

Water Content and Particle Texture of Synthetic Hydrotalcite-like Layered Double Hydroxides

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Hydrotalcite-like layered double hydroxides (LDHs) with compositions corresponding to $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2](\text{CO}_3)_{x/2}n\text{H}_2\text{O}$, where $(1-x)/x \approx 2, 3,$ and 4 , were prepared by complementary variable- and constant-pH coprecipitation methods. In the commonly used variable pH process, LDH precipitation was initiated at the elevated pH value of the starting carbonate solution and terminated at $\text{pH} \approx 10$. In contrast, the constant pH method allowed the entire precipitation process to be carried out at $\text{pH} 10$. Both synthesis methods yielded air-dried LDH carbonates containing two types of water, namely, interparticle pore water, wherein water is condensed between aggregated crystal platelets, and surface water, which is bound to intragallery and external basal planes. Interparticle pore water was readily removed by heating to 60°C , but the temperature for complete removal of surface water increased from 240 to 280°C ($5^\circ\text{C}/\text{min}$) with increasing Al^{3+} content. A bimodal loss of surface water was consistent with the presence of "intrinsic" surface water bound to intracrystal gallery surfaces and "extrinsic" surface water adsorbed at the external surfaces of the crystallites. The particle textures of the LDH reaction products, as reflected in crystal morphologies, surface areas, and interparticle pore size distributions, were highly dependent on the preparation method and the layer charge density. Fine grained crystals with rough surfaces and relatively high surface areas were obtained by the variable pH method, whereas the constant pH method afforded larger, well-formed hexagonal crystals. All of the products prepared by the variable pH method exhibited mesopores with radii in the range $50\text{--}300 \text{ \AA}$. In contrast, the constant pH method gave Mg_3Al - and Mg_4Al -LDH carbonate crystals with narrow mesopore distributions near 20 \AA radius. TEM images provided evidence for the accommodation of interparticle pore water in voids formed by edge-face crystal aggregation. Cofacial layer stacking disorders also were observed that contribute both to the binding of extrinsic surface water and to the formation of mesopores.

Introduction

Hydrotalcite-like layered double hydroxides, henceforth abbreviated LDHs, consist of positively charged brucite-like ($\text{Mg}(\text{OH})_2$ -type) layers separated by counteranions and water molecules. The chemical composition of this class of intercalation compounds can be expressed in general as $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+}[\text{A}^{n-}]_{x/n}z\text{H}_2\text{O}$, where M^{II} and M^{III} are the divalent and trivalent cations in the octahedral interstices of the hydroxide layer and A^{n-} is the charge-balancing interlayer gallery anion. Owing in part to their anion exchange properties,^{1–3} certain LDH derivatives are useful materials for pollution prevention and waste cleanup. They also are valued as precursors for the preparation of a number of industrially important catalysts.⁴ More recently, LDH intercalates have been investigated as catalyst supports, particularly for the immobilization of biomimetic catalysts with properties suitable for the in situ remediation of contaminated soils.⁵ Another important

feature of LDH compositions is their ionic/protonic conductivity,⁶ which makes them potentially useful for sensor and other device applications.

Many of the materials properties of LDH intercalates are related in part to the exceptional mobilities of the gallery anions. Ionic mobilities depend on the water content of the gallery region occupied by the anions, as well as on the particle texture and water contained in interparticle pores.⁷ The acid/base properties and ion-exchange behavior of LDH compounds also should depend on water content and particle texture. Therefore, it is important to understand the partitioning of water between structural sites in the gallery and noncrystallographic sites in LDH compounds. However, relatively few studies have been reported for LDH intercalates, as compared to the more extensive knowledge available for water in silica gels,⁸ clays,⁹ and

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zeolites.¹⁰ With few exceptions,^{11,12} the distinction between different types of water in LDH compounds has not been generally recognized. de Roy et al.¹² have identified two types of surface-bound water in LDH materials, namely, "intrinsic" water structurally intercalated between the brucite-like layers and "extrinsic" water bound to external surfaces. However, more detailed insights into the relationship between water content, particle texture and method of LDH synthesis are lacking.

The present work investigates the water content for a series of LDH carbonates of the type $[Mg_{1-x}Al_x(OH)_2](CO_3)_{x/2}zH_2O$ with compositions corresponding to $(1-x)/x$ values of approximately 2.0, 3.0, and 4.0. In addition to describing the relationship between water content and the layer composition (charge density), we also report the surface area and mesoporosity of LDH carbonates obtained by two different coprecipitation methods. In the first method, which is commonly used for LDH synthesis, the pH is allowed to vary at the initial stages of particle nucleation and precipitation. In the second, newly developed method of the present work, the pH is held constant at all stages of particle formation. These different synthesis methods result in substantial differences in textural properties for LDH products of equivalent chemical composition.

Experimental Section

LDH Synthesis by the Variable-pH Method. A mixed $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ solution (2.0 M, 250 mL) with a Mg^{2+}/Al^{3+} ratio of 2.0, 3.0, or 4.0 was added at a rate of ~ 20 mL/min to enough 1.0 M Na_2CO_3 solution at 40 °C so that the overall CO_3^{2-}/Al^{3+} ratio was 1.5. Regardless of the Mg^{2+}/Al^{3+} ratio, a white precipitate immediately formed upon addition of the first drop of the mixed metal nitrate solution to the basic Na_2CO_3 solution. Once the pH of the reaction mixture neared a value of 10.0, a solution of 2.0 M NaOH was added along with the mixed Mg^{2+}/Al^{3+} solution to hold the reaction pH at 10.0 (± 0.1). After complete delivery of the mixed nitrate solution, the reaction mixture was stirred vigorously for 4 h at 40 °C and then aged for 40 h at 70 °C with good stirring. Upon completion of the digestion period, the product suspension was cooled to room temperature and centrifuged. The resulting white product was then washed free of carbonate ion (as observed by $AgNO_3$ test) by repeatedly forming a slurry in deionized water and then centrifuging. All products were air-dried on glass plates.

LDH Synthesis by the Constant-pH Method. In this method a 500-mL quantity of H_2O was first heated at 40 °C, and the pH was adjusted to 10.0 by the addition of several drops of a solution formed by mixing equal volumes of 1.0 M Na_2CO_3 and 2.0 M NaOH. A mixed metal nitrate solution with a Mg^{2+}/Al^{3+} ratio of 2.0, 3.0, or 4.0 and the mixed base solution were then added to the reaction vessel at rates that maintained the reaction pH at 10.0 ± 0.1 . In this way the reaction pH was kept constant from the very beginning of the precipitation process. Once all of the mixed base solution was consumed, additional 2.0 M NaOH was added to keep the reaction pH at 10.0 for the rest of precipitation reaction. The reaction mixture was stirred vigorously for 4 h at 40 °C and then aged for 40 h at 70 °C with good stirring. The final products were washed and dried as described in the variable pH method.

Characterizing Methods. Elemental analyses were performed by ICP emission spectroscopy using solutions prepared

by dissolving approximately 40 mg of solid sample in 100 mL of 20% (v/v) HNO_3 .

X-ray diffraction patterns of LDH powders were recorded on a Rigaku diffractometer equipped with DMAXB software, and a goniometer fitted with a variable-temperature sample stage. The temperature dependence of the LDH samples was investigated using two complementary methods that gave equivalent results. One series of samples was heated for 10 min under N_2 at six temperatures in the range 50–250 °C and then cooled to room temperature to record the diffraction patterns. In a second series of experiments the samples were heated to the same six temperatures at a rate of 5 °C/min, and the powder patterns were recorded at these temperatures. The heating rates and amounts of sample used in these latter experiments approximated the conditions used to record the thermogravimetric data. Dehydrated samples were allowed to rehydrate in air until no further changes were observed in the diffraction patterns.

Differential thermal analysis (DTA) was carried out under N_2 on a DuPont 990 thermal analysis system. Zn metal was used as a calibration standard. Thermogravimetric analysis (TGA) was carried out on a Cahn 121 TG analyzer. Approximately 50 mg (TGA) and 15 mg (DTA) quantities of each LDH sample, either air-dried or predried at 60 °C for 10 h in an oven, were heated at rates of 5 °C/min (TGA) and 20 °C/min (DTA).

Transmission electron micrographs (TEM) were obtained with a JEOL 100 CX TEM at the Center for Electron Optics at MSU. Samples for TEM were prepared by dipping copper grids coated with holey carbon films into LDH powder or into sonicated LDH suspensions in ethanol or water.

Nitrogen adsorption/desorption isotherms at liquid nitrogen temperature were obtained on a Coulter Omnisorb (TM) 360 CX sorptometer using ultrahigh-purity nitrogen as the adsorbate and helium at the carrier gas. For surface area measurements and pore size distribution measurements, about 70 mg of each LDH carbonate was outgassed overnight at 100 or 200 °C under vacuum (10^{-5} Torr). For each outgassing temperature, the BET surface area was determined from the low pressure region ($0.05 < P/P_0 < 0.25$) of the adsorption isotherm. Mesopore volumes and pore size distributions were obtained from the nitrogen desorption isotherms using the BJH model.¹³ This model assumes that the pores are cylindrical in shape and that the pore diameter is in the range 20–500 Å.

Results and Discussion

In general, LDH intercalation compounds are formed by coprecipitation reaction of M^{2+} , M^{3+} , and A^{n-} ions from aqueous solution. The reaction stoichiometry, temperature, time, and pH are important synthesis variables that can influence the particle size and texture of the final products.⁴ In addition, the method of mixing the reagents can be important in mediating the nucleation and precipitation process.¹⁴ Hydrotalcite-type LDH carbonates typically are prepared by simply adding a solution of Mg^{2+} and Al^{3+} cations to a solution of Na_2CO_3 until the pH of the reaction mixture reaches a pH of ~ 10.0 , and then a solution of NaOH is used to maintain the pH value until the precipitation process is completed. In one synthetic method of the present work we use this "variable-pH" methodology to obtain representative $[Mg_{1-x}Al_x(OH)_2](CO_3)_{x/2}$ compositions with $(1-x)/x$ (Mg^{2+}/Al^{3+}) ratios of ~ 2.0 , 3.0, and 4.0. In addition, we utilized a new synthetic method, wherein the metal ion, carbonate, and hydroxide solutions are mixed under conditions of "constant pH" (10.0 ± 0.1) at

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Table 1. Properties of Air-Dried $Mg_{1-x}Al_x$ -LDH Carbonates Prepared by the Variable- and Constant-pH Methods

property	variable-pH method			constant-pH method		
	Mg_2Al	Mg_3Al	Mg_4Al	Mg_2Al	Mg_3Al	Mg_4Al
Al^{3+} substitution, ^a x	0.332	0.254	0.209	0.312	0.231	0.196
basal spacing, Å	7.69	7.77	7.82	7.55	7.84	8.00
unit cell a , ^b Å	3.04	3.06	3.07	3.04	3.06	3.08
layer unit area, ^c Å ²	8.01	8.09	8.14	8.03	8.13	8.22
layer charge density, $e^+/\text{Å}^2$	0.041	0.031	0.026	0.039	0.028	0.024

^a Comparison determined by chemical analysis. ^b $a = 2d_{110}$.

^c Area of a $Mg_{1-x}Al_x(OH)_2$ octahedral unit = $\sqrt{3}(a^2/2)$.

all stages of the nucleation/precipitation process. All other synthesis parameters were held constant for the two synthesis methods. Since pH can greatly influence initial particle nucleation, we expected the variable-pH and constant-pH synthesis methods to afford products with different textural properties.

Table 1 summarizes the compositions and structural parameters for the products prepared by both synthetic methods. It is seen that the Mg^{2+}/Al^{3+} compositions of the final products are close to the values used in the reaction stoichiometries, though the constant pH method tends to give somewhat higher levels of Al^{3+} substitution than the variable pH method. Notably, the in-plane unit-cell a dimension decreases with increasing isomorphous substitution of Mg^{2+} by Al^{3+} , reflecting the fact that the ionic radii for Al^{3+} and Mg^{2+} are 0.53 and 0.72 Å, respectively.¹⁵ The increase in basal spacing with decreasing Al^{3+} substitution is consistent with the decreased Coulombic attractive force between the positively charged brucite-like layers and the negatively charged interlayer anions.¹⁶ As expected, the unit layer charge and charge density increase in proportion to the Al content of the layers.

The water desorption behavior of $Mg_{1-x}Al_x$ -LDH carbonates was examined in part by thermogravimetric analysis (TGA). Regardless of the synthesis method, all air-dried samples exhibited two general types of water, namely, interparticle pore water formed by capillary condensation between LDH crystallites and adsorbed surface water bound to gallery and external surfaces. As shown in Figure 1, curve A, an air-dried Mg_3Al -LDH carbonate loses about 30 wt % H_2O , equivalent to ~ 6.3 mol of water/mol of Al, below 110 °C, and then an additional ~ 11 wt % H_2O or ~ 1.8 moles per Al between 110 and 250 °C. If the sample is predried at 60 °C for 10 h, then all the interparticle pore water is removed and only surface water is desorbed below 250 °C as shown in Figure 1, curve B. Above ~ 250 °C the LDH carbonate begins to undergo dehydroxylation of the brucite-like layers and loss of carbonate.

Since the amount of interparticle pore water in an LDH will vary depending on particle size and texture, it was desirable to remove the interparticle pore water by predrying at 60 °C prior to determining the amount of surface bound water associated with each LDH composition. The effect of Mg^{2+}/Al^{3+} ratio on surface-bound water molecule was determined for three LDH carbonates prepared by the variable-pH method. TGA curves analogous to that shown in Figure 1B for the

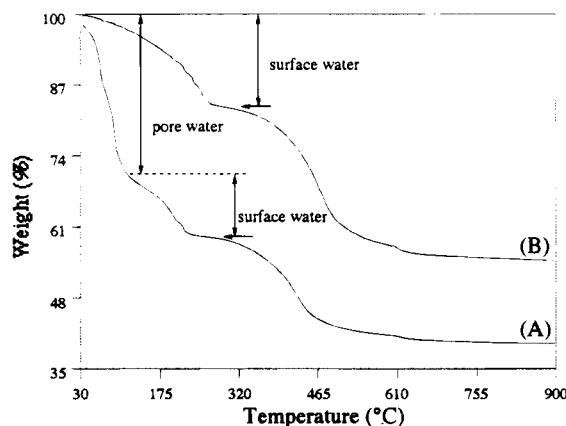


Figure 1. TGA curves (5 °C/min) for Mg_3Al LDH carbonates: (A) air-dried sample; (B) sample predried at 60 °C for 10 h. Sample A was prepared by the constant-pH method, whereas sample B was prepared by the variable-pH method.

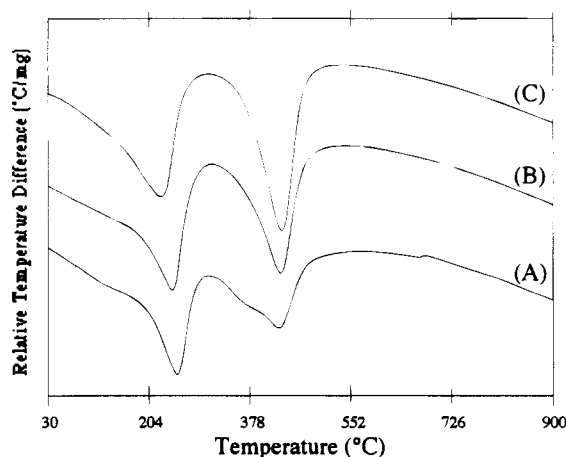


Figure 2. DTA curves for (A) Mg_2Al -, (B) Mg_3Al -, and (C) Mg_4Al -LDH carbonates prepared by the variable-pH method and dried at 60 °C in air.

Mg_3Al LDH carbonate also were obtained for Mg_2Al - and Mg_4Al -LDH carbonates dried at 60 °C, but the desorption temperature for complete removal of the surface-bound water increased from 240 to 280 °C with increasing Al content. An increase in the desorption temperature with increasing layer charge density most likely is caused in part by the greater steric constraints on the interlayer species and by a larger number of H-bonding interactions between the interlayer water molecules and carbonate anions. These observations on the thermal desorption of water from LDH carbonates are in agreement with previously reported NMR studies¹⁷ demonstrating that the strength of the bonding between the interlayer water and the LDH layers is related to the interlayer space available for the guest water molecules.

The loss of surface water from LDH carbonates free of interparticle pore water occurs in two concomitant steps, as judged from the weak inflection point at 210 °C in the TGA curves (cf. Figure 1B). Better evidence for a bimodal surface water desorption process is provided by the presence of two endothermic DTA peaks. As shown in Figure 2 a broad low temperature shoulder extending to ~ 180 °C is associated with the

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Table 2. Surface Water Content of the $Mg_{1-x}Al_x$ -LDH Carbonates Prepared by the Variable-pH Method and Predried at 60 °C

	LDH carbonate		
	Mg_2Al ($x = 0.332$)	Mg_3Al ($x = 0.254$)	Mg_4Al ($x = 0.209$)
total surface water, ^a n	0.76 (60– 280 °C) ^b	0.73 (60– 267 °C)	0.71 (60– 240 °C)
max intrinsic surface- water, ^c n'_{max}	0.50	0.62	0.69

^a Water content expressed in moles per $Mg_{1-x}Al_x(OH)_2$ octahedral unit. ^b Values in parentheses are the temperature ranges over which the surface water was desorbed. ^c $n'_{max} = 1 - (3x/2)$.

sharp endothermic maxima for surface water desorption from each LDH carbonate. The low-temperature shoulders are reproducible and cannot be attributed to instrumental baseline drift. In agreement with our TGA results for the loss of interlayer water, the positions of the endothermic maxima increase with increasing Al substitution in the order Mg_4Al -LDH (222 °C) < Mg_3Al -LDH (242 °C) < Mg_2Al -LDH (254 °C) LDH. On the basis of previously reported thermochemical studies,^{18–20} the endothermic peaks above 300 °C correspond to the decarbonation–dehydroxylation of the LDH carbonates.

The desorption of two types of surface-bound water from LDH intercalates has been observed by TGA and DTA by earlier workers,^{19,20} but this behavior has not been completely evaluated for carbonate derivatives of different layer charge. In recent studies of water adsorption by Zn_2Cr - and Zn_2Al -LDH chlorides, de Roy et al.¹² noted that the amount of surface-bound water exceeded the amount that could be crystallographically accommodated by intercalation between the brucite-like sheets. This prompted their assignment of two types of surface water, namely, “intrinsic” or structural water intercalated as a monolayer in the LDH galleries, and “extrinsic” or extracrystalline water. The bimodal water desorption behavior of our LDH carbonates, together with our quantitative estimates of their surface water content, also points to the presence of intrinsic and extrinsic surface water.

Table 2 summarizes the total surface-bound water for each of the $Mg_{1-x}Al_x$ LDH carbonates prepared by the variable pH method of the present work. The total surface water decreases slightly from 0.759 to 0.705 moles per octahedral $Mg_{1-x}Al_x(OH)_2$ unit upon decreasing the degree of Al^{3+} substitution from $x = 0.332$ to 0.209. Also shown in Table 2 is the *maximum* amount of intrinsic water (n'_{max}) that can be structurally accommodated as a monolayer in the galleries of an LDH of composition x . The value of n'_{max} is estimated from the relationship $n'_{max} = 1 - 3(x/2)$, where $3(x/2)$ represents the fraction of gallery sites occupied by the CO_3^{2-} oxygen atoms. It is evident that the experimentally determined amounts of surface water substantially exceeds n'_{max} , at least for values of $x = 0.332$ and 0.254, and that extrinsic water must be accommodated at external (nongallery) surfaces.

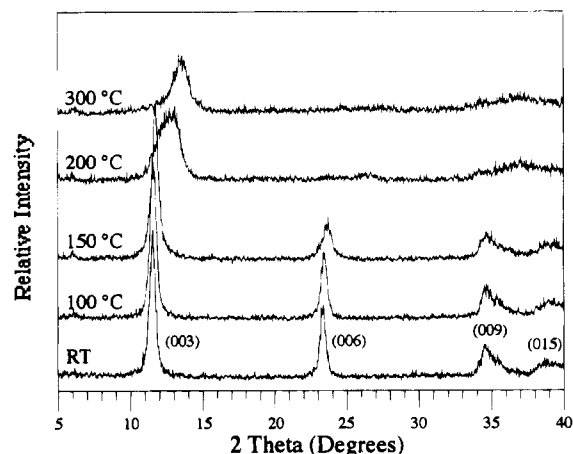


Figure 3. Temperature dependence of the XRD powder patterns for an air-dried Mg_2Al LDH carbonate prepared by the variable-pH method. The patterns were recorded under nitrogen at the temperature of heating. The heating rate was 5 °C/min to mimic the conditions used to obtain the TGA data in Figure 1.

Before discussing further the significance of extrinsic surface water in LDH carbonates, we further verify by XRD studies our interpretation of the TGA/DTA data for water desorption. Evidence for the loss of both interparticle pore water and surface water from air-dried $Mg_{1-x}Al_x$ LDH carbonates was obtained from a series of X-ray diffraction experiments at temperatures in the range 50–300 °C. The results for the Mg_2Al -LDH carbonate prepared by the variable pH method are given in Figure 3. The XRD patterns, which were recorded under nitrogen at a heating rate of 5 °C/min in order to approximate the conditions used to record the thermal analysis data, exhibit no significant change in basal spacing below 150 °C. This result is in agreement with earlier observations of Miyata²¹ and confirms our assignment of the water loss below 150 °C primarily to interparticle pore water. Above 150 °C the basal spacings begin to decrease, as expected for the loss of intragallery surface water. By 300 °C the spacing is reduced from an initial value of 7.69 Å to a value of ~6.5 Å, confirming the loss of gallery water over this temperature range. When all of the interlayer water is removed from the gallery, the first-order $00l$ reflection is broadened and the second and third $00l$ harmonics are greatly reduced in intensity. Apparently, the removal of interlayer water induces disorder in the layer stacking sequence, perhaps due to concomitant partial dehydroxylation of the layers as suggested previously.²² The decrease in basal spacing upon gallery dehydration is in agreement with previously reported shifts in LDH basal spacings upon the removal of gallery surface water.¹⁷ Similar changes in XRD patterns upon heat treatment also were observed for the analogous Mg_2Al - and Mg_4Al -LDH carbonates.

Fornés et al.²³ have recently reported the loss of interlayer water from a hydrotalcite-like $Mg^{2+}-Al^{3+}-CO_3^{2-}$ LDH dried under dynamic vacuum at ambient temperature. They also observed the rapid rehydration of the interlayer upon exposure of the anhydrous

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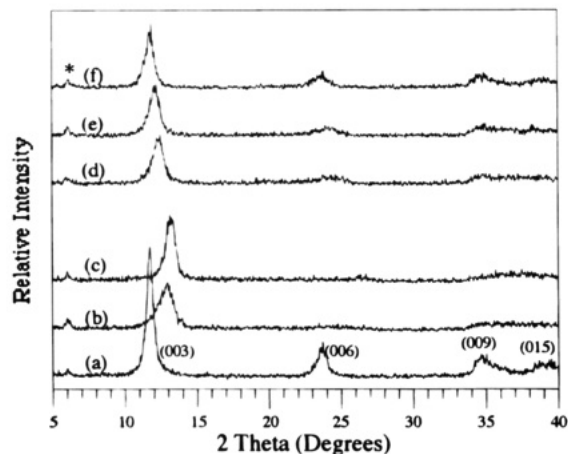


Figure 4. XRD patterns of a Mg_2Al LDH carbonate (variable-pH method) upon thermal dehydration and rehydration. Patterns a–c were recorded under N_2 at $150\text{ }^\circ\text{C}$ after heating times of 10 min, 1 h, and 2 h, respectively. Patterns d–f were recorded at $25\text{ }^\circ\text{C}$ after rehydration upon exposure of the dehydrated sample to the atmosphere for 1, 2, and 5 h, respectively. The feature indicated by an asterisk is an instrument artifact.

samples to atmospheric moisture. Our results show that substantially higher temperatures ($\sim 150\text{ }^\circ\text{C}$) are required to remove gallery water under N_2 at atmospheric pressure. In agreement with Fornés et al., we also observe rehydration of anhydrous LDHs upon reexposure to the moist atmosphere. As shown by the XRD patterns in Figure 4, the Mg_2Al LDH carbonate when heated 2 h at $150\text{ }^\circ\text{C}$ loses gallery surface water

and exhibits an equilibrium basal spacing of 6.70 \AA . Upon exposure of the dehydrated LDH to the atmosphere, the basal spacing characteristic of hydrated galleries (7.67 \AA) is restored within 5 h. Of course, the rehydration rates will depend on particle texture, composition, and humidity level, but these qualitative results unequivocally establish the reversibility of the gallery dehydration–rehydration process.

The above results for the water desorption behavior of $Mg_{1-x}Al_x$ -LDH carbonates are for derivatives prepared by the variable-pH method. We expect the intrinsic surface water content to be dependent primarily on layer charge density. However, the amount of interparticle pore water and extrinsic surface water should depend very much on particle texture. Hence, it was of interest to compare the particle properties of LDH carbonates prepared by the variable-pH and constant-pH methods. To obtain quantitative estimates of particle size and texture, we have combined transmission electron microscopy studies with nitrogen adsorption–desorption determinations of surface areas and pore size distributions for derivatives prepared by both synthesis methods.

As shown by the TEM images in Figure 5A, the Mg_3Al LDH carbonate prepared by the variable-pH method exhibits poorly shaped platelike particle morphologies together with a few well-formed hexagonal plates approximately 60 \AA thick by 250 \AA in diameter. Also, the surfaces of the crystals adopt a rough texture. In contrast, the same LDH composition prepared by the constant pH method showed smooth, well-formed, over-

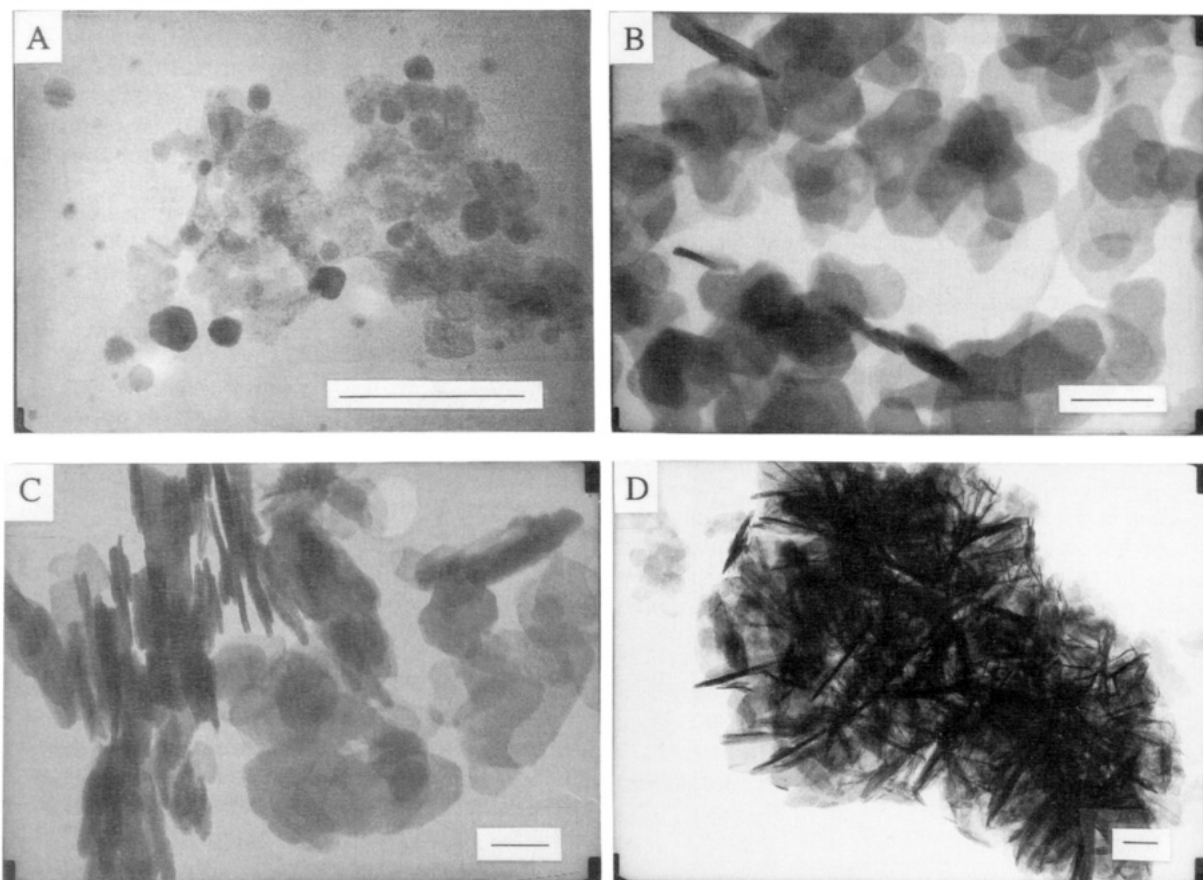


Figure 5. TEM images of Mg_3Al LDH carbonates prepared by (A) the variable-pH method and (B–D) the constant-pH method. Sample A was deposited from ethanol suspension onto a holey carbon grid. Sample B–D were deposited from water suspension. Scale bar is 1000 \AA .

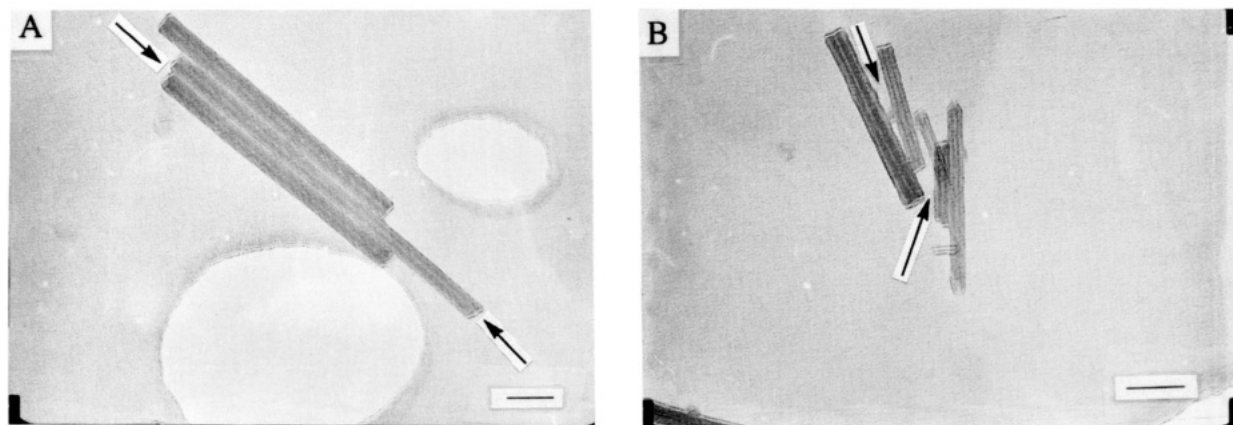


Figure 6. TEM images of a Mg_3Al LDH carbonate prepared by the variable-pH method showing interparticle textures: (A) Cofacial stacking of thin crystals with arrows indicating interfacial regions for accommodating pore water and extrinsic surface water. (B) Edge-face aggregation of thin crystals with arrows indicating regions for capillary condensation of interparticle pore water. Scale bar is 1000 Å.

lapping hexagonal crystals approximately 100 Å thick and 1000 Å in width (cf. Figure 5B–D). Also, there is some tendency for the platelets to aggregate in an edge–face manner, as illustrated by the micrographs in Figure 5C,D. As originally suggested by de Roy, the face–face overlapping of crystallites generates interfaces that can accommodate extrinsic surface water, as well as other adsorbates. In Figure 6A we provide direct TEM evidence for the existence of such interfaces. Note that the interfaces in this aggregate occur at intervals of approximately 60–300 Å, corresponding to one interface every 8–40 LDH layers. Also, the thickness of the interface (30–70 Å) is comparable to the length scale of the contiguous LDH layers. Thus, we suggest that these cofacial regions can accommodate interparticle pore water, as well as extrinsic surface water.

Edge–face or card-house type aggregation of platelets often is observed for cationic smectite clays, but it is less commonly recognized in anionic LDH materials. Evidence for edge to face aggregation of LDH layers is given by the TEM image in Figure 6B. It also is apparent from this micrograph that the edge–face contacts can give rise to pores in the 300–1000 Å size range. Clearly, it is these textural features that contribute to the pore water content of LDH compositions.

We next consider the N_2 adsorption–desorption properties of LDH carbonates prepared by the variable and constant pH methods. As shown in Figure 7A, the Mg_3Al –LDH carbonate formed by the variable pH method exhibits a type IV isotherm characteristic of a nonmicroporous material and a H1-type hysteresis loop indicative of interparticle mesoporosity.²⁴ In contrast, the derivative prepared by the constant pH method remains nonmicroporous, but the H2-type hysteresis loop signals a change in the textural pore distribution (cf. Figure 7B). Figure 8 provides plots of the pore size distributions for the two materials. The variable pH product, which is characterized by small crystallite size and rough surface texture (cf. Figure 5A), has a pore radius distribution between 80 and 250 Å. In contrast, the larger crystals formed by the constant pH method exhibits a sharp peak near 20 Å superimposed on a broad distribution that extends beyond 200 Å. Clearly,

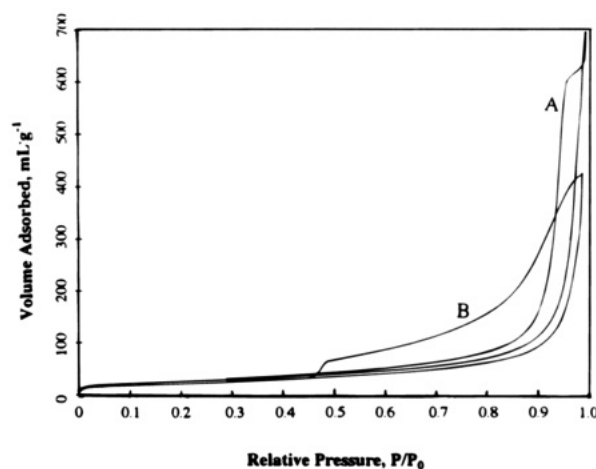


Figure 7. N_2 adsorption/desorption isotherms (at $-196^\circ C$) for Mg_3Al LDH carbonates prepared by (A) the variable-pH method and (B) the constant-pH method. Both sample were outgassed at $200^\circ C$ under dynamic vacuum.

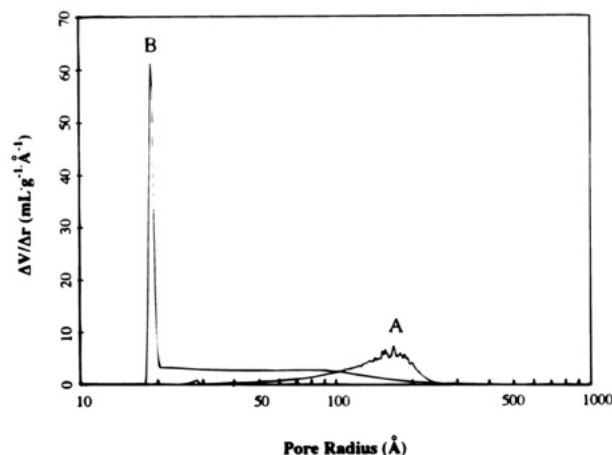


Figure 8. Pore size distributions obtained from the N_2 desorption isotherms of Mg_3Al LDH carbonates prepared by (A) the variable-pH method and (B) the constant-pH method.

the synthesis method can dramatically influence the textural pore distribution of the LDH.

Table 3 summarizes the BET N_2 surface areas and pore size distributions for all of the LDH carbonates prepared in this study. Decreasing the outgassing temperature from $200^\circ C$ to $100^\circ C$ decreases the surface

(24) Report of the Phys. Chem. Div., 1985 IUPAC, *Pure Appl. Chem.* 1985, 57, 603.

Table 3. BET/N₂ Surface Areas (S_{BET} , m²/g) and Mesopore Volumes (V_{ms} , mL/g) over Several Ranges of Pore Radii for Mg_{1-x}Al_x LDH Carbonates

property	variable-pH method			constant-pH method		
	Mg ₂ Al	Mg ₃ Al	Mg ₄ Al	Mg ₂ Al	Mg ₃ Al	Mg ₄ Al
S_{BET} , m ² /g						
100 °C outgassing	82	75	88	61	67	73
200 °C outgassing	111	91	104	65	77	80
V_{ms} , mL/g						
100 °C outgassing						
10–30 Å	0.000	0.000	0.000	0.002	0.117	0.138
30–50 Å	0.000	0.004	0.007	0.006	0.074	0.136
50–300 Å	0.91	0.83	0.73	0.61	0.38	0.46
200 °C outgassing						
10–30 Å	0.001	0.003	0.001	0.000	0.144	0.146
30–50 Å	0.001	0.008	0.010	0.003	0.088	0.142
50–300 Å	1.07	0.95	0.84	0.63	0.49	0.49

areas somewhat, but the pore volume distributions are not significantly affected by the outgassing temperature. It is noteworthy that surface areas are lower for the larger crystallite products prepared by the constant pH method, as expected based on the layer crystal morphologies revealed by the TEM results described earlier. Interestingly, the pore distributions for the Mg₃Al and Mg₄Al compositions are sensitive to synthesis methods, but the Mg₂Al derivative exhibits the same pore distribution regardless of the synthesis method. The narrow pore distribution centered near 20 Å for the Mg₃Al and Mg₄Al compositions may be the result of pore connectivity limitations associated with the voids formed by cofacial stacking of crystallites as observed by TEM. As noted earlier, the length scale of the interfacial regions between crystallites is comparable to that of the continuous layers. We tentatively speculate that the porosity associated with these cofacial regions may be a consequence of the incomplete formation of the LDH layers. That is, the LDH layers at the interface may be discontinuous. As illustrated in Figure 9, such layer discontinuities could give rise to necking of mesopores, as well as to open mesopores. These cofacial layer stacking defects, together with the edge-face layer aggregation mechanism associated with the interparticle pore water content of LDH materials, undoubtedly contribute to the overall mesoporosity observed by N₂ desorption. The relative abundance of the two types of particle textures, which are dependent on the method of synthesis, will determine the range and uniformity of the pore distribution.

Conclusions

Air-dried layered double hydroxides of general composition [Mg_{1-x}Al_x(OH)₂](CO₃)_nH₂O, whether prepared by the variable-pH or constant-pH method, contain two general types of water, namely, interparticle pore water

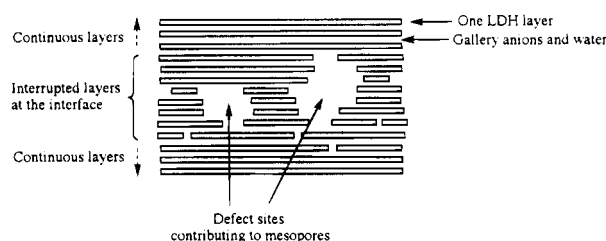


Figure 9. Possible model for the interfacial regions of LDH derivatives exhibiting textural porosity in the pore radius range near 20 Å. Water and gallery anions are not represented.

and surface-bound (extrinsic and intrinsic) water. Pore water is easily lost upon heating at 60 °C, whereas intrinsic surface water bound at positions in the gallery region is lost above 150 °C. Owing to increasing electrostatic interactions between the LDH layers and interlayer carbonate anions, the desorption temperature for intrinsic water increases with increasing Al³⁺ substitution. Extrinsic water adsorbed in multilayers at interfaces between cofacially stacked crystals is lost at temperatures between the temperature for loss of interparticle pore water (60 °C) and the onset temperature for loss of intrinsic water (150 °C). In general, increasing the layer charge by increasing the Al³⁺ substitution results in larger amounts of surface water, as well as in higher desorption temperatures.

The textural properties of LDH carbonates, as reflected in crystal morphologies, surface areas, and mesopore distributions, depend on the method of synthesis. Products prepared by the variable-pH method give fine-grained, higher surface area crystals with rough surfaces. In contrast, the constant pH method affords larger hexagonal crystals with smooth surfaces. Depending on Al³⁺ substitution and preparation method, two distinctive pore distributions are observed, namely, broad distributions with pore radii in the range 50–300 Å and narrow distributions with mesopore maxima near 20 Å radius. Regardless of the layer charge density, the variable-pH method affords broad textural pore distributions. The constant pH method affords broad mesopore distributions for Mg₂Al–LDH carbonates, but sharp distributions near 20 Å radius for Mg₃Al– and Mg₄Al–LDH carbonates. The dependence of particle texture on synthesis method may be useful in mediating the materials performance properties of LDH compositions for potential applications as ionic conductors, anion exchangers, and selective heterogeneous catalysts.

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