

THE FORMATION OF LAYERED DOUBLE HYDROXIDES ON ALUMINA SURFACE IN AQUEOUS SOLUTIONS CONTAINING DIVALENT METAL CATIONS

FRANTIŠEK KOVANDA^{1,*}, PETRA MAŠÁTOVÁ¹, PETRA NOVOTNÁ², AND KVĚTA JIRÁTOVÁ³

¹ Department of Solid State Chemistry, Institute of Chemical Technology Prague, Technická 5, 166 28 Prague, Czech Republic

² Department of Inorganic Technology, Institute of Chemical Technology, Technická 5, 166 28 Prague, Czech Republic

³ Institute of Chemical Process Fundamentals of the ASCR, v.v.i., Rozvojová 135, 165 02 Prague, Czech Republic

Abstract—Layered double hydroxides (LDHs) are often used as precursors for mixed-oxide catalysts and the deposition of a LDH layer on supporting materials would be advantageous because of better utilization of active components. The purpose of the present study was to investigate the formation of LDHs on Al₂O₃/Al supports prepared by the anodic oxidation of aluminum foil in dilute aqueous solutions of Co, Mn, and/or Ni nitrates. The LDH deposition was carried out under hydrothermal conditions at 80–180°C for periods ranging from 8 h to 7 days. In the initial stages of the reaction, a surface alumina hydration was observed. The LDH phase was detected after long-term deposition (3–7 days) at 120–160°C and only a small amount of Mn was incorporated in the LDHs deposited. In solutions containing only Co and Mn cations, scanning electron microscopy (SEM) images show a gradual growth of platy crystals resulting in the formation of discrete bulky aggregates with sizes up to several tens of micrometers. The adhesion of aggregates to the support probably decreased with increasing size and oversized aggregates fell away; none was found in SEM images of the samples obtained after prolonged reaction times. When Ni cations were present in the solution, they were incorporated preferentially into the LDH phase; an homogeneous layer was formed, with single platy crystals oriented perpendicular to the support. After calcination at 500°C, the products formed on Al₂O₃/Al support exhibited a shift of reduction maxima to higher temperatures in comparison with mixed oxides obtained by thermal decomposition of coprecipitated LDHs.

Key Words—Deposition, Hydrothermal Reaction, Layered Double Hydroxides, Supported Mixed Oxides.

INTRODUCTION

Layered double hydroxides (LDHs), also known as ‘hydrotalcite-like compounds’ or ‘anionic clays,’ are an important class of layered materials used in various applications, *e.g.* in heterogeneous catalysis (Cavani *et al.*, 1991; Basile and Vaccari, 2001; Li and Duan, 2006; Kovanda *et al.*, 2006a). The chemical composition of LDHs can be expressed by the general formula $[M_{1-x}^{II}M_x^{III}(\text{OH})_2]^{x+}[A_{x/n}^{n-}\cdot y\text{H}_2\text{O}]^{x-}$ where M^{II} and M^{III} are divalent and trivalent metal cations, A^{n-} is an n -valent anion, and x usually has values between 0.20 and 0.33. The M^{II}/M^{III} isomorphous substitution in octahedral sites of the hydroxide sheets results in a net positive charge, which is neutralized by the interlayers comprising anions and water molecules. The LDHs are usually prepared by coprecipitation, when a solution containing M^{II} and M^{III} metal cations in adequate proportions reacts with an alkaline solution. After thermal decomposition at moderate temperatures, LDHs give finely dispersed mixed oxides of M^{II} and M^{III} metals with large surface area and good thermal stability, criteria usually required for heterogeneous catalysts. When the powdered pro-

ducts are formed into pellets or extrudates, a considerable part of the catalyst grain volume is often not employed because of internal and external diffusion. Deposition of an active layer on a supporting material would, therefore, be advantageous.

Alumina is often used as a supporting material for deposition of active components such as noble or transition metals. The alumina-supported catalysts are commonly prepared by deposition of ionic precursors from aqueous solutions *via* impregnation or deposition-precipitation techniques followed by thermal activation. The formation of LDH phases was observed during impregnation of γ -alumina with aqueous solutions containing divalent metal cations (Ni²⁺, Co²⁺, or Zn²⁺) at near-neutral pH (Paulhiac and Clause, 1993; d’Espinoze de la Caillerie *et al.*, 1995; Merlen *et al.*, 1995). The impregnation procedure was carried out at ambient temperature in the presence of diluted ammonia and, upon calcination, thermally stable systems were obtained due to a strong ion-support interaction. A dissolution-reprecipitation mechanism was proposed, consisting of the adsorption of divalent metal cations on an alumina surface followed by alumina dissolution (rate-limiting step promoted by adsorbed ions) and precipitation of Al³⁺ cations, released from the support, with divalent metal cations in the solution. Simultaneous ion adsorption and alumina dissolution are expected; therefore, the amount of adsorbed cations is small and

* E-mail address of corresponding author:

Frantisek.Kovanda@vscht.cz

DOI: 10.1346/CCMN.2009.0570403

the formation of an LDH phase is almost quantitative. In this process, alumina is not only a supporting material but also the source of Al^{3+} .

An analogous approach was recently applied for preparation of oriented LDH films on Al-containing substrates, e.g. Zn-Al LDH on Al-bearing glass substrate (Gao *et al.*, 2006) or Ni-Al LDH on porous anodic alumina (Chen *et al.*, 2006). Thin films growing directly from a substrate have better adhesion and mechanical stability in comparison with the films obtained by colloidal-deposition techniques (e.g. spin-coating or dip-coating). A monolayer of LDH microcrystals, consisting of thin curved platelets oriented perpendicular to the substrate, was observed in SEM images. The microstructure of LDH films was affected by temperature and time of crystallization and the hydrophobic surfaces can be obtained in this way (Chen *et al.*, 2006; Yang *et al.*, 2008). The deposition of Zn-Al LDH on anodized aluminum foil and following LDH intercalation with laurate (dodecanoate) resulted in the formation of a hierarchical micro/nanostructured superhydrophobic film with very effective corrosion-resistant properties (Zhang *et al.*, 2008). The mixed oxides obtained by thermal decomposition of deposited LDHs maintain the original morphology of the precursor films (Chen *et al.*, 2008; Lü *et al.*, 2008). The LDH films deposited on metal substrates can also be prepared by electrochemical synthesis (Scavetta *et al.*, 2007; Gupta *et al.*, 2008; Yarger *et al.*, 2008).

In the present work, the formation of LDH phases at the interface between Al oxide and dilute aqueous solutions of Co and Mn nitrates was studied. The Co-Mn-Al LDH-related mixed oxides are promising catalysts for N_2O decomposition (Obalová *et al.*, 2005, 2007; Kovanda *et al.*, 2006b) and their deposition on a support would be advantageous for industrial applications. The method reported by Chen *et al.* (2006) was modified and used for LDH crystallization on porous alumina/aluminum support under hydrothermal conditions. The products formed were characterized by powder X-ray diffraction (XRD) and SEM; the reducibility of calcined products was also examined.

EXPERIMENTAL

Materials

Cobalt, Mn, Ni, and ammonium nitrates ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and NH_4NO_3), aqueous ammonia solution (25 wt.%), and sulfuric acid (96 wt.%), all supplied by Penta (Czech Republic), were used as purchased. Distilled water was used in the preparation of solutions.

The porous anodic alumina film was obtained by anodizing aluminum foil (purity >99.9%, thickness 0.1 mm) in H_2SO_4 solution (2.8 mol L^{-1}) for 60 min at room temperature and current density of 30 mA cm^{-2} . The aluminum foil ($10 \text{ cm} \times 13 \text{ cm}$) washed in ethanol

and distilled water was placed between two cathodes (aluminum plates, purity >99.9%, thickness 3 mm); the distance between the anode and cathodes was 2 cm. The anodized foil was washed thoroughly in distilled water, dilute aqueous solution of ammonia (5 wt.%), and again in distilled water and then dried at 60°C . The dried $\text{Al}_2\text{O}_3/\text{Al}$ samples ($2 \text{ cm} \times 6 \text{ cm}$) were used as a support for LDH deposition.

Preparation of samples

The method reported by Chen *et al.* (2006) was adopted for LDH deposition. The aqueous solution of Co and Mn nitrates with a Co:Mn molar ratio of 2:1 and a total metal ion concentration of 0.01 mol L^{-1} , containing NH_4NO_3 (0.06 mol L^{-1}), was prepared; the pH of 6.5 was maintained by adding dilute aqueous ammonia solution (1 wt.%). In some experiments, analogous solutions of Co and Ni nitrates (Co:Ni molar ratio of 1:1) or Co, Ni, and Mn nitrates (Co:Ni:Mn molar ratio of 1:1:1) were used. The $\text{Al}_2\text{O}_3/\text{Al}$ support was placed vertically into 100 mL Teflon-lined stainless steel bombs containing 75 mL of nitrate solution. The hydrothermal reaction was carried out at various temperatures (between 80 and 180°C) under autogenous pressure for periods ranging between 8 h and 7 days. The support was then taken out, rinsed with distilled water, and dried at 60°C .

Characterization

The elemental analysis of the products deposited was determined by atomic absorption spectroscopy. The sample (0.10–0.15 g) of $\text{Al}_2\text{O}_3/\text{Al}$ support after deposition was dissolved in 1 mL of hot hydrochloric acid (35 wt.%) and the solution obtained was diluted with distilled water to 25 mL; the concentration of Co, Mn, and Ni was determined using a Spectr AA880 instrument (Varian). The metals content was related to the weight increase in the dried support after deposition (considered as the approximate weight of the deposited product).

Powder XRD patterns were recorded using a Seifert XRD 3000P instrument with $\text{CoK}\alpha$ radiation ($\lambda = 0.179 \text{ nm}$, graphite monochromator, goniometer with Bragg-Brentano geometry) in the 10 – $80^\circ 2\theta$ range, and step size 0.05° . Qualitative analysis was performed using the HighScore software package (PANalytical, The Netherlands, version 1.0d).

Scanning electron micrographs of the samples were taken at various magnifications using an Hitachi S-4700 instrument. No conductive layer was applied in order to maintain all surface details at high resolution. The small accelerating voltage of $\sim 2 \text{ kV}$ was applied to avoid surface charging.

Selected samples were heated at 500°C for 4 h in air in order to obtain mixed oxides deposited on $\text{Al}_2\text{O}_3/\text{Al}$ support. The reference LDH-related mixed oxides were prepared under the same conditions, by heating coprecipitated LDH precursors. The Co-Al, Ni-Co-Al, and Ni-

Co-Mn LDH precursors with cation molar ratios of 2:1, 1:1:1, and 1:1:1, respectively, were obtained by coprecipitation of the corresponding nitrates; details of the synthesis are described elsewhere (Kovanda *et al.*, 2006b). Temperature programmed reduction (TPR) measurements of the calcined samples (0.2 g) were performed with a H_2/N_2 mixture (10 mol.% of H_2), flow rate of 50 mL min^{-1} , and a linear temperature increase of $20^\circ\text{C min}^{-1}$ up to 1000°C . A change in H_2 concentration was detected using a mass spectrometer Omnistar 300 (Pfeiffer Vakuum).

RESULTS AND DISCUSSION

An increase in the weight of the samples in relation to reaction temperature and time is demonstrated in Figure 1a. A marked weight increase was observed in samples prepared at 100 – 160°C and the sample weight increased with increasing time of hydrothermal treatment. The temperature of 80°C was probably too low for LDH deposition in very dilute nitrate solutions. Surprisingly, only a slight weight increase and small Co and Mn contents were found in the samples prepared at 180°C . The Co content in the samples increased with reaction temperature (up to 160°C) and time (Figure 1b); maximum values of almost 20 wt.% Co in the deposited layer were determined in the samples prepared at 140 and 160°C . On the other hand, much smaller Mn contents were found in all samples (Figure 1c), approximately one tenth of the amount of Co, even though the Co:Mn molar ratio in solution was 2:1. The small amount of solid Mn in the deposited product might be explained by a difference in the pH at which Co and Mn hydroxides are precipitated; the pH values of 7.5 and 8.5 are reported for precipitation of Co^{2+} and Mn^{2+} in 0.01 M solutions, respectively (Cavani *et al.*, 1991), whereas a pH of 6.5 was maintained in the solutions used for LDH deposition. The possible partial oxidation of Mn^{2+} cations and the formation of hydrated oxides during hydrothermal reaction cannot be excluded; a few dark brown spots on the surfaces of the samples were observed in some cases. On the other hand, such hydrated Mn oxides were not detected by XRD.

In the powder XRD patterns of all samples, two sharp diffraction peaks, corresponding to the Al in the support were found (Figure 2). No other phases were detected by XRD in the Al_2O_3/Al support and the samples obtained after 8 h of hydrothermal reaction. A hydroxalite-like LDH together with a boehmite-like phase were found in the samples obtained at 120 – 160°C after prolonged hydrothermal treatment (4–7 days). Powder XRD indicated the formation of boehmite ($AlOOH$) as a result of surface Al oxide hydration; later, a crystallization of LDH was also detected (Table 1). A partial incorporation of Co and Mn cations in the hydrated alumina can be expected. X-ray diffraction patterns with no basal diffraction lines were reported by Chen *et al.*

(2006) for Ni-Al LDH films formed on porous anodic alumina. In contrast, 003 and 006 diffraction lines were apparent in powder XRD patterns of the Co- and Mn-containing samples (Figure 2); therefore, the LDH

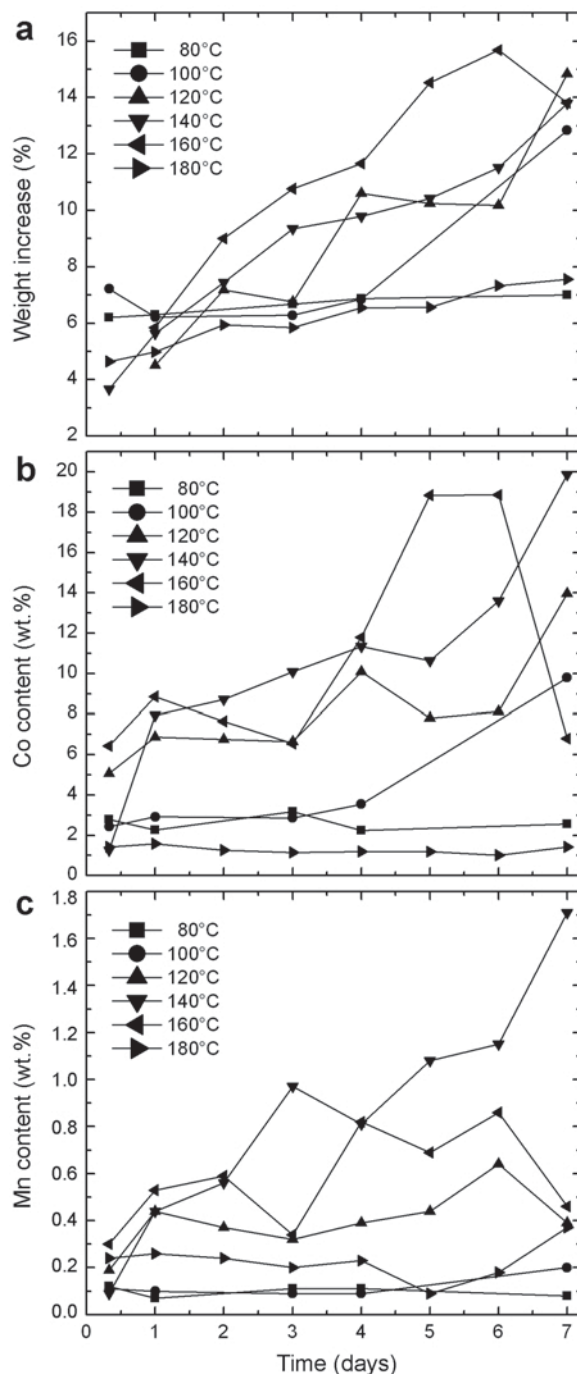


Figure 1. Weight increase of the Al_2O_3/Al support and the amount of Co and Mn in the products formed during hydrothermal reactions in Co- and Mn-containing aqueous solutions in relation to reaction temperature and time: (a) relative weight increase; (b) Co content; (c) Mn content.

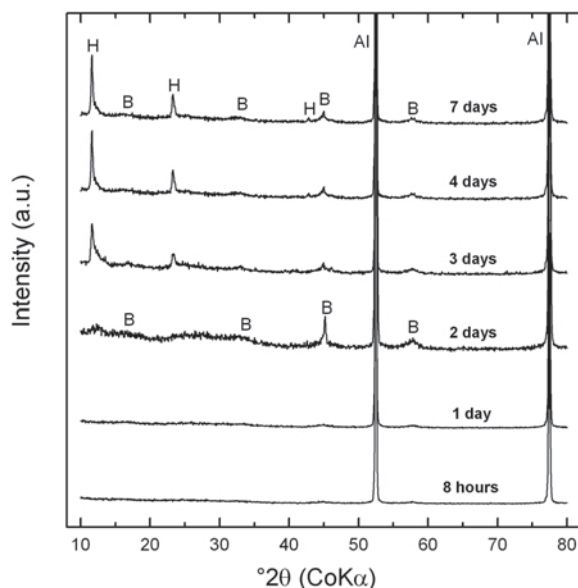


Figure 2. Powder XRD patterns of the samples treated for various times at 140°C. B – AlOOH (boehmite), H – hydrotalcite-like phase, Al – aluminum (support).

crystals formed were probably not strictly perpendicular to the support. No LDH was formed in the samples prepared at 180°C. The thermal stability of Co-containing LDHs is relatively low; they are decomposed at ~200–250°C (Kovanda *et al.*, 2006b). Hence, temperatures of 180°C may be too high for the formation of a stable LDH phase in the solution used.

In the initial stages of LDH formation, single, thin, platy crystals with orientation approximately perpendicular to the substrate were observed in SEM images (Figure 3a). The gradual growth of these crystals resulted in the formation of bulky aggregates up to several tens of micrometers in size (Figure 3b–c). The size of the aggregates formed increased with increasing reaction time. A marked decrease in weight of deposited product and especially in Co concentration was observed for the sample obtained after 7 days of reaction at 160°C (Figure 1). In addition, the powder XRD pattern of this

sample showed LDH diffraction lines of lesser intensity in comparison with the samples prepared at shorter reaction times (not shown here). In SEM images of the aforementioned sample, a much smaller number of aggregates was found; on the other hand, spots, indicating traces of aggregates removed, were visible (Figure 4). All these results indicate a partial removal from the support of the LDH crystals formed. The contact area between aggregates of LDH crystals and the support was rather limited and so adhesion of aggregates to the support probably decreased with increasing size, and oversized aggregates fell away.

When Ni cations were present in the solution, LDHs with significantly different morphologies were obtained (Figure 3d). A relatively homogeneous film consisting of thin curved platelets was formed, similar to that reported by Chen *et al.* (2006) for Ni-Al LDH. Elemental analysis of the LDHs deposited showed an increased incorporation of Ni in the solid (Table 2); the amount of Ni determined was more than twice as much as that of Co, even though the same Ni and Co concentrations were used in solution. Again, only a very small amount of Mn was detected in the product formed. As mentioned above, different values of precipitation pH for Ni, Co, and Mn hydroxides are reported: 7.0, 7.5, and 8.5, respectively (Cavani *et al.*, 1991). Therefore, a greater degree of precipitation of Ni²⁺ rather than Co²⁺ cations is to be expected under the experimental conditions used.

The samples prepared by hydrothermal reaction (4 days at 140°C) in aqueous solution containing Co, Mn, and/or Ni nitrates were heated at 500°C in air to obtain LDH-related mixed oxides deposited on Al₂O₃/Al substrate. Thermal decomposition of Co-containing LDHs results in the formation of spinel-like mixed oxides (Kovanda *et al.*, 2006b). Two characteristic reduction maxima were observed in TPR patterns of the Co-Al mixed oxide with a Co:Al molar ratio of 2:1 prepared by calcination of coprecipitated LDH precursor. The first at ~400°C is probably related to a reduction of a Co-rich Co₃O₄-type component and the second, at ~690°C, was ascribed to reduction of Co in Co-Al spinel-

Table 1. Phases detected by powder XRD in the samples in relation to reaction temperature and time.

Temperature (°C)	Time (days)				
	1	2	3	4	7
80	(s)	(s)	B	B	B
100	(s)	B	B	B	B, LDH
120	(s)	B	B	B, LDH	B, LDH
140	B	B	B, LDH	B, LDH	B, LDH
160	B	B	B, LDH	B, LDH	B, LDH
180	B	B	B	B	B

(s) – only aluminum support was detected; B – AlOOH (boehmite); LDH – hydrotalcite-like phase.

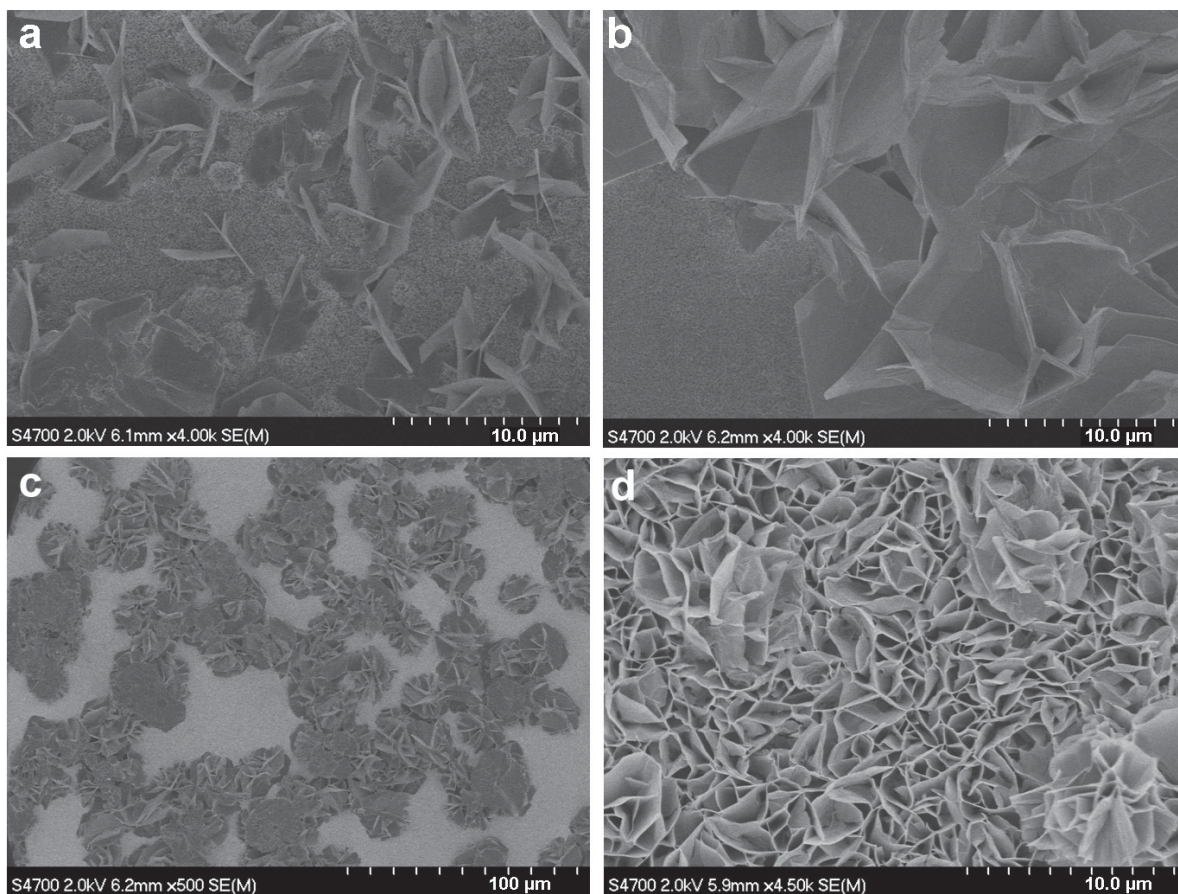


Figure 3. SEM images of LDH crystals grown on $\text{Al}_2\text{O}_3/\text{Al}$ support during hydrothermal reaction in aqueous solutions containing Co and Mn cations: (a) single, thin, platy crystals formed after 4 days at 120°C ; (b) aggregate of thin platy crystals formed after 7 days at 120°C ; (c) discrete, bulky aggregates formed after 7 days at 120°C (lower magnification); and (d) deposited layer consisting of LDH crystals formed after 4 days at 140°C in an aqueous solution containing Co, Ni, and Mn cations.

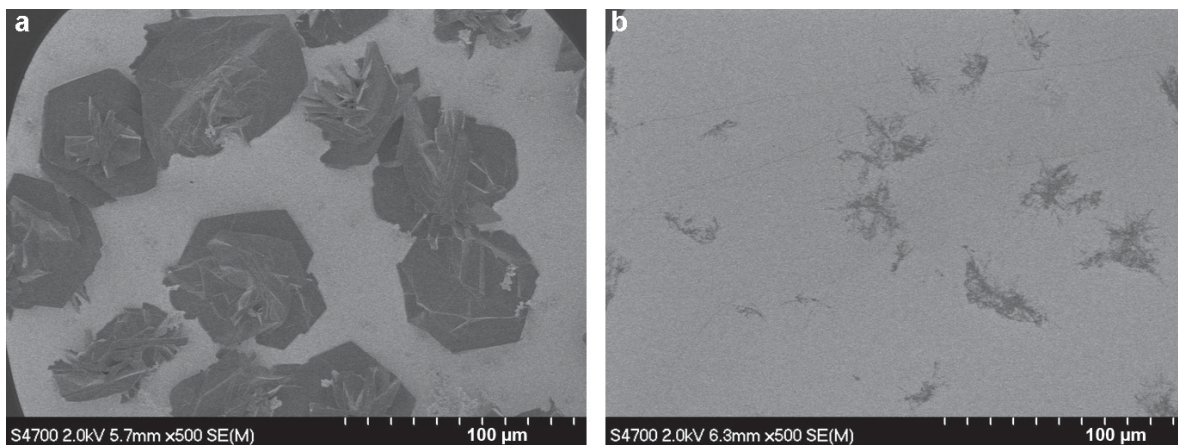


Figure 4. SEM images of the samples obtained at 160°C : (a) bulky aggregates of LDH crystals formed after 5 days; (b) traces of the aggregates removed found in the sample obtained after 7 days of reaction.

Table 2. Elemental analysis of the samples prepared by hydrothermal reaction at 140°C for 4 days in aqueous solutions containing Co, Mn, and/or Ni cations (total metal ion concentration 0.01 mol L⁻¹).

Nitrate solution	Relative weight increase* (%)	Wt.%		
		Ni	Co	Mn
Co-Mn (1:1)	13.4	—	18.5	0.7
Ni-Co (1:1)	18.7	13.1	5.8	—
Ni-Co-Mn (1:1:1)	16.4	12.8	5.3	0.1

* Difference in sample weight before and after hydrothermal reaction.

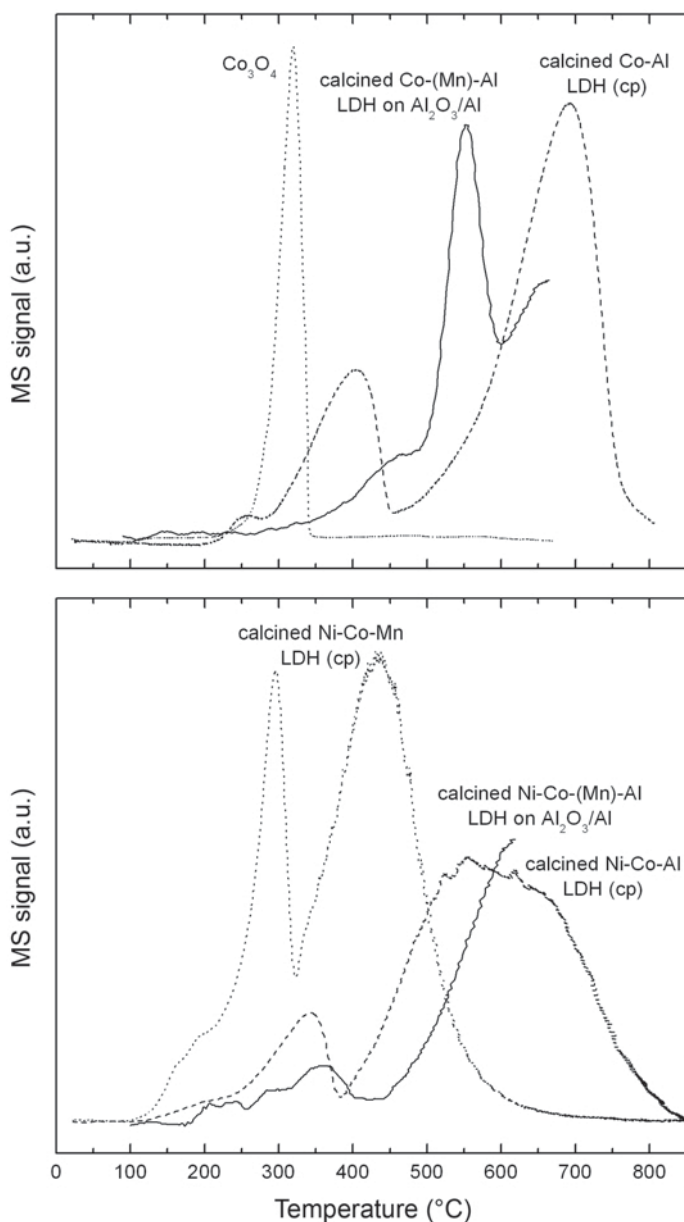


Figure 5. TPR patterns of the products formed on an $\text{Al}_2\text{O}_3/\text{Al}$ support and calcined at 500°C in comparison with those of mixed oxides prepared by heating coprecipitated LDH precursors (cp).

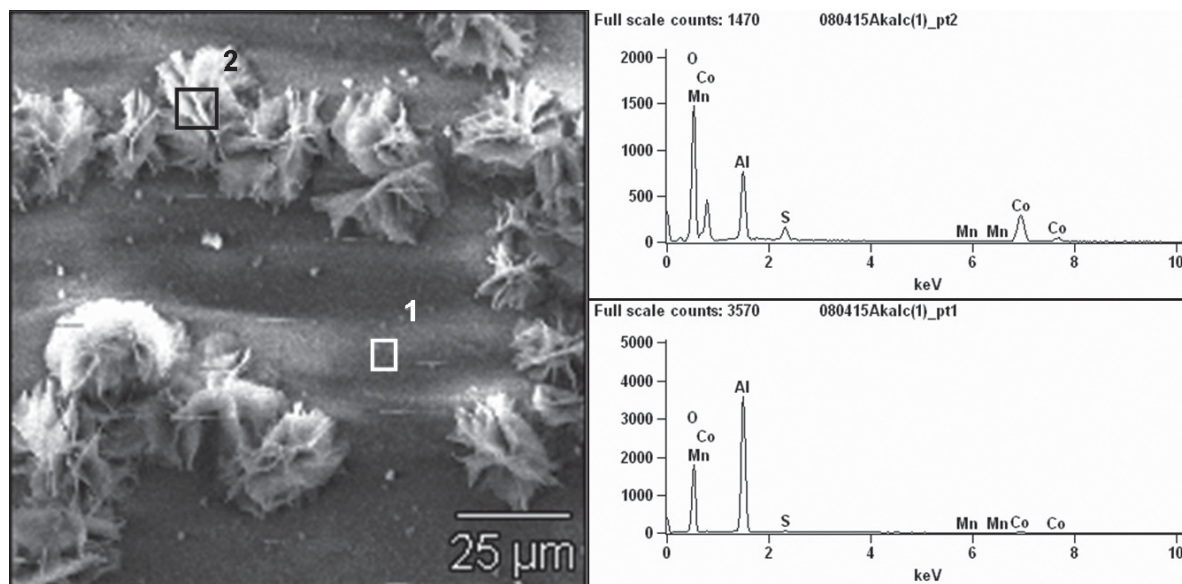


Figure 6. SEM image of the Co-(Mn)-Al LDH aggregates calcined at 500°C and EDX patterns of the selected sites: point 1 – Al₂O₃/Al support; point 2 – aggregate of calcined LDH crystals.

like mixed oxide (Ribet *et al.*, 1999). The Co-(Mn)-Al mixed oxide deposited on Al₂O₃/Al support was less reducible than the product prepared by calcination of coprecipitated Co-Al LDH; the first reduction maximum was shifted to 550°C (Figure 5). A similar shift of reduction maxima to higher temperatures was also observed with the Ni-containing mixed oxides deposited on Al₂O₃/Al support. The SEM images of LDHs deposited (Figure 3) show the bulky aggregates or structured layer composed of relatively large and well developed plate crystals. Compared to the coprecipitated LDH precursors, the products with better structural ordering and increased crystallite size were obtained after deposition under hydrothermal conditions. An improved crystallinity of the LDH precursors can affect the reducibility of related mixed oxides; *e.g.* the hydrothermal treatment of Ni-Al LDHs resulted in enhanced stability of Ni species in calcination products against reduction (Benito *et al.*, 2006; Kovanda *et al.*, 2009).

Table 3. Microprobe analysis of the deposited Co-(Mn)-Al LDH calcined at 500°C (point 1 – Al₂O₃/Al support, point 2 – aggregate of the calcined LDH crystals, see Figure 6).

Element	Point 1 (at.%)	Point 2 (at.%)
Co	1.92	44.7
Mn	0.16	0.08
Al	89.1	34.5
O	6.58	15.6
S	2.19	5.19

Microprobe analysis of the Al₂O₃/Al support with deposited LDH-related mixed oxides showed only small Co and Mn concentrations in spots corresponding to the support. In other spots corresponding to the aggregates of calcined LDH crystals, a considerably increased Co concentration was detected but a relatively small Co:Al ratio of ~1.3:1 was found (Figure 6, Table 3). The smaller Co:Al molar ratio, compared to the co-precipitated LDH-related mixed oxide (Co:Al = 2:1), might indicate a substantial enrichment of deposited mixed oxide with Al. On the other hand, a contribution to the detected radiation coming from the Al₂O₃/Al support cannot be ruled out. Therefore, estimation of Co/Al molar ratio and potential enrichment of the deposited mixed oxide with Al is difficult. Microprobe analysis indicated an increased amount of S in the deposited mixed oxide (Table 3). The sulfate anions were probably not completely washed from the support after anodic oxidation and could be intercalated into the LDHs formed. The presence of sulfate, together with the crystallinity of the calcination products and their potential enrichment with Al might explain the marked shift of reduction maxima to higher temperatures in TPR patterns of the mixed oxides deposited on Al₂O₃/Al support.

CONCLUSIONS

The Co-containing LDHs were deposited on an Al₂O₃/Al support by surface reaction with dilute aqueous solutions containing Co²⁺ cations under hydrothermal conditions. The formation of an LDH phase was facilitated by increasing reaction temperature and time; the surface hydration of Al oxide and the subsequent

formation of a boehmite-like phase took place before crystallization of the LDH. A gradual growth of thin platy LDH crystals resulted in the formation of discrete, bulky aggregates up to several tens of micrometers in size; their adhesion to the support probably decreased with increasing size and oversized aggregates fell away. No LDH formation was found in the samples obtained at 180°C. When Ni²⁺ cations were present in the solution, more Ni was incorporated into the product formed and LDHs with different morphologies were deposited (an homogeneous layer consisting of thin curved platelets was observed). The LDH-related mixed oxides deposited on Al₂O₃/Al support exhibited a marked shift of reduction maxima to higher temperatures in comparison with those obtained by calcination of coprecipitated LDH precursors; the presence of sulfate in the precursors, as well as the high crystallinity of calcination products and possibly their enrichment with Al may explain the findings.

ACKNOWLEDGMENTS

This work was supported by the Czech Science Foundation (104/07/1400) and by the Czech Ministry of Education, Youth and Sports (MSM 6046137302).

REFERENCES

- Basile, F. and Vaccari, A. (2001) Applications of hydrotalcite-type anionic clays (layered double hydroxides) in catalysis. Pp. 285–321 in: *Layered Double Hydroxides: Present and Future* (V. Rives, editor). Nova Science Publishers, New York.
- Benito, P., Labajos, F.M., and Rives, V. (2006) Microwave-treated layered double hydroxides containing Ni²⁺ and Al³⁺: The effect of added Zn²⁺. *Journal of Solid State Chemistry*, **179**, 3784–3797.
- Cavani, F., Trifirò, F., and Vaccari, A. (1991) Hydrotalcite type anionic clays: preparation, properties, and applications. *Catalysis Today*, **11**, 173–301.
- Chen, H., Zhang, F., Fu, S., and Duan, X. (2006) In situ microstructure control of oriented layered double hydroxide monolayer films with curved hexagonal crystals as superhydrophobic materials. *Advanced Materials*, **18**, 3089–3093.
- Chen, H., Zhang, F., Xu, S., Evans, D.G., and Duan, X. (2008) Facile fabrication and wettability of nestlike microstructure maintained mixed metal oxide films from layered double hydroxide film precursors. *Industrial and Engineering Chemistry Research*, **47**, 6607–6611.
- d'Espinose de la Caillerie, J.-B., Kermarec, M., and Clause, O. (1995) Impregnation of γ -alumina with Ni(II) or Co(II) ions at neutral pH: Hydrotalcite-type coprecipitate formation and characterization. *Journal of the American Chemical Society*, **117**, 11471–11481.
- Gao, Y.F., Nagai, M., Masuda, Y., Sato, F., Seo, W.S., and Koumoto, K. (2006) Surface precipitation of highly porous hydrotalcite-like film on Al from a zinc aqueous solution. *Langmuir*, **22**, 3521–3527.
- Gupta, V., Gupta, S., and Miura, N. (2008) Potentiostatically deposited nanostructured Co_xNi_{1-x} layered double hydroxides as electrode materials for redox-supercapacitors. *Journal of Power Sources*, **175**, 680–685.
- Kovanda, F., JirátoVá, K., and Kalousková, R. (2006a) Synthetic hydrotalcite-like compounds. Pp. 89–139 in: *Advances in Chemistry Research, Volume 1* (F.L. Gerard, editor). Nova Science Publishers, New York.
- Kovanda, F., Rojka, T., Dobešová, J., Machovič, V., Bezdička, P., Obalová, L., JirátoVá, K., and Grygar, T. (2006b) Mixed oxides obtained from Co and Mn containing layered double hydroxides: Preparation, characterization and catalytic properties. *Journal of Solid State Chemistry*, **179**, 812–823.
- Kovanda, F., Rojka, T., Bezdička, P., JirátoVá, K., Obalová, L., Pacultová, K., Bastl, Z., and Grygar, T. (2009) Effect of hydrothermal treatment on properties of Ni-Al layered double hydroxides and related mixed oxides. *Journal of Solid State Chemistry*, **182**, 27–36.
- Li, F. and Duan, X. (2006) Applications of layered double hydroxides. Pp. 193–223 in: *Layered Double Hydroxides. Structure and Bonding, Vol. 119* (X. Duan and D.G. Evans, editors). Springer, Berlin/Heidelberg.
- Lü, Z., Zhang, F., Lei, X., Yang, L., Xu, S., and Duan, X. (2008) In situ growth of layered double hydroxide films on anodic aluminum oxide/aluminum and its catalytic feature in aldol condensation of acetone. *Chemical Engineering Science*, **63**, 4055–4062.
- Merlen, E., Gueroult, P., d'Espinose de la Caillerie, J.-B., Rebours, B., Bobin, C., and Clause, O. (1995) Hydrotalcite formation at the alumina/water interface during impregnation with Ni(II) aqueous solutions at neutral pH. *Applied Clay Science*, **10**, 45–56.
- Obalová, L., JirátoVá, K., Kovanda, F., Pacultová, K., Lacný, Z., and Mikulová, Z. (2005) Catalytic decomposition of nitrous oxide over catalyst prepared from Co/Mg-Mn/Al hydrotalcite-like compounds. *Applied Catalysis B: Environmental*, **60**, 289–297.
- Obalová, L., Pacultová, K., Balabánová, J., JirátoVá, K., Bastl, Z., Valášková, M., Lacný, Z., and Kovanda, F. (2007) Effect of Mn/Al ratio in Co-Mn-Al mixed oxide catalysts prepared from hydrotalcite-like precursors on catalytic decomposition of N₂O. *Catalysis Today*, **119**, 233–238.
- Paulhiac, J.L. and Clause, O. (1993) Surface coprecipitation of Co(II), Ni(II), or Zn(II) with Al(III) ions during impregnation of γ -alumina at neutral pH. *Journal of the American Chemical Society*, **115**, 11602–11603.
- Ribet, S., Tichit, D., Coq, B., Ducourant, B., and Morato, F. (1999) Synthesis and activation of Co-Mg-Al layered double hydroxides. *Journal of Solid State Chemistry*, **142**, 382–392.
- Scavetta, E., Mignani, A., Prandstraller, D., and Tonelli, D. (2007) Electrosynthesis of thin films of Ni, Al hydrotalcite-like compounds. *Chemistry of Materials*, **19**, 4523–4529.
- Yang, F., Xie, B.Y., Sun, J.Z., Jin, J.K., and Wang, M. (2008) Preparation and wettability of Zn-Al layered double hydroxide film directly grown on highly porous anodic alumina oxide template. *Materials Letters*, **62**, 1302–1304.
- Yarger, M.S., Steinmiller, E.M.P., and Choi, K.-S. (2008) Electrochemical synthesis of Zn-Al layered double hydroxide (LDH) films. *Inorganic Chemistry*, **47**, 5859–5865.
- Zhang, F., Zhao, L., Chen, H., Xu, S., Evans, D.G., and Duan, X. (2008) Corrosion resistance of superhydrophobic layered double hydroxide films on aluminum. *Angewandte Chemie International Edition* **47**, 2466–2469.

(Received 20 November 2008; revised 18 March 2009; Ms. 0235; A.E. D.C. Bain)