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Preparation of Well-defined Nanometer-sized Layered Double Hydroxides by Novel pH Adjustment Method Using Ion-exchange Resin

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Well-defined finite particles of layered double hydroxides were successfully synthesized from aqueous solution of metal salts by the newly developed pH adjustment method, where hydroxide form ion-exchange resin was used to make acidic starting solution to basic for the hydroxide formation.

Layered double hydroxides (LDHs) are a class of layered materials consisting of positively charged brucite-like layer, where some M^{2+} cations are substituted with M^{3+} cations to give positive charge, and the charge compensating interlayer exchangeable anions.[1,2] Besides the mineralogical and structural interests, studies on the possible applications of LDHs have been conducted.[3–10] For such applications, the morphology of LDHs is a key issue to optimize the performance. In order to control the particle morphology of LDHs, several synthetic efforts have been applied so far. The LDH formation occurred during the pH increases; the addition of base into acidic solution containing M^{2+} and M^{3+} cations is a most popular synthetic strategy. During the coprecipitation, microwave irradiation[11] and sonication[12] were applied to obtain well-crystallized and pure LDHs. The syntheses in an emulsion[13] and in a colloid mill[14] under vigorous mixing have also been reported to control particle size and morphology.

In order to obtain high-quality homogeneous samples, the addition of base should be carefully done. In order to avoid heterogeneity of mixing (or pH change), homogeneous precipitation utilizing urea hydrolysis has been applied.[15–22] Homogeneous precipitation is a promising way to prepare well-crystallized and large particles of various oxides and hydroxides because pH rises homogeneously in the solution.[23] We have used hydrothermal conditions in the homogeneous precipitation method to prepare large platy hydrotalcite particles[19,20] as large as 25 µm and associated to a relatively narrow particle size distribution.[21–23] Even with the successful preparation of LDHs with controlled morphology, there is a need for new syntheses of LDHs toward narrower size distribution in a wider size range as well as for varied chemical composition. Here, we report a new synthetic method of LDHs, where anion-exchange resin was used to adjust the pH of the solution for the precipitation. As a result, nanometer-sized LDH particles with relatively narrow particle size distribution were obtained. In addition, the carbonate LDHs thus obtained gave stable aqueous suspension, and films were obtained by evaporating the solvents on substrate.

The synthetic procedures are as follows, 50 mL of aqueous stock solution of 0.9 M $MgCl_2 \cdot 6H_2O$ and 50 mL of aqueous solution of 0.3 M $AlCl_3 \cdot 6H_2O$ were mixed (at a molar Mg:Al ratio of 3:1). To this solution was added 180 mL of OH^- ion-exchange resin (anion-exchange capacity of 1.40 equiv L^{-1}, particle size of 0.53–0.63 mm; from Organo Co.), which was prepared by the titration of original Cl^- form by 1 M aqueous NaOH solution. The mixture was allowed to react for 2 h at room temperature with shaking. During the reaction, pH increased from 3 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 removed by filtration to obtain aqueous suspension. From the aqueous suspension, the solid products were separated by centrifugation (4000 rpm for 30 min) and dried at 60 °C.

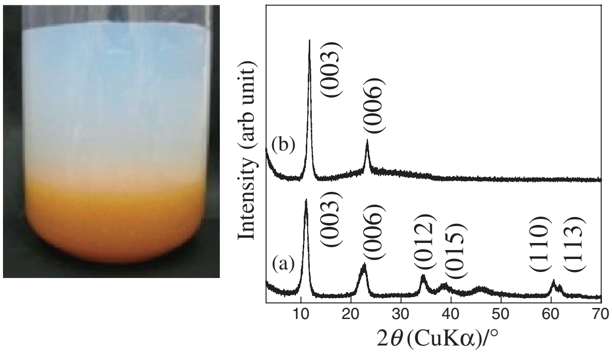

Figure 1. (Left) Photograph of the mixture after the reaction. (Right) XRD patterns of the products (a) collected by centrifugation and (b) collected by casting from the supernatant after the ultracentrifugation.

The XRD pattern of the product (Figure 1) shows the diffraction lines ascribable to Mg–Al–carbonate LDH (hydrotalcite) as indexed in a hexagonal lattice. In the infrared (IR) spectra of the product, adsorption bands ascribable to a brucite-like sheet (OH stretching vibration at around 3400 cm^{-1}) and interlayer carbonate ions (CO stretching vibration at 1350 cm^{-1} and bending vibration at 780 cm^{-1}) were observed. Thermogravimetric and differential thermal analysis (TG-DTA) curves showed endothermic reactions which accompanied weight losses due to dehydroxylation and decarbonation. The Mg:Al ratio of the product is 2.8:1, which is a typical value of hydrotalcite. All these observations confirmed the successful formation of hydrotalcite by the present reactions using ion-exchange resin.

One of the characteristics of hydrotalcite thus obtained is the size of the particle as shown by the TEM image (Figure 2), where hexagonal platy particles with the lateral size of ca. 80 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.). A certain part of the hydroxide was collected by centrifugation, while the supernatant is still turbid showing the presence of colloidal size particles. The solid hydroxide samples were collected by ultracentrifugation (25000 rpm for 20 min) to see the particle morphology. The particle

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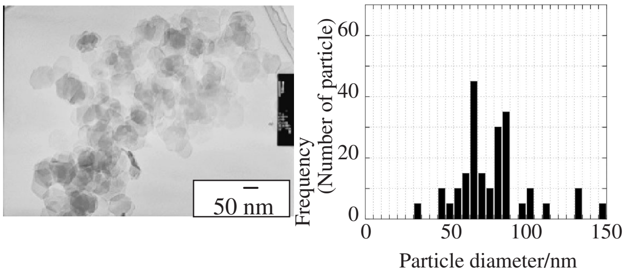

Figure 2. TEM image (left) of the centrifuged product and the corresponding particle size distribution (right).

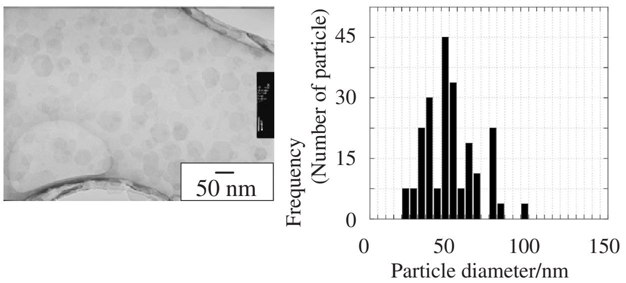

Figure 3. TEM image (left) of the sample collected by casting the supernatant and the particle size distribution (right).

shape is hexagonal platy, and the XRD pattern, TG-DTA, IR results, and the composition are the same as those observed for the sample collected by centrifugation. Even after the ultracentrifugation, the supernatant is still turbid showing the presence of swollen particle in it. Figure 3 shows the TEM image of the sample, which was collected by casting the supernatant after the ultracentrifugation. The hexagonal platy particle with smaller particle size (average particle size of 50 nm, which was determined from the TEM image for the 200 particles) was compared with those collected by centrifugation and ultracentrifugation.

We have recently obtained micrometer-sized Co–Al LDHs with narrow particle size distribution with the coefficient of variation of around 20% using urea hydrolysis in aqueous alcohols.[21–23] On the other hand, the present success is for the nanometer-sized LDH particles. The smaller size with narrower particle size distribution is desirable for applications including pharmaceuticals.[3–6,24]

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.[25–28] The SEM images of the cast film are shown in Figure 4, where hexagonal platy particles with the size of 50–100 mm were observed. 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.[18,29,30]

The presently developed synthetic method 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 chlorides (nickel chloride, copper chloride, cobalt chloride, and aluminum chloride) by the present method. It is also possible to use other salts like nitrate as the starting materials for the present LDH preparation. Simple hydroxides like nickel hydroxide were also synthesized to show the versatility of the present method. The detailed synthesis and characterization of these hydroxides will be reported separately.

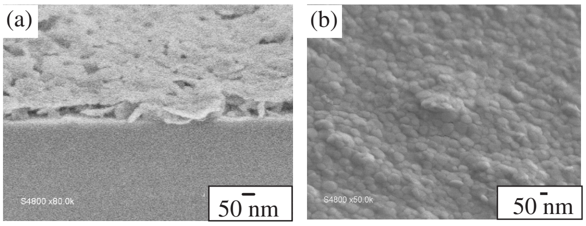

Figure 4. SEM images of the cast film prepared by casting the supernatant (a) edge and (b) surface of the film.

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