Formation of Chromium Interlayers in α-Zirconium Phosphate

Dugald J. MacLachlan* and David M. Bibby
Department of Chemistry, Victoria University of Wellington, Wellington, New Zealand

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Interlayered materials with basal spacings 15—26 Å, obtained when the half-sodium-exchanged form of α-zirconium bis(hydrogenphosphate) is refluxed with solutions of chromium(III) acetate, have been studied by thermal analysis, *X*-ray powder diffraction, electron microscopy, e.s.r. and i.r. spectroscopy; surface areas were also determined. The reaction causes expansion of the interlayer spacing, to a degree depending on the initial chromium content of the solution and the temperature. The results are interpreted in terms of the formation of a hydrous chromium acetate interlayer species which decomposes on heating between 300 and 400 °C. The surface area of the α-zirconium phosphate does not change appreciably on reaction with chromium(III) acetate indicating that interlayer crowding effects play a dominant role.

When thermally stable species are introduced between the layers of two-dimensional solids, materials with microporous cavities may be formed. Because of their size, these introduced species act as pillars, and prop the layers apart. If the distance between pillars is sufficiently large, permanent interlayer pore spaces are created. The pore space can be 'fine-tuned' by altering the pillar size and number.

Using this strategy it should be possible to design new porous materials incorporating a range of desired features. This approach has been used to advantage previously with the smectite family of clays where a wide range of molecular sorbents and catalysts has been synthesised.[1] Pillaring agents that have been employed include alkylammonium cations,[2] metal chelates,[3] and polyoxymetal cations.[4]

For any of these to be useful as sorbents or catalysts they must be stable. The low thermal stability of most materials pillared by organic cations precludes their use in many catalytic processes. Interest in the area of catalysis has therefore centred on inorganically pillared materials. Examples of these are the alumina[4a] and zirconia[4f] intercalated smectites which have been shown to act as petroleum cracking catalysts, with shape selectivities similar to those of commercial zeolites.[5]

α-Zirconium phosphate is a layered compound, with chemical properties similar to those of the smectite clays.[6] This material, and its transition-metal exchanged forms, was recently shown[7] to be catalytically active. The small intracrystalline pore sizes of α-zirconium phosphates restrict access to the interlayer region for most reagents. In order to increase the available surface area it is desirable to prop the layers apart.

Organically pillared α-zirconium phosphates have been synthesised.[8] While the sorption properties of these materials are promising, their application in many catalytic processes has been limited because of low thermal stabilities. Inorganic pillars include metal complexes of bipyridyl and phenanthroline.[9,10] Large silica pillars have been introduced into α-zirconium phosphate[11] by intercalating polysesquioxides of silicon which are then thermally decomposed *'in situ'*.

Polynuclear hydroxochromium interlayers have been formed in the interlayer spaces of smectite clays and shown to produce interesting levels of porosity and catalytic activity.[12] Because of the interesting properties of that material we have prepared and studied the properties of such interlayers in α-zirconium phosphate.

The exchange of Cr^{3+} into the half-sodium-exchanged form of α-zirconium phosphate using chromium(III) nitrate solutions has been studied previously by Alberti *et al.*[13] If mild conditions are used the process is one of simple ion exchange giving rise to a small increase in the interlayer distance to 11.6 Å for the maximum exchange phases. The use of chromium(III) acetate for the exchange reaction with α-zirconium phosphate and the production of poly(hydroxochromium acetate) interlayers is the subject of the present study.

Experimental

Materials.—The $ZrOCl_2 \cdot 8H_2O$ and chromium(III) acetate were supplied by BDH, the orthophosphoric acid from May and Baker. A zirconium phosphate gel was prepared by precipitation from a solution of zirconyl chloride with dilute phosphoric acid. Microcrystals of α-zirconium phosphate were formed by refluxing the gel in 12 mol dm^{-3} phosphoric acid for 336 h according to the procedure of Clearfield *et al.*[14] The half-sodium-exchanged form α-$[Zr(PO_4)_2]HNa \cdot 5H_2O$ was prepared as described previously[15] and was stored over a saturated solution of NaCl relative humidity 75%.

Intercalation Reaction.—Hydroxochromium(III) acetate-expanded α-zirconium phosphate was prepared by refluxing 2 g of the half-sodium-exchanged form of α-zirconium phosphate with chromium(III) acetate solutions. Exchange reactions carried out at 25 °C result in the formation of mixed-phase systems with lower basal spacings than those of reactions carried out under reflux.

The effect of varying the concentration of the chromium(III) acetate solutions was studied between 0.007 and 0.5 mol dm^{-3} representing a range of 1—80 mmol of chromium(III) acetate per gram of exchanger. The materials were separated and washed by centrifugation. *X*-Ray diffractograms were taken of wet and air-dried products and also of samples prepared on a glass slide and heated to different temperatures up to 500 °C.

The products were also studied using thermogravimetric analysis (t.g.a.) and thermal desorption-mass spectrometry (t.d.-m.s.). Surface areas were obtained for samples heated to different temperatures. Infrared spectra were recorded for selected samples. The samples were also examined using scanning electron microscopy (s.e.m.) and transmission electron microscopy (t.e.m.).

Analysis Procedure and Apparatus.—Chromium, phosphorus, and zirconium contents were determined by *X*-ray fluorescence (x.r.f.) on materials heated to 900 °C. Analysis of solution supernatants for phosphorus was by the molybdate blue method.[16] Carbon contents were determined by microanalysis. T.g.a. analyses were performed with a thermogravimetric microbalance at a heating rate of 10 °C min^{-1} in a flow of air. Surface areas were measured with a Quantachrome Corporation

Table 1. Sample compositions calculated from x.r.f. analysis (samples calcined at 900 °C)

Sample	mmol chromium(III) acetate per g of exchanger	% ZrO_2	% P_2O_5	% Cr_2O_3	Total	Acetate/Cr ratio[a]
1	0	37.2	41.3	—	[b]	—
2	1	35.4	40.6	23.6	99.6	0.0
3	2.5	30.8	35.4	33.3	99.5	0.2
4	5	28.9	33.3	35.6	97.8	0.3
5	10	29.0	33.5	37.2	99.7	0.4
6	20	28.7	32.4	36.3	97.4	0.4
7	40	29.5	33.6	35.1	98.2	0.5
8	80	33.3	37.5	29.6	100.4	0.6

[a] Calculated using combined microanalysis and x.r.f. results. [b] The half-sodium-exchanged form contains 21.0% Na_2O.

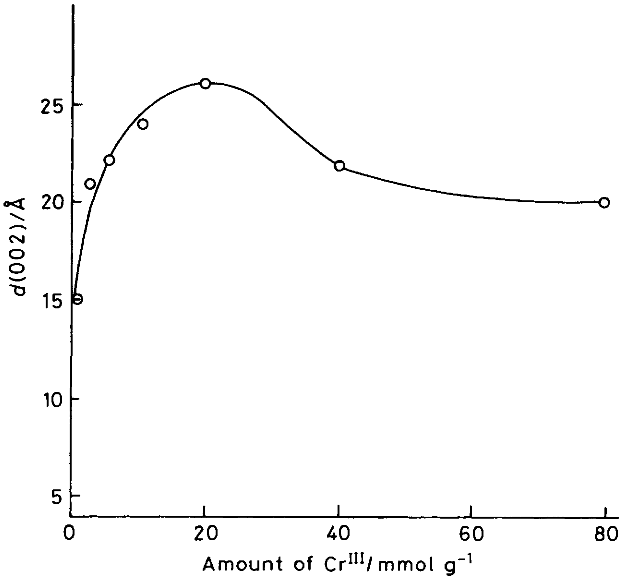

Figure 1. Curve showing the d_{002} spacing of α-$[Zr(PO_4)_2]NaH{\cdot}5H_2O$ treated with various amounts of chromium(III) acetate

Quantasorb surface area analyser, using the multipoint Brunauer–Emmett–Teller method.[17] The experimental system for obtaining t.d.-m.s. has been described elsewhere.[18] A heating rate of 5 °C min^{-1} and an argon atmosphere were utilised. The *X*-ray diffraction (x.r.d.) patterns were obtained with a Philips diffractometer using Cu-K_α radiation and a graphite monochromator. *X*-Band e.s.r. spectra of air-dried samples were obtained at room temperature on a Varian spectrometer operating at a microwave frequency of 9.7 GHz. I.r. spectra were recorded on a Perkin-Elmer 599B spectrometer as KBr disks. Diffuse reflectance spectra were obtained using a Unicam SP700 spectrometer with magnesium carbonate in the reference beam. The products were examined for homogeneity and morphology using both a Philips SEM505 scanning electron microscope and a Philips EM420ST transmission electron microscope.

Results

For brevity the ionic forms of α-zirconium phosphate will be indicated using the formalism of Alberti and Costantino,[19] whereby their ionic composition is indicated under a bar followed by their water content. Their interlayer distance will be reported in parentheses. Thus $[Zr(PO_4)_2]H_2{\cdot}H_2O$ and $[Zr(PO_4)_2]NaH{\cdot}5H_2O$ will be written as $\overline{HH}{\cdot}H_2O$ (7.6 Å) and $\overline{NaH}{\cdot}5H_2O$ (11.8 Å) respectively.

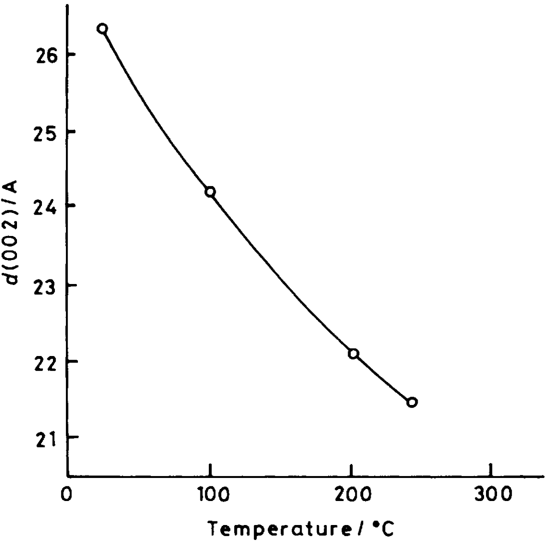

Figure 2. Curve showing the d_{002} spacing of sample 6 heated at various temperatures (by 300 °C the sample has become amorphous)

Refluxing chromium(III) acetate solutions with $\overline{NaH}{\cdot}5H_2O$ resulted in exchanged forms with expanded interlayer spacings. Seven samples were prepared from chromium(III) acetate solutions of different concentrations and are numbered as shown in the Table. The chromium content in the samples increases with the initial chromium(III) acetate concentration until a maximum is reached with sample 5, thereafter decreasing with increasing chromium(III) acetate concentration.

The basal spacings for the different concentrations of chromium(III) acetate are shown in Figure 1, and reach a maximum of ≈26 Å at around 20 mmol chromium(III) acetate per gram of exchanger, decreasing to ≈20 Å as the chromium(III) acetate concentration increased to 80 mmol per gram of exchanger. The reflections from the basal planes are broad and there is little evidence of higher-order reflections suggesting that these materials are disordered but not amorphous.

The variation of basal spacing with temperature for 20 mmol chromium(III) acetate per gram of exchanger, sample 6, is plotted in Figure 2. Heating to 100 °C causes the ≈26 Å basal spacing of the air-dried material to collapse to ≈24 Å. This change is probably associated with the loss of water. An interlayer distance of ≈21 Å is reached by 240 °C but by 300 °C no reflections due to basal planes or other diffraction maxima are observed. The exchanger has then become amorphous and, when heated in the atmosphere, is coated by a black carbon deposit. A new but as yet unidentified phase crystallises by 1 000 °C. The 20 mmol chromium(III) acetate per gram of

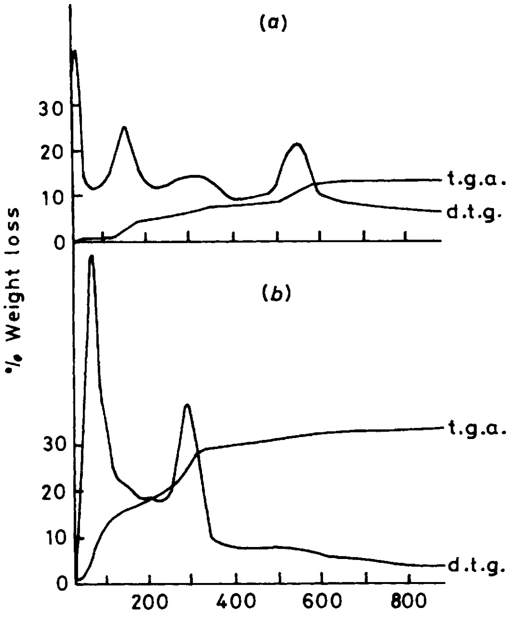

Figure 3. T.g.a. and d.t.g. curves for (*a*) sample 6 and (*b*) α-$Zr(HPO_4)_2 \cdot H_2O$ carried out with a heating rate of 10 °C min^{-1} in an atmosphere of air

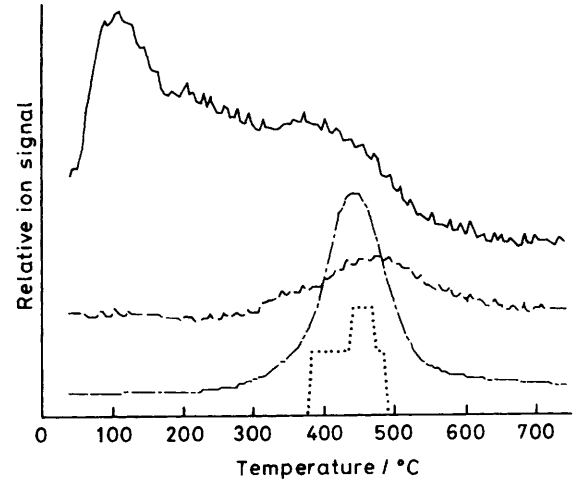

Figure 4. T.d.-m.s. curve of sample 6 carried out with a heating rate of 5 °C min^{-1} and a constant flow of argon. Ions (scaling factor in parentheses): *m/z* 18 (7 000) (——), 28 (2 000) (– – –), 44 (2 000) (— - - —), and 58 (100) (· · ·)

exchanger, sample 6, is used to illustrate the t.g.a. and t.d.-m.s. measurements and is representative of all the samples.

The most significant feature of the t.g.a. for sample 6 (Figure 3) is the loss of interlayer water or water associated with the exchanged species which occurs from room temperature until about 100 °C. Following this is a weight loss centred around 300 °C. A mass loss resulting from condensation of the phosphate groups which would be expected to occur between 500 and 700 °C is not observed.

The t.g.a. of the hydrogen form of the exchanger, $\overline{\mathrm{HH}} \cdot H_2O$ (7.6 Å), is shown for comparison in Figure 3. The main processes observed in this case are the loss of zeolitic water, which occurs on heating to 150 °C, followed by a further water loss which continues to 300 °C. The condensation of the phosphate groups to form a pyrophosphate occurs around 550 °C.

The mass peaks observed in the t.d.-m.s. of sample 6, Figure 4, indicate that the series of weight losses observed by t.g.a. are associated with *m/z* 18, arising from H_2O, centred on 100, 200, and 430 °C. These are tentatively ascribed to water losses due to (1) loosely bound water, (2) water associated with the layer lattice or involved in hydration of the chromium species, and (3) water from pyrolysis of the acetate anions. The loss at 430 °C was also associated with peaks due to *m/z* 28 (CO), 44 (CO_2), and 58 [$(CH_3)_2C{=}O$], confirming decomposition of the acetate anions. The differences in observed temperatures for weight losses in the t.g.a. and t.d.-m.s. curves are due to the differences in the heating rate, atmospheric pressure, and atmospheres employed.

The surface areas of the samples heated to 350 °C under vacuum are ≈ 70 m^2 g^{-1}, while that of $\overline{\mathrm{HH}} \cdot H_2O$ is ≈ 10 m^2 g^{-1}.

When examined by s.e.m. and t.e.m. the samples appear to be homogeneous, with the same morphology as the starting material.

In the i.r. spectra, apart from bands associated with the starting zirconium phosphate, new absorbances due to the acetate groups around 1 600 cm^{-1} are observed.

The e.s.r. spectra of all the samples consisted of a broad resonance at $g = 1.98$, while in the diffuse reflectance spectra bands were observed at 23 500 and 16 500 cm^{-1}, consistent with octahedrally co-ordinated chromium(III) ions.

Discussion

The Exchange Reaction.—The new exchanged materials obtained in this study have poor crystallinity, with reflections other than those from the basal planes either absent or of extremely low intensity, therefore hydrolysis of the zirconium phosphate layers must be considered. However, the analysis of the supernatant liquids shows only minor amounts of phosphorus, $<2\%$ of the total, suggesting that significant hydrolysis did not occur. This was supported by the absence of any Zr–OH absorbance in the i.r. around 3 700 cm^{-1},[20] and by the chemical analyses, which all exhibit phosphorus to zirconium ratios of two. When solutions of chromium(III) nitrate and sodium acetate of various compositions and with pH values encompassing those used in the present study are refluxed with $\overline{\mathrm{NaH}} \cdot 5H_2O$ (11.8 Å), well ordered phases based on simple ion-exchange reactions are observed. It is unlikely then that extensive hydrolysis of the layers followed by precipitation of a chromium(III) phosphate phase occurs. The reaction is more likely to be a complicated exchange process.

It has recently been shown[21] that under favourable conditions n-propylamine intercalates of α-zirconium phosphate undergo infinite swelling producing semi-amorphous gels. The poor crystallinity observed in the present study could in part be explained by a disordered stacking of the zirconium phosphate layers similar to that observed for these n-propylamine intercalates.

Interlayer Species.—The chromium is present as octahedrally co-ordinated chromium(III) as indicated by diffuse reflectance and e.s.r. spectroscopy. From the carbon content together with the t.d.-m.s. and i.r. data it is apparent that acetate ligands are involved in the interlayer complex. The ratio Cr/O_2CMe and the i.r. data do not support intercalation of the starting chromium(III) acetate. The exchange reaction must therefore be of a complex hydrolysis/condensation product of the chromium(III) acetate salt solution. The hydrolytic behaviour of chromium(III) salt solutions has been extensively studied.[22,23] For chromium(III) nitrate and chloride solutions at pH less than

2, the predominant chromium species are monomeric. As the pH is raised, or the solution refluxed, soluble polymeric species of increasing molecular weight are formed. This behaviour continues with increasing pH and temperature until precipitation of a chromium(III) hydroxide or hydroxide oxide occurs. The exact composition of the hydrolytic solution is very pH dependent. For chromium(III) acetate solutions the hydrolysis sequence is further complicated as acetate ligands can be involved in the polymeric products. Studies[24] of chromium(III) chloride solutions to which sodium acetate is added show that trimeric chromium(III) hydroxide acetates are formed. On addition of base, or on reflux, acetate ligands can be replaced by hydroxo groups and condensation of the trimers occurs to form hexamers as well as higher polymers.

While in the present study the nature of the chromium species in the solutions of chromium(III) acetate after reflux is not known, it is reasonable to expect that condensation reactions of the types described for the monomeric and trimeric chromium species occur. These condensation reactions would take place with a corresponding reduction in the ratio of acetate ligands to chromium atoms. The acetate to chromium ratios observed in the exchanged samples range from 0 to 0.6.

It would be unusual for a large polymer to be exchanged directly from solution as the interlayer spacings of $\overline{\mathrm{NaH}}\cdot5H_2O$ and $\overline{\mathrm{Cr}_{0.5}\mathrm{H}_{0.5}}\cdot4H_2O$ are 11.8 and 11.6 Å respectively. A more likely occurrence is that the polymeric chromium species is formed *'in situ'*. The reorganisation involved for *'in situ'* polymer growth and the effect of refluxing probably combine to produce the structural disorder observed by x.r.d. studies and the changes in basal spacings observed as the solution concentration changes. The size of the polymer depends on the concentration of the starting solution, as illustrated by Figure 1, and probably reflects the buffering properties, and degree of participation in the complex, of the acetate ligands.

Thermal Stability.—The t.g.a. for sample 6 shows that a loss of weakly bound water from the interlayer occurs at 100 °C. This is followed by decomposition of the interlayer chromium species which is centred around 300 °C. The t.d.–m.s. confirms this, showing that pyrolysis of acetate ligands occurs in the region of this weight loss as evidenced by the appearance of *m/z* 58 $[(CH_3)_2C{=}O]$ which is a major decomposition product of acetates. Presumably at this stage of the thermal degradation a chromium oxide, probably Cr_2O_3, is formed. The loss of water and decomposition of acetate on heating is not accompanied by an increase in surface area as measured by nitrogen absorption. It appears that in these samples the distance between chromium species formed on decomposition of the interlayer species is too small to give rise to an associated increase in surface area.

A comparison of the chromium interlayered α-zirconium phosphates obtained in this study can be made with chromium interlayered in smectite clays. When chromium(III) nitrate solutions are hydrolysed using sodium hydroxide as the base,[25] and OH^-/Cr^{3+} ratios of 2, smectite clay intercalates with basal spacings of 16.8 Å are formed. This represents a layer separation of 7.2 Å and the intercalate is stable up to 200 °C before collapse. The interlayer species here is probably very similar to that obtained with dilute chromium(III) acetate solutions which give rise to a 15.8-Å phase with α-zirconium phosphate and a layer separation of approximately 6.8 Å. In dilute solutions it is conceivable that the acetate ions exert little influence on the chromium hydrolysis reactions. Alberti *et al.*[13] also reported the existence of a 15-Å phase which sometimes occurred during their study on the formation of $\overline{\mathrm{Cr}_{0.5}\mathrm{H}_{0.5}}\cdot4H_2O$ (11.6 Å). Larger spacings have been achieved with smectite clays by employing sodium carbonate as the base[12] and ageing the solutions at 95 °C. These intercalates exhibited basal spacings approaching 27 Å at room temperature, representing a layer separation of 11 Å which is similar to those achieved in this study.

The layer charge of α-zirconium phosphate is *ca.* 10 times greater than that of smectite clays so the distance between interlayer chromium species is expected to be smaller. Thus porous materials with molecular sieve-like properties are readily obtained with smectite clays and not with α-zirconium phosphate as prepared in this study. α-Zirconium phosphate when treated with chromium(III) acetate forms materials more closely resembling chlorite minerals, which are smectites which contain a continuous hydroxometal interlayer, than pillared smectite clays.

Conclusions

We have shown that chromium interlayers can be formed with α-zirconium phosphate. These materials exhibit large basal spacings but are highly disordered. Crowding of the interlamellar space leads to surface areas which are not significantly larger than those of the starting material.

The so-formed solids can be thought of as α-zirconium phosphate analogues of chlorites but with a much wider range of interlayer distances and metal loadings.

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