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Note

Lithium ion exchange on α-titanium phosphate

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Polybasic acid salts such as zirconium phosphate have been extensively investigated as ion exchangers. Crystalline salts are less hydrolyzed than amorphous salts and are superior to the latter in the reproducibility of their ion-exchange properties. When amorphous titanium phosphate is refluxed in orthophosphoric acid, it is converted into a crystalline compound, $Ti(HPO_4)_2 \cdot H_2O$ (α-TP), which is isomorphous with crystalline zirconium phosphate (α-ZP).

In this paper, the behaviour of forward and backward lithium ion exchange on α-TP is reported.

EXPERIMENTAL

Preparation of α-TP

α-TP was prepared according to Alberti *et al.*[1] by refluxing amorphous TP in 10 *M* orthophosphoric acid for 200 h. The product was dried in a silica gel desiccator.

Analytical procedures

For the determination of phosphate group, 100 mg of α-TP were fused with sodium carbonate. The phosphate was extracted into hot water and precipitated with magnesia mixture* and the precipitate was ignited and weighed as magnesium pyrophosphate.

For the determination of titanium, 200 mg of α-TP were heated with concentrated sulphuric acid until complete dissolution had occurred. The solution was diluted with water and titanium cupferronate was precipitated and ignited. The PO_4:Ti ratio of the crystalline product was found to be 2.01.

From the result of differential thermal analysis (DTA), the weight loss at 120–180° corresponded to 1 mole of water per formula weight if the formula $Ti(HPO_4)_2 \cdot H_2O$ was assumed. From the X-ray diffraction pattern, the interplanar distance (*d*) values agreed with those reported by Alberti *et al.*[1]. X-ray powder patterns were taken by using Cu K_α radiation.

*[$\overline{H} + Li^+ \rightarrow \overline{Li} + H^+$] ion exchange (forward titration)***

The experiment was carried out by the batch method. Samples of α-TP

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* A mixture of $MgCl_2$, NH_4Cl and NH_4OH.

** The superscript bars refer to the stationary phase.

(250 mg) were equilibrated with 25 ml of 0.1 *N* LiCl + LiOH solution with various pH values. After shaking for 4 days at 25°, aliquots of the supernatant were analyzed for lithium and phosphate and their pH values were measured. Lithium was determined by flame spectrophotometry and phosphate was determined colorimetrically at 380 nm.

The solid phases after equilibration were stored over saturated LiCl (10% relative humidity) and over water (100% relative humidity).

$[\overline{Li} + H^+ \rightarrow \overline{H} + Li^+]$ *ion exchange (backward titration)*

An attempt was made to carry out the backward titration in lithium ion exchange of α-TP. The Li form of TP was prepared by dispersing α-TP in water and slowly titrating it potentiometrically with 0.1 *N* LiOH solution. The equilibrium pH was about 8. Maximum exchange was attained after 3 days. The product was stored over saturated LiCl.

The Li form of TP, corresponding to 250 mg of α-TP, was equilibrated with 25 ml of 0.1 *N* LiCl + HCl solutions with various pH values. Other procedures were the same as in the forward titration.

The solid phases were stored in a water-saturated desiccator and then subjected to thermal analysis and X-ray diffraction measurement.

RESULTS AND DISCUSSION

Fig. 1a shows the forward and backward titration curves. The maximum exchange capacity was about 90% of theoretical exchange capacity.

Crystalline zirconium phosphate prepared either by a refluxing procedure or by direct precipitation exhibited remarkable pH changes at 66% or 50% exchange[2-4]. On the other hand, α-TP showed no pH jump in this region. This monofunctional behaviour is related to the absence of a distinct phase of the monolithium form, as described below.

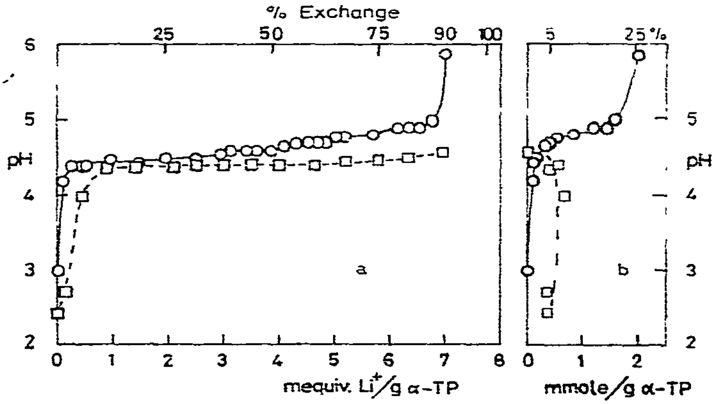

Fig. 1. Titration curves of crystalline titanium phosphate. ○, Crystalline titanium phosphate titrated with 0.1 *N* LiCl + LiOH; □, lithium-form titanium phosphate titrated with 0.1 *N* LiCl + HCl. Abscissae: (a) Li^+ uptake (mequiv./g α-TP); (b) phosphate released to the external solution (mmole/g α-TP). Ordinate: pH at equilibrium.

X-ray powder patterns for the samples conditioned at low (10%) and high relative humidity (100%) as well as the sample immediately after the forward titration were compared. The patterns were the same, *i.e.*, the water content, and hence the interlayer distance, remained the same under the various conditions used. Further, hardly any change in interlayer distance was observed at any stage of the forward titration, and the difference between the H and Li forms was not distinct (Table I).

These observations provided no evidence that the product at half-exchange is a new phase of the monolithium form. From the diffraction patterns, the product is rather considered to be a mixture of the H form and the dilithium form.

Fig. 1b shows the phosphate released to the external solution for 1 g of original exchanger. Contrary to the results of Alberti *et al.*[1], the phosphate was markedly released above the equilibrium pH of 5. At least 25% of total phosphate was released to the external solution at the final stage of the forward titration. This phenomenon was confirmed to be accompanied by the decomposition of the exchanger in contact with the alkaline solution.

On the other hand, the lithium uptake is 90% of the theoretical exchange capacity and is not balanced by the phosphate release, provided that only ideal ion exchange is involved in the process.

Hence information about the behaviour of titanium under these circumstances was required. The final product of the backward titration was in fact less crystalline compared with all other exchanged products and its PO_4:Ti ratio was only 1.9. Hence, it is clear that the phosphate was partly released and titanium remained in some form in the solid phase. There is a possibility that titanium, once released, may return to the solid phase as hydrated titanium oxide. A comparison was made of the

TABLE I

X-RAY DIFFRACTION PATTERNS (*d*, Å) OF CRYSTALLINE TITANIUM PHOSPHATE
Abbreviations: s = strong; m = medium; w = weak; v = very.

Final product of backward titration	*H form*		*50% exchange*	*Final product of forward titration (Li form)*	
	This work	*Alberti et al.*[1]		*This work*	*Alberti et al.*[1]
(11.39 s)*					
7.65 vs	7.56 s	7.56 s	7.62 vs	7.57 vs	7.56 vs
			4.39 vw	4.39 s	4.42 w
4.25 w	4.25 m	4.25 m	4.24 m		
			4.22 m	4.21 s	4.20 s
4.03 vw	4.05 w	4.05 w	4.05 m		
3.44 s	3.46 vs	3.45 vs	3.42 vs	3.42 vs	3.42 vs
3.15 m	3.15 vw	3.15 vw	3.15 vw		
				2.69 w	2.70 w
2.61 m	2.61 w	2.61 w	2.60 vw	2.60 w	2.59 w
			2.54 m	2.54 s	2.54 s
2.50 m	2.50 s	2.49 s	2.50 m		
			2.27 w	2.27 m	2.27 m
2.24 vw	2.25 m	2.24 m	2.24 w		
				2.13 w	2.12 w
2.02 vw	2.02 m	2.02 m	2.02 vw	2.00 w	2.00 w
1.87 w	1.87 m	1.86 m	1.73 vw	1.74 w	1.74 w

* See text (p. 266).

X-ray patterns of the ignited solid phase and ignited pure titanium dioxide, but clear evidence of the existence of "free" hydrated titanium oxide in the solid phase was not obtained.

In the backward titration, about 5% of total phosphate was released over the pH range 2.5–4.5 (Fig. 1b). This value is considerably higher than the release in the forward process over the same pH region

α-TP has a layered structure. In the X-ray powder diffraction patterns of α-TP, the *d*-value corresponding to the first strong reflection indicates the interlayer distance. This was found to be 7.56 Å and corresponded to the (002) plane. The interlayer distance was kept essentially constant at all stages of the forward titration.

From the half-way stage of the backward titration, however, broad or sometimes sharp peaks appeared in the region $2\theta < 10°$. They are not very reproducible and could not be assigned to any peak expected from the known lattice parameter of α-TP[5], whereas the remainder of diffractogram is reproducible and reasonably indexed.

In one experiment, the final product of the backward titration gave a strong peak ($2\theta = 7.76°$, $d = 11.39$ Å) immediately after the equilibration (Table I). The indexing of this peak was not possible, and the peak shifted and weakened after several months' storage. As the crystallinity became poor, water molecules may have become attached near the surface of exchanger particles and partly widened the interplanar distance. The appearance of these unidentified peaks may indicate that the decomposition of the exchanger begins and the crystallinity becomes poor.

In the case of α-zirconium phosphate, when more than 33% of the Li^+ was replaced with protons, gelatinous zirconium phosphate formed instead of α-ZP crystals[2]. At the completion of the backward titration, only the gel remains. This extreme case was not observed in the α-TP exchanger.

The results of the thermal analysis are given in Fig. 2. The half-exchanged

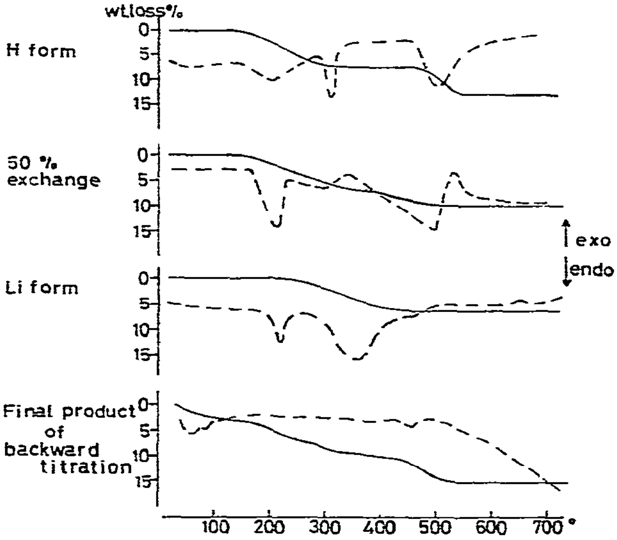

Fig. 2. Thermal analyses of various phases of titanium phosphate. Solid line, TG curve; broken line, DTA curve.

product and the final product of the forward titration were each found to have 1 mole of water of crystallization per formula weight. On the other hand, the final product of the backward titration showed rather featureless change in the thermogravimetric (TG) and DTA curves, reflecting its poor crystallinity compared with the original α-TP. It released 1.3 mole of water when heated to 300° on the assumption that anhydrous TP was $Ti(HPO_4)_2$. Excess of water is considered to be absorbed to a more or less amorphous portion of α-TP.

In the H form and lithium ion form of α-ZP, the interplanar distances and the number of molecules of water of crystallization varied widely. This did not occur for α-TP. Only the final product of the backward titration had slightly more water of crystallization, yet it still retained crystallinity. These results suggest that α-TP is rather rigid in its ion-exchange behaviour compared with α-ZP. Further studies on the exchange of alkali metal ions other than lithium ion are now in progress in order to extend the information along these lines.

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