



ELSEVIER

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com



International Symposium on Air & Water Pollution Abatement Catalysis (AWPAC) – Catalysis for renewable energy

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



Matériaux Ni–Al dérivés des hydrotalcites comme catalyseurs pour le reformage à sec du méthane à basse température

Radosław Dębek^{a,b,*}, Katarzyna Zubek^a, Monika Motak^a, Maria Elena Galvez^{b,c}, Patrick Da Costa^{b,c}, Teresa Grzybek^a

^a AGH University of Science and Technology, Faculty of Energy and Fuels, Al. A. Mickiewicza 30, 30-059 Cracow, Poland

^b Université Paris-6, UPMC, Sorbonne Universités, Institut Jean-Le-Rond-d'Alembert, 2, place de la Gare-de-Ceinture, 78210 Saint-Cyr-l'École, France

^c Institut Jean-Le-Rond-d'Alembert, UMR CNRS 7190, 2, place de la Gare-de-Ceinture, 78210 Saint-Cyr-l'École, France

ARTICLE INFO

Article history:

Received 17 December 2014

Accepted after revision 9 April 2015

Available online 26 October 2015

Keywords:

Dry reforming

Methane

CO₂

Hydrotalcite

Nickel

ABSTRACT

Nickel–aluminium and magnesium–aluminium hydrotalcites were prepared by coprecipitation 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). DRM 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.

© 2015 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

1. Introduction

Dry reforming of methane (DRM) has been lately considered as an outstanding alternative process for the production of synthesis gas, having several advantages over the conventional route, i.e. steam reforming. DRM produces a syngas with a H₂/CO molar ratio of around 1, suitable for Fischer–Tropsch synthesis, for methanol or dimethyl ether synthesis. Moreover, DRM offers an

interesting option for the valorisation of CO₂ streams and its conversion into fuels and/or chemicals [1,2]. However, there are still important barriers to overcome in view of the practical application of DRM, such as its high endothermicity and the lack of an active and long-term stable catalyst [3].

Research on the catalysts for dry methane reforming has been focused lately on nickel-based catalysts on suitable supports, since this transition metal shows an activity similar to that of noble ones, but is less costly and more available [3–5]. However, the problem of catalyst deactivation remains to be solved [6,7], and research efforts are directed towards the finding of support materials that lead to an improved catalyst stability. In

* Corresponding author at: AGH University of Science and Technology, Faculty of Energy and Fuels, Al. A. Mickiewicza 30, 30-059 Cracow, Poland.
E-mail address: debek@agh.edu.pl (R. Dębek).

this sense, hydrotalcites have been recently presented as promising catalyst precursors leading to enhanced catalytic performance with respect to traditional nickel-supported catalysts [8–11].

Hydrotalcite is a naturally occurring mineral, which has a layered structure and chemical formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$. The name hydrotalcite or layered double hydroxides (LDH) is also used to describe a large group of materials, in which the Mg^{2+} and Al^{3+} ions are replaced by some other di- and trivalent cations, with ionic radii similar to those of magnesium and aluminium [12,13]. The mixed oxides obtained after thermal decomposition of hydrotalcites exhibit several properties, which are beneficial to the DRM reaction, such as:

- high surface area;
- basic character;
- the fact that di- and trivalent cations are randomly distributed in hydrotalcite layers, leading to a homogeneous mixture of oxides [13,14].

For example, ceria-promoted Ni/Mg/Al mixed oxides obtained from coprecipitated hydrotalcite materials were found to be very active at 800 °C for the DRM reaction [8]. Gonzalez et al. [9] found an optimal Ni loading at around 19 wt. % for similar materials. In both cases, the mixed oxides were obtained from the thermal decomposition of hydrotalcites with different $\text{Ni}^{2+}/\text{Mg}^{2+}$, $\text{M}^{2+}/\text{M}^{3+}$ molar ratios [10,15]. However, to date, no information on the behaviour of simple Ni/Al mixed oxides obtained from hydrotalcites in the DRM reaction has been yet reported. Moreover, the materials presented so far in the existing literature are active only in the high-temperature range. On the other hand, they have been reported to show high catalytic activity in the CH_4 decomposition reaction at 550 °C [16,17,19], so that such materials should show good performance in the DRM process.

The aim of this work is therefore to synthesize and characterize two different hydrotalcite-derived materials:

- synthetic Mg–Al hydrotalcite and derived material with a chemical composition similar to that of naturally occurring mineral;
- Ni–Al hydrotalcite, and derived material with an $\text{M}^{2+}/\text{M}^{3+}$ molar ratio equal to 4–, to evaluate their activity towards DRM at low temperature, i.e. from 550 to 750 °C.

The goal is to evaluate the catalytic performance of these mixed oxides systems with high nickel content and a composition similar to that of an Ni/NiO traditional alumina or of a silica-supported catalyst.

2. Experimental

2.1. Catalyst preparation

Hydrotalcite-like materials containing magnesium and aluminium (HT-MgAl) or nickel and aluminium (HT-NiAl) in their brucite-like layers were synthesized through a

co-precipitation method. The solution of appropriate metal nitrates [$\text{Mg}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$ – Acros Organics, $\text{Al}(\text{NO}_3)_3$ – Chempur] and 1M NaOH (POCH) were added dropwise to a 0.05 M solution of sodium carbonate (POCH), under continuous stirring and at a fixed pH of 10 ± 0.2 . The co-precipitation was carried out at 60 °C. The obtained suspension was subsequently aged at 60 °C for 1 h under stirring, then filtered. The remaining solid was carefully washed with distilled water and then dried overnight at 80 °C. The so-prepared materials were finally calcined at 550 °C for 4 h under air.

2.2. Physicochemical characterization

Elemental analyses were performed by means of ICP-OES (SCA-CNRS facilities) in order to determine the Ni, Mg and Al contents in the different materials. X-ray diffraction (XRD) patterns were acquired in an Empyrean diffractometer from PANalytical, in the 2θ range 8–80° using a Cu X-ray source ($\lambda = 1.5046 \text{ \AA}$). Textural properties were evaluated from the N_2 adsorption isotherms acquired at –196 °C in a Belsorp Mini II equipment. Prior to each measurement, the samples were outgassed at 120 °C for 3 h. Temperature-programmed reduction (TPR) profiles were recorded with a BELCAT-M apparatus from BEL Japan, equipped with a thermal conductivity detector (TCD). The samples (50 mg) were first degassed at 100 °C for 2 h, then reduced at 7.5 °C/min using 5% H_2 in Ar.

2.3. Catalytic tests

The activity towards DRM of the synthesized hydrotalcite-derived materials was tested in a fixed-bed reactor. Prior to the experiments, each catalyst was reduced with hydrogen (3% H_2 in argon) at either 900 or 550 °C. In the first series of experiments, catalytic tests were carried out at 550 °C for 1 h with the substrate molar ratio $\text{CH}_4/\text{CO}_2/\text{Ar} = 2/1/7$ and GHSV equal to 20,000 h^{-1} . The total gas flow was equal to 100 cm^3/min . The products of the reaction were analyzed by gas chromatography (490 Varian MicroGC). In the second series of experiments, the nickel-containing sample was tested at 750, 700, 650, 600 and 550 °C for 1 h, while the other reaction conditions were unchanged. Additionally, the 4-h tests were carried out for the HT-NiAl catalyst at 550 and 700 °C. The reaction of methane decomposition at 550 °C was also investigated using a mixture of CH_4 in Ar as a feed gas ($\text{CH}_4/\text{Ar} = 2/8$).

3. Results and discussion

3.1. Textural, structural and chemical features of the hydrotalcite-derived materials

The XRD patterns for the different materials are presented in Fig. 1. The materials before calcination (Fig. 1A) exhibit three diffraction peaks at 11.4, 22.8 and 34.5°, characteristic of the hydrotalcite structure, respectively corresponding to the (003), (006) and (009) symmetry planes [14]. Based on the position of these reflections, the parameter c of the unit cell was calculated.

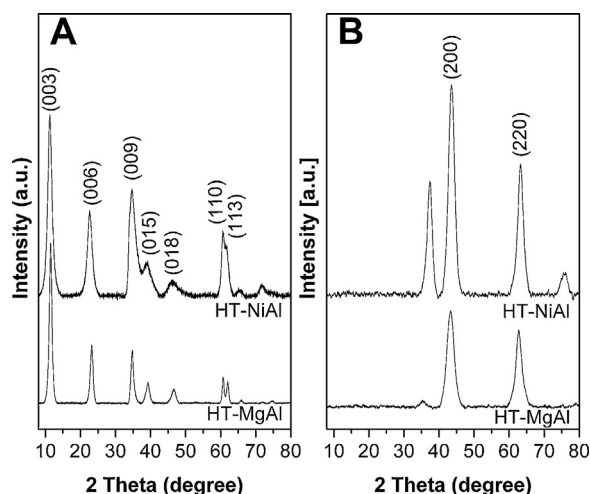


Fig. 1. X-ray patterns of fresh (A) and calcined (B) materials.

The diffraction corresponding to the (110) plane was used to calculate the parameter a of the unit cell. The values of these cell parameters are shown in Table 1. The parameter a for all catalysts was equal to 3.06 Å, which indicates that the average cation–cation distance in brucite-like layers of synthesized hydrotalcites remained unaltered, pointing to a successful incorporation of nickel cations into the brucite-like layers. Parameter c' , calculated from parameter c , which depended on the distances between the layers in the hydrotalcite structure, indicates the presence of carbonate and/or nitrate anions in the interlayer space of hydrotalcites [12].

The X-ray patterns of the calcined hydrotalcite materials, shown in Fig. 1B, present two main diffraction peaks at around 43.5 and 63°, which correspond to the (200) and (202) reflections of the periclase-like structure. This structure is typical of nano-oxides originating from the calcination of hydrotalcite-like materials under mild temperature conditions. The sample HT-NiAl also shows two intense reflections at around 37 and 76°. Both may be ascribed to nickel–aluminium mixed oxides [14].

The TPR profiles for calcined hydrotalcites are depicted in Fig. 2. No reduction peak can be observed for HT-MgAl hydrotalcite-derived material, since Ni is not present in its composition. In the case of the HT-NiAl catalyst, one wide and asymmetric reduction peak with a maximum at 553 °C is observed, arising from the reduction of bulk and surface nickel (II) species [18,19].

The values of the BET surface area, of the pore volume, and the mean pore diameter, calculated from the N_2

Table 1

Unit cell parameters for the hydrotalcite-derived materials, calculated from their respective XRD patterns.

Material	a (Å)	c (Å)	$c' = c/3$ (Å)
HT-MgAl	3.06	23.1	7.7
HT-NiAl	3.06	23.4	7.8

HT: hydrotalcite; Mg: magnesium; Al: aluminium; Ni: nickel.

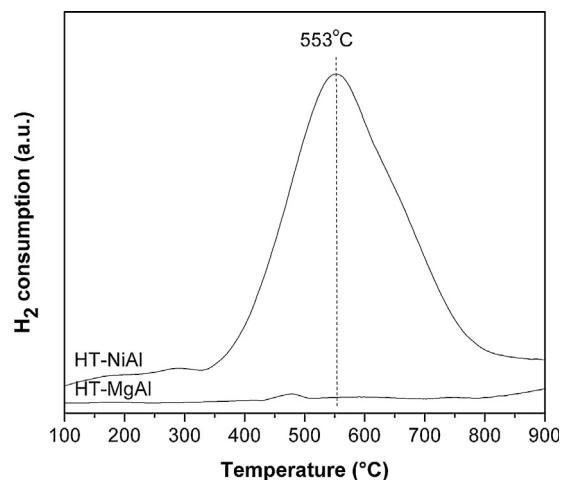


Fig. 2. H_2 -temperature-programmed reduction (TPR) profiles recorded for calcined hydrotalcite-derived materials.

adsorption isotherms, are presented in Table 2. Both materials HT-MgAl and HT-NiAl possess surface areas of around 125 m^2/g , in agreement with the data reported in the literature for similar hydrotalcite-derived oxides [8,11]. Let us note here that, according to the IUPAC classification, the adsorption isotherms for both materials were of type IV, with a H3 hysteresis loop, typical of mesoporous materials [20]. Ni loading, i.e. the substitution of Mg^{2+} by Ni^{2+} cations in the brucite-like layers, results in a decrease in the total pore volume, pointing to a certain extent of pore blockage. However, the surface area slightly increases as a consequence of the decrease in the mean pore diameter upon Ni introduction.

The results of elemental analysis are also shown in Table 2. An Mg/Al molar ratio around 2.7 in HT-MgAl is close to the nominal value assumed during preparation (Mg/Al = 3), and similar to that in naturally occurring minerals. In the case of HT-NiAl, the molar ratio of Ni/Al was equal to 3.76, also close to the nominal value of 4.

3.2. Activity and selectivity towards DRM

Methane conversion and CO_2 conversion measured during DRM experiments in the presence of the two hydrotalcite-derived materials at a temperature of 550 °C are depicted in Fig. 3A and B. As could be expected, the hydrotalcite-derived material HT-MgAl is not able to convert either CH_4 or CO_2 . However, at a temperature as low as 550 °C, the Ni-containing hydrotalcite-derived material HT-NiAl is able to convert 48 and 54% of CH_4 ,

Table 2

Elemental analysis and textural properties of the hydrotalcite-derived materials.

Material	Mg (%)	Ni (%)	Al (%)	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	d_{mean} (nm)
HT-MgAl	37.4	–	14.2	124	0.53	17
HT-NiAl	–	63.5	7.7	129	0.41	13

HT: hydrotalcite; Mg: magnesium; Al: aluminium; Ni: nickel.

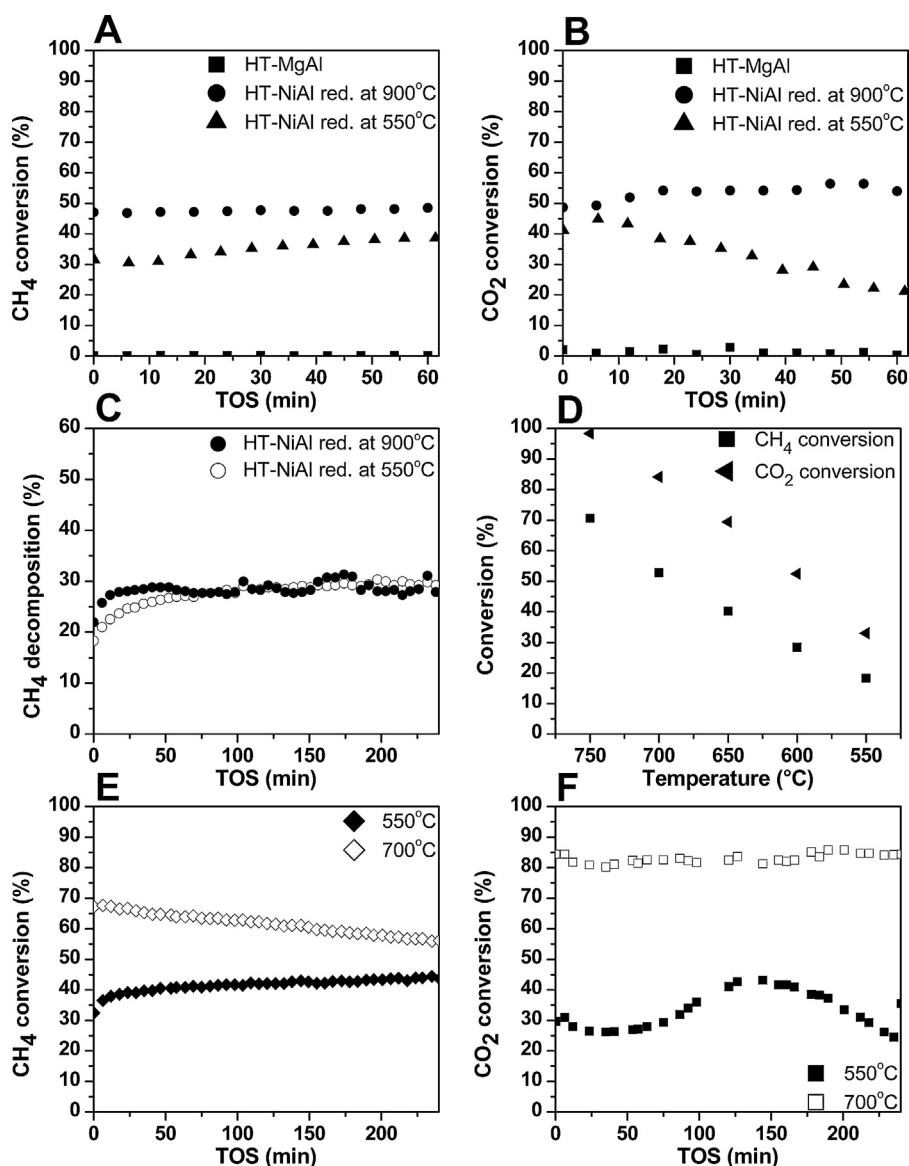


Fig. 3. Results of catalytic experiments: (A) CH₄ conversion and (B) CO₂ conversion in dry reforming of methane (DRM) at 550 °C; (C) direct CH₄ decomposition: CH₄ conversion in the temperature range 750–550 °C; (D) CO₂ and CH₄ conversion for DRM experiments in the temperature range 750–550 °C; (E) CH₄ conversion and (F) CO₂ conversion, through a 4-h DRM experiment at 550 and 700 °C.

depending on the temperature chosen for the reduction pre-treatment prior to the reaction. In this sense and at 550 °C, a reduction temperature of 900 °C seems to be beneficial to an increase in catalytic activity. On the other hand, the activation of the catalyst at 550 °C is not sufficient to reduce all of the nickel species to a metallic form. Moreover, the sharp decrease in CO₂ conversion observed for the catalyst pre-treated at 550 °C points to its fast deactivation. The spent HT-NiAl sample reduced at 900 °C was examined by XRD experiments after the DRM reaction (results not shown). The XRD diffractogram showed the presence of three phases: metallic nickel, graphitic carbon, and periclase-like mixed oxides. The presence of a spinel phase was not detected, thus the better performance of the Ni/Al catalysts reduced at 900 °C

with respect to the one activated at 550 °C can be attributed to the “deeper” reduction of nickel species, which was confirmed also by the H₂-TPR experiment.

Meaningful information on the selectivity of the catalysts towards DRM can be obtained through the evaluation of the H₂/CO molar ratio in the gas produced in the reaction. In general and under these conditions, the average value for a 1-h experiment was equal to 2.43, which is far from the expected equimolar mixture of H₂ and CO, and strongly suggests the occurrence of side reactions [3]. Since an excess of H₂ was observed, the most probable side reaction is CH₄ decomposition. This hypothesis was confirmed through tests with only methane as the feed gas over the HT-NiAl sample. The results of this methane decomposition experiment are presented in

Fig. 3C. The catalysts reduced at 550 and 900 °C showed both ca. 30% conversion of methane. This indicates that methane decomposition strongly influences the overall process. Moreover, the direct decomposition and conversion of CH₄ is not influenced by the temperature of the catalyst's pre-treatment. Rivas et al. [19] tested hydrothermalite-derived Ni/Al mixed oxides in the CH₄ decomposition reaction. The high activity of these materials was explained by the strong interaction of Ni species with alumina, which inhibits sintering of the active phase. Moreover, the presence of the graphic form of carbon on the spent catalyst stays in line with the results reported for Ni/Al hydrothermalite-derived mixed oxides tested in the decomposition reaction of CH₄ [16,17,19].

The results of catalytic DRM experiments performed in the temperature range from 550 to 750 °C for sample HT-NiAl activated at 900 °C are presented in Fig. 3D. The CH₄ and CO₂ conversion rates depicted in Fig. 3D were measured under steady-state conditions. The values of CH₄ and CO₂ conversion rates are respectively 70% and 95% at 750 °C. The higher conversion rate of CO₂ with respect to that of CH₄ is due to the excess of CH₄ in the feed gas. It must be noted here that in these tests, carried out under programmed temperature conditions, i.e. starting at 750 °C and cooling down to each temperature until 550 °C, the conversion of CH₄ and CO₂ registered at 550 °C was lower than for the isothermal experiment at 550 °C. This is most probably due to structural and phase changes in the material induced by its initial heating at 750 °C, e.g., the formation of a spinel phase or sintering of Ni crystallites. The values of the H₂/CO molar ratio registered during these programmed temperature experiments point to a slight excess of hydrogen in the products of the reaction, see Fig. 4. However, the H₂/CO values are much lower with respect to the tests carried out under isothermal conditions at 550 °C, with an average value of ca. 1.4 at 750 °C. The H₂/CO molar ratio decreases with temperature and reaches values of around 1 at 650, 600, and 550 °C. This also indicates that at higher temperature a different reaction mechanism is involved, which results in different product distributions. The value around 1 at 550 °C suggests that

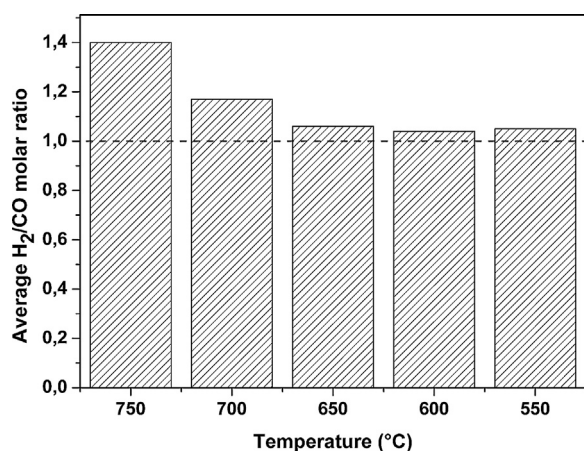


Fig. 4. H₂/CO ratios measured during the temperature-programmed experiments, in the range 750–550 °C.

CH₄ decomposition does not influence the overall process to a large extent, when the catalyst is first tested at 750 °C. Moreover, the values of H₂/CO around 1 may arise from the compatibility of CH₄ decomposition with the carbon gasification reaction (Boudouard reaction).

Fig. 3E and F report the results of catalytic stability on the HT-NiAl hydrothermalite-derived material, during 4-h DRM experiments performed at 550 and 700 °C. The conversions of CH₄ and CO₂ are higher when the reaction is carried out at 700 °C. However, methane conversion drastically decreases with time. The opposite situation can be observed for tests carried out at 550 °C, confirming faster catalyst deactivation at higher temperatures. Moreover, the average values of the H₂/CO molar ratio registered at 700 and 550 °C were equal to ca. 1.6 and 2.3, respectively. Therefore, CH₄ decomposition seems to strongly influence the DRM reaction at moderate temperatures, while at 700 °C, the process is most probably mostly affected by the simultaneous occurrence of the RWGS and Boudouard reactions.

4. Conclusions

In the present work, two hydrothermalite-derived materials were synthesized and tested as catalysts for the dry reforming of methane. Before their calcination, the synthesised materials showed the typical hydrothermalite layered structure. After calcination, the tested materials exhibited a periclase-like structure of mixed oxides. The nickel-containing hydrothermalite-derived material, HT-NiAl, was active in the DRM reaction at 550 °C, with average values of CH₄ and CO₂ conversions around 48 and 54%, when the material was pre-treated in H₂ at 900 °C. Pre-treatment at 550 °C was not effective enough to reduce all the NiO species to metallic nickel and resulted in lower conversions of methane and CO₂.

Temperature-programmed DRM experiments (in the sequence 750, 700, 650, 600 and 550 °C), showed that the catalysts' activity decreases with the reaction temperature. The hydrothermalite material HT-NiAl underwent several structural changes when first heated to 750 °C, which resulted in different conversions and product distribution than those measured in the isothermal experiment at 550 °C.

During the 4-h-duration DRM experiments, the catalyst HT-NiAl showed better performance at 700 °C than at 550 °C. However, at the former temperature, deactivation was faster than in the experiment performed at 550 °C. In any case, the results obtained evidence that hydrothermalite-derived materials are promising catalysts for the dry reforming of methane reaction at low temperatures (550–750 °C).

Acknowledgements

R. Dębek acknowledges for financial support the International Group of Research (GDRI) "Catalysis for polluting emissions after treatment and production of renewable energies" and the French Embassy in Poland. This work was also funded by the National Centre for Research and Development, Poland, in the framework of

the strategic project “Technologies Supporting Development of Safe Nuclear Power Engineering”, task “Development of high-temperature reactors for industrial purposes (HTRPL)”, grant number SP/J/1/166183/12, step task No. 15, ‘Preparation and physicochemical characterization of catalysts for dry reforming of methane’.

References

- [1] K. Asami, X.H. Li, K. Fujimoto, Y. Koyama, A. Sakurama, N. Kometani, Y. Yonezawa, *Catal. Today* 84 (2003) 27.
- [2] G. Centi, S. Perathoner, *Catal. Today* 148 (2009) 191.
- [3] Y.H. Hu, E. Ruckenstein, *Adv. Catal.* 48 (2004) 297.
- [4] A. Albarazi, P. Beaunier, P. Da Costa, *Int. J. Hydrogen Energy* 38 (2013) 127.
- [5] J. Nakamura, K. Aikawa, K. Sato, T. Uchijima, *Catal. Lett.* 25 (1994) 265.
- [6] Z.L. Zhang, V.A. Tsipouriari, A.M. Efstathiou, X.E. Verykios, *J. Catal.* 158 (1996) 51.
- [7] A.M. Efstathiou, A. Kladi, V.A. Tsipouriari, X.E. Verykios, *J. Catal.* 158 (1996) 64.
- [8] C.E. Daza, S. Moreno, R. Molina, *Int. J. Hydrogen Energy* 36 (2011) 3886.
- [9] A.R. Gonzalez, Y.J.O. Asencios, E.M. Assaf, J.M. Assaf, *Appl. Surf. Sci.* 280 (2013) 876.
- [10] Z.Y. Hou, T. Yashima, *Appl. Catal., A-Gen.* 261 (2004) 205.
- [11] A.I. Tsyganok, T. Tsunoda, S. Hamakawa, K. Suzuki, K. Takehira, T. Hayakawa, *J. Catal.* 213 (2003) 191.
- [12] F. Cavani, F. Trifiro, A. Vaccari, *Catal. Today* 11 (1991) 173.
- [13] C. Forano, U. Costantino, V. Prévot, C. Taviot Gueho, in: F. Bergaya, B.K.G. Theng, G. Lagaly (Eds.), *Handbook of Clay Science*, Elsevier, Amsterdam, London, 2006, p. xxi.
- [14] V. Rives, *Mater. Chem. Phys.* 75 (2002) 19.
- [15] O.W. Perez-Lopez, A. Senger, N.R. Marcilio, M.A. Lansarin, *Appl. Catal., A-Gen.* 303 (2006) 234.
- [16] R. Guil-Lopez, V. La Parola, M.A. Pena, J.L.G. Fierro, *Int. J. Hydrogen Energy* 37 (2012) 7042.
- [17] J. Ashok, M. Subrahmanyam, A. Venugopal, *Int. J. Hydrogen Energy* 33 (2008) 2704.
- [18] O. Clause, L. Bonneviot, M. Che, *J. Catal.* 138 (1992) 195.
- [19] M.E. Rivas, J.L.G. Fierro, R. Guil-Lopez, M.A. Pena, V. La Parola, M.R. Goldwasser, *Catal. Today* 133 (2008) 367.
- [20] G. Leofanti, M. Padovan, G. Tozzola, B. Venturelli, *Catal. Today* 41 (1998) 207.