SYNTHESIS OF α -ZIRCONIUM PHOSPHATE FROM ACETYL ACETONATE SOLUTION; A COMPARATIVE SYNTHESIS STUDY OF α -ZrP

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Abstract: Three main routes of synthesis; namely the reflux, the direct precipitation, and the sol-gel methods, are used to prepare α -zirconium phosphate α -Zr(HPO₄)₂·2H₂O or simply α -ZrP. Within each separate method of synthesis, different starting precursors and/or reaction conditions are tested for optimization to obtain the crystalline product. Different products were characterized using TGA-DTA data, SEM photos, N₂-gas absorption-desorption measurements, and FT-IR absorption spectra. The products showed different extents of crystallinity as roughly or qualitatively shown by their XRD patterns. The results are explained on the basis of each synthesis route and reaction conditions. In contrast to the familiar results that the initial un-refluxed product of rapid precipitation is basically amorphous ZrP, a careful washing strategy confirmed that this is a crystalline ZrP contaminated with a minority of solid H₃PO₄. This is shown by the XRD patterns of this product after intercalation with butylamine. For sol-gel experiments, reflux could not greatly improve the crystallinity of the products obtained from a mixture of Zr(OPr^{iso})₄ and phosphoric acid solutions while a product obtained in presence of acetylacetone, as a complexing agent, presented some better tendency for crystallization with reflux. All products of refluxing Zr(OPr^{iso})₄ with a 1:1 mixture of mono- and diethyl phosphates were amorphous. Chemical analysis shows a reasonable agreement between the experimental ratios of P/Zr and the calculated values. Compared to other methods of synthesis, the direct precipitation seems to be more efficient in obtaining a product of good yield and improved crystallinity.

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INTRODUCTION

The chemistry of tetravalent transition metal phosphates has been a subject of increasing interest because a variety of compounds with different structures and properties can be prepared¹. The layered-structure compositions of such phosphates are of most importance due to their present and promising uses as ion-exchangers, gas sensors, intercalation hosts, and several other applications²⁻⁵. Extensive studies on layered phosphates are done^{1,6}. Among this group of compounds, α -zirconium phosphate has received a noticeable interest for its important ion-exchange properties, especially in drastic conditions of high temperatures and strong acid media. In addition, due to both the controlled intercalation extent and the well-selected type of guest moiety, α -zirconium phosphate can also be applied in making a variety of intercalation products that cover a wide range of interlayer spacing for different uses as chemical sensors and as improved or highly selective ion-exchangers.

Two main methods are presently described in literature to prepare, α -Zr(HPO₄)₂·2H₂O. These are the rapid precipitation-reflux⁷ (I) and the direct precipitation methods⁸ (II). Other methods of preparation have been reported like the sol-gel method⁹ (III). The products are ZrP of different

degrees of crystallinity. Most reports, describing synthesis of ZrP from concentrated H₃PO₄ by rapid precipitation, adopt the addition of zirconium oxychloride (or chloride) solution to a large excess of concentrated H₃PO₄. These reports also consider prolonged reflux of the solid product to in hot concentrated phosphoric acid to reach variable extents of crystallinity. Many of these reports consider the initial product to be a hydroxo-phosphate composition that needs further reflux to improve its crystallinity^{2,10}.

On the other hand, crystalline α -ZrP could successfully be obtained by slow decomposition of zirconium complexes⁸. In this case, only the fluoro-complexes were considered in this respect. In a typical sol-gel synthesis procedure, H₃PO₄ (85%) was added to an equal volume of 1 molar zirconium n-propoxide in n-propanol. Compared to ZrOCl₂ in aqueous solution, zirconium n-propoxide is reported to allow shorter reaction times and lower crystallization temperatures.

As a continuation of their efforts to more investigation on the layered polyvalent metal phosphates, Clearfield and his co-authors used a direct hydrothermal method for the preparation of zirconium phosphate and zirconium arsenate in alkaline media¹¹.

This work aims to comparatively study more starting materials for both the direct precipitation and the sol-gel methods of ZrP synthesis. For the first method, different starting precursors can be investigated and different phosphate sources, other than H_3PO_4 , can be tried in the second method. In addition, the nature of the very initial product of rapid precipitation¹² and the common mixing sequence in this procedure will be investigated¹⁰. In each case, the nature of ZrP product and its extent of crystallinity will be studied by different characterization tools to optimize these procedures.

MATERIALS AND METHODS

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

Preparation of Zirconium Phosphates.

TABLE (1) summarizes the different routes and conditions of synthesis of zirconium phosphate samples in this work.

I. Rapid precipitation-reflux: The ZrP gel samples were prepared following the method of Gal and Gal¹³, where a solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, (freshly re-crystallized from 7M-HCl and air-dried), was slowly added, with constant stirring, to an excess of concentrated phosphoric acid. A white solid product, namely ZrP, was immediately formed. Samples of this product were treated in different ways as follows:

A) Pre-reflux precipitate (sample C_0)

A portion of the white solid formed above was repeatedly washed and centrifuged using 0.3 M- H_3PO_4 solution until free of chloride. This sample was named C_0 . Water was not used as the washing solution to avoid any possible hydrolysis of this sample.

B) Reflux products, (C_n samples)

Following the Clearfield and Stynes' method⁷, the white solid ZrP was refluxed in 12M phosphoric acid up to 7 days where different samples (C_1 , C_2 , C_3 , C_4 , C_5 , and C_6) were withdrawn at different times of reflux for characterization. The withdrawn samples were centrifuged at 4500 rpm for 10 minutes and washed with diluted phosphoric acid then with distilled water until a pH of 3-4.

C) Reverse-addition product. (sample C_R)

For a separate sample, C_R , the sequence of addition of the two reacting precursors to one another, described above, was reversed¹⁰. Concentrated phosphoric acid was slowly added to zirconyl chloride octahydrate solution while all other steps of reflux, centrifuge, and washing were done as mentioned in the procedure described in procedure B. After treatment, all the samples were stored over P_4O_{10} .

II. Direct-precipitation: ZrP was prepared according

to the Alberti and Torracca's method so modified to improve both the rapidity and the yield of the preparation⁸. Two samples of ZrP were prepared by slow decomposition of zirconium fluoride complexes in aqueous solutions. Hydrofluoric acid and sodium fluoride were the alternative sources of the fluoride ion for complexation as follows:

A) Precipitation from HF (sample A)

In a large Teflon beaker, 85 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ were dissolved in 1200 ml of distilled water and 80 ml of 40% hydrofluoric acid were then added with constant stirring. To this solution, 715 ml of 85% phosphoric acid were added. Instead of passing a stream of pre-humidified air¹⁴ through the solution after being warmed at ca 80 °C, the solution was simply exposed to an infrared source of energy for 4 days where crystals of α -zirconium phosphate were slowly formed on the surface and the walls of the container and frequently settled down to the bottom of the beaker. After about 5 days, now further precipitation was noticed and the obtained crystals were easily filtered and washed with distilled water on a No. 1 Whatman filter paper until a filtrate of pH of 4-5 was obtained. The white powder product; namely, sample A, was then stored over P_4O_{10} for drying.

B) Precipitation from NaF solution (sample A_s)

Of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 32 g was dissolved in 900 ml of 1.1 M-HCl, with constant stirring for 30 minutes, where the pH became steady¹⁵. 21 g of sodium fluoride were then added to this solution with stirring for further 30 minutes while the pH steadily increased and then leveled off to 1.6 after all the fluoride salt was completely dissolved. The Na/Zr ratio in this solution was 5.0:1 and the final Zr concentration was 0.11 molar. To this solution, 100 ml of 15 molar orthophosphoric acid, (H_3PO_4 , specific density 1.7) was quickly added with thorough stirring. Zr became 0.1 M while the Na/Zr ratio remained 5.0:1 and the molar ratio P/Zr was about 8:1. Despite the immediate formation of a white precipitate, stirring was continued for 2 hours to insure complete precipitation and the precipitate was then easily filtered on a No. 1 Whatman filter paper and thoroughly washed with a plenty of distilled water until free of chloride (tested by 0.1 molar AgNO_3 solution). The white powder; sample A_s , was then dried just under vacuum (where neither a drying-agent nor heating were needed) and kept for characterization.

III. Sol-gel synthesis: Three ZrP samples were prepared from zirconium isopropoxide, $\text{Zr}(\text{OPr}^{\text{iso}})_4$, and different phosphate precursors^{9, 16, 17}. In all cases, the Zr/P molar ratio was kept at 1:2.

For the first sample, namely L_A , a 85% H_3PO_4 was mixed with an equal volume of a 1M solution of $\text{Zr}(\text{OPr}^{\text{iso}})_4$ in isopropanol with constant stirring to form a white gel. This gel was refluxed at 80 °C in its

TABLE 1 Summary of the methods of preparation of zirconium phosphate samples.

Method of synthesis	Materials	Reaction conditions	Sample
I- Rapid precipitation, reflux	$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ added to H_3PO_4	Dilute H_3PO_4 washing, No reflux	C₀
		Dilute H_3PO_4 -washing Water-washing, No reflux	C₁
		As above, 1 hr-reflux	C₂
		14 hr reflux	C₃
		24 hr reflux	C₄
		72 hr reflux	C₅
		7 days reflux	C₆
	H_3PO_4 added to $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$	As for sample C₆	C_R
II- Direct-precipitation	$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, HF, and H_3PO_4	Complexation and decomposition	A
	$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, NaF, and H_3PO_4	Complexation and decomposition	A_s
III- Sol-gel	$\text{Zr}(\text{OPr}^{\text{iso}})_4$ and H_3PO_4	ZrP gel refluxed at 80 °C up to 7 days	L_A
	$\text{Zr}(\text{OPr}^{\text{iso}})_4$ /1:1 mixture of mono-, and diethyl phosphate esters	ZrP gel refluxed for different times	L_B
	$\text{Zr}(\text{OPr}^{\text{iso}})_4$, acetylacetone, and H_3PO_4	ZrP gel refluxed over night	L_C

mother liquor for different times.

In the second sol-gel synthesis, a nearly 1:1 molar mixture of mono-, and diethyl phosphate esters was used instead of orthophosphoric acid and the procedure was completed as above. These samples were designated as **L_B** samples.

The third sol-gel experiment started with a complex that is formed by adding acetylacetone to the isopropoxide precursor under nitrogen atmosphere. The formed zirconium acetylacetonate complex was slowly added to 1M phosphoric acid solution and the mixture was then refluxed. The formed precipitate was filtered, washed, and dried as described above. This sample is denoted as sample **L_C**.

Characterization: The P/Zr ratio of the products was gravimetrically determined as described elsewhere⁷.

Powder X-ray diffraction measurements were carried out in a chart recording Bruker D8 advance X-ray diffractometer using copper (K_α) Target with a secondary monochromator at 40 kV and 40 mA.

Samples of optimized crystallinity were vacuum-dried for 1 week and thermally analyzed using Perkin Elmer Thermogravimetric Analyzer TG A7. Differential thermal analysis (DTA) was also per-

formed using a Shimadzu DTA-50 machine. The heating rate in all runs was 10° C/min.

FT-IR absorption spectra of products were examined in the frequency range of 400-4000 cm⁻¹ using a Nexus 670 FTIR spectrophotometer (Nicolet-USA) using the KBr pellet technique.

The morphology of crystalline samples was scanned by a JEOL JXA-840A Electron Probe Microanalyzer.

The surface area was determined by the adsorption-desorption isotherms of sample optimum samples using a Coulter™ surface area analyzer SA3100TM with Coulter analysis software version 2.13. Nitrogen gas of purity 99.99% was used as the adsorbate gas at 77 °K by cooling with liquid nitrogen.

RESULTS AND DISCUSSION

Rapid-precipitation refluxed samples. FIGURE 1 shows the x-ray diffraction patterns of the white solid formed by adding ZrOCl_2 solution to concentrated phosphoric acid (12M) as refluxed in its mother liquor for different periods of time. The initial samples show less extents of crystallinity where their X-ray

diffraction patterns show broad reflections. Refluxing the ZrP-gel in concentrated phosphoric acid improved the crystallinity toward α -ZrP from sample C_1 through C_6 . Under conditions of high resolution, the intense reflections at $2\theta = 19.9, 25.1$, and 34° actually show doublets. Improved crystallinity is simply indicated by the higher intensity and greater sharpness of the individual peaks of the XRD patterns across these samples. With longer reflux times, the four broadened reflections observed in the initial gels grew in intensity indicating a progress of the crystallinity as a function of refluxing time.

FIGURE 1 XRD of the gels refluxed in 12M- H_3PO_4 for different periods of time.

The common strategy for the precipitation of ZrP-gels, following the reflux method, is the addition of $ZrOCl_2$ solution to a large excess of H_3PO_4 to insure a P/Zr molar ratio greater than 2 through all stages of the reaction^{7, 18, 19, 20, and 21}. A reversed sequence of addition of the Zr and P precursors should then start the reaction with a P/Zr ratio of less than 2 or even less than 1. This ratio continues to increase until it exceeds 2 for the overall mixture of reactants at the end of mixing with vigorous agitation of the reaction mixture.

FIGURE 2 shows a comparison between the XRD pattern of sample C_R and that of sample C_6 (α -ZrP-reflux). It is clear that both patterns seem identical. This figure indicates that the reflux process (increased acidity and phosphate concentration) favored a higher P/Zr ratio until α -ZrP crystals are formed regardless whether the starting gel contained some compositions of molar ratios of P/Zr of less than 2 or not¹².

FIGURE 3 shows the XRD pattern of sample C_0 . It is the same precipitate obtained in the very first stage of

FIGURE 2 XRD patterns of reverse addition sample, C_R and that of the long-refluxed sample, C_6 .

FIGURE 3 XRD pattern of the initial precipitate, C_0 , washed only with dilute H_3PO_4 .

preparing samples C_1 to C_6 ; where, instead of refluxing the gel in a hot concentrated phosphoric acid, the precipitate was just centrifuged and washed with dilute phosphoric acid until free of any chloride. By comparing the XRD pattern of the un-refluxed sample C_0 (FIGURE 3) with that of sample C_6 , (FIGURE 1), it is clear that both patterns show similar characteristics.

This similarity is in agreement with the results obtained by Trobajo¹², who precipitated ZrP solid from dilute (1.25M) phosphoric acid, while it is precipitated from 12M phosphoric acid in this study. For more examination of the nature of sample **C₀**, it was kept for a week in a closed atmosphere saturated with butyl amine vapor where the amine was intercalated in the ZrP host. A fully crystalline α -ZrP sample (**A**, prepared by direct precipitation as described in section II below) was also kept in the same conditions for comparison. The XRD patterns of the intercalation products and that of the pure sample **A** are shown in FIGURE 4. Sample **C₀** (the freshly precipitated air-dried white solid, precipitated from phosphoric acid) thus appears to be mixture of very fine crystalline particles of α -ZrP and a minority of solid phosphoric acid¹². This is also supported by the result of relatively larger P/Zr ratio of sample **C₀** over sample **A** as will be shown below. On extensive washing with water to get rid of excess acid, the very fine crystals of α -ZrP undergo hydrolysis into the almost amorphous hydroxo-phosphate (sample **C₁** in FIGURE 1 above). This is in contrast with the common idea, prevailed for more than half a century, that the rapid precipitation of zirconium phosphate should, in principle, result in the formation of amorphous solids with P/Zr molar ratios of less than two and that these amorphous solids can be fully or partially crystallized only by reflux in phosphoric acid.

FIGURE 4 XRD patterns of sample **A**, its *n*-butylamine-intercalation product (**A-BA**), and that of sample **C₀** intercalated with the same amine.

II. Direct precipitation samples. FIGURE 4 shows the XRD patterns of α -ZrP directly prepared by the direct precipitation with prior formation of zirconium (IV) fluoro complex using HF (sample **A**) or NaF (sample

A_S). The XRD patterns of both samples are very similar. Meanwhile, both samples show relatively sharper and higher peaks relative to those of the crystalline product obtained by reflux for one week following Clearfield's method (sample **C₆** in FIGURE 1).

FIGURE 5 XRD patterns of samples directly precipitated from HF, (**A**) and NaF solutions (**A_S**).

FIGURE 6 XRD patterns of ZrP precipitated from $\text{Zr}(\text{OPr}^{\text{iso}})_4$ and 85% H_3PO_4 and refluxed at 80 °C for different times (**L_A** samples).

This indicates more uniformity in the particle size distribution and even more crystallinity than the refluxing method. Because of the gradual decomposition of the fluoro-zirconate complex in the direct precipitation method, a slow precipitation of zirconium phosphate occurs as the fluoride is depleted. This leads to relatively larger and well-formed crystals²².

III. Sol-gel samples. FIGURE 6 shows the XRD patterns of ZrP samples obtained from a $\text{Zr(OPr}^{\text{iso}})_4$ and 85% phosphoric acid mixture after reflux at 80 °C for 1 and 7 days (L_A -samples). It is clear that refluxing the white solid, in its mother liquor up to one week at relatively low temperature, (80 °C), improved its crystallinity. A relatively more pronounced improvement of crystallinity is noticed for gels obtained from aqueous solutions of ZrOC1_2 ($t = 1$ week, $T = 95$ °C).

Nevertheless, both L-samples (sol-gel) and C-samples (reflux) are less crystalline as compared to A-samples (direct precipitation).

FIGURE 7 shows the x-ray diffraction patterns of samples L_B (precipitated from a nearly 1:1 mixture of mono and diethyl phosphate esters and boiling-refluxed in their mother liquor for different periods of time). The amorphous white precipitate shows almost no response to reflux even up to 2 days. Hydrolysis of phosphate ester-mixture may have not completed in these conditions. This did not favor the formation of crystalline zirconium phosphate. The third sol-gel product, sample L_C , present some better tendency of crystallization on reflux at 90 °C in its mother liquor as shown by their XRD pattern in FIGURE 8.

FIGURE 7 XRD patterns of gels precipitated from methyl/ethyl phosphate mixture and boiling-refluxed in their mother liquors.

Slow and well-controlled hydrolysis of zirconium propoxide after being complexed with the acetylacetone seems to have occurred and favored the formation of crystalline α -zirconium phosphate on reflux for only two days. This may be due to a slower decomposition of the zirconium precursor (zirconium acetylacetonate complex) on reaction with phosphate anion to form crystalline products. However, sample L_C still shows some amorphous character if compared to the fully crystalline product (sample A). In addition, the zirconium acetylacetonate complex needed higher temperature to decompose if compared to that of the zirconium fluoro-complex.

FIGURE 8 XRD pattern of sample L_C (sol-gel prepared from zirconium acetylacetonate complex).

Chemical Analysis

Some representative samples of each of the products obtained both by the reflux and the precipitation methods; namely samples C_6 , C_0 , and A were analyzed for their contents of phosphorus, zirconium, and water contents as P_2O_5 , ZrO_2 , and H_2O weight percent respectively. The results are listed in TABLE 2. The efficiency, η , of precipitation of the product in each case was calculated using the formula:

$$\eta = \frac{P}{E} \times 100$$

where P is the experimental weight of the product (collected and dried into a desiccator over P_2O_5) and E is the weight of product theoretically calculated for complete precipitation or full reaction of all ZrOCl_2 added. Direct precipitation ZrP (sample A) showed an experimental P/Zr atomic ratio of 2 which is exactly the same as the theoretical ratio. The ratio for the product of the reflux method is (1.96) after about a week of reflux. This may be due to the more crystallinity of the

TABLE 2 Analytical data for selected samples.

Sample	Method	P ₂ O ₅ (%)	ZrO ₂ (%)	P/Zr	H ₂ O (%)	η
C ₆	Reflux	49.11	43.48	1.96	7.52	69.00
C ₀	Pre-reflux	52.24	42.96	2.11	7.65	69.03
A	Precipitation	47.22	40.98	2.00	5.95	77.10

former product (sample A) that enables precise chemical composition and water content. The P/Zr ratio of sample C₀ is greater than that of sample C₆ and is still greater than the theoretical ratio for α-ZrP. This may support the fact¹² that the former sample is a mixture of α-ZrP and some minor content of solid phosphoric acid H₃PO₄.

Thermal Analysis

FIGURE 9 shows the thermal behavior of the direct-precipitated samples, (A; precipitated from HF solution, and AS; precipitated from NaF solution). Both samples were elected for thermal analysis as they show optimum crystallization α-ZrP products compared with other samples in this work (regarding their x-ray diffraction patterns).

FIGURE 9 TGA and DTA curves of samples A (direct-precipitated from HF solution) and AS (direct-precipitated from NaF solution).

The thermal behaviors of these samples are nearly identical. Both samples undergo three endothermic changes in the temperature range of 100 to 250 °C. The first one (situated near 150 °C) is ascribed to a phase transition from α-ZrP to ζ-ZrP. Conversion to the later form is completed below 150 °C before the water of hydration is released. The second endothermic change appears around 165 °C and up to 195 °C is due to the lattice water loss²³⁻²⁵. The third endothermic change is

at about 230 °C where the zeta phase of ZrP (ζ-ZrP) is converted to the neo one (η-ZrP). The overall changes below 300 °C are represented by the following equation

The broad endotherm at 450° C to 650° C is attributed to dehydroxylation or condensation of the orthophosphate groups into pyrophosphate. However, the broad endotherm continues up to temperatures higher than 650 °C as somewhat higher temperatures (up to about 800 °C) are required for crystallization of ZrP₂O₇.

Matching with the DTA curves, the TGA curves in FIGURE 9 show the weight losses due to the successive water molecules (dehydration, 30-165 °C and dehydroxylation, 450 °C upwards) per each ZrP molecule. The initial weight of the analyzed sample alters the step height in each case. Compared with TGA curves for several α-ZrP samples obtained by the refluxing procedure in a previous study²⁶, the TGA curves of samples A and AS can be considered as highly crystalline. This is revealed from the regular shape of weight loss on the TGA curves.

FIGURE 10 N₂/77 K adsorption-desorption curves of sample A.

FIGURE 10 shows the N₂/77° K adsorption-desorption curves of sample A. The isotherm shape presents a type II of the BET classification where the process of adsorption occurs to form a mono-multilayer on a surface of very poor porosity. The surface area, SBET, as calculated for the adsorption branch of the isotherm is calculated to be 49.8 m²/g. This moderate value corresponds to a highly crystalline product¹² of α-ZrP.

FT-IR Spectra

FIGURE 11 shows the FT-IR absorption spectra of each the two direct-precipitated samples, (**A** and **A_S**), a refluxed sample of good crystallinity (**C₆**), and a sample prepared by the sol-gel method and refluxed for 7 days, (**L_{7 days}**).

FIGURE 11 FT-IR absorption spectra of **A**, **A_S**, **C₆**, and **L_{7 days}** samples

Both of the refluxed samples show some adsorbed water as can be seen by the presence of a broad absorption band from about 3600 to about 2900 cm^{-1} that can be attributed to the hydrogen bonded water. This very strong broad band almost overlapped the two strong and sharp bands centered at 3590 and 3510 cm^{-1} , (both characteristic of the asymmetric OH stretch of zeolitic water). These two peaks are clearly seen in the spectra of the direct-precipitated samples (**A** and **A_S**) that may have adsorbed much moisture due to their higher degrees of crystallinity, if compared to the refluxed products (**C₆**, **L_{7 days}**).

The same applies for the P—OH stretch band that is clearly seen in the spectra of the directly precipitated products and centered at 3300 cm^{-1} while it can hardly be seen in the spectra of the refluxed products due to the presence of the very broad band of absorbed moisture²⁷.

In each of the four spectra, a strong band characteristic of symmetric P—OH stretch vibration of H_2O is also seen around 3150 cm^{-1} with which two relatively small absorption bands at 2100 and 2300 cm^{-1} are associated. The later two bands correspond to characteristically weak P—OH stretching vibrations. This is also found in other compounds²⁸. FIGURE 11 shows that these two bands are more apparent in all samples prepared in aqueous media (**A**, **A_S**, and **C₆**) than in the sample prepared in alcohol medium (**L_{7 days}**). The sharp moderate band at 1620 cm^{-1} is attributed to the O—H bonding of zeolitic water. This band seems sharper for the more crystalline samples (**A**, **A_S**).

For the spectra of all samples, there is a group of four strong closely located bands in the range of 1150-950 cm^{-1} . The first three of these bands are centered at about 1130, 1070, and 1035 cm^{-1} and are attributed to the PO₃ stretch while the fourth, located at about 965 cm^{-1} characterizes the P—O stretch. Another two moderate absorption bands are located at about 600 and 530 cm^{-1} . The former band is attributed to the out of plane bending of the PO-H band while the later is attributed to the bending of PO₃ groups. The band located at 660 cm^{-1} is assigned to a librational mode of water.

Scanning Electron Microscope Images, SEM

FIGURE 12 shows the SEM photos of samples **A** and **C₆** at the same magnification ratio. It is clear from these two photos that both samples are in the form of well-defined crystalline flaky particles or plate aggregations. The plates seem hexagonal (typical of α -ZrP).

On direct precipitation, very slow decomposition of zirconium-fluoro complex enabled the formation of larger and more morphologically homogeneous crystals of about 8 to 10 micrometers diameter range (slide (b)). The best crystalline α -ZrP that could be prepared by the reflux method shows only crystals of about 3 to 5 μm average diameter (slide (a)) with irregular size distribution.

FIGURE 12 Scanning electron micrographs of plate-like α -Zrp. (a) Sample **C₆** obtained by reflux. (b) Sample **A** obtained by direct precipitation.

In both cases, plate surfaces are well-seen and the average dimensions of the plates can be easily compared. The plate thickness is more difficult to calculate due to their preferential arrangement where the solid plates are placed parallel to the sample holder in the way of the electron beam.

CONCLUSION

Various methods were compared to prepare α -ZrP in this study. Direct precipitation from (either from HF medium or from Zr acetylacetonates) produced the most crystalline product. Sol-gel products from a 1:1 mixture of mono/dialkyl phosphate ester were of least crystallinity and the poorest response to reflux crystallization. Relatively longer times of reflux in concentrated aqueous phosphoric acid are needed for products of the conventional reflux method. Nevertheless, the very initials product of this method is a mixture of α -ZrP and some minor content of solid phosphoric acid H_3PO_4 . The obtained results indicate that the crystallinity of the prepared α -ZrP is tightly related both to the methods of the preparation and the starting materials.

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