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CHARACTERIZATION OF LAYERED DOUBLE HYDROXIDE Mg-Al-CO_3 PREPARED BY RE-HYDRATION OF Mg-Al MIXED OXIDE

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Emanation thermal analysis, differential thermal analysis, thermogravimetry, X-ray diffraction, scanning electron microscopy (SEM) and surface area and porosity determination from nitrogen adsorption/desorption measurements were used to characterize the Mg-Al-CO_3 LDH compound with the Mg:Al ratio 3:1 prepared by re-hydration of the Mg-Al mixed oxide. The mixed oxide was obtained after heating of the intial Mg-Al-CO_3 LDH compound in air at 500°C for 2 h. The samples were re-hydrated by two ways namely in a distilled water at 20°C for 5 days or by moistening at 60°C in air with RH 80% during 10 days, respectively. The characteristics of the re-hydrated LDH samples were compared with the initial Mg-Al-CO_3 compound.

The influence of the re-hydration conditions on the microstructure, surface morphology and thermal stability of the regenerated Mg-Al-CO_3 LDHs samples is discussed.

It was demonstrated that the re-generation of the layered structure by the hydration of the mixed oxide in water or in air, respectively, took place via the dissolution-crystallization mechanism and that the layered double hydroxide with different surface area and thermal behavior were formed after re-hydration in water or humid air, respectively. The emanation thermal analysis revealed differences in the microstructure changes of the re-hydrated sample during heating. XRD patterns and results of the methods used supported the ETA results.

Keywords: *DTA, emanation thermal analysis, layered double hydroxide, Mg-Al-CO_3, re-hydrated Mg-Al mixed oxide, TG, thermal behaviour, XRD*

Introduction

Layered double hydroxides (LDHs), known as anionic clays, are a family of compounds which deserve much attention in recent years. All hydrotalcite-like compounds can be described with general formula $M^{2+}_{1-x}M^{3+}_{x}(OH)_2A^{m-}_{x/m}(1-3x/2)H_2O$, where ($0.20<x\leq0.33$). The partial substitution of the divalent cations by trivalent ones involves a positive charge of the layer, balanced by anions between the hydroxyl layers, where water molecules also exist. A large number of LDHs have been synthesized, for example compounds containing metal cations M^{2+} such as Mg, Mn, Fe, Co, Ni, Cu, Zn, and Ca; and the metal cations M^{3+} such as Al, Cr, Mn, Fe, Co, La, and Y and the exchange anions A^{m-} such as CO_3^{2-}, SO_4^{2-}, OH^-, CrO_4^{2-}, ClO_4^-, halides, complex anions, organic anions, etc. [1–4].

The properties of the layered double hydroxides (LDHs) used as anionic sorbents, precursors for catalysts, heat adsorbents, etc. [1–3] are closely related with their structure. It is well known that surface properties of the mixed oxides formed during the heat treatment of the LDH compounds to elevated temperatures are dependent on their structure.

It was demonstrated by numerous authors [5–13] that during heating of the LDH Mg-Al-CO_3 (Mg:Al=3:1) the formation of several intermediate products takes place as the result of dehydration, dehydroxylation and decarbonisation. The calcination of Mg-Al-CO3 LDH at temperatures of 120–160°C give rise to dehydrated LDH samples. By heating LDH samples to temperatures of 200–250°C the formation of intermediate phase with grafted CO_3^{2-} anions into hydroxide layers take place. By heating of the Mg-Al-CO_3 LDH to temperatures of 400–800°C a mixed Mg-Al-oxide solid solution (MO) that possessed catalytic properties was formed. It should be mentioned that the layered structure of the LDH can be recovered by treatment of the mixed oxide MO with water or with water solutions that contain various anions. By this way the LDHs with various inorganic and organic anions as well as pillared structures can be prepared [1, 2, 14]. There is a number of papers describing the preparation of such products and mechanisms of the LDHs regeneration, based on various reaction conditions, e.g. pH, temperature, concentration of anions, composition of starting materials, etc [1, 4, 15–17]. The cation incorporation and substitution, stability and properties of

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hydrotalcite and its high temperature product MO during calcinations – re-hydration processes were also investigated [18–20].

It was of interest in this study to investigate the influence of the re-hydration conditions on the microstructure, surface morphology and thermal stability the Mg-Al-CO_3 LDHs obtained from mixed oxides MO by the regeneration process.

Experimental

Synthesis of the initial sample

The initial Mg-Al-CO_3 compound with the Mg:Al ratio 3:1 was prepared as described by Miyata [21]. The synthesis was performed under vigorous stirring by drop-wise mixing of an acid solution of 0.5M $Mg(NO_3)_2$ and 0.5M $Al(NO_3)_3$ (in molar ratio 3:1) with alkali solution of 1M NaOH and 0.5M Na_2CO_3. The synthesis was carried out at controlled pH of 10-10.5. The resulting gel was aged in a polypropylene bottle for 48 h at 80°C. The precipitate obtained was filtered, washed until washing water reached a pH value of 8–8.5 and then dried at room temperature.

In order to prepare regenerated samples, the initial LDH sample was converted to the mixed Mg-Al oxide by heating at 500°C for 2 h and it was subsequently re-hydrated for 5 days in liquid distilled water at 20°C (the sample was called R-water) or by moistening at 60°C in air with RH 80% during 10 days (the sample was called R-air).

Methods

Differential thermal analysis (DTA), thermogravimetry (TG) and emanation thermal analysis (ETA) were used to characterize the thermal behavior of the samples.

X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the samples structure and microstructure.

Surface area and porosity were determined from nitrogen adsorption/desorption measurements by using B.E.T and B.H.J. methods, respectively.

The powder XRD patterns were obtained by Rigaku X-ray diffractometer MultiFlex 2kW, by using CuK_α radiation separated by a crystal monochromator in the range 2Θ 3–70°, step size 0.03°.

Simultaneous DTA/TG measurements were performed by using Rigaku Thermoplus TG 8120 apparatus. The following conditions were used: heating rate: 10 K min^{-1}; air flow: 132 mL min^{-1}, sample mass: 16.0–16.5 mg; reference material: Al_2O_3

SEM micrographs were performed by using PHILIPS Electron Micrograph.

The ETA measurements were carried out by using NETZSCH DTA-ETA Equipment type 404. The labelled samples situated in a corundum crucible were heated at the rate of 6°C min^{-1} in the air flow (flow-rate 50 mL min^{-1}). The initial sample of $MgAlCO_3$ LDH was labelled by drops of the radionuclides of ^{228}Th and ^{224}Ra in acetone solution. After the labelling, acetone was evaporated at 80°C. The atoms of ^{228}Th adsorbed at sample surface served as a source of ^{224}Ra and ^{220}Rn. Specific activity of the labelled sample was 10^5 Bq g^{-1}. It was determined by means of TRIM code [22] that the maximum depth of the penetration of the radon ^{220}Rn recoiled atoms is 80 nm. A more detailed description of ETA as a less common method and its use in the characterization of the LDHs and other dispersed solids is given in [23–28].

Results and discussion

Figure 1 depicts XRD patterns of the initial sample and the samples obtained by the re-hydration of the mixed oxide (MO) in liquid distilled water – (the sample is called ‘R-water sample’) and by moistening in a humid air (the sample is called ‘R-air sample’), respectively. From XRD data of the initial sample following values of the lattice parameters were determined *c* (c=3 x d_{003})=2.349 nm and *a* (a=2 x d_{110})=0.306 nm These values were in a good agreement with the results previously reported in the literature and corresponding to the well crystallized hydrotalcite-like structure with Mg:Al ratio 3:1. The values of the spacings d_{003} and d_{110} of the ‘R-water sample’ and ‘R-air sample’ were very close to those of the initial sample, which indicated that unit cell parameters did not change during regeneration and that the sample have chemical composition identical to that of the initial sample. The shape of XRD patterns suggested that the structure of the two re-hydrated samples corresponds to the rhombohedral polytype (Figs 1b and c), whereas the XRD pattern of the initial sample confirmed a turbostratic random arrangement of the layers, manifested by a broad *0kl* diffraction lines with high-angle tail (Fig. 1a). The comparison of the width of the diffraction lines of the investigated samples suggested that the three samples possessed different size of the particles. The XRD diffraction lines of re-hydrated sample ‘R-water sample’ (Fig. 1b) were sharp and intensive, while the XRD lines of the ‘R-air sample’ were relatively of a low intensity, corresponding to a low crystalline samples (Fig. 1c). This result was in a good correlation with the surface area data of the samples (Table 1) and the SEM micrographs (Fig. 3).

Figure 2 depicts results of TG-DTA and ETA measurements of the initial Mg-Al-CO_3 LDH sample and of the samples obtained by re-hydration of the mixed oxide MO in water (R-water sample) or in air (R-air sample). The two DTA endothermic effects (Fig. 2a) observed during heating of the Mg-Al-CO_3 LDH sample were ascribed to processes of the interlayer dehydration, dehydroxylation and decarbonization, respectively [6–13].

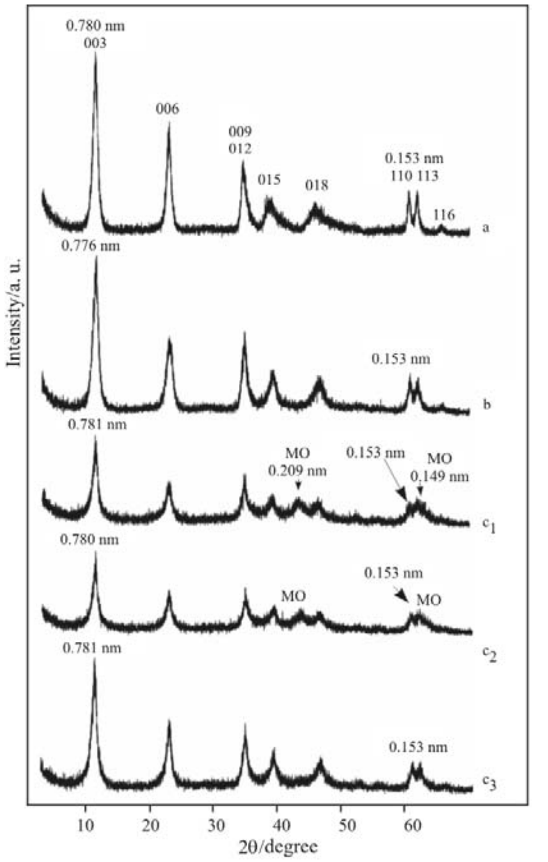

Fig. 1 XRD patterns of Mg-Al-CO_3 LDH samples: a – initial sample; b – sample prepared by hydration of MO in water; c – samples prepared by hydration of MO in air, where c_1 – 5 days, c_2 – 10 days and c_3 – 10 days treatment

Table 1 Surface area and porosity of initial $MgAlCO_3$ LDH and samples obtained by hydration of the mixed oxide in water or in air

Sample	BET/ $m^2\,g^{-1}$	Pore vol. (BHJ desorption)/$cm^3\,g^{-1}$	Pore radius/ nm
Initial sample	87	0.003	0.83
R-water sample	141	0.044	0.15
R-air sample	377	0.11	0.17

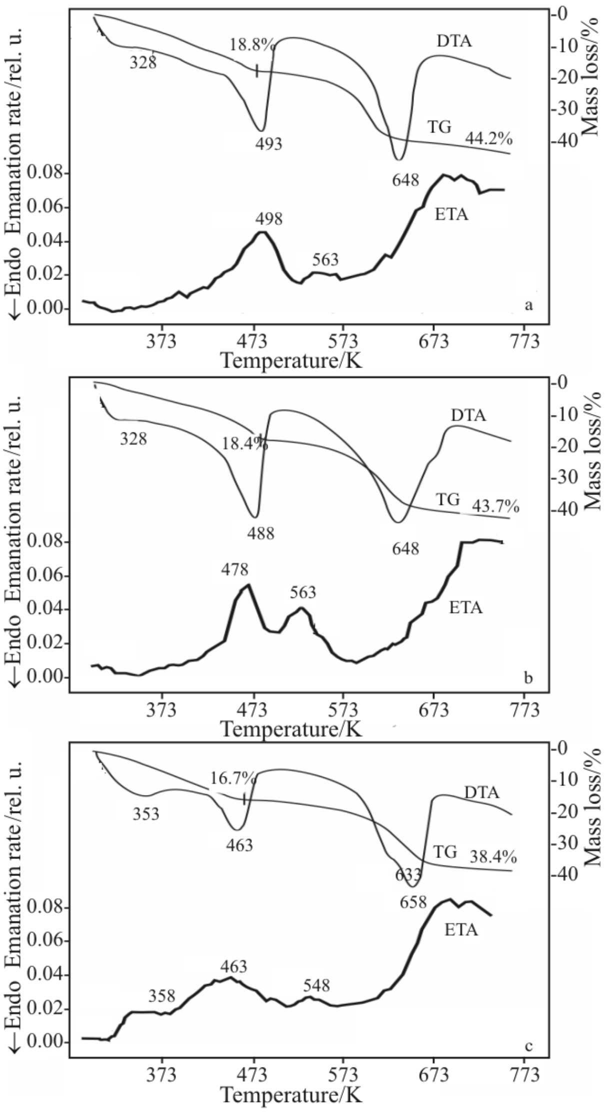

Fig. 2 DTA, TG and ETA data of the initial Mg-Al-CO_3 LDH samples: a – initial sample, b – R-water sample prepared by hydration of MO in water, and c – R-air sample prepared by hydration of MO in humid air lasting 10 days

From Fig. 2 it followed that the DTA-TG curves of the 'R-water sample' , 'R-air sample' and the initial LDH sample were similar regardless of little difference in the temperature maxima for the re-hydrated samples. However, the ETA results revealed significant differences in thermal behavior, the microstructure and surface area development of the investigated samples on heating.

In our previous work [29] it was demonstrated that the increase of the emanation rate, *E*, at the temperature range of 293–473 K was associated with the dehydration of the interlayer, whereas the abrupt decrease of the emanation rate in the range of 493–533 K was attributed to closure of the interlayer,

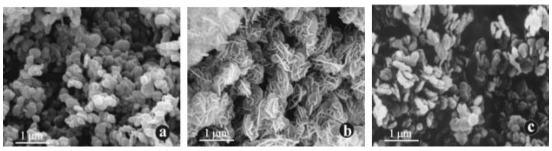

Fig. 3 SEM micrographs of initial sample of a – Mg-Al-CO_3 LDH, b – the samples obtained by hydration of mixed oxide in water and c – in air, respectively

due to the grafting of the CO_3^{2-} anions during the release of water molecules originating from OH hydroxyl groups.

The breaks observed on the ETA curves (at the temperatures of 463, 478 and 498 K for the 'R-air sample', 'R-water sample' and the initial LDH sample, respectively), coincided well with the corresponding endothermic DTA effects and the mass decrease of the samples estimated by TG curves (Figs 2b and c). We assumed that the increase of the emanation rate, *E*, accompanied the release of water due to dehydration and partial dehydroxylation of the samples. The decrease of the emanation rate observed in range of 478–508 K characterized the closure of the interlayer space due to grafting of CO_3^{2-} anions in the hydroxide layers.

The temperature of the increase of the emanation rate, *E*, during heating of the 'R-air sample' (Fig. 2c) was supposedly influenced by the size of particles [26, 29]. Taking into account the elevated surface area of the samples (Table 1), low crystallinity of the samples estimated by XRD (Fig. 1c_1) and the fact that no significant changes of the particle size were observed (Fig. 3b), we assumed that the crystallization of new LDH during regeneration in the moist air took place on the surface of the mixed oxide MO only. The XRD lines corresponding to the mixed oxide MO confirmed its presence in the 'R-air sample' (Fig. 1c_1) and supported this assumption. Moreover, from the XRD pattern (Fig. 1c_2) it followed that in the sample re-hydrated during more than 5 days, there was present some amount of the mixed oxide MO phase. We have therefore supposed that the newly formed LDH on the surface was acting as a barrier to prevent further hydration of the mixed oxide MO. Moreover, we have demonstrated that the remaining mixed oxide MO can be converted into LDH after hydration in water (Fig. 1c_3).

In the case of the 'R-water sample', the SEM micrograph confirmed that the observed particles were thinner than those of the initial LDH sample (Fig. 3b, a).This fact can be used to explain the increase of emanation rate of the 'R-water sample' (Fig. 2b).

The increase of the emanation rate, *E*, in the temperature range 293–533 K with an maximum at 528 K observed with the 'R-water sample' was not accompanied with the mass loss or with any DTA effect (Fig. 2b). A similar effect was observed in the range of 533–593 K for the case of the initial LDH sample ,and it was attributed to the destruction of the LDH layer structure by sticking of the hydroxide layers and a rearrangement of the atoms to an amorphous state [29]. For the 'R-water sample' the break on the ETA curve took place with a significant intensity at 528 K (Fig. 2b). The ETA results are in agreement with our previous statement [30] that the re-hydration of the mixed oxide MO in a water solution took place by the dissolution of the mixed oxide MO and subsequent crystallization of the LDH sample.

Conclusions

It was found that microstructure, surface morphology and thermal stability of the re-generated Mg-Al-CO_3 LDHs samples were depending on conditions used for the preparation of the sample by re-hydration of the mixed Mg-Al oxide. The layered double hydroxide with different surface area and thermal behavior were formed after re-hydration in water or humid air, respectively. The emanation thermal analysis results confirmed the dissolution-crystallization mechanism proposed for the re-generation of the layered structure by the hydration of mixed oxide and revealed differences in the microstructure changes of the re-hydrated sample during heating.

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References

1 F. Cavani, F. Trifiro and A.Vaccari, Catal. Today, 11 (1991) 173.
2 A.Vaccari, Appl. Clay Sci., 14 (1999) 61.
3 A. Khan and D. J. O'Hara, Mater. Chem., 12 (2002) 3191.
4 V. Rives and M. A. Ulibarri, Coord. Chem. Rev., 181 (1999) 61.
5 V. Rives, Mater. Chem. Phys., 75 (2002) 19.
6 F. Rey and V. Fornes, J. Chem. Soc. Faraday Trans., 88 (1992) 2233.
7 M. Bellotto, B. Rebours, O. Clause, J. Lynch, D. Bazin and E. Elkaim, J. Phys. Chem., 100 (1996) 8535.
8 F. M. Labajos, V. Rives and M. A. Ulibarri, J. Mater. Sci., 27 (1992) 1546.
9 M. Bellotto, B. Rebours, O. Clause, J. Lynch, D. Bazin and E. Elkaim, J. Phys. Chem., 100 (1996) 8535.

10 T. Stanimirova, N. Petrova, I. Vergilov and G. Kirov, J. Mater. Sci., 34 (1999) 4153.

11 J. C. A. A. Roelofs, J. A. van Bokhoven, A. J. van Dillen, J. Geus and K. de Jong, Chem. Eur. J., 8 (2002) 5571.

12 F. Malherbe and J. P. Besse, J. Solid State Chem., 155 (2000) 332.

13 T. Stanimirova, N. Piperov, N. Petrova and G. Kirov, Clay Miner., 39 (2004) 177.

14 W. Yang, Y. Kim, P. K. T. Liu, M. Sahimi and T. T. Tsotsis, Chem. Eng. Sci., 57 (2002) 1945.

15 Z. P. Xu and G. Q. Lu, Chem. Mater., 17 (2005) 1055.

16 J. Boclair and P. Braterman, Chem. Mater. 11 (1999) 298.

17 J. Boclair, P. Braterman, J. Jiang, S. Lou and F. Yarberry, Chem. Mater., 11 (1999)303.

18 T. Hibino, Y. Yamashita, K. Kosuge and A. Tsunashima, Clay Clays Miner., 43 (1995) 42.

19 T. Stanimirova and G. Kirov, Appl. Clay Sci., 22 (2003) 295.

20 S. Komarneni, N. Kozai and R. Roy, J. Mater. Chem., 8 (1998) 1329.

21 S. Miyata, Clay Clays Miner., 28 (1980) 50.

22 I. N. Beckman and V. Balek, J. Therm. Anal. Cal., 67 (2002) 49.

23 V. Balek and J. Tolgyessy, Wilson and Wilson's Comprehensive Analytical Chemistry, Part XII C, Elsevier, Amsterdam 1984, p. 304.

24 V. Balek, J. Šubrt, T. Mitsuhashi, I. N. Beckman and K. Gyoryová, J. Therm. Anal.Cal., 67 (2002) 15.

25 V. Balek, E. R.Vance, V. Zeleňák, Z. Málek and J. Šubrt, J. Therm. Anal. Cal., 88 (2007) 93.

26 V. Balek, M. Beneš, J. Šubrt, J. L. Pérez-Rodríguez, P. E. Sánchez-Jimenez, L. A. Pérez-Maqueda and J. Pascual Cosp, J. Therm. Anal. Cal., 92 (2008) 171.

27 V. Balek, J. Šubrt, I. M. Bountseva, H. Irie and K. Hashimoto, J. Therm. Anal. Cal., 92 (2008) 161.

28 F. Kovanda, V. Balek, V. Dorničák, P. Martinec, M. Mašlan, L. Bílková, D. Koloušek and I. M. Bountsewa, J. Therm. Anal. Cal., 71 (2003) 727.

29 T. Stanimirova, T Hibino and V. Balek, J. Therm. Anal. Cal., 84 (2006) 473.

30 T. Stanimirova, E. Dinolova and G. Kirov, J. Mater. Sci. Lett., 20 (2001) 453.

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