

# Basic Properties of $Mg^{2+}_{1-x}Al^{3+}_x$ Layered Double Hydroxides Intercalated by Carbonate, Hydroxide, Chloride, and Sulfate Anions

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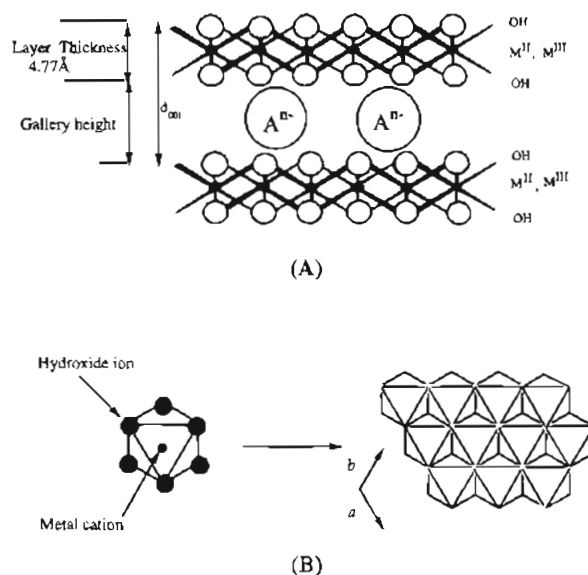
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A series of layered double hydroxide (LDH) intercalation compounds of the type  $[M^{II}_{(1-x)}M^{III}_x(OH)_2][A^{n-}]_{x/n}zH_2O$  have been prepared with  $(1-x)/x = 2.2-2.5$  and  $A^{n-} = CO_3^{2-}$ ,  $OH^-$ ,  $Cl^-$ , and  $SO_4^{2-}$  in order to establish the relationship between composition and the basic properties of the LDH structures. The base-catalyzed disproportionation of 2-methyl-3-butyn-2-ol (MBOH) to acetylene and acetone was used to judge basic reactivity. Structural characterization was achieved by thermogravimetric analysis, X-ray diffraction patterns, and BET- $N_2$  surface area measurements after thermal treatment of the intercalates at the temperatures employed in the catalytic reaction. The crystalline LDH intercalates are more reactive toward MBOH transformation than the amorphous oxides formed by thermal decomposition of the LDH structures. The anion basicity influences the LDH reactivity as evidenced by the fact that the carbonate and hydroxide intercalated materials are more active than the chloride derivative. The sulfate derivative exhibits exceptionally high reactivity despite very low surface area when activated at low temperatures. All crystalline LDH intercalates displayed high basic selectivity, but the oxides obtained from the thermal decomposition of the chloride and sulfate intercalates exhibited acidic sites in addition to the basic centers. In the chloride materials the acidity may arise from the replacement of hydroxyl groups in the brucite-like layers by the halide ion. For the thermally decomposed LDH sulfate the acidity most likely originates from magnesium sulfate phase formation.

## Introduction

Layered double hydroxides (LDHs) can be structurally characterized as containing brucite- (magnesium hydroxide-) like layers in which some divalent metal cations have been substituted by trivalent ions to form positively charged sheets. The metal cations occupy the centers of octahedra whose vertices contain hydroxide ion. These octahedra are connected to each other by edge sharing to form an infinite sheet. The cationic charge created in the layers is compensated by the presence of hydrated anions between the stacked sheets.<sup>1,2</sup> LDHs have the general formula  $[M^{II}_{(1-x)}M^{III}_x(OH)_2][A^{n-}]_{x/n}zH_2O$  where  $M^{II}$  is a divalent cation ( $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ , or  $Ca^{2+}$ );  $M^{III}$  is a trivalent ion ( $Al^{3+}$ ,  $Cr^{3+}$ ,  $Mn^{3+}$ ,  $Fe^{3+}$ ,  $Co^{3+}$ ,  $Ni^{3+}$ , or  $La^{3+}$ ) and  $A^{n-}$  is the gallery anion. Figure 1 schematically illustrates the LDH structure. These ionic layered materials also have been termed "hydrotalcite-like" compounds in reference to the structural similarity to the mineral hydrotalcite,  $[Mg_6Al_2(OH)_{16}][CO_3] \cdot 4H_2O$ , or by the term "anionic clays" in mirror image resemblance to the cationic clays whose negative charge of the aluminosilicate layers are counterbalanced by intercalated cations.

Single-crystal X-ray studies performed with natural layered double hydroxides show that the  $a$  parameter of the hexagonal cell unit corresponds to the distance between two metal cations in adjacent octahedra while the  $c$  parameter corresponds to two or three times the distance between adjacent hydroxyl layers depending on the layered stacking pattern.<sup>2</sup> The carbonate and water molecules are arranged in the gallery region so that the



**Figure 1.** Schematic representations of (a) a layered double hydroxide structure consisting of brucite-like layers intercalated by hydrated anions and (b) the AB packing of hydroxide ions giving rise to the octahedral interstices occupied by  $M^{2+}$  and  $M^{3+}$  metal cations.

plane containing the oxygen atoms is parallel to the brucite-like layers. Although the water molecules and carbonate anions are disordered, the oxygen atoms of them tend to be distributed around the threefold axis that intersects two hydroxyl groups of adjacent layers. For each octahedron of composition  $[M^{II}_{(1-x)}M^{III}_x(OH)_2][A^{n-}]_{x/n}$ , there is one interlayer site that may or may not be occupied by a water molecule or an anion.

Mixed metal oxides obtained by thermal decomposition of layered double hydroxides can promote base-catalyzed reactions. The properties of anionic clays as catalyst precursors were reviewed recently by Cavani *et al.*<sup>3</sup> The utilization of solid

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base catalysts in organic synthesis is relatively modest in comparison with the broad range of catalytic processes employing acid solids. However, research on LDHs and other basic solid catalysts<sup>4</sup> for the production of fine chemicals has been intensified lately. Owing to the intrinsic basicity of LDH materials, they also may find applications as catalysts for environmental pollution control (*e.g.*, dehydrohalogenations).

We recently reported<sup>5</sup> on the reactivity of thermally activated hydrotalcite-like  $\text{Mg}^{2+}/\text{Al}^{3+}/\text{CO}_3^{2-}$  layered double hydroxide using the disproportionation of 2-methyl-3-butyn-2-ol (MBOH)<sup>6</sup> as a probe. A solid of composition  $[\text{Mg}_{2.34}\text{Al}(\text{OH})_{6.68}](\text{CO}_3)_{0.5}\cdot 2.6\text{H}_2\text{O}$  was calcined at temperatures in the range 80–450 °C, and structure–reactivity relationships were established. Samples activated at low temperatures, where the LDH structure is retained (<250 °C), were more reactive than the mixed metal oxides formed by thermal decomposition of the LDH structure above 300 °C. This result suggested that the anions in the gallery region may play an important role in the basic behavior of LDH materials calcined below the decomposition temperature. Accordingly, the present work examines the effect of the gallery anion on the basic properties of LDH structures. We have synthesized a series of LDH compositions containing  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  in the brucite-like layers and simple anions ( $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{OH}^-$ , and  $\text{SO}_4^{2-}$ ) in the gallery region. Changes in structure and basic reactivity toward MBOH under different conditions of thermal activation were examined by TGA experiments, XRD powder patterns, and BET- $\text{N}_2$  surface area measurements.

## Experimental Section

**Synthesis of  $\text{Mg}^{2+}/\text{Al}^{3+}/\text{Cl}^-$ -LDH.** A  $\text{Mg}^{2+}/\text{Al}^{3+}$  LDH chloride was prepared by a coprecipitation reaction according to Miyata's procedure.<sup>7</sup> A mixture of  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$  (20.0g, 0.100 mol) and  $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$  (11.87 g, 0.0500 mol) was dissolved in 200 mL of deionized water. The aqueous solution was slowly added with stirring at 25 °C to 100 mL of a NaOH solution at pH 10 under a nitrogen flow. The pH was maintained at this value by the continuous addition of 2 M NaOH. The resulting suspension was stirred overnight under a nitrogen flow at 70 °C. The solid product was isolated by centrifuging, washing thoroughly with deionized water, and drying overnight at 80 °C. All synthesis steps were carried out using decarbonated water. The X-ray powder diffraction pattern indicated the basal spacing to be 7.74 Å at room temperature. Elemental analysis indicated the  $\text{Mg}^{2+}/\text{Al}^{3+}$  molar ratio to be 2.24. The sodium content was 0.02 wt % and the water content was approximately 14 wt % by TGA experiment. Thus, the LDH composition was  $[\text{Mg}_{2.24}\text{Al}(\text{OH})_{6.48}]\text{Cl}\cdot 2.05\text{H}_2\text{O}$ .

**Synthesis of  $\text{Mg}^{2+}/\text{Al}^{3+}/\text{SO}_4^{2-}$ -LDH.** A  $\text{Mg}^{2+}/\text{Al}^{3+}$  LDH sulfate was prepared by a method<sup>8</sup> analogous to the LDH chloride described above, except that  $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (25.2 g, 0.100 mol) and  $\text{Al}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}$  (16.4 g, 0.0250 mol) were used as the source of magnesium and aluminum. The X-ray powder diffraction pattern of the product under ambient conditions indicated the basal spacing to be 8.81 Å. Elemental analysis indicated the  $\text{Mg}^{2+}/\text{Al}^{3+}$  molar ratio to be 2.32. The sodium content was <0.01 wt % and the water content was approximately 16 wt % by TGA experiment. Thus, the LDH composition was  $[\text{Mg}_{2.32}\text{Al}(\text{OH})_{6.64}](\text{SO}_4)_{0.5}\cdot 2.6\text{H}_2\text{O}$ .

**Synthesis of  $\text{Mg}^{2+}/\text{Al}^{3+}/\text{CO}_3^{2-}$ -LDH.** The synthesis of  $[\text{Mg}_{2.44}\text{Al}(\text{OH})_{6.88}][\text{CO}_3]_{0.5}\cdot n\text{H}_2\text{O}$  was carried out by a coprecipitation reaction of  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{CO}_3^{2-}$  in aqueous solutions according to previously described methods.<sup>5</sup>

**Synthesis of  $\text{Mg}^{2+}/\text{Al}^{3+}/\text{OH}^-$ -LDH.** A  $\text{Mg}^{2+}/\text{Al}^{3+}$  LDH hydroxide was prepared by the restructuring reaction of the mixed metal oxide

formed by the thermal decomposition of the LDH carbonate. A 6-g quantity of  $[\text{Mg}_{2.44}\text{Al}(\text{OH})_{6.88}][\text{CO}_3]_{0.5}\cdot n\text{H}_2\text{O}$  was calcined at 500 °C for 4 h. The resulting metal oxide was suspended in 200 mL of decarbonated water and stirred at room temperature for 3 days under  $\text{N}_2$ . The solid was isolated by centrifuging and drying overnight at 80 °C under a nitrogen flow. The basal spacing was 7.59 Å at room temperature under ambient atmosphere. Elemental analysis indicated the  $\text{Mg}^{2+}/\text{Al}^{3+}$  molar ratio to be 2.49. Since the sodium content was 0.03 wt % and the water content was approximately 20 wt % by TGA experiment, the LDH hydroxide composition may be expressed as  $[\text{Mg}_{2.49}\text{Al}(\text{OH})_{6.98}]\text{OH}\cdot 3.1\text{H}_2\text{O}$ .

**Characterization Methods.** Samples for chemical analysis were dissolved in 20% (v/v)  $\text{HNO}_3$ , and the solutions were analyzed by ICP emission spectroscopy at the College of Veterinary Medicine, Michigan State University.

BET- $\text{N}_2$  surface areas were determined on a Quantasorb Jr. sorption system.

Infrared spectra of samples in KBr matrix were recorded on a Nicolet FT-IR/42 spectrometer in the range 4000–400  $\text{cm}^{-1}$ .

X-ray powder patterns were recorded on a Rigaku diffractometer using  $\text{Cu K}\alpha$  radiation (45 kV and 100 mA) and a scan speed of 4° in 2 $\theta$ /min. The divergent and scattering slits were set at 0.5°, and the receiving slit was 0.3°.

Samples for BET- $\text{N}_2$  surface area measurements and for X-ray diffraction studies were placed together inside a horizontal quartz tube in the center section of a tube furnace and heated under a flow of nitrogen at 80, 150, 250, 350 or 450 °C for 2 h. After this step, the samples were transferred to the BET sample cell and outgassed under vacuum at room temperature for 1 h.

Thermally dehydrated samples for XRD studies were transferred quickly to the sample compartment of the diffractometer in an effort to minimize rehydration, and the diffraction patterns were recorded. Since the basal spacings in some cases were found to be sensitive to atmospheric humidity, we decided to check the basal spacings obtained under ambient conditions against those obtained using a high temperature X-ray diffractometer attachment in combination with a Rigaku programmable temperature controller. The sample powders with a particle size between 150 and 75  $\mu\text{m}$  were supported on a copper plate. The copper plate was held in a platinum frame, into which a thermocouple was inserted. The entire assembly was inserted into a furnace made from an alumina frame and the platinum heater. The temperature was increased at a 3 °C/min ramp rate and held at 80, 150, or 250°C for 2 h under a flow of  $\text{N}_2$ . The X-ray diffraction patterns were recorded at high temperature employing the conditions described above, except that the scan speed was 2° in 2 $\theta$ /min.

Thermogravimetric experiments were carried out on a Cahn TGA System Model 121 using approximately 50 mg of samples with a particle size between 150 and 75  $\mu\text{m}$ . The temperature was ramped at rates of 3 and 5 °C/min from 30 °C to 900 °C under a flow of nitrogen gas. The determination of weight loss at constant temperature was performed by using a ramp rate of 3 °C/min and holding the temperature at the desired value for a duration of 2 h.

The calcination of samples at 900 °C for 4 h in air was carried out in a calibrated Fisher programmable ashing furnace, Model 497. Samples for surface area analysis were outgassed under vacuum at 150 °C for 2 h. The particle size of the samples for surface area and catalytic studies were the same, 150–75  $\mu\text{m}$  (100–200 mesh).

**Catalytic Reactions.** 2-Methyl-3-butyn-2-ol, abbreviated MBOH, (Aldrich Chemical Co.) was used without further purification. Chromatographic analysis confirmed the high purity of the reagent. The retention time and response factors of MBOH reaction products were determined using reference compounds from Aldrich Chemical Co. The response factor of acetylene was determined by disproportionation of MBOH over MgO (Matheson Coleman & Bell) assuming that the molar ratio of the acetone/acetylene reaction products was one.<sup>6</sup> MBOH conversion was carried out in a micro reactor equipped with an Omega Programmable Temperature Controller Model CN2011K and an on-line Perkin-Elmer 8500 gas chromatograph. The liquid reactant was placed in a saturator at 24 °C and the vapor was introduced into the reactor by means of a He flow of 11.3 mL/min. A 150-mg quantity of the LDH with a particle size between 150 and 75  $\mu\text{m}$  was placed in the reactor and activated at 80–450 °C under a He flow for 2 h. For

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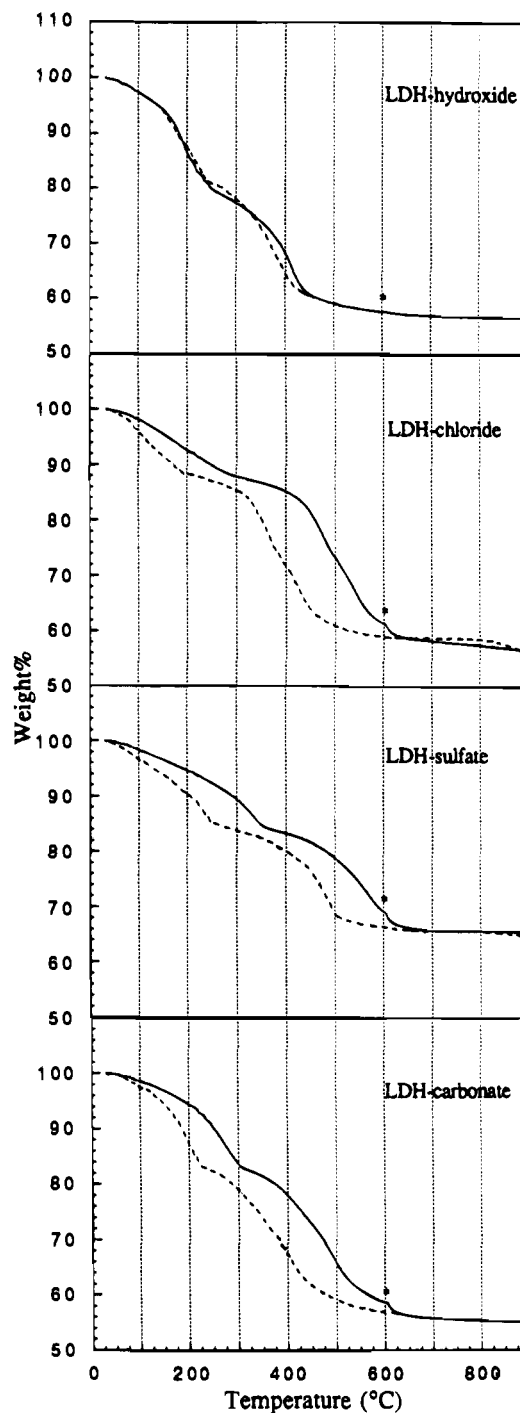
the sample calcined at 900 °C, the material was heated at 150 °C for 2 h in the micro reactor before the reaction. The reactor was adjusted to the desired temperature and the MBOH stream was introduced at a flow rate of approximately 0.65 mmol/h.<sup>9</sup> The products were analyzed by gas chromatography after reaching steady state conditions within a 2 h reaction time. The chromatograph was equipped with an FID detector and a 6 in. × 1/8 in. o.d. stainless steel column packed with 3% SP-1500 on Carbowack B (80/120 mesh).

## Results and Discussion

The primary objective of the present work is to establish for a series of  $Mg^{2+}/Al^{3+}$  LDH derivatives the relative reactivities as solid state bases. The basic properties of these compounds are likely to depend on the nature of the intercalated counter anion, the crystallinity of the LDH and the hydration state of the basal surfaces. Therefore, we have first thoroughly characterized each derivative of interest with regard to thermal and structural properties under conditions that approximate those encountered in the base-catalyzed reaction of 2-methyl-3-butyn-2-ol.

**Thermal and Structural Properties.** The LDH compositions prepared in this work have a  $Mg^{2+}/Al^{3+}$  ratio in the range 2.2–2.5 and contain intercalated  $Cl^-$ ,  $SO_4^{2-}$ ,  $CO_3^{2-}$ , and  $OH^-$  as counteranions. The TGA results shown in Figure 2 indicate that all of these LDH intercalates are thermally stable up to 240–300 °C. The weight loss below this temperature is ascribed to external surface water and to gallery water.<sup>2</sup> It was presumed that interparticle pore water was eliminated by overnight drying at 80 °C. Above 240–300 °C all four compounds begin to dehydroxylate to mixed metal oxides and, in the case of the chloride and sulfate intercalates, to salts containing these anions. Table 1 provides the TGA weight loss for the LDH intercalates using both dynamic heating and isothermal heating at several temperatures in the range 150–900 °C. Heating rates of 5 and 3 °C/min significantly underestimate the equilibrium weight loss obtained by isothermal heating. Although the dehydration/dehydroxylation properties are similar for all four intercalates, important differences are observed depending on the anion.

We consider first the dehydration properties of the LDH hydroxide. The XRD powder diffraction pattern obtained under ambient conditions for the sample calcined at 250 °C was the same as the sample dried at 80 °C (see Figure 3). On the basis of the TGA results, one might expect the LDH hydroxide to exhibit a lower basal spacing after heating at 250 °C due to the loss of a greater amount water molecules from the gallery region. Therefore, the possibility of the sample rehydrating in the air during the XRD experiment was checked using a special attachment to the X-ray instrument that permitted the intercalate to be calcined *in situ* and the diffraction pattern to be recorded at the calcination temperature. The XRD patterns obtained for the LDH hydroxide at elevated temperatures, as shown in Figure 4, are not coincident with those recorded in air. For instance, the sample calcined at 150 °C for 2 h has a  $d_{003}$  value of 6.73 Å, whereas at 250 °C the sample is essentially amorphous. One can conclude that the dehydration and structural degradation of the LDH hydroxide is complete at 250 °C, provided that the activation time is at least 2 h. Also, the rehydration and reconstitution of the LDH hydroxide upon exposure to air is a very fast (minutes) and completely reversible process. The fast process of layer hydration was observed also for LDH carbonate samples calcined under vacuum for 1 h at 200 and 300 °C and



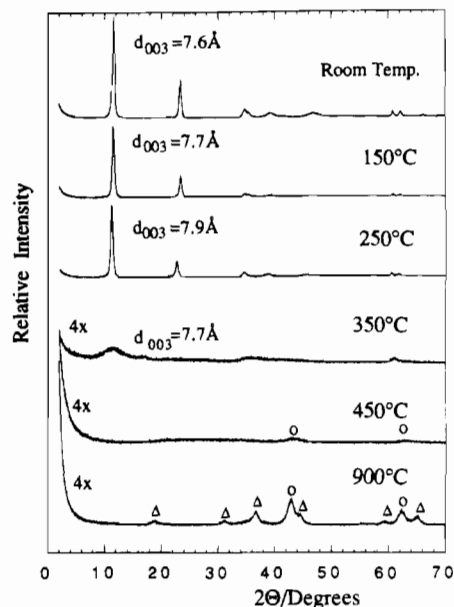
**Figure 2.** Thermogravimetric analysis (TGA) curves obtained at scanning rates of 5 °C/min (solid line) and at 3 °C/min (dashed line) for  $Mg^{2+}/Al^{3+}$  layered double hydroxides containing intercalated  $OH^-$ ,  $Cl^-$ ,  $SO_4^{2-}$  and  $CO_3^{2-}$ . The feature indicated by an asterisk is an instrument artifact.

exposed to the ambient atmosphere at room temperature for increasing times.<sup>10</sup>

The LDH–hydroxide contains approximately 20 wt % water, as judged by the steps in the TGA curves obtained at ramp rates of 5 and 3 °C/min (see Figure 2). On the basis of the general formula  $[M^{II}_{(1-x)}M^{III}_x(OH)_2][A^{n-}]_{x/n}$ , the maximum molar amount of interlayer water that can be structurally incorporated as a monolayer in an LDH hydroxide is  $1 - (x/n)$ .<sup>7</sup> Accordingly, we expected up to approximately 0.71 mol or 16% by weight

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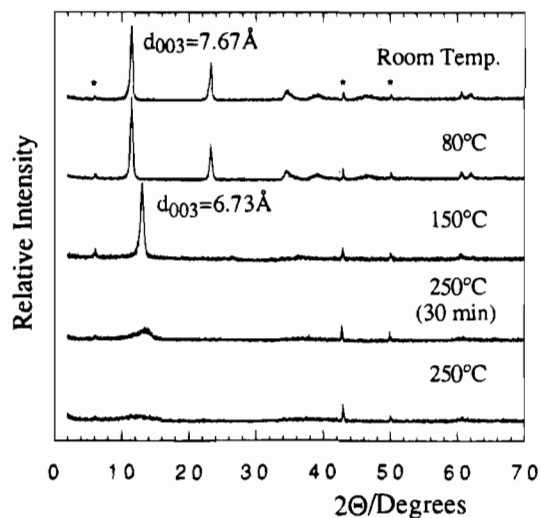


**Figure 3.** XRD patterns of  $\text{Mg}_{2.49}\text{Al}$  LDH hydroxide samples after heating for 2 h under nitrogen at the temperatures indicated and recording the diffraction patterns in air at room temperature within a few minutes after expose to the atmosphere. Diffraction peaks corresponding to  $\text{MgO}$  and  $\text{MgAl}_2\text{O}_4$  spinel are labeled  $\circ$  and  $\Delta$ , respectively.<sup>5</sup>

**Table 1.** Weight Loss (%) by LDH Intercalates As Determined by Dynamical and Isothermal Thermal Gravimetric Analysis

TEMPERATURE (°C)	Dynamical Heating		Isothermal Heating, 2h
	5°C/min	3°C/min	
<b>Part A : <math>\text{Mg}_{2.49}\text{Al}</math> LDH Hydroxide</b>			
150	5.50	6.19	15.9
250	20.0	19.8	23.6
350	25.9	26.3	34.8
450	39.1	38.8	40.4
900	43.4	42.9	----
<b>Part B : <math>\text{Mg}_{2.24}\text{Al}</math> LDH Chloride</b>			
150	4.34	8.73	11.3
250	10.0	12.9	14.6
350	13.2	20.0	30.1
450	18.5	36.2	39.6
900	43.4	44.0	----
<b>Part C : <math>\text{Mg}_{2.32}\text{Al}</math> LDH Sulfate</b>			
150	3.39	5.61	9.84
250	7.59	13.5	16.0
350	15.2	17.7	20.6
450	18.3	22.2	30.0
900	34.5	35.2	----
<b>Part D : <math>\text{Mg}_{2.34}\text{Al}</math> LDH Carbonate</b>			
150	3.04	5.45	11.6
250	9.72	17.7	20.9
350	18.5	26.4	33.6
450	27.3	38.3	40.8
900	45.0	44.9	----

of water in the gallery region. The 4 wt % water in excess could be related with surface water in the LDH hydroxide. The sample loses  $\sim 6$  wt % water at 150 °C at both ramping rates. If the temperature is held for 2 h at 150 °C the material releases 16% water and is almost completely dehydrated. The liberation of interlayer water from the LDH-hydroxide is accompanied



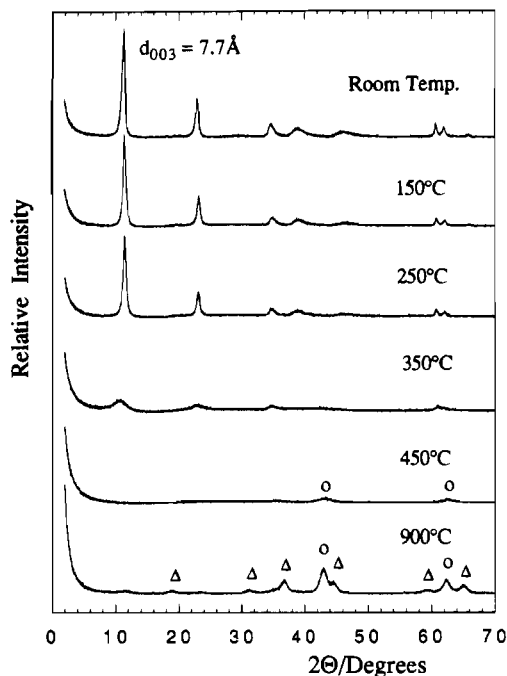
**Figure 4.** XRD patterns of  $\text{Mg}_{2.49}\text{Al}$  LDH hydroxide samples recorded with the use of a high temperature attachment. Patterns were recorded at the temperatures indicated after a calcination period of 2 h, unless otherwise noted. The features indicated by an asterisks are attachment artifacts.

by a decrease in basal spacing from 7.67 to 6.73 Å (cf. Figure 4). Also, the higher order 00*l* peaks are broadened, suggesting disorder in the layers stacking, as observed previously for hydroxalite-like compounds.<sup>11</sup> The water is absent from the gallery region when the sample is heated at 250 °C for 30 min. After 2 h at 250 °C the peak intensity decreases, the sample loses more than 20% weight, and the material becomes amorphous. Despite the low crystallinity of the LDH, the weight loss during the isotherm step is not consistent with dehydroxylation of the layers, leading to the conclusion that the material is structurally disordered but not decomposed after 2 h at 250 °C. Thus, one can describe the calcined LDH at 250 °C as an anhydrous hydroxide with a high level of structural disorder. The extent of dehydroxylation increases when the sample is calcined at 350 °C for 2 h. Formation of a  $\text{MgO}$  phase occurs at 450 °C, as evidenced by weak peaks characteristic of this metal oxide in the X-ray diffraction pattern.  $\text{MgAl}_2\text{O}_4$  and  $\text{MgO}$  crystalline phases are clearly evident by XRD for the sample calcined at 900 °C (Figure 3).

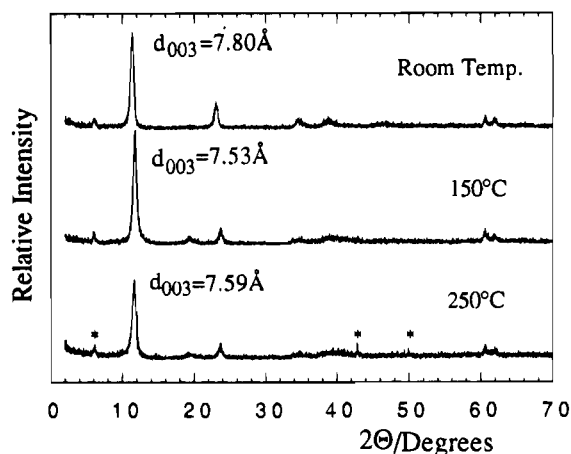
We next consider the thermal dehydration-dehydroxylation of the  $\text{Mg}_{2.24}\text{Al}$  LDH chloride. The TGA curve for the LDH chloride (cf., Figure 2) shows that the material is stable up to approximately 300 °C. Below this temperature, the LDH releases water. The TGA curve in the range 50–280 °C exhibits steps which we tentatively attribute to the loss of two types of water, namely, surface water at 50–150 °C, and interlayer water at 150–200 °C. An endothermic DTA peak for  $\text{Mg}^{2+}/\text{Al}^{3+}$ -LDH chlorides at 230 °C has been previously attributed to the liberation of interlayer water.<sup>7</sup>

As shown in Figure 5 the XRD powder diffraction patterns of the LDH chloride calcined at 80, 150, and 250 °C do not show significant change with temperature, at least when the patterns are recorded in air. The  $d_{003}$  peak intensities diminish when the temperature increases, but the basal spacing remains near  $\sim 7.7$  Å. If the thickness of the brucite layer (4.77 Å) is subtracted from the  $d_{003}$  value of the LDHs, one can estimate the gallery height to be 2.93 Å. This value is smaller than the diameter of the chloride ion (3.62 Å), suggesting the existence of a strong electrostatic interaction between the layers of high charge density and the guest in the gallery region even in the

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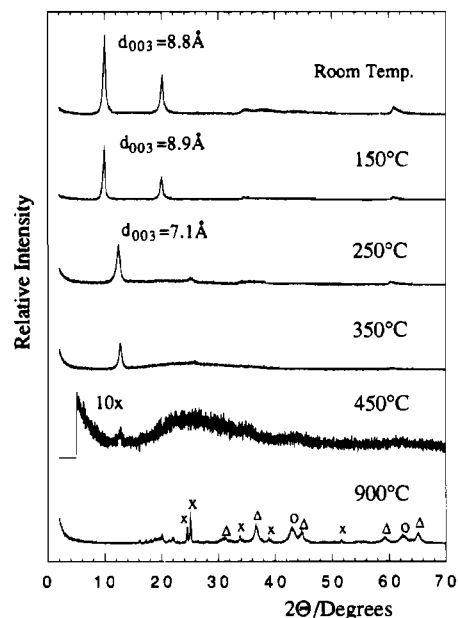
**Figure 5.** XRD of  $Mg_{2.24}Al$  LDH chloride samples after heating for 2 h under nitrogen at the temperatures indicated. All diffraction patterns were recorded in air at room temperature minutes after exposure to the atmosphere. Diffraction peaks corresponding to  $MgO$  and  $MgAl_2O_4$  spinel are labeled  $\circ$  and  $\Delta$ , respectively.<sup>5</sup>



**Figure 6.** XRD patterns of  $Mg_{2.24}Al$  LDH chloride samples recorded on a high temperature attachment after 2 h of calcination. All patterns were recorded at the temperatures indicated. The features indicated by an asterisks are attachment artifacts.

presence of interlayer water. In this case, we expect the basal spacing of the anhydrous LDH to be unaffected by the release of gallery water molecules. Consequently, the basal spacing should not be altered upon dehydration and subsequent rehydration in air.

The *in situ* high temperature XRD experiments shown in Figure 6 confirm the above model for the dehydration of the LDH chloride. The samples calcined at 150 and 250 °C for 2 h exhibit comparable basal spacing ( $d_{003} = 7.5 \text{ \AA}$ ). The total amount of water in the sample is 14 wt %, which corresponds to 2.05 mol of  $H_2O$  per mole of aluminum. The data in Table 1 show that the sample is partially dehydrated by isothermal heating at 150 °C, but completely dehydrated when heated at 250 °C for 2 h. The LDH chloride under dynamic heating is more sensitive to the heating rate than the hydroxide form (*cf.*, Figure 2). On the other hand the release of gallery water molecules from the LDH chloride, unlike the LDH hydroxide,



**Figure 7.** XRD patterns of  $Mg_{2.32}Al$  LDH sulfate samples after heating for 2 h under nitrogen at the temperatures indicated. All patterns were recorded in air minutes after exposure to the atmosphere. Diffraction peaks corresponding to  $MgO$ ,  $MgAl_2O_4$  spinel, and  $MgSO_4$  are labeled  $\circ$ ,  $\Delta$ , and  $\times$ , respectively.<sup>5,22</sup>

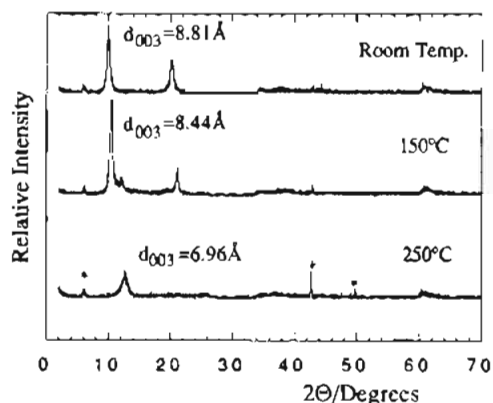
does not change the interlayer stacking distance. Even the 006 peak can be observed in the XRD of the LDH chloride samples activated at 150 and 250 °C for 2 h (*cf.*, Figure 6).

Above the decomposition temperature of approximately 300 °C, the TGA curve of LDH chloride shows two weight loss steps when ramped at 3 °C/min, namely, one in the range 300–380 °C and the other at 380–580 °C. The XRD patterns at 350 and 450 °C (Figure 5) reveal that the layered structure collapses at these temperatures and an amorphous material is produced. According to earlier workers,<sup>7,12</sup> the first step in the decomposition involves the liberation of water through dehydroxylation processes, and the second step is attributed to the release of  $Cl^-$  ions. Calcination of LDH chloride at 900 °C produces a product with the same XRD pattern as the product formed by calcination of the carbonate and hydroxide derivatives. The thermally transformed material is a mixture of spinel and magnesium oxide phases (*cf.*, Figure 5).

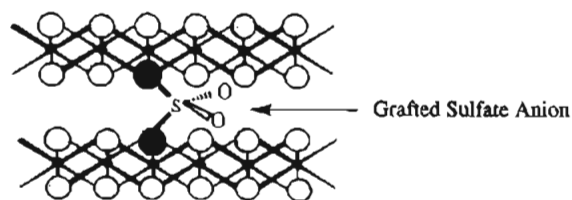
The LDH sulfate liberates surface and interlayer water in the temperature range 50–300 °C (*cf.*, Figure 2). The XRD patterns (Figure 7) recorded in air after calcination at 150 and 250 °C show that a  $\sim 1.8 \text{ \AA}$  contraction in basal spacing occurs above 150 °C. Also, the X-ray patterns obtained at the temperature of calcination (Figure 8) confirm the changes in the XRD peak positions above 150 °C. Brindley and Kikkawa<sup>13</sup> observed a similar contraction in basal spacing for a sulfate-exchanged natural hydroxalcite heated to 200 °C. The small gallery height (2.23 Å) of the anhydrous material can not be attributed to the free sulfate ion in the interlamellar spacing. The low  $d_{003}$  value found for sulfates intercalated in Zn–Cr and Cu–Cr LDHs when heated at 120 °C has been explained by the irreversible grafting of  $SO_4^{2-}$  anions into the framework.<sup>2</sup> Exposing our calcined LDH–sulfate samples to ambient humidity does not change the XRD pattern, indicating the lack of gallery rehydration. This result is consistent with irreversible sulfate grafting between the layers. The basal spacing of grafted LDH sulfates

(12) Clearfield, A.; Kieke, M.; Kwan, J.; Colon, J. L.; Wang, R.-C. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1991**, *11*, 361.

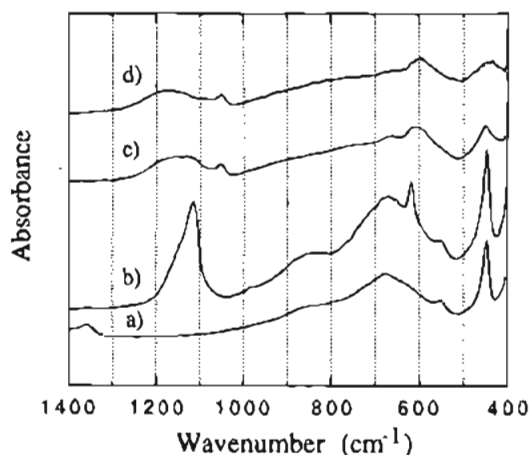
(13) Brindley, G. W.; Kikkawa, S. *Clays Clay Miner.* **1980**, *28*, 87.



**Figure 8.** XRD pattern of  $Mg_{2.32}Al$  LDH sulfate samples recorded on a high temperature attachment after 2 h of calcination. All patterns were recorded at the temperatures indicated. The features indicated by an asterisks are attachment artifacts.



**Figure 9.** Proposed grafting of sulfate to adjacent LDH layers of a 7.0-Å  $Mg_{2.32}Al$ -sulfate phase above 250 °C.



**Figure 10.** IR spectra (KBr matrix) for  $Mg_{2.24}Al$  LDH chloride (a) dried at 80 °C and  $Mg_{2.32}Al$  LDH sulfate (b) dried at 80 °C ( $d_{003} = 8.8$  Å), (c) calcined at 250 °C for 2 h, and (d) calcined at 350 °C for 2 h ( $d_{003} = 7.0$  Å). All spectra were recorded in air.

is similar to that reported for the anhydrous LDH carbonate ( $d_{003} \sim 6.7$  Å, see below) wherein the gallery height is determined by the oxygen ion diameter. Hence, we propose the  $C_{2v}$  structure shown in Figure 9 as one plausible possibility for the grafting of the sulfate ion.

Previously reported IR spectroscopic studies of LDH sulfates have shown that the anion is restricted (oriented) in the gallery space.<sup>2,8,14</sup> In general, the  $\nu_3$  and  $\nu_4$  bands near 1100 and 450  $cm^{-1}$  for tetrahedral sulfate are split in the intercalate, suggesting a lowering of symmetry from  $T_d$ . As shown in Figure 10b, the IR spectrum of the  $Mg^{2+}/Al^{3+}$  LDH sulfate ( $d_{003} = 8.8$  Å) below the sulfate grafting temperature exhibits a broad band with maximum at 1115  $cm^{-1}$  and shoulders at approximately 1150 and 1175  $cm^{-1}$  that are related to the  $\nu_3$  mode of the sulfate ion. Also, the IR inactive  $\nu_1$  mode under  $T_d$  symmetry is present as a very weak band at approximately 980  $cm^{-1}$ . The

assignment of a band related to the inactive  $\nu_2$  mode in  $T_d$  symmetry is difficult, because the LDH layer absorbs in the spectral region around 450  $cm^{-1}$  where this vibrational mode normally occurs. Figure 10a illustrates the absorption due to the LDH layers in the 450  $cm^{-1}$  region. The band at 620  $cm^{-1}$  is associated with the  $\nu_4$  sulfate mode, but owing to the background absorbance of the LDH layer, splitting of this mode can not be observed. Owing to these spectral limitations, we are not able to verify the  $C_{3v}$  symmetry suggested by earlier workers<sup>14,15</sup> for the ungrafted sulfate ion.

Figure 10, parts c and d, shows the IR spectra of the LDH-sulfate after grafting reaction at 250 and 350 °C. These derivatives have basal spacings of  $\sim 7$  Å consistent with grafted sulfate. The broad bands at 1170 and 1050  $cm^{-1}$  are attributable to the splitting of the degenerate  $\nu_3$  vibration of sulfate. The magnitude of the splitting (120  $cm^{-1}$ ) suggests a strong interaction between the sulfate anion and the layers. Therefore, it is likely that  $SO_4^{2-}$  grafting to the layers occurs through metal cation-sulfate bound formation. Other sulfate bands are obscured by the absorptions of the partially dehydroxylated LDH layers. The IR spectra do not permit unequivocal differentiation between  $C_{2v}$  or  $C_{3v}$  sulfate symmetry. However, we favor  $C_{2v}$  symmetry (*cf.*, Figure 9) on the basis of the basal spacing of 7.0 Å.

As indicated by the data in Table 1, the LDH sulfate exhibits a 16 wt % loss (2.6 mol of  $H_2O$ /mol of Al) of water at 250 °C where the layered structure is retained. The sample heated at 150 °C for 2 h releases approximately 10 wt % water and thereby can be characterized as a partially dehydrated material. The liberation of intragallery water causes a decrease of only 0.43 Å in the basal spacing. A larger contraction in gallery height is not expected due to the large diameter of the sulfate anion relative to the size of a water molecule. The XRD pattern (*cf.*, Figure 8) shows the presence of a small fraction of grafted layers ( $d \sim 7.0$  Å) in the sample activated at 150 °C for 2 h. When calcined at 250 °C for 2 h the sample releases all gallery water and essentially complete grafting of sulfate to the layers occurs.

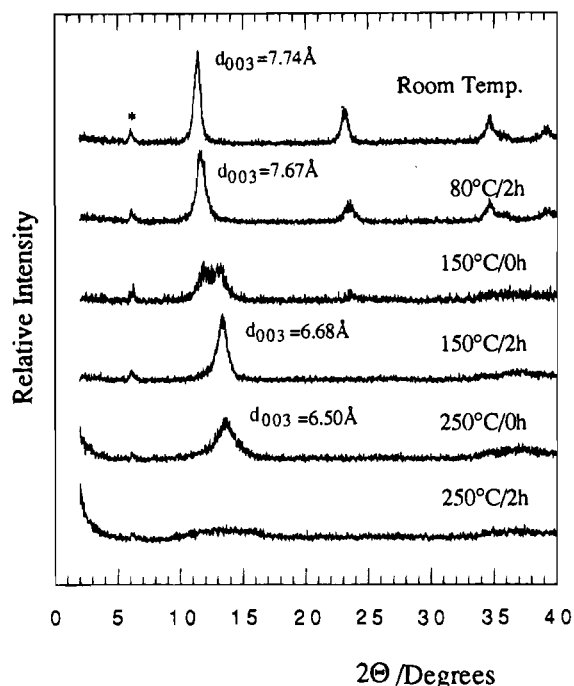
The formation of crosslinking sulfate groups between the layers at 250 °C could be an important factor in understanding the higher thermal stability of the LDH sulfate when compared with anionic clays containing  $CO_3^{2-}$  or  $OH^-$ . The TGA curve and XRD data show that the decomposition of the LDH sulfate begins above 300 °C, yet a small fraction of layered structure is still present at 450 °C (*cf.*, Figure 7). The grafted anions seem to hinder the condensation of adjacent hydroxyl groups. Thermal decomposition of the LDH sulfate at 900 °C results in the formation of a mixture of crystalline  $MgO$ ,  $MgAl_2O_4$ , and  $MgSO_4$  phases, but the amount of  $MgSO_4$  retained at 900 °C decreases with increasing time. The TGA curve recorded at 3 °C/min for the LDH sulfate shows a weight loss above 850 °C (*cf.*, Figure 2) that may be related to the decomposition of the magnesium sulfate phase and the liberation of  $SO_3$ .<sup>16</sup>

The rehydration and reconstitution reactions observed for thermally treated LDH intercalates led us to check the thermal properties of the LDH carbonate studied previously.<sup>5</sup> In order to obtain a more accurate comparison with other LDHs intercalates, we examined also the weight loss of a  $Mg_{2.34}Al$  hydrotalcite under isothermal condition (Table 1). The maximum amount of water that can be intercalated as a monolayer in a  $Mg_{(1-x)}Al_x(OH)_2$  LDH is structurally limited to  $1 - 3x/n$ , assuming that the carbonate anion can occupy three oxygen sites

(15) Drits, V. A.; Sokolova, T. N.; Sokolova, G. V.; Cherkashin, V. I. *Clays Clay Miner.* **1987**, *35*, 401.

(16) Marino, O.; Mascolo, G. *Thermochim. Acta* **1982**, *55*, 377.

(14) Bish, D. L.; Livingstone, A. *Mineral. Mag.* **1981**, *44*, 339.



**Figure 11.** XRD pattern of  $Mg_{2.34}Al$  LDH carbonate samples obtained with a high temperature attachment. All patterns were recorded at the temperatures and calcination times indicated. The features indicated by an asterisks are attachment artifacts.

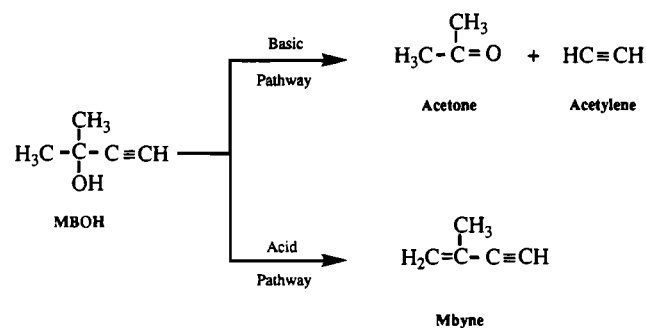
in the interlayer region. For a  $Mg_{2.34}Al$  carbonate, this relationship suggests that the sample contains at least 4.3% by weight of surface water.

The XRD patterns obtained *in situ* at 150 °C reveals that the sample is a mixture of about 50% hydrated and 50% anhydrous LDH carbonate (Figure 11). After calcination for 2 h at 150 °C, the XRD shows only a  $d_{003}$  peak (6.68 Å) attributable to an anhydrous gallery, though not all of the water (17% by weight or 2.6 mol of  $H_2O/mol$  of Al) is lost by isothermal heating (Table 1). The same XRD patterns are obtained under dynamic heating conditions if the temperature is ramped at 5 °C/min. However, the LDH carbonate seems to be more sensitive to the heating rate than the other LDH intercalates described above (see Figure 2). Rey and Fornés<sup>10</sup> also have observed a decrease in the gallery height for hydrotalcite-like samples calcined at 200 and 300 °C for 1 h under vacuum. Brindley and Kikkawa<sup>13</sup> reported an abrupt decrease in the basal spacing of natural hydrotalcite above 260 °C. Our  $Mg_{2.34}Al$  carbonate when heated at 250 °C for 2 h loses all gallery water (Table 1), but the XRD pattern (Figure 11) indicates the sample is structurally decomposed.

**Basic Properties.** The basic reactivity of our LDHs intercalates were evaluated by the catalytic conversions of 2-methyl-3-buten-2-ol (MBOH). Studies conducted by Lauron-Pernot *et al.*<sup>6</sup> showed that MBOH is a sensitive and selective substrate for acid–base solid surface characterization. Basic materials cause the molecule to disproportionate to acetone and acetylene. Acidic solids, such as silica–aluminas, convert MBOH primarily to 3-methyl-3-buten-1-yne (Mbyne), whereas amphoteric materials can lead to 3-methyl-3-buten-2-one and 3-hydroxy-3-methyl-2-butanone formation. Scheme 1 shows the principal organic products formed in the basic and acidic reaction pathways for MBOH conversion.

The most reactive LDH composition observed in this study for the base catalyzed disproportionation of MBOH is the meixnerite-like  $Mg^{2+}/Al^{3+}$  LDH hydroxide under conditions (80 °C) where most of the gallery water is retained (see Table 2). The next most active compound is the hydrotalcite-like  $Mg^{2+}/$

**Scheme 1**



$Al^{3+}$  LDH carbonate when outgassed at 150 °C, where most of the gallery water has been removed (see Table 3). Increasing the temperature of activation of the LDH hydroxide also affords exclusively basic compositions that convert MBOH to acetylene and acetone in quantitative yield, but the reactivity of the compositions decreases beginning with dehydration of the LDH structure at 150 °C. Thus, the intercalated anion and water play both play important roles in influencing the reactivity of a crystalline LDH structure. It is especially noteworthy that both the amorphous mixed  $Mg^{2+}/Al^{3+}$  oxide formed at 450 °C and the crystalline spinel and MgO phases formed at 900 °C are less active basic catalysts for MBOH conversion than the crystalline LDH structure. Although the total  $N_2$  BET surface area is increased upon conversion of the LDH–hydroxide or carbonate structures to an oxide, the specific activities on a surface area basis, as well as on a mass basis, are substantially decreased owing to a loss of intrinsic reactivity. This result is particularly significant as most LDH intercalates are traditionally used as precursors to oxide catalysts rather than as catalysts in their own right. It would appear that certain base-catalyzed reactions requiring temperatures below 150 °C, where the LDH hydroxide and carbonate structures are stable, would be better performed with the LDH itself, rather than its oxide decomposition products.

The  $Mg_{2.24}Al$  LDH chloride composition behaves differently from the meixnerite- and hydrotalcite-like analogous as a catalyst for MBOH conversion. As can be seen from the data presented in Table 4, the crystalline LDH chloride functions as a basic catalyst when placed in the anhydrous state by thermal activation at 150–250 °C. However, the specific activity is substantially lower than the LDH hydroxide or carbonate. Destructive partial dehydroxylation and dechlorination of the LDH chloride structure at temperatures  $\geq 350$  °C lowers the base-catalyzed activity further. Moreover, Mbyne also is formed as a coproduct, signaling the formation of acid sites in the oxides. The acid sites are retained up to activation temperatures of 450 °C but at 900 °C, the acid sites are absent.

The LDH chloride activated above 300 °C affects MBOH selectivity. In addition to basic reactivity, the thermally decomposed materials also possess active acid sites. A mechanism similar to that proposed to explain the high acidity of fluorinated cationic clays<sup>17</sup> can be useful in interpreting the MBOH results. As is schematically illustrate in Figure 12,  $Cl^-$  ions in the interlayer region can replace hydroxyl groups of the layers above 300 °C. Consequently, some hydroxyl groups will be bound to metal centers adjacent to halides ions. The resulting  $Cl-M-OH$  linkages can function as a Brønsted acid due to the electron-withdrawing effect of the chloride ions. The TGA curve recorded at 3 °C/min shows that the LDH–chloride loses

(17) Butruille, J.-R.; Michot, L. J.; Barrès, O.; Pinnavaia, T. J. *J. Catal.* **1993**, *139*, 664.

**Table 2.** Conversion of MBOH to Acetone and Acetylene by Base-Catalyzed Reaction with Thermally Activated Mg<sub>2.49</sub>Al LDH Hydroxide

activation temp (°C)	struct assignt	surface area (m <sup>2</sup> g <sup>-1</sup> )	reacn temp (°C)	% tot. convn	activity (mmol h <sup>-1</sup> m <sup>-2</sup> )	activity (mmol h <sup>-1</sup> g <sup>-1</sup> )
80	hydrated LDH		80	90.6	0.10	4.09
150	partially anhydrous LDH	39.4	80	18.3	0.024	0.94
			110	92.1	>0.12	>4.75
250	anhydrous LDH	43.9	80	7.3	0.0094	0.41
			110	74.7	0.096	4.22
350	partially dehydroxylated LDH	50.2	110	61.2	0.081	4.07
450	amorphous mixed oxide	50.8	110	50.2	0.072	3.66
900	spinel and MgO	81.6	110	55.6	0.030	2.41

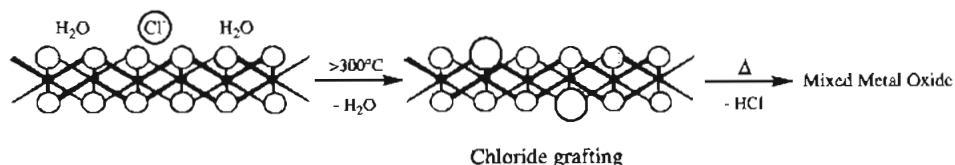
**Table 3.** Conversion of MBOH to Acetone and Acetylene by Base-Catalyzed Reaction with Thermally Activated Mg<sub>2.34</sub>Al LDH Carbonate

activation temp (°C)	struct assignt	surface area (m <sup>2</sup> g <sup>-1</sup> )	reacn temp (°C)	% tot. convn	activity (mmol h <sup>-1</sup> m <sup>-2</sup> )	activity (mmol h <sup>-1</sup> g <sup>-1</sup> )
80	hydrated LDH		80	22.4	0.011	1.01
150	mixture of hydrated and anhydrous LDH	89	80	47.7	0.026	2.33
			110	99.3	>0.055	>4.89
			150	100	>0.055	>4.89
250	anhydrous LDH	91	80	25.1	0.015	1.37
			150	99.9	>0.060	>5.46
350	partially dehydroxylated and decarbonated LDH	107	80	4.7	0.0029	0.31
			110	64.6	0.039	4.22
			150	93.5	~0.057	~6.10
450	amorphous mixed oxide	180	80	4.5	0.0018	0.33
			110	38.9	0.016	2.85
			150	99.5	>0.040	>7.28
890	spinel and MgO	83	80	2.7	0.0014	0.12
			110	39.9	0.021	1.73
			150	99.1	>0.052	>4.29

**Table 4.** Base- and Acid-Catalyzed Conversion of MBOH by Thermally Activated Mg<sub>2.24</sub>Al LDH Chloride

activation temp (°C)	struct assignt	surface area (m <sup>2</sup> g <sup>-1</sup> )	reacn temp (°C)	% tot. convn	% base-catalyzed selectivity	% acid-catalyzed selectivity <sup>b</sup>	activity (mmol h <sup>-1</sup> m <sup>-2</sup> )	activity (mmol h <sup>-1</sup> g <sup>-1</sup> )
150 <sup>a</sup>	partially anhydrous LDH	83.6	80	10.0	~100	tr	0.006	0.49
			150	99.8	~100	tr	>0.058	>4.88
250	anhydrous LDH	82.0	110	4.5	~100	tr	0.0027	0.23
			150	78.7	~100	tr	0.049	4.00
350	partially dehydroxylated and dechlorinated LDH	99.6	150	7.2	51.4	48.6	0.0045	0.45
			200	1h-71.7	72.7	27.3	...	...
				2h-63.8	78.1	21.9	0.040	3.95
450	amorphous mixed oxide-chloride	210.0	150	10.1	18.0	82.0	0.0034	0.72
			200	1h-61.5	27.7	72.3	...	...
				2h-50.9	54.3	45.7	0.017	3.65
				3h-51.3	64.7	35.3	...	...
900	spinel and MgO	89.4	110	74.3	100		0.036	3.33

<sup>a</sup> The reactivity of the sample activated at 80 °C is < 2%. <sup>b</sup> tr = insignificant amount of acid product (Mbyne).

**Figure 12.** Suggested mechanism for the replacement of hydroxide ions by chloride ions upon LDH chloride thermolysis above 300 °C.

approximately 2.7% mass at 800 °C. This weight loss can be related to the release of chloride anions. At 900 °C the decomposition product is a mixture of MgO and a spinel phase (Figure 5). The high basic selectivity of this material for MBOH conversion is consistent with the loss of halide anions and the disappearance of acidic functionality.

Miyata<sup>7</sup> has used titration methods to measure the acidity and basicity of metal oxides formed by LDH thermal decomposition at 500 °C. The chloride sample did not show basic properties. Acid sites of strength  $H_0 \leq 4.8$  and 1.5 and of  $H_0 \leq -3$  in low amount were detected. In contrast, our MBOH reaction reveals that the amorphous product formed at 450 °C initially exhibits both basic and acidic functionality, but the acid sites are slowly deactivated with increasing MBOH reaction time. The results in Table 4 also show similar MBOH reactivity

patterns for the LDH chloride and carbonate. However, the specific activities (based on unit area) for the chloride are lower than those found for hydrotalcite.

MBOH reactivity patterns over the LDH sulfates thermally activated below 350 °C (Table 5) are indicative of high basic functionality. The compound thermally activated above 450 °C, where the layer structure collapses and an acidic MgSO<sub>4</sub> phase is formed, promotes acid-catalyzed Mbyne formation. This catalytic evaluation of the acid-base properties of thermally activated LDH sulfate agrees with the titration results obtained by Miyata and Okada.<sup>8</sup> They observed that samples with  $M^{II}/M^{III} = 3$  and calcined in the range 200–700 °C possess basic sites of  $H_0 \geq 12.2$  strength. Weak acid sites ( $H_0 \leq 4.8$ ) appeared at 200 °C and sites of highest strength ( $H_0 \leq 1.5$ ) were formed at 400 °C. The decomposition of MgSO<sub>4</sub> at high



**Table 5.** Base- and Acid-Catalyzed Conversion of MBOH by Thermally Activated Mg<sub>2.32</sub>Al LDH Sulfate

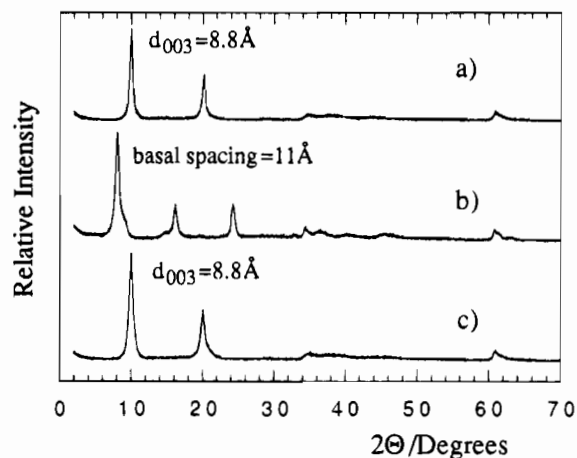
activation temp (°C)	struct assignt	surface area (m <sup>2</sup> g <sup>-1</sup> )	reacn temp (°C)	% tot. convn	% base-catalyzed selectivity	% acid-catalyzed selectivity <sup>c</sup>	activity (mmol h <sup>-1</sup> m <sup>-2</sup> )	activity (mmol h <sup>-1</sup> g <sup>-1</sup> )
150	anhydrous LDH and trace of grafted LDH layers	2.7	110	7.4	~100	tr	0.13	0.36
			150	88.5	~100	tr	1.58	4.26
250	grafted LDH layers and trace of anhydrous LDH	2.5	150	37.9	~100	tr	0.78	1.96
350	grafted LDH	2.3	150	2.3	~100	tr	0.06	0.13
			200	44.3	98.2	1.8	1.1	2.42
450	amorphous	2.2	150	18.7	100		0.53	1.16
			200	46.8	98.6	1.4	1.32	2.90
900/2h <sup>b</sup>	spinel, MgO, and MgSO <sub>4</sub>	24.0	150	7.8	9.7	87.0	0.014	0.34
900/4h		48.0	150	5.5	55.8	44.2	0.005	0.24

<sup>a</sup> The reactivity of the sample activated at 80 °C is < 2%. <sup>b</sup> The catalytic reaction produced also 3.3% 3-hydroxy-3-methyl-2-butanone. <sup>c</sup> tr = insignificant amount of acid product.

temperatures (>850 °C) is evidenced also by the results for MBOH conversion. The sample calcined at 900 °C for 2 h has a higher acid selectivity than that the material calcined for 4 h (Table 5). Catalysts formed from the calcined LDH sulfate are less reactive based on unit weight than those formed from hydrotalcite, but the structure-reactivity relationships are the same. However, owing to the atypical low surface area of the LDH sulfate, the activities on a surface area basis are very high for the LDH sulfate activated at 150 and 250 °C.

Regardless of the intercalated anion, all LDH intercalates activated below the temperature of structural collapse are more reactive than the metal oxides formed by their thermal decomposition. The lower activity of the metal oxides is probably related to the structural modifications (collapse of charged layers) and the change in composition caused by the loss of volatile reaction products. Our results show that the basic reactivity of an LDH intercalate is improved if a weakly basic gallery anion such as chloride is replaced by a strong base such as carbonate. Catalytic reactions involving crystalline LDH intercalates can be promoted by the basic hydroxyl groups associated with magnesium ions at edge sites and at external surface layers, but the guest anion may also take part in the catalytic process.

The LDH hydroxide, carbonate and chloride samples calcined at temperatures below 150 °C and characterized as a hydrated (for LDH-OH<sup>-</sup>) and partially dehydrated (for LDH-CO<sub>3</sub><sup>2-</sup> and LDH-Cl<sup>-</sup>) crystalline phases exhibit the best basic catalytic performance. Since these materials are nonporous, the anion at external surfaces edges of the stacked layers interacts with the reagent. This type of interaction has been proposed to explain the organic halide exchange reactions catalyzed by LDHs intercalated by Cl<sup>-</sup> or I<sup>-</sup>.<sup>18</sup> The basic strength of coordinatively unsaturated anions on the LDH surface is enhanced when compared with the solvated anions in solution. Also, the charge distribution and polarizability of the anion will differ depending on the location and magnitude of the layer charge. The influence of charged layers in enhancing the acid strength of cationic clays intercalated by hydrated cations has been reported in the literature<sup>19</sup> and analogous considerations should be important in determining the basicities of the surface anion. Lopez-Salinas *et al.*<sup>20</sup> also have observed differences in the reactivity behavior for [NiCl<sub>4</sub>]<sup>2-</sup> when free in suspension or intercalated in a hydrotalcite-like material. The reactivity of the intercalated anion complex for conversion of butyl bromide to butyl chloride is higher than that of the free [NiCl<sub>4</sub>]<sup>2-</sup>.



**Figure 13.** XRD pattern of Mg<sub>2.32</sub>Al LDH sulfate after being (a) dried at 80 °C, (b) equilibrated at 25 °C at 100% relative humidity and (c) redried at 80 °C.

All of the LDH XRD, TGA, and BET-N<sub>2</sub> data reported in this study were obtained under conditions that approximate the MBOH reaction conditions in an effort to define the catalytic material that the probe molecule encounters in the reaction system. But it is possible that some structural alterations in the LDH can occur during the catalytic process. LDH sulfates have been reported to exist at room temperature as two different phases. In addition to a hydrated material with basal spacing of ~8.8 Å, an ~11 Å phase is possible in which the gallery is expanded by water.<sup>2,13-15</sup> This behavior illustrates the flexibility of the intragallery region of LDH sulfate intercalates. Figure 13 shows that the hydrated (not grafted) LDH sulfate intercalate is swelled by water when allowed to equilibrate in air at 100% relative humidity. The expanded phase with a basal spacing of 11 Å is transformed back to the 8.8 Å phase if the sample is heated at 80 °C. Drits *et al.*<sup>15</sup> have observed the swelling of minerals in the hydrotalcite-manasseite group when saturated with ethylene glycol. Only the sulfate galleries are expanded in LDH samples composed of a SO<sub>4</sub><sup>2-</sup> and CO<sub>3</sub><sup>2-</sup> mixed-layer structure. If saturated with glycerol, the sulfate layer is only partially expanded. Hansen and Taylor<sup>21</sup> have reported the expansion of the hydrotalcite basal spacing to 14.4 Å when treated in glycerol vapor at 120 °C. One interesting observation in Hansen and Taylor's work is the proposal of carbonate decomposition in the presence of glycerol liberating carbon dioxide and forming hydroxide and/or glycerolate anions in the interlayer region.

Our XRD studies of LDH sulfate thermally activated at 150 °C and exposed to MBOH for 2 h at 110 °C provide no

(18) Martin, K. J.; Pinnavaia, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 541.

(19) Pinnavaia, T. J. *Science* **1983**, *220*, 365.

(20) Lopez-Salinas, E.; Tomita, N.; Matsui, T.; Suzuki, E.; Ono, Y. *J. Mol. Catal.* **1993**, *81*, 397.

(21) Hanse, H. B. C.; Taylor, R. M. *Clay Miner.* **1991**, *26*, 311.

(22) Powder Diffraction File, Set 21-546, Inorganic Volume, JCPDS, p 175.

indication of reagent intercalation. However, these data do not exclude the possibility of intercalation and interaction of MBOH with internal hydroxyl groups to explain the high activity of the sulfate sample. The catalysts could be very sensitive to swelling by MBOH under reaction conditions, and this could explain why the sulfate exhibits exceptional MBOH reactivity on a surface area basis.

The high catalytic conversion of LDH hydroxide activated at 80 °C may also be facilitated by MBOH intercalation. The XRD pattern of one of four LDH hydroxide sample after the MBOH catalytic test showed the complete absence of lines related to the layered structure. This result seems to suggest that MBOH could swell the layers during the catalytic reaction and provoke delamination or restructuring of the material.

### Summary

The reactivities of the simple  $\text{Mg}^{2+}_{1-x}\text{Al}^{3+}_x$  LDH carbonates and hydroxides as solid basic catalysts for MBOH disproportionation are superior to the oxides formed from the same LDH materials by thermal decomposition. These basic guest anions participate in the catalytic reaction through interaction with the reagent at the external basal and edge surfaces of the layers. The substantially higher reactivity of the LDH carbonate and hydroxide in comparison to the corresponding LDH chloride supports the important role played by the exchange anion in determining the basicity of a crystalline LDH.

Despite a very low surface area, a  $\text{Mg}^{2+}_{1-x}\text{Al}^{3+}_x$  LDH sulfate exhibits relatively high reactivity toward MBOH, which may be explained by MBOH intercalation under reaction conditions.

Swelling of the layered structure by reagent intercalation would increase the effective surface area of the catalyst and, consequently, the number of basic sites available for reaction. The decrease in the activity of the LDH sulfate calcined at 250, 350, or 450 °C is associated with the crosslinking of layers by the grafted sulfate group and the resulting inaccessibility of the internal hydroxide groups.

The collapse of the LDH structure by heating affords thermolysis products with acid–base selectivity different from the crystalline precursors. Exclusively basic metal oxides are formed by thermal decomposition of the LDH carbonate and hydroxide at 450–900 °C. In contrast, owing to  $\text{MgSO}_4$  phase formation, the LDH sulfate affords acidic sites when activated at 450–900 °C. In the case of the LDH chloride, structural decomposition can promote the substitution of hydroxyl groups by chloride anions in the brucite-like layers. This exchange of hydroxide by chloride enhances acidic properties, but upon the complete loss of the halide ion at high temperature, the acidic centers are eliminated.

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