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# *Communications*

## Pillaring of a Layered Double Hydroxide by Polyoxometalates with Keggin-Ion Structures

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Layered silicate clays (LSCs) are well recognized for their ability to form a variety of pillared intercalated derivatives[1,2] with novel properties for selective adsorption and catalysis.[3-5] Layered double hydroxides (LDHs)[6-9] represent another potentially important class of lamellar ionic solids for forming pillared derivatives. These materials consist of positively charged $Mg(OH)_2$-like layers separated by hydrated gallery anions. A very large range of compositions of the type $[M^{II}_{1-x}M^{III}_x(OH)_2][A^{n-}]_{x/n}\cdot yH_2O$ are possible, wherein the $M^{II}$ and $M^{III}$ metal ions occupy octahedral positions in the hydroxide layers and $A^{n-}$ is the gallery anion.

Although LDHs have the reverse polarity from LSCs with regard to layer and gallery ion charge, they are not as readily pillared as LSCs. The relatively high layer charge density of LDHs ($\geq$0.04 e$-$/Å$^2$ vs $\sim$0.01 e$-$/Å$^2$ for smectite LSCs) tends to promote "stuffing" of the galleries by the pillaring anions themselves, particularly when the gallery ion charge is in the range $-1$ to $-3$. Using $V_{10}O_{28}^{6-}$ as a prototypical oxo anion, we previously have demonstrated that polyoxometalates (POMs) with high charge can be effective reagents for the pillaring of LDHs.[10] $Mo_7O_{24}^{6-}$ also has been investigated as a potential LDH pillaring agent,[11] but this species affords products with a gallery height ($\sim$7.4 Å) similar to the value obtained with $V_{10}O_{28}^{6-}$ ($\sim$7.1 Å)[12] Pillared derivatives with even larger gallery heights and pore sizes are desired for catalytic reactions of organic molecules.

In the present work we report LDH pillaring by $\alpha$-$[XM_{12}O_{40}]^{n-}$ POMs with Keggin-type structures.[13] These reagents afford intercalates with gallery heights of $\sim$10 Å, substantially larger than those obtained for the $V^V$ and $Mo^{VI}$ isopoly intercalates. Also, our results show that the reactivity of $[XM_{12}O_{40}]^{n-}$ species toward intercalative ion exchange depends strongly on both the net charge and polyhedral form of the ion.

An aqueous hot suspension of $[Zn_2Al(OH)_6]NO_3\cdot 2H_2O$,[14,15] henceforth abbreviated $Zn_2Al[NO_3^-]$, was found to undergo facile and *complete* intercalative ion exchange reaction[16] with aqueous solutions of $\alpha$-$[H_2W_{12}O_{40}]^{6-}$ and $\alpha$-$[SiV_3W_9O_{40}]^{7-}$ Keggin ions. Conversely, no reaction was observed for the Keggin ions $\alpha$-$[PW_{12}O_{40}]^{3-}$ and $\alpha$-$[SiW_{12}O_{40}]^{4-}$. Also, only partial intercalation (<20%) was observed under equivalent conditions for the Keggin-like species $[PCuW_{11}O_{39}(H_2O)]^{5-}$.

The above results show that the accessibility of the LDH galleries depends, in part, on the charge on the POM. If

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[1] Vaughan, D. E. W. *Catal. Today* **1988**, *2*, 187.

[2] Pinnavaia, T. J. *Science* **1983**, *220*, 365.

[3] Adams, J. M. *Appl. Clay Sci.* **1987**, *2*, 309.

[4] *Catalysis Today—Pillared Clays*; Burch, R., Ed.; Elsevier: Amsterdam, **1988**; Vol. 2, No. 2-3, pp 185–368.

[5] Figueras, F. *Catal. Rev. Sci. Eng.* **1988**, *30*, 457.

[6] Reichle, W. T. *CHEMTECH* **1986**, 58.

[7] (a) Taylor, H. F. W. *Mineral. Mag.* **1973**, *39*, 377. (b) Rouxhet, P. G.; Taylor, H. F. W. *Chimia* **1969**, *23*, 480.

[8] Miyata, S.; Okada, A. *Clays Clay Miner.* **1977**, *25*, 14.

[9] Brindley, G. W.; Kikkawa, S. K. *Clays Clay Miner.* **1980**, *28*, 87.

[10] Kwon, T.; Tsigdinos, G. A.; Pinnavaia, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 3653.

[11] Drezdzon, M. A. *Inorg. Chem.* **1988**, *27*, 4628.

[12] We should also note that G. M. Woltermann, in U.S. Patent 4,454,244, has claimed products formed by the reaction of LDHs with aqueous solutions of $[V_{10}O_{28}]^{6-}$ and other polyoxometalates. Our investigations of several of these products indicates that they contain various phases, some of which are nonlayered or even X-ray amorphous.

[13] Pope, M. P. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, **1983**; pp 23–27.

[14] The host LDH was prepared by reaction of freshly precipitated aluminum hydroxide with an aqueous zinc chloride solution at pH 6.2 according to the general method of Taylor.[15] The reaction time at 100 °C was 7 days.

[15] Taylor, R. M. *Clay Miner.* **1984**, *19*, 591.

[16] The ion-exchange reactions were carried out by the dropwise addition of a boiling suspension of $Zn_2Al[NO_3^-]$ to a 40% excess of the POM in aqueous solution at room temperature. A nitrogen atmosphere was used to avoid possible reaction of the LDH with atmospheric $CO_2$. The final products also were stored under nitrogen.

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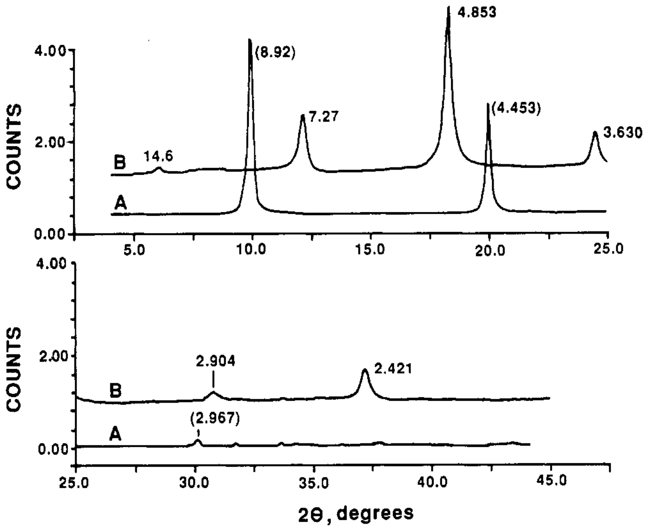


**Figure 1.** X-ray diffraction patterns for oriented film samples of LDH intercalates (A) $Zn_2Al[NO_3^-]$ and (B) $Zn_2Al[\alpha\text{-}H_2W_{12}O_{40}^{6-}]$. Values adjacent to the diffraction peaks are *d* spacings in angstroms for several 00*l* harmonics.

we assume a triangular arrangement of Keggin ions with a 9.8-Å diameter in the LDH galleries, then the area needed to accommodate each ion is 83 Å$^2$. Since for $Zn_2Al[NO_3^-]$ the area per unit layer charge is only 16.6 Å$^2$, Keggin ions with a charge less than 5− should be spatially incapable of balancing the host layer charge, at least when intercalated at the monolayer level. The absence of intercalative ion exchange for $\alpha\text{-}[PW_{12}O_{40}]^{3-}$ and $\alpha\text{-}[SiW_{12}O_{40}]^{4-}$ is consistent with these simple geometrical considerations. The partial replacement of $NO_3^-$ by Keggin ions with a 3− or 4− charge would require mixing of the Keggin ion and $NO_3^-$ ions within the same galleries, but such intracrystalline mixing of ions of very different sizes apparently is thermodynamically unfavorable.

The $Zn_2Al[\alpha\text{-}H_2W_{12}O_{40}^{6-}]$ and $Zn_2Al[\alpha\text{-}SiV_3W_9O_{40}^{7-}]$ intercalated products were crystallographically well-ordered phases. Figure 1 provides the X-ray diffraction patterns for oriented film samples of the $Zn_2Al[\alpha\text{-}H_2W_{12}O_{40}^{6-}]$ reaction product and the $Zn_2Al[NO_3^-]$ starting material. At least six orders of 00*l* harmonics corresponding to a basal spacing of 14.5 Å were observed for both the $\alpha\text{-}[H_2W_{12}O_{40}]^{6-}$ and the $[SiV_3W_9O_{40}]^{7-}$ intercalates. If the thickness of the LDH layer is taken to be 4.7 Å, then the gallery height is 9.8 Å, in accord with the expected size of a Keggin ion. Elemental analyses for the metatungstate derivative were in reasonable agreement with the formula unit $[Zn_{12}Al_6(OH)_{36}][\alpha\text{-}H_2W_{12}O_{40}]\cdot 22H_2O$. Anal. Calcd for $H_{82}Zn_{12}Al_6W_{12}O_{98}$ (wt %): Zn, 15.6; Al, 3.9; W. 40.0. Found: Zn, 14.8; Al, 3.1; W, 41.6.

Further evidence for the retention of the Keggin ion structure in the intercalated state was provided, in part, by the IR spectra of the $Zn_2Al[\alpha\text{-}SiV_3W_9O_{40}^{7-}]$ intercalate. As shown in Figure 2, the group frequencies[17] of the $M_3O_{13}$ triads for the intercalated Keggin ion are very similar to those observed for an authentic salt of the POM. Also, a solution prepared by the dissolution of $Zn_2Al[\alpha\text{-}SiV_3W_9O_{40}^{7-}]$ in nitric acid at pH 2.0 exhibited single $^{29}Si$ and $^{51}V$ NMR resonances with chemical shifts of −84 ppm vs TMS and −567 ppm vs $VOCl_3$, repectively. These shifts were identical with those for an authentic solution of the POM.

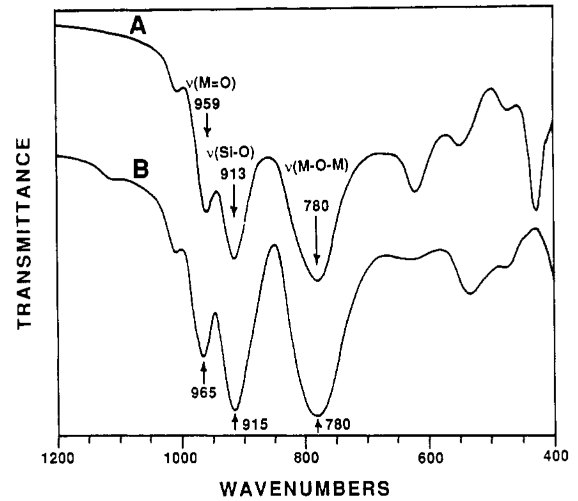
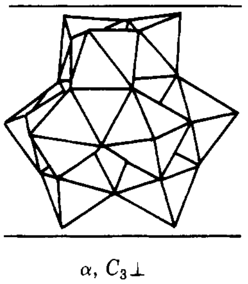
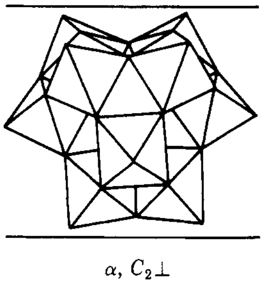


**Figure 2.** Infrared spectra showing the intratriad group frequencies of $[SiV_3W_9O_{40}]^{7-}$ (A) intercalated in a $Zn_2Al$ LDH and (B) as the potassium–hydronium salt. The assignment of the intratriad $M_3O_{13}$ frequencies are after ref 17.

$Zn_2Al[\alpha\text{-}H_2W_{12}O_{40}^{6-}]$ and $Zn_2Al[\alpha\text{-}SiV_3W_9O_{40}^{7-}]$ both exhibited Langmuir-type $N_2$ adsorption isotherms indicative of regularly microporous structures. The $N_2$ BET surface areas, which were determined after outgassing at 130 °C, were 63 and 155 m$^2$/g for the $\alpha\text{-}[H_2W_{12}O_{40}]^{6-}$ and $\alpha\text{-}[SiV_3W_9O_{40}]^{7-}$ intercalates, respectively. The respective pore volumes were 0.023 and 0.061 mL/g. The nonpillared $Zn_2Al[NO_3^-]$ precursor exhibited a surface area of only 26 m$^2$/g. Thus, POM intercalation substantially increases the accessibility of the intracrystalline surfaces. Hence, the term "pillared" is appropriate in describing the nature of these materials.

In the $Zn_2Al[\alpha\text{-}H_2W_{12}O_{40}^{6-}]$ and $\text{-}[\alpha\text{-}SiV_3W_9O_{40}^{7-}]$ intercalates described above, the oxygen framework of the POM defines a polyhedral form with $T_d$ symmetry.[13] The orientation of the α isomer in the LDH galleries is of structural interest. Inspection of polyhedral models suggest two possible orientations. One orientation places the $C_3$ axis of the framework orthogonal to the layers, and in the other orientation the $C_2$ axis is orthogonal.


$\alpha$, $C_3\perp$


$\alpha$, $C_2\perp$

The $C_3\perp$ orientation of the α-isomer allows the LDH hydroxyls to engage in H bonding to six oxygens of the upper $M_3$ triad and to three terminal oxygens on the opposing side of the POM. Conversely, the $C_2\perp$ orientation permits 12 H bonding interactions to 8 terminal and 4 bridging POM oxygen atoms. The larger number of H bonds should favor the $C_2\perp$ orientation.

Evidence in favor of the $C_2\perp$ orientation for the α-isomer was obtained by investigating the intercalation properties of $\beta\text{-}[SiV_3W_9O_{40}]^{7-}$, which has $C_{3v}$ oxygen framework symmetry. The intercalation of this isomer is relatively slow, and the intercalation rate decreases to essentially zero with increasing extent of exchange. Complete exchange was not possible even after several reaction cycles with fresh solutions of $\beta\text{-}[SiV_3W_9O_{40}]^{7-}$. As shown

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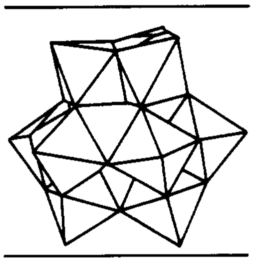
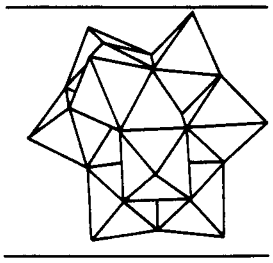
(17) (a) Thouvenot, R.; Fournier, M. Franck, R.; Rocchiccioli-Deltcheff, C. *Inorg. Chem.* **1984**, *23*, 598. (b) Rocchiccioli-Detcheff, C.; Fournier, M.; Franck, R.; Thouvenot, R. *Inorg. Chem.* **1983**, *22*, 207.



β, $C_3\perp$



β, $C_3$ inclined

in the drawing, the $C_3\perp$ orientation for the β polyhedral form allows for H bonding interactions equivalent to those for the $C_3\perp$ orientation of the α isomer. Thus, if $C_3\perp$ was the preferred orientation of α, then the β form should intercalate with equal facility. Since there is a substantial difference in intercalation properties of the α and β form, the $C_3\perp$ orientation for α is precluded.

When oriented with $C_3$ inclined, the β-isomer is capable of mimicking only half the H-bonding interactions encountered for a $C_2\perp$ orientation of α. One face of the POM experiences guest–host interactions equivalent to those found for the $C_3\perp$ orientation of α, but the H-bonding pattern on the opposite face of the POM is completely disrupted (see above). Thus, we conclude that guest–host interactions are important in determining the intercalative reactivity of LDHs toward Keggin-type species under the reaction conditions employed in this work and that the α isomer intercalates with the $C_2\perp$ orientation preferred.

We also have been successful in obtaining 100% yields of pure phases containing lacunary (defect) Keggin species[13] such as $\beta_1$-$[SiW_{11}O_{39}]^{8-}$ and $[PW_9O_{34}]^{9-}$. Basal spacings similar to those for $Zn_2Al$-$[\alpha$-$H_2MO_{12}O_{40}{}^{6-}]$ and $Zn_2Al$-$[\alpha$-$SiV_3W_{12}O_{40}{}^{7-}]$ were observed, indicating that the pillaring reaction is not unique to $XM_{12}O_{40}$ metalate anions with full $T_d$ framework symmetry. $[Zn_2Al(OH)_6]NO_3$ was selected as the host structure in the present work because of its hydrolytic stability at acidic pH. However, we also have formed Keggin ion pillared derivatives with more basic host structures such as the hydrotalcite-like $[Mg_2Al]$ and $[Mg_3Al]$ LDHs.[18] The properties of these and other pillared polyoxometalate derivatives will be the subject of future investigations.

**Acknowledgment.** This research was sponsored by the National Science Foundation (Grant DMR-8514154) and by the MSU Center for Fundamental Materials Research.

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(18) Dimotakis, E. D.; Pinnavaia, T. J., unpublished results.