A mechanochemical approach to get stunningly uniform particles of magnesium–aluminum-layered double hydroxides

Xiaqing Zhang, Fenglin Qi, Shuping Li*, Shaohua Wei, Jiahong Zhou

Jiangsu Key Laboratory of Biofunctional Material, College of Chemistry and Material Science, Nanjing Normal University, Nanjing 210097, China

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A mechanochemical approach is developed in preparing a series of magnesium–aluminum-layered double hydroxides (Mg–Al-LDHs). This approach includes a mechanochemical process which involved manual grinding of solid salts in an agate mortar and afterwards peptization process. In order to verify the LDHs structure synthesized in the grinding process, X-ray diffraction (XRD) patterns, transmission electron microscopy (TEM) photos and thermogravimetry/differential scanning calorimetry (TG–DSC) property of the product without peptization were characterized and the results show that amorphous particles with low crystallinity and poor thermal stability are obtained, and the effect of peptization is to improve the properties, more accurately, regular particles with high crystallinity and good thermal stability can be gained after peptization. Furthermore, the fundamental experimental parameters including grinding time, the molar ratio of Mg to Al element (defined as R value) and the water content were systematically examined in order to control the size and morphologies of LDHs particles, regular hexagonal particles or the spherical nanostructures can be efficiently obtained and the particle sizes were controlled in the range of 52–130 nm by carefully adjusting these parameters. At last, stunningly uniform Mg–Al-LDHs particles can be synthesized under proper R values, suitable grinding time and high degree of supersaturation.

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1. Introduction

Layered double hydroxides (LDHs) are a class of anionic clays which can be represented by the general formula of $\left[\text{M}^{2+}_{x} \text{M}^{3+}_{1-x} \text{O} (\text{OH})_{2}\right]^{x} \text{A}^{x} \cdot (\text{m} + \frac{x}{2}) \text{H}_2\text{O}$, in which $\text{M}^{3+}$ and $\text{M}^{2+}$ are trivalent and divalent metal ions, respectively [1,2]. LDHs are the only known inorganic materials with positively charged layers and the interlayer anions, especially these anions can be replaced through ion-exchange processes, and regular stacks of octahedral sheets build up the structural units of LDHs. The net positive charge on the layers, which is due to substitution of divalent ions with trivalent ones in the brucite-like metal hydroxide $\text{M(OH)}_2$, is balanced by the negative charge from the interlayer anions. The layered structure is also stabilized by hydrogen bonds among the interlayer water molecules, anions and as well as by electrostatic interactions between the layers and the anions [3].

Thanks to the layered structure and anion exchange capacity, LDHs can be found useful in various applications, such as catalysts, catalysts supports, ion exchangers, filters, decolorizing agents, industrial adsorbents, polymer stabilizers, optical hosts, rheological modifiers and so on [4]. There are a large number of synthesis methods to prepare LDHs, for example co-precipitation [5], reconstruction [6], calcination rehydration [7], sol–gel method etc. But these methods are time-consuming and even worse produce a large amount of wastes. Thus, the search for proper methods that allows the simple preparation and less pollution to the environment attracts the attention of the researchers. Mechanochemical method has been known for a long time and it induces the transformation by milling or manually grinding the solid salts. It is believed as a promising alternative one due to its simplicity and environmentally friendly [8].

It was reported lately that a solvent-free procedure to synthesize Zn–Al-LDHs by first grinding and then autoclaving ZnO and AlCl$_3$·6H$_2$O at 150 °C [9]. Khusnutdinov et al. used Mg(OH)$_2$, Al(OH)$_3$ and NaHCO$_3$ as precursors to prepare Mg–Al-LDHs by solid state reactions [10]. Tongamp et al. obtained LDHs by milling anhydrous Mg(OH)$_2$ and Al(OH)$_3$ for 1 h in a planetary ball mill and then milling again in the presence of water [11]. However, the as-prepared LDHs are usually loose powders of irregular aggregates which render most of the applications restricted [9–12]. Relevant research results showed that the degree of crystallinity and its morphology can greatly affect the potential applications of LDHs [13]. Thus synthesis of LDHs with high crystallinity and well-defined...
shapes by mechanochemical approach would certainly enhance their possibilities for practical applications [14]. Herein, we report a simple way to synthesize high crystallinity, homogenous and regular LDHs particles by mechanochemical method. In detail, this method involved manual grinding of the solid salts and afterwards peptization process. Furthermore we also emphatically discussed the influence of grinding time, R values and water content on their properties.

2. Experimental

2.1. Materials

Mg–Al–LDHs were synthesized by the mechanochemical method which includes grinding and peptization process. All chemicals – Mg(NO$_3$)$_2$·6H$_2$O (Guangdong Xilong Chemical Co.), Al(NO$_3$)$_3$·9H$_2$O (ShangHai Sinpeuo Fine Chemical Co.), NaOH (Guangdong Xilong Chemical Co.) and Na$_2$CO$_3$ (YangZhou HuBao Chemical Reagents) – were used as received and the reagents used in this experiment were analytically grade.

2.2. Synthesis of Mg–Al–LDHs

A typical synthesis process is described as follows: 0.025 mol Na$_2$CO$_3$ and 0.005 mol NaOH were manually ground for 5 min. Subsequently, 0.01 mol Al(NO$_3$)$_3$·9H$_2$O and given molar proportion Mg(NO$_3$)$_2$·6H$_2$O powder were added into the mixture, which were also ground at room temperature. After a period of grinding, the final powder was washed with distilled water five times to remove the unwanted electrolytes. At last, the suspension was peptized at 80°C for 24 h.

LDHs obtained by mechanochemical method were prepared by altering the molar ratio between Mg and Al (noted as R), the grinding and water content, respectively. In fact, Mg(NO$_3$)$_2$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O were mixed with different R values such as 2:1, 3:1 and 4:1, meanwhile, the grinding time was fixed as 60 min and no water adding; and the mixture was ground at room temperature for 30, 60 and 90 min while the R value was fixed as 3:1 and no water adding; the solid mixture was ground at different water content such as 0%, 2% and 8% mass fraction while R value was 3:1 and grinding time was equal to 60 min.

2.3. Characterization

The X-ray diffraction (XRD) patterns were obtained with a D/max-2500PC rotating anode X-ray powder diffractometer (Rigaku Co.), using Cu Kα radiation (λ = 1.5406Å) from 3° to 70° at a scanning rate of 1°/min. TEM images were obtained by a H-7650-HITACHI (Hitachi Medical Co.,) machine operating at 200 kV, samples for TEM were prepared by depositing a drop of sample solution onto a carbon-coated copper grid. The excess liquid was wicked away with filter paper, and the grid was dried in air. A model J-A1100 (Jarrell-Ash Co. USA) inductively coupled plasma (ICP) atomic emission spectrometer was employed for metal element analysis. The LDHs samples were characterized by their particle size distribution using Sirion 200 (FEI Co., Holland) Scanning Electron Microscopy (SEM) machine. Zeta potentials were obtained by the Zetasizer 3000 system (Malvern Instruments Ltd., England) with pH value of LDHs suspension being 9.5 ± 0.1 and the weight percentage of 0.1%. Thermogravimetric/Differential Scanning Calorimetry (TG–DSC) was measured on a STA-449C (Netzsch Co.) machine with a heating rate of 10°C/min in N$_2$ atmosphere.

3. Results and discussion

3.1. Structure of LDHs synthesized in the grinding process

In order to verify the structure synthesized in the grinding process, the sample without peptization which was obtained under the condition of R = 3:1, grinding time 60 min was chosen for characterization. More exactly, the selected sample was washed for five times with distilled water in the end of grinding, which directly formed the suspension of sample a. To compare, the corresponding sample after peptization at 80°C for 12 h was noted as sample b as well.

The influence of peptization process on the structure and morphologies of samples has been studied by XRD, TEM and TG–DSC. The concerned results of sample a and b are shown in Fig. 1. From XRD results, the diffraction peaks of two samples can be indexed to a hexagonal lattice with R–3m rhombohedra symmetry, commonly used for the description of LDHs structures [15], the basal reflections from (003) are indicative of LDH–CO$_3$ formation with an interlayer spacing of 0.78 nm. Moreover, the two curves are both consistent with the JCPDS X-ray diffraction file No.22-0700 [16], suggesting that both samples have the hydrotalcite sheet-like structure. It is known that for the same crystal phase, the sharpness and intensity of XRD peaks are proportional to their crystallinity [17]. Indeed, as we can see from Fig. 1A, the XRD peaks become sharper and the intensity increases remarkably after the peptization, indicating that the products crystalize much better via the peptization process. The morphology of LDHs obtained without peptization is amorphous (Fig. 1B), which is accordant with the report of other researchers [16]. LDHs material with high crystallinity and regular hexagonal plates can be formed through peptization process. The TG–DSC results are also shown in Fig. 1C. As a matter of fact for LDHs, the weight loss occurs essentially in two steps [18]. The first one, from room temperature up to ca. 230°C, corresponds to the removal of water physisorbed on the external surface of the crystallites as well as the water intercalated in the interlayer galleries. And it corresponds to about 20% of the total weight. There is a weak endothermic event in DSC of sample a at around 178°C, whereas for sample b, it is near 215°C. The second weight loss for LDHs involves dehydroxylation of the layers and loss of CO$_3$ [19]. Meanwhile, it presents a corresponding endothermic event in the DSC of sample b at around 385°C, certainly this value is higher than that of sample a (364°C). It reveals that the electrostatic attraction between the layers is becoming stronger after the peptization. Consequently, the removal of interlayer water molecules and CO$_3^{2–}$ ions becomes more difficult than before. In addition, the zeta potential measurements also showed that the increment of zeta potentials after the peptization (see Table 1), which meant the higher layer charge of sample b. Chemical compositions of a and b are shown in Table 1. Element N cannot be detected in sample b, on the contrary, trace N can be found in sample a. This indicates that NO$_3$– anions in the interlayer can be exchanged by CO$_3^{2–}$ completely via peptization process, which is due to LDHs that have a very strong affinity for carbonate anions.

The results of the above analysis clearly indicate that Mg–Al–LDHs material with high crystallinity, well-developed hexagonal shapes and high stability could be obtained after peptization. Furthermore, the peptization process probably plays a critical role in the formation of Mg–Al–LDHs with high crystallinity hexagons Table 2.

3.2. Effect of R values on the properties of LDHs

The effect of M$^{2+}$/M$^{3+}$ ratio (R values) on the structure and morphology of Mg–Al–LDHs has been also investigated. There are certain effects of R values on the structures and morphologies
Fig. 1. (A) XRD patterns of LDHs. (B) TEM images and the corresponding particle size distribution histograms of LDHs. (C) TG–DSC curves for LDHs: a, without peptization; b, with peptization.

Table 1
Composition, zeta potential and relevant data of LDHs sample a and b.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>M$^{2+}$ a (%)</th>
<th>M$^{3+}$ a (%)</th>
<th>C$_b$ (%)</th>
<th>N$_b$ (%)</th>
<th>Basal spacing (nm)</th>
<th>Zeta potential (mV)</th>
<th>Mean particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>21.4</td>
<td>7.7</td>
<td>4.1</td>
<td>1.4</td>
<td>0.779</td>
<td>+19.36</td>
<td>34.1</td>
</tr>
<tr>
<td>b</td>
<td>18.2</td>
<td>6.5</td>
<td>3.2</td>
<td>Nd</td>
<td>0.780</td>
<td>+35.19</td>
<td>125.4</td>
</tr>
</tbody>
</table>

a: molar percent; b: weight percent; Nd: not detected

of the given systems (Fig. 2). As shown in Fig. 2A, a layered structure with high crystallinity and a basal spacing of 0.781 nm was obtained when $R = 2:1$, and forming a roughly monodispersed suspension, the particles are well-defined hexagons with size distribution between 60 and 140 nm. As $R = 3:1$, it has been found that the LDHs have the highest crystallinity, meanwhile, the particles became thicker and larger than the one of $R = 2:1$. Those well-developed hexagonal plates with the size ranging from 80 to 200 nm, formed a very homogenous suspension. Nevertheless, when the $R$ value further increased to 4:1, the crystallinity of LDHs was turning to decrease. In addition, a morphology transformation from regular hexagonal shape to sphere and coagulated one could be observed from Fig. 2B. In fact, the chemical analysis revealed that the experimental M$^{2+}$/M$^{3+}$ values are higher than the expected

Table 2
Relevant key data of Mg-Al-LDHs by mechanochemical approach.

<table>
<thead>
<tr>
<th>$R$ value</th>
<th>Grinding time (min)</th>
<th>Water content (%)</th>
<th>Basal spacing (nm)</th>
<th>Mean particle size (nm)</th>
<th>Zeta potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>2.15:1</td>
<td>60</td>
<td>0</td>
<td>0.781</td>
<td>96.1</td>
</tr>
<tr>
<td>3:1</td>
<td>3.15:1</td>
<td>60</td>
<td>0</td>
<td>0.780</td>
<td>130.3</td>
</tr>
<tr>
<td>3:1</td>
<td>2.49:1</td>
<td>30</td>
<td>0</td>
<td>0.781</td>
<td>101.8</td>
</tr>
<tr>
<td>3:1</td>
<td>2.53:1</td>
<td>90</td>
<td>0</td>
<td>0.790</td>
<td>94.8</td>
</tr>
<tr>
<td>4:1</td>
<td>4.05:1</td>
<td>60</td>
<td>0</td>
<td>0.792</td>
<td>55.2</td>
</tr>
<tr>
<td>3:1</td>
<td>3.11:1</td>
<td>60</td>
<td>2%</td>
<td>0.782</td>
<td>68.1</td>
</tr>
<tr>
<td>3:1</td>
<td>3.13:1</td>
<td>60</td>
<td>8%</td>
<td>0.781</td>
<td>51.7</td>
</tr>
</tbody>
</table>
(nominal) ones. It is probably due to the aluminum ions become partially dissolved as aluminate species under high pH conditions [20].

From Fig. 2, we also can conclude that R values have much effect on the crystallinity of LDHs: the shape and peak area is similar between R = 2:1 and 3:1. To compare, the LDHs of R = 3:1 are in best crystallinity, whereas the LDHs of R = 4:1 are in low crystallinity. From the metal cations and interlayer anion point of view, the crystallinity of LDHs depends on the ratio of M^{2+}/M^{3+} in the given systems. Corresponding to the Mg/Al ratio in the naturally occurring LDH–hydrotalcite [21], the best crystalline phase of most LDHs material was obtained with a M^{2+}/M^{3+} ratio at 3:1. Y. Wang et al. thought that this specific ratio gave rise to a LDHs phase that may be energetically more stable than those with other R values; they speculated that the more M^{2+} cations were replaced by M^{3+}, the more positive charges would result on brucite layers, thus leading to stronger bonding between the brucite layers and the interlayer anions and therefore a more stable LDHs phase; on the other hand, additional energy would be introduced by the lattice distortion created by the size difference between the two cations upon a cation substitution. Therefore, the most stable LDHs phase is expected to be the one with an M^{2+}/M^{3+} ratio that best compromises these two competing factors and usually this ratio is equal to 3:1 [22]. As a matter of fact, their explanation has also been proved by our results which concerned that LDHs sample of R = 3:1 had the highest zeta potential (see Table 1).

The zeta potentials varied cause of the shift of R values. This is because that the positive layer charge of Mg–Al-LDHs results from the isomorphous substitution of Al^{3+} for Mg^{2+} in the hydroxide layer [Al{Mg_{1-x}(OH)}_{2}]^{x+}. Hence, the change of zeta potentials must be related with different deposit of Al^{3+} and Mg^{2+} into the LDH layers. For instance, the sample of R = 3:1 and R = 4:1, the decrease of Al^{3+} content in the LDH layers would result in the gradual reduction of zeta potentials [23], and therefore the stability of the samples reduced dramatically and then the coagulation appeared at system of R = 4:1. As for LDHs sample of R = 2:1, a molar ratio of M^{2+}/M^{3+} = 2 corresponds to the maximum substitution of M^{2+} by M^{3+} in brucite-like layers on condition that M^{3+} sites are not neighboring. Thus, in some cases the product with a molar ratio of M^{2+}/M^{3+} = 2 might contain amorphous phases that are not detectable by XRD measurements [24]. Accordingly, zeta potential will decrease slightly because of the formation of amorphous phases. Under the effect of electrostatic repulsion, particles with high zeta potentials will be more homogeneous and stable than those with lower ones, hence, high zeta potentials are necessary for stable LDHs system, which render R values in the range of 2:1 to 3:1.

The TG–DSC analysis is also displayed in Fig. 2C, and the weight loss occurs essentially in two steps [18]. Interestingly, the endothermic peak in DSC curves changed with variation of R values, i.e., the first endothermic peak appeared at 207 °C, 215 °C and 200 °C and the second one at 385 °C, 385 °C and 380 °C for samples of R = 2:1, 3:1 and 4:1, respectively. In fact, LDHs of R = 3:1

Fig. 2. (A) XRD patterns of LDHs under different R values. (B) TEM images and the corresponding particle size distribution histograms of LDHs under different R values. (C) TG–DSC curves for LDHs under different R values.
have the highest temperatures in endothermic event, whereas LDHs of $R=4:1$ have the lowest ones. And this result is accor-
dant with the measurement of zeta potentials, LDHs of $R=3:1$ have the highest zeta potential and LDHs of $R=4:1$ have the lowest one.

3.3. Effect of grinding time on the properties of LDHs

Grinding is known to mechanically activate the reactions. The mechanical energy produced from grinding will lead to the regular arrangement of the particles at the proper grinding, whereas structural imperfections in the particles will appear during longer grinding [25]. As a result, suitable grinding is necessary to ensure sufficient contacts and effective collisions between the reactants. Fig. 3 shows the XRD patterns and TEM photos of LDHs synthesized under different grinding time. The crystallinity became better when increasing grinding time from 30 min to 60 min, whereas the samples showed decreased peak heights together with broadening of the peaks when grinding further prolonged to 90 min. Under the shorter grinding (i.e., 30 min), the particles showed irregular hexagon and they seemed to be under-grown. It indicates that the mechanical energy from shorter grinding is too weak to give rise to the full-grown particles. Under longer grinding (i.e., 90 min), distortions in the plate stacking and delamination processes may account for the reduction in the peak's intensity, as well as in its widening [26]. Longer grinding may be associated with destroy of the hydroxyl layers or delamination, and the exposure of active broken edges upon the breakage of the layers will lead to the formation of secondary aggregates, then some aggregations may occur in the sample, see Fig. 3B [26]. Only under proper grinding, the suitable mechanical energy would make particles become quite uniform, together with regular hexagon and a narrow particle size distribution. Elemental analysis showed that shorter (30 min) or longer grinding (90 min) would lead to the deviation of $R$ values from those of raw materials, and this deviation is attributed to the under-growth or destruction of the hydroxyl layers. The particle size is also changed by grinding, as shown in Table 2, the excess mechanical energy produced from longer grinding would lead to the formation of small particles.

Thermal analysis was performed on these samples as well, shown in Fig. 3C. The change of endothermic peak with different grinding time was in keeping with the variation of zeta potentials, or rather, higher layer charge or high zeta potentials will lead to the strong attraction between LDH layers, interlayer anions and water. Subsequently, the loss of interlayer water and anions needs more energy accordingly, giving rise to the appearance of higher temperatures in endothermic event. Shown from Fig. 3C, LDHs with grinding time of 60 min had the highest zeta potential and then the highest endothermic temperatures in DSC curves (215 °C and 385 °C) and LDHs with grinding time of 90 min had the lowest zeta

![Fig. 3. (A) XRD patterns of LDHs under different grinding time. (B) TEM images and the corresponding particle size distribution histograms of LDHs under different grinding time. (C) TG–DSC curves for LDHs under different grinding time.](image-url)
potential and then the lowest endothermic temperatures in DSC curves (201 °C and 373 °C).

3.4. Effect of water content on the properties of LDHs

In the mechanochemical synthesis, grinding of solid mixtures is a basic technique, and it is influenced by the presence of water in starting materials [27]. Previous study indicates that the mechanochemical reaction is influenced by humid air or addition of water [28]. The aim of this chapter is to examine the effect of water content in starting powder mixture of nitrate and base on mechanochemical formation of Mg-Al-LDHs. In fact, the water content in the powder mixture was controlled to be 0, 2 and 8% mass fraction, respectively, and the results are shown in Fig. 4. Together with the data in Table 2, the gradual decrease of the diameters and the crystallinity has been found as a function of water content. It presents that the addition of water rather enhanced the aggregation of particles from TEM results. Watanabe et al. studied the mechanism of the incipient chemical reaction for milling of Ca(OH)₂ and SiO₂ powder mixture [29–31], and their study indicates that dehydration process is easy to take place under the existing excess water. Taking into account the findings of Watanabe et al., it is considered that the present particle aggregation under high water content is caused by the formation of oxygen bridging bonds through mechanochemical dehydration [32]. Element analysis results show that change of water content has no effect on R values, and zeta potentials remain almost constant as well. Previous study shows that the crystalline water in nitrates is considered to be released from the structure of solid salt to form the free one, and then supersaturated solutions are formed during the grinding, which in fact constructs some microaqueous reactors for the reactant molecules, and then ultra-fine particles are obtained in them [24]. When the water content increases, the amount of the microaqueous reactors increased accordingly. Since the mole number of the reactants remained constant in three reaction systems, increasing water content means less reactive molecules in each reactors and it results in the formation of smaller particles.

The TG–DSC curves are also examined and shown in Fig. 4. The variation of water content have almost no effect on zeta potentials of LDHs system, and then the value of endothermic peaks are quite the same within the error, i.e., the value of the first endothermic peak appeared at 215 °C, 209 °C and 208 °C, respectively. And the second endothermic peaks at 385 °C, 383 °C and 382 °C for these samples, respectively. Consequently, our study confirmed that thermal analysis is a powerful tool to indicate structural changes.

Fig. 4. (A) XRD patterns of LDHs under different water content. (B) TEM images and the corresponding particle size distribution histograms of LDHs under different water content. (C) TG–DSC curves for LDHs under different water content.
Interestingly, the morphologies of some LDHs obtained from mechanochemical method are stunningly uniform and the crystallites are well faceted, the entire phenomenon observed might be due to the effect of the high degree of supersaturation, it is known that the addition of water would weaken the degree of supersaturation, and then makes the morphology and the crystallinity even worse. The further studies concerned grinding processes are in progress now.

3.5. Conclusions

Stunningly uniform Mg–Al-LDH particles can be synthesized through a mechanochemical approach. Fundamental experimental parameters, i.e. grinding time, $R$ values and water content are studied in detail. Proper $R$ values, suitable grinding time and high degree of supersaturation are required to prepare well-defined and homogenous LDH particles. We speculate that it will be a general, green, and low cost method for preparing uniform LDHs.

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