J Mater Sci (2007) 42:9210–9215
DOI 10.1007/s10853-007-1866-5

Preparation of meixnerite (Mg–Al–OH) type layered double hydroxide by a mechanochemical route

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Received: 27 December 2006 / Accepted: 21 May 2007 / Published online: 27 July 2007

Abstract We have attempted to synthesize the meixnerite (Mg–Al–OH) type layered double hydroxide (LDH) by a two step milling operation of a mixture of $Mg(OH)_2$ and $Al(OH)_3$ with water. In the first-step, a mixture of the starting materials was milled for 1 h without water, and the product prepared in the first-step was milled for 2 h with water in the second-step milling operation. The milled products were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR), and thermo gravimetric-differential thermal analyses with mass spectroscopy (TG-DTA/MS). The surface morphology was characterized by scanning electron microscopy (SEM). Meixnerite with a small amount of carbonate was successfully synthesized mechanochemically at ambient conditions by milling for only 3 h in a planetary ball mill.

Introduction

There is a considerable interest in the preparation and application of layered double hydroxides (LDHs) or hydrotalcite-like compounds (HTLcs), which are represented by the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$. LDHs consist of brucite-like structure where Mg^{2+} ions are arranged in metal hydroxide sheets. Naturally occurring hydrotalcite is represented by the formula $[Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O]$ and a large number of LDHs or HTLcs have been synthesized with divalent and trivalent cations [1, 2]. LDHs have a wide range of applications in catalysis as catalyst supports, as catalysts in organic reactions, catalyst in natural gas conversion or as environmental catalyst for reduction of SO_X and NO_X emissions, CO_2 adsorption. They also find application in ion exchange and absorption reactions, pharmaceutics, photochemistry and electrochemistry. Detail discussions of LDHs applications are cited in following references [1, 3–5].

The preparation and/or synthesis of LDHs can be achieved by a number of synthetic techniques. The most commonly used are simple coprecipitation methods such as precipitation at low and high supersaturation, separate nucleation and aging steps, and urea hydrolysis. Other methods applied include ion-exchange, rehydration using the structural memory effect and hydrothermal methods etc. [1, 6–12]. The meixnerite form of LDH (Mg–Al–OH) is usually prepared by the thermal decomposition of the carbonate LDH of the form (Mg–Al–CO_3) and reconstruction of the resulting metal oxide in the presence of OH. Mg–Al–CO_3 LDH prepared by coprecipitation method is first heated at temperatures between 500 °C and 700 °C for around 5 h under N_2 gas to form Mg–Al oxide solution, which is then placed in sealed flask containing degassed water for up to 5 days. Re-hydration of the mixed oxide into the meixnerite form is reported to have increased strength and concentration of active OH^- ions and is applied as catalyst and in ion-exchange reactions [13–18].

This work was conducted with two purposes. One is to develop a simple process to prepare the meixnerite form of LDH (Mg–Al–OH) by a mechanochemical route from $Mg(OH)_2$, $Al(OH)_3$ and water as starting materials. Another is to study the possibility of synthesizing hydrated compounds with high ratio of water, which has been achieved by a two-step milling operation. One-step milling

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of the starting materials with water was also investigated to compare with the results obtained from the two-step operation to understand the difference.

Experimental

Mechanochemical route

Two kinds of chemical reagents, $Mg(OH)_2$ and $Al(OH)_3$ supplied by Wako Chemicals—Japan were prepared as starting materials in this experiment. These two samples were mixed at a molar ratio of 3:1 for Mg and Al (Mg:Al = 3:1). The 2.0 g mixture was milled by a planetary ball mill (Pulverisette-7, Fritsch, Germany), which has two mill pots (45 cm^3 inner volume each) made of stainless-steel with 7 steel-balls of 15 mm diameter. Mill speed in this work was kept constant at 700 rpm.

In the first-step, the sample mixture of $Mg(OH)_2$ and $Al(OH)_3$ was milled using the planetary ball mill without water for 1 h. In the second-step the milled mixture of starting materials was milled for another 2 h, this time with the addition of water to effect mechanochemically induced reaction between water, Mg and Al to form meixnerite type LDH. In the meixnerite structure ($Mg_6Al_2(OH)_{18}\cdot 4H_2O$)—there is 4.0 mol water, however in this work, when determining moles Mg, Al and H_2O for milling, (Mg:Al:H_20) at (3:1:2) was used as baseline mixing ratio but amount water was varied at 2.0, 3.0, 4.0. 5.0, and 6.0 mol or 0.3, 0.4, 0.5, and 0.6 mL water respectively to the 2.0 g milled mixture of $Mg(OH)_2$ and $Al(OH)_3$. The increased addition of water was to account for the necessary absorption by the solid sample during milling. Water was added in the second-step milling operation and effects on meixnerite preparation were investigated. As a reference, the starting materials, $Mg(OH)_2$ and $Al(OH)_3$ mixture was also milled by the same mill with varying amounts of water for 3 h in a single-step milling, and the data was compared with the data prepared by the two-step milling process.

The carbonation of the synthesized sample was conducted with the following procedure. 0.5 g of the prepared sample was soaked in Na_2CO_3 solution (1% in mass, 50 cm^3) and agitated for 1 h. After water washing and filtration, the sample was dried at 80 °C for 2 h.

Characterization techniques

X-ray powder diffraction (XRD) analysis was carried out using Rigaku, RINT-2200/PC system with a CuKα irradiation source (λ = 1.5405 Å) at 40 kV and 50 mA for the samples milled with and without water as well as the starting mixture to determine their phases and observe changes in phase formations. Samples were analyzed in a continuous scan mode between 5° and 65° 2θ. Morphology of the ground mixture was observed by SEM (Semi-Electro probe Micro analyzer) equipment, S-4100L (Hitachi). Fourier transformed infrared (FT-IR) (Digilab Excalibur Series, FTS-3000) spectra of the samples were measured using KBr as a diluent. The TG/MS analysis was performed using a thermobalance connected to a quadrupole mass spectrometer (Rigaku Thermo-Mass: Thermo plus TG-8120 with M-201QA). The measurements were carried out with helium gas at a flow rate of 300 mL/min. About 13 mg of the prepared and carbonated samples were heated from 20 °C to 1,000 °C at a heating rate of 20 °C/min in a platinum sample pan. A portion of the volatile products was led to the ion source of the mass spectrometer through a transfer line heated to 200 °C.

Results and discussion

Powder X-ray diffraction (XRD) and SEM

Figure 1 shows XRD patterns of $Mg(OH)_2$ and $Al(OH)_3$ mixture milled for 3 h in a single-step milling operation with different amounts of a water ranging from 2.0 mol to 5.0 mol. Characteristic patterns of LDHs were clearly observed to appear in the milled products, however, peaks of starting materials remain in the milled mixtures. The

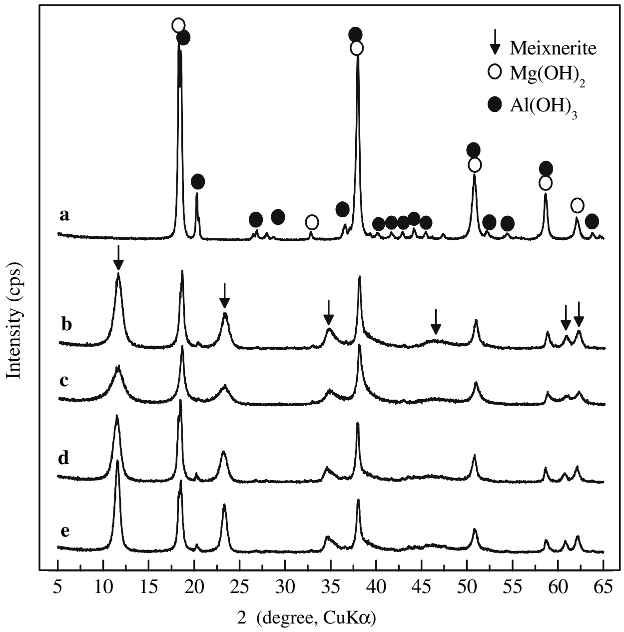

Fig. 1 XRD patterns—preparation of meixnerite in one-step process by milling 2.0 g mixture of $Mg(OH)_2$ and $Al(OH)_3$ (Mg:Al = 3:1) for 3 h with varying amounts of water; (**a**) $Mg(OH)_2$/$Al(OH)_3$ mixture before milling, (**b**) 2.0 mol (0.3 mL) water, (**c**) 3.0 mol (0.4 mL) water, (**d**) 4.0 mol (0.5 mL) water, (**e**) 5.0 mol (0.6 mL) water

relative peak intensity of starting materials and reaction product varies with the addition of water but it seems to be difficult to achieve a complete reaction by adjusting the water amount in a single-step operation. The presence of water from the start seems to affect $Mg(OH)_2$ and $Al(OH)_3$ from being effectively reduced to amorphous and/or near amorphous phases and create new active sites for further reaction as wet milling is not suitable for solid state reactions.

However, water is necessary for preparation of LDHs and a two-step milling operation is proposed to avoid hindrance of water in initial stages of milling. In the first-step, dry milling of both hydroxides without water is conducted, followed by further milling with water as the second-step. The results of the XRD measurements obtained from the milled mixtures with the changes in amount of water and milling time are presented in Fig. 2 and 3, respectively.

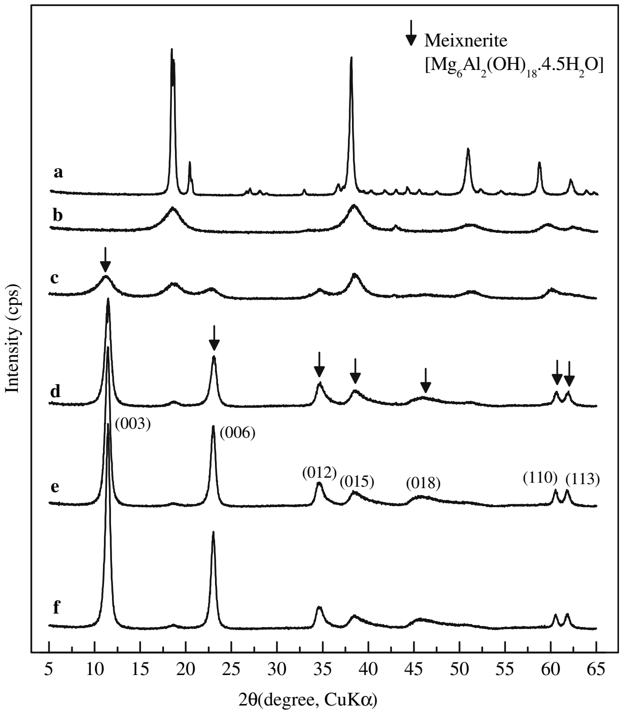

Fig. 2 XRD patterns of meixnerite prepared in a two-step milling process. (**a**) 2.0 g $Mg(OH)_2$ and $Al(OH)_3$ (Mg/Al = 3) mixture sample before milling, (**b**) sample mixture milled 1 h without water, (**c**–**f**) preparation of meixnerite by milling product in (**b**) for 2 h with 2.0, 3.0, 4.0, 5.0 mol water respectively

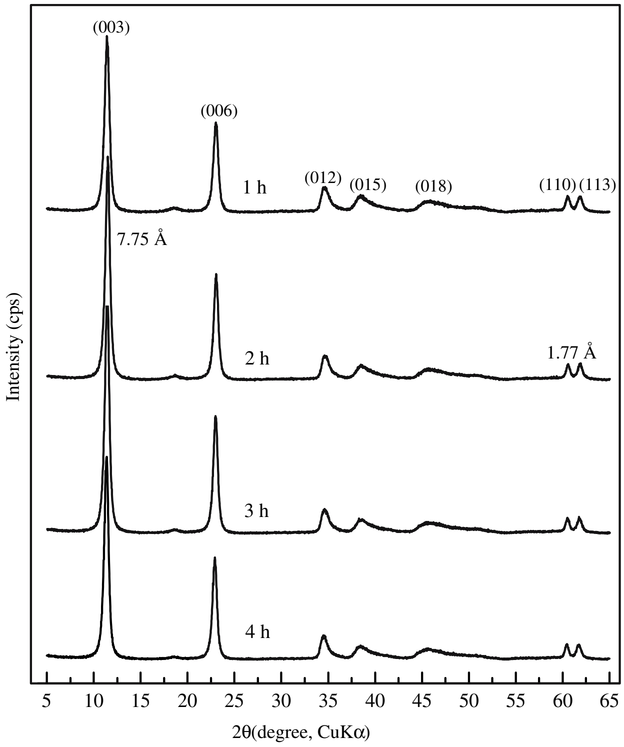

Fig. 3 XRD patterns—meixnerite preparation as a function of milling time for $Mg(OH)_2/Al(OH)_3$ (Mg/Al = 3) mixture sample (obtained by dry milling for 1 h in the first-step) with 5.0 mol (0.6 mL) water in the two-step

In Fig. 2b peak intensity of initial sample mixture was reduced to quite a low level compared with that of the starting sample by dry milling for 1 h. The wet milling was conducted by fixing time at 2 h and amount water addition varied at 2.0, 3.0, 4.0, and 5.0 mol. The stoichiometric amount of water for the meixnerite formation in this experiment is 2.25 mol. When water addition is just around such required amount as the case of 2.0 mol shown by Fig. 2c, characteristic patterns of LDH appears with low peak intensity and peaks of hydroxide mixtures remain in the final product. The peak intensities of the LDH gradually increase with increase in water addition from 3.0 mol to 5.0 mol with intensities reaching highest point at 5.0 mol water addition. These results indicate that not only the water addition is necessary but also more water than the required stoichiometric amount should be added to achieve a complete reaction for LDH formation because water absorbs on the surfaces of samples and it is almost impossible to introduce all the added water into the crystalline structures. Further increase in water addition showed a decrease in the peak intensity of LDH as excessive water resulted in wet milling affecting solid state reactions. XRD patterns of meixnerite form (Mg–Al–OH) LDH resembled well in the range $2\theta = 5$–65° and d_{003} basal spacing at 5.0 mol water addition and 2 h milling gave 7.75 Å [1, 17, 19]. At 2.0, 3.0, and 4.0 mol water addition, d_{003} basal spacing values were at 7.76, 7.79, and 7.90 Å respectively.

XRD patterns in Fig. 3 show meixnerite preparation by keeping amount water fixed at 5.0 mol (0.6 mL) and varying milling time at 1, 2, 3, and 4 h. It has been observed that the peak intensity increases with an increase in milling time and reaches highest point at 2 h milling. The peak intensity decreases with further increase in milling time. The d_{003} values remained constant at 7.80 Å for 1, 3, and 4 h, and 7.75 Å for 2 h milled samples. From the X-ray diffraction patterns discussed, a two-step milling process with a water addition of 5.0 mol and a milling time of 2 h, meixnerite form of LDH was confirmed. This shows that a two-step milling is effective for synthesizing hydrotalcite: The first step is to reduce the structure of starting materials to amorphous phase, which results from the solid state reaction between the two hydroxides and serves as the precursor for the formation of meixnerite phase. An easy formation of a pure product is obtained in the second-step milling where water molecules are introduced into the structures as crystal water. Without the first-step operation and the existence of precursor, the milling operation with water proceeds just as a wet milling. It is not easy to complete a solid state reaction by a wet operation. The proposed two-step operation has successfully solved the dilemma of introducing the water into the structure and avoiding the wet operation. Water existence facilitates the following reaction, to form $Mg_6Al_2(OH)_{18}.4H_2O$ or meixnerite type LDH. The compositions will be further addressed later with the analysis of carbonate.

Figure 4 shows a SEM photograph of the Mg–Al–OH LDH prepared in this work. Large and lumpy particles are observed in the photo. Generally, the morphology of the ground sample without water exhibits agglomeration of fine particles in several microns, though the size of primary particles is in nanoscale. The water existence leads to a further agglomeration into large particles.

TG-DTA/MS measurements

LDHs and/or HTLcs normally undergo a two-step weight loss upon heating. The low temperature region up to around 250 °C has been attributed to the loss of surface adsorbed (physisorbed) and intercalated (interlayer) water molecules and the high temperature region between 250 °C and 450 °C has been attributed to the decomposition of LDHs [1, 10, 11, 20–24]. Figure 5A1 and A2 show TG and DTA patterns respectively of the meixnerite form of LDH prepared from a mixture of $Mg(OH)_2$ and $Al(OH)_3$ with 5.0 mol water in a two-step milling process for 3 h. The first endothermic peak at 75 °C was due to the release of physisorbed water, and the second endothermic peak at 177 °C was due to the release of interlayer water, with a weight loss of around 17 wt% at 177 °C. The calculated amount of water in meixnerite constitutes about 12.5 wt%, higher weight loss recorded above was due to excess water used to prepare meixnerite during milling. Figure 5B1 and B2 show TG and DTA patterns of meixnerite heated at 80 °C for 2 h after preparation. From this pattern, a single endothermic peak was observed at 225 °C due to the release of interlayer water and recorded a weight loss at 13 wt%, as physisorbed water was released during heat treatment at 80 °C. The endothermic peak due to dehydroxylation is seen at 422 and 430 °C for milled sample mixtures before and after heated at 80 °C respectively, with each giving a weight loss of about 20 wt%. Endothermic peaks due to $Al(OH)_3$ and $Mg(OH)_2$ decomposition were not observed at 280 and 418 °C respectively, indicating that the starting materials when milled with

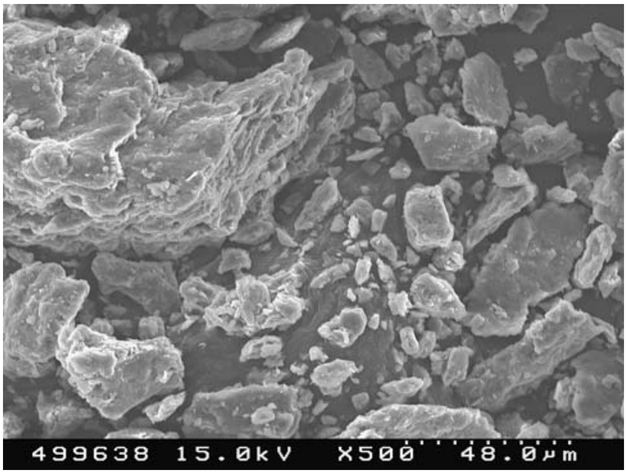

Fig. 4 SEM photograph of meixnerite form LDH [Mg–Al–OH] (Mg/Al = 3) prepared mechanochemically by milling 2.0 g mixture of $Mg(OH)_2$ and $Al(OH)_3$ with 5.0 mol (0.6 mL) water for 2 h at 700 rpm

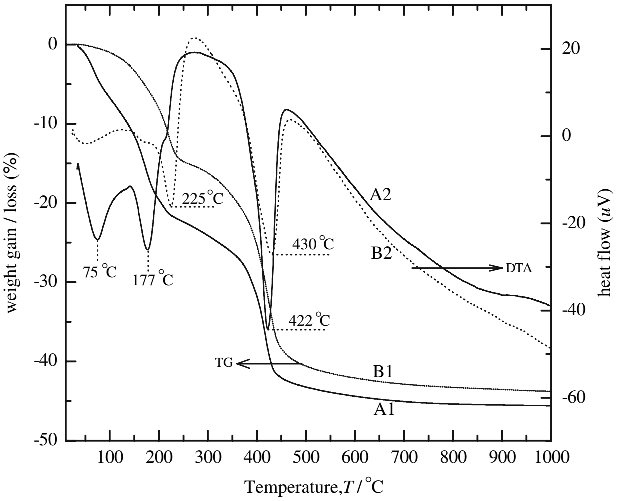

Fig. 5 TG-DTA pattern of meixnerite prepared mechanochemically in a two-step process by milling 2.0 g of $Mg(OH)_2$ and $Al(OH)_3$ mixture (Mg:Al = 3:1) with 5.0 mol (0.6 mL) water, both before and after heating at 80 °C. (A1)—TG before heat, (A2)—DTA before heat, (B1)—TG after heat, (B2)—DTA after heat

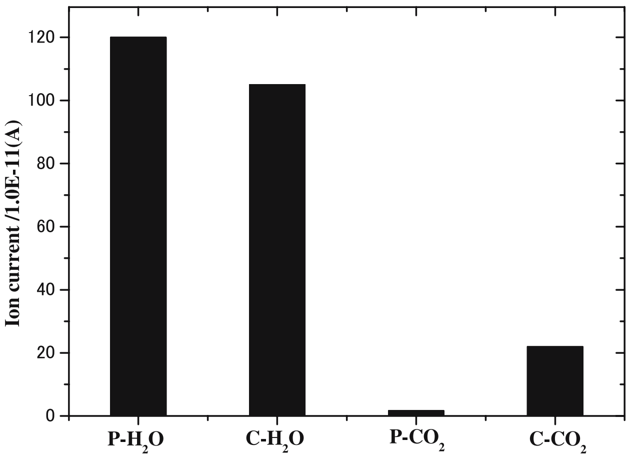

Fig. 6 Evolution of the gases H_2O and CO_2 at 420 °C by MS analysis from the as-prepared sample (indicated as P) and carbonated sample (indicated as C)

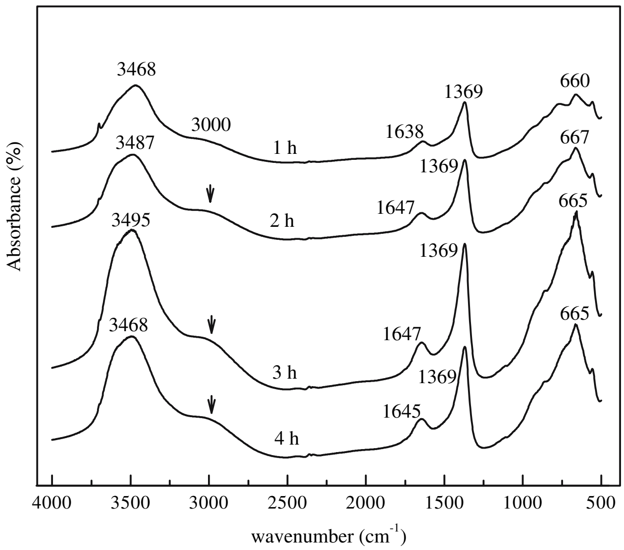

Fig. 7 FT-IR patterns of meixnerite prepared mechanochemically by milling 2.0 g of $Mg(OH)_2$ and $Al(OH)_3$ [3:1] mixture with 5.0 mol (0.6 mL) water for different periods of time

water have been converted to meixnerite, and un-reacted traces of starting materials may be below detection limit. The general TG-DTA features of meixnerite prepared in this work correspond well with that of LDHs and support well XRD data, also obtained in this work.

Figure 6 shows the evolutions of water and carbon dioxide at 420 °C from MS analysis of both the prepared and carbonated samples. Two samples were measured at exactly same conditions so that the obtained qualitative data of compositions from two samples could be comparable. First, the decrease in water amount resulting from the carbonation treatment has been observed. The most important is the datum for CO_2 of which the evolution has been observed only around 420 °C. Although the evolution due to CO_2 has been observed from the prepared sample, the intensity is about 5% to that of the carbonated sample, suggesting that the proposed method is quite effective for avoiding CO_2 absorption, considering that all the operations including milling and other sample handlings were conducted in air. The prepared sample is not a pure meixnerite. Since the carbonate amount is much lower than that of the carbonate type, it is reasonable to say that the compositions of the prepared sample are near that of meixnerite (hydroxide type) and far from that of the hydrotalcite (carbonate type). Meixnerite is used to refer to approximately the prepared sample.

Infrared spectroscopy (FT-IR)

Figure 7 shows the FI-IR spectra of the prepared samples with amount water addition fixed at 5.0 mol and milling time varied between 1 h and 4 h. The general features in the spectra clearly are consistent with that of LDHs which many researchers cover in their works [1, 10, 24–26] and some detailed discussion is performed in the following sentences. The infrared bands at 3,450–3,700 cm^{-1} are attributed to the stretching vibration of OH group. The peak at higher position corresponds to the free OH group of the starting hydroxide samples. The peak at lower position is related to the group with strong H-bonding inside. It is interesting to note that the sharp peak at higher position around 3,700 cm^{-1} has been nearly observed with 1 h ground sample, indicating the small amounts of the starting hydroxides remain in the 1 h ground sample. This peak has disappeared in the patterns of the samples ground over 2 h. Broad peaks have become dominate due to water compositions with strong H-bonding inside the structures. In other words, no free hydroxides exist in the prepared samples, indicating that the prepared sample is a LDH rather than a mixture of starting hydroxides. The peak around 1,370 cm^{-1} may be attributed to the interaction between CO_3 group and OH group confirming the existence of CO_2 from the atmosphere as milling was conducted under normal atmospheric conditions with distilled water [1, 11, 22–26].

Conclusion

The results in this work clearly show that LDHs or hydrotalcite like coumpounds could be prepared by mechanochemical means through milling within 3 h. Meixnerite form of LDH with small amount of carbonate was successfully prepared in a two-step milling process. In the first-step, $Mg(OH)_2$ and $Al(OH)_3$ as starting materials were milled without water for 1 h, and with water for 2 h in the second-step. This method offers a good solution to the mechanochemical synthesis of compounds involving the water use.

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