

Preparation of Layered Double-Hydroxide Nanomaterials with a Uniform Crystallite Size Using a New Method Involving Separate Nucleation and Aging Steps

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In particle formation, the method can be just as important as the chemical reaction involved. A new method of synthesizing hydrotalcite-like layered double hydroxides (LDHs) of the type $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2]^{x+}(\text{CO}_3^{2-})_{x/2} \cdot y\text{H}_2\text{O}$ ($x = 1.7\text{--}3.3$) is reported. The key features of this method are a very rapid mixing and nucleation process in a colloid mill followed by a separate aging process. The properties of the resulting LDHs are compared with those of materials produced using the conventional coprecipitation process at constant pH. The compositions and structural parameters of the materials synthesized using the two routes are very similar, although the crystallinity is slightly higher for the LDHs produced using the new method. The thermal behavior of the materials synthesized using the two routes is also similar. The major advantage of the new method is that it affords smaller crystallites with a higher aspect ratio, having a very narrow distribution of crystallite size. In the conventional coprecipitation process at constant pH, the mixing process takes considerable time such that nuclei formed at the beginning of the process have a much longer time to undergo crystal growth than those formed at the end of the process. The consequence is that a wide dispersion of crystallite sizes is obtained. In the colloid mill process, however, the mixing and nucleation are complete in a very short time and are followed by a separate aging process. Furthermore, we suggest that the extreme forces to which the nucleation mixture is subjected in the colloid mill prevent aggregation of the nuclei and result in the nuclei having a uniform small size. When the resulting mixture is aged in a separate process, well-formed crystallites with a similarly narrow range of diameters result.

Introduction

Layered double hydroxides (LDHs) are a class of synthetic anionic clays whose structure can be described as containing brucite ($\text{Mg}(\text{OH})_2$)-like layers in which some of the divalent cations have been replaced by trivalent ions, giving positively charged sheets.^{1,2} This charge is balanced by intercalation of anions in the hydrated interlayer regions. They can thus be considered complementary to aluminosilicate clays. LDHs can be represented by the general formula $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot y\text{H}_2\text{O}$. The identities of the di- and trivalent cations (M^{II} and M^{III} , respectively) and the interlayer anion (A^{n-}) together with the value of the stoichiometric coefficient (x) may be varied over a wide range, giving rise to a large class of isostructural materials. The parent material of this class is the naturally occurring mineral hydrotalcite, which has the formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$, and LDHs are consequently also known as hydrotalcites or, more accurately, hydrotalcite-like materials. LDHs have found a wide

variety of uses¹ including as anion exchangers, adsorbents, catalysts and catalyst supports, and additives to plastics. In addition to the composition and degree of crystallinity, the crystallite size and its distribution are important considerations for many potential applications of LDHs. For example, they can be used as an additive in agricultural plastic film since their infrared-absorbing properties lead to an improvement in the heat-retaining properties of the film, resulting in increased nighttime temperatures. In this case the particle size of the LDH should be in the nanometer range and the particle size distribution should be narrow;^{3,4} otherwise, the LDH additive has an adverse effect on both the mechanical properties and optical transparency of the plastic film.

LDH materials are traditionally synthesized by coprecipitation reactions from aqueous solution.¹ The method of mixing and the pH during the nucleation and precipitation process have been reported^{1,5} to be the

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most important synthesis variables and can have a marked influence on the particle size and texture of the resulting products. In the so-called variable-pH precipitation process,¹ hydrotalcite-type LDH carbonates are typically prepared by adding a solution containing Mg^{2+} and Al^{3+} cations to a solution of Na_2CO_3 until the pH of the reaction mixture reaches a specified value (typically around 10) and a solution of NaOH is then used to maintain the pH value until the precipitation is complete. More commonly used is the constant-pH coprecipitation method at low supersaturation,^{1,6} which involves simultaneous dropwise addition of mixed salt and base solutions to a reaction vessel at such a rate that the pH remains constant. In either case, once mixing is complete, the resulting suspension is subsequently aged at elevated temperatures. Yun and Pinnavaia have reported⁷ a detailed comparison of the properties of carbonate-containing magnesium–aluminum LDH materials produced using these two methods. The variable-pH method was shown to afford fine-grained crystals with rough surfaces and relatively high surface areas, whereas the constant-pH method gave larger well-formed hexagonal crystals. Precipitation at constant pH involves low supersaturation, leading to a relatively small number of nuclei so that crystallites with a large size are generally produced. It is difficult to control the particle size and distribution of LDHs using the traditional methods. Formation of crystallites involves two stages—nucleation and aging.⁸ The processes occurring while a crystal is undergoing aging in its mother liquor are very complex and can involve crystal growth, agglomeration, breakage, and other processes such as Ostwald ripening. Since the addition process takes considerable time in both the case of precipitation at variable pH and constant pH, nuclei formed at the start of the addition process have a much longer period of time to undergo aging than those formed at the end of the addition process. In other words, the formation of nuclei and aging take place simultaneously during the prolonged addition process. The inevitable consequence is that after aging a wide dispersion of crystallite sizes is obtained. Valim and co-workers have confirmed⁹ that, in the case of magnesium–aluminum and zinc–chromium LDH materials containing interlayer terephthalate or dodecyl sulfate anions, a wide distribution of crystallite sizes were obtained using coprecipitation at either variable or constant pH. The crystallinity of the materials was higher in the case of precipitation at constant pH, however.

In this paper, we report a new method for the synthesis of LDH materials developed in our laboratory,^{10,11} which involves a very rapid mixing and nucleation process in a colloid mill,^{12,13} followed by a separate aging process. The structural and morphological proper-

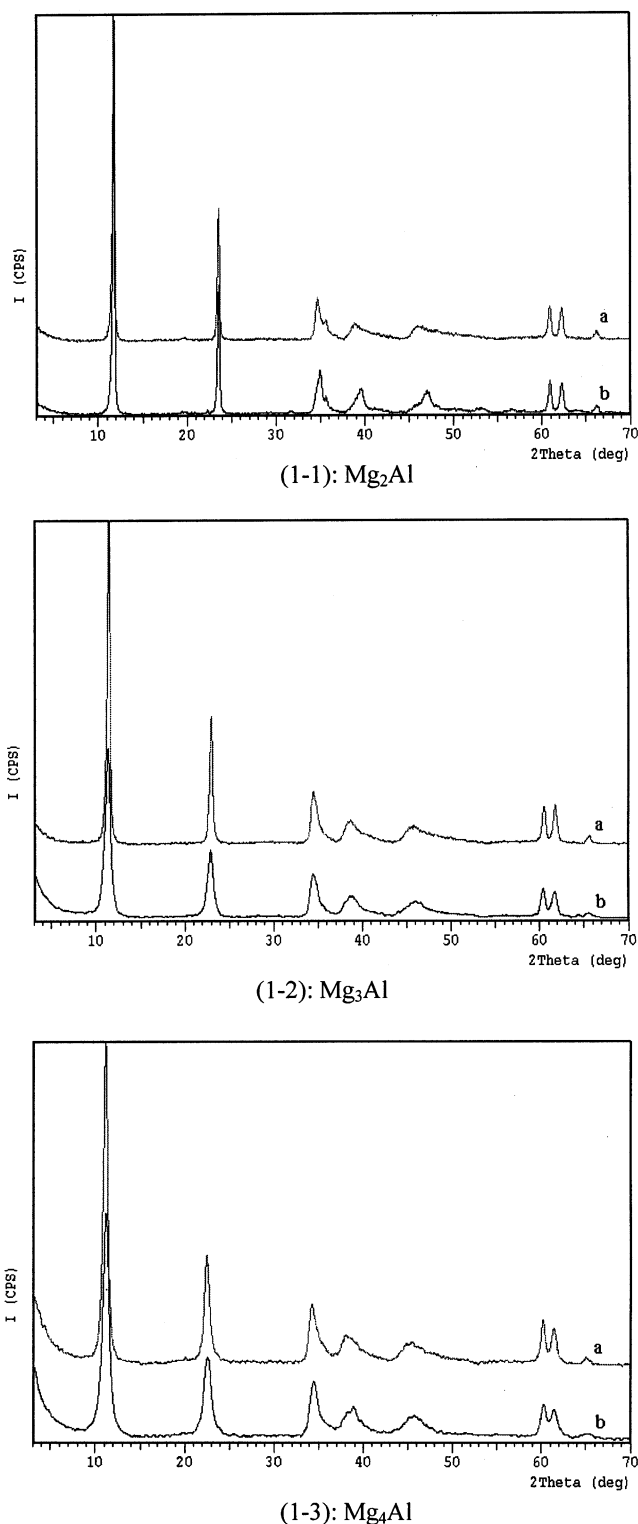


Figure 1. XRD patterns for Mg–Al–CO₃ LDHs with different Mg^{2+}/Al^{3+} ratios prepared using (a) our new method using rapid mixing and nucleation in a colloid mill followed by a separate aging step and (b) conventional coprecipitation at constant pH. The new method gives LDHs of higher crystallinity.

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ties of LDH carbonates with different compositions produced using the new method are compared with those produced using the constant-pH method employed by Yun and Pinnavaia⁷ and others.^{1,2} Materials prepared using the variable-pH method were not included in this study since Yun and Pinnavaia⁷ have previously

Table 1. Properties of LDHs Prepared Using the Two Different Methods

property	constant-pH method			new method with separate aging and nucleation steps		
	Mg ₂ Al	Mg ₃ Al	Mg ₄ Al	Mg ₂ Al	Mg ₃ Al	Mg ₄ Al
Al ³⁺ substitution, ^a <i>x</i>	0.371	0.287	0.239	0.367	0.285	0.231
Mg ²⁺ /Al ³⁺ ratio	1.69	2.48	3.18	1.73	2.51	3.33
basal spacing, nm	0.7537	0.7832	0.7909	0.7530	0.7823	0.7944
<i>d</i> ₁₁₀ , nm	0.1521	0.1533	0.1535	0.1521	0.1532	0.1538
lattice parameter ^b <i>a</i> , nm	0.3042	0.3066	0.3070	0.3042	0.3064	0.3076
lattice parameter ^c <i>c</i> , nm	2.280	2.341	2.360	2.284	2.341	2.371
crystallite size in <i>c</i> direction, ^d nm	29.6	11.6	9.6	30.9	21.8	14.0

^a Value of *x* in the formula [Mg_{1-*x*}Al_{*x*}(OH)₂](CO₃)_{*x*/2}·*y*H₂O, as determined by ICP. ^b *c* = average value calculated from (003), (006), and (009) reflections. ^c *a* = 2*d*₁₁₀. ^d Value calculated from the Scherrer equation (see text).

Table 2. Surface Water Content of LDHs Prepared Using the Two Different Methods

	constant-pH method			new method with separate aging and nucleation steps		
	Mg ₂ Al	Mg ₃ Al	Mg ₄ Al	Mg ₂ Al	Mg ₃ Al	Mg ₄ Al
weight loss during the first stage, %	14.10	12.48	8.91	14.62	14.59	12.25
temperature range of weight loss/°C	50–254	50–233	62–230	50–254	50–235	62–230
total surface water, ^a <i>n</i>	0.64	0.54	0.36	0.67	0.64	0.51
maximum intrinsic surface water, ^b <i>n</i> ' _{max}	0.44	0.57	0.64	0.45	0.57	0.65

^a Water content expressed in moles per Mg_{1-*x*}Al_{*x*}(OH)₂ octahedral unit. ^b *n*'_{max} = 1 – (3*x*/2) (see text).

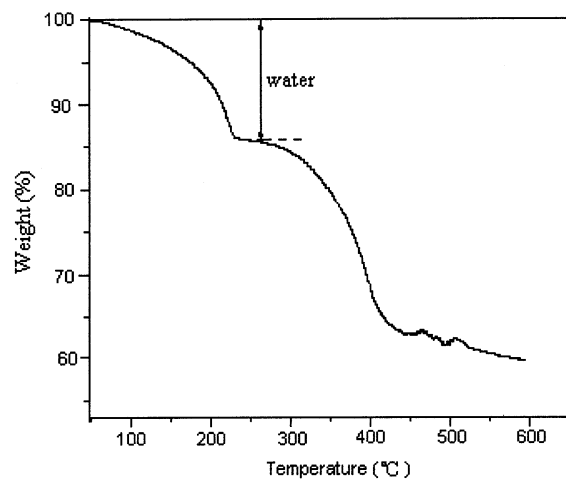


Figure 2. TG plot for Mg–Al–CO₃ LDHs with an initial Mg²⁺/Al³⁺ ratio of 3:1 prepared using our new method using rapid mixing and nucleation in a colloid mill followed by a separate aging step.

shown that this method gives materials of inferior crystallinity compared with those obtained using the variable-pH method, as discussed above.

Experimental Section

Precursor Solutions. Solution A: Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O with Mg²⁺/Al³⁺ ratios of 2.0, 3.0, and 4.0 were dissolved in deionized water (225 mL) to give solutions with an Mg²⁺ concentration of 1.6 M. Solution B: NaOH and Na₂CO₃ were dissolved in deionized water (225 mL) to form the mixed base solution. The concentrations of the base were related to the concentrations of metal ions in solution A as follows: [NaOH] = 1.6[Mg²⁺ + Al³⁺] and [CO₃²⁻] = 2.0[Al³⁺].

LDH Synthesis by the Constant-pH Method. Solution A (225 mL) and solution B (225 mL) were simultaneously added dropwise to a vessel containing stirred deionized water (180 mL) at such a rate that the pH of the reaction mixture was maintained at 9.5. The mixing process was carried out at room temperature. The resulting slurry was aged at 100 °C for 13 h. The precipitate was then filtered, washed well with deionized water, and dried at 100 °C for 24 h.

LDH Synthesis with Separate Nucleation and Aging Steps. Solution A (225 mL) and solution B (225 mL) were

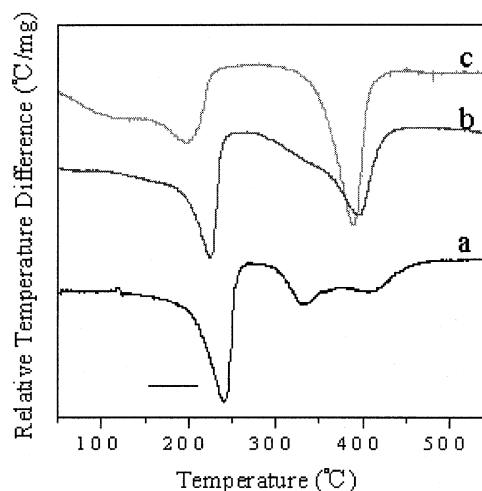


Figure 3. DTA curves for Mg–Al–CO₃ LDHs with initial Mg²⁺/Al³⁺ ratios of (a) 2:1, (b) 3:1, and (c) 4:1 prepared using our new method using rapid mixing and nucleation in a colloid mill followed by a separate aging step.

simultaneously added to a colloid mill^{12,13} rotating at 3000 rpm and mixed for 2 min. The resulting slurry was removed from the colloid mill and aged at 100 °C for 13 h. The final precipitate was filtered, washed thoroughly with deionized water, and dried at 100 °C for 24 h.

Characterization. Powder XRD patterns of the samples were recorded using a Rigaku XRD-6000 diffractometer under the following conditions: 40 kV, 30 mA, Cu Kα radiation. The samples, as unoriented powders, were step-scanned in steps of 0.04° (2θ) in the range from 3 to 70° using a count time of 10 s/step.

Elemental analyses were performed by ICP emission spectroscopy using solutions prepared by dissolving the samples in dilute HNO₃.

Thermogravimetric analysis and differential thermal analysis (TG-DTA) were carried out on a PCT-1A thermal analysis system produced locally. Samples were dried at 100 °C for 24 h prior to analysis.

Transmission electron micrographs (TEM) were recorded on an Hitachi H-800 TEM instrument.

The particle size distribution was determined using a Malvern Mastersizer 2000 laser particle size analyzer.

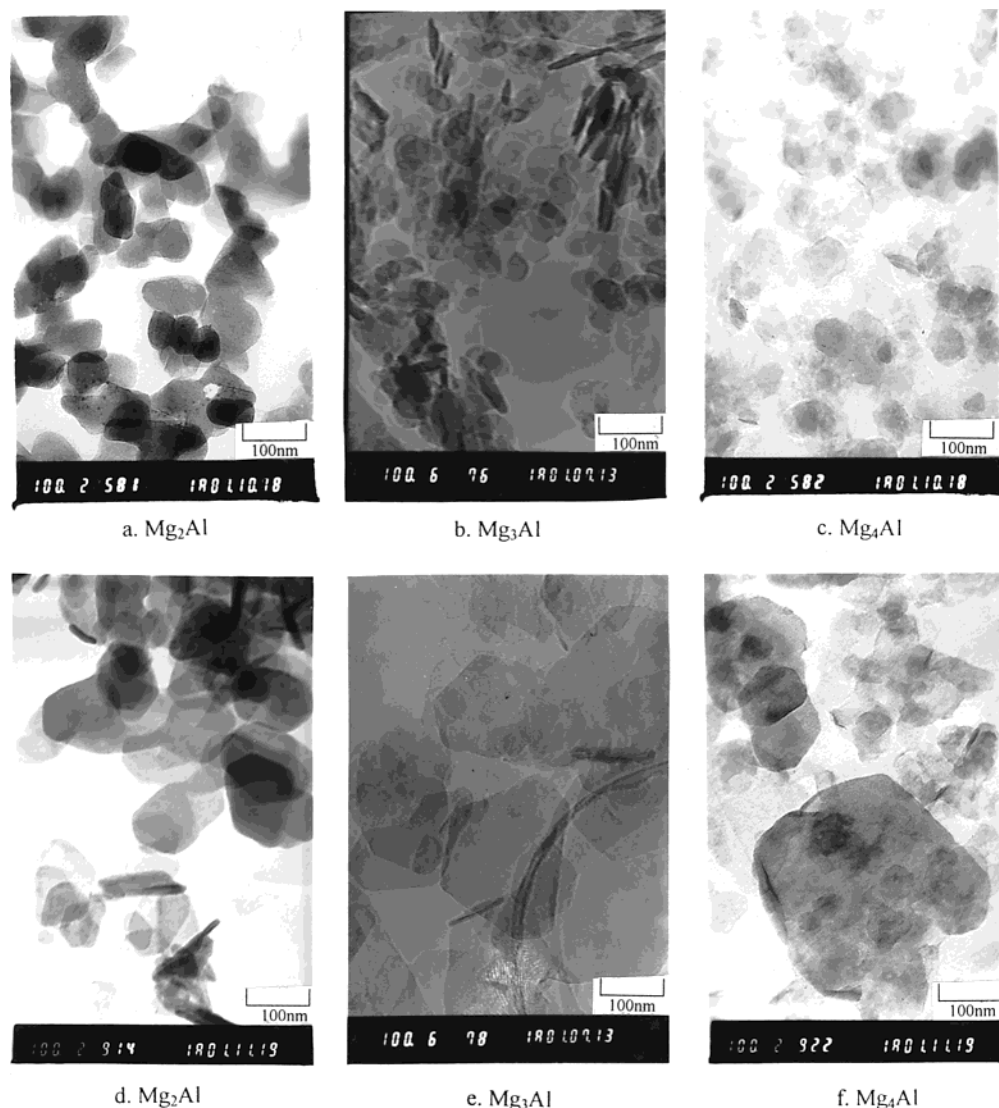


Figure 4. TEM micrographs of Mg–Al–CO₃ LDHs with different Mg²⁺/Al³⁺ ratios prepared using our new method using rapid mixing and nucleation in a colloid mill followed by a separate aging step [(a)–(c)] and conventional coprecipitation at constant pH [(d)–(f)]. The new method affords smaller crystallites with a much narrower range of length.

Results and Discussion

In general, LDH compounds are formed by coprecipitation reaction of M²⁺, M³⁺, and A^{n−} ions from aqueous solution. The method of mixing the reagents has an important influence on the nucleation and precipitation processes and will influence the crystallite size and crystallite size distribution. The difference between the constant-pH method used by Yun and Pinnavaia⁷ and others^{1,2} and our new method involving separate nucleation and aging steps lies in the different way of mixing the reagents. The constant-pH method involves simultaneous dropwise addition of mixed salt and base solutions to a reaction vessel under conditions of constant pH at all stages of the nucleation/precipitation process. The new method involves very rapid mixing under vigorously stirred conditions in a colloid mill^{12,13} to complete the nucleation process, followed by a separate aging process. The colloid mill consists of a conical rotor [basal diameters 18 cm (top) and 4 cm (bottom), height 15 cm] and a stator with a narrow gap (10 μm) between them. A rotor speed of 3000 rpm was employed in this work. The mixing takes place in the liquid thin film between the rotor and stator. The

reactants were rapidly added to the colloid mill and sheared in closed, continuous operation for 60 s. All other variables were constant for the two synthesis methods. The two methods were used to prepare LDH carbonates of the type [Mg_{1−x}Al_x(OH)₂](CO₃)_{x/2}·yH₂O with different (Mg²⁺/Al³⁺) ratios.

Table 1 lists the compositions and structural parameters for the products prepared using the two methods. The samples are denoted Mg_nAl, where *n* is the Mg²⁺/Al³⁺ molar ratio employed in the synthesis mixture. The Mg²⁺/Al³⁺ ratios of the final products are lower than the values used in the reaction mixtures. The constant pH method gives slightly higher levels of Al³⁺ substitution than the method with separate nucleation and aging steps, but the values are comparable.

The powder XRD patterns for the LDH carbonates prepared using the two different methods are shown in Figure 1. In each case, the XRD patterns exhibit the characteristic reflections of LDH materials with a series of (00*l*) peaks appearing as narrow symmetric lines at low angle, corresponding to the basal spacing and higher order reflections. The intensities of the diffraction peaks of LDHs prepared using our new method with separate

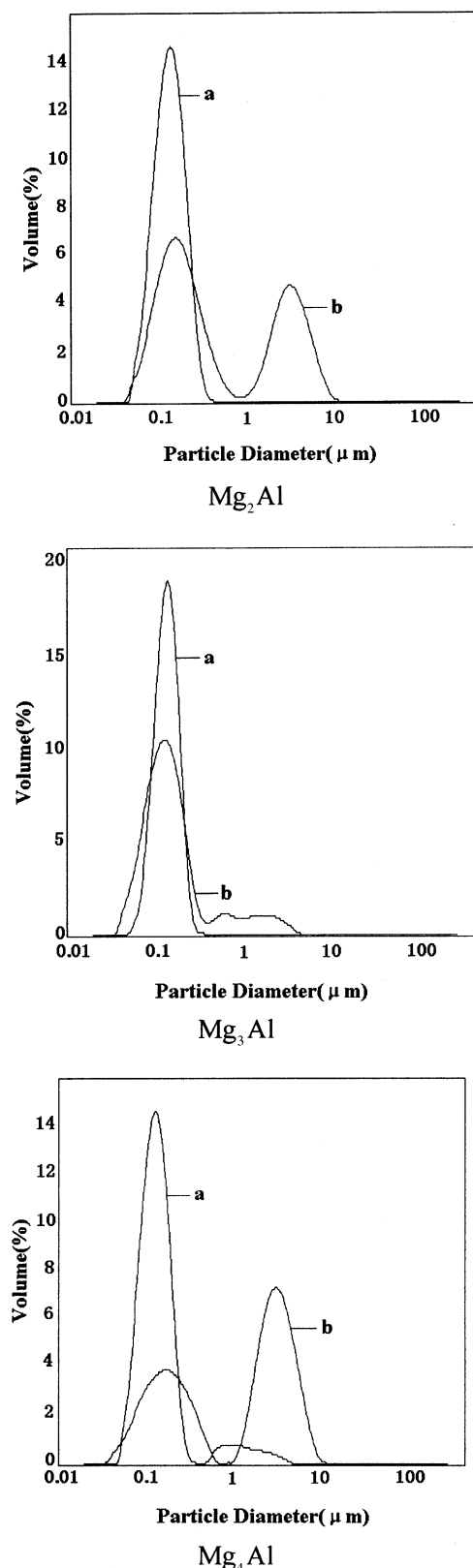


Figure 5. Profiles of particle diameter distribution for Mg–Al–CO₃ LDHs with different Mg²⁺/Al³⁺ ratios prepared using (a) our new method using rapid mixing and nucleation in a colloid mill followed by a separate aging step and (b) conventional coprecipitation at constant pH. The new method affords materials with a much narrower range of diameter.

nucleation and aging steps are higher than those of the corresponding peaks for LDHs prepared using the constant-pH method. This indicates that the LDHs

prepared using our new method have higher crystallinity. In each case no other crystalline phases have been formed. Assuming a 3R stacking of the layers and from the positions of the (003), (006), (110) reflections, the lattice parameters a and c may be calculated.¹⁴ As shown in Table 1, these are essentially independent of the synthesis method. The unit cell parameter a is the average distance between two metal ions in the layers and c is 3 times the distance from the center of one layer to the next. The value of a ($=2d_{110}$) is a function of the average radii of the metal cations while the value of c ($=3d_{003}$) is a function of the average charge of the metal cations, the nature of the interlayer anion, and the water content. The lattice parameter a decreases with increasing isomorphous substitution of Mg²⁺ by Al³⁺ as has been reported elsewhere,¹ reflecting the fact that the ionic radii for Mg²⁺ and Al³⁺ are 0.65 and 0.50 Å, respectively. The increase in lattice parameter c with increasing Mg²⁺/Al³⁺ ratio is consistent with the decrease in Coulombic attractive force between the negatively charged interlayer anions and the positively charged brucite-like layers and as the proportion of trivalent ions in the latter decreases. The structural properties of the LDHs produced using our new method are thus consistent with those produced using conventional methods. The average crystallite size in the c direction (the stacking direction, perpendicular to the layers) may be estimated from the values of the full-width at half-maximum (fwhm) of the (003) and (006) diffraction peaks by means of the Scherrer equation [$L = 0.89\lambda/\beta(\theta) \cos \theta$, where L is the crystallite size, λ is the wavelength of the radiation used, θ is the Bragg diffraction angle, and $\beta(\theta)$ is the fwhm].¹⁴ The values given in Table 1 (average value of L obtained from the data for the (003) and (006) diffraction peaks) show that irrespective of the synthesis method the crystallite sizes in the c direction decrease as the Mg²⁺/Al³⁺ ratio increases. The presence of a larger number of tripositive aluminum ions in the layers presumably accelerates the rate of stacking of the layers. Although the average crystallite size in the a direction is sometimes estimated from the fwhm of the (110) peak,¹⁵ the low intensity of this peak coupled with the approximations inherent in the Scherrer equation introduce a large uncertainty into the calculated value.

As shown in Figure 2 for one representative case, the thermal behavior of the LDHs is characterized by two transitions: the first one at low temperature corresponds to the loss of surface water (from both the internal gallery surfaces and the external (nongallery) surfaces); the second one at higher temperature is due to dehydroxylation of the brucite-like layers as well as decomposition of the carbonate anions. The content of surface water can be determined from the weight loss during the first stage in the TG curve for LDHs. Table 2 shows the corresponding data for samples previously dried at 100 °C. The amount of water per Mg_{1-x}Al_x(OH)₂ octahedral unit decreases on decreasing the degree of aluminum substitution (x) for samples produced by either method. The same trend was observed by Yun and Pinnavaia⁷ for LDHs produced using the variable-

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pH method, although in this case the reported water contents were higher. This may be due to the lower predrying temperature employed (60 °C) or the fact that the samples were fine-grained crystals with rough surfaces. The amounts of water incorporated are higher for the LDHs produced by our new method than for those produced using the conventional constant-pH method. The maximum amount of intrinsic water that can be structurally accommodated as a monolayer in the galleries of an LDH with the degree of aluminum substitution x is given by $n'_{\max} = 1 - 3(x/2)$ since $3(x/2)$ represents the fraction of gallery sites occupied by the CO_3^{2-} oxygen atoms.⁷ When x is large, the high carbonate content in the interlayer galleries leads to substantial crowding and a significant fraction of the surface water must be accommodated on the nongallery surfaces as reported by Yun and Pinnavaia⁷ for LDHs produced using the variable-pH method. As shown in Figure 3, the positions of the endothermic maxima in the DTA increase with increasing aluminum content for LDHs produced using our new synthetic procedure. The same trend was reported by Yun and Pinnavaia⁷ for LDHs produced using the variable-pH method. As discussed by Yun and Pinnavaia,⁷ the observed increase in the desorption temperature with increasing layer charge density is probably caused in part by the greater steric constraints on the interlayer water molecules and by a larger number of hydrogen-bonding interactions between the interlayer water molecules and carbonate anions. The thermal behavior of the LDHs synthesized using our new method is thus very similar to that of materials produced using conventional coprecipitation processes.

TEM micrographs of the LDHs obtained using the two different synthesis methods are illustrated in Figure 4. The expected hexagonal platelike nature of the crystallites is clearly apparent in each case. The average diameter of the platelets is smaller for the LDHs prepared using our new method and considerably more uniform in distribution than for the materials produced using the constant-pH method. The diameters of the LDH crystallites produced using our new method are in the range 60–80 nm. Although the thickness of the platelets is difficult to compare from the TEM micrographs, the values estimated using the Scherrer equation (see Table 1) are higher for the LDHs produced using our new method. Taken together, these two results indicate that the LDHs produced using our new method have a smaller aspect ratio (defined as platelet diameter/thickness) than those produced using the conventional constant-pH method.

The particle size distribution for each of the LDH samples was determined by low-angle laser light scattering, which gives accurate results for particle diameters in the range 0.05–3500 μm . For any given particle, the value of the particle diameter obtained using this

method is the diameter of a sphere of equivalent volume. The results for the particle size distribution by volume are shown in Figure 5. For each $\text{Mg}^{2+}/\text{Al}^{3+}$ ratio, the particle size distribution for the LDH material produced using our new method is considerably narrower than that for the LDH sample produced by precipitation at constant pH. The latter generally shows a bimodal distribution over a wide range. Thus, by having a rapid nucleation process in the colloid mill, followed by a separate aging process, it is indeed possible to produce materials with a narrow range of crystallite sizes. We believe that there are two features of our new synthesis procedure that are responsible for the narrow particle size distribution. First, the mixing process resulting in nucleation, which takes place in the colloid mill, is complete in a very short time. In contrast, in the conventional precipitation process at constant pH, the addition process takes considerable time such that nuclei formed at the start of the addition process have a much longer time to undergo crystal growth than those formed at the end of the addition process. In other words, the formation of nuclei and crystal growth take place simultaneously in the addition process. The inevitable consequence is that after aging a wide dispersion of crystallite sizes is obtained. Second, in the colloid mill the solutions are mixed in a thin liquid film under conditions of high-speed fluid shear and high pressures and friction between the stator and rotor (rotating at 3000 rpm) with the mixture also being subjected to intensive vibration. In this highly turbulent zone, the newly formed nuclei undergo energetic collisions and this, together with the large hydraulic shear forces to which the nucleation mixture is subjected, means that agglomeration of the nuclei is inhibited and their size remains at a minimum. The resulting mixtures of crystallite nuclei with a narrow range of particle size are then aged in a separate process, resulting in well-formed crystallites with a similarly narrow range of diameters.

Conclusions

LDHs can be prepared by rapid mixing of the precursor solutions in a colloid mill, which initiates nucleation, followed by a separate aging step. The compositions, structural parameters, and thermal behavior of the LDHs synthesized using this method are comparable to those of materials synthesized using conventional coprecipitation at constant pH. The colloid mill method, however, gives smaller crystals with a high aspect ratio. Particularly noteworthy is that the observed particle size distribution is much narrower when using this method. We are currently exploring the use of the colloid mill as a reaction vessel for the preparation of other inorganic materials produced by coprecipitation reactions.

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