Preparation of Heavy Metal Phosphates; Effect of Starting Precursors

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Abstract: Crystallization of heavy metal phosphates prepared from aqueous solutions is very slow. The situation could be improved when the salts were prepared from the respective metal alkoxide. The sol-gel synthesis of a group of these salts, (Zr, Ti, and Hf phosphates), from precursors of different natures was envisaged. By altering through metal precursors of different natures (inorganic or metallo-organic), and phosphate precursor of different natures (phosphoric acid or organic phosphate esters), we have shown that organic phosphates are also of advantage as the counterpart. Thermal analysis, FT-IR, and XRD results indicated more crystalline products when prepared from organic phosphates.

1. INTRODUCTION

Beside the well known uses of phosphates as fertilizers¹⁻³, detergent ingredients⁴, and as industrial corrosion inhibitors⁵, they also find wide applications as advanced materials of high technological importance^{6,7}. They exhibit many interesting physical properties such as superprotonic conductivity⁶, high ultraviolet transparency, and large thermal expansion coefficients^{8,9}.

Tetravalent metal phosphates, $M(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, where M refers to a tetravalent metal such as Zr, Ti, Hf, and Pb, are interesting for their ion-exchange behavior and their catalytic activity¹⁰⁻¹⁶. When solutions containing phosphate anion and tetravalent metal salts are mixed,

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amorphous gels of variable compositions result¹². The gels are transferred into microcrystals depending on the reflux conditions. Trivalent titanium was oxidized in H_3PO_4 where crystalline tetravalent metal phosphates were precipitated¹⁶. Livage et al prepared hydrated zirconium and titanium phosphates^{10,11} in order to have inorganic exchanger membrane by adding H_3PO_4 to the metal precursors (oxychloride in water or alkoxide in alcohol). The pronounced example of preparation; $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, was investigated by many others (see refs. 11-14 for example).

Preparation of these systems was studied mainly in aqueous media where water acts both to dissolve the inorganic precursors (H_3PO_4 and metal salts) and hydrolyze the metal cation¹⁷. In this case it seems difficult to control the hydrolysis and condensation of aqueous molecular precursors. In addition, the use of hydrated tetravalent metal phosphates in ion-exchange activities is governed by their crystallinity.

The possibility of preparing a group of tetravalent metal phosphates using different starting precursors for both the phosphate value and the metal cations then seems interesting. The dependence of the product crystallinity on the preparation route regarding the two methods; namely the traditional wet method and the sol-gel preparation in organic solvents will be in comparison.

2. EXPERIMENTAL DETAILS

2.1 Materials: We used 85% H_3PO_4 (Analar), 70% $\text{Zr}(\text{OPr})_4$ in propanol (Aldrich), 98%+ $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Laboratory Rasayan), 98%+ HfOC_2 (Aldrich), 99%+ $\text{Ti}(\text{OBu})_4$ (Aldrich), and a 1:1 mixture of monoethyl/diethyl phosphate esters; namely ET, prepared by one of us⁸. In this work, (*I*) refers to an inorganic precursor of either the metal (i.e.

an oxychloride) or the phosphate value (i.e. H_3PO_4). An (*O*) refers to an organic precursor of the metal (i.e. an alkoxide) or of the phosphate value (i.e. ET). So for example $\text{Zr}_{(I/O)}$ means a zirconium phosphate produced from zirconium oxychloride and ET while $\text{Zr}_{(O/I)}$ refers to zirconium phosphate produced from zirconium propoxide and phosphoric acid.

2.2 Procedure: H_3PO_4 was diluted to 50% and a 1 M aqueous solution of each of ZrOCl_2 , HfOCl_2 were prepared as well as a molar solution of $\text{Zr}(\text{OPr})_4$ and $\text{Ti}(\text{OBu})_4$ in their respective mother dry alcohols. Et was diluted with ethanol down to 25% by weight. The metal precursor solutions (both organic and inorganic) were mixed, with constant magnetic stirring, in an alternating manner both with the phosphoric acid solution (inorganic phosphate) and with the ET solution (organic precursor of phosphate) in the 1:2 M:P ratio as shown in table 1.

Each time a metal alkoxide was used, an appropriate amount of water was added to the mixture according to the stoichiometry of the reaction equation¹⁰. Stirring was continued overnight and the precipitates and gels were then dried for 21 days at 60 °C and under a reduced pressure for another week at the same temperature.

TABLE 1. Mixed precursors.

Phosphate	Ti		Zr		Hf	
H_3PO_4	None	<i>O</i>	<i>I</i>	<i>O</i>	<i>I</i>	None
ET	None	<i>O</i>	<i>I</i>	<i>O</i>	<i>I</i>	None

I: An inorganic precursor of the metal (i.e. an oxychloride).

O: An organic precursor (i.e. an alkoxide).

Two additional samples of the precipitates obtained by mixing Zr

alkoxide both with phosphoric acid, $Zr_{(O/T)}$, and with ET, $Zr_{(O/O)}$, were refluxed with their respective mother liquors where portion samples were removed at different times of reflux for drying and analysis.

Dry solid products were ground and checked for their crystallinity by XRD (Philips PW 1710 powder diffractometer aided with a Philips PW 1050 vertical goniometer and a graphite crystal monochromator (Cu K_{α} radiation). TA was preformed using a DSC PerkinElmer derivatogram model DTA 7/Unix system, Norwalk, Ct. A heating rate of $10^{\circ}\text{C}/\text{min}$ was employed in each run.

IR runs were performed for the refluxed samples of Zr in both its organic and inorganic starting mother liqueurs. The runs were performed using KBr pellet technique^{17,18} by means of Jasco Instruments FT-IR 300E.

3. RESULTS AND DISCUSSION:

It is clear that all the samples are amorphous as shown by their XRD patterns in Fig. 1. Switching from inorganic to organic precursors, shows some improvement of the crystallinity but, on general, the crystallinity is still poor. It seems that Zr, Ti, and Hf show the same trend in this respect. On refluxing the zirconium phosphate samples; $Zr_{(O/O)}$ and $Zr_{(O/T)}$, in their mother liquor solutions, the crystallinity improved with time This improvement is little.

It needed about a week of reflux time to get the crystalline species shown in Fig. 2. It seems that further very long reflux times in phosphoric acid will be needed before an appreciable crystallinity could be achieved^{12,17}.

FIGURE 1. XRD patterns of dried zirconium samples as prepared.

FIGURE 2. XRD of refluxed samples zirconium samples.

TGA curves of Zr samples shown in Fig. 3 for samples prepared from aqueous, (i.e. inorganic), phosphate precursors display water evolution up to 200 °C and a constant weight after 700 °C. This may be attributed to the volatility of phosphoric acid at this temperature (3). On the other hand, the samples prepared from organic phosphates show weight constancy at about 450 °C. The use of either inorganic or organic Zr precursors does not seem to be of a great effect on the TGA curves on using H_3PO_4 acid as the counterpart of the starting material.

Livage stressed the importance of an organic Zr precursor in improving the product zirconium phosphate¹⁷. In the our study, the nature of phosphate precursor was found to be of some importance. Fig. 4 shows the IR spectra of samples $\text{Zr}_{(\text{O/I})}$ and $\text{Zr}_{(\text{O/O})}$ as refluxed for one week. It is clear that the IR spectra of the two refluxed precipitates show no vibration bands for the alkoxy group^{11,17,18}. The samples seem to undergo almost complete hydrolysis or phosphatization that removed the reactive alkoxy ligands.

DSC curves of all samples are shown in Fig. 5 where a characteristic endothermic peak always appears around 250–350 °C. This peak

corresponds to the weight loss shown in Fig. 3 for the samples prepared from ET. On the other hand, the samples prepared from phosphoric acid solutions are weight stable at this temperature range and undergo some weight losses at higher temperatures above 600 °C which is out of scale for their DSC runs. Such a behavior is typical of phosphates salts^{3,11}.

FIGURE 3. TGA curves of zirconium phosphate samples.

FIGURE 4. IR spectra of Zr samples, 1 week-refluxed.

A comparison between the sample refluxed in its organic mother liquor and that prepared and refluxed in its inorganic phosphate solution show that the first one is more crystalline. This is indicated by the bending and vibrational bands of the amorphous P-O-H groups appearing 1250 and 2400 cm^{-1} respectively. These bands are more pronounced in the case of the sample prepared in aqueous phosphate than in ET. The organic nature of the starting precursor plays some rule in improving the crystallinity of the product as stated by Livage but it is the nature of the phosphate precursor in this case. In accordance with the results obtained by Livage, aging samples prepared from H_3PO_4 did not appreciably affect the crystallinity as much as it did in case of samples prepared from ET.

FIGURE 5: DSC curves of dried samples as prepared.

4. CONCLUSION:

The preparation of tetravalent metal phosphates could be improved by starting their sol-gel synthesis using organic phosphate precursors. The crystallinity of the product depends not only on the nature of the starting metal precursor but also on the nature of the counterpart phosphate starting material. Compared to the samples prepared from phosphoric acid, those prepared from ethyl phosphate were more crystalline as prepared and undergone more sensible crystallization on reflux.

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