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Controlled Particle Size and Size Distribution of Co–Al Layered Double Hydroxide via the Hydrothermal Urea Method in Aqueous Alcohols

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Hexagonal platy particles of Co^{II} and Al^{III} layered double hydroxide were precipitated from homogeneous solutions via urea hydrolysis under hydrothermal conditions. The particle sizes and size distribution were successfully controlled by adding alcohols to the starting mixture.

Layered double hydroxides (LDHs) are a class of layered materials consisting of a positively charged brucite like layer, and a charge compensating interlayer exchangeable anions.[1,2] Besides the mineralogical and structural interests, studies on the possible applications[3] of LDHs in the phamaceutical industry and biochemistry,[4–6] and as catalysts,[7–9] adsorbents[10] have been conducted. For these applications, the morphology of LDHs is a key issue to control the performance. In order to control the particle morphology of LDHs, several synthetic efforts have been used. Microwave irradiation[11] and sonication[12] were conducted to obtain highly crystalline and pure LDHs. The syntheses in an emulsion[13] and in a colloid mill under vigorous mixing[14] have also been reported to control particle size and morphology.

Homogeneous precipitation utilizing urea hydrolysis is a promising way to prepare large highly crystalline oxide and hydroxide particles because pH rises homogeneously in the solution. LDHs with particle sizes of 2–5 µm have been synthesized by the urea method.[15–17] We have used hydrothermal conditions in the urea method to prepare successfully large platy hydrotalcite particle[18] as large as 25 µm with a relatively narrow particle size distribution. Motivated by these successes, efforts are being made in our laboratory to synthesize LDHs with other compositions, with a narrower size distribution and with various sizes. Here, we report the effects of alcohols on the hydrothermal syntheses according to the previously reported protocol[18] on the morphology of LDH composed of Co^{II} and Al^{III} (Co–Al-LDHs). Due to the reported functions of Co–Al-LDHs, such as catalytic and magnetic ones,[19] the morphosyntheses of Co–Al-LDHs are worth investigating. Based on the reported synthetic protocol, we investigated the effects of additives on the product morphology and found that ethylene glycol and glycerol apparently affected the particle size and size distribution.

Typical synthetic procedure of Co–Al-LDHs is based on previous reports.[18,20] An aqueous stock solution of 0.01 M $CoCl_2 \cdot 6H_2O$, 0.01 M $AlCl_3 \cdot 6H_2O$, and 0.1 M $(NH_2)_2CO$ were mixed in a molar Co:Al:$(NH_2)_2CO$ ratio of 2:1:10. An alcohol was then added to the aqueous mixture. The alcohols used were glycerol, ethylene glycol, and poly(ethylene glycol) (MW = 600). The amount of glycerol was 0.01, 0.2, or 1 g to 40 mL of the aqueous solution of $CoCl_2$, $AlCl_3$, and $(NH_2)_2CO$. The amount of added ethylene glycol and poly(ethylene glycol) was 0.1, 1, or 10 g to 40 mL of the aqueous solution of $CoCl_2$, $AlCl_3$, and $(NH_2)_2CO$. The aqueous mixtures were allowed to react in a 100 mL Teflon-lined autoclave that was sealed in a stainless steel tank. The $(NH_2)_2CO$/Al ratio in the starting solution was fixed at 10, and the temperature and time were 100 °C and 1 day, respectively. After cooling to room temperature, the solid products were collected by centrifugation and washed with deionized water. The products were dried under reduced pressure.

As reported for the synthesis of hydrotalcite[18] and Co–Al-LDHs,[20] Co–Al-LDHs were successfully synthesized by the present hydrothermal synthesis even when an alcohol was added. The yield and the chemical composition of the products are summarized in Table 1. The values in Table 1 are consistent with those reported for the reaction in the absence of an alcohol.[20] Figure 1 shows the XRD patterns of the products prepared in the presence of glycerol. All of the XRD patterns exhibit the characteristic reflections correspond to Co–Al-LDHs. The lattice parameters are $a(2 \times d(110)) = 0.306$ nm, $c(3 \times d(003)) = 2.25$ nm, which are in good agreement with those of Co–Al-LDHs reported by Pérez-Ramírez et al.[21]

Figure 2 shows scanning electron micrographs (SEM) of the products prepared in the presence of glycerol and particle size distributions derived from the SEM images. The particle size distributions were obtained by the SEM images for no less than 100 particles. Hexagonal plates with diameters of 5–20 µm were observed for the products. The average particle size decreased (from 9.33 to 6.12 µm) with the increase in the added glycerol amount as seen in Fig. 2. Particle size distribution became narrower with an increase in the added glycerol amount. Smaller particles with a narrower particle size distribution were obtained when ethylene glycol was added instead of glycerol. The SEM images of the particles are shown in Fig. 3. The particle size distribution derived from the SEM images is also shown in Fig. 3. Swelling (or exfoliation) of LDH platelets is a topic of recent interest.[22,23] In addition, LDHs should be useful as a filler to improve the performance of various organic polymers,[24] and LDHs with very narrow

Table 1. Product Yield and the Chemical Composition of the Products

Added alcohol	Amount of the added alcohol/g	Co/Al ratio	Yield Co/%	Yield Al/%
Glycerol	0.01	1.8	81	91
Glycerol	0.1	2.0	92	96
Glycerol	1	1.9	98	99
Ethylene glycol	0.01	1.8	80	89
Ethylene glycol	0.1	2.0	91	92
Ethylene glycol	1	2.0	89	90

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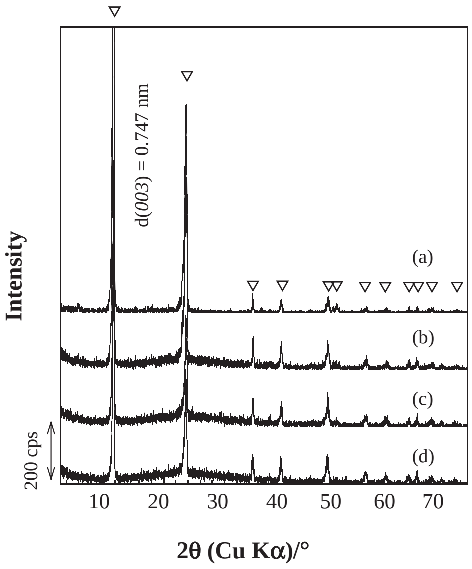

Fig. 1. XRD patterns of the precipitates obtained from water/glycerol mixture. Water/glycerol ratios are (a) 40 mL/0 g, (b) 40 mL/0.01 g, (c) 40 mL/0.2 g, and (d) 40 mL/1 g.

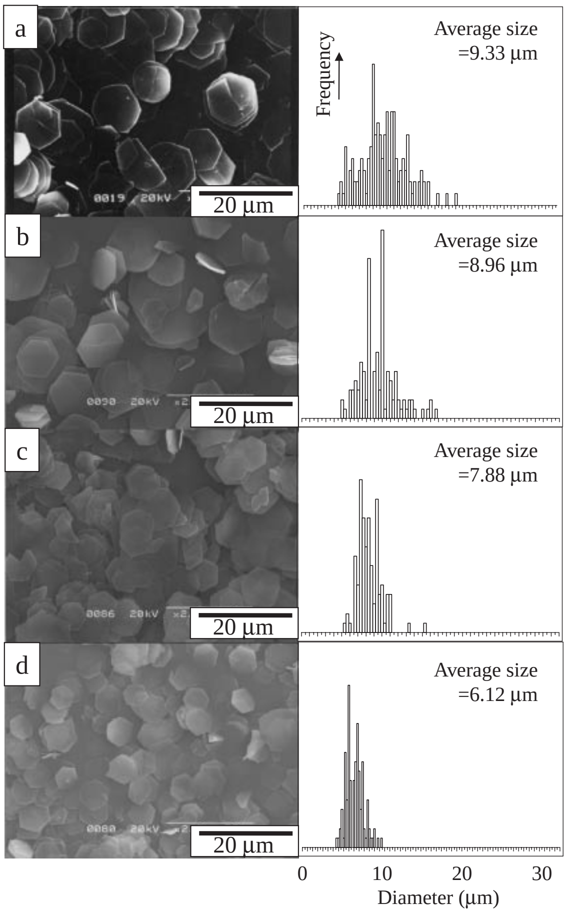

Fig. 2. SEM images and particle size distributions of the precipitates obtained from water/glycerol mixture. Water/glycerol ratios are (a) 40 mL/0 g, (b) 40 mL/0.01 g, (c) 40 mL/0.2 g, and (d) 40 mL/1 g.

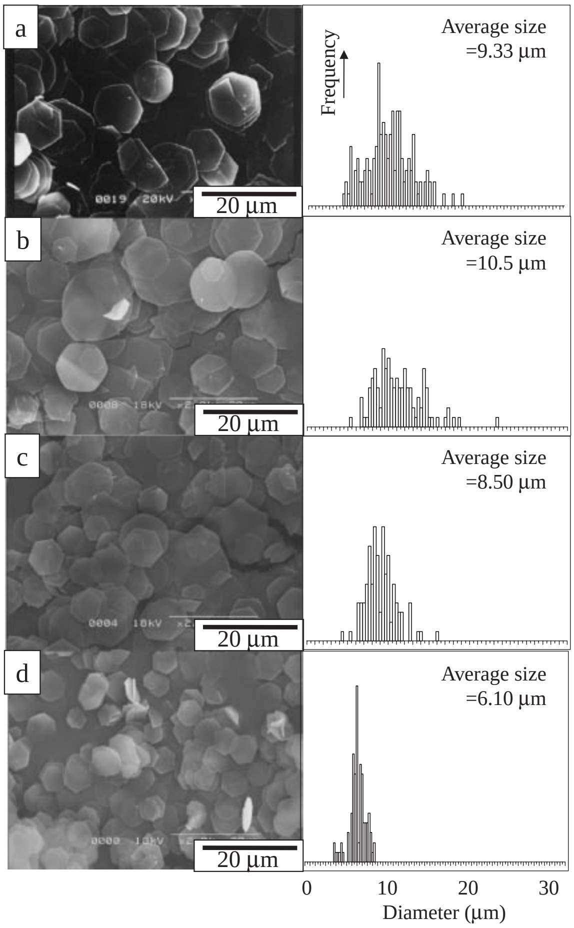

Fig. 3. SEM images and particle size distributions of the precipitates obtained from water/ethylene glycol mixture. Water/ethylene glycol ratios are (a) 40 mL/0 g, (b) 40 mL/0.10 g, (c) 40 mL/1.0 g, and (d) 40 mL/10 g.

particle size are needed for such applications.

On the other hand, poly(ethylene glycol) gave different results. The formation of Co_3O_4 was detected by using the XRD as well as SEM. In addition to the hexagonal platy particles, aggregates of smaller particles were observed in the SEM image (Fig. 4). The chemical origin of the oxidation of Co^{II} species is unclear at present, the formation of Co_3O_4 was detected in the syntheses of Co–Al-LDHs at higher temperature and higher Co^{II} content as reported previously.[20] Co_3O_4 is not desirable in the present study, further study involving poly(ethylene glycol) was not conducted.

Besse and co-workers have reported the syntheses of LDHs in water/alcohol mixtures by using both urea method and titration with NaOH.[25–27] Ethanol, propanol, iso-propanol, and ethylene glycol were used. The syntheses in the aqueous mixtures containing ethanol and propanol resulted in the formation of pseudoboehmite, while LDHs with smaller particle sizes (less than micron) were obtained as aggregates of small particles when the syntheses were performed in an aqueous mixture containing ethylene glycol. In the present study, Co–Al-LDH with a hexagonal platy morphology was obtained irrespective of the added amounts of ethylene glycol and glycerol. The aspect ratio of the products did not change apparently. The

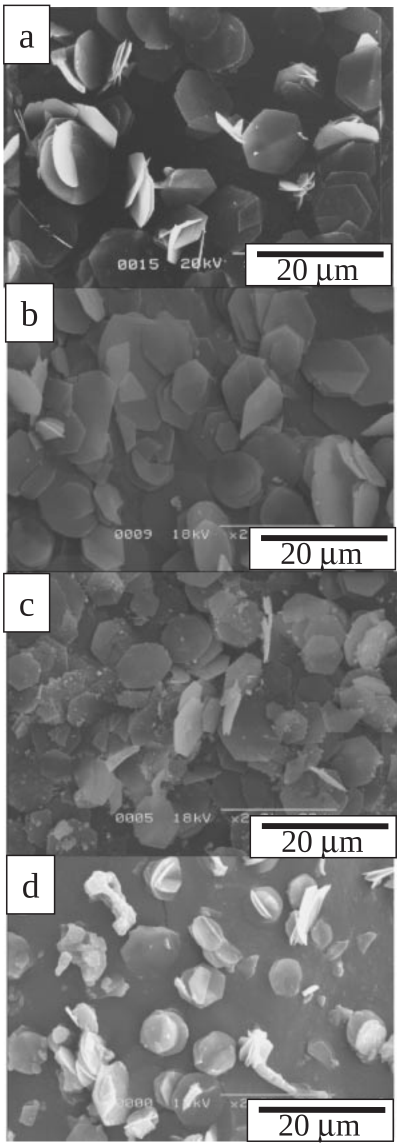

Fig. 4. SEM images of the precipitates obtained from water/poly(ethylene glycol) mixture. Water/poly(ethylene glycol) ratios are (a) 40 mL/0 g, (b) 40 mL/0.10 g, (c) 40 mL/1.0 g, and (d) 40 mL/10 g.

reaction was thought to be initiated from the precipitation of aluminum hydroxide and subsequent incorporation of bidentate cation with an increase in the pH.[28] Forano and co-workers proposed that the alcohols' role was to modify the particle morphology by being adsorbed on the growing particle surface.[25] Further studies on how to modify the crystal growth process should be considered after a systematic study on the preparation of LDHs with other water/alcohol mixtures.

Although it is difficult to compare the present particle size distribution with those of the reported products due to the lack of information, (SEM images of LDHs are available, while limited number of particles were shown there.) the present LDHs synthesized by using the urea method under hydrothermal conditions in the water/(ethylene glycol or glycerol) mixtures possess a very narrow particle size distribution.

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