On the Synthesis of α-Zirconium Phosphate

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Received February 4, 2000. Revised Manuscript Received March 9, 2000

Crystalline α -zirconium phosphate, Zr(HPO₄)₂.H₂O, was obtained by direct precipitation of soluble salts of zirconium(IV) with phosphoric acid. The fresh compound transforms, by hydrolysis, into amorphous or semicrystalline hydroxophosphates with a P/Zr molar ratio of less than two. These facts contradict the formation mechanism of zirconium phosphates admitted by researchers for over more than 40 years. The materials are characterized by chemical, textural, and thermal analysis, powder X-ray diffraction, and scanning electron microscopy.

Introduction

The metal salts of phosphoric acid have been known for over a century. In the last 40 years, they have been the object of continuous interest in the chemical literature. Initially, this was due to the report of the ion exchange properties of zirconium phosphate gels.^{1,2} Earlier, many other uses were developed: molecular sieves, catalysts, ion and proton conductors, and matrices for chemical modification. $3-7$ The initial impetus for this effort was a result of the discovery that zirconium phosphate could be prepared in crystalline form.8

The literature reports that amorphous gels are obtained by the rapid addition of ion phosphate containing solutions to zirconium(IV) salt solutions.⁹ If the molar ratio of phosphate to zirconium is less than two, quantitative precipitation of the zirconium still occurs (unless the ratio is less than one), but the product is a hydroxyphosphate.9,10 Even when the ratio of phosphate to zirconium exceeds two in the initial mix, the precipitate which first forms has a ratio lower than two.¹¹ If the precipitate is aged in the mother liquor, its phosphate content continues to increase with time until

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equilibrium is reached.¹¹ Increased acidity and phosphate ion concentration favor a higher P/Zr ratio. The maximum ratio even in the gel is two.⁸ De Boer¹² represented this compound as a monohydrogen phosphate, $Zr(HPO₄)₂$.

The first crystalline zirconium phosphate, $Zr(HPO_4)_2$. H₂O (α -ZrP), was obtained by reflux in H₃PO₄ of a zirconium phosphate gel.⁸ This layered phase^{13,14} can also be synthesized by hydrothermal methods¹⁵ or by direct precipitation with prior formation of zirconium- (IV) fluoro complexes.¹⁶ Some years later,¹⁷ a second layered phase, Zr(H₂PO₄)(PO₄)·2H₂O (γ-ZrP),¹⁸ was synthesized. Both compounds have been the object of multiple investigations as host agents of many chemical species.19 Recently, the synthesis of a third crystalline compound with a P/Zr molar ratio equal to two has been described, Zr(HPO₄)₂ (τ-ZrP), but its structure is threedimensional.¹⁵

That is to say, during the entire second half of this century it has been accepted that the rapid precipitation of zirconium phosphate originated amorphous solids with a P/Zr molar ratio of less than two, and which only became crystalline (or semicrystalline) materials after lingering treatment with H_3PO_4 . This paper seeks to demonstrate that this is not so. On the contrary, if the P/Zr molar ratio in the reaction mixture is greater than two, the product of the precipitation is small crystalline particles of α -ZrP that become amorphous zirconium hydroxophosphate in subsequent treatments following the initial formation of the solid.

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Experimental Section

Reagents. All chemicals were of reagent grade (Aldrich) and used without further purification.

Preparation of Zirconium Phosphates. Zirconium phosphate was first prepared from hydrochloric acid solutions of zirconyl chloride using an excess of phosphoric acid as precipitant. A total of 25 g of zirconyl chloride was dissolved in 430 mL of 2 M HCl. This solution was slowly added to 400 mL of 1.25 M H_3PO_4 with stirring (initial P/Zr molar ratio 3.6). The precipitate was centrifuged and washed with 0.3 M H₃-PO4 until free of the chloride ion. This solid was dried in air at room temperature (material 1). Material 2 was obtained from material 1 by means of treatment with NaOH(aq). A total of 5 g of material 1 was suspended in 500 mL of water. NaOH (0.1 M) was then slowly added with stirring until pH = 3. The residual solid was centrifuged, washed with water, and dried in air at room temperature (material 2). Crystalline α -zirconium phosphate was prepared from material 1 by reflux during 48 h in 10 M H_3 PO₄.

Intercalation Procedure. The *n*-butylamine intercalation compounds were obtained by exposure of the solid materials to an atmosphere saturated with amine vapor during 5 days at room temperature.

Analytical Procedures. The zirconium and phosphorus contents were determined with a SpectraSpectrometer DCP-AEC after dissolving a weighed amount of the sample in HF- (aq). Microanalytical data (C, H, and N) were obtained using a Perkin-Elmer model 2400B elemental analyzer. Powder X-ray diffraction measurements were carried out in a Philips diffractometer, model PW 1729/1720 (scan speed 0.125-3 deg min⁻¹, Cu K α radiation, $\lambda = 1.5418$ Å). Thermogravimetric min⁻¹, Cu Kα radiation, $\lambda = 1.5418$ Å). Thermogravimetric
analysis was carried out at a rate of 5 °C min⁻¹ (under a flow of nitrogen) using a Mettler 4000-TG50 instrument. N₂ adsorption-desorption isotherms were recorded at 77 K using an automatic volumetric system equipped with a turbomolecular pump (∼10-⁵ Torr) Micromeritics ASAP 2000 instrument. The measurement of the vapor pressure of the liquid nitrogen bath was carried out each hour for the N_2 adsorption branch. Scanning electron micrographs were performed using a JEOL JSM 6100 electron microscope, operating at 20 kV.

Results and Discussion

The origin of the results that are expounded next was a fortuitous fact. Our aim was to prepare amorphous zirconium phosphate. To do this, we prepared H_3PO_4 -(aq), to which an aqueous solution of Zr(IV) was slowly added. A white solid is thus obtained that must be washed to eliminate the excess of phosphoric acid. In an attempt to avoid the possible hydrolysis reaction, washing was carried out in situ with dilute phosphoric acid. To our surprise, the powder XRD pattern of the obtained solid dried in air at room temperature (material 1) is the one that appears in Figure 1a, which presents similar characteristics to that of crystalline α -zirconium phosphate (Figure 1b).

We later repeated the synthesis of zirconium phosphate rigorously following the bibliographic descriptions.8 We washed with dilute phosphoric acid and subsequently with water. An essentially amorphous solid is indeed obtained (Figure 1c).

The synthesis of α -ZrP via treatment of amorphous zirconium phosphate with dilute phosphoric acid at ambient temperature is not a likely occurrence. For years, it has been reported that the formation of crystalline zirconium phosphate starting from amorphous solids needs high concentrations of H_3PO_4 and/ or high temperatures. It seems more feasible that the α -ZrP appears directly in the precipitation process. In fact, this is so. Figure 1d shows the powder XRD pattern

Figure 1. Powder X-ray diffraction patterns of (a) material 1, (b) α -ZrP (reflux), (c) amorphous ZrP, and (d) freshly precipitate.

of the fresh precipitate (before any washing process). This coincides with that of α -ZrP.

The synthesis of material 1 was carried out on 10 different occasions. In all the cases, the P/Zr molar ratio in the solid was greater than two (it ranged between 2.5 and 2.8). Although crystalline compounds with a P/Zr ratio greater than two are known,²⁰ we suppose that material 1 is a mixture of α -ZrP and H₃PO₄(s). The percentage in weight of α -ZrP in the mixture should therefore be 80-85%. This hypothesis should be confirmed.

As can be observed in Figure 2, material 1 intercalates *n*-butylamine in the vapor phase. Its powder XRD pattern can be obtained by overlapping of the characteristic diagrams of α -ZrP/*n*-butylamine (*d* = 18.6 Å)²¹ and H_3PO_4/n -bultylamine ($d = 13.3$ Å) intercalate compounds. Moreover, the behavior of material 1 is identical to the sample obtained by a mechanical mixture of α -ZrP (75 wt %) and solid H_3PO_4 (Figure 2d).

The thermal behavior of material 1 also differs from what is characteristic of α -ZrP (reflux). Because of H₃-PO4 decomposition, the weight loss obtained at 800 °C $(30-35%)$ is higher than that calculated for α -ZrP (11.95%). Also, due to the presence of $H_3PO_4(s)$,⁸ the condensation of the monohydrogen phosphate to pyrophosphate groups takes place at very low temperatures (<200 °C; 500-600 °C in α -ZrP obtained by reflux). In Figure 3a, it can be observed that the (two-step) dehydration process is followed by the condensation reaction to pyrophosphate, and finally, H_3PO_4 decomposition takes place at 500-600 °C. This TG curve considerably differs from what is characteristic of α -ZrP (Figure 3b), where the processes of crystallization, water

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Figure 2. Powder X-ray diffraction patterns of samples obtained by intercalation of *n*-butylamine into (a) material 1, (b) α -ZrP (reflux), (c) H₃PO₄(s), and (d) mechanical mixture of α -ZrP (75 wt %) and H₃PO₄ (25 wt %).

loss, and condensation to pyrophosphate are separated by more than 300 °C.

Figure 4 confirms that the presence of phosphoric acid in material 1 reduces the thermal stability of α -ZrP. The powder XRD pattern of material 1 treated at 300 °C corresponds to ZrP_2O_7 .²² Similar behavior is observed in a mechanical mixture of α -ZrP (75 wt %) and solid H_3PO_4 (Figure 4b). At said temperature, the pure α -ZrP sample has only lost its crystallization water (Figure 4c), becoming the anhydrous phase (*ú*-ZrP) with an interlaminar distance of 7.4 \AA .²³

When material 1 (dried powder) is treated with NaOH(aq) until $pH = 3$, a new solid is obtained. This sample dried in air at room temperature (material 2) is high purity α -ZrP. Elementary analysis of material 2 (experimental: Zr 29.8, P 21.2; calculated for $Zr(HPO_4)_2$. H2O: Zr 30.28, P 20.56 wt %) and the TG/DTG curves (Figure 3c) confirm this fact.

The $N_2/77$ K adsorption-desorption isotherm shape of α -ZrP samples (Figure 5) corresponds to type II of the BDDT classification,²⁴ which indicates that the adsorption process takes place in a mono-multilayer with negligible porosity. The BET method application over the adsorption branches gives rise to values of S_{BET} $= 39.5 \text{ m}^2 \text{ g}^{-1}$ for material 2 and $S_{\text{BET}} = 18.3 \text{ m}^2 \text{ g}^{-1}$ for α -ZrP (reflux).

SEM images allow us to monitor the process visually. Material 1 (Figure 6a) is made up of plate aggregates of α -ZrP. Phosphoric acid acts as a uniting agent. After the elimination of phosphoric acid, hexagonal individual

Figure 3. TG $(-)$ and DTG $(-)$ curves for (a) material 1, (b) α -ZrP (reflux), and (c) material 2.

Figure 4. Powder X-ray diffraction patterns of samples treated in air at 300 °C: (a) material 1, (b) mechanical mixture of α -ZrP (75 wt %) and H₃PO₄ (25 wt %), and (c) α -ZrP (reflux).

plates, typical of α -zirconium phosphate, are observed in material 2 (Figure 6b). Statistical studies indicate that the average surfaces of the plates are \sim 1350 × 1350 A^2 . Figure 6c shows the SEM image of α -ZrP (reflux). The morphology of both solids is qualitatively identical.

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Figure 5. N₂/77K adsorption-desorption isotherms of (a) material 2 and (b) α -ZrP (reflux).

Quantitatively, it is observed that the zirconium phosphate digestion in 10 M H_3PO_4 at the reflux temperature results in an increase in the mean size of the plates $(\sim 2500 \times 2500 \text{ Å}^2)$.

Plate thickness is more difficult to calculate using the SEM technique as the layered nature of the solids gives a preferential arrangement. The solid layers are placed parallel to the sample carrier, hence perpendicular to the optical axis. These data can be obtained by the study of the powder XRD peak profile, by means of Sherrer's equation.25 For determination of the entire line profile, the half-maximum width is used, and the NaCl (d_{200}) reflection) is used as a reference. Typical interlaminar powder XRD reflection (d_{002}) is used in the study of both solids.²⁶ Thus, the obtained data is associated with the average thickness of the layered microcrystalline plates, which results in values of 235 Å for material 2 and 380 Å for α -ZrP (reflux). Because of the limitations of the method used, the results obtained must be considered as approximate.

The semiquantitative knowledge of the shape and average size of the crystallites allows calculation of the approximate specific surface area of these materials. In the case of material 2, the average crystallite external area is 4.9×10^6 Å² and the average crystallite volume is 4.3×10^8 Å³. In the case of α -ZrP (reflux), the ratio area:volume is 1.6×10^7 Å² to 2.4×10^9 Å³. Since α -ZrP has four formula units per unit cell, which has a volume of 724 $\AA^{3,14}$ it follows that the calculated specific surface area of these solids is 41.6 m^2 g⁻¹ for material 2 and 25.0 m^2 g⁻¹ for α -ZrP (reflux). The agreement with the experimental data (39.5 and 18.3 m^2 g⁻¹, respectively) is acceptable, keeping in mind the limitations of the method used to measure the crystallite size and the assumption made that the crystallites are regular and roughness-free.

Figure 6. SEM images of (a) material 1, (b) material 2, and (c) α -ZrP (reflux).

Conclusions

In excess of phosphorus, crystalline α -zirconium phosphate is directly obtained in the interaction of zirconium(IV) and phosphoric acid solutions. Subsequently, semicrystalline or amorphous hydroxophosphates are formed by the process of hydrolysis.

Acknowledgment. This work was funded by CICYT (Spain), Research Project No. MAT97-1185.

CM0010093

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