Synthesis of new types of polyoxometallate pillared anionic clays: ^{31}P and ^{27}Al MAS NMR study of the orientation of intercalated $PW_{11}VO_{40}{}^{4-}$

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A series of different new types of polyoxometallate pillared anionic clays are synthesized by ion-exchange reactions and characterized by elemental analysis, powder X-ray diffraction and IR spectroscopy; the observation of two ^{31}P MAS NMR peaks for $ZnAl$-$PW_{11}VO_{40}$ provides experimental evidence for the orientation of the intercalated polyoxometallates with the C_2 axis predicted to be orthogonal to the layers.

Layered anionic clays are a class of layered materials of current interest because of their wide application in catalysis.[1] Heteropoly acids which are strong protonic acids have also been thoroughly studied and are being used as technical catalysts.[2] However, for heteropoly acid catalysts, apolar molecules react only at surface sites, which leads to poor activity and low BET surface areas.[3] It would thus be very interesting to intercalate polyoxoanions into clays and prepare a new type of microporous material.[4] Although the phenomenon of intercalation of polyoxometallates (POMs) has been established and several routes have been used for the synthesis of pillared materials,[5,6] only few POMs have been inserted and the orientation of the intercalated anions has not yet been studied in detail.[7] Here we communicate our studies on the intercalation of new types of POMs such as trimetalloderivatives of 9-tungstosilicate and heteropolytungstate containing lanthanide elements and initial ^{31}P and ^{27}Al MAS NMR studies of $ZnAl$-$PW_{11}VO_{40}$, to determine the orientation of the polyoxoanions.

The host clay $ZnAl$-NO_3 was prepared by our own procedure.† Potassium salts of $PW_{11}VO_{40}{}^{4-}$,[8] $XW_{11}O_{39}Z$-$(H_2O)^{n-}$ (X = Si, B; Z = Co, Ni, Cu, Al),[9] SiW_9O_{37}-$Z_3(H_2O)^{10-}$ (Z = Co, Cu),[10] $Ln(XW_{11}O_{39})_2{}^{n-}$ (Ln = La, Ce^{III}; X = Si, P, B),[11] were synthesized according to literature methods. POM intercalated clays were prepared by ion-exchange reactions. A typical procedure is as follows. Under an N_2 atmosphere, an aqueous solution of a POM K^+ salt (*ca.* 9.0 g in 30 ml distilled water) was added to a stirred suspension of $ZnAl$-NO_3 (3.0 g) in 20 ml decarbonated, distilled water at 90 °C; the resulting suspension was left to stir under these conditions for 10–15 h and then the product was separated by centrifugation, washed with hot water several times and finally the crystalline product was dried at 120 °C for 10 h.

Intercalation was confirmed by powder X-ray diffraction, FT IR spectroscopy and elemental analysis. Fig. 1 shows the X-ray patterns of some representive products, which illustrate the formation of crystalline intercalated clays. It is noteworthy that for $PW_{11}VO_{40}{}^{4-}$ (whose intercalation is theoretically feasible but had previously not been experimentally realised[7]) the XRD pattern [Fig. 1(*b*)] shows clearly the formation of the desired product in a pure state.[6] The calculated gallery heights are in agreement with the diameter of Keggin type POMs (assuming the thickness of the brucite layer is 4.7 Å).[12]

The orientation of the intercalated Keggin type hetero-POMs has been predicted according to the degree of hydrogen-bonding between the sheet and hetero-POMs.[6] To our knowledge, this prediction has not yet been validated by experimental evidence. For some intercalated moieties, full structural refinement has been achieved by XRD, with different orientations possibly

resulting in layers of different heights,[13] although XRD patterns may be uninformative in differentiating orientations of nearly spherical Keggin type POMs. MAS NMR is a useful tool to probe the orientations of POMs supported on silica,[14] and pillaring cation species.[15] We therefore carried out ^{31}P and ^{27}Al MAS NMR studies of the $PW_{11}VO_{40}{}^{4-}$ intercalated clays. For ^{31}P measurements, a small flip angle (15°) and a long delay between scans (100 s) was chosen to allow observation of quantitative spectra;[14] the results clearly gave the first sound evidence for the predicted orientation. Fig. 2 shows that despite the fact that $PW_{11}VO_{40}{}^{4-}$ replaces $NO_3{}^-$, the ^{27}Al peak ($AlCl_3$ internal reference) remains unaltered. This fact indicates that Al in the sheet still retains its original coordination environment. The ^{31}P MAS NMR (H_3PO_4 internal reference), of pure α-
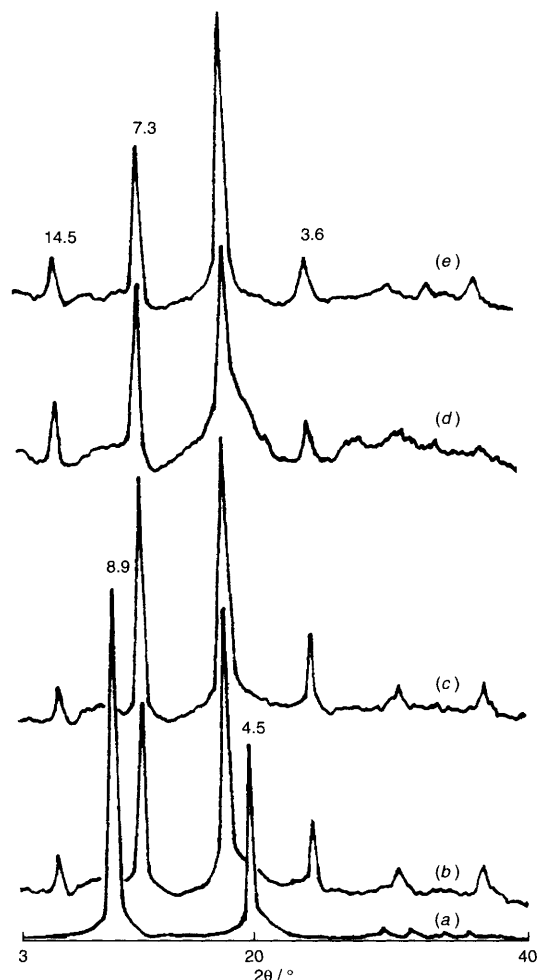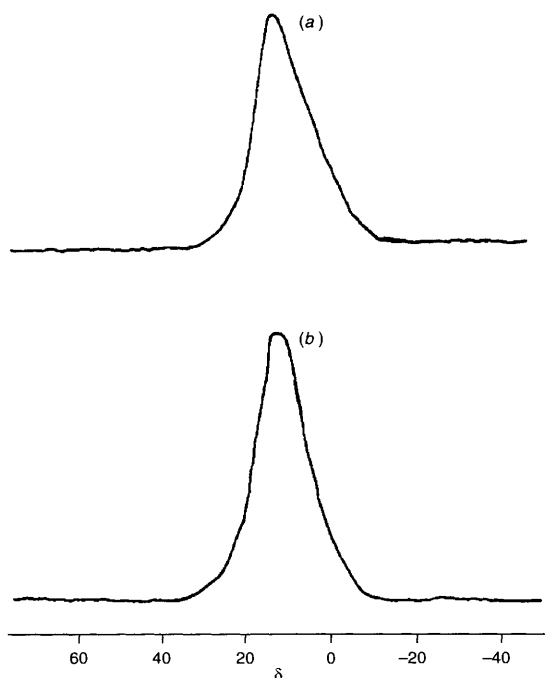

Fig. 1 Powder X-ray diffraction patterns (Cu-Kα) for representive products with spacings labelled in Å: (*a*) $ZnAl$-NO_3, (*b*) $ZnAl$-$PW_{11}VO_{40}$, (*c*) $ZnAl$-$SiW_{11}O_{39}Co(H_2O)$, (*d*) $ZnAl$-$SiW_9O_{37}Co_3(H_2O)_3$ and (*e*) $ZnAl$-$Ce^{III}(SiW_{11}O_{39})_2$

Fig. 2 ^{27}Al MAS NMR spectra (104.214 MHz) of (a) ZnAl–NO3 and (b) ZnAl–PW11VO40. Experimental conditions: spining rate 4 kHz; 512 scans with 2.5 s recycle time; 11 μs 90 ° pulse; 2.0 s delay before acquisition.
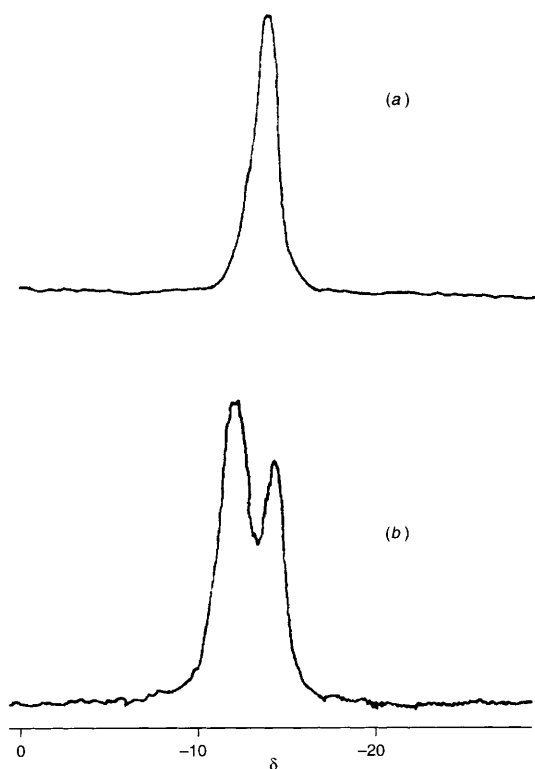
Fig. 3 ^{31}P MAS NMR spectra (161.903 MHz) of (a) $PW_{11}VO_{40}{}^{4-}$ and (b) ZnAl–PW11VO40. Experimental conditions: spining rate 4 kHz; 2000 scans with 100 s recycle time; 12 μs 90 ° pulse, 100 s delay before acquisition.

$PW_{11}VO_{40}{}^{4-}$ shows one peak at δ −12.170 [Fig. 3(a)] while the intercalated polyanion [Fig. 3(b)] shows two peaks (δ −11.876 and −14.031) with a relative area ratio of 2:1. For substituted Keggin type $PW_{11}VO_{40}{}^{4-}$ species, the 12 octahedra around the central P are not identical. If in the intercalated polyanion the C_2 axis is perpendicular to the sheet, there are two
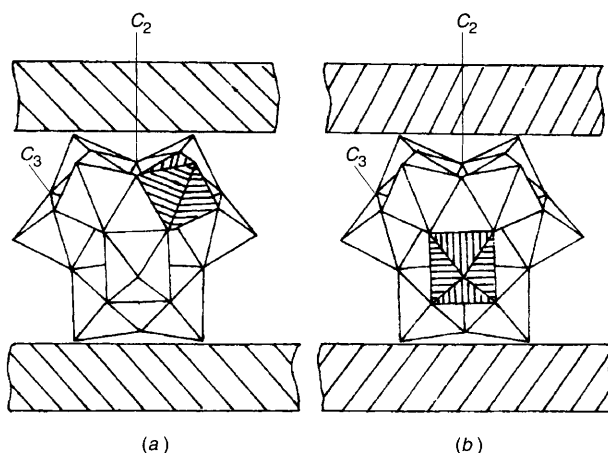
Fig. 4 Differentiation of VO6 octahedra in intercalated $PW_{11}VO_{40}{}^{4-}$; (a) near sheet and (b) in layer

different sites {near the sheet [Fig. 4(a)] or in the layer [Fig. 4(b)]} which the VO6 octahedra can adopt leading to the different ^{31}P chemical shifts whose relative areas should correspond to the ratio of the probability of the two types of V (2:1) in accord with the experimental result. If on the other hand the α-$PW_{11}VO_{40}{}^{4-}$ adopts a C_3 axis orientation, the probability ratio of V near the sheet and in the layer is 1:1, and can thus be discounted. So we can determine unambiguously that for $PW_{11}VO_{40}{}^{4-}$ the C_2 axis is orthogonal to the sheet. Further study on orientational preference of other pillared hetero-POMs can be carried out accordingly.

Footnote

† Zn(NO3)2·6H2O (30 g) and Al(NO3)3·9H2O (20 g) were added to 300 ml of decarbonated, distilled water. Under N2 a 15% NaOH solution was added dropwise to the vigorously stirred solution until the pH of the mixture was 9.0–9.5. The white product was separated and washed. Distilled water was then added and stirring produced a white slurry, which was digested for 10–15 h at 90–100 °C. Finally the product was separated and dried *in vacuo*.

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