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Direct Preparation of θ-Zirconium Phosphate

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Synopsis The effects of temperature and Zr concentration in solution on the composition and degree of crystallinity of zirconium phosphate have been examined. Pure θ-zirconium phosphate with an interlayer spacing of 10.4 Å has been prepared by direct precipitation.

Cations having a large ionic radius, such as Cs^+, Ba^{2+}, hydrated Mg^{2+} *etc.*, are not, or only slowly, exchanged by α-zirconium phosphate (α-ZrP) $Zr(HPO_4)_2\cdot H_2O$, owing to the small interlayer spacing (7.6 Å) of this exchanger.[1,2] These cations, however, can be easily exchanged by the highly hydrated form of α-ZrP with an interlayer spacing of 10.4 Å,[3] which was reported as $Zr(HPO_4)_2\cdot 8H_2O$ and labeled θ-ZrP.[2,4] This ion exchange characteristics of θ-ZrP is noteworthy since it enlarges the practical use of crystalline zirconium phosphate as an ion exchanger. Conventionally, θ-ZrP is obtained by regenerating suitable salt forms of α-ZrP with HCl solution.[3] In this case the phase can be prepared in a pure form only when the starting α-ZrP has a good but not too high degree of crystallinity. A recent paper[5] reported that the methanol intercalate of α-ZrP obtained from the salt form of the exchanger is washed with water to give rise to θ-ZrP. However, both methods are not simple in procedure since they include ion exchange (or intercalation) and regeneration processes.

The composition and degree of crystallinity of solution-grown zirconium phosphate are strongly dependent on the preparation conditions, such as temperature, digestion time, concentrations of solutes, stirring time *etc.* In this study the effects of some of these factors were examined to prepare θ-ZrP directly from solution.

Experimental

Several ZrP samples were prepared as follows. In all runs, the concentration of phosphoric acid solution was held constant at 6 mol dm^{-3} since it was suggested by Clearfield *et al.*[6] that an excess of phosphoric acid as precipitant is available for the growth of ZrP crystals. One volume aliquots of $ZrOCl_2$ aqueous solution at various concentrations were added dropwise to one volume of the phosphate solution at different temperatures with stirring and the reaction mixtures were kept for 48 h at those temperatures while being stirred. The resulting precipitates were filtered and washed with distilled water. X-Ray diffraction patterns were taken on the wet samples obtained.

Results and Discussion

Table 1 shows the composition and degree of crystallinity of the various products obtained under different experimental conditions. The approximate phase composition was estimated by the relative intensity of the peaks at 10.4 and 7.6 Å as in a previous report.[3] When the concentration of the starting $ZrOCl_2$ solution is fixed at 2 mol dm^{-3}, the refluxed product is α-ZrP, while at 94 °C a mixture of the α and θ phases is precipitated. For samples prepared at 94 °C, as the concentration of the $ZrOCl_2$ solution is decreased, the percentage of θ-ZrP increases until at 0.05 mol dm^{-3} 100% of θ-ZrP with high degree of crystallinity is obtained. When 0.05 mol dm^{-3} $ZrOCl_2$ solution is used, the samples obtained at below 94 °C are formed of θ-ZrP, whose degree of crystallinity increases with an increase of the precipitation temperature, while at boiling temperature the θ and α phases are coprecipitated.

From these results the effects of concentration and temperature on the crystallization of θ-ZrP are summarized as follows. (1) The increase in solute concentration makes the θ phase unstable. (2) The crystallization of θ-ZrP is promoted by increasing the precipitation temperature but at near boiling temperature the θ phase is less stabilized. (3) The optimum Zr concentration and temperature for the preparation of pure and highly crystalline θ-ZrP are determined by a combination of these two effects. The Zr concentration of 0.05 mol dm^{-3} and digestion temperature of 94 °C for the use of 6 mol dm^{-3} H_3PO_4 solution and

Table 1. Preparation conditions of ZrP samples and their characterization[a)]

Concentration of starting solution/mol dm^{-3}		Precipitation temperature/°C	Approximate phase/%		Crystallinity[b)] (X-ray)
ZrOCl	H_3PO_4		θ-ZrP(10.4 Å)	α-ZrP(7.6 Å)	
2	6	*ca.* 105 (reflux)	0	100	H
2	6	94	54	46	L
0.4	6	94	84	16	M
0.2	6	94	93	7	H
0.05	6	*ca.* 105 (reflux)	85	15	H
0.05	6	94	100	0	H
0.05	6	80	100	0	M
0.05	6	60	100	0	L

a) Digestion time, 48 h. b) H, high; M, medium; L, low.

48-h digestion time can be taken to meet this optimum condition satisfactorily. Longer times for digestion will contribute to further increase in the degree of crystallinity of the θ-ZrP.

The preferred formation of θ-ZrP in dilute solution and/or at moderate but not too high temperatures could be explained in terms of the type of hydration in this phase. In the monohydrated phase, α-ZrP, the water molecules are located midway between any two POH sites on the interlayer surface and tightly held by bifurcated hydrogen bonds.7) Therefore, this type of hydrate bonding is likely to be thermally stable and it also contributes to the increase of only 0.2 Å in the interlayer spacing over that of the anhydrous form of α-ZrP which is called ζ-ZrP.8) The remaining moles of water in this phase, on the other hand, would be located within the interlayer space and weakly held by hydrogen bonding to free hydrogen atoms of the water molecules covering the layer surface. It is therefore apparent that only in very dilute and/or moderately hot solution θ-ZrP with such unstable interlayer water would be formed in preference to α-ZrP.

The interlayer spacing of θ-ZrP is increased by 2.8 Å over that of α-ZrP. By using a value of 24.3 Å^2 for the occupied area per POH site in α-ZrP2,9) and about 14 Å^3 for the van der Waals volume of the water molecule,10) the water content in a mole of θ-ZrP can be evaluated to be 1 plus $24.3 \times 2.8/14$ or 5.9. This value is less than the value of 8 water molecules earlier reported2,4) but agrees well with a value of 6 ± 1 water molecules observed by Alberti *et al.*3) It is therefore more reasonable to conclude that θ-ZrP is formed as a hexahydrate $Zr(HPO_4)_2 \cdot 6H_2O$. A similar calculation for another highly hydrated phase which has an interlayer spacing of 11.5 Å and composition $Zr(HPO_4)_2 \cdot 8 \pm 1H_2O$3) yield a value of 7.8 water molecules, which is in good agreement with the observed value.

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