

PREPARATION OF LARGE PLATY PARTICLES OF Co-Al LAYERED DOUBLE HYDROXIDES

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Abstract—Cobalt (II) and Al (III) layered double hydroxides were precipitated from homogeneous solutions using urea hydrolysis under hydrothermal conditions. The particle sizes were controlled successfully by changing the reaction temperature and period. It was found that larger particles formed by reactions at lower temperatures over longer reaction periods because the slow urea hydrolysis at lower temperatures suppresses the formation of nuclei in the solution. When the reaction was conducted at 60°C for 100 days, particles >40 μm wide were obtained.

Key Words—Hydrothermal Synthesis, Layered Double Hydroxides, Particle-size Distribution, Urea Hydrolysis.

INTRODUCTION

Layered double hydroxides (LDHs) are a class of layered materials consisting of positively charged brucite-like sheets, where some M^{2+} cations are substituted by M^{3+} cations giving a positive charge, and the charge-compensating interlayer exchangeable anions (Trifiro and Vaccari, 2004; Miyata, 1983). As well as considering the mineralogical and structural interests, studies of the possible applications of LDHs as catalysts (Kaneda *et al.*, 1998), adsorbents (Pavan *et al.*, 1998), ceramic precursors (Hibino and Tsunashima, 1998; Del Arco *et al.*, 1999; Alejandre *et al.*, 1999; Li *et al.*, 2005), reaction media for controlled photochemical (Takagi *et al.*, 1993) and electrochemical reactions (Yao *et al.*, 1998a), bioactive nanocomposites (Choy *et al.*, 1999, 2000) and pharmaceutical uses (Del Arco *et al.*, 2004; Nakayama *et al.*, 2004) have been conducted.

For some of the practical applications, the morphology of the LDHs is key to controlling performance, *e.g.* for use as fillers (Leroux and Besse, 2001; Oriakhi *et al.*, 1996), it is believed that particles with high aspect ratios and narrow particle-size distributions are favored. Co-precipitation of LDHs from aqueous solutions containing $M(II)$ and $M(III)$ by the addition of base such as aqueous NaOH is a common method for the synthesis of LDHs (Cavani *et al.*, 1991). Though the co-precipitation method is applicable to the synthesis of various LDHs and their intercalation compounds, finite crystallites with wide particle-size distributions are generally formed. In order to overcome this limitation, microwave

irradiation (Fetter *et al.*, 1997) and sonification (Climent *et al.*, 2004) were conducted to obtain well-crystallized and pure LDHs. Synthesis in an emulsion (He *et al.*, 2004) and in a colloid mill under vigorous mixing (Zhao *et al.*, 2002) have also been reported to control particle size and morphology.

The homogeneous precipitation method, using urea hydrolysis, is a promising means of preparing well-crystallized, large particles of various oxides and hydroxides because the pH increases homogeneously in the solution. Layered double hydroxides with particle sizes of 2–5 μm have been synthesized by the urea method (Cai *et al.*, 1994; Costantino *et al.*, 1998, 1999; Yao *et al.*, 1998b). We previously used hydrothermal conditions to successfully prepare large platy hydroxide particles (up to 25 μm wide) (Ogawa and Kaiho, 2002) with a relatively narrow particle-size distribution. Motivated by this success, efforts are being made in our laboratory to synthesize LDHs of other compositions. We report the synthesis of a LDH incorporating Co(II) and Al(III) (Co-Al-LDHs). In the past, Co-Al-LDHs have been synthesized by the co-precipitation method and their physicochemical properties were reported by Pérez-Ramírez *et al.* (1999, 2001, 2002), Kannan and Swamy (1992, 1999), Kannan *et al.* (1995), Ulibarri *et al.* (1991), Leroux *et al.* (2001), Xu and Zeng (2001) and Thompson *et al.* (1999). Due to the reported functions of Co-Al-LDHs, *e.g.* catalytic and magnetic, the morphosyntheses of Co-Al-LDHs are worth investigating. To our knowledge, the Co-Al-LDH particles reported so far are <0.1 μm wide. In the present study, we synthesized Co-Al-LDHs from aqueous solutions of $CoCl_2$ and $AlCl_3$, and investigated the effects of the synthesis conditions on the morphology of the Co-Al-LDH particles. The reaction parameters such as temperature and time and the Co/Al ratios had significant effects on the morphology of the product.

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EXPERIMENTAL

Materials

Urea (extra pure grade, >99.0%; Wako Pure Chemical Industries, Ltd.) and cobalt and aluminum chloride hexahydrates ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, Kanto Chemical Co., Inc.) were used as received.

Sample preparation

An aqueous stock solution of 0.01 M CoCl_2 , 0.01 M AlCl_3 and 0.1 M $(\text{NH}_2)_2\text{CO}$ were mixed at the molar Co:Al: $(\text{NH}_2)_2\text{CO}$ ratio of $x:1:10$ ($x = 1, 2, 3, 4$ or 5) and allowed to react in a Teflon-lined autoclave (Taiatsu Glass Ind. Co.). We have checked the effects of the $(\text{NH}_2)_2\text{CO}$:Al ratio on the Mg-Al-LDH system and the $(\text{NH}_2)_2\text{CO}$:Al ratio is a factor in determining the products. Judging from the preliminary experimental results on the product yield and by-product formation, the $(\text{NH}_2)_2\text{CO}$:Al ratio in the starting solution was fixed at 10 in the present study. The mixture was aged at temperatures between 50 and 150°C. After cooling to room temperature, the solid products were collected by centrifugation (3500 rpm for 15 min) and washed with deionized water. The products were dried under reduced pressure. The pH of the solutions before and after the reaction and the yield of the product (%) are summarized in Table 1.

Characterization

X-ray diffraction (XRD) patterns of the products were obtained on a Rigaku Rad IIB diffractometer using monochromatic $\text{CuK}\alpha$ radiation and operated at 40 kV and 20 mA. Thermogravimetric-differential thermal analysis (TG-DTA) curves were recorded on a Rigaku TG8120 instrument at a heating rate of 10°C/min and using α -alumina as the standard material. Fourier transform infrared (FTIR) spectra were recorded on a

Shimadzu FT-IR8200 by the KBr disk method. Scanning electron micrographs of the Au-coated samples were obtained using an Hitachi S-2380N scanning electron microscope. The coating thickness was 200 Å. The chemical compositions of the products were determined by electron microprobe analysis (EMPA) on a JEOL JXA-733 with detector (NORAN 605H-3SES). The products yields were determined from the concentration of Co^{2+} and Al^{3+} in the supernatant liquid with inductively coupled plasma (ICP) emission spectroscopy (ICP) using a Rigaku SPECTRO CIROS CCD device.

RESULTS AND DISCUSSION

As reported for the synthesis of hydrotalcite (Ogawa and Kaiho, 2002), Co-Al-LDHs were synthesized successfully. Table 1 summarizes the yields and compositions of the products.

Effect of the reaction temperature

Figure 1 shows the XRD patterns of the products prepared under the different temperatures. All the XRD patterns exhibit characteristic reflections corresponding 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.* (2001, 2002). When the reaction was conducted at 100°C, the by-product was not detected in the XRD pattern. On the other hand, the presence of Co_3O_4 was detected in the XRD patterns of the products prepared at 125 and 150°C (Figure 1b,c). As a result, the products were brown-black in color while pure Co-Al-LDH is pink (Figure 2).

In the infrared (IR) spectra of the products, absorption bands ascribable to a brucite-like sheet (OH-stretching vibration at $\sim 3400 \text{ cm}^{-1}$) and interlayer carbonate ions (CO-stretching vibration at $\sim 1350 \text{ cm}^{-1}$)

Table 1. Summary of experimental conditions, yields and chemical compositions of the products.

Reaction temperature (°C)	Reaction time (days)	The molar ratio of Co/Al	pH (before the reaction)	pH (after the reaction)	The ratio of Co/Al in the platy particles	Yield (%)	
						Co	Al
100	1	3	4.05	7.07	2.1	90	96
125	1	3	4.05	8.23		99	96
150	1	3	4.05	8.33		99	95
100	1	1	3.94	7.81	1.9		
100	1	2	3.98	7.40	1.9		
100	1	4	4.10	6.87	2.1		
100	1	5	4.11	6.68			
90	2	3	4.05	6.86		84	96
80	2	3	4.05	6.18		53	77
70	2	3	4.05	4.66		×	×
60	2	3	4.05	4.04		×	×
60	14	2	3.98	6.73			
60	100	2	3.98	8.28		96	100
50	150	2	3.98	7.16		73	82

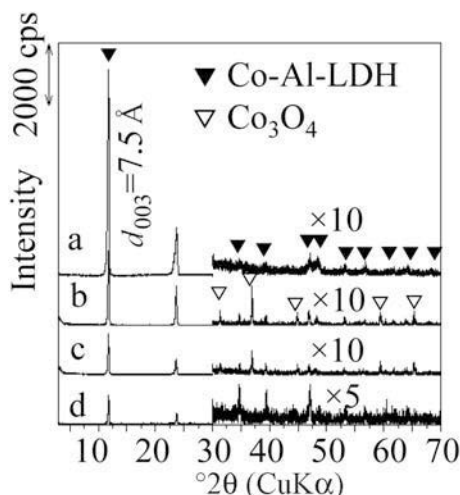


Figure 1. Powder XRD patterns of the products prepared at (a) 100, (b) 125 and (c) 150°C for 1 day, when the molar Co:Al ratio in the starting solution was 3, and (d) 50°C for 150 days when the molar Co/Al ratio in the starting solution was 2.

and bending vibration at $\sim 780\text{ cm}^{-1}$) were observed. These spectra are in good agreement with the spectrum reported by Klopogge and Frost (1999) for Co-Al-LDH. CO_3^{2-} was formed as a result of the urea hydrolysis and occluded in the products as the interlayer anions due to the high selectivity (Miyata, 1983). The bands observed in the wavenumber region between $800\text{ and }400\text{ cm}^{-1}$ are ascribable to Co-Al-O-stretching and bending and Co-O or Al-O-stretching vibrations (Hernandez-Moreno *et al.*, 1985). Due to the small amount of Co_3O_4 and the overlapping absorption bands, the presence of Co_3O_4 was not detected in the IR spectra of the products prepared by the reactions at 125 and 150°C, though its presence was detected by the XRD (Figure 1).

Thermogravimetric-differential thermal analysis curves were also recorded to confirm the formation of Co-Al-LDHs and Figure 4 shows the curves of the product prepared by the reaction at 100°C as a typical example. Two endothermic peaks at ~ 200 and 260°C were observed in the DTA curve, accompanying weight losses of 13 and 14%, respectively, in the corresponding TG curve. The first weight loss of 13% was attributed to the desorption of the adsorbed water. The second weight loss was associated with the evolution of carbon dioxide caused by the decomposition of the interlayer carbonate

anions as well as that of water due to dehydroxylation of the brucite-like sheet. These TG-DTA results are consistent with those of LDHs (Cavani *et al.*, 1991). Very similar TG-DTA curves were obtained irrespective of the reaction temperature, again showing that the products were mainly composed of Co-Al-LDH.

Figure 5 shows scanning electron micrographs of the products. Hexagonal plates with diameters of $5\text{--}15\ \mu\text{m}$ were observed for the product prepared by the reaction at 100°C . Similar plates with diameters of $3\text{--}5\ \mu\text{m}$ and granules of $100\text{--}300\text{ nm}$ width on the surface of the plates were observed for the products prepared by the reactions at 125 and 150°C . These granules are thought to be the Co_3O_4 phase present on the XRD patterns (Figure 1, traces b,c).

From the above-mentioned results, the reaction temperature was fixed at 100°C for 24 h in the following experiments, in order to obtain pure LDHs.

Effect of the molar ratio of Co:Al:urea

When the Co:Al ratio in the starting solution was changed to 1:1, 2:1, 3:1, 4:1 and 5:1, LDHs with similar XRD patterns were obtained. The Co:Al ratio of the platy particles were $\sim 2:1$ (summarized in Table 1) as determined by EMPA, irrespective of the Co:Al ratio of the starting solutions. We previously reported similar phenomena for the hydrothermal synthesis of hydroxycalcite (Ogawa and Kaiho, 2002). Costantino *et al.* (1998) reported that the $\text{Al}/(\text{Al}+\text{Mg})$ ratio of hydroxycalcite prepared using urea hydrolysis was constant even when the corresponding values in solutions were changed. These observations are inconsistent with the reported LDH characteristics; it was reported that $M(\text{II})/M(\text{III})$ ratios can be varied between 4:1 and 2:1 by changing the synthetic solution (Cavani *et al.*, 1991; Miyata, 1975). As for the Co-Al-LDHs, it was also possible to control the Co:Al ratios (Xu and Zeng, 2001; Leroux *et al.*, 2001). Cation ordering in the brucite-like sheet may be a reason for the present products to have a constant Co:Al value (2:1), though direct evidence of cation ordering has not yet been obtained.

Figure 6 shows scanning electron micrographs of the products and particle-size distributions derived from the SEM observations (of no fewer than 120 particles). Hexagonal plates are observed when Co:Al ratios were 1:1, 2:1 and 3:1, while disk-like particles are observed

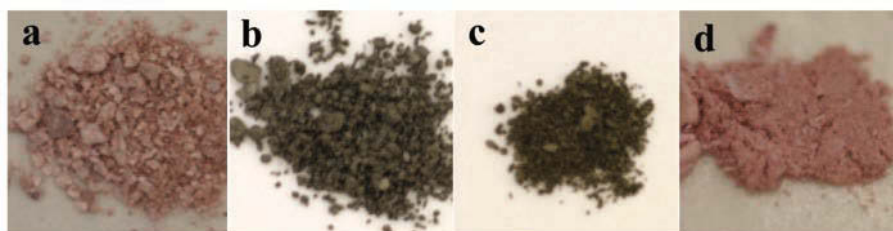


Figure 2. Photograph of the products prepared at (a) 100, (b) 125 and (c) 150°C for 1 day, when the molar Co:Al ratio in the starting solution was 3, and (d) 50°C for 150 days, when the molar Co/Al ratio in the starting solution was 2.

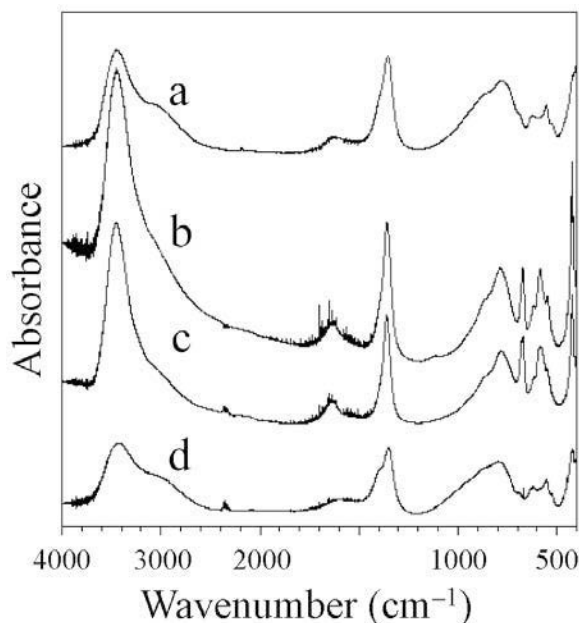


Figure 3. FTIR spectra of the products prepared at (a) 100, (b) 125 and (c) 150°C for 1 day, when the molar Co/Al ratio in the starting solution was 3, and (d) 50°C for 150 days, when the molar Co/Al ratio in the starting solution was 2.

when the Co:Al ratios were 4:1 and 5:1. When the Co:Al ratio was 5:1, stick-like by-products with lengths of <math><5\ \mu\text{m}</math> were observed. The amount of by-product was too small to be detected by XRD. The average particle size did not change notably depending on the Co:Al ratio except when the Co:Al ratio in the starting solution was 1.

Syntheses at 50 and 60°C

As mentioned above, hexagonal platy particles of Co-Al-LDH 5–15 μm wide have been prepared successfully. The size range is similar to that reported for

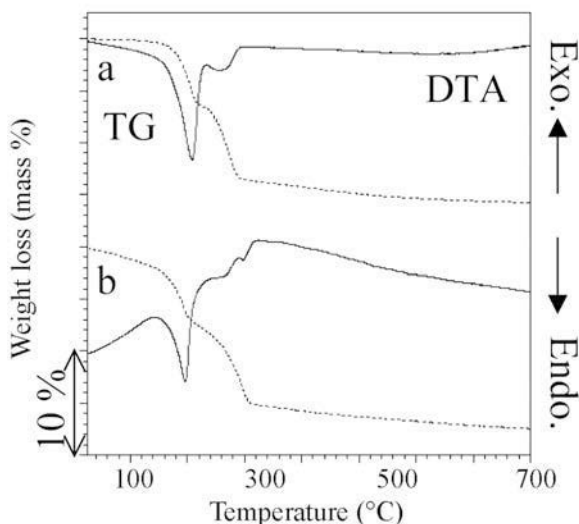


Figure 4. TG-DTA curves of the products prepared at 100°C for 1 day, when the molar Co/Al ratio in the starting solution was 3.

hydroxalcoite synthesized in similar hydrothermal conditions (Ogawa and Kaiho, 2002). The temperature is one of the most important factors in determining the particles' size, probably because of the urea hydrolysis rate. It was reported that the rate increases by ~ 200 times when the temperature is increased from 60 to 100°C (Shaw and Bordeaux, 1955). Taking this into account, a reaction at lower temperature was conducted to decrease the urea hydrolysis rate. The slow urea hydrolysis was expected to suppress the formation of nuclei in the solution at the initial stage, so that the limited number of

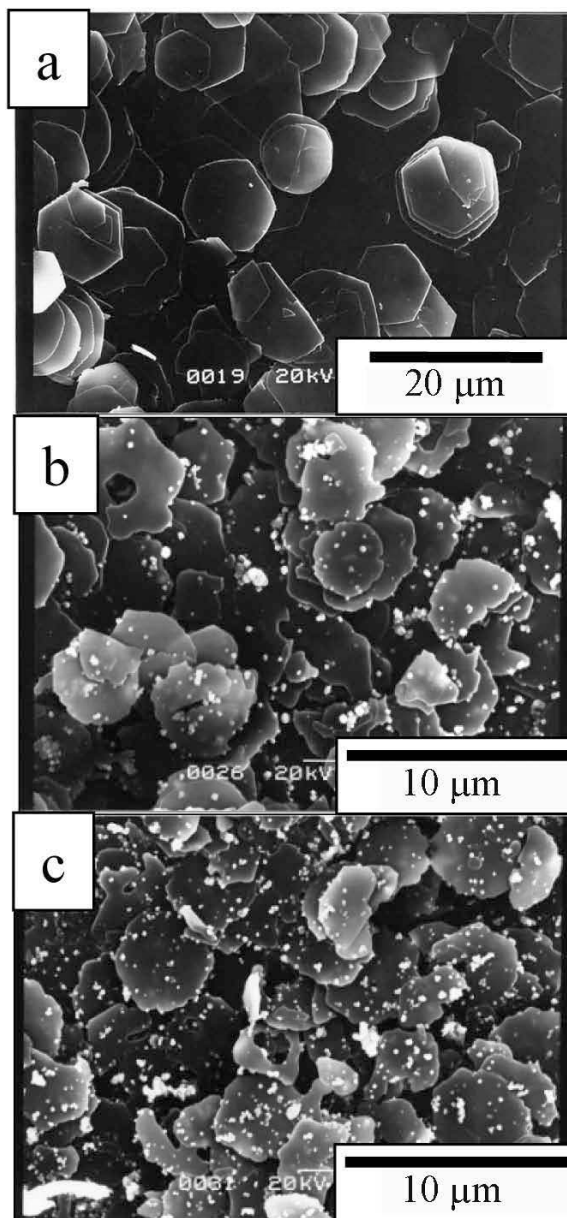


Figure 5. SEM images of the products prepared at (a) 100, (b) 125 and (c) 150°C for 1 day, when the molar Co/Al ratio in the starting solution was 3.

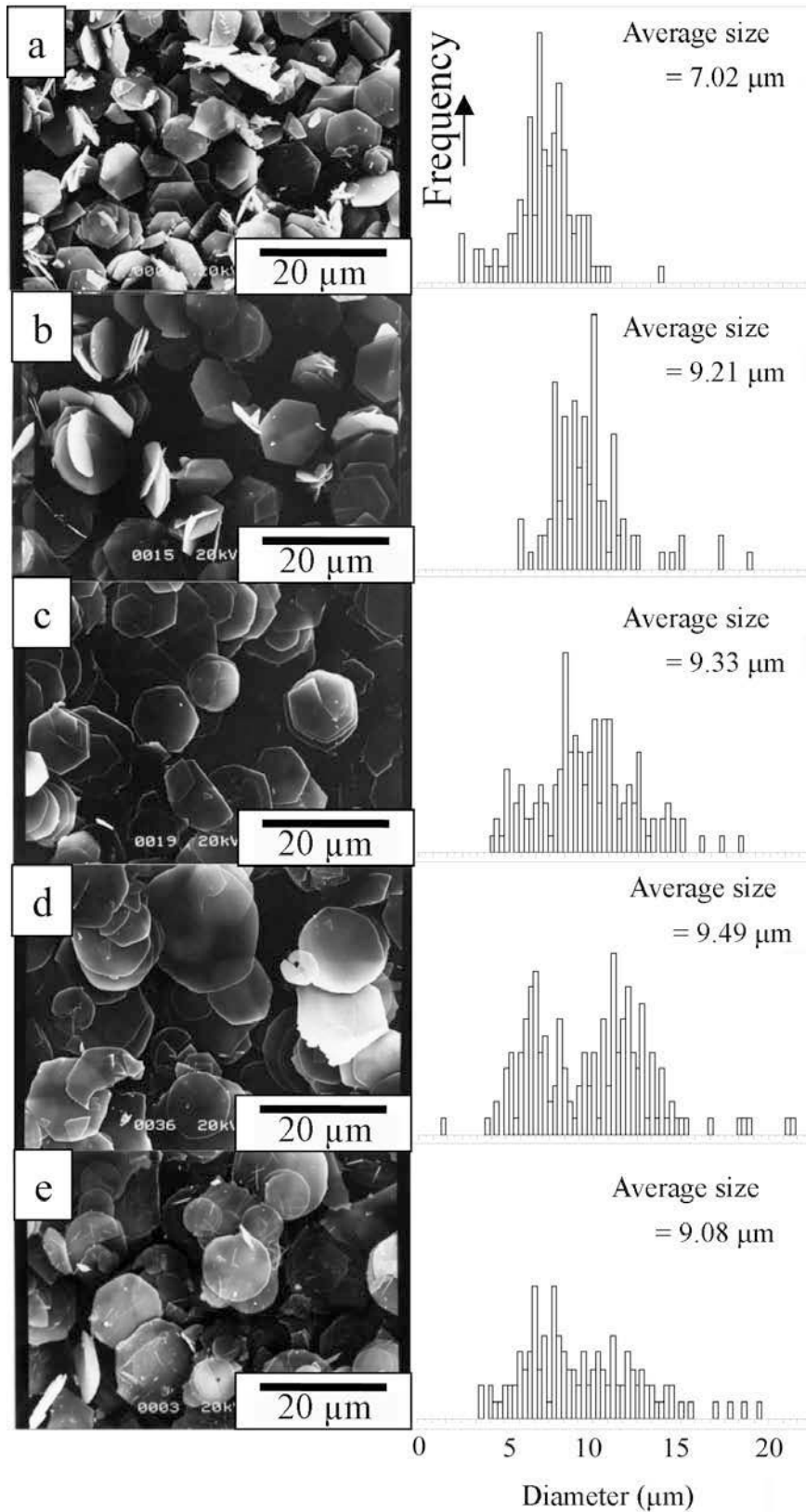


Figure 6. SEM images and particle-size distributions of the products prepared when the molar Co/Al ratio in the starting solution was (a) 1, (b) 2, (c) 3, (d) 4 and (e) 5.

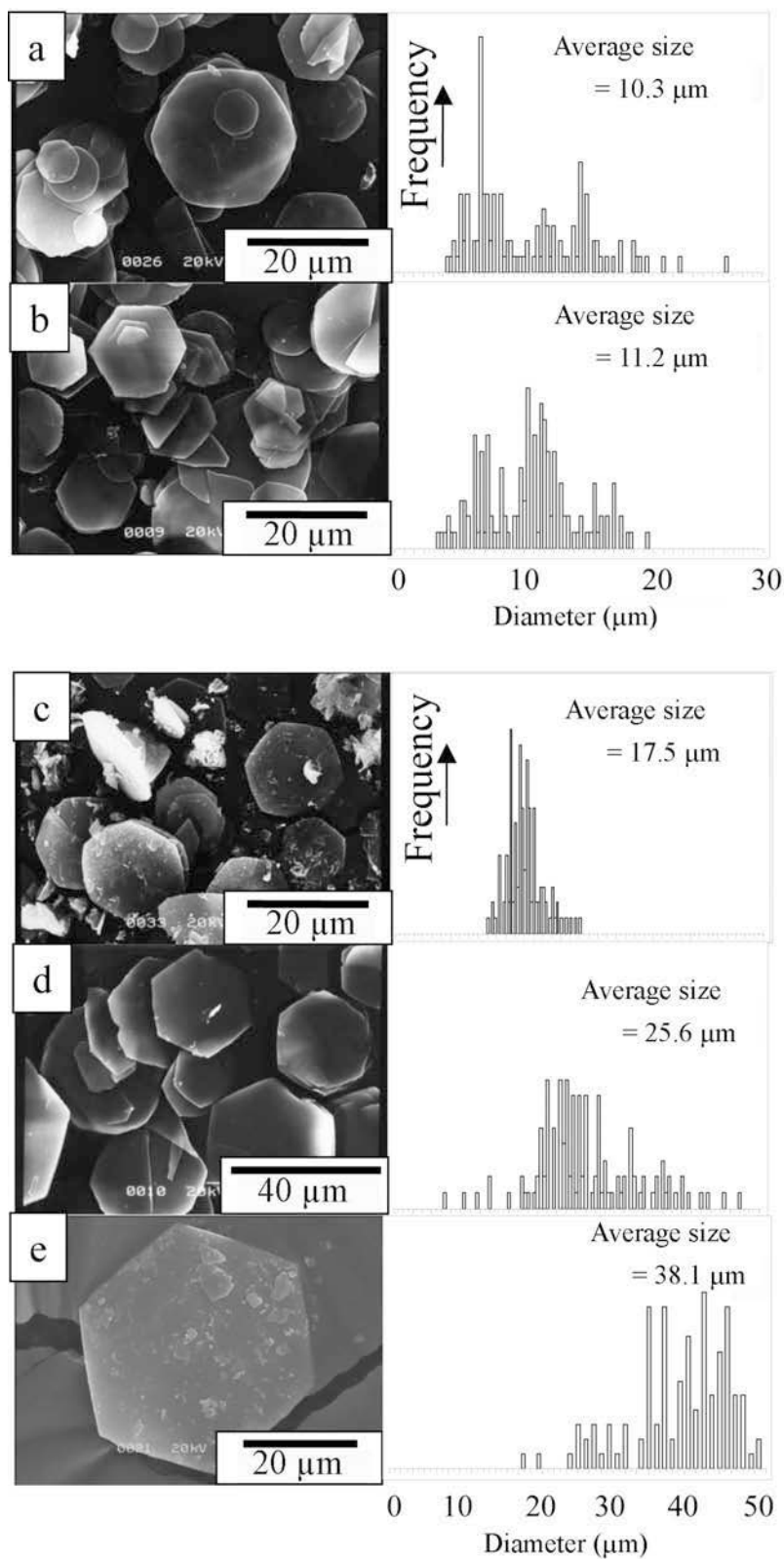


Figure 7. SEM images and particle-size distributions of the products prepared at (a) 80 and (b) 90°C for 2 days when the molar Co:Al ratio was 3. (c–e) Images of those products prepared at 60°C, 14 days (c), at 60°C, 100 days (d), and at 50°C for 150 days when the molar Co/Al ratio in the starting solution was 2.

nuclei formed can be grown to larger particles. When the reactions were conducted at 50, 60, 70, 80 and 90°C, Co-Al-LDHs formed, as proven by the XRD and IR results (data not shown). Figure 7a,b shows SEM images and particle-size distributions of the products prepared at 80 and 90°C. Hexagonal plates with diameters of ~5–25 µm are observed for both of the products. The product yields were small when the reactions were conducted at 60 and 70°C for 48 h. The pH of the solutions scarcely changed after the reactions (summarized in Table 1), suggesting that longer reaction time may be required for sufficient urea hydrolysis. Accordingly, synthesis at a lower temperature for a longer period was conducted.

Figure 7c,d shows SEM images and particle-size distributions of the products prepared at 60°C for 14 and 100 days. As previously, a very large hexagonal platy particle 47 µm wide and ~1 µm thick was obtained. Particles up to 47 µm wide were also obtained when the reaction was conducted at 50°C for 150 days allowing it to hydrolyze sufficiently (Figure 7e). The average particle size increased to 38.1 µm. The XRD pattern and FTIR spectrum (Figures 1d and 3d) reveal this product to be well-crystallized LDH. To our knowledge, the particles thus obtained are the largest synthetic LDHs so far reported.

As reported previously for the hydrothermal synthesis of hydrotalcite, hexagonal platy particles of Co-Al-LDH 47 µm wide and <1 µm thick were successfully synthesized by the reaction in a closed vessel. Since the reactions are easy to conduct, their applications in the synthesis of LDHs with different chemical compositions are promising. The aspect ratios of the particles seem to be almost constant irrespective of size. Other experimental techniques should be deployed to control the values.

CONCLUSIONS

Hexagonal platy particles of Co-Al-LDHs with the chemical composition $\text{Co}_2\text{Al}(\text{OH})_6(\text{CO}_3)_{0.5}n\text{H}_2\text{O}$ were synthesized from aqueous solutions of urea and Co and Al chlorides. Urea hydrolysis upon heating resulted in an increase in pH causing the precipitation of Co-Al-LDHs. The chemical composition of the products was difficult to control even when the composition of the starting solution was changed, though particle sizes were controlled by varying the reaction temperature and period. When the reaction was conducted at 60°C for 100 days, particles >40 µm wide were obtained successfully.

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