

THERMAL BEHAVIOR OF Mg–Al–CO₃ LAYERED DOUBLE HYDROXIDE CHARACTERIZED BY EMANATION THERMAL ANALYSIS

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Emanation thermal analysis (ETA) was used to characterize microstructure changes during heating of Mg–Al–CO₃ layered double hydroxide (LDH) in the temperature range of 293–1473 K. It was confirmed by ETA that the formation of an intermediate phase with grafted CO₃²⁻ anions in the hydroxide layers took place in the temperature range of 508–523 K and the formation of Mg–Al mixed oxide (MO) occurred in the range 623–773 K. The small peak of the emanation rate at 603 K indicated the degradation of the layered structure and the broad peak in the range of 1073–1273 K characterized the onset of the separation of the decomposition products of MO into MgO and Mg₂Al₄O₇. The ETA results revealed that dehydration of the product with grafted CO₃²⁻ anions occurred at lower temperatures than that of the initial Mg–Al–CO₃ LDH.

Keywords: DTA, EGA, emanation thermal analysis (ETA), layered double hydroxides, TG, thermal decomposition

Introduction

Layered double hydroxides (LDHs), also known as anionic clays are of increasing interest in recent years, because of the wide scope of their applications in the field of catalysis, adsorption, anionic exchange, water purification, flame retardants, etc. [1–3].

The structure of LDHs consists of consequent positively charged brucite-like layers and compensation of negative anion-water interlayers [4]. The LDH compounds are described with general formula $M_{1-x}^{2+} M_x^{3+} (\text{OH})_2 A_{x/m}^{m-} \cdot (1-3x/2)\text{H}_2\text{O}$, ($0.20 < x \leq 0.33$), where M^{3+} (Al, Cr, Mn, Fe, Co, Ga, La and Y) partially substitutes M^{2+} (Mg, Mn, Fe, Co, Ni, Cu, Zn and Ca) in the brucite-like layers. The positive charge surplus is balanced by the anions A^{m-} (CO₃²⁻, SO₄²⁻, OH⁻, CrO₄²⁻, ClO₄⁻, halides, complex anions, organic anions, etc.) in the interlayer space, where water molecules are also present [1, 3, 5, 6].

The LDHs properties are closely related with their thermal activation and the high temperature products formed during heating. The thermal decomposition of Mg–Al–CO₃ LDH is a sequence of dehydration, dehydroxylation and decarbonisation processes, giving rise to a series of intermediate products. It was supposed by a number of authors [5, 7–12] that the release of interlayer water on the sample heating was completed at 453–483 K and that the initial structural change took place during the dehydroxylation. It was demonstrated by various methods that the destruction of the first OH groups (in the range 483–523 K) caused

a grafting of carbonate anions and led to the formation of the product with smaller interlayer distance and specific properties [7, 10, 13]. The continuous dehydroxylation and the release of CO₂ (in the range of 623–1073 K) resulted in the destruction of the layered structure and the formation of periclase-like cubic (Mg, Al)O solid solution [1, 2, 7].

The processes and products of Mg–Al–CO₃ LDH thermal decomposition have been investigated by using such methods as thermogravimetry (TG), differential thermal analysis (DTA), calorimetry, X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), Nuclear magnetic resonance (NMR), evolving gas analysis (EGA), mass-spectroscopy (MS) and others [1, 2, 9–12, 14].

In the last two decades a non-conventional method called as emanation thermal analysis (ETA), based on the measurements of the radon release from previously labelled solid samples, was used to monitor the microstructure development during thermal decomposition of various chemical compounds such as oxalates, sulfates, carbonates, oxides, etc. [15–18]. Recently, the ETA was applied [19] to investigate in detail the thermal decomposition of synthetic pyroaurite-like anionic clay (Mg–Fe–CO₃ LDH). A good agreement between the ETA results characterizing the microstructure development under in situ heating of the samples and the results of B.E.T. surface area determinations was demonstrated.

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In this paper we describe the results of ETA to characterize the thermal behavior of Mg–Al–CO₃ LDH and re-hydrated form of its product with grafted CO₃²⁻ anions. The ETA results were compared with results of DTA, TG, EGA (mass-spectroscopy detection), XRD and FTIR.

Experimental

Synthesis of the initial sample

The initial Mg–Al–CO₃ compound with the Mg:Al ratio 3:1 was prepared as described by Miyata [5]. The synthesis was performed under vigorous stirring by dropwise mixing of an acid solution of 0.5 M Mg(NO₃)₂ and 0.5 M Al(NO₃)₃ (in molar ratio 3:1) with alkali solution of 1 M NaOH and 0.5 M Na₂CO₃. The synthesis was carried out at controlled pH of 10–10.5. The resulting gel was aged in polypropylene bottle for 48 h at 353 K. The obtained precipitate was filtered, washed until the washing water reached a pH value of 8–8.5 and then it was dried at room temperature.

Labelling of samples for ETA

For the ETA measurements the sample of the initial Mg–Al–CO₃ LDH was labelled by drops of the radionuclides of ²²⁸Th and ²²⁴Ra in acetone solution. After the labelling, acetone was evaporated at 353 K. The atoms of ²²⁸Th adsorbed on the sample surface served as a source of ²²⁴Ra and ²²⁰Rn. The specific activity of the labelled sample was 10⁵ Bq g⁻¹. The labelled samples were stored for four weeks prior to the ETA measurements under dry conditions to allow the radioactive equilibrium between the ²²⁸Th and ²²⁴Ra nuclides to be established. It was determined by means of TRIM code [20] that the maximum depth of the labelling by ²²⁴Ra and ²²⁰Rn recoiled atoms is 80 nm.

ETA measurements

The ETA measurements were carried out simultaneously with the DTA by using Netzsch Equipment, Type 404. The labelled samples situated in a corundum crucible were heated at the rate of 6 K min⁻¹ in the air flow (flow-rate 50 mL min⁻¹). The air flow carried the radon released from the sample into the measuring chamber of radon radioactivity. The resulting ETA curves are presented as temperature dependence of the radon release rate, called emanation rate, E (in relative units); $E=A_{\alpha}/A_{\text{total}}$, where A_{α} is α -radioactivity of radon released in a time unit from the labelled sample and A_{total} is the total γ -radioactivity of the labelled sample. Semiconductor and NaI (TI) detectors were used for the α - and γ -radioactivity measurements, respectively.

Simultaneous DTA, TG and EGA(MS) measurements

Simultaneous DTA, TG and EGA-mass-spectroscopy detection EGA(MS) measurements were performed at the heating rate of 6 K min⁻¹ by using the equipment Netzsch Type STA 409, coupled with Balzers mass spectrometer, the evolved gases detected were $m/e=18$ (H₂O) and $m/e=44$ (CO₂).

Powder XRD patterns

The powder XRD patterns were recorded on a Rigaku X-ray diffractometer MultiFlex 2 kW. The measurements were obtained using CuK α radiation separated by a crystal monochromator in the range 2θ 3–70°, continuous scan at 4° min⁻¹.

FTIR spectra

FTIR spectra were recorded with a Nicolet Magna-IR 750 spectrometer using the KBr pellet technique (spectral range, 400–4000 cm⁻¹; resolution, 16 cm⁻¹; 150 scans).

Results and discussion

Thermal behavior of initial Mg–Al–CO₃ LDH

Figure 1 depicts results of DTA and ETA (a), TG/DTG (b) and EGA(MS) (c) that characterize the thermal behavior of the initial Mg–Al–CO₃ LDH heating in air in the range from 293 to 1473 K. From the results of TG (Fig. 1b) and EGA(MS) measurements (Fig. 1c) it followed that the mass loss in the temperature range of 293–523 K corresponding to 17.0% of the initial sample mass was caused by water release from the sample. The comparison of the ETA, DTA and TG results (Figs 1a and b) revealed, the mass loss of the sample in the mentioned temperature range was accompanied by an enhancement of the emanation rate radon release (ETA curve in Fig. 1a) indicating an increase of surface area and the formation of additional radon diffusion paths.

On the basis of the Allmann's structural refinement we calculated that in the Mg–Al–CO₃ LDH sample with Mg:Al=3:1 ratio, the amount of the interlayer water was 14.5 mass%, at which mass loss the temperature reads 478 K. The additional mass loss of 2.5% observed between 478 K and 523 K (Fig. 1b) was ascribed to the release of water molecules originating from OH hydroxyl groups [8, 10, 12]. As it is seen in the Fig. 1a, the emanation rate increased gradually from 363 to 508 K and accompanied by the interlayer water dehydration. Thus, it can be assumed that the radon migration ability was facilitated by the release of interlayer water molecules. Moreover, the

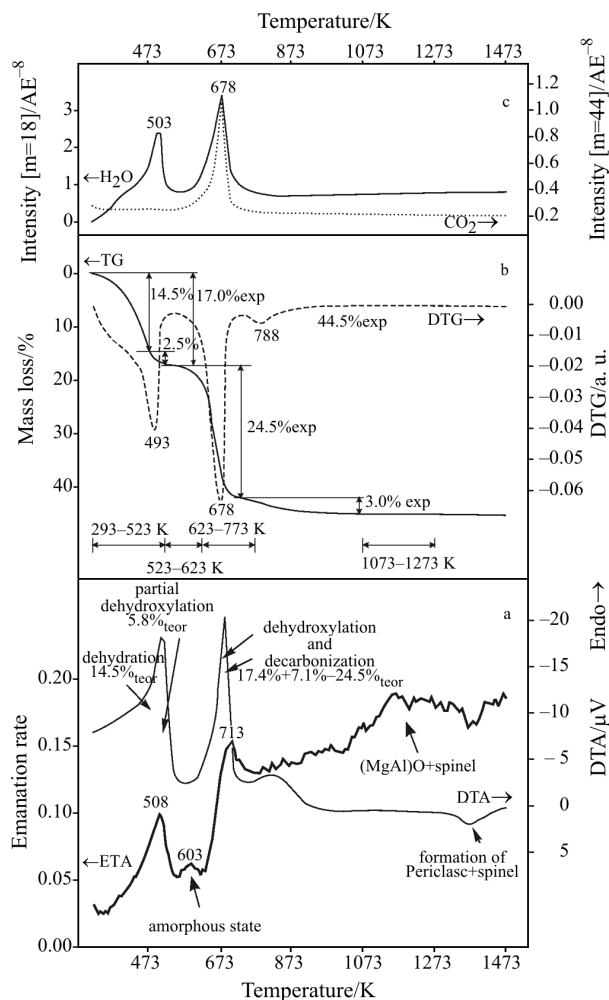


Fig. 1 Comparison of the results of ETA/DTA, TG/DTG and EGA(MS) measurements obtained during heating of the initial Mg–Al–CO₃ LDH in range of 293–1473 K: a – results of ETA (bold line) and DTA (slender line) measurements, b – results of TG (full line) and DTG (dashed line) measurements, c – results of EGA(MS) – release of H₂O (full line) and CO₂ (dotted line)

XRD pattern of the dehydrated product showed an unchanged interlayer distance (Fig. 2b), which allowed to describe the products' structure as pillared structure, in which the CO₃²⁻ anions without changing their position and symmetry (Fig. 3b) play a role of pillars. The resulting pillared interlayer probably serves as a diffusion path for the radon release.

From Fig. 1a, it is seen that after the release of the interlayer water and water molecules formed from OH groups, the emanation rate, E , decreased abruptly at the temperature range from 508 to 523 K. It is known that the partial dehydroxylation at temperature range of 483–523 K occurred being accompanied by the rearrangement of the CO₃ groups [10, 14]. The FTIR spectra of the sample heated at 523 K showed that the carbonate adsorption band ν_3 at 1383 cm⁻¹

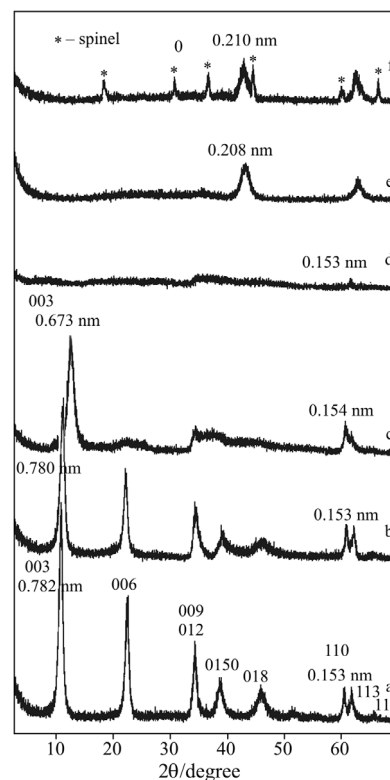


Fig. 2 Powder XRD patterns of the a – initial Mg–Al–CO₃ LDH sample and the intermediate products obtained by heating of the initial sample to the temperatures, b – 463 K, c – 523 K, d – 593 K, e – 773 K and f – 1173 K

split into two main bands (1584 and 1354 cm⁻¹). In addition, the absorption band (1036 cm⁻¹) corresponding to the inactive IR vibration ν_1 appeared (Fig. 3c). These changes of the FTIR spectra were attributed to the change in the carbonate group symmetry from D_{3h} to C_{2v} , which was caused by the grafting of the CO₃ groups in the hydroxide layers [7, 10, 21].

The product resulting after the CO₃ groups' rearrangement was characterized by a significantly reduced basal spacing $d_{003}=0.673$ nm as compared with that of 0.782 nm for initial sample (Fig. 2). Taking into account the thickness of the brucite structure layer (0.48 nm), the interlayer height decreased from 0.303 to 0.192 nm during heating at 523 K. Thus, the abrupt decrease of the emanation rate observed on the ETA curve in the range of 508–523 K is attributed to the decrease of the interlayer volume serving as the radon diffusion channel.

On further heating in the temperature range of 523–623 K, a continuous destruction of the layered structure took place, which resulted in the formation of an X-ray amorphous intermediate product (Fig. 2d). Since no mass loss was observed by TG in this temperature range (Fig. 1b), the small increase peaked at 603 K on the ETA curve (Fig. 1a) is ascribed to a rearrangement of amorphous state during heating.

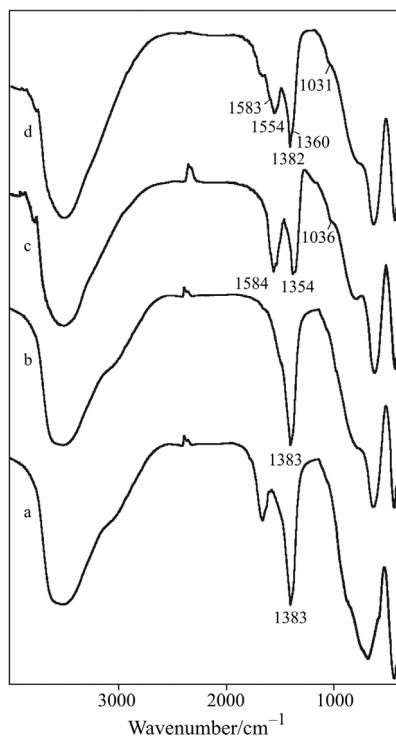


Fig. 3 FTIR spectra of the a – initial Mg–Al–CO₃ LDH sample; b – intermediate products obtained by heating of the initial sample to the temperatures of 463 K, c – 523 K, d – after the re-hydration of the LDH heated at 523 K

The results depicted on Figs 1b and 1c showed that the dehydroxylation and decarbonation of the sample is complete in the temperature range of 623–773 K. The observed increase of the emanation rate in this temperature range (Fig. 1a) can be ascribed to the thermal degradation of the LDH and the formation of nano-sized Mg–Al mixed oxide (Fig. 2e). This is in agreement with the assumption that the thermal degradation process was accompanied by the formation of additional diffusion paths for radon, indicated by an increase of emanation rate, E . It was demonstrated by electron microscopy observations [11] that cracks of various sizes (length of 10–40 μm and the width of 0.2 μm , and/or length up to 0.2 μm and width of 1–2 nm) were formed during heating of the synthetic as well as natural samples of Mg–Al–CO₃ LDH up to 773 K. It can be assumed that these cracks as well as the interface boundaries of the formed mixed oxide serve as additional diffusion channels for radon migration.

In the temperature range of 1073–1273 K no mass loss was observed (Fig. 1b), and the XRD pattern of the sample heated at 1173 K confirmed the appearance of the spinel phase (MgAl₂O₄) along with the presence of the periclase-like mixed Mg–Al oxide phase (Fig. 2f). Thus, we assumed that the broad peak observed on the ETA curve (Fig. 1b) indicated the onset of the sep-

aration of periclase (MgO) and spinel phases formed as the result of the LDHs thermal decomposition.

The final crystallization of the periclase and spinel phases occurred at 1373 K, as indicated by the exothermal DTA effect (Fig. 1a). At this temperature a dent of the emanation rate, E was observed, indicating an ordering of newly formed structures and closing the radon diffusion paths formed previously.

Thermal behavior of re-hydrated products

Taking into account that the product with grafted CO₃²⁻ anions obtained by heating of Mg–Al–CO₃ LDH at 523 K was reported as an excellent heat adsorbent [14], it was of interest to compare the thermal behavior of the LDH and re-hydrated form of this product. In order to prepare the re-hydrated sample, the initial sample was heated at 523 K for 2 h and re-hydrated by moistening for 7 days at 333 K in air with RH 80%.

In Fig. 4 the ETA-DTA, TG/DTG and EGA(MS) results of the initial Mg–Al–CO₃ LDH sample and of

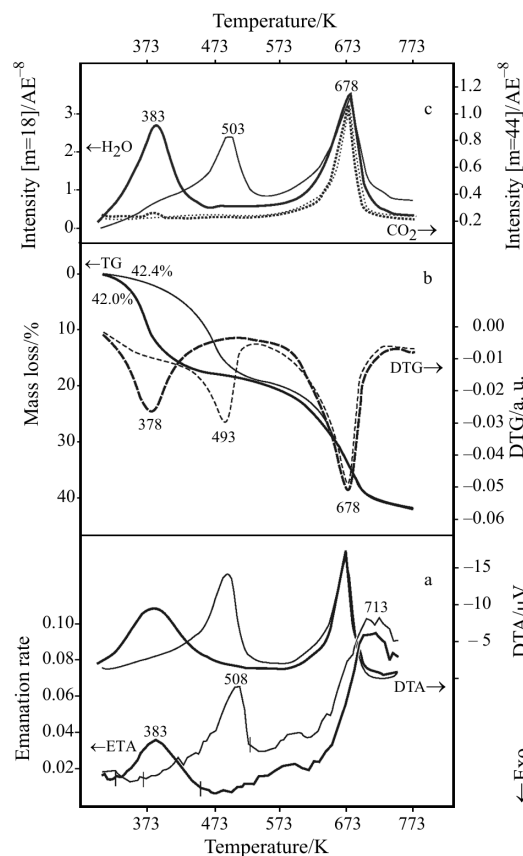


Fig. 4 Comparison of the ETA/DTA, TG/DTG and EGA(MS) results obtained during heating (range of 293–773 K) of the initial sample (slender lines) and the sample obtained after the re-hydration of the LDH heated at 523 K (bold lines); a – results of ETA and DTA measurements, b – results of TG (full lines) and DTG (dashed lines) measurements, c – results of EGA(MS) – release of H₂O (full line) and CO₂ (dotted line)

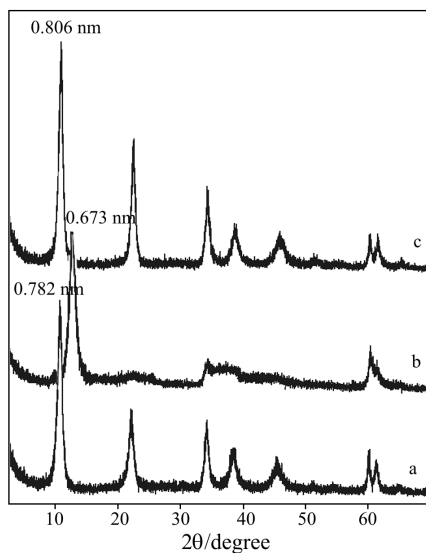


Fig. 5 XRD patterns of the a – initial Mg–Al–CO₃ LDH sample; b – the intermediate product obtained by heating of the initial sample at 523 K, c – after the re-hydration of the LDH heated at 523 K

the re-hydrated sample are compared. In contrast to the ETA results of the initial sample, the emanation rate, E , of the re-hydrated sample decreased in the temperature range of 383–453 K with a gentler slope than that observed for the initial sample between 508 and 523 K (Fig. 4a). The different thermal behaviour observed with the re-hydrated sample can be explained by its specific structure. It was showed by the XRD that the re-hydrated sample showed larger interlayer distance than that of the initial sample (Fig. 5). The FTIR spectra showed that the CO₃²⁻ anions were still grafted in hydroxide layers – carbonate ν_3 vibration band was still split and ν_1 was registered (Fig. 3d). This fact implied that the interlayer of the re-hydrated sample contained only water molecules provoking a weak interaction between the hydroxide layers and interlayer. It can be assumed that the decrease of the emanation rate, E , observed in the range from 383 to 453 K is due to a gradual closure of the interlayer space along with interlayer water release. At the same time, the results in Fig. 4 shows that the release of interlayer water from the re-hydrated sample takes place at lower temperatures (323–453 K) than that of the initial sample (363–523 K), respectively. This information is useful for the activation of the LDHs samples to be applied as heat adsorbents.

Conclusions

By using the ETA, DTA, TG, EGA(MS), XRD and FTIR detailed information about thermal behaviour of Mg–Al–CO₃ LDH on heating in air was obtained. The

ETA brought additional information about the microstructure development and formation of intermediate phases with layered structure and their changes on heating. Moreover, the onset temperatures of the separation of the LDH final decomposition products and their final crystallization were determined from the ETA results. It was assumed that during heating of the re-hydrated LDH product, a gradual closure of the interlayer space took place along with the water release, which was in contrast to thermal behavior of the initial LDH sample, that was characterized by an abrupt interlayer closure. It was found that the temperature ranges where the water released from the re-hydrated form of the product with grafted CO₃²⁻ anions and the initial LDH samples took place on heating were different: i.e. 323–453 and 363–523 K, respectively. This information is useful in the determination of optimized conditions for the preparation of the LDH samples to be applied as heat adsorbents.

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