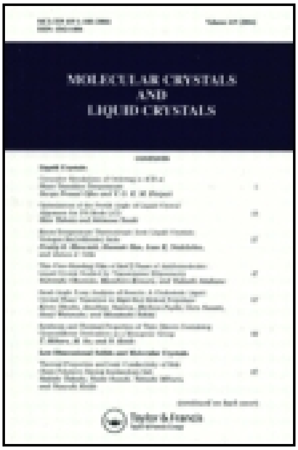

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# Insertion of Chromium Oligomeric Species in $Hf(HPO_4)_2{\cdot}H_2O$ (α-HfP)

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The reactions of chromium (III) acetate $Cr(OAc)_3$ ($OAc=CH_3OCO$) solutions with suspensions of *n*-propylamine / α-hafnium phosphate [$Hf(HPO_4)_2{\cdot}2C_3H_7NH_2{\cdot}H_2O$] (Apr-HfP) have been investigated over a wide range of $Cr(OAc)_3$ concentrations and heating conditions. The interlayered materials obtained have been studied by chemical and thermal analysis, X-ray powder diffraction, electron microscopy and IR 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. The results are interpreted in terms of the formation of hydrous chromium acetate interlayer species which decompose on heating between 350-450°C. The surface area of the α-hafnium phosphate increases after the reaction with chromium (III) acetate and in the samples thermally treated.

Keywords: pillaring; α-hafnium phosphate; hydrous chromium acetate.

## INTRODUCTION

Pillared layered solids are formed by intercalation of large polymeric cations in the interlayer region of layered solids. After calcination, the precursor cations are transformed to the respective metal oxide macroclusters, which prop the layers permanently apart. The presence of inorganic species acting as pillars and interacting strongly with the layers gives rise to thermally stable materials of high surface area and pore volume accesible for ion exchange, adsorption and catalysis[1,2].

A broad spectrum of pillaring ions (Zr, Cr, Al, etc.) and a range of layered hosts, provides the opportunity for creating numerous chemical combinations[3-7]. Of the layered metal (IV) phosphates, α-zircomium phosphate (α-ZrP) has been the most extensively studied, partly because its structure has been fully determined[8,9]. Also the chromiun pillars in α-titamium phosphate (α-TiP) have been studied[10].

The use of chromium (III) acetate for the exchange reaction with α-hafnium phosphate and the production of poly (hydroxochromium acetate) interlayers is the subjet of the present study.

## EXPERIMENTAL

### Materials

All chemicals used were commercial products of the best available purity.

The Apr-HfP was freshly prepared by contacting α-HfP with propylamine vapour during 6 days. The intercalate obtained had a composition of $Hf(HPO_4)_2{\cdot}2C_3H_7NH_2{\cdot}H_2O$.

Hafnium phosphate gel was prepared by precipitation from a solution of hafnium chloride with dilute phosphoric acid. Microcrystals of α-hafnium phosphate were formed by refluxing the gel in 12 mol dm$^{-3}$ phosphoric acid according to the procedure of Nakai et al[11]

### Intercalation Reactions

Hydroxochromium (III) acetate-expanded α-hafnium phosphate was prepared by contacting *n*-propylamine/α-hafnium phosphate with $Cr(OAc)_3$ aqueous solutions of differing chromium concentrations (3.1-80.0 mmol of $Cr^{3+}$ added / g of $HfP_2O_7$). The solid was present in the solution in the ratio of 1g : 250 ml. After being refluxed for 4 days, the suspensions were centrifugated and the solids separated, washed with demineralized water and air-dried.

### Analytical Procedures

Chromium concentrations in solution before and after uptake were monitored by colorimetry by using a Spectronic Genesys™ 5. The analysis of the concentration of phosphorous and hafnium was carried out on a Spectraspec spectrometer DCP-AEC. Analysis of solution supernatants for phosphorus was made spectrophotometrically by the molybdate method. Microanalysis data (C and N) were obtained with a Perkin-Elmer Model 2400 elemental analyser. Thermal analysis was performed by a Mettler TA 4000 (TG 50 from room temperature to 900°C, atmosphere of nitrogen, heating rate 5°Cmin$^{-1}$). Textural analysis was made by $N_2$/77K adsorption-desorption isotherms, using a Micromeritics ASAP 2000 instrument with turbomolecular pump ($\approx 10^{-5}$ torr). X-ray measurements have been carried out in a Philips diffractometer, Model PW 1729/1720 with CuK$_\alpha$ radiation ($\lambda$=1.5418Å) and a graphite monocromator. IR spectra were obtained on a Perkin-Elmer infrared spectrometer, Model Paragon 1000 by the KBr pellet technique. The samples were examined for homogeneity and morphology using a scanning electron microscope (SEM) Model JEOL 6100.

## RESULTS

Refluxing chromium (III) acetate solutions of different concentrations with Apr-HfP resulted in exchanged forms with expanded interlayers (Table).

TABLE Composition and $d_{002}$ of the samples obtained (air-dried).

| Sample | mmol chromium (III) added per g of $HfP_2O_7$ | mmol chromium (III) uptake per g of $HfP_2O_7$ | ratio OAc/$Cr^{3+}$ | $d_{002}$ (Å)[a] |
|---|---|---|---|---|
| 1 | 3.1 | 3.1 | 0.2 | 12.9 |
| 2 | 7.2 | 6.0 | 0.4 | 14.0 |
| 3 | 20.3 | 14.2 | 0.5 | 17.0 |
| 4 | 40.1 | 17.9 | 0.8 | 18.0 |
| 5 | 60.3 | 13.0 | 0.6 | 16.2 |
| 6 | 80.0 | 6.8 | 0.5 | 15.9 |

([a] determined from three orders of 00ℓ basal spacing).

The chromium content in the samples increases with the initial chromium (III) acetate concentration until a maximum is reached (sample 4), thereafter decreasing with increasing chromium (III) acetate concentration.

The basal spacings for the different concentrations of chromium (III) acetate reach a maximum of 18.0 Å at around 40.1 mmol $Cr^{3+}$/g $HfP_2O_7$, decreasing to 15.9 Å for the addition of 80.0 mmol $Cr^{3+}$/g $HfP_2O_7$.

The values of the basal spacings for sample 5 at room temperature, 200 and 400°C are 16.2 Å, 13.2 Å and 10.7Å respectively.

The Figure shows the TG and DTG curves of sample 5 and the $\alpha$-$Hf(HPO_4)_2 \cdot H_2O$.

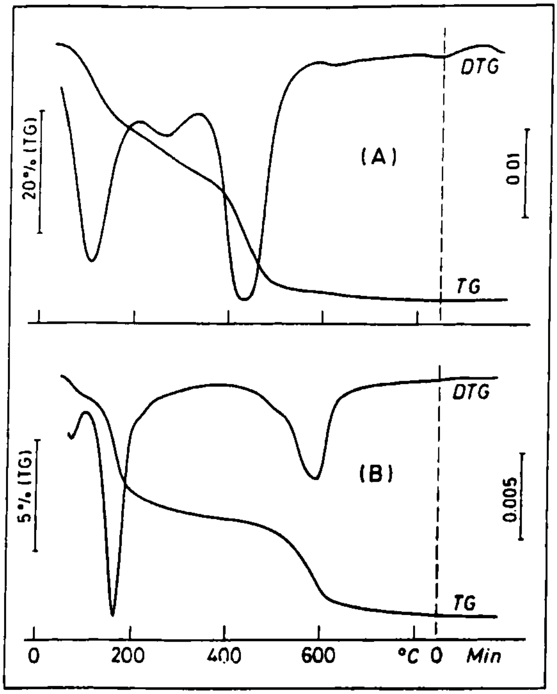

FIGURE TG and DTG curves of (A) sample 5; (B) α-$Hf(HPO_4)_2{\cdot}H_2O$.

The surface areas of the sample 5 treated at 25, 200 and 400°C are 45, 120 and 38 $m^2g^{-1}$ while that to α-$Hf(HPO_4)_2{\cdot}H_2O$ is 12 $m^2g^{-1}$. When examined by SEM the samples appear to be homogeneous, with the same morphology as the starting material. In the IR spectra, apart from bands associated to the starting hafnium phosphate, new absortions due to the acetate groups around 1558 and 1456 $cm^{-1}$ are observed.

## DISCUSSION

The new materials obtained in this study have poor crystallinity. The reflections from the basal planes are broad but the presence of higher-order reflections suggests that these materials are disordered but not amorphous, so that, hydrolysis of the hafnium phosphate should 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 Hf-OH absorbance in the IR spectra around 3700cm$^{-1}$ and by the chemical analysis, which exhibits phosphorous to hafnium ratios of two[12].

The negligeable nitrogen content in the intercalated species indicates that propylamonium has been completely exchanged.

From the carbon content of the intercalated species together with TG and IR data it is apparent that acetate ligands are involved in the interlayer complex. The ratio Cr/OAc does not support intercalation of the starting chromium (III) acetate and the IR spectra confirm the OAc group. 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[13,14]. 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 and acetate ligands can be involved in the polymeric products. Studies of chromium (III) chloride solutions to which sodium acetate is added, show that trimeric chromium (III) hydroxide acetates are formed[15]. 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.

Despite the nature of the chromium species in the solutions of chromium (III) acetate after reflux is not known in the present study, 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 corresonding reduction in the ratio of acetate ligands to chromiun atoms. The acetate to chromiun ratios observed in the exchange samples range from 0.2 to 0.8.

The TG curve for sample 5 (Figure (A)) shows that a loss of weakly bound water from the interlayer occurs at 100°C. This is followed by decomposition of the interlayer chromiun species which is centered around 430°C showing that pyrolysis of acetate ligands occurs in the region of this weight loss. Presumably at this stage of the thermal degradation a chromium oxide, probably $Cr_2O_3$, is formed. A mass loss resulting from condensation of the phosphate groups which would be expected to occur between 500-600°C is not observed.

The loss of crystallization water produces an increase in the values of specific surface calculated from BET and t-plot methods of sample 5 treated at 200°C, but the decomposition of acetate on heating is not accompanied by an increase in surface area as measured by nitrogen adsorption. 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 increase in surface area.

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## REFERENCES

[1.] R. Setton, in *Chemical Reactions in Organic and Inorganic Constrained Systems*, edited by NATO ASI Series C, Reidel. Dordrecht (1986), vol. 165.

[2.] R. Burch, *Catal. Today* (1988), vol. 2, p. 185.

[3.] P. Maireles-Torres, P. Olivera-Pastor, E. Rodríguez-Castellón, A. Jimenez-Lopez and A.A.G. Tomlinson, *J. Mate. Chem.*, **1**, 739 (1991).

[4.] F. Gonzalez, C. Pesquera, C. Blanco, I. Benito and S. Mendioroz, *Inorg. Chem.*, **31**, 729 (1992).

[5.] K. Ohtsuka, Y. Hayashi and M. Suda, *Chem. Mater.*, **5**, 1823 (1993).

[6.] D. Petridis, T. Bakas, A. Simopoulos and N.H. Cangas, *J. Inorg. Chem.*, **28**. 2439 (1989).

[7.] S. Yamanaka, *Ceram. Bull.*, **70**, 1056 (1991).

[8.] A. Clearfield and G.D. Smith, *Inorg. Chem.*, **8**, 431 (1969).

[9.] J. Albertsson, A. Oskarsson, R. Tellgren and J.O. Thomas, *J. Phys. Chem.*, **81**, 1574 (1977).

[10.] P. Mairelles- Torres, P. Olivera-Pastor, E. Rodríguez-Castellón, A. Jimenez-Lopez and A.A.G. Tomlinson, in *Pillared Layered Structures*, edited by I.V. Mitchell (Elsevier Applied Science, London, 1990), p. 137.

[11.] I. Nakai, K. Imai, T. Kawashima, K. Ohsumi, F. Izumi and I. Tomita, *Anal. Sci.*, **6**, 689, (1990).

[12.] T. Yamaguchi, Y. Nakano and K. Tanabe, *Bull. Chem. Soc. Jpn.*, **51**, 2482 (1978).

[13.] C.B. Baes, in *The Hydrolysis of Cations*, (Wiley, New York, 1976).

[14.] F.P. Rotzinger, H. Stunzi and W. Morty, *Inorg. Chem.*, **25**, 489 (1986).

[15.] H. Erdmann, *Leder*, **14**, 249 (1963).