



Intercalation of *N,N*-dimethyl-1-phenylethylamine into α -Zirconium Phosphate

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(Received: 16 October 2000; in final form: 4 September 2001)

Key words: intercalation, de-intercalation, ion exchange, zirconium phosphate, phenylethylamine, layered compound

Abstract

The intercalation and deintercalation of *N,N*-dimethyl-1-phenylethylamine (*N,N*-amine) into α -zirconium phosphate was investigated by pH titration. *N,N*-amine was taken up easily in one step to give a new phase $\text{Zr}(\text{HPO}_4)(\text{HPO}_4 \cdot \text{N,N}\text{-amine}) \cdot \text{H}_2\text{O}$, which was characterized by X-ray diffractometry, IR spectroscopy, and thermal analysis. The release of *N,N*-amine from the solid was found to be irreversible due to structural changes in both the intercalation and deintercalation reactions.

Introduction

The layered structure of α -zirconium phosphate makes the compound useful not only as an inorganic ion-exchanger, but also as a host compound for intercalation reactions [1]. Many organic compounds have been investigated as possible guests, the size and polarity of which determine the intercalation behavior.

The intercalation of ring-structured amino derivatives (aromatic or heterocyclic) exhibiting pharmacological activity has been reported by a number of researchers; Kijima *et al.* have investigated the uptake of a range of amino acids, and Costantino *et al.* have examined the intercalation of heterocyclic compounds incorporating an imidazole ring [2, 3]. Derivatives of 2-phenylethylamine are widely known to have physiological and psychological effects, and one of the present authors has successfully intercalated 1- and 2-phenylethylamine into α -zirconium phosphate and detailed the intercalation mechanism [4].

In this study, *N,N*-dimethyl-1-phenylethylamine (abbreviated *N,N*-amine) was used as a guest for intercalation and deintercalation with α -ZrP.

Experimental

Reagents

Zirconium (IV) oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, reagent grade), potassium fluoride (KF, reagent grade, 99%), phosphoric acid (H_3PO_4 , reagent grade, 85%) and perchloric acid (HClO_4 , reagent grade, 60%) were purchased from Wako Pure Chemical Industry Co. Ltd., and hydrochloric acid (reagent grade, concentration 35–37%) was obtained from Kokusan Chemical Co. Ltd. (*R*)-*N,N*-dimethyl-1-phenylethylamine was obtained from Tokyo Kasei Co. Ltd. All chemicals were used without further purification.

Preparation of α -zirconium phosphate

α -Zirconium phosphate (abbreviated α -ZrP) was prepared according to the direct precipitation method reported in a previous study [5]: 32.0 g of zirconium oxychloride octahydrate was dissolved in 168 mL of distilled water, followed by the addition of 60 mL of 60% perchloric acid. Then 22.32 g of potassium fluoride was added under continuous stirring with a magnetic stirrer, with the subsequent drop-wise addition of 172 mL of phosphoric acid, still under continuous stirring. The solution was placed in a water bath (50 °C) and prehumidified air was bubbled through the solution for 48 hours. The precipitate obtained was washed with distilled water until the pH of the supernatant became approximately 5. The α -ZrP product was then confirmed by X-ray powder diffractometry.

Procedure for intercalation and deintercalation of *N,N*-amine

Intercalation reactions were carried out in batches by pH titration.

Intercalation (forward titration)

Intercalation (forward) was carried out according to two procedures. In the first procedure, the amine and an *N,N*-ammonium chloride solution were employed. The total concentration of amine and its chloride solution was 0.1 mol/l with a molar ratio of between 0 and 9, corresponding to 100 mg of α -ZrP was 100 mg in a 10.0 mL solution. The mixture was shaken continuously at 25 °C for a specified period of time. The second procedure involved titrating with *N,N*-amine alone in order to examine the selectivity of α -ZrP for *N,N*-amine.

To prepare the new phase, a slight excess of *N,N*-amine relative to the ion-exchange capacity of α -ZrP was added to a weighed amount of the exchanger. The mixture was shaken at 25 °C for at least 96 h, and then the solid phase

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was centrifuged, washed with distilled water and air-dried at room temperature. The new phase obtained is referred to here as ZrP-NN.

Deintercalation (backward titration)

Deintercalation was also carried out according to two separate procedures. In the first procedure, a weighed amount of ZrP-NN (143 mg) was placed in an ampule. Hydrochloric acid (0.1 mol/l) and *N,N*-ammonium chloride solution (6.64 mL) were then added to the ZrP-NN. The volume of added hydrochloric acid was varied between 0.3 and 3.3 mL, and the total volume was adjusted to 10 mL with distilled water. The second procedure was identical except for the use of hydrochloric acid alone. The mixture was shaken continuously at 25 °C for a specified period of time.

Analytical procedure

X-ray powder diffractometry

The change in the interlayer distance of the solid phase was examined by X-ray powder diffractometry (RAD-II C, Rigaku Denki Co. Ltd.) using Ni-filtered CuK α radiation ($\lambda = 0.1542$ nm). The interlayer distance was examined under wet conditions with the sample covered with Mylar film to prevent it from drying. Dry samples were prepared by drying wet samples in air at room temperature.

Infrared spectroscopy

Infrared spectra were obtained by the KBr method on a Perkin-Elmer 1600 FT-IR spectrophotometer.

Thermal analysis

Thermogravimetric and differential thermal analysis (TG-DTA) was conducted on a RIGAKU TAS-200 thermo-analyzer in a static air atmosphere or under flowing nitrogen using α -alumina as a reference compound at temperatures between 25 and 600 °C at a heating rate of 10 °C/min. Ignition loss was measured using a platinum crucible.

Results and discussion

Intercalation (forward)

The following experiments were performed in order to determine the equilibration time. First, 10 mL of *N,N*-amine aqueous solution (0.1 mol/l) was added to 100 mg of α -ZrP in an ampule. The mixture was then shaken continuously at 25 °C in a water bath for 4–14 days. After a designated time, the pH value of the supernatant was measured and the change in the interlayer distance of the solid phase was recorded by X-ray diffractometry. The equilibration time was obtained within 8 days. In the following work, a reaction time of 10 days was employed.

To estimate the pK_b of the *N,N*-amine, the amine was titrated with hydrochloric acid. The apparent pK_b value of the *N,N*-amine was found to be approximately 4.8, which is consistent with that of ammonia. The intercalation of ammonia ($pK_b = 4.65$), cyclohexylamine ($pK_b = 3.36$) and

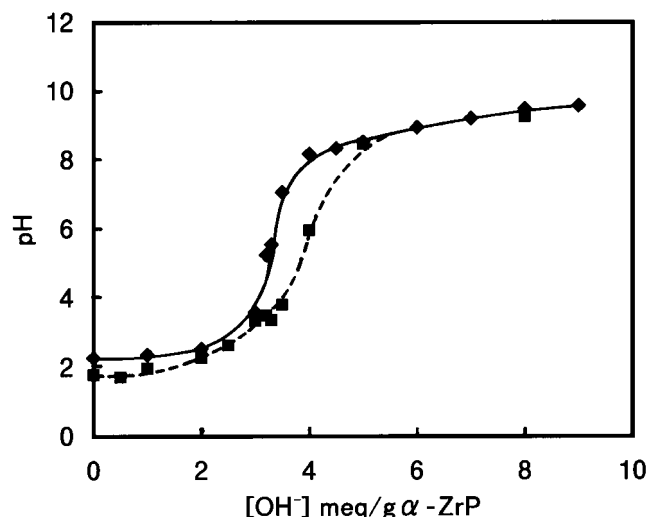
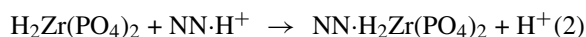
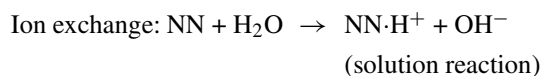
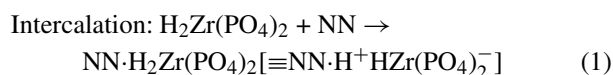


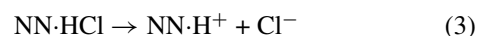
Figure 1. Titration curves with *N,N*-dimethyl-1-phenylethylamine and its chloride. ■: forward, ◆: backward.

dl-phenylethylamine ($pK_b = 4.92$) has been investigated in previous works [4–7]. These compounds were found to be taken up easily into the interlayer region of α -ZrP, indicating that the intercalation of *N,N*-amine occurs easily if molecular size is not an issue. The amine hydrochloride aqueous solution can be prepared easily by adding hydrochloric acid to *N,N*-amine solution and adjusting the pH to an equivalence point of approximately 5.

Figure 1 shows the titration curve for α -ZrP with *N,N*-amine and its chloride. As (S)-*N,N*-amine gave the same titration curve, only (R)-*N,N*-amine was used in the following experiments. *N,N*-amine was taken up at relatively low pH, as expected from the pK_b of the *N,N*-amine ($pK_b \cong 4.8$)(curve (a)). In an aqueous solution, two reactions are possible between α -ZrP and *N,N*-amine, as follows:



When *N,N*-ammonium chloride is present, the following reaction is involved:



The decrease in pH indicates that the resultant cationic species will react easily with exchangeable protons in α -ZrP. The uptake reaction proceeded in a single step, intercalating 3.3 mEq of *N,N*-amine into 1 g of α -ZrP, indicating that half the protons in α -ZrP are involved in the intercalation of *N,N*-amine. This titration behavior differs from that of 1- and 2-phenylethylamine and cyclohexylamine [4, 6].

Figure 2 shows the titration curve for *N,N*-amine (curve (a)), which indicates that all the added amines up to 3.3 mEq/g are taken up in one step. This finding is the

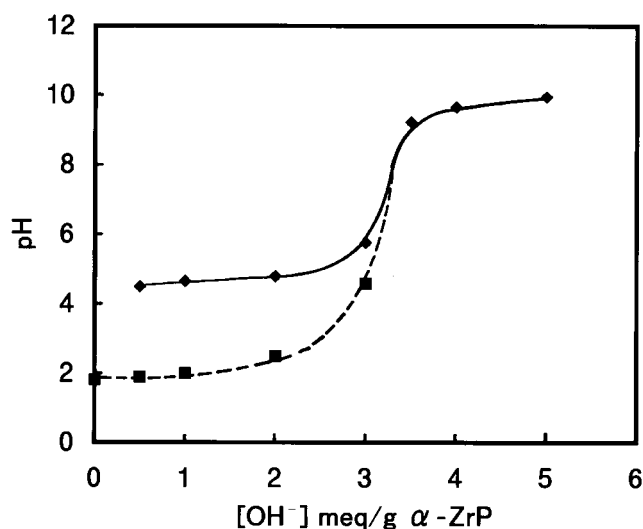


Figure 2. Titration curves with only *N,N*-dimethyl-1-phenylethyl-amine.

same as for the system using the amines and *N,N*-ammonium chloride.

α -ZrP takes up 4.4 mEq/g of 1-phenylethylamine and 6.6 mEq/g of 2-phenylethylamine. However, only 3.3 mEq/g *N,N*-amine is intercalated into α -ZrP, reflecting the steric hindrance of methyl groups.

It is known that α -ZrP has a layered structure and the interlayer distance changes with the progress of intercalation, as observed in the lowest diffraction angle region of X-ray diffractometry (XRD) patterns obtained during the uptake reaction. Figure 3(a) shows the structural change in the solid phase with the uptake of *N,N*-amine. The numerals in the ordinate correspond to those in the abscissa in Figure 1. From the XRD patterns it can be seen that the interlayer distance of the solid phase dilated to 16.0 Å, the intensity of the peak increased with the progress of *N,N*-amine intercalation, and there is a decrease in the intensity of the peak corresponding to an interlayer distance of 7.6 Å attributable to the original α -ZrP. This variation in the XRD patterns indicates that the uptake reaction proceeds in a single step, which is consistent with the results obtained from the titration curve of *N,N*-amine.

This structural change was the same as that observed in the system using *N,N*-amine alone. Hence, the results of the IR analysis are consistent with the thermal analysis results.

Assuming that the intensity of the peak in an XRD pattern is proportional to the amount of each phase present, the ratio of phases can be estimated. The proportion of each phase in the solid with increasing intercalation of *N,N*-amine is shown in Figure 3(b). A phase with an interlayer distance of 16.0 Å (Phase A) increased with *N,N*-amine content up to 3 mEq/g while a second phase with an interlayer distance of 7.6 Å decreases. Beyond 3 mEq/g, only the 16.0 Å phase was observed.

Hydration plays an important role in maintaining the interlayer distance of the solid in the intercalation of ammonia [5]. In this case, XRD patterns obtained under wet and dry conditions for the same sample are identical, indicating that hydration does not affect the interlayer distance.

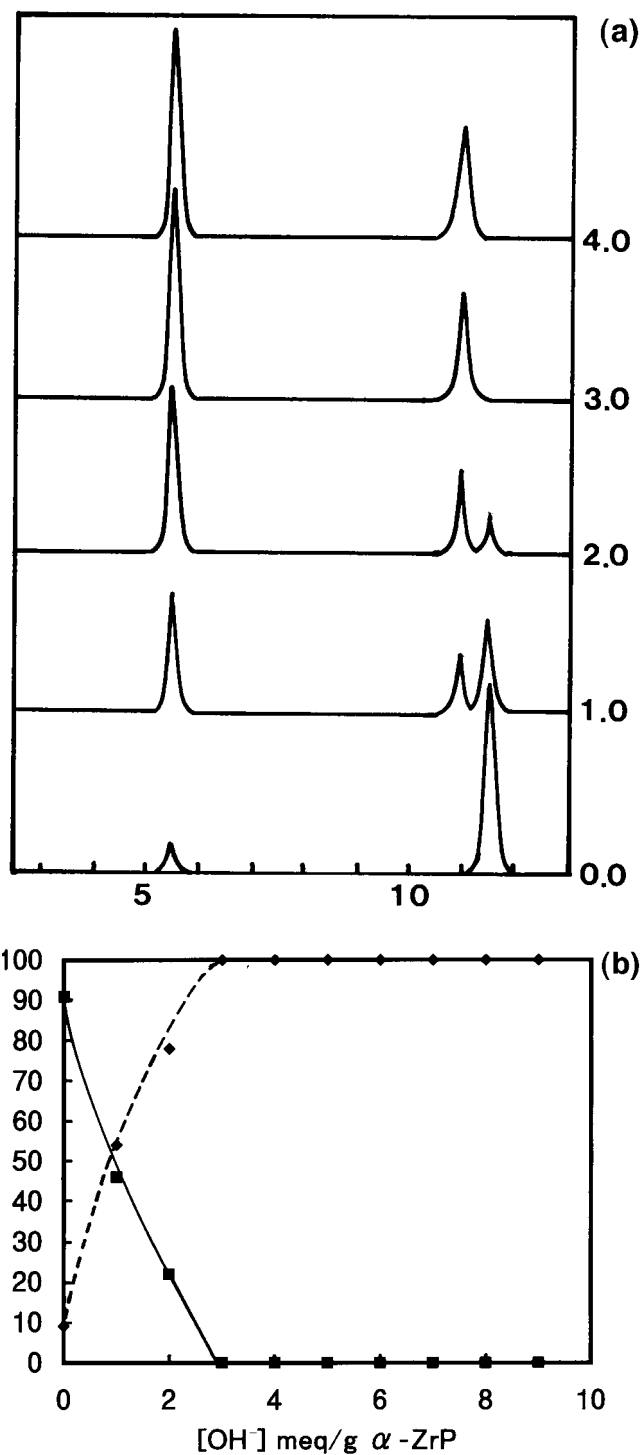


Figure 3. (a) Typical X-ray powder patterns of the solid phase. The numerals in the ordinate correspond to those in the abscissa in Figure 1. (b) Approximate ratio of the phases present during the pH titration with *N,N*-dimethyl-1-phenylethylamine and its chloride.

The interlayer distance of Phase A obtained in this study is slightly larger than that of 1-phenylethylamine (15.6 Å), and smaller than that of 2-phenylethylamine (16.3 Å). In previous studies, the 16.0 Å and 7.6 Å phases appeared when one molecule of 1- or 2-phenylethylamine replaced one of the two protons in α -ZrP. Hence, the interlayer distance of Phase A indicates that *N,N*-amine is present as a monolayer in the interlayer region of zirconium phosphate.

According to the literature, the molar ratio of a guest to a host (loading ratio) can be roughly estimated based on the free volume created in the interlayer region [4], calculated by the following equation:

$$V_f = 24.3(d - 6.3) - 37n$$

where $24.3 (\text{\AA}^2)$ is the area covered by one $-\text{POH}^+$, d is the interlayer distance of an intercalate, $6.3 (\text{\AA})$ is the thickness of the α -zirconium phosphate macroanion, $37 (\text{\AA}^3)$ is the volume of a hydrating water molecule, and n is the hydration number.

As Phase A has an interlayer distance of 16.0\AA and one hydrating water, V_f is equal to $199 \text{\AA}^3 (= 24.3(16.0 - 6.3) - 37)$. This means that one POH^+ site (active site) can accommodate a molecule smaller than 199\AA^3 . An N,N -amine molecule is 62\AA^3 larger than a 1-phenylethylamine molecule due to the two methyl groups. As the total volume of one N,N -amine is estimated to be 228\AA^3 , 1.15 active sites are required to accommodate one molecule of N,N -amine.

A dimethylamino group reacts with one $-\text{POH}^+$. If the group covers more than 24\AA^2 , other active sites will be blocked. Assuming that two methyl groups bond to a nitrogen point in the ZrP layer, the coverage is approximately 24\AA^2 . However, the coverage is estimated to be about 31\AA^2 if three methyl groups are arranged on a plane parallel to that of ZrP. Only one active site is required in the former, whereas 1.3 sites are required in the latter.

Figure 4 shows the IR spectra of α -ZrP, N,N -amine and ZrP-NN. The IR spectra of ZrP-NN is almost identical to the composite spectra of N,N -amine and α -ZrP [8, 9]. Absorption bands attributable to $-\text{OH}$ stretching are present in the $3600\text{--}2800 \text{ cm}^{-1}$ region, and sharp bands at 3000 cm^{-1} and 1650 cm^{-1} are assigned to hydrating water [8]. Bands observed at 1150 , 1170 and 1200 cm^{-1} in the spectrum for N,N -amine were not present in the ZrP-NN spectrum, although weak absorption bands appeared at 1320 , 760 and 705 cm^{-1} . These findings indicate that N,N -amine exists in α -ZrP as an ammonium ion [4, 10].

Figure 5 shows thermoanalytical curves for the ZrP-NN complex. The TG curve indicates that thermal decomposition occurred in four steps. Dehydration occurred in the first and second stages, followed by the evolution of N,N -amine and the decomposition of a fraction of the N,N -amine observed as a black residue in the platinum pan. Two exothermic reactions at $300\text{--}350 \text{ }^\circ\text{C}$ are ascribed to the oxidation of the amines on the surface of the platinum pan. The decomposition reaction in the fourth step is thought to be caused by dehydration associated with the condensation of phosphate as pyrophosphate.

As a black residue remained after the TG-DTA measurements, the ignition loss of ZrP-NN was examined using a platinum crucible by burning the carbon off completely under prolonged heating. The resultant solid was colorless. The weight loss was found to be $39.6 \text{ wt}\%$ in total, which agrees with the presence of 1 mole of N,N -amine and two moles of water in ZrP-NN. As 1 mol water was withheld in the condensation of pyrophosphate, the remaining ZrP-NN still contained one mole of hydrating water.

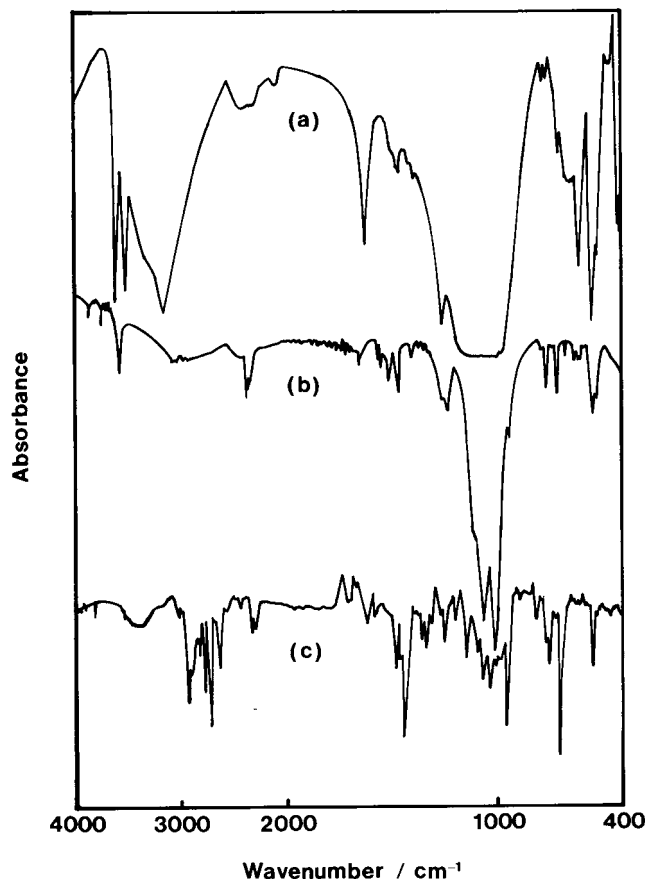


Figure 4. IR spectra of (a) α -zirconium phosphate, (b) N,N -ZrP, and (c) N,N -dimethyl-1-phenylethylamine.

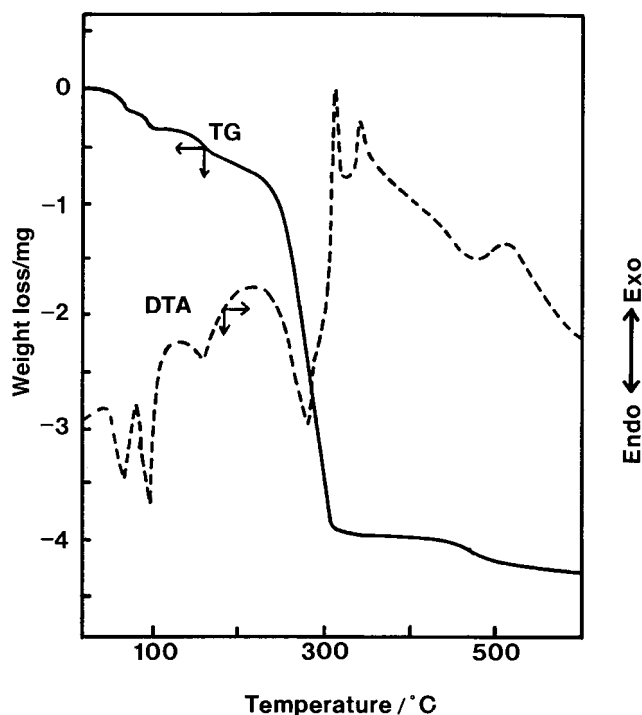


Figure 5. Tg and DTA curves of N,N -ZrP.

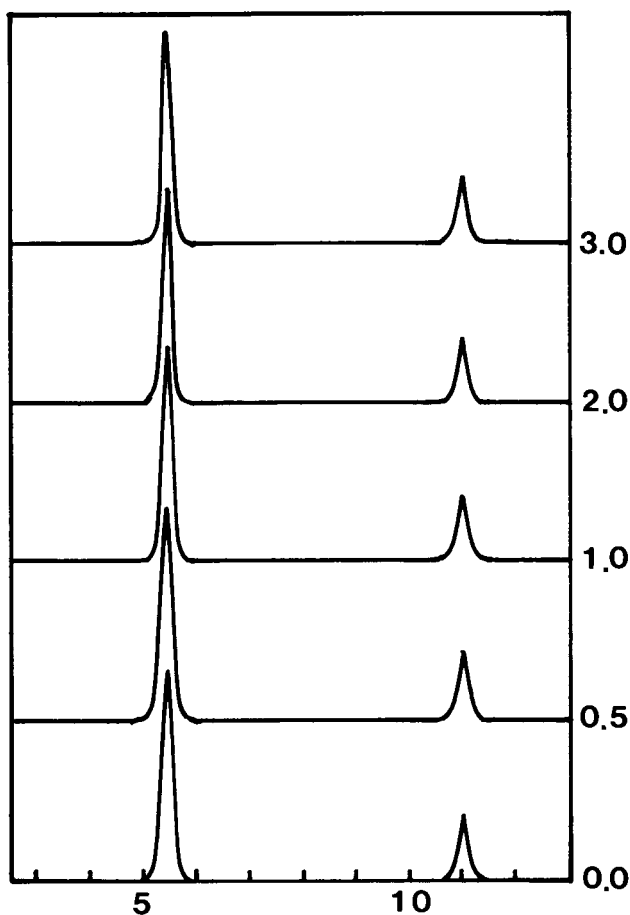


Figure 6. Typical X-ray powder patterns of the solid phase. The numerals in the ordinate correspond to those in the abscissa in Figure 2.

The composition of ZrP-NN as determined by elemental analysis is as follows: C: 24.20%, H: 4.01%, N: 2.90%. The molar ratio of each element in ZrP-NN in reference to nitrogen is C : H : N = 9.8 : 19 : 1. Taking account of the residue (presumably carbon), the chemical formula of the complex obtained is $\text{Zr}(\text{C}_{10}\text{H}_{15}\text{N}-\text{HPO}_4)(\text{HPO}_4)\cdot\text{H}_2\text{O}$.

Deintercalation (backward)

Deintercalation was performed by adding 5 mL of distilled water and 5 mL of HCl (0.1 mol/l) to 143.6 mg of ZrP-NN in an ampule. The mixture was then shaken continuously at 25 °C in a water bath for 14 days in order to ensure equilibrium, which was expected to be attained within 12 days.

Curve (b) in Figure 1 shows the backward titration for *N,N*-amine and *N,N*-ammonium chloride solution. It is clear that the intercalation reaction is irreversible. The reaction proceeded in a more acidic solution than did the forward titration, and the low pH indicates that hydrogen ions remained in the solution phase. Furthermore, the ionic mole fraction of *N,N*-ammonium in the solid was higher than that expected from the forward process. The hydrogen ion concentration in the forward and backward titrations was calculated to be 5.4×10^{-3} and 2.3×10^{-2} mol/l at the

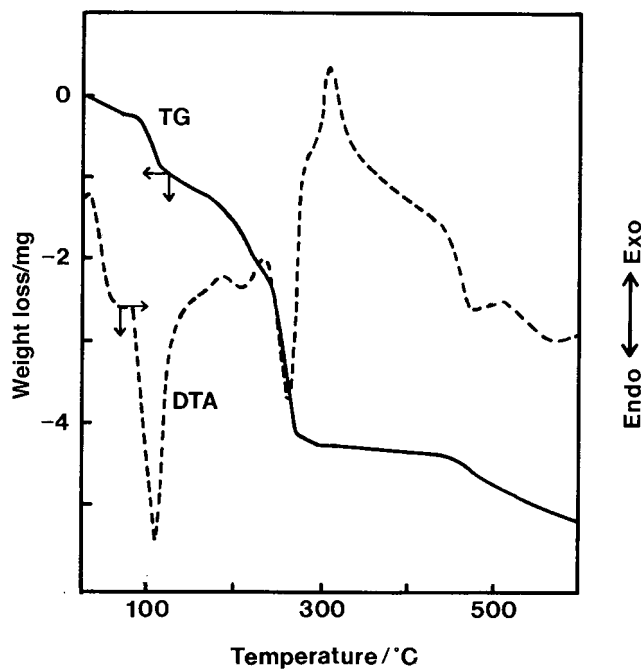


Figure 7. Tg and DTA curves of the sample obtained at 0 meq/g of the backward titration.

0 meq/g point, corresponding to the *N,N*-ammonium ionic mole fraction of 0.08 and 0.35, respectively.

Curve (b) in Figure 2 shows the backward titration with hydrochloric acid alone. The reaction was also irreversible in this system. For example, at the 0.5 meq/g $[\text{OH}^-]$ point, the ionic mole fraction of ammonium ions in the solid is estimated to be 8% in the forward titration and 27% in the backward titration.

The cause of this hysteresis was examined by X-ray diffractometry and IR and thermal analyses on the solid phase during the deintercalation reaction.

The structural change of the solid phase in the backward titration is very similar in both systems. Figure 6 shows the XRD patterns for the hydrochloric acid reaction. Although an α -phase appeared during the reaction, the ammonium phase was dominant. These findings agree well with the characteristics obtained for this titration.

The IR spectra of the compounds show that at the beginning of the reaction, new peaks appeared in the 3600–2800 cm^{-1} region. These can be assigned to hydrating water in α -ZrP. The intensity of these absorption peaks increased with the proportion of α -phase. The bands near 1500 cm^{-1} and 700 cm^{-1} are assigned to *N,N*-amine (cf. IR spectra in the forward direction). These peaks appeared in the final stage of the reaction, indicating that the *N,N*-ammonium ion remained in the solid phase.

Figure 7 shows the thermoanalytical curves of the sample for 0 meq/g in the titration curve. The first step at about 100 °C and the fourth step at around 500 °C are due to dehydration. The ratio of weight loss between the first and fourth steps is about 2.6, indicating that the sample contains 2.6 mol of water per mol of sample; the fourth weight loss is caused by the condensation of $-\text{HPO}_4$ to pyrophosphate. From the second and third steps it can be deduced that no

N,N-amine remained in the sample, which is consistent with the IR results.

These facts obtained above indicated that a considerable amount of *N,N*-amine in the solid phase remained and prevented the solid from forming the original α -ZrP. This type of hysteresis is common to the system involving α -ZrP, and has been reported earlier [5].

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