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PREPARATION OF LAYERED DOUBLE HYDROXIDES

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ABSTRACT

Layered double hydroxides (LDHs) are class of materials with useful properties associated with their anion exchange abilities for a wide range of applications including bio and environmental problems. Synthetic methods have been examined to prepare LDHs with controlled structure, composition and particle morphology. Co-precipitation is a method used most widely while efforts have been made to conduct under controlled reactions conditions. In the present review article, synthetic methods for LDHs are overviewed with the emphasis on the authors' contribution.

Key words: Layered double hydroxide, Urea, Homogeneous precipitation, Particle size distribution, Hydrothermal reaction, Nanoparticles

INTRODUCTION

Layered double hydroxides (LDHs) are a class of layered materials whose structure is composed of brucite ($Mg(OH_2)$) like layers in which some of the divalent cations have been replaced by trivalent ions, giving positively charged sheets and the charge compensating interlayer anions as shown in Fig. 1. The chemical formula of LDH is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively, x is the ratio $M^{3+}/(M^{2+}+M^{3+})$ and A^{n-} is the interlayer anion. Attracted by the versatilities of chemical composition and the surface chemical properties of LDHs, the preparation, characterization and properties of LDHs have actively been investigated (He et al., 2006; Evans and Slade, 2006). Practical applications of LDH in such areas as catalysts (Sels et al., 1999; Choundary et al., 2002; Prevot et al., 2001; Yu et al., 2007; Kaneda et al., 1998), ion exchange/adsorption (Inomata and Ogawa, 2006), pharmaceutics and electrochemistry have been proposed so far (Li and Duan, 2006; Hoyo, 2007), so that efforts have been made to design the composition as well as the structures of the LDHs and their intercalates.

In addition to the structures, the particle size and its distributions are key issues in order to achieve optimum performance of LDHs in several applications. For example, nanometer sized particles are useful for bio-related applications including drug delivery (Choy et al., 1999 and 2000; del Arco et al., 2004; Nakayama et al., 2004; Aisawa et al., 2004) and thin films have been investigated for electrochemical and photochemical studies (Shichi et al., 2003; Takagi et al., 1993; Liu et al., 2008; Yao et al., 1998; Morigi et al., 2001; Scavette et al., 2007). Rheological characteristics of LDH suspension are worth investigating for such applications as paint and polymer additives (Moujahid et al., 2003; Kottegoda and Jones, 2005; Lee and Cheng, 2004). All these processing and properties are closely related to the original particle morphology. In the present review article, the recent progresses in the syntheses of LDHs with controlled particle morphology will be summarized after the general introduction of the preparative methods for LDHs.

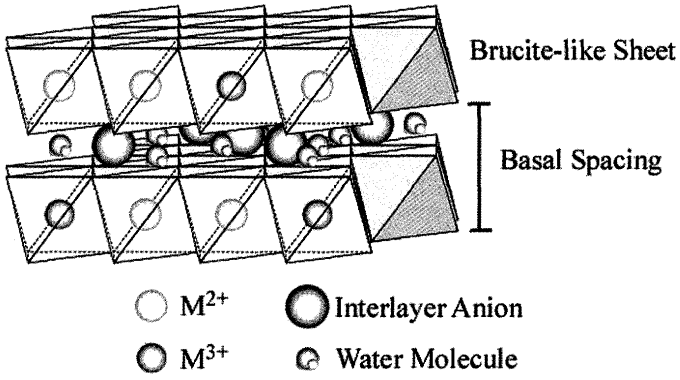

FIG. 1. Schematic structure of layered double hydroxide.

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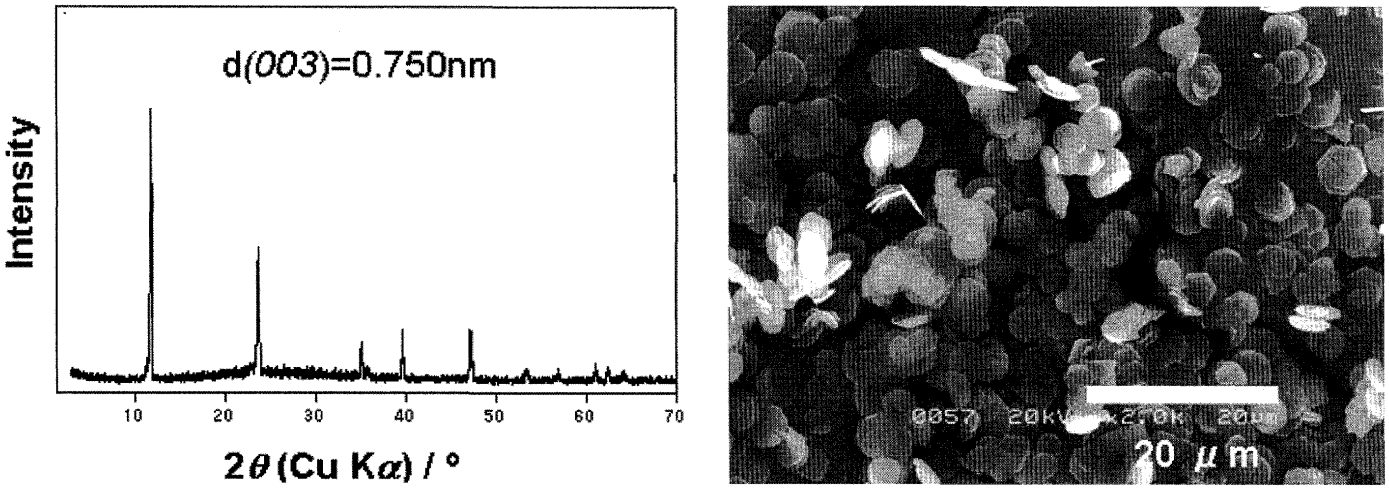

FIG. 2. XRD pattern and SEM image of hydrotalcite prepared by the homogeneous precipitation method using urea.

General idea of Co-precipitation

Co-precipitation of LDHs from aqueous solutions containing M^{2+} and M^{3+} by the addition of bases such as aqueous NaOH is a common method for the synthesis of LDHs (Trifflo and Vaccari, 2004; Reichle, 1986). Though the co-precipitation method has been employed to synthesize various LDHs and their intercalation compounds, the products are generally finite crystallites (nanometer scale) with broad particle size distributions. In order to control particle morphology of LDHs, various synthetic conditions such as sonication (Seida et al., 2002; Climent et al., 2004; Ni et al., 2010), microwave irradiation (Benito et al., 2007 and 2009; Herrero et al., 2009) and colloid mill (Zhao et al., 2002; Feng et al., 2003) have been used for the precipitation. The synthesis of LDH in surfactant solution like emulsion has been conducted so far (He et al., 2004; Hu et al., 2007; Bellezza et al., 2009). However, the information on the particle size and size distribution are limited and the success in the controlled particle morphology is limited. Accordingly, there remain rooms for further study on the morphosyntheses of LDHs.

Homogeneous Precipitation

Homogeneous precipitation using urea hydrolysis is a well known method to obtain well-defined inorganic particles (Sugimoto, 2001). During the heating, urea hydrolyze to rise pH homogeneously in solution, which often results in the monodispersed particles. The urea method has been applied to prepare LDHs with relatively narrow particle size distribution compared to co-precipitation method (Cavani et al., 1991; Costantino et al., 1998; Narita et al., 2001; Adachi-Pagano et al., 2003; Iyi et al., 2009). Urea and hexamethylenetetramine (Iyi et al., 2004) have been used to make solution basic for LDH precipitation. We have conducted the urea method under hydrothermal conditions to control morphology of LDH, and succeeded in the synthesis of large platy particles of LDH with the size of as large as > 40 μm (Ogawa and Kaiho, 2002; Kayano and Ogawa, 2006a). As an example, the XRD pattern and the SEM image of hydrotalcite prepared by the hydrothermal reaction using urea are shown in Fig. 2. Recently, we have reported that the hydrothermal reaction in aqueous alcohol was an possible way to control the particle size distribution more precisely (Kayano and Ogawa, 2006b; Arai and Ogawa, 2009).

As an example, synthetic procedure of Co-Al-LDHs is described here. Aqueous stock solutions of $CoCl_2 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$, and $(NH_2)_2CO$ were mixed at a molar Co:Al:$(NH_2)_2CO$ ratio of 2:1:10. The aqueous mixture (homogeneous solution) was allowed to react in a Teflon-lined autoclave that was sealed in a stainless steel tank. The vessels were heated in a laboratory oven. After cooling to room temperature, the solid products were separated by centrifugation and washed with water. The products were dried under reduced pressure. Alcohols such as glycerol were added to the aqueous solution of $CoCl_2$, $AlCl_3$, and $(NH_2)_2CO$ to control the particle size and size distribution.

All the precipitates obtained were pink colored and main product was Co-Al-LDH as determined by XRD, TG-DTA and IR results (Pérez-Ramírez et al., 2001; Kloprogge and Frost, 1999). The particle size was successfully controlled by the reaction temperature and period. It was found that larger particle formed by the reactions at lower temperature and longer reaction period because the slow urea hydrolysis at lower temperature was expected to suppress the formation of nuclei in the solution. When the reaction was conducted at 60 °C for 100 days, particle with the lateral size of larger than 40 μm was successfully obtained as shown in the SEM image (Fig. 3).

The particle sizes and size distribution of Co-Al LDHs were also controlled by adding alcohols (ethylene glycol and glycerol) to the starting solution mentioned above (Kayano and Ogawa, 2006b). The glycerol gave best result in terms of the particle size distribution of the products (Kayano and Ogawa, 2006b). Accordingly, we examined the preparation of LDH from aqueous glycerol solution further to see the effects of the synthetic conditions on the particle morphology.

Hexagonal platy particles of Co-Al-LDH were obtained when glycerol/water ratio in the starting solution was 1 g/40 mL and heating was conducted at 80°C. Average particle

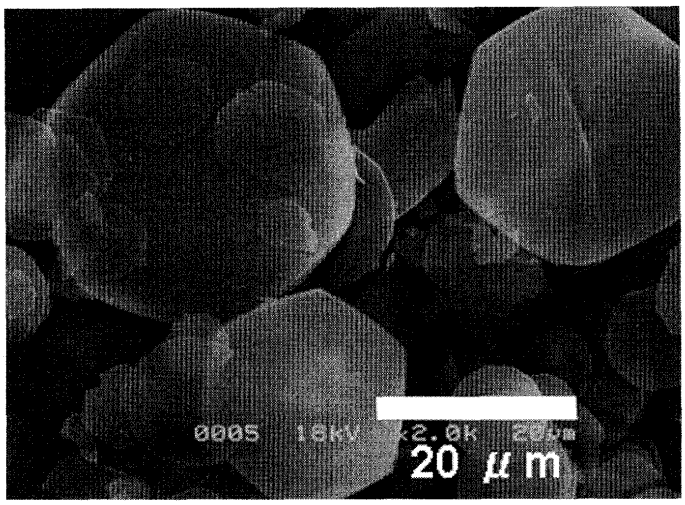

FIG. 3. A SEM image of large platy particle of Co-Al-LDH.

diameters were 3.8, 9.3, and 10.1 μm with the coefficient of variation (CV) values of 22.5, 23.3, and 24.7% when the heating time was 1, 2, and 7 days, respectively. It was shown that pH after the reaction increased with prolonged heating time (pH 6.09, 6.27 and 8.50, for 1,2, and 7 days, respectively), resulting in higher product yields. The particle growth almost completed within a few days during the reaction at 80°C as shown by the product yield and the particle size.

Since the urea hydrolysis rate depends on the temperature, the synthesis temperature is one of the most important factors to determine the particle size. It was reported that the urea decomposition rate increased by ~200 times when the temperature increased from 60 to 100°C (Shaw and Bordeaux, 1955). The slow urea hydrolysis was expected to suppress the formation of nuclei in the solution as a result of the slow pH rise at the initial stage, so that the limited number of nuclei formed and they can be grown to larger particles. The particle prepared at 80°C for 1 day (pH 6.09 after the reaction) was larger than that prepared at 100°C for 1 day (pH 8.50 after the reaction).

The reaction condition was optimized in terms of the glycerol amount in the staring solution for the synthesis at 100 °C for 1 day. The glycerol/water ratios examined were 10, 15 or 20 g/40 mL. When the glycerol/water ratio was 0, 1 or 10 g/40 mL, the products possessed hexagonal platy morphology. When the glycerol/water ratio was 10 g/40 mL, hexagonal plates were rather roundish. When the glycerol/water ratio was 15 or 20 g/40 mL, indefinite shape and stick-like particles of approximately 1 μm length were obtained besides the circular plate, which is the main product. The difference between hexagonal plate and circular plate is worth discussion from the viewpoints of crystal growth mechanisms and the properties. The addition of large amount of glycerol did not affect the particle size distribution of the products, while average particle size decreased with the increase in the glycerol/water ratio.

After the reaction at 50°C for 150 days, Co-Al LDH formed, which is circular plate with the average diameter of ca. 1 μm (Arai and Ogawa, 2009), which was much smaller than that (38 μm) of the products prepared in the absence of glycerol (Kayano and Ogawa, 2006a). A SEM image is shown in Fig. 4. After the reaction of both of two syntheses, pH values were approximately 7.15, and the product yields are almost the same. Note that the pH value obtained for aqueous glycerol is difficult to be compared. However, we gave the value just for comparison that the urea hydrolysis proceed at the same degree even in the aqueous glycerol. The particle diameter distribution of the product prepared with glycerol heating at 50°C for 150 days was 13.2% coefficient of variation, which was the smallest CV value.

Thus, Co-Al-LDH particle possessed circular platy morphology when glycerol/water ratio was 10 g/40 mL, while hexagonal platy particle was obtained at the glycerol/water ratio of below 1 g/40 mL. Average particle size of Co-Al-LDH varied from 1 to 38 μm. Larger particles formed at lower

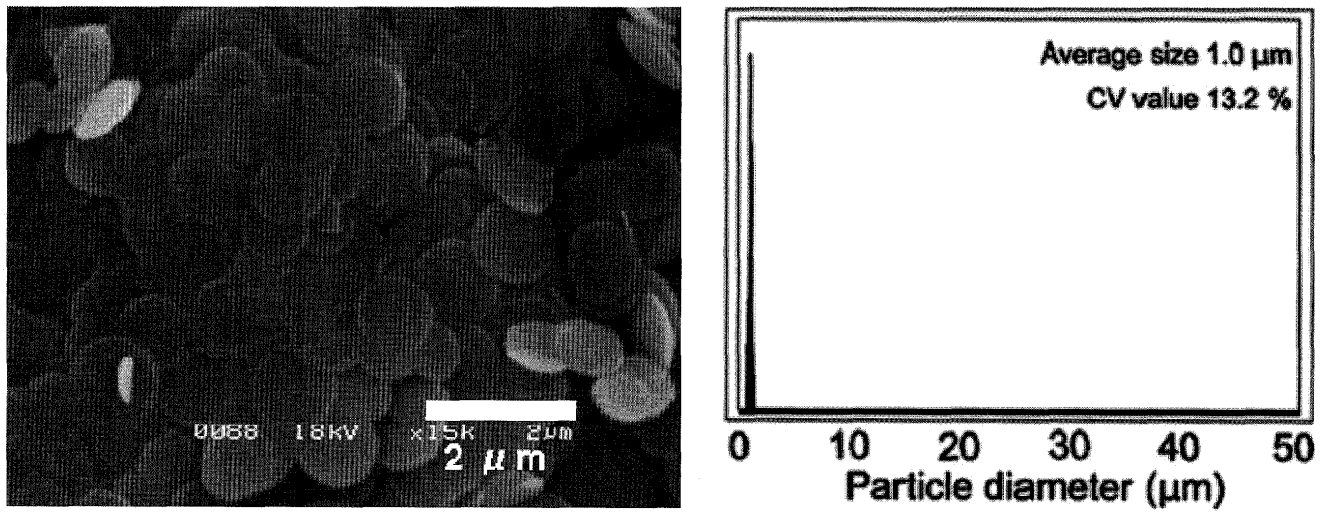

FIG. 4. A SEM image of Co-Al-LDH with narrow particle size distribution.

temperature synthesis. Particle size became smaller with the increase in the glycerol/water ratio of the synthesis solution. The narrowest particle size distribution was achieved by the reaction at 50°C for 150 days from aqueous glycerol solution of the composition of glycerol/water ratio at 10 g/40 mL.

Co-precipitation using ion exchange resin

As discussed above, since the process of pH change is dominant step to synthesize LDHs, the way of pH control has been carefully conducted. We have recently reported a unique way to raise solution pH, where OH^- form of anion exchange resin was used as the base supply. Well-defined finite particles of LDHs were successfully synthesized from aqueous solution of metal salts by the newly developed pH adjustment method, where hydroxide from exchange resin was used to make acidic starting solution to basic for the LDH formation (Nitoh et al., 2010).

The synthetic procedures are as follows, aqueous stock solution of $MgCl_2 \cdot 6H_2O$ and aqueous solution of $AlCl_3 \cdot 6H_2O$ were mixed (at the molar Mg:Al ratio of 3:1). To this solution was added OH^- form ion exchange resin, which was prepared by the titration of original Cl^- form with aqueous NaOH solution. The mixture was allowed to react at room temperature with shaking. During the reaction, pH increased to 8 as a result of the anion exchange of Cl^- with OH^-. Cl^- was adsorbed on the ion exchange resin and OH^- was liberated to the solution. After the reaction, the ion exchange resin was easily removed by filtration to obtain aqueous suspension. From the aqueous suspension, the solid products were separated by centrifugation and dried.

The product is Mg-Al-carbonate LDH (hydrotalcite) as characterized by XRD, IR, TG-DTA and SEM. One of the characteristics of hydrotalcite thus obtained is the size of the particle as shown by the TEM image (Fig. 5), where hexagonal platy particle with the lateral size of ca. 50 nm and narrow particle size distribution were observed. As a result of the small particle size, the aqueous dispersion of the present LDH is stable for a long duration (It is difficult to find precipitate after standing the suspension for several days.).

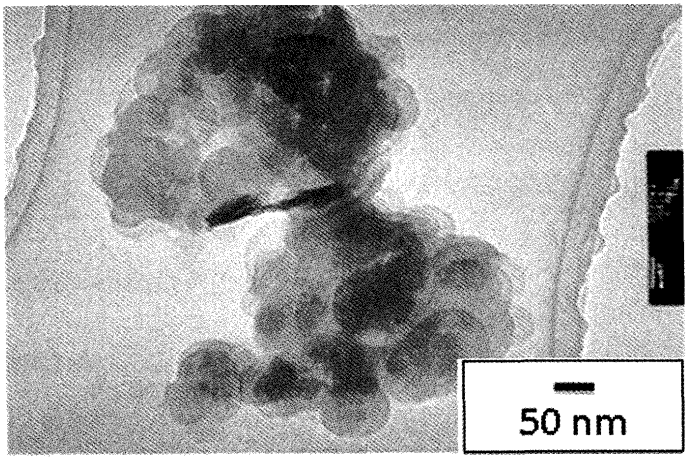

FIG. 5. A TEM image of nanometer size hydrotalcite prepared using ion exchange resin.

From the suspensions, the LDH particles were deposited on a flat substrate by casting to form macroscopically homogeneous films. Preparation of the suspension and film of LDHs is a topic of current interest for materials applications as already mentioned (Iyi et al., 2008; Zhang, 2008). The present casting process is a very simple synthetic way to prepare thickness controlled LDH films. The film is homogeneous and transparent, so that the photochemical and electrochemical studies are worth conducting (Shichi et al., 2003; Takagi et al., 1993; Liu et al., 2008; Yao et al., 1998; Morigi et al., 2001; Scavette et al., 2007).

The synthetic method using anion exchange resin was applied to prepare LDHs with other chemical compositions. ZnAl-, NiAl-, CuAl- and CoAl-LDHs with finite particle sizes (platy particle with the lateral size less than 100 nm) have successfully been synthesized from aqueous solutions of metal salts by the present method. Simple hydroxides like nickel hydroxide were also synthesized to show the versatility of the present method.

Hydrothermal reactions with hydroxides as starting materials

We have developed another simple synthetic method of LDHs, where magnesium hydroxide (brucite) and aluminum hydroxide (gibbsite) were used as the inorganic sources for the synthesis of the Mg-Al LDH-deoxycholate intercalation compounds (Asai and Ogawa, 2000). The selectivity of bulky and monodentate deoxycholate anion as the interlayer anion of LDH was very low and other synthetic methods, conventional coprecipitation, anion exchange and reconstruction were not applicable for the syntheses. So that the hydrothermal synthesis starting from magnesium hydroxide (brucite) and aluminum hydroxide (gibbsite) was developed to successfully prepare deocycholate-LDH intercalation compounds. The method is an easy, environmentally friendly method potentially applicable to the preparation of a series of LDH with different structures and properties. The hydrothermal LDH synthesis from aqueous suspension of magnesium hydroxide and aluminum hydroxide was applied to the synthesis of the sulfide containing Mg-Al LDHs, where thioacetoamide was used as the sulfide source (Ogawa and Saito, 2003). The reaction is as follows; brucite and gibbsite powders were mixed with an aqueous stock solution of thioacetoamide with vigorous stirring. The mixture was transferred into a Teflon-lined autoclave and heated at 150°C for 1 day. Light green colored precipitates were obtained by the reactions. During the hydrothermal reactions, magnesium hydroxide and aluminum hydroxide were thought to be dissolved and subsequently precipitate as LDH with containing polysulfide anions (S_2^- and S_3^-). The polysulfide anions were thought to be derived from the decomposition of thioacetoamide. The product exhibited blue color corresponding to the S_2^- and S_3^- ion and turns to colorless when the sample was stored in air for several days or heat treated in air at 120°C, showing that the occluded polysulfide anions were oxidized to sulfate anion by atmospheric oxygen. The thermal analyses in air showed a exothermic reaction accompanying a weight gain at around 150°C and the infrared spectrum showed an appearance of absorption bands ascribable to sulfate (SO_4^{2-}) anion, showing the oxidation of the sulfide anions to sulfate anion as schematically shown in

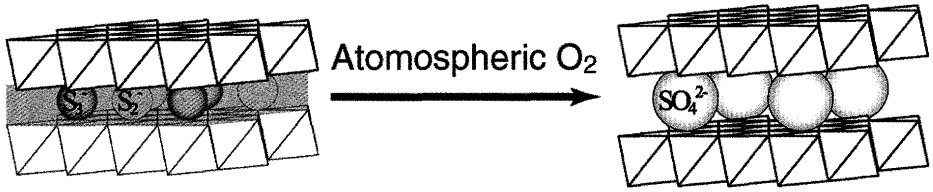

FIG. 6. Schematic structure of polysulfide containing Mg-Al-LDH.

Fig. 6.

The synthetic method was extended for the preparation of Zn-Al LDHs. Benzenesulfonate was used as the interlayer anion to be directly incorporated into the interlayer space of the LDH by the hydrothermal reactions of aqueous suspension of zinc oxide and gibbsite (Ogawa and Sugiyama, 2009). The synthetic procedure of Zn/Al LDH containing benzensulfonate (abbrevaiated as BS) is shown below; zinc oxide, gibbsite powders and benzenesulfonic acid were mixed in distilled water with vigorous magnetic stirring. The aqueous mixture (slurry) was transferred into a Teflon-lined autoclaveand heated at 150°C for 1 day. After the hydrothermal reaction, precipitate was separated by centrifugation.

XRD, IR, TG-DTA confirmed the formation of Zn-Al LDH containing BS in the interlayer space. A SEM image of the product is shown in Fig. 7. It is thought that the present synthesis involved the dissolution of zinc oxide and gibbsite under the hydrothermal condition and spontaneous formation of LDH phases incorporating BS. The starting materials remain when the hydrothermal reaction of zinc oxide and gibbsite in aqueous slurry was conducted in the absence of BS. Thus, BS plays a role as the incorporating guest species as well as to dissolve zinc oxide and gibbsite. BS made the solution pH lower, so that the dissolution of zinc oxide and gibbsite was promoted. The remaining starting materials can be eliminated by employing the modified conditions such as prolonged reaction time and higher reaction temperature.

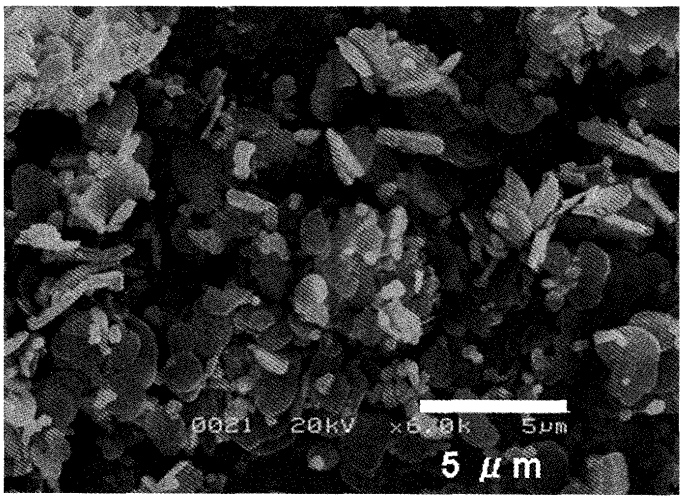

FIG. 7. A SEM image of Zn-Al-LDH-benzenesulfonate prepared from aqueous slurry of zinc oxide and gibbsite.

A similar synthetic method, the hydrothermal treatment of gibbsite and MgO at 180°C, was reported for the preparation of LDHs (Newman et al., 2002). Later on, Xu and Lu reported the LDH formation by the hydrothermal treatment of aqueous slurries containing MgO and Al_2O_3 at 110°C (Xu and Lu, 2005). The hydrothermal reactions at a range of temperature (100, 150, 180 and 240°C) were investigated *in-situ* by means of a synchrotron irradiation (Mitchell et al., 2007). More recently, Zn-Al LDHs containing chloride anion was prepared from ZnO and $AlCl_3 \cdot 6H_2O$ by the hydrothermal treatment at 150°C for one day (Chitrakar et al., 2007). These reactions are simple and versatile methods to prepare LDHs, while the approach are limited for the preparation of chloride, carbonate and nitrate anion intercalated materials besides our reports on the preparation of deoxycholate (Ogawa and Asai, 2000) and polysulfides (Ogawa and Saito, 2003) containing LDHs.

Solid-solid reactions

Recently, the preparation of LDH by the solid-state reactions from magnesium hydroxide, aluminum hydroxide and magnesium nitrate was reported (Tongamp et al., 2008 and 2009). If compared with reported LDH syntheses using aqueous media, the solid-state synthesis of LDH has such advantages as i) solid-liquid separation is not necessary, ii) carbonate contamination is less plausible, iii) the starting materials are not expensive if compared with those used for the conventional syntheses. Accordingly, the solid-state formation of organic anion intercalated LDHs is worth investigating (Kuramoto and Ogawa, 2011).

CONCLUSIONS

Due to the wide range of application of layered double hydroxides, the preparation of LDHs for controlled particle size and composition have been investigated. Efforts have been carefully done for the precisely controlled syntheses, as a result, a variety of LDHs with controlled particle size from nm to micrometer are possible to synthesize. Further studies on the preparation of LDHs to meet the requirements of specific applications will be conducted.

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