Synthesis of Heteropolyoxometalate-Pillared Mg/Al, Mg/Ga, and Zn/Al Layered Double Hydroxides via LDH−Hydroxide Precursors

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We report the synthesis of acidic (Zn/Al−POM) and basic (Mg/Al−POM and Mg/Ga−POM) materials by a general route previously demonstrated only for basic LDH materials. In each case, $H_2W_{12}O_{40}^{6-}$ or $PW_{11}O_{39}^{7-}$ pillared materials with significant BET surface areas were obtained. Stringent control over the M^{2+}:M^{3+} ratio in the layers of the POM-pillared products was not possible, and loss of M^{2+} was found to be the most severe for the Mg/Ga and Zn/Al materials. Infrared analysis indicated that complete exchange of adipate anions in the precursor material by POM anions was achieved except for the Zn/Al analogues. Removal of the residual adipate anions after washing the product with a dilute base solution was possible, but a concomitant decrease in surface area could not be avoided.

Introduction

Layered double hydroxides (LDHs) pillared by polyoxometalate (POM) anions have attracted considerable attention as a potentially important class of catalytically active, microporous materials.[1−6] The physical and chemical properties of these hybrid catalysts may readily be altered by changing the identity or mole fraction of the divalent and trivalent metal cations in the positively charged LDH layers.[7] In addition, there are a wide variety of POM anions with different charges and catalytic properties which may be used as pillars.[8−10] Ideally, it should be possible to adjust the synthesis conditions in order to tailor-make an LDH−POM catalyst that possesses the desired microporosity and catalytic activity to suit a particular application.

The greatest obstacle to the widespread use of POM-pillared LDH catalysts is the lack of a general method for synthesizing a variety of microporous materials with different chemical compositions, narrow pore size distributions, and high specific surface areas. Acidic LDH−POMs (those with layer compositions that are stable in solution at pH values of about 3−5, e.g. Zn/Al and Ni/Al) are often synthesized by direct coprecipitation[11,12] or by anion exchange reactions involving the nitrate or chloride form of the LDH in a mildly acidic aqueous medium (typically pH 3.5−5).[1,2,13,14] The same reaction conditions applied to basic LDH layers (i.e. those layers that are stable in solution only above pH 7, e.g. Mg/Al or Mg/Ga) generally result in a lowering of the M^{2+}:M^{3+} ratio below that of the desired value. Since $Mg(OH)_2$ is fairly soluble at pH 8 and below, any attempt to form basic LDH−POM materials at low pH (i.e. where POM anions are stable) by direct coprecipitation will result in the trivalent metal hydroxide first precipitating out of solution and then subsequently reacting with the Mg^{2+} that remains in solution. Any unincorporated Mg^{2+} at the end of the "coprecipitation reaction" will be lost during the final washing step (i.e., ICP analysis shows up to 1000 times as much Mg^{2+} as Ga^{3+} in the mother liquor).[15] Similarly, attempting to exchange nitrate or chloride anions present in either a Mg/Al or Mg/Ga LDH with POM anions (in an acidic medium) will result in $Mg(OH)_2$ becoming more soluble, thus allowing Mg^{2+} cations to be leached out of the layers and ultimately lost during the final washing step.

Control over the final M^{2+}:M^{3+} ratio of the POM-pillared product is desirable, however, since this ratio determines the charge density of the LDH layers and therefore influences the lateral spacing between the POM pillars. To synthesize a series of LDH−POM materials with different micropore size distributions, it is therefore necessary to retain, as much as possible, the desired M^{2+}:M^{3+} ratio from the initial step of a synthesis through to the ultimate product.

A second major problem is that the Keggin structure of the POM anions is hydrolytically unstable at weakly acidic to basic pH,[16,17] and thus the pillaring reactions are typically accompanied by the co-formation of an impurity phase, which is thought to be a magnesium-rich salt of the POM anion that deposits on the surface of the LDH crystallites.[6] Deposition of the POM salt phase may block the LDH micropores, resulting

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in the very low surface areas that are generally observed for these products.[3,4] The formation of this salt phase, however, may be greatly reduced by performing the anion exchange reaction at elevated temperature and with minimal subsequent aging time following the complete anion exchange.

Yun and Pinnavaia[6] recently reported a synthesis route that proceeds through the carbonate form of the LDH and minimizes the above problems. The layered structure of the LDH−carbonate is initially decomposed at 500 °C under flowing nitrogen to form a mixed-oxide solid solution.[18−21] LDHs heated below 600 °C exhibit a memory effect and reconstitute in aqueous solution to re-form the original LDH structure;[6,18] since the carbonate is driven off as CO_2 during the heating step and no other anions are present during the rehydration phase, the product obtained from calcined $Mg_6Al_2(OH)_{16}CO_3$ is a synthetic form of meixnerite, $Mg_3Al(OH)_8OH$. It was found that conversion of the meixnerite-like phase to a second intermediate, by the substitution of adipate anions for the interlamellar hydroxyl groups, greatly facilitated the desired POM anion exchange reaction. This method was shown to yield LDH materials pillared with POM anions possessing the Keggin, Dawson, and Finke structures, in which total BET N_2 surface areas of up to 136 $m^2\ g^{-1}$ were obtained. In addition, as much as 50% of the total surface area, or up to 70 $m^2\ g^{-1}$, was attributed to micropores.[6]

To determine whether this method was more generally applicable, as well as the optimum synthesis conditions for obtaining highly crystalline POM-pillared LDH phases, we recently synthesized the series of POM-pillared LDH materials $Mg_3Al{-}POM$, $Zn_3Al{-}POM$, and $Mg_3Ga{-}POM$ with the POM species $H_2W_{12}O_{40}{}^{6-}$ and $PW_{11}O_{39}{}^{7-}$. These combinations of layers and pillars demonstrate the applicability of this method to the synthesis of high-surface-area LDH materials with both acidic (Zn/Al) and basic (Mg/Al and Mg/Ga) LDH layers.

Experimental Section

Materials. The reagents $Mg(NO_3)_2{\cdot}6H_2O$ (BDH Assured), $Al(NO_3)_3{\cdot}9H_2O$ (MCB Reagents, ACS reagent), $Zn(NO_3)_2$ (BDH, 98%), NaOH (BDH, Assured), Na_2CO_3 (BDH, AnalaR), adipic acid (Aldrich, 99%), dodecatungstophosphoric acid (BDH, AnalaR), tungstic acid (Aldrich, 99%), and 28% ammonium hydroxide solution (BDH, Assured) were used as received without additional purification.

$(NH_4)_6(\alpha\text{-}H_2W_{12}O_{40})$. Ammonium metatungstate was prepared according to a literature method.[22] A 90.8 g sample of tungstic acid in 250 mL of distilled deionized water was heated to 80−90 °C, and 10.5 mL of 28% ammonium hydroxide solution was added at this temperature. Following complete addition, the mixture was stirred for an additional 2 h at the addition temperature. Crystals of $(NH_4)_6(\alpha\text{-}H_2W_{12}O_{40})$ were obtained by evaporating the filtrate to dryness overnight in an oven at 80 °C.

$Na_3PW_{12}O_{40}$. The sodium salt of the heteropoly acid $H_3PW_{12}O_{40}$ was prepared by reaction with a stoichiometric amount of sodium carbonate at 50 °C. After complete addition of the carbonate solution, the heteropoly salt solution was evaporated to dryness overnight in an oven at 90 °C.

Pillaring Strategy. A synthetic method that was first reported[6] for the pillaring of LDH materials with a 3:1 Mg:Al ratio in the LDH layers has been adapted as a general route for the synthesis of LDH materials with different layer compositions. The initially formed product is an LDH−carbonate, which is produced via the well-known coprecipitation reaction.[23] Since carbonate anions are notoriously difficult to remove by ion exchange methods, this material is thermally decomposed by calcination at temperatures between 450 and 550 °C. At these temperatures, the LDH structure is reversibly decomposed, and interlayer carbonate anions and surface hydroxyl groups are evolved as CO_2 and water, respectively, resulting in a mixed-metal-oxide solid solution. The mixed oxide displays a memory effect and will reconstitute upon stirring in water for a period of 5 days. With careful exclusion of anions from the solution during the reconstitution phase, including carbonate anions from atmospheric CO_2 sources, the mixed oxide will incorporate the hydroxide anions present in deionized water as the LDH structure re-forms. The resulting product is another intermediate in the pillaring strategy, a LDH−hydroxide (LDH−OH). To facilitate the incorporation of bulky polyoxometalate anions, however, the LDH−OH is further modified by reaction with adipic acid at elevated temperature. The interlayer hydroxide anions react with the adipic acid, producing a LDH−adipate, in which the layer repeat distance is expanded slightly from about 8.0 to 12.9 Å. The final step involves anion exchange of POM anions to replace the adipate anions in the precursor, yielding the desired polyoxometalate-pillared layered double hydroxide.

In the following sections a detailed description of the conditions that were used to synthesize each Mg/Ga-containing intermediate has been provided. Synthesis of the Mg/Al and Zn/Al analogues was carried out under nearly identical conditions: therefore, a detailed account has not been given. Any modifications to the synthetic procedure that were necessary in order to optimize the synthesis of the Mg/Al and Zn/Al materials are presented under Results and Discussion. The notation used to describe each intermediate or product has the general form $M^{2+}{}_R M^{3+}{-}A^{n-}$, where M^{2+} and M^{3+} are the divalent and trivalent metal cations present in the LDH layers, R is the initial M^{2+}:M^{3+} ratio present in the mixed-metal nitrate salt solution (not the ratio determined experimentally by ICP analysis), and A^{n-} is the desired interlayer anion species.

The $Mg_3Ga{-}$Carbonate Precursor ($Mg_3Ga{-}CO_3$). A 2-L, three-neck round-bottom flask was equipped with a pH probe and an addition funnel. The flask was charged with 600 mL of freshly distilled deionized (DDI) water, and the pH was adjusted to 10.0 by the addition of 2 M NaOH. A mixed-metal nitrate solution (16.07 g of $Ga(NO_3)_3{\cdot}9H_2O$ and 48.15 g of $Mg(NO_3)_2{\cdot}6H_2O$ in 390 mL of DDI water) was added dropwise with vigorous stirring at a constant temperature of 40 °C. The pH was maintained at 10.0, first by the co-addition of a mixed Na_2CO_3/NaOH base solution (final CO_3:Ga ratio was 1.5) and then by the co-addition of 2 M NaOH solution. After complete addition of the mixed-metal nitrate solution, the resulting thick white suspension was allowed to stir for 2 h at 40 °C and then for an additional 40 h at 70 °C. The final product was washed by repeated cycles of centrifuging and shaking in fresh DDI water (three cycles) and then dried overnight in an oven at 90 °C. ICP elemental analysis indicated that the product had the approximate composition $[Mg_{3.08}Ga(OH)_{8.16}](CO_3)_{0.5}$.

The $Mg_3Ga{-}$Hydroxide Precursor ($Mg_3Ga{-}OH$). The first step of the procedure that was used to prepare the LDH−hydroxide precursor was to decompose the hydroxycarbonate of magnesium and gallium by heating at 500 °C in a quartz tube furnace under flowing nitrogen for 5 h. One gram of the resulting mixed-oxide solid solution was quickly transferred to a sealed round-bottom flask and stirred at room temperature in 100 mL of fresh DDI water under flowing nitrogen for 5 days. The product, which is denoted $Mg_3Ga{-}OH$, was not isolated or washed; the slurry was kept under nitrogen and used directly in the next step.

The $Mg_3Ga{-}$Adipate Precursor ($Mg_3Ga{-}$adipate). The temperature of the above slurry was increased to 55 °C, a 200% excess of adipic acid (0.96 g) dissolved in 100 mL of slightly warmed DDI water was added all at once, and the mixture was stirred at 50 °C under flowing nitrogen for 1 h. The $Mg_3Ga{-}$adipate precursor was not isolated or washed, except for a small amount that was used to prepare POXRD slides for subsequent analysis.

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The $Mg_3Ga-H_2W_{12}O_{40}$ Product. After 1 h of stirring, the above LDH−adipate slurry was allowed to settle, and then approximately 50 mL of clear liquid was removed. Once stirring resumed, the temperature was increased to approximately 94 °C (2 °C below the boiling point in Calgary) and an additional 100 mL of boiling DDI water was added all at once. Hot POM solution (e.g. 1.65 g of $(NH_4)_6H_2W_{12}O_{40}$ in 50 mL of DDI water) was placed in a pressure-equalized addition funnel above the flask and added rapidly but dropwise at ambient pH to the vigorously stirred LDH−adipate slurry. After complete addition, a further aging period at near-reflux temperature was allowed prior to the product being quickly cooled in an ice bath, centrifuged, and then washed two times with freshly distilled deionized water. The final product was air-dried at room temperature, ground, sieved, and stored in separate vials until needed.

Physical Measurements. ^{27}Al and ^{71}Ga MAS NMR spectra were obtained at 78.2 and 91.5 MHz, respectively, on a Bruker AXM2 300 spectrometer under an external magnetic field of 7 T. Rotors containing the packed samples were spun at the magic angle (54° 44′ relative to the external magnetic field) at a spinning rate of 10 or 14 kHz for the ^{27}Al or ^{71}Ga samples, respectively. Typical acquisition parameters were 7000 scans with a 0.7 μs excitation pulse and 1 s delay for the ^{27}Al NMR spectra and 120 000 scans with a 0.8 μs pulse 0.5 s delay between successive scans for the ^{71}Ga NMR spectra. Measurements involving thermally treated samples were carried out after the thermal treatment, i.e. after the sample had been cooled to room temperature.

Preferred-orientation X-ray diffraction (POXRD) patterns were obtained, using a Scintag XDS 2000 diffractometer, from LDH samples suspended in water and then evaporated to dryness on glass slides. Samples were step-scanned from 3 to 65° 2θ in 0.025° steps with a counting time of 1 s/step. Infrared (IR) spectra of the samples pressed in KBr pellets were obtained at a resolution of 4 cm^{-1} between 4000 and 350 cm^{-1} on a Mattson Instruments Genesis Series FT-IR spectrometer, using 32 sample scans and 32 background scans. Chemical analysis for Mg, Zn, Al, and W was performed using a Thermo Jarrell Ash Atom Scan 16 ICP spectrometer. Elemental analysis for carbon and nitrogen 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.

Results and Discussion

The current work is a continuation of our study of the physicochemical properties and catalytic activity of polyoxometalate-pillared layered double hydroxide materials containing gallium in the LDH layers. Previous results have indicated that the same synthesis conditions used to produce aluminum-containing LDH materials may also be applied to the gallium-containing analogues with good results,[15,24] but the amount of literature dealing with the gallium-containing LDHs remains small. This paper also attempts to evaluate the potential of the synthetic route that proceeds through $LDH-CO_3$, mixed oxide, LDH−OH, and LDH−adipate precursors as a general method for the synthesis of POM-pillared LDH materials of significantly different layer compositions. For this reason, the more acidic Zn/Al LDH materials have also been included in this study along with the Mg/Al and Mg/Ga species.

The d_{003} spacings, chemical compositions, and BET surface areas for the POM-pillared products are summarized in Table 1. POXRD patterns for $Mg_3Al-H_2W_{12}O_{40}$, $Mg_3Ga-H_2W_{12}O_{40}$, and $Zn_3Al-H_2W_{12}O_{40}$ are presented in Figure 1 and for $Mg_3Al-PW_{11}O_{39}$, $Mg_3Ga-PW_{11}O_{39}$, and $Zn_3Al-PW_{11}O_{39}$ in Figure 2. For each LDH−POM, a d_{003} value between 14.6 and 15.0 Å was obtained, indicating that the Keggin ions have been successfully intercalated between the LDH layers.[25,26] In addition to the d_{003} reflection, five or six higher order diffraction lines are also observed and indexed in each case, indicating that all LDH−POM products are very well ordered materials. A broad reflection, which has been attributed to a partially hydrolyzed salt of the POM anion, is also apparent in each pattern around 11 Å and has been marked with an asterisk in Figures 1 and 2. Only the $Zn/Al-PW_{11}O_{39}$ product displays an unusual POXRD pattern (see Figure 2c); most noticeably, the d_{003} reflection is much less intense, and the byproduct peak centered around 11 Å is composed of several sharp peaks compared to one broad peak in the other patterns.

Table 1. Chemical Compositions and Physical Data for the POM-Pillared LDHs

sample	d_{003} (Å)	wt % carbon[a]	$M^{II}:M^{III}:W$[b]	BET surface area ($m^2\ g^{-1}$)
$Mg_3Al-PW_{11}O_{39}$	15.0	0.0	2.1:1.0:1.4	108
$Mg_3Ga-PW_{11}O_{39}$	14.9	0.1	1.6:1.0:1.0	77
$Zn_3Al-PW_{11}O_{39}$	14.6	2.1	1.7:1.0:1.4	104
$Mg_3Al-H_2W_{12}O_{40}$	14.9	0.0	2.4:1.0:2.2	113
$Mg_3Ga-H_2W_{12}O_{40}$	14.8	0.2	1.8:1.0:1.5	118
$Zn_3Al-H_2W_{12}O_{40}$	14.7	2.2	1.7:1.0:1.9	92

[a] Carbon analysis on a Control Equipment Corp. (CEC) 440 elemental analyzer. [b] ICP analysis on a Thermo Jarrell Ash Atom Scan 16 spectrometer.

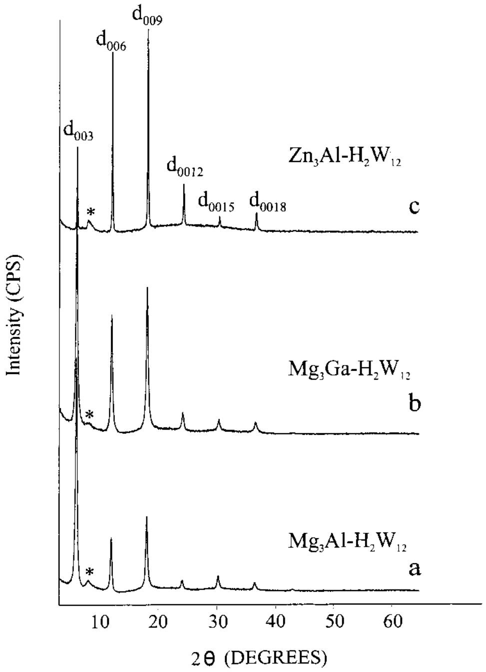

Figure 1. Preferred orientation X-ray diffraction (POXRD) patterns of (a) $Mg_3Al-H_2W_{12}O_{40}$, (b) $Mg_3Ga-H_2W_{12}O_{40}$, and (c) $Zn_3Al-H_2W_{12}O_{40}$. ∗ denotes impurity phase.

Further evidence for the intercalation of the Keggin ions is provided by FT-IR spectroscopy. The FT-IR absorption spectra for $Zn_3Al-PW_{11}O_{40}$, $Zn_3Al-H_2W_{12}O_{40}$, and $Zn_3Al-H_2W_{12}O_{40}$ washed with 0.1 M NaOH are presented in Figure 3. In each case, strong bands arising from metal−oxygen stretching modes within the LDH layers (■) appear at about 624 and 427 cm^{-1}. Superimposed on top of the LDH spectrum between 450 and 1100 cm^{-1} are the characteristic bands of the POM anion pillars, which occupy the gallery region between the LDH layers. In Figure 3a, the absorption band that normally appears around

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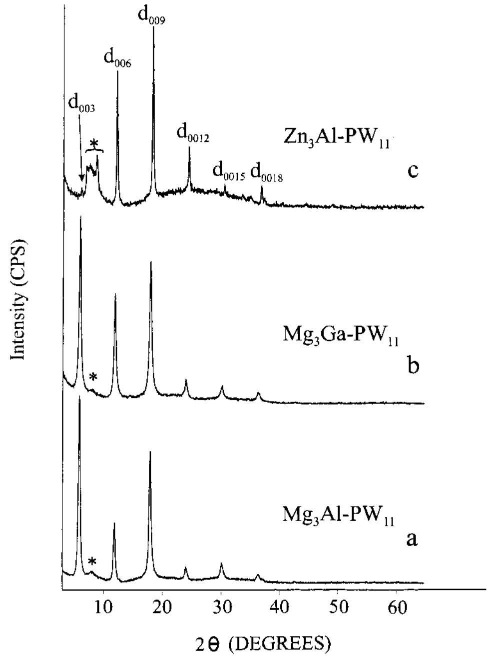

Figure 2. Preferred orientation X-ray diffraction (POXRD) patterns of (a) $Mg_3Al-PW_{11}O_{39}$, (b) $Mg_3Ga-PW_{11}O_{39}$, and (c) $Zn_3Al-PW_{11}O_{39}$. $*$ denotes impurity phase.

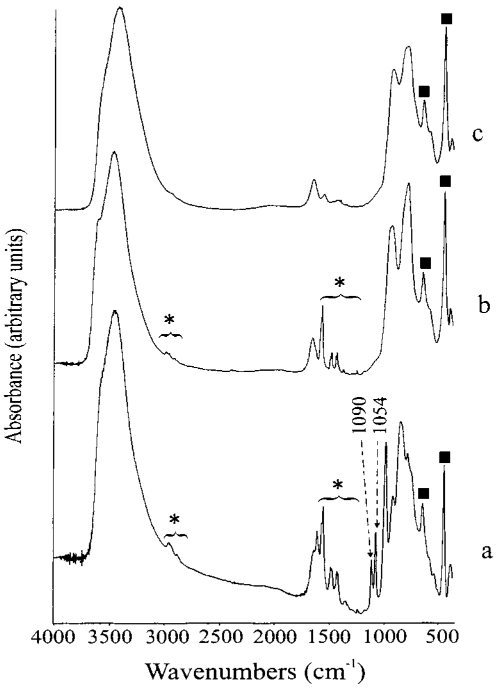

Figure 3. FT-IR spectra of (a) $Zn_3Al-PW_{11}O_{39}$, (b) $Zn_3Al-H_2W_{12}O_{40}$, (c) $Zn_3Al-H_2W_{12}O_{40}$ washed with 0.1 M NaOH solution. $*$ denotes peaks due to the residual adipate anions; ■ denotes peaks due to the LDH layers.

1080 cm^{-1} in the FT-IR spectrum of the intact $PW_{12}O_{40}{}^{3-}$ Keggin unit ($\nu(P-O_a)$) has been split into two separate bands at about 1090 and 1054 cm^{-1}. Splitting of the $\nu(P-O_a)$ band occurs when the Keggin unit undergoes a partial decomposition and loses a single WO_6 octahedron to form the lacunary (or defect) Keggin species, $PW_{11}O_{39}{}^{7-}$, which in this case is the actual pillaring species. The spectrum appearing in Figure 3b is consistent with the FT-IR spectrum of an intact $H_2W_{12}O_{40}{}^{6-}$ structure, and thus metatungstate anions possessing the full Keggin structure are the actual pillaring species in $Zn_3Al-H_2W_{12}O_{40}$.

The FT-IR spectra of both the $Zn_3Al-PW_{11}O_{39}$ and $Zn_3Al-H_2W_{12}O_{40}$ materials (Figure 3a,b) also display bands ($*$) that are characteristic of residual adipate anions, suggesting that the POM anion exchange reaction did not proceed to completion despite the fact that a large POM excess was used. Below 1100 cm^{-1}, the spectra obtained from the $Mg_RAl-POM$ and $Mg_RGa-POM$ analogues were virtually identical in appearance to those obtained from the corresponding $Zn_RAl-POM$ materials, and therefore they have not been included in Figure 3. Unlike that of the $Zn_RAl-POM$ products, however, the intensity of absorption bands attributed to residual adipate anions was very low in the spectra obtained from $Mg_RAl-POM$ and $Mg_RGa-POM$ materials. Elemental analysis to determine the amount of carbon present in each LDH−POM was performed, with the results appearing in Table 1. It is apparent that the interlayer adipate anions were completely replaced by POM anions in the final step of the synthesis for the $Mg_RAl-POM$ and $Mg_RGa-POM$ products even though very large excesses of adipate were initially used. In each case the weight percent (wt %) carbon is essentially zero. In contrast, the $Zn_RAl-POM$ products contain approximately 2% carbon by weight, indicating that significant amounts of adipate anions were retained following the anion exchange step. The presence of residual adipate anions, however, did not seriously affect the BET surface areas of the products, which were determined to be very similar to the values observed for the other products in which adipate anions were not retained.

Attempts to remove the residual adipate anions by washing the product with 0.1 M NaOH were successful in producing well-ordered LDH−POM phases containing only 0.29 wt % carbon. The FT-IR spectrum of this material, shown in Figure 3c, illustrates the nearly complete removal of adipate anions after the POM anion exchange reaction. Surprisingly, the remainder of the absorption spectrum was virtually unaffected after the product was washed with the dilute base solution, except for a slight reduction in the intensity of the POM bands compared to the bands arising from the LDH layers. Unfortunately, the surface area of this product was reduced to approximately 30 $m^2\ g^{-1}$ compared to 92 $m^2\ g^{-1}$ for the product that was washed only with deionized water. Since the basic nature of the washing solution is unlikely to affect the LDH layers (the POXRD patterns indicate that the layers are virtually unaffected), it is suggested that POM pillars situated near the edges of the sheets decomposed upon exposure to the base solution, allowing the layers to collapse around the edges and block the entrances to the micropores.

The ease of removal of residual adipate anions by washing with dilute base solution suggests that the anions were simply adsorbed on the exterior surface of the LDH crystallites and did not occupy the gallery space. The observation of large specific surface areas of up to 104 $m^2\ g^{-1}$ displayed by $Zn_3Al-POM$ materials supports the view that the gallery region does not become stuffed with a mixture of POM anions and adipate anions. In addition, the ICP elemental analysis results clearly indicate that the required number of POM anions necessary to balance the LDH surface charge is present for both $Zn_3Al-POM$ products. Specifically, the W:Al ratio for $Zn_3Al-PW_{11}O_{39}$ was found to be 1.4:1 (theoretical value is 1.4:1) and for $Zn_3Al-H_2W_{12}O_{40}$ the experimentally determined ratio was 1.9:1 (theoretical value is 2.0:1). Experiments are currently underway in our laboratory to determine if the presence of residual adipate anions on the $Zn_3Al-POM$ LDH crystallites has a detrimental effect on the physical properties or catalytic activity of the materials.

The aging period following POM anion exchange had an impact on the specific surface area of the various pillared LDH−POM materials. To investigate the effect of aging, the product of a $Mg_3Ga-H_2W_{12}O_{40}$ synthesis was divided into two parts, where the first half was stirred for 5 min at 95 °C following exchange and the second half was stirred at the same temperature for an additional 3 h. Comparison between the FT-IR spectra (not shown) of the $Mg_3Ga-H_2W_{12}O_{40}$ sample aged for 5 min and of the sample aged for 3 h indicates that the adipate anions are completely exchanged after only 5 min aging time. The POXRD patterns of both products appeared to be virtually identical as well. The only difference between the two samples was that the product that was stirred for 3 h displayed a BET surface area of 118 $m^2\ g^{-1}$ compared to only 95 $m^2\ g^{-1}$ for the product that was stirred for 5 min. An extended aging period appears to result in a more highly microporous product.

It is apparent from the M^{2+}:M^{3+} ratios given in Table 1 that the current synthesis route generally yields LDH−POM products whose chemical compositions vary from those of the desired product. ICP elemental analysis of the Mg_3Al-CO_3, Mg_3Ga-CO_3, and Zn_3Al-CO_3 precursors has revealed that, under appropriate coprecipitation conditions (pH 10.0 for Mg/Al and Mg/Ga, pH 7.7 for Zn/Al), nearly 100% of the divalent and trivalent metal cations are incorporated into the LDH−carbonate, and thus a M^{2+}:M^{3+} ratio of 3:1 is actually obtained in each case. During the subsequent steps, however, control over the pH is no longer possible, and dissolution of M^{2+} from the layers occurs to varying degrees depending upon the layer composition. Loss of M^{2+} is least severe for the Mg_3Al−POM samples and, rather surprisingly, occurs to about the same extent in both the Mg_3Ga−POM and Zn_3Al−POM samples. The observed Zn:Al ratio in the Zn_3Al-OH intermediate is consistent with a previous report,[27] which states that Zn_RAl-OH formed by the rehydration of calcined Zn_RAl-CO_3 has a M^{2+}:M^{3+} ratio near 2:1, regardless of the ratio initially present in the carbonate-containing material.

As previously stated, the theoretical W:M^{3+} ratios are 1.4:1 for the LDHs pillared with $PW_{11}O_{39}{}^{7-}$ and 2:1 for those pillared with $H_2W_{12}O_{40}{}^{6-}$, and in fact values very close to these were obtained experimentally for the Mg_3Al−POM and Zn_3Al−POM samples. Only the ratios of the gallium-containing analogues were abnormally low, with values of 1:1 and 1.5:1, for the $PW_{11}O_{39}{}^{7-}$- and $H_2W_{12}O_{40}{}^{6-}$-pillared products, respectively. Since FT-IR analysis of these samples failed to indicate the presence of interlayer adipate or carbonate anions, the low ratios may be attributed to the presence of a separate gallium-containing phase, possibly amorphous α-GaO(OH), which has been reported in other instances.[15]

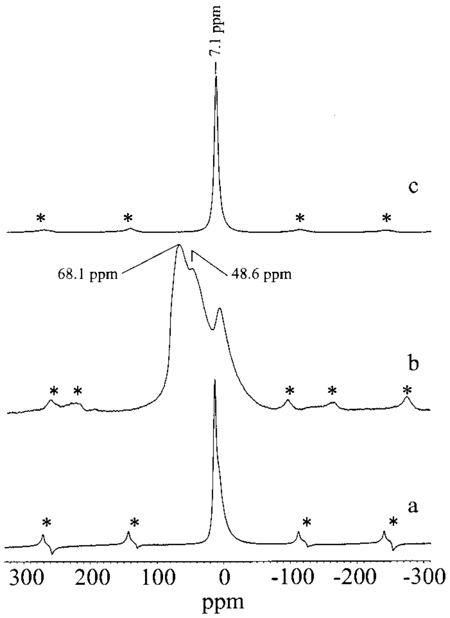

Figure 4. ^{27}Al MAS NMR spectra of (a) Zn_3Al-CO_3, (b) Zn/Al mixed metal oxide, and (c) $Zn_3Al-PW_{11}O_{39}$. $*$ denotes spinning sidebands.

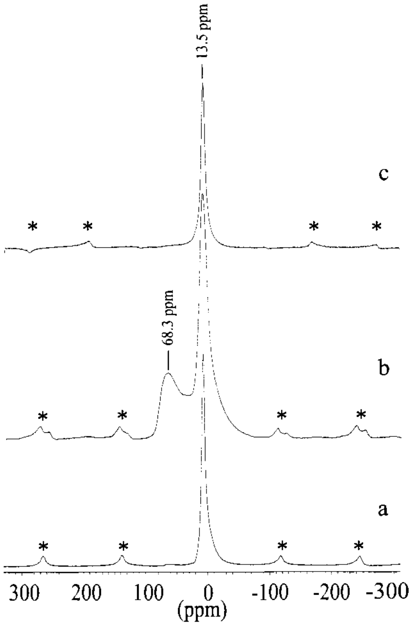

Figure 5. ^{27}Al MAS NMR spectra of (a) Mg_3Al-CO_3, (b) Mg/Al mixed metal oxide, and (c) $Mg_3Al-PW_{11}O_{39}$. $*$ denotes spinning sidebands.

To understand better the processes that are occurring over the course of the synthesis, a solid state, MAS NMR study of the LDH−CO_3, mixed-metal-oxide solid solution and LDH−POM was undertaken. The ^{27}Al MAS NMR of the Zn_3Al-CO_3 (Figure 4a) and Mg_3Al-CO_3 (Figure 5a) samples indicated the presence of octahedral aluminum only ($\delta \sim 7-14$ ppm). After the carbonates were calcined at 500 °C for 5 h, the NMR spectra showed evidence of both tetrahedral ($\delta \sim 68$ ppm) and octahedral aluminum for both the zinc- (Figure 4b) and magnesium-containing (Figure 5b) analogues. In addition, the zinc/aluminum mixed metal oxide (Figure 4b) formed by thermal decomposition also contained a significant amount of pentavalent aluminum ($\delta \sim 49$ ppm),[28] which was not formed in the magnesium/aluminum mixed oxide (Figure 5b). It is believed that as the interlayer carbonate anions are evolved as CO_2 during heating, the Al^{3+} cations migrate into the gallery space and adopt a tetrahedral coordination. The Zn_3Al-CO_3 material appears to be a special case, and it has been suggested that the decomposition of bridged bidentate complex anions (such as $CO_3{}^{2-}$) with metal anions in the LDH layers may be necessary for the formation of pentavalent aluminum.[28] No explanation currently exists to account for the nonobservation of pentavalent aluminum in the spectrum of the Mg/Al mixed oxide.

Subsequent reconstitution of the LDH structure by stirring in degassed water under nitrogen for 5 days returned all aluminum to an octahedral coordination, regardless of whether

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(27) Kooli, F.; Depege, C.; Ennaqadi, A.; deRoy, A.; Besse, J. P. *Clays Clay Miner.* **1997**, *45*, 92.

(28) Velu, S.; Ramkumar, V.; Narayanan, A.; Swamy, C. S. *J. Mater. Sci.* **1997**, *32*, 957.

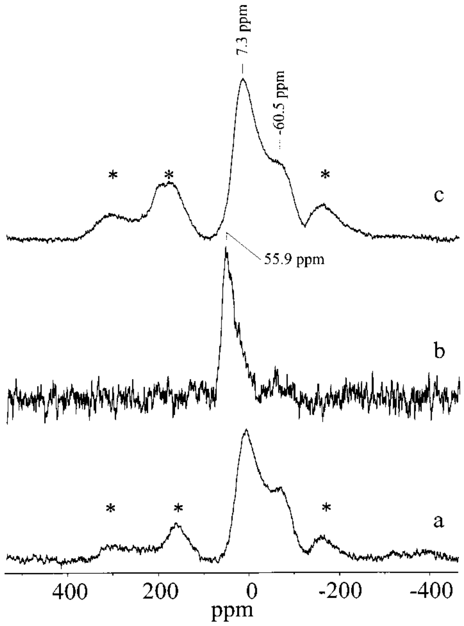

Figure 6. ^{71}Ga MAS NMR spectra of (a) Mg_3Ga-CO_3, (b) Mg/Ga mixed metal oxide, and (c) $Mg_3Ga-H_2W_{12}O_{40}$. $*$ denotes spinning sidebands.

pentavalent aluminum was detected in the mixed oxide. The PW_{11}-pillared products with Zn/Al-containing layers (Figure 4c) and Mg/Al-containing layers (Figure 5c) both displayed ^{27}Al NMR spectra nearly identical to that of the corresponding LDH−carbonate precursor. One difference, however, is that the spectral peak is more symmetric for the LDH−POM, possibly due to a less distorted octahedral orientation of the aluminum cation once the M^{2+}:M^{3+} ratio has decreased from 3:1 in the $LDH-CO_3$ to nearly 2:1 in the LDH−POM.

The ^{71}Ga MAS NMR spectra (Figure 6) were complicated by the presence of very strong spinning sidebands, possibly indicating that the gallium existed in a more distorted octahedral environment compared to that of the other analogues. Upon adjusting the acquisition parameters, we observed a single resonance with a strong shoulder (possibly the result of second-order quadrupolar effects) at a position that is characteristic of gallium in an octahedral environment (7.3 ppm). Once again, decomposition of the LDH formed a mixed metal oxide with a single resonance that is believed to be that for tetrahedral gallium ($\delta \sim 56$ ppm). Interestingly, there was no evidence of gallium in an octahedral environment following decomposition (Figure 6b) as there had been in the ^{27}Al MAS NMR spectra (see above) of $Mg_3Al-POM$ and $Zn_3Al-POM$. It is possible that line broadening as a result of rapid quadrupolar relaxation might have caused the signal for octahedral gallium to vanish into the noise; therefore additional experiments are being performed to try to verify these results. Upon rehydration and anion exchange to form the POM-pillared product, however, all gallium returned to an octahedral coordination (Figure 6c).

Conclusions

The LDH−OH precursor route has been used for the first time to produce acidic (Zn/Al) and basic (Mg/Al and Mg/Ga) LDH materials pillared with PW_{11} and H_2W_{12} POM anions. The results of the solid state MAS NMR study of the LDH−POM and the $LDH-CO_3$ and mixed oxide precursors have demonstrated unequivocally that the current synthetic route may be employed to produce polyoxometalate-pillared LDH materials with a wide variety of layer compositions. The Zn/Al and Mg/Ga LDH materials have been shown to undergo the same series of transformations that have previously been reported only for the Mg/Al analogues. All LDH−POM products synthesized using the LDH−hydroxide precursor route exhibited large surface areas and significant microporosity regardless of the LDH layer composition or pillaring anion.

Stringent control over the M^{2+}:M^{3+} ratios proved to be impossible under the conditions used in this work; the final ratios were consistently smaller than those found in the synthesis mixtures. Loss of M^{2+} was most severe in the Zn/Al and Mg/Ga LDHs and was the least severe with Mg/Al LDHs. MAS NMR studies showed that, for each type of LDH, thermal decomposition converts at least some of the octahedrally coordinated M^{3+} into tetrahedral and/or pentavalent forms, but upon reconstitution and POM exchange, only octahedral M^{3+} is detected. Furthermore, the POM-pillared products obtained from Zn_3Al-CO_3 LDH precursors retained significant quantities of adipate anions after the final washing step. It is believed that these adipate anions are simply adsorbed on the surface of the LDH crystallites and that they do not occupy positions between the LDH layers. Attempts to remove the residual adipate anions by washing in basic solution were successful; however, much of the microporous surface area was lost by this action.

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