Mechanochemical Synthesis of Layered Double Mg–Al Hydroxides

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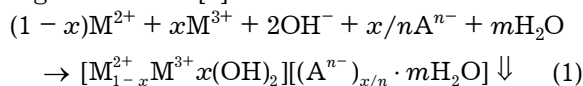
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Abstract

Samples of layered double Mg–Al hydroxides with different Mg/Al ratios were obtained by means of the mechanical activation of the mixture $x\mathrm{Mg(OH)_2} + y\mathrm{AlCl_3} \cdot 6\mathrm{H_2O}$ with the x/y reagents ratio equal to 3/1, 4/1, 5/1 and 6/1 in a planetary mill AGO-2. It was shown that activation for 25 min with additional mixing and activation for 10 min in the presence of an inert additive KCl allows one to obtain layered double Mg–Al hydroxides without admixtures of initial reagents.

INTRODUCTION

Layered double hydroxides (LDH) belong to the class of inorganic compounds having the composition $[\mathrm{M}^{2+}_{1-x}\mathrm{M}^{3+}_{x}(\mathrm{OH})_2][(\mathrm{A}^{n-})_{x/n} \cdot m\mathrm{H_2O}]$; their structure is composed of positively charged metal hydroxide layers $[\mathrm{M}^{2+}_{1-x}\mathrm{M}^{3+}_{x}(\mathrm{OH})_2]^{x+}$ alternating with the layers containing anions and water molecules $[(\mathrm{A}^{n-})_{x/n} \cdot m\mathrm{H_2O}]^{x-}$. Layered double hydroxides are widely used as precursors to obtain oxide catalysts, as medical preparations, ion exchangers, adsorbents *etc.* [1].

Several methods of LDH synthesis are known: anion exchange, co-precipitation, rehydration, sol-gel procedure. The most widespread among them is co-precipitation method which consists in the combined deposition of M^{2+} and M^{3+} cations from the salt solutions with the help of alkalis under controlled pH according to reaction [1]:

$$(1 - x)\mathrm{M}^{2+} + x\mathrm{M}^{3+} + 2\mathrm{OH}^- + x/n\mathrm{A}^{n-} + m\mathrm{H_2O}$$

$$\rightarrow [\mathrm{M}^{2+}_{1-x}\mathrm{M}^{3+}x(\mathrm{OH})_2][(\mathrm{A}^{n-})_{x/n} \cdot m\mathrm{H_2O}] \Downarrow \quad (1)$$

One of the main disadvantages of this synthesis method is the contamination of the formed products with carbonate ions. To avoid this, deionised water is used for synthesis; the precipitation process is carried out in the atmosphere of an inert gas. Another disadvantage of this method is poor filtering ability of the precipitates; thus synthesized double hydroxides are poorly crystallized. To increase the degree of crystallinity, additional operations are used: hydrothermal treatment [2], as well as the treatment with microwave radiation [3]. The above-indicated disadvantages stimulate search for new methods of LDH synthesis.

The authors of [4] demonstrated the possibility to synthesize the anion forms of Mg–Al LDH under mechanical activation of a mixture of magnesium hydroxide and the hydrates of aluminium salts (chloride, nitrate and sulphate) with the initial molar ratio Mg/Al equal to 3/1. The molar ratio in the product samples was 1/2. The authors of [5] demonstrated the possibility of the formation of Mg–Al–OH LDH as a result of the joint activation of $\mathrm{Mg(OH)_2}$ and $\mathrm{Al(OH)_3}$ (at a ratio of 1/3) for 3 h in a planetary mill in the presence of water.

The proposed mechanochemical method allows one to obtain rather well crystallized Mg–Al samples. In addition, this method does not involve the use of large amounts of water and solutions; the compounds formed after the synthesis are well filtering.

The goal of the present work was to investigate the possibility of the synthesis of

the chloride kind of Mg−Al LDH with different Mg to Al molar ratios under mechanical activation of the mixture $Mg(OH)_2 + AlCl_3 \cdot 6H_2O$.

EXPERIMENTAL

The mechanochemical synthesis of Mg−Al LDH was carried out by activating the mixture $Mg(OH)_2 + AlCl_3 \cdot 6H_2O$ at the Mg/Al molar ratio equal to 1/1, 2/1, 3/1, 4/1, 5/1, and 6/1. The reagent grade of $AlCl_3 \cdot 6H_2O$ used for synthesis was "ch." (pure). The initial $Mg(OH)_2$ was calcined at 500 °C for 2 h to remove the admixed carbonate ions, then the formed MgO was hydrated in an autoclave under hydrothermal conditions at 130 °C for 24 h. The mechanochemical activation of the mixture was carried out in a mill of the planetary type AGO-2 with the acceleration of 40g in steel cylinders for different intervals of time. Steel balls 6 mm in diameter were used as milling bodies. The mass of the balls was 200 g, the ratio of the ball load mass to the mass of the reaction mixture was 20/1. In order to remove water-soluble compounds, the activation products were washed with distilled water on a paper filter and then dried in the air for 24 h. The X-ray phase analysis of thus obtained samples was carried out using DRON-3 diffractometer at the scanning rate of 2°/min. Thermal analysis was carried out using a Paulic−Paulic−Erdei derivatograph within temperature range from the room temperature to 1173 K in the air. The weighed portion was 0.2 g, heating rate 10 °C/min. The IR spectra were recorded with an Infralum FT-801 spectrometer in tablets with KBr. The chemical composition of the product samples was determined with the help of chelatometry and mercurimetry.

RESULTS AND DISCUSSION

According to the data of X-ray phase analysis, the LDH phase is formed after 10 min long activation of the mixture of $Mg(OH)_2$ and $AlCl_3 \cdot 6H_2O$ with the initial reagents ratios equal to 3/1, 4/1, 5/1 and 6/1. The formation of the LDH phase is evidenced by the appearance of intense and broadened basal reflections with the d/n ratio equal to 7.85 (003) and 3.9 Å (006),
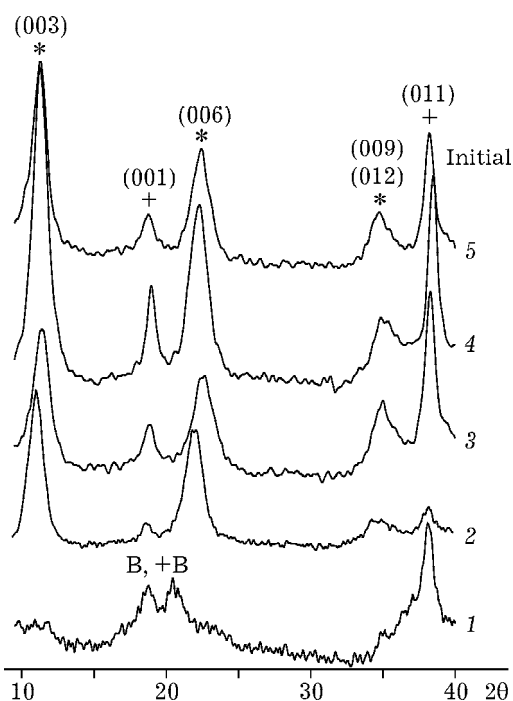

Fig. 1. X-ray diffraction patterns of the samples after mechanical activation (AGO-2, 40g, 10 min) and washing with water. Al/Mg molar ratio: 2/1 (*1*), 3/1 (*2*), 4/1 (*3*), 5/1 (*4*), 6/1 (*5*). Designations: *LDH, +Mg(OH)$_2$, B − bayerite (Al(OH)$_3$).

which is characteristic of the chloride form of Mg−Al LDH. The X-ray diffraction patterns also contain the reflections of $MgCl_2 \cdot 6H_2O$ (4.1, 2.98, 2.88, 2.72, 2.64, and 2.33 Å). For the initial Mg/Al ratio equal to 5/1 and 6/1, the reflections of the initial $Mg(OH)_2$ are present. For the molar ratios Mg/Al equal to 1/1 and 2/1, no formation of the LDH phase was observed. After activation of these samples, the diffraction patterns contained the reflections of magnesium and aluminium chloride hexahydrates: 3.29 (113) and 2.30 Å (321), respectively.

After washing the activation products of the initial molar ratios 3/1, 4/1, 5/1 and 6/1 with water, the X-ray diffraction patterns exhibit the reflections characteristic of LDH and the initial $Mg(OH)_2$ (4.77 Å (001), and 2.37 Å (011)) (Fig. 1). At the ratio Mg/Al = 1/1, activation products are to a substantial extent soluble in water. For the reagent ratio equal to 2/1, the reflections observed in the diffraction patterns of the sample after washing are those characteristic of the crystal modification of $Al(OH)_3$ (bayerite) (d/n is 4.76 and 4.34 Å) and $Mg(OH)_2$ (d/n is 4.77 and 2.37 Å).

The presence of the initial unreacted $Mg(OH)_2$ in the reaction product is likely to be connected with the fact that separate particles of the mixture stick together during activation and get accumulated in the lower part of the cylinder, which substantially decreases the efficiency of activation. Such a behaviour of the reaction mixture is connected with the high hygroscopicity of the initial $AlCl_3 \cdot 6H_2O$, which causes particle sticking in the mixture. To bring the mixture back to the zone affected by the milling bodies, additional mixing was carried out during activation (the cylinders were opened, and the mixture was stirred with the balls). According to the XPA data (Fig. 2), the use of the additional mixing operation and a simultaneous increase in the activation time to 25 min allow one to obtain LDH without any admixtures of the initial reagents. However, this method is connected with additional operations, which brings complications to the synthesis of LDH.

To prevents the particles from sticking together and to the cylinder walls, an additive was introduced into the reaction mixture. This was KCl which is inert to the initial reagents. Visual observations confirmed this assumption: the mixture after activation was a friable powder; it did not get stuck to cylinder walls. The X-ray diffraction patterns after the activation
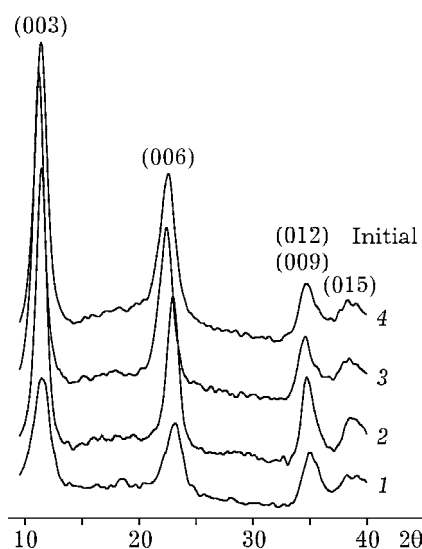

Fig. 2. X-ray diffraction patterns of the samples after mechanical activation (AGO-2, 40*g*, 25 min) with additional mixing and washing with water. Mg/Al molar ratio: 3/1 (*1*), 4/1 (*2*), 5/1 (*3*), 6/1 (*4*).

of the mixture for 10 min in the presence of KCl additive, followed by washing with water, contain only the reflections of Mg−Al LDH ((003), (006), (009), (012), and (015)). The pattern is identical to that shown in Fig. 2. So, the introduction of an inert KCl additive allows us to decrease the time of activation substantially and to eliminate additional stirring of the mixture. It should also be noted that the X-ray diffraction patterns of the samples after activation in the presence of KCl contain weak reflections that may be related to the $KCl \cdot MgCl_2 \cdot 6H_2O$ phase. One cannot exclude that the inert KCl additive affects the activation through binding the hygroscopic $MgCl_2 \cdot 6H_2O$ into a less hygroscopic double salt $KCl \cdot MgCl_2 \cdot 6H_2O$.

To investigate how the amount of an inert KCl additive introduced into the initial mixture affects the formation of double hydroxide, we used a mixture with the initial reagents ratio $Mg(OH)_2/(AlCl_3 \cdot 6H_2O)$ equal to 5/1. It was discovered that with the inert additive content within the range 9−19 %, the X-ray diffraction patterns exhibit only LDH reflections; their intensity remains almost unchanged. This allows us to state that the dilution of the reaction mixture by increasing the mass of the additive under the experimental conditions does not affect the completeness of the mechanochemical interaction.

The data of chemical analysis are shown in Table 1. The formulas of the samples were calculated on the basis of the assumption that the formed layered double hydroxides are described by the classical formula with metal cations occupying 2/3 of the octahedral cavities of the hydroxide lattice. In this case, the composition of metal hydroxide layers may be represented as $[Mg_{1-x}Al_x(OH)_2]^{x+}$. One can see in Table 1 that the Mg/Al ratio in the synthesized samples increases with an increase in the $Mg(OH)_2/(AlCl_3 \cdot 6H_2O)$ molar ratio of the initial mixture. The data obtained provide evidence that the synthesized products contain both chloride and hydroxide ions in the interlayer spacings. The concentration of the former decreases with a decrease in $AlCl_3 \cdot 6H_2O$ content of the initial reaction mixture.

For the synthesized compounds, we detected an increase in the interlayer spacing (*c*/3

TABLE 1

Chemical composition and the determined formulas for the obtained samples of layered double hydroxides

Initial Mg/Al molar ratio	Concentration, mass %			Mg/Al	Formula	$c/3$, Å
	Mg	Al	Cl			
2 : 1	11.2	20.8	2.3	0.5	$0.9Mg(OH)_2 + 2Al(OH)_3 + 0.1MgCl_2 \cdot 6H_2O$	
3 : 1	17.9	12.8	6.0	1.6	$[Mg_{0.6}Al_{0.4}(OH)_2](OH)_{0.25}Cl_{0.15} \cdot H_2O$	7.62
4 : 1	22.2	7.9	6.3	3.0	$[Mg_{0.75}Al_{0.25}(OH)_2](OH)_{0.1}Cl_{0.15} \cdot H_2O$	7.70
5 : 1	24.9	7.3	5.4	3.8	$[Mg_{0.79}Al_{0.21}(OH)_2](OH)_{0.1}Cl_{0.1} \cdot H_2O$	7.80
6 : 1	24.2	6.9	3.6	4.0	$[Mg_{0.8}Al_{0.2}(OH)_2](OH)_{0.15}Cl_{0.05} \cdot H_2O$	7.88

parameter) with an increase in the initial molar ratio Mg/Al and the ratio of Mg/Al in the products (see Table 1). Such a dependence of the lattice parameter c on the M^{2+}/M^{3+} ratio was described in [1, 6]. These data provide evidence that the formation of a series of solid solutions occurs rather than a mixture of X-ray amorphous magnesium hydroxide and LDH of fixed composition.

For the initial Mg/Al ratio equal to 2/1, the resulting mixture contained the initial $Mg(OH)_2$, bayerite and a small amount of magnesium chloride that was not washed away with water completely due to the insufficient time of washing.

The IR spectrum (Fig. 3) of the initial reaction mixture contains a narrow intensive band corresponding to the stretching vibrations of brusite (3700 cm^{-1}); a broad band (3450 cm^{-1})

Fig. 3. IR spectra of the obtained Mg−Al LDH samples. Initial mixture: Mg/Al molar ratio 4/1; Mg/Al molar ratio: 4/1 (*1*), 5/1 (*2*), 6/1 (*3*).

summing up the stretching vibrations of hydroxo groups of crystallization and sorbed water; a band related to the deformation vibrations of water (1620 cm^{-1}); a band at 600 cm^{-1} related to the stretching vibrations of Mg−O. After the mechanochemical interaction, the absorption band at 3700 cm^{-1} disappears, the absorption band at 3450 cm^{-1} broadens. The latter band sums up the stretching vibrations of hydroxo groups in the hydroxide layers of LDH, as well as the vibrations of water molecules situated in the interlayer space and those sorbed on the surface of samples. The occurrence of absorption at 1420 cm^{-1} is due to the carbonate ion admixture; this ion is formed due to the absorption of CO_2 from the air by brusite.

Heating of the synthesized samples above 100 °C causes the following changes (Fig. 4). Within temperature range 100−250 °C, two endoeffects are observed (at 180 and 220 °C); they are connected with the removal of water sorbed on the surface and water present in the interlayer space, respectively. The mass loss corresponding to these processes is 20 %. At a temperature of 380 °C, the endoeffect connected with the decomposition of hydroxide layers is observed. With an increase in the Mg/Al ratio in the samples, the position of this effect shifts from 370 (Mg/Al = 1.6) to 405 °C (Mg/Al = 4). This is connected with the fact that with the transition to larger Mg/Al ratios the metal hydroxide layers of the products contain a larger amount of fragments with Mg−OH bonds. Magnesium hydroxide has a higher decomposition temperature than $Al(OH)_3$ (410 and 330 °C, respectively). Mass loss during the decomposition of hydroxide layers is about 20 %.

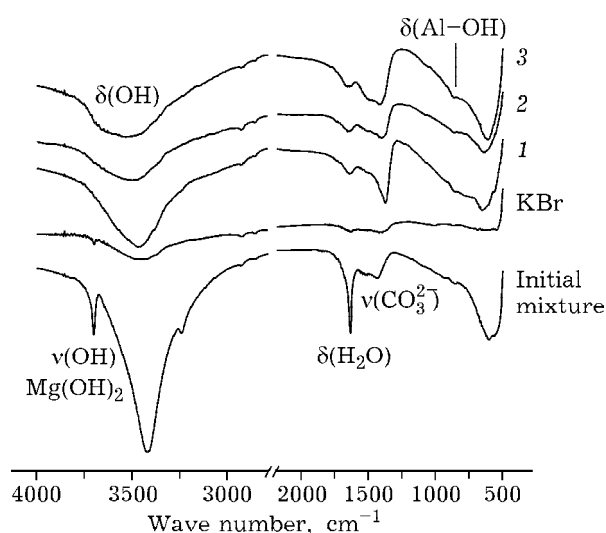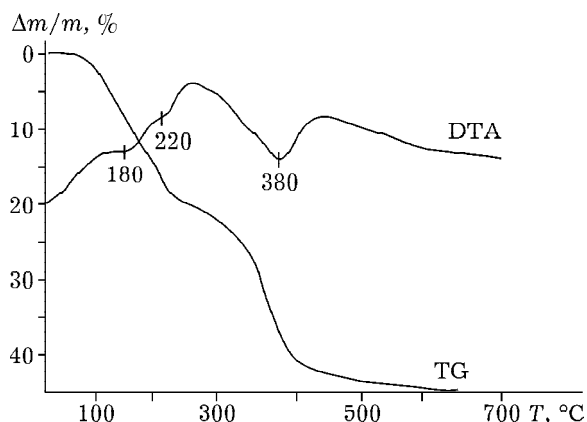Somewhat different picture is observed during the thermal decomposition of the sample

Fig. 4. Thermogram of the Mg–Al LDH sample with the initial Mg/Al molar ratio in the mixture equal to 4/1.
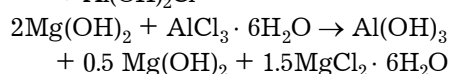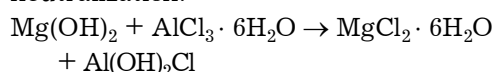
with the initial Mg/Al ratio equal to 2/1. The TG and DSC curves allow us to reveal three stages of mass loss. The first endo effect with the minimum at 140 °C is connected with the loss of sorbed water. The minima of the DSC curve at 230 and 350 °C are characterized by the thermal decomposition of $Al(OH)_3$ and $Mg(OH)_2$, respectively [7, 8]. This agrees with the XPA data (see Fig. 1) providing evidence that a mixture of magnesium and aluminium hydroxides was formed after mechanical activation and washing.

On the basis of the obtained experimental data, we proposed a scheme of the mechanochemical interaction in the mixture $xMg(OH)_2 + yAlCl_3 \cdot 6H_2O$. In the initial system, OH ions are represented only by the hydroxide lattice of brusite layers. Mechanochemical activation leads to the partial substitution of magnesium in brusite by aluminium. To conserve the zero charge, hydroxide and chloride ions get inserted into the interlayer space. The occurrence of hydroxide ions in the interlayer space points to the fact that the interaction includes the stage of acid-base character.
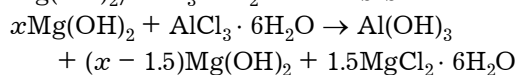
$AlCl_3 \cdot 6H_2O$ which is present in the reaction mixture is very hygroscopic and contains some amount of saturated aluminium chloride solution. As a result of its hydrolysis, a mixture of basic chlorides and hydrochloric acid are formed. In the course of mechanochemical activation, an increase in defect content and dispersity of brusite occurs; its surfaces get renewed permanently, which simplifies the interaction of

H_3O^+ (formed by the dissociation of $Al(H_2O)_6^{3+}$ with the surface hydroxo groups of $Mg(OH)_2$:
$$Mg(OH)_2 + 2H_3O^+ \rightarrow 4H_2O + Mg^{2+}$$
The formed magnesium cations together with chloride ions and water molecules form the bischofite phase ($MgCl_2 \cdot 6H_2O$). Further evolution of the system depends on the initial reagents ratio $Mg(OH)_2/(AlCl_3 \cdot 6H_2O)$.

For small initial Mg/Al ratios (1/1, 2/1), the interaction finishes at the stage of acid-base neutralization:
$$Mg(OH)_2 + AlCl_3 \cdot 6H_2O \rightarrow MgCl_2 \cdot 6H_2O$$
$$+ Al(OH)_2Cl$$
$$2Mg(OH)_2 + AlCl_3 \cdot 6H_2O \rightarrow Al(OH)_3$$
$$+ 0.5\,Mg(OH)_2 + 1.5MgCl_2 \cdot 6H_2O$$
For larger initial ratios (Mg/Al equal to 3/1, 4/1, 5/1, and 6/1), the phase of unreacted brusite remains in the system after neutralization of $AlCl_3 \cdot 6H_2O$. The amount of this phase increases while the initial ratio of components $Mg(OH)_2/AlCl_3 \cdot 6H_2O$ increases:
$$xMg(OH)_2 + AlCl_3 \cdot 6H_2O \rightarrow Al(OH)_3$$
$$+ (x - 1.5)Mg(OH)_2 + 1.5MgCl_2 \cdot 6H_2O$$
where $x = 3, 4, 5$, and 6.

Further on, under the conditions of mechanical activation, the interaction of $Al(OH)_3$, unreacted $Mg(OH)_2$ and $MgCl_2 \cdot 6H_2O$ occurs, resulting in the formation of hydrotalcite structure of the final product. The possibility of such an interaction was indicated in literature. Thus, the possibility of the mechanochemical interaction of magnesium and aluminium hydroxides with the formation of the hydroxide form of Mg–Al LDH was shown in [5]. It may be assumed that the formed hydroxide form of LDH interacts with magnesium chloride with the formation of the final product.

CONCLUSION

The obtained experimental data provide evidence that the mechanochemical activation of the mixture $xMg(OH)_2 + yAlCl_3 \cdot 6H_2O$ with the reagents ratio x/y equal to 3/1, 4/1, 5/1, and 6/1 in AGO-2 planetary mill ($40g$) for 10 min leads to the formation of Mg–Al LDH. The use of activation for 25 min with additional mixing and activation for 10 min in the presence of an inert KCl additive allow us to obtain Mg–Al LDH without admixtures of initial reagents. On

the basis of the obtained data, we propose a scheme including at the first stage the acid-base interaction of magnesium hydroxide and the products of $AlCl_3 \cdot 6H_2O$ hydrolysis. At the second stage, under the conditions of mechanical activation, the interaction of the formed $Al(OH)_3$, unreacted $Mg(OH)_2$ and $MgCl_2 \cdot 6H_2O$ occurs.

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