Nitin Kumar, Maryam Shojaee, JJ Spivey,

Catalytic bi-reforming of methane: from greenhouse gases to syngas,

Current Opinion in Chemical Engineering,

Volume 9,

2015,

Pages 8-15,

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https://doi.org/10.1016/j.coche.2015.07.003.

(https://www.sciencedirect.com/science/article/pii/S2211339815000428)

Abstract: The bi-reforming reaction to produce syngas from CH4 and CO2 offers significant advantages over dry reforming and oxy-CO2 with respect to catalyst deactivation by carbonization. This approach has potential for powerful new alternatives and is entering the stage of increasing advanced research toward commercialization of the technology. Research is ongoing to develop catalysts that are resistant to high temperatures and the presence of a more oxidative environment due to steam. All current research on bi-reforming catalysis is focused on Ni-based catalysts, a logical extension based on commercial materials on steam/methane reforming and dry reforming. However, recent work on thermally stable crystalline oxides has promise, particularly in resisting carbon deposition while remaining stable at the demanding conditions of bi-reforming.

Eun-hyeok Yang, Na Young Kim, Young-su Noh, Sung Soo Lim, Jae-Sun Jung, Jae Suk Lee, Gi Hoon Hong, Dong Ju Moon,

Steam CO2 reforming of methane over La1−xCexNiO3 perovskite catalysts,

International Journal of Hydrogen Energy,

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2015,

Pages 11831-11839,

ISSN 0360-3199,

https://doi.org/10.1016/j.ijhydene.2015.06.021.

(https://www.sciencedirect.com/science/article/pii/S0360319915015037)

Abstract: Steam CO2 reforming of methane was carried out over cerium substituted perovskite catalysts. Among the catalysts studied, La0.9Ce0.1NiO3 showed the best performance with 49% of methane and 14% of CO2 conversion under the tested conditions. The chemical and structural properties of the catalysts before and after the reaction were studied by N2 physisorption, X-ray diffraction, CO2-TPD, TPH, TPR, TGA and TEM. It was found that most of Ce existed as CeO2 rather than being incorporated in perovskite lattice because of large difference in ionic radii between La3+ and Ce4+. Few substitution of Ce in A site resulted in high degree of reduction for active Ni species with good catalytic activity which was further decreased with increasing Ce concentration; substitution of large amount of Ce species led to methanation of CO2 and formation of large nickel cluster. TPH and TGA analysis revealed that Ce substituted catalyst has better resistance to coke deposition compared to non-promoted perovskite catalyst.

Keywords: Cerium substitution; Hydrogen production; Perovskite; Steam CO2 reforming

Tao Wu, Qing Zhang, Weiye Cai, Peng Zhang, Xuefeng Song, Zhuang Sun, Lian Gao,

Phyllosilicate evolved hierarchical Ni- and Cu–Ni/SiO2 nanocomposites for methane dry reforming catalysis,

Applied Catalysis A: General,

Volume 503,

2015,

Pages 94-102,

ISSN 0926-860X,

https://doi.org/10.1016/j.apcata.2015.07.012.

(https://www.sciencedirect.com/science/article/pii/S0926860X15300612)

Abstract: Well dispersed Ni and Cu–Ni alloy nanoparticles (∼7nm) embedded in nanosheets of hierarchical SiO2 hollow spheres (surface area>400m2/g) have been synthesized through a hydrothermal process and have shown superior catalytic performance in methane dry reforming (DRM) reaction to the impregnated control sample based on SiO2 nanospheres. The catalytic activity and the sintering and coke resistant properties of the hierarchical composite catalysts in the high temperature DRM catalysis are ascribed to the strong metal–support interaction and the well dispersed small metal nanoparticles.

Keywords: Hierarchical; Ni/SiO2; Cu–Ni/SiO2; Methane dry reforming; Catalysis

Xiaogang Zheng, Shiyu Tan, Lichun Dong, Shaobo Li, Hongmei Chen,

Corrigendum to “Plasma-assisted catalytic dry reforming of methane: Highly catalytic performance of nickel ferrite nanoparticles embedded in silica” [J. Power Sources 274C (2014) 286–294],

Journal of Power Sources,

Volume 276,

2015,

Page 388,

ISSN 0378-7753,

https://doi.org/10.1016/j.jpowsour.2014.12.029.

(https://www.sciencedirect.com/science/article/pii/S0378775314020473)

Whitney S. Jablonski, Stephanie M. Villano, Anthony M. Dean,

A comparison of H2S, SO2, and COS poisoning on Ni/YSZ and Ni/K2O-CaAl2O4 during methane steam and dry reforming,

Applied Catalysis A: General,

Volume 502,

2015,

Pages 399-409,

ISSN 0926-860X,

https://doi.org/10.1016/j.apcata.2015.06.009.

(https://www.sciencedirect.com/science/article/pii/S0926860X15300259)

Abstract: A systematic comparison of sulfur poisoning on Ni/YSZ and Ni/K2O-CaAl2O4, a commercially available reforming catalyst, demonstrated the heightened and rapid degradation of Ni/YSZ methane reforming activity. Ni/K2O-CaAl2O4 has nearly 15 times the hydrogen uptake capacity of Ni/YSZ which implies a difference in active nickel area. Because of this difference in active nickel surface area, Ni/K2O-CaAl2O4 was diluted in pure α-Al2O3 to achieve the same active nickel surface area as Ni/YSZ. The turnover frequencies (TOF) for steam methane reforming without sulfur on Ni/YSZ and Ni/K2O-CaAl2O4 were similar, although there was some deactivation on Ni/K2O-CaAl2O4 possibly as a result of coking which was observed visually. Sulfur deactivation on both catalysts was examined for H2S, SO2, and COS at concentrations of 1, 3, and 5ppm. Ni/YSZ deactivated rapidly to an activity close to zero. Ni/K2O-CaAl2O4 deactivated quickly in the first 20min, but then reached a non-zero steady state activity. The relative deactivation rates for the sulfur species examined were COS>SO2≥H2S. Reaction temperatures of 650°C, 750°C, and 800°C were evaluated, but temperature did not strongly affect deactivation rates for either catalyst. The overarching result of this study is that Ni/YSZ methane reforming activity is more sensitive to sulfur deactivation than a commercial reforming catalyst. The effect is so strong, that the use of Ni/YSZ with any hydrocarbon fuel may require removal of sulfur to sub-ppm levels.

Keywords: Methane steam reforming; Methane dry reforming; CO2 reforming; Hydrogen sulfide; Sulfur dioxide; Ni/YSZ; Solid oxide fuel cell; SOFC; Nickel catalyst; YSZ support; Sulfur poisoning; Carbonyl sulfide; Sulfur; Poisoning

Yasotha Kathiraser, Usman Oemar, Eng Toon Saw, Ziwei Li, Sibudjing Kawi,

Kinetic and mechanistic aspects for CO2 reforming of methane over Ni based catalysts,

Chemical Engineering Journal,

Volume 278,

2015,

Pages 62-78,

ISSN 1385-8947,

https://doi.org/10.1016/j.cej.2014.11.143.

(https://www.sciencedirect.com/science/article/pii/S1385894714016568)

Abstract: In recent decades, CO2 utilization has become increasingly important in view of the escalating global warming phenomenon. In view of this, conversion of CO2 to syngas via CO2 (dry) reforming of methane (DRM) reaction has been gaining prominent research interest. This paper presents a review on the kinetic and mechanistic aspects for DRM reaction with focus on Ni based catalysts. Ni-based catalysts are commercially attractive due to the low cost and wide availability of Ni metal. Kinetic studies over the Ni based catalysts are vital in scaling up of the DRM process in order to assess its industrial viability. Many differing opinions have been formed for the rate determining steps (RDS) of the reaction kinetics. In this review, a survey of the differing RDS presented in literature based on the widely used Langmuir Hinshelwood Hougen Watson (LHHW) models for Ni-catalyzed DRM reactions are categorized and presented along with the importance of experimental techniques for justifying mechanistic formulation.

Keywords: CO2 reforming of methane; Ni catalyst; Reaction kinetics; Rate determining steps; Characterization techniques

Zhenghong Bao, Yongwu Lu, Jun Han, Yebo Li, Fei Yu,

Highly active and stable Ni-based bimodal pore catalyst for dry reforming of methane,

Applied Catalysis A: General,

Volume 491,

2015,

Pages 116-126,

ISSN 0926-860X,

https://doi.org/10.1016/j.apcata.2014.12.005.

(https://www.sciencedirect.com/science/article/pii/S0926860X1400756X)

Abstract: Bimodal pore NiCeMgAl catalysts were synthesized via the refluxed co-precipitation method. Methane reforming using carbon dioxide over this bimodal pore NiCeMgAl catalyst for syngas production was systematically studied by optimizing the active component NiO-loading, calcination temperature, reduction temperature and gas hourly space velocity (GHSV). The Ni15CeMgAl sample with 15wt% NiO loading, was found to be active enough at 750°C with a high CH4 conversion of 96.5%. The proper reduction temperature for the NiCeMgAl catalyst is either 550–650°C or 850°C. Higher calcination temperature favors the formation of NiAl2O4 and MgAl2O4 spinel structures. The Ni active sites derived from the NiAl2O4 spinel structure had longer stability than those from the free NiO. Compared with non-bimodal pore NiCeMgAl catalyst, bimodal pore NiCeMgAl catalyst has a longer stability in the feed gas without dilution. The large pores in the bimodal pore Ni15CeMgAl catalyst were supposed to contribute to the quick molecule transfer during the dry reforming of methane (DRM) reaction when the GHSV was less than 96,000h−1. The evolution of the Ni15CeMgAl catalyst before and after the DRM reaction was investigated by BET, XRD, TEM, and TGA techniques. A schema of the DRM reaction on the bimodal pore Ni15CeMgAl catalyst was proposed, and the correlation between the structure evolution and catalytic performance change was also discussed.

Keywords: Nickel catalyst; Bimodal pore; Reflux; Dry reforming of methane

Jaekyeong Yoo, Yongju Bang, Seung Ju Han, Seungwon Park, Ji Hwan Song, In Kyu Song,

Hydrogen production by tri-reforming of methane over nickel–alumina aerogel catalyst,

Journal of Molecular Catalysis A: Chemical,

Volume 410,

2015,

Pages 74-80,

ISSN 1381-1169,

https://doi.org/10.1016/j.molcata.2015.09.008.

(https://www.sciencedirect.com/science/article/pii/S1381116915300844)

Abstract: A mesoporous nickel–alumina aerogel catalyst (NAA) was prepared by an epoxide-initiated gelation method and a subsequent supercritical carbon dioxide drying method. For comparison, a mesoporous nickel–alumina xerogel catalyst (NAX) was also prepared by an epoxide-initiated gelation method without supercritical carbon dioxide drying. Both catalysts were applied to the hydrogen production by tri-reforming of methane. The effect of preparation method on the physicochemical properties and catalytic activities of the catalysts was investigated. Although both catalysts exhibited a well-developed mesoporous structure, NAA catalyst retained higher surface area and larger pore volume than NAX catalyst. It was also revealed that NAA catalyst retained higher nickel dispersion and larger methane adsorption capacity than NAX catalyst. In the hydrogen production by tri-reforming of methane, both catalysts exhibited a stable catalytic performance. However, NAA catalyst showed higher hydrogen yield and higher CH4 conversion than NAX catalyst. High nickel dispersion and strong affinity with methane of NAA catalyst was responsible for its high catalytic performance.

Keywords: Hydrogen production; Tri-reforming of methane; Nickel–alumina aerogel catalyst; Nickel dispersion; Methane adsorption capacity

Eun-hyeok Yang, Young-su Noh, S. Ramesh, Sung Soo Lim, Dong Ju Moon,

The effect of promoters in La0.9M0.1Ni0.5Fe0.5O3 (M=Sr, Ca) perovskite catalysts on dry reforming of methane,

Fuel Processing Technology,

Volume 134,

2015,

Pages 404-413,

ISSN 0378-3820,

https://doi.org/10.1016/j.fuproc.2015.02.023.

(https://www.sciencedirect.com/science/article/pii/S0378382015000958)

Abstract: Nickel-based catalysts are typically used for syngas production via reforming reactions. The reforming of methane using carbon dioxide, called dry reforming of methane (DRM), is an effective way to produce syngas from these two notable greenhouse gases. However, Ni-based catalysts used for DRM undergo severe coke deposition. In the current study, perovskite-type oxide catalysts were prepared using the modified EDTA-cellulose method and characterized by the N2 physisorption, TPR, CO2-TPD, XRD, TGA, SEM and TEM-EDX techniques. The influence of partial substitution of La by Sr/Ca was investigated in the dry reforming reaction for the production of synthesis gas, and the basicity of the catalysts was varied by substituting the A site with either Sr or Ca, which modified the catalytic activity under the tested conditions. It was found that the perovskite catalysts demonstrated superior carbon resistance during the reaction, with La0.9Ca0.1Ni0.5Fe0.5O3 catalyst exhibiting the best catalytic performance among the prepared perovskite catalysts.

Keywords: Strontium; Calcium; Iron; Perovskite; Reforming; Gas to liquid (GTL); CH4; CO2

Na Young Kim, Eun-Hyeok Yang, Sung-Soo Lim, Jae Sun Jung, Jae-Suk Lee, Gi Hoon Hong, Young-Su Noh, Kwan Young Lee, Dong Ju Moon,

Hydrogen production by steam reforming of methane over mixed Ni/MgAl + CrFe3O4 catalysts,

International Journal of Hydrogen Energy,

Volume 40, Issue 35,

2015,

Pages 11848-11854,

ISSN 0360-3199,

https://doi.org/10.1016/j.ijhydene.2015.06.104.

(https://www.sciencedirect.com/science/article/pii/S036031991501589X)

Abstract: Steam reforming of methane (SRM) was performed over a mixed Ni/MgAl + CrFe3O4 catalyst. The catalyst was prepared by physical mixing method and it was compared to Ni/MgAl and iron or chromium promoted M/Ni/MgAl catalysts prepared by impregnation method. Catalysts were characterized by various analytical techniques such as nitrogen physisorption, TPR, XRD, TGA and SEM. The catalytic activity in a fixed-bed reactor was investigated at a temperature range of 500–700 °C, 1 bar pressure and feed molar ratio of H2O/CH4 = 2. TPR and XRD illustrated that segregated Ni particles were observed with promoted M-Ni/MgAl catalysts and it leads to reduce the active Ni metal. The addition of the Cr/Fe3O4 catalyst activates steam and easily reacts with methane. Consequently, physically mixed catalysts showed higher hydrogen selectivity and methane conversion than the other catalysts.

Keywords: Steam reforming; WGS reaction; Hydrogen production; Physically mixed catalyst

Y. Shiratori, M. Sakamoto, T. Uchida, H. Le, T. Quang-Tuyen, K. Sasaki,

Hydrotalcite-dispersed paper-structured catalyst for the dry reforming of methane,

International Journal of Hydrogen Energy,

Volume 40, Issue 34,

2015,

Pages 10807-10815,

ISSN 0360-3199,

https://doi.org/10.1016/j.ijhydene.2015.07.016.

(https://www.sciencedirect.com/science/article/pii/S0360319915017449)

Abstract: A paper-structured catalyst (PSC) is a flexible planar catalyst that can be stacked on the anode of SOFCs and exhibits excellent catalytic activity for the reforming of hydrocarbon fuels at the operating temperature of the SOFC. Although our final goal is the realization of direct internal reforming (DIR) SOFCs fueled by biogas by applying a PSC, the tolerance of PSCs to sulfur impurities in biogas (H2S) must be improved for the practical application of PSCs to DIR-SOFCs operated by biogas. In this study, an inorganic fiber network in which a layered double hydroxide (Mg/Al-hydrotalcite denoted as HT) is dispersed was prepared by a paper-making process, and Ni was then loaded in this paper matrix via an impregnation process. This Ni-loaded HT-dispersed PSC exhibited considerably higher tolerance to H2S than that of HT-free PSC.

Keywords: Biogas; Dry reforming; H2S poisoning; Paper-structured catalyst; Mg/Al-hydrotalcite

Sofia D. Angeli, Fotis G. Pilitsis, Angeliki A. Lemonidou,

Methane steam reforming at low temperature: Effect of light alkanes’ presence on coke formation,

Catalysis Today,

Volume 242, Part A,

2015,

Pages 119-128,

ISSN 0920-5861,

https://doi.org/10.1016/j.cattod.2014.05.043.

(https://www.sciencedirect.com/science/article/pii/S092058611400426X)

Abstract: Steam reforming of natural gas for the production of hydrogen at low operation temperature offers significant financial and environmental advantages. However, the presence of higher hydrocarbons as minor components of natural gas can significantly affect the formation of coke and thus the effectiveness of the catalyst. In this study, the effect of the presence of C2–C3 alkanes in the feedstock on the carbon accumulation during low temperature steam reforming of methane is investigated over Ni and Rh catalysts supported on lanthanum doped ceria–zirconia mixed oxide. Both catalysts showed high resistance to coke formation and especially in the case of Rh/La/CeO2–ZrO2, the carbon accumulation detected was low even after 10h on stream in steam reforming of all mixtures of hydrocarbons tested. The presence of higher alkanes in methane increased the amount of carbon on Ni(10)CeZrLa compared to pure methane as well as the nature of the carbonaceous species. Increase in the C-number of the additive alkane had almost no influence on the total amount of carbon formed (C/H feed ratio=constant) but favored the formation of filamentous carbon.

Keywords: Methane steam reforming; Natural gas; Coke; Ni catalyst; Rh catalyst; Alkanes

J. Estephane, S. Aouad, S. Hany, B. El Khoury, C. Gennequin, H. El Zakhem, J. El Nakat, A. Aboukaïs, E. Abi Aad,

CO2 reforming of methane over Ni–Co/ZSM5 catalysts. Aging and carbon deposition study,

International Journal of Hydrogen Energy,

Volume 40, Issue 30,

2015,

Pages 9201-9208,

ISSN 0360-3199,

https://doi.org/10.1016/j.ijhydene.2015.05.147.

(https://www.sciencedirect.com/science/article/pii/S0360319915013609)

Abstract: The wet impregnation method was used to prepare ZSM5 supported nickel and/or cobalt monometallic and bimetallic catalysts with a 7 wt.% total metal loading. The CO2 reforming of methane reaction was carried out in the 600 °C–800 °C temperature range over the different catalysts (GHSV 60000 mL g−1 hr−1). The cobalt containing catalysts favored the reverse water gas shift reaction at high temperature and cobalt acted as a synergist to nickel, as overall, bimetallic catalysts showed better catalytic performance. Carbon deposition was less expressed over catalysts with high cobalt content. Following 12 h on stream at 700 °C, the bimetallic catalyst with cobalt to nickel ratio of 2, showed high CO2 and CH4 conversions (∼60%) accompanied with the lowest carbon deposition (5%). The thermal analysis of aged catalysts showed that among the deposited carbon species, it is the carbon present in the proximity of nickel and/or cobalt catalytic sites that is responsible of deactivation.

Keywords: Catalyst deactivation; Dry reforming; Nickel; Cobalt; Zeolites; Carbon deposition

Katharina Mette, Stefanie Kühl, Andrey Tarasov, Hendrik Düdder, Kevin Kähler, Martin Muhler, Robert Schlögl, Malte Behrens,

Redox dynamics of Ni catalysts in CO2 reforming of methane,

Catalysis Today,

Volume 242, Part A,

2015,

Pages 101-110,

ISSN 0920-5861,

https://doi.org/10.1016/j.cattod.2014.06.011.

(https://www.sciencedirect.com/science/article/pii/S0920586114004313)

Abstract: The influence of redox dynamics of a Ni/MgAl oxide catalyst for dry reforming of methane (DRM) at high temperature was studied to correlate structural stability with catalytic activity and coking propensity. Structural aging of the catalyst was simulated by repeated temperature-programmed reduction/oxidation (TPR/TPO) cycles. Despite a very high Ni loading of 55.4wt.%, small Ni nanoparticles of 11nm were obtained from a hydrotalcite-like precursor with a homogeneous distribution. Redox cycling gradually changed the interaction of the active Ni phase with the oxide support resulting in a crystalline Ni/MgAl2O4-type catalyst. After cycling the average particle size increased from 11 to 21nm – while still a large fraction of small particles was present – bringing about a decrease in Ni surface area of 72%. Interestingly, the redox dynamics and its strong structural and chemical consequences were found to have only a moderate influence on the activity in DRM at 900°C, but lead to a stable attenuation of carbon formation due to a lower fraction of graphitic carbon after DRM in a fixed-bed reactor. Supplementary DRM experiments in a thermobalance revealed that coke formation as a continuous process until a carbon limit is reached and confirmed a higher coking rate for the cycled catalyst.

Keywords: Dry reforming of methane; Nickel; Coking; Ni, Mg, Al hydrotalcite; High temperature; Redox dynamics

Muhammad Usman, W.M.A. Wan Daud, Hazzim F. Abbas,

Dry reforming of methane: Influence of process parameters—A review,

Renewable and Sustainable Energy Reviews,

Volume 45,

2015,

Pages 710-744,

ISSN 1364-0321,

https://doi.org/10.1016/j.rser.2015.02.026.

(https://www.sciencedirect.com/science/article/pii/S1364032115001148)

Abstract: This review will explore the influences of the active metal, support, promoter, preparation methods, calcination temperature, reducing environment, particle size and reactor choice on catalytic activity and carbon deposition for the dry reforming of methane. Bimetallic (Ni−Pt, Ni−Rh, Ni−Ce, Ni−Mo, Ni−Co) and monometallic (Ni) catalysts are preferred for dry reforming compared to noble metals (Rh, Ru and Pt) due to their low-cost. Investigation of support materials indicated that ceria−zirconia mixtures, ZrO2 with alkali metals (Mg2+, Ca2+, Y2+) addition, MgO, SBA-15, ZSM-5, CeO2, BaTiO3 and Ca0.8Sr0.2TiO3 showed improved catalytic activities and decreased carbon deposition. The modifying effects of cerium (Ce), magnesium (Mg) and yttrium (Y) were significant for dry reforming of methane. MgO, CeO2 and La2O3 promoters for metal catalysts supported on mesoporous materials had the highest catalyst stability among all the other promoters. Preparation methods played an important role in the synthesis of smaller particle size and higher dispersion of active metals. Calcination temperature and treatment duration imparted significant changes to the morphology of catalysts as evident by XRD, TPR and XPS. Catalyst reduction in different environments (H2, He, H2/He, O2/He, H2−N2 and CH4/O2) indicated that probably the mixture of reducing agents will lead to enhanced catalytic activities. Smaller particle size (<15nm) had a significant influence on the suppression of carbon deposition and catalytic activity. Fluidized bed reactor exhibited the highest activity and stability, lower carbon deposition and higher conversion compared to a fixed-bed reactor. Moreover, membrane reactor, solar reactor, high-pressure reactor and microreactor were also investigated with specific features such as: pure H2 production, detailed reaction information with enhanced safety, higher pressure applications and dry reforming reaction with/without catalyst under sunlight. The study of parameters would improve the understanding of various preparation and reaction conditions leading to various catalytic activities.

Keywords: Dry reforming of methane; Landfill gas; Syn-gas; Carbon deposition; Ni catalyst

Sung Su Kim, Sang Moon Lee, Jong Min Won, Hee Jae Yang, Sung Chang Hong,

Effect of Ce/Ti ratio on the catalytic activity and stability of Ni/CeO2–TiO2 catalyst for dry reforming of methane,

Chemical Engineering Journal,

Volume 280,

2015,

Pages 433-440,

ISSN 1385-8947,

https://doi.org/10.1016/j.cej.2015.06.027.

(https://www.sciencedirect.com/science/article/pii/S1385894715008669)

Abstract: In this study, a series of catalysts of composition Ni/X% CeO2–Y% TiO2, (where X and Y range from 0% to 100%), was prepared by impregnation. The effects of different ratio of CeO2/TiO2 on the catalytic activity and stability were examined during methane dry reforming. Ni/TiO2 showed better initial activity than Ni/CeO2. However, Ni/CeO2 was much more stable. The Ni/CeO2–TiO2 catalyst, which has optimum Ce/Ti ratio, showed excellent activity and stability in dry reforming. XPS analysis, H2 TPR, and a reverse water gas shift reaction (RWGS) test confirmed that higher dispersion of Ni sites on the surface of the support could improve the catalytic activity, and that great reducibility of catalyst could improve the stability of catalyst.

Keywords: Reforming; Ni; CeO2–TiO2; Catalysis; Hydrogen; Carbon deposition

Radosław Dębek, Monika Radlik, Monika Motak, Maria Elena Galvez, Wincenty Turek, Patrick Da Costa, Teresa Grzybek,

Ni-containing Ce-promoted hydrotalcite derived materials as catalysts for methane reforming with carbon dioxide at low temperature – On the effect of basicity,

Catalysis Today,

Volume 257, Part 1,

2015,

Pages 59-65,

ISSN 0920-5861,

https://doi.org/10.1016/j.cattod.2015.03.017.

(https://www.sciencedirect.com/science/article/pii/S0920586115001789)

Abstract: NiMgAl mixed oxides promoted with cerium species were synthesized from their corresponding hydrotalcite precursors and subsequently characterized by elemental analysis, XRD, H2-TPR, CO2-TPD and N2 sorption techniques. The catalytic activity of the prepared catalysts was tested in the reaction of CO2 methane reforming and compared to the performance of two reference catalysts: 10Ni/Al2O3 and 10Ni/CZ (ceria-zirconia). The hydrotalcite derived materials showed a significant catalytic activity at 550°C towards the dry reforming reaction. However, the simultaneous occurrence of undesired side reactions was as well observed, mainly CH4 decomposition and RWGS reaction. In this sense, the addition of cerium by ion-exchange with [Ce(EDTA)]− complexes resulted in higher activity and selectivity, due to an increase in the reducibility of nickel species and to the introduction of new intermediate and strong basic sites (acid-base pairs and low coordinated oxygen species). The reference catalysts showed considerable loss of catalytic activity during 5h experiments, lower CO2 conversion (10Ni/CZ) and high excess of CO in the products of the reaction (10Ni/Al2O3), pointing to a generally better performance of the hydrotalcite derived catalysts.

Keywords: Nickel; Ceria; Hydrotalcite; CO2; Reforming; Hydrogen

Jessica L. Ewbank, Libor Kovarik, Fatoumata Z. Diallo, Carsten Sievers,

Effect of metal–support interactions in Ni/Al2O3 catalysts with low metal loading for methane dry reforming,

Applied Catalysis A: General,

Volume 494,

2015,

Pages 57-67,

ISSN 0926-860X,

https://doi.org/10.1016/j.apcata.2015.01.029.

(https://www.sciencedirect.com/science/article/pii/S0926860X15000447)

Abstract: Nickel catalysts prepared by a variety of different methods are commonly used for reforming reactions such as methane dry reforming. Two preparation methods, controlled adsorption and dry impregnation, are implemented to explore the effect of preparation method on the formation of active sites on alumina supported nickel catalysts. By varying only the preparation method, comparison of catalysts that differ primarily in metal–support interactions, strong metal–support interaction (controlled adsorption) and weak metal–support interactions (dry impregnation), are obtained. For controlled adsorption, optimal synthesis conditions are identified using point of zero charge measurements, pH-precipitation experiments, and adsorption isotherms. Using these conditions, a catalyst with a higher dispersion and strong metal–support interactions is prepared. Physicochemical characterization by N2 physisorption, H2 chemisorption, temperature programmed reduction (TPR), transmission electron microscopy (TEM), and environmental TEM (ETEM) shows that the types of nickel sites formed strongly depend on the synthesis method. Methane dry reforming reactivity studies show stable catalytic performance for at least 9h and provide additional insight into the types of active centers present. After reductive pretreatment, the nickel catalyst prepared by dry impregnation is found to primarily have nickel present as a surface NiAl2O4. In contrast, the active centers for the nickel catalyst prepared by controlled adsorption consist of nickel particles that are encapsulated by a nickel aluminate layer with 1–2nm in thickness. Combustion analysis and XPS of spent catalysts reveal different amounts and nature of carbonaceous deposits as a function of the synthesis method.

Keywords: Rational synthesis; Nickel; Alumina; Adsorption; Metal–support interactions

Xiao-Gang Zheng, Shi-Yu Tan, Li-Chun Dong, Shao-Bo Li, Hong-Mei Chen, Shun-An Wei,

Experimental and kinetic investigation of the plasma catalytic dry reforming of methane over perovskite LaNiO3 nanoparticles,

Fuel Processing Technology,

Volume 137,

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ISSN 0378-3820,

https://doi.org/10.1016/j.fuproc.2015.02.003.

(https://www.sciencedirect.com/science/article/pii/S0378382015000703)

Abstract: Plasma-assisted catalytic conversion of CH4 and CO2 into synthesis gas was performed in a dielectric barrier discharge reactor coupled with perovskite La–Ni nanoparticles (LaNiO3 NPs). Compared to supported catalysts such as Ni/γ-Al2O3, La–Ni/γ-Al2O3 and Ni/La2O3, LaNiO3 NPs showed better catalytic performance. The results show that the low flow rate of feed gases and high input power were favorable for the conversions of CH4 and CO2 as well as the selectivities of desired products, but led to lower energy efficiency. A global kinetic model according to argon dilution in plasma-catalytic system was proposed and employed to foresee the CH4 and CO2 conversion assisted by plasma-catalysts hybrid effect. The kinetic model indicates that the reactant conversion rate was an exponential function of the discharge energy.

Keywords: Kinetic model; LaNiO3; Dry reforming of methane; Dielectric barrier discharge

Ali Nakhaei Pour, Maryam Mousavi,

Combined reforming of methane by carbon dioxide and water: Particle size effect of Ni–Mg nanoparticles,

International Journal of Hydrogen Energy,

Volume 40, Issue 38,

2015,

Pages 12985-12992,

ISSN 0360-3199,

https://doi.org/10.1016/j.ijhydene.2015.08.011.

(https://www.sciencedirect.com/science/article/pii/S0360319915020601)

Abstract: The effect of Ni–Mg particle size on product selectivity, catalyst activity and coke formation on Ni/MgO/α-Al2O3 catalyst were studied in simultaneous steam and CO2 reforming of methane to syngas. The Ni–Mg particle sizes in the range of 13.7–29.7 nm were prepared via incipient wetness impregnation method using α-Al2O3 as support. Experimental results for turn over frequency (TOF) show that the intrinsic catalyst performances were dependent on Ni–Mg particle size. However, the products selectivities and H2/CO ration were found to be independent of Ni–Mg particle size. The experimental results reveal that the coke formation rates on the surface of catalysts are increased by increasing Ni–Mg particle size. Nevertheless, the correlated site carbon atom deposition rates (carbon atoms deposited on one site of catalyst) is shown an opposite trend.

Keywords: CO2-steam reforming; Ni catalysts; Methane; Syngas; Size dependent

Hale Ay, Deniz Üner,

Dry reforming of methane over CeO2 supported Ni, Co and Ni–Co catalysts,

Applied Catalysis B: Environmental,

Volume 179,

2015,

Pages 128-138,

ISSN 0926-3373,

https://doi.org/10.1016/j.apcatb.2015.05.013.

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Abstract: Ceria supported Ni, Co monometallic and Ni–Co bimetallic catalysts were prepared by incipient wetness impregnation method, calcined at two different temperatures (700°C and 900°C) and tested for dry reforming of methane reaction at 700°C. The activities of ceria-based Ni containing catalysts decreased with increasing calcination temperature accompanied by a decrease in coke deposition. While Ni/CeO2 and Ni–Co/CeO2 catalysts exhibited comparable high activities, Co/CeO2 catalysts exhibited very low activity. The lower activity of Co/CeO2 catalyst was attributed to strong metal support interaction (SMSI). The SMSI effect was confirmed with TEM images showing a layer of support coating the metal particles. The diversity of the deposited carbon structures in terms morphology (straight long filaments, highly entangled and curly shaped filaments, filaments with knuckle-like structure and carbon onions) was noted. In addition to the carbon buildup, the deactivation was observed to be due to the loss of active metals in the carbon filaments.

Keywords: Dry reforming of methane; Ni; Co; Ni–Co; Ceria supported; Calcination temperature

Xiaoqing Zhang, Chunhui Yang, Yanping Zhang, Yan Xu, Shuyong Shang, Yongxiang Yin,

Ni–Co catalyst derived from layered double hydroxides for dry reforming of methane,

International Journal of Hydrogen Energy,

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(https://www.sciencedirect.com/science/article/pii/S0360319915024805)

Abstract: Ni/Co monometallic and bimetallic layered double hydroxides (LDH) were in-situ synthesized on the surface of γ-Al2O3 by urea precipitation method. Then they were decomposed and reduced by H2/Ar atmospheric plasma jet at 400 °C for 15 min to become into catalysts. The LDH precursors were verified by XRD, SEM, FT-IR and Raman, while the catalysts were characterized by N2 adsorption-desorption, XRD, TEM and H2-TPR. After that their catalytic activity and stability were evaluated in dry reforming of methane (DRM) reaction. Both Ni and 2Ni–1Co showed better catalytic performance than other catalysts. Finally, the weight and species of carbon deposition on spent catalyst were tested by TG-DTA analysis. The deposition of inert carbon was the main reason for deactivation of catalysts in DRM. Moreover, a highly uniform dispersion and small particle size of active component are achieved by in situ co-precipitation method, and γ-Al2O3 provided large specific surface area for these Ni/Co catalysts.

Keywords: LDH precursor; Ni–Co bimetallic catalyst; In-situ urea precipitation; Dry reforming of methane; Carbon deposition

Nada H. Elsayed, Nathan R.M. Roberts, Babu Joseph, John N. Kuhn,

Low temperature dry reforming of methane over Pt–Ni–Mg/ceria–zirconia catalysts,

Applied Catalysis B: Environmental,

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(https://www.sciencedirect.com/science/article/pii/S0926337315002660)

Abstract: Low temperature dry reforming of methane was studied over platinum (0.2–2wt.%) and/or nickel (8wt.%) and magnesium (8wt.%) immobilized onto a ceria–zirconia support. Ceria–zirconia (0.6:0.4) solid solutions were synthesized by precipitation and the metals were loaded by the incipient wetness method. XRD patterns demonstrated that the support was a cubic fluorite structure and Ni and Mg were deposited onto it. Temperature-programmed reduction showed that Pt addition substantially decreased the reduction temperature and the impact became less prominent with increasing Pt loading. The Ni–Mg/(Ce0.6Zr0.4)O2 had the highest number of basic sites and the amounts decreased with the addition of platinum. The lowest CH4 and CO2 conversion (X10) temperatures were achieved at 454°C and 437°C, respectively, using a 0.5% Pt–Ni–Mg/(Ce0.6Zr0.4)O2 catalyst. This catalyst was optimum because it balanced between the enhanced reducibility and decreasing number of basic sites, which both occurred with increasing Pt loading. Dry reforming experiments also indicated that Pt decreased the reaction onset temperature for methane and CO2 and correlated to a slight decrease in the H2:CO ratio (though still higher than for the 0.5% Pt–Ce0.6Zr0.4O2 control catalyst). Steady-state reaction experiments were conducted between 430 and 470°C for the best catalyst and the results showed TOFs increasing from 2.69 to 4.74s−1 with increasing temperature and minimal deactivation when left on stream for 100.5h. A comparison to literature indicates that the Pt/Ni/Mg/Ce0.6Zr0.4O2 catalyst has among the highest activities, especially if Ir and Rh catalysts are not included.

Keywords: Dry reforming; Low temperature; (CeZr)O2

Changzhen Wang, Nannan Sun, Ning Zhao, Wei Wei, Yuhan Sun, Chenggong Sun, Hao Liu, Colin E. Snape,

Coking and deactivation of a mesoporous Ni–CaO–ZrO2 catalyst in dry reforming of methane: A study under different feeding compositions,

Fuel,

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https://doi.org/10.1016/j.fuel.2014.11.097.

(https://www.sciencedirect.com/science/article/pii/S0016236114012083)

Abstract: A previously developed mesoporous Ni–CaO–ZrO2 catalyst (NCZ) was submitted to dry reforming of methane (DRM), and the influence of feeding compositions on the properties of accumulated carbon was comprehensively studied. To this end, the used catalysts (NCZ-x) were characterized with a particular focus on the carbon residuals, using X-ray diffraction, N2 adsorption, transmission electron microscope, scanning electron microscopy, thermogravimetric analysis and X-ray photoelectron spectroscopy, etc. The results indicate that by varying the composition of the feeding gas, the morphology and chemical inertness of the accumulated carbon changed considerably, and the deactivation of the NCZ catalyst under CH4-rich conditions can be associated with the formation of coating carbon species that leads to the coverage of highly active Ni nano particles (NPs).

Keywords: Nickel catalyst; CO2 reforming; Carbon deposition; Deactivation; Feeding composition

Jianzhong Qi, Yanping Sun, Zongli Xie, Mike Collins, Hao Du, Tianying Xiong,

Development of Cu foam-based Ni catalyst for solar thermal reforming of methane with carbon dioxide,

Journal of Energy Chemistry,

Volume 24, Issue 6,

2015,

Pages 786-793,

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https://doi.org/10.1016/j.jechem.2015.10.001.

(https://www.sciencedirect.com/science/article/pii/S2095495615000704)

Abstract: Using solar energy to produce syngas via the endothermic reforming of methane has been extensively investigated at the laboratory- and pilot plant-scales as a promising method of storing solar energy. One of the challenges to scaling up this process in a tubular reformer is to improve the reactor's performance, which is limited by mass and heat transfer issues. High thermal conductivity Cu foam was therefore used as a substrate to improve the catalyst's thermal conductivity during solar reforming. We also developed a method to coat the foam with the catalytically active component NiMg3AlOx. The Cu foam-based NiMg3AlOx performs better than catalysts supported on SiSiC foam, which is currently used as a substrate for solar-reforming catalysts, at high gas hourly space velocity (≥400,000 mL/(g·h)) or at low reaction temperatures (≤ 720 °C). The presence of a γ-Al2O3 intermediate layer improves the adhesion between the catalyst and substrate as well as the catalytic activity.

Keywords: Cu foam-based Ni catalyst; Monolithic catalyst; Solar thermal reforming of methane

Karam Jabbour, Nissrine El Hassan, Anne Davidson, Pascale Massiani, Sandra Casale,

Characterizations and performances of Ni/diatomite catalysts for dry reforming of methane,

Chemical Engineering Journal,

Volume 264,

2015,

Pages 351-358,

ISSN 1385-8947,

https://doi.org/10.1016/j.cej.2014.11.109.

(https://www.sciencedirect.com/science/article/pii/S1385894714015770)

Abstract: Monometallic 5wt% Ni containing catalysts were prepared by a two-solvent (cyclohexane/water) deposition method using cheap and widely available natural diatomites (Ni/AW2 and Ni/MN3) as supports. The fresh samples were characterized by SEM, EDX microanalysis, N2 adsorption–desorption isotherms, XRD and tested after reduction (in hydrogen) in dry reforming of methane. Spent catalysts were further characterized by TPH coupled with mass spectrometry. Although slightly less active than a reference Ni/Aerosil (Ni/SiO2) catalyst prepared in similar conditions, the Ni/diatomites catalysts showed good activity with 90% methane conversion reached on Ni/MN3 at 800°C and a high selectivity towards dry reforming reaction (H2:CO molar ratio around unity over the entire temperature range). The catalysts were also relatively stable during catalytic measurements conducted at 650°C for 12h. In addition, depending on the nature of the diatomite and on the conditions of thermal activation, carbon deposits with lower toxicity (easier to remove by reactivation) than those formed on the Ni/Aerosil were obtained.

Keywords: Synthesis gas; Dry reforming; Nickel; Diatoms; Carbon deposits

Suntorn Sangsong, Monrudee Phongaksorn, Sabaithip Tungkamani, Thana Sornchamni, Rungroj Chuvaree,

Dry Methane Reforming Performance of Ni-based Catalyst Coated onto Stainless Steel Substrate,

Energy Procedia,

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2015,

Pages 137-142,

ISSN 1876-6102,

https://doi.org/10.1016/j.egypro.2015.11.450.

(https://www.sciencedirect.com/science/article/pii/S1876610215021827)

Abstract: In this work, the Ni-based catalysts (10wt.%Ni/Al2O3-MgO and 10wt.%Ni/MgO) were synthesized by sol-gel method. Each catalyst was prepared as catalyst pellets and catalyst-coated plate, stainless steel plate coated with catalyst. The catalyst-coated plates were fabricated using spray coating. The dry methane reforming (DMR) performances of catalyst-coated plate were investigated and compared with DMR performances of catalyst pellets. As the mass transfer was improved, the methane consumption rate per gram of catalyst coated onto metal plate was ten times greater than those of catalyst pellets approximately. The carbon deposition was also significantly prevented when the catalyst was constructed as a thin-film layer on the plate under our developing condition. Therefore, this catalyst-coated plate can be further developed for multichannel reactor.

Keywords: Nickel Based Catalysts; Spray Coating; Dry Methane Reforming

Ting Xie, Xiaoyuan Zhao, Jianping Zhang, Liyi Shi, Dengsong Zhang,

Ni nanoparticles immobilized Ce-modified mesoporous silica via a novel sublimation-deposition strategy for catalytic reforming of methane with carbon dioxide,

International Journal of Hydrogen Energy,

Volume 40, Issue 31,

2015,

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ISSN 0360-3199,

https://doi.org/10.1016/j.ijhydene.2015.06.008.

(https://www.sciencedirect.com/science/article/pii/S0360319915014640)

Abstract: A kind of Ni nanoparticles (NPs) immobilized Ce-modified mesoporous silica was synthesized via a novel sublimation-deposition strategy and evaluated in catalytic reforming of methane with carbon dioxide. The as-prepared catalysts were characterized systematically to elucidate their morphological structure and surface properties. Small Ni NPs ranging from 2.1 nm to 4.3 nm have been successfully assembled in the mesoporous silica with a homogenous distribution. As compared with conventional Ni-impregnated catalysts, the catalysts exhibit more stable and near equilibrium conversion for CH4 and CO2 for 20 h at 750 °C with negligible carbon deposition. The confinement effect deriving from the mesoporous channels of silica support, as well as the high dispersion and reducibility of Ni NPs due to strong Ni–SiO2 interaction contribute to the enhanced coking- and sintering-resistance. Furthermore, the addition of ceria further improves the coke resistance, leading to the consistent catalytic performance of the catalysts in dry reforming of methane. We believe that the successful application of sublimation-deposition strategy can also play a role in the design of robust catalysts with excellent catalytic activity and durability for many other coking- and sintering-resistant reactions.

Keywords: Dry reforming of methane; Confinement effect; Coking-resistance; Sintering-resistance

Masoud Khajenoori, Mehran Rezaei, Fereshteh Meshkani,

Dry reforming over CeO2-promoted Ni/MgO nano-catalyst: Effect of Ni loading and CH4/CO2 molar ratio,

Journal of Industrial and Engineering Chemistry,

Volume 21,

2015,

Pages 717-722,

ISSN 1226-086X,

https://doi.org/10.1016/j.jiec.2014.03.043.

(https://www.sciencedirect.com/science/article/pii/S1226086X1400197X)

Abstract: Ceria promoted nickel catalysts supported on nanocrystalline MgO were prepared and employed in methane reforming with carbon dioxide. The prepared catalysts were characterized by XRD, BET, SEM, TPO and TPR techniques. The effect of nickel loading on the catalytic performance of catalysts was investigated and the results showed that 10%Ni–7%CeO2/MgO catalyst possessed the highest catalytic activity. The results also showed that increasing in CO2/CH4 molar ratio decreased the amount of deposited carbon and increased the methane conversion.

Keywords: Coke formation; Dry reforming; Activity; CeO2 promoter

Mira Nawfal, Cédric Gennequin, Madona Labaki, Bilal Nsouli, Antoine Aboukaïs, Edmond Abi-Aad,

Hydrogen production by methane steam reforming over Ru supported on Ni–Mg–Al mixed oxides prepared via hydrotalcite route,

International Journal of Hydrogen Energy,

Volume 40, Issue 2,

2015,

Pages 1269-1277,

ISSN 0360-3199,

https://doi.org/10.1016/j.ijhydene.2014.09.166.

(https://www.sciencedirect.com/science/article/pii/S036031991402761X)

Abstract: Catalytic performance of Ru/NixMg6−xAl2 800 800 mixed oxides, with x = 2, 4 and 6, x being the molar ratio, towards Methane Steam Reforming, was studied. NixMg6−xAl2 800 oxide, used as support, was prepared via hydrotalcite route. It was thermally stabilized at 800 °C, impregnated with 0.5 wt.% ruthenium using ruthenium (III) nitrosyl nitrate Ru(NO) (NO3)3 precursor and then calcined again at 800 °C under an air flow. Ruthenium impregnation significantly enhanced the reactivity of the oxides in Methane Steam Reforming. In fact, it was found, that even with a low ruthenium content (0.5 wt.%), ruthenium oxide particles are formed but are well dispersed over the surface of the oxide NixMg6−xAl2 800. Ru/Ni6Al2 800 800 showed better catalytic performances, towards Methane Steam Reforming, than ruthenium impregnated on the two other supports. Indeed, nickel content is higher in Ni6Al2 800 than in the other studied supports and therefore the probability of Ni–Ru interaction should be greater and consequently catalytic performances could be improved.

Keywords: Hydrotalcite; Methane steam reforming; Ruthenium; Nickel; Hydrogen production

Yuxuan Zeng, Xinbo Zhu, Danhua Mei, Bryony Ashford, Xin Tu,

Plasma-catalytic dry reforming of methane over γ-Al2O3 supported metal catalysts,

Catalysis Today,

Volume 256, Part 1,

2015,

Pages 80-87,

ISSN 0920-5861,

https://doi.org/10.1016/j.cattod.2015.02.007.

(https://www.sciencedirect.com/science/article/pii/S0920586115000772)

Abstract: A coaxial dielectric barrier discharge (DBD) reactor has been developed for plasma-catalytic dry reforming of CH4 and CO2 into higher value synthesis gas (syngas). The influence of reaction conditions (e.g. CO2/CH4 molar ratio and total feed flow rate) and supported metal catalysts M/γ-Al2O3 (M=Ni, Co, Cu and Mn) on the performance of the plasma process has been investigated in terms of the conversion of feed gases, the selectivity and yield of major gas products, and the energy efficiency of the plasma process. The combination of plasma with the Ni/γ-Al2O3 and Mn/γ-Al2O3 catalysts significantly enhanced the conversion of CH4 and exhibited a plasma-catalytic synergy for this and the overall energy efficiency of the process. The maximum CH4 conversion of 19.6% was achieved for the plasma-catalytic dry reforming over the Ni/γ-Al2O3 catalyst at a discharge power of 7.5W and a gas flow rate of 50mlmin−1. However, the presence of any of these catalysts in the plasma did not show any synergy for CO2 conversion. In addition, the integration of plasma and the γ-Al2O3 supported catalysts was found to enhance the yield of CO and H2, whilst the Ni/γ-Al2O3 catalyst exhibited the best activity for syngas production.

Keywords: Plasma-catalysis; Dry reforming; Dielectric barrier discharge; Non-thermal plasma; Synthesis gas

L. Fan, L. van Biert, A. Thallam Thattai, A.H.M. Verkooijen, P.V. Aravind,

Study of Methane Steam Reforming kinetics in operating Solid Oxide Fuel Cells: Influence of current density,

International Journal of Hydrogen Energy,

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2015,

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https://doi.org/10.1016/j.ijhydene.2015.02.096.

(https://www.sciencedirect.com/science/article/pii/S0360319915004760)

Abstract: In literature, little is reported on the experimental studies of Methane Steam Reforming (MSR) kinetics in Solid Oxide Fuel Cells (SOFCs) when a current is drawn. This work investigates MSR reaction kinetics in a complete SOFC with a Ni–Gd0.1Ce0.9O2−δ (Ni−GDC) anode under varying gas compositions, operating temperatures and current densities in order to obtain reliable experimental data for Computational Fluid Dynamics (CFD) modeling studies. Consistent with previous work, the methane conversion XCH4 decreases as the temperature decreases. A slight increase in the MSR reaction rate is observed when a current is drawn. A positive dependency of the MSR reaction rate on methane concentration was found. Current has an insignificant influence on the methane reaction order. Under open-circuit working condition, steam concentration has a slightly positive influence at higher temperature and a slightly negative influence at lower temperature on the MSR reaction rate. The influence of steam concentration on the reaction rate becomes more negative when a current is drawn. It is probably due to the blockage of reaction sites by the adsorbed oxygen/water molecules/ions.

Keywords: SOFC; Reforming; Ni-GDC; Operating cell; Activation energy; Current density

Tae Wan Kim, Ji Chan Park, Tak-Hyoung Lim, Heon Jung, Dong Hyun Chun, Ho Tae Lee, Sungjun Hong, Jung-Il Yang,

The kinetics of steam methane reforming over a Ni/γ-Al2O3 catalyst for the development of small stationary reformers,

International Journal of Hydrogen Energy,

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https://doi.org/10.1016/j.ijhydene.2015.02.014.

(https://www.sciencedirect.com/science/article/pii/S0360319915003195)

Abstract: To develop small stationary reformers for on-site H2 production, the active catalyst and its reaction kinetics were examined in order to study the steam methane reforming reaction. A 20 wt% Ni/γ-Al2O3 was found to be a highly active catalyst within the investigated range of contact time from 1.16 to 3.64 gcath/mol, which was good for developing the small stationary reformers. BET, XRD, and TEM analysis revealed that the high activity of the 20 wt% Ni/γ-Al2O3 catalyst compared to the 15 wt% Ni/γ-Al2O3 catalyst was strongly ascribed to the high number of Ni metal particles and the ratio of the number of the Ni metal species between the catalysts was calculated to be 1.33. Furthermore, the SMR reaction kinetics of the reversible first-order reaction between reactants and products was applied. This showed that the activation energies obtained by the two catalysts were the same because of the similar pore diffusion and heat transfer restrictions, and the similar Ni particle size in the catalyst pores. Also, it was found that the ratio of the pre-exponential factor was 1.30, which was exactly proportional to the ratio of Ni loading in the catalysts because it was strongly related to the collision density.

Keywords: Steam methane reforming; Kinetics; Ni loading; Ni particle size; Activation energy; Pre-exponential factor

Miklós Németh, Zoltán Schay, Dávid Srankó, Johanna Károlyi, György Sáfrán, István Sajó, Anita Horváth,

Impregnated Ni/ZrO2 and Pt/ZrO2 catalysts in dry reforming of methane: Activity tests in excess methane and mechanistic studies with labeled 13CO2,

Applied Catalysis A: General,

Volume 504,

2015,

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https://doi.org/10.1016/j.apcata.2015.04.006.

(https://www.sciencedirect.com/science/article/pii/S0926860X15002392)

Abstract: In the present work, 1%Ni/ZrO2, 3%Ni/ZrO2 and 1%Pt/ZrO2 catalysts prepared by impregnation with the concomitant addition of NaHCO3 were investigated and compared by structural investigations such as TEM, XRD, TPR, XPS and DRIFTS methods. Temperature programmed dry reforming (DRM) experiments were done (i) at atmospheric pressure in plug flow reactor and an in situ DRIFTS cell or (ii) under sub atmospheric pressure (∼50mbar) in a closed loop circulation system using labelled 13CO2 to trace the fate of carbon compounds. The calcined and reduced fresh catalysts contained nanoparticles in the range of 2–18nm. According to the TPR results, in 3%Ni/ZrO2 catalyst most of Ni is in strong interaction with the support. The presence of sodium was suggested to induce the appearance of strongly bound bridged CO sites during CO chemisorption in DRIFTS measurements for all samples and to cause BE shift in XPS spectrum of the highly dispersed Pt/ZrO2 only. In the catalytic tests in plug flow reactor the 3wt%Ni/ZrO2 sample turned to be the most active catalyst, but coke was deposited on its surface measured by the subsequent temperature programmed oxidation (TPO) measurements. In situ low temperature DRIFTS-DRM measurements suggested that stability of surface carbonates is less when dispersed electron-rich Pt nanoparticles are on the ZrO2 support, while more carbonates accumulate on Ni/ZrO2 samples. Based on our isotope labeled 13CO2+12CH4 experiments in circulation system, the same initial reaction pathways could be suggested for the Ni and Pt catalysts. The reactive surface carbon species from the two different sources (CH4 and CO2) were completely scrambled on 3wt%Ni/ZrO2 at 600°C, suggesting that common reaction intermediates do exist.

Keywords: Mechanism of dry reforming; Ni/ZrO2; Pt/ZrO2; Circulation system; DRIFTS; Coke formation; 13CO2 isotope labeled experiments

Radosław Dębek, Katarzyna Zubek, Monika Motak, Maria Elena Galvez, Patrick Da Costa, Teresa Grzybek,

Ni–Al hydrotalcite-like material as the catalyst precursors for the dry reforming of methane at low temperature,

Comptes Rendus Chimie,

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2015,

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https://doi.org/10.1016/j.crci.2015.04.005.

(https://www.sciencedirect.com/science/article/pii/S1631074815001137)

Abstract: Nickel–aluminium and magnesium–aluminium hydrotalcites were prepared by co-precipitation and subsequently submitted to calcination. The mixed oxides obtained from the thermal decomposition of the synthesized materials were characterized by XRD, H2-TPR, N2 sorption and elemental analysis and subsequently tested in the reaction of methane dry reforming (DRM) in the presence of excess of methane (CH4/CO2/Ar=2/1/7). DMR in the presence of the nickel-containing hydrotalcite-derived material showed CH4 and CO2 conversions of ca. 50% at 550°C. The high values of the H2/CO molar ratio indicate that at 550°C methane decomposition was strongly influencing the DRM process. The sample reduced at 900°C showed better catalytic performance than the sample activated at 550°C. The catalytic performance in isothermal conditions from 550°C to 750°C was also determined.

Keywords: Dry reforming; Methane; CO2; Hydrotalcite; Nickel

Saeed Khajeh Talkhoncheh, Mohammad Haghighi,

Syngas production via dry reforming of methane over Ni-based nanocatalyst over various supports of clinoptilolite, ceria and alumina,

Journal of Natural Gas Science and Engineering,

Volume 23,

2015,

Pages 16-25,

ISSN 1875-5100,

https://doi.org/10.1016/j.jngse.2015.01.020.

(https://www.sciencedirect.com/science/article/pii/S1875510015000219)

Abstract: In this study, Ni-based nanocatalysts over various types of supports, NH4NO3 ion exchanged clinoptilolite, CeO2 and Al2O3, have been prepared by impregnation method and studied for CO2 reforming of CH4 into syngas. The physicochemical properties of the samples were characterized by XRD, FESEM, EDX, BET and FTIR analyses. XRD analysis is showed that the interaction between NiO and CeO2 results in well dispersion of NiO. Based on the BET analysis, Ni/Al2O3 nanocatalyst has the highest specific surface area in comparison to other nanocatalysts. FESEM images illustrate that, all the samples have nanoscale morphology. EDX analysis demonstrates the homogenous dispersion of Ni on Ni/Al2O3 and Ni/CeO2 nanocatalysts. The activity and stability of the synthesized nanocatalysts for CO2 reforming of CH4 were tested at temperature range of 550–850 °C. Ni/Al2O3 nanocatalyst illustrates much higher conversions (93% and 96% for CH4 and CO2 at 850 °C) and yields (90% and 93% for H2 and CO). Also, the activity of Ni/Al2O3 remained stable during 1440 min. Among the prepared samples, Ni/Al2O3 nanocatalyst has the best performance due to the desired physicochemical properties; while Ni/Clinoptilolite, as an inexpensive and economical nanocatalyst, has relatively good activity.

Keywords: Dry reforming; Hydrogen; Ni; Ceria; Clinoptilolite; Alumina

Monika Radlik, Małgorzata Adamowska-Teyssier, Andrzej Krztoń, Krzysztof Kozieł, Waldemar Krajewski, Wincenty Turek, Patrick Da Costa,

Dry reforming of methane over Ni/Ce0.62Zr0.38O2 catalysts: Effect of Ni loading on the catalytic activity and on H2/CO production,

Comptes Rendus Chimie,

Volume 18, Issue 11,

2015,

Pages 1242-1249,

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https://doi.org/10.1016/j.crci.2015.03.008.

(https://www.sciencedirect.com/science/article/pii/S1631074815000806)

Abstract: The activity of ceria–zirconia-supported nickel catalysts (Ni/CZ) with various loadings of nickel (2, 4 and 10wt. %) was studied in the case of low-temperature dry reforming of methane (DRM). XRD, SBET, SEM, TPD-CO2 and thermogravimetry were used to determine the physicochemical properties of the catalysts and of the carbon deposits formed on the surface. It was found that the agglomerates of the Ni-active phase are formed on the surface of the support for high loadings of nickel. The best conversions of CO2 and CH4 and an optimum ratio H2/CO=1 were obtained for the catalysts with the highest Ni content. It was also found that loading has an influence on the amount of carbon deposits formed in the DRM process.

Keywords: Methane; Hydrogen; Dry reforming; Ceria–zirconia; Nickel loading

S. Marmarshahi, A. Niaei, D. Salari, F. Abedini, M. Abbasi, N. Kalantari,

Evaluating the Catalytic Performance of La1-xCexNi1-yZnyO3 Nanostructure Perovskites in the Carbon Dioxide Reforming of Methane,

Procedia Materials Science,

Volume 11,

2015,

Pages 616-621,

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https://doi.org/10.1016/j.mspro.2015.11.095.

(https://www.sciencedirect.com/science/article/pii/S221181281500437X)

Abstract: In this research nanostructure perovskites La1-xCexNi1-yZnyO3 were prepared by sol-gel auto-combustion method and their application were evaluated for methane reforming with carbon dioxide and syngas production. Catalysts were designed by Response Surface Method (RSM) based on central composite design (CCD) with three factors of catalyst characteristics, x, y and Tc. The prepared catalysts were examined in methane reforming process at 750 ˚C temperature and atmospheric pressure. Analysis of variance (ANOVA) showed that parameters don’t have any linear effect on catalytic activity and their effect is proportional to square form. Among this investigated parameters, Ni content effect is considerable and calcination temperature (Tc) has a partial effect. In this research R2 value was 94.88%. The optimum catalyst which determined by RSM was La0.60Ce0.40Ni0.81Zn0.19O3 in 747 ˚C calcination temperature that corresponds to empirical result. The XRD characterization of optimum catalyst showed that perovskite catalyst was formed in rhombohedra phase with nanostructure crystals and the SEM of optimum catalyst confirmed the nano scale of prepared particles.

Keywords: Nanoparticle; Dry reforming; Mixed metal oxide; RSM.

Rafik Benrabaa, Axel Löfberg, Jesús Guerrero Caballero, Elisabeth Bordes-Richard, Annick Rubbens, Rose-Noëlle Vannier, Hamza Boukhlouf, Akila Barama,

Sol–gel synthesis and characterization of silica supported nickel ferrite catalysts for dry reforming of methane,

Catalysis Communications,

Volume 58,

2015,

Pages 127-131,

ISSN 1566-7367,

https://doi.org/10.1016/j.catcom.2014.09.019.

(https://www.sciencedirect.com/science/article/pii/S156673671400377X)

Abstract: Silica-supported NiFe2O4 spinel was prepared by sol–gel method using tetramethyl orthosilicate as a precursor of silica. B.E.T., XRD, MEB–EDS, TEM, XPS and Raman scattering techniques were used for its characterization. The reducibility by hydrogen was investigated by TPR and HT-XRD. These properties are compared to those of unsupported NiFe2O4. Both acidic and redox sites were found by studying the decomposition of isopropanol. First experiments in the dry reforming of methane by CO2 showed that owing to more acidic properties supporting NiFe2O4 on silica provides a more active and selective catalyst that seems less prone to coking.

Keywords: NiFe2O4; Sol–gel method; Isopropanol decomposition; Dry reforming of methane

Junshe Zhang, Fanxing Li,

Coke-resistant Ni@SiO2 catalyst for dry reforming of methane,

Applied Catalysis B: Environmental,

Volumes 176–177,

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https://doi.org/10.1016/j.apcatb.2015.04.039.

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Abstract: Nanostructured Ni@SiO2 core–shell catalyst is prepared from nickel oxide nanoparticles by a facile method. Calcination of as-synthesized core–shell nanoparticles creates a micro/meso-porous structure in the amorphous silica shell. The catalytic performance of core–shell catalyst toward dry reforming of methane was first evaluated in a thermogravimeter coupled with a mass spectrometer. Coking is negligible in a reforming period of 40h on stream at 850°C, while more than 0.32gcokegcat−1 is produced on a commercial Ni-based reforming catalyst in 6.4h at the same reforming condition. Dry reforming was also performed in a continuous flow, fixed-bed reactor at 750°C. Characterization of spent catalyst further confirms that Ni@SiO2 catalyst has high coke-resistance for dry reforming. The amount of coke deposited on the core–shell catalyst in 24.5h is 0.012gcokegcat−1.

Keywords: Coke-resistance; Nickel oxide nanoparticles; Core–shell catalyst; Dry reforming of methane; Carbon dioxide

Igor Luisetto, Simonetta Tuti, Chiara Battocchio, Sergio Lo Mastro, Armida Sodo,

Ni/CeO2–Al2O3 catalysts for the dry reforming of methane: The effect of CeAlO3 content and nickel crystallite size on catalytic activity and coke resistance,

Applied Catalysis A: General,

Volume 500,

2015,

Pages 12-22,

ISSN 0926-860X,

https://doi.org/10.1016/j.apcata.2015.05.004.

(https://www.sciencedirect.com/science/article/pii/S0926860X1500294X)

Abstract: The catalytic performances of Ni/CeO2–Al2O3 catalysts for the dry reforming of CH4 (DRM) were investigated. Catalysts with different Ni dispersion and different amount of CeAlO3 species were prepared by different methods and characterized by BET, XRD, XPS, Raman, TPR and TPO techniques. Catalytic activity was studied during time on stream in the range 873–1073K with a mixture of CH4:CO2:Ar=40:40:20vol.% and GHSV 90,000cm3g−1h−1. The intrinsic catalytic activity increased with the increasing of Ni crystallite size. Carbon was deposited as nano-fibres and graphite when catalysts worked at lower temperature, and the largest amount was found on the catalyst with the largest Ni crystallite size. The formation of graphitic deposits is limited by the presence of CeAlO3 species formed during catalyst activation. CA preparation method results particularly attractive because it allows to obtain catalysts with small Ni crystallite size and high content of CeAlO3 species, which both have a role in suppressing the carbon deposition and therefore in obtaining stable catalytic performances.

Keywords: Ni/CeO2–Al2O3; Dry reforming; Nickel particle size; CeAlO3; Carbon deposition

Tri Huu Nguyen, Agata Łamacz, Andrzej Krztoń, Agnieszka Ura, Karolina Chałupka, Magdalena Nowosielska, Jacek Rynkowski, Gérald Djéga-Mariadassou,

Partial oxidation of methane over Ni0/La2O3 bifunctional catalyst II: Global kinetics of methane total oxidation, dry reforming and partial oxidation,

Applied Catalysis B: Environmental,

Volume 165,

2015,

Pages 389-398,

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https://doi.org/10.1016/j.apcatb.2014.10.019.

(https://www.sciencedirect.com/science/article/pii/S0926337314006328)

Abstract: The global kinetics (power rate law) of methane total oxidation (TO) over La2O3 catalyst was performed at 773, 823 and 873K. The global kinetics of methane dry reforming (DR) at 648, 673, 698 and 723K and partial oxidation (POM) at 993, 1013, 1023 and 1053K were conducted over Ni0/La2O3 catalyst. The initial rate method and isolation method were used to determine initial rates, rate constants, and partial orders to reactants and establish the Arrhenius equations for TO, DR, POM. The experimental apparent activation energies were 87.8, 116.4 and 112.8kJmol−1 for DR, TO and POM, respectively. For TO, the reaction order to CH4 was varying with conversion whereas that to O2 was zero. For DR, the reaction order to CH4 was constant, whereas that to CO2 was dependent on the concentration of CO2. The values of rate constants revealed the following order: kDR≫kPOM, kTO. It was found that the rate constant of POM reaction is linked to that of methane TO: kPOM≈2kTO. The catalytic cycle of methane TO is the “rate determining cycle” (rdc) of the POM process.

Keywords: POM; Global kinetics; Power rate law; Nickel; La2O3

Rong-jun ZHANG, Guo-fu XIA, Ming-feng LI, Yu WU, Hong NIE, Da-dong LI,

Effect of support on the performance of Ni-based catalyst in methane dry reforming,

Journal of Fuel Chemistry and Technology,

Volume 43, Issue 11,

2015,

Pages 1359-1365,

ISSN 1872-5813,

https://doi.org/10.1016/S1872-5813(15)30040-2.

(https://www.sciencedirect.com/science/article/pii/S1872581315300402)

Abstract: Ni-based catalysts with different supports were prepared and characterized by N2 physisorption, XRD, H2-TPR, H2 chemisorption, and so on; the effect of support on the performance of Ni-based catalyst in methane dry reforming was then investigated. The results indicated that the support has a significant influence on the state of NiO species. SiO2, TiO2 and ZrO2 as a support have a weak interaction with NiO, which facilitates the reduction of the corresponding catalysts; however, the weak interaction may also lead to quick deactivation due to the agglomeration of active metal species. Al2O3 and MgO have a strong interaction with NiO, which may promote the formation of NiAl2O4 spinel and NiO-MgO solid solution, respectively, and make the reduction of corresponding catalysts very difficult. Al2O3 modified by MgO is provided with both proper textural properties and interaction strength between metal and support, which are in favor of the dispersion and stabilization of NiO species. As a result, NiO supported on MgO-modified Al2O3 exhibits superior catalytic performance in methane dry reforming even under very high gas hourly space velocity; it is quite stable during a long term test of more than 100 h.

Keywords: methane; carbon dioxide; dry reforming; syngas; support effect

X.Y. Gao, J. Ashok, S. Widjaja, K. Hidajat, S. Kawi,

Ni/SiO2 catalyst prepared via Ni-aliphatic amine complexation for dry reforming of methane: Effect of carbon chain number and amine concentration,

Applied Catalysis A: General,

Volume 503,

2015,

Pages 34-42,

ISSN 0926-860X,

https://doi.org/10.1016/j.apcata.2015.07.005.

(https://www.sciencedirect.com/science/article/pii/S0926860X15300582)

Abstract: Aliphatic amines of different carbon numbers (i.e., carbon number in one linear hydrocarbon chain, Nc) and concentrations (Ca) were used in the preparation of silicon dioxide (SiO2) supported nickel catalysts by incipient wetness impregnation (IWI) method. The results showed that both the size and the metal-support interaction (MSI) were affected by the carbon chain number and the amine concentration. On one hand, the use of the aliphatic amine with a larger carbon chain number achieved a smaller size and higher dispersion due to the stronger steric hindrance; this smaller size and higher dispersion further enhanced the MSI because of the larger contact area of Ni with the silica support. On the other hand, a higher amine concentration decreases the size and improve the dispersion because of the faster nucleation rate; also when higher concentration of amine was used, more hydrogen bonds were formed between the -NH2 and the silanol group and more electron transfer was found between Ni and the -NH2, leading to a stronger MSI. With a small size, high dispersion and strong MSI, NiSi-OAm showed the most stable catalytic performances (CO2 conversion of 78% and CH4 conversion of 70% within 20h) with low carbon deposition (1.8 mgC/gcath) for dry reforming of methane (DRM) reaction.

Keywords: Ni; Aliphatic amine; Carbon chain; –NH2 terminal group; Dry reforming of methane

María Elena Gálvez, Abdulkader Albarazi, Patrick Da Costa,

Enhanced catalytic stability through non-conventional synthesis of Ni/SBA-15 for methane dry reforming at low temperatures,

Applied Catalysis A: General,

Volume 504,

2015,

Pages 143-150,

ISSN 0926-860X,

https://doi.org/10.1016/j.apcata.2014.10.026.

(https://www.sciencedirect.com/science/article/pii/S0926860X14006498)

Abstract: A non-conventional synthesis route for the preparation of Ni/SBA-15 catalyst for methane dry reforming (MDR), comprising the addition of ascorbic acid as reducing agent, was considered and compared to impregnation and precipitation conventional preparation methods. The catalyst prepared following this novel route evidenced successful confinement of Ni-species inside the pores of SBA-15, both NiO and Ni-phyllosilicates. Due to its particular characteristics, this catalyst showed enhanced activity, selectivity and stability in MDR experiments. Concretely, deactivation of the catalyst was substantially hindered, due to improved selectivity, preferential carbon growth on the external surface of the catalyst, and special ability of the catalyst to favor the formation of amorphous carbon.

Keywords: Methane dry reforming; Ni catalyst; SBA-15; Ascorbic acid; Synthesis gas; Hydrogen

Linus A. Schulz, Lea C.S. Kahle, Karla Herrera Delgado, Stephan A. Schunk, Andreas Jentys, Olaf Deutschmann, Johannes A. Lercher,

On the coke deposition in dry reforming of methane at elevated pressures,

Applied Catalysis A: General,

Volume 504,

2015,

Pages 599-607,

ISSN 0926-860X,

https://doi.org/10.1016/j.apcata.2015.03.002.

(https://www.sciencedirect.com/science/article/pii/S0926860X15001477)

Abstract: The reaction pathways leading to coke formation in dry reforming on Ni and Pt-based catalysts were investigated. Using isotope-labeled reactants (i.e., CH4+13CO2 ⇌ 2CO+2H2) showed that initially 13CO2 is converted faster than CH4 and that this higher activity leads to a higher concentration of 13CO compared with 12CO in the product stream, suggesting little isotope scrambling among products at this stage. Gasification of carbon deposits was found to be an important pathway enhancing the catalyst stability. Analysis of the pathways leading to carbon deposits suggests that coke is formed predominantly via reverse Boudouard reaction on Ni, while both metals contribute to CH4 dissociation. The pronounced reversibility of the CH and CO bond formation and cleavage was also shown by the presence of 13CH4 formed from 13CO2 and 12CO formed from 12CH4. Numeric calculations complementing the experimental results led to the proposal of a reaction pathway for the surface reactions, accounting for the differences between Ni and Pt.

Keywords: Dry reforming of methane; Reverse water gas shift; Ni; Pt; Hexaaluminate support; Coke formation; Isotope labeling; Reaction flow analysis

R.Y. Chein, Y.C. Chen, C.T. Yu, J.N. Chung,

Thermodynamic analysis of dry reforming of CH4 with CO2 at high pressures,

Journal of Natural Gas Science and Engineering,

Volume 26,

2015,

Pages 617-629,

ISSN 1875-5100,

https://doi.org/10.1016/j.jngse.2015.07.001.

(https://www.sciencedirect.com/science/article/pii/S1875510015300275)

Abstract: Thermodynamic equilibrium of dry reforming of methane (DRM) was studied by Gibbs free energy minimization at elevated pressures. CH4 and CO2 conversions, carbon formation, H2 yield, H2/CO ratio and H2O formation were used to characterize the DRM performance using the reaction temperature as the primary parameter. The result shows that DRM is unfavorable at high pressure. CO2 and CH4 conversions decrease while the carbon formation increases as the pressure increases. With increasing CO2/CH4 ratio in the reaction, CH4 conversion is enhanced, carbon formation is suppressed, but CO2 conversion is lower due to the excess CO2 supply. The simulation results indicated that the introduction of inert gas in the system did not produce a significant effect on DRM performance. The performances of combined DRM and partial oxidation of methane (POM) and combined DRM and methane-steam reforming (MSR) were also studied to suppress the carbon formation. It was found that carbon formation can be reduced by introducing oxygen. However, the resulted H2/CO ratio is less than 1. Introducing H2O into the reaction system can eliminate carbon formation when amount of H2O is large. However, the system must be operated at high temperature to produce high CH4 and CO2 conversions.

Keywords: Dry reforming of methane (DRM); Gibbs free energy minimization; High pressures; CH4 conversion; CO2 conversion; Carbon formation

Marie-Nour Kaydouh, Nissrine El Hassan, Anne Davidson, Sandra Casale, Henri El Zakhem, Pascale Massiani,

Effect of the order of Ni and Ce addition in SBA-15 on the activity in dry reforming of methane,

Comptes Rendus Chimie,

Volume 18, Issue 3,

2015,

Pages 293-301,

ISSN 1631-0748,

https://doi.org/10.1016/j.crci.2015.01.004.

(https://www.sciencedirect.com/science/article/pii/S1631074815000053)

Abstract: Dry reforming of methane has been carried out on SBA-15 catalysts containing 5wt% Ni and 6wt% Ce. The effect of the order of Ni and Ce impregnation on the catalytic activity has been studied. Both metals were added using the “two-solvent” method that favors metal dispersion inside the pores. Characterizations by XRD (low and high angles), N2 sorption, SEM and TEM of the materials after metal addition and calcination indicate good preservation of the porosities and high NiO and CeO2 dispersion inside the porous channels. Reduction was carried out before the catalytic tests and followed by TPR measurements. The most active reduced catalyst was the Ni–Ce/SBA-15 sample prepared by impregnating cerium first, then nickel. All catalysts were highly active and selective towards H2 and CO at atmospheric pressure. Full CH4 conversion was obtained below 650°C. The higher performances compared to those reported in the literature for mesoporous silica with supported Ni and Ce catalysts are discussed.

Résumé

Le reformage à sec du méthane a été étudié sur des catalyseurs SBA-15 contenant 5 % en poids de Ni et 6 % en poids de Ce. L’effet de l’ordre d’imprégnation de Ni et Ce sur l’activité catalytique a été étudié. Ces deux métaux ont été ajoutés en utilisant la méthode « à deux solvants », qui favorise la dispersion du métal à l’intérieur des pores. Les caractérisations par DRX (petits et grands angles), adsorption de N2, MEB et MET des matériaux après ajout du métal et calcination montrent une bonne préservation de la porosité et une grande dispersion des nanoparticules de NiO et CeO2 à l’intérieur des pores. La réduction des catalyseurs suivie par RTP a été effectuée avant tests catalytiques. Le catalyseur le plus actif est le Ni–Ce/SBA-15 réduit, préparé par imprégnation, tout d’abord du cérium, puis du nickel. Les catalyseurs étaient très actifs et sélectifs en H2 et CO sous pression atmosphérique, avec une conversion complète de CH4 atteinte avant 650°C. Les performances supérieures à celles décrites dans la littérature pour des catalyseurs à base de silice mésoporeuse contenant du Ni et du Ce sont discutées.

Keywords: Methane dry reforming; Mesoporous SBA-15 silica; Nickel; Cerium; Impregnation; Reformage à sec du méthane; Silice mésoporeuse SBA-15; Nickel; Cérium; Imprégnation

Jesús Manuel García-Vargas, Jose Luis Valverde, Javier Díez, Fernando Dorado, Paula Sánchez,

Catalytic and kinetic analysis of the methane tri-reforming over a Ni–Mg/β-SiC catalyst,

International Journal of Hydrogen Energy,

Volume 40, Issue 28,

2015,

Pages 8677-8687,

ISSN 0360-3199,

https://doi.org/10.1016/j.ijhydene.2015.05.032.

(https://www.sciencedirect.com/science/article/pii/S0360319915011763)

Abstract: In this work, the influence of the temperature and feed composition on the catalytic behaviour of a Ni–Mg/β-SiC catalyst in the methane tri-reforming was analysed and modelized. This catalyst was characterized by Atomic Absorption Spectrophotometry (AAS), Temperature Programmed Reduction (TPR), N2 adsorption, Temperature Programmed Desortion of CO2 (TPD) and X-Ray Diffraction (XRD). 36 catalytic experiments at different temperatures and feed compositions were performed, modifying the quantity of CH4, CO2, H2O and O2 present in the feed. The predominance of each one of the reactions that took place during the tri-reforming process was evaluated as a function of the temperature, finding at low temperatures a higher contribution of both the steam reforming and the water gas shift reactions. On the contrary, at higher temperatures, a higher contribution of the dry reforming was detected. Finally, a kinetic model was raised and experimental data were fitted to it. Steam reforming, dry reforming and water gas shift reactions were considered as the kinetically relevant equations. A good agreement between experimental and predicted data was observed.

Keywords: Tri-reforming; Nickel; Magnesium; Kinetics

Elham Baktash, Patrick Littlewood, Reinhard Schomäcker, Arne Thomas, Peter C. Stair,

Alumina coated nickel nanoparticles as a highly active catalyst for dry reforming of methane,

Applied Catalysis B: Environmental,

Volume 179,

2015,

Pages 122-127,

ISSN 0926-3373,

https://doi.org/10.1016/j.apcatb.2015.05.018.

(https://www.sciencedirect.com/science/article/pii/S0926337315002635)

Abstract: Alumina coated nickel nanoparticles were prepared employing atomic layer deposition (ALD) on nickel oxide (NiO) nanoparticles and subsequent reduction of the NiO core. The materials showed impressive activity and stability for dry reforming of methane at elevated temperatures (700–800°C), especially when compared to the uncoated and reduced NiO nanoparticles. The stabilization against sintering at high temperatures is the crucial factor explaining the high catalytic activity of alumina coated Ni nanoparticles.

Keywords: Dry reforming of methane (DRM); Nickel oxide; Atomic layer deposition (ALD); Nanoparticles; Core–shell structures

Yang Qi, Zhenmin Cheng, Zhiming Zhou,

Steam reforming of methane over Ni catalysts prepared from hydrotalcite-type precursors: Catalytic activity and reaction kinetics,

Chinese Journal of Chemical Engineering,

Volume 23, Issue 1,

2015,

Pages 76-85,

ISSN 1004-9541,

https://doi.org/10.1016/j.cjche.2013.11.002.

(https://www.sciencedirect.com/science/article/pii/S1004954114002146)

Abstract: Ni/Mg–Al catalysts derived from hydrotalcite-type precursors were prepared by a co-precipitation technique and applied to steam reforming of methane. By comparison with Ni/γ-Al2O3 and Ni/α-Al2O3 catalysts prepared by incipient wetness impregnation, the Ni/Mg–Al catalyst presented much higher activity as a result of higher specific surface area and better Ni dispersion. The Ni/Mg–Al catalyst with a Ni/Mg/Al molar ratio of 0.5:2.5:1 exhibited the highest activity for steam methane reforming and was selected for kinetic investigation. With external and internal diffusion limitations eliminated, kinetic experiments were carried out at atmospheric pressure and over a temperature range of 823–973K. The results demonstrated that the overall conversion of CH4 and the conversion of CH4 to CO2 were strongly influenced by reaction temperature, residence time of reactants as well as molar ratio of steam to methane. A classical Langmuir–Hinshelwood kinetic model proposed by Xu and Froment (1989) fitted the experimental data with excellent agreement. The estimated adsorption parameters were consistent thermodynamically.

Keywords: Methane steam reforming; Hydrogen; Hydrotalcite; Catalyst; Kinetics

Patrick Littlewood, Xiao Xie, Michael Bernicke, Arne Thomas, Reinhard Schomäcker,

Ni0.05Mn0.95O catalysts for the dry reforming of methane,

Catalysis Today,

Volume 242, Part A,

2015,

Pages 111-118,

ISSN 0920-5861,

https://doi.org/10.1016/j.cattod.2014.07.054.

(https://www.sciencedirect.com/science/article/pii/S092058611400580X)

Abstract: The behaviour of nickel manganese catalysts Ni0.05Mn0.95O for the dry (carbon dioxide) reforming of methane was investigated from 500 to 800°C. Prepared catalysts showed ex-solution nickel nanoparticles on the manganese surface, which sintered during reaction, deactivating the catalyst. By pre-sintering the catalyst at 750°C in an inert atmosphere, deactivation from sintering and carbon deposition was avoided at temperatures below 800°C. The resistance of the sintered catalyst against carbon deposition was assumed to be caused by SMSI effects. After dispersing the Ni0.05Mn0.95O catalyst on silica, the catalyst exhibits a leap in activity at 600°C followed by slow deactivation, attributed to a spontaneous phase change to Ni/Mn2SiO4.

Keywords: Dry reforming; Methane; Carbon dioxide; Nickel; Manganese; Olivine

Abdulkader Albarazi, Maria Elena Gálvez, Patrick Da Costa,

Synthesis strategies of ceria–zirconia doped Ni/SBA-15 catalysts for methane dry reforming,

Catalysis Communications,

Volume 59,

2015,

Pages 108-112,

ISSN 1566-7367,

https://doi.org/10.1016/j.catcom.2014.09.050.

(https://www.sciencedirect.com/science/article/pii/S1566736714004087)

Abstract: Ceria–zirconia doped Ni/SBA-15 catalysts for methane dry reforming were prepared following different synthesis routes. Textural, structural and chemical features of such catalysts are strongly influenced by the synthesis procedure chosen for its preparation. Co-precipitation results in the formation of nickel-phyllosilicate species, as a result of a strong interaction between the active phase and the SBA-15 support. Their presence results in slightly lower catalytic activity but notably enhanced stability than for the catalysts prepared by means of impregnation, which evidenced a predominant presence of NiO. Moreover, direct methane decomposition is not favored in the presence of the co-precipitated catalyst, resulting in minimal carbon formation and deposition on their surface, which is the main cause of its deactivation.

Keywords: Methane dry reforming; Nickel; Ceria–zirconia; SBA-15

Xiaogang Zheng, Shiyu Tan, Lichun Dong, Shaobo Li, Hongmei Chen,

Plasma-assisted catalytic dry reforming of methane: Highly catalytic performance of nickel ferrite nanoparticles embedded in silica,

Journal of Power Sources,

Volume 274,

2015,

Pages 286-294,

ISSN 0378-7753,

https://doi.org/10.1016/j.jpowsour.2014.10.065.

(https://www.sciencedirect.com/science/article/pii/S0378775314016747)

Abstract: Spinel nickel ferrite nanoparticles (NiFe2O4 NPs) embedded in silica (NiFe2O4#SiO2) was prepared to enhance the reaction performance of the dry reforming of methane in a coaxial dielectric barrier discharge reactor. NiFe2O4 NPs of around 10 nm were effectively embedded in porous SiO2 NPs (∼100 nm in diameter). Compared to the supported Ni-based catalysts (Ni/γ-Al2O3, Ni–Fe/γ-Al2O3, Ni–Fe/SiO2, and NiFe2O4), the NiFe2O4#SiO2 catalyst placed at the discharge zone exhibited excellent catalytic performance and high resistance to carbon formation during dry reforming under ambient conditions without the involvement of extra heat. The synergetic effect between the non-thermal plasma and the NiFe2O4#SiO2 catalyst favored the conversion of CH4 and CO2 into syngas. The results indicated that the special structure of the as-synthesized NiFe2O4#SiO2 catalyst was capable of restraining the aggregation of Ni–Fe alloy and suppressing the carbon formation in the reforming process.

Keywords: Dry reforming of methane; Synergistic effect; Nickel ferrite; Embedded structure; Non-thermal plasma

Moisés R. Cesário, Braúlio S. Barros, Claire Courson, Dulce M.A. Melo, Alain Kiennemann,

Catalytic performances of Ni–CaO–mayenite in CO2 sorption enhanced steam methane reforming,

Fuel Processing Technology,

Volume 131,

2015,

Pages 247-253,

ISSN 0378-3820,

https://doi.org/10.1016/j.fuproc.2014.11.028.

(https://www.sciencedirect.com/science/article/pii/S0378382014005074)

Abstract: Ni–CaO–mayenite (Ca12Al14O33) catalysts for the CO2 Sorption Enhanced Steam Methane Reforming (SE-SMR) have been developed using the microwave assisted self-combustion method of preparation. The sorption of CO2 by CaO shifts the steam reforming and the Water Gas Shift reaction (WGS) towards H2 production and favors the heat balance of the global reaction. The CO2 sorption has been studied on materials with different CaO/Ca12Al14O33 ratios and for different types of preparation. The specific surface area of materials, the temperature of Ni phases' reducibility and CO2 sorption are all essential for material efficiency. The Ni–CA75MM catalyst was the most active and stable in methane steam reforming with CO2 sorption, even at an unusually low temperature (650°C).

Keywords: Steam methane reforming; CO2 sorption; Microwave assisted self-combustion method; Hydrogen

Honggen Peng, Youhe Ma, Wenming Liu, Xianglan Xu, Xiuzhong Fang, Jie Lian, Xiang Wang, Changqing Li, Wufeng Zhou, Ping Yuan,

Methane dry reforming on Ni/La2Zr2O7 treated by plasma in different atmospheres,

Journal of Energy Chemistry,

Volume 24, Issue 4,

2015,

Pages 416-424,

ISSN 2095-4956,

https://doi.org/10.1016/j.jechem.2015.06.015.

(https://www.sciencedirect.com/science/article/pii/S2095495615000200)

Abstract: A series of Ni/La2Zr2O7 pyrochlore catalysts prepared by impregnation method and treated by dielectric barrier discharge (DBD) plasma in different atmospheres and varied sequences were prepared and applied for dry reforming of methane (DRM). It is found that all of the plasma treated catalysts show evidently improved activity and coke resistance in comparison with the non-plasma treated one. The best performance is achieved on Ni/La2Zr2O7–H2P–C, a catalyst treated in H2 plasma before calcination. TGA-DSC and SEM demonstrate that carbon deposition is significantly suppressed on all of the plasma treated samples. Moreover, XRD and TEM results testify that both NiO and Ni sizes on the calcined and reduced samples treated by plasma are also decreased, which results in higher Ni metal dispersion on the reduced and used catalysts and enhances the interactions between Ni sites and the support. It is believed that these are the inherent reasons accounting for the promotional effects of plasma treatment on the reaction performance of the Ni/La2Zr2O7 pyrochlore catalysts.

Keywords: Methane dry reforming; Ni-based catalysts; Pyrochlore support; DBD plasma; Coke resistance

Nitin Kumar, Maryam Shojaee, JJ Spivey,

Catalytic bi-reforming of methane: from greenhouse gases to syngas,

Current Opinion in Chemical Engineering,

Volume 9,

2015,

Pages 8-15,

ISSN 2211-3398,

https://doi.org/10.1016/j.coche.2015.07.003.

(https://www.sciencedirect.com/science/article/pii/S2211339815000428)

Abstract: The bi-reforming reaction to produce syngas from CH4 and CO2 offers significant advantages over dry reforming and oxy-CO2 with respect to catalyst deactivation by carbonization. This approach has potential for powerful new alternatives and is entering the stage of increasing advanced research toward commercialization of the technology. Research is ongoing to develop catalysts that are resistant to high temperatures and the presence of a more oxidative environment due to steam. All current research on bi-reforming catalysis is focused on Ni-based catalysts, a logical extension based on commercial materials on steam/methane reforming and dry reforming. However, recent work on thermally stable crystalline oxides has promise, particularly in resisting carbon deposition while remaining stable at the demanding conditions of bi-reforming.

Jesús Manuel García-Vargas, José Luís Valverde, Javier Díez, Paula Sánchez, Fernando Dorado,

Preparation of Ni–Mg/β-SiC catalysts for the methane tri-reforming: Effect of the order of metal impregnation,

Applied Catalysis B: Environmental,

Volume 164,

2015,

Pages 316-323,

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https://doi.org/10.1016/j.apcatb.2014.09.044.

(https://www.sciencedirect.com/science/article/pii/S0926337314005785)

Abstract: The influence of the order of Ni and Mg impregnation has been analyzed in terms of catalytic activity and stability of β-SiC supported catalysts for the tri-reforming of methane. Catalysts were characterized using different techniques such as Temperature Programmed Reduction, X-Ray Diffraction, Transmission Electron Microscopy and Temperature Programmed Oxidation. The addition of Mg clearly changed the reduction profile, increasing the temperature required to obtain Ni0. Higher reduction temperatures were needed when Mg was firstly loaded or when both metals, Ni and Mg, were simultaneously loaded, which was attributed to the occurrence of interactions between Ni and Mg. Catalyst prepared by first Ni impregnation showed the worst catalytic behaviours, probably due to a poor interaction between Ni and Mg, a possible blockage of Ni particles by Mg ones and the occurrence of Ni2Si after reaction. Catalysts prepared with the highest Mg/Ni molar ratio (1/1) showed smaller Ni particle sizes, lower coke rate formation and higher basicity and Ni-Mg interaction. Ni-Mg/SiC 1/1 was selected as the best catalyst due to its high catalytic activity and stability and low coke generation.

Keywords: Methane; Tri-reforming; Nickel; Magnesium; TPO

Eun-hyeok Yang, Na Young Kim, Young-su Noh, Sung Soo Lim, Jae-Sun Jung, Jae Suk Lee, Gi Hoon Hong, Dong Ju Moon,

Steam CO2 reforming of methane over La1−xCexNiO3 perovskite catalysts,

International Journal of Hydrogen Energy,

Volume 40, Issue 35,

2015,

Pages 11831-11839,

ISSN 0360-3199,

https://doi.org/10.1016/j.ijhydene.2015.06.021.

(https://www.sciencedirect.com/science/article/pii/S0360319915015037)

Abstract: Steam CO2 reforming of methane was carried out over cerium substituted perovskite catalysts. Among the catalysts studied, La0.9Ce0.1NiO3 showed the best performance with 49% of methane and 14% of CO2 conversion under the tested conditions. The chemical and structural properties of the catalysts before and after the reaction were studied by N2 physisorption, X-ray diffraction, CO2-TPD, TPH, TPR, TGA and TEM. It was found that most of Ce existed as CeO2 rather than being incorporated in perovskite lattice because of large difference in ionic radii between La3+ and Ce4+. Few substitution of Ce in A site resulted in high degree of reduction for active Ni species with good catalytic activity which was further decreased with increasing Ce concentration; substitution of large amount of Ce species led to methanation of CO2 and formation of large nickel cluster. TPH and TGA analysis revealed that Ce substituted catalyst has better resistance to coke deposition compared to non-promoted perovskite catalyst.

Keywords: Cerium substitution; Hydrogen production; Perovskite; Steam CO2 reforming

Tao Wu, Qing Zhang, Weiye Cai, Peng Zhang, Xuefeng Song, Zhuang Sun, Lian Gao,

Phyllosilicate evolved hierarchical Ni- and Cu–Ni/SiO2 nanocomposites for methane dry reforming catalysis,

Applied Catalysis A: General,

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(https://www.sciencedirect.com/science/article/pii/S0926860X15300612)

Abstract: Well dispersed Ni and Cu–Ni alloy nanoparticles (∼7nm) embedded in nanosheets of hierarchical SiO2 hollow spheres (surface area>400m2/g) have been synthesized through a hydrothermal process and have shown superior catalytic performance in methane dry reforming (DRM) reaction to the impregnated control sample based on SiO2 nanospheres. The catalytic activity and the sintering and coke resistant properties of the hierarchical composite catalysts in the high temperature DRM catalysis are ascribed to the strong metal–support interaction and the well dispersed small metal nanoparticles.

Keywords: Hierarchical; Ni/SiO2; Cu–Ni/SiO2; Methane dry reforming; Catalysis

Ana Gouveia Gil, Zhentao Wu, David Chadwick, K. Li,

Ni/SBA-15 Catalysts for combined steam methane reforming and water gas shift—Prepared for use in catalytic membrane reactors,

Applied Catalysis A: General,

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https://doi.org/10.1016/j.apcata.2015.09.009.

(https://www.sciencedirect.com/science/article/pii/S0926860X15301423)

Abstract: This study focuses on the preparation, characterization and catalytic performance evaluation of Ni/SBA-15 catalysts for the combined steam methane reforming (SMR) and water gas shift (WGS) reaction. Specific efforts have been directed towards the impact of the SBA-15 preparation methods on further incorporating the resultant catalysts into the micro-structured ceramic hollow fibres for the development of more advanced membrane reactors. The effect of Ni loading (5–25wt.%) on the catalytic performance was investigated using the SBA-15 prepared via a sol–gel method. Furthermore, the effect of SBA-15 preparation methods (sol–gel and hydrothermal methods) on the catalyst properties and performance were also systematically investigated in a packed-bed reactor, using a fixed Ni loading of 25wt.%. For the purpose of comparison, a commercially available SBA-15 powder was also employed. Apart from the different distribution and particle size of Ni, the interaction between Ni and SBA-15 is considered as the major reason for the difference in catalytic performance.

Keywords: Ni/SBA-15 catalyst; Micro-structured ceramic hollow fibre; Steam methane reforming; Water–gas shift

Daeil Park, Changwook Lee, Dong Ju Moon, Taegyu Kim,

Design, analysis, and performance evaluation of steam-CO2 reforming reactor for syngas production in GTL process,

International Journal of Hydrogen Energy,

Volume 40, Issue 35,

2015,

Pages 11785-11790,

ISSN 0360-3199,

https://doi.org/10.1016/j.ijhydene.2015.05.030.

(https://www.sciencedirect.com/science/article/pii/S036031991501174X)

Abstract: Design and thermal-fluidic analysis of CH4 steam-CO2 reforming (SCR) reactor for gas to liquid-floating production storage and offloading (GTL-FPSO) is presented in this paper. The temperature distribution through the SCR reactor should be uniform in order to optimize the catalytic reforming reaction. The numerical analysis of heat, flow and catalytic reactions was used to design the SCR reactor. The kinetic constants for catalytic analysis were calculated from Arrhenius plot that was obtained by SCR experiments on Ni/Al2O3 pellet catalysts. The catalysts were prepared by impregnating Ni into commercial Al2O3 pellets. The reaction temperatures ranged from 1023 K to 1173 K. The CH4 and CO2 conversions increased with the temperature, while H2/CO ratio of syngas decreased with the increase of temperature. And the metallic foam catalyst showed a higher CH4 conversion than a pellet catalyst. The commercial FLUENT code was used to predict the temperature distribution in the SCR reactor. It was shown that the performance of SCR reactor depends strongly on the temperature distribution through the catalysts.

Keywords: Steam-CO2 reforming; Supported catalyst; Thermal-fluidic analysis; Hydrogen; GTL-FPSO

O. Corigliano, P. Fragiacomo,

Technical analysis of hydrogen-rich stream generation through CO2 reforming of biogas by using numerical modeling,

Fuel,

Volume 158,

2015,

Pages 538-548,

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https://doi.org/10.1016/j.fuel.2015.05.063.

(https://www.sciencedirect.com/science/article/pii/S0016236115005700)

Abstract: A well-known and widespread method for producing a hydrogen-rich gas stream consists of reforming processes that convert a hydrocarbon, by adopting a substance, usually steam, to act as reforming promoter. CO2 dry reforming allows the use of CO2 as a reforming agent, which appeals owing to the undeniably negative environmental impact of CO2. This technology opens up interesting perspectives in the field of energy and environmental sustainability since it offers reintegration of CO2-rich gas streams into reforming processes as well as conversion of hydrocarbon. In this context biogas can be used exclusively as it consists mainly of CH4 and CO2, which is environmentally sustainable as gas generated from originally pollutant organic waste. The paper reports a wide performance analysis at the possible and different operating conditions by using a numerical simulation model of a CO2 dry reforming of biogas, set up ad hoc in Matlab. The numerical simulations are conducted in relation to the main control parameters such as the CO2/CH4 ratio, pressure and temperature. Hydrogen yield and feeding gas conversions are taken into account for the performance testing, while the assessment of safe operation involves consideration of the activities causing carbon deposition. The paper aims at performing several parametric energy and technical analyses to assess the various outcomes in order to acquire an important tool for choosing more favorable functioning in relation to possible uses.

Keywords: CO2 reforming; Biogas; Hydrogen; Numerical modeling

Eun-hyeok Yang, Young-su Noh, S. Ramesh, Sung Soo Lim, Dong Ju Moon,

The effect of promoters in La0.9M0.1Ni0.5Fe0.5O3 (M=Sr, Ca) perovskite catalysts on dry reforming of methane,

Fuel Processing Technology,

Volume 134,

2015,

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https://doi.org/10.1016/j.fuproc.2015.02.023.

(https://www.sciencedirect.com/science/article/pii/S0378382015000958)

Abstract: Nickel-based catalysts are typically used for syngas production via reforming reactions. The reforming of methane using carbon dioxide, called dry reforming of methane (DRM), is an effective way to produce syngas from these two notable greenhouse gases. However, Ni-based catalysts used for DRM undergo severe coke deposition. In the current study, perovskite-type oxide catalysts were prepared using the modified EDTA-cellulose method and characterized by the N2 physisorption, TPR, CO2-TPD, XRD, TGA, SEM and TEM-EDX techniques. The influence of partial substitution of La by Sr/Ca was investigated in the dry reforming reaction for the production of synthesis gas, and the basicity of the catalysts was varied by substituting the A site with either Sr or Ca, which modified the catalytic activity under the tested conditions. It was found that the perovskite catalysts demonstrated superior carbon resistance during the reaction, with La0.9Ca0.1Ni0.5Fe0.5O3 catalyst exhibiting the best catalytic performance among the prepared perovskite catalysts.

Keywords: Strontium; Calcium; Iron; Perovskite; Reforming; Gas to liquid (GTL); CH4; CO2

Unalome Wetwatana Hartley, Suksun Amornraksa, Pattaraporn Kim-Lohsoontorn, Navadol Laosiripojana,

Thermodynamic analysis and experimental study of hydrogen production from oxidative reforming of n-butanol,

Chemical Engineering Journal,

Volume 278,

2015,

Pages 2-12,

ISSN 1385-8947,

https://doi.org/10.1016/j.cej.2015.02.016.

(https://www.sciencedirect.com/science/article/pii/S1385894715001886)

Abstract: A Gibbs free energy minimization method was applied to analyze the thermodynamics of hydrogen production via oxidative reforming of n-butanol. The conditions studied were a temperature range of 300–1100°C under atmospheric pressure with steam to n-butanol molar feed ratios (SBR) ranging from 0 to 12 and oxygen to n-butanol molar feed ratios (OBR) of 0–6. The thermoneutral conditions can be obtained at OBR of 2.70–2.80 at 700°C and 2.65–2.75 at 800°C, respectively. The maximum hydrogen yield of 5.56mol/molButanol can be achieved at 700°C with SBR of 12, conditions under which carbon formation and methane generation are predicted to be relatively low. The thermodynamic predictions were in good agreement with experimental results using Ni/Al2O3 and Rh/Al2O3 catalysts, from which the reaction was studied at different SBR, OBR, and temperatures. Under atmospheric pressure at 700°C with OBR of 2.70 and SBR of 9, the product yields from the reaction in the presence of Rh/Al2O3 were close to the thermodynamic values.

Keywords: n-Butanol; Oxidative reforming; Thermodynamic analysis; Hydrogen production

F.J. Gutiérrez Ortiz, F.J. Campanario, P.G. Aguilera, P. Ollero,

Hydrogen production from supercritical water reforming of glycerol over Ni/Al2O3–SiO2 catalyst,

Energy,

Volume 84,

2015,

Pages 634-642,

ISSN 0360-5442,

https://doi.org/10.1016/j.energy.2015.03.046.

(https://www.sciencedirect.com/science/article/pii/S0360544215003400)

Abstract: Hydrogen production from the supercritical water reforming of glycerol was studied in a tubular fixed-bed reactor by using a Ni-based catalyst supported on Al2O3 and SiO2. Tests were carried out at a pressure of 240 bar, temperatures of 500–800 °C, glycerol feed concentrations of 5–30 wt.%, and weight hourly space velocity from 1.25 to 22.5 gGly h−1 gCat−1 (residence time from 1.6 to 4.8 s through the bed). The dry gas is mainly composed of H2, CO2, CO, CH4. The results showed that the glycerol conversion was almost complete, except at the highest glycerol feed concentration and lowest temperature. Hydrogen yields were very close to those values predicted by equilibrium at a short residence time. Nickel on catalyst was completely reduced, and structured carbon nanotubes were encountered at glycerol concentrations higher than 20 wt.%. This study illustrates that the reforming of glycerol using supercritical water over a Ni catalyst makes it possible to reduce the reforming temperature needed when no catalyst is used (from 800 °C to 600 °C), achieving a high-yield hydrogen production, very close to equilibrium, and requiring less energy.

Keywords: Reforming; Supercritical water; Glycerol; Hydrogen; Catalyst; Nickel

Subhasis Das, Sharvani Thakur, Arijit Bag, Manveer Singh Gupta, Prasenjit Mondal, Ankur Bordoloi,

Support interaction of Ni nanocluster based catalysts applied in CO2 reforming,

Journal of Catalysis,

Volume 330,

2015,

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https://doi.org/10.1016/j.jcat.2015.06.010.

(https://www.sciencedirect.com/science/article/pii/S0021951715002079)

Abstract: Surface-tuned mesoporous alumina has been prepared using a template-assisted solvo thermal method, and Ni nanoclusters (4–5nm) have been synthesized on this support using a very facile organic matrix decomposition approach to dry reforming of methane. The catalyst system demonstrates very good catalytic activity toward CH4 and CO2 conversion (>90%), with a H2/CO ratio in syngas of almost unity, remarkable stability for more than 100h, and is proven to be a very interesting catalyst system in dry reforming with methane. Both fresh and spent catalyst have been thoroughly characterized using different techniques such as N2 physisorption studies, X-ray diffraction, X-ray photoelectron spectroscopy, high-resolution transmission electron microscopy, temperature-programmed reduction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and thermogravimetric analysis to determine the structure–activity relationship. Characterization results show that Ni nanoclusters are highly dispersed on the surface of modified alumina. In addition, an excellent metal-support interaction evolves that clearly enhances the stability of the Ni clusters, providing better resistivity toward sintering. The presence of balanced acidic and basic sites in the surface-modified alumina drastically lowers coke formation and enhances the catalyst lifetime. The structures of adsorbed methane and carbon dioxide on the catalyst surface and the corresponding energy of adsorption have been computed using density functional theory calculations. It has been found that CO2 is adsorbed and dissociated into CO and O, while methane is adsorbed as CH3∗ and H∗ on the catalyst system.

Keywords: C–H activation; Surface-modified alumina; Dry reforming; Density functional theory calculations; Reaction kinetics

Na Young Kim, Eun-Hyeok Yang, Sung-Soo Lim, Jae Sun Jung, Jae-Suk Lee, Gi Hoon Hong, Young-Su Noh, Kwan Young Lee, Dong Ju Moon,

Hydrogen production by steam reforming of methane over mixed Ni/MgAl + CrFe3O4 catalysts,

International Journal of Hydrogen Energy,

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ISSN 0360-3199,

https://doi.org/10.1016/j.ijhydene.2015.06.104.

(https://www.sciencedirect.com/science/article/pii/S036031991501589X)

Abstract: Steam reforming of methane (SRM) was performed over a mixed Ni/MgAl + CrFe3O4 catalyst. The catalyst was prepared by physical mixing method and it was compared to Ni/MgAl and iron or chromium promoted M/Ni/MgAl catalysts prepared by impregnation method. Catalysts were characterized by various analytical techniques such as nitrogen physisorption, TPR, XRD, TGA and SEM. The catalytic activity in a fixed-bed reactor was investigated at a temperature range of 500–700 °C, 1 bar pressure and feed molar ratio of H2O/CH4 = 2. TPR and XRD illustrated that segregated Ni particles were observed with promoted M-Ni/MgAl catalysts and it leads to reduce the active Ni metal. The addition of the Cr/Fe3O4 catalyst activates steam and easily reacts with methane. Consequently, physically mixed catalysts showed higher hydrogen selectivity and methane conversion than the other catalysts.

Keywords: Steam reforming; WGS reaction; Hydrogen production; Physically mixed catalyst

Ana Gouveia Gil, Zhentao Wu, David Chadwick, K. Li,

A catalytic hollow fibre membrane reactor for combined steam methane reforming and water gas shift reaction,

Chemical Engineering Science,

Volume 137,

2015,

Pages 364-372,

ISSN 0009-2509,

https://doi.org/10.1016/j.ces.2015.06.051.

(https://www.sciencedirect.com/science/article/pii/S0009250915004595)

Abstract: A catalytic hollow fibre membrane reactor (CHFMR) was developed in this study for combined steam methane reforming (SMR) and water gas shift (WGS) reaction. This is achieved by incorporating a Ni/SBA-15 catalyst into a plurality of micro-channels with open entrance from inner surface of Al2O3 hollow fibres, followed by coating of a 3.3µm Pd membrane on the outer surface of the hollow fibre using an electroless plating method. In addition to systematic characterizations of each reactor component, i.e. Ni/SBA-15 catalyst, micro-structured ceramic hollow fibre and Pd separating layer, the effect of how the reactor was assembled or fabricated on the catalytic performance was evaluated. Electroless plating of the Pd membrane impaired the catalytic performance of the deposited Ni/SBA-15 catalyst. Also, the over-removal of hydrogen from the reaction zone was considered as the main reason for the deactivation of the Ni-based catalyst. Instead of mitigating such deactivation using “compensating” hydrogen, starting the reaction at higher temperatures was found more efficient in improving the reactor performance, due to a better match between hydrogen production (from the reaction) and hydrogen removal (from the Pd membrane). An effective methane conversion of approximately 53%, a CO2 selectivity of 94% and a H2 recovery of 43% can be achieved at 560°C. In order for a more significant “shift” phenomenon, alternative methodology of fabricating the reactor and more coke resistant catalysts are recommended.

Keywords: Catalytic hollow fibre membrane reactor; Steam methane reforming; Water-gas shift; H2 production; Ni/SBA-15 catalyst; Pd membrane

Xingyi Lin, Rule Li, Miaomiao Lu, Chongqi Chen, Dalin Li, Yingying Zhan, Lilong Jiang,

Carbon dioxide reforming of methane over Ni catalysts prepared from Ni–Mg–Al layered double hydroxides: Influence of Ni loadings,

Fuel,

Volume 162,

2015,

Pages 271-280,

ISSN 0016-2361,

https://doi.org/10.1016/j.fuel.2015.09.021.

(https://www.sciencedirect.com/science/article/pii/S0016236115009175)

Abstract: A series of supported Ni/Mg/Al catalysts with Ni loadings of 3–18wt% were prepared from Ni–Mg–Al layered double hydroxides and tested for the CH4–CO2 reforming. The influence of Ni loading on the catalyst activity and stability was studied. It is found that the catalyst activity increased with increasing the Ni loading. However, the CO disproportionation became significant as the Ni loading increased. The long-term stability of the Ni/Mg/Al catalysts was influenced by the Ni loading as well as the reaction temperature. At a high temperature of 1023K, the catalyst stability increased with increasing the Ni loading, whereas it decreased with increasing the Ni loading at a low temperature of 873K. The characterization on the spent Ni/Mg/Al catalysts showed that the sintering of Ni metal particles increased with increasing the Ni loading, and it became more severe at 873K than at 1023K. On the other hand, the coke deposition at 1023K tended to decrease with increasing the Ni loading, and an opposite tendency was observed at 873K. The coke deposition particularly the encapsulating carbon was considered to be responsible for the catalyst deactivation. A Ni loading of 12wt% would be suitable for the Ni/Mg/Al catalyst considering its high activity, good stability, and less coke deposition at high temperature.

Keywords: Methane; Carbon dioxide; Synthesis gas; Ni catalyst; Layered double hydroxides

Yusuke Hiramitsu, Masahiko Demura, Ya Xu, Masanari Yoshida, Toshiyuki Hirano,

Catalytic properties of pure Ni honeycomb catalysts for methane steam reforming,

Applied Catalysis A: General,

Volume 507,

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ISSN 0926-860X,

https://doi.org/10.1016/j.apcata.2015.09.044.

(https://www.sciencedirect.com/science/article/pii/S0926860X15301770)

Abstract: Honeycomb catalysts were assembled, using only 30μm-thick Ni foils, to develop genuine monolithic catalysts for hydrogen production via methane steam reforming. A high cell density (900 cpsi) and geometric surface area (59.4cm2/cm3) were achieved on the honeycomb catalyst. The catalyst exhibited high CH4 conversion (over 97%) at 1073K for a long period of up to 8321.1h under low steam-to-carbon ratio (1.34) and space velocity (335h−1) conditions. A H2 production rate of 74.2ml/min was achieved, and carbon deposition was hardly detected in spite of the low steam-to-carbon ratio. The catalyst was gradually deactivated due to the oxidation of Ni, but was repeatedly regenerated by reduction in flowing hydrogen. These findings proved the high potential of the Ni honeycomb catalyst for application to a small-scale hydrogen production system. Monitoring the temperature profile along the axial direction showed good heat transfer between the catalyst and the surrounding gas, which was attributed to the high thermal conductivity of Ni and to the high cell density of the catalyst. The high geometric surface area and good heat transfer are considered responsible for the good performance of the catalyst.

Keywords: Hydrogen production; Metallic honeycomb catalyst; Cell density; Geometric surface area; Temperature profile

Y. Shiratori, M. Sakamoto, T. Uchida, H. Le, T. Quang-Tuyen, K. Sasaki,

Hydrotalcite-dispersed paper-structured catalyst for the dry reforming of methane,

International Journal of Hydrogen Energy,

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ISSN 0360-3199,

https://doi.org/10.1016/j.ijhydene.2015.07.016.

(https://www.sciencedirect.com/science/article/pii/S0360319915017449)

Abstract: A paper-structured catalyst (PSC) is a flexible planar catalyst that can be stacked on the anode of SOFCs and exhibits excellent catalytic activity for the reforming of hydrocarbon fuels at the operating temperature of the SOFC. Although our final goal is the realization of direct internal reforming (DIR) SOFCs fueled by biogas by applying a PSC, the tolerance of PSCs to sulfur impurities in biogas (H2S) must be improved for the practical application of PSCs to DIR-SOFCs operated by biogas. In this study, an inorganic fiber network in which a layered double hydroxide (Mg/Al-hydrotalcite denoted as HT) is dispersed was prepared by a paper-making process, and Ni was then loaded in this paper matrix via an impregnation process. This Ni-loaded HT-dispersed PSC exhibited considerably higher tolerance to H2S than that of HT-free PSC.

Keywords: Biogas; Dry reforming; H2S poisoning; Paper-structured catalyst; Mg/Al-hydrotalcite

Mingjue Yu, Yi-An Zhu, Yong Lu, Gangsheng Tong, Kake Zhu, Xinggui Zhou,

The promoting role of Ag in Ni-CeO2 catalyzed CH4-CO2 dry reforming reaction,

Applied Catalysis B: Environmental,

Volume 165,

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Pages 43-56,

ISSN 0926-3373,

https://doi.org/10.1016/j.apcatb.2014.09.066.

(https://www.sciencedirect.com/science/article/pii/S0926337314006006)

Abstract: The catalytic performance of Ag promoted Ni/CeO2 catalyst has been investigated in methane and carbon dioxide dry reforming reaction. The temperature-dependent catalytic activity and time-on-stream catalytic performance at 760°C under different feeding conditions have been explored. Pristine Ni/CeO2 is not stable as a result of coke deposition and surface reconstruction. In addition, co-feeding of H2 can adversely influence the long-term stability of Ni/CeO2. Ag severely reduces the intrinsic catalytic activity of Ni/CeO2 catalyst, while enhances the long-term stability by diminishing coke deposition. Ag is applicable as a promoter under various reaction conditions, from N2 diluted feedstock to H2 co-fed and carrier-gas free feedstock. Kinetic studies show that Ag elevates the activation energy from 91 to ca. 140kJ/mol by a loading of 0.3mol.%, excessive Ag loading does not affect activation energy. The role of Ag is to block step sites on Ni surface that is associated with carbon nucleation and growth, and to promote gasification of coke formed. Besides, Ag alters the type of coke formed over Ni surface from recalcitrant whisker/encapsulating carbon to easily gasifiable amorphous carbonaceous species.

Keywords: Methane; Carbon dioxide; Dry reforming; Solid solution; Surface alloy

Moom Sinn Aw, Milena Zorko, Petar Djinović, Albin Pintar,

Insights into durable NiCo catalysts on β-SiC/CeZrO2 and γ-Al2O3/CeZrO2 advanced supports prepared from facile methods for CH4–CO2 dry reforming,

Applied Catalysis B: Environmental,

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https://doi.org/10.1016/j.apcatb.2014.09.012.

(https://www.sciencedirect.com/science/article/pii/S0926337314005396)

Abstract: This study explores CeZrO2 deposited over commercial β-SiC, and a highly ordered 3D β-SiC synthesised in the laboratory via electrophoretic deposition, as well as γ-Al2O3 in order to prepare three types of dual support for NiCo bimetallic catalyst in CH4–CO2 dry reforming (DR). CeZrO2 was deposited over γ-Al2O3 and β-SiC by dry impregnation (DI), wet impregnation (WI) and 2-step deposition precipitation (DP). XRD analysis indicated that the constituents of the dual supports were retained after calcination, as well as before and after the DR reaction. CeZrO2 remained as a mixed oxide solid solution, whilst alumina formed spinel structures with Ni and Co before the catalysts were reduced in H2 during the pretreatment step prior to the activity tests. During 550h stability tests, WI, 2-step SICAT/CeZrO2 and 2-step γ-Al2O3/CeZrO2 solids were identified as the most promising catalysts, maintaining high DR activities without deactivation. Notably, 2-step SiC(SICAT) and 2-step γ-Al2O3/CeZrO2 samples recorded the highest yield (H2=77%, CO=90%; H2=71%, CO=81%), with a coke content of 7.7 and 0.6wt.%, respectively. Carbon deposition for the former is high; contrarily, for WI SiC(SICAT) solid, it accumulated a lower amount of 2.6wt.%. No agglomeration of CeZrO2 and NiCo phases was observed, evidencing excellent robustness and thermal resistance of these dual supports.

Keywords: Bimetallic catalyst; Carbon dioxide; Methane dry reforming; Syngas; CeZrO2 solid solution

Xiwei Xu, Enchen Jiang, Mingfeng Wang, Youjie Xu,

Dry and steam reforming of biomass pyrolysis gas for rich hydrogen gas,

Biomass and Bioenergy,

Volume 78,

2015,

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ISSN 0961-9534,

https://doi.org/10.1016/j.biombioe.2015.03.015.

(https://www.sciencedirect.com/science/article/pii/S0961953415000951)

Abstract: Biomass pyrolysis gas (including H2, CO, CH4, CO2, C2H4, C2H6 and etc.) reforming for hydrogen production over Ni/Fe/Ce/Al2O3 catalysts was presented in this study. This study investigated how the operating conditions, such as the calcinations temperature of catalysts, the reaction temperature, the gas hourly space velocity (GHSV) and the ratio of H2O/C, affect the conversion of CH4 and CO2 and the selectivity of hydrogen from dry and steam reforming of pyrolysis gas. The experimental results indicated that, under the conditions: the reaction temperature of 600 °C, the GHSV of 900 h−1 and H2O/C of 0.92, the reaction efficiency is the optimal. Especially, the concentration of H2, CO, CH4, CO2, and C2Hn (C2H4 and C2H6) were 36.80%, 10.48%, 9.61%, 42.62%, 0.49% respectively. The conversion of CH4 and CO2 reached 45.9% and 51.09%, respectively. There were all kinds of reactions during the processing of reforming of pyrolysis gas. And the main reactions changed with the operation condition. It was due to the promoting or inhibiting interaction among different constituents in the pyrolysis gas and the different activity of catalysts in the different operation condition.

Keywords: Pyrolysis gas; Dry reforming; Steam reforming; Hydrogen; Ni/Fe/Ce/Al2O3 catalysts; Carbon deposition

Sofia D. Angeli, Fotis G. Pilitsis, Angeliki A. Lemonidou,

Methane steam reforming at low temperature: Effect of light alkanes’ presence on coke formation,

Catalysis Today,

Volume 242, Part A,

2015,

Pages 119-128,

ISSN 0920-5861,

https://doi.org/10.1016/j.cattod.2014.05.043.

(https://www.sciencedirect.com/science/article/pii/S092058611400426X)

Abstract: Steam reforming of natural gas for the production of hydrogen at low operation temperature offers significant financial and environmental advantages. However, the presence of higher hydrocarbons as minor components of natural gas can significantly affect the formation of coke and thus the effectiveness of the catalyst. In this study, the effect of the presence of C2–C3 alkanes in the feedstock on the carbon accumulation during low temperature steam reforming of methane is investigated over Ni and Rh catalysts supported on lanthanum doped ceria–zirconia mixed oxide. Both catalysts showed high resistance to coke formation and especially in the case of Rh/La/CeO2–ZrO2, the carbon accumulation detected was low even after 10h on stream in steam reforming of all mixtures of hydrocarbons tested. The presence of higher alkanes in methane increased the amount of carbon on Ni(10)CeZrLa compared to pure methane as well as the nature of the carbonaceous species. Increase in the C-number of the additive alkane had almost no influence on the total amount of carbon formed (C/H feed ratio=constant) but favored the formation of filamentous carbon.

Keywords: Methane steam reforming; Natural gas; Coke; Ni catalyst; Rh catalyst; Alkanes

Shaohua Zhang, Chuan Shi, Bingbing Chen, Yali Zhang, Jieshan Qiu,

An active and coke-resistant dry reforming catalyst comprising nickel–tungsten alloy nanoparticles,

Catalysis Communications,

Volume 69,

2015,

Pages 123-128,

ISSN 1566-7367,

https://doi.org/10.1016/j.catcom.2015.06.003.

(https://www.sciencedirect.com/science/article/pii/S1566736715002307)

Abstract: Nickel catalysts catalyzing the DRM reaction have the problems of sintering and coking. Herein we proposed an idea of stabilizing nickel by Ni17W3 alloy, and α-WC formed during the DRM reaction participated in the CO2 activation, leading to a better coke resistance of Ni17W3/SiO2 catalyst. Due to better Ni dispersion and less coke deposition, Ni17W3/SiO2 catalyst exhibits an improved catalytic stability for the DRM reaction compared with the model Ni/SiO2 catalyst.

Keywords: Methane; Carbon dioxide; Tungsten carbide; Nickel

Katharina Mette, Stefanie Kühl, Andrey Tarasov, Hendrik Düdder, Kevin Kähler, Martin Muhler, Robert Schlögl, Malte Behrens,

Redox dynamics of Ni catalysts in CO2 reforming of methane,

Catalysis Today,

Volume 242, Part A,

2015,

Pages 101-110,

ISSN 0920-5861,

https://doi.org/10.1016/j.cattod.2014.06.011.

(https://www.sciencedirect.com/science/article/pii/S0920586114004313)

Abstract: The influence of redox dynamics of a Ni/MgAl oxide catalyst for dry reforming of methane (DRM) at high temperature was studied to correlate structural stability with catalytic activity and coking propensity. Structural aging of the catalyst was simulated by repeated temperature-programmed reduction/oxidation (TPR/TPO) cycles. Despite a very high Ni loading of 55.4wt.%, small Ni nanoparticles of 11nm were obtained from a hydrotalcite-like precursor with a homogeneous distribution. Redox cycling gradually changed the interaction of the active Ni phase with the oxide support resulting in a crystalline Ni/MgAl2O4-type catalyst. After cycling the average particle size increased from 11 to 21nm – while still a large fraction of small particles was present – bringing about a decrease in Ni surface area of 72%. Interestingly, the redox dynamics and its strong structural and chemical consequences were found to have only a moderate influence on the activity in DRM at 900°C, but lead to a stable attenuation of carbon formation due to a lower fraction of graphitic carbon after DRM in a fixed-bed reactor. Supplementary DRM experiments in a thermobalance revealed that coke formation as a continuous process until a carbon limit is reached and confirmed a higher coking rate for the cycled catalyst.

Keywords: Dry reforming of methane; Nickel; Coking; Ni, Mg, Al hydrotalcite; High temperature; Redox dynamics

Muhammad Usman, W.M.A. Wan Daud, Hazzim F. Abbas,

Dry reforming of methane: Influence of process parameters—A review,

Renewable and Sustainable Energy Reviews,

Volume 45,

2015,

Pages 710-744,

ISSN 1364-0321,

https://doi.org/10.1016/j.rser.2015.02.026.

(https://www.sciencedirect.com/science/article/pii/S1364032115001148)

Abstract: This review will explore the influences of the active metal, support, promoter, preparation methods, calcination temperature, reducing environment, particle size and reactor choice on catalytic activity and carbon deposition for the dry reforming of methane. Bimetallic (Ni−Pt, Ni−Rh, Ni−Ce, Ni−Mo, Ni−Co) and monometallic (Ni) catalysts are preferred for dry reforming compared to noble metals (Rh, Ru and Pt) due to their low-cost. Investigation of support materials indicated that ceria−zirconia mixtures, ZrO2 with alkali metals (Mg2+, Ca2+, Y2+) addition, MgO, SBA-15, ZSM-5, CeO2, BaTiO3 and Ca0.8Sr0.2TiO3 showed improved catalytic activities and decreased carbon deposition. The modifying effects of cerium (Ce), magnesium (Mg) and yttrium (Y) were significant for dry reforming of methane. MgO, CeO2 and La2O3 promoters for metal catalysts supported on mesoporous materials had the highest catalyst stability among all the other promoters. Preparation methods played an important role in the synthesis of smaller particle size and higher dispersion of active metals. Calcination temperature and treatment duration imparted significant changes to the morphology of catalysts as evident by XRD, TPR and XPS. Catalyst reduction in different environments (H2, He, H2/He, O2/He, H2−N2 and CH4/O2) indicated that probably the mixture of reducing agents will lead to enhanced catalytic activities. Smaller particle size (<15nm) had a significant influence on the suppression of carbon deposition and catalytic activity. Fluidized bed reactor exhibited the highest activity and stability, lower carbon deposition and higher conversion compared to a fixed-bed reactor. Moreover, membrane reactor, solar reactor, high-pressure reactor and microreactor were also investigated with specific features such as: pure H2 production, detailed reaction information with enhanced safety, higher pressure applications and dry reforming reaction with/without catalyst under sunlight. The study of parameters would improve the understanding of various preparation and reaction conditions leading to various catalytic activities.

Keywords: Dry reforming of methane; Landfill gas; Syn-gas; Carbon deposition; Ni catalyst

Sung Su Kim, Sang Moon Lee, Jong Min Won, Hee Jae Yang, Sung Chang Hong,

Effect of Ce/Ti ratio on the catalytic activity and stability of Ni/CeO2–TiO2 catalyst for dry reforming of methane,

Chemical Engineering Journal,

Volume 280,

2015,

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https://doi.org/10.1016/j.cej.2015.06.027.

(https://www.sciencedirect.com/science/article/pii/S1385894715008669)

Abstract: In this study, a series of catalysts of composition Ni/X% CeO2–Y% TiO2, (where X and Y range from 0% to 100%), was prepared by impregnation. The effects of different ratio of CeO2/TiO2 on the catalytic activity and stability were examined during methane dry reforming. Ni/TiO2 showed better initial activity than Ni/CeO2. However, Ni/CeO2 was much more stable. The Ni/CeO2–TiO2 catalyst, which has optimum Ce/Ti ratio, showed excellent activity and stability in dry reforming. XPS analysis, H2 TPR, and a reverse water gas shift reaction (RWGS) test confirmed that higher dispersion of Ni sites on the surface of the support could improve the catalytic activity, and that great reducibility of catalyst could improve the stability of catalyst.

Keywords: Reforming; Ni; CeO2–TiO2; Catalysis; Hydrogen; Carbon deposition

Fang Guo, Jun-Qiang Xu, Wei Chu,

CO2 reforming of methane over Mn promoted Ni/Al2O3 catalyst treated by N2 glow discharge plasma,

Catalysis Today,

Volume 256, Part 1,

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https://doi.org/10.1016/j.cattod.2015.02.036.

(https://www.sciencedirect.com/science/article/pii/S092058611500173X)

Abstract: The N2 plasma treated Ni/Al2O3 catalyst was enhanced by manganese (Mn) promoter with doping content ranging from 5wt% to 15wt%. Compared to the plasma treated nickel catalyst without Mn additive, the introduction of Mn promoter further increased the CH4 conversion of studied catalysts about 10% at 700°C for CO2 reforming of methane. After 360min reaction of time-on-stream, the deactivation degree value was decreased to 1.46%. Relatively lower value of 5–10wt% doping amount of Mn was appropriate. Mn promoter further intensified the reducibility of plasma treated catalyst according to the shift to lower temperature of the reduction peak shown in H2-TPR profiles. CO2-TPD results suggested that the modification effect of Mn promoter on the basicity of plasma treated catalyst was speculated to account for the concentration increase of absorbed CO2. It was beneficial to the carbon deposition elimination and it increased the coking-resistant ability of catalyst surface, while this result was in good agreement with the CO2-TPSR and TG results. The lower temperature and smaller area of CO peak was observed over plasma treated Ni-Mn/Al2O3 catalyst in CO2-TPSR test, i.e., less coke formation on the Mn promoted sample.

Keywords: Manganese promoter; Coke resistance; Plasma; Ni-based catalyst; CO2 reforming of methane; TPSR

Halit Eren Figen, Sema Z. Baykara,

Hydrogen production by partial oxidation of methane over Co based, Ni and Ru monolithic catalysts,

International Journal of Hydrogen Energy,

Volume 40, Issue 24,

2015,

Pages 7439-7451,

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https://doi.org/10.1016/j.ijhydene.2015.02.109.

(https://www.sciencedirect.com/science/article/pii/S0360319915005108)

Abstract: Fossil fuels which supply most of the world energy demand are depletable, and they cause greenhouse gas emissions which eventually lead to global warming and climate change. Hydrogen, a clean and versatile energy carrier, can be converted into useful forms of energy in several ways. Catalytic partial oxidation of methane is a very promising process for hydrogen and synthesis gas production, besides steam reforming of methane, the leading technology. In the present work, catalysts for partial oxidation of methane have been developed and studied in terms of structural properties and chemical performance. For this purpose Co, Co–Ni, Co–Ru, Co–Ni–Ru, and Ni catalysts loaded onto cordierite ceramic monolithic supports were prepared via modified sol-gel-impregnation method. The catalysts were characterized by, SEM-EDS, XRD, BET, and ICP-OES techniques. Activity tests of the catalysts were performed in a tubular reactor at 450 ml/min total flow rate from 600 °C to 850 °C. Co–Ni–Ru was the most successful catalyst, with selectivity values of 93.10% H2 and 93.81% CO, and CH4 conversion of 98.71%, and hydrogen production efficiency of 95.89% at 850 °C. During the activity tests of this catalyst 2.13% CO2 was present in the product stream.

Keywords: Hydrogen production; Methane; Partial oxidation; CPOM; Catalyst; Monolith support

Jessica L. Ewbank, Libor Kovarik, Fatoumata Z. Diallo, Carsten Sievers,

Effect of metal–support interactions in Ni/Al2O3 catalysts with low metal loading for methane dry reforming,

Applied Catalysis A: General,

Volume 494,

2015,

Pages 57-67,

ISSN 0926-860X,

https://doi.org/10.1016/j.apcata.2015.01.029.

(https://www.sciencedirect.com/science/article/pii/S0926860X15000447)

Abstract: Nickel catalysts prepared by a variety of different methods are commonly used for reforming reactions such as methane dry reforming. Two preparation methods, controlled adsorption and dry impregnation, are implemented to explore the effect of preparation method on the formation of active sites on alumina supported nickel catalysts. By varying only the preparation method, comparison of catalysts that differ primarily in metal–support interactions, strong metal–support interaction (controlled adsorption) and weak metal–support interactions (dry impregnation), are obtained. For controlled adsorption, optimal synthesis conditions are identified using point of zero charge measurements, pH-precipitation experiments, and adsorption isotherms. Using these conditions, a catalyst with a higher dispersion and strong metal–support interactions is prepared. Physicochemical characterization by N2 physisorption, H2 chemisorption, temperature programmed reduction (TPR), transmission electron microscopy (TEM), and environmental TEM (ETEM) shows that the types of nickel sites formed strongly depend on the synthesis method. Methane dry reforming reactivity studies show stable catalytic performance for at least 9h and provide additional insight into the types of active centers present. After reductive pretreatment, the nickel catalyst prepared by dry impregnation is found to primarily have nickel present as a surface NiAl2O4. In contrast, the active centers for the nickel catalyst prepared by controlled adsorption consist of nickel particles that are encapsulated by a nickel aluminate layer with 1–2nm in thickness. Combustion analysis and XPS of spent catalysts reveal different amounts and nature of carbonaceous deposits as a function of the synthesis method.

Keywords: Rational synthesis; Nickel; Alumina; Adsorption; Metal–support interactions

Xiao-Gang Zheng, Shi-Yu Tan, Li-Chun Dong, Shao-Bo Li, Hong-Mei Chen, Shun-An Wei,

Experimental and kinetic investigation of the plasma catalytic dry reforming of methane over perovskite LaNiO3 nanoparticles,

Fuel Processing Technology,

Volume 137,

2015,

Pages 250-258,

ISSN 0378-3820,

https://doi.org/10.1016/j.fuproc.2015.02.003.

(https://www.sciencedirect.com/science/article/pii/S0378382015000703)

Abstract: Plasma-assisted catalytic conversion of CH4 and CO2 into synthesis gas was performed in a dielectric barrier discharge reactor coupled with perovskite La–Ni nanoparticles (LaNiO3 NPs). Compared to supported catalysts such as Ni/γ-Al2O3, La–Ni/γ-Al2O3 and Ni/La2O3, LaNiO3 NPs showed better catalytic performance. The results show that the low flow rate of feed gases and high input power were favorable for the conversions of CH4 and CO2 as well as the selectivities of desired products, but led to lower energy efficiency. A global kinetic model according to argon dilution in plasma-catalytic system was proposed and employed to foresee the CH4 and CO2 conversion assisted by plasma-catalysts hybrid effect. The kinetic model indicates that the reactant conversion rate was an exponential function of the discharge energy.

Keywords: Kinetic model; LaNiO3; Dry reforming of methane; Dielectric barrier discharge

Nada H. Elsayed, Nathan R.M. Roberts, Babu Joseph, John N. Kuhn,

Low temperature dry reforming of methane over Pt–Ni–Mg/ceria–zirconia catalysts,

Applied Catalysis B: Environmental,

Volume 179,

2015,

Pages 213-219,

ISSN 0926-3373,

https://doi.org/10.1016/j.apcatb.2015.05.021.

(https://www.sciencedirect.com/science/article/pii/S0926337315002660)

Abstract: Low temperature dry reforming of methane was studied over platinum (0.2–2wt.%) and/or nickel (8wt.%) and magnesium (8wt.%) immobilized onto a ceria–zirconia support. Ceria–zirconia (0.6:0.4) solid solutions were synthesized by precipitation and the metals were loaded by the incipient wetness method. XRD patterns demonstrated that the support was a cubic fluorite structure and Ni and Mg were deposited onto it. Temperature-programmed reduction showed that Pt addition substantially decreased the reduction temperature and the impact became less prominent with increasing Pt loading. The Ni–Mg/(Ce0.6Zr0.4)O2 had the highest number of basic sites and the amounts decreased with the addition of platinum. The lowest CH4 and CO2 conversion (X10) temperatures were achieved at 454°C and 437°C, respectively, using a 0.5% Pt–Ni–Mg/(Ce0.6Zr0.4)O2 catalyst. This catalyst was optimum because it balanced between the enhanced reducibility and decreasing number of basic sites, which both occurred with increasing Pt loading. Dry reforming experiments also indicated that Pt decreased the reaction onset temperature for methane and CO2 and correlated to a slight decrease in the H2:CO ratio (though still higher than for the 0.5% Pt–Ce0.6Zr0.4O2 control catalyst). Steady-state reaction experiments were conducted between 430 and 470°C for the best catalyst and the results showed TOFs increasing from 2.69 to 4.74s−1 with increasing temperature and minimal deactivation when left on stream for 100.5h. A comparison to literature indicates that the Pt/Ni/Mg/Ce0.6Zr0.4O2 catalyst has among the highest activities, especially if Ir and Rh catalysts are not included.

Keywords: Dry reforming; Low temperature; (CeZr)O2

Baitao Li, Xueyan Qian, Xiujun Wang,

Oxidative CO2 reforming of methane over stable and active nickel-based catalysts modified with organic agents,

International Journal of Hydrogen Energy,

Volume 40, Issue 25,

2015,

Pages 8081-8092,

ISSN 0360-3199,

https://doi.org/10.1016/j.ijhydene.2015.04.104.

(https://www.sciencedirect.com/science/article/pii/S0360319915010162)

Abstract: This study targeted the novel silica-supported nickel-based catalyst (Ni/SiO2) modified by organic agents. The synergic modification effect of ethylene glycol (EG) and citric acid (CA) on the nickel catalyst was investigated. EG was used to pretreat the silica support and CA was used in the impregnation solution to synthesize the nickel based catalysts with different CA loadings. NiCA-x/SiO2-EG (x: molar ratio of CA/Ni ranging from 0.25 to 1.5) catalysts achieved an excellent stability and higher catalytic activity than the catalysts without EG in oxidative CO2 reforming of methane (CH4/CO2/O2 = 40/20/10, total flow rate = 60 ml/min, reaction temperature = 750 °C, and reaction pressure = 1 atm). EG addition modified the surface properties of silica support. The use of CA in the impregnation solution had a clear effect on the dispersion of NiO and Ni in the silica matrix. For the catalysts with the same content of CA, the catalysts with EG modification showed the synergic effect of EG and CA by improving the chemical interaction between Ni and support, resulting in higher dispersion of nickel. The temperature programmed reduction revealed that the reduction peak shifted to higher temperature with increasing CA loading, which was attributed to the smaller metallic Ni size of the reduced catalysts. The transmission electron microscopy, X-ray diffraction and Fourier transform infrared spectroscopy confirmed that the addition of organic additive modified the silica surface and retained the metallic Ni species, and thus preventing the metal aggregation at high reaction temperature. The NiCA-1.5/SiO2-EG catalyst exhibited the highest activity, which was due to the small metallic metal size (4 nm) and the strong interaction between silica support and metal species.

Keywords: Methane reforming; Nickel-based catalysts; Citric acid; Ethylene glycol

Jannike Solsvik, Zhongxi Chao, Hugo A. Jakobsen,

Modeling and simulation of bubbling fluidized bed reactors using a dynamic one-dimensional two-fluid model: The sorption-enhanced steam–methane reforming process,

Advances in Engineering Software,

Volume 80,

2015,

Pages 156-173,

ISSN 0965-9978,

https://doi.org/10.1016/j.advengsoft.2014.09.011.

(https://www.sciencedirect.com/science/article/pii/S0965997814001604)

Abstract: A dynamic one-dimensional multicomponent model for two-phase flows which includes heat- and mass transfer processes are studied in the Euler framework. The model is intended for reactive gas–solid flows in bubbling fluidized bed reactors. A model is desired that allows for a more complex description of the fluidized bed reactors (e.g. prediction of the bed expansion) relative to the conventional fluidized bed reactor models such as, e.g., Kunii–Levenspiel type of models. The model should not predict details in the flow as the two- and three-dimensional Euler two-fluid models in order to ensure reasonable simulation costs. In particular, the two- and three-dimensional Euler two-fluid models challenges the current available computational capacity for studies of reactive flows. The novel sorption-enhanced steam methane reforming (SE-SMR) technology is simulated in the bubbling bed regime. Simulation results of the one-dimensional Euler two-fluid model is compared to both a two-dimensional Euler model and a conventional fluidized bed model consisting of mass and heat balances. Furthermore, a sensitivity study to operation conditions and transport coefficients is performed for the one-dimensional Euler two-fluid model. The present simulation results reveal that the chemical process performance of the reactor is to a large extent determined by the imposed temperature in the reactor. Further, the one-dimensional Euler model provides an improvement of the simpler conventional fluidized bed reactor models by prediction of the bed expansion. Compared with the two-dimensional Euler model, cross-sectional averaging results in a significant reduction in the computational time but on the cost of loss of flow details.

Keywords: Fluidized bed; One-dimensional model; Gas–solid flow; Reactive flow; Two-fluid model; SE-SMR

Karam Jabbour, Nissrine El Hassan, Anne Davidson, Pascale Massiani, Sandra Casale,

Characterizations and performances of Ni/diatomite catalysts for dry reforming of methane,

Chemical Engineering Journal,

Volume 264,

2015,

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https://doi.org/10.1016/j.cej.2014.11.109.

(https://www.sciencedirect.com/science/article/pii/S1385894714015770)

Abstract: Monometallic 5wt% Ni containing catalysts were prepared by a two-solvent (cyclohexane/water) deposition method using cheap and widely available natural diatomites (Ni/AW2 and Ni/MN3) as supports. The fresh samples were characterized by SEM, EDX microanalysis, N2 adsorption–desorption isotherms, XRD and tested after reduction (in hydrogen) in dry reforming of methane. Spent catalysts were further characterized by TPH coupled with mass spectrometry. Although slightly less active than a reference Ni/Aerosil (Ni/SiO2) catalyst prepared in similar conditions, the Ni/diatomites catalysts showed good activity with 90% methane conversion reached on Ni/MN3 at 800°C and a high selectivity towards dry reforming reaction (H2:CO molar ratio around unity over the entire temperature range). The catalysts were also relatively stable during catalytic measurements conducted at 650°C for 12h. In addition, depending on the nature of the diatomite and on the conditions of thermal activation, carbon deposits with lower toxicity (easier to remove by reactivation) than those formed on the Ni/Aerosil were obtained.

Keywords: Synthesis gas; Dry reforming; Nickel; Diatoms; Carbon deposits

Suntorn Sangsong, Monrudee Phongaksorn, Sabaithip Tungkamani, Thana Sornchamni, Rungroj Chuvaree,

Dry Methane Reforming Performance of Ni-based Catalyst Coated onto Stainless Steel Substrate,

Energy Procedia,

Volume 79,

2015,

Pages 137-142,

ISSN 1876-6102,

https://doi.org/10.1016/j.egypro.2015.11.450.

(https://www.sciencedirect.com/science/article/pii/S1876610215021827)

Abstract: In this work, the Ni-based catalysts (10wt.%Ni/Al2O3-MgO and 10wt.%Ni/MgO) were synthesized by sol-gel method. Each catalyst was prepared as catalyst pellets and catalyst-coated plate, stainless steel plate coated with catalyst. The catalyst-coated plates were fabricated using spray coating. The dry methane reforming (DMR) performances of catalyst-coated plate were investigated and compared with DMR performances of catalyst pellets. As the mass transfer was improved, the methane consumption rate per gram of catalyst coated onto metal plate was ten times greater than those of catalyst pellets approximately. The carbon deposition was also significantly prevented when the catalyst was constructed as a thin-film layer on the plate under our developing condition. Therefore, this catalyst-coated plate can be further developed for multichannel reactor.

Keywords: Nickel Based Catalysts; Spray Coating; Dry Methane Reforming

Ting Xie, Xiaoyuan Zhao, Jianping Zhang, Liyi Shi, Dengsong Zhang,

Ni nanoparticles immobilized Ce-modified mesoporous silica via a novel sublimation-deposition strategy for catalytic reforming of methane with carbon dioxide,

International Journal of Hydrogen Energy,

Volume 40, Issue 31,

2015,

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ISSN 0360-3199,

https://doi.org/10.1016/j.ijhydene.2015.06.008.

(https://www.sciencedirect.com/science/article/pii/S0360319915014640)

Abstract: A kind of Ni nanoparticles (NPs) immobilized Ce-modified mesoporous silica was synthesized via a novel sublimation-deposition strategy and evaluated in catalytic reforming of methane with carbon dioxide. The as-prepared catalysts were characterized systematically to elucidate their morphological structure and surface properties. Small Ni NPs ranging from 2.1 nm to 4.3 nm have been successfully assembled in the mesoporous silica with a homogenous distribution. As compared with conventional Ni-impregnated catalysts, the catalysts exhibit more stable and near equilibrium conversion for CH4 and CO2 for 20 h at 750 °C with negligible carbon deposition. The confinement effect deriving from the mesoporous channels of silica support, as well as the high dispersion and reducibility of Ni NPs due to strong Ni–SiO2 interaction contribute to the enhanced coking- and sintering-resistance. Furthermore, the addition of ceria further improves the coke resistance, leading to the consistent catalytic performance of the catalysts in dry reforming of methane. We believe that the successful application of sublimation-deposition strategy can also play a role in the design of robust catalysts with excellent catalytic activity and durability for many other coking- and sintering-resistant reactions.

Keywords: Dry reforming of methane; Confinement effect; Coking-resistance; Sintering-resistance

Masoud Khajenoori, Mehran Rezaei, Fereshteh Meshkani,

Dry reforming over CeO2-promoted Ni/MgO nano-catalyst: Effect of Ni loading and CH4/CO2 molar ratio,

Journal of Industrial and Engineering Chemistry,

Volume 21,

2015,

Pages 717-722,

ISSN 1226-086X,

https://doi.org/10.1016/j.jiec.2014.03.043.

(https://www.sciencedirect.com/science/article/pii/S1226086X1400197X)

Abstract: Ceria promoted nickel catalysts supported on nanocrystalline MgO were prepared and employed in methane reforming with carbon dioxide. The prepared catalysts were characterized by XRD, BET, SEM, TPO and TPR techniques. The effect of nickel loading on the catalytic performance of catalysts was investigated and the results showed that 10%Ni–7%CeO2/MgO catalyst possessed the highest catalytic activity. The results also showed that increasing in CO2/CH4 molar ratio decreased the amount of deposited carbon and increased the methane conversion.

Keywords: Coke formation; Dry reforming; Activity; CeO2 promoter

Yuxuan Zeng, Xinbo Zhu, Danhua Mei, Bryony Ashford, Xin Tu,

Plasma-catalytic dry reforming of methane over γ-Al2O3 supported metal catalysts,

Catalysis Today,

Volume 256, Part 1,

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Pages 80-87,

ISSN 0920-5861,

https://doi.org/10.1016/j.cattod.2015.02.007.

(https://www.sciencedirect.com/science/article/pii/S0920586115000772)

Abstract: A coaxial dielectric barrier discharge (DBD) reactor has been developed for plasma-catalytic dry reforming of CH4 and CO2 into higher value synthesis gas (syngas). The influence of reaction conditions (e.g. CO2/CH4 molar ratio and total feed flow rate) and supported metal catalysts M/γ-Al2O3 (M=Ni, Co, Cu and Mn) on the performance of the plasma process has been investigated in terms of the conversion of feed gases, the selectivity and yield of major gas products, and the energy efficiency of the plasma process. The combination of plasma with the Ni/γ-Al2O3 and Mn/γ-Al2O3 catalysts significantly enhanced the conversion of CH4 and exhibited a plasma-catalytic synergy for this and the overall energy efficiency of the process. The maximum CH4 conversion of 19.6% was achieved for the plasma-catalytic dry reforming over the Ni/γ-Al2O3 catalyst at a discharge power of 7.5W and a gas flow rate of 50mlmin−1. However, the presence of any of these catalysts in the plasma did not show any synergy for CO2 conversion. In addition, the integration of plasma and the γ-Al2O3 supported catalysts was found to enhance the yield of CO and H2, whilst the Ni/γ-Al2O3 catalyst exhibited the best activity for syngas production.

Keywords: Plasma-catalysis; Dry reforming; Dielectric barrier discharge; Non-thermal plasma; Synthesis gas

Kai Li, Jing-Lin Liu, Xiao-Song Li, Xiao-Bing Zhu, Ai-Min Zhu,

Post-plasma catalytic oxidative CO2 reforming of methane over Ni-based catalysts,

Catalysis Today,

Volume 256, Part 1,

2015,

Pages 96-101,

ISSN 0920-5861,

https://doi.org/10.1016/j.cattod.2015.03.013.

(https://www.sciencedirect.com/science/article/pii/S0920586115001741)

Abstract: To seek an efficient route for syngas production from oxidative CO2 reforming of methane (OCRM) via post-plasma catalytic technique, three routes were compared using spark-shade plasma (input power=106W, with F1 of 1.36 SLM at CH4:O2:CO2=1:0.6:0.7) and Ni/CeO2/Al2O3 catalyst (catalyst temperature=800°C, with or without F2 of 0.52 SLM CH4). Compared with Route 1 (plasma only, F1 only), XO2,XCH4,CH2+CO and H2/CO ratio of Route 2 (plasma+catalyst, F1 only) increased to 100%, 99%, 76% and 1.2, respectively; but XCO2 kept at about 35%, which was close to the thermodynamic-equilibrium values. In Route 3 (plasma+catalyst, F1+F2), XCO2 increased dramatically to 67%, CH2+CO and H2/CO ratio further increased to 86% and 1.5, respectively, though XCH4 decreased to 77%. Both SCO and SH2 arrived at nearly 100%. Assuming that the plasma could supply the heat energy for the subsequent catalytic reaction at 800°C, syngas energy cost as low as 0.5eV/molecule and energy efficiency as high as 91% were achieved.

Keywords: Plasma; Ni catalyst; Methane reforming; Syngas

Tae Wan Kim, Ji Chan Park, Tak-Hyoung Lim, Heon Jung, Dong Hyun Chun, Ho Tae Lee, Sungjun Hong, Jung-Il Yang,

The kinetics of steam methane reforming over a Ni/γ-Al2O3 catalyst for the development of small stationary reformers,

International Journal of Hydrogen Energy,

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https://doi.org/10.1016/j.ijhydene.2015.02.014.

(https://www.sciencedirect.com/science/article/pii/S0360319915003195)

Abstract: To develop small stationary reformers for on-site H2 production, the active catalyst and its reaction kinetics were examined in order to study the steam methane reforming reaction. A 20 wt% Ni/γ-Al2O3 was found to be a highly active catalyst within the investigated range of contact time from 1.16 to 3.64 gcath/mol, which was good for developing the small stationary reformers. BET, XRD, and TEM analysis revealed that the high activity of the 20 wt% Ni/γ-Al2O3 catalyst compared to the 15 wt% Ni/γ-Al2O3 catalyst was strongly ascribed to the high number of Ni metal particles and the ratio of the number of the Ni metal species between the catalysts was calculated to be 1.33. Furthermore, the SMR reaction kinetics of the reversible first-order reaction between reactants and products was applied. This showed that the activation energies obtained by the two catalysts were the same because of the similar pore diffusion and heat transfer restrictions, and the similar Ni particle size in the catalyst pores. Also, it was found that the ratio of the pre-exponential factor was 1.30, which was exactly proportional to the ratio of Ni loading in the catalysts because it was strongly related to the collision density.

Keywords: Steam methane reforming; Kinetics; Ni loading; Ni particle size; Activation energy; Pre-exponential factor

L.L. Makarshin, V.A. Sadykov, D.V. Andreev, A.G. Gribovskii, V.V. Privezentsev, V.N. Parmon,

Syngas production by partial oxidation of methane in a microchannel reactor over a Ni–Pt/La0.2Zr0.4Ce0.4Ox catalyst,

Fuel Processing Technology,

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ISSN 0378-3820,

https://doi.org/10.1016/j.fuproc.2014.10.031.

(https://www.sciencedirect.com/science/article/pii/S037838201400455X)

Abstract: Operation of a microchannel reactor during the partial oxidation of methane has been studied. Methods for the deposition of a durable (Ni–Pt)/LaCeZrO catalyst on the Fecralloy microchannel plates working under thermocycling (up to 900°C) conditions up were developed. It was shown that the temperature profile along the microchannel plate length is not flat. A part of methane is combusted into H2O and CO2 at the front edge of the microchannel plate, which is accompanied by a big heat release. On the rest part of the microchannel plate, endothermic reactions of methane steam and dry reforming occur yielding CO and Н2. As a result, the front edge of the microchannel plate (up to 2mm in length) undergoes a heavy thermal corrosion. Test runs of the microchannel reactor with one microchannel plate demonstrated 82% methane conversion and 60% selectivity toward carbon monoxide at gas space velocity of 820,000h−1. Scaling of the MC reactor increased hydrogen production proportionally to the number of the MC plates. The specific hydrogen production related to the volume occupied by the MC plates is about 123L/(h·cm3).

Keywords: Microchannel reactor; Microchannel plate; Methane; Partial oxidation; Syngas; Hydrogen production

E. Ruiz-Trejo, P. Boldrin, J.L. Medley-Hallam, J. Darr, A. Atkinson, N.P. Brandon,

Partial oxidation of methane using silver/gadolinia-doped ceria composite membranes,

Chemical Engineering Science,

Volume 127,

2015,

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https://doi.org/10.1016/j.ces.2015.01.047.

(https://www.sciencedirect.com/science/article/pii/S0009250915000767)

Abstract: Methane was partially oxidised to CO using oxygen permeated through a 1 mm thick silver/Ce0.9Gd0.1O2−x (Ag/CGO) composite membrane operating at 500–700°C with air at 1bar pressure. The membranes were fabricated by sintering ultrafine nanoparticles of gadolinia-doped ceria (<5nm) coated with silver using Tollens׳ reaction. This unique combination led to dense composites with low content of silver (7vol%), no reaction between the components and predominant metallic conductivity. When feeding 4% methane at 700°C to a 1-mm thick Ag/CGO using Ni as reforming catalyst, the conversion reached 21% and the CO selectivity 92% with an estimated oxygen flux of 0.18mLmin−1cm−2 (NTP). The samples were stable in carbon-containing atmospheres and under a large pO2 transmembrane pressure difference at temperatures below 700°C for 48h.

Keywords: Methane partial oxidation; Cermet membrane; Silver; Gadolinia-doped ceria; Oxygen separation

Rafik Benrabaa, Axel Löfberg, Jesús Guerrero Caballero, Elisabeth Bordes-Richard, Annick Rubbens, Rose-Noëlle Vannier, Hamza Boukhlouf, Akila Barama,

Sol–gel synthesis and characterization of silica supported nickel ferrite catalysts for dry reforming of methane,

Catalysis Communications,

Volume 58,

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ISSN 1566-7367,

https://doi.org/10.1016/j.catcom.2014.09.019.

(https://www.sciencedirect.com/science/article/pii/S156673671400377X)

Abstract: Silica-supported NiFe2O4 spinel was prepared by sol–gel method using tetramethyl orthosilicate as a precursor of silica. B.E.T., XRD, MEB–EDS, TEM, XPS and Raman scattering techniques were used for its characterization. The reducibility by hydrogen was investigated by TPR and HT-XRD. These properties are compared to those of unsupported NiFe2O4. Both acidic and redox sites were found by studying the decomposition of isopropanol. First experiments in the dry reforming of methane by CO2 showed that owing to more acidic properties supporting NiFe2O4 on silica provides a more active and selective catalyst that seems less prone to coking.

Keywords: NiFe2O4; Sol–gel method; Isopropanol decomposition; Dry reforming of methane

M.M. Rahman,

H2 production from aqueous-phase reforming of glycerol over Cu–Ni bimetallic catalysts supported on carbon nanotubes,

International Journal of Hydrogen Energy,

Volume 40, Issue 43,

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(https://www.sciencedirect.com/science/article/pii/S0360319915022636)

Abstract: Aqueous-phase reforming of glycerol was investigated over a series of Ni and Cu–Ni bimetallic catalysts supported on multiwalled carbon nanotubes (MWNT). The reaction was carried out in a continuous flow fixed bed reactor (240 °C, 40 atm) with a solution of 1 wt% glycerol in DI water at a flow rate of 0.05 mL/min. Amongst the catalysts tested, bimetallic 1Cu–12Ni/MWNT catalyst gave the higher H2 selectivity (86%) and glycerol conversion (84%) than the benchmark 12Ni/MWNT catalyst. Irrespective of Cu and Ni ratio, bimetallic Cu–Ni catalysts showed higher selectivity and glycerol conversion towards H2 production than the Ni catalyst. The presence of Cu in bimetallic catalysts resulted in suppression of undesirable methanation reaction. Catalysts characterized by XRD and XPS showed a significant peak shift of Ni in bimetallic Cu–Ni catalysts than the Ni catalyst, suggesting a strong interaction between Cu and Ni. Also H2–TPR analysis showed that introducing Cu increased Ni reducibility. The bimetallic interaction is thought to be responsible for the lowered methane yield and ultimately, higher hydrogen yield observed.

Keywords: Bimetallic catalyst; Aqueous phase reforming; Glycerol; Hydrogen

Junshe Zhang, Fanxing Li,

Coke-resistant Ni@SiO2 catalyst for dry reforming of methane,

Applied Catalysis B: Environmental,

Volumes 176–177,

2015,

Pages 513-521,

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https://doi.org/10.1016/j.apcatb.2015.04.039.

(https://www.sciencedirect.com/science/article/pii/S0926337315002271)

Abstract: Nanostructured Ni@SiO2 core–shell catalyst is prepared from nickel oxide nanoparticles by a facile method. Calcination of as-synthesized core–shell nanoparticles creates a micro/meso-porous structure in the amorphous silica shell. The catalytic performance of core–shell catalyst toward dry reforming of methane was first evaluated in a thermogravimeter coupled with a mass spectrometer. Coking is negligible in a reforming period of 40h on stream at 850°C, while more than 0.32gcokegcat−1 is produced on a commercial Ni-based reforming catalyst in 6.4h at the same reforming condition. Dry reforming was also performed in a continuous flow, fixed-bed reactor at 750°C. Characterization of spent catalyst further confirms that Ni@SiO2 catalyst has high coke-resistance for dry reforming. The amount of coke deposited on the core–shell catalyst in 24.5h is 0.012gcokegcat−1.

Keywords: Coke-resistance; Nickel oxide nanoparticles; Core–shell catalyst; Dry reforming of methane; Carbon dioxide

X.Y. Gao, J. Ashok, S. Widjaja, K. Hidajat, S. Kawi,

Ni/SiO2 catalyst prepared via Ni-aliphatic amine complexation for dry reforming of methane: Effect of carbon chain number and amine concentration,

Applied Catalysis A: General,

Volume 503,

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https://doi.org/10.1016/j.apcata.2015.07.005.

(https://www.sciencedirect.com/science/article/pii/S0926860X15300582)

Abstract: Aliphatic amines of different carbon numbers (i.e., carbon number in one linear hydrocarbon chain, Nc) and concentrations (Ca) were used in the preparation of silicon dioxide (SiO2) supported nickel catalysts by incipient wetness impregnation (IWI) method. The results showed that both the size and the metal-support interaction (MSI) were affected by the carbon chain number and the amine concentration. On one hand, the use of the aliphatic amine with a larger carbon chain number achieved a smaller size and higher dispersion due to the stronger steric hindrance; this smaller size and higher dispersion further enhanced the MSI because of the larger contact area of Ni with the silica support. On the other hand, a higher amine concentration decreases the size and improve the dispersion because of the faster nucleation rate; also when higher concentration of amine was used, more hydrogen bonds were formed between the -NH2 and the silanol group and more electron transfer was found between Ni and the -NH2, leading to a stronger MSI. With a small size, high dispersion and strong MSI, NiSi-OAm showed the most stable catalytic performances (CO2 conversion of 78% and CH4 conversion of 70% within 20h) with low carbon deposition (1.8 mgC/gcath) for dry reforming of methane (DRM) reaction.

Keywords: Ni; Aliphatic amine; Carbon chain; –NH2 terminal group; Dry reforming of methane

R.Y. Chein, Y.C. Chen, C.T. Yu, J.N. Chung,

Thermodynamic analysis of dry reforming of CH4 with CO2 at high pressures,

Journal of Natural Gas Science and Engineering,

Volume 26,

2015,

Pages 617-629,

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https://doi.org/10.1016/j.jngse.2015.07.001.

(https://www.sciencedirect.com/science/article/pii/S1875510015300275)

Abstract: Thermodynamic equilibrium of dry reforming of methane (DRM) was studied by Gibbs free energy minimization at elevated pressures. CH4 and CO2 conversions, carbon formation, H2 yield, H2/CO ratio and H2O formation were used to characterize the DRM performance using the reaction temperature as the primary parameter. The result shows that DRM is unfavorable at high pressure. CO2 and CH4 conversions decrease while the carbon formation increases as the pressure increases. With increasing CO2/CH4 ratio in the reaction, CH4 conversion is enhanced, carbon formation is suppressed, but CO2 conversion is lower due to the excess CO2 supply. The simulation results indicated that the introduction of inert gas in the system did not produce a significant effect on DRM performance. The performances of combined DRM and partial oxidation of methane (POM) and combined DRM and methane-steam reforming (MSR) were also studied to suppress the carbon formation. It was found that carbon formation can be reduced by introducing oxygen. However, the resulted H2/CO ratio is less than 1. Introducing H2O into the reaction system can eliminate carbon formation when amount of H2O is large. However, the system must be operated at high temperature to produce high CH4 and CO2 conversions.

Keywords: Dry reforming of methane (DRM); Gibbs free energy minimization; High pressures; CH4 conversion; CO2 conversion; Carbon formation

Jesús Manuel García-Vargas, Jose Luis Valverde, Javier Díez, Fernando Dorado, Paula Sánchez,

Catalytic and kinetic analysis of the methane tri-reforming over a Ni–Mg/β-SiC catalyst,

International Journal of Hydrogen Energy,

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2015,

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ISSN 0360-3199,

https://doi.org/10.1016/j.ijhydene.2015.05.032.

(https://www.sciencedirect.com/science/article/pii/S0360319915011763)

Abstract: In this work, the influence of the temperature and feed composition on the catalytic behaviour of a Ni–Mg/β-SiC catalyst in the methane tri-reforming was analysed and modelized. This catalyst was characterized by Atomic Absorption Spectrophotometry (AAS), Temperature Programmed Reduction (TPR), N2 adsorption, Temperature Programmed Desortion of CO2 (TPD) and X-Ray Diffraction (XRD). 36 catalytic experiments at different temperatures and feed compositions were performed, modifying the quantity of CH4, CO2, H2O and O2 present in the feed. The predominance of each one of the reactions that took place during the tri-reforming process was evaluated as a function of the temperature, finding at low temperatures a higher contribution of both the steam reforming and the water gas shift reactions. On the contrary, at higher temperatures, a higher contribution of the dry reforming was detected. Finally, a kinetic model was raised and experimental data were fitted to it. Steam reforming, dry reforming and water gas shift reactions were considered as the kinetically relevant equations. A good agreement between experimental and predicted data was observed.

Keywords: Tri-reforming; Nickel; Magnesium; Kinetics

Faris Jasim Al-Doghachi, Zulkarnain Zainal, Mohd Izham Saiman, Zaidi Embong, Yun Hin Taufiq-Yap,

Hydrogen Production from Dry-Reforming of Biogas over Pt/Mg1-xNixO Catalysts,

Energy Procedia,

Volume 79,

2015,

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ISSN 1876-6102,

https://doi.org/10.1016/j.egypro.2015.11.460.

(https://www.sciencedirect.com/science/article/pii/S187661021502192X)

Abstract: Dry reforming of biogas carried out over Pt/Mg1-xNixO catalysts, where x= 0, 0.03, 0.07, and 0.15 with 1 wt% Pt for each, prepared by the co-precipitation method from aqueous solution of Ni(NO3)2.6H2O and Mg(NO3)2.6H2O using K2CO3, then the platinum(II)acetylacetonate impregnated on MgO–NiO. The synthesized catalysts analyzed by XRD, FT-IR, XRF, XPS, BET and TEM. at 700 oC, the catalysts reduced by H2 prior to each reaction. The order of conversions of CO2 and CH4 at 900 oC of the reduced catalysts after being on the stream for 200h was as follows: Pt/Mg0.85Ni0.15O > Pt/Mg0.93Ni0.07O > Pt/Mg0.97Ni0.03O > Pt/MgO with a CH4:CO2 mole ratio of 2:1 that displayed the best resistance to deactivation by carbon formation and formed high selectivity of H2 and CO. The dry reforming reaction was also carried out with the presence of low concentrations of oxygen (1.25%) flow and showed an enhancement in the conversion of CH4

Keywords: Synthesis gas; H2 production; Dry-Reforming of biogas; MgO-NiO catalyst

Vimala Dhanala, Sunil K. Maity, Debaprasad Shee,

Oxidative steam reforming of isobutanol over Ni/γ-Al2O3 catalysts: A comparison with thermodynamic equilibrium analysis,

Journal of Industrial and Engineering Chemistry,

Volume 27,

2015,

Pages 153-163,

ISSN 1226-086X,

https://doi.org/10.1016/j.jiec.2014.12.029.

(https://www.sciencedirect.com/science/article/pii/S1226086X14006984)

Abstract: Present work provides a systematic investigation of oxidative steam reforming (OSR) and comparisons with steam reforming (SR) of isobutanol over γ-Al2O3 supported nickel catalysts. Catalysts characterization results demonstrated that majority of nickel oxide was present as dispersed NiAl2O4. The hydrogen yield and selectivity to CO and methane were somewhat lesser for OSR compared to SR. The H2/CO mole ratio in the range of 8–10 was observed under the experimental conditions. The experimental results were matched well with equilibrium products compositions. The spent catalysts were further characterized to elucidate chemical and morphological changes of the catalysts during SR and OSR.

Keywords: Oxidative steam reforming; Thermodynamic equilibrium analysis; Bio-butanol; Synthesis gas; Ni/γ-Al2O3

Partho S. Roy, Chan S. Park, Arun S.K. Raju, Kiseok Kim,

Steam-biogas reforming over a metal-foam-coated (Pd–Rh)/(CeZrO2–Al2O3) catalyst compared with pellet type alumina-supported Ru and Ni catalysts,

Journal of CO2 Utilization,

Volume 12,

2015,

Pages 12-20,

ISSN 2212-9820,

https://doi.org/10.1016/j.jcou.2015.09.003.

(https://www.sciencedirect.com/science/article/pii/S2212982015300123)

Abstract: Metal-foam-coated 0.09wt% [Pd(7)–Rh(1)]/(CeZrO2–Al2O3) catalyst was compared with commercially available alumina-supported 8.0wt% Ru and 13.0wt% Ni catalysts for steam reforming of a model biogas. The experiments were conducted in a tubular reactor using a feedstock with the steam-to-methane ratio of 1.50 at 1atm pressure and 20,000h−1 GHSV. CH4 reforming reactions by steam alone and by CO2 alone were also studied over these catalysts in order to explain the catalyst activity. The Pd–Rh catalyst is superior in a number of ways, including better activity for CH4 and CO2 conversion in spite of much less ingredient loading per unit volume. The Pd–Rh catalyst also exhibited higher syngas production index [(H2 LHV+CO LHV)/(Feed CH4 LHV)], lower syngas H2/CO ratio and coke formation. The results were supported by BET measurement, CO chemisorption and electron microscopy. The experimental results demonstrate that the metal-foam-coated Pd–Rh/(CeZrO2–Al2O3) catalyst performs better for syngas production through steam-biogas reforming compared to the Ru and Ni catalysts.

Keywords: Steam-biogas reforming; Metal-foam-coated Pd–Rh catalyst; Catalytic activity comparison; Syngas production index; Coke formation

Maria A. Goula, Nikolaos D. Charisiou, Kiriakos N. Papageridis, Andreas Delimitis, Eleni Pachatouridou, Eleni F. Iliopoulou,

Nickel on alumina catalysts for the production of hydrogen rich mixtures via the biogas dry reforming reaction: Influence of the synthesis method,

International Journal of Hydrogen Energy,

Volume 40, Issue 30,

2015,

Pages 9183-9200,

ISSN 0360-3199,

https://doi.org/10.1016/j.ijhydene.2015.05.129.

(https://www.sciencedirect.com/science/article/pii/S0360319915013427)

Abstract: Nickel on Al2O3 supported catalysts with low and high metal loading (8 and 16 wt. %) were synthesized, using the conventional incipient wetness and wet impregnation methods, as well as a slightly modified Equilibrium Deposition Filtration (EDF) technique. Calcined, reduced and used catalysts' properties were determined by applying several characterization techniques such as, N2 adsorption-desorption, ICP-AES, XRD, TEM H2-TPR and carbon analysis. The catalytic performance for the biogas dry reforming reaction was studied concerning CH4 and CO2 conversion, H2 and CO yield and the produced gas mixture's H2 to CO molar ratio. It was proven that the variation of the synthesis method, affects the catalyst's reducibility, as well as the nickel species' particle size. Catalysts with the low Ni loading present an improved performance when reduced at higher temperature (800 °C). Catalytic behavior was quite different for the 8Ni/Al-edf catalyst, in comparison to the samples prepared by the conventional incipient wetness or wet impregnation methods.

Keywords: Biogas dry reforming; Nickel catalysts; Catalyst's synthesis; Hydrogen; Syngas

Yang Qi, Zhenmin Cheng, Zhiming Zhou,

Steam reforming of methane over Ni catalysts prepared from hydrotalcite-type precursors: Catalytic activity and reaction kinetics,

Chinese Journal of Chemical Engineering,

Volume 23, Issue 1,

2015,

Pages 76-85,

ISSN 1004-9541,

https://doi.org/10.1016/j.cjche.2013.11.002.

(https://www.sciencedirect.com/science/article/pii/S1004954114002146)

Abstract: Ni/Mg–Al catalysts derived from hydrotalcite-type precursors were prepared by a co-precipitation technique and applied to steam reforming of methane. By comparison with Ni/γ-Al2O3 and Ni/α-Al2O3 catalysts prepared by incipient wetness impregnation, the Ni/Mg–Al catalyst presented much higher activity as a result of higher specific surface area and better Ni dispersion. The Ni/Mg–Al catalyst with a Ni/Mg/Al molar ratio of 0.5:2.5:1 exhibited the highest activity for steam methane reforming and was selected for kinetic investigation. With external and internal diffusion limitations eliminated, kinetic experiments were carried out at atmospheric pressure and over a temperature range of 823–973K. The results demonstrated that the overall conversion of CH4 and the conversion of CH4 to CO2 were strongly influenced by reaction temperature, residence time of reactants as well as molar ratio of steam to methane. A classical Langmuir–Hinshelwood kinetic model proposed by Xu and Froment (1989) fitted the experimental data with excellent agreement. The estimated adsorption parameters were consistent thermodynamically.

Keywords: Methane steam reforming; Hydrogen; Hydrotalcite; Catalyst; Kinetics

Ana L. García-Lario, María Aznar, Isabel Martinez, Gemma S. Grasa, Ramón Murillo,

Experimental study of the application of a NiO/NiAl2O4 catalyst and a CaO-based synthetic sorbent on the Sorption Enhanced Reforming process,

International Journal of Hydrogen Energy,

Volume 40, Issue 1,

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https://doi.org/10.1016/j.ijhydene.2014.10.033.

(https://www.sciencedirect.com/science/article/pii/S0360319914028365)

Abstract: A CaO-based synthetic sorbent and a NiO/NiAl2O4 catalyst are synthesized and tested under Sorption Enhanced Reforming (SER) conditions in a fixed bed reactor. The effect of temperature, steam-to-methane ratio (S/C) and sorbent-to-catalyst proportion (Z) are studied. A SER based plant simulation model is implemented to evaluate if the operating conditions chosen allow for a self-sustained plant from a thermal energy consumption standpoint. The most appropriate temperature for SER test is 650 °C. At 600 °C the catalyst seems to be not sufficiently active, while at 700 °C, a longer breakthrough period results. SER equilibrium is reached even at the lowest S/C ratio of 1.6, obtaining H2 purity of 82 vol.% (dry basis). For the SER based plant simulation developed, the low S/C ratio of 1.6 allows a self-sustained plant where the energy required in the calciner for CaCO3 decomposition is supplied by burning the off-gas from the H2 purification unit.

Keywords: Hydrogen; Nickel; Synthetic sorbent; Nickel aluminate; Sorption Enhanced Reforming; Self-sustained plant

Patrick Littlewood, Xiao Xie, Michael Bernicke, Arne Thomas, Reinhard Schomäcker,

Ni0.05Mn0.95O catalysts for the dry reforming of methane,

Catalysis Today,

Volume 242, Part A,

2015,

Pages 111-118,

ISSN 0920-5861,

https://doi.org/10.1016/j.cattod.2014.07.054.

(https://www.sciencedirect.com/science/article/pii/S092058611400580X)

Abstract: The behaviour of nickel manganese catalysts Ni0.05Mn0.95O for the dry (carbon dioxide) reforming of methane was investigated from 500 to 800°C. Prepared catalysts showed ex-solution nickel nanoparticles on the manganese surface, which sintered during reaction, deactivating the catalyst. By pre-sintering the catalyst at 750°C in an inert atmosphere, deactivation from sintering and carbon deposition was avoided at temperatures below 800°C. The resistance of the sintered catalyst against carbon deposition was assumed to be caused by SMSI effects. After dispersing the Ni0.05Mn0.95O catalyst on silica, the catalyst exhibits a leap in activity at 600°C followed by slow deactivation, attributed to a spontaneous phase change to Ni/Mn2SiO4.

Keywords: Dry reforming; Methane; Carbon dioxide; Nickel; Manganese; Olivine

Abdulkader Albarazi, Maria Elena Gálvez, Patrick Da Costa,

Synthesis strategies of ceria–zirconia doped Ni/SBA-15 catalysts for methane dry reforming,

Catalysis Communications,

Volume 59,

2015,

Pages 108-112,

ISSN 1566-7367,

https://doi.org/10.1016/j.catcom.2014.09.050.

(https://www.sciencedirect.com/science/article/pii/S1566736714004087)

Abstract: Ceria–zirconia doped Ni/SBA-15 catalysts for methane dry reforming were prepared following different synthesis routes. Textural, structural and chemical features of such catalysts are strongly influenced by the synthesis procedure chosen for its preparation. Co-precipitation results in the formation of nickel-phyllosilicate species, as a result of a strong interaction between the active phase and the SBA-15 support. Their presence results in slightly lower catalytic activity but notably enhanced stability than for the catalysts prepared by means of impregnation, which evidenced a predominant presence of NiO. Moreover, direct methane decomposition is not favored in the presence of the co-precipitated catalyst, resulting in minimal carbon formation and deposition on their surface, which is the main cause of its deactivation.

Keywords: Methane dry reforming; Nickel; Ceria–zirconia; SBA-15

Xiaogang Zheng, Shiyu Tan, Lichun Dong, Shaobo Li, Hongmei Chen,

Plasma-assisted catalytic dry reforming of methane: Highly catalytic performance of nickel ferrite nanoparticles embedded in silica,

Journal of Power Sources,

Volume 274,

2015,

Pages 286-294,

ISSN 0378-7753,

https://doi.org/10.1016/j.jpowsour.2014.10.065.

(https://www.sciencedirect.com/science/article/pii/S0378775314016747)

Abstract: Spinel nickel ferrite nanoparticles (NiFe2O4 NPs) embedded in silica (NiFe2O4#SiO2) was prepared to enhance the reaction performance of the dry reforming of methane in a coaxial dielectric barrier discharge reactor. NiFe2O4 NPs of around 10 nm were effectively embedded in porous SiO2 NPs (∼100 nm in diameter). Compared to the supported Ni-based catalysts (Ni/γ-Al2O3, Ni–Fe/γ-Al2O3, Ni–Fe/SiO2, and NiFe2O4), the NiFe2O4#SiO2 catalyst placed at the discharge zone exhibited excellent catalytic performance and high resistance to carbon formation during dry reforming under ambient conditions without the involvement of extra heat. The synergetic effect between the non-thermal plasma and the NiFe2O4#SiO2 catalyst favored the conversion of CH4 and CO2 into syngas. The results indicated that the special structure of the as-synthesized NiFe2O4#SiO2 catalyst was capable of restraining the aggregation of Ni–Fe alloy and suppressing the carbon formation in the reforming process.

Keywords: Dry reforming of methane; Synergistic effect; Nickel ferrite; Embedded structure; Non-thermal plasma

Chao He, Jianwei Zheng, Ke Wang, Haiqiang Lin, Jing-Yuan Wang, Yanhui Yang,

Sorption enhanced aqueous phase reforming of glycerol for hydrogen production over Pt-Ni supported on multi-walled carbon nanotubes,

Applied Catalysis B: Environmental,

Volume 162,

2015,

Pages 401-411,

ISSN 0926-3373,

https://doi.org/10.1016/j.apcatb.2014.07.012.

(https://www.sciencedirect.com/science/article/pii/S092633731400410X)

Abstract: In this study, multi-walled carbon nanotubes supported Pt and Pt-based bimetallic catalysts were prepared and their catalytic activities were investigated to screen effective and economical catalyst for H2 production in catalytic aqueous phase reforming (CAPR) of glycerol. Nickel promoted Pt catalyst with optimized Ni:Pt molar ratio afforded highest glycerol conversion rate (81.21%) and carbon conversion to gas (15.3%) although hydrogen gasification ratio (7.2%) was poorer than that of noble metals promoted Pt-based bimetallic catalysts. Adding CaO significantly enhanced the fraction and selectivity of H2 over Pt-Ni catalyst and those of CH4 were reduced to a negligible level, which was possibly attributed to the facilitated water-gas shift reaction and inhibited methanation through in-situ CO2 sorption via carbonation. Results suggested that Pt-Ni bimetallic catalysts improved dehydrogenation–decarboxylation and dehydration–hydrogenation reactions, leading to high glycerol conversions. Introducing CaO further favored C–C bond cleavage towards high H2 yield. The catalytic performance can be completely recovered after regenerating the catalyst and adding sacrificial CaO. In terms of reduced consumption of precious metal catalyst, excellent catalyst performance and hydrothermal stability, combination of Pt-Ni bimetallic catalyst and CaO additive was identified as an effective catalytic system for H2 production in CAPR of glycerol.

Keywords: Bimetallic catalyst; Platinum-nickel; Platinum-palladium; Water-gas shift; CO2 removal

Xiaogang Zheng, Shiyu Tan, Lichun Dong, Shaobo Li, Hongmei Chen,

Corrigendum to “Plasma-assisted catalytic dry reforming of methane: Highly catalytic performance of nickel ferrite nanoparticles embedded in silica” [J. Power Sources 274C (2014) 286–294],

Journal of Power Sources,

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https://doi.org/10.1016/j.jpowsour.2014.12.029.

(https://www.sciencedirect.com/science/article/pii/S0378775314020473)

Whitney S. Jablonski, Stephanie M. Villano, Anthony M. Dean,

A comparison of H2S, SO2, and COS poisoning on Ni/YSZ and Ni/K2O-CaAl2O4 during methane steam and dry reforming,

Applied Catalysis A: General,

Volume 502,

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ISSN 0926-860X,

https://doi.org/10.1016/j.apcata.2015.06.009.

(https://www.sciencedirect.com/science/article/pii/S0926860X15300259)

Abstract: A systematic comparison of sulfur poisoning on Ni/YSZ and Ni/K2O-CaAl2O4, a commercially available reforming catalyst, demonstrated the heightened and rapid degradation of Ni/YSZ methane reforming activity. Ni/K2O-CaAl2O4 has nearly 15 times the hydrogen uptake capacity of Ni/YSZ which implies a difference in active nickel area. Because of this difference in active nickel surface area, Ni/K2O-CaAl2O4 was diluted in pure α-Al2O3 to achieve the same active nickel surface area as Ni/YSZ. The turnover frequencies (TOF) for steam methane reforming without sulfur on Ni/YSZ and Ni/K2O-CaAl2O4 were similar, although there was some deactivation on Ni/K2O-CaAl2O4 possibly as a result of coking which was observed visually. Sulfur deactivation on both catalysts was examined for H2S, SO2, and COS at concentrations of 1, 3, and 5ppm. Ni/YSZ deactivated rapidly to an activity close to zero. Ni/K2O-CaAl2O4 deactivated quickly in the first 20min, but then reached a non-zero steady state activity. The relative deactivation rates for the sulfur species examined were COS>SO2≥H2S. Reaction temperatures of 650°C, 750°C, and 800°C were evaluated, but temperature did not strongly affect deactivation rates for either catalyst. The overarching result of this study is that Ni/YSZ methane reforming activity is more sensitive to sulfur deactivation than a commercial reforming catalyst. The effect is so strong, that the use of Ni/YSZ with any hydrocarbon fuel may require removal of sulfur to sub-ppm levels.

Keywords: Methane steam reforming; Methane dry reforming; CO2 reforming; Hydrogen sulfide; Sulfur dioxide; Ni/YSZ; Solid oxide fuel cell; SOFC; Nickel catalyst; YSZ support; Sulfur poisoning; Carbonyl sulfide; Sulfur; Poisoning

Yasotha Kathiraser, Usman Oemar, Eng Toon Saw, Ziwei Li, Sibudjing Kawi,

Kinetic and mechanistic aspects for CO2 reforming of methane over Ni based catalysts,

Chemical Engineering Journal,

Volume 278,

2015,

Pages 62-78,

ISSN 1385-8947,

https://doi.org/10.1016/j.cej.2014.11.143.

(https://www.sciencedirect.com/science/article/pii/S1385894714016568)

Abstract: In recent decades, CO2 utilization has become increasingly important in view of the escalating global warming phenomenon. In view of this, conversion of CO2 to syngas via CO2 (dry) reforming of methane (DRM) reaction has been gaining prominent research interest. This paper presents a review on the kinetic and mechanistic aspects for DRM reaction with focus on Ni based catalysts. Ni-based catalysts are commercially attractive due to the low cost and wide availability of Ni metal. Kinetic studies over the Ni based catalysts are vital in scaling up of the DRM process in order to assess its industrial viability. Many differing opinions have been formed for the rate determining steps (RDS) of the reaction kinetics. In this review, a survey of the differing RDS presented in literature based on the widely used Langmuir Hinshelwood Hougen Watson (LHHW) models for Ni-catalyzed DRM reactions are categorized and presented along with the importance of experimental techniques for justifying mechanistic formulation.

Keywords: CO2 reforming of methane; Ni catalyst; Reaction kinetics; Rate determining steps; Characterization techniques

Ji-Eun Min, Yun-Jo Lee, Hae-Gu Park, Chundong Zhang, Ki-Won Jun,

Carbon dioxide reforming of methane on Ni–MgO–Al2O3 catalysts prepared by sol–gel method: Effects of Mg/Al ratios,

Journal of Industrial and Engineering Chemistry,

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https://doi.org/10.1016/j.jiec.2014.12.012.

(https://www.sciencedirect.com/science/article/pii/S1226086X14006777)

Abstract: Carbon dioxide reforming of methane on Ni–MgO–Al2O3 catalysts has been investigated systematically at various Mg/Al ratios, focusing on catalytic activity and coke resistance. Ni catalysts supported on MgO–Al2O3 were prepared by sol–gel method using citric acid as a gelling agent. The characterization of the catalyst was carried out by XRD, TEM, TPR, N2 adsorption, H2 chemisorption, O2 titration, CO2-TPD and TGA. In the comparison with a catalyst prepared by coprecipitation method, it was found that the catalyst prepared by the sol–gel method showed higher coke resistance. In the variation of Mg/Al ratios, high coke resistance was obtained with increasing MgO loading, while high catalytic activity was observed with the catalysts of medium MgO/(MgO+Al2O3) ratio (0.44–0.86), of which the superior catalytic activity is likely attributed to high specific surface area and well dispersed Ni particles.

Keywords: Carbon dioxide reforming of methane; Mg/Al mixed oxide; Ni-based catalyst; Sol–gel method

Zhenghong Bao, Yongwu Lu, Jun Han, Yebo Li, Fei Yu,

Highly active and stable Ni-based bimodal pore catalyst for dry reforming of methane,

Applied Catalysis A: General,

Volume 491,

2015,

Pages 116-126,

ISSN 0926-860X,

https://doi.org/10.1016/j.apcata.2014.12.005.

(https://www.sciencedirect.com/science/article/pii/S0926860X1400756X)

Abstract: Bimodal pore NiCeMgAl catalysts were synthesized via the refluxed co-precipitation method. Methane reforming using carbon dioxide over this bimodal pore NiCeMgAl catalyst for syngas production was systematically studied by optimizing the active component NiO-loading, calcination temperature, reduction temperature and gas hourly space velocity (GHSV). The Ni15CeMgAl sample with 15wt% NiO loading, was found to be active enough at 750°C with a high CH4 conversion of 96.5%. The proper reduction temperature for the NiCeMgAl catalyst is either 550–650°C or 850°C. Higher calcination temperature favors the formation of NiAl2O4 and MgAl2O4 spinel structures. The Ni active sites derived from the NiAl2O4 spinel structure had longer stability than those from the free NiO. Compared with non-bimodal pore NiCeMgAl catalyst, bimodal pore NiCeMgAl catalyst has a longer stability in the feed gas without dilution. The large pores in the bimodal pore Ni15CeMgAl catalyst were supposed to contribute to the quick molecule transfer during the dry reforming of methane (DRM) reaction when the GHSV was less than 96,000h−1. The evolution of the Ni15CeMgAl catalyst before and after the DRM reaction was investigated by BET, XRD, TEM, and TGA techniques. A schema of the DRM reaction on the bimodal pore Ni15CeMgAl catalyst was proposed, and the correlation between the structure evolution and catalytic performance change was also discussed.

Keywords: Nickel catalyst; Bimodal pore; Reflux; Dry reforming of methane

Jaekyeong Yoo, Yongju Bang, Seung Ju Han, Seungwon Park, Ji Hwan Song, In Kyu Song,

Hydrogen production by tri-reforming of methane over nickel–alumina aerogel catalyst,

Journal of Molecular Catalysis A: Chemical,

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https://doi.org/10.1016/j.molcata.2015.09.008.

(https://www.sciencedirect.com/science/article/pii/S1381116915300844)

Abstract: A mesoporous nickel–alumina aerogel catalyst (NAA) was prepared by an epoxide-initiated gelation method and a subsequent supercritical carbon dioxide drying method. For comparison, a mesoporous nickel–alumina xerogel catalyst (NAX) was also prepared by an epoxide-initiated gelation method without supercritical carbon dioxide drying. Both catalysts were applied to the hydrogen production by tri-reforming of methane. The effect of preparation method on the physicochemical properties and catalytic activities of the catalysts was investigated. Although both catalysts exhibited a well-developed mesoporous structure, NAA catalyst retained higher surface area and larger pore volume than NAX catalyst. It was also revealed that NAA catalyst retained higher nickel dispersion and larger methane adsorption capacity than NAX catalyst. In the hydrogen production by tri-reforming of methane, both catalysts exhibited a stable catalytic performance. However, NAA catalyst showed higher hydrogen yield and higher CH4 conversion than NAX catalyst. High nickel dispersion and strong affinity with methane of NAA catalyst was responsible for its high catalytic performance.

Keywords: Hydrogen production; Tri-reforming of methane; Nickel–alumina aerogel catalyst; Nickel dispersion; Methane adsorption capacity

Massimiliano Lo Faro, Patrizia Frontera, PierLuigi Antonucci, Antonino Salvatore Aricò,

Ni–Cu based catalysts prepared by two different methods and their catalytic activity toward the ATR of methane,

Chemical Engineering Research and Design,

Volume 93,

2015,

Pages 269-277,

ISSN 0263-8762,

https://doi.org/10.1016/j.cherd.2014.05.014.

(https://www.sciencedirect.com/science/article/pii/S0263876214002433)

Abstract: This study deals with an investigation of the catalytic performance of a bimetallic system based on Ni and Cu prepared by two different methods. It was found that the oxalate method permits to obtain crystallites with lower dimension compared to the sol–gel method, even after the calcination of powders carried out at the same temperature. Furthermore, the catalytic behavior of the two samples was different. The Ni–Cu prepared by oxalate method showed higher performance and stability than the Ni–Cu prepared by sol–gel in autothermal reforming (ATR) of methane achieving a fuel conversion of about 80%.

Keywords: Ni–Cu bimetallic catalyst; Ba-doped catalyst; Solid oxide fuel cells; Autothermal reforming; Methane to syngas

Xiaochong Xue, Sufang Wu,

The microstructure and stability of a Ni-nano-CaO/Al2O3 reforming catalyst under carbonation–calcination cycling conditions,

International Journal of Hydrogen Energy,

Volume 40, Issue 16,

2015,

Pages 5617-5623,

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https://doi.org/10.1016/j.ijhydene.2015.02.032.

(https://www.sciencedirect.com/science/article/pii/S0360319915003377)

Abstract: The paper investigated the effect of carbonation–calcination cycling conditions on the microstructure and CO2 sorption property of a sorption complex catalyst. The carbonation operation condition consisted of temperature of 600 °C with 20% CO2–80% N2 and 20% CO2–80% steam atmosphere to simulate the methane reforming reaction conditions; the calcination condition was 800 °C with 100% N2. The Brunauer–Emmer–Teller (BET) surface area and thermogravimetric analysis (TGA) were measured to investigate the microstructure and variation in sorption property of the catalyst after multiple cycles under each condition. Results showed that the microstructure and CO2 sorption capacity of the sorption complex catalyst decayed significantly in the initial carbonation–calcination cycles, especially under a steam atmosphere. X-ray diffraction analysis revealed that a stable compound Ca12Al14O33 formed gradually during the initial carbonation–calcination cycle seven at a temperature of 800 °C. A model is proposed to explain the observed effect of carbonation–calcination cycling on Ca12Al14O33 formation. Furthermore, based on our findings, a new sorption complex catalyst was prepared by pretreating at a high temperature of 900 °C. Evaluation of the catalyst prepared by the ReSER hydrogen production process through 10 circulations revealed significant improvement instability.

Keywords: Hydrogen; Steam methane reforming; Catalyst; Carbonation–calcination cycles; Calcium aluminate; Stability

Xiaoyan Wu, Xiaoliang Zhou, Yu Tian, Xiaowei Kong, Jun Zhang, Wei Zuo, Xuesong Ye, Kening Sun,

Preparation and electrochemical performance of silver impregnated Ni-YSZ anode for solid oxide fuel cell in dry methane,

International Journal of Hydrogen Energy,

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Pages 16484-16493,

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https://doi.org/10.1016/j.ijhydene.2015.09.121.

(https://www.sciencedirect.com/science/article/pii/S0360319915300446)

Abstract: The Ni/YSZ composite anode has been widely explored for solid oxide fuel cells (SOFCs). However, it is susceptible to carbon coking in hydrocarbons because of the high catalytic activity of Ni for carbon formation. In this paper, Ag particles were incorporated into Ni/YSZ anode to suppress the carbon deposition in hydrocarbons. The results showed that the performance of the modified cells was greatly increased as compared to the unmodified ones. The long term stability experiment was conducted for 100 h at 0.30 A/cm2 in dry CH4 at 1023 K indicating the anti-coking ability of the anode was greatly improved. The particle size and morphology of silver particles are the essential factors influencing the cell performance such as the maximum power density and long-term stability. Therefore, silver can be suggested as a promising candidate material for modifying the Ni/YSZ anode with regard to improving electrochemical performance and suppressing the carbon deposition.

Keywords: Solid oxide fuel cells; Ni/YSZ anode; Silver; Impregnation; Methane; Carbon deposition

Chuanmin Ding, Xiaofeng Gao, Yulin Han, Xishun Ma, Junwen Wang, Shibin Liu, Kan Zhang,

Effects of surface states over core-shell Ni@SiO2 catalysts on catalytic partial oxidation of methane to synthesis gas,

Journal of Energy Chemistry,

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ISSN 2095-4956,

https://doi.org/10.1016/S2095-4956(15)60283-2.

(https://www.sciencedirect.com/science/article/pii/S2095495615602832)

Abstract: In the present work, core-shell Ni@SiO2 catalysts were investigated in order to evaluate the relevance of catalytic activity and surface states of Ni core as well as Ni nanoparticles size to catalytic partial oxidation of methane (POM). The catalysts were characterized by N2 adsorption, H2-TPR, XRD, TEM and XPS techniques. The catalytic performance of the core-shell catalysts was found to be dependent on the surface states of catalyst, which influenced the formation of products. It was considered that carbon dioxide formed on the oxidized nickel sites (NiO) and carbon monoxide produced on the reduced sites (Ni). The surface states of active metal in the dynamic were influenced both by the size of Ni core and the porosity of silica shell. However, the catalytic activity would be debased when the size of Ni core was under a certain extent, which can be ascribed to the fact the carbon deposition increased with the increasing content of NiO. The effects of surface states of Ni@SiO2 catalyst on the catalytic performance were discussed and the reaction pathway over Ni core encapsulated inside silica shell was proposed.

Keywords: partial oxidation of methane; surface state of catalyst; reaction pathway

E. Gallegos-Suárez, A. Guerrero-Ruiz, M. Fernández-García, I. Rodríguez-Ramos, A. Kubacka,

Efficient and stable Ni–Ce glycerol reforming catalysts: Chemical imaging using X-ray electron and scanning transmission microscopy,

Applied Catalysis B: Environmental,

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ISSN 0926-3373,

https://doi.org/10.1016/j.apcatb.2014.10.007.

(https://www.sciencedirect.com/science/article/pii/S0926337314006201)

Abstract: Nickel–ceria composite catalysts prepared by a microemulsion method showed outstanding catalytic behavior in hydrogen production by glycerol steam reforming. Contrarily to usual Ni-based catalysts, the system allows long-term stability and nearly absence of by-products, particularly methane and carbon monoxide. With the help of scanning transmission electron microscopy and energy dispersive X-ray spectroscopy we confirmed the key role played by an intimate intermixing of Ni and Ceria components at reaction conditions. In addition, chemical imaging maps as well as more conventional techniques, such as Temperature Programmed Oxidation (TPO) and X-ray Photoelectron Spectroscopy (XPS) were used to identify the carbon containing (including coke) species nature and to establishing their chemical relevance. Combination of these techniques points out that the optimum interphase contact, reached for a specific 20:80 molar Ni:Ce formulation, allows; (i) to keep the Ni particle size controlled with absence of significant formation of coke and thus without deleterious effects on the long-term stability of the catalysts; and (ii) to eliminate undesirable side reactions such as methanation.

Keywords: Ni; Glycerol; Metal–support interaction; Hydrogen production

Mohamad Hassan Amin, Sudarsanam Putla, S. Bee Abd Hamid, Suresh K. Bhargava,

Understanding the role of lanthanide promoters on the structure–activity of nanosized Ni/γ-Al2O3 catalysts in carbon dioxide reforming of methane,

Applied Catalysis A: General,

Volume 492,

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Pages 160-168,

ISSN 0926-860X,

https://doi.org/10.1016/j.apcata.2014.12.038.

(https://www.sciencedirect.com/science/article/pii/S0926860X1400800X)

Abstract: The present work was undertaken to investigate the effect of different lanthanide promoters on the structure–activity properties of Ni/γ-Al2O3 catalyst for CO2 reforming of CH4. Accordingly, a number of lanthanides, namely Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Tm were incorporated into the Ni/γ-Al2O3 catalyst by means of sol–gel method. An extensive physicochemical characterisation was performed using XRD, TG-DTA, BET surface area, BJH, XPS, Raman, H2-TPR, and TEM techniques. Surprisingly, low initial conversions of CH4 and CO2 were obtained for promoted Ni/γ-Al2O3 catalysts compared with un-promoted catalyst, which is due to the presence of smaller pore sizes in the promoted catalysts. The observed initial activity order for conversions of CH4 and CO2 is un-promoted >Eu>Tb>Ho>Tm>Er>Dy>Pr>Sm>Gd>Nd. Interestingly, promoted Ni/γ-Al2O3 catalysts exhibited an outstanding efficiency in time-on-stream studies up to 60h than the un-promoted catalyst. This significant observation is mainly due to low amounts of amorphous coke deposited on the surface of promoted Ni/γ-Al2O3 catalysts compared with un-promoted catalyst. Among all investigated lanthanides, the Er-promoted Ni/γ-Al2O3 catalyst showed the best performance in CH4 conversion, which is attributed to optimum Ni particle size, more reducibility, and low amounts of amorphous coke formation. It was shown that the catalytic efficacy of Ni/γ-Al2O3 catalysts is highly dependent on the nature of the promoter. These notable findings are expected to bring new opportunities in the design of novel promising catalytic materials for CO2 reforming of CH4.

Keywords: CO2 reforming of methane; Ni/γ-Al2O3 catalyst; Lanthanide; Promoter

J. Estephane, S. Aouad, S. Hany, B. El Khoury, C. Gennequin, H. El Zakhem, J. El Nakat, A. Aboukaïs, E. Abi Aad,

CO2 reforming of methane over Ni–Co/ZSM5 catalysts. Aging and carbon deposition study,

International Journal of Hydrogen Energy,

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2015,

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https://doi.org/10.1016/j.ijhydene.2015.05.147.

(https://www.sciencedirect.com/science/article/pii/S0360319915013609)

Abstract: The wet impregnation method was used to prepare ZSM5 supported nickel and/or cobalt monometallic and bimetallic catalysts with a 7 wt.% total metal loading. The CO2 reforming of methane reaction was carried out in the 600 °C–800 °C temperature range over the different catalysts (GHSV 60000 mL g−1 hr−1). The cobalt containing catalysts favored the reverse water gas shift reaction at high temperature and cobalt acted as a synergist to nickel, as overall, bimetallic catalysts showed better catalytic performance. Carbon deposition was less expressed over catalysts with high cobalt content. Following 12 h on stream at 700 °C, the bimetallic catalyst with cobalt to nickel ratio of 2, showed high CO2 and CH4 conversions (∼60%) accompanied with the lowest carbon deposition (5%). The thermal analysis of aged catalysts showed that among the deposited carbon species, it is the carbon present in the proximity of nickel and/or cobalt catalytic sites that is responsible of deactivation.

Keywords: Catalyst deactivation; Dry reforming; Nickel; Cobalt; Zeolites; Carbon deposition

Radosław Dębek, Monika Radlik, Monika Motak, Maria Elena Galvez, Wincenty Turek, Patrick Da Costa, Teresa Grzybek,

Ni-containing Ce-promoted hydrotalcite derived materials as catalysts for methane reforming with carbon dioxide at low temperature – On the effect of basicity,

Catalysis Today,

Volume 257, Part 1,

2015,

Pages 59-65,

ISSN 0920-5861,

https://doi.org/10.1016/j.cattod.2015.03.017.

(https://www.sciencedirect.com/science/article/pii/S0920586115001789)

Abstract: NiMgAl mixed oxides promoted with cerium species were synthesized from their corresponding hydrotalcite precursors and subsequently characterized by elemental analysis, XRD, H2-TPR, CO2-TPD and N2 sorption techniques. The catalytic activity of the prepared catalysts was tested in the reaction of CO2 methane reforming and compared to the performance of two reference catalysts: 10Ni/Al2O3 and 10Ni/CZ (ceria-zirconia). The hydrotalcite derived materials showed a significant catalytic activity at 550°C towards the dry reforming reaction. However, the simultaneous occurrence of undesired side reactions was as well observed, mainly CH4 decomposition and RWGS reaction. In this sense, the addition of cerium by ion-exchange with [Ce(EDTA)]− complexes resulted in higher activity and selectivity, due to an increase in the reducibility of nickel species and to the introduction of new intermediate and strong basic sites (acid-base pairs and low coordinated oxygen species). The reference catalysts showed considerable loss of catalytic activity during 5h experiments, lower CO2 conversion (10Ni/CZ) and high excess of CO in the products of the reaction (10Ni/Al2O3), pointing to a generally better performance of the hydrotalcite derived catalysts.

Keywords: Nickel; Ceria; Hydrotalcite; CO2; Reforming; Hydrogen

Mingchen Tang, Long Xu, Maohong Fan,

Progress in oxygen carrier development of methane-based chemical-looping reforming: A review,

Applied Energy,

Volume 151,

2015,

Pages 143-156,

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https://doi.org/10.1016/j.apenergy.2015.04.017.

(https://www.sciencedirect.com/science/article/pii/S0306261915004729)

Abstract: This work comprehensively reviews the recent advances for chemical-looping reforming of CH4 (CLR) technology, which breaks down the traditional CH4 reforming process (including steam and dry reforming) into two separate half-steps, namely CH4 oxidation and replenishment of oxygen carrier (OC) with appropriate oxidizing agents. In order to steer the conversion of CH4 toward partial oxidation (POM) for synthesis gas (H2+CO) production rather than total oxidation for producing CO2 and H2O, the appropriate selection of OC becomes a critical issue. Moreover, instead of the commonly used air to re-oxidize the oxygen-depleted OC after reaction with CH4, steam and CO2 have been proposed as two alternatives, opening up the opportunities to produce extra H2 and CO. However, owing to much weaker oxidization ability of steam and CO2 than air, the low oxidation degree and slow oxidation rate seem to remain as challenges. Furthermore, the resistance of OC to attrition, agglomeration and carbon deposition is also of great importance. In these regards, the latest major milestones are compiled.

Keywords: Chemical-looping reforming; CO2 capture; Partial oxidation of CH4; Oxygen carrier; Syngas production

A. Djaidja, H. Messaoudi, D. Kaddeche, A. Barama,

Study of Ni–M/MgO and Ni–M–Mg/Al (M=Fe or Cu) catalysts in the CH4–CO2 and CH4–H2O reforming,

International Journal of Hydrogen Energy,

Volume 40, Issue 14,

2015,

Pages 4989-4995,

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https://doi.org/10.1016/j.ijhydene.2014.12.106.

(https://www.sciencedirect.com/science/article/pii/S036031991403537X)

Abstract: The catalysts Ni–M/MgO prepared by impregnation of the MgO support and (Ni–M–Mg)2Al by co-precipitation method using NH4OH as precipitating agent (M=Cu or Fe), were characterized by BET surface area, X-ray diffraction (XRD), temperature programmed reduction (TPR), temperature programmed oxidation (TPO), Transmission electronic microscopy (TEM) and tested in CH4/CO2 and CH4/H2O reactions. XRD analysis showed the presence of NixMg1 − xO (x = 0.05 or 0.1), NiAl2O4 and/or MgAl2O4 solid solutions. NiO was not observed on all catalysts what could confirm the formation of solid solutions. The reducibility of the catalysts increased in the presence of Cu or Fe due to the reduction assistance of these elements. The reactivity results showed very high performances (with CH4 conversion and yields of H2 and CO up to 90%) and a good resistance for coke formation. For the CO2 reforming of methane, the TPO profiles and TEM analysis showed mainly four types of coke: CHx species, surfaces carbon, nickel carbide and carbon nanotubes. However, for the H2O reforming, the nanotubes carbon was not detected. The coke deposit decreased in the presence of Fe or Cu species due probably to the formation of Ni–Fe or Ni–Cu alloys where in the active phase is highly dispersed. In this work, we observed also that the presence of Mg, basic element, in the catalyst composition decreased coke formation in the form of nanotube. In the other hand, the deactivation of catalysts in the case of H2O reforming is more related to actives sites oxidation.

Keywords: Ni catalysts; Spinal; CO2 reforming; H2O reforming

Ali Nakhaei Pour, Maryam Mousavi,

Combined reforming of methane by carbon dioxide and water: Particle size effect of Ni–Mg nanoparticles,

International Journal of Hydrogen Energy,

Volume 40, Issue 38,

2015,

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https://doi.org/10.1016/j.ijhydene.2015.08.011.

(https://www.sciencedirect.com/science/article/pii/S0360319915020601)

Abstract: The effect of Ni–Mg particle size on product selectivity, catalyst activity and coke formation on Ni/MgO/α-Al2O3 catalyst were studied in simultaneous steam and CO2 reforming of methane to syngas. The Ni–Mg particle sizes in the range of 13.7–29.7 nm were prepared via incipient wetness impregnation method using α-Al2O3 as support. Experimental results for turn over frequency (TOF) show that the intrinsic catalyst performances were dependent on Ni–Mg particle size. However, the products selectivities and H2/CO ration were found to be independent of Ni–Mg particle size. The experimental results reveal that the coke formation rates on the surface of catalysts are increased by increasing Ni–Mg particle size. Nevertheless, the correlated site carbon atom deposition rates (carbon atoms deposited on one site of catalyst) is shown an opposite trend.

Keywords: CO2-steam reforming; Ni catalysts; Methane; Syngas; Size dependent

Hale Ay, Deniz Üner,

Dry reforming of methane over CeO2 supported Ni, Co and Ni–Co catalysts,

Applied Catalysis B: Environmental,

Volume 179,

2015,

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ISSN 0926-3373,

https://doi.org/10.1016/j.apcatb.2015.05.013.

(https://www.sciencedirect.com/science/article/pii/S0926337315002581)

Abstract: Ceria supported Ni, Co monometallic and Ni–Co bimetallic catalysts were prepared by incipient wetness impregnation method, calcined at two different temperatures (700°C and 900°C) and tested for dry reforming of methane reaction at 700°C. The activities of ceria-based Ni containing catalysts decreased with increasing calcination temperature accompanied by a decrease in coke deposition. While Ni/CeO2 and Ni–Co/CeO2 catalysts exhibited comparable high activities, Co/CeO2 catalysts exhibited very low activity. The lower activity of Co/CeO2 catalyst was attributed to strong metal support interaction (SMSI). The SMSI effect was confirmed with TEM images showing a layer of support coating the metal particles. The diversity of the deposited carbon structures in terms morphology (straight long filaments, highly entangled and curly shaped filaments, filaments with knuckle-like structure and carbon onions) was noted. In addition to the carbon buildup, the deactivation was observed to be due to the loss of active metals in the carbon filaments.

Keywords: Dry reforming of methane; Ni; Co; Ni–Co; Ceria supported; Calcination temperature

Xiaoqing Zhang, Chunhui Yang, Yanping Zhang, Yan Xu, Shuyong Shang, Yongxiang Yin,

Ni–Co catalyst derived from layered double hydroxides for dry reforming of methane,

International Journal of Hydrogen Energy,

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(https://www.sciencedirect.com/science/article/pii/S0360319915024805)

Abstract: Ni/Co monometallic and bimetallic layered double hydroxides (LDH) were in-situ synthesized on the surface of γ-Al2O3 by urea precipitation method. Then they were decomposed and reduced by H2/Ar atmospheric plasma jet at 400 °C for 15 min to become into catalysts. The LDH precursors were verified by XRD, SEM, FT-IR and Raman, while the catalysts were characterized by N2 adsorption-desorption, XRD, TEM and H2-TPR. After that their catalytic activity and stability were evaluated in dry reforming of methane (DRM) reaction. Both Ni and 2Ni–1Co showed better catalytic performance than other catalysts. Finally, the weight and species of carbon deposition on spent catalyst were tested by TG-DTA analysis. The deposition of inert carbon was the main reason for deactivation of catalysts in DRM. Moreover, a highly uniform dispersion and small particle size of active component are achieved by in situ co-precipitation method, and γ-Al2O3 provided large specific surface area for these Ni/Co catalysts.

Keywords: LDH precursor; Ni–Co bimetallic catalyst; In-situ urea precipitation; Dry reforming of methane; Carbon deposition

Changzhen Wang, Nannan Sun, Ning Zhao, Wei Wei, Yuhan Sun, Chenggong Sun, Hao Liu, Colin E. Snape,

Coking and deactivation of a mesoporous Ni–CaO–ZrO2 catalyst in dry reforming of methane: A study under different feeding compositions,

Fuel,

Volume 143,

2015,

Pages 527-535,

ISSN 0016-2361,

https://doi.org/10.1016/j.fuel.2014.11.097.

(https://www.sciencedirect.com/science/article/pii/S0016236114012083)

Abstract: A previously developed mesoporous Ni–CaO–ZrO2 catalyst (NCZ) was submitted to dry reforming of methane (DRM), and the influence of feeding compositions on the properties of accumulated carbon was comprehensively studied. To this end, the used catalysts (NCZ-x) were characterized with a particular focus on the carbon residuals, using X-ray diffraction, N2 adsorption, transmission electron microscope, scanning electron microscopy, thermogravimetric analysis and X-ray photoelectron spectroscopy, etc. The results indicate that by varying the composition of the feeding gas, the morphology and chemical inertness of the accumulated carbon changed considerably, and the deactivation of the NCZ catalyst under CH4-rich conditions can be associated with the formation of coating carbon species that leads to the coverage of highly active Ni nano particles (NPs).

Keywords: Nickel catalyst; CO2 reforming; Carbon deposition; Deactivation; Feeding composition

Jianzhong Qi, Yanping Sun, Zongli Xie, Mike Collins, Hao Du, Tianying Xiong,

Development of Cu foam-based Ni catalyst for solar thermal reforming of methane with carbon dioxide,

Journal of Energy Chemistry,

Volume 24, Issue 6,

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Pages 786-793,

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https://doi.org/10.1016/j.jechem.2015.10.001.

(https://www.sciencedirect.com/science/article/pii/S2095495615000704)

Abstract: Using solar energy to produce syngas via the endothermic reforming of methane has been extensively investigated at the laboratory- and pilot plant-scales as a promising method of storing solar energy. One of the challenges to scaling up this process in a tubular reformer is to improve the reactor's performance, which is limited by mass and heat transfer issues. High thermal conductivity Cu foam was therefore used as a substrate to improve the catalyst's thermal conductivity during solar reforming. We also developed a method to coat the foam with the catalytically active component NiMg3AlOx. The Cu foam-based NiMg3AlOx performs better than catalysts supported on SiSiC foam, which is currently used as a substrate for solar-reforming catalysts, at high gas hourly space velocity (≥400,000 mL/(g·h)) or at low reaction temperatures (≤ 720 °C). The presence of a γ-Al2O3 intermediate layer improves the adhesion between the catalyst and substrate as well as the catalytic activity.

Keywords: Cu foam-based Ni catalyst; Monolithic catalyst; Solar thermal reforming of methane

Dong Tian, Wei Liu, Yonghong Chen, Weili Yu, Lianghao Yu, Bin Lin,

A robust NiO–Sm0.2Ce0.8O1.9 anode for direct-methane solid oxide fuel cell,

Materials Research Bulletin,

Volume 71,

2015,

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https://doi.org/10.1016/j.materresbull.2015.06.042.

(https://www.sciencedirect.com/science/article/pii/S0025540815300027)

Abstract: In order to directly use methane without a reforming process, NiO–Sm0.2Ce0.8O1.9 (NiO–SDC) nanocomposite anode are successfully synthesized via a one-pot, surfactant-assisted co-assembly approach for direct-methane solid oxide fuel cells. Both NiO with cubic phase and SDC with fluorite phase are obtained at 550°C. Both NiO nanoparticles and SDC nanoparticles are highly monodispersed in size with nearly spherical shapes. Based on the as-synthesized NiO–SDC, two kinds of single cells with different micro/macro-porous structure are successfully fabricated. As a result, the cell performance was improved by 40%–45% with the new double-pore NiO–SDC anode relative to the cell performance with the conventional NiO–SDC anode due to a wider triple-phase-boundary (TPB) area. In addition, no significant degradation of the cell performance was observed after 60h, which means an increasing of long term stability. Therefore, the as-synthesized NiO–SDC nanocomposite is a promising anode for direct-methane solid oxide fuel cells.

Keywords: Ceramics; Chemical synthesis; Thermogravimetric analysis(TGA); Electrochemical properties

Mira Nawfal, Cédric Gennequin, Madona Labaki, Bilal Nsouli, Antoine Aboukaïs, Edmond Abi-Aad,

Hydrogen production by methane steam reforming over Ru supported on Ni–Mg–Al mixed oxides prepared via hydrotalcite route,

International Journal of Hydrogen Energy,

Volume 40, Issue 2,

2015,

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https://doi.org/10.1016/j.ijhydene.2014.09.166.

(https://www.sciencedirect.com/science/article/pii/S036031991402761X)

Abstract: Catalytic performance of Ru/NixMg6−xAl2 800 800 mixed oxides, with x = 2, 4 and 6, x being the molar ratio, towards Methane Steam Reforming, was studied. NixMg6−xAl2 800 oxide, used as support, was prepared via hydrotalcite route. It was thermally stabilized at 800 °C, impregnated with 0.5 wt.% ruthenium using ruthenium (III) nitrosyl nitrate Ru(NO) (NO3)3 precursor and then calcined again at 800 °C under an air flow. Ruthenium impregnation significantly enhanced the reactivity of the oxides in Methane Steam Reforming. In fact, it was found, that even with a low ruthenium content (0.5 wt.%), ruthenium oxide particles are formed but are well dispersed over the surface of the oxide NixMg6−xAl2 800. Ru/Ni6Al2 800 800 showed better catalytic performances, towards Methane Steam Reforming, than ruthenium impregnated on the two other supports. Indeed, nickel content is higher in Ni6Al2 800 than in the other studied supports and therefore the probability of Ni–Ru interaction should be greater and consequently catalytic performances could be improved.

Keywords: Hydrotalcite; Methane steam reforming; Ruthenium; Nickel; Hydrogen production

L. Fan, L. van Biert, A. Thallam Thattai, A.H.M. Verkooijen, P.V. Aravind,

Study of Methane Steam Reforming kinetics in operating Solid Oxide Fuel Cells: Influence of current density,

International Journal of Hydrogen Energy,

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https://doi.org/10.1016/j.ijhydene.2015.02.096.

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Abstract: In literature, little is reported on the experimental studies of Methane Steam Reforming (MSR) kinetics in Solid Oxide Fuel Cells (SOFCs) when a current is drawn. This work investigates MSR reaction kinetics in a complete SOFC with a Ni–Gd0.1Ce0.9O2−δ (Ni−GDC) anode under varying gas compositions, operating temperatures and current densities in order to obtain reliable experimental data for Computational Fluid Dynamics (CFD) modeling studies. Consistent with previous work, the methane conversion XCH4 decreases as the temperature decreases. A slight increase in the MSR reaction rate is observed when a current is drawn. A positive dependency of the MSR reaction rate on methane concentration was found. Current has an insignificant influence on the methane reaction order. Under open-circuit working condition, steam concentration has a slightly positive influence at higher temperature and a slightly negative influence at lower temperature on the MSR reaction rate. The influence of steam concentration on the reaction rate becomes more negative when a current is drawn. It is probably due to the blockage of reaction sites by the adsorbed oxygen/water molecules/ions.

Keywords: SOFC; Reforming; Ni-GDC; Operating cell; Activation energy; Current density

Miklós Németh, Zoltán Schay, Dávid Srankó, Johanna Károlyi, György Sáfrán, István Sajó, Anita Horváth,

Impregnated Ni/ZrO2 and Pt/ZrO2 catalysts in dry reforming of methane: Activity tests in excess methane and mechanistic studies with labeled 13CO2,

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Abstract: In the present work, 1%Ni/ZrO2, 3%Ni/ZrO2 and 1%Pt/ZrO2 catalysts prepared by impregnation with the concomitant addition of NaHCO3 were investigated and compared by structural investigations such as TEM, XRD, TPR, XPS and DRIFTS methods. Temperature programmed dry reforming (DRM) experiments were done (i) at atmospheric pressure in plug flow reactor and an in situ DRIFTS cell or (ii) under sub atmospheric pressure (∼50mbar) in a closed loop circulation system using labelled 13CO2 to trace the fate of carbon compounds. The calcined and reduced fresh catalysts contained nanoparticles in the range of 2–18nm. According to the TPR results, in 3%Ni/ZrO2 catalyst most of Ni is in strong interaction with the support. The presence of sodium was suggested to induce the appearance of strongly bound bridged CO sites during CO chemisorption in DRIFTS measurements for all samples and to cause BE shift in XPS spectrum of the highly dispersed Pt/ZrO2 only. In the catalytic tests in plug flow reactor the 3wt%Ni/ZrO2 sample turned to be the most active catalyst, but coke was deposited on its surface measured by the subsequent temperature programmed oxidation (TPO) measurements. In situ low temperature DRIFTS-DRM measurements suggested that stability of surface carbonates is less when dispersed electron-rich Pt nanoparticles are on the ZrO2 support, while more carbonates accumulate on Ni/ZrO2 samples. Based on our isotope labeled 13CO2+12CH4 experiments in circulation system, the same initial reaction pathways could be suggested for the Ni and Pt catalysts. The reactive surface carbon species from the two different sources (CH4 and CO2) were completely scrambled on 3wt%Ni/ZrO2 at 600°C, suggesting that common reaction intermediates do exist.

Keywords: Mechanism of dry reforming; Ni/ZrO2; Pt/ZrO2; Circulation system; DRIFTS; Coke formation; 13CO2 isotope labeled experiments

Hua-Ping Ren, Yong-Hong Song, Wei Wang, Jian-Gang Chen, Jie Cheng, Jinqiang Jiang, Zhao-Tie Liu, Zhong-Wen Liu, Zhengping Hao, Jian Lu,

Insights into CeO2-modified Ni–Mg–Al oxides for pressurized carbon dioxide reforming of methane,

Chemical Engineering Journal,

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(https://www.sciencedirect.com/science/article/pii/S1385894714010833)

Abstract: The mixed oxide of NiO, MgO, and Al2O3 (NMA) with a MgO/Al2O3 molar ratio of 3 was prepared from the hydrotalcite-like precursor, and ceria was introduced into NMA with Ce/Al molar ratios between 0.1 and 1.0 via the co-precipitation (NMACe) and the incipient impregnation (Ce/NMA) method, respectively. The NMACe and Ce/NMA were comparatively investigated to reveal the impact of ceria on NMA for carbon dioxide reforming of methane (CDR) under severe conditions. All of the catalysts were highly active for the pressurized CDR. On the contrary, a significant impact of the content and introduction method of CeO2 on the catalytic stability was observed. Thus, the calcined, reduced, and/or used catalysts were systematically characterized by spectroscopic and adsorption techniques. Results indicate that the H2-TPR pattern of NMA was significantly influenced by the addition of CeO2, the extent of which is dependent on its content and introduction method. As a result, the degree of reduction and dispersion of Ni were clearly varied for different catalysts. Although the (111) planes of cubic CeO2 were preferentially exposed over all of the catalysts, the content of Ce3+ over Ce/NMA was apparently higher than that over NMACe, and the appropriate interactions between Ni and NMA were achieved over Ce/NMA with a Ce/Al ratio of 0.5. Because of the inhibited coke deposition, the alleviated graphitization of the deposited coke, and the delayed sintering of Ni, Ce/NMA with a Ce/Al ratio of 0.5 showed highly active and stable performance for the titled reaction under highly demanding operation conditions.

Keywords: Carbon dioxide; Methane; Nickel; Hydrotalcite; Ceria

Radosław Dębek, Katarzyna Zubek, Monika Motak, Maria Elena Galvez, Patrick Da Costa, Teresa Grzybek,

Ni–Al hydrotalcite-like material as the catalyst precursors for the dry reforming of methane at low temperature,

Comptes Rendus Chimie,

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(https://www.sciencedirect.com/science/article/pii/S1631074815001137)

Abstract: Nickel–aluminium and magnesium–aluminium hydrotalcites were prepared by co-precipitation and subsequently submitted to calcination. The mixed oxides obtained from the thermal decomposition of the synthesized materials were characterized by XRD, H2-TPR, N2 sorption and elemental analysis and subsequently tested in the reaction of methane dry reforming (DRM) in the presence of excess of methane (CH4/CO2/Ar=2/1/7). DMR in the presence of the nickel-containing hydrotalcite-derived material showed CH4 and CO2 conversions of ca. 50% at 550°C. The high values of the H2/CO molar ratio indicate that at 550°C methane decomposition was strongly influencing the DRM process. The sample reduced at 900°C showed better catalytic performance than the sample activated at 550°C. The catalytic performance in isothermal conditions from 550°C to 750°C was also determined.

Keywords: Dry reforming; Methane; CO2; Hydrotalcite; Nickel

Saeed Khajeh Talkhoncheh, Mohammad Haghighi,

Syngas production via dry reforming of methane over Ni-based nanocatalyst over various supports of clinoptilolite, ceria and alumina,

Journal of Natural Gas Science and Engineering,

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https://doi.org/10.1016/j.jngse.2015.01.020.

(https://www.sciencedirect.com/science/article/pii/S1875510015000219)

Abstract: In this study, Ni-based nanocatalysts over various types of supports, NH4NO3 ion exchanged clinoptilolite, CeO2 and Al2O3, have been prepared by impregnation method and studied for CO2 reforming of CH4 into syngas. The physicochemical properties of the samples were characterized by XRD, FESEM, EDX, BET and FTIR analyses. XRD analysis is showed that the interaction between NiO and CeO2 results in well dispersion of NiO. Based on the BET analysis, Ni/Al2O3 nanocatalyst has the highest specific surface area in comparison to other nanocatalysts. FESEM images illustrate that, all the samples have nanoscale morphology. EDX analysis demonstrates the homogenous dispersion of Ni on Ni/Al2O3 and Ni/CeO2 nanocatalysts. The activity and stability of the synthesized nanocatalysts for CO2 reforming of CH4 were tested at temperature range of 550–850 °C. Ni/Al2O3 nanocatalyst illustrates much higher conversions (93% and 96% for CH4 and CO2 at 850 °C) and yields (90% and 93% for H2 and CO). Also, the activity of Ni/Al2O3 remained stable during 1440 min. Among the prepared samples, Ni/Al2O3 nanocatalyst has the best performance due to the desired physicochemical properties; while Ni/Clinoptilolite, as an inexpensive and economical nanocatalyst, has relatively good activity.

Keywords: Dry reforming; Hydrogen; Ni; Ceria; Clinoptilolite; Alumina

Jane Estephane, Marc Ayoub, Khaled Safieh, Marie-Nour Kaydouh, Sandra Casale, Henri El Zakhem,

CO2 reforming of CH4 over highly active and stable yRhNix/NaY catalysts,

Comptes Rendus Chimie,

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(https://www.sciencedirect.com/science/article/pii/S163107481400280X)

Abstract: Ni7.5/NaY catalysts were prepared using two different methods, the incipient wetness impregnation method and the “two-solvent” method. These catalysts were characterised by N2 sorption, XRD, TEM and TPR. Their activity and stability in the dry reforming of methane were tested at atmospheric pressure under an equimolar mixture of methane and carbon dioxide. Three different Ni species, very small, spherical, and layers of nickel silicate were observed by TEM. The preparation by the two-solvent method led to a better dispersion of the active phase as well as to better activity and stability. These catalysts were promoted with small amounts (0.1wt%) of rhodium. Rhodium facilitates the reducibility and greatly enhances catalytic activity. A complete conversion (100%) for CH4 and CO2 over the Rh promoted catalyst is achieved at 584°C and 559°C respectively, while for the non-promoted Ni7.5/NaY catalyst, only a 60% conversion rate for CH4 and CO2 is reached at the same temperatures.

Résumé

Des catalyseurs Ni7,5/NaY ont étés préparés par imprégnation à sec et par la méthode à deux solvants. Ces catalyseurs ont étés caractérisés par physisorption d’azote, DRX, MET et RTP. Leur activité et stabilité ont été testées dans le reformage à sec du méthane sous pression atmosphérique et un mélange équimolaire de méthane et de dioxyde de carbone. Trois différentes espèces de nickel, sphériques, de très petites tailles ou des feuillets de silicate de nickel ont été détectées par MET. La méthode à deux solvants permet de mieux disperser la phase active et d’augmenter l’activité catalytique. Ces catalyseurs ont été promus par un faible pourcentage de rhodium. Ce dernier facilite la réduction et augmente significativement l’activité et la stabilité. Une conversion totale (100 %) du méthane et du dioxyde de carbone a été obtenue à 584°C et 559°C respectivement, sur le catalyseur promu par du Rh, tandis que sur le catalyseur Ni7,5/NaY non promu, la conversion du CH4 et du CO2 n’est que de 60 % aux mêmes températures.

Keywords: Dry reforming; Nickel; Rhodium; Syngas; Zeolite NaY; Reformage à sec; Nickel; Rhodium; Syngas; Zéolithe NaY

S. Marmarshahi, A. Niaei, D. Salari, F. Abedini, M. Abbasi, N. Kalantari,

Evaluating the Catalytic Performance of La1-xCexNi1-yZnyO3 Nanostructure Perovskites in the Carbon Dioxide Reforming of Methane,

Procedia Materials Science,

Volume 11,

2015,

Pages 616-621,

ISSN 2211-8128,

https://doi.org/10.1016/j.mspro.2015.11.095.

(https://www.sciencedirect.com/science/article/pii/S221181281500437X)

Abstract: In this research nanostructure perovskites La1-xCexNi1-yZnyO3 were prepared by sol-gel auto-combustion method and their application were evaluated for methane reforming with carbon dioxide and syngas production. Catalysts were designed by Response Surface Method (RSM) based on central composite design (CCD) with three factors of catalyst characteristics, x, y and Tc. The prepared catalysts were examined in methane reforming process at 750 ˚C temperature and atmospheric pressure. Analysis of variance (ANOVA) showed that parameters don’t have any linear effect on catalytic activity and their effect is proportional to square form. Among this investigated parameters, Ni content effect is considerable and calcination temperature (Tc) has a partial effect. In this research R2 value was 94.88%. The optimum catalyst which determined by RSM was La0.60Ce0.40Ni0.81Zn0.19O3 in 747 ˚C calcination temperature that corresponds to empirical result. The XRD characterization of optimum catalyst showed that perovskite catalyst was formed in rhombohedra phase with nanostructure crystals and the SEM of optimum catalyst confirmed the nano scale of prepared particles.

Keywords: Nanoparticle; Dry reforming; Mixed metal oxide; RSM.

Igor Luisetto, Simonetta Tuti, Chiara Battocchio, Sergio Lo Mastro, Armida Sodo,

Ni/CeO2–Al2O3 catalysts for the dry reforming of methane: The effect of CeAlO3 content and nickel crystallite size on catalytic activity and coke resistance,

Applied Catalysis A: General,

Volume 500,

2015,

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ISSN 0926-860X,

https://doi.org/10.1016/j.apcata.2015.05.004.

(https://www.sciencedirect.com/science/article/pii/S0926860X1500294X)

Abstract: The catalytic performances of Ni/CeO2–Al2O3 catalysts for the dry reforming of CH4 (DRM) were investigated. Catalysts with different Ni dispersion and different amount of CeAlO3 species were prepared by different methods and characterized by BET, XRD, XPS, Raman, TPR and TPO techniques. Catalytic activity was studied during time on stream in the range 873–1073K with a mixture of CH4:CO2:Ar=40:40:20vol.% and GHSV 90,000cm3g−1h−1. The intrinsic catalytic activity increased with the increasing of Ni crystallite size. Carbon was deposited as nano-fibres and graphite when catalysts worked at lower temperature, and the largest amount was found on the catalyst with the largest Ni crystallite size. The formation of graphitic deposits is limited by the presence of CeAlO3 species formed during catalyst activation. CA preparation method results particularly attractive because it allows to obtain catalysts with small Ni crystallite size and high content of CeAlO3 species, which both have a role in suppressing the carbon deposition and therefore in obtaining stable catalytic performances.

Keywords: Ni/CeO2–Al2O3; Dry reforming; Nickel particle size; CeAlO3; Carbon deposition

Tri Huu Nguyen, Agata Łamacz, Andrzej Krztoń, Agnieszka Ura, Karolina Chałupka, Magdalena Nowosielska, Jacek Rynkowski, Gérald Djéga-Mariadassou,

Partial oxidation of methane over Ni0/La2O3 bifunctional catalyst II: Global kinetics of methane total oxidation, dry reforming and partial oxidation,

Applied Catalysis B: Environmental,

Volume 165,

2015,

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https://doi.org/10.1016/j.apcatb.2014.10.019.

(https://www.sciencedirect.com/science/article/pii/S0926337314006328)

Abstract: The global kinetics (power rate law) of methane total oxidation (TO) over La2O3 catalyst was performed at 773, 823 and 873K. The global kinetics of methane dry reforming (DR) at 648, 673, 698 and 723K and partial oxidation (POM) at 993, 1013, 1023 and 1053K were conducted over Ni0/La2O3 catalyst. The initial rate method and isolation method were used to determine initial rates, rate constants, and partial orders to reactants and establish the Arrhenius equations for TO, DR, POM. The experimental apparent activation energies were 87.8, 116.4 and 112.8kJmol−1 for DR, TO and POM, respectively. For TO, the reaction order to CH4 was varying with conversion whereas that to O2 was zero. For DR, the reaction order to CH4 was constant, whereas that to CO2 was dependent on the concentration of CO2. The values of rate constants revealed the following order: kDR≫kPOM, kTO. It was found that the rate constant of POM reaction is linked to that of methane TO: kPOM≈2kTO. The catalytic cycle of methane TO is the “rate determining cycle” (rdc) of the POM process.

Keywords: POM; Global kinetics; Power rate law; Nickel; La2O3

Rong-jun ZHANG, Guo-fu XIA, Ming-feng LI, Yu WU, Hong NIE, Da-dong LI,

Effect of support on the performance of Ni-based catalyst in methane dry reforming,

Journal of Fuel Chemistry and Technology,

Volume 43, Issue 11,

2015,

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ISSN 1872-5813,

https://doi.org/10.1016/S1872-5813(15)30040-2.

(https://www.sciencedirect.com/science/article/pii/S1872581315300402)

Abstract: Ni-based catalysts with different supports were prepared and characterized by N2 physisorption, XRD, H2-TPR, H2 chemisorption, and so on; the effect of support on the performance of Ni-based catalyst in methane dry reforming was then investigated. The results indicated that the support has a significant influence on the state of NiO species. SiO2, TiO2 and ZrO2 as a support have a weak interaction with NiO, which facilitates the reduction of the corresponding catalysts; however, the weak interaction may also lead to quick deactivation due to the agglomeration of active metal species. Al2O3 and MgO have a strong interaction with NiO, which may promote the formation of NiAl2O4 spinel and NiO-MgO solid solution, respectively, and make the reduction of corresponding catalysts very difficult. Al2O3 modified by MgO is provided with both proper textural properties and interaction strength between metal and support, which are in favor of the dispersion and stabilization of NiO species. As a result, NiO supported on MgO-modified Al2O3 exhibits superior catalytic performance in methane dry reforming even under very high gas hourly space velocity; it is quite stable during a long term test of more than 100 h.

Keywords: methane; carbon dioxide; dry reforming; syngas; support effect

María Elena Gálvez, Abdulkader Albarazi, Patrick Da Costa,

Enhanced catalytic stability through non-conventional synthesis of Ni/SBA-15 for methane dry reforming at low temperatures,

Applied Catalysis A: General,

Volume 504,

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Pages 143-150,

ISSN 0926-860X,

https://doi.org/10.1016/j.apcata.2014.10.026.

(https://www.sciencedirect.com/science/article/pii/S0926860X14006498)

Abstract: A non-conventional synthesis route for the preparation of Ni/SBA-15 catalyst for methane dry reforming (MDR), comprising the addition of ascorbic acid as reducing agent, was considered and compared to impregnation and precipitation conventional preparation methods. The catalyst prepared following this novel route evidenced successful confinement of Ni-species inside the pores of SBA-15, both NiO and Ni-phyllosilicates. Due to its particular characteristics, this catalyst showed enhanced activity, selectivity and stability in MDR experiments. Concretely, deactivation of the catalyst was substantially hindered, due to improved selectivity, preferential carbon growth on the external surface of the catalyst, and special ability of the catalyst to favor the formation of amorphous carbon.

Keywords: Methane dry reforming; Ni catalyst; SBA-15; Ascorbic acid; Synthesis gas; Hydrogen

Linus A. Schulz, Lea C.S. Kahle, Karla Herrera Delgado, Stephan A. Schunk, Andreas Jentys, Olaf Deutschmann, Johannes A. Lercher,

On the coke deposition in dry reforming of methane at elevated pressures,

Applied Catalysis A: General,

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ISSN 0926-860X,

https://doi.org/10.1016/j.apcata.2015.03.002.

(https://www.sciencedirect.com/science/article/pii/S0926860X15001477)

Abstract: The reaction pathways leading to coke formation in dry reforming on Ni and Pt-based catalysts were investigated. Using isotope-labeled reactants (i.e., CH4+13CO2 ⇌ 2CO+2H2) showed that initially 13CO2 is converted faster than CH4 and that this higher activity leads to a higher concentration of 13CO compared with 12CO in the product stream, suggesting little isotope scrambling among products at this stage. Gasification of carbon deposits was found to be an important pathway enhancing the catalyst stability. Analysis of the pathways leading to carbon deposits suggests that coke is formed predominantly via reverse Boudouard reaction on Ni, while both metals contribute to CH4 dissociation. The pronounced reversibility of the CH and CO bond formation and cleavage was also shown by the presence of 13CH4 formed from 13CO2 and 12CO formed from 12CH4. Numeric calculations complementing the experimental results led to the proposal of a reaction pathway for the surface reactions, accounting for the differences between Ni and Pt.

Keywords: Dry reforming of methane; Reverse water gas shift; Ni; Pt; Hexaaluminate support; Coke formation; Isotope labeling; Reaction flow analysis

Marie-Nour Kaydouh, Nissrine El Hassan, Anne Davidson, Sandra Casale, Henri El Zakhem, Pascale Massiani,

Effect of the order of Ni and Ce addition in SBA-15 on the activity in dry reforming of methane,

Comptes Rendus Chimie,

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https://doi.org/10.1016/j.crci.2015.01.004.

(https://www.sciencedirect.com/science/article/pii/S1631074815000053)

Abstract: Dry reforming of methane has been carried out on SBA-15 catalysts containing 5wt% Ni and 6wt% Ce. The effect of the order of Ni and Ce impregnation on the catalytic activity has been studied. Both metals were added using the “two-solvent” method that favors metal dispersion inside the pores. Characterizations by XRD (low and high angles), N2 sorption, SEM and TEM of the materials after metal addition and calcination indicate good preservation of the porosities and high NiO and CeO2 dispersion inside the porous channels. Reduction was carried out before the catalytic tests and followed by TPR measurements. The most active reduced catalyst was the Ni–Ce/SBA-15 sample prepared by impregnating cerium first, then nickel. All catalysts were highly active and selective towards H2 and CO at atmospheric pressure. Full CH4 conversion was obtained below 650°C. The higher performances compared to those reported in the literature for mesoporous silica with supported Ni and Ce catalysts are discussed.

Résumé

Le reformage à sec du méthane a été étudié sur des catalyseurs SBA-15 contenant 5 % en poids de Ni et 6 % en poids de Ce. L’effet de l’ordre d’imprégnation de Ni et Ce sur l’activité catalytique a été étudié. Ces deux métaux ont été ajoutés en utilisant la méthode « à deux solvants », qui favorise la dispersion du métal à l’intérieur des pores. Les caractérisations par DRX (petits et grands angles), adsorption de N2, MEB et MET des matériaux après ajout du métal et calcination montrent une bonne préservation de la porosité et une grande dispersion des nanoparticules de NiO et CeO2 à l’intérieur des pores. La réduction des catalyseurs suivie par RTP a été effectuée avant tests catalytiques. Le catalyseur le plus actif est le Ni–Ce/SBA-15 réduit, préparé par imprégnation, tout d’abord du cérium, puis du nickel. Les catalyseurs étaient très actifs et sélectifs en H2 et CO sous pression atmosphérique, avec une conversion complète de CH4 atteinte avant 650°C. Les performances supérieures à celles décrites dans la littérature pour des catalyseurs à base de silice mésoporeuse contenant du Ni et du Ce sont discutées.

Keywords: Methane dry reforming; Mesoporous SBA-15 silica; Nickel; Cerium; Impregnation; Reformage à sec du méthane; Silice mésoporeuse SBA-15; Nickel; Cérium; Imprégnation

Elham Baktash, Patrick Littlewood, Reinhard Schomäcker, Arne Thomas, Peter C. Stair,

Alumina coated nickel nanoparticles as a highly active catalyst for dry reforming of methane,

Applied Catalysis B: Environmental,

Volume 179,

2015,

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ISSN 0926-3373,

https://doi.org/10.1016/j.apcatb.2015.05.018.

(https://www.sciencedirect.com/science/article/pii/S0926337315002635)

Abstract: Alumina coated nickel nanoparticles were prepared employing atomic layer deposition (ALD) on nickel oxide (NiO) nanoparticles and subsequent reduction of the NiO core. The materials showed impressive activity and stability for dry reforming of methane at elevated temperatures (700–800°C), especially when compared to the uncoated and reduced NiO nanoparticles. The stabilization against sintering at high temperatures is the crucial factor explaining the high catalytic activity of alumina coated Ni nanoparticles.

Keywords: Dry reforming of methane (DRM); Nickel oxide; Atomic layer deposition (ALD); Nanoparticles; Core–shell structures

Siddhartha Sengupta, Goutam Deo,

Modifying alumina with CaO or MgO in supported Ni and Ni–Co catalysts and its effect on dry reforming of CH4,

Journal of CO2 Utilization,

Volume 10,

2015,

Pages 67-77,

ISSN 2212-9820,

https://doi.org/10.1016/j.jcou.2015.04.003.

(https://www.sciencedirect.com/science/article/pii/S221298201500027X)

Abstract: Modifying the support of the alumina (Al2O3) supported Ni and Ni–Co catalysts with limited amounts of CaO and MgO had an effect on the catalytic activity during the reforming of CH4 with CO2 at 873K. The presence of CaO had a favorable effect on the catalytic activity of the supported catalysts. In contrast, the presence of MgO had an adverse effect due to the strong interaction of MgO with the Ni and Co phases under the present synthesis conditions. Characterization of the supported Ni and Ni–Co catalysts revealed that modifying the support with CaO or MgO had an effect on the reducibility, amount and type of H2 and CO2 chemisorbed and the nature of the metal crystallite. The characterization studies also revealed that the limited interaction of CaO with Ni phase in supported Ni and Ni–Co catalysts gave rise to additional sites that were able to chemisorb H2 and CO2 at higher temperatures without having a significant effect on the reducibility of the catalysts. The presence of these additional sites may be the reason for the improved activity of the modified-Al2O3 supported Ni and Ni–Co catalysts containing CaO.

Keywords: Reforming; CH4; CO2; Ni–Co/Al2O3; Basic promoters; Carbon deposition

Moisés R. Cesário, Braúlio S. Barros, Claire Courson, Dulce M.A. Melo, Alain Kiennemann,

Catalytic performances of Ni–CaO–mayenite in CO2 sorption enhanced steam methane reforming,

Fuel Processing Technology,

Volume 131,

2015,

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ISSN 0378-3820,

https://doi.org/10.1016/j.fuproc.2014.11.028.

(https://www.sciencedirect.com/science/article/pii/S0378382014005074)

Abstract: Ni–CaO–mayenite (Ca12Al14O33) catalysts for the CO2 Sorption Enhanced Steam Methane Reforming (SE-SMR) have been developed using the microwave assisted self-combustion method of preparation. The sorption of CO2 by CaO shifts the steam reforming and the Water Gas Shift reaction (WGS) towards H2 production and favors the heat balance of the global reaction. The CO2 sorption has been studied on materials with different CaO/Ca12Al14O33 ratios and for different types of preparation. The specific surface area of materials, the temperature of Ni phases' reducibility and CO2 sorption are all essential for material efficiency. The Ni–CA75MM catalyst was the most active and stable in methane steam reforming with CO2 sorption, even at an unusually low temperature (650°C).

Keywords: Steam methane reforming; CO2 sorption; Microwave assisted self-combustion method; Hydrogen

Honggen Peng, Youhe Ma, Wenming Liu, Xianglan Xu, Xiuzhong Fang, Jie Lian, Xiang Wang, Changqing Li, Wufeng Zhou, Ping Yuan,

Methane dry reforming on Ni/La2Zr2O7 treated by plasma in different atmospheres,

Journal of Energy Chemistry,

Volume 24, Issue 4,

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https://doi.org/10.1016/j.jechem.2015.06.015.

(https://www.sciencedirect.com/science/article/pii/S2095495615000200)

Abstract: A series of Ni/La2Zr2O7 pyrochlore catalysts prepared by impregnation method and treated by dielectric barrier discharge (DBD) plasma in different atmospheres and varied sequences were prepared and applied for dry reforming of methane (DRM). It is found that all of the plasma treated catalysts show evidently improved activity and coke resistance in comparison with the non-plasma treated one. The best performance is achieved on Ni/La2Zr2O7–H2P–C, a catalyst treated in H2 plasma before calcination. TGA-DSC and SEM demonstrate that carbon deposition is significantly suppressed on all of the plasma treated samples. Moreover, XRD and TEM results testify that both NiO and Ni sizes on the calcined and reduced samples treated by plasma are also decreased, which results in higher Ni metal dispersion on the reduced and used catalysts and enhances the interactions between Ni sites and the support. It is believed that these are the inherent reasons accounting for the promotional effects of plasma treatment on the reaction performance of the Ni/La2Zr2O7 pyrochlore catalysts.

Keywords: Methane dry reforming; Ni-based catalysts; Pyrochlore support; DBD plasma; Coke resistance

Davi C. Carvalho, Nuryana A. Ferreira, Josué M. Filho, Odair P. Ferreira, João M. Soares, Alcineia C. Oliveira,

Ni–Fe and Co–Fe binary oxides derived from layered double hydroxides and their catalytic evaluation for hydrogen production,

Catalysis Today,

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ISSN 0920-5861,

https://doi.org/10.1016/j.cattod.2014.08.010.

(https://www.sciencedirect.com/science/article/pii/S0920586114005781)

Abstract: Binary oxides based on Co–Fe and Ni–Fe were synthesized thermal treatment of layered double hydroxides (LDH) having distinct Ni/Fe and Co/Ni ratios. The solids were characterized through X-ray diffraction (XRD), Raman and Mössbauer spectroscopy, nitrogen adsorption–desorption isotherms, thermoprogrammed reduction (TPR) and thermoprogrammed desorption of CO2 (TPD-CO2), scanning electron microscopy (SEM) and evaluated in dry reforming of methane. XRD results revealed the spinel oxides such as NiFe2O4 and CoFe2O4 coexisting with γ-Fe2O3, α-Fe2O3, Co3O4 and NiO monoxides. These phases were confirmed by Raman and Mössbauer spectroscopy. Nitrogen adsorption–desorption isotherms showed a porosity within micro-to-meso pores range, with some samples displaying macropores. Catalytic evaluation in the dry reforming of methane by varying the temperature in the 650 and 750°C range suggested in situ Co°/CoFe2O4 and Ni°/NiFe2O4 phases formation, which gives best results with the temperature increment, resulting in H2/CO ratios close to 1. The elevated resistance to coking showed by Co–Fe series is particularly remarkable, however, sintering effects were observed over these solids.

Keywords: Spinel oxides; Hydrotalcites; Dry reforming; Methane; Characterizations

Tarak Mondal, Kamal K. Pant, Ajay K. Dalai,

Oxidative and non-oxidative steam reforming of crude bio-ethanol for hydrogen production over Rh promoted Ni/CeO2-ZrO2 catalyst,

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https://doi.org/10.1016/j.apcata.2015.04.004.

(https://www.sciencedirect.com/science/article/pii/S0926860X15002379)

Abstract: The catalytic oxidative and non-oxidative steam reforming of crude bio-ethanol for hydrogen production was studied in a tubular fixed bed reaction system over 30wt.%Ni/CeO2-ZrO2 and 1wt.%Rh-30wt.%Ni/CeO2-ZrO2 catalysts. The catalysts were prepared by impregnation-co-precipitation method and characterized by BET, XRD, TPR, TGA, XPS, XANES and EXAFS techniques. Characterization results revealed that the addition of Rh promotes reducibility of NiO at lower temperature for the bimetallic catalysts. Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) analysis depicted that NiO with 6-fold local co-ordination is present in all the samples. Ethanol conversion, hydrogen yield and product selectivity were investigated at 600°C and space time of 9.17kgcath/kgmol[EtOH]) at atmospheric pressure. In steam reforming of crude bio-ethanol, 81% ethanol conversion was achieved with 59% hydrogen selectivity on Ni/CeO2-ZrO2 catalyst, whereas, higher ethanol conversion (86%) with 73% hydrogen selectivity was achieved using Rh-Ni/CeO2-ZrO2 catalysts. In oxidative steam reforming of crude bio-ethanol, hydrogen yield and selectivity reduced due to the partial oxidation of oxygenate compounds present in the feed. The used catalysts were also analysed by BET, TGA/DTA, TPR, TPO, Raman spectroscopy, SEM, and TEM techniques to identify the cause of catalyst deactivation. The results indicate that the catalyst deactivation occurred mainly due to amorphous and filamentous carbon deposition on the catalysts surface, due to the presence of the impurities in the feed.

Keywords: Steam reforming; Crude bio-ethanol; Rh promoted Ni/CeO2-ZrO2 catalyst; Catalyst deactivation; Carbon deposition

Andrea Di Carlo, Domenico Borello, Mario Sisinni, Elisa Savuto, Paolo Venturini, Enrico Bocci, Koji Kuramoto,

Reforming of tar contained in a raw fuel gas from biomass gasification using nickel-mayenite catalyst,

International Journal of Hydrogen Energy,

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(https://www.sciencedirect.com/science/article/pii/S0360319915013415)

Abstract: Catalytic steam reforming of tar is a very efficient process to clean the gas produced by biomass gasification. Ni catalysts remain an affordable solution for this problem, even if this catalytic material suffers degradation due to carbon deposition and sulphur poisoning. In this study, the properties of a new catalyst Ni/Mayenite (Mayenite as binder), prepared by impregnation method and tested with a real gas obtained from a bench scale fluidized bed steam gasification of biomass, were investigated. Experiments were carried out in a microreactor fed by a slipstream coming from the bench scale gasifier to evaluate gas cleaning and upgrading options. Preliminary tests were carried out at three different temperatures, 700, 750 and 800 °C. In all the tests, the catalysts showed high activities reaching to a conversion rate of 90% in the case at highest temperature (800 °C). The conversion efficiency remained stable around this value during a 3 h test. A decrease in the performance was observed at 700 and 750 °C, even if the conversion remained stable around a lower value. An increase of H2 (>50%) and a decrease of CH4 were observed at all the temperatures, due to the occurrence of steam reforming reaction. A long duration test (12 h) was carried out at 800 °C and demonstrated that, at this temperature, the conversion was stable for a longer period.

Keywords: Biomass gasification; Tar; Steam reforming catalyst; Fluidized bed

M. Benito, I. Ortiz, L. Rodríguez, G. Muñoz,

Ni–Co bimetallic catalyst for hydrogen production in sewage treatment plants: Biogas reforming and tars removal,

International Journal of Hydrogen Energy,

Volume 40, Issue 42,

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https://doi.org/10.1016/j.ijhydene.2015.06.163.

(https://www.sciencedirect.com/science/article/pii/S0360319915016924)

Abstract: A Ni–Co bimetallic catalyst supported on lanthana promoted alumina was prepared by excess volume solution method. The catalyst was characterised by XRD, N2 adsorption isotherms, XRF, TPO, SEM and XPS. The catalyst was tested in a simulated biogas stream with a CH4:CO2 1:1, usually presented after anaerobic digestion in sewage treatment plants, and in a simulated air gasification stream containing toluene as a tar model compound. The catalyst was submitted to catalytic activity vs. temperature tests in order to determine the optimum temperature to maximize conversion and selectivity in both processes. At 700 °C, equilibrium conversion in the case of biogas conversion was achieved, and total toluene and methane conversion in gasification stream was reached, maximizing hydrogen production with the lack of complex tar by-products formation. Long-term reaction experiments up to 100 h demonstrated the stability of catalyst performance. Post-reaction characterisation of catalytic samples by SEM-EDX and XPS revealed the lack of coke deposits on the catalyst, responsible of catalyst deactivation in the most of catalytic systems reported in the literature. At the light of the results obtained, the catalyst developed could be applied to produce renewable hydrogen from anaerobic digestion units of sewage plants, through the energy valorisation of biogas stream and sludge gasification.

Keywords: Hydrogen; Catalyst; Sewage treatment plants; Biogas; Energy valorisation; Tar

Kah Weng Siew, Hua Chyn Lee, Maksudur R. Khan, Jolius Gimbun, Chin Kui Cheng,

CO2 reforming of glycerol over La-Ni/Al2O3 catalyst: A longevity evaluative study,

Journal of Energy Chemistry,

Volume 24, Issue 3,

2015,

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ISSN 2095-4956,

https://doi.org/10.1016/S2095-4956(15)60324-2.

(https://www.sciencedirect.com/science/article/pii/S2095495615603242)

Abstract: This paper reports on the longevity of glycerol-dry (CO2) reforming over the lanthanum (La) promoted Ni/Al2O3 catalysts. The XRD results showed that the Ni particle was well-dispersed in the presence of La promoter. In addition, via the NH3-TPD analysis, it was found that the La promoter has reduced the acidity of Ni catalyst which may have explained the mitigation of carbon laydown. It was determined that the 3.0 wt% La-promoted Ni/Al2O3 catalyst possessed the largest BET specific surface area of 97 m2·g−1. Consequently, it yielded the best catalytic longevity performance with conversion attained more than 90%, even after 72 h of reaction duration. Significantly, it can be confirmed that the presence of CO2 during the glycerol dry reforming was essential in reducing carbon deposition, most likely via gasification pathway. This has ensured a stability of catalytic activity for a long reaction period (72 h).

Keywords: CO2 reforming; glycerol; lanthanum; longevity; syngas

Seyed Reza Yahyavi, Mohammad Haghighi, Sirous Shafiei, Mozaffar Abdollahifar, Farhad Rahmani,

Ultrasound-assisted synthesis and physicochemical characterization of Ni–Co/Al2O3–MgO nanocatalysts enhanced by different amounts of MgO used for CH4/CO2 reforming,

Energy Conversion and Management,

Volume 97,

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Pages 273-281,

ISSN 0196-8904,

https://doi.org/10.1016/j.enconman.2015.03.064.

(https://www.sciencedirect.com/science/article/pii/S0196890415002824)

Abstract: The Ni–Co/Al2O3–MgO nanocatalysts with different Al/Mg ratios were synthesized via sonochemistry method and applied in CH4/CO2 reforming. In order to investigate the effect of ultrasonic irradiation, Ni–Co/Al2O3–MgO nanocatalyst with Al2O3/MgO=1.5 was also prepared via impregnation method. All samples were characterized by XRD, FESEM, PSD, BET and FTIR techniques. However, it should be noted that the sonochemistry method results in a better dispersion, smaller particle size, higher specific area and uniform morphology as well as better catalytic performance in comparison with the impregnation. Although among the prepared samples via sonochemistry, the Ni–Co/Al2O3–MgO nanocatalyst with Al2O3/MgO=5 showed higher dispersion, better morphology, smaller crystal size, superior active phase distribution and higher specific surface area. Due to the better textural properties, the Ni–Co/Al2O3–MgO nanocatalyst with Al2O3/MgO=5 shows a good catalytic performance, consequently.

Keywords: Impregnation; Ultrasound; Ni–Co/Al2O3–MgO; CH4/CO2 reforming; Synthesis gas

A. Derya Deniz Kaynar, Doruk Dogu, Nail Yasyerli,

Hydrogen production and coke minimization through reforming of kerosene over bi-metallic ceria–alumina supported Ru–Ni catalysts,

Fuel Processing Technology,

Volume 140,

2015,

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ISSN 0378-3820,

https://doi.org/10.1016/j.fuproc.2015.09.004.

(https://www.sciencedirect.com/science/article/pii/S0378382015301569)

Abstract: Steam reforming of kerosene was investigated to produce syngas as a fuel for solid-oxide fuel cells. Catalytic performances of synthesized bi-metallic Ru–Ni containing ceria–alumina supported catalysts were compared with mono-metallic catalysts containing only Ni or Ru, in the reforming reaction of kerosene. These catalysts had mesoporous structures with narrow pore size distributions. Performance of the catalyst containing 1% Ru and 15% Ni was the most stable with minimum coke and CH4 formation, as compared to the mono-metallic catalysts and bi-metallic catalysts containing less Ni. Incorporation of 1% Ru into Ni based catalysts significantly improved catalyst stability. All of the catalysts were very active, giving complete conversion of kerosene at 800°C. Increase of H2O/C ratio in the feed stream also caused more stable operation with less CH4 and CO formation. Results also proved that high hydrogen yields could be obtained by steam reforming of kerosene, producing a synthesis gas which might be used as a fuel in solid oxide fuel cells.

Keywords: Steam reforming; Kerosene; Ruthenium; Nickel; Catalyst

Wenlong Mo, Fengyun Ma, Yuee Liu, Jingmei Liu, Mei Zhong, Aisha Nulahong,

Preparation of porous Al2O3 by template method and its application in Ni-based catalyst for CH4/CO2 reforming to produce syngas,

International Journal of Hydrogen Energy,

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2015,

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https://doi.org/10.1016/j.ijhydene.2015.09.149.

(https://www.sciencedirect.com/science/article/pii/S0360319915024799)

Abstract: Four supports (SH0.01, SH0.02, SH0.03 and SH0.05) were synthesized by template method and compared with commercial carrier γ-Al2O3 (SH0), and the corresponding NiO/Al2O3 catalysts denoted as SHC0.01, SHC0.02, SHC0.03, SHC0.05 and SHC0 were prepared by hydrolysis-deposition method. BET results showed that the pore volumes of all carriers were about 0.41 cm3 g−1, and the SH0.02 support with surface area up to 477 m2 g−1 and average pore diameter of 3.3 nm only. NH3-TPD results indicated that SH0.02 held the weakest surface acidity. XRD characterization results certificated that the SHC0.02 catalyst presented well NiO dispersion, and its Ni grain size was only 5.8 nm. H2-TPR characterization results demonstrated that the proportion of NiO reduction peak area of SHC0.02 in the total reduction peak area was 86%. Evaluation experiments showed that the SHC0.02 catalyst performed the highest activity and selectivity than others. And the filamentous carbon deposited from long time stability test didn't cause catalyst deactivation, but massive accumulation of which would make bed pressure drop increase.

Keywords: CH4/CO2 reforming; Ni-based catalyst; Mesoporous Al2O3; Template method

Jun Ren, Xiang Qin, Jin-Zhou Yang, Zhi-Feng Qin, Hai-Long Guo, Jian-Ying Lin, Zhong Li,

Methanation of carbon dioxide over Ni–M/ZrO2 (M=Fe, Co, Cu) catalysts: Effect of addition of a second metal,

Fuel Processing Technology,

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https://doi.org/10.1016/j.fuproc.2015.04.022.

(https://www.sciencedirect.com/science/article/pii/S0378382015001824)

Abstract: Ni/ZrO2 catalysts with an added second metal were prepared by impregnation method and used in CO2 methanation. X-ray diffraction, hydrogen temperature programmed reduction, hydrogen temperature programmed desorption, X-ray photoelectron spectroscopy, and in situ infrared spectroscopy measurements were taken to characterize the surface and bulk properties of the catalysts. Compared with Co and Cu, Fe could efficiently enhance the catalytic activity of Ni/ZrO2 in CO2 methanation at low temperatures. The optimal amount of Fe was 3wt.%. CO2 methanation over Ni–Fe/ZrO2 catalysts may proceed through dissociation of CO2 into CO and subsequent reaction of CO with hydrogen to generate methane. Addition of Fe not only can improve the dispersion and degree of reduction of Ni, but also can enhance the partial reduction of zirconia. These effects further promote adsorption and dissociation of H2 and CO2, thus enhancing the activity of the catalyst in CO2 methanation.

Keywords: Bimetallic catalyst; CO2 methanation; ZrO2 support; Low-temperature activity

Ahmed Al-Fatesh,

Suppression of carbon formation in CH4–CO2 reforming by addition of Sr into bimetallic Ni–Co/γ-Al2O3 catalyst,

Journal of King Saud University - Engineering Sciences,

Volume 27, Issue 1,

2015,

Pages 101-107,

ISSN 1018-3639,

https://doi.org/10.1016/j.jksues.2013.09.006.

(https://www.sciencedirect.com/science/article/pii/S1018363913000482)

Abstract: Bimetallic catalysts, containing 5wt% Ni+5wt% Co supported on γ-Al2O3 combined with different amounts of Sr promoter ranging from 0 to 1wt%, for dry reforming reaction were prepared by the impregnation method. The dry reforming reaction was carried out at atmospheric pressure using CO2/CH4/N2 feed ratio of 17/17/2, F/W=60mL/min gcat and reaction temperature range of 500–700°C. The performance of the developed catalyst was evaluated by estimating the CH4 and CO2 conversions, and by performing a long run stability test. The fresh and spent catalysts were characterized by BET, TGA, TPD, TPR, and TPO. The bimetallic catalysts provided higher activity than the monometallic-catalysts. When the bimetallic was promoted with Sr, the activity decreased slightly however, the stability enhanced. The best stability, estimated by the deactivation factor, and less carbon deposition, measured by TGA, were obtained when 5Ni5CoSr0.75 catalyst was used.

Keywords: CH4; CO2; Bimetallic Ni–Co; Sr; γ-Al2O3

Tarak Mondal, Kamal K. Pant, Ajay K. Dalai,

Catalytic oxidative steam reforming of bio-ethanol for hydrogen production over Rh promoted Ni/CeO2–ZrO2 catalyst,

International Journal of Hydrogen Energy,

Volume 40, Issue 6,

2015,

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https://doi.org/10.1016/j.ijhydene.2014.12.070.

(https://www.sciencedirect.com/science/article/pii/S0360319914034673)

Abstract: Catalytic steam reforming of bio-ethanol in presence of oxygen for hydrogen production was studied over Ni/CeO2–ZrO2 and Rh–Ni/CeO2–ZrO2 catalysts. The catalysts were prepared by an impregnation-co-precipitation method and characterized by various characterization techniques. Characterization results revealed that addition of ZrO2 improves the oxygen storage capacity of CeO2 which improves catalytic activity. The effects of temperature, ethanol/water/oxygen molar ratio, and space time on ethanol conversion and product selectivities were investigated using a tubular fixed bed reactor at atmospheric pressure. Complete ethanol conversion was achieved at 600 °C with a maximum hydrogen yield of 4.6 mol/mol on the 1%Rh–30%Ni/CeO2–ZrO2 catalyst. Ethanol conversion and H2 selectivity were increased with increasing contact time, while CO and CH4 selectivity decreased. Investigation revealed Rh promoted catalyst exhibited better catalytic activity than 30%Ni/CeO2–ZrO2 catalyst for oxidative steam reforming of ethanol, indicating that addition of Rh improved the catalytic activity significantly by promoting water gas shift reaction.

Keywords: Oxidative steam reforming; Hydrogen production; Bio-ethanol; Rh promoted Ni/CeO2–ZrO2 catalyst; Catalyst characterization

Monica Dan, Maria Mihet, Zsolt Tasnadi-Asztalos, Arpad Imre-Lucaci, Gabriel Katona, Mihaela D. Lazar,

Hydrogen production by ethanol steam reforming on nickel catalysts: Effect of support modification by CeO2 and La2O3,

Fuel,

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https://doi.org/10.1016/j.fuel.2015.01.050.

(https://www.sciencedirect.com/science/article/pii/S0016236115000642)

Abstract: Ethanol steam reforming at low temperatures and high water:ethanol ratios was studied on Ni (8wt.%) catalysts deposited on CeO2 (6wt.%) or La2O3 (6wt.%) promoted alumina and zirconia supports. The catalysts were prepared by successive impregnation: first the rare earth oxide and then the Ni, and characterized by XRD, H2 chemisorption, TPR and H2-TPD. Promotion of both alumina and zirconia with CeO2 and La2O3 leads to changes in the Ni – support interaction resulting in much better dispersion and stabilization of the Ni nanoparticles on the catalyst surface. For La2O3 promoted catalysts 100% ethanol conversion was obtained in the experimental conditions used in this work, at temperatures as low as 300°C. The ethanol conversion was improved by the addition of CeO2 to zirconia supported catalyst, but was not significantly influenced by the addition of CeO2 to alumina supported one. A thermodynamic study of ethanol steam reforming was performed (CHEMCAD process simulator and Gibbs reactor with calculations based on free energy minimization), in order to find the thermodynamic equilibrium composition of reaction products in the particular experimental reaction conditions used in this work. The reaction products mixture at 350°C contains higher proportion of hydrogen and lower proportion of methane than the equilibrium concentration predicted by thermodynamic analysis. The best hydrogen yield was obtained for Ni/La2O3–ZrO2 catalyst. All catalysts except Ni/ZrO2 are stable in 24h time on stream experiments.

Keywords: Hydrogen; Ethanol steam reforming; CeO2 promoted catalysts; La2O3 promoted catalyst; Thermodynamic evaluation of ethanol steam reforming

Yi-Wei Wu, Wei-Chieh Chung, Moo-Been Chang,

Modification of Ni/γ-Al2O3 catalyst with plasma for steam reforming of ethanol to generate hydrogen,

International Journal of Hydrogen Energy,

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https://doi.org/10.1016/j.ijhydene.2015.04.053.

(https://www.sciencedirect.com/science/article/pii/S0360319915009416)

Abstract: Hydrogen provides clean energy when combusted since it is carbon-free. Generation of hydrogen via reforming of hydrocarbons is of high potential to power the fuel cell. Reforming of ethanol with the help of catalyst is viable due to abundant sources of ethanol. In this study, Ni/γ-Al2O3 is evaluated for its catalytic activity on steam reforming of ethanol. In the meantime, a dielectric barrier discharge (DBD) is used to pretreat Ni/γ-Al2O3 catalyst to enhance the catalytic activity and the resistance of coke formation. Results show that at a temperature of 710 K, the ethanol conversions achieved with untreated and plasma-treated catalysts are 68.0 and 88.6%, respectively. Ethanol conversion achieved with plasma treated catalyst reaches 96.2% with the carbon balance of 97% at 810 K, indicating that plasma treatment is an effective approach to enhance the catalytic activity and durability. Moreover, hydrogen yield reaches 320 mg/h gcat for plasma-treated catalyst and is 10% higher than that achieved with the untreated one.

Keywords: Steam reforming of ethanol; Hydrogen production; Ni-based catalyst; DBD

Sangho Lee, Minseok Bae, Joongmyeon Bae, Sai P. Katikaneni,

Ni–Me/Ce0.9Gd0.1O2−x (Me: Rh, Pt and Ru) catalysts for diesel pre-reforming,

International Journal of Hydrogen Energy,

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https://doi.org/10.1016/j.ijhydene.2014.12.113.

(https://www.sciencedirect.com/science/article/pii/S0360319914035447)

Abstract: In this paper, catalyst compositions and preparation methods of Ni–Me/Ce0.9Gd0.1O2-x (Me: Rh, Pt and Ru) are investigated for diesel pre-reforming. Ni loading is optimized with respect to catalytic activity and coke formation. Incipient wetness method and glycine nitrate process are compared for catalyst preparation. Rh, Pt and Ru are added to improve the catalytic stability. Micro-reactor test, temperature programmed oxidation and temperature programmed reduction are used to compare catalysts. The optimized composition of Ni–Me/Ce0.9Gd0.1O2−x is 19.5 wt.% Ni and 0.5 wt.% Ru on Ce0.9Gd0.1O2−x. Higher than 20 wt.% of Ni loading is limited by the coke formation. Ru helps coke oxidation at low temperature. Glycine nitrate process is superior to the incipient wetness method with respect to the catalysts stability. 2000 h of pre-reforming operation is carried out using the optimized catalyst. 70.6 mol% H2 and 4.7 mol% CH4 are produced in a stable manner.

Keywords: Diesel; Heavy hydrocarbons; Pre-reforming; Hydrogen; Methane rich syngas

J. Ashok, Y. Kathiraser, M.L. Ang, S. Kawi,

Bi-functional hydrotalcite-derived NiO–CaO–Al2O3 catalysts for steam reforming of biomass and/or tar model compound at low steam-to-carbon conditions,

Applied Catalysis B: Environmental,

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https://doi.org/10.1016/j.apcatb.2015.02.017.

(https://www.sciencedirect.com/science/article/pii/S0926337315000685)

Abstract: In this paper, the bi-functional properties of NiO–CaO–Al2O3 (Ni–Ca–Al) catalysts derived from hydrotalcite-like precursors were explored for steam reforming of toluene and biomass reactions. The influence of CO2 sorption property of NiO–CaO–Al2O3 catalysts was also explored by changing Ca/Al molar composition ratio for steam reforming reaction. The steam reforming of toluene reaction was investigated at low steam-to-carbon conditions (S/C=1). An optimum catalyst composition of Ni–Ca–Al(8:62:30) gave superior catalytic performance in terms of stability and activity in both the reforming reactions. At S/C value of 1, Ni–Ca–Al(8:62:30) catalyst displayed a stable toluene conversion of near 70% for a period of 24h tested in toluene reforming reaction. At 650°C, about 85% of biomass was converted to gaseous products over Ni–Ca–Al(8:62:30), which is the highest among all the catalysts tested. The XRD analysis of reduced and spent catalysts shows that the rate of agglomeration of active metallic Ni species over Ni–Ca–Al(8:62:30) catalyst is considerably lesser when compared to other catalysts. The TPR and XPS analyses reveals that the calcined and reduced Ni–Ca–Al catalysts are in Ca(Ni, Al)O solid solution form, respectively. CO2− TPD studies shows that the basicity of Ni–Ca–Al(8:62:30) catalyst is higher compared to other Ni–Ca–Al catalysts. The rate of carbon deposition over Ni–Ca–Al(8:62:30) catalyst during steam reforming of toluene reaction is 2.5mgCg−1h−1, which is also the lowest among all the catalysts. Hence, the low carbon deposition rate is one of the reasons for its stable catalytic performance compared to the rest.

Keywords: Hydrotalcite; Steam reforming; Biomass; Tars; NiO–CaO–Al2O3

Manoj Pudukudy, Zahira Yaakob, Mohd Sobri Takriff,

Methane decomposition over Pd promoted Ni/MgAl2O4 catalysts for the production of COx free hydrogen and multiwalled carbon nanotubes,

Applied Surface Science,

Volume 356,

2015,

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ISSN 0169-4332,

https://doi.org/10.1016/j.apsusc.2015.08.246.

(https://www.sciencedirect.com/science/article/pii/S016943321502070X)

Abstract: This article reports the synthesis, characterization and catalytic performance of Pd promoted Ni/MgAl2O4 spinel catalysts for the thermal decomposition of methane into hydrogen and carbon nanotubes. The as-synthesized catalysts were characterized for their structural, textural, morphological properties. The catalytic properties of the Ni/MgAl2O4 catalyst were found to be enhanced with Pd promoter. It effectively increased the surface area of the catalyst without affecting the pore parameters and improved the fine dispersion of NiO particles on the surface of the magnesium aluminate. The reduction temperature of Ni/MgAl2O4 was found to be lowered after Pd deposition. Moreover, the Pd promoted catalyst provided high catalytic activity and stability for methane decomposition. A maximum hydrogen yield of ∼57% was obtained over the Pd catalyst at a reaction temperature of 700°C without any deactivation for 420min of time on stream. Moreover highly uniform, interwoven and thin multi-walled carbon nanotubes with high graphitization degree were deposited over the catalysts.

Keywords: Hydrogen; Methane decomposition; Magnesium aluminate; Palladium; Multiwalled carbon nanotubes

Tarak Mondal, Kamal K. Pant, Ajay K. Dalai,

Oxidative and non-oxidative steam reforming of crude bio-ethanol for hydrogen production over Rh promoted Ni/CeO2-ZrO2 catalyst,

Applied Catalysis A: General,

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ISSN 0926-860X,

https://doi.org/10.1016/j.apcata.2015.04.004.

(https://www.sciencedirect.com/science/article/pii/S0926860X15002379)

Abstract: The catalytic oxidative and non-oxidative steam reforming of crude bio-ethanol for hydrogen production was studied in a tubular fixed bed reaction system over 30wt.%Ni/CeO2-ZrO2 and 1wt.%Rh-30wt.%Ni/CeO2-ZrO2 catalysts. The catalysts were prepared by impregnation-co-precipitation method and characterized by BET, XRD, TPR, TGA, XPS, XANES and EXAFS techniques. Characterization results revealed that the addition of Rh promotes reducibility of NiO at lower temperature for the bimetallic catalysts. Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) analysis depicted that NiO with 6-fold local co-ordination is present in all the samples. Ethanol conversion, hydrogen yield and product selectivity were investigated at 600°C and space time of 9.17kgcath/kgmol[EtOH]) at atmospheric pressure. In steam reforming of crude bio-ethanol, 81% ethanol conversion was achieved with 59% hydrogen selectivity on Ni/CeO2-ZrO2 catalyst, whereas, higher ethanol conversion (86%) with 73% hydrogen selectivity was achieved using Rh-Ni/CeO2-ZrO2 catalysts. In oxidative steam reforming of crude bio-ethanol, hydrogen yield and selectivity reduced due to the partial oxidation of oxygenate compounds present in the feed. The used catalysts were also analysed by BET, TGA/DTA, TPR, TPO, Raman spectroscopy, SEM, and TEM techniques to identify the cause of catalyst deactivation. The results indicate that the catalyst deactivation occurred mainly due to amorphous and filamentous carbon deposition on the catalysts surface, due to the presence of the impurities in the feed.

Keywords: Steam reforming; Crude bio-ethanol; Rh promoted Ni/CeO2-ZrO2 catalyst; Catalyst deactivation; Carbon deposition

Chuanmin Ding, Ganggang Ai, Kan Zhang, Qinbo Yuan, Yulin Han, Xishun Ma, Junwen Wang, Shibin Liu,

Coking resistant Ni/ZrO2@SiO2 catalyst for the partial oxidation of methane to synthesis gas,

International Journal of Hydrogen Energy,

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(https://www.sciencedirect.com/science/article/pii/S0360319915007156)

Abstract: Carbon deposition, which may reduce the number of active sites or remove metal particles from the catalyst surface, is an urgent issue for the partial oxidation of methane (POM) to synthesis gas. To solve this problem, Ni/ZrO2@SiO2 catalysts were prepared by a modified Stöber method. The investigation was focused mainly on the role of ZrO2 addition and mesopore silica shell in preventing carbon deposition. The structural properties and carbon deposition of catalysts were characterized by XRD, TEM, N2 adsorption and TG techniques. The oxygen transfer capacity and reducibility of catalysts were evaluated by oxygen storage capacity (OSC) and temperature programmed reduction (TPR). Inspiringly, the Ni/ZrO2@SiO2 catalyst was proved to be more active and possessed less carbon deposition due to the higher reducibility and oxygen storage/release capacity. Importantly, compared with the support catalysts, the catalysts coated by mesopore silica shell showed exceptional resistance to coking, because the edge and corner atoms favor to carbon deposition were selectively blocked by silica shell, in addition, the size of the pore channel prevented growth up of carbon filament.

Keywords: Partial oxidation of methane; Carbon deposition; Silica shell; Synthesis gas

Yi Shen, Aik Chong Lua,

Synthesis of Ni and Ni–Cu supported on carbon nanotubes for hydrogen and carbon production by catalytic decomposition of methane,

Applied Catalysis B: Environmental,

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https://doi.org/10.1016/j.apcatb.2014.08.038.

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Abstract: Nickel and nickel–copper alloy supported on carbon nanotubes (CNTs) were examined as catalysts for hydrogen production by methane decomposition. The Ni/CNT and Ni–Cu/CNT catalysts were characterized using field emission scanning electron microscopy, energy dispersive X-ray microscopy, transmission electron microscopy and X-ray diffraction. The performance of the catalysts was dependent on the catalyst composition and reaction temperature. The Ni78Cu22/CNT catalyst exhibited the excellent catalytic performance with a stable methane conversion of 0.8 at 700°C, a carbon yield rate of 0.08gC/(mingNi) at 743°C and a carbon yield of 602gC/gNi at 700°C. Carbon materials with various morphologies, i.e., herringbone carbon nanofibers (CNFs), platelet CNFs, bamboo-shaped CNFs, branched CNFs, multi-branched CNFs and onion-like carbons, depending on the catalyst composition and reaction temperature, were obtained. The morphology of the produced carbon material was correlated with the growth mechanism of the carbon material on the catalyst.

Keywords: Hydrogen production; Catalytic decomposition of methane; Ni–Cu/CNT catalyst; Carbon morphology

Haibo Zhao, Lei Guo, Xixian Zou,

Chemical-looping auto-thermal reforming of biomass using Cu-based oxygen carrier,

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Abstract: Chemical-looping reforming (CLR) of biomass, which utilizes active lattice oxygen from oxygen carrier (OC), provides a novel route to convert biomass into synthesis gas. This research utilized Cu-based OC rather than commonly-used Fe- or Ni-based OC in the process. The possible advantage is the exothermic reactions between CuO and gasification products are beneficial to auto-thermal reforming of biomass in fuel reactor. Batch fluidized bed experiments with different carriers (silica sand, Fe-based or Cu-based OCs) were conducted at different temperatures. It was found that when using Cu-based OCs, the gas yield and carbon conversion efficiency increased significantly, but the gasification efficiency and low heating value decreased accordingly, which are ascribed to the high-reactivity Cu-based OCs prompt the carbon conversion and also consume more reducible gases. The presence of Cu-based OCs help reduce C2Hm and tar in syngas. Additionally, the tar content decreased with temperature increase, while C2Hm content first increased then decreased.

Keywords: Biomass; Synthesis gas; Chemical looping reforming; Copper oxide oxygen carrier; Fluidized bed reactor

Andrea Di Carlo, Domenico Borello, Mario Sisinni, Elisa Savuto, Paolo Venturini, Enrico Bocci, Koji Kuramoto,

Reforming of tar contained in a raw fuel gas from biomass gasification using nickel-mayenite catalyst,

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Abstract: Catalytic steam reforming of tar is a very efficient process to clean the gas produced by biomass gasification. Ni catalysts remain an affordable solution for this problem, even if this catalytic material suffers degradation due to carbon deposition and sulphur poisoning. In this study, the properties of a new catalyst Ni/Mayenite (Mayenite as binder), prepared by impregnation method and tested with a real gas obtained from a bench scale fluidized bed steam gasification of biomass, were investigated. Experiments were carried out in a microreactor fed by a slipstream coming from the bench scale gasifier to evaluate gas cleaning and upgrading options. Preliminary tests were carried out at three different temperatures, 700, 750 and 800 °C. In all the tests, the catalysts showed high activities reaching to a conversion rate of 90% in the case at highest temperature (800 °C). The conversion efficiency remained stable around this value during a 3 h test. A decrease in the performance was observed at 700 and 750 °C, even if the conversion remained stable around a lower value. An increase of H2 (>50%) and a decrease of CH4 were observed at all the temperatures, due to the occurrence of steam reforming reaction. A long duration test (12 h) was carried out at 800 °C and demonstrated that, at this temperature, the conversion was stable for a longer period.

Keywords: Biomass gasification; Tar; Steam reforming catalyst; Fluidized bed