



Research paper

Effect of anion addition on the syntheses of Ca–Al layered double hydroxide via a two-step mechanochemical process

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ABSTRACT

A pure phase of Ca–Al–X (X = CO₃²⁻ or Cl⁻) layered double hydroxide (LDH) was synthesized via a two-step solvent-free mechanochemical process. Milling Ca and Al hydroxides only gave katoite as the main phase in the product. Further addition of carbonate or chloride during milling operation allowed easy formation of Ca–Al–X LDH. The as-prepared samples were characterized by X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FT-IR), thermogravimetry (TG), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). The characterization results confirmed the formation of highly crystalline Ca–Al LDH phase. The idea to add a third phase to help stabilize desired compound as LDH in this work may be of help for the synthesis of other substance in general.

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1. Introduction

Layered double hydroxides (LDH), also known as anionic clays or hydrocalcite-like compounds represented as $[M_1^{2+}_x M_2^{3+}_x (\text{OH})_2]^{x+} (\text{A}^-)_{x/n} \cdot m\text{H}_2\text{O}$, have been widely used in environmental protection (Martino et al., 2013), pharmaceutical preparation (Rives et al., 2014), organic synthesis (French et al., 2010), elastomer doping (Basu et al., 2013), etc. Ca–Al LDH, also called hydrocalumite, was first introduced as AFm phases in the chemistry of cement and can be represented as $[\text{Ca}_2\text{Al}(\text{OH})_6(\text{X})_{(x)} \cdot y\text{H}_2\text{O}]$, in which X can be substituted by OH⁻, Cl⁻, NO₃⁻, CO₃²⁻, SO₄²⁻ or Al(OH)₄⁻ (Renaudin et al., 1999). Ca–Al LDH with various anions have been used in environmental protection (Zhou et al., 2011; Qian et al., 2012; Rojas, 2014; Qiu et al., 2015), organic synthesis (Zheng et al., 2015) and as functional materials (Mora et al., 2011; Zhang et al., 2011). The structure or structure change of the Ca–Al LDH in the chemistry of cement has been understood clearly and more attention was paid for the synthesis and the exploitations of its properties and potential applications. Since formation of Ca–Al LDH phase from cement needed a reaction time more than a month, various methods have been developed instead. Rojas (2014) synthesized Ca–Al–NO₃ LDH by a co-precipitation method and used it for the removal of heavy metal. Pérez-Barrado et al. (2013) used microwave irradiation to synthesize hydrocalumite and found that the use of microwaves help the crystalline growth of hydrocalumite. Pérez-Barrado et al. (2015) conducted a work with the focus on the reconstruction and delamination of Ca–Al LDH

using ultrasound and obtained smaller lamella size LDH particles. Ca–Al–Cl LDH, also known as Friedel's salt or Ca–Al–Cl LDH, was first introduced in the chemistry of cement which belongs to the family of LDH and can be used in environmental protection (Li et al., 2013) or organic synthesis catalyst (Cota et al., 2010). Various solution ways have been used to synthesize Ca–Al–Cl LDH, such as co-precipitation (Grover et al., 2010), microwave and ultrasound irradiations (Granados-Reyes et al., 2014), which have disadvantages in energy consumption and environmental pollution.

Tongamp et al. (2007, 2008) offered a solvent-free mechanochemical way for the synthesis of Mg–Al LDH. Extensions to new kinds of LDH such as Ca–Sn (Ferencz et al., 2014), Li–Al (Qu et al., 2016) LDH by this method were reported (Qu et al., 2015). Just recently, Ferencz et al. (2015) reported their synthesis of Ca–Al–CO₃ LDH, using calcium hydroxide (Ca(OH)₂) and aluminum hydroxide (Al(OH)₃) as raw materials, by a two-step mechanochemical process with 15.6 wt.% katoite and 84.4 wt.% Ca–Al–CO₃ LDH in the final product. Previous studies in chemistry of cement have confirmed that Ca–Al LDH was initially formed as a metastable compound and converted to cubic katoite (Ca₃Al₂(OH)₁₂), which was the most stable calcium aluminate hydrate, during concrete curing (Scrivener and Pratt, 1984; Taylor, 1997; Plank et al., 2010; Wang et al., 2015). Co-grinding of Ca(OH)₂ and Al(OH)₃ could easily give katoite with no LDH phases (Kano et al., 1998; Kim and Saito, 1998). Our preliminary test indicated clearly that milling the hydroxides only gave katoite but no LDH phase.

The binary Ca–Al phase differs from the Mg–Al phase from which pure hydroxide phase as meixnerite (Mg–Al–OH) type layered double hydroxide was easily synthesized by the two-step mechanochemical

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operation. There is a need to clarify the relationship between katoite and Ca–Al LDH and to search for the necessary conditions for the synthesis of each, particularly via the mechanochemical route. During our work on the mechanochemical synthesis of Ca–Al LDH, it was found that the addition of a third phase to Ca and Al hydroxides allowed the easy formation of stable Ca–Al LDH phases. For example, Ca chloride and carbonate additions led to formation of pure phase of Ca–Al–X ($X = \text{CO}_3^{2-}$ and Cl^-) by the two-step mechanochemical process, serving as the necessary conditions for the synthesis of Ca–Al LDH. The fundamental results obtained are reported in this paper.

2. Experimental procedure

2.1. Materials and methods

$\text{Ca}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, calcium carbonate (CaCO_3), and calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) (Sinopharm Group Co Ltd., Shanghai, Analytical reagent) were used as raw materials with no further purification. Ball-milling operation was conducted by using a planetary ball mill (Pulverisette-7, Fritsch, Germany), which has two mill pots (45 cm³ inner volume each) made of zirconia with 7 zirconia balls of 15 mm in diameter. Rotational speed in this work was kept constant at 600 r/min.

The conditions to synthesize Ca–Al LDH were the same as described by Tongamp et al. (2007) which involved a two-step dry and wet milling operation. In the first dry grinding step, two grams of the mixture of $\text{Ca}(\text{OH})_2$, CaCO_3 and $\text{Al}(\text{OH})_3$ or $\text{Ca}(\text{OH})_2$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$ were milled at molar ratios of 3/1/2, 3.25/0.75/2, 3.75/0.25/2 and 4/0/2, respectively and ground for 2 h. In the second wet grinding step, 0.8 mL water for Ca–Al– CO_3 LDH and 0.4 mL water for Ca–Al–Cl LDH was added into the milled sample for another 1 h milling. The obtained samples were nearly dry powders or in a somewhat caked state and were crushed into powder in a mortar before characterization.

2.2. Characterizations

XRD patterns of samples were recorded on a Rigaku MAX-RB RU-200B diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5403 \text{ \AA}$) to determine their phases and observe changes in phase formations. Microstructures of the prepared sample were observed by SEM (JSM-5610LVJEOL). TG-DSC analyses were performed simultaneously by a thermal analyzer (STA449F3, NETZSCH) in nitrogen gas from 30 °C to 1000 °C at a heating rate of 20 °C/min. FT-IR spectra of the samples were registered on Nicolet 6700, Thermo, using KBr as a diluent over 4000–500 cm^{-1} .

3. Results and discussion

XRD patterns of Ca–Al– CO_3 LDH prepared by a two-step milling operation with different molar ratios are shown in Fig. 1. In the patterns of the reference sample ($\text{Ca}(\text{OH})_2/\text{CaCO}_3/\text{Al}(\text{OH})_3$ at 4/0/1), namely without adding of CaCO_3 , reflection of katoite (JCPDS 24-0217) were observed, which was the main impurity when preparing Ca–Al LDH by milling operation or hydrothermal process (Granados-Reyes et al., 2014; Ferencz et al., 2015). With an increase in the molar ratio of CaCO_3 , the reflection intensities of katoite decreased and those of Ca–Al– CO_3 LDH increased concomitantly. The pattern of sample ($\text{Ca}(\text{OH})_2/\text{CaCO}_3/\text{Al}(\text{OH})_3$ at 3.25/0.75/2) gave a nearly pure phase of Ca–Al– CO_3 LDH with negligible phase of katoite, while that of sample ($\text{Ca}(\text{OH})_2/\text{CaCO}_3/\text{Al}(\text{OH})_3$ at 3/1/2) showed a main phase of Ca–Al– CO_3 LDH with observable existence of remaining CaCO_3 . The presence of CaCO_3 was necessary to obtain a stable phase of Ca–Al LDH to prevent the formation of the katoite phase. Renaudin et al. (1999) prepared a Ca–Al– CO_3 LDH sample by hydrothermal treatment of $\text{Ca}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ and CaCO_3 in a silver capsule under 2 Kbar isotropic pressure and 100 °C for 1 month and obtained a material described by the formula of $\text{Ca}_4\text{Al}_2\text{O}_6\text{CO}_3 \cdot 11\text{H}_2\text{O}$ or $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$ for

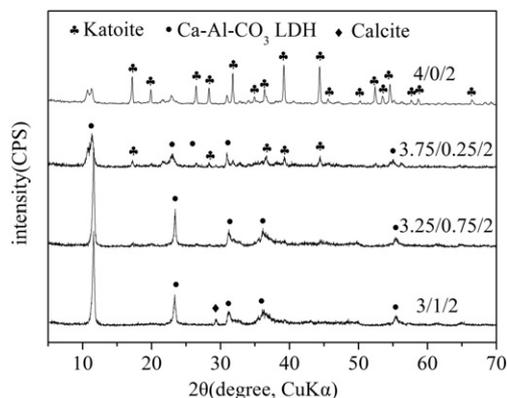


Fig. 1. XRD patterns of Ca–Al– CO_3 LDH prepared by a two-step milling operation with different $\text{Ca}(\text{OH})_2/\text{CaCO}_3/\text{Al}(\text{OH})_3$ molar ratios.

Ca–Al– CO_3 LDH, indicating that one mole CaCO_3 could be incorporated into Ca–Al LDH structure. A small reflection of CaCO_3 was observed here to remain in the sample ($\text{Ca}(\text{OH})_2/\text{CaCO}_3/\text{Al}(\text{OH})_3$ at 3/1/2), suggesting mechanochemical treatment was not easy as hydrothermal one to complete the reaction with all the CaCO_3 incorporated into the structure. Ferencz et al. (2015) conducted a two-step mechanochemical synthesis of Ca–Al– CO_3 LDH, using $\text{Ca}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ and H_2O as raw materials and reported the product with compositions as 15.6 wt.% katoite and 84.4 wt.% Ca–Al– CO_3 LDH when NaOH was used. The carbonate in Ca–Al– CO_3 LDH may come from the ambient air, due to the NaOH addition to absorb CO_2 . Finally, it could be concluded that a third component such as CO_3^{2-} was essential for the synthesis of Ca–Al– CO_3 LDH by mechanochemical approach.

Fig. 2 shows XRD patterns of Ca–Al–Cl LDH prepared by the two-step milling operation with different $\text{Ca}(\text{OH})_2/\text{CaCl}_2 \cdot 2\text{H}_2\text{O}/\text{Al}(\text{OH})_3$ molar ratios at constant 600 r/min. Compared to the reference sample ($\text{Ca}(\text{OH})_2/\text{CaCl}_2 \cdot 2\text{H}_2\text{O}/\text{Al}(\text{OH})_3$ molar ratio of 4:0:2) without $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ addition, where katoite phase was the main one, addition of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in as low as 0.25 M ratio gave well-crystallized Ca–Al–Cl LDH, although the weak reflection of katoite phase were still observable. When the molar ratio of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was increased to 0.75 and 1, a pure phase of Ca–Al–Cl LDH was obtained without observable katoite phase and no differences appeared between XRD patterns of samples at $\text{Ca}(\text{OH})_2/\text{CaCl}_2 \cdot 2\text{H}_2\text{O}/\text{Al}(\text{OH})_3$ ratio of 3.25/0.75/2 and 3/1/2. Compared to the XRD pattern of Ca–Al– CO_3 LDH, it was easy to obtain a pure phase of Ca–Al–Cl LDH, possibly because the reactivity of water soluble $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ might be higher than that of the water-insoluble CaCO_3 and higher stability of Ca–Al–Cl LDH than Ca–Al– CO_3 LDH. A differing pattern such as shoulder reflection around 23° 2θ was observed with Ca–Al–Cl LDH from that of Ca–Al– CO_3 LDH, possibly due to the different layered

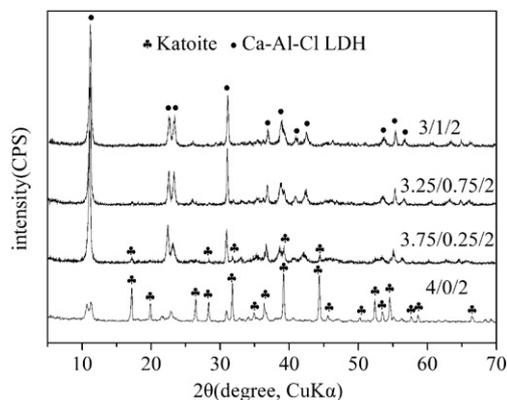


Fig. 2. XRD patterns of Ca–Al–Cl LDH prepared by a two-step milling operation with different $\text{Ca}(\text{OH})_2/\text{CaCl}_2 \cdot 2\text{H}_2\text{O}/\text{Al}(\text{OH})_3$ molar ratios.

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