# Direct Synthesis of a Polyoxometallate-pillared Layered Double Hydroxide by Coprecipitation

**Eiichi Narita,***[a] **Padmananda D. Kaviratna**[b] **and Thomas J. Pinnavaia***[b]

[a] *Department of Chemical and Biological Engineering, Hachinohe National College of Technology, Tamonoki, Hachinohe 039-11, Japan*

[b] *Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, MI 48824, USA*

The coprecipitation reaction of $Zn^{2+}$ and $Al^{3+}$ ions in moderately acidic $\alpha$-$[SiW_{11}O_{39}]^{8-}$ solution directly affords a layered double hydroxide derivative with an approximate composition of $[Zn_{24}Al_8(OH)_{64}][\alpha\text{-}SiW_{11}O_{39}]$ and an exceptionally well-ordered gallery height of 9.8 Å.

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Layered double hydroxides (LDHs) consist of positively charged brucite-like layers separated by charge-balancing hydrated gallery anions.[1–3] A broad range of compositions of the type $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2][A^{n-}]_{x/n}\cdot yH_2O$ ($x$ = 0.17–0.33) are possible, wherein the $M^{2+}$ and $M^{3+}$ metal ions occupy octahedral positions in the hydroxide layers and $A^{n-}$ is an exchangeable gallery anion.[4,5] Recently, several pillared LDH derivatives have been prepared in which $A^{n-}$ is a polyoxometallate (POM). These microporous compounds allow guest molecules to access the intracrystal gallery surfaces. Some of the derivatives exhibit large gallery heights suitable for catalytic oxidation of organic compounds.[6]

Most of the POM-pillared LDHs reported to date have been prepared by ion exchange methods. For instance, well-ordered LDHs that incorporate iso- or hetero-polyoxometallate anions as pillaring agents, such as $V_{10}O_{28}{}^{6-}$ and $\alpha$-1,2,3-$[SiV_3W_9O_{40}]^{7-}$, have been obtained by ion exchange reaction of simple LDH precursors of the type $[Zn_2Al]$–$Cl^-$ and $[Zn_2Al]$–$NO_3$.[7] Ion exchange reactions also have been extended to the synthesis of basic pillared derivatives without competing hydrolysis of the POM anions by the use of organic anion-intercalated precursors.[8] Although ion exchange reactions normally are quite convenient to carry out, they require the synthesis of a suitable LDH precursor. Moreover,

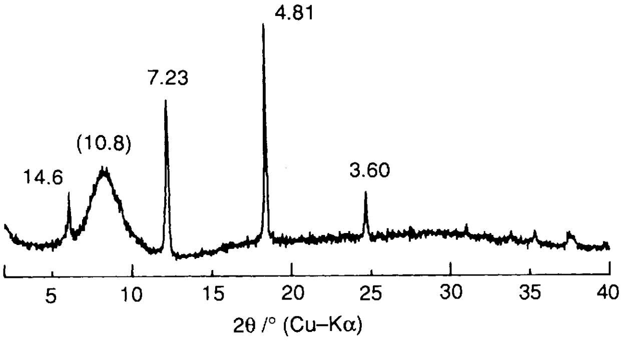

**Fig. 1** X-Ray powder diffraction pattern for oriented film sample of the LDH intercalate, $[(Zn_3Al)]$–$[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ obtained by direct coprecipitation at a POM/Al ratio = 2.0, pH 6, and 100 °C. Values adjacent to the diffraction peaks are *d* spacings in Å for several 001 harmonics. Value in parentheses is for the byproduct assigned to $Zn^{2+}/Al^{3+}$/POM salt.

exchange reactions can be slow, particularly if the exchanging anion is larger than the anion initially occupying the LDH galleries.

A second method for the preparation of POM-pillared LDH derivatives utilizes the reconstitution of mixed metal oxide solid solutions.[9] In this method an LDH–$CO_3^{2-}$ precursor is thermally decomposed to form the oxide solid solution, and then the oxide is reconstituted into a pillared LDH by hydrothermal reaction with the pillaring POM anion. Pillared LDHs containing $V_{10}O_{28}^{6-}$ have been prepared by this method from $[Mg_2Al]$–$CO_3^{2-}$ and $[Zn_2Al]$–$CO_3^{2-}$ parents.[9] Analogous reactions also have been used to prepare pillared forms containing Keggin-like hetero-POM anions with higher gallery heights.[10] However, reconstitution reactions in general require multistep procedures and are even more inefficient than ion exchange.

Accordingly, a more direct method for the preparation of POM-pillared LDH derivatives is desirable. In this work we describe the first direct synthesis of a POM-pillared LDH by coprecipitation reaction of $Zn^{2+}$ and $Al^{3+}$ ions in the presence of a moderately acidic lacunary Keggin ion, $\alpha\text{-}[SiW_{11}O_{39}]^{8-}$.

First, $\alpha\text{-}K_8[SiW_{11}O_{39}]\cdot12H_2O$ (1.2 mmol) was dissolved in 120 ml of decarbonated, deionized water under an argon atmosphere. The pH of the POM solution was adjusted to 6.0 by the addition of 0.2 mol $l^{-1}$ $HNO_3$. Then, 20 ml of a mixed aqueous solution of $Zn(NO_3)_2$ (1.2 mmol) and $Al(NO_3)_3$ (0.60 mmol) was added dropwise to the vigorously stirred POM solution at 100 °C. The pH of the mixture was maintained near 6.0 by simultaneous addition of 0.20 mol $l^{-1}$ NaOH to the POM solution. After reaction for 1 h the solid product was separated by centrifugation, washed thoroughly with deionized water, and dried in air at 90 °C.

As can be seen in Fig. 1, the X-ray powder diffraction pattern of the reaction product contained several 001 harmonics characteristic of a pillared LDH phase with a basal spacing of 14.6 Å, a value in good agreement with previously reported spacings of 14.5 and 14.6 Å for the same compound prepared by ion exchange and reconstitution reaction methods.[10] The basal spacing of 14.6 Å corresponds to a gallery height of 9.9 Å and to an $\alpha\text{-}[SiW_{11}O_{39}]^{8-}$ orientation in which the $C_2$ axis is perpendicular to the host layers. It is noteworthy that the observed X-ray reflections are much sharper than those for the same compound prepared by ion exchange and reconstitution reactions, indicating improved stacking order or scattering domain size along the stacking direction.

The X-ray powder diffraction pattern shown in Fig. 1 also contains a broad reflection at 2θ 6.5–10° due to the formation of a by-product. We tentatively assign the by-product to a quasi crystalline $Zn^{2+}/Al^{3+}$ salt of the POM. This assignment is supported by the fact that reactions of either $Zn(NO_3)_2$ or $Al(NO_3)_3$ with $\alpha\text{-}[SiW_{11}O_{39}]^{8-}$ under analogous conditions afford a precipitate with a diffraction pattern that contains the broad reflection, but not the sharp reflections characteristic of the POM-pillared LDH. The intensity of the byproduct peak could be reduced twofold by increasing the pH of the reaction mixture to a maximum value of 7.5. Decreasing the pH to 5.5 increased the relative amount of byproduct formed. However, over the entire pH range 5.5–7.5, the diffraction pattern for the LDH–POM phase remained sharp. Below pH 5.5, the LDH–POM did not form, while above pH 8.0, only LDH phases interlayered by POM hydrolysis products were formed. Reducing the reaction temperature to 60 °C increased the X-ray scattering intensity of the byproduct and broadened the line widths for the pillared LDH. Varying the POM/Al molar ratio over the range 0.25–2.0 had no effect on the quality of the reaction product, as judged by X-ray diffraction.

**Table 1** Chemical compositions, basal spacing, and $N_2$ BET surface area for LDH reaction products formed by coprecipitation

| Sample | Chemical composition (molar ratio) Zn : Al : W | Basal spacing/Å | Surface area/ $m^2$ $g^{-1}$ |
|---|---|---|---|
| (A) LDH–α-$[SiW_{11}O_{39}]^{8-}$ [b] | 0.77 : 0.23 : 0.27<br>(0.32)[a] | 14.6 | 97 |
| (B) LDH–$NO_3^-$ [b] | 0.69 : 0.31 : 0 | 7.7 | 33 |

[a] Value in parentheses is the theoretical value calculated from the ion-exchange capacity. [b] 100 °C, 0.5 h, pH 6.

The results of elemental analyses and Brunauer–Emmett–Teller (BET) surface area measurements for a typical coprecipitated reaction product are given in Table 1, together with those for non-pillared LDH–$NO_3^-$ formed under analogous reaction conditions. It is significant that the Zn/Al molar ratio for the pillared product incorporated $\alpha\text{-}[SiW_{11}O_{39}]^{8-}$ was about 3, despite the initial Zn/Al molar ratio being 2.0. However, the Zn/Al molar ratio of the non-pillared LDH–$NO_3^-$ was about 2. Thus, a part of the $Al^{3+}$ is not incorporated into the LDH–POM product, and the overall composition of the pillared LDH product is approximately $[Zn_{24}Al_8(OH)_{64}][\alpha\text{-}SiW_{11}O_{39}]$.

The surface area was found to increase from 33 $m^2$ $g^{-1}$ for the non-pillared LDH–$NO_3^-$ to 97 $m^2$ $g^{-1}$ for the pillared LDH–POM. Further evidence for the retention of the lacunary Keggin-ion structure in the intercalated state was provided by IR spectroscopy. The group frequencies [ν(W=O) 950 $cm^{-1}$; ν(Si–O) 907 $cm^{-1}$; ν(W–O–W) 715, 800 $cm^{-1}$) of the $M_3O_{13}$ triads for the intercalated Keggin ion are very similar to those observed for an authentic salt of the POM ion.

Normally, coprecipitation reactions of the type reported here afford amorphous or poorly ordered phases, owing in part to hydrolysis of the POM at basic pH or hydrolysis of the LDH at acidic pH. However, through a judicious choice of $M^{II}$, $M^{III}$ and POM anions coprecipitation of a crystalline LDH–POM intercalate can be achieved over a slightly acidic pH range where most POM anions are stable. The LDH that are stable at acid pH include those containing the more acidic $M^{II}$ and $M^{III}$ layer cations such as $Ni^{2+}$, $Zn^{2+}$, $Al^{3+}$ and $Cr^{3+}$. The formation of a poorly ordered byproduct normally accompanies the formation of pillared LDH. However, the production of byproduct can be minimized by optimizing the pH and temperature of the reaction and by mixing a suitable organic solvent. More importantly, the advantages of rapidly preparing large quantities of material for catalytic applications by direct coprecipitation far outweight the lower yields arising from byproduct formation.

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