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The Hydrothermal Synthesis of Hydrotalcite by Using Different Partially Soluble and Insoluble in Water Magnesium and Aluminium Components

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Abstract:

In this work, the influence of different partially soluble and insoluble in water Mg and Al components on the formation of hydrotalcite by using only hydrothermal synthesis was examined. Hydrothermal synthesis duration was 4, 24 and 72 h at 200 °C and Mg/Al ratio was equal to 3:1. The starting materials were: $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, $\text{Mg}_5(\text{CO}_3)_4 \cdot (\text{OH})_2 \cdot 4\text{H}_2\text{O}$, $\text{Al}(\text{OH})_3$ and $\gamma\text{-Al}_2\text{O}_3$. It was determined that Mg and Al containing compounds have most important influence on the formation of hydrotalcite by hydrothermal conditions. $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ as raw material is not recommendable for the synthesis of hydrotalcite, because even after 24 h of isothermal curing at 200 °C temperature hydrotalcite is not formed and magnesium aluminum hydroxide hydrate is dominant in the synthesis products. Besides, initial magnesium containing component is decomposed into magnesium carbonate and hydroxide. It was examined that hydrotalcite is formed already after 4 h of hydrothermal synthesis at 200 °C temperature when Mg/Al molar ratio is equal to 3:1 in the $\text{Mg}_5(\text{CO}_3)_4 \cdot (\text{OH})_2 \cdot 4\text{H}_2\text{O} - \gamma\text{-Al}_2\text{O}_3 / \text{Al}(\text{OH})_3 - \text{H}_2\text{O}$ system. However, together with this compound a fair amount of an intermediate compounds (boehmite and magnesium carbonate) are formed. The duration of isothermal curing determines the formation of a hexagonal plates which are characteristic to hydrotalcite.

Keywords: Magnesium aluminium hydroxide hydrate, Hydrotalcite, Hydrothermal synthesis, X-Ray Diffraction

1. Introduction

Hydrotalcite can be ascribed to layered double hydroxides (LDHs) minerals group. LDHs are described by general formula $\text{Me}^{2+}_{1-x}\text{Me}^{3+}_x(\text{OH})_2]^{x+}(\text{A}^-)_{x/n} \cdot m\text{H}_2\text{O}$, where Me^{2+} and Me^{3+} are di- and trivalent metals cations, and A^- is an anion [1]. Recently, more and more interest is taken in this group of compounds due to the unique properties of calcined LDHs [2–4]. This large family of compounds are widely use in the industry of organic and inorganic chemistry, cement, medicine and biotechnologies [5–10].

Naturally occurring mineral hydrotalcite, $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$, is hydroxycarbonate of magnesium and aluminum, which was discovered in Sweden around 1842. This compound was first suggested by Manasse, who was the first to recognize that carbonate anions were an essential feature of this mineral [1].

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A number of synthetic techniques have been used to prepare hydrotalcite in a laboratory [1]. Commonly, a preparation method involving many steps is used to obtain this compound: firstly, co-precipitation method is employed (first stage). An aqueous solutions of Mg and Al containing components with Na_2CO_3 and NaOH solutions are mixed under vigorous stirring. The addition of both solutions takes about 1 or 2 hours. And only when the hydrothermal synthesis is used (second stage) [11–15]. Furthermore, above all mentioned steps, the calcination of initial compounds is used, mostly, when raw materials are nitrates or even calcination-rehydration method [16, 17]. However, the obtained product of this n-stage synthesis is mostly impure, as a result, it is always thoroughly washed with hot distilled water until undesirable ions, such as Na^+ , SO_4^{2-} , Cl^- or NO_3^- are removed [11–17]. Thus, all synthesis steps take much time and the technology of this preparation method is complicated.

Only fragmentary data of complex hydrotalcite hydrothermal synthesis is published in literature [11–17]. Hydrothermal synthesis includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures. Hydrothermal synthesis can be defined as a method of synthesis of single crystals which depends on the solubility of minerals in hot water under high pressure [18]. It has been shown to be effective in intercalation of organic guest with low affinity for LDHs into the interlayers [1]. The method is also particularly suitable for the growth of large good-quality crystals while maintaining good control over their composition [18]. Thus, it is very important to ease the preparation of hydrotalcite by finding the favorable conditions (temperature, raw materials and etc.).

The aim of this paper is to study the influence of different partially soluble and insoluble in water Mg and Al components on the formation of hydrotalcite by using only hydrothermal synthesis.

2. Experimental procedure

The following materials were used in this work: magnesium carbonate hydroxide hydrate (Sigma-Aldrich Chemie GmbH, Germany; the purity is 99 %), basic magnesium carbonate (Reachim, Russia; the purity is 99 %), $\gamma\text{-Al}_2\text{O}_3$ ($\gamma\text{-Al}_2\text{O}_3$ 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 %).

The ratio of Mg/Al in primary mixtures was equal to 3:1, i.e. the same as the stoichiometric composition of hydrotalcite. Dry primary mixtures were mixed with water in the stainless steel vessels (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, 24 or 72 hours. The products of the synthesis was filtered, rinsed with ethyl alcohol to prevent carbonization of material, dried at a temperature of 100 °C \pm 5, 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 2–60° (2 θ) in steps of 2 θ = 0.02°.

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) coupled with energy dispersive X-ray spectrometry (EDS) of the samples was performed using a accelerating voltage of 30 kV and a working distance of 9.2 mm for SEM observation and a 200 s accumulation time for EDS analysis.

3. Results and Discussion

In the first stage of this work, the products are synthesized by using partially soluble in water magnesium carbonate hydroxide hydrate, $4\text{MgCO}_3\cdot\text{Mg}(\text{OH})_2\cdot 5\text{H}_2\text{O}$, and aluminum hydroxide, $\text{Al}(\text{OH})_3$, mixture with water after 4 and 24 hours at $200\text{ }^\circ\text{C}$ temperature.

It was determined that after 4 hours of isothermal curing magnesium carbonate hydroxide hydrate is not fully decomposed into MgCO_3 (d-spacing – 0.274, 0.251, 0.210, 0.194, 0.170 nm; endothermic peaks at $432\text{ }^\circ\text{C}$ and $629\text{ }^\circ\text{C}$ temperatures; absorption bands at 1401 , 886 and 748 cm^{-1}) and $\text{Mg}(\text{OH})_2$ (d-spacing – 0.477, 0.237, 0.719 nm; endothermic peak at $302\text{ }^\circ\text{C}$ temperature; absorption band at 3698 cm^{-1}) (Fig. 1, a–c). $\text{Mg}_6\text{Al}_2(\text{OH})_{18}\cdot 5\text{H}_2\text{O}$ phase (d-spacing – 0.774, 0.385, 0.258, 0.230 nm; endothermic peaks at $206\text{ }^\circ\text{C}$ and $302\text{ }^\circ\text{C}$ temperatures; absorption bands at 3499 and 554 cm^{-1}) is found in the synthesis products (Fig. 1, a–c). However, hydrotalcite is not formed even after 24 h of hydrothermal treatment (Fig. 2, a–c).

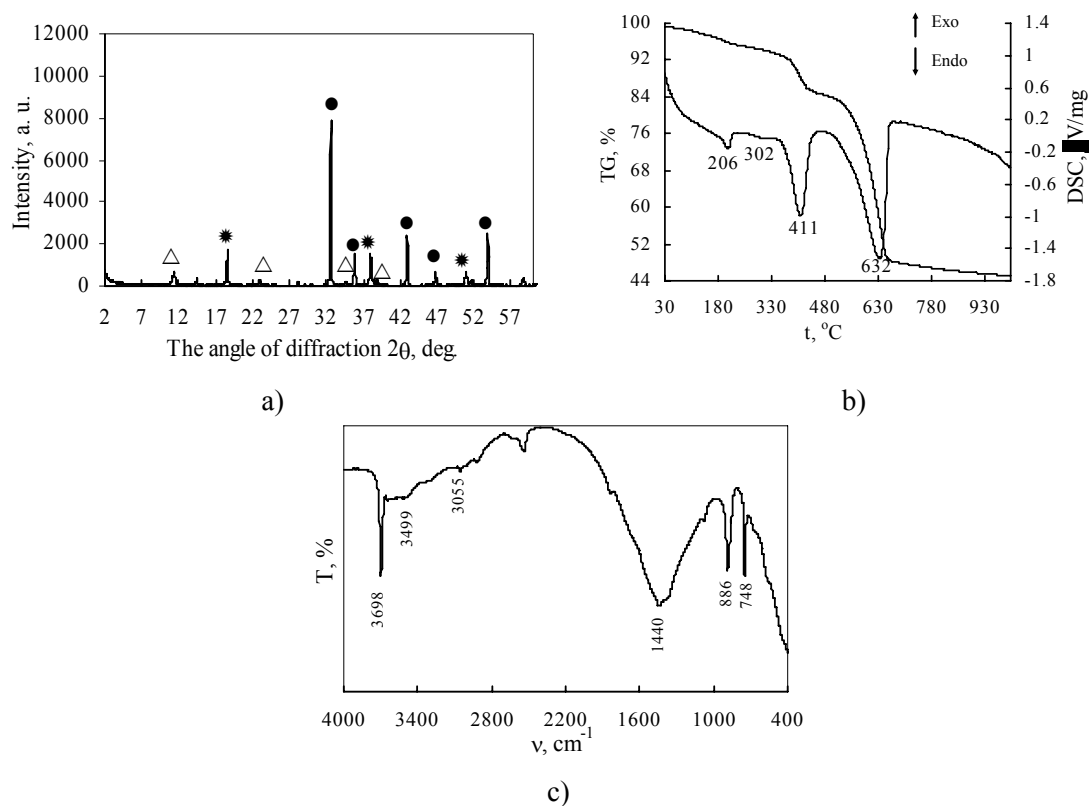


Fig. 1. X-ray diffraction pattern (a), STA curves (b), FT-IR spectrum (c) of synthesis products when starting materials are $4\text{MgCO}_3\cdot\text{Mg}(\text{OH})_2\cdot 5\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$. Duration of hydrothermal synthesis at $200\text{ }^\circ\text{C}$ is equal to 4 h. Indices: ● – magnesium carbonate, △ – magnesium aluminium hydroxide hydrate, * – magnesium hydroxide.

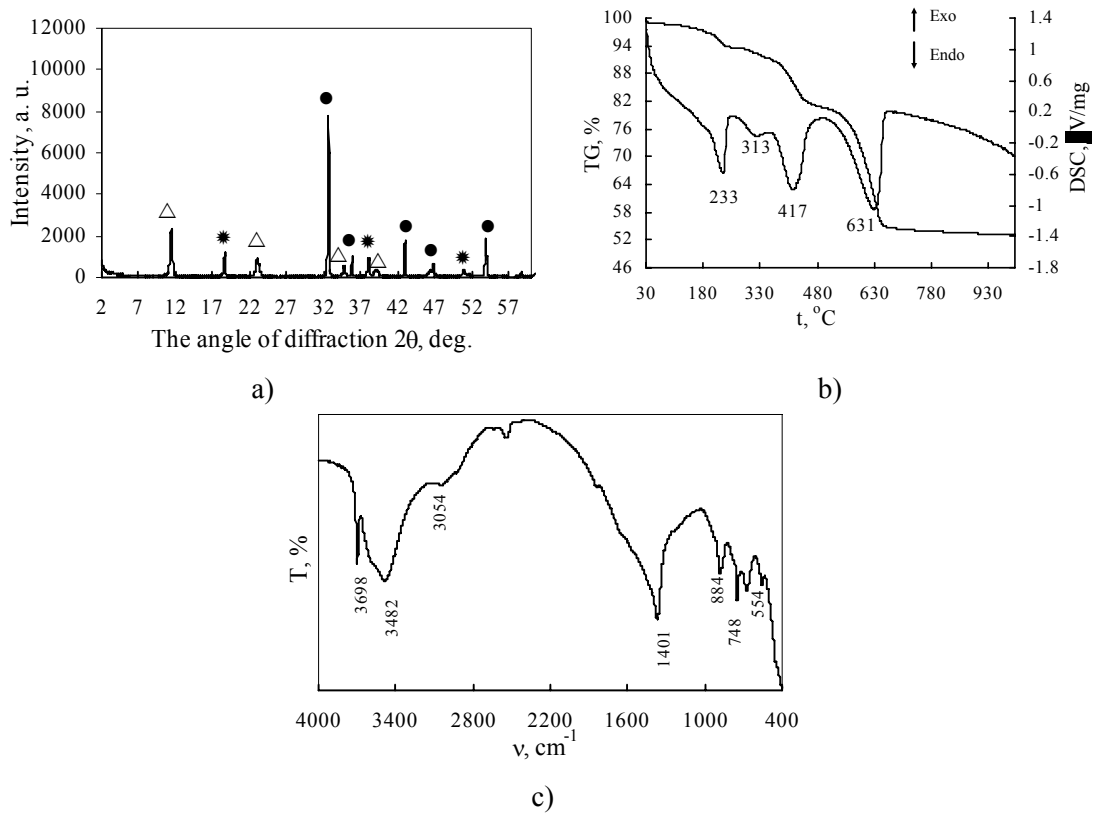


Fig. 2. X-ray diffraction pattern (a), STA curves (b), FT-IR spectrum (c) of synthesis products when starting materials are $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$. Duration of hydrothermal synthesis at $200\text{ }^\circ\text{C}$ is equal to 24 h. Indices: ● – magnesium carbonate, △ – magnesium aluminium hydroxide hydrate, * – magnesium hydroxide.

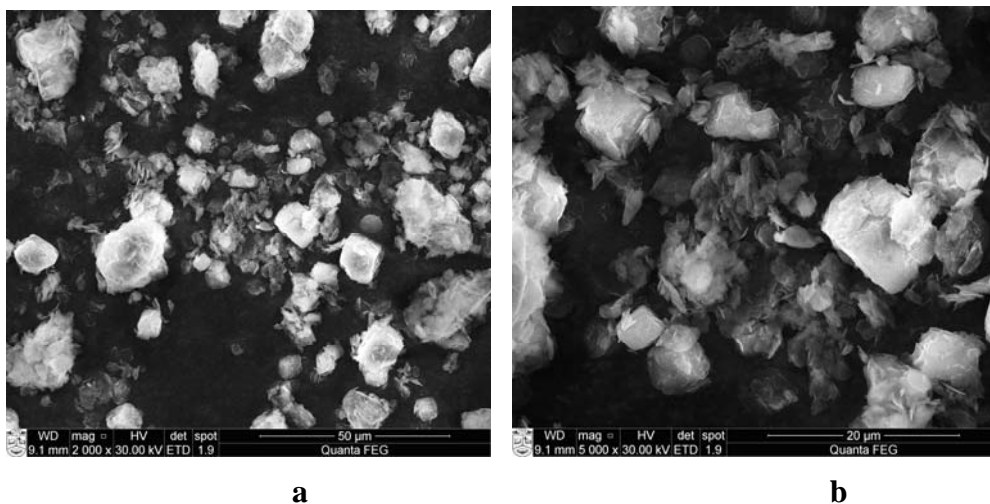


Fig. 3. SEM images of synthesis products when the duration of hydrothermal synthesis at $200\text{ }^\circ\text{C}$ is equal to 24 h and the magnitude is: a – 2000, b – 5000.

SEM images showed an aggregates with indefinite structure which can be ascribed to $\text{Mg}_6\text{Al}_2(\text{OH})_{18} \cdot 5\text{H}_2\text{O}$, thin $\text{Mg}(\text{OH})_2$ plates and rhombohedral MgCO_3 crystals form. The crystals size varied from 2.5 to 10 μm (Fig. 3, a, b).

On purpose to accelerate the interaction between Mg and Al containing components and to reduce the amount of $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ decomposition products, more reactive Al containing compound ($\gamma\text{-Al}_2\text{O}_3$) is used in the synthesis.

It was determined that the reaction between Mg and Al containing compounds speeded up already after 4 h of isothermal curing, because the higher crystallinity of magnesium aluminum hydroxide hydrate (d-spacing – 0.774, 0.385, 0.285, 0.230 nm) is obtained compared with the results given by using $\text{Al}(\text{OH})_3$ (Fig. 4, a). It is interesting that after 24 h of hydrothermal synthesis diffraction peaks which are characteristic to this compound remain almost the same (Fig. 4, b). It is clearly demonstrated in DSC curve: the areas of endothermic effect at 227 and 313 °C temperatures which is related with the loss of OH⁻ groups from magnesium aluminum hydroxide hydrate structure also remain almost the same (Fig. 5; ~60 and 20 $\mu\text{V}/\text{mg}$, respectively), though the decrease of absorption band intensity of the latter compound is observed in FT-IR spectrum at 3493 cm^{-1} (Fig. 6, b).

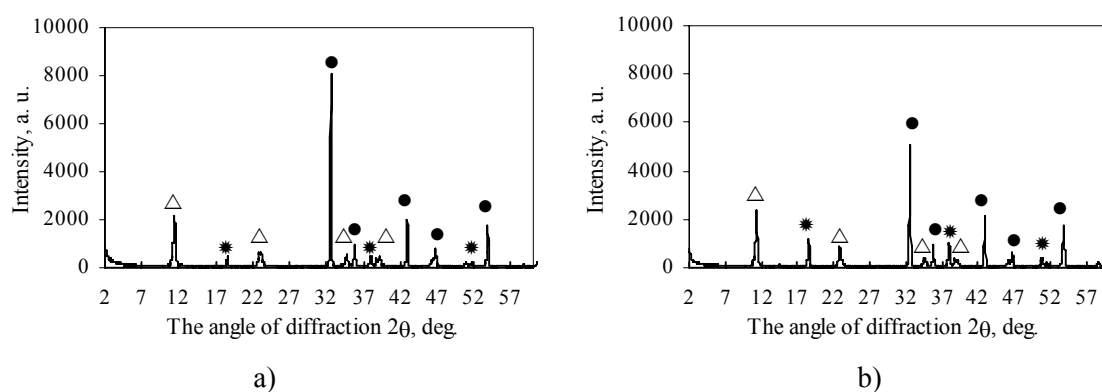


Fig. 4. X-ray diffraction pattern of synthesis products when starting materials are $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ and $\gamma\text{-Al}_2\text{O}_3$. The duration of hydrothermal synthesis at 200 °C is equal to 4 (a) and 24 h (b). Indices: ● – magnesium carbonate,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

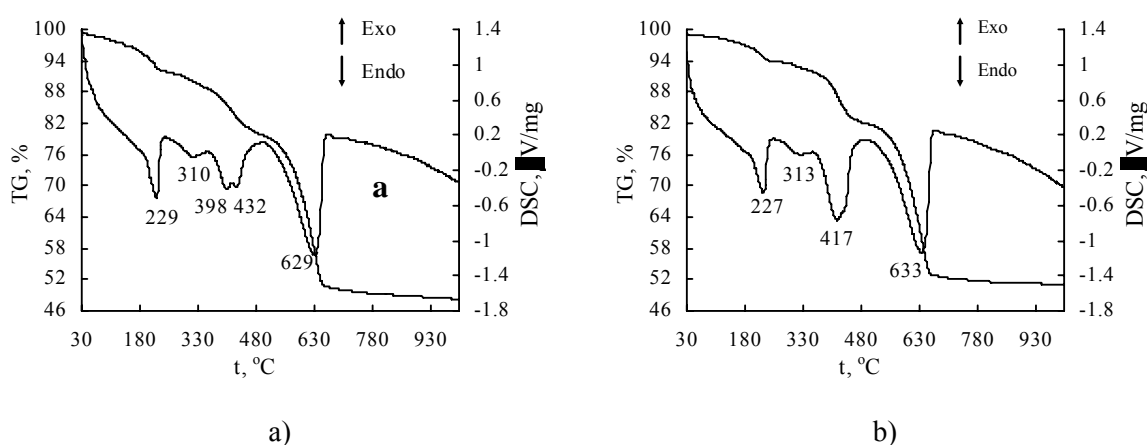


Fig. 5. STA curves of synthesis products when starting materials are $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ and $\gamma\text{-Al}_2\text{O}_3$. The duration of hydrothermal synthesis at 200 °C is equal to 4 (a) and 24 h (b)

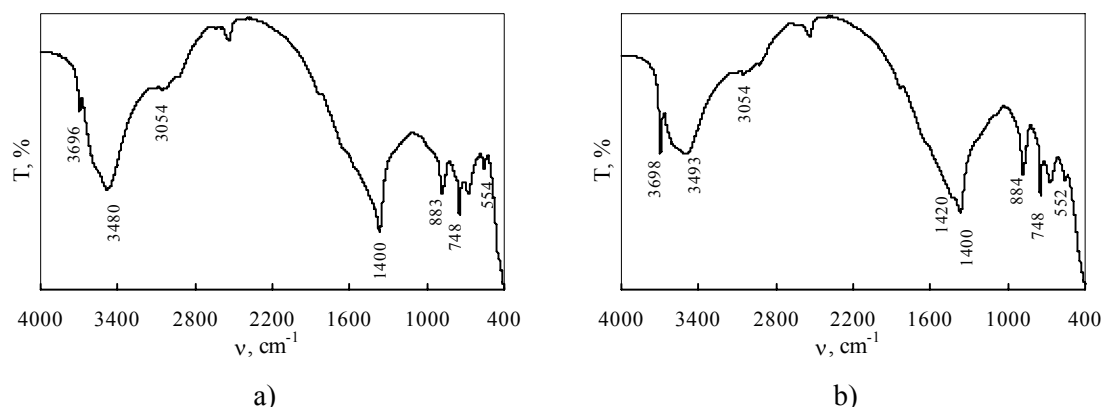


Fig. 6. FT-IR spectrum of synthesis products when starting materials are $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ and $\gamma\text{-Al}_2\text{O}_3$. The duration of hydrothermal synthesis at 200°C is equal to 4 (a) and 24 h (b).

As it was expected, magnesium hydroxide is almost completely bonded already in the beginning of the synthesis. This is shown in XRD data: low intensity peaks (d-spacing – 0.447, 0.237, 0.179 nm) characteristics to this compound are identified (Fig. 4, a). A FT-IR spectrum shows a shoulder at 3696 cm^{-1} (Fig. 6, a). Meanwhile the endothermic effect at 398°C temperature which can be assigned to its dehydration is observed (Fig. 5, a). Prolonging the duration cause the increasing in the intensity of diffraction peaks (Fig. 4, b). This is due to the faster decomposition of $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$. The absorption band of the latter compound reflecting $O-H$ bond vibrations is identified at 3054 cm^{-1} (Fig. 6, b).

It is interesting that the characteristic basal spacing of magnesium carbonate (d-spacing – 0.274 nm) decreases in two times as the time pass by (24 h) compared with the results given by using $\text{Al}(\text{OH})_3$ (Fig. 4, b). Meanwhile, the other peaks which are characteristic to this compound both after 4 hours and 24 hours of isothermal curing remain almost the same (Fig. 4). It is clearly demonstrated by FT-IR spectrum: the absorption bands at 1420 , 1400 , 884 and 748 cm^{-1} are due to $C-O_3^{2-}$ bond vibrations and are very similar (Fig. 6, b). Besides, the area of endothermic peak at 633°C temperature which reflects the two stage decarbonization remains the same and it is approximately equal to $400\text{ }\mu\text{V}/\text{mg}$ (Fig. 5, b). More intense thermal conversion is visible in DSC curve because this process overlaps with magnesium hydroxide dehydration at 417°C temperature (Fig. 5, b).

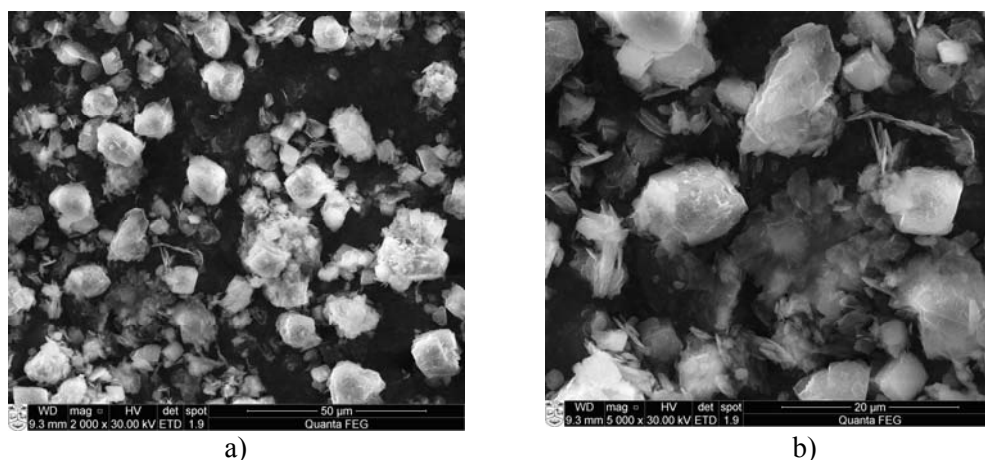


Fig. 7. SEM images of synthesis products when the duration of hydrothermal synthesis at 200°C is equal to 24 h and the magnitude is: a – 2000, b – 5000.

The SEM analysis data showed that the crystals with similar morphology are identified same as in the samples with $\text{Al}(\text{OH})_3$: an $\text{Mg}_6\text{Al}_2(\text{OH})_{18}\cdot 5\text{H}_2\text{O}$ aggregates with indefinite structure, thin $\text{Mg}(\text{OH})_2$ plates and rhombohedral MgCO_3 crystals form. The crystals size varied in 2–10 μm range (Fig. 7, a, b).

Thus, hydrotalcite is not formed by all hydrothermal synthesis conditions in the $4\text{MgCO}_3\cdot\text{Mg}(\text{OH})_2\cdot 5\text{H}_2\text{O} - \text{Al}(\text{OH})_3/\gamma\text{-Al}_2\text{O}_3 - \text{H}_2\text{O}$ system, because the initial Mg containing component is decomposed into magnesium carbonate and hydroxide while the stable magnesium aluminum hydroxide hydrate is dominant in the synthesis products.

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. 8. It was determined that the recrystallization to magnesium oxide at 520 °C temperature is not characteristic to basic magnesium carbonate ($\text{Mg}_5(\text{CO}_3)_4\cdot(\text{OH})_2\cdot 4\text{H}_2\text{O}$). For this reason, in the next stage of this work the latter compound and $\text{Al}(\text{OH})_3$ are used for hydrotalcite synthesis.

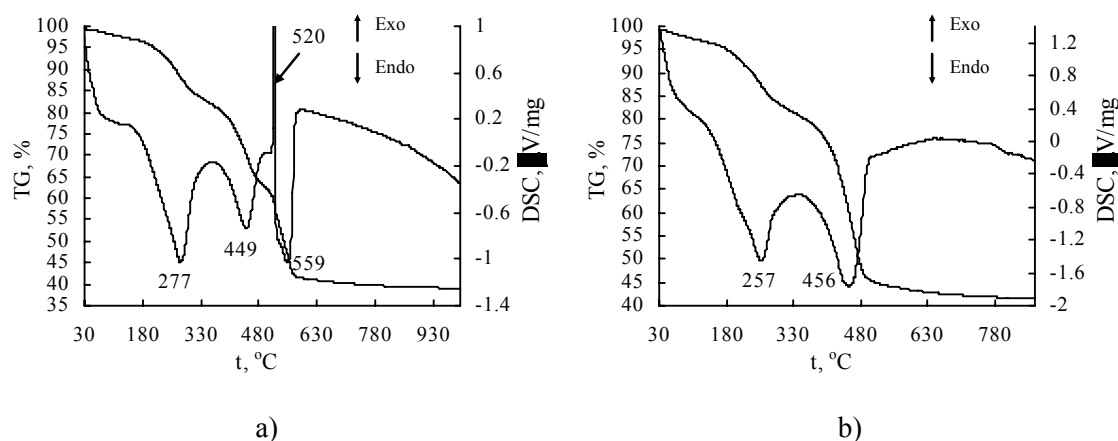


Fig. 8. STA curves of $4\text{MgCO}_3\cdot\text{Mg}(\text{OH})_2\cdot 5\text{H}_2\text{O}$ (a) and $\text{Mg}_5(\text{CO}_3)_4\cdot(\text{OH})_2\cdot 4\text{H}_2\text{O}$ (b).

It was determined that hydrotalcite, $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot 4\text{H}_2\text{O}$, is formed already after 4 h of isothermal synthesis in the $\text{Mg}_5(\text{CO}_3)_4\cdot(\text{OH})_2\cdot 4\text{H}_2\text{O} - \text{Al}(\text{OH})_3 - \text{H}_2\text{O}$ system (Fig. 9, a). The characteristic peaks of this compound (d-spacing – 0.766, 0.381, 0.250, 0.229, 0.194 nm) are identified in the XRD curve. Moreover, magnesium carbonate (d-spacing – 0.274, 0.257, 0.210, 0.194, 0.170 nm) and boehmite (d-spacing – 0.615, 0.309, 0.235, 0.186 nm) are formed together with hydrotalcite.

It should be underlined, that layered double hydroxide group contains many compounds, which characteristic d-spacing are very close to each other and the crystal structure is similar. For this reason the peaks of XRD overlaps one another. Thus, it is impossible to identify clearly the composition of a compound only with reference to XRD analysis data. In this case, FT-IR method gives an useful information and it allows us to identify not only a functional group of compound that we are interested in, but also single ones or even the reaction course.

It was determined that during hydrothermal synthesis monoclinic crystal system of basic carbonate regroups into more orderly orthorhombic crystal system. It is clearly visible in SEM analysis images: after 4 h of isothermal curing the rhombohedral crystal form is dominant. Moreover, rhombic plates characteristic to boehmite and thin plates with hexagonal symmetry of hydrotalcite are identified (Fig. 9, d).

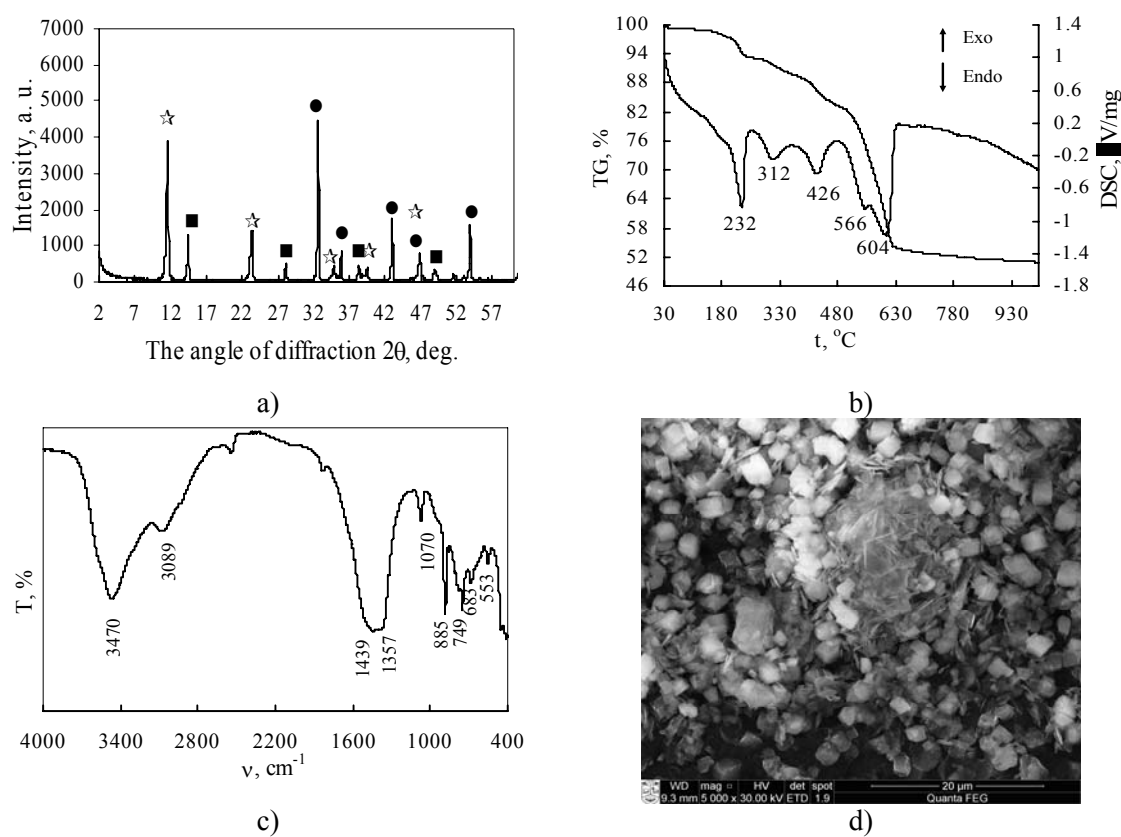


Fig. 9. X-ray diffraction pattern (a), STA curve (b), FT-IR spectrum (c) and SEM images (d) of synthesis products when starting materials are $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ and $Al(OH)_3$. The duration of hydrothermal synthesis at 200 °C is equal to 4 h. Indices: ☆ – hydrotalcite, ● – magnesium carbonate, ■ – boehmite.

Simultaneous thermal analysis confirms the formation of the latter compound. These thermal conversions were identified after 4 h of hydrothermal synthesis (Fig. 9, b):

- At 232 °C temperature loosely held interlayer water of hydrotalcite is lost.
- At 312 °C temperature a partial dehydroxylation of hydrotalcite brucite-like sheets takes place. It should be noted that OH^- group bonded with Al^{3+} is lost. This process overlaps with boehmite dehydration.
- At 426 °C temperature the decarbonization of hydrotalcite and magnesium carbonate proceeds.
- In the temperature range 566–604 °C, recrystallization of boehmite to $\gamma-Al_2O_3$ involving two steps takes place. It should be underlined that this process overlaps with the formation of mixed metal oxides characteristic to hydrotalcite at 604 °C temperature.

The following absorption bands are identified by FT-IR analysis (Fig. 9, c):

- The band at 3470 cm^{-1} is due to $O-H$ bond vibrations which are characteristic to hydrotalcite.
- The broad peak at 3089 cm^{-1} is attributed to the H-bonding, $HO-(H)-CO_3^{2-}$ vibrations, which can be ascribed to the main synthesis product.
- The sharp, intense vibrational bands of carbonates that appears at 1439, 885 cm^{-1} can be assigned to magnesium carbonate. It should be underlined that the bands at 1357 and 683 cm^{-1} is also due to $C-O_3^{2-}$ bond vibrations, but it is characteristic to hydrotalcite.

- The bands at 1070, 749 and 553 cm^{-1} can be assigned to Al–O bond vibrations, which proceed in boehmite crystal structure.

It was observed that the formed magnesium carbonate is more reactive after prolonging the duration than using magnesium carbonate hydroxide hydrate as the initial Mg containing component (Fig. 10). It is clearly demonstrated by SEM images, the formation of the latter compound crystals is decreasing as the time pass by and the plate structure of hydroxalcite become more orderly (Fig. 11). It is interesting that only prolonging the duration cause for the endothermic effect, which is characteristic to hydroxalcite and can be assigned to the formation of mixed metal oxides, to highlight at 694 and 664 $^{\circ}\text{C}$ temperatures (Fig. 12). FT-IR analysis data shows that the intensity of absorption bands at 1435 and 884 cm^{-1} which can be assigned to $\text{C} - \text{O}_3^{2-}$ bond vibrations is decreasing (Fig. 13, b).

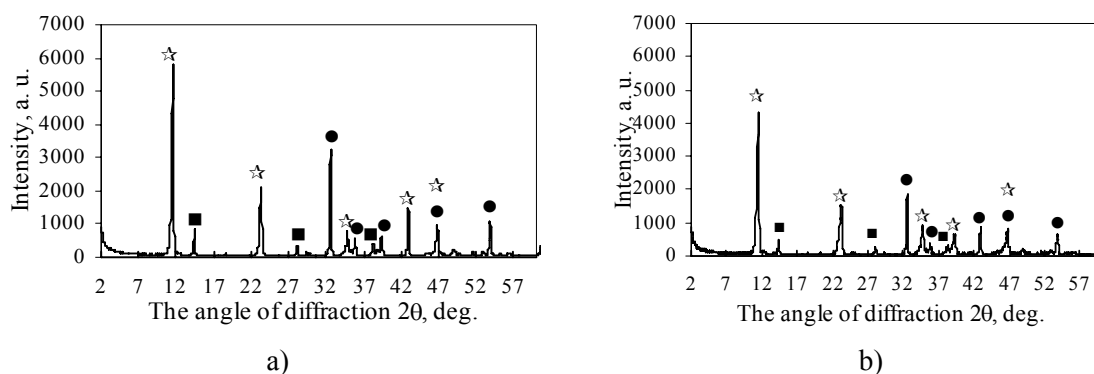


Fig. 10. X-ray diffraction pattern of synthesis products when starting materials are $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$. The duration of hydrothermal synthesis at 200 $^{\circ}\text{C}$ is equal to 24 (a) and 72 h (b). Indices: ☆ – hydroxalcite, ● – magnesium carbonate, ■ – boehmite.

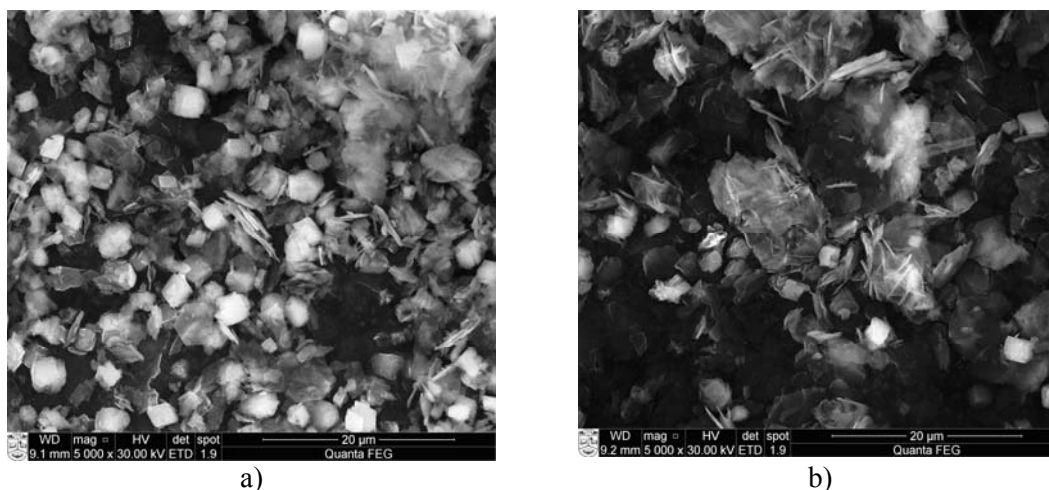


Fig. 11. SEM images of synthesis products when starting materials are $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$. The duration of hydrothermal synthesis at 200 $^{\circ}\text{C}$ is equal to 24 (a) and 72 h (b).

The crystallinity of boehmite is decreasing by continuing the synthesis to 72 hours as it is shown in XRD curve (Fig. 10, b). This tendency is observed also by FT-IR and SEM analysis (Fig. 11, 13). It should be noted, that the endothermic effect of boehmite which is

related to the latter compound recrystallization to γ - Al_2O_3 is clearly visible at 581 °C temperature (Fig. 12, b). Meanwhile, after 24 h of synthesis this process proceeds in two steps (Fig. 12, a; 566 and 602 °C). The main reason is the formation of boehmite crystal aggregates.

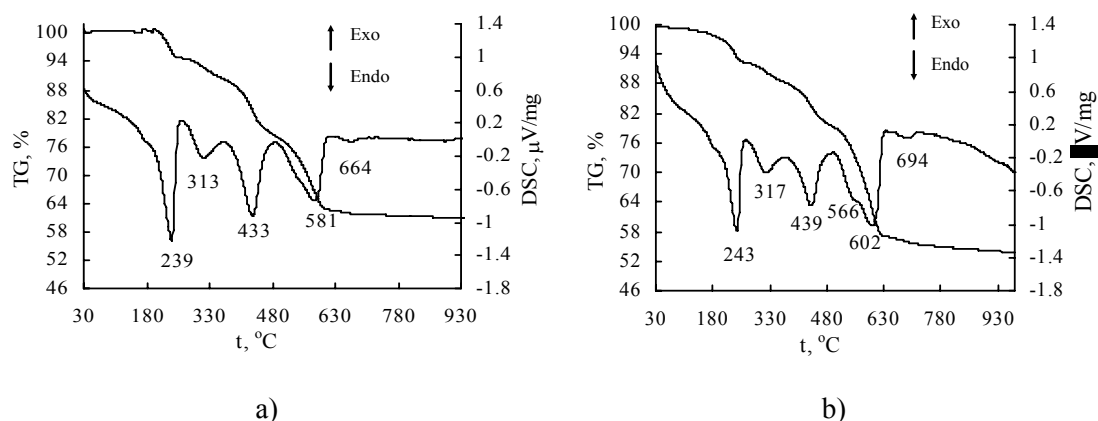


Fig. 12. STA curves of synthesis products when starting materials are $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$. The duration of hydrothermal synthesis at 200 °C is equal to 24 (a) and 72 h (b).

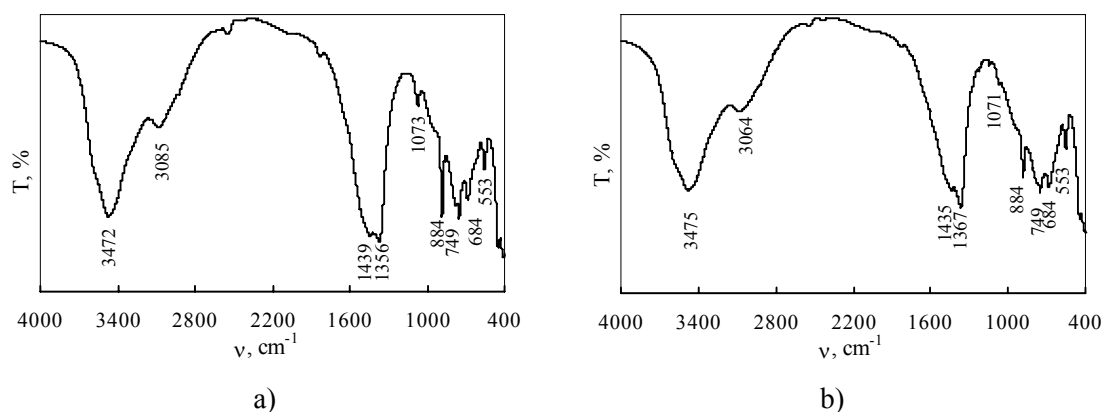


Fig. 13. FT-IR spectrum of synthesis products when starting materials are $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$. The duration of hydrothermal synthesis at 200 °C is equal to 24 (a) and 72 h (b).

Previous results showed that γ - Al_2O_3 stimulates the formation of stable compounds already in the beginning of the synthesis. On purpose to accelerate the interaction between Mg and Al components and to shorten the duration of hydrothermal synthesis as Al containing component γ - Al_2O_3 was used.

As it was expected, the formation of hydrotalcite is faster 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, because already after 4 hours 1.5 times greater crystallinity of this compound is obtained rather than using $\text{Al}(\text{OH})_3$ (Fig. 14, a). It is clearly demonstrated in DSC curve (Fig. 15, a): at 244, 322 and 439 °C temperatures, the areas of endothermic effects are significantly increased from 94.4 to 149.3 $\mu\text{V}/\text{mg}$ (Fig. 9, b; 232 °C), from 44.7 to 69.9 $\mu\text{V}/\text{mg}$ (Fig. 9, b; 312 °C) and also from 65.18 to 102.2 $\mu\text{V}/\text{mg}$ (Fig. 9, b; 426 °C). Furthermore, the recrystallization of mixed metal oxides to spinel phase is clearly visible at 835 °C temperatures when γ - Al_2O_3 is used. Meanwhile, FT-IR spectrum shows that absorption bands at 3467, 3086, 1366 and 684 cm^{-1} are more intense (Fig. 16, a).

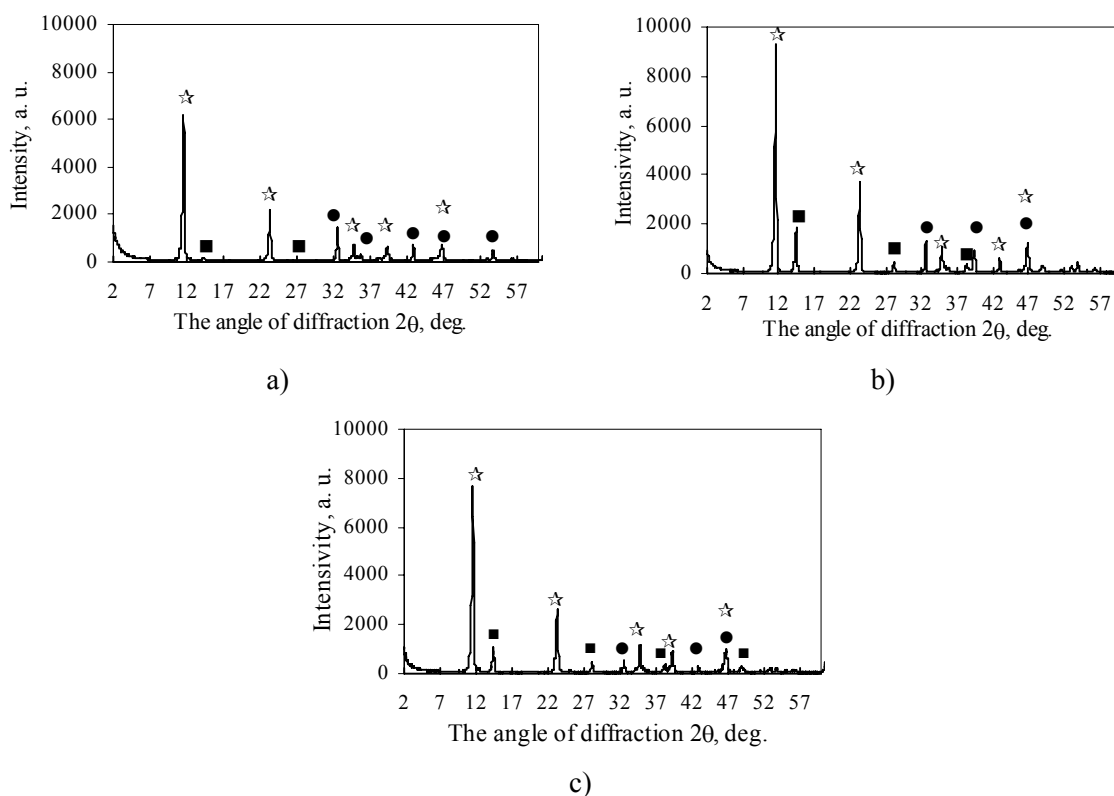


Fig. 14. X-ray diffraction pattern of synthesis products when starting materials are $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ and $\gamma\text{-Al}_2\text{O}_3$. The duration of hydrothermal synthesis at 200°C is equal to 4 (a), 24 (b) and 72 h (c). Indices: ☆ – hydrotalcite, ● – magnesium carbonate, ■ – boehmite.

It was determined that the prolonging the duration to 72 hours cause the crystallinity of hydrotalcite only slightly to increase by comparing with the results obtained after 4 hours (Fig. 14, c). Moreover, the areas of endothermic effects at 253 and 437°C temperatures, which can be attributed to the decarbonization and dehydration of hydrotalcite, change from 149.3 to $200.5 \mu\text{V}/\text{mg}$ (Fig. 15, a; 244°C) and from 102.2 to $129.5 \mu\text{V}/\text{mg}$ (Fig. 15, a; 439°C). It should be noted that the area of thermal conversion at 324°C temperature, which reflects a partial dehydroxylation of the main synthesis product, approximately is equal to $68 \mu\text{V}/\text{mg}$ (Fig. 15, a; 322°C). This is due to the overlapping with boehmite dehydration. Meanwhile, FT-IR spectrum shows that absorption bands, which are characteristic to hydrotalcite, only slightly are changed (Fig. 16, c; 3474 , 3088 , 1367 , 684 cm^{-1}).

It was observed that the intensity of the peaks which can be assigned to magnesium carbonate is decreased in four times as the time pass by (72 h) rather than using aluminum hydroxide (Fig. 14, c; d-spacing – 0.274 , 0.210 , 0.170 nm). It was clearly demonstrated by FT-IR spectrum: the absorption bands at 1412 and 881 cm^{-1} , the region of antisymmetric stretching of carbonates, are barely visible (Fig. 16, c). Moreover, the area of endothermic effect which is related with MgCO_3 decarbonization is decreased from 161.4 to $129.5 \mu\text{V}/\text{mg}$ (Fig. 12, b; 433°C). It should be underlined that also the decarbonization of hydrotalcite proceeds at this temperature.

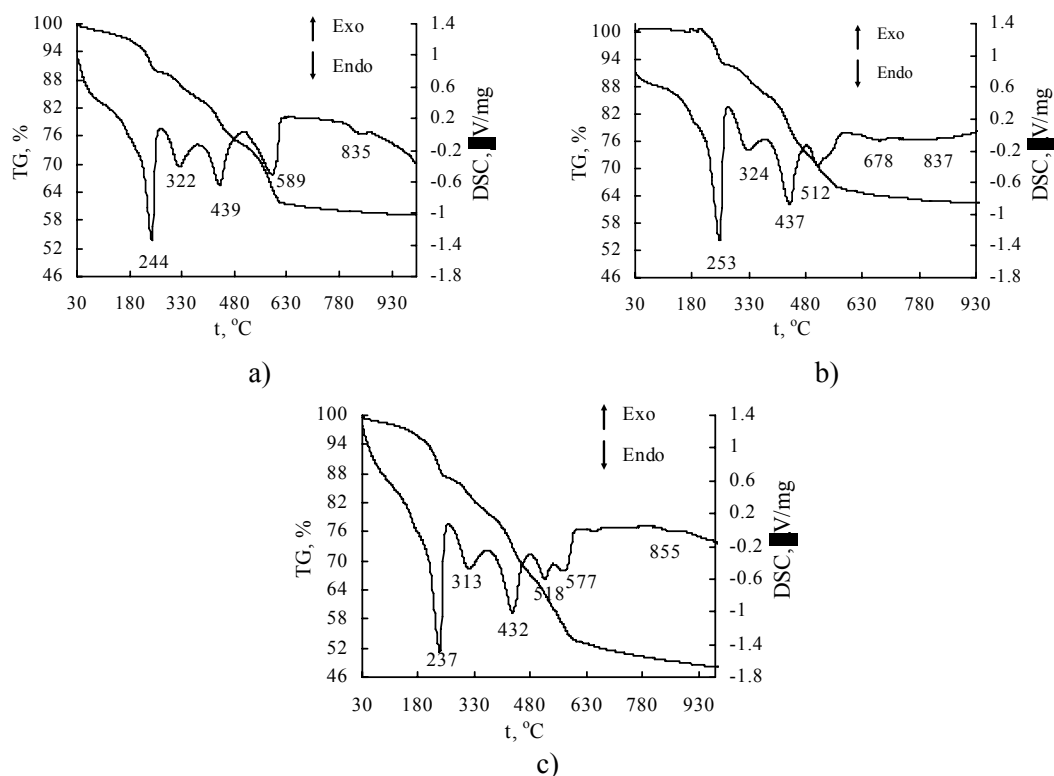


Fig. 15. STA curves of synthesis products when starting materials are $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ and $\gamma-Al_2O_3$. The duration of hydrothermal synthesis at 200 °C is equal to 4 (a), 24 (b) and 72 h (c).

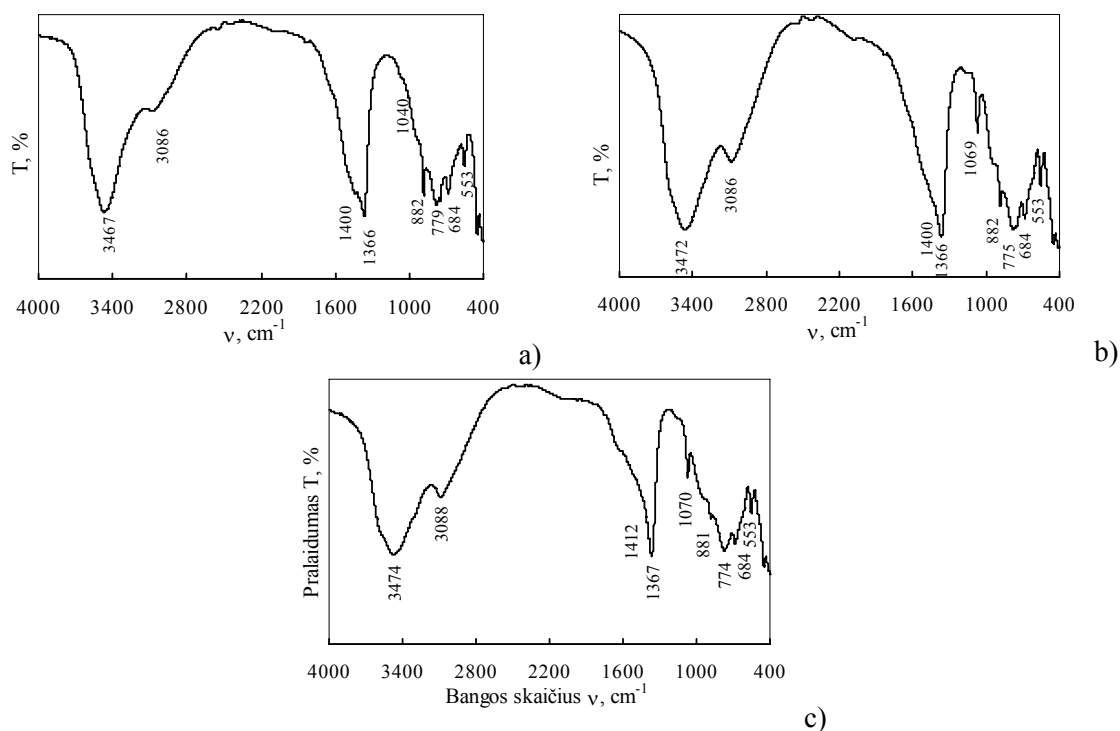


Fig. 16. FT-IR spectrum of synthesis products when starting materials are $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ and $\gamma-Al_2O_3$. The duration of hydrothermal synthesis at 200 °C is equal to 4 (a), 24 (b) and 72 h (c).

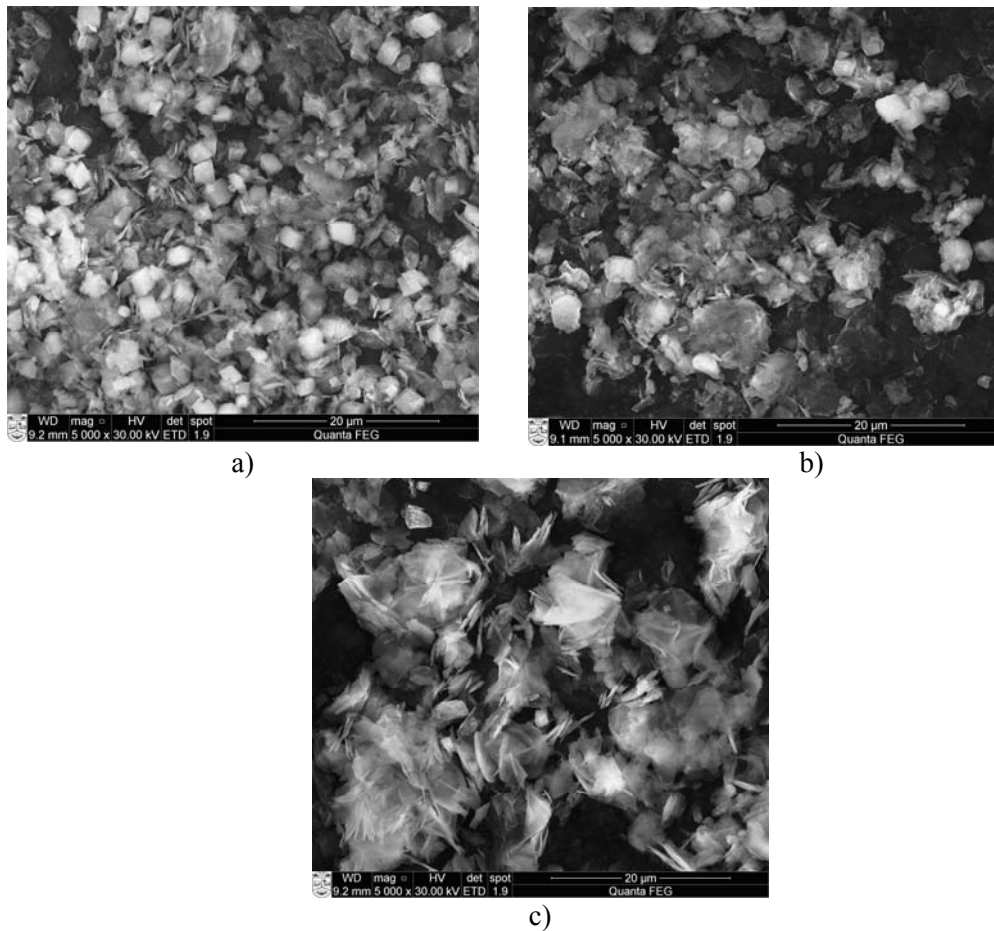


Fig. 17. SEM images of synthesis products when starting materials are $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ and $\gamma-Al_2O_3$. The duration of hydrothermal synthesis at 200 °C is equal to 4 (a), 24 (b) and 72 h (c).

SEM analysis data showed that after 4 h the small crystals are dominant in the synthesis products. Prolonging the duration cause the processes of recrystallization: after 72 h of synthesis the increase in crystal size is observed and the crystal structure of hydrotalcite becomes more orderly.

4. Conclusions

It was determined that Mg and Al containing compounds have most important influence on the formation of hydrotalcite by hydrothermal conditions. $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ as raw material is not recommendable for the synthesis of hydrotalcite, because even after 24 h of isothermal curing at 200 °C temperature hydrotalcite is not formed and magnesium aluminum hydroxide hydrate is dominant in the synthesis products. Besides, initial magnesium containing component is decomposed into magnesium carbonate and hydroxide.

It was examined that hydrotalcite is formed already after 4 h of hydrothermal synthesis at 200 °C temperature when Mg/Al molar ratio is equal to 3:1 in the $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$

– γ - $\text{Al}_2\text{O}_3/\text{Al}(\text{OH})_3\text{–H}_2\text{O}$ system. However, together with this compound a fair amount of an intermediate compounds (boehmite and magnesium carbonate) are formed.

The thermal stability of hydrotalcite was studied: at 237 °C temperature – OH^- group from the crystal structure is lost while at 317 °C temperature – the dehydroxylation of the brucite-like sheets proceeds and it overlaps with boehmite dehydration. Furthermore, the endothermic effect at 434 °C temperature reflects the decarbonization both of hydrotalcite and magnesium carbonate. At 678 °C temperature the thermal conversion is identified which can be assigned to the formation of mixed metal oxides and it overlaps with boehmite recrystallization to γ - Al_2O_3 , while the endothermic effect at 836 °C temperature can be related with the recrystallization of mentioned oxides to spinel phase.

The duration of isothermal curing determines the formation of hexagonal plates which are characteristic to hydrotalcite. It should be noted that prolonging the duration from 4 to 72 h cause the increase in crystal size from 2 to 4 μm .

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Садржај: У овом раду, испитиван је утицај различитих у води делимично растворљивих и нерастворљивих магнезијумових и алуминијумових једињења на формирање хидроталцита хидротермалном методом. Хидротермална синтеза је трајала 4, 24 и 72 сата на 200°C, док је однос Mg/Al био 3:1. Полазне компоненте су биле: $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, $\text{Mg}_5(\text{CO}_3)_4 \cdot (\text{OH})_2 \cdot 4\text{H}_2\text{O}$, $\text{Al}(\text{OH})_3$ и $-\text{Al}_2\text{O}_3$. Утврђено је да садржај Mg и Al једињења има значајнији утицај на формирање хидроталцита од

услова хидротермалне методе. $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ као необрађен материјал није препоручљив за синтезу хидроталцита, јер ни након 24 сата изотермског третмана на 200°C хидроталцит није формиран а доминантан продукт је магнезијум алуминијум хидрокси хидрат. Поред тога, полазно једињење магнезијума се разлаже на магнезијум карбонат и магнезијум хидроксид. Доказано је да се хидроталцит формира хидротермалном синтезом већ након 4 сата на 200°C када је моларни однос Mg/Al 3:1, као $\text{Mg}_5(\text{CO}_3)_4 \cdot (\text{OH})_2 \cdot 4\text{H}_2\text{O} - \gamma\text{-Al}_2\text{O}_3 / \text{Al}(\text{OH})_3 - \text{H}_2\text{O}$ систем. Међутим, поред овог једињења формиран је значајан удео интермедијерних једињења ($\gamma\text{-AlO}(\text{OH})$ и магнезијум карбонат). Трајање изотермског третмана одређује формирање хексагоналних плочица карактеристичних за хидроталцит.

Кључне речи: магнезијум алуминијум хидрокси хидрат, хидроталцит, хидротермална синтеза, дифракција X-зрака
