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Review article

Mechanochemical approaches to synthesize layered double hydroxides: a review

Jun Qu, Qiwu Zhang *, Xuewei Li, Xiaoman He, Shaoxian Song

School of Resources and Environmental Engineering, Wuhan University of Technology, Luoshi Road 122, Wuhan, Hubei 430070, China

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ABSTRACT

Layered double hydroxides (LDH) have been extensively studied because of their unique characteristics. The available reviews have dealt with the applications of LDH normally prepared with aqueous solution approaches. Recently mechanochemical ways to synthesize LDH and intercalated LDH have received more and more attention from researchers and several mechanochemical processes have been reported. This article reviews the recent advances in the preparation and intercalation of layered double hydroxides by mechanochemical approaches. Although conventional solution methods for the syntheses of LDH were widely studied, several problems remain to be resolved; such as treatment of aqueous waste, high energy consumption, complex operation etc. It is believed that mechanochemical methods may have potentials to effectively overcome the difficulties and also to synthesize various new types of LDH with further development of this new technique.

1. Introduction

Layered double hydroxides (LDH) or hydrotalcite-like compounds belong to the group of clay minerals which can be represented by the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+}, M^{3+} can be substituted by Mg^{2+}, Ca^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+} and Fe^{3+}, Al^{3+}, Bi^{3+}, In^{3+}, La^{3+}, Ga^{3+}, respectively, and A^{n-} is exchangeable anion, including Cl^-, OH^-, CO_3^{2-}, SO_4^{2-}, NO_3^-. Many of the binary LDH reported in patents and literatures are shown in Table 1. Typical properties such as base catalysis character, ion-exchange capability, memory effect and adjustable element compositions allow wide-ranging applications in the fields of environmental protection, pharmacy or nanocomposite syntheses (Cavani et al., 1991; Li and Duan, 2006). Several review papers are available to summarize the research results mostly with focuses on the applications for elastomer composites (Basu et al., 2014), anion adsorption (Theiss et al., 2014) and intercalation of drugs (Rives et al., 2014). A novel approach based on mechanochemical treatment to synthesize LDH and related intercalates have been reported recently. Besides the evident advantage of easy operation, this approach demonstrates potentials to overcome the difficulties related to solution operation such as the different rates of precipitation with pH regulation. It is believed that a review focused on this approach will be helpful for understanding the nature and advantage of the mechanochemical method, as well as to facilitate the developments of LDH syntheses and applications.

LDH were discovered by Hochstetter (Hochstetter and Prakt, 1842) in Sweden in 1842. Almost all the reported LDH were synthesized by aqueous solution operation including co-precipitation (Martino et al., 2013), hydrothermal method (Jin et al., 2007) or urea decomposition-homogeneous precipitation (Benalioua et al., 2015). The essence of these processes is similar, involving the precipitations of different metal ions. However, solution operation may result in some problems. Different precipitation rate of metal ions particularly with multicomponents in ternary system or quaternary system may easily take place (Cavani et al., 1991), which results in the formation of intermediate phases as impurities to the final product. When it comes to the synthesis of carbonate-free LDH, additional measure, such protective N_2 atmosphere, is also needed to prevent carbon dioxide dissolution from the air (Zhang et al., 2004). Furthermore, the solution operation usually needs heating and produces a mass of pollutant effluents of aqueous wastes to be purified, thus, increasing the cost of production.

As to the most promising branch of organic and inorganic nano LDH composite materials, which were mainly produced by the ion-exchange (Taviot-Gueho et al., 2010) and the hydration reconstruction processes (Aisawa et al., 2003) in aqueous solutions, there exists some limitations for the intercalation of large molecules. Intercalating capacity will be significantly limited if the molecular size and the gallery space do not match (Basu et al., 2014). Hydration reconstitution is a special characteristic of LDH. The oxides of LDH (LDO) produced by heating to remove structural water can absorb the anions and water molecule from solution and recover their layered structures. Although hydration reconstruction can be used to produce various intercalated LDH (Aisawa et al., 2003), there exists concern for the decrease in specific surface area of the products and the formation of irreversible spinel phase resulting from the heating operation of preparing LDO (Cheng et al., 2010).

* Corresponding author.
E-mail address: zhangqw@whut.edu.cn (Q. Zhang).

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Table 1
Part of binary LDHs reported in patents and literatures (Miyata et al., 1974; Miyata et al., 1975; Basu et al., 2014).

		M^{2+}, M^{+}												
		Mg	Fe	Co	Ni	Cu	Zn	Ca	Sr	Be	Cd	Pb	Mn	Li
M^{3+}	Al	■	■	■	■	■	■	■	■	■		■	■	■
	Cr	■		■	■	■	■	■						
	Fe	■	■	■	■	■	■	■	■		■			
	Co	■	■	■	■		■							
	Ni				■									
	Bi	■	■		■		■							
	Sb	■			■					■				
	Ga	■	■	■	■	■	■	■						
	In	■			■		■							
	V	■					■							
	Cr	■		■			■			■		■		
	Y	■			■				■					
	La	■			■		■	■						
M^{4+}	Ti	■		■	■		■							
	Sn						■	■						
M^{6+}	Mo						■							

Mechanochemistry was usually used as a modification method of material science to gain highly dispersed, high surface energy particles (Salmones et al., 2008; Bugatti et al., 2013; Wang et al., 2013). Mechanochemical approach offered an alternative for the synthesis and intercalation of LDH (Khusnutdinov and Isupov, 2008; Tongamp et al., 2008; Iwasaki et al., 2012a; Zhang et al., 2013; Zeng et al., 2014). Three different mechanochemical processes have been exploited to synthesize LDH: 1) single-step grinding; 2) mechano-hydrothermal; 3) two-step grinding (dry and wet grinding). The mechanochemical intercalation of LDH can be manufactured by the following three ways: 1) liquid-assisted grinding of LDH with intercalation compound; 2) grinding raw material with intercalation compound and then with hydrothermal treatment in the liquid phase; 3) grinding amorphous raw materials with intercalation compound and water in the second step of the two-step grinding process. Recent research suggests that mechanochemistry will be of great importance in manufacturing of LDH with new element combinations and inserting new species of compounds into the gallery space of LDH.

In this paper the authors aim to:

1) Review the syntheses of different LDH by mechanochemistry, the processes and the characterization methods of the products.
2) Introduce a brief review of the intercalation of LDH by mechanochemical approaches.
3) Discuss reasonable directions for future work.

2. Characterization methods used in mechanochemical processes to synthesize LDH

Various kinds of analytical methods, including XRD, in situ XRD, FT-IR, SEM-EDX, TEM, have been used to characterize the sample prepared or the phase transformation of raw materials during grinding. These characterization techniques also helped to understand the mechanisms of the syntheses.

2.1. XRD

X-ray diffractometry (XRD) is one of the most commonly used characterization methods. LDH phases are mainly identified by XRD patterns because of its multiple relationships of different diffraction reflections indicating the layered structure of LDH. XRD analysis of LDH prepared mechanochemically can reflect the crystallinity and lattice distortion of LDH induced by mechanochemical stress. When preparing intercalated LDH, the increase in d_{003} value calculated by the XRD patterns, can be a strong evidence for the successful intercalation. Reflection area is important in judging for the crystallinity of the samples. The heights of XRD reflections may be used to compare the crystallinities of the LDH, since they are proportional to reflection area (Kannan et al., 1996).

Tongamp et al. (2007) used XRD to identify the LDH phase and degree of crystallinity in the as-prepared sample. The one-step wet grinding of $Mg(OH)_2$ and $Al(OH)_3$ gave Mg–Al LDH together with considerable amount of unreacted $Mg(OH)_2$ and $Al(OH)_3$. In the two-step process, XRD pattern showed amorphous state of the material after dry grinding of the raw materials and then high crystalline of LDH after the wet grinding. The optimum conditions for Mg–Al LDH prepared by two-step grinding process was dry grinding for an hour, followed by wet grinding for 3 h with 5 mol water ($Mg:Al:H_2O = 3:1:5$).

Qi et al. (2013) identified the successful intercalation of methotrexatum into layered double hydroxide by XRD analysis of the products, which was prepared by manual grinding of magnesium and aluminum nitrate, and then grinding with NaOH solution and methotrexatum powder. The XRD patterns showed R(Mg:Al:MTX) = 2:1:0.5 was suitable for the intercalation of MTX into LDH.

2.2. In situ XRD

In situ XRD experiment has been used to illustrate the standard intercalation method of organic molecules into LDH with excess of solvent by the group of O'Hare (Fogg et al., 1998; Lei et al., 2001; Khan and O'Hare, 2002). Milanesio et al. (2010) presented the complete intercalation of EUS among the layer of the LDH using the in situ XRD experimental setup by liquid assistance grinding of LDH and EUS with small amount of solution. The growth of (00 *l*) ($2\theta = 4.20, 8.32, 12.38$) with the disappearance of the typical reflections of LDH-NO_3 and EUS indicated the formation of LDH-EUS.

Conterosito et al. (2013) illustrated the whole intercalation process of eusolex, tiaprofenic acid, ketoprofen, fluorescein into LDH by liquid assistance grinding of LDH and the compounds to be intercalated as shown in Fig.1. In situ XRD showed high efficiency to confirm the optimum conditions for intercalation of LDH, avoiding the excess of solvent and energy waste promising wide use in the synthesis of other materials.

2.3. MAS-NMR

Ay et al. (2009) compared the ^{27}Al MAS NMR spectra of Mg–Al LDH prepared by manual grinding of $Mg(NO_3)_2$, $Al(NO_3)_3$ and NaOH solution and by the traditional co-precipitation method as shown in Fig.2. Both samples revealed a single, sharp resonance centered at 9–10 ppm with Full Width at the Half-Height indicating the presence of the hexacoordinate aluminum atoms with uniform chemical surroundings rather than perturbed aluminum atoms (Arco et al., 2000). The results showed the identical structures for the LDH prepared by mechanochemistry and the traditional solution method.

2.4. SEM-EDX

SEM-EDX could be used to give a direct view on the morphology of the materials and identify the elements distribution in the material. Ferencz et al. (2014) used SEM-EDX to confirm the distribution of Sn in the Ca–Sn LDH prepared by two-step dry and wet grinding of