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FORMATION AND THERMAL DECOMPOSITION OF PYRIDINE INTERCALATES OF α- and γ-ZIRCONIUM PHOSPHATES

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ABSTRACT

The intercalation of pyridine into α-ZrP takes place with an accompanying uptake of one more mole of water to form a dihydrate $Zr(HPO_4)_{1.55}(C_5H_5NHPO_4)_{0.45} \cdot 2\,H_2O$ which has an interlayer spacing of 10.9 Å and contains two types of water with different thermostabilities. The pyridine intercalate of γ-ZrP with 12.3 Å spacing is formed by the replacement of interlayer water by the gest molecules without any appreciable change in interlayer spacing and its composition is $Zr(HPO_4)_{1.56}(C_5H_5NHPO_4)_{0.44} \cdot 0.7\,H_2O$. The α-intercalate undergoes dehydration at below 140°C, accompanied by its separation into a pyridine-free phase (ζ-ZrP) and a pyridine enriched one, and this dehydration is immediately followed by the desorption of pyridine, resulting in the overall conversion of the initial phase to ζ-ZrP. The γ-intercalate, on the other hand, releases its water without any phase separation at similar temperatures but its depyridination temperature at 250°C is about 110°C higher than that for the other. A molecular packing model is proposed to explain the interlayer spacings, compositions, and thermal decomposition properties of both intercalates.

INTRODUCTION

The family of layered, ion exchanger zirconium phosphate (ZrP) is represented by two basic phases: α-ZrP, $Zr(HPO_4)_2 \cdot H_2O$, with an interlayer spacing of 7.6 Å [1]; and a dihydrate, $Zr(HPO_4)_2 \cdot 2\,H_2O$, with an interlayer spacing of 12.3 Å, labelled γ-ZrP [2]. These two phases are also known to behave as good intercalating agents of a variety of polar organic molecules. Much attention has been paid to the intercalation behavior of α-ZrP toward various compounds, including alkyl amines [3–7] and amides [3]. The intercalation of pyridine into α-ZrP has also been studied by Yamanaka et al. [5]. Very few papers, however, have been published on the intercalation properties of γ-ZrP, i.e., concerning the intercalation of alkanols and alkyl amines [7].

Although the crystal structure of α-ZrP was elucidated by Clearfield and Smith [1], the structure of γ-ZrP has not yet been resolved and it has been postulated that the essential difference between the two phases is the relative

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position of the phosphate groups in adjacent layers, and within the layers the structure is the same [2]. Recently, however, several authors [7–9] suggested that these two phases differ from one another also in the structure of the layers.

The situation described above arouses our interest in a comparative study on the intercalation compounds of α- and γ-ZrP. The present paper describes first the intercalation of pyridine into α- and γ-ZrP and second the thermal decomposition behavior of the resulting intercalates.

EXPERIMENTAL

Reagents

The α-ZrP sample used, $Zr(HPO_4)_2 \cdot H_2O$, was the same as referred to as ZrP-H in ref. 10. The γ form of ZrP, $Zr(HPO_4)_2 \cdot 2\,H_2O$, was prepared by the method of ref. 2. $ZrOCl_2$ solution (1 mole dm^{-3}, 225 cm^3) was added dropwise to 450 cm^3 of a boiling solution of 6 mole dm^{-3} in NaH_2PO_4 and 2 mole dm^{-3} in HCl, and the resulting precipitate was refluxed for 14 days. After filtration, the refluxed material was regenerated with 2 N HCl and washed with distilled water to remove chloride ion and then dried in air at room temperature. Pyridine was dried and distilled prior to use.

Equilibrations

Exactly 0.1 g of ZrP was added to 20 cm^3 of aqueous pyridine solution at various concentrations. After shaking at 25 ± 0.5°C for 3 days, the mixture was centrifuged and half of the resulting solid was dried in air by equilibrating in a room kept at $P/P_0 = 0.60 \pm 0.05$ in humidity at 25°C for a month or more. The pH of the supernatants was measured using a Toa autotitrator and the uptake amounts of pyridine were obtained as differences between the initial and final concentrations determined by the colorimetric method using the absorbance at 256 nm. Room temperature X-ray diffraction patterns were taken of the wet and dried samples with a Toshiba diffractometer using CuK_α rays.

Heating experiment

Thermogravimetry (TG) was made on the dried samples using a Shinkuriko thermogravimetric analyzer with a heating rate of 10°C min^{-1}. X-Ray diffraction measurements at elevated temperatures were conducted using a Nippon-denshi high temperature X-ray diffractometer as follows. The dried sample was placed on a platinum plate and heated by applying an electric current to the plate. The sample temperature was calibrated by referring to the IV → III, III → II, and II → I transition temperatures of powdered NH_4NO_3 [11] which were detected by observing one or two preselected diffraction peaks characteristic of each lower temperature phase to disappear during stepped heating. X-Ray diffraction patterns in the 2θ range 7–15° were taken with a scanning rate of $1° \ 2\theta \ \mathrm{min}^{-1}$ at about 20° or 40°C intervals, while the sample temperature was increased stepwise to each predetermined value and then held for 10 min prior to each scanning.

RESULTS

Intercalation process

Yamanaka et al. [5] reported that the intercalation of pyridine (Py) into α-ZrP proceeded without any appreciable change in water content and a monohydrate phase $Zr(HPO_4)_{1.55}(PyHPO_4)_{0.45} \cdot H_2O$ with an interlayer spacing of 10.9 Å was formed. In preparing the pyridine intercalate of α-ZrP for the thermal decomposition experiment, the intercalation behaviour was re-examined. The titration and X-ray data obtained agreed well with the previous report. However, the TG data described later, which were used to determine the pyridine and water contents in the intercalate, indicated that the intercalation takes place with an accompanying uptake of one more mole of water to form a dihydrate, $Zr(HPO_4)_{1.55}(PyHPO_4)_{0.45} \cdot 2\,H_2O$, containing two types of water in equal amounts. The pyridine content obtained from the TG data was equal to that obtained by the solution analysis. As seen from the TG and X-ray data described later, the different conclusion of Yamanaka et al. [5] is probably because the intercalated sample was dried in excess prior to the TGA analysis whereas it was used in a wet state in the X-ray measurements. Thus, the intercalation process of pyridine into α-ZrP can be given as

$$Zr(HPO_4)_2 \cdot H_2O\ (7.6\,\text{Å}) \xrightarrow{\text{Py in } H_2O} Zr(HPO_4)_{1.55}(PyHPO_4)_{0.45} \cdot 2\,H_2O\ (10.9\,\text{Å}) \tag{1}$$

As Fig. 1 shows, the titration curve for γ-ZrP was similar to that for α-ZrP and indicated only one end point at an addition level of about 2 mmole g^{-1}. The X-ray observations on the solid phases obtained in the course of the pyridine uptake process for γ-ZrP were also similar to those for α-ZrP [5]. With an increase in addition level up to 2 mmole g^{-1}, the host phase, γ-ZrP, decreased, while an intercalated phase with an interlayer spacing of 12.3 Å appeared and increased remarkably. At higher addition levels, only the intercalated phase was observed. The same X-ray pattern was observed on both the wet and dried samples (Table 1). The first reflection in the intercalate agrees closely with that in γ-ZrP [2] but many of the reflections at

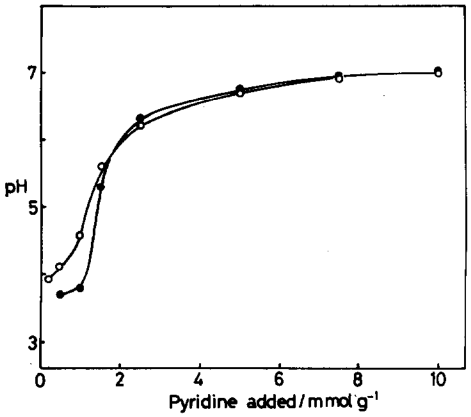

Fig. 1. Potentiometric titration curves for α- and γ-ZrP with pyridine: ○, α-ZrP; ●, γ-ZrP.

higher 2θ values are different. From the TG data described later, the composition of the intercalate was determined to be $Zr(HPO_4)_{1.56}(PyHPO_4)_{0.44} \cdot 0.67\,H_2O$. A value of 0.44 for the pyridine content was also in good agreement with 0.45, obtained from the solution analysis. On the basis of the above data and observations, the intercalation process of pyridine into γ-ZrP can be written as

$$Zr(HPO_4)_2 \cdot 2\,H_2O\ (12.3\ \text{Å}) \xrightarrow{\text{Py in } H_2O} Zr(HPO_4)_{1.56}(PyHPO_4)_{0.44} \cdot 0.7\,H_2O\ (12.3\ \text{Å}) \qquad (2)$$

Reactions (1) and (2) assume that the pyridine molecules are intercalated as pyridinium ions into the α- and γ-ZrP crystals. This was confirmed by a preliminary experiment on the IR absorption of the intercalated solids obtained, in which the 1640 and 1545 cm^{-1} bands attributable to pyridinium ion [12] were observed. According to Yamanaka et al. [5], reaction (1) would

TABLE 1

X-Ray diffraction pattern of the pyridine intercalate of γ-ZrP

d (Å)	I/I_0
12.3	100
6.39	14
5.12	14
4.49	8
3.63	24
3.29	38
2.68	6

proceed predominantly by the transfer of the protons of phosphate groups to unionized pyridine and only partly by the ion exchange between the protons and the pyridinium cations formed in strongly acidic solution. The same explanation will be applicable to reaction (2).

Thermal decomposition of the intercalated phases

Figure 2 shows the weight loss vs. temperature curves for the two intercalated phases of α- and γ-ZrP, which will hereafter be referred to as α- and γ-intercalates, respectively. The weight loss vs. temperature data obtained on both intercalates using the same heating processes as used in the X-ray measurements were in fair agreement with those of Fig. 2. The α-intercalate showed four distinct weight losses during heating up to 1000°C and was finally converted to α-ZrP_2O_7. The first and second weight losses are equal in amount and both are due to the desorption of water. This fact suggests that the α-intercalate possesses two types of water with different thermostabilities, one desorbed at below 70°C and the other desorbed at higher temperatures. These two types of water will be denoted as types I and II, respectively. As explained previously [5], the third weight loss which commences at 142°C can be attributed to the desorption of pyridine and the fourth starting at 440°C can be correlated with the condensation of phosphate groups and the decomposition of carbonized pyridine.

The X-ray patterns of the α-intercalate at different temperatures are shown in Fig. 3. At 35°C, in the course of the first dehydration process, the α-intercalate was converted totally to a mixture of phases whose interlayer spacings are 10.4 Å and 9.94 Å. These two phases will be termed M and M′,

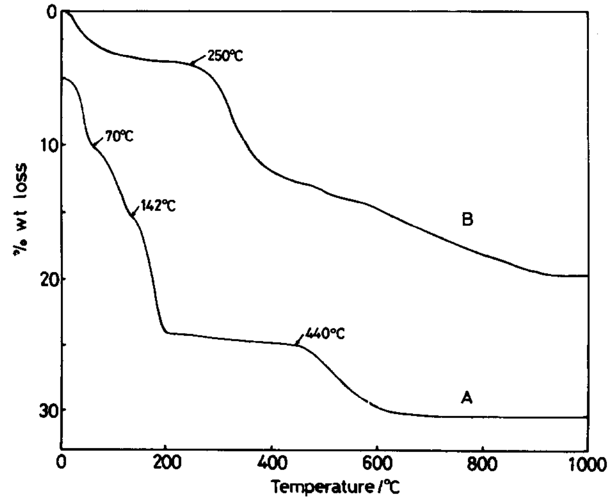

Fig. 2. TG curves for the pyridine intercalates of (A) α-ZrP, and (B) γ-ZrP. The vertical scale for (A) is shifted by 5%.

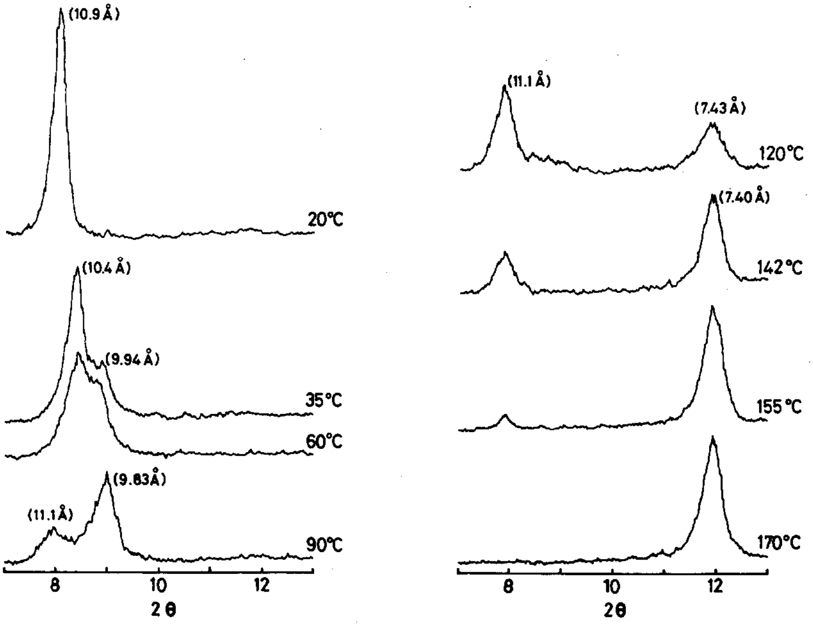

Fig. 3. X-Ray diffraction patterns of the pyridine intercalate of α-ZrP at various temperatures. The interlayer spacing (Å) corresponding to each diffraction peak is given in parentheses.

respectively. This finding indicates that the water of type I is present within the interlayer region of the α-intercalate and readily removed even by heating up to 35°C. The M and M′ phases were also observed at 60°C, but for a very little shift in position and slight decrease in intensity of each diffraction peak. During the second dehydration process below 140°C, these two phases were gradually converted to phases with spacings of 11.1 Å and 7.40 Å, respectively. It is apparent that the latter phase corresponds to anhydrous ζ-ZrP with a spacing of 7.41 Å [13]. The 11.1 Å phase, on the other hand, can be regarded as being an anhydrous phase with an increased pyridine content, but not identical with the anhydrous form of the original α-intercalate. This interpretation is compatible with the fact that the 11.1 Å phase has expanded its layers over the dihydrated α-intercalate. It is probable that the formation of interlayer holes due to dehydration induces the migration of pyridine molecules within the interlayer space, resulting in separation of the initial phase into a pyridine-free pase and a pyridine-enriched one. With a further increase in temperature, the 11.1 Å phase was also depyridinated into ζ-ZrP and at 170°C only the latter phase was observed. As suggested also by the TGA data, the decomposition behavior at higher temperatures would be the same as that of α-ZrP [13]. The decomposition process of the α-intercalate can thus be summarized as

$$\begin{aligned}&\mathrm{ZrP(Py)}\cdot 2\,\mathrm{H_2O}\ (10.9\,\text{Å}) \xrightarrow[-\mathrm{H_2O(I)}]{30\text{–}70^\circ\mathrm{C}} \mathrm{M}\ (10.4\,\text{Å})\\ &\quad + \mathrm{M}'\ (9.94\,\text{Å}) \xrightarrow[-\mathrm{H_2O(II)}]{70\text{–}140^\circ\mathrm{C}} \overline{\mathrm{ZrP(Py)}}\ (11.1\,\text{Å})\\ &+ \zeta\text{-ZrP}\ (7.4\,\text{Å}) \xrightarrow[-\mathrm{Py}]{140^\circ\mathrm{C}<} \zeta\text{-ZrP}\ (7.4\,\text{Å}) \rightarrow \alpha\text{-}\mathrm{ZrP_2O_7}\end{aligned} \qquad (3)$$

In eqns. (3) and (4) the abbreviations ZrP(Py) and $\overline{\mathrm{ZrP(Py)}}$ are used to represent the intercalates with the same pyridine contents as in the original ones and that with an increased amount of pyridine, respectively.

As shown in Fig. 2, the TG curve for the γ-intercalate showed three distinct weight losses, and the final product was the same as previously. The first weight loss at below 150°C is due to the desorption of water. With the aid of the observation that the condensation of phosphate groups in γ-ZrP occurs in two steps between 350 and 880°C, in agreement with a previous report [14], the second weight loss observed between 250 and 400°C could be attributed mostly to depyridination and partly to the first step of condensation. The third weight loss at higher temperatures could be explained in the same way as the fourth weight loss for the α-intercalate.

Figure 4 plots the interlayer spacing and the ratio $\%I=(I/I_0)\times 100$ for the γ-intercalate, as a function of temperature, where I is the intensity of the first X-ray reflection peak and I_0 is the I value at room temperature. In the light of the TG data described above, the first decrease in the interlayer spacing at below 100°C can be correlated with the transformation of the γ-intercalate to its anhydrous form. In the temperature range 260–350°C, this anhydride showed a remarkable and continuous decrease in the inter-

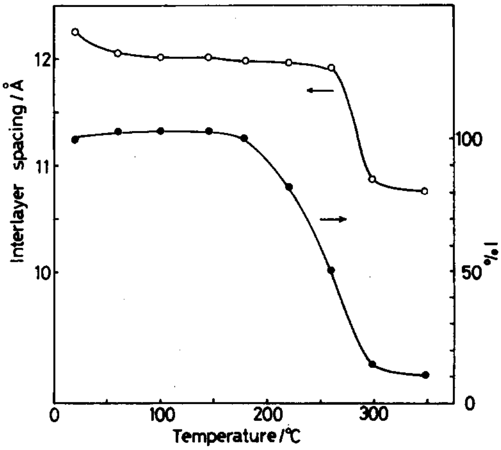

Fig. 4. Interlayer spacings and $\%I$ (see text) of the pyridine intercalate of γ-ZrP as a function of temperature.

layer spacing and crystallinity and was finally converted to a poorly crystalline phase with a spacing of 10.8 Å, due to the desorption of pyridine. The 10.8 Å phase showed a tendency to become amorphous with further increase in temperature. The remarkable decrease in the %*I* value at below 200°C indicates that the anhydrous pyridine intercalate would become progressively disordered prior to depyridination. Thus, the decomposition process of the γ-intercalate can be represented as

$$\mathrm{ZrP(Py)\cdot 0.7\,H_2O\ (12.3\,\text{Å})} \xrightarrow[-\mathrm{H_2O}]{30\text{–}100^\circ\mathrm{C}} \mathrm{ZrP(Py)\ (12.0\,\text{Å})} \xrightarrow[\text{disordering}]{180^\circ\mathrm{C}}$$

$$\text{disordered }\mathrm{ZrP(Py)\ (11.9\,\text{Å})} \xrightarrow[-\mathrm{Py}]{250\text{–}350^\circ\mathrm{C}} \mathrm{ZrP\ (10.8\,\text{Å})}$$

$$\rightarrow \alpha\text{-}\mathrm{ZrP_2O_7} \qquad (4)$$

It is noticed that the depyridinated form of the γ-intercalate has more expanded layers compared to the anhydrous phase of γ-ZrP, which has an interlayer spacing of 9.4 Å, and is labelled β-ZrP [2].

DISCUSSION

The α-intercalate has expanded its layer by 3.5 Å over that in the anhydrous form of its host phase (ζ-ZrP). This value corresponds closely to 3.4 Å for the Van der Waals thickness of pyridine [15,16], indicating that the interlayer space in the intercalate would be occupied by a monolayer of pyridine molecules placed nearly flat to the ZrP planes. If we assume that pyridine molecules 7.3 Å in diameter are hexagonally closest-packed as a monolayer, the effective area per molecule is $2\sqrt{3} \times (7.3/2)^2$ or 46.1 Å^2. Since the occupied area per POH site in α-ZrP is 24.3 Å^2 [10], the pyridine content, x, in mole per formula weight of α-ZrP can be evaluated to be $2 \times (24.3/46.1)/2$ or 0.53. The observed and calculated values of x for the α-intercalate yield a value of 85% for the interlayer occupancy of pyridine about 142 Å^3 in molecular volume. It is more interesting that the difference of 0.08 mole between the calculated and the observed values of x corresponds in volume to 0.8 mole of water about 14 Å^3 in volume [17]. This means that nearly one mole of water per formula weight of α-ZrP occupies the vacant space in a loosely packed layer of pyridine and that the remaining one mole of water contributes little to the expansion of the ZrP layers. Such a packing manner is permissible by assuming that most of the latter one mole of water is placed midway between any two POH sites on the layer surface and held by bifurcated hydrogen bonds, similar to water in α-ZrP [18]. This is because the water molecules held by such a hydrogen bond are predicted to expand the ZrP layers only slightly, as suggested by the difference of 0.2 Å between the interlayer spacings of α- and ζ-ZrP. This type of water is likely to originate in the host phase and to be thermally stable, and it can therefore be assigned to water of type II. On the other hand, the water molecules located within the interlayer space would be weakly held by hydrogen bonding to one hydrogen atom of the layer surface water and by hydrophobic interaction with the pyridine molecules. The unstable type of water which is probably taken up together with pyridine is assignable to water of type I. The above assignment of intracrystalline water is also consistent with the TG observation that the amounts of water of types I and II in α-intercalate are equal.

Since the difference of 2.9 Å between the interlayer spacings of γ-intercalate and β-ZrP also suggests the flat configuration of pyridine molecules, a similar consideration will be applicable to the case of γ-intercalation. On the plausible assumption that the water molecules in γ-ZrP are weakly held by interlayer hydrogen bonding to the POH sites [2,9], the observed decrease of 1.3 moles of water in the intercalation process could be explained in terms of the replacement of interlayer water by the large gest molecules and the remaining 0.7 mole of water could be regarded as being located within the intercalation layer. Then the expected maximum value of x for the γ-intercalate is 0.44 plus 0.07 or 0.51, yielding a value of 23.5 $Å^2$ for the occupied area per POH site in γ-ZrP. This value is a little less than that for α-ZrP but is much more than 17.8 $Å^2$ reported previously [7].

The intercalation compounds of α- and γ-ZrP with strong base *n*-butylamine have similar temperatures of deamination at 230°C [6,7]. In contrast to this, the depyridination temperature for the γ-intercalate at 250°C is about 110°C higher than that for the α-intercalate. As suggested by the phase separation observed at low temperatures, the pyridine molecules intercalated into α-ZrP may be so weakly held that the intercalate is stabilized by the introduction of interlayer water into the vacant space between the gest molecules. On the other hand, the high thermostability of the γ-intercalate is probably because the pyridine molecule with a flat configuration fits the interlayer space of the host crystal so closely as to be strongly held without any reinforcement by water molecules. Further investigation, however, will be necessary to explain fully the different thermostabilities of both intercalates due to the structural differences of their host phases.

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