



Mechano-hydrothermal preparation of Li-Al-OH layered double hydroxides

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ABSTRACT

A mechano-hydrothermal (MHT) method was used to synthesize Li-Al-OH layered double hydroxides (LDHs) from $\text{LiOH} \cdot \text{H}_2\text{O}$, $\text{Al}(\text{OH})_3$ and H_2O as starting materials. A two-step synthesis was conducted, that is, $\text{Al}(\text{OH})_3$ was milled for 1 h, followed by hydrothermal treatment with $\text{LiOH} \cdot \text{H}_2\text{O}$ solution. Effects of the $\text{LiOH}/\text{Al}(\text{OH})_3$ molar ratio ($R_{\text{Li/Al}}$) and hydrothermal temperature (T_{ht}) on the crystallinity, morphology, and composition of the product were examined. The resulting LDHs were characterized by X-ray diffraction, transmission electron microscopy, scanning electron microscopy, Fourier transform infrared, and elemental analyses. The results showed that pre-milling plays a key role in the LDH formation during subsequent hydrothermal treatment. The Li/Al molar ratio of the obtained LDHs keeps constant at 0.5, independent from the $R_{\text{Li/Al}}$ (0.5–5.0) in the starting materials. An increase in the T_{ht} (20–80 °C) can enhance the crystallinity and morphology regularity of the products. The so-obtained Li-Al-OH LDHs exhibit high crystallinity and well-dispersity, which may have wider applications than the aggregate ones obtained using conventional mechanochemical and Li^+ -imbibition methods.

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1. Introduction

Anionic clays, a large class of layered hydroxide compounds composed of positively charged Brucite [$\text{Mg}(\text{OH})_2$]-like layers and exchangeable interlayer anions, have received great attention owing to their unique structure, special properties, and extensive applications [1–9]. Anionic clays have a great variety of members; based on their composition and structure, they can be divided into two groups [2,4], namely, layered double hydroxides (LDHs) [5,9] and layered hydroxide salts (LHSS) [4]. LDHs are commonly represented by the general formula $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2][\text{A}^{n-}]_{x/n} \cdot m\text{H}_2\text{O}$ [1,2,4,9], where M^{II} and M^{III} are the di- and trivalent metal cations, respectively, and A^{n-} is the anion of n charge. Actually, LDHs should be represented by the more general formula $[\text{M}^{\text{II}}_{1-x-y-z}\text{M}^{\text{III}}_x\text{M}^{\text{IV}}_y\text{M}^{\text{I}}_z(\text{OH})_2][\text{A}^{n-}]_{(x+2y-z)/n} \cdot m\text{H}_2\text{O}$, owing to the fact that various LDHs containing the monovalent metal cation (M^{I}) Li^+ and tetravalent metal cations (M^{IV}) such as Ti^{4+} , Zr^{4+} , Se^{4+} , V^{4+} , and Si^{4+} have been widely reported [2,5–9]. For example, Li-Al-Ti- CO_3 LDHs have been synthesized recently by Kong et al. [10]. Notably, when $y = 0$, $x = 2/3$, and $z = 1/3$, forming a unique group of

LDHs (Li-Al-A LDHs) with the formula $[\text{Li}_{1/3}\text{Al}_{2/3}(\text{OH})_2][\text{A}^{n-}]_{1/n} \cdot m\text{H}_2\text{O}$ [2,11,12]. Commonly, Li-Al-A LDHs are considered to be derived from crystalline aluminum hydroxides $[\text{Al}(\text{OH})_3]$ including Gibbsite and Bayerite, thereby often called $\text{Al}(\text{OH})_3$ (Gibbsite or Bayerite)-based anionic clays or LDHs [2,11–13]. Crystalline $\text{Al}(\text{OH})_3$ (Gibbsite or Bayerite) has a similar structure to Brucite, except that 1/3 of the octahedral metal cation sites are vacant, namely, Al^{3+} ions only occupy 2/3 of the octahedral cation sites, thereby having a layer composition of $[\square_{1/3}\text{Al}_{2/3}(\text{OH})_2]$ (\square represents the vacancy). The vacancies in the layers may be filled by Li^+ to yield excess positive charges that are neutralized by interlayer anions, forming Li-Al-A LDHs with a general formula of $[\text{Li}_x\text{Al}_2(\text{OH})_6][\text{A}^{n-}]_{x/n} \cdot m\text{H}_2\text{O}$ ($x \leq 1$) [2,11], where the A^{n-} may be CO_3^{2-} , OH^- , Cl^- , Br^- , NO_3^- , SO_4^{2-} , and so on. Actually, Li-Al LDHs may be also considered to be derived from Brucite, in which 2/3 of Mg^{2+} ions are isomorphically substituted for Al^{3+} ions and 1/3 of Mg^{2+} ions for Li^+ ions and probably some vacancies. In addition, Li-Al LDHs are the only known compounds in the $\text{Al}(\text{OH})_3$ -based anionic clays so far [2,3].

A Li-Al- CO_3 LDH was first synthesized by Besson et al. in 1974 through boiling mixtures of $\text{Al}(\text{OH})_3$ and lithium carbonate (Li_2CO_3), and then by Serna et al. in 1977 through the hydrolysis of aluminum-tri-(sec-butoxide) in the presence of Li_2CO_3 [14]. Since then, Li-Al LDHs have been widely studied [2,3], involving their

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synthesis [12,15–25], structure [11,13,16,19,26–28], properties [23,29–38], and potential applications [20–24,32,38–43]. Extensive potential applications of Li-Al LDHs have been demonstrated, such as in catalysts [21,41], sorbents for wastewater treatment [20,22,38–40] and CO₂ capture [43], corrosion protection [24,42], lithium ion batteries [23], and separations [32]. Many solution-phase chemical methods to synthesize Li-Al LDHs have been developed, such as the “imbibition” (intercalation) of Li⁺ (lithium salts or LiOH) into Al(OH)₃ (Gibbsite, Bayerite, or Nordstrandite) [15–19], co-/homo-precipitation [21,22], hydro-/solvo-thermal treatment [20,21,23], and the reaction between metallic Al or Al-Li alloy and LiOH or LiNO₃/NaOH in solution [12,24]. These solution-phase chemical methods have some disadvantages. For instance, the imbibition of Li⁺ into Al(OH)₃ (Li⁺-imbibition method) commonly generates irregular aggregate (or stone-like) products [18,19], co-/homo-precipitation routes produce large amounts of waste [25], and hydro-/solvo-thermal methods usually require a high reaction temperature (120–150 °C) and a long reaction period (10–24 h) [20,21,23]. A solvent-free mechanochemical (MC) route has been developed [44,45] and frequently used to synthesize M^{II}-M^{III} and M^{II}-M^{IV} LDHs [46–57]. In comparison with traditional solution-phase chemical methods, MC method has some advantages, such as easy operation, energy-saving, and no effluent emission [25]. However, its disadvantage is that the LDH products are commonly with low crystallinity and irregular aggregate (or stone-like) shapes [25,45,48,50,55,56], which limits their applications to a great extent. Recently, Qu et al. [25] utilized the MC route to synthesize Li-Al-OH LDHs, and the so-obtained product exhibits stone-like aggregates. To improve the crystallinity, morphology, and dispersity of MC products, we have developed a mechano-hydrothermal (MHT) method by combining a pre-milling process with a hydrothermal treatment [58,59]. The MHT process is advantageous in terms of low reaction temperature and short reaction time compared with the conventional hydrothermal method, and its target products are of high crystallinity, good dispersion, and regular shape compared with the conventional MC method. So far, there have been no reports on the MHT synthesis of Li-Al LDHs.

In the current work, the MHT method was used to synthesize Li-Al-OH LDHs from Gibbsite [γ -Al(OH)₃] and LiOH·H₂O as starting materials. Effects of the LiOH/Al(OH)₃ molar ratios ($R_{\text{Li/Al}}$) and hydrothermal temperature (T_{ht}) on the crystallinity, morphology, and composition of the product were examined. In addition, the MHT results are compared with those of conventional MC and hydrothermal (HT) methods. A Li-Al-OH LDH with high crystallinity, well-dispersity, and regular hexagon morphology is obtained using the MHT route. The so-obtained Li-Al-OH LDHs may have wider applications than the stone-like ones obtained using conventional MC and Li⁺-imbibition methods.

2. Experimental section

2.1. Preparation of Li-Al-OH LDHs

Gibbsite (γ -Al(OH)₃, analytical reagent) was purchased from Shanghai Meixing Chemical Co., Ltd., China. LiOH·H₂O (analytical reagent) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. The chemicals were used as received. Water used was purified with a Hitech-Kflow water purification system (China).

A two-step operation was performed to synthesize the target sample. In the first-step, Al(OH)₃ was milled for 1.0 h under ambient conditions, using a planetary ball mill (QM3STC, Nanjing Nanda Instrument Plant, China) with four stainless-steel mill pots (500 cm³ inner volume each) and 10 mm diameter steel-balls. The ball/Al(OH)₃ weight ratio was about 49, and the mill speed was constant at 450 rpm. In the second-step, 0.3 g of the so-milled

Al(OH)₃ was placed in a 50 ml Teflon-lined stainless-steel autoclave filled with 30 ml of 60 mM LiOH·H₂O solution, in which the Li/Al molar ratio ($R_{\text{Li/Al}}$) was 0.5. After the vessel was sealed and thoroughly shaken, it was statically placed in an oven and hydrothermally treated under a designed temperature (T_{ht} , 20–80 °C) for 1 h. The product thus obtained was collected using centrifugation, washed with water, and dried at 60 °C. To examine the effect of $R_{\text{Li/Al}}$, the MTH synthesis was performed under the same conditions except the $R_{\text{Li/Al}}$ being changed to 2.0, 3.0, 4.0, and 5.0.

For comparison, the conventional MC [47] and HT [26] methods were adopted to synthesize the target sample, respectively, using Al(OH)₃ and LiOH·H₂O as starting materials. For the MC synthesis, a two-step milling operation was performed. The Al(OH)₃ was first milled for 1.0 h under the same conditions as mentioned above, followed by further milling with LiOH·H₂O for another 1 h. For the HT synthesis, the mixture of unmilled Al(OH)₃ and LiOH solution was hydrothermally treated at 80 °C for 6 h.

For clarity, the LDH samples obtained by MHT, MC, and HT methods are denoted as MHT-, MC-, and HT-LDHs, respectively.

2.2. Characterization

X-ray diffraction (XRD) patterns of the so-prepared samples were recorded on a D/max-rAdiffractometer (Bruker AXS, Co., Ltd., Germany) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 40 mA, in the 2θ range of 10–70° with a scanning rate of 10°/min. The morphology of the samples was analyzed by a field emission-scanning electron microscope (FE-SEM, JSM-6700F, JEOL, Japan) and a transmission electron microscope (TEM, JEM-2100, JEOL, Japan). Fourier transform infrared (FT-IR) spectra of the samples were collected using KBr pellets on a Vector-22 FT-IR spectroscopy (Bruker AXS, Co., Ltd., Germany) in reflectance mode, from 400 to 4000 cm⁻¹, with a resolution of 2 cm⁻¹. The Al and Li contents of the samples were determined using a ICAP-9000 inductively coupled plasma-atomic emission spectrometry (ICP-AES, Jarrel-Ash, Thermo Electron Co., USA) after the samples were dissolved in a dilute HCl. Zeta potentials were measured using a DXD-II microelectrophoresis instrument (Jiangsu Optical Instrument Co., China) with a flow-through sample cell. Particle size distributions were measured using a SALD-7100 laser scattering particle size analyzer (Shimadzu). The N₂ adsorption-desorption isotherms were determined using an Autosorb IQ-MP system (Quantachrome Instruments, USA), with the samples degassed at 120 °C for 5 h under vacuum prior to the measurements. The specific surface area (A_s), pore-size distribution, and pore volume (V_p) of the samples were estimated from the isotherms by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively.

3. Results and discussion

A MHT method was adopted to synthesize Li-Al-OH LDHs, in which a pre-milling process was combined with a hydrothermal treatment. That is, the starting material Al(OH)₃ was first milled for 1.0 h, and the milled Al(OH)₃ mixed with a LiOH solution was then hydrothermally treated under a given temperature (T_{ht}) for 1 h. The pre-milling for Al(OH)₃ can produce more active sites, which is favorable of the LDH-phase formation during the subsequent hydrothermal treatment [58,59]. In addition, the pH values of the reaction systems before and after the hydrothermal treatment were determined to be the same at ~12.6.

The effect of T_{ht} (20–80 °C) on the formation of Li-Al-OH LDHs was examined at $R_{\text{Li/Al}} = 0.5$ using XRD. As shown in Fig. 1, at $T_{\text{ht}} = 20 \text{ °C}$, the characteristic diffraction peaks of the LDH-phase [11,15,20,25] are clearly observed and those of the starting material Al(OH)₃ (Fig. S1 in the Supporting Information, SI) disappear,

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