Synthesis and characterization of layered double hydroxides with different cations (Mg, Co, Ni, Al), decomposition and reformation of mixed metal oxides to layered structures

Kristina Klemkaite¹,²*, Igoris Prosycevas³, Ricardas Taraskevicius⁴, Alexander Khinsky², Aivaras Kareiva¹

¹Department of General and Inorganic Chemistry, Vilnius University, LT-03225 Vilnius, Lithuania
²Amigus, LT-49473 Kaunas, Lithuania
³Institute of Materials Science, Kaunas University of Technology, LT-50131 Kaunas, Lithuania
⁴Institute of Geology and Geography, Nature Research Centre, LT-03223 Vilnius, Lithuania

Abstract: Three layered double hydroxides (LDH) \([\text{Mg}_{1-x}\text{Al}_x\text{(OH)}_2]^{x+}(\text{Am}^-)^{x/m} \cdot n\text{H}_2\text{O}\) and \([\text{M}^{II}_{1-x}\text{M}^{III}_x\text{(OH)}_2]^{x+}(\text{Am}^-)^{x/m} \cdot n\text{H}_2\text{O}\) (M II – Mg, Co, Ni; M III – Al; A - CO₃²⁻) were successfully synthesized by the low supersaturation method. The as-synthesized LDH samples were thermally decomposed and the derived mixed metal oxides reformed back to layered structures in water and magnesium nitrate media at different temperatures. All synthesized samples were characterized by X-ray diffraction (XRD) analysis, thermogravimetric (TG) analysis, X-ray fluorescence (XRF) analysis and scanning electron microscopy (SEM). The results of XRD and XRF analyses showed that single-phase layered double hydroxides were formed during synthesis and reformation. It was demonstrated, that a partially substituted by cobalt and nickel LDH samples also show memory effect. The crystallite size of regenerated LDH depends on the regeneration media, temperature and chemical composition. The LDH samples after regeneration consist of large particles with sharp edges along with a large amount of smaller particles.

Keywords: Layered double hydroxides • Chemical synthesis • Hydration • Regeneration • Memory effect

1. Introduction

Layered double hydroxide (LDH) or hydrotalcite (HT) type materials are widely used in catalysis, ion-exchange, adsorption, and pharmaceutics [1]. The general formula for the LDH materials is \([\text{M}^{II}_{1-x}\text{M}^{III}_x\text{(OH)}_2]^{x+}(\text{Am}^-)^{x/m} \cdot n\text{H}_2\text{O}\), where M are bivalent or trivalent cations with similar radii, and A are interlayer anions, mostly CO₃²⁻. Their structure is similar to that of brucite (Mg(OH)₂) type octahedral layers. The cations in the layer can be changed using a wide range of main group cations (e.g. Mg, Al) or transition metal cations (e.g. V, Cr, Mn, Fe, Co, Ni). These cations normally are in the divalent or trivalent state, although preparation of LDH with tetravalent cations has also been previously reported [2,3]. All these materials having various compositions share typical common characteristics: layered structure and the formation of mixed-metal oxides after thermal treatment. Interest in these compounds has increased in recent years because of the possibilities for post-synthetic modifications [4-8].

The most common method applied for preparation of LDH is co-precipitation, wherein precipitating agents such as NaOH or/and NaHCO₃ are added to the solution of metal salts [4]. LDH possess a unique layered structure. On the other hand, during calcination at high temperatures the layered structure could easily be destroyed. However, the regeneration (or reconstitution)

* E-mail: kristina.klemkaite@chf.stud.vu.lt
of the LDH layered structure is possible after soaking of mixed-metal oxides formed after thermal treatment in an aqueous solution containing anions to be intercalated. Such reverse reactions from mixed oxides to layered double hydroxides are referred in literature as “memory effect” with a topotactical character of the regeneration reaction [9,10]. Based on estimation of reaction kinetics and results of scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis it has been proven that regeneration is a process of dissolution of mixed oxides and subsequent crystallization of layered double hydroxides [11,12]. The dissolution-crystallization mechanism explains well the formation of LDH with new anions and implies a possibility of changing the cation composition during the regeneration process. The regeneration of LDH structure could be used as intermediate treatment to functionalize LDH by intercalation of anions in the interlayer. This effect has been applied for the removal of anions [13] and to improve the catalytic properties of the specimens [14].

Recently, processes such as hydration, rehydration and reconstruction were well explained for Mg/Al hydrotalcite [15]. In our case, the term “regeneration” is used to describe the process of the formation of layered double hydroxide with different chemical composition compared with originally synthesized material, as this definition is often used in literature [12,16]. The main aim of the present work was to study the influence of regenerating medium for different LDH. Three compositions of LDH structures were selected. Firstly, the Mg/Al composition was identical to the natural hydrotalcite. Secondly, the Mg/Co/Al composition was selected as basis for automotive applications [17,18]. Finally, the Mg/Ni/Al composition was selected as basis for gasification, catalytic partial oxidation or steam reforming applications [19-22]. The main features of synthesis, thermal decomposition of LDH and reformation of mixed-metal oxides to layered structures were also investigated.

2. Experimental Procedure

2.1. Sample preparation

The layered double hydroxide with natural hydrotalcite composition was prepared by coprecipitation under low supersaturation from a solution of the appropriate metal nitrates with a molar ratio of Mg:Al equal to 3:1 and a solution of NaHCO₃:NaOH with molar ratio of 1:2. Materials Al(NO₃)₃•9H₂O, Mg(NO₃)₂•6H₂O, Ni(NO₃)₂•6H₂O, Co(NO₃)₂•6H₂O from Lach - Ner, s.r.o. Neratovice, Czech Republic were used. The solution of metal nitrates was added to the solution of NaHCO₃+NaOH (pH ≈ 12) very slowly and under vigorous stirring. After mixing the obtained gel was aged at 80°C for 6 h. The resulting slurry was filtered and washed with distilled water and dried at room temperature (sample was labelled as Mg/Al). The mixed-metal oxide was obtained by heating the synthesized Mg/Al specimen for 3 h at 650°C and was labelled as Mg/Al₆₅. The hydration of mixed-metal oxide was carried out at 20°C for 6 h with continuous stirring in deionised water pH ≈ 6 (2 g of mixed oxide in 40 mL of water) and the sample was denoted as Mg/Alₓ₂₀. The regeneration in 1 mol L⁻¹ magnesium nitrate solution with pH ≈ 3.7 was performed under the same conditions as with deionised water (2 g of mixed oxide in 40 mL of 1 mol L⁻¹ Mg(NO₃)₂) and the sample was denoted as Mg/Alₓₙ₂₀. The influence of regeneration temperature was investigated in the same solutions at 80°C. The sample hydrated at 80°C was named as Mg/Alₙ₈₀ and regenerated in Mg(NO₃)₂ solution at the same temperature was named as Mg/Alₙ₈₀.

Layered double hydroxides containing cobalt or nickel were prepared under the same conditions as the Mg/Al sample, except that 15% of 1 mol L⁻¹ magnesium nitrate solution was replaced by 1 mol L⁻¹ cobalt nitrate solution or 1 mol L⁻¹ nickel nitrate solution. The obtained samples were named as Mg/Co/Al and Mg/Ni/Al, respectively. After decomposition at 650°C (named as Mg/Co/Al₆₅ and Mg/Ni/Al₆₅), the hydration was performed in water at 20°C and 80°C for 6 h and regeneration in Mg(NO₃)₂ solution at the same temperatures. The samples containing cobalt were named as Mg/Co/Alₓ₂₀, Mg/Co/Alₓ₈₀, Mg/Co/Alₙ₂₀, Mg/Co/Alₙ₈₀, and the specimens containing nickel were named as Mg/Ni/Alₓ₂₀, Mg/Ni/Alₓ₈₀, Mg/Ni/Alₙ₂₀, Mg/Ni/Alₙ₈₀. After the reformation processes, the samples were washed with distilled water and dried in air.

2.2. Characterization methods

The XRD patterns of the synthesized, calcined and regenerated in water or magnesium nitrate were recorded with a conventional Bragg-Brentano geometry (θ - 2θ scans) on a DRON-6 automated diffractometer equipped with a secondary graphite monochromator. Cu Kα radiation (λ = 1.541838 Å) was used as a primary beam. The patterns were recorded from 5 to 70° in steps of 0.02°, with the measuring time of 0.5 s per step. Silicon was used as a reference sample. The cell parameters c and a of the rhombohedral structure were determined from the positions of the (003), (006) and (110) diffraction lines, respectively. The lattice parameter a = 2d(110) corresponds to an average cation–cation distance calculated from the 110 reflection, while the c parameter corresponds to three times the thickness of d₀₀₃ parameter. In this case c was calculated from two diffraction lines using equation c = 3/2 [d₀₀₃+2d₀₀₆] [23].

Synthesis and characterization of layered double hydroxides with different cations (Mg, Co, Ni, Al) decomposition and reformation of mixed metal oxides to layered structures
K. Klemkaite et al.

The average crystallite size of layered double hydroxides was calculated by X-Fit program from the full-width at half-maximum (FWHM) intensity of the (003), (006) and the (110) diffraction peaks.

Thermogravimetric (TG) and differential scanning calorimetric (DSC) analyses were carried out with a Netzsch instrument “STA 409 PC Luxx” using a heating rate of 10°C min⁻¹ in air atmosphere and the temperature range from 30°C up to 900°C. Ceramic sample holders and Pt-Rh crucibles were used.

Metal loadings of the layered double hydroxides were analyzed by X-ray fluorescence technique (XRF) on a Spectro Analytical Instrument GmbH&Co.KG., with a Pd window X-ray tube. The analysis was carried on a 32 mm disc. XRF apparatus uses the Turboquant calibration method that is able to analyze all elements from Na to U. Mean values of relative standard deviation for analysed elements were: Mg – 1.54%; Al – 1.42%; Co – 3.7% and Ni – 2.4%. The surface morphology of the samples was studied by SEM (EVO 50 EP, Carl Zeiss SMT AG, Germany). The analysis of images was done with the ImageJ software.

3. Results and Discussion

3.1. Synthesis of Layered Double Hydroxide

All three layered double hydroxides Mg/Al, Mg/Co/Al and Mg/Ni/Al were successfully synthesized by coprecipitation method. As seen from the XRD patterns (Fig. 1), the hydrotalcite type phase was identified in all synthesized layered double hydroxides [4,7]. More intensive and sharper reflections of the (003) and (006) planes at low 2θ values (11-23°), and broad asymmetric reflections at higher 2θ values (34-66°) can be observed in the XRD patterns. The (009) reflection overlaps with the (102), resulting in a broad signal. Therefore, we can conclude that it is possible to obtain hydrotalcite-like layered structures with the Co²⁺ or Ni²⁺, Mg²⁺ and Al³⁺ cations in the chosen range of compositions. However, the intensities of some reflections for different LDH samples are slightly different, possibly indicating different degrees of their crystallinity. Determined cell parameters c and a are shown in Table 1. The published interlayer distance of carbonate-containing Mg/Al LDH is 7.8 Å [23]. The d₀₀₃-values obtained for the synthesized LDH samples are very similar. Only a very low increase of the basal spacing is seen in the LDH samples containing cobalt and nickel. The calculated values of crystallite size of LDH samples are also shown in Table 1. The dimensions in the a-direction are larger than that in the c-direction, as can be expected from the plate-like shape of hydrotalcite crystals [4]. Introduction of cobalt or nickel to the layered double hydroxides composition caused a considerable decrease in the crystallite size, which is in a good agreement with literature data [24]. The formation of smaller nano-sized primary crystallites could be a result of cobalt or nickel influence on the nucleation and crystal growth process during the precipitation of LDH.

The compositions of the synthesized layered double hydroxides were analyzed by the X-ray fluorescence technique to determine differences of calculated and experimentally received compositions of materials (Table 2). As seen, the transition metals were detected in all LDH samples for the preparation of which the cobalt and nickel were used. The determined LDH molar compositions are very close to the nominal. However, the Al content is slightly lower than expected and this could be associated with partial solubility of aluminium ions as aluminate species under these synthesis conditions. LDH with cobalt has a lower content of Mg and this effect was already observed by S. Ribet [25]. The general formula for LDH is \[\text{M}^{2+}_{1-x} \text{M}^{3+}_x (\text{OH})_2(\text{Am}^-)_x/m \text{H}_2\text{O}\] and it indicates that it

| Sample name | d₀₀₃ (Å) | d₀₀₆ (Å) | d₁₁₀ (Å) | Cell parameters (Å) | Crystallite size (Å) |
|-------------|----------|----------|----------|---------------------|---------------------|
| Mg/Al       | 7.77     | 3.86     | 1.53     | 23.25               | 3.06               |
| Mg/Co/Al    | 7.93     | 3.92     | 1.53     | 23.59               | 3.07               |
| Mg/Ni/Al    | 7.87     | 3.89     | 1.53     | 23.40               | 3.05               |

Figure 1. XRD patterns of original layered double hydroxides synthesized by coprecipitation method with various cations composition. A – Mg/Al; B – Mg/Co/Al; C – Mg/Ni/Al. Reflections from Si crystal used as a reference are marked with asterisk.
is possible to synthesize a number of compounds  
with different stoichiometries. In the natural hydrotalcites  
the value of $x$ is generally equal to 0.25. Thus, the XRF  
results clearly confirmed that it is possible to synthesize  
LDH with the above formula having more than two metals  
[4]. There are, however, many difficulties in determining  
the exact value of $x$ in LDH. An elemental analysis of  
the metal content of a solid phase will not give correct  
values if the LDH is not monophasic, i.e., mixed with  
$\text{M}^{\text{ii}}\text{(OH)}_2$, $\text{M}^{\text{iii}}\text{(OH)}_2\text{M}^{\text{iv}}\text{OOH}$ or other phases which could  
segregate when the synthesis mixture contains either  
very high or very low $\text{M}^{\text{ii}}/\text{M}^{\text{iii}}$ ratios. However, more often  
these phases are amorphous and cannot be detected  
by XRD [26].  

The obtained $x$ values of synthesized LDH by XRF  
technique are in the expected range. They are not lower  
than 0.2 and not higher than 0.3. So, the results of  
XRF analysis let us conclude that single-phase layered  
double hydroxides have formed during co-precipitation  
synthesis. The carbonate content in synthesized  
samples was calculated from the $\text{M}^{\text{ii}}/\text{M}^{\text{iii}}$ atomic ratios,  
assuming that carbonate is the only charge balancing  
interlayer anion. The water content in the formula was  
determined from the results of TG analyses which are  
presented below.  

### 3.2. Thermal decomposition of LDH  
All layered double hydroxides undergo thermal  
decomposition at higher temperatures. Thermal  
gravimetric analysis of the natural hydrotalcite type  
sample Mg/Al and LDH with cobalt Mg/Co/Al and nickel  
Mg/Ni/Al was performed (Fig. 2). The researchers in [24]  
have demonstrated that mass changes up to 200°C are  
due to the removal of interlayer and adsorbed water.  
Below this temperature dehydroxylation is minor and  
no decarbonation occurs. As seen from Fig. 2, the  
endothermic processes of removal of water continue till  
250°C and two DTG minima at 88 and 220°C appear  
for all samples. The mass loss in this temperature  
interval was used for the calculation of water content  
(see Table 2). The decomposition of intralayer hydroxyl  
and carbonate anions occurs in the temperature range  
of 250-500°C. The presence of a single mass loss in  
this range confirms the coupling of dehydroxylation  
and decarbonation processes [24]. The presence of  
the transition metals in the synthesized LDH samples  
showed very minor effect on the thermal stability.  
Therefore, the same temperature (650°C) for thermal  
treatment of all samples was chosen. The annealing  
temperature is very important because it is crucial for  
successful reconstitution of the layered structure. During  
the calcination of LDH, the temperature should be  
higher than that of the layer collapse but lower than that  
of formation of spinel phase. This solid phase is stable  
and cannot be converted to LDH in water. Thus, for  
layered double hydroxides the calcinations temperature  
is usually set between 400 and 700°C.  

The XRD analysis of heat-treated samples revealed  
the formation of poorly crystalline magnesium oxide  
(Pdf # 75-1525) with peaks at $2\theta \approx 36, 43$ and $63^\circ$  
(Fig. 3). These peaks are slightly shifted to higher $2\theta$  
angles in comparison with a pure magnesium oxide.  
This is a consequence of the incorporation of aluminium  
in the framework of the MgO, resulting in the formation  
of a mixed-metal oxide [27]. No peaks assigned to  
the transition metal oxides were observed. The XRD  
patterns of the samples Mg/Al$_{65}$, Mg/Co/Al$_{65}$, Mg/Ni/Al$_{65}$ do not show the formation of spinel-type crystalline  
phases. Consequently, the possibility to reform them to  
layered double hydroxides still remains.  

### 3.3. Reformation of mixed metal oxides to  
layered double hydroxides  
Mixed metal oxides were reformed to layered double  
hydroxides in water or magnesium nitrate solution. The  
XRD patterns of samples treated at room and 80°C  
temperatures are shown in Figs. 4 and 5, respectively. As  
seen, the diffractions from layered double hydroxides are  

| Sample name | (M$_2^{\text{ii}}$+Mg)/Al | M$_2^{\text{ii}}$/ (M$_2^{\text{ii}}$+Mg) | Cations content in the LDH | Proposed formula$^a$ |
|-------------|-------------------------|-----------------|--------------------------|------------------|
| Mg/Al       | 3.26                     | 0.77            | Mg                       | [M$_{3.26}$Al$_{0.77}$\(\text{OH})_2\] \(\text{CO}_3\) \(\text{H}_2\text{O} \) |
| Mg/Al$_{20}$| 3.71                     | 0.79            | Mg or Co                  | [M$_{3.71}$Al$_{0.79}$\(\text{OH})_2\] \(\text{CO}_3\) \(\text{H}_2\text{O} \) |
| Mg/Co/Al$_{65}$ | 2.86                    | 16.85           | Mg or Ni                  | [M$_{2.86}$Co$_{16.85}$\(\text{OH})_2\] \(\text{CO}_3\) \(\text{H}_2\text{O} \) |
| Mg/Co/Al$_{20}$ | 3.71                    | 13.32           | Mg or Co                  | [M$_{3.71}$Co$_{13.32}$\(\text{OH})_2\] \(\text{CO}_3\) \(\text{H}_2\text{O} \) |
| Mg/Ni/Al$_{65}$ | 3.23                    | 14.41           | Mg or Ni                  | [M$_{3.23}$Ni$_{14.41}$\(\text{OH})_2\] \(\text{CO}_3\) \(\text{H}_2\text{O} \) |
| Mg/Ni/Al$_{20}$ | 3.34                    | 14.35           | Mg or Ni                  | [M$_{3.34}$Ni$_{14.35}$\(\text{OH})_2\] \(\text{CO}_3\) \(\text{H}_2\text{O} \) |

$^a$ M$_2$ is cobalt or nickel respectively in Mg/Co/Al, Mg/Co/Al$_{20}$ or Mg/Ni/Al, Mg/Ni/Al$_{20}$ samples.  
$^b$ Cations, adsorbed and interlayer water contents are measured, all others are calculated.
dominating in all cases. These results let us conclude, that in all cases reformation to layered structure occurs. However, the XRD patterns of Mg/Ni/Al\textsubscript{W20}, Mg/Ni/Al\textsubscript{N20} and Mg/Co/Al\textsubscript{W20} show incomplete regeneration after treatment of the samples in water or magnesium nitrate at room temperature for 6 h. The formation of side magnesium oxide phase is confirmed by XRD measurements.

The cell parameters $c$ and $a$ were also determined for regenerated samples from the position of the (003), (006) and (110) diffraction lines (Table 3). Sample containing transition metals shows decrease in the basal spacing after reconstitution in water, contrary to the Mg/Al-containing samples. Nickel or cobalt in the synthesized LDH causes the changes in the structure of materials. These samples show mixed oxide even after reconstitution with water and at the same time it could be the reason for decrease of basal spacing compared to samples without transition metals. However, the relative error in the determination of $d_{003}$ can be estimated higher than few percent. So no definitive conclusion on this observation could be made. The reconstitution in the magnesium nitrate solution had the highest influence on the $c$ parameter of LDH. The basal spacing represents the thickness of a single layer and is normally related to the size of charge balancing interlayer anions. For the samples reformed in the magnesium nitrate solution, the basal spacings $d_{003}$ are higher than 8 Å. This corresponds to the values of basal spacing of nitrate containing LDH [28]. There are only a few studies where the influence of the third metal cation for the regeneration process is investigated [29]. The influence of reformation on Mg/(Co or Ni)/Al composition of regenerated LDH samples was also studied by XRF (Table 2). It can be

| Sample         | Reconstitution media | Temperature of reconstitution (°C) | $d_{003}$ (Å) | $d_{006}$ (Å) | $d_{110}$ (Å) | Cell parameters | Crystallite size (003) (Å) |
|----------------|----------------------|-----------------------------------|--------------|--------------|--------------|-----------------|--------------------------|
| Mg/Al\textsubscript{W20} | H\textsubscript{2}O   | 20                                | 7.79         | 3.86         | 1.52         | 23.28          | 3.05             | 62                       |
| Mg/Al\textsubscript{N20} | Mg(NO\textsubscript{3})\textsubscript{2} | 20                                | 8.03         | 3.98         | 1.53         | 23.99          | 3.07             | 70                       |
| Mg/Al\textsubscript{W80} | H\textsubscript{2}O   | 80                                | 7.81         | 3.88         | 1.53         | 23.34          | 3.06             | 117                      |
| Mg/Al\textsubscript{N80} | Mg(NO\textsubscript{3})\textsubscript{2} | 80                                | 8.20         | 4.02         | 1.53         | 24.36          | 3.07             | 69                       |
| Mg/Co/Al\textsubscript{W20} | H\textsubscript{2}O   | 20                                | 7.88         | 3.90         | 1.53         | 23.52          | 3.06             | 91                       |
| Mg/Co/Al\textsubscript{N20} | Mg(NO\textsubscript{3})\textsubscript{2} | 20                                | 8.08         | 3.99         | 1.53         | 24.10          | 3.07             | 61                       |
| Mg/Co/Al\textsubscript{W80} | H\textsubscript{2}O   | 80                                | 7.89         | 3.91         | 1.53         | 23.57          | 3.06             | 131                      |
| Mg/Co/Al\textsubscript{N80} | Mg(NO\textsubscript{3})\textsubscript{2} | 80                                | 8.12         | 4.01         | 1.54         | 24.22          | 3.08             | 80                       |
| Mg/Ni/Al\textsubscript{W20} | H\textsubscript{2}O   | 20                                | 7.82         | 3.86         | 1.52         | 23.31          | 3.04             | 58                       |
| Mg/Ni/Al\textsubscript{N20} | Mg(NO\textsubscript{3})\textsubscript{2} | 20                                | 8.11         | 3.93         | 1.52         | 23.97          | 3.04             | 28                       |
| Mg/Ni/Al\textsubscript{W80} | H\textsubscript{2}O   | 80                                | 7.84         | 3.89         | 1.53         | 23.44          | 3.06             | 94                       |
| Mg/Ni/Al\textsubscript{N80} | Mg(NO\textsubscript{3})\textsubscript{2} | 80                                | 8.27         | 4.05         | 1.52         | 24.57          | 3.05             | 47                       |
Synthesis and characterization of layered double hydroxides with different cations (Mg, Co, Ni, Al), decomposition and reformation of mixed metal oxides to layered structures

concluded that the composition was modified very little. All samples after treatment in magnesium nitrate have a higher concentration of magnesium. Apparently, the lower amount of cobalt calculated in the Mg/Co/Al N20 is associated with increase of magnesium content in composition. Thus, the most affected sample after regeneration is LDH containing cobalt.

The determined crystallite sizes of regenerated LDH samples are presented in Table 3. Evidently, the crystallite size depends on the reconstitution media, temperature and chemical composition of regenerated LDH. However, the reasons for wide distribution of crystallite size at different conditions is still unclear and should be answered in the future. In most of the cases, by increasing the temperature of reconstitution media to 80°C the crystallite size also increases. Especially this effect is evident during hydration in water media. The crystallite size increases for Mg/Al, Mg/Al/Co and Mg/Al/Ni LDH samples are 62 to 117 Å, 91 to 131 Å, and 58 to 94 Å, respectively. Of course, the increase of crystallite size could influence the porosity and surface morphology of LDH after decomposition. The results mentioned above let us conclude that the process of regeneration of layered double hydroxide in liquid media gives an opportunity not only to reform mixed metal oxides to LDH, but also to change the structural features of reformed LDH samples in comparison to as-synthesized ones. The porosity studies on calcined and regenerated LDH samples are currently under investigation.

The influence of reformation process on the surface morphology of the samples with representative nickel containing layered double hydroxide was investigated.

Figure 3. XRD patterns of mixed oxides after calcination original layered double hydroxides at 650°C. A - Mg/Al 65, B - Mg/Co/Al 65, C - Mg/Ni/Al 65. Crystalline phase: MgO (Pdf # 75-1525).

Figure 4. XRD patterns of reconstituted layered double hydroxides at 20°C. (A1 - Mg/Al W20; A2 - Mg/Al N20; B1 - Mg/Co/Al W20; B2 - Mg/Co/Al N20; C1 - Mg/Ni/Al W20; C2 - Mg/Ni/Al N20) Crystalline phases: O - MgO, * - Si, all others-LDH.

Figure 5. XRD patterns of reconstituted layered double hydroxides at 80°C. (A1 - Mg/Al W80; A2 - Mg/Al N80; B1 - Mg/Co/Al W80; B2 - Mg/Co/Al N80; C1 - Mg/Ni/Al W80; C2 - Mg/Ni/Al N80) Crystalline phases: * - Si, all others-LDH.

Figure 6. SEM micrograph of as-synthesized Mg/Al/Ni LDH.

Figure 7. SEM micrograph of Mg/Al/Ni LDH after hydration in water.
using SEM (Figs. 6-8). It can be seen from Fig. 6, that as-synthesized Mg/Ni/Al LDH is composed of large (1-3 µm) flat plate-like crystals. The surface of regenerated Mg/Ni/Al agglomerated particles (~10 µm) is covered by smaller (1-3 µm) crystals (see Fig. 7). A layered structure in these particles still persists. Fig. 8 shows the SEM micrograph of regenerated Mg/Ni/Al in magnesium nitrate LDH sample. As seen, many small particles (~1 µm) are partially aggregated. In some areas aggregates of fibrous particles can be also found. In conclusion, the morphology of regenerated Mg/Ni/Al and Mg/Ni/Al LDH samples is slightly different in comparison with as-synthesized Mg/Ni/Al sample. The LDH samples after regeneration consist of large particles with sharp edges along with a large amount of smaller particles.

4. Conclusions

Three layered double hydroxides (LDH) were successfully synthesized by the low supersaturation method, thermally decomposed and derived mixed metal oxides reformed to layered structures in water and nitrate media. It was demonstrated, that a partial substitution of magnesium by cobalt and nickel does not lead to fundamental changes in LDH behaviour during the cycle synthesis-thermal decomposition-regeneration. On the other hand, an incomplete regeneration of some transition metal containing samples at room temperature independent of the regeneration media has been observed. Besides, during reformation of mixed metal oxides to LDH, no essential loss of transition metals was determined. However, slightly different chemical compositions of layered structures having higher concentration of magnesium after reformation of mixed metal oxides in magnesium nitrate were observed. Moreover, hydration causes the formation of LDH with higher crystallite size in comparison to the LDH samples reformed in magnesium nitrate media. In most of the cases, by increasing temperature of reconstitution media to 80ºC the crystallite size also increased. The morphology of regenerated LDH samples is also slightly different in comparison with as-synthesized LDH sample. The LDH samples after reconstitution consist of large particles with sharp edges along with a large amount of smaller particles. A layered structure in the LDH particles after regeneration still persists.

Acknowledgements

A. Baltusnikas and Dr. A. Selskis are thanked for XRD and SEM measurements, respectively. We also would like to thank N. Laurinaitis for technical assistance.

References

[1] F. Li, X. Duan, In: D.M.P. Mingos (Ed.), Structure and Bonding (Springer-Verlag, Berlin, Heidelberg, 2006) 193
[2] S. Velu, K. Suzuki, M. Okazaki, S. Tomura, F. Ohashi, Chem. Mater. 11, 2163 (1999)
[3] S. Velu, K. Suzuki, M.P. Kapoor, S. Tomura, F. Ohashi, T. Osaki, Chem. Mater. 12, 719 (2000)
[4] F. Cavani, F. Trifiro, A. Vaccari, Catal. Today 11, 173 (1991)
[5] S.P. Newman, W. Jones, New J. Chem. 22, 105 (1998)
[6] A. Vaccari, Appl. Clay Sci. 14, 161 (1999)
[7] V. Rives, M.A. Ulibarri, Coord. Chem. Rev. 181, 61 (1999)
[8] J. He, M. Wei, B. Li, Y. Kang, D.G Evans, X. Duan, In: D.M.P. Mingos (Ed.) (Structure and Bonding, Springer-Verlag, Berlin, Heidelberg, 2006) 89
[9] T. Sato, H. Fujita, T. Endo, M. Shimada, A. Tsunashima, React. Solid. 5, 219 (1988)
[10] A.J. Marchi, C.R. Apesteguia, Appl. Clay Sci. 13, 35 (1998)
Synthesis and characterization of layered double hydroxides with different cations (Mg, Co, Ni, Al), decomposition and reformation of mixed metal oxides to layered structures

F. Millange, R.I. Walton, D. O’Hare, J. Mater. Chem. 10, 1713 (2000)
T. Stanimirova, E. Dinolova, G. Kirov, J. Mater. Sci. Lett. 5, 453 (2001)
L.P. Cardoso, J.B. Valim, J. Phys. Chem. Solids 65, 481 (2004)
K. Takehira, T. Shishido, Catal. Surv. Asia 11, 1 (2007)
M. Mokhtar, A. Inayat, J. Ofili, W. Schwieger, Appl. Clay Sci. 50, 176 (2010)
J.F.N. Filho, F. Silve´rio, M.J. dos Reis, J.B. Valim, J. Mater. Sci. 43, 6986 (2008)
A. Corma, A.E. Palomares, F. Rey, Appl. Catal. B. Environ. 4, 29 (1994)
A.E. Palomares, J.M. López-Nieto, F.J. Lázaro, A. López, A. Corma, Appl. Catal. Part B. Environ. 20, 257 (1999)
F. Basile, L. Basini, M. D’Amore, G. Fornasari, A. Guarinoni, D. Matteuzzi, G. Del Piero, F. Trifiro, A. Vaccari, J. Catal. 173, 247 (1998)
K. Schulze, W. Makowski, R. Chyzy, R. Dziembaj, G. Geismar, Appl. Clay Sci. 18, 59 (2001)
M. Marquevich, X. Farriol, F. Medina, D. Montane, Catal. Lett. 85, 41 (2003)
M. Li, X. Wang, S. Li, S. Wang, X. Ma, Int. J. Hydrogen Energy 35, 6699 (2010)
J. Pérez-Ramirez, G. Mul, F. Kapteijn, J.A. Moulijn, J. Mater. Chem. 11, 821 (2001)
J. Pérez-Ramirez, S. Abello, N.M. van der Pers, J. Phys. Chem. 111, 3642 (2007)
S. Ribet, D. Tichit, B. Coq, B. Ducourant, F. Morato, J. Solid State Chem. 142, 382 (1999)
D.G. Evans, R.C.T. Slade, In: D.M.P. Mingos (Ed.), (Structure and Bonding, Springer-Verlag, Berlin, Heidelberg, 2006) 1
A.E. Palomares, A. Uzcátegui, A. Corma, Catal. Today 137, 261 (2008)
H.W. Olfs, L.O. Torres-Dorante, R. Eckelt, H. Kosslick, Appl. Clay Sci. 43, 459 (2009)
T. Stanimirova, T. Stolikova, G. Kirov, Geochem. Miner. Petr. 45, 119 (2007)