canonical Monte Carlo simulation study, S. Lyu, I. Deroche, T. Örs, J.-L. Paillaud

9. Molecular Simulation of Acoustic Response of Fluid Adsorption in Nanoporous Materials, L. Didier, A. Sam, R. Venegas, B. Coasne

10. Measurements of thermal effects during intrusion and extrusion of electrolyte solutions in pure silica zeolites, C. Dirand, I. Bezverkhyy, J-P. Bellat

11. Determination of Microporous and Mesoporous Surface Areas and Volumes of Mesoporous Zeolites by Corrected t-plot Analysis, L. Desmurs, A. Galarneau, C. Cammarano, V. Hulea

12. Structural and Energetic Characterization of Silica-Alumina Gels, L. Gehrke, C. Bläker, C. Pasel, D. Bathen

13. Energy consumption of VSA carbon capture; from lab scale to a pilot plant, M. Gholami, J. F. M. Denayer

14. Gas by Molecular Separation Trapdoor mechanism in multicationic zeolites, C. Grimaud, A. Tuel, C. Daniel, D. Farrusseng

15. Enhancing gas adsorption through HKUST-1 hybridization with activated carbons, L. Jimenez-Lopez, R. Morales, V. Fierro, A. Celzard

16.   Study of glycine behavior in a comet, Y.Kviring, Y.Kviring, J. Simon, M. Salazar

17.   Molecular dynamics simulation of glycine in contact with ice, Y. Kviring, JM. Simon, JM Salazar

18.   Design of an unprecedent filtration device based on an elastic adsorbent for the adsorption intensification process of metal ions, M. Masquelier, C. Gourmand, L. Jierry and C. Bertagnolli

19.   Extruding diffusion constants from your extrudates: pore geometry and adsorbate kinetics, S. R. McIntyre, E. Hunter-Sellars, P. A. Sáenz-Cavazos, A. R. Houghton, D. R. Williams

20.   Recent developments in molecular Density Functional Theory: towards a more versatile tool for the characterization of nanoporous materials, C. Miqueu, R. Labeyrie, A. Barthes

21.   Competitive CO_2/H_2O Dynamic Column Breakthrough of CALF-20 under Adiabatic Conditions, Tai Nguyen, Sabereh Rezaei , Kasturi Nagesh Pai, Andrew Liu

22.   Correlation between gas storage capacity and surface area in MOFs?, M. Perbet, R. Morales, A. Cezelard, V. Fierro, E.A. Quadrelli, D. Farrusseng

23.   Investigation of catalytic COS formation on zeolites, S. Pfeifer, C. Pasel, C. Bläker, T. Eckardt, J. Eggebrecht, D. Bathen

24.   Impact of airborne nanoparticles on workers' health: a new method based on Krypton gas adsorption, O. Rastoix, S. Merouane, C. Vallieres, D. Rousset

25.   Sieving of H_2 and its isotopes by zeolites: Molecular simulations achievements and failures. J. Marcos Salazar, G.C.Q da Silva, J.M. Simon

26.   Aspects of a novel sensitive method for meso-macropore analysis based on nitrogen adsorption at the triple point temperature (63 K) M. Terlinden, F. Kleitz, M. Thommes

27.   Development and application of a novel pore network model for physisorption characterization, J. Söllner, M. Thommes

28.   CPO-27(Ni) pelletization: Impact on structural, textural, and thermal properties, G. Trierweiler Gonçalves, L. Michelin, L. Josien, J.-L. Paillaud, G. Chaplais

29.   Frontal analysis method with fractional sampling technique using a tandem HPLC system, S. Zarei, J. W. Lee, A. Seidel-Morgenstern

30.   Machine Learning Perturbation Theory for an accurate prediction of adsorption enthalpies, Michael Badawi, Dario Rocca, Basile Herzog, Tomas Bučko, Michael Badawi

31.   Role of water content in amine-grafting of silica gel beads for CO2 adsorption, B. M. O. Ogunedo, S. A. Nabavi

32.   Carbon-based Materials as Promising Adsorbents for Gas Phase Phosphorus Recovery, G. Lehnard, T. E. Müller

33.   Water and carbon dioxide co-absorption isotherms evaluation through dynamic column breakthrough analysis, Guzzo, S., P. Schulze, A. Seidel-Mongerstern

34.   Adsorption of dextrin on iron oxides in iron ore flotation process, Jean Wilfried Hounfodji, Wassim Abid, Juliette Lainé, Yann Foucaud, Michael Badawi

35.   Analysis of Sorption Isotherms of Zeolites with the Excess Surface Work – Thermodynamical and Quantum Mechanical Description, J. Adolphs

36.   Evaluating Light Olefin/Paraffin Separation Performance of MOF-808-based Adsorbents, Mahsa Najafi, Harun Kulak, Ivo F.J. Vankelecom, Joeri F.M. Denayer

37.   Understanding the Interplay of Pore Width and Amine Loading of PEI-Loaded Silica on CO_2 Adsorption, Tobias Beger, Juliane Titus, Sven Schardt, Olaf Deutschmann, Roger Gläser

38.   Textural analysis of various biochar using several probe gases, M. Guilmont, E. Ghomri, C. Vaulot, Y. Le Brech, N. Thevenin, R. Gadiou

39.   Energy consumption of VSA carbon capture; from lab scale to a pilot plant, M. Gholami, J. F. M. Denayer

Abstracts of oral presentations

Separation of water and ethanol mixtures by nanoporous organosilica;

a molecular dynamics study

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Ethanol is a widely used biofuel that offers a lower-emission alternative to gasoline, but the separation of ethanol from water in the production process is energy-intensive and affects the overall energy balance of biofuels. Membrane-based separation techniques, such as reverse osmosis and ultrafiltration, have emerged as efficient and low-energy methods for various applications. However, the separation of ethanol-water mixtures presents challenges due to their miscibility and unique properties. Here we use molecular dynamics simulations to evaluate the efficiency of organosilica nanoporous membranes for separating water-ethanol mixtures. Organosilica membranes were chosen as their surfaces present a tunable hydrophilicity, allowing for controlling the interaction with the mixture. Our results obtained for a large range of mixture compositions show that even slightly hydrophobic nanopores favor the transport of ethanol while blocking that of water (**Fig. 1**). We attribute this self-induced selectitity of the organosilica to the high energetical cost for water to reach the vicinity of hydrophobic surfaces, which we quantify in terms of hydrogen bonds. By emphasizing the efficiency of nanoporous organosilica in separating water-ethanol mixtures, our findings will contribute to the development of more efficient separation technologies for biofuel production and depolution.
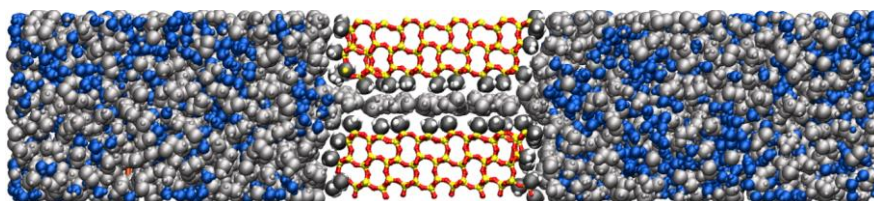
Fig. 1. Snapshots of the water (blue)-ethanol (gray) mixture in contact with a hydrophobic organosilica nanopore decorated in surface with methyl (CH3) groups.

Double-Layer Simulated Moving Bed Chromatography for Ternary Separations: Langmuir Isotherms

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Batch and recycle chromatography are widely applied for 'center-cut' separations, in which the target component migrates in the middle of the elution train. It is well known that continuous separation processes, such as simulated moving bed (SMB) chromatography, are efficient and cost effective compared to batch or semi-continuous chromatographic separation processes in solving binary or pseudo-binary separation problems. However, even in this case it is still challenging to design a suitable continuous chromatographic process due to its operational and structural complexity.

Recently a new double-layer SMB process concept was introduced for solving the continuous 'center-cut' separation problem [1, 2]. Considering an operational similarity between SMB chromatography and fractional distillation, the dividing wall distillation process [3], which is nowadays well established and widely used for multi-component fractional distillation, was adopted for a novel continuous SMB configuration. A modified short-cut design method for new design concept will be presented for Langmuir adsorption isotherms. This new concept and two early suggested alternative center-cut SMBs (SMB cascade [4] and integrated 8-zone SMB [5]) will be compared exploiting a simplified theoretical approach based on the equilibrium model of chromatography and results of a detailed simulation study assuming linear adsorption isotherms.

References:

[1]. J. W. Lee, *Ind. Eng. Chem. Res.* **59**, 9619 (2020).
[2]. J. W. Lee, *Ind. Eng. Chem. Res.* **60**, 8911 (2021).
[3]. R. O. Wright, N. J. Elizabeth, *U.S. Patent* **2 471 134 A**, (1949).
[4]. P. C. Wankat, *Ind. Eng. Chem. Res.* **40**, 6185 (2001).
[5]. J. Nowak, D. Antos, A. Seidel-Morgenstern, *J. Chromatogr. A* **1253**, 58 (2012).

A molecular dynamics approach to calculate protein adsorption data

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The use of biomolecules in pharmaceuticals is on the rise, with biopharmaceuticals accounting for up to 31.4% of the pharmaceutical industry's turnover in Germany in 2020, primarily in the form of peptides or proteins [1]. Downstream processing, in particular ion-exchange chromatography, represents a significant portion of the production cost and offers substantial optimization potential. To achieve economically efficient production, a thorough understanding of these processes is crucial.

While molecular dynamics simulations have been frequently employed to evaluate adsorption, most research has focused on qualitatively studying the interactions between individual molecules and adsorbents or surfaces. Free energy calculations provide a means to obtain statistical data on the interactions between a single molecule and other partners. This approach has been successfully applied to various systems, demonstrating the ability to calculate bulk properties through statistical analysis [2]. A proof of concept has shown that molecular dynamic simulations can generate complete adsorption isotherms [3]. However, the computational demands of these simulations have necessitated certain simplifications that affect the accuracy of the calculations. Recent advances in parallelization, increased computational resources, and further optimization of the simulated systems have the potential to overcome these limitations.

This study provides a detailed quantitative insight of the orientation of proteins in the adsorbed state and its effect on bulk protein adsorption data. Additionally, experimental data are used to validate and further explore the influence on the adsorption system.

References:

[1] J. Lücke, M. Bädecker, M. Hildinger, Med. Biotech. i. D. (2022).
[2] D. Markthaler, S. Jakobtorweihen, N. Hansen, Living J. Comput. Mol. Sci. 1, 1-25 (2019)
[3] S. Jakobtorweihen, J. Heuer, T. Waluga, J. Chromatogr. A. 1620, 460940. (2020).

Characterization of carbon monolith for wastewater treatment under flow

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J. Sanchez-Marcano[2], **A. Galarneau**[1]

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Zeolite monoliths (LTA, FAU-X nanocrystals) obtained by pseudomorphic transformation of silica monoliths prepared by a combination of spinodal decomposition and sol-gel processes shown tremendous performance for the removal of radionuclides (Sr, Cs) from contaminated water in continuous flow with perfect breakthrough curves [1,2], if monoliths feature trimodal porosity (micro-, nano-, macroporosity).

In the present study, to remove pharmaceutical micropollutants from wastewater, carbon monoliths (CM) with trimodal porosity (micro-, meso-, macroporosity) were synthesized by replica of silica monoliths. The complex structure of CM was resolved thanks to different technics: SEM, X-Ray microtomography, nitrogen sorption at 77 K, Hg porosimetry, water permeability. Sorption capacity of CM for a mixture of antibiotics (ciprofloxacin, amoxicillin, sulfamethoxazole, tetracycline, 20 mg L^{-1} each) was as high as 815 mg g^{-1}. In a recirculation flow configuration, with a flow rate of 1 mL min^{-1}, CM (6 mm diameter, 5 mm length) was able to remove 93% of the antibiotics contained in 200 mL solution. These CM could represent a highly efficient solution for the purification of real wastewater containing pharmaceutical molecules, which are generally found at much lower concentrations (from a few ng L^{-1} to µg L^{-1}).
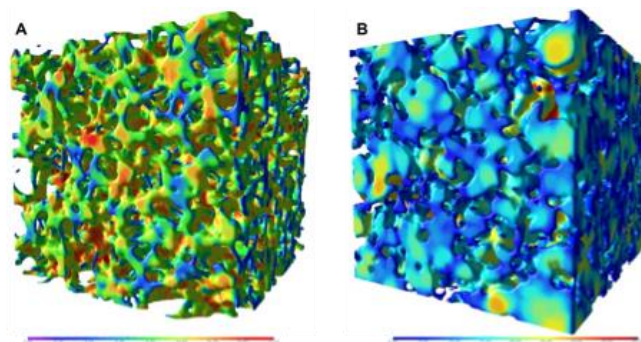
Fig. 1. Microtomography of Carbon Monolith: (A) Skeleton, (B) Macroporous network.

References:

[1] B. Said et al., Microporous Mesoporous Mater., **232**, 39-52 (2016).
[2] Y. Didi et al., Microporous Mesoporous Mater., **285**, 185-194 (2019).

Quantitative Assessment of Hydrophilicity/Hydrophobicity in Mesoporous Silica by Combining Adsorption, Liquid Intrusion and Solid-State NMR spectroscopy

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Abstract

We have developed a comprehensive strategy for assessing the surface chemistry of nanoporous materials by combining advanced adsorption studies, novel liquid intrusion techniques and solid-state NMR spectroscopy. The methodology was established on a well-defined system of model materials, the highly ordered mesoporous silica SBA-15, both pristine and functionalized with different amounts of trimethylsilyl (TMS) groups. The surface density of trimethylsilyl groups, was determined by quantitative ^1H solid-state NMR spectroscopy under Magic Angle Spinning (MAS). ^1H two-dimensional single quantum double quantum MAS NMR spectra reveal an intimate mixture of TMS and residual silanol groups on the surface. A full textural characterization of the materials was obtained by high-resolution argon at 87 K adsorption, coupled with the application of dedicated methods based on non-local-density functional theory. We further present a methodology to determine the effective contact angle of water adsorbed on the pore surfaces, which constitutes a powerful parameter for the characterization of the surface chemistry inside porous materials. The surface chemistry was found to vary from hydrophilic to a hydrophobic as the TMS functionalization content was increased, leading to contact angles from 0 ° (complete wetting) to 120 ° (non-wetting). For wetting and partial wetting surfaces, the contact angle was determined from the water sorption isotherms by applying the modified Kelvin equation on the desorption branch of the observed hysteresis loop, reflecting the thermodynamic liquid-vapour transition. On non-wetting surfaces, we investigated the pore filling of water by the application of a novel liquid water intrusion/extrusion experiment, applying the Washburn equation on the water intrusion branch which reflects the thermodynamic equilibrium vapor-liquid transition for a non-wetting fluid. Molecular simulations provide density profiles of water on pristine and TMS-grafted silica surfaces, which agree with the obtained experimental data. The methodology presented here can in principle be used for assessing the hydrophilicity/hydrophobicity of a wide range of nanoporous materials for optimizing their properties towards applications in chromatographic separation or heterogeneous catalysis.

The impact of the pore wall hydrophobicity on the density of confined water: A combined nitrogen and water sorption study.

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Recent findings have brought to the scientific community's attention the fact that properties of water, such as density and dielectric constant, vary significantly under confinement. The modulation of water properties with pore size has been extensively studied. However, the effect of pore-wall hydrophobicity remains an unresolved topic. Our research focuses on the impact of subtle changes in the hydrophobicity of nanoporous materials on the properties of confined water. To accomplish this, we synthesized and characterized nanoporous organosilica of MCM-41 type, using a direct synthesis method, with a controlled percentage of organic groups (methyl, ethyl, or phenyl) on the surface [1].

By combining nitrogen and water sorption techniques, we determined the density of water within the nanopores. The results in Figure 1 indicate that the density of water is significantly lower when confined in amphiphilic nanopores compared to hydrophilic MCM-41 with the same pore size. Other changes in the properties of water under amphiphilic confinement, such as its mobility [2], melting temperature and crystalline structure confirm that one can obtain a significantly different solvent by modulating the surface of the confining material [3].
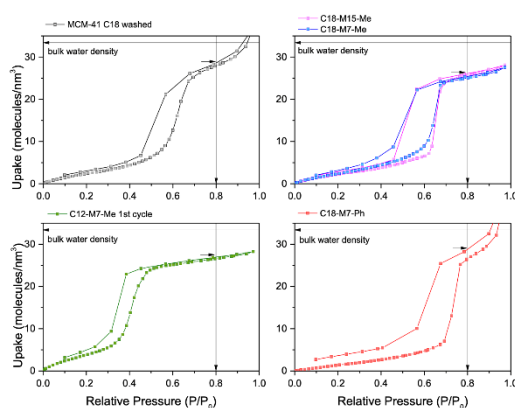
Fig. 1. Water adsorption-desorption isotherms normalized by the pore volume for the determination of the density of confined water. (P0 =0.0317 bar at 298.15 K) (left). (right)

This notion is especially important in the design of new nanoporous materials for applications in aqueous media, such as water treatment, the encapsulation of biomolecules, and supported catalysis, where a small change in the hydrophobic-hydrophilic balance can greatly impact their performance [1].

References:

[1] Osta, O.; Bombled, M.; Partouche, D.; Gallier, F.; Lubin-Germain, N.; Brodie-Linder, N.; Alba-Simionesco, C. Direct Synthesis of Mesoporous Organosilica and Proof-of-Concept Applications in Lysozyme Adsorption and Supported Catalysis. ACS Omega **2020** 5 (30), 18842-18848.

[2] Aîcha Jani et al., "Dynamics of Water Confined in Mesopores with Variable Surface Interaction," The Journal of Chemical Physics 154, no. 9 (March 7, 2021): 094505, accessed August 20, 2021, https://aip.scitation.org/doi/10.1063/5.0040705.

[3] Osta, O.; Bombled, M., Darpentigny, J., Brodie-Linder, N.; Alba-Simionesco, C. Effect of the pore-wall hydrophobicity on water's freezing and melting (Manuscript in preparation).

Understanding the evolution of microporosity during hierarchization treatments of side pocket containing zeolites

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Zeolites are materials widely used in industrial catalytic applications. The diffusion of molecules, which sizes approach that of the micropores can be strongly hindered by the narrow pore system. This, together with the often extended diffusion path length, impacts negatively the catalytic efficiency of a given process. Zeolite hierarchization allows for creating secondary porosity in the mesopore range, interconnected to the microporous system, diminishing the diffusion path lengths and allowing for maximizing effectiveness factors in catalysis.

In an ideal zeolite hierarchization process solely intracrystalline mesopores are generated whilst micropore volume remains preserved. Many hierarchization methods have been disclosed to create secondary porosity in zeolites, and their impact on the development of mesopore has been widely described in the litterature[1]. Yet, diligent characterization of the evolution of the microporous texture is generally neglected. Indeed, the impact of such post-synthetic modifications on the distribution and accessibility of micropores is only scarcely highlighted[2-3].

In this communication, we firstly present the impact of hierarchization treatments on the evolution of the micropore system of zeolites featuring pseudo-one dimensional porosity with side pockets. A set of hierarchical MOR and EUO structured modified zeolites by different hierarchization treatments (steaming, acid leaching, ammonium fluoride etching) was prepared. The adsorption of probe molecules with different kinetic diameters (N_2, Ar, *n*-nonane, *n*-hexane, toluene, 2.3-DMB) was investigated on these samples with the aim to understand the evolution of the microporous system. It was found that hierarchization treatments generally lead to a slight decrease of the micropore volume determined by N_2 or Ar physisorption. For the MOR structured zeolites the bimodal size distribution (side pockets and main channels) was importantly impacted as a function of the applied post-synthetic treatment. Steaming treatments destroy preferentially the side pockets, whereas acid leaching was found to have a stronger impact on the main channels. Ammonium fluoride etching allows for majorly preserving main channels compared to acid leaching but has a stringer impact on the amount and distribution of side pockets.

The enlarged microporosity index (φ_{Ar}) could be deduced from argon physisorption isotherms measured on *n*-nonane preadsorbed samples. A φ_{Ar} value of 0 corresponds to samples for which *n*-nonane molecules are hardly confined and block the access to micropores for Ar molecules. The value 1 is reached for samples with enlarged microporosity, for which the micropore size no longer allows for the confinement of *n*-nonane molecules.

References:

[1] J. Perez-Ramirez & al, Chem. Soc. Rev, 37, 2530 (2008).
[2] H. Issa & al, J.Catal, 374, 409 (2019).
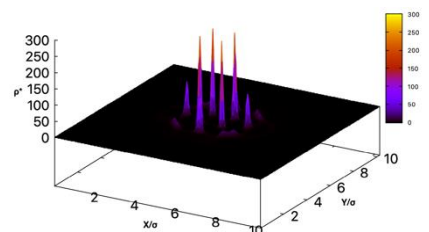[3] A. A. C. Reule & al, J.Catal, 349,98 (2017).

Towards a DFT approach to Mechanical Properties in Nanoporous Materials.

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In order to investigate the mechanical properties of the solid skeleton in nanoporous materials, we apply here two approaches based on the classical density functional theory (cDFT). cDFT has been primarily employed for determining the structural and thermodynamic properties of inhomogeneous fluids. It has also been explored in few studies for solid phases [1,2]. In a first approach, we implement the usual Gaussian parametrization within cDFT to obtain a face-centered cubic (FCC) solid phase. As an application of this strategy, we compute the phase diagram of a Lennard-Jones gas-liquid-FCC system, providing valuable insights into the equilibrium behavior of our system.

In parallel, inspired by the work of Lutsko et al. [3], an alternative method of spontaneous crystallization without imposing a specific structure is explored. Notably, Lutsko recently proposed a new free energy functional that incorporates a non-local hard-sphere contribution, demonstrating improved stability compared to the well-known tensorial White-Bear II (WBII) functional. Furthermore, our approach adopts a density approximation scheme using trilinear interpolation, which was also introduced by Lutsko [4]. This combination of the novel free energy functional and the density

Spontaneous localization of the density field obtained by using cDFT at fixed number of particles in a 2D system at T*=0.4 VR-Mie potential

approximation scheme contributes to the overall stability of our investigations into spontaneous crystallization. Inspired by these results and with the aim to investigate the deformation of porous solids, we apply this strategy in the canonical ensemble instead of the most conventional grand canonical one. Several dispersive contributions based on different potentials, including the VR-Mie and WCA, are tested.

By combining the classical density functional theory (cDFT) approach with Gaussian parametrization and the exploration of the spontaneous crystallization, this research endeavors to provide a solid foundation for the investigation of various mechanical properties associated with the solid skeleton of nanoporous materials.

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Cation-exchanged LTA Zeolites for the Separation of Propane and Propylene

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The separation of propane and propylene represents one of the most energy-intensive separations in chemical industry. As an alternative to cryogenic distillation, adsorption using microporous zeolites might offer an alternative. LTA zeolites have been shown to be promising adsorbents, but a systematic study of the effect of the extra-framework cations on propylene and propane adsorption is lacking.

In this work, we synthesized LTA zeolites exchanged with different cations (Na^+, Li^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}). All exchanged samples were synthesized with Na^+ as counterion and then partially exchanged with the other cation (30% and 50%). A comparison was made with pure Si-LTA. Adsorption isotherms were measured using a manometric system, coupled to a Tian-Calvet calorimeter, allowing the simultaneous measurement of the adsorption pseudo-differential enthalpy. While Si-LTA shows no preferential adsorption of propane or propylene and is essentially homogeneous for both probe molecules, propylene shows a strong interaction with divalent cations. On the other hand, LTA zeolites with monovalent cations (Na^+ / Li^+) show slow diffusion of propane, opening perspectives for a kinetic separation.
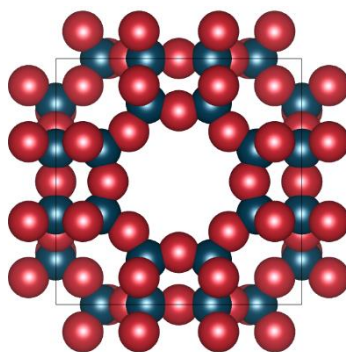

Fig. 1. View along the LTA pore opening

Binary adsorption of light hydrocarbons on zeolites at low temperatures

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The separation of light alkanes and alkenes (C2-C4) at trace concentrations is of great importance in petrochemical industry and in technical environmental protection. Because of similar structural and thermophysical properties of the alkane and the corresponding alkene, the separation with conventional methods, such as low-temperature rectification or extraction, is very expensive. Adsorption processes at low temperatures, based on different interactions of the alkane and alkene with the adsorbent surface, may be an alternative. Due to different temperature dependencies of these interactions, a temperature optimum may be found for separation. As yet, no systematic data are available on binary adsorption of light hydrocarbons at low temperatures. With this in mind, this work investigates the adsorption thermodynamics of light hydrocarbons on various faujasite zeolites over a wide temperature range. Another goal is to predict binary adsorption based on experimentally determined pure component data. The results of the predictions will then be compared with the experimental data.

Dynamic breakthrough experiments of light hydrocarbons and their mixtures on different adsorbents were carried out in a fixed-bed adsorption column at temperatures between -75 °C and 0 °C. From mass balances around the adsorption column, equilibrium loadings were calculated and adsorption isotherms derived. In order to assess the temperature dependency of binary adsorption more precisely, different thermodynamic models are used and discussed. Furthermore, the Ideal Adsorbed Solution Theory (IAST) is applied to predict the adsorption behavior. The adsorption selectivity depending on temperature is calculated and discussed.

First results are available for the adsorption of ethane/ethene and propane/propene mixtures on a series of faujasite zeolites. While the temperature influence on the pure component adsorption of the C2 alkane and alkene is markedly different, the adsorption behavior of propane and propene is similar with changing of the temperature. In binary mixture adsorption of alkanes and alkenes, the alkane is displaced by the stronger adsorbing alkene. The displacement is more pronounced at low temperatures. IAST provides a good prediction of the general behavior of mixed adsorption. The selectivity for the alkene is best at the lowest temperature.

D$_2$/H$_2$ separation by adsorption in zeolites under cryogenic conditions: understanding the mechanism from experiment and molecular simulation

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Separation of hydrogen isotopes is of interest in nuclear industry and in other fields. Currently it is achieved by the Girdler sulfide process which is highly energy consuming. In recent years an alternative approach has appeared which uses the selective adsorption in microporous materials under cryogenic conditions (< 100 K). This separation process, known as quantum sieving, is based on the preferential adsorption of the heavier isotopes in micropores whose size is comparable with the kinetic diameter of hydrogen isotopes molecules (~ 0.29 nm). The zeolites are considered as promising materials in this application due to the suitable range of pore size, tunable surface chemistry and high stability.

To understand the parameters governing D$_2$/H$_2$ selectivity in zeolites we performed since 2017 a series of studies using experimental approach and/or molecular simulation. The thermodynamic equilibrium selectivity was determined using a co-adsorption technique. This data was completed by the single gas adsorption isotherms measured in a wide temperature range (40 - 100 K) which allowed to determine the isosteric heat of adsorption of D$_2$ and H$_2$ as a function of loading. The molecular simulations were realized using the grand canonical Monte Carlo (GCMC) technique. To account for the quantum effects appearing in the cryogenic conditions the Feynman-Hibbs effective interaction potential was employed. Using these approaches, we characterized the properties of the following zeolites: NaX [1,2], LTA [3] and CHA [4,5].

In our talk we will present the major results from our previous studies along with the recent ones concerning Li- and Na-exchanged low silica X zeolites (FAU framework with Si/Al = 1). The role of the zeolites properties (pore size, Si/Al ratio, cation nature) in the D$_2$/H$_2$ separation will be discussed in detail and on this basis the different separation mechanisms will be proposed.

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Adsorption Chiller for Industrial Application

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Globally, about 30% of industrial energy input is lost as waste heat, of which about 27% (2.422 TWh/a) is low-temperature waste heat between 60-100 °C. [1] At the same time, approximately 17% of the electricity produced annually worldwide is used for refrigeration, [2] which results in a CO_2 output of approximately 2.24 Gt CO_2/a (6% of global emissions).

In summary, there is a significant industrial demand for cooling and, at the same time, large amounts of low-temperature waste heat are available. However, their utilization is thermodynamically challenging due to the low temperature level.

The thermally driven adsorption chiller is up to this challenge, as it can efficiently generate cooling from waste heat even with very low driving temperatures starting at 55 °C, using the climate-neutral refrigerant water instead of banned F-Gases. Compared to compression-based systems, they can reduce electricity consumption by approximately 70-80%. Aspects of application and technical development will be presented, e.g. kinetic measurements or impact of the choice of the adsorption material.
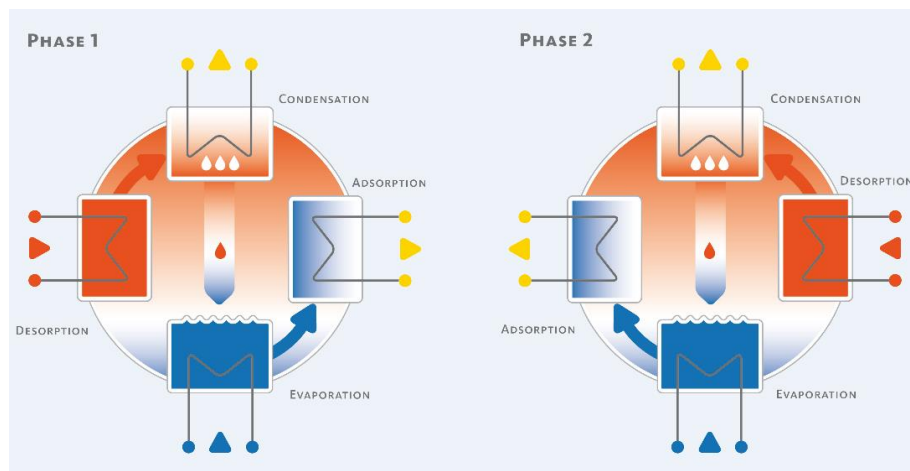
Fig. 1. The two main phases of an alternating operating adsorption chiller

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Hidden Adsorption – TSA in industrial gas processing plants

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Industrial gas processes, such as separation, purification and recovery are integral to a wide range of sectors, including petrochemicals, air separation or hydrogen production. However, when dealing with the separation of trace components many standard and known separation units are limited in their use. In general, these pre-purification steps are just a small fraction of the entire industrial gas process but represent one of the most important ones. Without a proper pre-purification the core separation process would not be able to function. The use of Temperature Swing Adsorption (TSA) as the pre-purification unit offers an optimal solution by harnessing the principles of adsorption.

TSA relies on the temperature-dependent adsorption and desorption characteristics of adsorbents to selectively separate unwanted components from gas mixtures. This dynamic process enables optimal selectivity, reduced energy consumption and better process economics. Therefore, at Linde almost all industrial gas processes use TSA as the optimal pre-purification unit.

To illustrate the advantages and potential of the TSA an example for an industrial gas application will be presented, demonstrating the possibilities that can be achieved by using adsorptive processes as pre-purification unit.

Shaping of HKUST-1 for CO$_2$ capture from biogas

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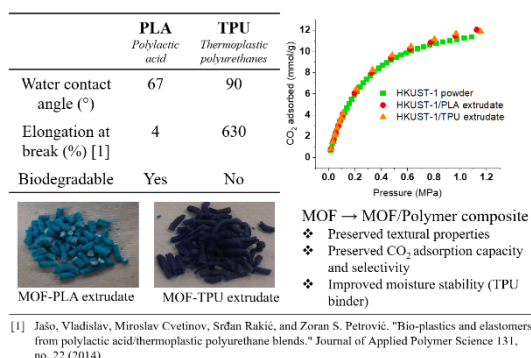
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HKUST-1 is one of the frequently studied Metal-Organic Frameworks (MOFs) as an adsorbent for CO$_2$/CH$_4$ separation, owing to its high CO$_2$ adsorption capacity and selectivity. However, the synthesis of HKUST-1 often results in the formation of powders that require post-treatments for shaping. Initially, HKSUT-1 was first shaped using a bio-based binder, polylactic acid (PLA) via two processes (extrusion and 3D printing).

During the extrusion process, HKUST-1 was mixed with 10% PLA by mass, while the 3D composite had a higher PLA content of 70%. Characterization via XRD confirmed the preservation MOF particles within the composites. But, if SEM analysis revealed that HKUST-1 particles in the extrudate composite remain accessible to gas, this was hindered in the 3D composite because of particle encapsulation. N$_2$ adsorption isotherm measurements demonstrated that BET surface area of the extruded composite remains closed to that of pristine HKUST-1 (1528 m^2/g), in contrast to the 3D composite (70 m^2/g). It was concluded that the 3D composite was unsuitable as gas adsorbent.

Using the same extrudate shaping procedure, another type HKUST-1 composite was next elaborated, substituting PLA by an hydrophobic binder, thermoplastic polyurethane (TPU). CO$_2$ and CH$_4$ adsorption isotherms measured up to 10 bar, highlight the preservation of adsorption capacities of HKUST-1 for both extrudate composites. Additionally, the aging analysis reveals that both pristine MOF and MOF/PLA extrudate, when exposed to humid air over one month, experiences a 20% reduction in their CO$_2$ adsorption capacity. On the contrary, under the same controlled humid conditions, no change of the adsorption capacity of the MOF/TPU composite was observed. This was attributed to the effect of the hydrophobic nature of TPU.

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Fig. 1: Comparison between TPU and PLA properties and their respective MOF/polymer composite

# Transition metal-exchanged GIS zeolites for CO_2/CH_4 separation

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CO_2/CH_4 separation is crucial for biogas purification, which produces biomethane as a green energy resource [1]. Adsorption-based separation is one of the most promising approaches for CO_2/CH_4 separation, and further exploration of adsorbents is necessary to achieve optimal performance in terms of CO_2/CH_4 selectivity, capacity, and regeneration under relevant conditions.

Gismondine (GIS) zeolite is a three-dimensional porous zeolite consisting of 8-membered rings of corner-sharing tetrahedral TO_4 units (T = Si or Al). It has garnered attention from researchers due to its remarkable CO_2 separation selectivity and capacity [2]. Synthetic GIS zeolites primarily contain sodium as the cation sites (Na-GIS), which may strongly interact with CO_2 and result in challenging regeneration [3]. We propose that transition metal cation sites, capable of forming π back donation with CO_2, could facilitate regeneration because of moderate CO_2 affinity while maintaining satisfactory capacity and selectivity [4].

To investigate the effect of transition metal cation exchange on CO_2/CH_4 separation, we prepared Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} exchanged GIS (referred to as Co-GIS, Ni-GIS, Cu-GIS, and Zn-GIS, respectively). CO_2 adsorption isotherms demonstrate that Cu-GIS exhibits a relatively high CO_2 adsorption capacity among the cation-exchanged GIS zeolites. CO_2/CH_4 breakthrough measurements show that Cu-GIS displays comparable selectivity but faster regeneration ability under inert gas flow compared to sodium Na-GIS. This research suggests that Cu-GIS could be a promising candidate for CO_2/CH_4 separation applications.
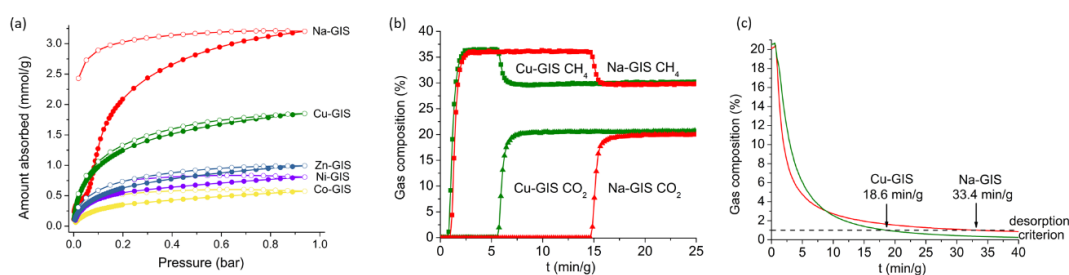
Fig. 1. (a) The CO_2 adsorption isotherms at 298 K of GIS zeolites. (b) The breakthrough results of CO_2/CH_4/helium mixture at 298 K for GIS zeolites. (c) Desorption of CO_2 in dynamic helium flow.

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Direct Air Capture with solid amine sorbents: understanding the effect of water on process performance

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Direct Air Capture (DAC), contrary to point source capture, aims at removing CO_2 directly from the atmosphere. It can thus be installed everywhere in principle and is a must to reach global climate objectives set by IPCC. Due to the technico-economic challenges of such a separation, it is though still a growing technology. Climeworks is a leader in this field and has the ambition to scale this technology to remove 1Gt/y of CO_2 in 2050: the Orca (4kt/y since 2021, Fig. 1) and Mammoth (40kt/y, to start end 2023) plants in Iceland are the first steps of this journey.

Fig. 1. Picture of Climeworks Orca plant running since 2021 in Iceland

From technological standpoint, DAC with solid amine sorbents is challenging from several aspects: the effect of water on process performance is one of them. Water enhances the CO_2 adsorption capacity but its effects on the process are multiple and complex (impact on CO_2 diffusion, coadsorption with CO_2 [1], hysteresis in process conditions …). The goal of this contribution is to outline and discuss these effects.

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Chitosan-based activated carbons for CO_2 capture and biogas upgrading

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Chitosan was selected as the precursor for preparing activated carbons (ACs) with a high N content. These ACs were intended to serve as potential adsorbents for the capture of CO_2 and upgrading of biogas. The activation process of chitosan began with subjecting the material to pyrolysis under a 200 mL/min nitrogen flow at a temperature of 900 °C for 1h in a tubular furnace. Subsequently, the resulting char, which had low textural properties (BET surface area, A_{BET}, below 10 m^2/g), underwent activation for 1h using a flow of NH_3 gas (approximately 120 mg/min) at 900 °C. The burn off was around 80%. To characterize the obtained sample, N_2 and H_2 adsorption-desorption isotherms were conducted at a temperature of 77K. The A_{BET} was estimated using the N_2 isotherm at 77K, while the pore size distribution (PSD), specific surface area (S_{NLDFT}), and cumulative pore volume were determined using the 2-dimensional model based on Non-Local Density Functional Theory (2D-NLDFT) method using N_2+H_2 isotherms. The results of the characterization indicated that the AC is predominantly microporous (>98 %) with A_{BET} and S_{NLDFT} values of 1000 and 1200 m^2/g, respectively. To assess the adsorptive uptake and selectivity for CO_2/N_2 and CH_4/CO_2 separations, experimental isotherms were conducted using a high-pressure volumetric adsorption (HPVA) equipment from Micromeritics. These isotherms covered a pressure range of up to 35 bar and a

Figure 1. Selectivity values for CO_2/N_2 and CO_2/CH_4

temperature range from 0 to 75 °C. At 1bar and 25 °C, the CO_2 uptake was 2.6 mmol/g in accordance with previous reported uptakes [1,2]. The selectivity values were roughly constant within the evaluated pressure range. However, the selectivity was higher in the CO_2/N_2 separation, around 21, compared to the CO_2/CH_4 separation, around 6, as illustrated in Figure 1.
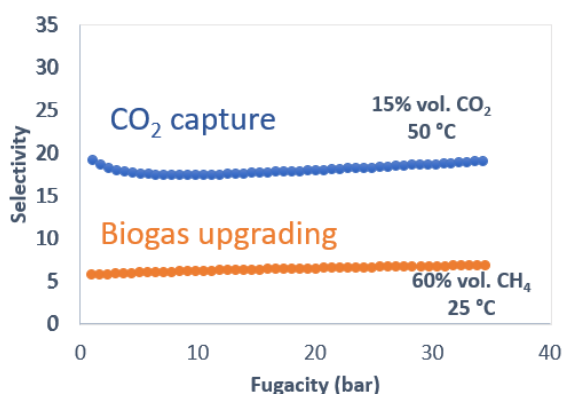
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A Hybrid System for Capturing CO₂ directly from the air

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To meet net-zero targets by 2050, the deployment of carbon dioxide removal (CDR) technologies is required. Among the portfolio of CDR technologies, direct air capture (DAC) has emerged as a promising approach to mitigate CO_2 emissions from mobile and dispersed sources, which cannot be addressed by other carbon capture technologies. DAC presents unique technical challenges due to the ultra-dilute nature of CO_2 in the atmosphere (presently 0.042 vol%). For comparison, CO_2 composition in post combustion gas streams is 4-15 vol% which is 100 to 375 times more concentrated than CO_2 in air. The low concentration of CO_2 in air makes the capture process more energy and material intensive, and more expensive than capturing CO_2 from fossil fuels plants, since much larger volumes of air must be processed to extract significant amounts of CO_2. Currently, the estimated cost for DAC varies in the range of \$250/tCO_2 to \$600/tCO_2. Given the expensive nature of DAC, and its key role in achieving net zero targets by 2050, it is essential to identify technological options that deliver optimal techno-economic performance.

Today, the development of CO_2 capture systems has focused mainly on single-stage separation technologies. For CO_2 capture, aqueous amine scrubbing is the benchmark technology and is widely deployed in industry for natural-gas sweetening. In terms of DAC, aqueous amine absorption process can achieve up to 90% CO_2 capture from a few % CO_2 gas streams feed. Despite its high technology readiness level, solvent degradation and significant energy requirement for solvent regeneration constitute crucial limitations of the absorption technology in carbon capture applications. Due to these drawbacks, alternative CO_2 separation technologies exist. Adsorption-based technology for DAC has been proposed but is far from running optimally. Overall, achieving 90% CO_2 capture from ppm level feed is extremely demanding for a single technology. However, the energy consumption and subsequently economic performance are in fact a major challenge for all separation technologies. When added to the inherent limitations of an individual technology, high energy consumption often translates into economic infeasibility. In this context, opportunities exist to develop hybrid processes for CO_2 capture from the air, which could reduce the costs associated with capture of CO_2 with an increased operational flexibility. Hybrid processes are developed to overcome the challenges that standalone processes face ; in this case to treat dilute, large volume, low pressure streams.

This work aims to assess the design of a hybrid process for capturing CO_2 directly from ambient air. The hybrid process proposed in this study integrates adsorption and absorption. The latter is a proven technology at the large scale, while the former benefits from high separation factors and the versatility given by the wide range of sorbent materials available. For the first stage, a four-step temperature vacuum swing adsorption process is considered (TVSA), using commercial sorbents, while for the second stage, an aqueous amine absorption process is developed. For the first stage, we compared the performance of different adsorbents in terms of CO_2 purity and recovery and energy requirement for completing the purification. We found that the intermediate concentration of the CO_2-enriched stream coming out from the first (adsorption) stage ranges from 0.5 to 21 % depending on the adsorbent and the operating conditions. For the second stage, we developed a meta model to serve as a design tool for the optimisation of the process. This model was abstracted from rigorous process simulations modelled in the Aspen Plus process simulator. Techno-economic optimisation on the second stage was performed resulting in a capture cost of \$79/t$_{CO_2}$ including the solvent degradation mitigation technique cost. Moving forward, we will integrate the TVSA model of the first stage with the absorption model of the second stage to evaluate and optimise the overall performance of the hybrid system.

Electrospun Carbon Nanofibers as Selective Adsorbent for the Separation of CO_2

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Vast CO_2 emissions are the main reason for the anthropogenic climate change. The capture of CO_2 from point sources such as flue gas or biogas using adsorption-based processes like pressure swing adsorption (PSA) or temperature swing adsorption (TSA) is a feasible option to reduce the net CO_2 emissions into the atmosphere. For such processes, adsorbents with a high CO_2 capacity, stability and CO_2 selectivity are needed.

In this work, electrospun polyacrylonitrile (PAN) nanofibers carbonized at various temperatures ranging from 600 °C to 1000 °C are evaluated for their CO_2 separation capabilities from flue gas and biogas. General characterization of the carbon nanofibers (CNFs) was performed with elemental analysis and XPS for the surface chemistry as well as Argon and CO_2 adsorption for the pore size distribution. [1] Isotherms of various gases show a significant reduction in the adsorption capacity when the carbonization temperature is increased above a certain threshold. This threshold is specific for each gas and corresponds to the molecular size. [2] With increasing carbonization temperature, the ultramicropores of the CNFs shrink, which, at a certain carbonization temperature, excludes a gas from the pores based on its molecular dimensions. [1,2]

To evaluate the CNFs as an adsorbent for the selective adsorption of CO_2 from flue gas or biogas, column breakthrough experiments with CO_2/N_2 [3] and CO_2/CH_4 [4] were conducted. The breakthrough curves are analyzed in regard to the adsorption kinetics using a modeling approach with the linear driving force (LDF) model. The kinetic analysis reveals a decreasing adsorption rate with increasing carbonization temperature. Up to 800 °C, the reduction in the adsorption rate of CO_2 is small, whereas the adsorption rate of CH_4 decreases by several orders of magnitude, resulting in severe kinetic limitations on CNFs carbonized at 800 °C. By integration of the breakthrough curves, the adsorbed amount and the adsorption selectivity are determined. Due to the size exclusion of the larger CH_4 molecule, a maximum of the CO_2/CH_4 selectivity is found for the CNFs carbonized at 800 °C (40). In contrast to the CO_2/CH_4 separation, the separation of CO_2 and N_2 is governed by the surface chemistry of the carbon rather than the size exclusion effect. Overall, an excellent CO_2/N_2 selectivity of up to 200 is found. The CO_2/N_2 selectivity correlates well with the amount of surface functional groups, which increases for lower carbonization temperatures. In conclusion, electrospun PAN-based CNFs are a versatile adsorbent that can be tailored for the selective capture of CO_2 from various gas mixtures.

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Effective microwave-assisted regeneration of MOF/graphene oxide composites for post-combustion CO_2 capture

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The development of effective CO_2 capture systems is critical to mitigate the rising levels in the short-term and moving toward a cleaner energy future. Metal-organic frameworks (MOFs) as solid sorbents are particularly promising for CO_2 due to their high adsorption capacity and high selectivity towards CO_2. Considering the main energy output from capture technologies comes from the adsorbent regeneration after CO_2 saturation, MOFs offer lower energy penalty for regeneration comparing to the currently used aqueous alkanolamine solutions.

In this work, we combine MOFs with graphene oxide (GO) to minimize the energy required for regeneration by using microwave swing adsorption (MSA) process. The incorporation of GO will enhance the typically very low electrical conductivity of the bare MOF and will increase the microwave absorption, warranting a faster regeneration by MSA. MIL-91(Ti) [1], CALF-20 [2] and MIL-160(Al) [3] are some of the MOFs selected based on the potential features required for post-combustion CO_2 capture (e.g. uptake, selectivity, stability and scalability) and are combined with different GO contents by *in situ* synthesis. It is observed that 5wt% GO/MOF composites feature semi-conducting behavior while bare MOFs are insulating. As a consequence, these composites, in particularly MIL-91(Ti)/GO 5% composites, show a CO_2 desorption twice faster with microwave irradiation then the pure MOF with conventional direct electric heating. This underlines the promising use of MOF/GO composites with microwave-assisted regeneration as a more sustainable alternative for industrial CO_2 post-combustion capture with a significant reduction of regeneration time and energy.

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MOFs as sustainable sorbents for CO₂ capture solutions

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Greenhouse gases (GHG) emission is one of the challenging environmental issues which the world is facing in the present decade. Carbon dioxide is considered the largest anthropogenic GHG source. To reduce the industrial CO_2 emissions and energy consumption, the implementation of carbon capture utilization or storage (CCUS) technologies are necessary. Currently, the only technology (TRL9) is the post-combustion CO_2 capture by adsorption/regeneration in amine-based solvents, but it suffers from high energy penalties leading to adverse environmental impacts (makeup, products of degradation). Thus, finding novel means to significantly reduce this capture energy and the by-products emissions can open gateways to deployment.

In this regard, Metal-Organic Frameworks (MOFs) have shown high promise for CO_2 adsorption-based capture approaches[1]. But, MOFs still lack investigation under real conditions where impurities can drastically affect their performance. In the framework of MOF4AIR, a multidisciplinary H2020 EU project, the performances and stability of a series of MOFs have been evaluated in conditions close to real industrial ones in view of their use in post-combustion capture process based on a Vacuum Pressure Swing Adsorption (VPSA) process.

Trivalent metal (such as Al) carboxylate MOFs are considered as one of the promising candidates for several potential industrial applications because of their higher hydrolytic stability compared to divalent metal carboxylate MOFs. In this communication, the focus will be on the study of promising microporous Al-MOFs, in particular MIL-160(Al)[2,3]. The scale-up and shaping of this MOF, up to the kilo-scale[4], will be presented together with a highlight on the performances in CO_2 capture. Results on both powder and shaped MOFs (at different scales) will be demonstrated. The effect of water on CO_2 adsorption, and comparison with some benchmark MOFs will also be discussed.

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Mediation of water vapour transport in nanopores via salt solutions: thermodynamic and kinetic study

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The general goal of this project is to exploit wetting and de-wetting cycles of salt solutions confined in porous electrodes to generate energy from low grade waste heat. Here, we investigate the fundamentals of how nanoporous media containing salt solutions respond to changes in humidity in order to establish design rules for such electrodes. We perform customized optical and mass uptake experiments to understand the kinetics of wetting and de-wetting and the thermodynamics of water vapour sorption by using model nanoporous silica membranes (Vycor) as our samples of interest. The wetting kinetics of pristine Vycor does not adhere to either capillarity driven or condensation limited mechanism. A qualitatively similar behaviour is exhibited by LiCl filled Vycor, though the wetting kinetics is significantly faster than pristine Vycor, featuring a clear dependence on LiCl concentration evolution during the pore-wetting process.
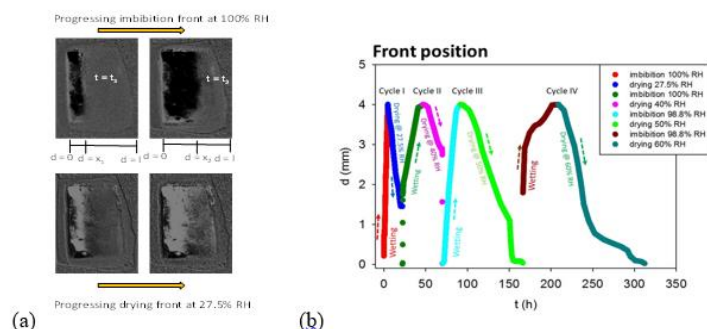
Fig. 1. (a) 1D wetting/drying front of water vapour in sealed Vycor membrane (b) wetting/drying front positions as a function of time and relative humidity

In this study, we unravel the mechanism of vapour phase pore-wetting of pristine Vycor and explore the impact of salt solution concentration evolution on capillary and osmotic pressures with implications in both wetting and de-wetting kinetics.

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Impact of tortuosity and surface diffusion on transport through porous media

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Mass transport in porous material including convection and diffusion plays a significant role in many environmental and industrial processes (catalysis, separation, etc.). The diffusion coefficients are determined by liquid chromatography in static conditions by using the Peak Parking (PP) method. In static conditions the molecule is parked in the middle of the column and let freely to diffuse during a time called the parking time and the peak is then recorded to calculate the effective diffusion coefficient. To separate the contribution of the macropores and the mesopores the Maxwell model is used [1, 2]. In adsorbing conditions, the intra-particle diffusion coefficient has two contributions: in-pore diffusion D_p and surface diffusion D_s. The in-pore diffusion D_p depends mainly on the tortuosity of the porous material which reflects the complexity of the porous network. Tortuosity of hierarchical material was determined by random walk simulation and compared to experimental data as well as to Maxwell equation [3]. The surface diffusion coefficient D_s is usually determined using models considering parallel diffusion in the pores and at the surface, but this assumption is rather crude. In this study, to address this problem, another approach is proposed using the Brownian motion of molecules in the pore space [4, 5]. These two approaches lead to similar equations relating the effective diffusion coefficient D, the in-pore diffusion D_p and surface diffusion D_s. To separate both contributions experiments were conducted with a series of polystyrenes having different affinities for silica's by using tetrahydrofuran (THF) in non-adsorbing conditions [6] and a mixture of heptane and THF for adsorbing conditions [7]. The surface diffusion is analyzed as a function of the surface affinity of the probes considered here.

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An Efficient Implementation of Maxwell-Stefan Theory for Modeling Gas Separation Processes

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Separation process modeling of fixed-bed adsorbers and thin-layered membranes consists typically of macroscopic mass and energy balances, with simplifying principles to be able to describe mass transfer processes at the particle level (i.e., lumped-kinetics models). However, for several gas separation processes, such as kinetically-controlled adsorption and membranes, the dynamics of the microscopic scale occur very slowly, and a detailed description of mass transfer is unavoidable for their accurate description. The Maxwell-Stefan Theory (M-S) is a powerful approach based on the principle of Irreversible Thermodynamics applied to describe diffusion processes at the microscopic level (i.e., particles, crystals) **[1,2]**. It has been employed for modeling fixed-bed adsorbers with slow kinetics and membrane processes **[3]**. The M-S approach requires a competitive adsorption equilibria ansatz for its application. In this work, we present a computationally efficient formulation that implements the M-S approach for these kinds of gas separations by applying the thermodynamically-consistent Ideal Adsorbed Solution Theory (IAST) **[4]**. We formulate transient mass balances as systems of Differential-Algebraic Equations (DAEs) that result from applying a Method of Lines Approach (MOL) for their numerical solution. IAST is incorporated in this solution principle by applying an accurate calculation approach developed in **[5,6]**. The advantages and robustness of the developed solution method are illustrated with several examples for describing particle adsorption dynamics and transport in thin-layered membranes.

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Improvement of axial dispersion estimation in porous media for gases under pressure: Experimental and modelling methods

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In issues of gas mixture separation by dynamic adsorption on fixed bed, the shape of the breakthrough curve of solute depends on many parameters: the advective flow of the gas stream, the diffusion of solute molecules and finally the kinetics of the fluid/solid transfer by adsorption. For a further better investigation of the adsorption kinetics mechanism, only the effects of advective flow and diffusion of solutes in the fluid on the breakthrough curve are explored in a first time by using inert porous materials. Usually the axial dispersion is considered as the macroscopic result of the coupling of solute diffusion in the fluid and advection, which impacts the mixing of the solute in the fluid matrix. Since the first works of Danckwerts [1] until today, the study of axial dispersion in porous media has been the subject of numerous publications [2].

Most of the previous works report empirical correlations for the evaluation of the axial dispersion coefficient as a function of Reynolds number, Schmidt number and molecular diffusion without, however, specifying the direct influence of the fluid pressure on this dispersion coefficient [3]. The purpose of this experimental study is to estimate the value of the macroscopic axial dispersion coefficient in an inert porous media (glass beads), under various experimental conditions, in a pressure range from 0.6 to 3.5 MPa: flow rate, concentration of binary gas mixture (methane, nitrogen), porosity of the porous media as well as the height of the fixed bed. The originality of this study lies in the implementation of a new original methodology to take into account the effect of the dead volume of experimental device on the axial dispersion. In the absence of adsorption, this new methodology allows a better estimation of the corrected breakthrough curve than the Point By Point (PBP) method developed in previous works [4]. The estimation of the axial dispersion is performed by numerical simulation of the experimental breakthrough curves by the Fickian advection-dispersion transport equation. The obtained axial dispersion coefficients within the pressure range of 0.6 to 3.6 MPa exhibit magnitudes on the order of $10^{-7} m^2.s^{-1}$. It is of interest to note that a correlation between axial dispersion and molecular diffusion is observed when the pressure exceeds 1.5 MPa. These results highlight the relationship between axial dispersion and molecular diffusion, especially at higher pressures, where the impact of interstitial velocity on axial dispersion is less pronounced.

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The limits of surface and pore volume characterization

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Not only the IUPAC recommends the use of argon at 87 K instead of nitrogen at 77 K for the characterization of porous materials[1], also the ISO 9277[2] describes problems when using the BET method for the determination by the use of N_2. Therefore, regardless of the fact that N_2 interaction problems with a material surface can influence specific area and pore size distribution results, N_2 near 77 K is still the most common technique due e.g. for comparison reasons. However, when it comes to samples with narrow ultramicropores or a very small surface area, such as thin films or non-porous samples, N_2 and Ar reach their limits.
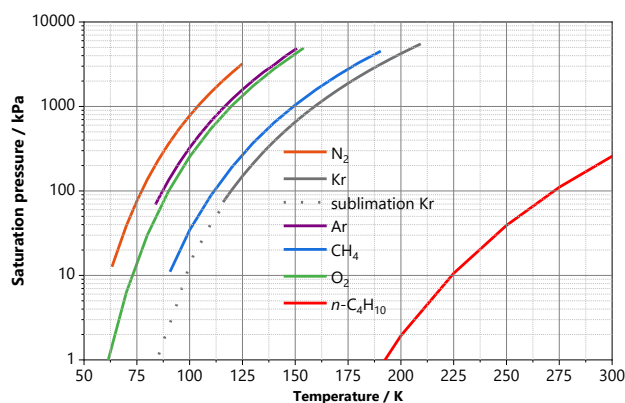

Figure 1. Saturation pressure vs T for typical adsorptives

A common approach to characterize small surface areas is the reduction of the saturation pressure p_0 to minimize the amount of free gas molecules. Therefore, IUPAC recommends the use of Kr with a fixed p_0 value of 0.35kPa at 77.35 K, but this does not take into account the dependence of the coolant on ambient pressure. Since the p_0 value of the supercooled liquid krypton adsorbate (see Fig. 1) cannot be measured directly, it has to be calculated either from a temperature measurement of the coolant or an exact temperature control. For accurate measurements, we used a new temperature control (cryoTune 77), which allows the use of the correct p_0 for the undercooled liquid adsorbates of Kr and Ar near 77 K.

For the characterization of macropores we recommend the use of *n*-butane. This new developed method is based on the reduction of the measuring temperature. At p/p_0=0.995, N_2 at 77 K fills pore diameters of about 400 nm, *n*-butane at 273 K of 500 nm, but *n*-butane at 195 K of 1000 nm. Our results will demonstrate that method by use of a cryoTune 195 regarding the limits of both pore filling and sample amount available.

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Unraveling Hierarchical Pore Networks Using Differential High-Resolution Mercury Intrusion

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Mercury intrusion has been employed for the characterization of hierarchical materials for many decades. Reverberi, *et.al*., described a method for determining the distribution of pore openings, or throats, for internal cavities of differing sizes in 1966 [1]. In this technique, the material is first saturated with mercury, stepwise intruding mercury up to the maximum analysis pressure, followed by extrusion back to near atmospheric pressure, and a repeat intrusion back to maximum pressure. Additional extrusion and intrusion cycles are performed, with each successive extrusion cycle reaching progressively lower pressures.

In the present study, a novel method for characterizing the pore network of hierarchical materials using high-resolution differential mercury intrusion is described. This method allows for a better understanding of the internal structure of these materials, to improve behavior modeling and expanded usage. The volume of pore cavities filled through progressively larger pore cavities is determined, which can be used to distinguish between lots that behaved as desired and those that did not, using a quick, detailed analysis method.
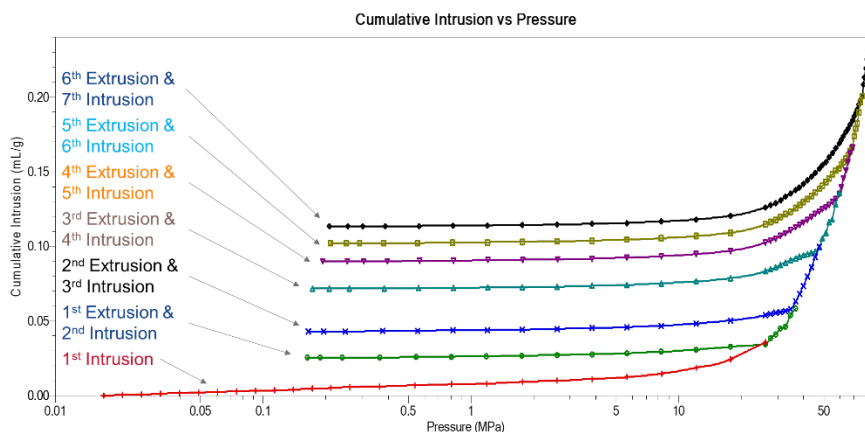
Fig. 1. Successive pore filling with each intrusion cycle.

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Vapour Adsorption Studies of Porous Materials

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The presence of pollutants in the air is becoming an area of significant interest and there has been an increasing concern about air quality and its impact on health due to the presence of volatile organic compounds (VOC) in the air. VOC molecules include toluene, formaldehyde, methylene chloride, tetrachloroethylene, xylene, acetone, and benzene which may appear in different forms as in solvents, paints, or packaging materials. It is important to find a solution for the removal of volatile organic pollutants from the air. Porous materials are considered a cost-effective route to capture VOC pollutants and the reason for their success is the high fraction of pore volume and adsorption sites for trapping volatile species. Zeolites and activated carbons are widely used due to their low cost and ease of availability.

VOC concentrations can vary in different environments but are significantly lower than the moisture concentration. Therefore, water molecules would be competing for the same adsorption sites as VOCs and it would be important to assess the impact of humidity on the choice of porous materials for removing certain VOC molecules. This study will look at the impact of humidity on a series of common industrial porous materials which are potentially usable for capturing VOCs.

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Frontal analysis method for determining adsorption isotherm

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Chromatographic separation processes are required for the purification of numerous valuable compounds. For designing and optimizing efficient processes, quantitative knowledge of the adsorption isotherms is essential. These thermodynamic functions are typically determined experimentally first for single-component systems. Competitive isotherm models can be applied subsequently for estimating the equilibria in the real multi-component systems.

To measure isotherms for components dissolved in a solvent, frontal analysis is one of the most frequently applied methods, i.e. the recording of breakthrough curves [1].

In this study we investigate the adsorption behavior of cyclopentanone (C5), cyclohexanone (C6) and cycloheptanone (C7) in a water/acetonitrile (80/20) mixture at 25 °C on an octadecylsilica reversed stationary phase (RP18).

In order to record the breakthrough curves, a fractional sampling method was applied using a tandem HPLC system. The feed mixtures were continuously introduced into the first HPLC system containing the stationary phase to be chatacterized to generate the breakthrough curve. Applying an injection valve installed at the outlet of this column, a constant volume could be injected automatically in a periodic manner into a second HPLC system for composition analysis. The shape of the inlet concentration profiles is also needed for accurate breakthrough curve interpretation. Due to unavoidable mixing in void volumes of the system, these profiles are not perfectly rectangular. They were experimentally measured by removing the first column.

Adsorption isotherms were measured for the three single-component systems covering a wide concentration range close the solubilty limits. Based on this single component knowledge, competitive adsorption isotherms could be predicted exploiting various mixture isotherm models. To predict also the performance of finite kinetics of the chromatographic separation process, as an additional parameter an apparent axial dispersion coefficients was estimated by adjusting solutions of the equilibrium-dispersion model (Aspen Chromatography, Version 12, AspenTech Inc., USA) to the breakthrough curves recorded. In these simulations, extra-dispersion in a dummy column placed in front of the main column was considered for capturing the shapes of the inlet profiles.

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New Carbamoyl Surface-modified ZrO_2 Nanohybrids for selective Au Extraction from E-Waste

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Efficient and selective extractions of precious metal ions such as Au(III) and Pd(II) were investigated using zirconia nanoparticles surface modified with different organic carbamoyl phosphonic acid ligands. The modification was made on the surface of commercial ZrO_2 that is dispersed in aqueous suspension and was achieved by optimizing the Bronsted acid-base reaction in ethanol/H_2O solution (1:2), resulting in inorganic-organic systems of ZrO_2-L^n (L^n: organic carbamoyl phosphonic acid ligand). The binding mode, amount control and stability of the organic ligand on the surface of zirconia nanoparticles were confirmed by various solid-state characterizations [1].

Batch adsorption results showed that:

(i) ZrO_2 surface modified with di-carbamoyl phosphonic acid ligands had the highest adsorption efficiency to extract metals than mono-carbamoyl ligands,

(ii) higher hydrophobicity of the ligand led to better adsorption efficiency.

ZrO_2, whose surface has been modified with a di-N,N-butyl carbamoyl pentyl phosphonic acid ligand (DBCPPA) (Fig.1), has shown promising efficiency and, more remarkably, selectivity for the recovery of gold over platinum in real industrial E-waste effluents. In terms of thermodynamic and kinetic adsorption data, ZrO_2-DBCPPA fits the Langmuir adsorption model and pseudo-second-order kinetic model for the adsorption of Au(III) with maximum experimental adsorption capacity q_{max}= 6.8 mg.g^{-1}.
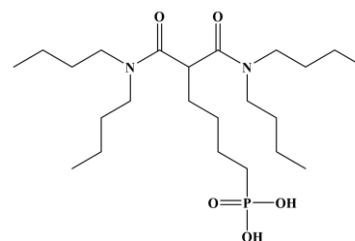
Fig. 1 Structure of Di-N,N-butyl carbamoyl pentyl phosphonic acid ligand (DBCPPA). [2]

Perspectives such as dispersing these hybrid nano-absorbents in electrospun fibers to improve recyclability will also be discussed.

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Mesoporous adsorbent for palladium recovery: synthesis, characterization and adsorption properties

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Palladium belongs to the platinum group metals (PGM) and is necessary for many key industries (information technologies, electronics or catalysts[1]). The supply of these metals also depends only on a few countries (South Africa provides 84% of all platinoids and Russia 40% of palladium[2]). That is why, since 2011, platinum group metals have been classified as critical raw materials by the European Union[2]. By taking into account the pollution associated with mining, it becomes highly desirable to develop the recycling of these metals, in particular from waste electrical and electronic equipment (WEEE). To complete usual WEEE recycling treatments processes, adsorption processes are promising for the recovery of residual trace metals due to their flexibility in design and operation. Conventional adsorbents used in hydrometallurgy (ion exchange resins, membranes) present several drawbacks, including insufficient selectivity. In addition, in some cases, they generate secondary pollution[3].

Our approach consists in developing an adsorbent based on mesoporous silica (MCM-41) that is easily functionalizable but also stable both mechanically and chemically. The selectivity and capacity of the adsorbent is provided by ligand immobilized within the material, *Figure 1*. This material is characterized (DRX, BET, TEM) and adsorption properties are evaluated under various adsorption conditions (ligand nature and content, acid nature and concentration, contact time, etc.). Concerning palladium recovery from an aqua regia medium, a maximum capacity of 104 $mg_{Pd}.g^{-1}$ is obtained in two hours with a trioctylamine impregnated material.
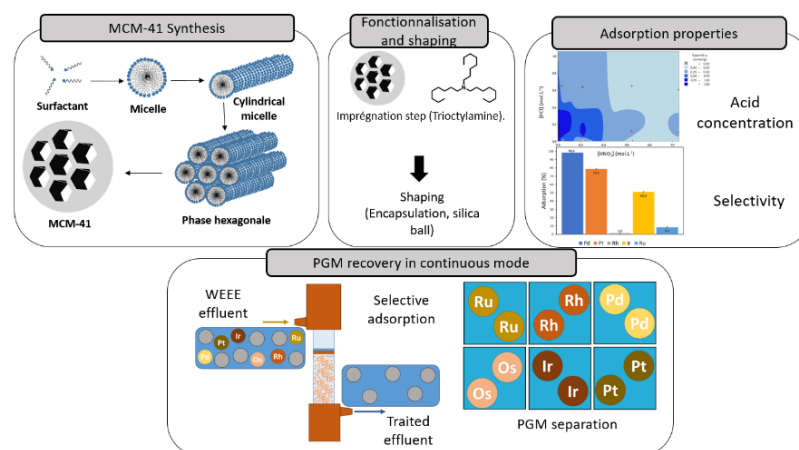

Figure 1: *Synthesis and characterization of the adsorbent. PGM separation.*

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Abstracts of poster presentations

Partially Mg-exchanged GIS for optimized CO_2/CH_4 and CO_2/N_2 separations

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The small-pore zeolites have received much attention in the last few years. Their framework topology comprised of eight-member rings (8MR) with a pore diameter of 3.0–4.5 Å. Thus, they could have suggested them as essential materials for separating small gases [1]. Generally, post-synthesis treatment can alter their separation and adsorption properties [2]. Small-pore zeolite P1 has a gismondine (GIS) type framework, its pore diameter of 3.0 Å can be adjusted for the separation of CO_2 over others gases such as N_2 and CH_4. In this context, we present a template-free synthesis of GIS followed by partially ion-exchange with Mg^{2+} cations. Then, the CO_2 separations of different gas mixtures over the alkali-exchanged adsorbents were compared.
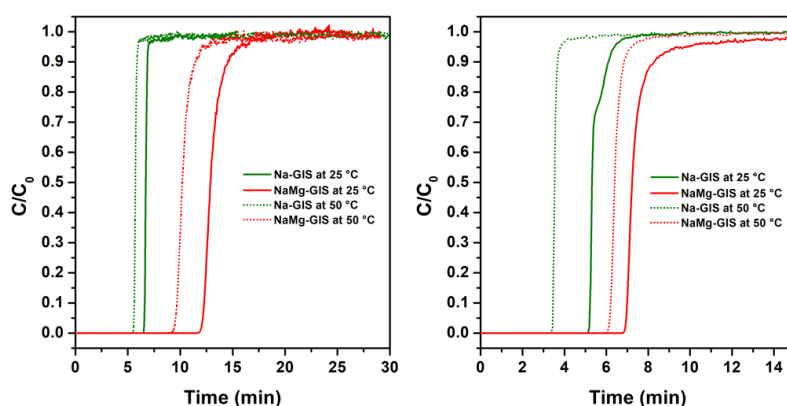
Fig. 1. CO_2 breakthrough at 25 and 50 °C obtained from competitive dynamic adsorption experiments, $CO_2/N_2/He$, 5/25/70 (left) and $CO_2/CH_4/He$, 20/30/50 (right).

Using breakthrough curve analysis, NaMg-GIS showed high separation performance compared to parent Na-GIS. The exchange of Na^+ cations with bivalent cation Mg^{2+} has led to increased space in GIS channels and high framework distortion leading to high CO_2 uptake and making it difficult for N_2 and CH_4 to pass through the 8-membered ring window as a consequence.

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Evaluation of CO_2-CH_4 separation performances by clay-based adsorbent materials for biogas up-grading

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Biogas is a valuable renewable energy carrier, which can be exploited directly as a fuel or injected into the natural gas pipeline grid after being separated from carbon dioxide (CO_2) and other contaminants such as water and hydrogen sulphide (H_2S) [1]. Among different CO_2 capture technologies, the adsorption-based processes (Vacuum Pressure Swing Adsorption -VPSA) account for 18% of installations operating nowadays in Europe [2]. As compared to other separation processes, the main advantages of VPSA are: electrified process with moderate energy consumption, high purity of the produced bio-methane, long lifespan and the compatibility with small scale biogas production facilities.

A great progress has been made in the field of development of new inorganic or hybrid porous materials for CO_2 capture [3]. However, for most of these synthetic materials the use at an industrial scale is limited, in particular because of their high production cost, their sensitivity to impurities and humidity in the gaseous streams [4]. Therefore, the development of inexpensive and scalable adsorbents for CO_2 capture is of high importance for the deployment of bio-CH_4 sector.

Clays are a class of promising low-cost materials, which to date have not been extensively explored in the context of CO_2/CH_4 separation, owing to high specific surface area (several hundreds of m^2/g) and their high crystal densities, some nano-clays can exhibit interesting CO_2 adsorption performances approaching those of commercial adsorbents [5].

In this work, different model clays (purified natural montmorillonites, synthetic hectorites and laponites) were investigated. Their textural properties, including the micropore volume and particles "aspect ratio" were evaluated by molecular probes physisorption (N_2@77K and Ar@87K), employing the revised t-plot, alpha-s and Derivative Isotherm Summation-DIS methods. The latter consists of the deconvolution of high-resolution argon adsorption isotherms with a set of theoretical isotherm components, allowing to quantify the contribution of particles edges and basal faces in the total specific surface area. The CO_2/CH_4 separation performances such as selectivity and volumetric adsorption capacities, were evaluated from pure gas adsorption isotherms, by applying the Ideal Adsorbed Solution Theory (IAST). Adsorption kinetics were evaluated during the fixed volume manometric experiment during isotherm acquisition.

It was observed that the specific surface area is the principal control of gas adsorption by clay systems and that nano-clays with S_{BET} 300-400m^2/g, adsorb above 1 mmol/g of CO_2 at 1 bar and 30°C. Moreover, synthetic nano-clays exhibit CO_2/CH_4 selectivity as high as that of reference material (13X zeolite) while offering significantly faster CO_2 adsorption kinetics. For a series of studied clay systems, the correlations between textural properties and gas adsorption characteristics were established.

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Efficiency of metal-loaded zeolite Y in dye degradation

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Synthetic dyes are a major source of pollution in aquatic ecosystems. Dye reduction using metal nanoparticles is considered an eco-friendly strategy, as it allows low-cost degradation of toxic organic pollutants into non-toxic products [1]. Dye reduction using metal nanoparticles is considered an environmentally friendly strategy, as it enables toxic organic pollutants to be degraded into non-toxic products at low cost [2].

Y zeolite, prepared by hydrothermal route, was used to stabilize Cu, Zn and Ag nanoparticles obtained by ion exchange, followed by treatment with $NaBH_4$ solution as reducing agent.

The designed nanocatalysts were tested in the catalytic reduction of methylene blue (MB) dye in a simple and a binary system to evaluate their efficiency in wastewater treatment. Samples were characterized by XRD, FTIR, UV-vis, SEM and EDS.

The results showed that the conversion of methylene blue (MB) to a colorless product (leuco-methylene blue) depended on the nature of the metal and its dispersion in the zeolite. The efficiency of our catalysts decreases in the following order: Ag/Y > Cu/Y > Zn/Y, MB reduction time was significantly reduced as the $NaBH_4$ concentration increased.

Furthermore, the Ag-Y catalyst was used in three consecutive experiments without any significant loss of activity, confirming its efficiency and stability.

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Preparation and Characterization of ion-exchanged offretite zeolites with cooper, silver and zinc for antibacterial applications

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Zeolites are crystalline microporous aluminosilicates consisting of $[AlO4]^{5-}$ and $[SiO4]^{4-}$, The substitution of an Si_4^+ ion by an Al_3^+ ion in the framework of a zeolite creates a negative charge that must be compensated for by a cation (alkali cation, alkaline-earth cation, ammonium (NH_4^+), quaternary ammonium (R_4N^+))[1-3]. This phenomenon is at the origin of a zeolite's ion exchange properties. In this study, we investigated the hydrothermal synthesis of offretite zeolite using various organic compounds, including tetramethylammonium hydroxide (TMAOH), tetraethylammonium hydroxide (TEAOH), 1,6-diaminohexane (DAH), trimethylamine (TrMA), and dimethylamine (DMA). Different techniques have been used for the structural and textural characterization of our solids: X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX), and thermal analysis (TGA-DTA). TMAOH proved to be the best template for obtaining pure offretite free from any impurities. Subsequently, the prepared offretites were ion-exchanged with Ag^+, Zn^{2+}, and Cu^{2+} ions to evaluate their antibacterial properties. The results obtained were remarkable, demonstrating significant activity against the bacterial strains tested.

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Immersion Microcalorimetry to study the sulfur-carbon interaction

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Within the last decade, sulfur-carbon composites have attracted much attention since they are promising components of electrode material for the next generation of Li-ion batteries [1]. For such applications, sulfur is confined into porous carbon: the carbon ensures the conductivity and the pores are supposed to retain the polysulfides that are formed during the electrochemical cycles [2]. Various hosts are considered such as mesoporous carbon, microporous carbon or carbon nanotubes. While there are numerous studies using impregnation of carbons in order to prepare efficient electrodes for lithium-sulfur batteries, the problem itself of the interaction of sulfur with carbon and its consequences on filling efficiency is rarely addressed. Our approach, based on immersion microcalorimetry, aims to answer two fundamental questions: (i) Is all the carbon surface in contact with sulfur? and (ii) What is the type and energy of interaction between sulfur and carbon? The first answer is important for applications whereas the second one may help the modelling of the electrode behaviour. Our final aim to open a path to the rationale of the impregnation of porous carbon by sulfur.

In this contribution, immersion microcalorimetry studies will be presented. To the best of our knowledge, it is the first time that this method is used at high temperature and with liquid sulfur. It allows the evaluation of the energy of interaction of sulfur with the porous material and to follow the kinetics of wetting. It will be shown that, below the polymerization transition, the kinetics of wetting is rather fast and that S_8 rings are able to enter the micropores [3]. Moreover, physicochemical characterizations of various carbon-sulfur composites show that the sulfur loading in the porous carbon hosts is related to the impregnation temperature and that the sulfur stability is linked to the pore network.

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Hydrogen isotopes separation by selective adsorption on FAU zeolites: influence of Si/Al ratio and cationic composition

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In the nuclear industry, the separation of hydrogen isotopes is carried out by selective adsorption at cryogenic temperature (40-100 K) on microporous materials whose pore size is comparable to the size of hydrogen isotopes molecules (~ 2.9 Å) [1]. This phenomenon, called quantum sieving, stems from the preferential retention of heavier isotopes in the pores of the material due to appearance of quantum effects during adsorption of these molecules at low temperature.

Zeolites appear as a promising class of sorbents for hydrogen isotopes separation due to their high stability, the diversity of the framework structure available and the possibility to modulate their properties through the variation of the cationic composition. Faujasite (FAU type) zeolites are widely used in industry, but their properties in D_2/H_2 separation were previously characterized only at 77 K [2]. The aim of the present study is to better understand the role of Si/Al ratio and cationic composition of FAU zeolites in this process.

The D_2/H_2 selective adsorption properties of different FAU zeolites in a wide temperature range (40 – 77 K) have been characterized under equilibrium conditions using an original self-made coadsorption experiment. NaX (Si/Al = 1.25) and LSX (Si/Al = 1) are considered with two different cationic composition for LSX (Na^+ and Li^+). The amounts adsorbed and D_2/H_2 selectivities are linked to the Si/Al ratio and the nature of the charge compensating cations.

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# Quantification of Water and Silanol Species on Various Silicas by IR Spectroscopy

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Michelin is a world leader in manufacturing and developing environmentally friendly tyres. In this context, they have decided to incorporate silica instead of carbon black as fillers to reduce rolling resistance by improving the rubber's mechanical properties.

As a key component of the reaction, this approach focused initially on characterizing the various adsorption sites. In this regard, several commercial silicas (two different batches of Zeosil® 1165MP, Zeosil® Premium, ULTRASIL® 7000GR, and ULTRASIL® 4000GR) were studied using the H-D exchange method with reactants of different sizes and were followed by InfraRed spectroscopy to determine the OH accessibility at the molecular level. [1]
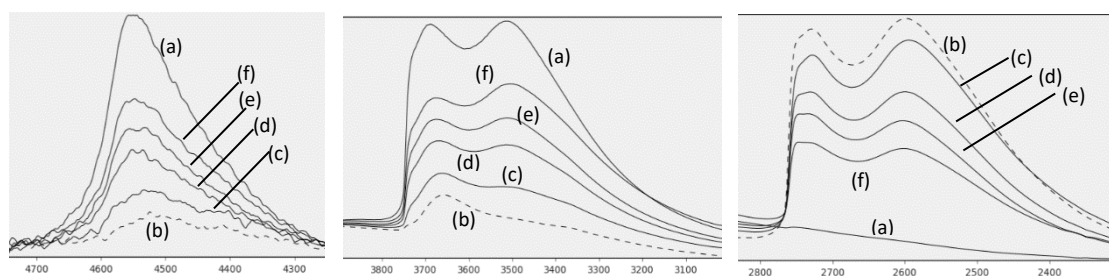
Fig. 1. IR spectra of silica D recorded after dehydration (a), then after H/D exchange by D2O treatment (b-dotted line), and then after back-exchange successively by 3-ethyl-pentan-3-ol (c), 2-methyl-propan-2-ol (d), propan-2-ol (e) and methanol (f).

By qualitatively and quantitively studying the evolution of different vibrational bands due to the H-D exchange and retro-exchange, the accessibility of different silanol groups (internal, external/isolated, and associated) of different silicas to different alcohols was deduced, the silanol and water populations were quantified.

The obtained results will help in future work in understanding the reactivity of silanol groups, and consequentially the different silicas, when studying their interactions with rubber and coupling agents (Silane).

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Radon adsorption in purely siliceous zeolites:

Grand Canonical Monte Carlo simulation study

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Zeolites, crystalline microporous aluminosilicates are frequently applied as adsorbents in decontamination (for volatile organic compounds, persistent organic pollutants, …), or separation of various gaseous mixtures. Whereas a number of investigations of noble gases mixtures separation using zeolites have been published [1,2] the radon adsorption in zeolites has been scarcely described [3]. However, finding a material able to selectively adsorb radon represents a real challenge for both, fundamental research (specifically the domain of subatomic physics) as well as applied research area (decontamination).

We have investigated radon adsorption in the purely siliceous zeolites (zeosils), in order to link its adsorption properties to their structural features, such as the framework density, dimensionality, pore diameter or ring size. Using the Grand Canonical Monte Carlo (GCMC) technique with adapted interatomic potentials for describing the interactions [4], we have simulated (1) radon adsorption isotherms in zeosils at room temperature, as well as (2) the evolution of isosteric heat of adsorption, as function of loading. Furthermore, based on a detailed analysis of obtained data, we could bring out a relationship between radon affinity and selected structural properties. Thus, we could select a couple of zeolite topologies with best radon adsorption performances. Moreover, an investigation of the adsorption properties of xenon within the zeosils, allowed us to select the zeolite topology with the highest separation xenon / radon potential. In order to optimize the adsorbent, the next step concentrates on the influence of the chemical composition on the adsorption performances of previously identified zeolite topologies.

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Molecular Simulation of Acoustic Response of Fluid Adsorption in Nanoporous Materials

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Fluid adsorption and transport in nanoporous materials are at the heart of efficient technologies impacting our economy/ecology: energy storage/conversion, environment protection, health/human welfare, agribusiness/food science, etc. In particular, nanoporous solids shaped as membranes are expected to play a leading role in the "*seven key chemical separations to change the world*"[1] but also to address increasingly complex problems such as bio/agropollutants removal, greenhouse gas mitigation, drinkable water production, etc.

Yet, despite a promised bright future, with more and more separation/catalytic processes to treat, the design of efficient nanoporous membranes is hampered by difficulties in extending their use to severe conditions [e.g. high temperature/pressure, harsh environments, and irradiation]. In practice, extending applications to extreme conditions requires on-line monitoring of material integrity and fluid adsorption/flow (to detect early any material modification or process malfunction). In this context, despite its generalized use in materials science, acoustics is often assumed to be unsuited for nanophenomena due to their large wavelength. Yet, the adsorption/permeation footprint of a nanoconfined fluid is included in an average way in the signal emitted by the system subjected to fluid pressure or acoustic excitation[2].

In this work, we employ molecular modeling and theoretical approach to unravel the acoustic signature of adsorption/transport in nanoporous materials. Different fluid models (coarse-grained versus molecular descriptions) and with different interactions (CH_4 versus CO_2) are studied in a prototypical nanoporous material (zeolite) to probe pore size/interaction effects. By varying, statically or dynamically, the pressure gradient inducing flow and the mean pressure/temperature, the role of transport type (Knudsen, diffusion, viscous flow) and adsorption type (partially and entirely filled pores) will be probed.

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Measurements of thermal effects during intrusion and extrusion

of electrolyte solutions in pure silica zeolites

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Since the 2000s, many studies have been focused on the energy performance of heterogeneous lyophobic systems (HLS). These systems have shown promising properties in the field of mechanical energy absorption, storage and generation. However, few studies have been dedicated to the determination of the heats of intrusion and extrusion in these systems. This is due to the lack of commercial equipment capable of carrying out this type of measurement at high pressure.

To measure the thermal effects during intrusion and extrusion, we have developed an experimental device based on differential calorimetry coupled to high-pressure manometry (up to 4000 bar). We are now able to determine the isobaric compressibility coefficient of electrolyte solutions at different concentrations and the heats of intrusion and extrusion of these solutions into various hydrophobic nanoporous materials (zeolites, MOFs, etc.). This information allows to better understand the mechanism of intrusion and extrusion processes and it helps evaluating the hydrothermal stability of HLS.

In our contribution we will present the measurements of the heats of intrusion and extrusion of various aqueous solutions of alkaline chlorides MCl (M^+: Li^+, Na^+, K^+, Rb^+, Cs^+) in CHA and MFI zeolites. It is shown that the exothermic or endothermic nature of the intrusion phenomenon depends on the concentration of the electrolyte and/or on the nature of the zeolite framework. In addition, it is observed that at constant concentration (H_2O/M^+ molar ratio = 12) the heat of intrusion-extrusion strongly depends on the nature of the alkaline cation in the electrolyte.

Determination of Microporous and Mesoporous Surface Areas and Volumes of Mesoporous Zeolites by Corrected t-plot Analysis

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Zeolites are catalysts involved in many industrial applications. Their microporosity yet impedes diffusion of bulky molecules, enhances secondary reactions and coking. To overcome these drawbacks, zeolites with additional mesoporosity are developed. In this context, it is important to develop/use methods able to evaluate accurately the textural properties of mesoporous zeolites. N_2 adsorption isotherms at 77 K are commonly used to characterize porous materials. Application of the classical *t*-plot to N_2 isotherms can be in theory used for determining the micro- and mesopore surface areas and pore volumes. However, computational studies proved that classical *t*-plot analysis overestimates the mesopore surface areas and underestimates the micropore volumes for micro-/mesoporous materials [1-3]. Measurements performed with mechanical mixtures of zeolites (FAU-Y, MFI, *BEA, MOR) and MCM-41 allows to provide corrections for t-plot analysis [4] to assess real micro- and mesopore surface areas and volumes as a function of the microporosity level in the mesoporous zeolites (Figure 1). Additional catalytic test reactions allow to determine the best compromise between micro- and mesopores [5].
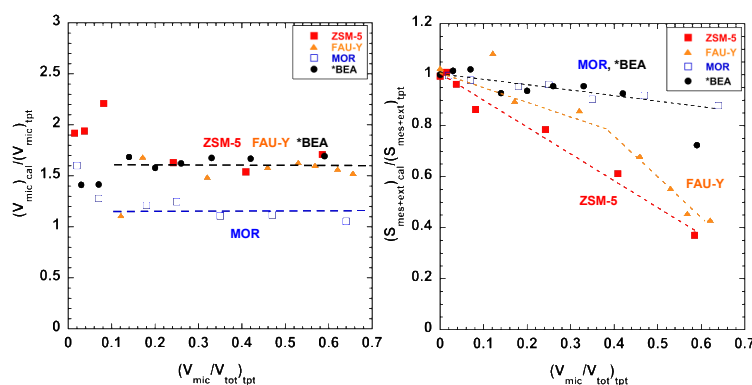
Fig. 1. Correction of t-plot (left) for microporous volume, (right) for surface area [4].

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Structural and Energetic Characterization of Silica-Alumina Gels

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The characteristic adsorption properties of porous materials are dominated by their structural characteristics and their surface chemistry. While the structural characterization of silica-alumina gels with nitrogen adsorption at 77 K, argon adsorption at 87 K or mercury porosimetry is extensively studied, a simple approach for the characterization of the surface chemistry of silica-alumina gels does not exist so far. The surface of silica-alumina gels consists of siloxane and silanol groups. The silanol groups occur in three different forms, namely isolated, geminal and vicinal silanol groups. These groups can only be distinguished by combining time-consuming and complex measurements such as nuclear magnetic resonance (NMR) or Fourier-transformed infrared (FTIR) spectroscopy. In order to provide a simple methodology, a measurement method to analyze the surface chemistry with calorimetric measurements is developed.

Adsorption isotherms and load-dependent heats of adsorption are measured simultaneously using a sensor gas calorimeter. Since the heat of adsorption is a measure of the strength of the prevailing interactions, the obtained data can be used for an energetic characterization. To quantify and eliminate the influence of the structural properties on the energetic characteristics, argon isotherms at 87 K were measured. For the detailed analysis of the surface chemistry, ^{1}H-NMR and ^{29}Si-NMR measurements were performed.

In this study, cyclpopentane, pyrrolidine and acetone are used as adsorptives for the energetic characterization. While cyclopentane forms similarly strong interactions with all silanol groups, pyrrolidine and acetone can form interactions of different strengths with the various silanol groups resulting in plateaus in the load-dependent heat of adsorption. The plateaus represent interactions of equal strength and can be attributed to the adsorption at specific silanol groups. The value and length of the plateau can then indicate the number and type of the respective silanol group. By comparing the load-dependent heats of adsorption and considering the ^{1}H-NMR and ^{29}Si-NMR data, the energetic plateaus can be assigned to the interactions with the different silanol group.

The method is tested on silica-alumina gels with different number and distribution of silanol groups as well as pore size distributions. Within the presentation, selected results are presented and discussed.
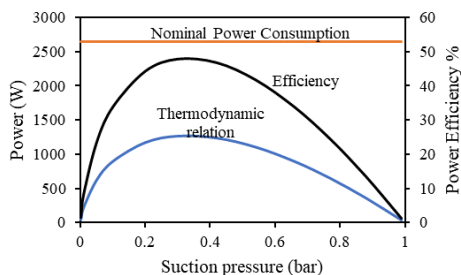
Energy consumption of VSA carbon capture; from lab scale to pilot plant

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Energy consumption is one of the key parameters in decision making for a carbon capture process, and with the momentum toward electrification of this process, it is crucial to be able to estimate the power consumption accurately. Two general approaches have been used to address the energy consumption which include the direct measurement of the consumed power by a power meter, or using a thermodynamic relation (work of compression from a vacuum to atmospheric pressure) with an efficiency factor [1]. A comparison of the results obtained using these two approaches shows shows that the thermodynamic equation underestimates the power consumption [2]. This is because of a typical efficiency factor of 70 % that is considered to convert the ideal work of evacuation to the required power. Comparing the nominal power consumption of an industrial vacuum pump with the calculated work from the thermodynamic relation implies that there is a suction pressure under which condition efficiency is close to 50 % (fig. 1). Since the vacuum pressure during desorption is not a fixed value, it is not straightforward to estimate the evacuation power efficiency and consequently the required power. Here a method has been developed that helps estimating the required power of evacuation by considering variable efficiency under evacuation.

Fig. 1. The efficiency of an industrial vacuum pump

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Gas Separation by Molecular Trapdoor mechanism in multicationic zeolites

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The separation of small gas molecules by adsorption is an essential operation for energy-related industries. Today processes rely on thermodynamic-type separation (PSA, TSA). On the other hand, molecular sieving is a mechanism based on the differences in size and/or shape between the pore aperture and guest molecules. Based on this principle, ETS-4 showed great selectivity for example towards N_2 over O_2 [1], as opposed to the selectivity usually observed in activated carbons. An alternative mechanism known as "Molecular trapdoor" was reported for chabazite zeolites, which can lead to "size-inverse" separation [2]. For example, in Cs-Chabazite, CO_2 is adsorbed whereas CH_4 is excluded. This "size-inverse" selectivity cannot be explained by sieving and was attributed to the interaction between the zeolite cation and the guest molecule.
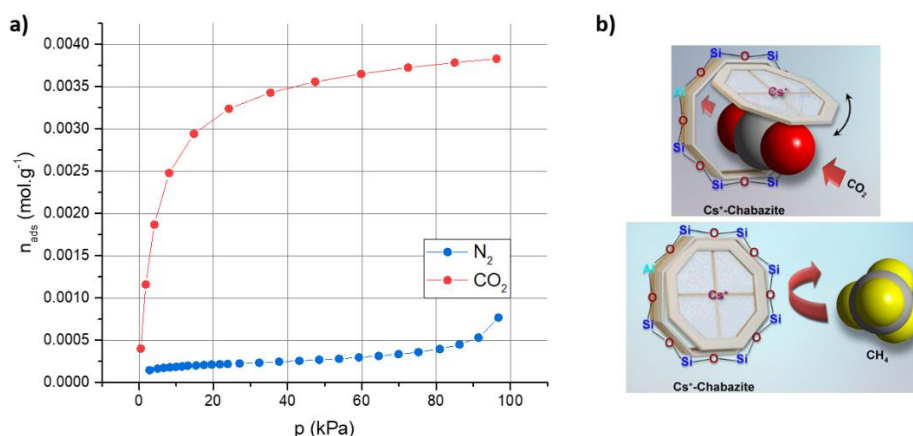

*Fig 2. a) **Adsorption isotherms of N_2 (77K) and CO_2 (298K) on K-CHA. b) Trapdoor mechanism in Cs-CHA** [2].*

Our objective is to study adsorption mechanisms in mixed cationic small pore zeolites such as LTA and CHA. To this end, we have synthesized various cationic exchanged zeolites (Na, Mg, K, Ca) and we have measured single component isotherms of small molecules (CH_4, CF_4, CO_2 and N_2).

As preliminary results, we have confirmed that N_2 cannot diffuse in K-CHA whereas CO_2 gets adsorbed. We will present original results on mixed cationic zeolites and various gases with different characteristics (polarity, size).

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Enhancing gas adsorption through HKUST-1 hybridization with activated carbons

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This study explores the potential of HKUST-1 composites for gas adsorption. We conducted an investigation to assess the impact of hybridizing metal-organic frameworks (MOFs) with 4 different activated carbons (ACs) having specific surface area (A_{BET}) ranging from 985 to 3305 m^2/g on the textural properties and gas sorption capacities of the resulting composites [1]. The incorporation of these ACs led to modifications in the pore size distribution and A_{BET} of the resulting hybrids, which aligns with findings from previous studies [2], [3]. The primary objective of this research is to evaluate the effectiveness of these hybrid, synthesized using AC to HKUST-1 ratios between 1% and 10%, in adsorbing CO_2 and H_2. Fig 1a) shows the nitrogen adsorption-desorption isotherms at 77K and Fig 1 b) illustrates the changes in A_{BET} for the hybrids prepared by addition of increasing percentages of Filtrasorb 400 to HKUST-1. Additionally, we will present a comprehensive characterization of the materials, along with experimental data on the sorption capacities of the composites under different pressure and temperature conditions.
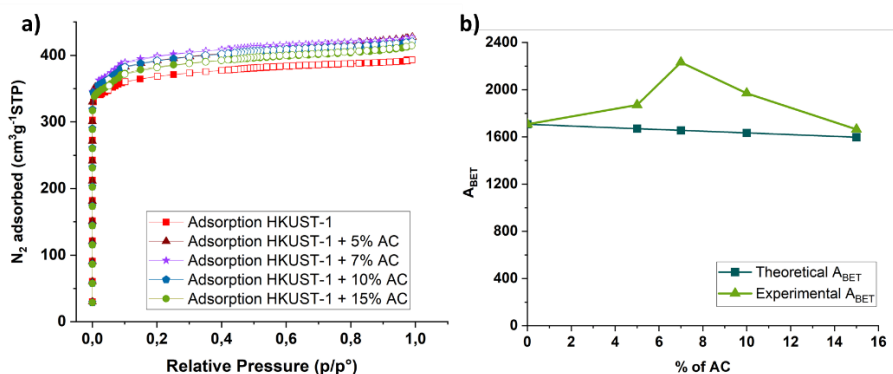

Fig. 1. **a) nitrogen adsorption-desorption isotherms at 77K of the for the hybrids prepared by addition of increasing percentages of Filtrasorb 400 to HKUST-1; b) illustrates the changes in A_{BET} comparing the theoretical and experimental values.**

References:
[1]		P. Ramirez-Vidal *et al.*, 'A Step Forward in Understanding the Hydrogen Adsorption and Compression on Activated Carbons', *ACS Appl. Mater. Interfaces*, vol. 13, no. 10, pp. 12562–12574, Mar. 2021, doi: 10.1021/acsami.0c22192.
[2]		E. Rojas-Garcia, A. A. Castañeda-Ramírez, D. Angeles-Beltrán, R. López-Medina, and A. M. Maubert-Franco, 'Enhancing in the hydrogen storage by SWCNT/HKUST-1 composites: Effect of SWCNT amount', *Catal. Today*, vol. 394–396, pp. 357–364, Jul. 2022, doi: 10.1016/j.cattod.2021.08.004.
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Study of glycine behavior in a comet.

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Thanks to hydrogen bonds, water molecules can form various crystalline structures, one of which is known to all of us as ice and the second as clathrate hydrates, which are crystalline compounds formed under certain thermobaric conditions from water and gas. However, when we talk about ice, we are most likely talking about one of the Ih phrases, since almost all ice on earth belongs to this type. There are 18 more different forms of ice that form at different temperatures and pressures. Some of these phases form at low pressure and at super cold temperatures, under these conditions, ice exists in some celestial bodies (comets) of interest to us in outer space, through modeling we can access the so-called "no man's land". In our work, we studied the interaction of two forms of the simplest amino acid, glycine (neutral and zwitterion) with water in its various forms, according with the conditions. Interactions are studied by using molecular dynamics simulations with the Gromacs package. For a correct description of the interaction of glycine molecules with water, we used the TIP4P-FB model of water [1], that describes, quite correctly, the most important parameters of water and its crystalline formations, as well as the Amber99SB-ILDN force field [2]. This last is most preferable for studying interactions between water and glycine.

We carried out simulations in which glycine was initially placed at the interface between ice Ih and water, while the simulation box consisted of half amorphous water and half ice Ih, before which the selected water model was successfully tested for the ability to form new hexagons on the interface between ice and water. As a result, we observed diffusion in the case when the neutral form of glycine was chosen, while glycine practically did not prevent the growth of ice from water molecules of amorphous water. And in the case of a similar simulation with zwitterion, we saw the total destruction of the ice crystal lattice (Figure 1). All simulations were carried out using the NPT ensemble under the same conditions T= 200K and P= 1 Bar, simulation time was 30 ns, excluding equilibration cycles.

The analysis of changes in the crystal lattice of ice was carried out using Q4, Q6 (Figure 1), F4 structural parameters [3-4] and FFT. Similar simulations were carried out with clathrates, but no changes in the structures of clathrates were observed, and no formation of new cells was observed, the conditions were the same as for ice. We are currently studying phase transitions between different forms of ice (LDA- ice Ic – ice sd- ice Ih) and the behavior of glycine molecules at the interface between different ice phases.
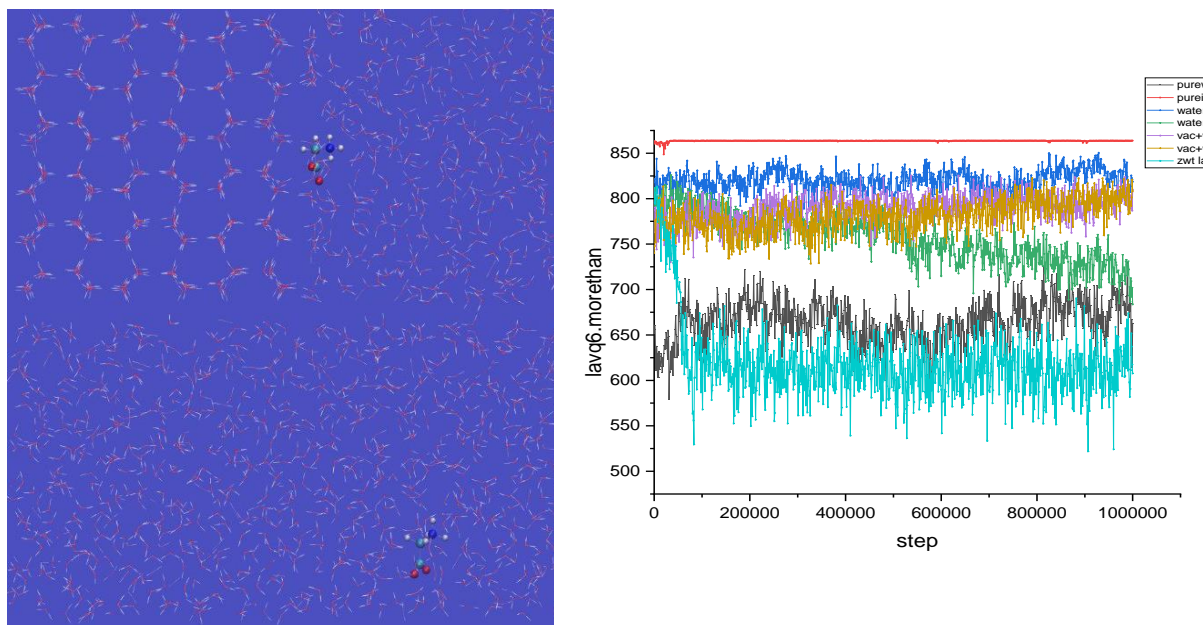
Figure1. Snapshots of the first step in the production cycle and the last one and values of Q6 parameters for chosen systems

References:

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Molecular dynamics simulation of glycine in contact with ice

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We carried out molecular dynamics simulations (GROMACS package) of glycine in contact with amorphous water and ice using the NPT ensemble under at a temperature T= 200K and pressure P= 1 Bar. Glycine was simulated using both its neutral form and the zwitterionic one. For a correct description of the interaction of glycine molecules with water, we used the TIP4P-FB model of water [1], that correctly describes most important parameters of water and its crystalline formations, as well as the Amber99SB-ILDN force field [2]. This last is most preferable for studying interactions between water and glycine. The amino acid was located at the interface between hexagonal ice Ih and water. In the case of the zwitterionic form of glycine, we saw the total destruction of the ice crystal lattice (Figure 1). For the neutral case, ice remains and the presence of glycine practically did not prevent the growth of ice from amorphous water. Additionally, we observed diffusion of glycine that leaves the interface to the bulk water.
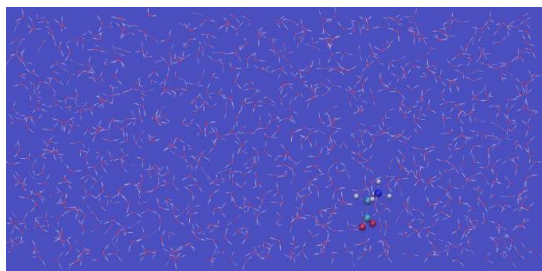
Fig. 1. Snapshots of the zwitterionic glycine in contact with water after de structuration of hexagonal ice

References:

[1] Wang, L. P., Martinez, T. J., & Pande, V. S. (2014). Building force fields: An automatic, systematic, and reproducible approach. Journal of Physical Chemistry Letters, 5(11), 1885–1891.
https://doi.org/10.1021/jz500737m

[2] Zhang, H., Yin, C., Jiang, Y., & Van Der Spoel, D. (2018). Force Field Benchmark of Amino Acids: I. Hydration and Diffusion in Different Water Models. Journal of Chemical Information and Modeling, 58(5), 1037–1052. https://doi.org/10.1021/acs.jcim.8b00026

Design of an unprecedent filtration device based on an elastic adsorbent for the adsorption intensification process of metal ions

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Efficient recovery of metal ions from water is crucial due to their environmental impact and economic value. Addressing this challenge involves developing innovative methods for (*i*) a fast filtration of high volumes and a (*ii*) cost-effective extraction, ensuring sustainable resource management and minimizing pollution. Recently, our group has shown that open cell polymer foam coated with a bio-based polyphenolic film is an excellent adsorbent for metal ions (Figures 1A, 1B). In addition, its compressibility does not limits its performance and results in an increase of the specific surface of adsorption in a given volume [1]. Herein, an original elastic adsorbent is proposed as a complementary approach to traditional techniques for traces metal recovery and process intensification (Figure 1C). The preparation and characterization of the adsorbent will be shown. Polydopamine is used as model of polyphenol coating [2] and Pb(II) as model of metal ions to establish a proof of concept. The influence of the compression of the adsorbent at various frequencies as a function of time will be given. A comparison study with a static mode (without compression) will be also provided.
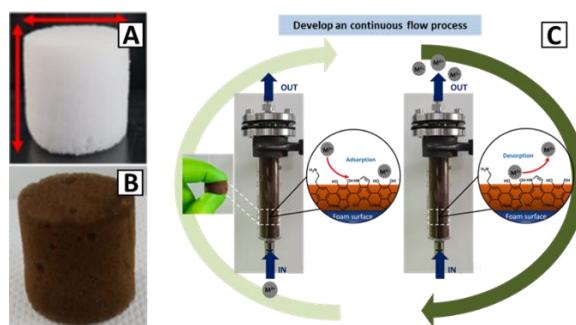
Figure 1. (**A**) Uncoated melamine foam, (**B**) melamine foam coated with polydopamine, (**C**) filtration system filled with melamine foams coated with polydopamine

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Extruding diffusion constants from your extrudates:

pore geometry and adsorbate kinetics

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The diffusion of molecules within the confines of material pores remains a relatively poorly understood research area. This lack of understanding persists despite the diffusion process's critical role in many adsorption phenomena, such as adsorbate selectivity and uptake kinetics. As such, a new model for the analysis of diffusion constants, obtained using a chromatographic Zero-Length Column method, is derived and utilised to accurately determine the micro and macropore diffusion of small molecules in zeolites. Additionally, the work bridges the gap between diffusion analysis techniques such as pulsed field-gradient NMR.

The proposed mathematical model was derived from the system mass balance and accounted for fluid-phase contributions, which can be significant in liquid systems[1].

$$\frac{C}{C_0} = \sum \frac{2L - \gamma(\beta_n)^2}{(L - (\gamma(\beta_n)^2)^2 + (\beta_n)^2} e^{-\frac{D\beta_n^2}{R^2}t}$$

Experimental studies of adsorbate desorption from crystals and extrudates of zeolite NaY and ZSM-5 were combined with this mathematical model to determine limiting uptake kinetics.
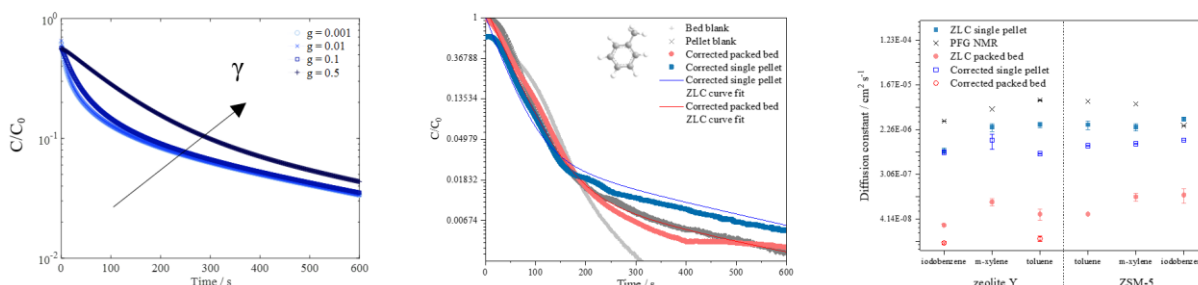
Fig. 1. (A) Simulated diffusion curves with increasing fluid hold-up, γ **(B)** Diffusion models fitted to experimental toluene data from zeolite Y (**C**) A comparison of NMR and ZLC diffusion constants.

Diffusion constants were found to increase in extrudate materials, with more extensive macropore diffusion contributing towards the overall diffusion coefficient. This extrudate diffusion was less affected by surface diffusion, resulting in an increased correlation with diffusion constants obtained from Pulsed-Field Gradient NMR.

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Recent developments in molecular Density Functional Theory: towards a more versatile tool for the characterization of nanoporous materials

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Among theoretical developments, the molecular density functional theory (DFT) has emerged as one of the most powerful and convenient molecular approach for the description of the thermodynamic properties of inhomogeneous fluids. The development of DFT for classical fluids originates in the late 70's [1] and its use is nowadays widespread for the description of fluid interfaces or fluids confined in nanopores, the characterization of porous materials [2], the analysis of freezing/melting transitions in simple fluids as well as in colloidal dispersions [3], etc. The success of DFT approaches is explained by the fact that they preserve detailed information on the microstructure of inhomogeneous fluids but with a much lower computational expense than molecular simulations. Much progress has been made in recent years in the development of both: i) the formulation of more realistic free energy functionals, necessary to account for complex fluids [4], ii) and more efficient numerical algorithms to apply DFT to complex geometries [5]. However, most applications - and especially the ones dedicated to the interpretation of adsorption isotherms of the gas probes in porosimetry - have on the one hand assumed specific simple continuous pore geometries, and on the other hand, were restricted to simple models for the fluids. In this work, in order to use DFT in more complexly structured materials such as zeolites or MOFs, a novel methodology is proposed, and multi-dimensional geometries are now reachable within realistic times. Adsorption of several gases in zeolite 13X is used as a test-case to show the ability of the proposed method. Adsorption of CO_2 and water in carbonaceous materials is also considered to illustrate the case of the adsorption of more complex fluids.
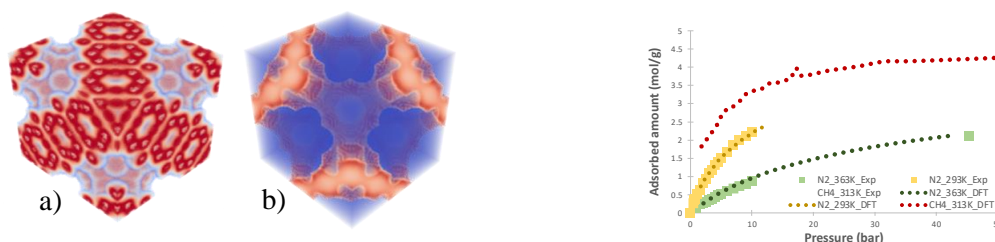
Fig. 1. (left) Nitrogen adsorption in a 13X zeolite cavity, a) fluid-solid interaction potential, b) corresponding fluid density profiles. (Right) Experimental and modeled adsorption isotherms in 13X.

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Competitive CO₂/H₂O Dynamic Column Breakthrough of CALF-20 Under Adiabatic Conditions

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Water vapour always presents in the industrial flue gas along with carbon dioxide, nitrogen and other contaminations. The presence of water vapour makes the CO_2 separation from the flue gas more difficult. Understanding the competition of CO_2 and H_2O and their interactions is crucial to effectively design an adsorption process. In this study, the competitive adsorption of CO_2 and H_2O on CALF-20 was performed. The binary CO_2/H_2O dynamic column breakthrough (BT) experiments were used to evaluate the competitive adsorption. Initially, the bed was regenerated at 120℃ using nitrogen. All breakthrough experiments were conducted under adiabatic conditions using an insulation. Different sets of experiments were carried out-at feed gas condition ranged 3-5% H_2O, 16% CO_2 and balanced N_2 at 40 ℃. In each set of experiment, the initial moisture concentration in the bed was varied from 0% to 1.5% to study the effect of the amount of H_2O pre-adsorbed in the bed. All temperature, composition and flowrate histories were recorded during the test. Commercial Aspen Adsorption and a built in-house model were used to predict the competitive CO_2/H_2O dynamic column breakthrough adsorption. A good agreement between the experimental and simulated breakthrough was observed.

# Correlation between gas storage capacity and surface area in MOFs?

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Microporous materials, in particular Metal Organic Frameworks (MOFs), are promising candidates for enhanced gas storage. Recently, capacity targets were achieved for H_2 or CH_4 storage which would enable novel mobility applications.

For activated carbons (AC), it is well known that a linear trend exists between the specific surface and gas storage capacity [1]. However, MOFs present more diverse pore structure and surface composition than ACs. In particular, MOF may exhibit Coordinated Unsaturated Metal Sites (CUS) which are known to be strong adsorption sites [2]. Here, we aim at studying the relative effect of CUS versus specific surface area in MOF and test if a linear trend still holds, despite their variety in structure and composition. We chose a series of well-known MOFs presenting different specific surfaces – some of them exhibiting CUS – and experimentally measured their adsorption capacities for different gases including N_2, CO_2, CH_4 and H_2, following a method already tested on hydrogen with activated carbons (cf. figure 1, preliminary results).
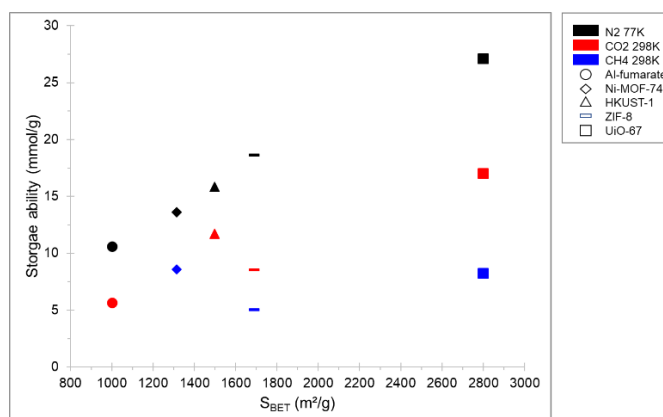
Fig. 1. Storage capacity of various MOFs as function of the specific surface area.

We expect our results to provide relevant insights on structure-properties of MOF for gas storage applications in order to allow the establishments of main guidelines. Results will be discussed with Molecular Modelling data available in literature.

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Investigation of catalytic COS formation on zeolites

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The main component of natural gas is methane. Besides that, trace amounts of sulfur containing components, carbon dioxide and higher hydrocarbons can be also included. The raw gas must be purified to fulfill pipeline standards and high purity specifications of the final product, such as Liquefied Natural Gas (LNG). An industrially common method for this purpose is the fixed bed adsorption technology using cyclic temperature swing adsorption processes (TSA). In these processes toxic and corrosive sulfur components such as hydrogen sulfide (H_2S) and carbonyl sulfide (COS) can be removed. Due to the good capacity and regenerability, zeolites are used. Unfortunately, the desorption phase of the fixed bed, COS formation may occur due to a catalytic reaction of H_2S and CO_2. After desorption, the treated purge gas is recombined with the raw gas and returned to the process. However, no reduction of the COS concentration is achieved by the treatment, so that the COS undesirably enters the product gas stream as a polluting component. For the design and optimization of such processes a deep knowledge of the adsorption behavior of the components to be separated and the COS formation is required. Furthermore, the adsorption properties of the adsorbents used must be well known. The aim of this research project is to systematically investigate the adsorption and desorption behavior and the catalytic activity of commercial and newly developed zeolites.

For this purpose, experiments are performed in a fixed-bed adsorption unit with process temperatures between 0 °C and 200 °C. By using mass balances, the equilibrium loads are determined from the measured outlet concentrations. A comparison of the adsorption behavior of the respective components and the total amount of COS formed allows conclusions to be drawn both about the adsorption mechanisms occurring and about the selectivity and catalytic activity of the adsorbent. In the contribution first results of the investigation of the COS formation will be presented and discussed.

Impact of airborne nanoparticles on workers' health:
a new method based on Krypton gas adsorption

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Engineered nanomaterials in powder form are increasingly used in industry, leading to legitimate concerns about their impact on health. Furthermore, several studies have shown evidence of surface area being a relevant criteria to estimate potential toxicological effects of nanoparticles [1-2]. Therefore, measuring the surface area of airborne nanoparticles could be a useful tool for occupational exposure assessment related to biological effects but still remains a complex analytical challenge.

To characterize the specific area of airborne nanostructured particles, a filter-based method of particle collection followed by gas adsorption analysis has been developed. Polycarbonate 0.8 µm pore-size filters cover all the required physical properties, specifically weight and surface stability under degassing conditions. Krypton gas was used as it is more suitable for low specific area measurement. Using this configuration, the instrument detection limit was established below 170 cm².

The proposed method is currently being validated on aerosols samples generated from commercial powders using a suitable generation bench (Fig. 1).
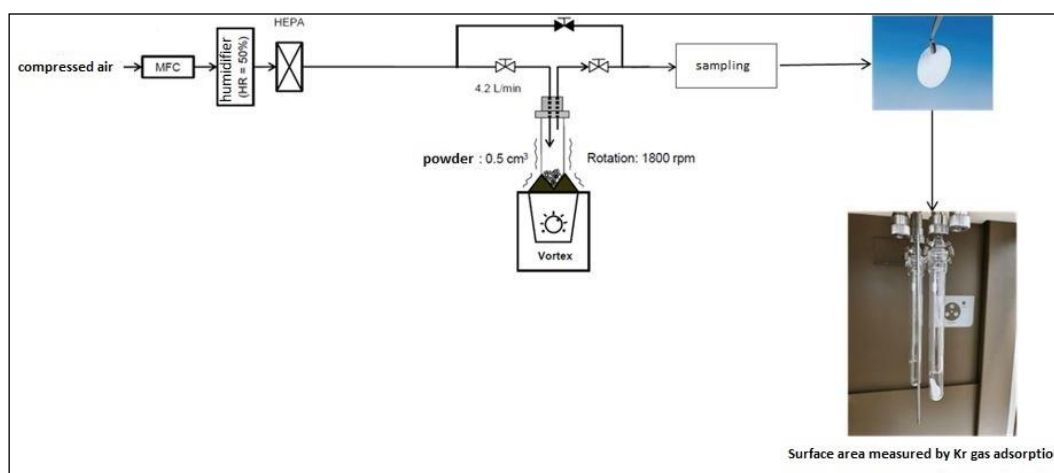

Fig. 1: diagram of the bench used to generate aerosol from a commercial powder.

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Sieving of H_2 and its isotopes by zeolites:

Molecular simulations achievements and failures

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Molecular simulations of the adsorption of H_2 molecules in zeolites commonly em- ploy non-polarizable empirical force fields. Such models provide coherent results with experiments above 77K. Unfortunately, below this temperature the spherical hydrogen representation fails to reproduce experimental results. This tendency is accentuated for cationic zeolites. In this case, the disagreement may arise from the interplay of the atomistic heterogeneity and the electric field produced by the host structure. These aspects, typical of nanoporous materials, are generally excluded in classical force fields. And have lead, by some authors, to an overestimation of the interaction between the cations and H_2. Worthwhile to mention that even when a temperature correction is used (i.e., the Feynman-Hibbs approximation) the agreement at middle range pressures is satisfactory at low and high pressures the failure cannot be disguise. Here, these issues are revisited by performing DFT and ab initio simulations for the faujasite $Na_{86}X$ at 40K with and without guest hydrogen molecules. These calculations allowed to determining the electrical field generated by the zeolitic structure. Our results show that the electrical field of the host structure induces a dipole moment on the hydrogens of ≈0.32 D. Despite this small value, is shown an enhancement of adsorbed molecules. The formation of a dipolar moment in the H_2 suggests that at cryogenic temperatures the agreement with experiments passes through the use of polarizable models of H_2. Here are detailed recent advances along this direction for providing a reliable analytical force field for H_2 interacting with faujasite structures.

Aspects of a novel sensitive method for meso-macropore analysis based on nitrogen adsorption at the triple point temperature (63 K)

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Major progress has been made during the last decade concerning textural characterization by physical adsorption, also because of the development and availability of theoretical procedures based on statistical mechanics (e.g. non-local density functional theory NLDFT and molecular simulation) coupled with high-resolution experimental protocols for the adsorption of various subcritical fluids (e.g. argon, nitrogen at 77 and 87K). With these fluids It is possible to assess surface areas as low as 0.5–1 m^2, but in order to assess even lower surface areas (as important for nanoporous thin films, membranes, materials with low specific surface area.), krypton adsorption at 77 K is generally the recommended method   which allows one to determine absolute surface areas $<$ 0.01 m^2 . However, at 77 K and 87 K, krypton is well below of its bulk triple point (I,e. at 77 K ca. 38 K) [1,4] and coupled with the effect of confinement on the phase behavior, krypton pore size analysis is possible only up to ~10 nm   (i.e., at 87K). Hence, for   physisorption characterization o f thin films/membranes exhibiting larger meso/macropores, novel methodologies are needed. A contribution towards this goal would be to establish thermodynamic conditions where the pore condensation region for a given adsorptive/ adsorbent system is shifted to the lowest possible relative pressure (i.e. expected at or just above the bulk triple point temperature) and in addition, the sensitivity of the measurement is sufficiently high.

Within this context, we have developed a novel methodology based on nitrogen adsorption at the triple point temperature (63 K). For the method development, we utilize a series of highly ordered mesoporous molecular sieves (KIT-6 silica) and macroporous controlled pore glasses (CPG). We have successfully applied our new method or the textural characterization of meso-/macro- porous anodic alumina films exhibiting pores $>$ 30 nm. While for such films krypton adsorption only allows one to determine the surface area, with the new method it is not only possible to obtain reliable surface area information (the sensitivity of nitrogen adsorption at 63 K is at least ca. 8 times higher than at 77K) but also to obtain the complete meso-macropore size distribution.

Summarizing, we suggest a novel methodology based on nitrogen adsorption at the triple point temperature, which significantly increases the sensitivity of adsorption measurements further intrinsically extends reliable physisorption characterization into the macropore size range.

Development and application of a novel pore network model for physisorption characterization

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Physical adsorption characterization is one of the most widely used techniques to characterize porous materials due to being reliable, well understood and, since the introduction of NLDFT kernels, able to assess micro- and mesopores within one unified approach. Major advances in the structural characterization have been achieved in the last two decades by coupling these methods with high-resolution experimental adsorption isotherms. Still, open questions about the pore size and pore network characterization of disordered and hierarchical materials remain. Porous materials used in applications consist of interconnected networks, exhibiting pronounced cooperative behaviour during adsorption/desorption visible in the hysteresis behavior. Even though several network models have been suggested in the past, so far it was not possible to feature all known contributions to hysteresis such as pore blocking/percolation and cavitation induced evaporation, delayed condensation due to metastable pore fluid as well as initiated condensation.

Within this framework we have developed a novel network model based on bond percolation which is able to account for cooperative effects during both, adsorption and desorption as well as during desorption hysteresis scans. This enables one to model the whole isotherm including hysteresis scans within one unified framework. The model yields a pore size distribution (PSD), which is corrected for network effects, as well as important pore network parameters such as for instance the connectivity, which represents the average number of connections of a mesopore. The model can continuously transition in between the borderline cases of the independent pore model and highly disordered pore networks. We provide several application examples, selected to be a diverse set of various adsorbents (vycor glas, chromatography monolith, KIT-6, SE3030) to show the possibilities using the model. For all materials, the primary ad- and desorption curves as well as the desorption scans were captured well, yielding an extended textural characterization,

Summarizing, we can state, based on our results, that the developed pore network model advances significantly the available toolbox for comprehensive and reliable pore size and pore network characterization of disordered and hierarchically structured materials.

CPO-27(Ni) pelletization: Impact on structural, textural, and thermal properties

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CPO-27 is a Metal-Organic Framework (MOF) that assembles divalent metal cations to the organic linker 2,5-dihydroxyterephthalate (dhtp) *via* the oxygen atoms of both the carboxylate and phenolate groups. Each M^{2+} is also coordinated to an oxygen atom of an adsorbed water molecule, which may be desorbed upon heating, generating an unsaturated metal site [1] with great potential to achieve alkane/alkene separation. Despite the density of information found in the literature regarding the syntheses approaches and the physical-chemical properties obtained, a lack of information remains on the impact of shaping on the material's properties. Indeed, it is important to outline the importance of shaping for the viability of the industrial applications [2]. The aim of this work is to assess the impact of compression on the textural, thermal and structural properties of CPO-27(Ni). Pellets were prepared by compressing the powder at a range of compression forces (5 to 90 kN). The compressed samples were characterized by powder XRD, TGA and N_2 adsorption/desorption at -196.15 °C. The results reveal a significant change of the textural properties for the compressed samples compared to the starting CPO-27 (**Fig. 1**), especially for those compressed at higher forces. It is noteworthy that the samples compressed at lower forces (10 kN and below) show similar textural properties with rather low crystallinity loss.
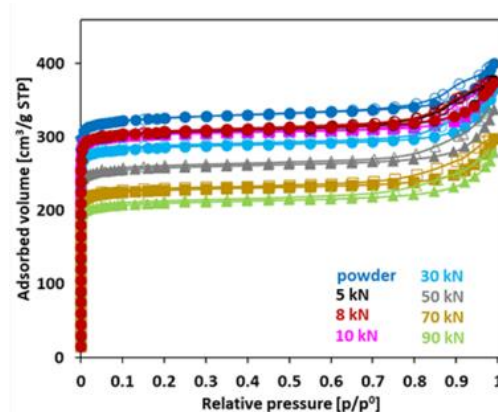
Fig. 1. Nitrogen adsorption/desorption isotherms of CPO-27(Ni) samples measured at -196.15 °C in powder and in compressed pellets at different forces.

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# Frontal analysis method with fractional sampling technique using a tandem HPLC system

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Chromatographic separation processes are widely used for the purification of valuable compounds from complex mixtures. For the design and optimization of these processes, knowledge of the adsorption isotherms is essential. In general, the adsorption isotherm parameters are experimentally determined in single-component systems, and the extended multi-component isotherm models with the same parameters are applied to estimate the adsorption equilibria in a multi-component system. Frontal analysis (FA) is one of the frequently applied methods for measuring parameters of adsorption isotherms of single-component to competitive multi-component systems [1].

In this work, the adsorption equilibria of three different component systems, cycloketones, benzenes with alipatic carbon chains, and methoxybenzenes, were investigated using FA. In order to observe the breakthrough curves precisely, a fractional sampling method was applied using a tandem HPLC system (Fig. 1). The feed mixtures were continuously introduced into the first column to form a breakthrough curve. A fixed-volume injection valve was connected at the outlet of the column to collect the samples intermittently and injected them directly into the second HPLC system to analyze the concentrations. The adsorption isotherm parameters measured in the single-component systems were applied to explain the competitive adsorption behaviors of the multi-component mixtures.
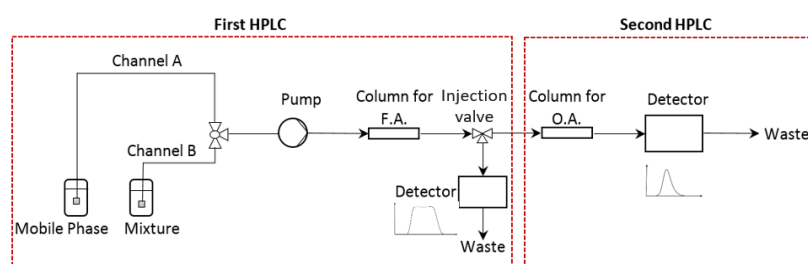
Fig. 1. Schematic of configuration of a tandem HPLC system applied for frontal analysis.

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Machine Learning Perturbation Theory for an accurate prediction of adsorption enthalpies

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In an effort to further improve the accuracy of ab initio simulations and reach the chemical accuracy at a moderate computing cost, we propose a method that couples machine learning techniques with thermodynamic perturbation theory to estimate finite-temperature properties using correlated approximations [1]. We apply this approach to compute the enthalpies of adsorption in zeolites and show that reliable estimates can be obtained by training a machine learning model with few energies computed at the Random Phase Approximation or the Couple-Cluster levels of theory, which are among the most accurate quantum methods available today [2,3]. This approach paves the way to the broader use of computationally expensive quantum-chemical methods to predict the finite-temperature properties of condensed matter systems. In close connection with experiments, this theoretical methodology opens the path to an integrated approach for the development of optimized nanoporous materials and processes in the fields of adsorption and environment.
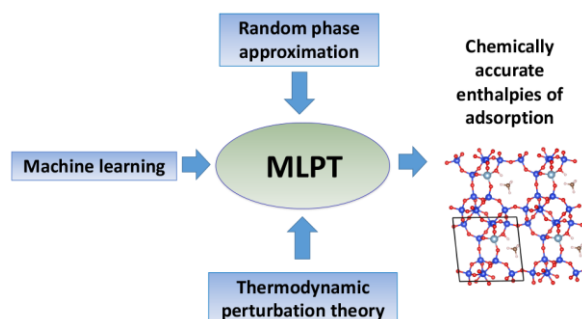
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Role of water content in amine-grafting of silica gel beads for CO$_2$ adsorption

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Industrial decarbonisation is crucial for reducing atmospheric carbon levels. CO$_2$ adsorption using amine-functionalized adsorbents (AFAs) offers an energy-efficient alternative. Synthesis of these adsorbents involves impregnation or grafting methods. Impregnation attaches amines through Van der Waals forces and hydrogen bonding, while grafting forms covalent bonds for increased thermal stability[1], [2].

While mesoporous SiO$_2$-based support structures like SBA-15, MCM-41, and MCM-48 have been extensively studied for AFAs due to their substantial surface area and pore volume, silica gel beads, another SiO$_2$-based support, present notable attributes. Despite its cost-effectiveness, ample surface area and pore volume, silica gel has been comparatively underexplored as an AFA support. An existing study highlights the time-intensive nature of functionalizing silica gel with amines, taking up to 120 hours for a batch [3].

This study overcomes this challenge by introducing a more efficient approach to synthesising AFAs, utilising silica gel as the support material. This study highlights the significance of water content in the synthesis process, potentially offering insights into advancing AFA production methodologies. The synthesised samples underwent comprehensive characterisation, including surface characteristics, CO$_2$ isotherms, elemental analysis and functional group confirmation, CO$_2$ capture capacity, thermal stability, and cyclic stability. The obtained results indicate a reduction in synthesis time, along with improvements in amine loading and CO$_2$ adsorption capacities.

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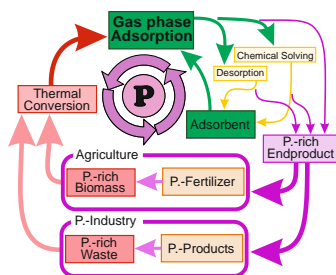
Carbon-based Materials as Promising Adsorbents for Gas Phase Phosphorus Recovery

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Phosphorus is a non-substitutable element for life on earth. To ensure food security, 458 kt of phosphorus are used as fertilizer in Germany alone each year to compensate for the loss of phosphorus in agriculture as a result of crop harvesting [1]. Due to the global population growth, the demand for phosphorus fertilizers will double by 2050 [2]. In addition, the increasing use of biomass for energy production and industrial purposes, will intensify the competition for the critical resource phosphorus. In the quest for long-term sustainability, ways must be found to provide a renewable supply of phosphorus and to establish a circular economy. One important route is the recovery of phosphorus during the thermal utilization of biomass. Under carefully selected conditions, phosphorus compounds are released into the gas phase [3].

So far there are no established processes for the selective removal of phosphorus compounds from gas streams.

Fig. 1. Closing phosphorus cycle via gas phase adsorption process

Carbon-based materials are promising adsorbents for this application. Taking advantage of their large surface area, and tailoring of adsorption properties by doping with metal salts, carbon materials were investigated for selective adsorption of phosphorus compounds. For this purpose, carbon-based materials were doped with different metal salts, including Al-, Mg- and Ga-salts, and the influence of specific acid sites on the adsorption properties was investigated. The adsorbents were characterized by BET and TPD [4]. Phosphorus adsorption experiments were performed and the adsorption capacity, strength and binding modes were analysed. Furthermore, the potential to recover the adsorbent was investigated and found to be highly dependent on the initial synthesis of the carbon-based material.

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# Water and carbon dioxide co-absorption isotherms evaluation through dynamic column breakthrough analysis

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The growing interest in capturing carbon dioxide from dilute streams, including the air, has led to the exploration of various solutions, including the application of CO_2 sorbents. A promising example is the sorbent Fiban A1, which comprises a fiber composed of an anion exchange resin with quaternary ammonium functional groups ($-N^+(CH_3)_3Cl^-$), where the chloride ions are exchanged for carbonate ions. This sorbent chemically absorbs carbon dioxide when dry and releases it when wet. In ambient air, it undergoes spontaneous drying and subsequently adsorbs CO_2. This offers the option to exploit a moisture-induced cycle that contrasts thermal and pressure swing processes [1]. Carbon dioxide in completely dry air is not absorbed by the fibers because the chemical adsorption process involves water as well, focused on the reaction:

$$CO_3^{2-} + H_2O + CO_2 \leftrightarrow 2HCO_3$$
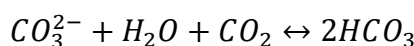
For this reason, it is interesting to study how humidity influences the CO_2 loadings.

This study focuses on the preliminary characterization of the sorbent. Specifically, the dynamic breakthrough experiments are employed to determine adsorption and desorption isotherm curves of water and carbon dioxide.
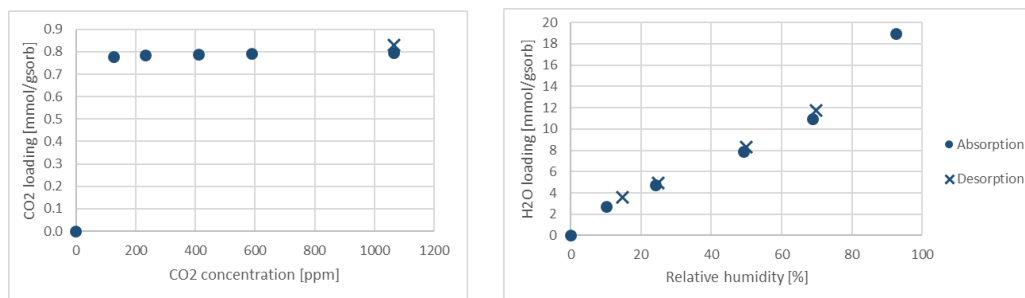
Fig. 1. CO_2 (15%RH) and H_2O isotherm absorption curves at 25 °C.

The CO_2 co-absorption experiments conducted so far have been at 15% relative humidity (RH). Higher humidities will be explored in the future. By comparing the experimental results with appropriate isothermal models, it is possible to evaluate the performance of the fiber at the studied temperature in the cyclic CO_2 direct air capture (DAC) process.

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# Adsorption of dextrin on iron oxides in iron ore flotation process

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Iron mineral flotation is a crucial process in the mining industry, particularly in the extraction and processing of iron ores. Iron minerals, such as hematite (Fe_2O_3) and magnetite (Fe_3O_4), are essential raw materials for the production of steel, which is used in many sectors, including construction, automotive, energy and many others [1,2]. The role of dextrin, a complex polymer derived from starch, in the flotation process of iron ores is investigated in this study. Specifically, the research investigates the adsorption behavior of dextrin onto two types of iron oxides: hematite and magnetite. Based on a Total Organic Carbon (TOC), we evaluated the operating conditions such as contact time, pH of the medium. Furthermore, we determined the adsorption isotherms of dextrin on both hematite and magnetite surfaces. Our results indicate that at pH =7 and contact time t=2h we obtain a better adsorption capacity. Isotherms display a L4-shape according to the classification proposed by Giles et *al.*, which is similar to type IV or type VI isotherms described by the International Union of Pure and Applied Chemistry (IUPAC) [3,4].
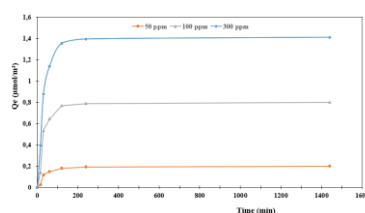
Fig. 1. Influence of contact time between dextrin and hematite

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Analysis of Sorption Isotherms of Zeolites with the Excess Surface Work – Thermodynamical and Quantum Mechanical Description

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The thermodynamic principles of excess surface work [1-3] and the combined approach with disjoining pressure [4, 5] (ESW-DP) are well documented. Applications can be find beside industrial patetnts e.g. in concrete science, zeolites and MOFs [6 -8]. Thermodynamically, the excess surface work is defined as the sum of the surface free energy and the isothermal isobaric sorption work characterized by an energy minimum at the monolayer capacity. It has been shown that one solution to the ESW equation is the double log linear representation of the change in chemical potential as a function of the amount adsorbed. This is also known as the De Boer-Zwicker equation from 1929 [9]. Brunauer, Emmett, and Teller [10] mentioned the linear behaviour of this equation but could not find an explanation. A quantum mechanical approach using perturbation theory was used in the χ-equation of J. B. Condon [11]. This χ-equation is essentially the same as the De Boer-Zwicker equation. Therefore, the ESW approach can be explained not only thermodynamically but also quantum mechanically.

Applications are presented on zeolites MCM 41, MCM 36 and SBA 15. Water vapor sorption on hydrophilic and hydrophobic surfaces can be described in more detail with the χ-equation and the linear solution of ESW (de Boer-Zwicker equation), respectively [12]. A reference isotherm is not necessary at all.

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Evaluating Light Olefin/Paraffin Separation Performance of MOF-808-based Adsorbents

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Light olefins, such as ethylene and propylene, are highly demanded feedstocks in the chemical and petroleum industry, primarily for polymer production [1,2]. Presently, cryogenic distillation techniques are employed for the separation and purification of these olefins from their paraffin counterparts. These techniques are energy-intensive, due to the similarity of physical and chemical properties of the hydrocarbons. Hence, it is crucial to explore more efficient separation techniques, such as membranes, to mitigate the carbon emissions associated with these processes [2]. The class of mixed-matrix membranes (MMMs), containing a selective polymer and metal-organic framework (MOF) fillers, can enable the desired tuning of permeability and selectivity [3,4]. MOF-808 is a Zr-based MOF possesses a large surface area and pore volume. Its structure offers a stable and adaptable platform for incorporating various functionalities into its framework, facilitated by the coordination sites present on its Zr clusters [5]. The present research focuses on examining the adsorptive characteristics of both untreated and various types of functionalized MOF-808 materials. The primary objective is to assess the impact of functionalization on the adsorption properties and evaluate the potential of these materials as fillers in mixed matrix membranes (MMMs). We conducted pulse inverse gas chromatography (IGC) at a temperature range of 30-80 °C to determine adsorption thermodynamics, including Henry coefficients, thermodynamic selectivity, and isosteric heats of adsorption at infinite dilution. Figure 1 shows the elution chromatograms of single ethane, ethene, propane, and propene over MOF-808 at 80 °C. The pulse IGC results show that certain functionalities can improve MOF-808s selectivity for the unsaturated molecules. The heats of adsorption of C_3s increased slightly after the functionalization of MOF-808. Isotherm measurements of single gas components at low-pressure range show the adsorption capacities of modified MOFs are higher compared to the pristine MOF. The results of this study offer perspectives for the design of MMMs with remarkable separation potential for light olefin/paraffin mixtures.
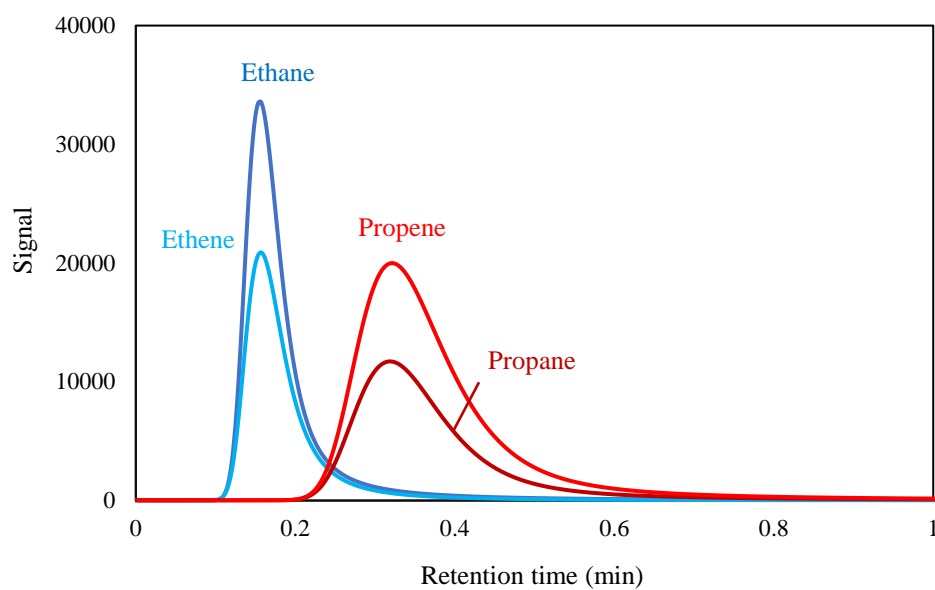
Fig. 1. Elution chromatograms of ethane, ethene, propane, and propene over MOF-808 at 80 °C

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Understanding the Interplay of Pore Width and Amine Loading of PEI-Loaded Silica on CO_2 Adsorption

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Developing carbon capture technologies like Direct Air Capture (DAC) can help decrease atmospheric CO_2 levels. Amine-based sorbents on porous supports are well-suited for adsorption from sources with low partial pressure of CO_2. Amine-functionalization of porous support materials is commonly achieved via impregnation of aminopolymers, e.g., polyethylene imine (PEI). The goal of this work is to understand the interplay between the textural properties of the support and its polymer loading on the CO_2 uptake in relation to adsorption temperature. In particular, effects like reduced amine accessibility due to pore blocking are investigated and adsorption kinetics are modelled based on obtained adsorption data.

Commercial spherical silica (Chromatorex®) with a pore width between 7 and 50 nm has been wet impregnated with 20, 33 and 43 wt.-% of branched PEI ($M_n \approx 600 - 2000$ g mol^{-1}) following a modified procedure of Xu et al. [1]. The sorbents were characterized by nitrogen sorption, CHN elemental analysis, and CO_2 adsorption with 450 ppm CO_2 in He at $30 - 70$ °C.

Generally, larger pores were found to be beneficial at comparable PEI loading although adsorption temperature additionally affects equilibrium uptake capacity (q_e). For samples with pore widths ≥ 10 nm, 50 °C yields the highest q_e as a result of a change in adsorption mechanism with increased polymer chain mobility and amine site accessibility at elevated temperatures ("molecular basket"). Amine efficiency (f_N) is clearly negatively correlated with increasing PEI loadings, as reflected by the decrease in average f_N from 0.15 at 20 wt.-% to 0.05 at 43 wt.-%. We assume this is due to decreased amine accessibility as increased polymer loading leads to pore blocking. Moreover, we found that smaller polymers were more effective at CO_2 capture as they inherit a larger number of primary amines. Over a span of 10 cycles, no differences in regards to leaching could be observed in comparison of different polymer chain lengths which all showed a decrease in q_e of 2 %. Using a DETCHEM simulation, we have been able to model the CO_2 adsorption uptake and match the recorded q_e in adsorption and saturation for different adsorption temperatures creating access to thermodynamic parameters such as the activation energy.

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# Textural analysis of various biochar using several probe gases

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Biochar are used in many applications, commonly in agro-environment to enhance the soil quality or for other applications such as carbon supported catalysts. The project entitled QUALICHAR funded by ADEME (French Agency of Environment and Energy Management) focuses on the valorization of selected conventional lignocellulosic biomasses (oak, douglas, pectin fir, beech, spruce), crop residue (corn raids) and unconventional biomasses (digestate, poultry droppings and cattle manure) into biochars by pyrolysis. The aim of this study is to understand the porosity development of the biochar depending on the process used and the biomass nature. Nitrogen (N_2) adsorption at 77 K is commonly used to measure BET surface, pore size distribution and total pore volume. However due to the biochar specific porosity, the nitrogen quadrupole moment and its slow diffusion kinetics [1] other probe gases (CO_2, Ar)[2] were used to characterize the biochars. This work tends to show that pyrolysis temperature is more impactful regarding porosity than type of process or biomass nature.
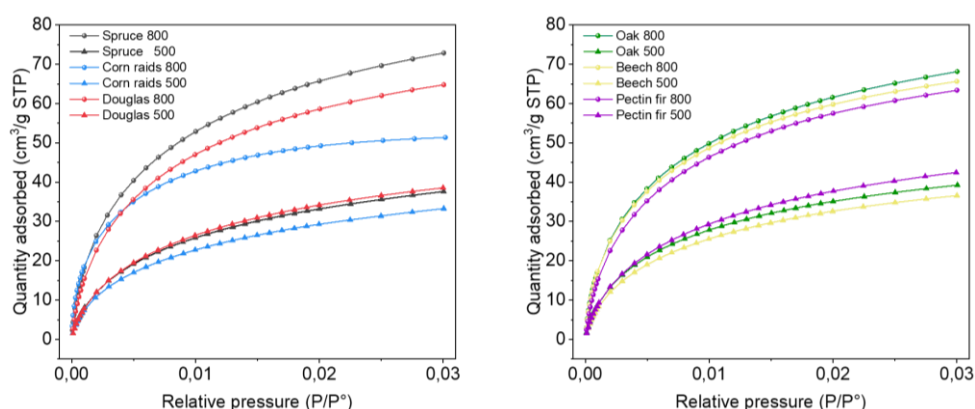
Fig. 1. CO_2 isotherm at 273K of biochar produced from lignocellulosic biomass by slow pyrolysis

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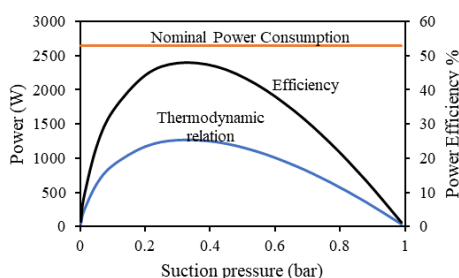
Energy consumption of VSA carbon capture; from lab scale to a pilot plant

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Energy consumption is one of the key parameters in decision making for a carbon capture process, and with the momentum toward increasing energy efficiency of this process, it is crucial to be able to estimate the power consumption accurately. Two general approaches have been used to address the energy consumption which include the direct measurement of the consumed power by a power meter, or using a thermodynamic relation (work of compression from a vacuum to atmospheric pressure) with an efficiency factor [1]. A comparison of the results obtained using these two approaches shows that the thermodynamic equation underestimates the power consumption [2]. This is because of a typical efficiency factor of 70 % that is considered to convert the ideal work of evacuation to the required power. Comparing the nominal power consumption of an industrial vacuum pump with the calculated work from the thermodynamic relation implies that there is a suction pressure under which condition efficiency is close to 50 % (fig. 1). Since the vacuum pressure during desorption is not a fixed value, it is not straightforward to estimate the evacuation power efficiency and consequently the required power. Here, a method has been developed that helps estimating the required power of evacuation by considering variable efficiency under evacuation.

Fig. 1. The efficiency of an industrial vacuum pump

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