Sodium Ion Exchange on Crystalline Zirconium Titanium Phosphate

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A new ion exchanger, crystalline zirconium titanium phosphate with variable zirconium to titanium mole ratios has been prepared and the sodium ion exchange behavior studied. In the zirconium-rich exchanger a half-exchanged monosodium phase was produced. This differs from the titanium-rich exchanger where a disodium phase was formed without formation of the intermediate monosodium phase. The pH titration curves were complicated but a trend emerged with variation in the Zr/Ti ratio. On the basis of the X-ray evidence and the shapes of the titration curves it is thought that the synthesized phosphates are solid solutions rather than a mechanical mixture of the two metal phosphates.

Considerable work have been reported on the ion exchange behavior of alkali metal ions on inorganic ion exchangers of the α-zirconium phosphate type.[1] Among the exchangers, α-titanium phosphate, $Ti(HPO_4)_2 \cdot H_2O$ (designated as α-TP) has the same layer structure as α-zirconium phosphate (α-ZP) with approximately the same interlayer distance of 7.56 Å. The ion exchange properties however differ in some respects from that of α-ZP. For example, in H^+–Na^+ ion exchange, both a monosodium phase and a disodium phase exist for α-ZP, which are immiscible with each other when they coexist. In X-ray powder diffractometry of α-TP, the monosodium phase[2] was not observed as was the case of H^+–Li^+ exchange.[3] The ion sieve effect exhibited by exchangers of this type also differs in that in acid media α-ZP can absorb K^+ ions but α-TP cannot.

Synthesis of the crystalline mixed phosphate of zirconium and titanium having variable zirconium to titanium mole ratios has been attempted and the sodium ion-exchange behavior studied.

Experimental

Synthesis of the Exchangers. Hydrochloric acid solutions (2 mol dm^{-3}) of zirconium dichloride oxide and titanium tetrachloride were prepared. The zirconium to titanium mole ratio in the mixed solutions was varied between experiments. The solution was added dropwise, with stirring to H_3PO_4 (2 mol dm^{-3}) kept at 60—70 °C. The resultant colorless gel was allowed to stand overnight, filtered and washed with 2% H_3PO_4 solution until free from chloride ion. The obtained amorphous salt was refluxed at the boiling point in concentrated H_3PO_4 for 48 to 200 h. The product was centrifuged and washed with deionized water until the pH of the supernatant solution exceeded 3. The microcrystalline product was stored over silica gel. The exchanger will be designated as ZTP hereafter.

Analysis of the Exchangers. The zirconium to titanium mole ratio in the exchangers was determined as follows. A weighed amount (100 mg) of the exchanger was dissolved in hot concd H_2SO_4 (20 cm^3). After cooling, the solution was diluted to 200 cm^3, and the ice-cooled 5% cupferron aqueous solution (10 cm^3) added. The precipitate was filtered and washed with 1.2 mol dm^{-3} HCl, ignited and weighed as the sum of ZrO_2 and TiO_2.

In a separate experiment, the exchanger (120 mg) was dissolved in hot concd H_2SO_4 (20 cm^3). After cooling, the solution was added to 1.5% H_2O_2 (200 cm^3). To this was added $NH_4H_2PO_4$ (1.5 g) and the resulting gelatinous precipitate aged on a steam bath at 50—60 °C for 2 h. The precipitate was filtered and washed with 1% NH_4NO_3, ignited and weighed as ZrP_2O_7. The zirconium to titanium mole ratio was estimated from the results of both experiments.**

Ion Exchange. The experiment was conducted by the batch method. Mixed solutions of 0.1 mol dm^{-3} NaCl and 0.1 mol dm^{-3} NaOH at variable mixing ratios were prepared to give solutions of differing values of pH keeping the sodium concentration constant. ZTP (250 mg) was placed in contact with each of the above mentioned solutions (25 cm^3), and shaken for 4 days at 25 °C. The solution was centrifuged, and the supernatant liquid subjected to pH measurement. Analysis for sodium was by flame photometry, and for phosphorus colorimetrically by the phosphomolybdic acid method. X-ray powder diffractometry was conducted on the exchangers obtained at various stages of ion exchange. Thermal analysis (TG and DSC) was performed to determine the number of waters of crystallization per formula weight of the exchanged phase.

Results and Discussion

Synthesized Exchangers. In Table 1, the zirconium to titanium mole ratios in the starting mixture and in the product together with the theoretical exchange capacity of the exchangers are shown. In each exchanger, the Zr/Ti ratio in the product was less than that in the starting mixture.

The X-ray powder patterns of the exchangers resembled that of α-ZP and α-TP, but the interlayer distance (d_{002}) estimated from the first reflection peak

TABLE 1. COMPOSITION OF SYNTHESIZED ION EXCHANGER, $Zr_xTi_{1-x}(HPO_4)_2 \cdot H_2O$

Notation	Mixing mole ratio (Zr/Ti) of starting materials	Mole ratio (Zr/Ti) of products	x	Estimated exchange capacity (meq/g)
ZTP(3.25)	3.38	3.25	0.77	6.87
ZTP(0.93)	1.13	0.93	0.48	7.17
ZTP(0.25)	0.37	0.25	0.20	7.50

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** There is the possibility that a small amount of titanium coprecipitates with the zirconium phosphate. Volumetric determination of titanium after reduction to the +3 state by liquid zinc amalgam gave a somewhat lower Zr/Ti ratio.[4]

at the lowest angle was 7.63 Å in each case. This figure is slightly larger than that for α-ZP and α-TP. Furthermore, a mechanical mixture of α-ZP and α-TP gave a more complicated powder pattern in which a single reflection from the (002) plane existed but several reflections at higher angles appeared separately as shown in Fig. 1.

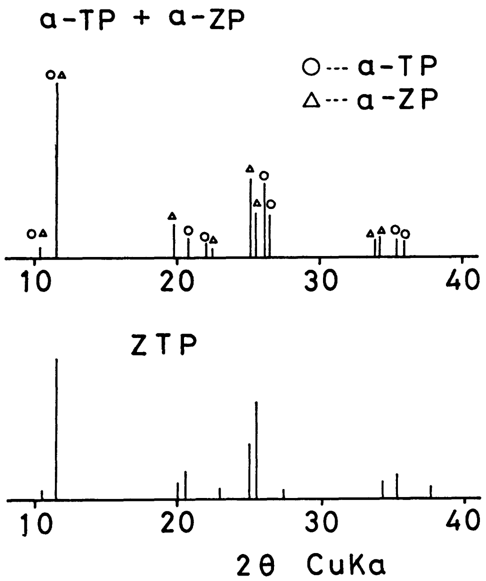

Fig. 1. Comparison of X-ray powder diffraction patterns between α-TP, α-ZP, and ZTP.

Table 2. Results of thermogravimetry

Exchanger	Water of crystallization (mol/mol ZTP)	Dehydration due to condensation of phosphate (mol/mol ZTP)
ZTP(3.25)	1.09	1.05
ZTP(0.93)	1.05	1.00
ZTP(0.25)	1.03	1.04

The results of thermogravimetric analysis are given in Table 2. The weight loss at 100—250 °C is ascribed to the water of crystallization, and the loss at 400—550 °C to condensation of the phosphate group. These data indicate that ZTP with all Zr/Ti mole ratios is monohydrate. Thus, ZTP is assumed to be isomorphous with α-ZP and α-TP. Analogously with α-ZP, the three oxygen atoms of the phosphate group are bonded to the three metal atoms in a layer. In ZTP, the three metal atoms consist of Zr and/or Ti. Since the crystal ionic radius of Zr^{4+} and Ti^{4+} differs considerably (0.79 and 0.68 Å respectively), the structure of the lattice is assumed to be less ordered than that of α-ZP or α-TP, and the remaining P–O bond of each phosphate group, to which an exchangeable H atom is bonded, may tilt from the perpendicular. This may result in a slight expansion of the interlayer distance and lead to the phosphate groups in ZTP having different values of acidity. The synthesized exchangers will be designated as ZTP(3.25), ZTP(0.93), and ZTP(0.25), depending upon the Zr/Ti ratios. The refluxing time was 200 h for ZTP(0.93) and 48 h for the others but the degree of crystallization did not greatly differ.

Ion Exchange. Figure 2 illustrates the pH-titration curves for sodium ion exchange and the phosphate release curves indicate the extent of hydrolysis of the exchanger. The titration curve for ZTP(3.25) has a point of inflection at approximately 3.5 meq Na^+ absorbed/g ZTP corresponding to approximately one half of the calculated exchange capacity of 6.87 meq/g.

In the titration curve for ZTP(0.93), the inflection is observed at approximately 3 meq/g, which is less than one half of the theoretical capacity of 7.2 meq/g. In the

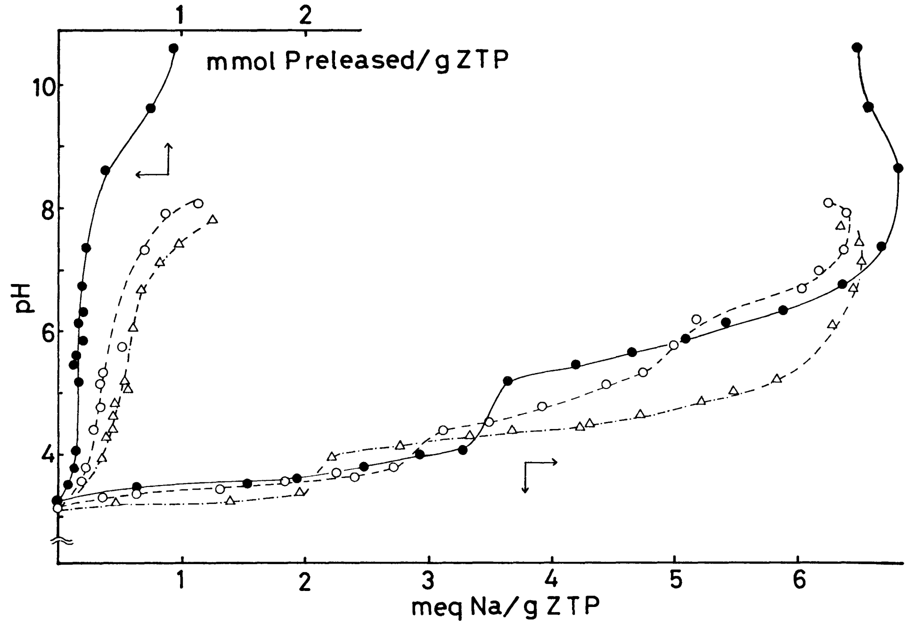

Fig. 2. The pH-titration curves for sodium ion exchange and the phosphate release curves.
-●-: ZTP (3.25), --○--: ZTP (0.93), and —·—△—·—: ZTP (0.25).

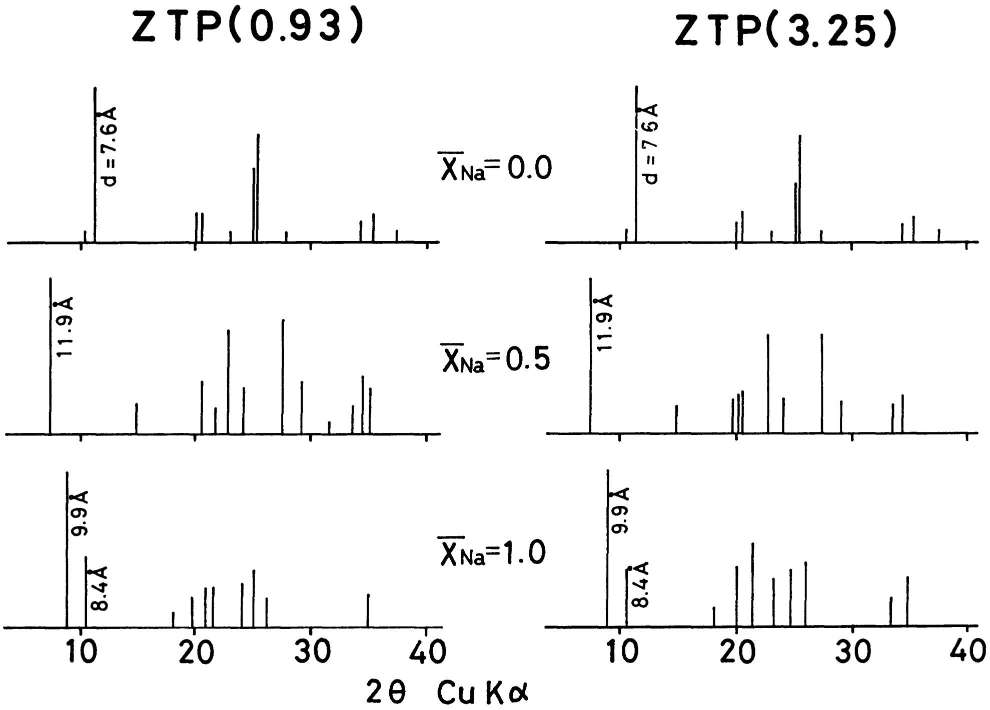

Fig. 3. The X-ray powder diffraction patterns of ZTP (3.25) and ZTP (0.93) at various stages of exchange. $\bar{X}_{Na}$ denotes the ionic fraction of sodium ion in the exchanger.

titration curve for ZTP(0.25), the inflection point is at approximately 2.2 meq/g, a value far less than half of the exchange capacity of 7.50 meq/g. This shift of the inflection has neither been observed in α-ZP nor in α-TP. Furthermore, the rise in pH at the inflection was very small compared to the clear and large pH change in the case of α-ZP. The cause for the "inflection shift" is not clear, but if the exchanger was a mechanical mixture of α-ZP and α-TP, the pH titration curve should be the composite curve for both exchangers. This however was not the case in the present study, and the curves indicate the solid-solution character of ZTP, in which the acidity of the phosphate protons varies depending upon the Zr/Ti mole ratio.

The ease of hydrolysis increased as the titanium mole fraction of the exchanger increased. As a result, the observed exchange capacity did not increase as suggested from the theoretical value.

Figure 3 illustrates the X-ray powder patterns for the exchangers (ZPT(3.25) and ZTP(0.93)) at several stages of exchange. The ionic fraction of sodium in the exchanger phase is denoted by $\bar{X}_{Na}$. In ZTP(3.25) and ZTP(0.93), the trend was very similar, namely, as the exchange of sodium ion proceeded, a new phase having an interlayer distance of 11.9 Å appeared. The diffraction peak intensity increased until, at the mid point of exchange, only this phase was observed.*** Up to $\bar{X}_{Na}=0.61$ for ZTP(3.25) and $\bar{X}_{Na}=0.54$ for ZTP(0.93), two peaks appeared at 9.9 and 8.4 Å. Finally at $\bar{X}_{Na}=0.95$ for ZTP(3.25) and $\bar{X}_{Na}=0.90$ for ZTP(0.93), the peak at 11.9 Å completely disappeared leaving the peaks at 9.9 and 8.4 Å.

For the sodium ion exchange on α-ZP, the point of inflection is found at the point of half exchange. Clearfield *et al.*[5] reported that the monosodium salt having an interlayer distance of 11.8 Å and the disodium salt having an interlayer distance of 9.9 Å exist, where the monosodium salt is a pentahydrate when stored at a relative humidity of 100%. Dried overnight at 35 °C or over diphosphorus pentaoxide this salt is converted to a monohydrate with an interlayer distance of 7.9 Å.

Similar phenomena were observed for ZTP(3.25) and ZTP(0.93). The monosodium form of ZTP(3.25) when stored at a relative humidity of 75%, it contained 4.7 mol of water of crystallization per formula weight. Dehydration of this monosodium form took place in two steps. Dried at 50 °C for 1 h it converted to the monohydrate having an interlayer distance of 7.9 Å (Fig. 4). The disodium salt when dried at 50 °C overnight, lead to the disappearance of the peak at 9.9 Å, the peak at 8.4 Å remained. The results for ZTP(0.93) were essentially the same. The indication is that the two peaks correspond to two types of disodium forms having different waters of crystallization, although the accurate number of the hydration could not be estimated. The monohydrate of the disodium form of α-ZP has an interlayer distance of 8.42 Å and thus the disodium form of ZTP with a spacing of 8.4 Å is most probably a monohydrate. The monohydrates of the monosodium and disodium forms did not regain the interlayer spacings when stored over saturated aqueous sodium chloride solution (relative humidity ≈75%).

In Fig. 5, the X-ray powder patterns for ZTP(0.25) at several stages of exchange together with those of the

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*** Under some conditions of drying, the reflection peak appeared at 7.9 Å instead of 11.9 Å. The interlayer distance is relatively sensitive to the water content of the exchanger, and consequently to the drying conditions.[4]

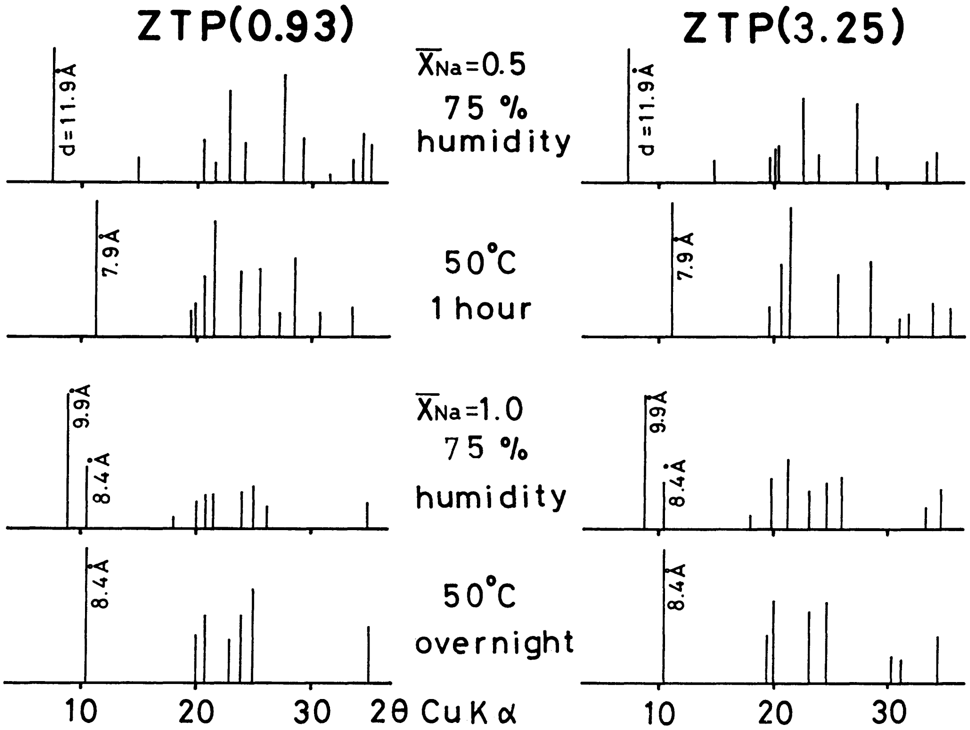

Fig. 4. Change in X-ray powder diffraction patterns of ZTP (3.25) and ZTP (0.93) depending on storage conditions.

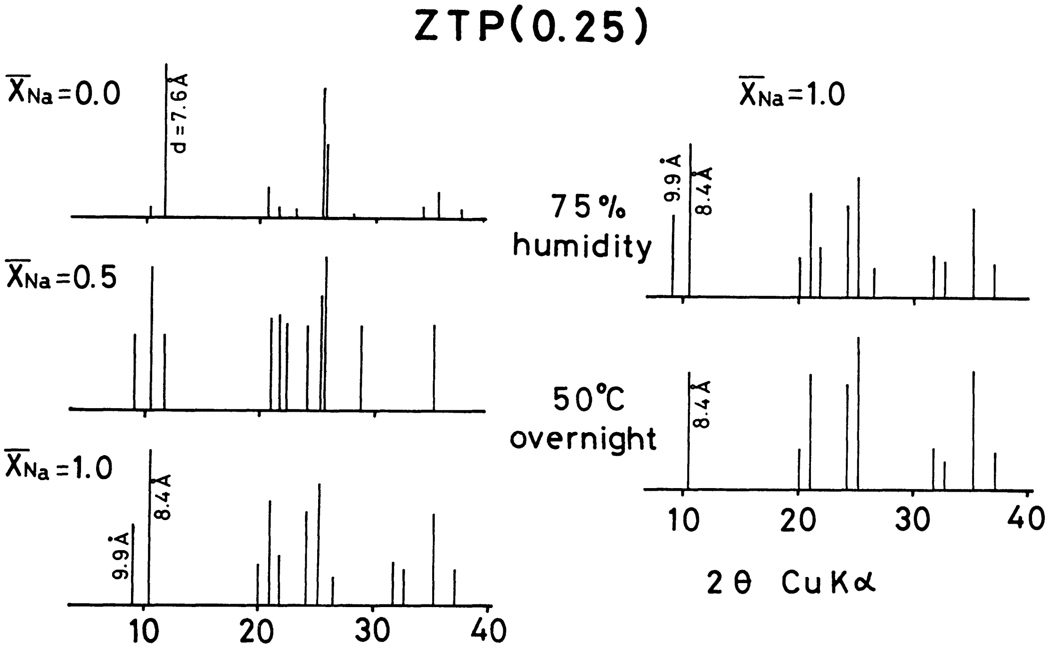

Fig. 5. The X-ray powder diffraction patterns of ZTP (0.25) at various stages of exchange and those of sodium form under different storage conditions.

disodium form under different storage conditions are shown. The X-ray pattern at $\bar{X}_{Na}=1.0$ was the same as for the foregoing two exchangers. The monosodium form however was not observed in this case, *i.e.*, as exchange proceeded, the disodium form phases were formed without the formation of the intermediate. In fact, at $\bar{X}_{Na}=0.5$, two peaks of the disodium form, 9.9 Å and 8.4 Å coexisted with the peak at 7.6 Å, which belongs to the unexchanged hydrogen form. Nevertheless, a small pH jump existed in the titration curve. In this case, the absence of a monosodium form does not correspond to a smooth titration curve without structure.

Further experimentation is continuing on the ion exchange behavior of other alkali metal ions such as lithium and potassium, and will be reported in due course.

Conclusions

A crystalline phosphate ion exchanger containing both zirconium and titanium has been synthesized. The sodium ion exchange behavior on the exchanger is interesting in that the presence or absence of the monosodium phase is dependent upon the Zr/Ti mole ratio in the exchanger. As an ion exchanger, ZTP is preferred to α-TP since it has higher resistance to hydrolysis.

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