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The Formation of Different Mg–Al LDHs (Mg/Al = 2:1) Under Hydrothermal Conditions and Their Application for Zn²⁺ ions Removal

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Abstract:

The formation of different Mg-Al LDHs (Mg/Al = 2:1) under hydrothermal conditions (200 °C; 4–24 h) was investigated in the $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O} - \gamma\text{-Al}_2\text{O}_3/\text{Al}(\text{OH})_3 - \text{H}_2\text{O}$ and $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O} - \gamma\text{-Al}_2\text{O}_3 - \text{H}_2\text{O}$ systems. It was determined that chemical nature of the initial Mg containing components changes the formation mechanism of the synthesis products during isothermal curing. Magnesium aluminum hydroxide hydrate is crystallized by using $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ as starting material while hydroxide hydrate in the $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ presence. The sequence of the compounds formation is presented. It should be noted that different modifications of Al containing components have only a slight influence on the meixnerite-type LDH hydrothermal synthesis. It was determined that after 45 min of sorption all Zn²⁺ ions are incorporated into the crystal structure of hydrotalcite. It should be underlined that crystallinity of the latter compound do not change during ion exchange experiments. Thus, the latter compound can be used as adsorbent for Zn²⁺ ion removal. Synthesized samples were characterized by powder X-Ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), simultaneous thermal analysis (STA) and scanning electron microscopy (SEM).

Keywords: Hydrothermal synthesis; Meixnerite-type layered double hydroxide; Hydrotalcite; Zn²⁺ ion removal.

1. Introduction

Layered double hydroxides (LDHs) can be described by general formula $[\text{M}(\text{II})_{1-x}\text{M}(\text{III})_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M(II) – divalent (e. g. Zn²⁺, Fe²⁺, Mg²⁺, Ni²⁺, Cu²⁺) and M(III) – trivalent metals (e. g. Al³⁺, Ga³⁺, Fe³⁺, Cr³⁺), and Aⁿ⁻ is an anion (e. g. Cl⁻, CO₃²⁻, OH⁻, NO₃⁻, SO₄²⁻) [1,2]. x has usually values between 0.20 and 0.33 [3]. Their structure is based on brucite-like layers, in which a divalent metal cation is located in the center of oxygen octahedra and two-dimensional infinite layers are formed by edge-sharing of the octahedra. Partial isomorphous substitution of trivalent cations for divalent ones results in a positive charge on the layers. Organic or inorganic anions are intercalated between the layers in order to maintain charge balance, and crystallization water is also generally found in the interlayer galleries [4]. Recently, LDHs attracted more attention due to their unique properties which are widely applied in anion exchange reactions and basic catalysis [5-8].

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Layered double hydroxides may be synthesized by using various methods. The most common way to obtain these compounds is simple coprecipitation and its modifications (e. g. precipitation at low and high supersaturation, urea hydrolysis and etc.) [9-13]. Meanwhile, mentioned methods have some disadvantages, such as pH value, i. e. alkaline solution should be maintained during preparation, temperature and time for LDHs to precipitate (the addition of metal salt solutions takes from one to two hours) [14]. S. K. Sharma and the others claimed that the pH value mostly varies from 7 up to 10 in the temperature range of 60 – 80 °C [15].

The important parameters determining the applications of LDHs are degree of crystallinity and textural properties, which depend on the used synthesis method [15,16]. These properties are influenced by various parameters such as the nature of the bivalent and trivalent cations and their ratio, aging time, temperature and etc. As a result, the hydrothermal treatment received much attention in the preparation of LDHs, because it allows to control crystallite size, crystallinity, the shape of crystals by changing temperature, synthesis time or divalent and trivalent metals molar ratio [17,18]. However, the literature concerning this LDHs synthesis method is limited.

Hydrotalcite has important characteristics that make it interesting for various applications. Firstly, hydrotalcite was widely studied and successfully used as basic catalyst for several reactions such as self condensation, cross-aldol condensation of aldehydes and ketones, Knoevenagel condensation, Claisen-Smith condensation, Michael addition. Secondly, this compound has a good ion-exchange capacity which leads to use it also for the removal of heavy metals from waste water.

H. Wang and co-workers [19] studied the defluoridation of drinking water by the latter compound. The results showed that calcined hydrotalcite samples exceeded greater F⁻ uptake than uncalcined samples [19]. Other researchers [2] also compared the uptake of Br⁻ anions between calcined and uncalcined HT samples and got the same results. M. Park and co-workers [20] investigated the adsorption of Cu²⁺ and Pb²⁺ cations by hydrotalcite and found that removal of mentioned cations from aqueous solutions resulted in precipitation of Cu₇Cl₄(OH)10·H₂O, PbCO₃PbCl₂ and Pb(OH)Cl compounds on the surface of HT, i. e. the surface adsorption proceeded.

In previous work was observed that during isothermal curing an intermediate compounds (boehmite and magnesium carbonate) was formed when Mg/Al ratio was equal to 3:1 [21].

In order to decrease the amount of undesirable compounds and the cost of hydrothermal treatment, this work is focused on investigation of different Mg–Al LDHs with a Mg/Al ratio 2:1 under hydrothermal conditions. The application for removing Zn²⁺ ions is also studied in this paper.

2. Experimental

The different Mg–Al LDHs samples were prepared by using the following reagents as raw materials: magnesium carbonate hydroxide hydrate (Sigma-Aldrich Chemie GmbH, Germany; the purity is 99 %), basic magnesium carbonate (Reachim, Russia; the purity is 99 %), γ -Al₂O₃ (γ -Al₂O₃ was produced by burning aluminium hydroxide (Reachim, Russia) at 475 °C for 5 hours) and aluminium hydroxide (Lar-Ner, Czech Republic; the purity is 63–67%).

It should be underlined that Mg containing raw materials (magnesium carbonate hydroxide hydrate and basic magnesium carbonate) have the similar empirical formula, however the thermal properties of these compounds are different as it is shown in Fig. 1. It was determined that Mg(OH)₂ dehydration begins at 277 °C temperature. Moreover, the decarbonization was observed at 449 °C temperature (Fig. 1, a). Meanwhile, only two

endothermic effects reflecting dehydration (257 °C) and decarbonization (456 °C) are visible in the $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ STA curve (Fig. 1, b). It should be noted that the recrystallization to magnesium oxide at 520 °C temperature is not characteristic to basic magnesium carbonate ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$).

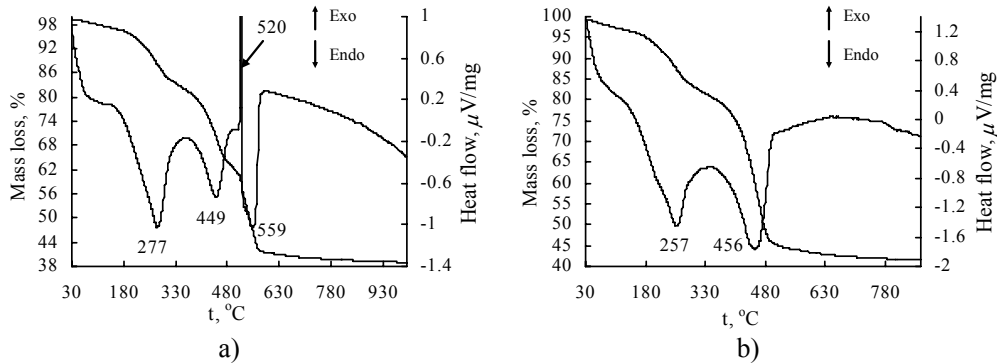


Fig. 1. STA curves of $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ (a) and $\text{Mg}_5(\text{CO}_3)_4 \cdot (\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (b).

Dry primary mixtures having a Mg/Al ratio equal to 2:1 were mixed with water (water/solid ratio of the suspension $W/S = 10.0$). Hydrothermal synthesis was carried out in unstirred suspensions under the saturated steam pressure at 200 °C temperature; the duration of isothermal curing was 4 and 24 hours. The products of the synthesis were filtered, rinsed with ethyl alcohol to prevent carbonization of material, dried at $50 \text{ °C} \pm 5$ temperature, and sieved through a sieve with a mesh width of 50 μm.

The X-ray powder diffraction (XRD) data were collected with a DRON-6 X-ray diffractometer with Bragg-Brentano geometry using Ni-filtered $\text{Cu K}\alpha$ radiation and graphite monochromator, operating with the voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range $2\text{--}60^\circ$ (2θ) in steps of $2\theta = 0.02^\circ$.

Simultaneous thermal analysis (STA: differential scanning calorimetry – DSC and thermogravimetry – TG) was also employed for measuring the thermal stability and phase transformation of synthesized products at a heating rate of 15 °C/min, the temperature ranged from 30 °C up to 1000 °C under air atmosphere. The test was carried out on a Netzsch instrument STA 409 PC Luxx. The ceramic sample handlers and crucibles of Pt-Rh were used.

FT-IR spectrum have been carried out by using a Perkin Elmer FT-IR Spectrum X system. The specimen was prepared by mixing 1 mg of the sample with 200 mg of KBr. The spectral analysis was performed in the range of $4000\text{--}400 \text{ cm}^{-1}$ with spectral resolution of 1 cm^{-1} .

Scanning electron microscopy (SEM) (FEI Quanta 200 instrument) of the samples was performed using 30 kV accelerating voltage and a working distance of 9.2 mm, detector – ETD.

Ion exchange experiments were carried out at 25 °C in a Grant SUB14 thermostatic adsorber by stirring 1 g of hydrotalcite in 100 ml of $\text{Zn}(\text{NO}_3)_2$ aqueous solution, containing 0.3 g/dm^3 of Zn^{2+} ions, for 45 min. The percentage of Zn^{2+} ions exchange was determined using a Perkin-Elmer Analyst 4000 spectrometer based on the changes of the concentrations of the cations in the solution and the cations in the hydrotalcite.

3. Results and Discussion

3.1 Characterization of meixnerite-type LDH in the $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O} - \text{Al}(\text{OH})_3/\gamma\text{-Al}_2\text{O}_3 - \text{H}_2\text{O}$ systems

It was determined, that after 4 hours of isothermal curing at 200 °C temperature magnesium carbonate (d -spacing – 0.274, 0.251, 0.210, 0.194, 0.170 nm; endothermic peaks at 429 °C and 636 °C temperatures; absorption bands at 1439, 1420, 885 and 748 cm^{-1}), magnesium hydroxide (d -spacing – 0.477, 0.237, 0.179 nm; endothermic peaks at 402 °C temperatures; absorption band at 3697 cm^{-1}) and also magnesium aluminum layered double hydroxide (d -spacing – 0.780, 0.387, 0.258, 0.230 nm; endothermic peaks at 217 and 306 °C temperatures; absorption bands at 3486, 554 cm^{-1}) are formed by using $\text{Al}(\text{OH})_3$ as raw material (Figs. 2, 3, 4, a). It should be noted, that magnesium hydroxide and magnesium carbonate are the products of initial Mg component decomposition.

It should be underlined that the intensity of diffraction peaks characteristic to $\text{Mg}_6\text{Al}_2(\text{OH})_{18} \cdot 4.5\text{H}_2\text{O}$ increased in 1.5 times after prolonging the hydrothermal treatment duration up to 24 hours (Fig. 2, b). These data were confirmed by FT-IR spectrum: the absorption maximum reflecting Mg-OH and Al-OH bond vibration at 3479 cm^{-1} is broader (Fig. 3, b). Meanwhile, the absorption band at 554 cm^{-1} , which can be ascribed to Al-O bond vibration, is more visible. Moreover, STA analysis data showed the increase of endothermic effects at 238 and 315 °C temperatures characteristic to Mg-Al-OH LDH dehydroxylation (Fig. 4, b).

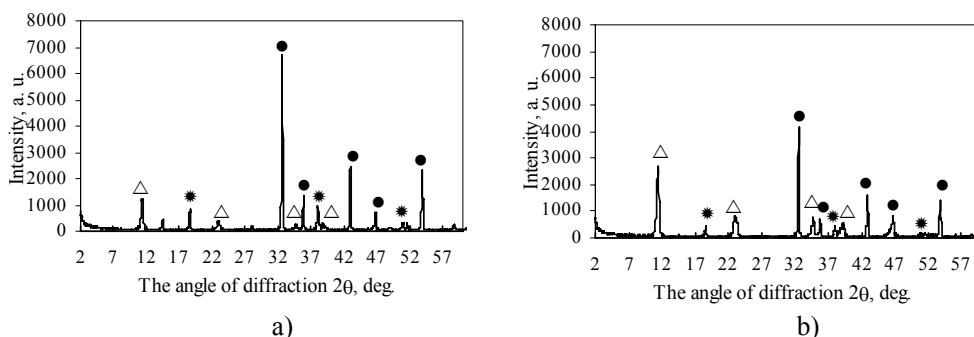


Fig. 2. X-ray diffraction pattern of synthesis products when raw materials are $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$. Duration of hydrothermal synthesis at 200 °C is equal to 4 (a) and 24 h (b). Indices: Δ – magnesium aluminum hydroxide hydrate, \bullet – magnesium carbonate $*$ – magnesium hydroxide.

It is interesting that after 24 h of hydrothermal synthesis the intensity of diffraction peaks of both magnesium carbonate and magnesium hydroxide is decreased (Fig. 2, b). It is clearly visible in FT-IR spectrum: only a shoulder at 3697 cm^{-1} reflecting Mg-OH bond vibrations and also the decrease in absorption bands intensity at 1430, 1414, 881 and 748 cm^{-1} characteristic to C-O_3^{2-} bond vibrations are observed (Fig. 3, b). Furthermore, the absorption maximum at 3055 cm^{-1} due to O-H bond vibrations can be assigned to $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, the initial magnesium component.

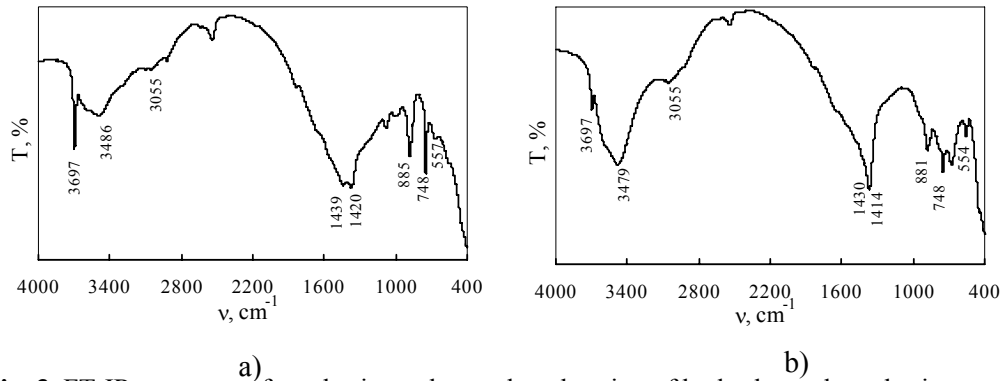


Fig. 3. FT-IR spectrum of synthesis products when duration of hydrothermal synthesis at 200 °C is equal to 4 (a) and 24 h (b). Raw materials are $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$.

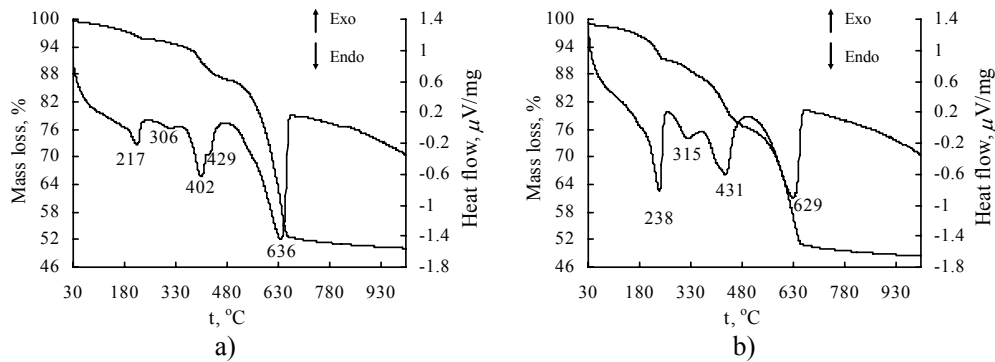


Fig. 4. STA curves of synthesis products when raw materials are $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$. The duration of hydrothermal synthesis at 200 °C is equal to 4 (a) and 24 h (b).

Simultaneous thermal analysis data is in good agreement with XRD and FT-IR (Fig. 4). After 24 h of isothermal curing, the intensity of endothermic effect at 629 °C temperature reflecting MgCO_3 decarbonization is decreased. It should be noted that it is a two-step process, e. g. decarbonization also identified at 431 °C temperature and overlaps with dehydration of $\text{Mg}(\text{OH})_2$ (Fig. 4, b).

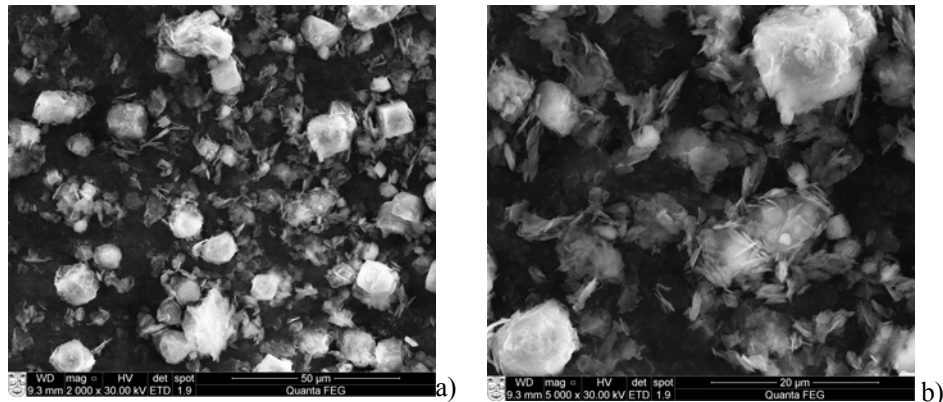


Fig. 5. SEM images of synthesis products when the duration of hydrothermal synthesis at 200 °C is equal to 24 h and the magnitude is: a – 2000, b – 5000. Raw materials are $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$.

The images of SEM analysis showed three different crystal morphology: an magnesium aluminum layered double hydroxide aggregates with indefinite structure, thin $\text{Mg}(\text{OH})_2$ plates and rhombohedral MgCO_3 crystals. The crystals size varied from 2 to 10 μm (Fig. 5).

Thus, due to a low reactivity of both magnesium containing component and intermediates (MgCO_3 , $\text{Mg}(\text{OH})_2$) $\text{Mg}_6\text{Al}_2(\text{OH})_{18}\cdot 4.5\text{H}_2\text{O}$ is dominant in the synthesis products. Unfortunately, a fair amount of MgCO_3 and $\text{Mg}(\text{OH})_2$ were found.

On purpose to exceed better interaction between Mg and Al containing components, $\gamma\text{-Al}_2\text{O}_3$ is used as initial Al containing component.

It was determined that the intensity of diffraction peaks characteristic to Mg–Al–OH LDH remain almost the same after 4 hours of hydrothermal treatment compared with results obtained by using $\text{Al}(\text{OH})_3$ (Fig. 6, a). Meanwhile, the areas of endothermic effects at 229 $^\circ\text{C}$ and 314 $^\circ\text{C}$ temperatures, are significantly increased from 26.89 to 72.41 $\mu\text{V}/\text{mg}$ (Fig. 4, a, 217 $^\circ\text{C}$) and from 6.94 to 18.61 $\mu\text{V}/\text{mg}$ (Fig. 4, a, 306 $^\circ\text{C}$) in the STA curve (Fig. 7, a). Furthermore, FT-IR spectrum data showed that absorption maximum at 3483 cm^{-1} is broader (Fig. 8, a). The basic diffraction maximum (d -spacing – 0.780 nm) markedly increased in 1.5 times after prolonging the synthesis duration up to 24 hours (Fig. 6, b).

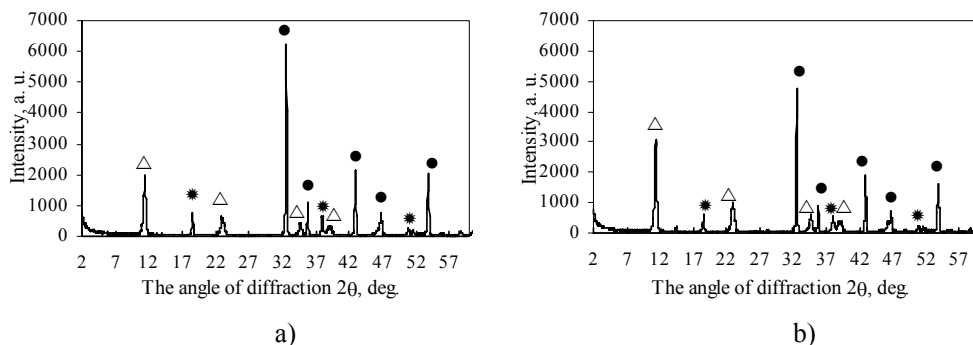


Fig. 6. X- ray diffraction pattern of synthesis products when the duration of hydrothermal synthesis at 200 $^\circ\text{C}$ is equal to 4 (a) and 24 h (b). Raw materials are $4\text{MgCO}_3\cdot\text{Mg}(\text{OH})_2\cdot 5\text{H}_2\text{O}$ and $\gamma\text{-Al}_2\text{O}_3$ Indices: Δ – magnesium aluminum hydroxide hydrate, \bullet – magnesium carbonate $*$ – magnesium hydroxide.

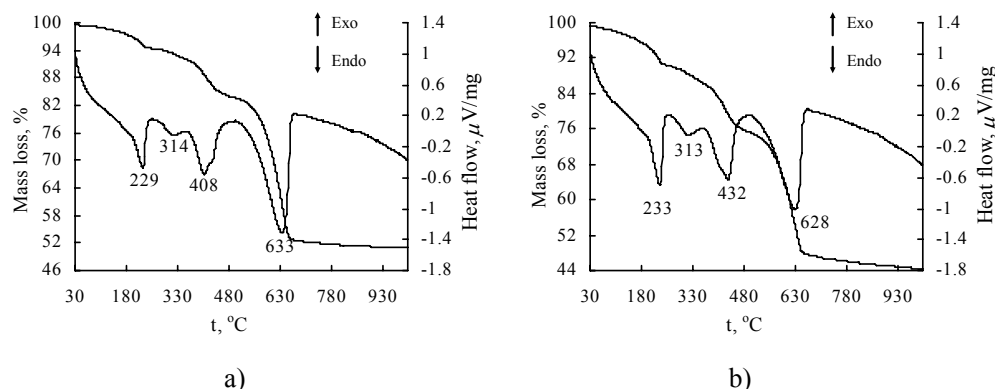


Fig. 7. STA curves of synthesis products when raw materials are $4\text{MgCO}_3\cdot\text{Mg}(\text{OH})_2\cdot 5\text{H}_2\text{O}$ and $\gamma\text{-Al}_2\text{O}_3$. The duration of hydrothermal synthesis at 200 $^\circ\text{C}$ is equal to 4 (a) and 24 h (b).

It should be underlined that after 24 hours of isothermal curing only a slight decrease in magnesium hydroxide (Fig 7, b; endothermic peak at 432 $^\circ\text{C}$ temperature) and magnesium carbonate (Fig. 7, b; endothermic peaks at 432 $^\circ\text{C}$ and 633 $^\circ\text{C}$ temperatures) amount were

observed (Fig. 6, b). $Mg(OH)_2$ is not fully reacted during all experimental conditions, though the absorption band at 3696 cm^{-1} decreases (Fig. 8, b). The same tendency noticed in the case with $MgCO_3$ (Fig. 8, b; absorption bands at 1400 , 884 , 748 cm^{-1}). Meanwhile, $O-H$ bond vibrations at 3055 cm^{-1} can be assigned to $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ (Fig. 8, b).

SEM analysis data shows the same crystal morphology as in the samples with aluminum hydroxide (Fig. 9). Furthermore, the prolonging of the hydrothermal synthesis duration causes the increase in crystal size from small to larger crystals.

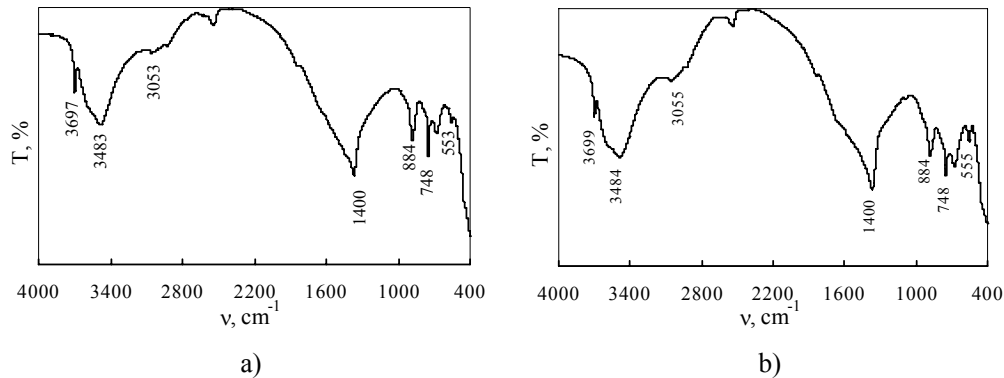


Fig. 8. FT-IR spectrum of synthesis products when duration of hydrothermal synthesis at $200\text{ }^\circ\text{C}$ is equal to 4 (a) and 24 h (b). Raw materials are $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ and $\gamma-Al_2O_3$.

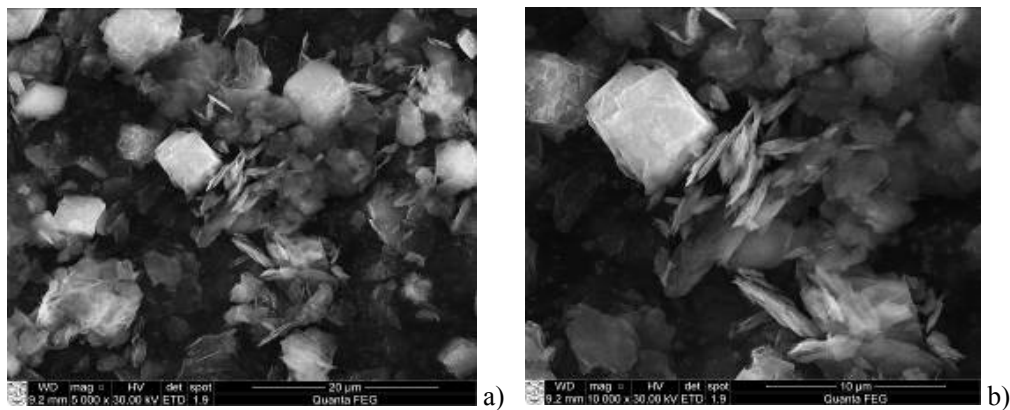
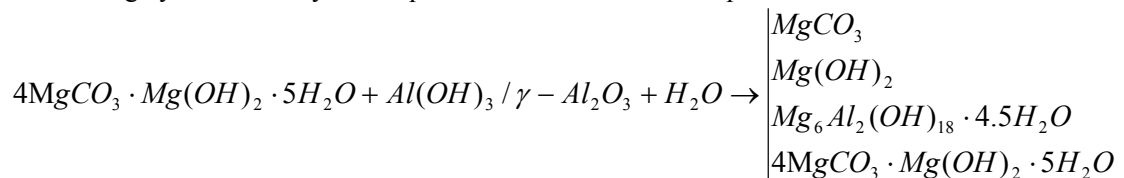


Fig. 9. SEM images of synthesis products when the duration of hydrothermal synthesis at $200\text{ }^\circ\text{C}$ is equal to 24 h and the magnitude is: a – 2000, b – 5000. Raw materials are $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ and $\gamma-Al_2O_3$.

During hydrothermal synthesis products formation can be represented as:



As seen from the reaction, in the beginning of it, the initial Mg component not fully decomposes into MgCO_3 and $\text{Mg}(\text{OH})_2$. During interaction between formed products and Al containing compounds Mg–Al–OH LDH is formed, as a result the prolonging of synthesis duration (24 h) causes the increase of latter compound amount in synthesis products. It should be noted that only a part of magnesium hydroxide is combined to $\text{Mg}_6\text{Al}_2(\text{OH})_{18}\cdot 4.5\text{H}_2\text{O}$.

3.2 Characterization of hydrotalcite in the $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2\cdot 4\text{H}_2\text{O} - \gamma\text{-Al}_2\text{O}_3 - \text{H}_2\text{O}$ system

Chemical nature of the initial Mg containing components changes the formation mechanism of the synthesis products.

It was determined that after 4 h of isothermic curing hydrotalcite (d -spacing – 0.765, 0.381, 0.257, 0.229 nm), hydrated Al_2O_3 – boehmite (d -spacing – 0.615, 0.309, 0.235, 0.186 nm) and MgCO_3 (d -spacing – 0.274, 0.257, 0.210, 0.194, 0.170 nm) were formed (Fig. 10).

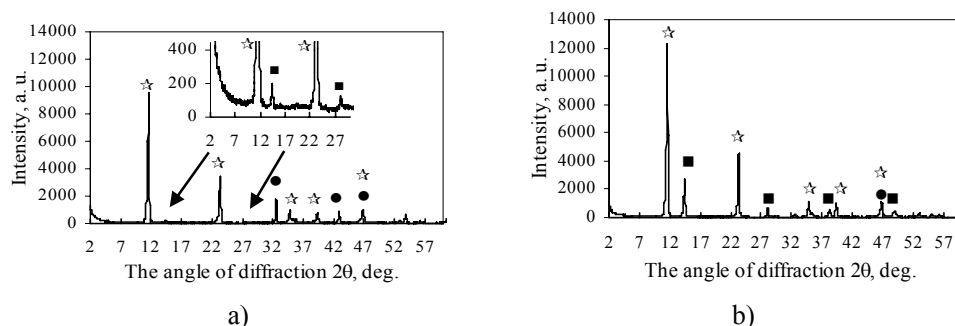


Fig. 10. X-ray diffraction pattern of synthesis products when the duration of hydrothermal synthesis at 200 °C is equal to 4 (a) and 24 h (b). Raw materials are $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2\cdot 4\text{H}_2\text{O}$ and $\gamma\text{-Al}_2\text{O}_3$. Indices: ☆ – hydrotalcite, ● – magnesium carbonate, ■ – boehmite.

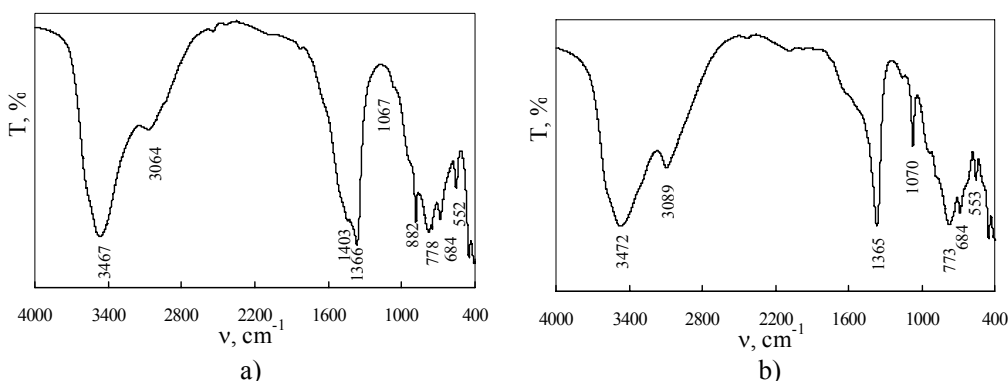


Fig. 11. FT-IR spectrum of synthesis products when duration of hydrothermal synthesis at 200 °C is equal to 4 (a) and 24 h (b). Raw materials are $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2\cdot 4\text{H}_2\text{O}$ and $\gamma\text{-Al}_2\text{O}_3$.

FT-IR signals are sufficiently strong to clearly identify all the important functional groups of compounds. The following absorption bands are identified by this analysis (Fig. 11):

- The absorption band at 3467 cm^{-1} reflecting $O - H$ bond vibrations are characteristic to hydrotalcite.

- The broad peak at 3064 cm^{-1} is due to the H-bonding ($HO - (H) - CO_3^{2-}$ vibrations) and can be ascribed to the Mg-Al- CO_3 LDH.
- The absorption bands of carbonates are observed at $1403, 882\text{ cm}^{-1}$ and can be assigned to magnesium carbonate. It should be noted, that these vibrations disappear after prolonging the synthesis duration. Moreover, the bands at 1366 and 684 cm^{-1} is also due to $C - O_3^{2-}$ bond vibrations and can be ascribed to hydrotalcite.
- The absorption bands at $1067, 778$ and 552 cm^{-1} reflecting $Al-O$ bond vibrations proceed in boehmite crystal structure.

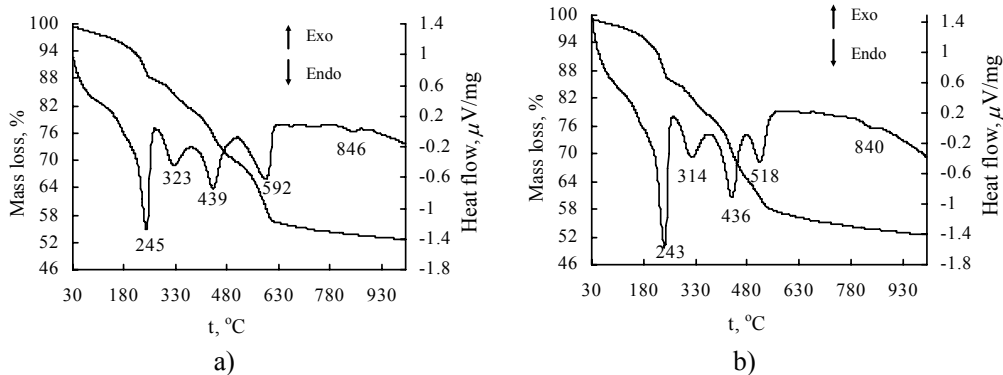


Fig. 12. STA curves of synthesis products when raw materials are $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ and $\gamma-Al_2O_3$. The duration of hydrothermal synthesis at $200\text{ }^\circ\text{C}$ is equal to 4 (a) and 24 h (b).

Simultaneous thermal analysis data confirms the formation of hydrotalcite. These thermal conversions were identified after 4 h of hydrothermal synthesis (Fig. 12):

- At $245\text{ }^\circ\text{C}$ temperature the interlayer water of Mg-Al- CO_3 LDH is lost.
- $323\text{ }^\circ\text{C}$ temperature reflects a partial dehydroxylation of hydrotalcite brucite-like sheets. It should be underlined that OH^- group bonded with Al^{3+} is lost. This process overlaps with boehmite dehydration.
- At $439\text{ }^\circ\text{C}$ temperature the decarbonization of hydrotalcite and magnesium carbonate is observed.
- At $592\text{ }^\circ\text{C}$ temperature, the recrystallization of boehmite to $\gamma-Al_2O_3$ takes place. It should be noted that it overlaps with the formation of mixed metal oxides and can be assigned to hydrotalcite.
- $846\text{ }^\circ\text{C}$ temperature reflects mixed metal oxides recrystallization to spinel phase, which is characteristic to Mg-Al- CO_3 LDH.

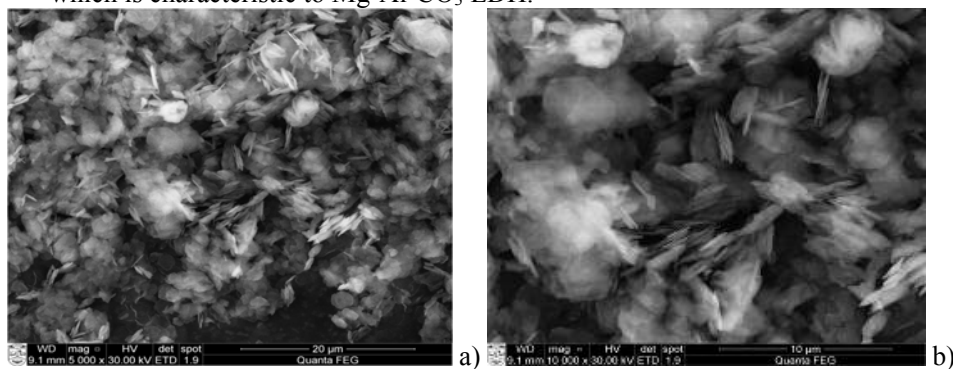
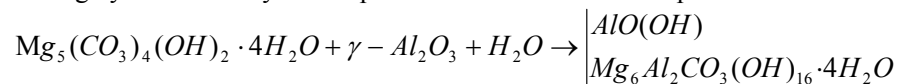


Fig. 13. SEM images of synthesis products when the duration of hydrothermal synthesis at $200\text{ }^\circ\text{C}$ is equal to 24 h and the magnitude is: a – 5000, b – 10000. Raw materials are $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ and $\gamma-Al_2O_3$.

It should be underlined that the crystallinity of hydrotalcite increased after prolonging the synthesis duration up to 24 hours. Furthermore, a fair amount of boehmite still remain. Meanwhile, magnesium carbonate is fully reacted (Fig. 5). It is clearly visible from SEM images: after 24 hours of hydrothermal synthesis rhombohedral $MgCO_3$ crystals are undetected and a hexagonal hydrotalcite plates are more visible.

During hydrothermal synthesis products formation can be represented as:



Thus, another LDH – hydrotalcite – is formed in the $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O - \gamma - Al_2O_3 - H_2O$ mixture. Unfortunately, a fair amount of boehmite still remain even after 24 hours of isothermal curing. It should be noted that magnesium carbonate is fully reacted. As a result, during synthesis more CO_3^{2-} - free anions, which intercalate in LDH interlayer, are produced.

3.3. A test reaction for Zn^{2+} ion removal

In order to evaluate sorption capacity of hydrotalcite (200 °C, 3h), adsorption of Zn^{2+} ions from $Zn(NO_3)_2$ solution was performed. It was determined that in alkaline solution the sorption proceeds effectively at the beginning of reaction. After 30 s, the amount of adsorbed Zn^{2+} ions in the crystal lattice of hydrotalcite is equal to 19.54 Zn^{2+} mg /g when the initial concentration of Zn^{2+} ions is 0.3 g/dm^3 (Fig. 14, a). Meanwhile, ion-exchange equilibrium is reached already after 5 minutes and 75 % of Zn^{2+} ions are incorporated into the crystal structure of hydrotalcite (Fig. 14, b). It was observed that the crystallinity of hydrotalcite does not change during the ion exchange experiments.

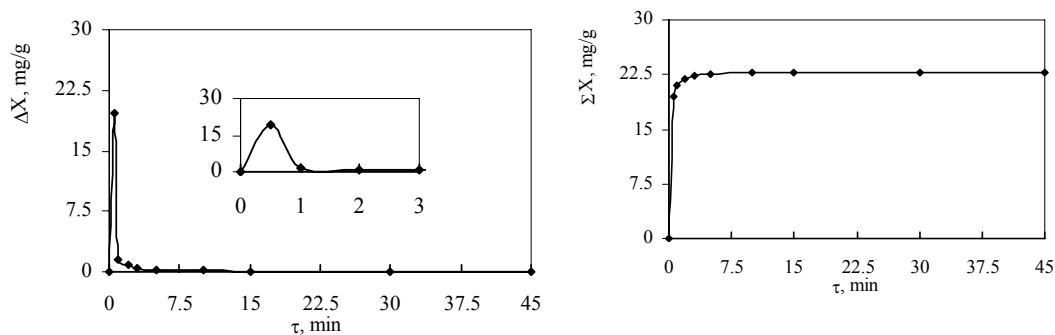


Fig. 14. Differential (a) and integral (b) kinetic curves of Zn^{2+} ions adsorption from $Zn(NO_3)_2$ solution at the initial concentration of Zn^{2+} ions of 0.3 g/dm^3 , at 25 °C.

It should be noted that the cation exchange reactions are not reversible process. In order to confirm this fact, after sorption process hydrotalcite substituted with Zn^{2+} ions was dried up and immersed in distilled water. It was proved that Zn^{2+} ions did not appear in the solution after 240 minutes at 25 °C.

Thus, hydrotalcite can be used as adsorbent for Zn^{2+} ion removal. The results presented here show that the latter compound has a good ion-exchange capacity and further research is needed to understand better its exchange and selectivity properties. In the future work, the synthesized hydrotalcites will be used for cleaning heavy metals from waste water.

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4. Conclusions

1. Different modifications of Al containing components has only a slight influence on the course of meixnerite-type LDH formation by using hydrothermal treatment. For this reason, the synthesis of the latter compound is a little more efficient when γ -Al₂O₃ is used as initial Al containing component.
2. It was determined that partial soluble magnesium carbonate hydroxide hydrate is not stable under hydrothermal conditions and decomposes into MgCO₃ and Mg(OH)₂ compounds, which reacted very heavily with Al containing components. As a result, a fair amount of low-reactive intermediates (MgCO₃, Mg(OH)₂) were remain in the synthesis products even after 24 hours of isothermal curing.
3. The crystallinity of magnesium carbonate hydroxide hydrate markedly increased in 1.5 times after prolonging the synthesis duration up to 24 hours.
4. Chemical nature of the initial Mg containing components changes the formation mechanism of the synthesis products. It was determined that magnesium aluminum hydroxide hydrate are formed by using 4MgCO₃·Mg(OH)₂·5H₂O as starting material. Meanwhile, the hydrotalcite are observed in the Mg₅(CO₃)₄(OH)₂·4H₂O presence. This is due to the different properties of formed MgCO₃. During hydrothermal reaction Mg₅(CO₃)₄(OH)₂·4H₂O produces magnesium carbonate of CO₃²⁻-free anions. These anions intercalate in LDH interlayer to form hydrotalcite while the other Mg containing raw material forms more stable, low-reactive MgCO₃.
5. After 24 hours of isothermal curing the intensity of hydrotalcite diffraction peaks only slightly increases while the crystallinity of boehmite significantly increased in 2 times. It should be noted that magnesium carbonate is fully reacted after prolonging the synthesis duration.
6. It was determined that after 45 min of sorption ~75 % of the Zn²⁺ ions are incorporated into the crystal structure of hydrotalcite. It was determined that the cation exchange reactions are not reversible and specific to chemisorption process. It should be underlined that crystallinity of the latter compound does not change during ion exchange experiments.

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Садржај: *Формирање различитих односа Mg-Al LDHs (Mg/Al = 2:1) под хидротермалним условима (200 °C; 4–24 h) је испитивано у $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O} - \gamma\text{-Al}_2\text{O}_3/\text{Al}(\text{OH})_3 - \text{H}_2\text{O}$ и $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O} - \gamma\text{-Al}_2\text{O}_3 - \text{H}_2\text{O}$ систему. Утврђено је да хемијска природа почетних једињења са садржајем Mg мења механизам формирања продуката синтезе током изотермског синтерованња. Хидрат магнезијум-алуминијум-хидроксид је искристалисан употребом $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ као почетног материјала док је искристалисан хидрат хидроксида у присуству $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. Представљен је редослед формирања једињења. Треба запазити и то да компоненте које садрже различите модификације Al имају слаб утицај на хидротермалну синтезу LDH. Утврђено је да након 45 мин сорпције, сви Zn^{2+} јони су уграђени у кристалну структуру хидроталцита. Потребно је подвући да се кристаличност насталих једињења не мења током јоно-измењивачких експеримената. Тако, добијена једињења могу бити употребљена као адсорбери за уклањање јона Zn^{2+} . Синтетисани узорци су карактерисани рендгенском дифракцијом, ФТИР-ом, симултаном термијском анализом и скенирајућом електронском микроскопијом.*

Кључне речи: *хидротермална синтеза, хидроталцит, уклањање јона Zn^{2+} .*
