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THE THERMAL DECOMPOSITION OF ZIRCONIUM PHOSPHATES

III. γ-ZIRCONIUM PHOSPHATE AND ITS ALKALI METAL ION-EXCHANGE FORMS

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ABSTRACT

The conversion of γ-zirconium phosphate (γ-$Zr(HPO_4)_2 2H_2O$) to the α form (α-$Zr(HPO_4)_2H_2O$) is reported. The mono exchanged forms of γ-zirconium phosphate (γ-$Zr(MPO_4)(HPO_4)xH_2O$) with alkali metal ions have been prepared and characterised. DTG is used to illustrate the effect of change in crystallinity of the γ-form. The nature of the exchanged cation on the decomposition temperature and surface area of the orthophosphates are reported and the anomalous behaviour of the lithium and caesium exchanged forms discussed.

INTRODUCTION

The properties of the crystalline form of α-zirconium phosphate (α-$Zr(HPO_4)_2H_2O$) have been discussed in some detail[1,2], the γ-form (γ-$Zr(HPO_4)_2 2H_2O$), however, has not recieved the same attention although described by Clearfield et al.[3]. The preparation of the ion-exchanged forms of γ-zirconium phosphate in which half the available hydrogen has been replaced by alkali metal ions was reported previously by us[4]. The interlayer distance between reactive phosphate groups in γ-zirconium phosphate is 12.2 Å as opposed to only 7.6 Å in the α-form, there also being an additional water molecule in the γ-form. The essential difference between the α and γ-forms is the relative position of the phosphate groups in adjacent layers[1,5]. In the previous paper in this series[4], the hydrogen and cation-exchanged materials of the general formula γ-$Zr(HPO_4)(MPO_4)xH_2O$ were partially characterised. The work has been extended to include caesium. Characterisation includes surface area and scanning electron microscopy (SEM) in an attempt to define the morphology.

DTG analyses of the γ-ion exchanged forms are given and used to show the effect of the degree of crystallinity on the decomposition. It was previously reported[4] that γ-zirconium phosphates dehydrated under the dry nitrogen used in thermal analyses experiments, and also that the degree of hydration of the ion-exchanged forms appeared uncertain[4]. We have therefore attempted to stabilise the amount of hydration by standing over a partial pressure of water vapour. It should be noted, however, that SEM and surface area studies apply to the dehydrated forms, as the water of crystallisation is easily removed under vacuum.

As it was possible to convert the γ- to the α-form, the surface areas of the two hydrogen and monoexchanged forms are compared.

EXPERIMENTAL

(i) *Preparation of γ-zirconium phosphate*

The preparation used was similar to that of Clearfield et al.[3], however, the concentration of the zirconyl chloride solution was decreased to allow for a slight water loss over the long reflux period. After initial precipitation, the zirconium phosphate was refluxed in its mother liquor for 2 and 21 days. Samples were allowed to air dry in shallow covered dishes. Samples were also stood over a partial pressure of 12 mm Hg of water vapour.

(ii) *Preparation of α- from γ-zirconium phosphate*

The α crystalline form was prepared by refluxing the γ-form for 30 h in a 50% phosphoric acid/water solution, in the absence of sodium and chloride ions.

(iii) *Preparation of γ-ion exchanged forms (γ-$Zr(HPO_4)(MPO_4)XH_2O$)*

The lithium, sodium, potassium, and caesium exchanged forms were prepared by titrating the appropriate hydroxide against a suspension of γ-zirconium phosphate in distilled water to a constant pH 7 over a period of ~3 h. Titration was carried out using an automatic titration unit with the cell under a flow of nitrogen to exclude carbon dioxide. The product in each case was filtered off and dried as in (i).

(iv) *Chemical analysis*

This was carried out as previously reported for α-zirconium phosphate[2]. Results are given in Table 1.

(v) *Thermal analysis*

DuPont 900 and 950 thermal analysis units were used, details of which have been previously described[2,7].

(vi) *X-Ray powder diffraction*

X-ray analysis was carried out using nickel filtered copper K_α radiation and a 11.48 cm powder camera. Samples were dried at 200°C and sealed in silica tubes. Measurements and intensities were determined using a scanning densitometer. Results are given in Table 2.

TABLE 1

CHEMICAL ANALYSIS OF γ-ZIRCONIUM PHOSPHATE AND ITS ION-EXCHANGED FORMS BASED ON $Zr(HPO_4)(MPO_4)$ WHERE $M = H, Li, Na, K, Cs$

M	*% Zr*		*% PO_4*		*% M*		*xH_2O*	
	Found	*Theory*[a]	*Found*	*Theory*	*Found*	*Theory*	*Air*	*12 mg Hg Water vapour*
H	32.5	32.6	66.9	66.7			2	2
Li	30.9	32.0	66.9	65.3	2.5	2.4	1.5	4.5
Na	29.7	30.3	62.3	61.9	7.5	7.5	1.2	2.6
K	28.1	28.8	60.9	58.8	11.5	12.1	0.25	0.33
Cs	24.28	22.3	46.1	45.6	23.1	31.9	1.4	4.7

[a] Based on an atomic weight of 92.97 for zirconium to allow for the presence of 2% hafnium.

TABLE 2

X-RAY DATA ON ZIRCONIUM PHOSPHATES
2.1 = β-$Zr(HPO_4)(LiPO_4)$; 2.2 = β-$Zr(HPO_4)(NaPO_4)$; 2.3 = β-$Zr(HPO_4)(KPO_4)$; 2.4 = β-$Zr(HPO_4)(CsPO_4)$.

2.1		*2.2*		*2.3*		*2.4*	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
9.80	70	10.34	75	10.82	85	11.91	70
7.02	100	5.62	100	5.70	100		
4.80	10	4.77	40	5.36	5		
4.57	70	4.15	5	4.92	30		
4.24	30	3.92	40	4.80	30		
3.77	85	3.79	85	4.24	30		
3.57	30	3.40	100	3.95	90		
3.38	100	3.30	15	3.85	75		
3.20	40	3.25	25	3.40	100	3.38	100
				3.34	10		
				3.26	40		

TABLE 3

Sample formula	*Surface area ($m^2\ g^{-1}$)*	*Particle size (nm)*	*Morphology*
β-$Zr(HPO_4)_2$ (1)	28.6	$<1\times10^3$	
β-$Zr(HPO_4)_2$ (2)	27.9	15×10^3	Fibrous
α-$Zr(HPO_4)_2$[a]	6.5	5×10^3	Hexagonal plates
β-$Zr(HPO_4)(LiPO_4)$	9.2	$<1\times10^3$	
β-$Zr(HPO_4)(NaPO_4)$	27.8	18×10^3	Fibrous
β-$Zr(HPO_4)(KPO_4)$	28.9	14×10^3	Fibrous
β-$Zr(HPO_4)(CsPO_4)$	20.5	25×10^3	Fibrous

[a] Prepared from γ-$Zr(HPO_4)_2$ sample (2).

(vii) *Scanning electron microscopy*

A Cambridge Stereoscan electron microscope was used to photograph the particles and establish their morphology. Results are given in Table 3.

(viii) *Surface area*

Surface areas were determined using a "single point" adsorption apparatus similar to that described by Klyachko-Gurvich[8]. Details of the apparatus and calculation will be described in a later paper[9]. Results are given in Table 3.

RESULTS AND DISCUSSION

(i) *γ-Zirconium phosphate*

The effect of extending the reflux time in the preparation of the γ-form was to increase crystallinity, as shown by the particle size determined from scanning electron microscope results (Table 3). Refluxing affects the thermal properties as illustrated by the DTG traces (Fig. 1) showing a down-ward temperature shift of all three peaks with the increase in crystallite size. This difference is not shown by the surface area results, however, as the result obtained by Horseley[6] (using a BET apparatus) of 27.6 m^2 g^{-1} compares very well with both samples measured (Table 3). This indicates

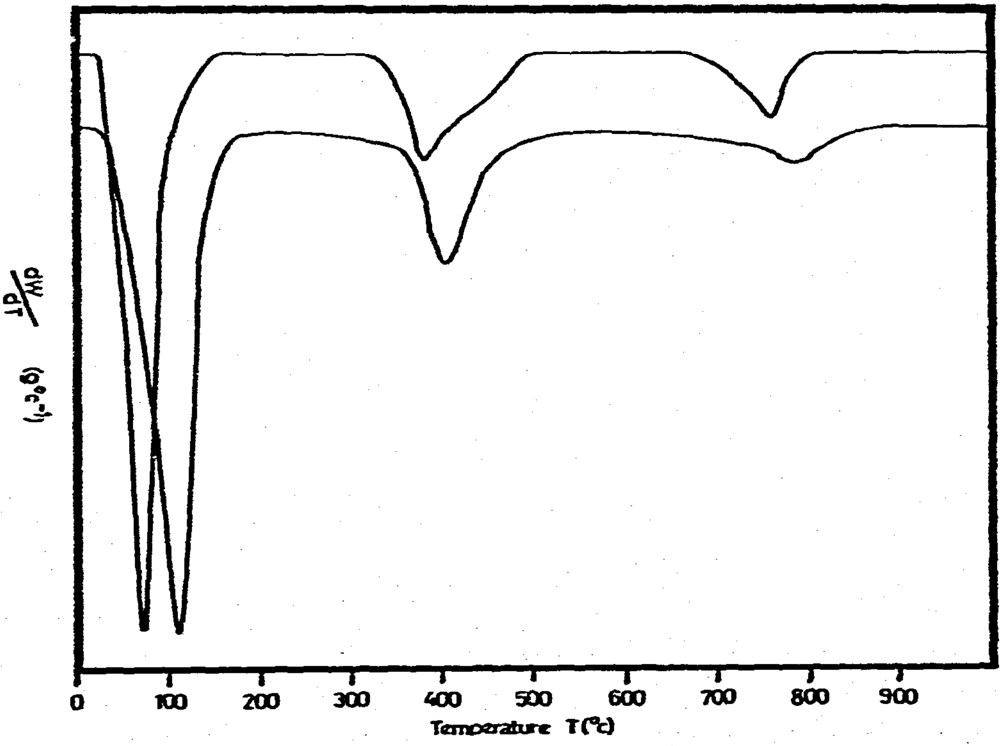


Fig. 1. DTG traces of γ-$Zr(HPO_4)_2 \cdot 2H_2O$ showing the effect of increased crystallinity. The top graph refers to 21 days reflux, the bottom graph to 2 days reflux.

that the surface areas quoted are predominantly due to porosity, i.e., the nitrogen molecules are penetrating between the layers of the γ-lattice. This is in direct contrast to results obtained by Horseley[14] for the α-form, where surface areas are much lower, and tend to be unique to each preparation, as the smaller lattice spacing will not allow the nitrogen molecules to penetrate between layers.

The γ-form has a fibrous crystal structure as opposed to the hexagonal plates of the α-form (Table 3)[2]. The difference in thermal properties has been reported previously[4,7]. The conversion obtained from γ- to α-zirconium phosphate is probably due to the γ-form being unstable at reflux temperature (~110°C) without the presence of sodium ions to stabalise the relative position of the phosphate groups. It may also be partially due to the excess of phosphate, and absence of chloride, as work by Matijevic et al.[10,11] concerning the effect of anions indicates that phosphate (and sulphate) favour hexagonal crystal configurations, whereas chloride (as present in the γ-form preparation) tends to favour needle formation.

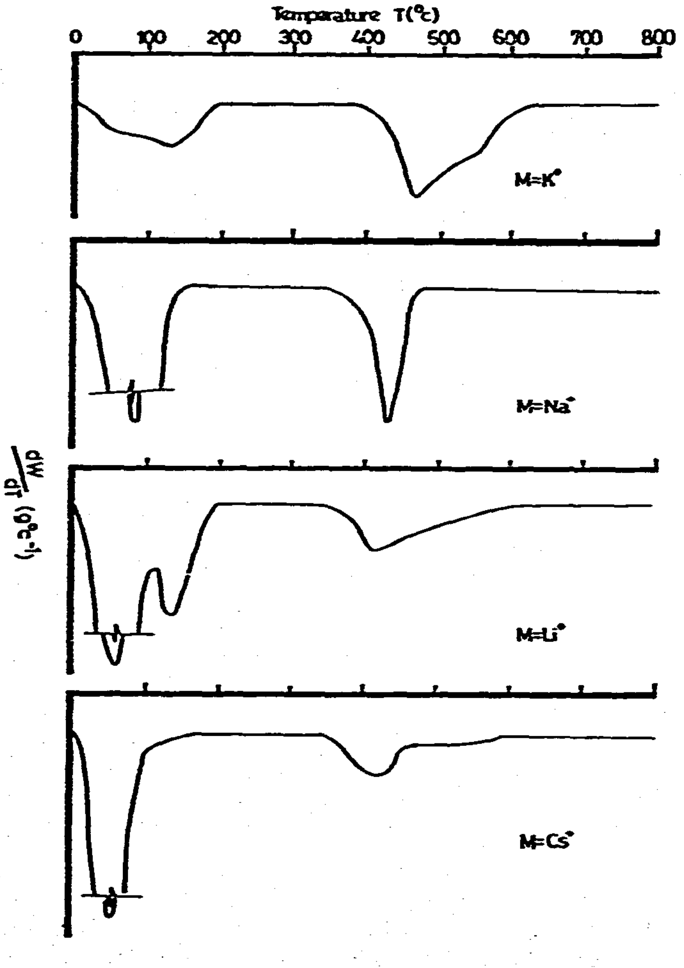
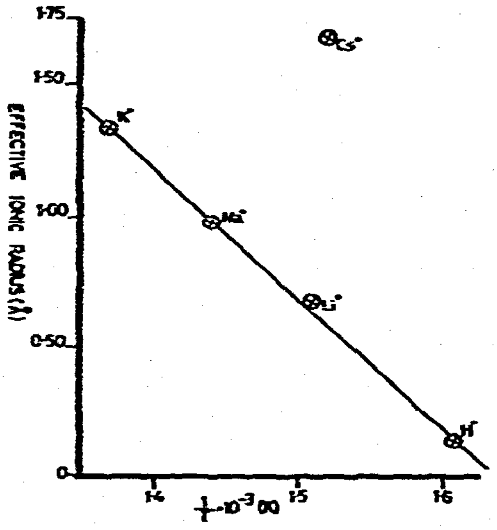


Fig. 2. DTG curves of γ-$Zr(HPO_4)(MPO_4)\cdot xH_2O$.

(ii) *Ion-exchanged forms* γ-$Zr(HPO_4)(MPO_4)\cdot xH_2O$

The caesium exchanged γ-zirconium phosphate only contains 21.8% caesium (theoretical amount 31.4%) although the same preparative method was used as in the other ion-exchanged forms. This low exchange value is reflected in the large size of the caesium ion which may have difficulty entering the cationic positions in the lattice, i.e., between phosphate groups of adjacent layers[3]. However, it is interesting to note that, in the case of the α-form which has an even smaller lattice spacing, work by Alberti et al.[12,15] shows the caesium exchanged form being prepared by substitution in the monosodium exchanged form. It may be, therefore, that the theoretical exchange value can be obtained using a similar method or perhaps by titrating in the presence of chloride[16]. Figure 2 shows the DTG traces of the various mono ion-exchanged materials. It can be seen from these and Fig. 3 (a graph of reciprocal temperature against effective ionic radius) that the peak temperature of the caesium form is obviously low, i.e., the peak temperature, measured from DSC traces, corresponding to the decomposition of the orthophosphate. This is due to discontinuities of the crystal structure caused by the low exchange of caesium.



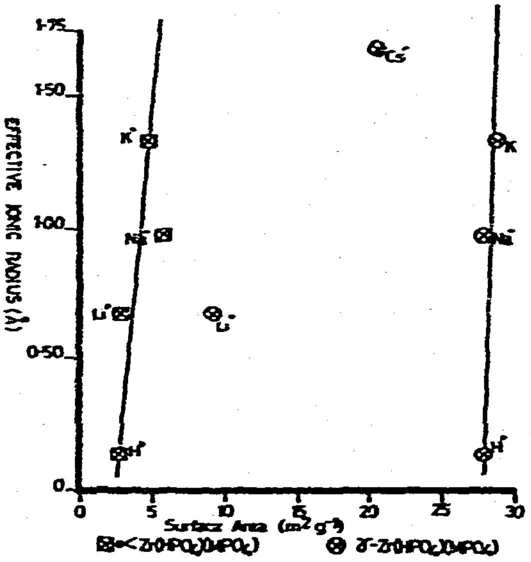


Fig. 3. Graph of effective ionic radius against reciprocal temperature.

Fig. 4. Graph of effective ionic radius against surface area.

The basis for the plot given in Fig. 4 is work done by Dollimore et al.[13] on the decomposition of metal oxalates, in which decomposition temperature is related to the lattice energy of the solid. For the zirconium phosphate system we have:

$$2Zr(HPO_4)(MPO_4) \rightarrow 2ZrP_2O_7 + H_2O + M_2O \tag{1}$$

(where M is the appropriate metal ion)

The lattice energy E_0 is given by:

$$E_0 = \frac{e^2 x}{r_i}$$

where e = charge on the ion;
r_i = separation of ions;
x = constant.

thus when $e = 1$

$$T_D = \frac{\text{constant}}{r_m + r_{\text{phosphate}}}$$

where T_D = peak decomposition temperature;
r_m = radius of metal cation;
$r_{\text{phosphate}}$ = radius of phosphate ion.

∴ rearranging

$$\frac{1}{T_D} = \frac{r_m}{\text{constant}} + \frac{r_{\text{phosphate}}}{\text{constant}}$$

It should be noted that the crystallinity of the sample can affect the peak temperature to some extent as shown earlier (Fig. 1). This can account for the value of the lithium ion being slightly low, but is not sufficient to explain the very low value given by caesium.

The surface area results for the mono ion-exchanged materials again illustrate that the values determined mainly indicate porosity (Table 3), as the nitrogen molecules can enter the lattice of the Na, K and Cs materials giving very similar values (Cs being slightly lower than H, Na, K due to its larger crystal size). The value for lithium is interesting. A value greater than for H, Na, K, or Cs would be expected due to the loss of crystallinity shown by scanning electron microscopy and comparison of DTG analyses (Fig. 3). The low value, however, is probably due to the small size and high polarising power of the lithium ion which draws adjacent layers sufficiently close that the lattice collapses, destroying much of the crystallinity and preventing nitrogen molecules from entering. The area determined is, therefore, due to the outer surface. A value similar to that of the α-Zr(HPO$_4$)(LiPO$_4$) would be expected if crystallinity had not been appreciably reduced[6]. Comparing the mono ion exchanged α-zirconium phosphates with the mono γ-exchanged forms in Fig. 4 where, although the crystal size is of a similar order of magnitude, the very much greater surface areas of the γ-forms (with the exception of lithium) show the penetration of the nitrogen molecules into the lattice.

The X-ray diffraction data show the corresponding increase of interlayer distance with ionic radius from lithium to caesium (of first d spacing value in each case). The powder photograph of the caesium-exchanged material, however, is less well-defined, and appears a mixture. This would be expected from the low exchange value found for caesium, and may be analogous to the solid solution systems found by Alberti et al.[15] on producing various stages of ion exchange on the α-form.

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