

## Structure and activity of M-Al layered double hydroxides in CO<sub>2</sub> methanation reaction as function of the divalent metal

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The effect of divalent metal (Ni or Co) on the structure, phase composition, thermal stability, and reducibility of co-precipitated Al-containing layered double hydroxides (LDHs) as catalyst precursors for CO<sub>2</sub> removal by methanation reaction was examined. The catalytic activity was estimated by varying reduction and reaction temperature and space velocity as well. It was observed that the divalent metal in Al-containing LDHs affects the crystallisation degree of the formed layered compounds, their specific surface area, and temperature of LDH decomposition with parallel phase transformation to resultant mixed metal oxides. It was found that Co<sup>2+</sup> ions stabilised in CoAl<sub>2</sub>O<sub>4</sub> spinel structure hampered their reduction to metal state, thus leading to deficiency of Co<sup>0</sup> active metal surface phase. This phenomenon determined a low activity of Co/Al<sub>2</sub>O<sub>3</sub> catalyst, especially at low reduction temperatures. In contrast, the interaction between Ni<sup>2+</sup> and Al<sup>3+</sup> ions resulted in generation of readily reducible Ni<sup>2+</sup>-O species, which favoured a higher activity of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst after reduction at the same temperatures. Spinel-type phases were formed at different temperatures as a function of the divalent metal and determined catalyst activity in the purification of H<sub>2</sub>-rich streams from traces of CO<sub>2</sub> by methanation reaction.

**Key words:** CoAl and Ni-Al layered double hydroxides, structure, mixed metal oxides, reducibility; CO<sub>2</sub> methanation.

### INTRODUCTION

Carbon dioxide (CO<sub>2</sub>) is a major greenhouse gas and makes a significant contribution to global warming and climate change. The pressing necessity for greenhouse gas emissions control concentrates scientists' attention to decrease CO<sub>2</sub> accumulation in the atmosphere. On this occasion, mitigation and effective utilisation of the CO<sub>2</sub> emissions have become major areas of research worldwide [1,2]

Among catalysed reactions, the catalytic hydrogenation of CO<sub>2</sub> over transition metal catalysts to form methane, simply called methanation (CO<sub>2</sub> + 4H<sub>2</sub> = CH<sub>4</sub> + 2H<sub>2</sub>O), is one of the most appropriate and efficient techniques for CO<sub>2</sub> removal. Direct synthesis of methane from CO<sub>2</sub> is favourable not only for reduction of greenhouse gas emissions, but also for fuel and chemicals production [2,3]. Moreover, CO<sub>2</sub> methanation is used as a promising technique for purification of H<sub>2</sub>-rich streams from traces of CO<sub>2</sub> to prevent catalyst poisoning especially in the ammonia synthesis industry [4] and in the fuel cell anode technology [5].

Although many different metals supported on various oxide carriers have been used, nickel and

ruthenium are two of the most effective. Despite the highest activity observed of Ru metal, it is not of practical interest due to its high cost [6]. Nickel catalysts at a large scale of concentrations (25–77 wt.%) are a choice of the industrial methanation because of their high activity, effectivity, selectivity toward methane formation in preference to other hydrocarbons, and relatively low cost [7–9].

Layered double hydroxides are lamellar materials belonging to a great group of natural or synthetic inorganic layered compounds, named anionic clays or hydrotalcite-like materials, because of the similarity existing between their structures and that of mineral hydrotalcite, (Mg<sub>6</sub>Al<sub>2</sub>(OH)<sub>16</sub>CO<sub>3</sub>·4H<sub>2</sub>O). The structure of LDHs can be expressed by the general formula [M<sup>2+</sup><sub>1-x</sub>M<sup>3+</sup><sub>x</sub>(OH)<sub>2</sub>]<sup>x+</sup>[A<sup>n-</sup><sub>x/n</sub>mH<sub>2</sub>O]<sup>x-</sup>, where bivalent M<sup>2+</sup> (Mg<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, etc.) and trivalent M<sup>3+</sup> (Al<sup>3+</sup>, Cr<sup>3+</sup>, In<sup>3+</sup>, etc.) metal cations are located in the brucite-like hydroxide layers. Due to charge disequilibrium, a substituted trivalent M<sup>3+</sup> cation for a M<sup>2+</sup> ion gives rise to infinite repetition of positively charged sheets alternating with A<sup>n-</sup> ions which are required to balance the net positive charges of the hydroxide layers. The charge compensating exchangeable anions A<sup>n-</sup>, such as CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, etc., as well as water molecules,

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are situated in the interlayer gallery of the layered structure. Herewith,  $x$  represents the fraction of the M<sup>3+</sup> cation, more precisely  $x = M^{3+}/(M^{3+} + M^{2+})$ , the most reliable composition range being approximately  $0.2 \leq x \leq 0.4$ , and  $m$  is the number of co-intercalated water molecules which prevent inter-anion repulsion. The LDH compounds are characterised by uniform homogeneous distribution of the M<sup>2+</sup> and M<sup>3+</sup> metal cations at the octahedral sites of the brucitelike layer on an atomic level. The cations are crosslinked through hydroxyl groups to form a bimetal hydroxide sheet similar to that of brucite [10–13].

Our research efforts have been directed to assess the potential use of Ni-Al layered systems as catalysts for CO<sub>2</sub> removal in place of conventional Ni-based catalysts. It has been established that depending on the Ni<sup>2+</sup>/Al<sup>3+</sup> molar ratio and temperature of treatment in hydrogen ambience, Ni-Al LDHs are promising precursors for catalysts for fine CO<sub>2</sub> removal from hydrogen-rich gas streams through the CO<sub>2</sub> methanation reaction both as-synthesised [14] and after thermal treatment to cause formation of finely dispersed Ni-Al mixed oxides [15].

While numerous studies have been focused on CO<sub>2</sub> methanation over Ni catalysts, there are only scarce attempts to elucidate the role of Co catalysts in the same reaction [16,17].

In this regard, the object of the present investigation is to elucidate the effect of divalent cation, Ni<sup>2+</sup> and Co<sup>2+</sup>, in co-precipitated Al-containing LDHs on phase composition, structure, thermal stability, reducibility, and activity estimation in CO<sub>2</sub> methanation by varying reduction and reaction temperature and space velocity as well.

Until now, an extensive comparative study of CO<sub>2</sub> methanation on non-calcined co-precipitated Co-Al and Ni-Al LDH has not been reported in the literature.

## EXPERIMENTAL

### *Sample preparation*

Carbonate forms of LDH precursors of identical composition (M<sup>2+</sup>/Al<sup>3+</sup> molar ratio of 3.0, M<sup>2+</sup> = Co<sup>2+</sup> or Ni<sup>2+</sup>) were obtained by co-precipitation of mixed Co-Al or Ni-Al aqueous nitrate solution with Na<sub>2</sub>CO<sub>3</sub> as precipitating agent at constant pH = 8 and temperature of 80 °C under vigorous stirring. The initial salts of analytical grade, provided by Alfa Aesar (USA), were used as received without further purification. Detailed description of the preparation procedure is presented in Ref. 14. The obtained precipitate was further dried at 80 °C for 20 h, named as-synthesised precursor, and designated

as CoAl or NiAl (Table 1). After reaction run, the spent catalysts were labelled as CoAl-s or NiAl-s.

Dried layered systems were step-wise treated in air for 2 h in the temperature range 200–1000 °C at a heating rate of 3 °C/min in order to understand phase composition changes.

### *Sample characterisation*

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

Specific surface areas were measured employing the single point BET method using a FlowSorb II 2300 Micromeritics apparatus with a N<sub>2</sub>/He mixture (30/70) at the boiling temperature of liquid nitrogen.

Thermal analysis (DTA-TG) was carried out simultaneously on a Stanton Redcroft conventional TG-DTA system. Measurements were carried out under airflow (ca. 3 ml/h) at a heating rate of 10 deg/min.

The phase composition of as-synthesised, calcined, and spent samples was established by powder X-ray diffraction (PXRD) analysis. Data were collected on a Bruker D8 Advance powder diffractometer employing CuK $\alpha$  radiation. Crystalline phases were identified by means of International Centre for Diffraction Data (ICDD) powder diffraction files.

The temperature-programmed reduction (TPR) behaviour of the investigated samples (~0.025 g) was evaluated by means of a laboratory setup using a thermal conductivity detector. The temperature was linearly raised from 25 to 850 °C at a heating rate of 10 deg/min. The TPR experiments were accomplished by a gaseous mixture of 10% H<sub>2</sub> in Ar at a flow rate of 25 cm<sup>3</sup>/min. The samples were heated in nitrogen to 80 °C at a rate of 30 deg/min to remove adsorbed water. Then the nitrogen was replaced by a gaseous mixture of 10% H<sub>2</sub> in Ar and the temperature was raised again at a rate of 10 deg/min up to 850 °C. The selected conditions were compatible with the criteria proposed by Monti and Baiker [18] that avoid mass transfer and temperature control limitations.

Gas-phase hydrogenation of CO<sub>2</sub> to CH<sub>4</sub> was carried out in a fixed-bed flow reactor setup under atmospheric pressure. For each catalytic measurement, 0.8 g of as-synthesised precursor of 0.4–0.8 mm particle size were loaded into a quartz reactor. Quartz glass pellets of 1.0–1.25 mm size were used to fill up reactor to eliminate mass transfer effects. Catalyst activation was successively performed by *in situ* reduction at 400, 450, 530, and 600 °C for 3 h with pure hydrogen (Messer MG, Chimco Gas) at a constant gas hourly space velocity (GHSV) of 2000

h<sup>-1</sup> and a heating rate of 1.7 deg/min. The catalytic activity measurements were accomplished by CO<sub>2</sub>/H<sub>2</sub>/Ar gaseous mixture (0.65/34.35/65 vol.%, Messer MG, Chimco Gas) in the temperature interval 220–400 °C and GHSV from 3000 to 22000 h<sup>-1</sup> after each reduction temperature. Residual CO<sub>2</sub> was determined using an online-connected Uras 3G gas analyser (Hartmann-Braun AG) in the range 0–0.0050 vol.% CO<sub>2</sub> (0–50 ppm). During reaction water was removed by a cooling trap (–40 °C) between the reactor and the gas analyser. The catalytic activity was evaluated by the GHSV value at which CO<sub>2</sub> residual concentration at the reactor outlet was 10 ppm, the latter being an admissible limit in the feedstock of industrial ammonia production. In addition, it satisfies the requirements for safety work of the fuel cell anodes.

Mass-gas analysis of the outlet gas mixture was performed on a MS-10 spectrometer with precision of 1×10<sup>-4</sup> vol.%.

## RESULTS AND DISCUSSIONS

Chemical analysis data of the samples listed in Table 1 reveal that the M<sup>2+</sup>/Al<sup>3+</sup> molar ratio of the dried precipitates is consistent with that of the initial mixed Co-Al and Ni-Al nitrate solutions.

For better understanding of the effect of divalent cation (Ni<sup>2+</sup> or Co<sup>2+</sup>) on phase composition, structure, thermal stability, and reducibility of the corresponding co-precipitated Al-containing LDHs, a number of physicochemical characterisations were performed.

**Table 1.** Sample notation, chemical composition, and colour of the as-synthesised hydrotalcite-like samples

Notation	Chemical composition as M <sup>2+</sup> /Al <sup>3+</sup> (molar ratio)		Colour
	theoretical	experimental	
CoAl	3.0	2.87	green
NiAl	3.0	2.98	beige

PXRD patterns of the as-synthesised precursors (Fig. 1a) exhibit common features with reflections located at the angles typical of a hydrotalcite-like phase that contains carbonate anions in the inter-layer space (ICDD-PDF file 00-014-0191): sharp and symmetrical for (003), (006), (110), and (113), and broad and asymmetrical for (009), (015), and (018), respectively. Applying PXRD data processing, the average crystallite sizes (*L*) from full-width at half-maximum values of the most intensive diffraction line (003) and the lattice parameters of the precursors were estimated (Table 2).

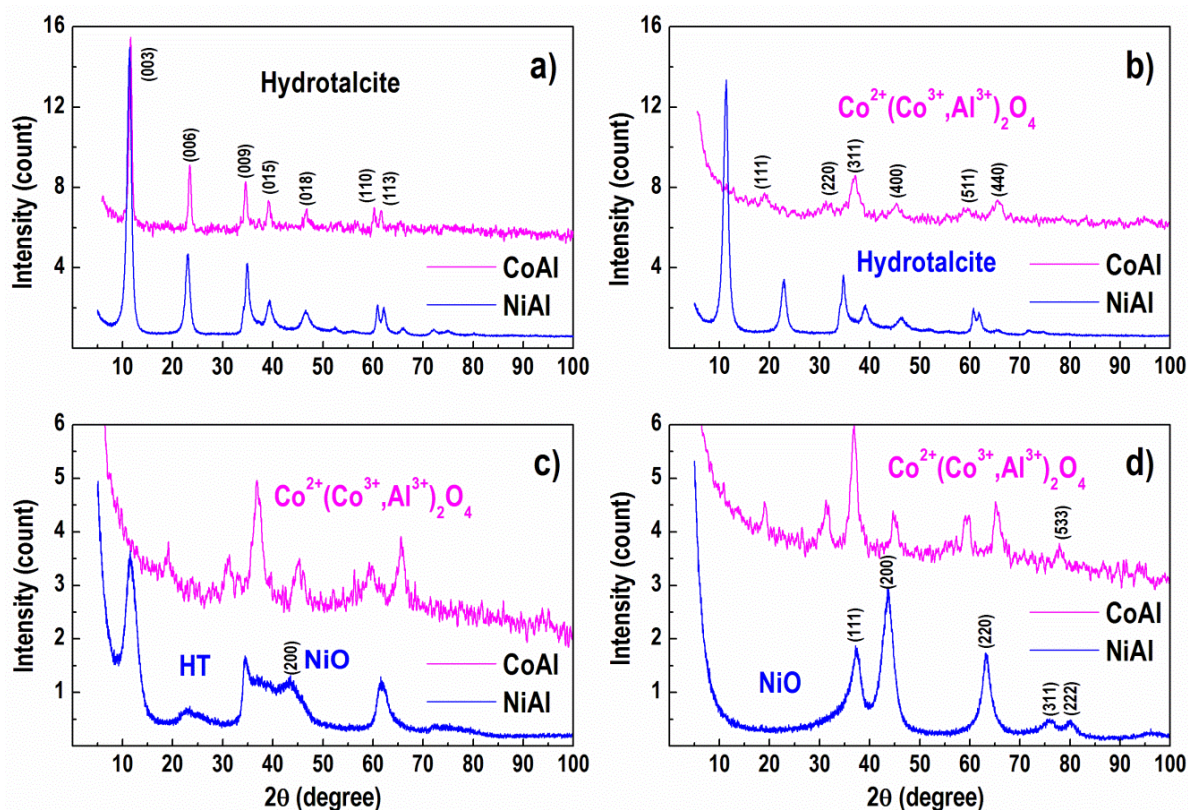


Fig. 1. PXRD patterns of the precursors thermally treated at 80 °C (a), 200 °C (b), 250 °C (c), and 350 °C (d).

**Table 2.** Lattice parameters, specific surface area, and average particle size of the as-synthesized samples

Sample	<i>a</i> (nm)	<i>c</i> (nm)	<i>V</i> (nm <sup>3</sup> )	SSA (m <sup>2</sup> /g)	<i>L</i> <sub>(003)</sub> (nm)
CoAl	0.3076 ± 0.0019	2.311 ± 0.002	0.189 ± 0.041	60	15.7
NiAl	0.3044 ± 0.0002	2.310 ± 0.001	0.186 ± 0.001	71	11.0
hydrotalcite*	0.3070	2.3230	0.190		

\*JCPDS file 01-014-0191

Collected data in Table 2 indicate that the CoAl sample demonstrates larger LDH crystallites than NiAl that are in conformity with narrower diffraction lines and lower specific surface area (SSA) values. The NiAl sample has smaller unit cell *a* and *c* parameters than the CoAl one. Differences in the *a*-parameter can be attributed to a smaller octahedral ionic radius of the Ni<sup>2+</sup> ions (0.069 nm) compared to Co<sup>2+</sup> (0.074 nm) [19].

Furthermore, different values of *c*-parameter can be ascribed to carbonate and water molecule amount in the interlayer space, which is apparently affected by the divalent ion present in the octahedral brucite-like hydroxide layers of the HT structure [11]. Variations of the lattice parameters were in good agreement with octahedral ionic radii of the metal ions present in the layered network. A double effect of Co<sup>2+</sup> partial oxidation to Co<sup>3+</sup> ions in the brucite-like layer during synthesis of the CoAl material should also be noticed. On the one hand, the Co<sup>3+</sup> ions, having a greater ionic radius (0.063 nm) with respect to Al<sup>3+</sup> (0.050 nm), cause an increase in the *a*-parameter value by comparison with standard hydrotalcite (Table 2). On the other hand, Co<sup>3+</sup> higher oxidation state enhances positive charge density of the brucite-like layer to require an excess of carbonate anions for charge compensation and water molecules to prevent interanionic repulsion in the interlayer gallery (*c*-parameters). As previously reported [20], Co<sup>3+</sup> ion presence is supported by the beige colour of the CoAl sample (Table 1). It should also be considered that the samples under study were prepared at 80 °C followed by aging in the mother liquor at the same temperature for 60 min. Obviously, the preparation temperature is a precondition to realise partial oxidation. Partial oxidation of Co<sup>2+</sup> to Co<sup>3+</sup> ions during preparation of the Co-Al layered materials has also been reported [21].

Carbonate-containing CoAl and NiAl samples were thermally decomposed (Fig. 2) by two transitions routes each of them being realised in two stages accompanied by weight losses, which is in agreement with that reported for stable layered compounds with molar ratio of M<sup>2+</sup>/M<sup>3+</sup> = 2–3 [21,22]. During low-temperature transition at 182 °C (CoAl) and 195 °C (NiAl) a reversible dehydration of the interlayer space occurred that is attributed to re-

moval of adsorbed water (<100 °C), and elimination of interlayer structural water (100–200 °C). The second decomposition step is irreversible and takes place at higher temperatures, namely 230 and 336 °C for CoAl and NiAl, respectively, due to simultaneous dehydroxylation (removal of water from the brucite sheet) and decarbonation (CO<sub>2</sub> loss from the interlayer carbonate anion) of the HT framework.

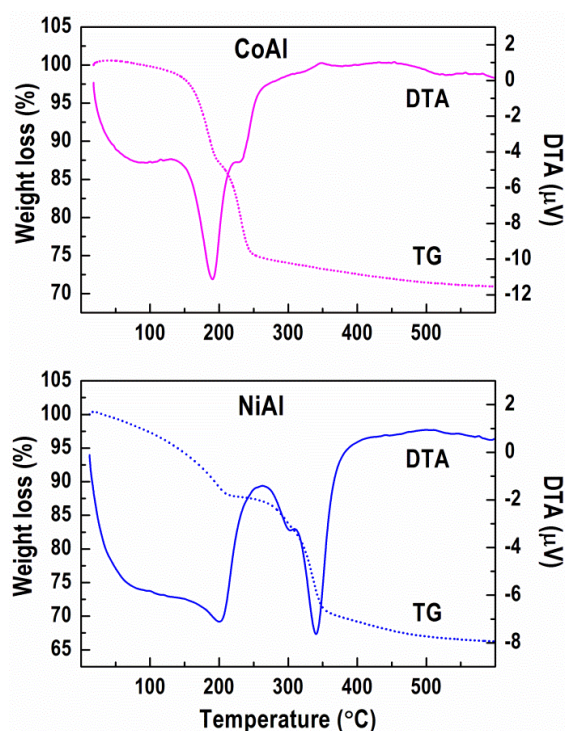


Fig. 2. DTA-TG profiles of the as-synthesised precursors.

Dehydroxylation results in destruction of the HT layer structure accompanied by formation of CoAl and NiAl mixed metal oxides.

In brief, the layered structure collapses at a lower temperature with CoAl (250 °C) than NiAl (350 °C). Thermal analysis data reveal that the total weight loss over the entire temperature range was higher with NiAl (34.0%) than CoAl (29.0%). This finding shows specifically the effect of divalent metal type on the thermal behaviour of the layered solids: the presence of Ni<sup>2+</sup> ions in the NiAl layered system increases the temperature of sample decomposition in comparison with CoAl. The result indicates a relatively low stability of the CoAl solid and attributes it to oxidation of Co<sup>2+</sup> ions.



In accordance with PXRD data, the characteristic diffraction lines of HT layered structure disappear completely after treatment of the CoAl sample at 200 °C (Fig. 1b) suggesting dehydroxylation of the brucite-type layers and decarbonation of the interlayer space because of destroyed layered structure. New reflections were registered that can be related to a spinel-like Co<sub>3</sub>O<sub>4</sub> phase (ICDD-PDF file 00-043-1003) and/or a spinel-like mixed oxide Co<sup>2+</sup>(Co<sup>3+</sup>,Al<sup>3+</sup>)<sub>2</sub>O<sub>4</sub>, attributable to facile oxidisability of the Co<sup>2+</sup> ion, and thermodynamic stability of Co<sub>3</sub>O<sub>4</sub> in air [23]. An isomorphous replacement of some of the larger Co<sup>3+</sup> ions, located at Oh sites of the Co<sub>3</sub>O<sub>4</sub> phase, by the smaller Al<sup>3+</sup> ions causes the formation of a non-stoichiometric very stable spinel-like mixed oxide Co<sup>2+</sup>(Co<sup>3+</sup>,Al<sup>3+</sup>)<sub>2</sub>O<sub>4</sub> [24,25]. Both spinel-like phases demonstrate similar reflections and intensities, thus it is not possible to distinguish between them. In contrast, PXRD patterns of NiAl sample calcined at 200 °C (Fig. 1b) display reflections similar to that of the as-synthesised counterpart signifying stability of the layered structure up to 200 °C. A decrease in peak intensity with concomitant shifting of the reflections to higher angles was observed that might be attributed to interlayer water molecule losses [26]. While the thermal treatment of CoAl sample at 250 °C only enhances the crystallinity of spinel-like mixed oxide Co<sup>2+</sup>(Co<sup>3+</sup>,Al<sup>3+</sup>)<sub>2</sub>O<sub>4</sub>, (Fig. 1c), the same temperature induces creation of an intermediate meta-stable dehydrated HT layered phase and appearance of additional broad diffraction lines of cubic NiO phase (ICDD-PDF file 00-047-1049) for NiAl solid. A further increase of the decomposition temperature to 350 °C (Fig. 1d) and especially to 800 °C (Fig. 3a) provokes better resolution of the diffraction peaks of Co<sup>2+</sup>(Co<sup>3+</sup>,Al<sup>3+</sup>)<sub>2</sub>O<sub>4</sub> phase for CoAl, indicating that Al<sup>3+</sup> cations are no more statistically distributed as they are located mainly at Oh positions of the mixed oxide spinel-like structure. Characteristics reflections of the HT layered structure disappeared completely after treatment of NiAl solid at 350 °C (Fig. 1d). Rather amorphous calcination products such as NiO phase were formed showing collapse of the layered structure [26,27]. PXRD patterns of NiAl sample calcined at 800 °C (Fig. 3a) exhibited reflections of a single oxide cubic NiO phase. The Al<sup>3+</sup> ions can be incorporated either in an amorphous nickel aluminate phase, or in a separate amorphous alumina phase [27].

A further increase of the annealing temperature to 1000 °C (Fig. 3b) promoted crystallisation as seen by the sharper diffraction lines of a mixed spinel-like Co<sup>2+</sup>(Co<sup>3+</sup>,Al<sup>3+</sup>)<sub>2</sub>O<sub>4</sub> oxide phase, while the pattern of the NiAl solid treated at the same

temperature shows the co-existence of two phases: a dominating NiO entity and a NiAl<sub>2</sub>O<sub>4</sub> one.

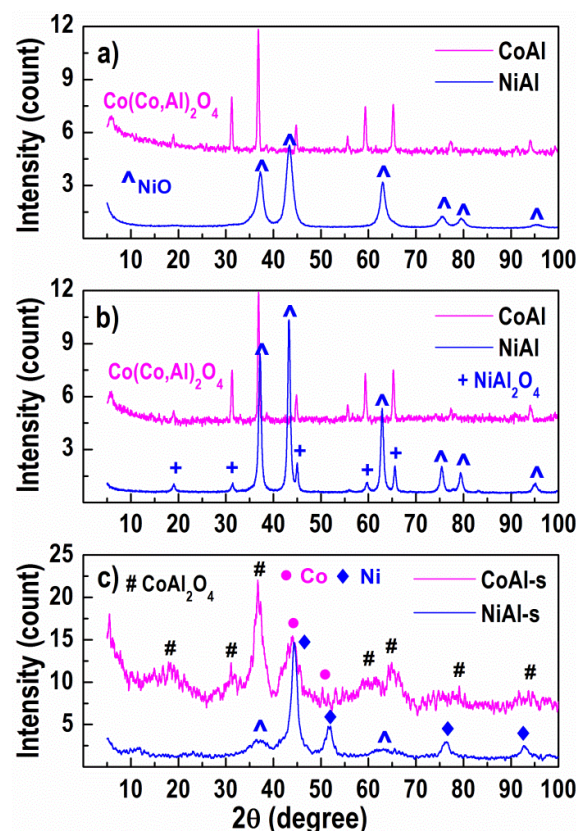


Fig. 3. PXRD of the precursors calcined at 800 °C (a) and 1000 °C (b), and of the spent catalysts preliminary reduced at 600 °C (c).

Briefly, while thermal decomposition of the CoAl precursor gave rise to CoAl<sub>2</sub>O<sub>4</sub> spinel formation, NiO and NiAl<sub>2</sub>O<sub>4</sub> spinel phases were the final products upon destruction of the NiAl sample.

A TPR technique was applied to investigate reducibility of the as-synthesised precursors. Experiments were carried out to elucidate reducible metal–O species present in the samples and to reveal the effect of divalent metals on the reduction of layered materials.

Since the reduction process was carried out dynamically at increasing temperatures by starting from the as-prepared state of the precursor, it is obvious that two parallel processes such as thermal decomposition and reduction of the obtained oxides take place during the TPR experiments. It has been reported that the thermal decomposition of the carbonate containing LDHs occurs in a similar range of temperatures either in air or hydrogen ambience [28].

The TPR profile of CoAl sample (Fig. 4) is characterised by low and high temperature regions between 180 and 400 °C and above 650 °C. Reduction in the former region is typically attributed to

transformation of Co<sub>3</sub>O<sub>4</sub> or spinel-like mixed oxide Co<sup>2+</sup>(Co<sup>3+</sup>,Al<sup>3+</sup>)<sub>2</sub>O<sub>4</sub> to CoO phase (Co<sup>3+</sup> → Co<sup>2+</sup>), followed by reduction of Co<sup>2+</sup> ions to metal Co<sup>0</sup> state (Co<sup>2+</sup> → Co<sup>0</sup>). Reduction of Co-Al spinels, Co<sub>2</sub>AlO<sub>4</sub> → CoAl<sub>2</sub>O<sub>4</sub>, is typical of the latter region [29–31]. Higher temperatures imply a stronger interaction between the Co and Al species, as in the reduction of cobalt aluminate [32,33]. It has been suggested that the Al<sup>3+</sup> ions polarise the more or less covalent Co–O bonds in the spinel-like mixed oxide thus increasing the effective charge of the Co ions [34] and, consequently, the lattice energy and the reduction temperature are increased as stated in Ref. 29.

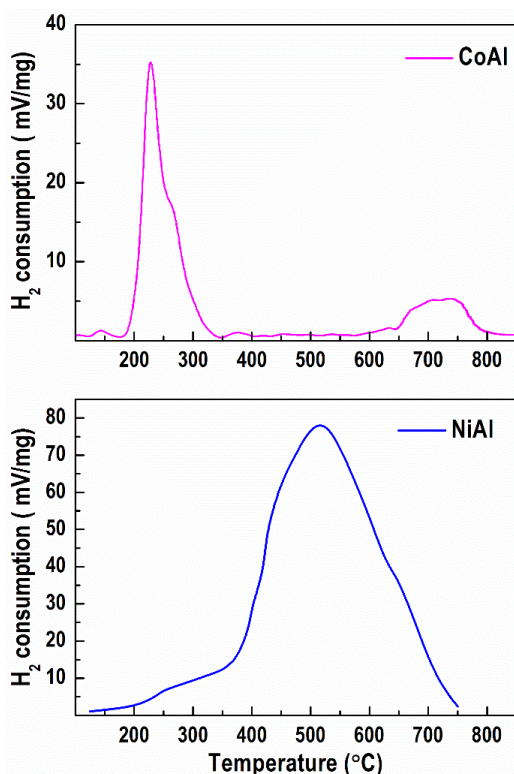


Fig. 4. TPR profiles of the as-synthesized precursors.

Contrary to CoAl, a broad asymmetric TPR profile spreading throughout a wide temperature range from 200 to 750 °C was registered with the NiAl sample. Low-temperature shoulders at ≈250, 400, and 430 °C, a well-resolved temperature maximum ( $T_{\max}$ ) at ≈520 °C as well as a high-temperature shoulder at ≈630 °C could be distinguished. A common explanation of the TPR results is searched in models proposed for decomposition and reduction of Ni-Al LDH compounds [35,36]. It was suggested that Ni-Al LDH give rise to mixed oxides that contain: (i) a NiO phase, which has a small amount of Al<sup>3+</sup> ions; (ii) a quasi-amorphous non-stoichiometric Ni-Al spinel-like phase, which hypothetically

is located at the interface between NiO and the alumina-type phase, and (iii) an alumina-type phase doped with small amounts of Ni<sup>2+</sup> ions, probably ‘grafted’ on the spinel-like phase. Based on this the low-temperature shoulders and  $T_{\max}$  can be ascribed to reduction of NiO intimately mixed with a small quantity of Al<sup>3+</sup> ions (i). The high-temperature shoulder is attributed to reduction of a poorly organised Ni–Al spinel-like phase (ii). A small amount of alumina-type phase doped with Ni<sup>2+</sup> ions (iii) may also be present.

In general, TPR profiles of the studied solids suggest two types of species, namely readily and hardly reducible entities. It is anticipated that their amounts and ratio may have impact on catalytic performance. In this connection, the layered compounds were reduced at 400, 450, 530, and 600 °C and then the methanation activity was evaluated. The measurements disclosed that both catalysts hydrogenate CO<sub>2</sub> successfully to 0–10 ppm at reaction temperatures between 400 and 320 °C and GHSV within 3000–22000 h<sup>-1</sup> (not shown). Bearing in mind that lower temperatures are thermodynamically favourable for the reaction, the activity of the catalysts is presented for reaction temperatures from 300 to 220 °C (Fig. 5 and 6).

Figures 5a-d show that the NiAl catalyst hydrogenated CO<sub>2</sub> to levels below 4 ppm at 300 °C and GHSV up to 22000 h<sup>-1</sup> irrespective of reduction temperature. In contrast to this, the Co-Al catalyst demonstrated a very low activity after reduction at 400 °C (Fig. 5a). Reduction at 600 °C, however, gave comparable levels of purification with both catalysts (Fig. 5d).

A similar activity was observed at 280 °C after reduction at each selected temperature if the activity was estimated by GHSV at which the concentration of CO<sub>2</sub> at reactor outlet is 10 ppm (Fig. 6a). Unlike CoAl, the NiAl catalyst remained active at a higher GHSV (20500 h<sup>-1</sup>) after reduction at 400 °C, whereas the former showed some activity at a lower GHSV (6.500 h<sup>-1</sup>). Reduction at 600 °C gave priority to NiAl because of 0-ppm CO<sub>2</sub> levels. Gradually the activity of the CoAl catalyst increased reaching a GHSV of 15500 h<sup>-1</sup> after reduction at 600 °C (Fig. 6a). A reaction temperature as low as 260 °C (Fig. 6b) caused a decrease in overall activity of both catalysts. The NiAl catalyst manifested a higher activity after reduction in the range 400–530 °C, however, at a lower GHSV. Almost equal CO<sub>2</sub> hydrogenation levels with both catalysts were achieved upon raising the reduction temperature up to 600 °C.



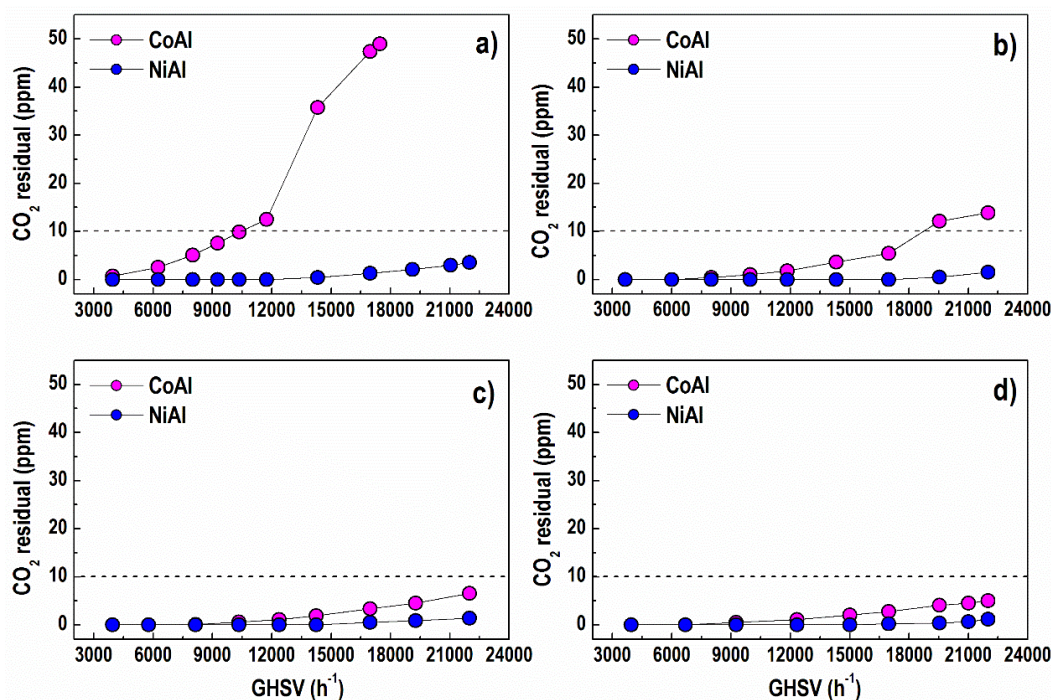


Fig. 5. Methanation activity of the catalysts at 300 °C after reduction: 400 °C (a), 450 °C (b), 530 °C (c), and 600 °C (d).

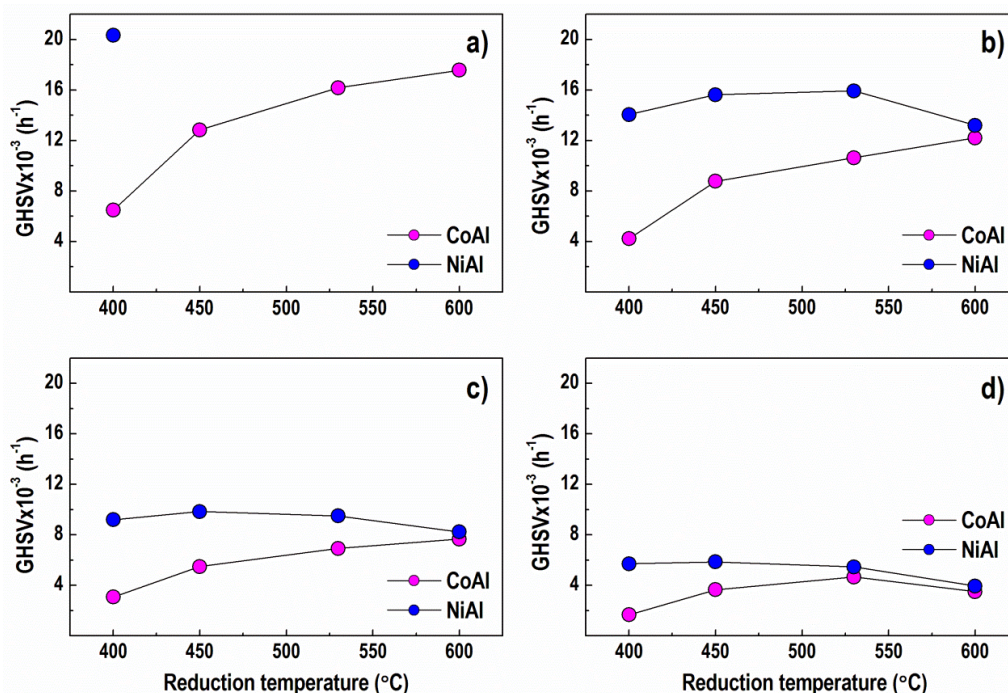


Fig. 6. Catalyst methanation activity at a 10-ppm level of CO<sub>2</sub> at a variable reaction temperature: 280 °C (a), 260 °C (b), 240 °C (c), and 220 °C (d).

Further decrease of the reaction temperature to 240 °C (Fig. 6c) enabled another drop of purification activity at the same degree. Experiments revealed that at the lowest reaction temperature of 220 °C (Fig. 6d) both catalysts exhibited a poor methanation activity independent of reduction temperature. CO<sub>2</sub> purification reached similar levels for

both catalysts at higher temperatures of reduction (530 and 600 °C). Obviously, kinetic limitations play a decisive role.

PXRD patterns of the spent CoAl catalyst (CoAl-s) (Fig. 3c) display reflections of low crystallinity mostly of CoAl<sub>2</sub>O<sub>4</sub> phase and metal Co<sup>0</sup> phase. In contrast to them, PXRD patterns of the

NiAl-s catalyst exhibit diffraction lines characteristic mainly of metallic nickel phase Ni<sup>0</sup> (ICDD-PDF file 00-004-850) as well as low intensity reflections of NiO phase (ICDD-PDF file 00-047-1049).

Differences in the catalytic performance of both catalysts are explained by different divalent metal presence and different redox properties of the metal species. A possible understanding of the methanation activity may be found in the TPR and PXRD data. Reduction of the Ni or Co ions in the precursor samples proceeds at different temperatures. This is attributed to different strength of interaction between Ni/Co and the Al<sup>3+</sup> moieties. The TPR profile of the NiAl sample displays significantly higher hydrogen consumption than the CoAl solid suggesting a facilitated reduction of Ni<sup>2+</sup>-O species. The NiAl catalyst showed a higher activity after reduction at lower temperatures (400 and 450 °C), which is ascribed to readily reducible Ni<sup>2+</sup>-O species. The occurrence of the latter in the solid was expected, because the formation of a hardly reducible NiAl<sub>2</sub>O<sub>4</sub> spinel-like phase was accomplished at temperatures over 800 °C (PXRD, Fig. 3a,b). This phenomenon determines the existence of non-spinel Ni<sup>2+</sup> ions that are reduced at lower temperatures to favour a higher activity of the NiAl catalyst in comparison with CoAl at the same reduction temperatures. Further reduction treatment of NiAl at high temperatures (530 and 600 °C) induced aggregation or sintering of the reduced metal Ni<sup>0</sup> thus leading to diminished CO<sub>2</sub> removal. Oppositely, the PXRD and TPR techniques indicated that Co<sup>2+</sup> and Al<sup>3+</sup> ions form a CoAl<sub>2</sub>O<sub>4</sub> normal spinel at 350 °C. A lower activity of CoAl catalyst could be discussed as a probability that a small fraction of Co<sup>2+</sup> ions would be reduced to the metal state. The remainder Co<sup>2+</sup> ions would be included in stable and hardly reducible cobalt aluminate phases prevailing in thermally treated or reduced samples at temperatures over 300 °C.

On the other hand, it is known that the catalytic activity is directly related to the number of available metal sites on the surface [37,38]. Consequently, a forming Co-Al spinel phase would hamper the reduction of Co<sup>2+</sup> ions and reduce the number of metal active Co<sup>0</sup> sites that are obtained during reduction-activation. Moreover, SSA data on spent catalysts reveal that NiAl-s possesses an almost twofold higher surface area (94 m<sup>2</sup>/g) than that of CoAl-s catalyst (50 m<sup>2</sup>/g). Overall characteristics of the catalysts point out a smaller number of active sites on the surface of the CoAl catalyst in comparison with NiAl, which determine a low methanation activity of the CoAl solid. This assumption was confirmed by the results of the activity tests at each

applied reaction temperatures especially after reduction of CoAl at lower temperatures.

#### Mass-gas analysis

The NiAl catalyst manifested a high level of CO<sub>2</sub> removal, which causes some doubt that this activity includes some partial hydrogenation of CO<sub>2</sub> to CO. For this purpose, the outlet gas mixture after the catalytic tests was collected and analysed. Data indicated that methane was the single reaction product thus confirming that CO<sub>2</sub> hydrogenation was the only reaction that proceeded on the catalysts at great excess of hydrogen.

#### CONCLUSIONS

Results from the study of Co-Al and Ni-Al layered double hydroxides discovered a strong dependence of structure, phase composition, thermal stability, and reducibility on the nature of divalent metal in the Al-containing samples. Divalent metal ions affect the crystallisation degree of the formed layered compounds, their specific surface area, and the thermal decomposition process of the layered structure accompanied by concomitant phase transformation to mixed metal oxides.

Formation of the spinel-type phases proceeded at different temperatures as a function of the type of divalent metal thus defining catalyst properties in the reaction of CO<sub>2</sub> methanation. Co<sup>2+</sup> ions stabilised in spinel structures hamper their reduction to metal state, leading to deficiency of active Co<sup>0</sup> phase on the surface. This phenomenon determined a low activity of Co/Al<sub>2</sub>O<sub>3</sub> catalyst, especially at low reduction temperatures. In contrast, interaction between Ni<sup>2+</sup> and Al<sup>3+</sup> ions generated readily reducible Ni<sup>2+</sup>-O species, which favoured a higher activity of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst at the same reduction temperatures. The overall hydrogenation activity of Ni/Al<sub>2</sub>O<sub>3</sub> makes the catalyst appropriate for low temperature CO<sub>2</sub> methanation.

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## СТРУКТУРА И АКТИВНОСТ НА M-AL СЛОЕСТИ ДВОЙНИ ХИДРООКСИДИ В РЕАКЦИЯТА НА МЕТАНИРАНЕ НА CO<sub>2</sub> КАТО ФУНКЦИЯ НА ДВУВАЛЕНТНИЯ МЕТАЛ

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(Резюме)

Изследван е ефектът на вида на двувалентния метал (Ni или Co) върху структурата, фазовия състав, термичната стабилност и редуцируемостта на сътаени Al-съдържащи слоести двойни хидроксида (СДХ) като прекурсори на катализатори за фино почистване от CO<sub>2</sub> чрез реакцията на метаниране. Направена е оценка на каталитичната активност чрез промяна на температурата на редукция, реакционната температура и обемната скорост. Разкрито е, че природата на двувалентния метал в Al-съдържащите СДХ влияе върху кристалността на образуваните СДХ, специфичната им повърхност и температурата на разлагане на слоеста структура до съответните смесени метални оксиди. Установено е, че стабилизирането на Co<sup>2+</sup> йоните в шпинелната CoAl<sub>2</sub>O<sub>4</sub> структура възпрепятства редукцията им до метално състояние, което води до недостатъчно количество от активна метална Co<sup>0</sup> фаза на повърхността. Този факт определя ниската метанираща активност на Co/Al<sub>2</sub>O<sub>3</sub> катализатор, особено при по-ниски температури на редукция. В контраст на това, взаимодействието между Ni<sup>2+</sup> и Al<sup>3+</sup> йоните предизвиква формиране на лесно редуцируеми Ni<sup>2+</sup>-O структури, което благоприятства по-висока активност на Ni/Al<sub>2</sub>O<sub>3</sub> катализатор при същите температури на редукция. Образоването на шпинело-подобни фази е функция на вида на двувалентния метал и е определящо за активността на катализаторите при фино почистване от CO<sub>2</sub> на богати на водород газови смеси чрез реакцията на метаниране.