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Effects of pH and Mg:Ga Ratio on the Synthesis of Gallium-Containing Layered Double Hydroxides and Their Polyoxometalate Anion Exchanged Products

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We have synthesized a series of $[\mathrm{Mg}^{2+}{}_{(1-x)}\mathrm{M}^{3+}{}_{x}(\mathrm{OH})_2][\mathrm{TA}^{2-}{}_{(x/2)}]\cdot z\mathrm{H_2O}$ ($\mathrm{M}^{3+} = \mathrm{Ga}^{3+}$ or Al^{3+} and TA $= \mathrm{C_6H_4(COO^-)_2}$) from mixed-metal chloride solutions with initial M^{3+} mole fractions of 0.20, 0.25, and 0.33, at constant pH values of 6.8, 7.7, 8.6, and 10.0. Terephthalate-containing products were obtained only under conditions that resulted in a Mg:M^{3+} ratio of 2:1 in the mixed metal hydroxide layers, indicating that a high layer charge density is necessary to incorporate terephthalate anions between the inorganic layers. Anion-exchange reactions were subsequently performed to produce LDHs intercalated with $\mathrm{PW_{11}O_{39}}^{7-}$ and $\mathrm{H_2W_{12}O_{40}}^{6-}$ anions, yielding products that displayed sharp powder diffraction patterns. In each case, the surface area of the POM-intercalated product was found to be approximately 40−45 $\mathrm{m^2/g}$, indicating that the micropore system is totally blocked and that the materials are virtually nonporous; this may result from the high layer charge density of the LDH−terephthalate precursors.

Introduction

Layered double hydroxides (LDHs) are a class of ionic lamellar solids with positively charged layers and exchangeable hydrated gallery anions.[1] The general LDH formula is $[\mathrm{M}^{2+}{}_{(1-x)}\mathrm{M}^{3+}{}_{x}(\mathrm{OH})_2][\mathrm{A}^{n-}{}_{(x/n)}]\cdot z\mathrm{H_2O}$, where M^{2+} and M^{3+} are divalent and trivalent metal cations such as Mg^{2+}, Cu^{2+}, Zn^{2+} and Al^{3+}, Fe^{3+}, Cr^{3+}, respectively, x is the ratio $\mathrm{M}^{3+}/(\mathrm{M}^{2+} + \mathrm{M}^{3+})$, and A^{n-} is a simple or complex organic or inorganic anion such as Cl^-, $\mathrm{NO_3}^-$, $\mathrm{CO_3}^{2-}$, $\mathrm{SO_4}^{2-}$, or $\mathrm{C_8H_4O_4}^{2-}$. The most common method of synthesis is coprecipitation of the metal salts from a mixed solution at constant pH and in the presence of the anionic species that is to be intercalated.[2]

Currently, there is a great deal of interest in supporting catalytically active polyoxometalate (POM) anions possessing the Keggin structure between the positively charged LDH layers.[3−9] POM anions are sufficiently large to create gallery heights of close to 10 Å, which provides sufficient room to allow physical and chemical processes to occur at the interior active sites. Unfortunately, the Keggin structure is unstable at typical coprecipitation pH values,[10,11] and therefore a direct synthesis is generally not feasible. Furthermore, anion-exchange reactions that involve large incoming POM anions and LDH materials that contain small exchangeable anions, such as Cl^-, $\mathrm{NO_3}^-$, or $\mathrm{CO_3}^{2-}$, proceed with difficulty and yield primarily the original LDH plus a magnesium rich salt of the POM which deposits on the surface of the LDH crystallites.[12]

One promising route to the formation of LDH−POM materials was proposed by Drezdzon[13] in which an LDH precursor containing a large organic anion is initially prepared by the standard coprecipitation method. The choice of organic anion should result in a precursor gallery height that is close to the value expected in the final LDH−POM. Subsequent anion exchange under mildly acidic conditions results in protonation of the organic anion, thus weakening the electrostatic attraction to the LDH layers, and facilitating the incorporation of the Keggin anions while minimizing the competing hydrolysis reaction. A variety of Mg/Al, Zn/Al, and Zn/Cr containing LDHs intercalated with organic anions such as terephthalate, benzoate, p-hydroxybenzoate, and *p*-toluenesulfonate have been synthesized as potential precursor materials.[13−15]

In this work, we describe the synthesis of LDH-terephthalate precursors in which the trivalent metal cation is Ga^{3+}. The substitution of Al^{3+} by Ga^{3+} has been shown in other cases to affect the catalytic properties of inorganic oxide materials. For example, Ga−H−ZSM-5 has previously been shown to promote the conversion of light paraffins to aromatics via the Cyclar process,[16] and gallium-containing pillar interlayered clay minerals (PILCs) are known to be active for the dehydrogenation of propane to propene.[17]

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To the best of our knowledge, this is the first time that a study has been reported on the synthesis of the binary Mg/Ga system. A comparison to the synthesis of the corresponding Al^{3+} species is presented. Subsequent exchange of the terephthalate anion by either $PW_{11}O_{39}{}^{7-}$ (PW_{11}) or $H_2W_{12}O_{40}{}^{6-}$ (H_2W_{12}) was also performed for the first time starting with Mg/Ga containing precursors.

Experimental Section

Materials and Methods. The reagents NaOH (BDH Assured), $MgCl_2{\cdot}6H_2O$ (BDH Assured), $AlCl_3{\cdot}xH_2O$ (BDH Assured), and terephthalic acid (Aldrich, 98%) were used as obtained without additional purification. An aqueous solution of approximately 8.44 M $GaCl_3$ was also used in the synthesis of all gallium-containing species. The ammonium metatungstate was used as received from Aldrich. $Na_7PW_{11}O_{39}$ was prepared from $H_3PW_{12}O_{40}$ (BDH, AnalR) and Na_2CO_3 (BDH, ACS Reagent).

Preferred-orientation X-ray diffraction (POXRD) patterns were obtained, using a Scintag 2000 diffractometer, from slurried samples evaporated to dryness on glass slides. Samples were step-scanned from 3 to 30° 2θ in 0.025° steps with a counting time of 1 s/step. Fourier transformed infrared (FT-IR) spectra were obtained between 1800 and 400 cm^{-1} on a Mattson Instruments 4030 Galaxy Series FT-IR spectrometer, from a CsI disk using 124 sample scans and 32 background scans. Chemical analysis for Mg, Ga, Al, and W was performed using a Thermo Jarrell Ash Atom Scan 16 ICP spectrometer. Carbon content analysis was performed using a CEC Corp. elemental analyzer. Surface area measurements were made using the BET method on an ASDI RXM 100 instrument at an adsorption temperature of 77 K, after pretreating the 60−80 mesh sample at 125 °C for 1 h under high vacuum.

Materials Preparation. The synthesis of $Mg_6Ga_2(OH)_{16}$-$TA{\cdot}zH_2O$ (TA = $C_8H_4O_4{}^{2-}$, terephthalate anion) at pH 10.0 (i.e., $MgGa[TA]_3$, see discussion for explanation of code) is described here. Synthesis at other pH values were performed in a similar manner, the amount of $GaCl_3$ was kept constant, but the quantity of $MgCl_2$ was adjusted to give the desired ratio for the different syntheses.

A 1-L, four-neck, round-bottom flask was equipped with a 250-mL pressure equalized addition funnel, a thermometer, a pH probe, a suba-seal septum to allow N_2 flow into and out of the system, a magnetic stirrer, and an electric heating mantle. The flask was charged with 250 mL of freshly distilled, deionized (DDI) water and 2.82 g (100% excess) of terephthalic acid. NaOH solution was added via a syringe needle through the septum to the vigorously stirred mixture until a final pH of 12.7 was obtained and the terephthalic acid had completely dissolved. In a separate flask, a solution containing 100 mL of DDI water, 2.00 mL of 8.44 M $GaCl_3$, and 10.31 g of $MgCl_2{\cdot}6H_2O$ was prepared and thoroughly mixed. The mixed-metal chloride salt solution was added dropwise to the stirred terephthalate solution at room temperature via the addition funnel, resulting in the immediate formation of a white precipitate accompanied by a decrease in pH of the terephthalate solution. Simultaneous addition of NaOH solution through the septum was manually performed to maintain a constant pH of 10.0 (±0.2) over the course of the 30 min addition period. Following the complete addition of the mixed-metal salt solution, the thick suspension was stirred at room temperature for an additional 2 h, and then aged at 70 °C (±5 °C) for approximately 18 h. The final pH once the suspension had cooled to 28 °C was 9.7. The crystals were washed by repeatedly centrifuging, decanting the supernate and shaking in fresh DDI water until most of the chloride had been removed. Final product was stored under DDI water until needed.

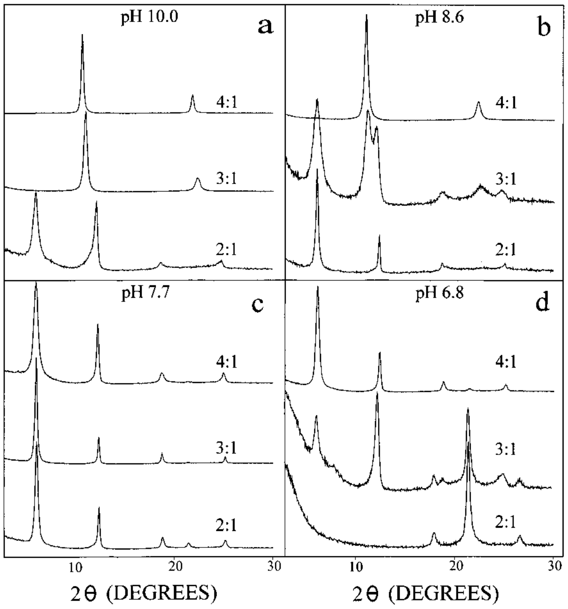

Figure 1. POXRD patterns for $MgGa[TA]_R$ products precipitated at (a) pH 10, (b) pH 8.6, (c) pH 7.7, and (d) pH 6.8. The Mg:Ga molar ratio, *R*, is given on each pattern and the coprecipitation pH appears in each box.

Replacement of Terephthalate Anions with Polyoxometalate Anions. Moist $Mg_6Ga_2(OH)_{16}TA$ (15.307 g, about 2.76 g dried weight) was placed in a 1-L round-bottom flask and slurried in 250 mL of DDI water under nitrogen until homogeneous. The pH of the LDH slurry was adjusted to about 5.5 by the addition of 20% HNO_3. 7.13 g of $Na_7PW_{11}O_{39}$ was dissolved in 100 mL of DDI water and then added dropwise to the LDH slurry with coaddition of nitric acid to maintain constant pH 5.5−6.0. After complete addition, the slurry was stirred at room temperature for 2 h, and then at 70 °C for an additional 18 h.

Results and Discussion

Synthesis of Precursor LDHs. A series of 12 Mg/Ga containing LDHs was prepared by coprecipitation of mixed metal chloride salt solutions with initial Mg:Ga ratios of 2:1, 3:1, and 4:1 at constant pH values of 6.8, 7.7, 8.6, and 10.0, in the presence of a 2-fold excess of terephthalate anions. Aluminum-containing analogues were synthesized under similar experimental conditions for comparison. The resulting products have been abbreviated $M^{2+}M^{3+}[A^{n-}]_R$, where R is the M^{2+}:M^{3+} ratio in the initial mixed metal salt solution and A^{n-} is the desired interlamellar anion (but not necessarily the anion that was actually incorporated). POXRD patterns corresponding to $MgGa[TA]_R$ and $MgAl[TA]_R$ products obtained at each of the four precipitation pH values are presented in Figures 1 and 2, respectively. The d_{003} reflection values and BET N_2 surface areas have been summarized in Table 1.

Initial attempts to synthesize layered double hydroxides of the series $MgGa[TA]_R$ and $MgAl[TA]_R$ were performed at pH 10.0. Synthesis at pH 10.0 is typical for Mg/Al samples because true coprecipitation conditions exist only at pH 10 and above. Below pH 10, it is believed that precipitation of the trivalent metal hydroxide occurs first, followed by reaction with Mg^{2+} cations in solution.[18] As shown in Table 2, the actual M^{2+}:M^{3+} ratio in the product formed at pH 10.0 is very close to the ratio that was initially present in the mixed-metal salt solution. One exception is the $MgGa[TA]_2$

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Table 1. d_{003} Spacing and BET N_2 Surface Area of MgGa[TA]$_R$ and MgAl[TA]$_R$ Layered Double Hydroxides Coprecipitated at Various pH

	coprecipitation pH							
M^{2+}:M^{3+} molar ratio, *R*, in synthesis mixture	6.8		7.7		8.6		10.0	
	d_{003}/Å	area/m^2 g^{-1}	d_{003}/Å	area/m^2 g^{-1}	d_{003}/Å	area/m^2 g^{-1}	d_{003}/Å	area/m^2 g^{-1}
Mg:Ga = 4	14.13	32	14.02	35	7.946	40	8.13	61
Mg:Ga = 3	14.13[a]	70	14.19	39	14.19	41	7.91	39
Mg:Ga = 2	*a*	96	14.14	45	14.28	19	14.31	27
Mg:Al = 4	14.08	5	14.03	22	14.07	0.1[b]	8.07	
Mg:Al = 3	14.13	68	14.09	62	14.16	0.1[b]	7.93	8
Mg:Al = 2	14.23	35	14.09	68	14.30	38	14.25	34

[a] Strong presence of gallium oxide hydroxide. [b] Diffuse POXRD pattern.

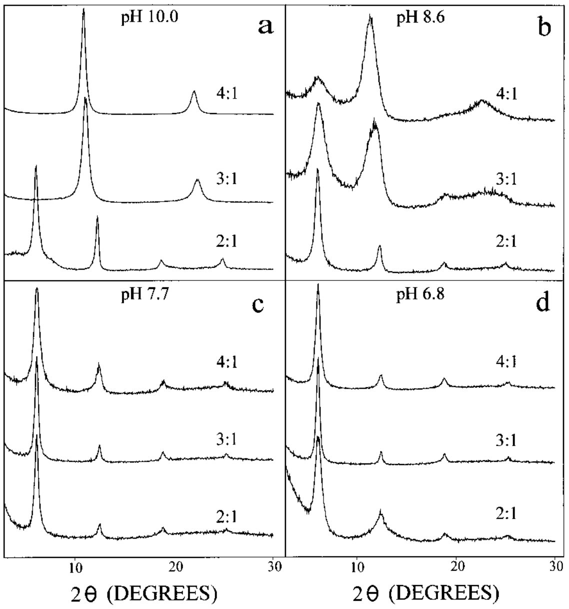

Figure 2. POXRD patterns for MgAl[TA]$_R$ products precipitated at (a) pH 10, (b) pH 8.6, (c) pH 7.7, and (d) pH 6.8. The Mg:Ga molar ratio, *R*, is given on each pattern and the coprecipitation pH appears in each box.

Table 2. M^{2+}:M^{3+} Molar Ratios of MgGa[TA]$_R$ and MgAl[TA]$_R$ Layered Double Hydroxides Coprecipitated at Various pH Measured by ICP

M^{2+}:M^{3+} molar ratio, *R*, in synthesis mixture	coprecipitation pH			
	6.8	7.7	8.6	10.0
Mg:Ga = 4	1.23	1.33	3.00	4.00
Mg:Ga = 3	0.54	1.25	2.53	2.99
Mg:Ga = 2	0.20	0.96	1.88	2.29
Mg:Al = 4	1.09	1.98	2.80	
Mg:Al = 3	1.16	1.63	2.51	3.08
Mg:Al = 2	0.63	1.44	2.04	2.14

sample, which was determined by ICP analysis to be MgGa[TA]$_{2.3}$. The magnesium enrichment in the MgGa[TA]$_2$ sample is probably attributed to the partial loss of Ga^{3+} due to the formation of soluble $Ga(OH)_4^-$, which forms at about pH 9.[19] It is apparent from the powder patterns in Figure 1a that terephthalate-intercalated LDH materials ($d_{003} = 14.3$ Å, $2\theta = 6.17°$)[13,20] can form at pH 10.0 only if the Mg:Ga ratio is about 2:1. LDHs with larger Mg:Ga ratios, specifically MgGa[TA]$_3$ and MgGa[TA]$_4$, display d_{003} reflections that are characteristic of a LDH chloride phase ($d_{003} = 8.1$ Å, $2\theta = 10.88°$).[2] The FT-IR spectrum (not shown) of MgGa[TA]$_4$ prepared at pH 10.0, but using the metal nitrate salts instead of the chloride salts, exhibits a strong band in the nitrate region; this observation supports the view that the metal salt counterion has been intercalated in preference to the terephthalate dianion. The behavior of MgAl[TA]$_2$, MgAl[TA]$_3$, and MgAl[TA]$_4$ precipitated at pH = 10.0, as shown in Figure 2a, is virtually identical with that described for the corresponding MgGa[TA]$_R$.

The results for both MgM^{3+}[TA]$_R$ series precipitated at pH 10.0 are consistent with those previously published by Kooli et al. for the MgAl[TA]$_R$ and MgAl[BA]$_R$ series (BA = $C_7H_5O_2^-$, benzoate anion), where it was found that the carboxylate anion was incorporated at pH 10.0 only if the Mg:Al ratio was less than or equal to 2:1. The difference between the 2:1 LDH (which incorporates TA) and the 3:1 and 4:1 (which do not) is proposed to be related to the layer charge density. A similar charge density dependence has previously been noted for the MgAl[$Fe(CN)_6^{4-}$]$_R$ system,[21] where the large tetravalent $Fe(CN)_6^{4-}$ anions were incorporated between the layers only for Mg:Al < 3:1.

Additional syntheses were performed at lower pH values in an attempt to produce terephthalate-containing materials with higher M^{2+}:M^{3+} ratios. The POXRD patterns obtained for MgGa[TA]$_R$ samples precipitated at pH 8.6, 7.7, and 6.8 are presented in Figure 1b–d, and the corresponding patterns for the MgAl[TA]$_R$ samples are presented in Figure 2b–d. As shown in Table 2 for both the MgGa[TA]$_R$ and MgAl[TA]$_R$ analogues, incomplete incorporation of Mg^{2+} is observed below pH 10.0. $Mg(OH)_2$ is fairly soluble at pH 8 and below, and thus a large amount of Mg^{2+} remains in solution and is lost during the washing step (i.e., ICP analysis shows up to 1000 times as much Mg^{2+} as Ga^{3+} in the mother liquor).

The MgGa[TA]$_3$ produced at pH 8.6 has a measured Mg:Ga ratio of about 2.5:1, which appears to be close to the upper limit for the partial incorporation of TA into the interlamellar space, as evidenced by the presence of d_{003} reflections characteristic of both LDH–terephthalate and LDH–chloride phases (Figure 1b, middle pattern). A Mg:Ga ratio greater than 2.5:1 results in a LDH–chloride (top pattern), whereas below this value only a LDH–terephthalate is formed (bottom pattern). The FT-IR spectra shown in Figure 3 correspond to the samples in Figure 1b. Note that the intensity of the bands associated with terephthalate increases in the order MgGa[TA]$_4$ < MgGa[TA]$_3$ < MgGa[TA]$_2$, indicating that these samples are actually a LDH–chloride, a

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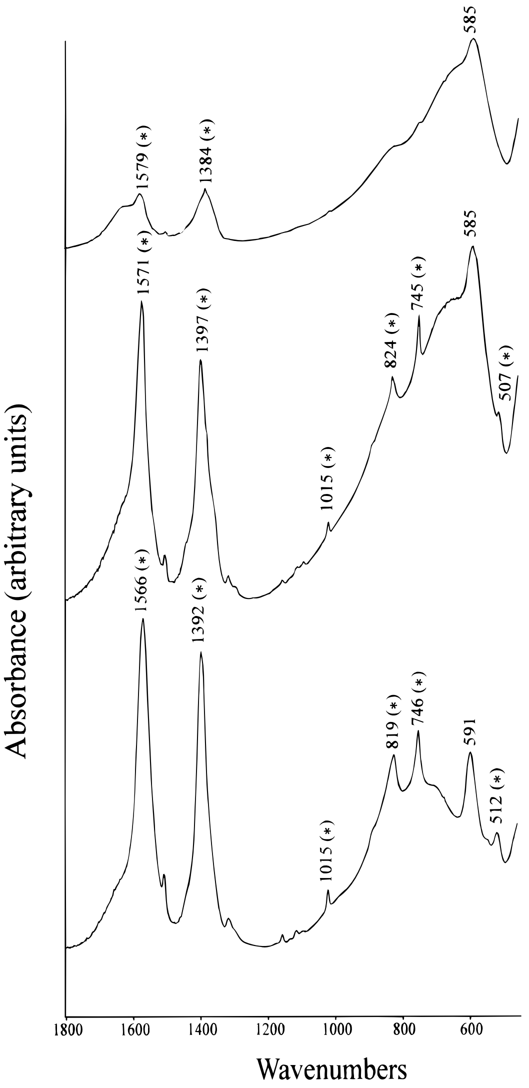

Figure 3. Fourier transformed infrared spectra (from CsI pellets) of (a) MgGa[TA]$_4$, (b) MgGa[TA]$_3$, and (c) MgGa[TA]$_2$, precipitated at pH 8.6. Asterisks denote peaks attributed to terephthalate anion.

mixture of LDH−chloride, and LDH−terephthalate, and finally a "pure" LDH−terephthalate, respectively.

The behavior of the MgAl[TA]$_R$ analogues at pH 8.6 (see Figure 2b) is rather different than that described above for the MgGa[TA]$_R$ series. POXRD patterns corresponding to very poorly crystallized LDH-TA samples are evident over all Mg:Al ratios, and there is no evidence for the coformation of a separate LDH−chloride phase. This is in contrast to the gallium-containing materials, which incorporate TA anions only when the Mg content is low. BET surface areas for the MgAl[TA]$_3$ and MgAl[TA]$_4$ samples, which displayed the most diffuse POXRD patterns, were only 0.1 m^2/g, much lower than the corresponding gallium containing species despite the fact that the M^{2+}:M^{3+} ratios were virtually identical.

Table 3. Mg^{2+}:M^{3+} Molar Ratios Calculated for Total M^{3+} Content and Layer M^{3+} Content at pH 7.7

M^{2+}:M^{3+} molar ratio, *R*,	wt %			Mg:M^{3+} molar ratio	
in synthesis mixture	M^{3+a}	Mg^a	C^b	total	layer
Mg:Ga = 4	29.56	13.73	13.05	1.33	2.08
Mg:Ga = 3	29.30	12.73	12.85	1.25	1.96
Mg:Ga = 2	36.22	12.05	10.94	0.96	2.18
Mg:Al = 4	13.86	17.83	16.23	1.98	1.99
Mg:Al = 3	9.40	14.51		1.63	
Mg:Al = 2	10.43	18.22	18.10	1.44	2.14

[a] ICP analysis on Thermo Jarrell Ash Atom Scan 16 spectrometer. [b] C analysis on CEC Corp. elemental analyzer.

Rather surprisingly, the best crystallized LDH−TA samples were obtained at a precipitation pH of 7.7 for the MgGa[TA]$_R$ series. As shown in Figure 1c, sharp POXRD patterns were obtained at all ratios, however, an additional peak at $2\theta = 21.4°$ was also observed for most of the MgGa[TA]$_R$ products; this peak must arise from gallium oxide hydrate, GaO(OH), which is isomorphous with diaspor α-AlO(OH).[22] The formation of a separate pure gallium phase immobilizes some of the gallium, and thus the measured Mg:Ga ratios reported in Table 2 do not accurately reflect the true composition of the LDH layers. The actual Mg:Ga ratio of the layers was determined by analyzing the product for wt % C and assuming that all of the carbon could be attributed to charge balancing terephthalate anions in the interlamellar space. Since the layer charge is due entirely to the presence of gallium within the layers, the wt % C provides an estimate of the moles of gallium in the layers, per gram of product. From ICP analysis the total moles of gallium (i.e., layer plus nonlayer) per gram of product is also known; therefore, it is possible to arrive at the fraction of gallium that actually exists in the layers. By assuming that all Mg detected by ICP analysis occurred in the layers, the ratio of Mg:Ga in the layers could be calculated; the results are tabulated in Table 3. It is significant to note that the Mg:Ga ratio in the layers was virtually constant at 2:1 regardless of the metal cation ratio in the initial synthesis mixture.

The POXRD patterns for the corresponding MgAl[TA]$_R$ products in Figure 2c reveal very few differences. Well-formed terephthalate-containing LDHs were obtained regardless of the Mg:Al ratio in the initial salt solution, but in no case was there evidence of a separate crystalline pure aluminum phase. ICP results indicate moderately higher Mg:M^{3+} ratios for the Al species compared to the corresponding gallium analogues, but the measured ratio is always lower than the ratio in the initial salt solution. Assuming that an X-ray amorphous pure aluminum phase did in fact precipitate, the Mg:Al content of the layers produced at pH 7.7 was determined, again indicating that the ratio present in the layers is virtually constant at about 2:1.

Figure 1d indicates that the intensity of the GaO(OH) reflections increases as the coprecipitation pH is further decreased to pH 6.8. ICP analysis indicates that the Mg:Ga ratio of the MgGa[TA]$_2$ product synthesized at pH 6.8 is actually 0.20:1, and thus virtually no Mg^{2+} was incorporated into this product. As can be seen from the POXRD pattern, it is apparently a pure GaO(OH) sample (there is no reflection around $2\theta = 6.17°$, $d_{003} = 14.3$ Å). The GaO(OH) formed in these synthesis is a relatively high surface area material, and the measured BET N$_2$ surface areas correlate to the intensity of the 21.4° peak. A maximum value of 96 m^2/g was obtained for the "pure" GaO(OH) product synthesized at pH 6.8. These results indicate that the synthesis of MgGa[TA]$_R$ products occurs at pH 7.7 or higher, whereas below this

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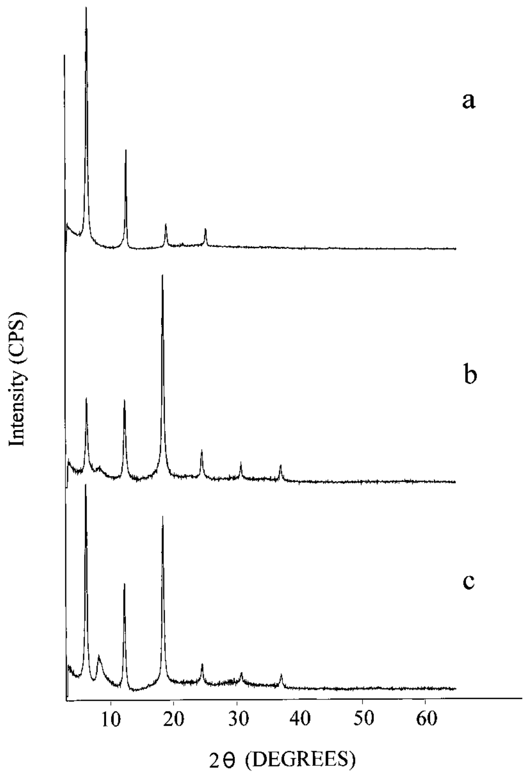

Figure 4. POXRD patterns of (a) MgGa[TA]$_3$ precursor prepared at pH 7.7, (b) MgGa[$PW_{11}O_{39}^{7-}$] anion-exchange product, and (c) MgGa[$H_2W_{12}O_{40}^{6-}$] anion-exchange product.

value the formation of GaO(OH) becomes dominant. This behavior appears to deviate from that of the Al containing analogues, which continue to form terephthalate-containing LDHs even at pH 6.8 (Figure 2d), and the appearance of a separate phase was not detected by XRD. $Mg(OH)_2$ solubility did, however, produce Mg:Al ratios as low as 0.63:1, which lie outside the theoretical limits for LDH formation. It therefore seems likely that some aluminum in the sample was not present in the layers, but instead as an amorphous, and therefore undetectable, separate phase.

Anion Exchange with POMs. The POXRD patterns of a MgGa[TA]$_3$ precursor and the corresponding anion-exchanged species, MgGa[$PW_{11}O_{39}^{7-}$]$_3$ and MgGa[$H_2W_{12}O_{40}^{6-}$]$_3$ are presented in Figure 4a–c, respectively. There is a slight increase in the d_{003} value from 14.2 Å in the terephthalate precursor to 14.6 and 14.8 Å for anion-exchanged products containing PW_{11} and H_2W_{12}. These POXRD patterns are remarkable for the relatively low intensity of the byproduct that appears around $2\theta = 8.08°$ ($d = 11$ Å); others have suggested that this byproduct is a poorly ordered Mg-rich salt of the Keggin ion.[4,12]

The specific surface area increased only slightly from 39 m^2/g for the precursor to about 45 m^2/g for both of the POM-exchanged products. Micropore size distribution experiments failed to reveal an accessible microporous structure in the POM anion-exchanged products, and it is likely that the interior surface area is blocked due to crowding of inorganic anions between the sheets. Pore blockage is probably attributable to the fact that the Mg:Ga ratio in the layers of the precursor is 2:1, and thus the surface charge density is very high, requiring the POM anions to “stuff” the interlayer region in order to satisfy electroneutrality. Carbon analysis performed on the samples indicate 0.12 wt % C in the case of the H_2W_{12}-exchanged product, and 0.67 wt % C in the case of the PW_{11}-exchanged product. It appears that the extent of exchange is nearly complete for the former (H_2W_{12}), whereas some organic anions must be retained in the latter (PW_{11}). In addition, the W:Ga ratio for MgGa[H_2W_{12}]$_3$ was 1.86:1 (theoretical value is 2.0:1) which supports the view that exchange is nearly complete. For the MgGa[PW_{11}]$_3$ LDH, the W:Ga ratio was determined to be 0.93:1 (theoretical value is 1.57:1), indicating that there are insufficient POM anions present to counterbalance the positive charge of the layers, and therefore the interlayer region must also contain residual terephthalate anions. In both cases, the Mg:Ga ratio as determined by ICP analysis increased from 1.25:1 in the terephthalate precursor to 1.99:1 for MgGa[H_2W_{12}]$_3$ and to 1.46:1 for MgGa[PW_{11}]$_3$. The increased Mg:Ga ratios can be attributed to dissolution of GaO(OH) at the low pH (pH = 5.5) used during the anion-exchange reaction.[19]

Concluding Remarks

Binary Mg/Ga-containing layered double hydroxides have been reported for the first time. The samples were precipitated from mixed metal chloride salt solutions in the presence of terephthalate anions, resulting directly in organic anion containing materials in which the aromatic rings are orientated perpendicular to the layers. Subsequent anion-exchange reactions were successful in replacing the terephthalate anions with polyoxometalate anions; the synthesis and characterization of MgGa[POM]$_R$ materials have not previously been reported.

Mg/Ga and Mg/Al LDHs precipitated at pH values between 6.8 and 10.0 in the presence of terephthalate anions have been shown to exhibit very similar behavior, with minor exceptions at the lower pH values. Under true coprecipitation conditions at pH 10.0, the M^{2+}:M^{3+} ratio of the initial salt solution is retained in the layers. LDHs intercalated with terephthalate anions form only when the Mg:M^{3+} ratio is equal to 2:1, whereas chloride containing LDH forms if the ratio is greater than 2:1. We tentatively believe that a high layer charge density is necessary for the incorporation of hydrophobic anionic species such as the terephthalate anion in order to create a continuous hydrophobic layer between the inorganic sheets. The anions are thus aligned perpendicular to the mixed-metal hydroxide layers in order to minimize the hydrophobic forces.

Due to the low Mg:Ga LDH precursor ratios obtained by this method, the resulting POM-exchanged products have a blocked pore structure, and thus the surface areas are relatively low. Contamination by other phases such as the M^{2+}/M^{3+} POM salt is minimized, as evidenced by the low intensity of the X-ray diffraction peak that is centered around $2\theta = 8.08°$ ($d = 11$ Å) in Figure 4b,c. The anion exchange of organic anion intercalated layered double hydroxide precursors does appear to be a viable route for synthesis of MgGa[POM]$_R$ ($R < 2$).

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