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Alkali Metal Ion Exchange on Crystalline Zirconium Titanium Phosphate

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Ion-exchange studies of crystalline zirconium titanium phosphate with variable zirconium-to-titanium mole ratios have been extended to sodium-ion exchange on the exchangers with Zr-to-Ti mole ratios of 0.37 and 0.61, and to lithium and potassium ion exchange on the exchanger with a Zr-to-Ti mole ratio close to unity. In the sodium-ion exchange, a mono-sodium phase formed up to about a half of the exchange; then a disodium phase with a different amount of water of crystallization formed. In the lithium-ion exchange, the reaction proceeded with the formation of fully exchanged phases whose water content varied depending upon the environment in which the exchanger was placed during or after the reaction. The exchange amount of potassium ions was much less than that of sodium or lithium ions, and the ion exchange proceeded in parallel with an extensive hydrolysis of the exchanger. The half-exchanged phase could not be confirmed in this case. For the three alkali metal ions studied, the selectivity series was found as a function of loading, *i.e.*, within the range of the load from 0 to 1.3 meq/g, the selectivity is in the order of $Na^+ > K^+ > Li^+$, between 1.3 and 4.5 meq/g, it is $Na^+ > Li^+ > K^+$, and above 4.5 meq/g loading, it turns out to be $Li^+ > Na^+ > K^+$.

The sodium-ion-exchange behavior on crystalline zirconium titanium phosphate (ZTP) with three different Zr-to-Ti mole ratios has been reported in some detail, and it was revealed¹⁾ that, in the titanium-rich exchanger, a disodium phase was formed without the formation of the intermediate monosodium phase, as was the case in H^+–Li^+ or H^+–Na^+ exchange on α-titanium phosphate(α-TP). The investigation has now been extended to sodium-ion exchange on ZTP with some other Zr/Ti mole ratios, and further to lithium and potassium-ion exchange on ZTP with the Zr/Ti mole ratio close to unity. A comparison of the exchange behavior of these alkali metal ions with each other is of interest from the viewpoint of ion selectivity as well as the ion-sieve effect.

Experimental

ZTP Exchangers. The ZTP exchangers used in this experiment were prepared as has been described earlier¹⁾ with the refluxing time of 200 h. The Zr/Ti mole ratio in the starting solutions was varied between the sodium-ion experiment and the lithium- and potassium-ion experiment.

Analysis of the Exchangers. The sum of Zr and Ti was determined gravimetrically by means of precipitation with cupferron.¹⁾ In a separate experiment, the exchanger (300 mg) was dissolved in hot concd H_2SO_4 (40 cm³). After cooling, 10% H_2O_2 (10 cm³) was added to the solution. The mixture was heated, and the resulting clear solution was diluted to 150 cm³. Then the solution was transferred into a reduction vessel containing a liquid zinc amalgam, carbon dioxide gas was introduced to repalce the air, and the vessel was shaken vigorously for 10 min under slight warming. Titanium(IV) was thus quantitatively reduced to a trivalnet state. Then the aqueous phase was titrated with a standard $NH_4Fe(SO_4)_2$ solution in the presence of a saturated KSCN solution (10 cm³), the Zr-to-Ti mole ratio being calculated from the results.²⁾

Ion Exchange. The experiment was conducted by means of the batch method in the way described previosuly. Mixed solutions of MCl (0.1 mol dm⁻³) and MOH (0.1 mol dm⁻³), where M is Li, Na, or K, were prepared in variable mixing ratios. The sodium experiment was carried out at 25 °C, whereas the lithium and potassium experiments were made at 25, 45, and 60 °C. After equilibration with the exchanger in interest, the solution was centrifuged, and then the pH of the supernatant liquid was measured. Analyses for Na, Li, and K was performed by flame photometry with a Hitachi atomic absorption/flame spectrophotometer, while P was analyzed colorimetrically by the phosphomolybdic acid method. X-Ray powder diffractometry was made on exchangers obtained at various stages of ion exchange by using a Rigaku Geigerflex X-ray diffractometer.

Results and Discussion

Synthesized Exchangers. Three kinds of ZTP exchangers have been prepared, as is shown in Table 1. ZTP(Zr/Ti=0.37) and ZTP(0.61) were used for the Na^+-ion exchange, and ZTP(1.02), for the Li^+- and K^+-ion exchange.

The interlayer distance (d_{002}), as estimated from the X-ray powder patterns, was approximately 7.6 Å in all three cases. As has been reported,¹⁾ the exchangers are considered as solid solutions of zirconium and titanium phosphate and as isomorphous with α-zirconium phosphate(α-ZP) and α-TP.

Sodium-ion Exchange. Figure 1 illustrates the pH-titration curves for Na^+-ion exchange and the corresponding phosphate-release curves. The titration

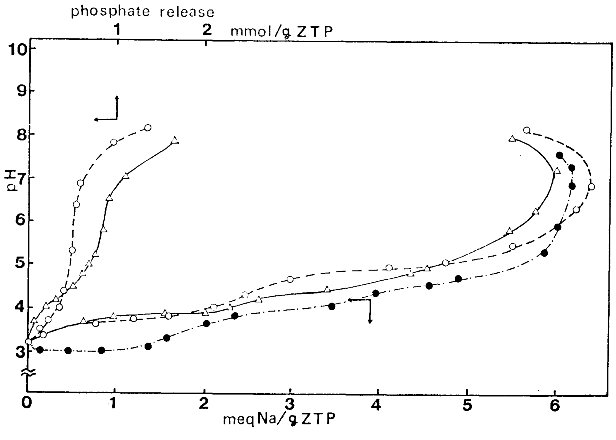

Fig. 1. The pH-titration curves for sodium ion exchange and the phosphate release curves.
—○—: ZTP (0.61), —△—: ZTP (0.37), —·●·—: α-TP.

Table 1. Composition of synthesized ion exchanger, $\mathrm{Zr}_x\mathrm{Ti}_{1-x}(\mathrm{HPO}_4)_2\cdot\mathrm{H_2O}$

Notation	Mixing mole ratio (Zr/Ti) of starting materials	Mole ratio (Zr/Ti) of products	x	Estimated exchange capacity (meq/g)
ZTP(0.37)	0.50	0.37	0.27	7.41
ZTP(0.61)	0.67	0.61	0.37	7.30
ZTP(1.02)	1.0	1.02	0.51	7.15

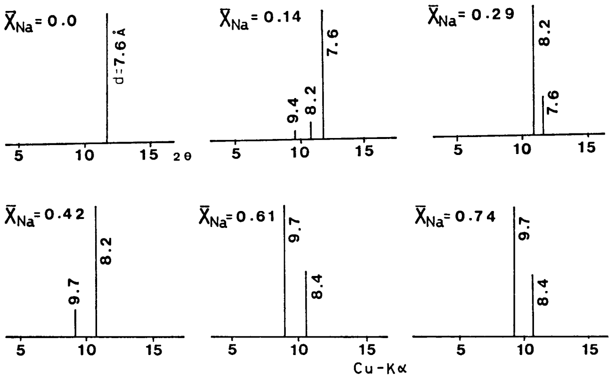

Fig. 2. The lowest angle regions of the X-ray powder diffraction patterns of ZTP(0.37) at several stages of exchange. $\bar{X}_{\mathrm{Na}}$ denotes the ionic fraction of sodium ion in the exchanger.

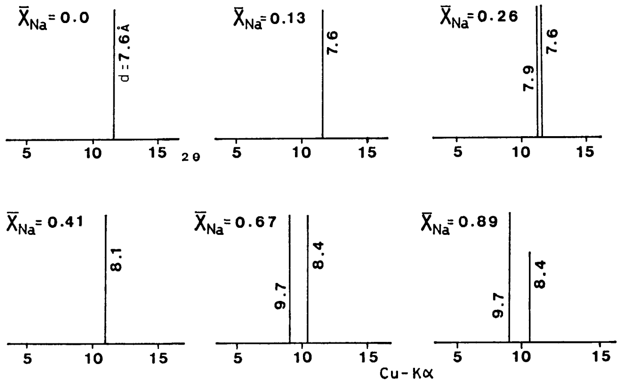

Fig. 3. The lowest angle regions of the X-ray powder diffraction patterns of ZTP(0.61) at several stages of exchange.

curve for ZTP(0.37) has a small point of inflection at approximately 2.3 meq Na^+/g ZTP. The curve for ZTP(0.61) also has an inflection at approximately 2.4 meq Na^+/g ZTP. The titration curve for Na^+-ion exchange on α-TP given by Takaguchi[3] is included in the figure, where an inflection exists at approximately 2 meq Na^+/g TP. The titration curve for Na^+-ion exchange on α-TP is similar to those given by previous investigations, but the existence of any inflection was not very clear[4,5] previously, except for the recent study by Clearfield and Frianeza.[6] The shift of the inflection toward a lower sodium loading with a decrease in the Zr content has been observed in the experiment[1] for ZTP(3.25) [3.5 meq/g], ZTP (0.93) [3 meq/g], and ZTP(0.25) [2.2 meq/g]. The data given in the present study again confirms the trend.

The X-ray powder patterns for ZTP(0.37) and ZTP (0.61) at several stages of exchange were measured; their lowest angle regions are shown in Figs. 2 and 3. The reflection peak at the lowest angle corresponds to the interlayer distance (d_{002}). The ionic fraction of sodium in the exchanger phase is denoted by $\bar{X}_{\mathrm{Na}}$. As is shown in Fig. 2, in ZTP(0.37), the intensity of the peak at 7.6 Å representing the unexchanged phase decreased with an increase in sodium loading, and a peak appeared at 8.2 Å. This peak seems to correspond to the monohydrate of monosodium salt (d= 7.9 Å), with some excess of water obtained in the dehydration process of pentahydrate (d=11.9 Å). Beyond a 50% exchange, the unexchanged phase was no longer present and the peaks at 8.4 and 9.7 Å arose. These peaks indicate disodium phases with different amounts of water of crystallization.[1] These patterns suggest that ZTP(0.37) still behaves toward the Na^+ ion like α-ZP in that the monosodium phase exists as an intermediate.

In ZTP(0.61), the interlayer distance remained almost constant until $\bar{X}_{\mathrm{Na}}$=0.26, where the peak at 7.9 Å appeared at the expense of the peak at 7.6 Å (Fig. 3). Thus, it shows the formation of the solid solution of ZTP with the Na^+ ion up to about 25% exchange. At $\bar{X}_{\mathrm{Na}}$=0.41, the 7.6 Å peak disappeared, leaving only the peak at 8.1 Å. The d-values for the monosodium form seem to vary between 7.9 and 8.2 Å depending upon the drying condition of the samples used for X-ray examination. If the sample was dried in a silica-gel desiccator, d-values of around 7.9 Å were obtained, whereas the samples only air-dried gave somewhat higher values.

In conclusion, for the Na^+-ion exchange process, the monosodium phase is present in ZTP(0.37) and ZTP(0.61), as was the case for α-ZP, ZTP(3.25), and ZTP(0.93).

Lithium-ion Exchange. The ion-exchange experiment was conducted by using ZTP(1.02), its formula being $\mathrm{Zr}_{0.505}\mathrm{Ti}_{0.495}(\mathrm{HPO}_4)_2\cdot\mathrm{H_2O}$. The pH-titration curves and the phosphate-release curves measured at 25, 45, and 60 °C are given in Fig. 4. At any temperature examined, the titration curve reached a plateau at a pH close to about 5 soon after the exchange started. In the case of the experiment at 25 °C, the plateau continued until the exchange proceeded up to 80% of the theoretical exchange capacity. Thereafter, the curve steeply rose to the pH of 7.5 and recorded the maximum exchange of 88.5%. At a higher pH value, the exchange amount of the Na^+ ion decreased as a result of the hydrolysis of the exchanger. The absence of any pH jump at a half-exchange reminds one of the lithium-ion exchange on α-TP.[7] As the temperature rose, the hydrolytic decomposition of the exchanger proceeded further, resulting in a decrease in the maximum exchange

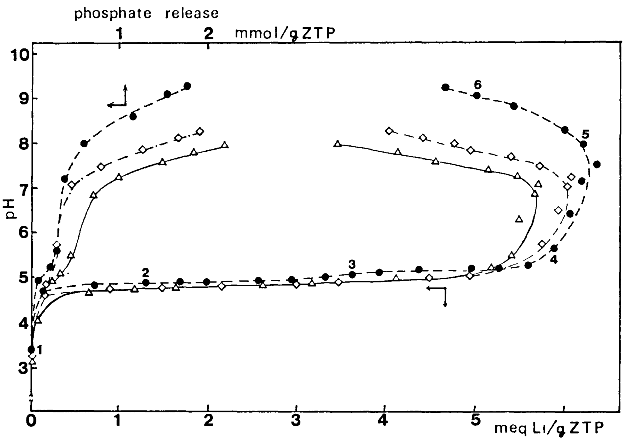

Fig. 4. The pH-titration curves for lithium ion exchange and the phosphate release curves.
—●—: 25 °C, —·◇·—: 45 °C, —△—: 60 °C. The exchanger is ZTP(1.02) in all the cases.

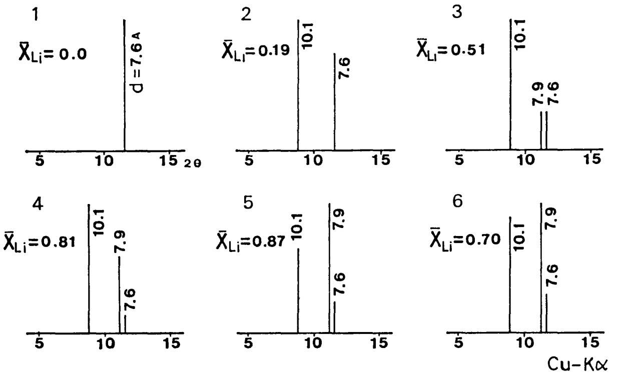

Fig. 5. The lowest angle regions of the X-ray powder diffraction patterns of ZTP(1.02) at several stages of lithium exchange at 25 °C. The numbers 1 to 6 indicate the extent of reaction shown in the titration curve in Fig. 4. $\bar{X}_{\mathrm{Li}}$ denotes the ionic fraction of lithium ion in the exchanger.

amount of the Li$^+$ ion, which was 84% at 45 °C and 79% at 60 °C compared to the theoretical value. As far as the ion-exchange behavior is concerned, however, the temperature dependence is very little, as is clearly observed in the fact that there is almost the same pH value in the plateau region. In other words, the exchange equilibrium is attained within 4 d even at 25 °C, but hydrolysis tends to proceed even further if the exchanger is in contact with alkaline solutions for a longer period.

The lowest-angle regions of the X-ray powder patterns of the exchanger at several stages of Li$^+$-ion exchange are reproduced in Fig. 5. Numbers 1 to 6 indicate the extent of exchange shown in the titration curve (Fig. 4). Unlike the Na$^+$-ion exchange on ZTP (0.61), a hardly no formation of the solid solution was observed in the present case; that is, as soon as the exchange started, the reflection peak at 10.1 Å appeared, followed by the peak at 7.9 Å. These two peaks retained considerable intensities up to the maximum exchange, namely, to the end of the reaction. At the same time, the peak at 7.6 Å representing the unexchanged phase also survived with much smaller intensity. It is considered that the increasing steric hindrance occurred as the hydrated Li$^+$ ions replaced protons, and that this resulted in incomplete substitution. The peaks at 10.1 and 7.9 Å correspond to the tetra- and mono-hydrate of dilithium salt, (Zr, Ti)$(\mathrm{LiPO_4})_2\cdot 4\mathrm{H_2O}$ and (Zr, Ti)$(\mathrm{LiPO_4})_2\cdot \mathrm{H_2O}$, as assumed from the lithium-exchanged phases formed in α-ZP.8) In fact, if the exchanged solid was heated at 100 °C for 30 min, the peak at 10.1 Å completely disappeared and the peak at 7.9 Å remained.

From the shape of the titration curves and the X-ray evidence, it may be concluded that, in the Li$^+$-ion exchange on ZTP(1.02), the reaction proceeds with the formation of fully exchanged phases whose water content varies depending upon the environment during or after the exchange process.

It is interesting to compare the Li$^+$-ion exchange behavior on ZTP with that on α-ZP and α-TP. In α-ZP, two exchangeable protons are said to have differing acidities, and a half-exchanged phase is often observed for the reaction with many counter ions. This exchanger also allows variations in the water content at various stages of ion exchange, and it leads to a change in the interlayer spacing. In α-TP, on the other hand, the formation of a half-exchanged phase is difficult to confirm.† Especially for the Li$^+$-ion exchange, the water content is rather unchanged throughout the reaction and the interlayer spacing is also kept constant. The case of ZTP(1.02) is just intermediate inbetween α-ZP and α-TP. It resembles α-TP in that a monolithium phase is absent, but it resembles α-ZP in that the water content varies during exchange, resulting in a change in the interlayer distance. However, taking the exchange behavior of Na$^+$ ion into consideration, the existence or absence of a half-exchanged form is not always simply related to the difference in the acidity of the two exchangeable protons of ZTP. To elucidate the mechanism of the direct formation of the fully exchanged phase, further investigation, including that of the diffusion kinetics of cations in the exchanger solid, are needed.

Potassium-ion Exchange. The same exchanger as used for the Li$^+$-ion exchange, ZTP(1.02), was utilized. The potassium-uptake curves and the phosphate-release curves obtained at 25, 45, and 60 °C are shown in Fig. 6. It is clear that potassium uptake on ZTP(1.02) is not so easy compared to the sodium and lithium uptake. Thus, up to pH 7 about 2 meq K$^+$ ions per g of exchanger were taken up. This value falls to between the corresponding potassium uptakes on α-TP and α-ZP, about 1 meq/g3) and 3 meq/g9) respectively. These values are much less than the exchange amount of alkali metal ions with smaller ionic radii for this pH. The equilibrium pH reached a plateau at about 7.1, where the K$^+$-ion exchange proceeded in parallel with the hydrolysis of the exchanger. No step-by-step exchange such as has been observed in the K$^+$-ion exchange on α-ZP9) was found in the case of ZTP(1.02).

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† Clearfield and Frianeza reported the formation of two sodium-ion-exchanged phases.6)

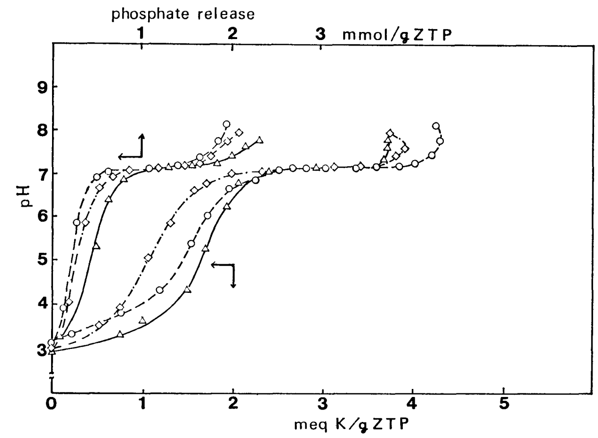

Fig. 6. The pH-titration curves for potassium ion exchange and the phosphate release curves.
—○—: 25 °C, —·◇·—: 45 °C, —△—: 60 °C.
The exchanger is ZTP(1.02) in all the cases.

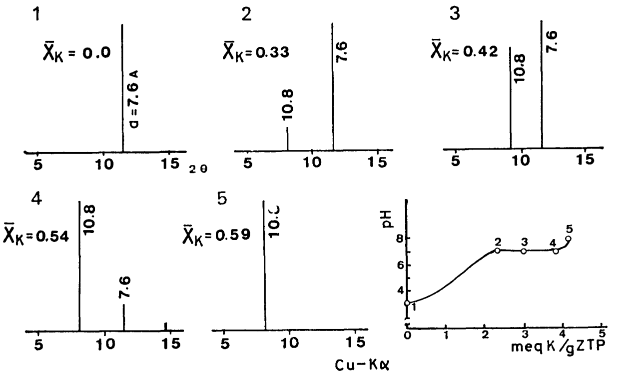

Fig. 7. The lowest angle regions of the X-ray powder diffraction patterns of ZTP(1.02) at several stages of potassium exchange at 25 °C. The numbers 1 to 5 indicate the extent of reaction shown in the titration curve given at the bottom right. $\bar{X}_K$ denotes the ionic fraction of potassium ion in the exchanger.

The maximum exchange was about 60% of the theoretical capacity at 25 °C and even less at higher temperatures. The phosphate release in alkaline solutions was much more extensive in the K^+ uptake than in the Li^+ and Na^+ ion exchange, reflecting the large ionic radius of the K^+ ion, which encounters cavity openings of comparable size.

In Fig. 7, the lowest angle region of the X-ray powder diffractograms of various exchanged solids for the 25 °C experiment are given schematically. Up to an exchange of about 33%, where the equilibrium pH is still below 7, no new solid phase can be observed, indicating the formation of a solid solution; *i.e.*, the K^+ ions are incorporated with ZTP without changing its structure. Above this point, the reflection corresponding to $d_{002}=10.8$ Å appeared, while the peak at 7.6 Å diminished. It should be noted that the exchanger decomposes to such an extent that, at $\bar{X}_K=0.59$, no reflection from the unexchanged phase was observed any longer. The X-ray powder patterns obtained in the 45 and 60 °C experiments were similar to those described above, except that the degree of crystallinity became poorer in the exchange at a higher pH.

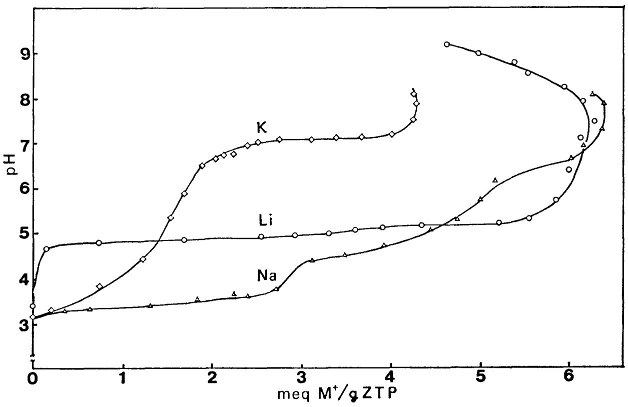

Fig. 8. The alkali metal ion uptake curves at 25 °C. For sodium ion uptake, ZTP(0.93) exchanger was used. For other two ions, ZTP(1.02) was employed.

In the K^+-ion exchange on α-ZP, monopotassium salt, $Zr(KPO_4)(HPO_4)\cdot H_2O$, with an interlayer distance of 7.95 Å, and dipotassium salt, $Zr(KPO_4)_2\cdot 3H_2O$, with an interlayer distance of 10.8 Å, were produced during the exchange process.[9] In the present study, the new solid phase confirmed has the interlayer distance of 10.8 Å, which most probably corresponds to a trihydrate of dipotassium salt, $(Zr,Ti)(KPO_4)_2\cdot 3H_2O$. This means that the half-exchanged phase could not be confirmed in this case either.

Ion-selectivity Series. Comparison is now possible between the ion-exchange behavior of three alkali metal ions on this particular inorganic exchanger. Titration curves measured under quite similar conditions are reproduced in Fig. 8. The selectivity series depends on the load of exchanger. Thus, within the range of loads from 0 to 1.3 meq/g, the selectivity is in the order: $Na^+>K^+>Li^+$, while between 1.3 and 4.5 meq/g, it is $Na^+>Li^+>K^+$. Above 4.5 meq/g loading, it turns out to be $Li^+>Na^+>K^+$, and practically no potassium ions are taken up at all.

It is noticeable that the lithium-ion selectivity increases relative to other ions as the load of the exchanger increases. However, this is a result of the rather constant equilibrium pH for lithium exchange compared to the case of sodium or potassium. In lithium exchange, essentially a single exchanged crystal form seems to exist. Thus, the tetrahydrate of dilithium salt is the most probable form on the exchange site. On the other hand, in the case of sodium exchange, the shape of the titration curve seems to be related to two exchanged forms, mono- and disodium salts. Further, in potassium exchange, the initial formation of a solid solution, followed by the formation of a potassium salt phase, may be responsible for the unique shape of its titration curve.

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