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Structure and reducibility of the mixed metal oxides obtained from Ni-Al layered double hydroxides. Catalytic activity in CO_2 methanation reaction

M. V. Gabrovska[1]*, R. M. Edreva-Kardjieva[1], D. D. Crişan[2], K. K. Tenchev[1],
D. A. Nikolova[1], M. Crişan[2]

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

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The effect of nickel amount on the structure, reducibility and activity of the mixed metal oxides generated by controlled thermal treatment of co-precipitated Ni-Al layered double hydroxides as catalyst precursors for CO_2 removal by methanation reaction, was examined by variation of the Ni^{2+}/Al^{3+} molar ratio ($Ni^{2+}/Al^{3+} = 0.5$, 1.5, and 3.0), the reduction and reaction temperatures. The powder X-ray diffraction of the thermally treated samples (200−1000 °C) established the formation of nano-sized NiO- and spinel $NiAl_2O_4$-like phases in different proportion and degree of crystallinity. The calcination temperature of 500 °C was selected as most convenient one because of the high dispersion of the mixed oxide phases predetermining the high dispersion of the metallic nickel.

It was revealed that after preliminary '*in situ*' reduction at 400, 450, 530 and 600 °C, all studied catalysts hydrogenated CO_2 effectively at reaction temperatures from 400 to 280 °C and space velocities between 3000 and 22000 h^{-1}. All three catalysts demonstrated similar activity at lower reduction and reaction temperatures due to the formation of readily reducible Ni^{2+}–O species which generated sufficient number of accessible Ni^0 surface active sites. Partial regeneration of the original layered structure was registered in the higher nickel containing solids after finishing of the catalytic test.

The advantage of the catalyst with the lowest nickel amount is disclosed at low reaction and reduction temperatures. Its performance dominates after reduction at higher temperatures because of the role of $NiAl_2O_4$ spinel-like phase to act as a "reservoir" generating fresh Ni^0. The decrease of activity in the rest of the catalysts is attributed mainly to the Ni^0 sintering.

Key words: Ni-Al layered double hydroxides, Ni-Al mixed oxides, structure, reducibility, CO_2 removal by methanation.

INTRODUCTION

The Ni-Al layered double hydroxides (LDHs), which are also known as takovite-like (TKl) compounds, belong to a great group of natural or synthetic inorganic lamellar compounds with chemical composition expressed by the 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, while the 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. Herewith, x represents the fraction of the Al^{3+} cation, and m is the number of the water molecules [1].

The research efforts have been focused on the assessment of the potential use of these layered systems as catalysts, either as-synthesized or mainly after thermal treatment. Typically, the thermal decomposition of the materials, includes dehydration, dehydroxylation and loss of the charge compensating anions, results in formation of finely dispersed Ni-Al mixed oxides of $Ni^{2+}(Al^{3+})O$ type. The latter represent promising catalysts due to their high specific surface area, high distribution of both Ni^{2+} and Al^{3+} ions after calcination despite of the high content of Ni^{2+} ions, high metal (inter)dispersion after

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

reduction, small crystal size, and stability against sintering [1−4].

The effective utilization of CO_2 originating from the production processes and flue gases of CO_2-intensive sectors is an important area of research because CO_2 is a major greenhouse gas and makes a significant contribution to global warming and climate change. Among the catalytic reactions, the catalytic hydrogenation of CO_2 over supported nickel metal catalysts to form methane, simply called methanation, is a particularly promising technique for CO_2 removal [5, 6]. The methanation reaction is commonly applied in ammonia plants at the final stage of purification of the synthesis gas in which low concentrations of CO and CO_2 (0.1−0.5%) are catalytically removed by a reaction with hydrogen. The reaction is of crucial importance due to the poisonous effect of carbon oxides on the ammonia synthesis. At present, the methanation became also attractive for reducing the residual carbon oxides in hydrogen-rich reforming gases, and to satisfy the requirements of polymer electrolyte fuel cell anodes [7, 8]. Although many different catalytic systems based on supported group VIII metals (e. g. Ru, Rh) on various oxide carriers (TiO_2, SiO_2, Al_2O_3, CeO_2, ZrO_2) have been applied to catalyze the reaction, the industrial methanation catalyst is essentially nickel metal at a large scale of concentrations (25−77 wt.%) due to its high activity, selectivity toward methane formation in preference to other hydrocarbons, high thermal stability, and relatively low cost [5, 9].

In a series of articles [10−13] Kruissink et al. have claimed that a thermal treatment of co-precipitated Ni-Al precursors of Ni^{2+}/Al^{3+} = 2.0−3.0 molar ratio in the interval of 450−900 °C and a following high-temperature reduction at 500−600 °C lead to the formation of very active catalysts for CO methanation at ≈300 °C. However, the authors have reported neither variations of the reduction and reaction temperatures, nor variations of the flow rates of the gaseous reaction mixture to obtain a detailed picture of catalyst performance.

In our recent paper [14] it was established that the Ni-Al LDHs with TKl structure are potential catalyst precursors for the fine CO_2 removal from hydrogen-rich gas streams through the methanation reaction, depending on the Ni^{2+}/Al^{3+} molar ratio and temperature of treatment in hydrogen ambience of the as-synthesized precipitates without preliminary calcination to the related oxides. It was found that after reduction at 400 and 450 °C the catalyst of the highest nickel amount has demonstrated the highest conversion degree at all reaction temperatures and space velocities, while the catalyst of the lowest nickel prevailed in the methanation activity after reduction within 530–600 °C.

The objective of this study is to examine the phase composition of the mixed oxides obtained by a controlled thermal treatment of the Ni-Al TKl systems aiming to select the catalyst with the most beneficial characteristics for the methanation reaction ($CO_2 + 4H_2 = CH_4 + 2H_2O$) by variation of the Ni^{2+}/Al^{3+} molar ratio, the reduction and reaction temperatures.

EXPERIMENTAL

Sample preparation

Carbonate forms of TKl precursors with Ni^{2+}/Al^{3+} molar ratios of 0.5, 1.5 and 3.0 were obtained by co-precipitation of the mixed Ni-Al nitrate solution with Na_2CO_3 at constant temperature of 80 °C and pH = 8 under vigorous stirring. More detailed description of the preparation procedure was presented in Ref. 14. The obtained precipitate was further dried at 80 °C for 20 h and named takovite-like precursor, designated as *x*NiAl, where *x* represents the Ni^{2+}/Al^{3+} molar ratio, for example 3.0NiAl (Table 1). The precursors were calcined in air at 500 °C for 2 h before the catalytic activity test. The catalysts after the reaction run (the tested catalysts) were labeled as *x*NiAl-t.

The unsupported NiO was prepared as a reference sample by the same preparation procedure. The sample was calcined in air at 500 °C for 2 h and denoted as reference NiO.

Table 1. Chemical composition of the as-synthesized TKl samples

Sample	Chemical composition				
	(wt. %)				Ni^{2+}/Al^{3+} molar ratio
	Ni	Al	NiO	Al_2O_3	
0.5NiAl	21.3	19.6	42.3	57.7	0.49
1.5NiAl	32.9	10.1	68.7	31.3	1.48
3.0NiAl	42.6	6.5	81.5	18.5	2.98

Sample characterization

Powder X-ray diffraction data was collected on a Bruker D8 Advance diffractometer employing CuK_α radiation (λ = 0.15418 nm), operated at U = 40 kV and I = 40 mA. The mean crystallite sizes (*L*) were determined using computer program X'Pert HighScore (PW3209) Version 1.0f (2004). The crystalline phases were identified using Joint Committee on Powder Diffraction Standards (JCPDS) files.

Specific surface area 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.

Temperature-programmed reduction was evaluated in the measurement cell of a SETARAM differential scanning calorimeter (DSC-111) directly connected to a gas chromatograph. The temperature was linearly raised from 25 to 700 °C at a heating rate of 10°C/min. The experiments (~0.025 g sample) were accomplished by a gaseous mixture of 10% H_2 in Ar at a flow rate of 25 cm^3/min.

Gas-phase hydrogenation of CO_2 to CH_4 was carried out in a fixed-bed flow reactor set-up under ambient pressure. The activation of the catalysts was performed by preliminary '*in situ*' reduction in the equipment at 400, 450, 530, and 600 °C for 3 h with pure hydrogen at a gas hourly space velocity (GHSV) of 2000 h^{-1} and a heating rate of 1.7°/min. The catalytic activity measurements were accomplished by means of gaseous mixture of $CO_2/H_2/Ar$=0.65/34.35/65 vol.% in the temperature interval 220−400 °C and GHSV from 3000 to 22000 h^{-1} after each reduction procedure. A liquate N_2 trap after reactor eliminated water as a reaction product. The amount of residual CO_2 was determined using online-connected Uras 3G gas analyzer (Hartmann-Braun AG) in the range 0−0.0050 vol.% CO_2 (0−50 ppm).

RESULTS AND DISCUSSION

The chemical composition of the TKl samples, measured by ICP analysis, is listed in Table 1.

Powder X-ray diffraction (PXRD)

In our recent paper [14] it was documented that a well-crystallized TKl structure containing carbonate anions in the interlayer space is formed only in 3.0NiAl precipitate (Fig. 1a): sharp and symmetrical reflections for (003), (006), (110) and (113) planes and broad and asymmetric for (012), (015), and (018), respectively. It was established that a decrease in nickel loading of 1.5NiAl sample causes lowering of the peak intensities and broadening of the TKl reflections (Fig. 1b), as well as the coexistence of two phases in 0.5NiAl solid (Fig. 1c): a poorly crystallized TKl phase accompanied by a gibbsite one. It was found that the increase in Ni amount of the samples leads to (i) increase of the lattice param-

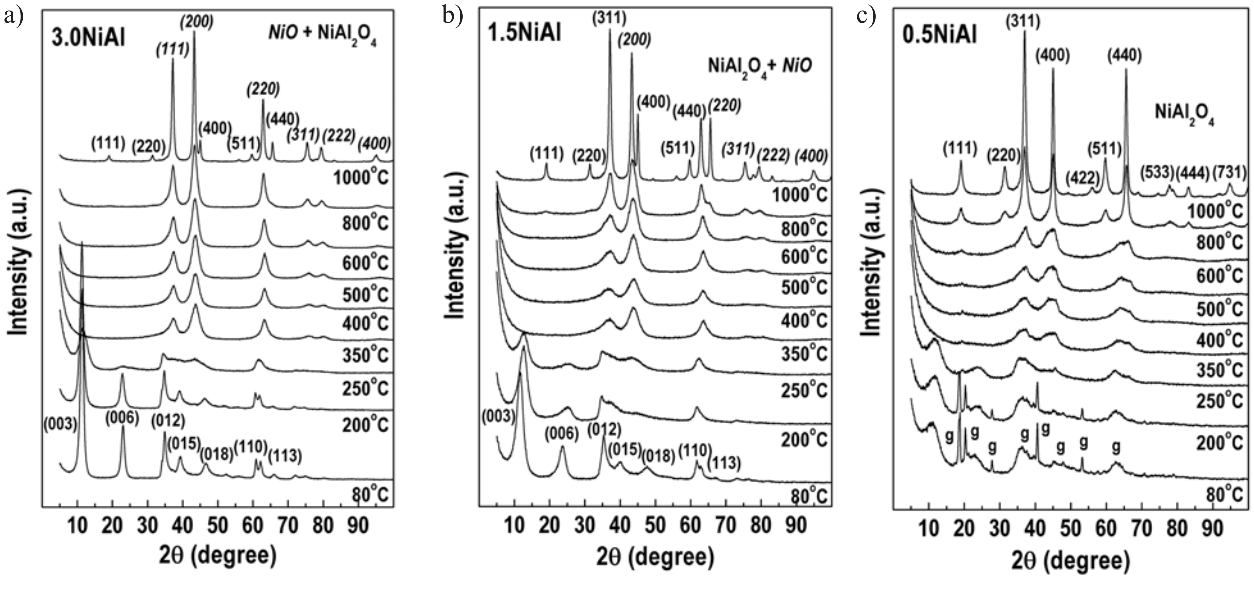

Fig. 1. PXRD patterns of the samples thermally treated at various temperatures: (a) 3.0NiAl, (b) 1.5NiAl and (c) 0.5NiAl, where **g** is gibbsite

eters, (ii) crystallite growth and (iii) decrease of the specific surface area (SSA).

The investigated Ni-Al layered systems were thermally treated in the temperature range 200−1000 °C for 120 min in an air atmosphere. The corresponding PXRD patterns were used for elucidation of the structure evolution with the temperature increase, i.e. appearance, formation and transformation of the resultant phases.

PXRD patterns of the calcined at 200 °C solids (Figs. 1−3) displayed reflections similar to the as-synthesized ones, however slightly shifted to higher angles. This finding is ascribed to the beginning of the interlayer water molecules losing. The diffraction lines of the thermally treated at 250 °C samples indicate partial decomposition of the TKl structure in all samples. It is observed an appearance of badly organized reflections (200) of NiO phase (JCPDS file 00-047-1049) in 1.5NiAl and 3.0NiAl samples, being better organized in the later. An additional broad reflections (111), (311) and (440) of a non-stoichiometric spinel-type $NiAl_2O_4$ phase (JCPDS file 00-010-0339) are detected in 0.5NiAl. The characteristic diffraction lines of TKl structure disappear completely at 350 °C and rather amorphous calcination products are formed in all samples. This observation is attributed to both dehydroxylation of the brucite-type layers and decarbonation of the interlayer space as result of the destruction of the layered structure [15−17]. With further increase in the temperature to 500 and 600 °C, the diffraction peaks of NiO and $NiAl_2O_4$ phases become narrower and more intense, due to the growth of crystallites and improvement of crystallization. PXRD patterns of the calcined at 800 °C solids detect reflections of: (i) a well formed single $NiAl_2O_4$ phase in 0.5NiAl; (ii) an appearance of badly organized $NiAl_2O_4$ phase in 1.5NiAl sample together with a better crystallized NiO phase, and (iii) a well formed single NiO phase in 3.0NiAl solid. The diffraction lines of the calcined at 1000 °C materials show existence of two phases in 1.5NiAl and 3.0NiAl samples: NiO and $NiAl_2O_4$, however, differing in proportion. NiO is a predominant phase in 3.0NiAl solid and conversely, spinel $NiAl_2O_4$ phase is the dominant phase in 1.5NiAl and 0.5NiAl materials. No separate Al-containing phase was observed may be because of segregation of Al^{3+} cations to an amorphous components.

The calculated crystallographic parameters of NiO phase (a_{NiO}) in calcined 1.5NiAl and 3.0NiAl solids up to 1000 °C (Fig. 2a) demonstrate values which are lower than of both reference NiO (a_{NiO} = 0.4176 nm) and standard NiO (a_{NiO} = 0.4177 nm) according to JCPDS file 00-047-1049. As it was reported [18], this finding is a consequence of the partial incorporation of Al^{3+} ions into the cubic framework of the NiO, reducing its cell dimensions (a_{NiO}) of the pure NiO because of the smaller radius of Al^{3+} ions (0.053 nm) as compared to Ni^{2+} ones (0.069 nm) [19]. The increase of Al^{3+} cations' incorporation into NiO lattice on decreasing Ni^{2+}/Al^{3+} molar ratio is in line with decreasing the NiO lattice parameter in the samples.

The mean crystallite sizes of NiO (L_{NiO}) and $NiAl_2O_4$ ($L_{NiAl_2O_4}$) phases in 1.5NiAl and 3.0NiAl samples were determined from the full-width at half-maximum values of (200) diffraction line for NiO phase and (311) line for $NiAl_2O_4$, respectively. It is observed that the increase of the calcination temperature up to 500 °C and the nickel content lead to the slightly enlargement of NiO crystallite sizes (Fig. 2b). The treatment of both samples at 800 and

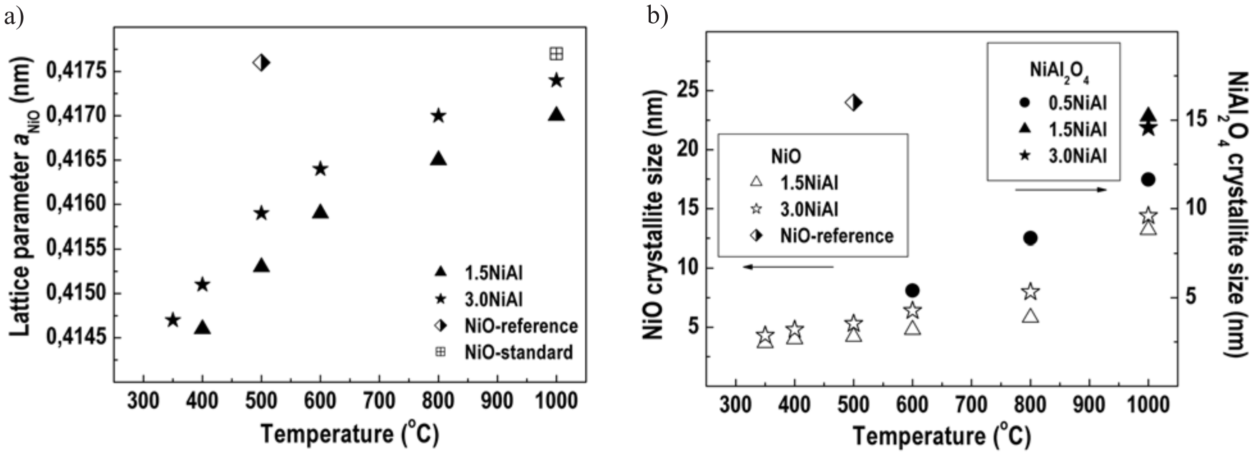

Fig. 2. Crystallographic characteristics of the samples thermally treated at various temperatures: (a) lattice parameter of NiO (a_{NiO}) and (b) crystallite size (L) of NiO and $NiAl_2O_4$ phases

1000 °C causes sharply increase and alignment of the NiO crystallite sizes, suggesting complete separation of NiO and $NiAl_2O_4$ phases. The values of L_{NiO} and $L_{NiAl_2O_4}$ comply with the degree of crystallization of both phases in the studied solids remaining in the nano-scaled region.

The PXRD analyses documented that the decomposition of the TKl structure at 500 °C attracts special attention. The resulting structurally disordered oxide mixture crystallizes to form NiO-like phase in 3.0NiAl and 1.5NiAl samples with L_{NiO} of 5.3 and 4.2 nm, respectively, and poorly organized $NiAl_2O_4$-like phase in 0.5NiAl. In addition the SSA (m^2/g) values of the calcined Ni-Al samples at 500 °C demonstrate well developed surface: 141 (0.5NiAl) > 128 (1.5NiAl) > 112 (3.0NiAl) in comparison with 15 m^2/g of the reference NiO sample.

Obviously, the NiO-like phase obtained by calcination of the Ni-Al TKl compounds exhibits a high thermal stability in comparison with the reference NiO. The Al^{3+} ions are concentrated onto and in the NiO surface, forming other phases such as alumina or spinel-type phases, so that the NiO surface is wholly modified [20]. The spinel-type phase plays a major role in the thermal properties of the mixed oxides, because there is no possibility of direct physical contact between two adjacent nickel crystallites. In such a way the growth and sintering of the NiO is hindering, thus increasing the SSA [21].

The high dispersion of NiO-like phase is presumed to generate also highly dispersed metallic nickel particles after the activation of the precursors by reduction with hydrogen. All these arguments lead to the conclusion that the thermal treatment of Ni-Al TKl systems as precursors of catalysts for CO_2 removal by methanation should be carried out at a temperature of 500 °C.

Temperature programmed reduction (TPR) study

The reducibility of the calcined at 500 °C precursors was investigated by means of TPR technique. TPR experiments were applied to elucidate the nature of reducible Ni^{2+}–O species present in the samples and to reveal the temperature at which reduction to metallic Ni^0 occurs depending on the nickel loading in the solids.

The TPR profile of the reference sample NiO, displays a large temperature peak in the range 280−550 °C with T_{max} at 393 °C and a shoulder at ≈450 °C. It may be assumed that full reduction of bulk Ni^{2+} ions to Ni^0 has occurred (Fig. 3). The appearance of broad asymmetric TPR profiles spreading throughout a wide temperature range from 290 to 700 °C in all solids documented the presence of Al^{3+} ions. A shift of LT shoulders as well as T_{max} towards higher temperatures upon decreasing of Ni content (increase of Al), are clearly observed with the samples under study.

The TPR profile of the highest nickel containing sample 3.0NiAl demonstrates low-temperature (LT) shoulders at ≈310 °C and ≈390 °C, temperature maxima (T_{max}) ≈550 °C and high-temperature (HT) shoulder at ≈645 °C. The profile of 1.5NiAl indicates a presence of LT shoulders at ≈312 °C and ≈405 °C, shoulder at ≈545 °C, T_{max} at ≈615 °C and HT shoulder at ≈670 °C. LT shoulders at ≈335 °C and ≈440 °C, T_{max} at ≈615 °C and HT shoulder at ≈670 °C are registered in 0.5NiAl sample.

The impeded reducibility as compared to the reference NiO pointed undoubtedly to the presence of $A1^{3+}$ ions in the NiO lattice. According to the models, proposed for decomposition and reduction of the LDH compounds [20−22], the LT shoulders from TPR profiles of all solids are ascribed to reduction of NiO intimately mixed with a small quantity of Al^{3+} ions (Phase I). The T_{max} of 3.0NiAl sample is attributed to reduction of the quasi-amorphous Ni-Al spinel-like phase (Phase II) which decorates the surface of the NiO particles and/or acts as their support. The T_{max} of 1.5NiAl and 0.5NiAl solids, as well as the HT shoulders of all samples are assigned to the reduction of the alumina-type phase doped with some amount of Ni^{2+} ions (Phase III), probably 'grafted' on the spinel-like phase. All TPR profiles identify incomplete reduction of Phase III because the profiles do not recover the baseline. It is associated with the appearance of hardly reducible spinel-like $NiAl_2O_4$ phases.

It may be generalized that the reduction of the Ni^{2+} ions in the mixed Ni-Al oxides, is realized at different temperatures due to different amounts,

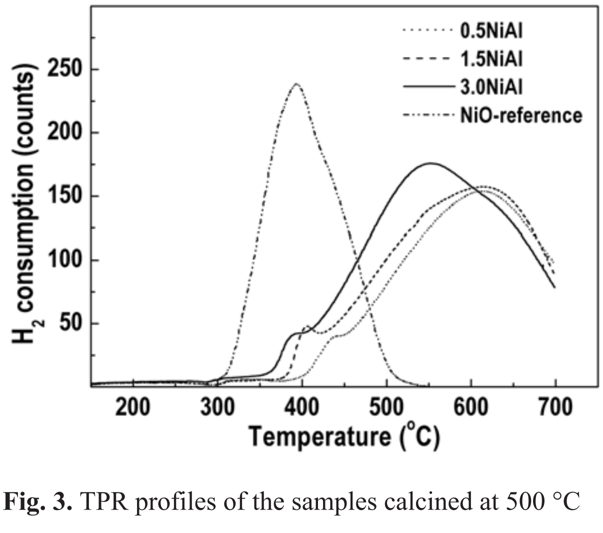

Fig. 3. TPR profiles of the samples calcined at 500 °C

location and strength of interaction of Ni^{2+}–O and Al^{3+} moieties.

CO$_2$ removal by methanation reaction

The catalytic activity of the calcined at 500 °C catalysts is evaluated by the highest GHSV at which the residual concentration of CO$_2$ at the reactor outlet is 0.0010 vol.% (10 ppm). This level is an admissible limit in modern industrial ammonia production. The catalytic runs show that after preliminary reduction at 400, 450, 530 and 600 °C all three catalysts hydrogenate CO$_2$ successfully to residual content of CO$_2$ levels of 0−10 ppm at reaction temperatures between 400 and 280 °C and GHSV within 3000–22000 h^{-1}. The differences in activity become evidently at lower reaction temperatures, namely at 260, 240 and 220 °C (Fig. 4).

As it can be seen, the 0.5NiAl catalyst demonstrates higher methanation activity at a reaction temperature of 260 °C after reduction at 400 °C. The catalyst purifies the reaction mixture from CO$_2$ to residual content of 10 ppm at GHSV = 12000 h^{-1}. Further increase of the reduction temperature brings about effective purging of the reaction mixture at GHSV = 22000 h^{-1} to residual content of 5.7 ppm CO$_2$ after reduction at 450 °C and 0 ppm CO$_2$ after reduction at 530 and 600 °C. The rest of catalysts comply with the following order of activities: 1.5NiAl>3.0NiAl after reduction at all examined temperatures.

Lowering of the reaction temperature to 240 °C leads to similar activity of all catalysts after reduction at 400 °C and to indistinguishable one, after reduction at 450 °C. In contrast, an enhancement in activity is registered after reduction at 530 °C, being more pronounced in the 0.5NiAl catalyst. Further increase of the reduction treatment to 600 °C reveals the priority of the 0.5NiAl catalyst which removes CO$_2$ to 10 ppm level at GHSV = 15000 h^{-1}. The activity of the rest of catalysts decrease in the order: 1.5NiAl>3.0NiAl.

The CO$_2$ removal at reaction temperature of 220 °C shows lower values almost independent of the reduction temperature. The purification seems effective only at low space velocities (4−5 h^{-1}).

The interpretation of the demonstrated activity may be partially found in the TPR experiments (Fig. 3). TPR profiles suggest the existence of two types of Ni^{2+}-O species on the surface of the all mixed oxides under study: readily and hardly reducible. The methanation activity of the catalysts after reduction at 400 and 450 °C may be easily ascribed to the presence of readily reducible Ni^{2+}-O species. The close activity indicates that the amount of active Ni^0 species is enough even in the 0.5NiAl in spite of the different nickel loading.

The higher activity of 0.5NiAl catalyst after reduction above 500 °C may be attributed to the retarding effect of Al^{3+} ions on the Ni^0 sintering due to the presence of spinel-type NiAl$_2$O$_4$ phase at higher temperatures. The sintering of the reduced metal lead to decrease of the activity, more pronounced in the catalyst with the highest nickel content 3.0NiAl. Moreover, it is suggested by McArthur [23] that nickel aluminates or some similar compounds act

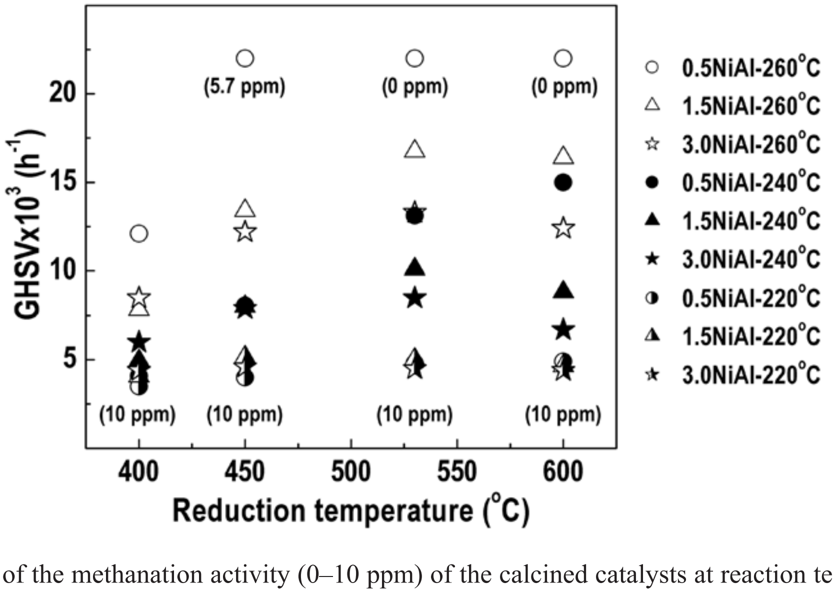

Fig. 4. Comparison of the methanation activity (0–10 ppm) of the calcined catalysts at reaction temperatures of 260, 240 and 220 °C *vs* reduction temperatures

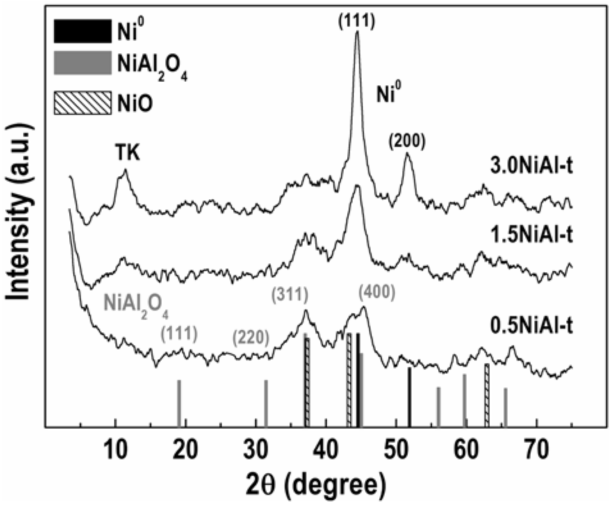

Fig. 5. PXRD patterns of the catalysts after the reaction run (tested samples)

somewhat as a "reservoir" which, upon gradual reduction in the presence of hydrogen-containing gases, continually generates fresh metallic nickel, thus accounting for the remarkable activity maintenance of the catalyst.

All these considerations are related to the incorporation of Al^{3+} cations into NiO lattice.

Additional explanation of the methanation activity is suggested by the diffractograms of the catalysts after the reaction run (Fig. 5), namely reduction at 600 °C, testing in the range 400–220 °C and passivation after cooling down to room temperature by a gas mixture of O_2/N_2. Some findings must be pointed: (i) Formation of Ni^0 phase (JCPDS file 00-004-850), in all the tested catalysts, being better organized in 3.0NiAl-t; (ii) Presence of NiO-like phase in 1.5NiAl-t and 0.5NiAl-t catalysts; (iii) Prevalent $NiAl_2O_4$ phase in 0.5NiAl-t; (iv) Registration of the reflections characteristics of TKl structure in 1.5NiAl-t and 3.0NiAl-t catalysts, more expressive in 3.0NiAl-t.

The appearance of diffraction lines typical of TKl compounds may be attributed to the property of the mixed oxides generated from LDHs to regenerate the initial layered structure in the presence of water with natural content of dissolved CO_2 [24, 25]. Evidently, a hydrolysis of the unreduced surface Ni^{2+} ions is realized upon the methanation reaction medium. The hydrolyzed Ni^{2+} species together with some Al^{3+} ions partially re-crystallized in original TKl structure. The partial formation of TKl phase may be implied as an additional reason for the lowest activity of 3.0NiAl and 1.5NiAl catalysts, namely, the amount of Ni^0 on the catalyst surface should be diminished thus provoking decrease in activity.

The low degree of crystallization of the tested catalysts hinders the determination of the Ni^0 size. The SSA (m^2/g) measurements suggest greater dispersion of the phases in 0.5NiAl-t catalyst: 122 (0.5NiAl-t) > 114 (1.5NiAl-t) > 79 (3.0NiAl-t). Moreover, the SSA of 3.0NiAl-t catalyst (79 m^2/g) shows value very close to the SSA of takovite-like 3.0NiAl solid (71 m^2/g) [14] thus evidencing the partial formation of TKl structure.

CONCLUSIONS

The structure, reducibility and CO_2 methanation activity of the Ni-Al mixed oxides generated by controlled thermal treatment of Ni-Al takovite-like LDHs depend on the amount, location and strength of interaction of Ni^{2+}–O and Al^{3+} species and temperature. NiO- and spinel $NiAl_2O_4$-like phases are formed in the nano-sized region in different proportion and degree of crystallinity as a function of the nickel content.

The calcination temperature of 500 °C is selected as most convenient one because of the high dispersion of the mixed oxide phases predetermining the high dispersion of the metallic nickel. All preliminary reduction temperatures of the three catalysts provoke effectively CO_2 hydrogenation down to 280 °C and high space velocities. Partial regeneration of the original layered structure was registered in the higher nickel containing solids after finishing of the catalytic test.

The advantage of the catalyst with the lowest nickel amount is revealed at low temperature of reaction (260 °C) and reduction (400 °C). Its performance dominates at higher reduction temperatures due to the role of spinel $NiAl_2O_4$-like phase to act as a "reservoir" generating fresh metallic nickel. The decrease of activity in the rest of the catalysts is mainly attributed to sintering of the reduced metal nickel.

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СТРУКТУРА И РЕДУЦИРУЕМОСТ НА СМЕСЕНИ МЕТАЛНИ ОКСИДИ, ПОЛУЧЕНИ ОТ Ni-Al СЛОИСТИ ДВОЙНИ ХИДРОКСИДИ. КАТАЛИТИЧНА АКТИВНОСТ В РЕАКЦИЯТА НА МЕТАНИРАНЕ НА CO$_2$

М. В. Габровска[1]*, Р. М. Едрева-Кърджиева[1], Д. Д. Кришан[2],
К. К. Тенчев[1], Д. А. Николова[1], М. Кришан[2]

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

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(Резюме)

Изследван е ефектът от количеството на никела върху структурата, редуцируемостта и активността на смесените метални оксиди, получени чрез контролирана термична обработка на съутаени Ni-Al слоисти двойни хидроксиди, като прекурсори на катализатори за очистване от CO$_2$ чрез реакцията на метаниране, променяйки молното съотношение Ni^{2+}/Al^{3+} (Ni^{2+}/Al^{3+} = 0.5, 1.5 и 3.0) и температурите на редукция и реакция. Чрез прахова дифракция на рентгенови лъчи на термично обработваните образци (200−1000 °C) е установено образуването на нано-размерни NiO- и шпинело NiAl$_2$O$_4$-подобни фази в различно съотношение и степен на кристалност. Като най-подходяща за накаляване на образците е избрана температурата от 500 °C поради високата дисперсност на смесените оксидни фази, което предопределя висока дисперсност и на металния никел след редукция.

Разкрито е, че след предварителна редукция *in situ* при 400, 450, 530 и 600 °C, всички изследвани катализатори ефективно хидрогенират CO$_2$ при реакционни температури от 400 до 280 °C и обемни скорости между 3000 и 22000 ч$^{-1}$. И трите катализатора показват сравнима активност при по-ниски редукционни и реакционни температури поради образуването на лесно редуцируеми Ni^{2+}-O видове, които пораждат достатъчен брой от достъпни Ni^0 активни места на повърхността. Регистрирано е частично възстановяване на първоначалната слоиста структура в образците с по-високо съдържание на никел след приключване на каталитичният тест.

Предимството на катализатора с най-ниско съдържание на никел пролича при ниски редукционни и реакционни температури. Неговата производителност доминира след редукция при по-високи температури поради ролята на NiAl$_2$O$_4$ шпинело-подобна фаза да действа като „резервоар“, пораждащ нови количества метален никел. Понижаването на активността на останалите катализатори се приписва главно на синтероването на металният никел.