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Mechano-hydrothermal synthesis of Mg_2Al–NO_3 layered double hydroxides

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ABSTRACT

A mechano-hydrothermal method was developed to synthesize Mg_2Al–NO_3 layered double hydroxide (LDH) from MgO, Al_2O_3 and $NaNO_3$ as starting materials. A two-step synthesis was conducted, that is, a mixture of MgO and Al_2O_3 was milled for 1 h, followed by hydrothermal treatment with $NaNO_3$ solution. The resulting LDHs were characterized by X-ray diffraction, transmission electron microscopy, scanning electron microscopy, Fourier transform infrared and elemental analyses. Pre-milling played a key role in the LDH formation during subsequent hydrothermal treatment. The process is advantageous in terms of low reaction temperature and short reaction time compared with the conventional hydrothermal method, and the target products are of high crystallinity, good dispersion and regular shape compared with the conventional mechanochemical method.

1. Introduction

Layered double hydroxides (LDHs) [1], also known as hydrotalcite-like compounds or anionic clays, are a family of layered materials with general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^{n-}_{x/n}]^{x-}\bullet mH_2O$, where M^{II} and M^{III} are di- and trivalent metal cations, respectively, A^{n-} are interlayer anions (or galley anions) of charge n, x is the molar ratio of $M^{III}/(M^{II}+M^{III})$ and m is the molar amount of co-intercalated water. Structurally, they consist of positively charged layers of mixed metal hydroxides that require the presence of interlayer anions to maintain overall charge neutrality. A major advantage of LDHs as functional materials or their precursors is that their composition is flexible [1]: the identity of the di- and trivalent metal ions, their atomic ratio, and the nature of the interlayer anion can be varied over a wide range without altering the basic structure of the material. As a result, LDHs have potential applications in diverse areas, such as catalysts or catalyst precursors, anion exchangers, flame retardants, stabilizers for polymers, and electroactive and photoactive materials, as well as in the medical field as antacids and for controlled release [1]. Therefore, much work has focused on synthesizing LDH materials using various methods, including the coprecipitation [1–5], hydrothermal [6–8], solvothermal [9], mechanochemical [10–16], microemulsion [17], urea [18] and reconstruction [19] methods.

Among the above methods, coprecipitation is the most common. However, a significant disadvantage of this conventional method is that large amounts of waste are produced [12,14]. Therefore, the mechanochemical method has gained considerable attention [10–16]. Advantages of this method include its simplicity and atomic economy, however, resultant LDH samples have low crystallinity and irregular aggregate shapes which limits their applications to a great extent. The hydrothermal method [6–8] is also a common preparation route of LDH materials. It yields well-crystallized and well-dispersed LDH particles with well-defined hexagonal shapes but is time consuming with high reaction temperature.

Herein, a new mechano-hydrothermal method to synthesize Mg–Al–NO_3 LDH from MgO, Al_2O_3 and $NaNO_3$ as starting materials is described. A pre-milling process was combined with a hydrothermal treatment, to obtain highly crystallized and well-dispersed LDH particles in a short time and using a mild process.

2. Experimental

2.1. Preparation of Mg_2Al–NO_3 LDH

All chemicals used were of analytical grade. Water was purified with a Hitech-Kflow water purification system (China). MgO and Al_2O_3 were prepared by calcining $Mg(NO_3)_2\bullet 6H_2O$ and $Al(OH)_3$, respectively, at 550 °C for 3.5 h in air with reference to Xu and Lu [7].

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A mechano-hydrothermal method was used to synthesize LDHs *via* a two-step process. In the first-step, 4.0 g (0.100 mol) MgO and 2.5 g (0.025 mol) Al_2O_3 was milled for 1 h under ambient conditions in air using a planetary ball mill (QM3STC, Nanjing Nanda Instrument Plant, China) with four stainless-steel mill pots (500 cm^3 inner volume each) and 10 mm diameter steel-balls. The mill speed was constant at 450 rpm with a ball/mixture mass ratio of approximately 49. In the second-step, 0.3 g of the milled mixture of MgO and Al_2O_3 was placed in a 50 mL Teflon-lined stainless-steel autoclave with 30 mL of 0.078 mol/L $NaNO_3$ solution. After the vessel had been sealed and shaken thoroughly, it was placed in an oven under static conditions and treated hydrothermally at the design temperature (T_{ht}) for a designed time interval (t_{ht}). The product thus obtained was collected after centrifugation, washed with water and dried at 60 °C.

Hydrothermal and mechanical treatments alone for mixtures of MgO, Al_2O_3 and $NaNO_3$ solution were carried out as references.

Furthermore, the mechanochemical method was used to synthesize the LDH by a two-step milling operation [11,13,16]. A mixture of 4.0 g (0.10 mol) MgO and 3.0 g (0.03 mol) Al_2O_3 was pre-milled for 1 h, followed by milling with 5.1 g (0.02 mol) $Mg(NO_3)_2$•$6H_2O$ for a further 5.0 h. The product thus obtained was washed with water and dried at 60 °C.

2.2. Characterization

X-ray diffraction (XRD) patterns of the prepared samples were recorded on a D/max-rA model diffractometer with Cu Kα radiation (λ = 1.5418 Å) at 40 kV and 40 mA in the 2θ range of 10–70° with a scanning rate of 0.08°/min. Sample morphology was analyzed by scanning electron microscopy (SEM) using a JEOL JSM-6700F model field emission-scanning electron microscope and transmission electron microscopy (TEM) using a JEOL JEM-2100 transmission electron microscope. Fourier transform infrared spectroscopy (FT-IR) spectra of the samples were collected using KBr pellets on a Bruker Vector-22 Fourier transformation infrared spectroscope in reflectance mode, from 400 to 4000 cm^{-1}, with a resolution of 2 cm^{-1}. The C, H and N contents of the samples were determined using a Vario EI III cube V2.0.1 elemental analyzer. The Mg and Al contents of the samples were determined by inductively coupled plasma atomic emission (ICP-AE) spectroscopy (Jarrel-ASH, ICAP-9000) after the samples had been dissolved in a dilute acid. The zeta potential was measured using a DXD-II microelectrophoresis instrument with flow-through sample cell. The particle size distribution (volume basis) was measured with a SALD-7100 laser scattering particle size analyzer.

3. Results and discussion

3.1. Powder XRD analysis

Powder XRD examination of the pre-milled mixture of MgO and Al_2O_3 without hydrothermal treatment showed that no LDH-phase was produced and the crystallinities of both the MgO and Al_2O_3 did not decrease visibly by the pre-milling process, as only characteristic reflections of the two starting materials were visible in its XRD patterns (Fig. S1 in the Supporting Information). Fig. 1 shows the powder XRD patterns of the samples obtained by the mechano-hydrothermal method with a T_{ht} of 80 °C for different t_{ht}. After hydrothermal treatment for 1 h, strong characteristic peaks of MgO also remained in the product. However, the very weak characteristic diffraction peaks of the LDH-phase could be observed, and the d_{003} value was 0.88 nm, which is close to the reported value for Mg–Al–NO_3 LDHs [20]. This indicates the formation of a Mg–Al–NO_3 LDH phase. The peak intensities of Al_2O_3 were much lower than those of MgO (Fig. S1 in the Supporting Information), so the reflection peaks of Al_2O_3 could not be observed clearly in Fig. 1. With an increase in t_{ht}, the MgO peak intensities decreased while those of the LDH-phase increased, showing that the ratio of starting materials transforming to the LDH-phase increases. When the t_{ht} was prolonged to 6 h, the characteristic MgO reflections disappeared, showing that the two starting materials reacted completely. Moreover, the resultant LDH sample presented all the characteristic peaks of hydrotalcite (JCPDS card no. 51-1528), indicating the LDH sample was crystalline. It is worth noting that the brucite phase ($Mg(OH)_2$) was not detected in the synthesis.

The effect of T_{ht} on crystallinity of the target LDH product was examined at a constant t_{ht} of 6 h, with results shown in Fig. 2. At T_{ht} = 60 °C, characteristic peaks of the LDH-phase appeared, showing that the LDH-phase can form. However, characteristic peaks of MgO also remained in the product, that is, the starting materials did not react completely. For a T_{ht} above 80 °C, the characteristic MgO peaks disappeared, showing complete conversion of the starting materials to the LDH-phase. Moreover, with an increase of T_{ht} from 60 to 120 °C, the characteristic peak intensities of the resultant LDH products increased, that is, the LDH sample crystallinity increased. In addition, it is worth noting that the characteristic peaks of $Mg(OH)_2$ were not visible for all LDH samples obtained under various T_{ht}.

Powder XRD patterns of products obtained by hydrothermal treatment alone for the mixture of MgO, Al_2O_3 and $NaNO_3$ solution as starting materials are shown in Fig. 3. After 24 and 48 h of hydrothermal treatment alone, the characteristic diffraction peaks

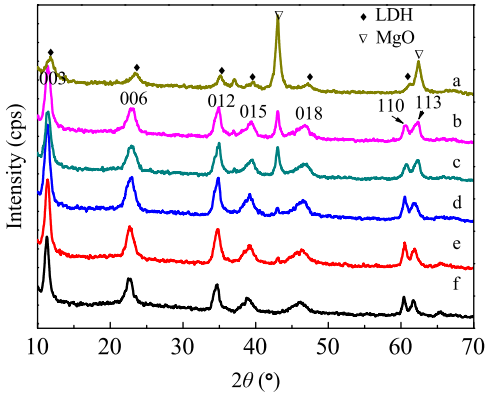

Fig. 1. XRD patterns of samples obtained by mechano-hydrothermal method with hydrothermal treatment at 80 °C for (a) 1.0, (b) 1.5, (c) 2.0, (d) 2.5, (e) 3.0 and (f) 6.0 h.

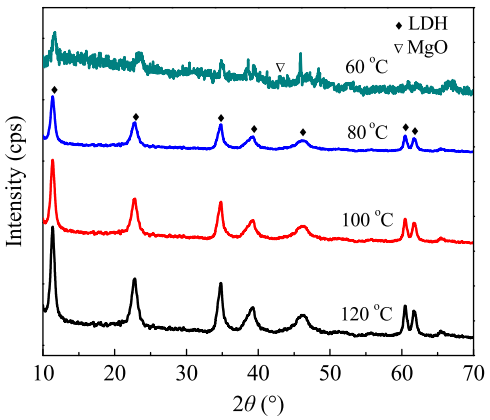

Fig. 2. XRD patterns of products synthesized by mechano-hydrothermal method under various hydrothermal temperatures for 6 h.