The Synthesis of Crystalline Zirconium Phosphate with Large Particle Size by the Direct-precipitation Method

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The direct-precipitation method was studied as a possible way to synthesize crystalline zirconium phosphate of a large and uniform crystal size. The yield and the crystal size were examined as functions of the initial hydrofluoric-acid and phosphoric-acid concentrations and the warming temperature. The conditions for preparing the largest crystal were: $ZrOCl_2 \cdot 8H_2O$, 0.13 M; hydrofluoric acid concentration, 0.715 M; phosphoric acid concentration, 5 M; temperature, 50 °C. Those for preparing the material with uniform crystal-size distribution and a possibly large-mean crystal size were: $ZrOCl_2 \cdot 8H_2O$, 0.13 M; hydrofluoric acid concentration, 0.715 M; phosphoric acid concentration, 9 M; temperature, 60 °C. The product was confirmed to be crystalline $Zr(HPO_4)_2 \cdot H_2O$ by means of chemical, thermal, and X-ray analyses, and by an examination of the titration curve.

The crystalline zirconium phosphate (ZP) cation exchanger has been extensively studied since the work of Clearfield and Stynes,[1] who first prepared the material by refluxing amorphous zirconium phosphate for a long time in a phosphoric acid solution. The investigation of ion-exchange kinetics, however, has just started, and only a little information[2-9] is available to date. The present authors intend to carry out kinetic studies for elucidating the ion-exchange mechanism of ZP. To accomplish this purpose, it is necessary to prepare a material which has not only a high degree of crystallinity, but also a large and uniform size and an excellent yield. Horsley and Nowell[10] have compared four alternative methods for preparing ZP: (A) the reflux method proposed by Clearfield and Stynes;[1] (B) the direct precipitation method proposed by Alberti and Torracca;[11] (C) the rapid precipitation method, which is a modification of (B), and (D) the method of direct precipitation in the presence of oxalic acid. They concluded that Method (C) was the best, mainly because the crystallinity of its products was the best. However, no detailed investigations from the point of view of the crystal-size distribution of the products have yet been reported. The present authors have attempted to establish a good procedure for obtaining material with a large and uniform crystal size. A preliminary experiment suggested that Method (B) above was most promising, for it provided crystals larger than those obtained by the other methods.

This report will describe the results of the investigation undertaken to establish the best conditions for the synthesis based on Method (B) by varying such factors as the concentrations of hydrofluoric acid and of phosphoric acid and the temperature of precipitation.

Experimental

Procedure for the Preparation of ZP. Five and a half grams of $ZrOCl_2 \cdot 8H_2O$ were dissolved in distilled water in a polyethylene beaker (5.5 cm in inside diameter, 6.7 cm high). The desired amounts of hydrofluoric acid as a complexing agent for zirconium and of phosphoric acid were added successively with vigorous stirring, to make the total volume 130 cm^3. The solution thus prepared was then allowed to warm in a thermostatic water bath for longer than 100 h in order to decompose the fluoro-complex of zirconium. The volume of the solution gradually decreased during the warming and reached about 70 cm^3 under the recommended conditions: hydrofluoric acid concentration; 0.13 M, phosphoric acid concentration; 9 M, temperature; 60 °C (see below). The white flaky product was separated centrifugally, washed with distilled water until the pH of the filtrate became about 5, and stored over P_2O_5 for two weeks. The yield was calculated on the basis of the zirconium recovery.

Measurement of Crystal Size. The flaky product was observed to be composed of many crystals of rectangular platelets, 50—450 μm in length and 8—90 μm in width. About a hundred well-shaped crystals were randomly selected from them, and their cross sections were measured by means of an optical microscope.

Analysis. Zirconium was precipitated by cupferron from a dil hydrofluoric acid solution in which 0.5 g of ZP had been dissolved, and was determined by ignition to the oxide.[12] The phosphate ion was precipitated as ammonium molybdophosphate from the above filtrate, reprecipitated as ammonium magnesium phosphate, and determined by ignition to $Mg_2P_2O_7$.[13] The water content was calculated from the weight loss on ignition.

Titration Curve. A half gram of ZP was immersed in 100 cm^3 of a solution (ionic strength 0.1 M, (1 M=1 mol/dm^3)) for a week at a room temperature, followed by the pH measurement and by the chemical analysis of the solution. To obtain a titration curve, this procedure was undertaken for various solutions which had been prepared by the desired combinations of 0.1 M NaOH and 0.1 M NaCl (forward titration) or of 0.1 M HCl and 0.1 M NaCl (backward titration). The amount of ion taken up by the exchanger was evaluated from the difference between the initial and the final concentrations of the Na^+ ions present in the solution. The Na^+ ions were converted to the corresponding pure chlorides and indirectly determined by titrating Cl^- ions by means of Fajans' method.

Apparatus. The thermal analysis was undertaken with a Shimadzu micro thermal analyzer, Model DT-20B, connected to a thermal balance, Model TGC-20H, for thermogravimetric analysis (TGA), and a high-temperature sample-holder, Model MDH-20, for differential thermal analysis (DTA). α-Alumina was used as the standard for DTA. The measurement was carried out in air at a heating rate of 5 °C/min. X-Ray diffraction patterns were taken using Ni-filtered Cu $K\alpha$ radiation.

Results and Discussion

In the direct precipitation method, there is a lower limit of the molar ratio of F/Zr in the mixed solution

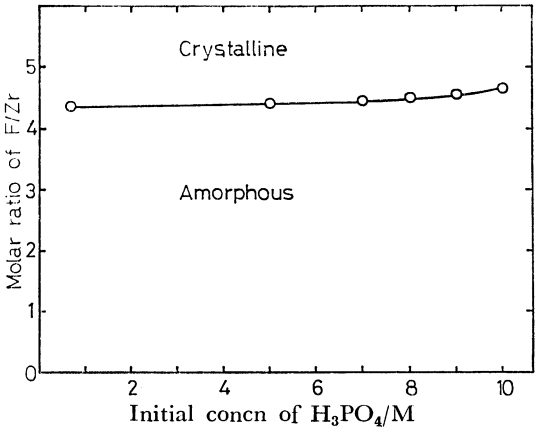

Fig. 1. Dependence of lower limit of F/Zr molar ratio on the concentration of H_3PO_4.

for obtaining crystalline material. When the F/Zr was lower than this limit, amorphous zirconium phosphate was precipitated. Figure 1 indicates that the limit depended slightly on the concentration of phosphoric acid. If the ratio is higher than 4.5, the crystalline form will be precipitated, irrespective of any other factors.

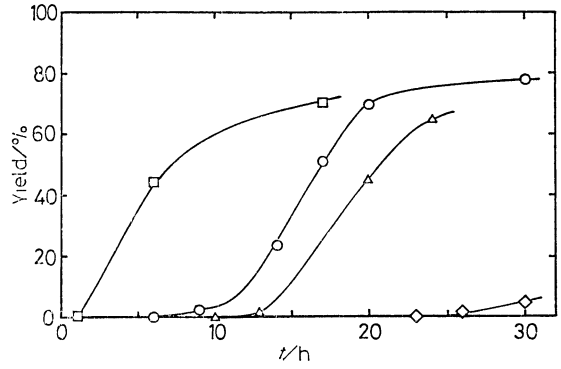

Fig. 2. Effect of F/Zr ratio on the rate of precipitation.
Conditions: T, 70 °C; concn of H_3PO_4, 5 M. F/Zr, □: 4.8, ○: 5.5, △: 6.8, ◇: 11.9.

The effect of the F/Zr ratio on the rate of precipitation was measured at an initial phosphoric acid concentration of 5 M and at 70 °C. Figure 2 indicates that the time needed for the first appearance of the precipitate (induction period) tended to become longer with the increase in the F/Zr ratio, while the progress of the precipitation, once it set in, was independent of the F/Zr ratio in the 4.8—6.8 region. From these results, a F/Zr ratio of 5.5 was selected by taking into account the margin for producing crystalline material and the rapidity of the procedure.

The dependence of the initial concentration of phosphoric acid on the formation rate of precipitate was investigated; the results are shown in Fig. 3. The progress of precipitation was little affected by the phosphoric acid concentration, but the induction period became longer with a decrease in the initial concentration of phosphoric acid.

As to the effect of the temperature, Fig. 4 reveals

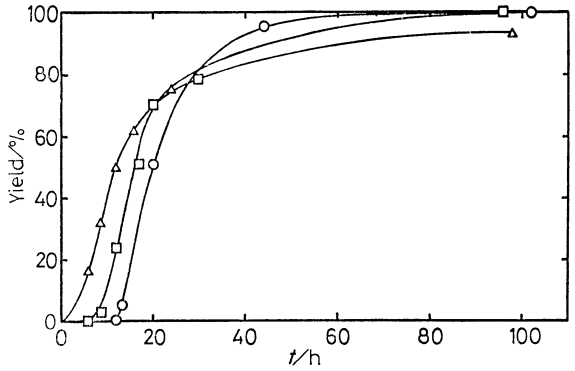

Fig. 3. Dependence of the initial concentration of H_3PO_4 on the formation rate of precipitate.
Conditions: F/Zr, 5.5; T, 70 °C. Concn of H_3PO_4, ○: 1 M, □: 5 M, △: 10 M.

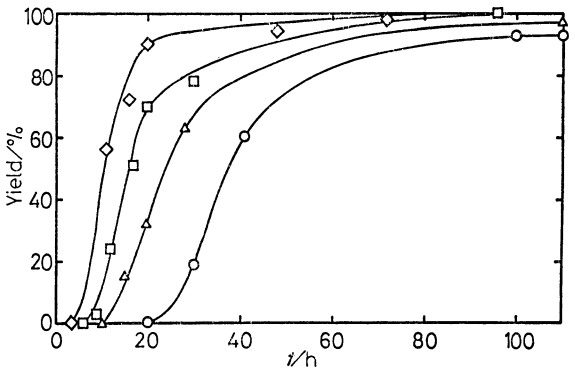

Fig. 4. Effect of temperature on the formation rate of precipitate.
Conditions: F/Zr, 5.5; concn of H_3PO_4, 5 M.
T, ○: 50 °C, △: 60 °C, □: 70 °C, ◇: 80 °C.

that, in addition to the shortening in the induction period, the progress of precipitation became faster as temperatures became warmer. These results suggest that, among the three factors examined, only the increasing temperature governs the progress of precipitation, while the concentrations of both hydrofluoric

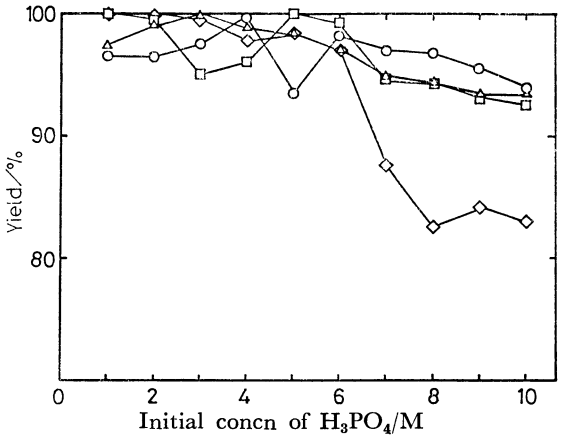

Fig. 5. Yield as functions of H_3PO_4 concentration and temperature.
F/Zr, 5.5.
T, ○: 50 °C, △: 60 °C, □: 70 °C, ◇: 80 °C.

acid and phosphoric acid affect only the length of the induction period. Furthermore, it is obvious from Figs. 3 and 4 that the precipitation reaction was completed within 100 h, whatever the conditions. Therefore, the yield after warming for longer than 100 h was measured as functions of the phosphoric acid concentration and the temperature. Figure 5 shows that the yield decreased a little with the concentration of phosphoric acid, but that it was higher than 90% under any conditions except in the case of 80 °C, where the yield decreased considerably when the concentration of phosphoric acid exceeded 7 M. Thus, the temperature should be fixed below 80 °C.

On the other hand, it is very important to ascertain the effect of the preparative conditions on the crystal size of the precipitate. The mean size of the crystals is plotted as a function of the initial concentration of phosphoric acid at different temperatures in Fig. 6, while its standard deviations under several representative conditions are shown in Table 1. The mean

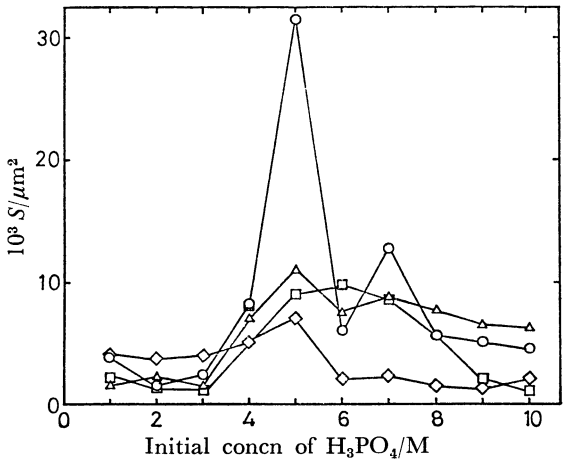

Fig. 6. Mean size of the crystals as functions of H_3PO_4 concentration and temperature.
F/Zr, 5.5.
T, ○: 50 °C, △: 60 °C, □: 70 °C, ◇: 80 °C.

TABLE 1. MEAN CRYSTAL SIZE OF ZP AND ITS STANDARD DEVIATION

Concn of H_3PO_4 M	$10^3 S$ μm^2	Standard deviation × 2 μm^2
1	1.4	0.7
5[a)]	31.5	18.1
5	10.1	4.9
9	6.5	2.3
10	6.3	3.1

Conditions of synthesis: F/Zr; 5.5, T; 60 °C except for a). a) F/Zr; 5.5, T; 50 °C.

crystal size was at its maximum near 5 M phosphoric acid. When we compared the two sides of the maximum, the mean crystal size was larger for the higher than for the lower concentrations of phosphoric acid. Furthermore, it decreased as the temperature rose. A comparison of the mean crystal size and its standard deviation shows that, in the case of 5 M phosphoric acid, though the mean crystal size was the largest, the uniformity of the crystals was poor, but in other cases it was comparatively good.

These observations can be understood as follows. The precipitate did not appear until the concentration of phosphoric acid approached about 8—9 M by the evaporation of water with hydrofluoric acid. This observation seems to reflect the length of the induction period. As the precipitation results from the decomposition of fluoro-complex of zirconium, the fact that the progress of precipitation depends only on the warming temperature, and not on the initial hydrofluoric acid and the phosphoric acid concentrations, can be understood if free hydrofluoric acid is considered to be expelled during the induction period. As a natural consequence, the lower the initial concentration of phosphoric acid, the higher the concentration of zirconium at the stage of precipitation. This fact makes it possible to interpret the slight decrease in the yield with the increase in the initial concentration of phosphoric acid. The higher rate of the generation of the free zirconium ion at the stage of precipitation—this corresponds to the conditions of a lower initial concentration of phosphoric acid and a higher temperature—facilitates the formation of many nuclei of the precipitate and leads to the small crystals. This argument is compatible with the observations of the mean crystal size except for the occurrence of the maximum in Fig. 6. Further investigations should be carried out to learn the reason for this important irregularity.

On the basis of these results, the conditions for the synthesis which provides the largest crystals are found to be; phosphoric acid concentration, 5 M; warming temperature, 50 °C. If the uniformity of the crystal size is required in addition to the large size of the crystals, the most favorable conditions are; phosphoric acid concentration, 9 M; warming temperature, 60 °C.

The following fact is worth noticing. The ZP thus prepared was in the form of flakes consisting of crystals of various sizes which adhered closely together. When converted to the sodium form, the flakes were broken down into fine particles. The ZP flakes, as prepared, were coverted to the sodium form by treating them with a mixture of 0.1 M NaCl and 0.1 M NaOH solutions (pH=11 at equilibrium). The particle-size distribution of the sodium-form exchangers thus prepared was examined by sieving, as is shown in Table 2. It is

TABLE 2. PARTICLE-SIZE DISTRIBUTION OF SODIUM-FORM EXCHANGERS

Mesh size	>70	70—100	100—145	145—200	200—280	280>
(1)[a)]	1	4	13	22	20	40
(2)[b)]	0	3	9	31	35	22

Conditions of synthesis: a) F/Zr, 5.5; concn of H_3PO_4, 5 M; T, 50 °C; b) F/Zr, 5.5; concn of H_3PO_4, 9 M; T, 60 °C.

evident from this table that (2) possessed a better uniformity in particle size than (1), though there existed very few particles larger than 100 mesh. Moreover, (2) contained fine powder, which cannot be used for column operation, only a half as much as (1). This particle-size distribution corresponds roughly to that of the crystals in the hydrogen form. Further breaking was not observed by reconversion to the hydrogen form or by repeated regeneration cycles. This phenomenon may be due to the separation of crystals by the stress exerted by the change in the interlayer distance in the structure of ZP by conversion.

Chemical, thermal, and X-ray analyses were performed in order to characterize the materials which had been prepared by the procedures recommended above.

The composition of the product was independent of the conditions for synthesis and was found to be $Zr(HPO_4)_2 \cdot H_2O$. (Found: ZrO_2, 41.23; P_2O_5, 47.27; H_2O, 11.88%).

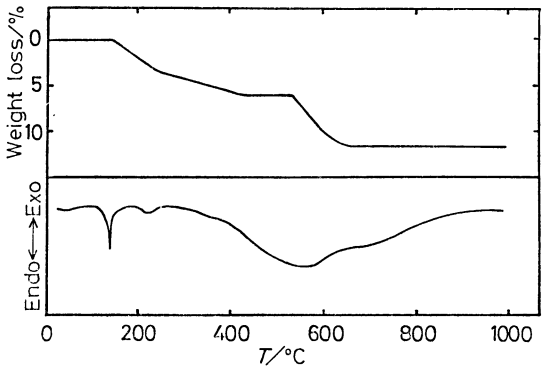

Fig. 7. TGA and DTA curves of ZP. Heating rate: 5 °C/min.

Figure 7 shows the TGA and DTA curves of the product. The TGA curve indicates that the product lost weight rapidly up to about 200 °C and then gradually up to 400 °C, where the weight became constant. The weight loss in this stage corresponds to one mole of water for each mole of ZP. Further heating to 650 °C gave rise to the release of a second mole of water, which resulted in the formation of pyrophosphate. In the DTA curve, there appeared a large and sharp endothermic peak at 150 °C, which was considered to correspond to the release of water. An exothermic peak attributed to the recrystallization by Clearfield and Stynes[1] did not appear. These curves closely resemble those of Sample (B) prepared by Horsley and Nowell.[10]

The results of X-ray analysis agreed well with the published data of α-ZP reported by Clearfield and Stynes.[1]

Forward and backward titration curves of ZP with sodium ion were constructed, as is shown in Fig. 8. The titration curves show two reversible exchange stages.

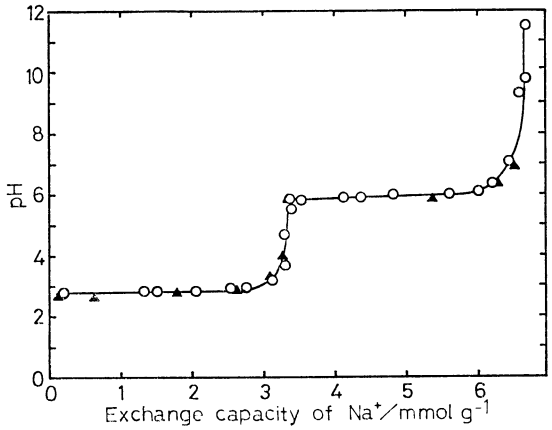

Fig. 8. Titration curves of ZP with sodium ion. ○: Forward titration, 0.1 M (NaOH+NaCl); ▲: Backward titration, 0.1 M (HCl+NaCl).

On the contrary, Clearfield *et al.*[14] reported that the titration curves exhibited a hysteresis loop, which resulted from the presence of different phases in the forward and backward titrations. These differences in titration and DTA curves can be explained by assuming that the crystallinity of the present product is better than that of Clearfield's.

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