

Structural and morphological characterization of $\text{Mg}_{0.8}\text{Al}_{0.2}(\text{OH})_2\text{Cl}_{0.2}$ hydrotalcite produced by mechanochemistry method

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ABSTRACT

Chlorine intercalated Mg–Al layered double hydroxides (Mg–Al–Cl–LDH) with a chemical formula $\text{Mg}_{0.8}\text{Al}_{0.2}(\text{OH})_2\text{Cl}_{0.2}$ were successfully produced by the one-step mechanochemistry method and subsequent water washing followed by drying in oven for 1 h at 80 °C. The samples were characterized by X-ray diffraction (XRD), Fourier Transform Infrared spectroscopy (FT–IR), field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS), elemental mapping analysis, transmission electron microscopy (TEM), X-ray fluorescence (XRF), and the differential thermogravimetric analysis (DTGA). Results revealed that the structural characteristics of Mg–Al–Cl–LDH were affected strongly by milling time. At the beginning of milling (up to 1 h), Hydrotalcite (HT) and Brucite were the dominant phases, while the progressive mechanical activation was completed as milling time increased, which resulted in the formation of nanostructured Mg–Al–Cl–LDH. Based on XRD and FTIR data, $\text{Mg}_{0.8}\text{Al}_{0.2}(\text{OH})_2\text{Cl}_{0.2}$ with high purity was obtained at 5 h milling. The interlayer spacing of LDH is also strongly influenced by milling time so that it escalated from 7.737 ± 0.001 to 8.005 ± 0.002 (1–15 h) and then decreased to 7.937 ± 0.001 for 20 h milled sample. Electron microscopic observation displayed that the final product had hexagonal platelet structure with lateral dimension of 20–100 nm. Therefore, the synthesis of $\text{Mg}_{0.8}\text{Al}_{0.2}(\text{OH})_2\text{Cl}_{0.2}$ via mechanochemistry owing to simplicity and versatility can be a promising candidate for use in catalyst carriers, drug delivery, and gene delivery.

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1. Introduction

Hydrotalcites (HTs) with layered double hydroxides (LDH) structure are anionic clays, which may collapse at temperatures between 200–400 °C owing to dehydration, dehydroxylation, and decarboxylation [1]. HTs have basic properties whose chemical formula is $\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2 \text{A}^n_{x/n-}$, where A^n- represents the charge balancing anions such as CO_3^{2-} , Cl^- , SO_4^{2-} , OH^- or NO_3^- [2]. Among those compensating anions, the carbonate ion is easily trapped in LDH as soon as exposed to air and moisture. This form of HTs is usually utilized as CO_2 absorbents, ion exchangers, fire retardants, and base catalyst [3]. HTs layer structure can be modified by substitution of other anions like Cl^- (Mg–Al–Cl–LDH) for

their biological significance [4]. Generally, Mg–Al–Cl–LDH possesses versatile properties for gene delivery, comprising rich functionality, extensive availability, good biocompatibility, controlled release of carried gene, and potential capability of target delivery [5]. This type of HTs can then be entirely decomposed by acidic body fluid and releases the adsorbed drug or gene after they reach the delivery point [6].

In past decade, many different chemical methods have been applied for fabrication of HTs. These methods include co-precipitation at different pH [7], hydrolysis [8], sol–gel [9], Microwave-assisted structure reconstruction [10], hydrothermal [11], sonication [12] and mechanical alloying (MA) [13]. Among various processes, mechanical alloying has recently been receiving particular attention as an alternative method to prepare commercially nanostructured materials with proper structural characteristics due to its simplicity and versatility [14]. In this process, melting is not necessarily occur and a homogenous product with nanostructural features is produced from blended reagents mixture [15]. In terms of environmental and topochemical viewpoints, the reactions between solid reactants without a solvent are essential and

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the large amounts of solutions can be eliminated, and also noxious gases emissions and the release of wastewater can be avoided employing MA method [16]. Hence, when the mass production of LDH is required, MA method can be used.

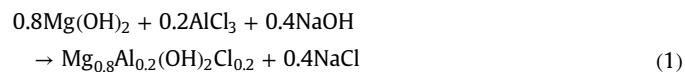
A number of experiments have been reported involving the intercalation of different anions into the interlayer LDH via MA method. Isupov et al. [17] reported the formation of Mg–Al–LDHs by mixing magnesium hydroxide with aluminum nitrate, sulfate, and chloride in high energy ball mill. A similar process was reported by Khusnutdinov et al. [13] to obtain hydroxycarbonate form of HT-like via MA process. The synthesis of Zn–Al–LDHs through grinding and followed by autoclaving the solid precursors at 150 °C for 1 day was investigated by Chitrakar et al. [18].

In this paper, considering the above characteristics of Mg–Al–Cl–LDH, chlorine intercalated Mg–Al layered double hydroxides ($\text{Mg}_{0.8}\text{Al}_{0.2}(\text{OH})_2\text{Cl}_{0.2}$) is expected to be a better LDH for exchanging with biomolecules such as DNA as compared to conventional HTs. However, no specific documentation has been demonstrated on $\text{Mg}_{0.8}\text{Al}_{0.2}(\text{OH})_2\text{Cl}_{0.2}$ using mechanochemical activation so far. Therefore, the present work aims at investigating the synthesis of $\text{Mg}_{0.8}\text{Al}_{0.2}(\text{OH})_2\text{Cl}_{0.2}$ using one step mechanochemical process as a simple, efficient, and inexpensive method. Furthermore, phase behavior of the system, and structural features including crystallite size, lattice strain, crystallinity degree, interlayer spacing, unit cell volume of lattice as well as morphological properties of products are investigated through XRD, FT-IR, FES-EM, EDS, Elemental mapping analysis, XRF, TEM, and DTGA techniques.

2. Experimental procedures

2.1. Synthesis of Mg–Al–Cl–LDH

Magnesium hydroxide (95%, Sigma-Aldrich), Aluminum chloride (99%, ACROS), and Sodium hydroxide pellets (97%, ACROS) were purchased and used as received. To synthesize $\text{Mg}_{0.8}\text{Al}_{0.2}(\text{OH})_2\text{Cl}_{0.2}$, the desired amounts of $\text{Mg}(\text{OH})_2$, AlCl_3 , and NaOH were milled at different milling times (1, 3, 5, 10, 15, and 20 h) in a high energy ball mill (8000 M Mixer/Mill) using hardened chromium steel vials (vol. 65 ml) under air atmosphere. The weight ratio of ball-to-powder (BPR) was 10:1. The mole ratio of magnesium to aluminum was equal 5. The powders were washed three times with deionized water (20 ml) on a paper filter, and then were aged under lab oven at 80 °C for 1 h. The target composition was adjusted according to the following reaction (1):



2.2. Characterization techniques

Phase identification was carried out on a Bruker D8 Advance ECO using $\text{Cu-K}\alpha$ radiation ($\lambda \approx 1.54 \text{ \AA}$). The patterns were scanned from 5 to 80 degrees 2θ at a step size of 0.03 degrees. The XRD profiles were compared to standards compiled by the Joint Committee on Powder Diffraction and Standards (JCPDS), which involved card #14-0191 for Hydrotalcite, #44-1482 for Brucite and #05-0628 for Halite. The crystallite size and lattice strain of the products were calculated by the Williamson-Hall equation (2) [19]:

$$B \cos \theta = \frac{0.9\lambda}{D} + \eta \sin \theta \quad (2)$$

where λ is the X-ray wavelength (0.154056 nm), D is the crystallite size, η is the internal micro-strain, θ is the Bragg angle (°), and B is the

peak width (in radians). The values of η and D were obtained by plotting $B \cos \theta$ versus $\sin \theta$, where η represents the slope and $0.9 \lambda / D$ the intercept of the line. Based on equation (3), the crystallinity degree (X_c) was obtained by taking the sum total of relative intensities of individual characteristic peaks [20]:

$$X_c = \frac{\text{SUM}(I_1 : I_n)_{\text{HT}}}{\text{SUM}(I_1 : I_n)_{\text{Standards}}} \times 100 \quad (3)$$

where $I_1 : I_n$ is the total of relative intensities of characteristic peaks of HT for both the synthesized powders and standard.

The interlayer spacing (d) can be calculated by averaging the basal peaks according to the equation (4) [21]:

$$d = \frac{1}{n} (d_{(003)} + 2d_{(006)} + \dots + nd_{(00n)}) \quad (4)$$

The lattice parameters (a , and c) can be determined for (003) and (110) Miller's planes from the following relation (5):

$$\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \quad (5)$$

where h , k , and l are the Miller indices. The unit cell volume (6) of samples was also calculated using the following equation [20]:

$$V = (a^2 c) \sin 60^\circ \quad (6)$$

The functional groups and structural changes of the samples were carried out by Fourier transform infrared spectroscopy (FT-IR, Bruker Tensor 27, USA). All spectra were recorded at ambient temperature in the range $4000\text{--}400 \text{ cm}^{-1}$. The morphological features of the milled specimens were characterized using FE-SEM (FEI Helios Nanolab 400 SEM). A more detailed morphological analysis was also executed using TEM (JEOL JEM 1200 EXII) that operated at the acceleration voltage of 120 kV. EDS and elemental mapping analysis attached to the FESEM was used to determine the elemental composition and distribution of components. The elemental analysis of HT was tested using the Supermini 200 (Rigaku) X-ray fluorescence (XRF) analyzer. Thermal analysis was performed with a TGA (TA Q50 Thermogravimetric Analyzer) during heating in an argon atmosphere at a rate of $10 \text{ }^\circ\text{C/min}$ from room temperature to $800 \text{ }^\circ\text{C}$.

3. Results and discussions

3.1. XRD analysis

The x-ray diffraction patterns for all different milling times runs (1–20 h) before and after washing followed by drying can be seen in Fig. 1. Based on Fig. 1a, the main products of mechanical activation were sodium chloride, Brucite and HT for all the samples. The presence of Brucite after 1 h milling indicates mechanochemical reaction was not completed, while it almost disappeared with increasing of milling time up to 5 h. Fig. 1b shows the XRD profiles of the samples after washing and drying at $80 \text{ }^\circ\text{C}$ for 1 h. The X-ray profile of the 1 h milled sample exhibits the most intense peaks of Brucite and HT, but the peaks corresponding to the sodium chloride vanished entirely. This trend continued for the 3 h milled specimen with considerable changes in intensity of peaks so that the intensity of HT peaks increased, and conversely Brucite ones declined. It shows that the milling time was not enough to have pure HT and some Brucite was still remaining in this sample. In the XRD pattern of the 5 h milled sample, an obvious phase evolution occurred and as a result, a pure phase composition indicating HT was formed. Further increase in the milling time up to 20 h led to further sharpening of the major diffraction peaks and growth in crystalline order of the HT phase with a partial trace

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