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New Route to Layered Double Hydroxides Intercalated by Organic Anions: Precursors to Polyoxometalate-Pillared Derivatives

Hydrotalcite-like layered double hydroxides[1] (LDHs) of the type $[M^{II}_{1-x}M^{III}_{x}(OH)_2][X^{n-}]_{x/n}\cdot zH_2O$ represent the only known family of ionic lamellar solids with positively charged layers. It recently has been shown that LDHs interlayered by polyoxometalate anions (POMs) represent a new class of pillared materials for selective adsorption and catalysis.[2-5] However, these pillared intercalates are intrinsically difficult to synthesize in highly crystalline form, in part, because LDH hosts are basic, whereas most POMs suitable for pillaring are acidic (e.g., $V_{10}O_{28}^{6-}$, $SiV_3W_9O_{40}^{7-}$). Thus, hydrolysis reactions of the LDH or POM can result in products that are poorly ordered, even X-ray amorphous,[6] or that contain multicrystalline phases interlayered by different anions.

One promising route to the synthesis of pillared LDH–POM intercalates is based on the ion-exchange reaction of a POM anion with an LDH precursor intercalated by a large organic anion.[4] In this case, the organic anion is very readily replaced by the POM, and competing hydrolysis reactions are minimized. Since LDH ion-exchange reactions are topotactic, any layer stacking defects in the precursor also will appear in the pillared product. In order to achieve regularly microporous materials, such defects should be minimized. However, a general method for the preparation of well-ordered organic anion derivatives of LDHs is lacking.

Here we describe a new method for the synthesis of exceptionally well-ordered LDH intercalates containing carboxylate and other organic anions. Some of these derivatives are excellent precursors for the preparation of regularly microporous derivatives pillared by Keggin-type POM anions. Our approach is based on the reaction of an organic acid with the hydroxide exchange form of the LDH in the presence of glycerol as a swelling agent. To our knowledge, this is the first example of the use of a swelling agent for the preparation of LDH intercalates.

A synthetic analogue of the naturally occurring mineral meixnerite,[7] $[Mg_3Al(OH)_8]OH\cdot 2H_2O$, was selected as a representative hydroxide ion exchange form of an LDH. This compound was conveniently prepared for the first time from hydrotalcite, $[Mg_3Al(OH)_8][CO_3]_{0.5}\cdot 2H_2O$, by first calcining the hydrotalcite at 500 °C for 3 h to form a mixed magnesium–aluminum oxide solid solution,[8-10] and then slurrying the mixed oxide in degassed water (25 °C, 16 h, 2 wt % solids) under a CO_2-free nitrogen atmosphere to form the crystalline $[Mg_3Al]$–OH intercalate. The addition of two volumes of glycerol to the slurry resulted in the extensive swelling of the LDH interlayers, as evidenced by the absence of Bragg scattering of Cu Kα X-rays ($\lambda = 1.542$ Å) above $2\theta = 1.0°$. However, the hydroxide in the hydrated state exhibited a set of sharp 00*l* reflections, as shown by the XRD pattern in Figure 1A. Thus, the basal spacing of the intercalate increased from 7.8 Å as a hydrate to >40 Å in the glycerated form.

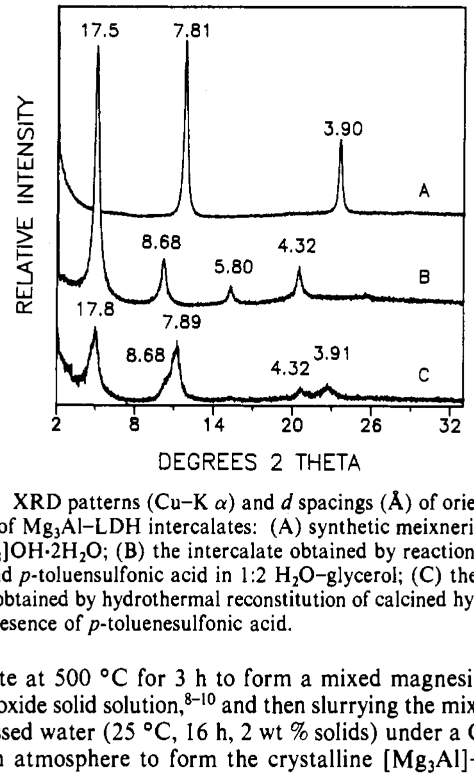

Figure 1. XRD patterns (Cu-K α) and *d* spacings (Å) of oriented film samples of Mg_3Al–LDH intercalates: (A) synthetic meixnerite, $[Mg_3Al(OH)_8]OH\cdot 2H_2O$; (B) the intercalate obtained by reaction of meixnerite and *p*-toluensulfonic acid in 1:2 H_2O–glycerol; (C) the reaction product obtained by hydrothermal reconstitution of calcined hydrotalcite in the presence of *p*-toluenesulfonic acid.

The reactions of meixnerite in 1:2 (v/v) H_2O–glycerol with long-chain carboxylic acids (e.g. nonanoic acid) or with α,ω-dicarboxylic acids (e.g., adipic acid) in stoichiometric ratios proceeded smoothly at ambient temperature to form the corresponding organic anion intercalates as single phases in quantitative yield with respect to interlayer (exchangeable) hydroxide. Equally facile and complete reactions were observed for *p*-toluenesulfonic and squaric acids. In each case, glycerol was needed for complete and clean reaction. Mixed phases, including unreacted meixnerite, were observed in the absence of the swelling agent. Thus, the swelling agent greatly facilitates access to the exchangeable hydroxide anions on the basal surfaces of the LDH host.

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Table I. Representative Mg_3Al–LDH Intercalates Containing Organic Anions

anion	basal spacing, Å	domain size,[a] Å
$[CH_3(CH_2)_7CO_2]^-$	20.2	101
$[O_2C(CH_2)_4CO_2]^{2-}$	14.4	203
$[p\text{-}CH_3C_6H_4SO_3]^-$	17.4	197
$[C_4O_4]^{2-}$	10.1	171

[a] The size of the scattering domain along the *c*-axis was determined from the width of the second or third 00*l* X-ray harmonic of oriented film samples.

Table I provides the basal spacings for selected reaction products, along with estimates of the scattering domain size in the *c*-axis direction (perpendicular to the layers). The latter quantity, which provides an indication of the extent of long-range layer stacking, was obtained from the width of the second or third 00*l* harmonic and the Scherrer relationship $d = 0.9\lambda/[D \cos \theta]$, where λ is the X-ray wavelength, D is the width of the diffraction line, and θ is the diffraction angle. Each reaction product exhibited a preferred orientation XRD pattern containing four or more 00*l* harmonics. Metal ion and carbon–hydrogen analyses were consistent with the complete replacement of hydroxide by the organic anion.

The reaction products obtained here are crystallographically well-ordered relative to those obtained by previously reported synthetic methods. For instance, the hydrothermal crystallization of gels formed by the coprecipitation of metal(II) and metal(III) hydroxides in the presence of organic anions is an effective route to LDH intercalates interlayered by terephthalate or arenesulfonates,[4] but this method affords alkyl carboxylate or α,ω-dicarboxylate derivatives with diffuse or amorphous X-ray patterns.[4,11] Ion-exchange reactions of simple LDH precursors in water, though quite suitable for the synthesis of LDH alkanesulfonates,[12,13] also are not generally useful for the preparation of crystalline LDH carboxylates.

The hydrothermal reconstitution of calcined LDH carbonates (hydrotalcites) in the presence of various anions has been recognized as a general pathway to LDH intercalates.[14-17] However, this latter method, when applied to organic anion derivatives, can afford mixed phases,[16] or the degree of crystallinity can vary with anion loading.[17] Parts B and C of Figure 1 compare the XRD patterns for $[Mg_3Al]$-*p*-toluenesulfonate intercalates prepared from synthetic meixnerite in 1:2 H_2O–glycerol and from the hydrothermal reconstitution of calcined hydrotalcite.[16] The former method yields a single, well-crsytallized phase, whereas the latter provides a less ordered intercalate, together with the LDH hydroxide (d = 7.8 Å) as a coproduct.

To illustrate the utility of well-ordered organic anion derivatives as precursors to pillared derivatives, we consider the synthesis of a $[Mg_3Al]$–LDH interlayered by the Keggin ion species $H_2W_{12}O_{40}^{6-}$. We have previously shown that a pillared $[Zn_2Al]$–$[H_2W_{12}O_{40}^{6-}]$ intercalate with a basal spacing of d = 14.5 Å can be prepared by the ion-exchange reaction of an acidic $[Zn_2Al]$–NO_3^- precursor (d = 8.9 Å) with the POM anion in aqueous solution.[3] In contrast, the analogous reaction with the basic $[Mg_3Al]$–NO_3^- precursor yields only amorphous hydrolysis products. Yet, the $[Mg_3Al]$–adipate and –toluenesulfonate intercalates prepared here are excellent precursors for the synthesis of a pillared $H_2W_{12}O_{40}^{6-}$ analogue (d = 14.8 Å) by aqueous ion-exchange reaction. The overall conversion of hydrotalcite to the POM-pillared derivative is shown in the Scheme I. Figure 2 illustrates the XRD patterns for the adipate precursor and the $[Mg_3Al]$–$H_2W_{12}O_{40}^{6-}$-pillared products.

Scheme I

$$\begin{array}{c} [Mg_6Al_2(OH)_{16}](CO_3).4H_2O \\ \Big\downarrow {\scriptstyle 500\ ^{\circ}C\ ,\ 3\ h} \\ Mg_{0.667}Al_{0.222}\square_{0.111}O \\ \Big\downarrow {\scriptstyle H_2O,\ 25\ ^{\circ}C\ ,\ 30\ h} \\ [Mg_3Al(OH)_8][OH].2H_2O \\ \Big\downarrow {\scriptstyle [C_6H_8O_4]^{2-}\ ,\ glyc.} \\ [Mg_6Al_2(OH)_{16}][C_6H_8O_4] \\ \Big\downarrow {\scriptstyle H_2W_{12}O_{40}^{6-}\ ;\ H_2O\ /\ glyc.} \\ [Mg_{18}Al_6(OH)_{48}][H_2W_{12}O_{40}].yH_2O \end{array}$$

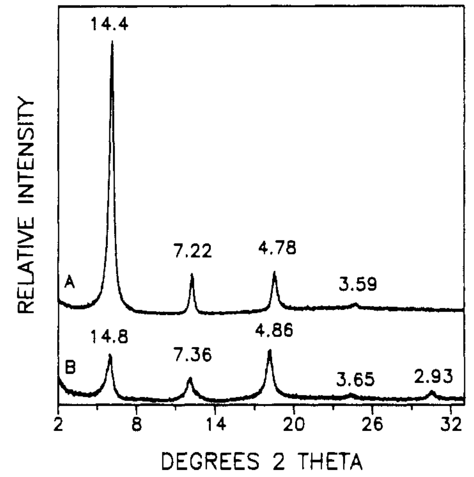

Figure 2. Preferred orientation XRD patterns (Cu–K α) and d spacings (Å): (A) a $[Mg_3Al(OH)_8]$–adipate reaction precursor; (B) the pillared $[Mg_3Al(OH)_8]_6[H_2W_{12}O_{40}]\cdot xH_2O$ reaction product.

Analogous reactions of the $[Mg_3Al]$–adipate and –toluenesulfonate intercalates with the lacunary Keggin species $SiW_{11}O_{39}^{8-}$ yielded the corresponding POM-pillared product as a single crystalline phase (d = 14.8 Å). The $H_2W_{12}O_{40}^{6-}$- and the $SiW_{11}O_{39}^{8-}$-pillared phases both exhibited type I N_2 adsorption isotherms indicative of microporous materials. BET surface areas for the $[Mg_3Al]$–$H_2W_{12}O_{40}^{6-}$ and –$SiW_{11}O_{39}^{8-}$ intercalates were 107 and 155 m^2/g, respectively. A more complete characterization of the pore structures of these pillared materials is under investigation.

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Department of Chemistry and Center for Fundamental Materials Research
Michigan State University
East Lansing, Michigan 48824

Emmanuel D. Dimotakis
Thomas J. Pinnavaia*

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