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Synthesis of Heteropolyoxometalate Pillared Layered Double Hydroxides via Calcined Zinc-Aluminium Oxide Precursors

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An amorphous zinc-aluminium oxide solid solution, $Zn_{0.67}Al_{0.33}O_{1.17}$, prepared by the thermal decomposition of the acidic layered double hydroxide (LDH), $[Zn_{0.67}\cdot Al_{0.33}(OH)_2](CO_3)_{0.17}\cdot 0.33H_2O$, was found to react with Keggin-like heteropolyoxometalate anions such as α-$[Si\cdot W_{11}O_{39}]^{8-}$ and α-1,2,3-$[SiV_3W_9O_{40}]^{7-}$ in acid solution to form pillared LDH structures with gallery heights of 9.9 Å.

Layered double hydroxides consist of 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) (Abbreviated as $[M^{2+}{}_{(1-x)/x}M^{3+}]$-$A^{n-}$), wherein the M^{2+} and M^{3+} metal ions occupy octahedral positions in the hydroxide layers and A^{n-} is the gallery anion.[1–4)] Ordinarily, the intracrystal basal surfaces are inaccessible to molecules larger than water owing to the low gallery heights of these intercalates. Recently, pillared LDH derivatives interlayered by polyoxometalate anions have been prepared in which A^{n-} is sufficiently robust and laterally spaced to provide intracrystalline access to organic adsorbates.[5–8)] The first pillared derivatives were synthesized by ion exchange with $[Zn_2Al]$-Cl^-, $[Zn_2Cr]$-Cl^- and $[Ni_2Al]$-Cl^- LDH precursors.[5)] The use of ion exchange reactions as a route to pillared LDH derivatives, however, is limited to these more acidic LDH precursors. Reactions of basic $[Mg_3Al]$-Cl^- and $[Mg_4\cdot Al]$-NO_3^- LDHs with polyoxometalate (POM) anions generally lead to the hydrolysis of POM. However, the hydrolysis can be reduced by pre-exchange of the inorganic anion with organic anion precursors such as *p*-toluenesulfonate and terephthalate.[7a)]

Although ion exchange reactions normally are quite convenient to carry out, they can be slow, particularly if the exchanging anion is larger than

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the initial LDH gallery height. Expanding the LDH galleries by intercalation of a water-soluble swelling agent can facilitate the exchange process, but such swelling is limited to derivatives intercalated by hydroxide.7b) Thus, there is a need to develop alternative routes to POM-pillared LDH derivatives, particularly those in which the LDH host layers are intrinsically acidic such as hydroxides of Mn^{2+}, Ni^{2+}, or Zn^{2+}.

Hydrotalcite-like $[Mg_{1-x}Al_x]$-CO_3^{2-} LDHs are known to decompose to magnesium-aluminium oxide solid solution by heating to 400–800 °C. The resulting oxides readily rehydrate and adsorb anions to reconstruct the original LDHs. This reconstitution reaction has been used to prepare $[Mg_{1-x}\cdot Al_x]$-LDH forms intercalated by both inorganic8,9) and organic anions,10,11) but its utility toward other LDH derivatives is unexplored. Here we describe the thermal decomposition of an acidic $[Zn_2Al]$-CO_3^{2-} LDH to form a Zn/Al oxide solid solution and the subsequent reconstitution reactions of the oxide to LDHs pillared by α-$[SiW_{11}O_{39}]^{8-}$ and α-1,2,3-$[SiV_3W_9O_{40}]^{7-}$.

The parent LDH, $[Zn_{0.67}Al_{0.33}(OH)_2](CO_3)_{0.17}\cdot 0.33H_2O$, was formed by coprecipitation reaction of Zn^{2+}, Al^{3+},and CO_3^{2-} at pH 6.2.12) The LDH was then calcined in air at 500±2 °C for 3 h to form a mixed oxide. Restructuring of the oxide into a POM-pillared LDH derivative was accomplished by adding the calcined product in small portions to a 10 mmol dm^{-3} POM solution with vigorous stirring at a POM/Al mole ratio of 1.0. The dropwise addition of 0.2 mol dm^{-3} HNO_3 maintained the pH at the desired value and prevented POM hydrolysis. Upon the addition of the oxide, the mixture was allowed to stir for 0.5 h. All reactions were carried out under argon to avoid possible reaction of the calcined oxide with atmospheric CO_2. The final products were washed with water and dried in air at 90 °C.

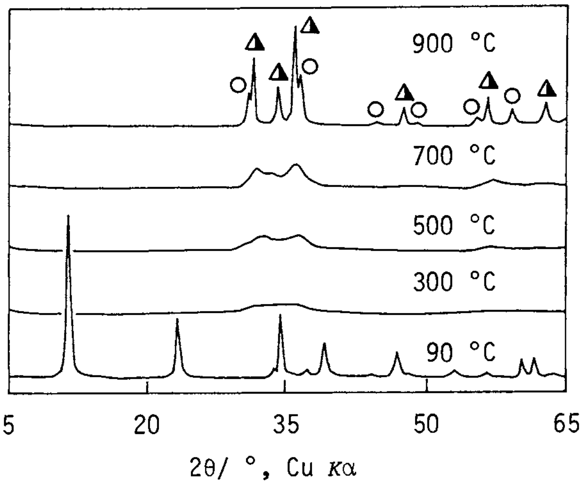

Fig. 1. XRD patterns for $[Zn_{0.67}Al_{0.33}\cdot(OH)_2](CO_3)_{0.17}\cdot 0.33H_2O$ (bottom) and for the products formed by calcining the LDH. O: Gahnite($ZnO\cdot Al_2O_3$), ▲: Zincite(ZnO).

According to TG-DTA analysis of the parent LDH, weight loss occurred in two stages. The loss below 220 °C corresponded to the loss of $0.33H_2O$ per metal ion. The loss between 220–500 °C corresponded to concomitant decomposition of carbonate and partial dehydroxylation. These latter reactions occur at a substantially lower temperature than for basic $[Mg_{1-x}Al_x]$-CO_3^{2-} derivatives.12) The more facile carbonate decomposition for the $[Zn_2Al]$-LDH reflects an increase in acidic character upon replacing Mg^{2+} by Zn^{2+}.

Figure 1 illustrates the changes in XRD patterns that occurred upon the thermal decomposition of the $[Zn_2 \cdot Al]-CO_3^{2-}$ LDH. At 90 °C, the LDH structure still exhibited several orders of 001 reflections. However, a very diffuse pattern corresponding to a zinc-aluminium solid solution was observed at 300 °C. The pattern remained diffuse until recrystallization to a mixture of gahnite ($ZnO \cdot Al_2O_3$) and zincite (ZnO) occurred at 900 °C. Significantly, when the oxide formed at 200–500 °C were dispersed in aqueous Na_2CO_3 for 3 h, they reformed the initial LDH phase. The mixed gahnite/zincite product obtained at 900 °C, however, did not reconstruct into an LDH.

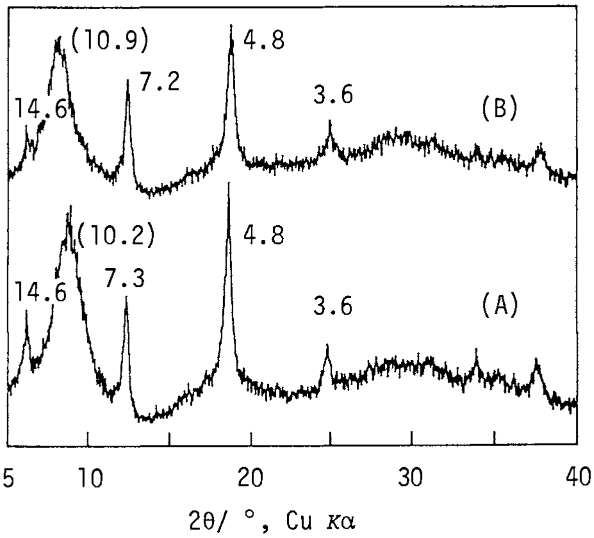

Fig. 2. XRD patterns for oriented film samples of the LDH intercalates: (A) $[Zn_2 \cdot Al]-[\alpha\text{-}SiW_{11}O_{39}]^{8-}$, (B) $[Zn_2Al]-[\alpha\text{-}1,2,3\text{-}SiV_3W_9O_{40}]^{7-}$. Values adjacent to the diffraction peaks are *d* spacing in angstroms. Values in parenthesis are for by-products assigned to mixed Zn^{2+}/Al^{3+} POM salts.

The addition of the zinc-aluminium oxide solid solution (500 °C), to a boiling solution of $\alpha\text{-}[SiW_{11}O_{39}]^{8-}$ at pH 6 resulted in the formation of an LDH phase that incorporated the POM as a pillaring agent. The XRD pattern of the white product, Fig. 2A, contained several 001 harmonics. The 14.6 Å basal spacing was identical to the same product prepared by ion exchange.[6)] An additional broad reflection was observed between 7.5–11° 2θ due to a by-product which we attribute on the basis of reference experiments to a mixture of quasicrystalline Zn^{2+} and Al^{3+} salts of the POM. Analogous chemistry was observed for the reaction of the oxide with $\alpha\text{-}1,2,3\text{-}[SiV_3W_9O_{40}]^{7-}$

Table 1. Pillared $[Zn_2Al]$-LDH products

Sample	Guest POM	Chemical composition (Molar ratio) Zn	: Al	: V	: W	B.E.T. surface area $m^2\ g^{-1}$
A	$\alpha\text{-}[SiW_{11}O_{39}]^{8-}$	0.63	: 0.37	: 0	: 0.42	98
				(0)[a)]	(0.50)	
B	$\alpha\text{-}[SiV_3W_9O_{40}]^{7-}$	0.67	: 0.33	: 0.13	: 0.41	113
				(0.14)	(0.42)	

a) Theoretical values calculated from ion-exchange capacity.

at pH 3 (*cf.* Fig. 2B).

Elemental analyses and B.E.T. surface area measurements are given in Table 1. A substantial increase in surface area was introduced by the pillaring process. Further evidence for the retention of the POM structure in the intercalated state was provided by IR spectra. As shown in Fig. 3, the group frequencies of the M_3O_{13} triads for the intercalated Keggin ion are very similar to those observed for an authentic salt of POM ions.[13]

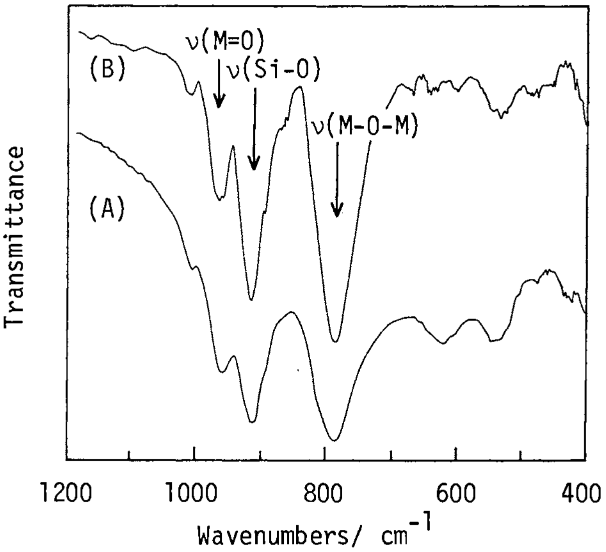

Fig. 3. IR spectra showing the intratriad group frequencies for the $[SiV_3W_9O_{40}]^{7-}$ anion as (A) the $[Zn_2Al]$-LDH intercalate and (B) the potassium/hydronium salt.

In summary, polyoxometalate derivatives of acidic LDHs can be conveniently prepared by reconstruction of the corresponding mixed metal oxide solid solution in the presence of the POM anion. This result, together with earlier studies of the synthesis of basic $[Mg_{1-x}Al_x]$-LDH derivatives,[8] indicate that the reconstruction reaction of a mixed metal oxide solid solution is a *general* route to both acidic and basic LDH derivatives pillared by POM anions. However, the acidic pillared products tend to be better ordered than the basic pillared derivatives, as judged from XRD linewidths.

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