



Synthesis of Li–Al layered double hydroxides via a mechanochemical route



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ABSTRACT

In this study, we introduced a solvent-free mechanochemical route to synthesize Li–Al layered double hydroxide through a two-step grinding of LiOH and Al(OH)₃, in which the mixture powder with Li/Al molar ratio at 1/2 was first dry ground for 2 h and then wet ground for another 1 h with water addition without any heating operation. The as-prepared samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), thermogravimetry (TG), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). The products possessed highly crystalline of Li–Al LDH phase with no evident impure phases, presenting an easy and effective preparation of Li–Al LDH by using solvent-free mechanochemical approach.

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1. Introduction

Layered double hydroxides are a group of synthetic anionic clays which are widely used in environmental protection (Theiss et al., 2014), pharmaceutical preparation (Hoyo, 2007), organic synthesis (French et al., 2010), elastomer compositing (Basu et al., 2014), etc. The general formula of LDH can be represented as $[M_1^{2+}_x M_2^{3+}_{1-x}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M^{2+} represents not only divalent metal elements but also univalent element such as Li^+ and Na^+ ; M^{3+} can be substituted by Fe^{3+} , Al^{3+} , Bi^{3+} , Ti^{4+} , Sn^{4+} , and Mo^{6+} (Basu et al., 2014). Li–Al LDH are the only reported M(I)M(III) type LDH which possesses the highest layer charge density (Wang et al., 2013) among all types of LDH, indicating its higher anion-exchange capacity than typical M^{2+}/M^{3+} LDH. Previous studies have shown that Li–Al LDH could not only be used in environmental protection such as Cr(VI) removal (Hsu et al., 2007), but also widely in lithium ion batteries (Wei et al., 2013), corrosion protection (Syu et al., 2013), and catalysts for organic synthesis (French et al., 2010).

Traditional methods to synthesize Li–Al LDH are usually operated in an aqueous solution through an “imbibition” process (Fogg et al., 2002), where Li^+ is intercalated into aluminum hydroxides including gibbsite, bayerite, nordstrandite and doyleite (Besserguenev et al., 1997; Fogg et al., 2002; Yang et al., 2004; Williams and O'Hare, 2006). The “imbibition” process involves the destruction of H-bonding networks of

Al(OH)₃ to form the layers of LDH (Wang et al., 2013) so that activation energy as high as 27 kJ mol^{-1} for the reaction between Li^+ and Al(OH)₃ (Fogg and O'Hare, 1999) is required for these pathways. Therefore synthesis reaction for Li–Al LDH is usually performed at temperature over 80 °C, with continuous stirring for hours or days and using relatively high concentration of lithium solution. Co-precipitation is another method to prepare Li–Al LDH especially for the carbonate type of Li–Al LDH where lithium salt, aluminum salt and carbonate salt are stirred together in water at 60–90 °C for 12–18 h (Sissoko et al., 1985). The solution ways mentioned above all involve a complicated process with long period of reaction time, heating treatment, intensive water-washing to remove the unreacted raw materials and solid liquid separation to gain final dry powder products. Alternative to manufacture Li–Al LDH is required with purpose to realize a much more environment-friendly process without emission of large amounts of wastes.

Previous studies suggested that it is feasible to synthesize LDH by a solvent-free mechanochemical approach (Tongamp et al., 2007; Qu et al., 2015). The mechanochemical process was based on mainly a solid phase reaction which could prevent the CO₂ dissolution from the ambient. It is promising to manufacture LDH in large scale by mechanochemistry because of the obvious advantages such as easy operation, energy-saving and no effluent emission. Mg–Al–OH (Tongamp et al., 2007), Mg–Al–NO₃ (Tongamp et al., 2008), Ca–Sn (Ferencz et al., 2014), and Ca–Al (Ferencz et al., 2015) LDH have been synthesized by this method. In this work, for the first time, we report the fundamental data obtained with Li–Al LDH synthesized via a solvent-free mechanochemical route.

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2. Experimental procedures

2.1. Milling operation

LiOH (Aladdin Industrial Corporation, Shanghai, 98%) and $\text{Al}(\text{OH})_3$ (Sinopharm Group Co Ltd., Shanghai, Analytical reagent) were used as raw materials in this experiment. Two grams of the mixture of LiOH and $\text{Al}(\text{OH})_3$ was milled at molar ratio of 1/2 for Li and Al to prepare Li–Al LDH, also with molar ratios of 0.2/2 and 1/1 as comparison, using a planetary ball mill (QM-3SP04, Nanjing NanDa Instrument Plant), which has four mill pots (50 cm³ inner volume each) made of stainless-steel with 7 steel-balls of 17 mm diameter. Milling speed in this work was kept constant at 500 rpm.

The milling involved a two-step operation. In the first step, called dry milling, 2 g mixture of LiOH and $\text{Al}(\text{OH})_3$ was ground for 2 h. In the second step, part of water was put in the milled sample another 1 h. With theoretical chemical formula of Li–Al LDH ($\text{LiAl}_2(\text{OH})_7 \cdot 2\text{H}_2\text{O}$), 2.0 mol water is needed for synthesizing Li–Al LDH. In this work, the amounts of water added were varied at 1.0, 2.0, 3.0, 4.0 and 5.0 mol or 0.2, 0.4, 0.6, 0.8 and 1.0 ml water respectively. Since water was consumed almost completely by forming LDH product, the obtained samples were nearly dry powders or somewhat caked sample. No further drying and other treatments were needed to treat the prepared samples for next step of characterizations.

2.2. Characterizations

XRD patterns of samples were recorded on a Rigaku MAX-RB RU-200B diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5403 \text{ \AA}$). Microstructures of the prepared sample were observed by SEM (JSM-5610LV JEOL) spectroscopy. TG-DSC analysis was performed by a simultaneously thermal analyzer (STA449F3, NETZSCH). FT-IR spectra of the samples were scanned on Nicolet 6700, Thermo, using KBr as a diluent over 4000–500 cm^{-1} .

3. Results and discussion

Fig. 1 shows XRD patterns of Li–Al LDH prepared by a two-step milling operation (dry grinding for 2 h and then wet grinding with water for another 1 h) with different amounts of water addition in the range from 1.0 to 5.0 mol in the second wet grinding operation. In the pattern of sample (a), namely the starting materials ($\text{LiOH}/\text{Al}(\text{OH})_3$ at 1/2), peaks of $\text{LiOH} \cdot \text{H}_2\text{O}$ were observed together with that of starting LiOH, due to its high capacity of absorbing water. After dry grinding of the

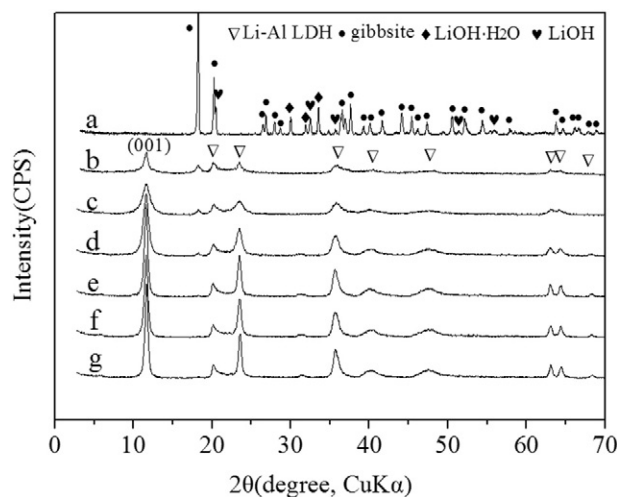


Fig. 1. XRD patterns—(a) an un-milled mixture of $\text{LiOH}/\text{Al}(\text{OH})_3$ (1/2); (b) the mixture milled for 2 h without water; (c–g) preparation of Li–Al LDH by milling sample (b) for another 1 h with 1.0, 2.0, 3.0, 4.0, and 5.0 mol water addition, respectively.

mixture sample for 2 h, represented as pattern b, typical pattern of LDH was clearly observed with evident existence of gibbsite. After wet grinding and with an increase in the amount of water added in wet milling, the peak intensity of LDH gradually increased and that of the gibbsite phase decreased and disappeared with water addition over 3.0 mol. The d_{001} basal value gave 7.65, 7.62, 7.62, 7.61 and 7.57 Å at 1.0, 2.0, 3.0, 4.0 and 5.0 mol water addition, respectively. Considering no other anions were involved in the preparation process except tiny CO_3^{2-} from the CO_2 dissolution, the anions in the interlamination of Li–Al LDH could only be CO_3^{2-} and OH^- . Previous studies (Poepfelmeier and Hwu, 1987; Thiel et al., 1993; Drewien et al., 1996; Wang et al., 2013) gave 7.54–7.56 Å of d_{001} basal value for Li–Al–OH LDH and 7.6 Å for Li–Al– CO_3 LDH. The decrease in d_{001} basal value from 7.65 Å to 7.57 Å with the increase in water in Fig. 1 suggested the dominant existence of OH^- anions in more addition of water. Wet grinding with more water helped to form more orderly LDH phase. Since 3.0 mol water was enough for the reaction between LiOH and $\text{Al}(\text{OH})_3$ to prepare pure phase of LDH product, it was maintained in the following experiments in wet grinding operation.

Fig. 2 shows XRD patterns of the prepared Li–Al LDH product with different times at wet milling, $\text{LiOH}/\text{Al}(\text{OH})_3$ ratio at 1/2 with dry milling for 2 h and 3.0 mol water in the wet milling. Even with wet grinding for 0.5 h, no impure phases were observed from the XRD pattern. The peak intensities in (001) were 10,442 cps, 11,529 cps, 13,919 cps, 15,886 cps and 18,036 cps for 0.5 h, 1 h, 2 h, 3 h and 4 h samples respectively. Prolonged grinding was helpful to form highly crystalline Li–Al LDH. The d_{001} basal value for different wet grinding times was around 7.60, 7.63, 7.62, 7.61, and 7.61 Å at 0.5, 1, 2, 3, and 4 h respectively.

By keeping 2 h of dry grinding, 1 h of wet grinding with 3.0 mol water, the effect of molar ratio of Li/Al on the preparation of LDH was investigated by comparing three mixtures with the ratio of 1/1, 1/2 and 0.5/2, respectively and the results were shown in Fig. 3. Although LDH phase was observed from all three patterns, only the ratio of Li/Al at 1/2 gave a pure phase without observable impurity phases. Starting materials remained in the products when more or less Li/Al ratio than 1/2 was used. Gibbsite phase was left when less Li as 0.5/2 was used and $\text{LiOH} \cdot \text{H}_2\text{O}$ was left in the product when more Li as 1/1 was used. Traditional wet chemical routes to prepare Li–Al LDH usually need excess raw materials, where the unreacted raw materials should be washed away to obtain pure LDH phase after the synthesis reaction (Drewien et al., 1996). It is different for mechanochemical process where the exact amount of the required molar ratio was used to prepare the products, with no impurity phases of gibbsite or LiOH left with product. Furthermore, no washing treatment or drying operation was needed. This

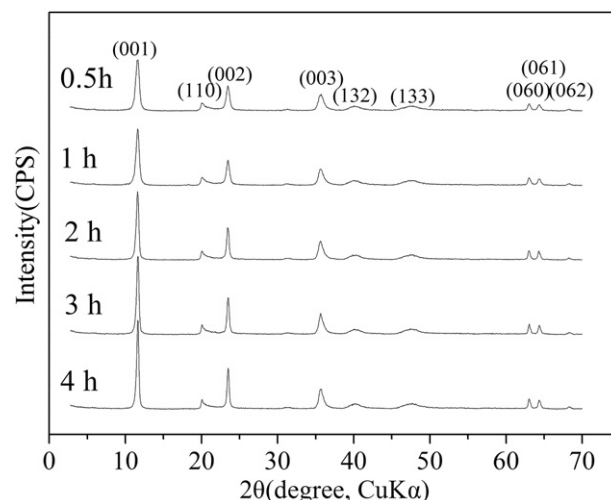


Fig. 2. XRD patterns Li–Al LDH sample prepared at different milling times for wet step.

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