Bulgarian Chemical Communications, Volume 47, Special issue C (pp. 66–72) 2015

Purification of hydrogen-rich streams from CO_2 by methanation

M. V. Gabrovska[1]*, R. M. Edreva-Kardjieva[1], M. G. Shopska[1], D. A. Nikolova[1],
L. P. Bilyarska[1], D. Crişan[2], M. Crişan[2]

[1]*Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St. Bldg. 11, 1113 Sofia, Bulgaria*
[2]*Ilie Murgulescu Institute of Physical Chemistry, Romanian Academy, 202 Splaiul Independentei St.,*
060021 Bucharest-12, Romania

Received: September 12, 2015; Revised December 14, 2015

Magnesium effect on structure and activity of coprecipitated Ni-Al layered double hydroxides as catalyst precursors for purification of hydrogen-rich streams from CO_2 by methanation was examined. Various M^{2+}/Al^{3+} ($M^{2+} = Ni^{2+}$, $Ni^{2+}+Mg^{2+}$) molar ratios (1.5 and 3.0), reduction and reaction temperatures as well as gas hourly space velocities (GHSV) were applied. Magnesium content was identical, at the expense of nickel, in both modified samples.

All catalysts prepared by reduction at 400, 450, 530, or 600°C hydrogenated carbon dioxide successfully to 0–10 ppm levels at reaction temperatures in the range of 400–320°C and GHSV from 3000 to 22000 h^{-1}. Highly loaded nickel catalysts (3.0NiAl and 3.0NiMgAl) manifested a tendency to be more active than low loaded materials (1.5NiAl and 1.5NiMgAl).

At lower reaction temperatures (280 and 260°C) after reduction at 400 and 450°C, non-modified 3.0NiAl and 1.5NiAl catalysts' activity was attributed to larger specific surface areas and smaller particle sizes of metal nickel (higher Ni dispersion). Further treatment of the catalysts at 530 and 600°C induced sintering of the nickel metal particles, thus leading to a decrease of methanation activity.

The Mg-containing catalysts had the advantage of preserving nickel metal dispersion after reduction above 500°C due to a retarding effect on Ni sintering.

The Mg-modified highly loaded Ni catalyst (3.0NiMgAl) can be recommended as a suitable material for deep CO_2 removal from hydrogen-rich gas streams through the methanation reaction at low temperatures, such as 240 and 220°C.

Keywords: Ni-Al layered double hydroxides, Mg modifier, CO_2 removal by methanation

INTRODUCTION

Coal conversion and utilization technologies are gaining considerable attention because of increasing prices and demand of oil. Synthetic natural gas (SNG) production from coal is considered promising for obtaining valuable gaseous fuel with high combustion efficiency and environment friendliness [1–5]. The methanation reaction represents a key step in coal-to-SNG production, where the catalytic hydrogenation of carbon oxides (CO and CO_2) provides an efficient alternative to conventional natural gas [6].

The hydrogenation of carbon dioxide to methane, also called the Sabatier reaction or methanation, can be used as a particularly promising technique for purification of H_2-rich streams from traces of CO_2 to prevent catalyst poisoning especially in the fuel cell anode technology and ammonia synthesis industry [7−11]. The methanation reaction is commonly applied in ammonia plants at the final stage of purification of the synthesis gas in which low-concentration carbon monoxide and carbon dioxide (0.1–0.5%) are catalytically removed. The reaction is of crucial importance due to the poisonous effect of carbon oxides on ammonia synthesis [8].

Although many metals such as Ni, Co, Fe, Ru, Rh, etc., supported on various oxide carriers (e.g., SiO_2, TiO_2, Al_2O_3, ZrO_2, and CeO_2) have been used to catalyse the reaction, nickel and ruthenium are the most effective [11]. Nickel catalysts have been extensively investigated because of the metal availability and economic considerations. With regard to this, industrial methanation catalysts are essentially based on metal nickel demonstrating high activity, selectivity toward methane formation in preference to other hydrocarbons, high thermal stability, and relatively low cost [7, 12, 13].

Methanation catalysts are exposed to extreme conditions owing to the highly exothermic nature of the CO_2 methanation reaction and the fact that steam is one of the reaction products: $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$, $\Delta H_{300°C} = -175.4$ kJ.mol^{-1} [7]. Overheating, sintering, and deactivation of the catalysts occur due to nickel crystallite growth with resultant reduction of the active nickel surface area. These phenomena require usage of mechanically and

---

* To whom all correspondence should be sent
E-mail: margo@ic.bas.bg

thermally stable supports such as stable to sintering alumina.

A major requirement in manufacturing Ni/Al_2O_3 catalysts is the catalyst to be sufficiently active to ignite the reaction at low temperatures, i.e. to contain a relatively large portion of nickel metal, usually over 60 wt.%. Ni-Al layered double hydroxides (LDHs) with takovite-like (TKl) structure can be obtained from Ni and Al salts at Ni^{2+}/Al^{3+} molar ratios between 1.0 and 5.6 in the fresh precipitates corresponding to 59.5–88.0 and 40.5–12.0 wt.% of NiO and Al_2O_3, respectively, as it has been documented in Ref. 14. In our recent study [15], we specified that Ni-Al LDHs with TKl structure are effective catalyst precursors for complete CO_2 removal from hydrogen-rich gas stream by methanation reaction.

Ni-Al LDHs belong to a great group of natural and synthetic inorganic lamellar compounds with a chemical composition of general formula $[Ni^{2+}_{1-x}Al^{3+}_{x}(OH)_2]^{x+}[A^{n-}_{x/n}]\cdot mH_2O$, where Ni^{2+} and Al^{3+} ions are located in the brucite-like hydroxide layers. Charge compensating exchangeable anions (A^{n-}) such as CO_3^{2-}, NO_3^{-}, SO_4^{2-}, Cl^{-}, etc. as well as water molecules are situated in the interlayer space of the layered structure. Here, x represents the fraction of Al^{3+} cations, and m is the number of water molecules. Ni-Al layered systems represent promising catalysts due to their high specific surface area, good distribution of both Ni^{2+} and Al^{3+} ions despite the high content of Ni^{2+} ions, high metal dispersion after reduction, and small crystallite size. A wide variety of M^{2+} or M^{3+} cations may be incorporated or replaced at the octahedral sites of the brucite-type sheets by other entities having similar ionic radius, thus forming different layered compounds [16–19].

An inspection of the literature suggests that MgO is an effective promoter to minimize the sintering of nickel metal particles [20].

The purpose of the present investigation was to elucidate magnesium dopant effect on the properties and catalytic activity of Ni-Al LDHs with TKl structure in the model reaction of CO_2 methanation.

EXPERIMENTAL

Sample preparation

Carbonate forms of TKl precursors with M^{2+}/Al^{3+} molar ratios of 1.5 and 3.0, where $M^{2+} = Ni^{2+}$ or $M^{2+} = Ni^{2+} + Mg^{2+}$ were prepared. All precursors were synthesized by coprecipitation of mixed Ni(Mg)-Al nitrate solution with Na_2CO_3 at constant pH = 8.0 and temperature of 80°C. '*Pro analyze*' purity grade nitrate salts of the corresponding metals, $Ni(NO_3)_2\cdot6H_2O$, $Mg(NO_3)_2\cdot6H_2O$, and $Al(NO_3)_3\cdot9H_2O$ were used. A more detailed description of the preparation procedure is reported in Ref. 15. A modification of the brucite-like hydroxide layer by partial isomorphous Mg^{2+} substitution for the Ni^{2+} ions was applied. Magnesium content was identical, at the expense of nickel, in both modified samples. The obtained precipitate was further dried at 80°C for 20 h and named 'as-synthesized' precursor, designated as *x*NiAl, where *x* represents the M^{2+}/Al^{3+} molar ratio, for example 3.0NiAl (Table 1).

Sample characterization

The chemical composition of the 'as-synthesized' materials was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a JY 38 (Jobin-Yvon) spectrometer.

Powder X-ray diffraction (PXRD) data were collected on a TUR-M 62 conventional HZG-4 powder diffractometer employing CoK_α radiation ($\lambda = 0.15418$ nm). The crystalline phases were identified using Joint Committee on Powder Diffraction Standards (JCPDS) files.

Specific surface area (SSA) of the 'as-synthesized' samples was measured employing the single point BET method using a FlowSorb II 2300 Micromeritics apparatus with a N_2-He mixture (15% N_2) at the boiling temperature of liquid nitrogen.

Gas-phase hydrogenation of CO_2 to CH_4 was carried out in a fixed-bed flow reactor set-up under ambient pressure. The amount (about 0.8 g) and particle size (0.4–0.8 mm) of the loaded 'as-synthesized' precursors were determined based on preliminary accomplished experiments aimed at eliminating mass transfer effects. Catalyst activation was performed by *in situ* reduction in the equipment at two stages.

The first stage consisted of heating the precursors in a flowing mixture of 5 vol.% hydrogen in argon to 150°C and keeping this temperature for 60 min, then heating to 240°C and holding for 60 min. The second stage involved further reduction of the precursors in a pure hydrogen flow consecutively at steps of 400, 450, 530, and 600°C for 3 h. Both reduction procedures were realized at a constant gas hourly space velocity (GHSV) of 2000 h^{-1} and a heating rate of 1.7 deg.min^{-1}. Catalytic activity measurements were accomplished after each reduction step at atmospheric pressure with a $CO_2/H_2/Ar$ mixture of 0.65/34.35/65.0 vol.% in the temperature interval of 220–400°C and GHSV from 3000 to 22000 h^{-1}. The catalysts were kept in a steady state for 30 min at each reaction temperature. The GHSV was varied at each reaction temperature until 0–50-ppm CO_2 levels were attained. Residual CO_2

amount was determined using an online-connected Uras 3G gas analyser (Hartmann-Braun AG). A cooling trap (–40°C) between the reactor and the gas analyser removed the water obtained as a co-product during the reaction. The catalyst bed temperature was measured by a shielded chromel-alumel thermocouple. Gas-mass analysis of the outlet gas mixture was performed on a MS-10 spectrometer.

Hydrogen chemisorption measurements were carried out using a volumetric laboratory set-up at room temperature and hydrogen pressure range of 0–13.33 kPa. The samples were submitted beforehand to *in situ* reduction in the equipment at 400, 450, 530, and 600°C for 3 h with a gaseous mixture of H_2/Ar (1/2, v/v) at a flow rate of 6.5 $l.h^{-1}$ and a heating rate of 2 $deg.min^{-1}$. Monolayer coverage (capacity for hydrogen adsorption) was determined by extrapolating the linear part of the isotherm to zero pressure. The total amount of adsorbed hydrogen was used to determine nickel metal specific surface area and to calculate nickel particles size in the reduced precursors at the above-mentioned temperatures. Particle size calculations were carried out presuming complete reduction of the Ni^{2+} ions to Ni^0 as well as a cubic form of the reduced nickel metal particles. Adsorption stoichiometry of one hydrogen atom bonded to one surface nickel metal atom was assumed, the surface density of Ni atoms being taken as 1.54×10^{19} $atoms.m^{-2}$ Ni [21].

RESULTS AND DISCUSSION

Chemical analysis data listed in Table 1 reveal that the M^{2+}/Al^{3+} molar ratio of the dried ‘as-synthesized’ samples is consistent with that of the mixed nitrate solutions used in the preparation procedure.

Powder X-ray diffraction

Diffraction patterns of the ‘as-synthesized’ samples are displayed in Figs. 1a-d. A well-crystallized TKl structure containing carbonate anions in the interlayer space was registered only in the 3.0NiAl precursor (Fig. 1a): sharp and symmetrical reflections for the (003), (006), (110), and (113) planes and broad and asymmetric reflections for (012), (015), and (018) (JCPDF file 00-015-0087). Because of lower nickel loading (Fig. 1b), 1.5NiAl causes sample crystallinity to diminish due to decreased crystallite sizes accompanied by increased specific surface area (Table 1). No aluminium hydroxide/oxyhydroxide phase was detected despite that the Ni^{2+}/Al^{3+} ratio in the sample is lower than 2.0, a typical value of stoichiometric TKl structure.

Table 1. Sample notation, chemical composition, and specific surface area of the ‘as-synthesized’ samples

Sample	Chemical composition						SSA m^2g^{-1}
	wt.%			molar ratio			
	Ni	Mg	Al	Ni^{2+}/Al^{3+}	Ni^{2+}/Mg^{2+}	M^{2+}/Al^{3+}	
1.5NiAl	32.9	–	10.1	1.5	–	1.5	91
3.0NiAl	42.6	–	6.5	3.0	–	3.0	71
1.5NiMgAl	20.2	5.4	10.1	0.9	1.5	1.5	102
3.0NiMgAl	31.4	5.4	6.8	2.1	2.4	3.0	86

PXRD patterns of Mg-containing samples (Figs. 1c,d) are similar to the corresponding Ni-Al entities. However, they are broader and of lower intensity, which is more appreciable for 3.0NiMgAl. This result is evidence for partial replacement of the smaller Ni^{2+} ions having an octahedral ionic radius r of 0.069 nm by the larger Mg^{2+} ions (r = 0.072 nm) [22]. Consequently, the modification of the Ni-Al system with Mg^{2+} ions causes partial amorphization of the TKl structure associated with specific surface area development (Table 1).

CO_2 removal by methanation reaction

The catalytic tests showed successful CO_2 hydrogenation to 0–10-ppm levels at reaction temperatures in the range of 400–320°C and GHSV from 3000 to 22000 h^{-1} on all catalysts after their reduction at 400, 450, 530, and 600°C. Differences in activity became evident at lower reaction temperatures such as 300°C (Fig. 2).

Highly loaded Ni catalysts demonstrated a higher methanation activity at a reaction temperature of 300°C than catalysts of low Ni content (Figs. 2a-d). The 3.0NiMgAl catalyst showed the highest activity (0-ppm level) after reduction at all studied temperatures. The 3.0NiAl catalyst hydrogenated CO_2 below a 4-ppm level even on raising the GHSV to 22000 h^{-1} irrespective of reduction temperature. A decrease of the Ni loading in the catalysts led to a decrease in activity, particularly with the 1.5NiMgAl catalyst after reduction at 400°C (Fig. 2a) where a CO_2 residual content of 22-ppm level at GHSV = 22000 h^{-1} was registered. However, increasing the reduction temperature up to 450°C (Fig. 2b), 530°C (Fig. 2c), and markedly to 600°C (Fig. 2d) has brought about a successful purification of the stream by all the catalysts at high GHSV levels keeping the residual CO_2 in the range of 0–6 ppm.

Taking into account that the lower temperatures are thermodynamically and economically favourable to carry on the reaction, catalyst activities were examined in an extended reaction temperature range within 280–220°C (Fig. 3).

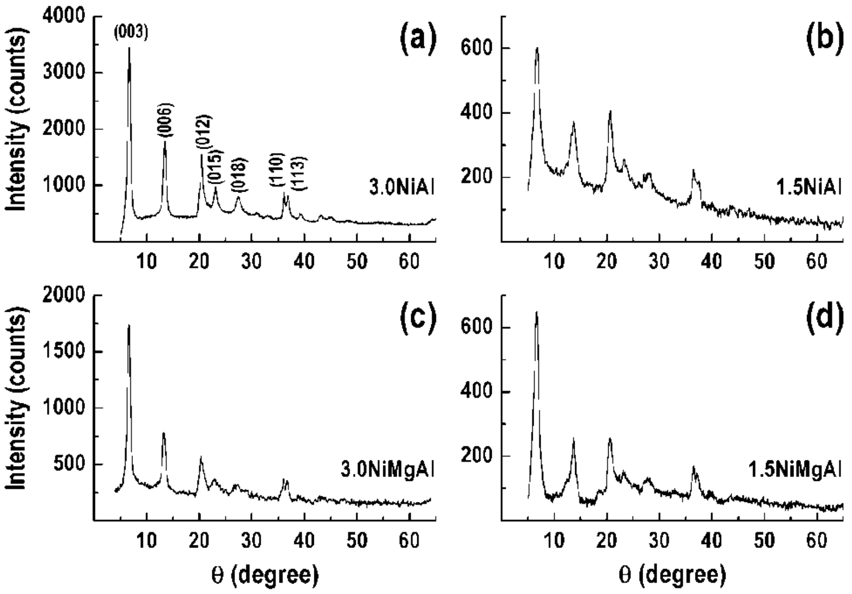

Fig. 1. PXRD patterns of the 'as-synthesized' samples: (a) 3.0NiAl, (b) 1.5NiAl, (c) 3.0NiMgAl, (d) 1.5NiMgAl.

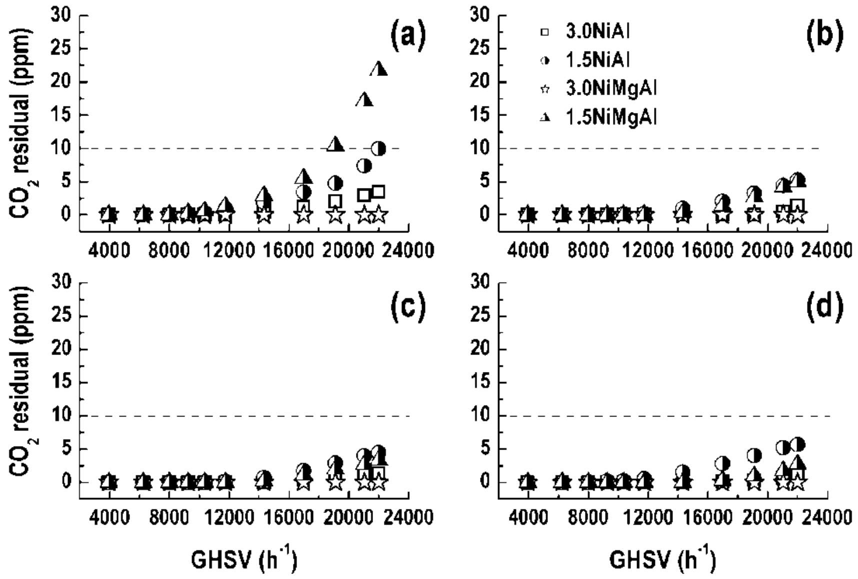

Fig. 2. Dependence of the methanation activity at 300°C on GHSV of the catalysts reduced at 400°C (a), 450°C (b), 530°C (c), and 600°C (d).

Similar relations of activity were observed at lower reaction temperatures (280–240°C) after catalyst reduction in the range of 400–600°C (Fig. 3a, b) if the activity is evaluated by the highest GHSV at which a residual 10-ppm level of CO_2 concentration at the reactor outlet is attained. The latter is an admissible limit in the feedstock of industrial ammonia production. It satisfies the requirements for safety work of fuel cell anodes as well. The 3.0NiMgAl catalyst showed again the highest methanation activity of 0-ppm level at $T \geq 260°C$ and GHSV of 22000 h^{-1} after treatment at all reduction temperatures. An exception was observed at a reaction temperature of 240°C if the catalyst was reduced at 400°C where a 10-ppm residual CO_2 level was registered (Fig. 3c). The non-modified 3.0NiAl catalyst remained also active at 280°C since raising the reduction temperature above 400°C gave rise to CO_2 levels below 10-ppm. In the region of 280–260°C, the Mg-containing low-loaded catalyst 1.5NiMgAl exhibited an increased activity after reduction at 450°C. CO_2 removal demonstrated by the 1.5NiAl catalyst was generally the lowest at reaction temperatures below 300°C; the latter has shown a slight variation in activity yet after reduction at 530°C.

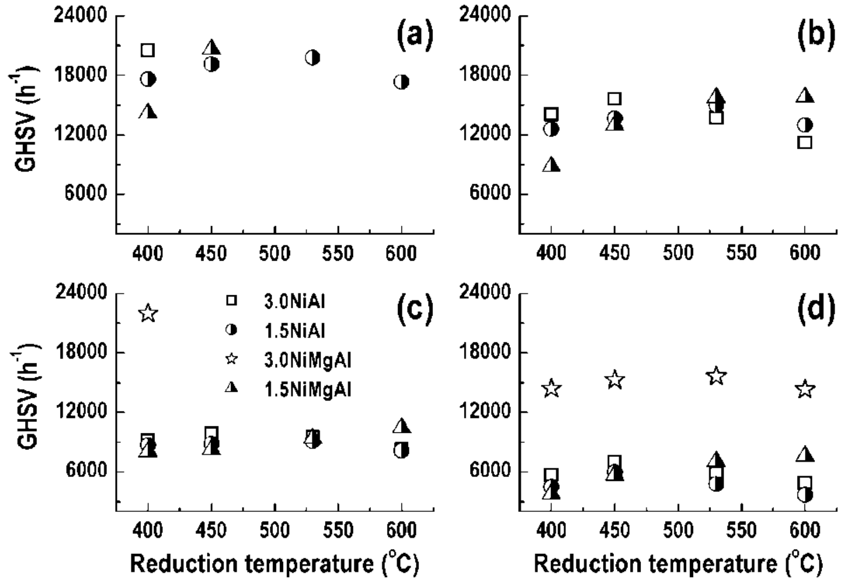

Fig. 3. Comparison of the methanation activity of the catalysts at various reaction temperatures: (a) 280°C, (b) 260°C, (c) 240°C, and (d) 220°C represented as dependence of necessary GHSV to keep a 10-ppm CO_2 level in H_2 on reduction temperature.

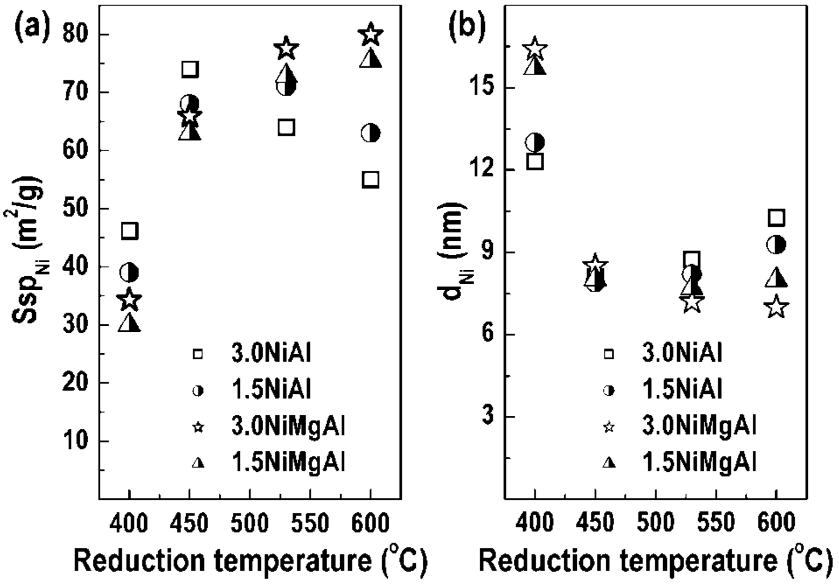

Fig. 4. Dependence of nickel metal specific surface area (a) and nickel metal particle size (b) on reduction temperature.

Lowering the reaction temperature to 220°C (Fig. 3d) caused a fall in activity with all the catalysts regardless of applied low space velocities. Nevertheless, the 3.0NiMgAl catalyst was still sufficiently active since the GHSV giving rise to 10-ppm CO_2 is quite high (about 15000 h^{-1}). The rest of catalysts manifested a similar activity after reduction at all studied temperatures.

H_2 chemisorption measurements

An explanation of the observed dependences of methanation activity could be found using results of H_2 chemisorption measurements. Considering that the model reaction takes place on the metal surface, nickel metal specific surface area (SSA_{Ni}) and, accordingly, nickel metal particle size (d_{Ni}) have predominant importance on hydrogenation activity.

According to the H_2 chemisorption data a larger SSA_{Ni} (Fig. 4a) and, therefore, a smaller d_{Ni} (higher Ni^0 dispersion) (Fig. 4b) of the 3.0NiAl and 1.5NiAl samples after reduction at 400 and 450°C presume a larger number of active centres on which the reaction takes place. Further treatment of these samples at 530 and 600°C induces sintering of the nickel metal particles by a particle-migration mechanism [23, 24]. This phenomenon provokes a decrease of the SSA_{Ni} and, accordingly, of the number of nickel metal atoms on the catalyst surface, thus leading to a decrease in methanation activity. In contrast, a gradual increase in SSA_{Ni} and a decrease of d_{Ni} were observed with the Mg-containing samples on raising the reduction temperature above 500°C. These results may be related to minimized migration of Ni^0 due to the presence of magnesium as a barrier/spacer to sintering of Ni^0 particles [25]. As nickel particle size becomes smaller, a greater number of nickel atoms will be exposed to the surface thus provoking a higher catalytic activity. This finding is predetermined by the structure sensitivity of the reaction as stated for methanation of 1% CO in hydrogen over nickel catalyst (MCR-2X, Haldor Topsøe A/S) at 250°C and a total pressure of 1 bar [26].

Mass-gas analysis

Carbon dioxide high-level removal invokes some doubt that measured activities include some partial hydrogenation of CO_2 to CO. For this purpose, the outlet gas mixture after the catalytic tests was collected and analysed. The data indicated methane as the only product. This result confirmed that CO_2 hydrogenation on the studied catalysts was complete.

CONCLUSIONS

A powder X-ray diffraction study revealed formation of Ni-Al takovite-like layered double hydroxides of different degree of crystallization depending on the Ni^{2+}/Al^{3+} ratio and the presence of magnesium additive. Modification of Ni-Al layered double hydroxides with magnesium caused partial amorphization of the layered structure. No aluminium hydroxide/oxyhydroxide phase was registered.

Variations of CO_2 methanation activity with changes of space velocity depended on nickel content, magnesium presence, and reduction and reaction temperatures.

Comparison of the catalytic activities showed that after reduction at 530 and 600°C the Mg-modified highly loaded Ni catalyst (3.0NiMgAl) dominated in CO_2 purification at reaction temperatures from 260 to 220°C due to (i) an increase of nickel metal specific surface area and (ii) retarding the effect of magnesium on metal nickel sintering.

The main effect of the magnesium dopant in Ni-Al layered double hydroxides is expressed in preserving nickel metal dispersion after reduction above 500°C.

Bearing in mind that lower temperatures are thermodynamically and economically favourable for the studied reaction, the Mg-modified highly loaded Ni catalyst 3.0NiMgAl can be recommend as a suitable candidate for deep CO_2 removal from hydrogen-rich gas streams through the methanation reaction at low temperatures, such as 240 and 220°C.

***Acknowledgements**: This article has been realized in the frame of interacademic collaboration between Institute of Catalysis, Bulgarian Academy of Sciences, and Ilie Murgulescu Institute of Physical Chemistry, Romanian Academy.*

REFERENCES

1. J. Kopyscinski, T. Schildhauer, S. Biollaz, *Fuel*, **89**, 1763 (2010).
2. Z. Liu, B. Chu, X. Zhai, Y. Jin, Y. Cheng, *Fuel*, **95**, 599 (2012).
3. M. Gassner, F. Marechal, *Energy Environ. Sci*., **5**, 5768 (2012).
4. T. Kienberger, C. Zuber, K. Novosel, C. Baumhakl, J. Karl, *Fuel*, **107**, 102 (2013).
5. D. Hu, J. Gao, Y. Ping, L. Jia, P. Gunawan, Z. Zhong, G. Xu, F. Gu, F. Su, *Ind. Eng. Chem. Res*., **51**, 4875 (2012).
6. C. Krier, M. Hackel, C. Hägele, H. Urtel, C. Querner, A. Haas, *Chem. Ing. Tech*., **85**, 523 (2013).
7. F. Mills, F. Steffgen, *Catal. Rev.-Sci. Eng*., **8**, 159 (1974).
8. K. Xavier, R. Sreekala, K. Rashid, K. Yusuff, B. Sen, *Catal. Today*, **49**, 17 (1999).
9. G. Xu, X. Chen, Z-G. Zhang, *Chem. Eng. J*., **121**, 97 (2006).
10. W. Wang, J. Gong, *Front. Chem. Sci. Eng*., **5**, 2 (2011).
11. W. Wang, Sh. Wang, X. Ma, J. Gong, *Chem. Soc. Rev*., **40**, 3703 (2011).
12. M. Vannice, *Catal. Rev.-Sci. Eng*., **14**, 153 (1976).
13. G. Bridger, C. Woodward, Production of methanation catalysts, *Stud. Surf. Sci. Catal*., Vol. 1, p. 331, Elsevier, Amsterdam, 1976.
14. P. de Korte, E. Doesburg, C. de Winter, L. van Reijen, *Solid State Ionics*, **16**, 73 (1985).
15. M. Gabrovska, R. Edreva-Kardjieva, D. Crişan, P. Tzvetkov, M. Shopska, I. Shtereva, *React. Kinet. Mech. Catal*., **105**, 79 (2012).
16. F. Cavani, F. Trifirò, A. Vaccari, *Catal. Today*, **11**, 173 (1991).
17. A. Vaccari, *Catal. Today*, **41**, 53 (1998).
18. A. Vaccari, *Appl. Clay Sci*., **14**, 161 (1999).
19. B. Zümreoglu-Karan, A. Ay, *Chem. Pap.*, **66**, 1 (2012).
20. T. Qing, X. Guo, X. Han, *CN Patent* 101 391 218 (2009).
21. J. Anderson, Structure of metallic catalysts, Academic Press, New York. 1975.
22. R. Shannon, *Acta Crystallogr. A*, **32**, 751 (1976).
23. H. Tamagawa, K. Oyama, T. Yamaguchi, H. Tanaka, H. Tsuiki, A. Ueno, *J. Chem. Soc. Faraday Trans. I*, **83**, 3189 (1987).
24. C. Bartholomev, R. Pannel, *J. Catal*., **65**, 390 (1980).

25. P. Babu, K. Ghuge, S. Rammohan, V. Krishnan, A. Bhat, *Catal. Lett.*, **15**, 95 (1992).
26. J. Rostrup-Nielsen, K. Pedersen, J. Sehested, *Appl. Catal. A-Gen.*, **330**, 134 (2007).

ОЧИСТВАНЕ НА БОГАТИ НА ВОДОРОД ГАЗОВЕ ОТ CO_2 ЧРЕЗ МЕТАНИРАНЕ

М. В. Габровска[1]*, Р. М. Едрева-Кърджиева[1], М. Г. Шопска[1], Д. А. Николова[1],
Л. П. Билярска[1], Д. Кришан[2], М. Кришан[2]

[1] *Институт по катализ, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 11, 1113 София, България*
[2] *Институт по физикохимия „Илие Мъргулеску“, Румънска академия, бул. „Индепенденцей“ 202,*
060021 Букурещ-12, Румъния

Постъпила на 12 септември 2015 г.; Преработена на 14 декември 2015 г.

(Резюме)

Изследван е ефектът на магнезия върху структурата и активността на съутаени Ni-Al слоести двойни хидроксиди като прекурсори на катализатори за очистване на богати на водород газови потоци от въглероден диоксид чрез реакцията на метаниране. Изследванията са провеждани чрез промяна на молното съотношение M^{2+}/Al^{3+} в прекурсорите (M^{2+}/Al^{3+} = 1.5 и 3.0, където $M^{2+} = Ni^{2+}$ или $M^{2+} = Ni^{2+} + Mg^{2+}$), температурата на редукция, реакционната температура и обемната скорост. Съдържанието на магнезий е идентично (за сметка на никела) и в двата модифицирани образеца.

Всички катализатори успешно хидрогенират CO_2 до стойности 0–10 ppm при реакционни температури в интервала 400–320°C и обемни скорости от 3000 до 22000 $ч^{-1}$, след редукция при 400, 450, 530 и 600°C. Катализаторите с високо съдържание на никел (3.0NiAl и 3.0NiMgAl) проявяват тенденция да са по-активни.

След редукция при 400 и 450°C, активността на немодифицираните 3.0NiAl и 1.5NiAl катализатори при по-ниски реакционни температури (280 и 260°C) се приписва на по-голяма специфична повърхност на металния никел и по-малки размери на металните никелови частици (висока никелова дисперсност). По-нататъшната обработка на катализатори при 530 и 600°C предизвиква синтеруване на металните никелови частици, което води до намаляване на метаниращата активност.

Предимството на Mg-съдържащите катализатори се проявява в запазване дисперсността на металния никел при редукция над 500°C, дължащо се на забавящия ефект на магнезия върху синтеруването на металния никел.

Модифицираният с Mg катализатор с високо съдържание на никел (3.0NiMgAl) може да се препоръча като подходящ кандидат за дълбоко очистване от CO_2 на богати на водород газови смеси чрез реакцията на метаниране при ниски реакционни температури като 240 и 220°C.