# Reaction in the System $N(CH_3)_4$-$ZrO_2$-$P_2O_5$-$H_2O$. Preparation and Characterization of Framework Zirconium Phosphates $(NH_4)_xH_{1-x}Zr_2(PO_4)_3$ and $HZr_2(PO_4)_3$

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The hydrothermal reaction in the system $ZrO_2$-$P_2O_5$-$H_2O$ in the presence of tetramethylammonium ions was examined within the temperature range 160—350 °C. This reaction resulted in the formation of framework zirconium phosphates $(NH_4)_xH_{1-x}Zr_2(PO_4)_3 \cdot yH_2O$ ($0.6 \leq x \leq 1$, $y \leq 0.3$) as well as some other phases, including two tetramethylammonium intercalates. The framework phases were rhombohedral with lattice constants of, *e.g.*, $a=8.669$ and $c=24.23$ Å for $x=1.0$. These phases were deammonated at 400—640 °C and converted to the proton-exchanged form $HZr_2(PO_4)_3$. The protons of this phase are easily exchanged by unhydrated $Li^+$ and $Na^+$ ions, but not by $K^+$ and $Cs^+$, owing to the sieving effect of the bottleneck in the $(Zr_2P_3O_{12})^{-1}$ framework. The acid strength of the proton form is a little weaker than that of $\alpha$-zirconium phosphate.

Inclusion phenomena have attracted increasing attention in inorganic chemistry. In previous papers concerned with molecular inclusion, we reported the adsorption of amino acids by layered zirconium phosphates[1] and the complexation of copper(II)-montmorillonite with a modified cyclodextrin.[2] Recently, another type of application has been made in preparing several useful micro-porous compounds, such as zeolite ZSM-5[3] and framework aluminophosphates,[4] by a method in which their organic base-including precursors were hydrothermally crystallized prior to the decomposition of the complexing moieties.

Zirconium phosphate, other than with a layered structure, can be obtained with a framework structure. This phase is the end member of the zirconium phosphate silicate $M_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($0 \leq x \leq 3$, M=univalent cation). It is represented by a composition of $x=2$ and M=Na (NASICON) with a fast $Na^+$ ion conductivity and has an open three-dimensional skeleton framework with four cavities per formula weight.[5] It is, therefore, of interest to apply the inclusion crystallization method to the NASICON system.

An attempt was, thus, made to examine a hydrothermal reaction in the system $ZrO_2$-$P_2O_5$-$H_2O$ in the presence of tetramethylammonium (TMA) ions.

In the present study, we obtained framework zirconium phosphates $(NH_4)_xH_{1-x}Zr_2(PO_4)_3$ and $HZr_2(PO_4)_3$ in addition to two tetramethylammonium intercalates. Alberti has already reported that the proton exchanged form of $MZr_2(PO_4)_3$ is obtained by washing $LiZr_2(PO_4)_3$ with dilute HCl.[6] After the present work was underway, we learned that Ono[7] prepared the ammonium- and the proton-exthanged forms of $MZr_2(PO_4)_3$ by a hydrothermal reaction using the system $NH_3$-$ZrO_2$-$P_2O_5$-$H_2O$. Clearfield, Roberts and Subramanian[8] also reported the hydrothermal synthesis of these two phases using the amine or ammonium exchanged forms of $\alpha$-zirconium phosphate as a starting material or the reaction of $NH_4Cl$ with $Zr(NaPO_4)_2$.

## Experimental

Hydrothermal experiments were carried out as follows. To a 1:1 mixed aqueous solution of 1 mol dm$^{-3}$ $ZrOCl_2$ and 1 mol dm$^{-3}$ tetramethylammonium bromide, a 1 mol dm$^{-3}$ phosphoric acid solution was added to keep the P/Zr ratio constant at 1.5 or 4. After the pH value of the reaction mixture had been adjusted to 0.8—9 with a 10% tetramethylammonium hydroxide solution, the mixture was sealed in a gold capsule or stainless steel bomb (fitted with a Teflon liner) and kept for 2—10 d at 160, 220, 280, 310, or 350 °C. The resulting solids were centrifuged, washed with distilled water and dried at 40 °C in air. Measurements of X-ray diffraction, TG traces, and infrared (IR) transmission were made using the same instruments and procedures as described elsewhere.[1] A wet analysis of zirconium and phosphorus was conducted by modifying the method of Clearfield, Blessing and Stynes.[9] An analysis of C, H, N loss on ignition was made using a conventional method. Ion exchange experiments were performed by the following procedure: 0.01—0.02 g of solid was contacted with 3 cm$^3$ of distilled water, followed by the addition of 0.5 cm$^3$ of a 1.0 mol dm$^{-3}$ MCl solution. After each equilibration at 25 °C, the pH of the supernatant was measured, which enabled us to evaluate the number of protons released to the solution. A qualitative measurement of the acid strength was made in the same manner as previously described.[10]

## Results and Discussion

The products resulting from the hydrothermal reactions were characterized primarily by their X-ray diffraction patterns and the results are summarized in Fig. 1. The two phases which give X-ray diffraction profiles similar to those of $NaZr_2(PO_4)_3$ and $KZr_2(PO_4)_3$[5] are denoted as NASICON(I) and NASICON(II), respectively. The numbers for the other phases designate the first interplanar spacing in their respective powder patterns. In the temperature range below 300 °C, the three phases labelled 12.6, 10.5, and 9.9 were obtainable as a single phase and the phases labelled 9.2 and 8.6 coexisted with the NASICON(I) phase. At higher temperature the NASICON(II) phase was obtained as a single phase at pH 1—9 and a mixture of some less crystalline phases, including the NASICON(I) phase, appeared at pH 0.8.

Among the three single phases labelled by numbers,

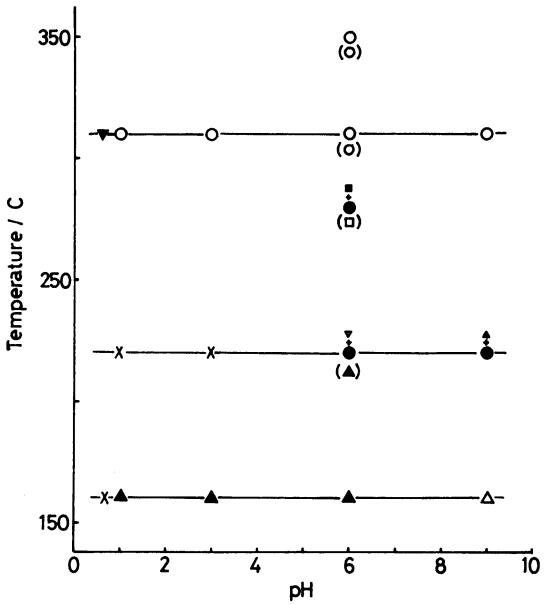


Fig. 1. Reaction diagram for the system TMA-$ZrO_2$-$P_2O_5$-$H_2O$.
●: NASICON(I), ○: NASICON(II), △: 12.6, ▲: 10.5, □: 9.9, ■: 9.2, ▽: 8.6, ×: amorphous, ▼: a mixture of some low crystalline phases, including phase NASICON(I). The phases obtained using reaction mixtures with a P/Zr ratio of 4 are shown in parentheses.

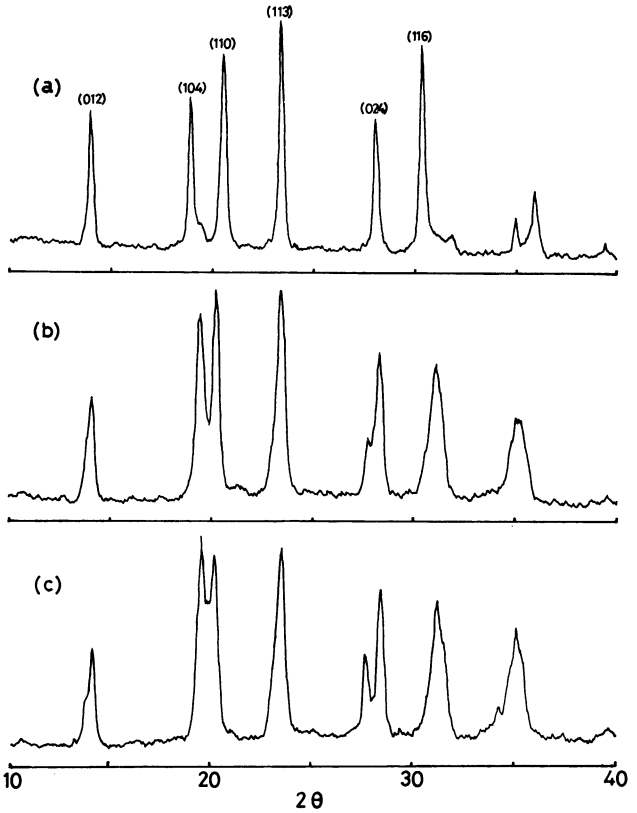


Fig. 2. X-Ray diffraction patterns of (a) sample A, (b) sample A-1, and sample A-2 for Cu$K\alpha$ rays. Main reflections are indexed for sample A.

composition analysis was made on phases 10.5 and 9.9 with high crystallinity. N, C, H analyses of these two phases yielded: N, 1.89; C, 6.23; H, 2.49 and N, 1.83; C, 6.12, H, 2.39 wt% or 1:3.85:18.4 and 1:3.90:18.3 in molar ratio, respectively. Both phases were also found to convert to $\alpha$-$ZrP_2O_7$ upon heating to 1000 °C. On the basis of the above results, in connection with the TG data, phases 10.5 and 9.9 can be identified as the TMA intercalates of $\alpha$-zirconium phosphate, with compositions of $ZrH_{1.52}(TMA)_{0.48}(PO_4)_2 \cdot 0.6\ H_2O$ and $ZrH_{1.54}(TMA)_{0.46}(PO_4)_2 \cdot 0.4H_2O$, respectively. These two intercalates expanded their layers by as little as 3.1 or 2.5 Å over that of the anhydrous form of $\alpha$-zirconium phosphate. These values are much less than 6.9 Å for the van der Waals diameter of the TMA ion. This is probably because the methyl groups of intercalated TMA ions would dip under the surface of the phosphate layer, due to an ionic attraction with the surface oxygens.

A similar but more detailed characterization was made on the NASICON(II) -type samples obtained. Table 1 lists data concerning the composition and structure of two typical samples prepared under different conditions. Both samples exhibited similar X-ray diffraction patterns, one of which is shown in Fig. 2(a). An organic analysis of sample A (obtained from a phosphorus-rich reaction mixture) yielded: N, 2.23; C, 0.32; H, 0.62 wt% or 1:0.17:3.89 in molar ratio, indicating that the NASICON(II) phase includes $NH_4^+$ ions, probably produced by the thermal decomposition of the TMA ions. An analysis of the deammonated form of sample A gave: $ZrO_2$, 51.2; $P_2O_5$, 44.5 wt% or 1:1.51 in P/Zr ratio. From the above data and the TG traces (described later), the composition of sample A was determined (Table 1). Sample B, obtained from a reaction mixture with a P/Zr ratio of 1.5, yielded solids containing fewer ammonium ions. The observed X-ray diffraction peaks for both samples were indexed on the basis of hexagonal cells with the lattice constants listed in Table 1. It has been noticed that the ammonium-exchanged form of $MZr_2(PO_4)_3$ contracted along the $a$ axis and expanded along the $c$ axis, compared to the Li, Na, or K forms.[5]

Figure 3 shows the TG curves for samples A and B. Upon heating, the ammonium form releases its water at 280—350 °C and undergoes deammonation at 400—

Table 1. Preparation conditions of $(NH_4)_xH_{1-x}(PO_4)_3$ and their characterization

| Sample | Hydrothermal cond. p/Zr | pH | $T$/°C | t/h | Composition | Lattice const.[a] $a$/Å | $c$/Å |
|---|---|---|---|---|---|---|---|
| A | 4 | 6 | 310 | 60 | $(NH_4)_{1.0}Zr_2(PO_4)_3 \cdot 0.07H_2O$ | 8.669 | 24.23 |
| B | 1.5 | 6 | 350 | 120 | $(NH_4)_{0.62}H_{0.38}Zr_2(PO_4)_3 \cdot 0.13H_2O$ | 8.694 | 24.19 |

a) Rhombohedral.

TABLE 2. STRUCTURAL AND ION EXCHANGE PROPERTIES OF THE CALCINED FORMS OF $(NH_4)_xH_{1-x}(PO_4)_3$

| Sample | Calcination cond. Precursor | $T$/°C | $t$/h | X-ray pattern | Ion exchange capacity/meq g$^{-1}$ for $Li^+$ | $Na^+$ | $K^+$ | $Cs^+$ |
|---|---|---|---|---|---|---|---|---|
| A | | | | | | 0.015 | | |
| A-1 | A | 600 | 1 | NASICON-like | 1.95 | 1.99 | 0.088 | 0.039 |
| A-2 | A | 600 | 2 | NASICON-like | 1.78 | 1.83 | | |
| A-3 | A | 600 | 12 | NASICON-like | 1.25 | 1.47 | 0.087 | 0.042 |
| B | | | | | | 0.008 | | |
| B-1 | B | 520 | 12 | NASICON-like | 1.54 | 1.43 | 0.027 | 0.009 |

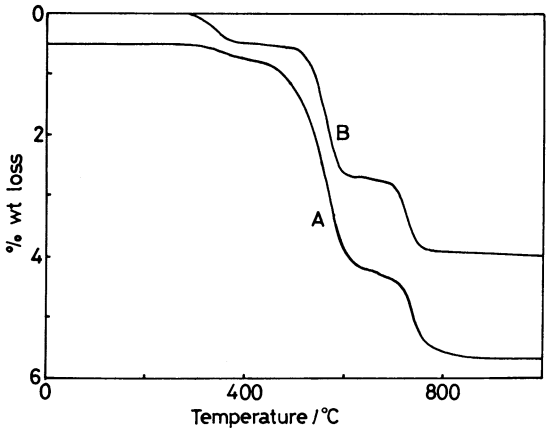


Fig. 3. TG curves for (A) sample-A and (B) sample-B with a heating rate of 10°C min$^{-1}$. The vertical scale for (A) is shifted by 0.5%.

640°C to convert to the proton analogue $HZr_2(PO_4)_3$. This conversion was confirmed by an IR observation. During the second weight loss, the $NH_4^+$ deformation band at 1440 cm$^{-1}$ disappears and the band due to OH stretching appears at 3645 cm$^{-1}$. The third weight loss at higher temperatures is due to the condensation of the phosphate groups.

Ion-exchange-capacity measurements on samples A and B and their calcined products were made using the procedure described before. In each run, the pH of an equilibrated solution decreased from an initial value of *ca.* 4.5 to 2—3.5 in 24—30 h and remained constant for longer times. The data obtained are summarized in Table 2. The X-ray diffraction profiles of the calcined products were characterized by the shift of the two diffraction peaks corresponding to the (104) and (110) reflections of the ammonium form as well as by the broadening or splitting of the peaks corresponding to its (012) and (124) reflections, as shown in Fig. 2 (b) and (c). For sample A-1, calcined at 600 °C for 1 h, the ion exchange capacities for $Li^+$ and $Na^+$ ions are close to 2.14 mmol g$^{-1}$ for the theoretical capacity of $HZr_2(PO_4)_3$, while those for $K^+$ and $Cs^+$ are 25—55 times smaller than the theoretical value. The X-ray diffraction and IR patterns of sample A-1 were changed to those for $LiZr_2(PO_4)_3$ or $NaZr_2(PO_4)_3$ after treatment with their corresponding chloride solution, but little affected by using KCl and CsCl solutions. These findings indicate that the protons in $HZr_2(PO_4)_3$ are exchanged by unhydrated $Li^+$ and $Na^+$ ions which are 0.74 and 1.02 Å in ionic radius, respectively. Also, protons other than surface protons are unreplaceable by $K^+$ and $Cs^+$ ions which are 1.38 and 1.70 Å in ionic radius, respectively. Because of their isomorphous structures, the diameter of a bottleneck formed by three $ZrO_6$ octahedral edges and three $PO_4$ tetrahedral edges for $HZr_2(PO_4)_3$ would be close to that for $NaZr_2(PO_4)_3$, *i.e.*, twice the difference of the Na-O distance[11] and $O^{2-}$-ion radius (or 2.3 Å). This diameter is large enough to allow $Li^+$ and $Na^+$ ions to diffuse into the cavity in the $(Zr_2P_3O_{12})^-$ framework, but too small for $K^+$ and $Cs^+$ ions. Thus, that the selectivity of $HZr_2(PO_4)_3$ for $Li^+$ and $Na^+$ uptakes is much higher than that for the others can be attributed to an ion-sieving effect of the intracrystalline bottleneck. It has also been noticed that the number of protons replaceable by $Li^+$ and $Na^+$ ions decreases with an increase in calcination time. However, the number of protons replaceable by $K^+$ and $Cs^+$ remains unaltered. One possible explanation for this behavior may be that the condensation of inner $HPO_4^{2-}$ group in $HZr_2(PO_4)_3$ proceeds in preference to that of the surface ones.

TABLE 3. ACID STRENGTH OF $HZr_2(PO_4)_3$ AND α-ZIRCONIUM PHOSPHATE IN WATER[a)]

| | Ho +4.8 | +3.3 | +1.5 | −3.0 | −5.6 | |
|---|---|---|---|---|---|---|
| $HZr_2(PO_4)_3$ | + | +* | − | − | − | This work |
| α-zirconium phosphate | + | + | − | − | − | Ref. 10 |

a) +, Acidic color; −, basic color; +*, see text.

The acid strength of $HZr_2(PO_4)_3$ in water as well as in benzene was qualitatively determined using sample A-1. This compound was found to have, qualitatively, the same acid strength of Ho≥3.3 in both liquids. The data obtained are shown in Table 3, along with those for α-zirconium phosphate.[10] For Ho=+3.3, however, the triphosphate solid rapidly became pale red on contact with the indicator, but turned pale gray in 1 h or more. Such fading was not observed for the α-zirconium phosphate. These results indicate that the acid strength of $HZr_2(PO_4)_3$ in a little weaker than that of α-zirconium phosphate.

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