Studies of Inorganic Ion Exchangers. II.[1] Effects of Sulfuric Acid on the Synthesis of $Ti(HPO_4)_2\cdot 0—1/2H_2O$

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In order to develop an inorganic ion exchanger for industrial use, sulfuric acid has been added to the reaction system of amorphous titanium(IV) phosphate and phosphoric acid. The effects of the additive on the formation of titanium(IV) hydrogenphosphate, a compound observed to have ion exchange affinities towards K^+ and Cs^+, have been investigated. $Ti(HPO_4)_2\cdot 0—1/2H_2O$ has been synthesized using the sulfuric acid solution of $TiOSO_4$, an intermediate in the production process of titanium dioxide. The addition of sulfuric acid to phosphoric acid and a resulting mole ratio of H_2SO_4/H_3PO_4 greater than 0.14, produced a borderline in the formation of the monohydrate and hemihydrate within the temperature range of 148—155 °C. Titanium(IV) hydrogenphosphate crystallized as fine particles (1—3 μ) by the double decomposition between the sulfuric acid solution of $TiOSO_4$ and phosphoric acid. The X-ray diffraction pattern of the product obtained using the sulfuric acid solution of $TiOSO_4$ above 160 °C compared favourably with that of the hemihydrate already reported. The composition was shown by the formula of $Ti(HPO_4)_2\cdot 0—1/2H_2O$. In the X-ray diffraction pattern of $Ti(HPO_4)_2\cdot 0—1/2H_2O$, two characteristic diffraction lines appeared at 11.6 and 9.21 Å; thus it has been assumed that the product is not a pure crystallite but a mixture of two or more species.

Some phosphates of polyvalent metals have been known as inorganic ion exchangers, zirconium phosphate being especially useful in analytical chemistry.[2,3] Previous investigations of the ion exchange properties of some phosphates,[4,5] lead to this investigation of titanium phosphate. The crystalline titanium(IV) bis(hydrogenphosphate) monohydrate, $Ti(HPO_4)_2\cdot H_2O$, can absorb Li^+ and Na^+,[6,7] but not the ions of larger radius, such as K^+ and Cs^+. In a previous work,[1] titanium(IV) bis(hydrogenphosphate) hemihydrate, $Ti(HPO_4)_2\cdot 1/2H_2O$, was formed by refluxing amorphous titanium(IV) phosphate with concentrated phosphoric acid. The X-ray diffraction pattern of the hemihydrate differed considerably from that of the monohydrate, and larger *d*-values appeared. It has been observed that this compound has ion exchange capacities towards K^+ and Cs^+. In the present work, an attempt has been made to prepare $Ti(HPO_4)_2\cdot 1/2H_2O$ by the reaction of concentrated phosphoric acid with the sulfuric acid solution of titanium oxide sulfate, $TiOSO_4$, the intermediate in the production process of titanium dioxide. The effects of sulfuric acid on the formation of titanium phosphate have been investigated by refluxing amorphous titanium(IV) phosphate with a mixture of H_2SO_4 and H_3PO_4. Subsequently, $Ti(HPO_4)_2\cdot 0—1/2H_2O$ has been synthesized using the sulfuric acid solution of $TiOSO_4$ or titanium(IV) oxide monohydrate (metatitanic acid, $TiO_2\cdot H_2O$).

Experimental

Starting Materials. Amorphous titanium(IV) phosphate has been prepared by the method described in a previous paper.[1] Synthesising conditions and analytical data are given in Table 1.

The sulfuric acid solution of $TiOSO_4$, which is the polish for titanium dioxide as a white pigment and does not contain iron as an impurity, was obtained from Ishihara Sangyo Kaisha Ltd. The composition is shown as a footnote in Table 2. $TiO_2\cdot H_2O$ used was a commercial grade powder.

Preparation of Titanium(IV) Bis(hydrogenphosphate). An appropriate quantity of titanium compound and other materials (amorphous titanium(IV) phosphate, H_2SO_4 soln of $TiOSO_4$, $TiO_2\cdot H_2O$: 25 g, 30 ml, 9.18 g) were placed in a three-necked flask, and H_3PO_4–H_2SO_4 solution (900 ml) was added. The mixture was refluxed for 50 h after which a condenser and a thermometer were connected to the flask. The resulting precipitate was separated centrifugally from the mother liquor, water added, the mixture vigorously shaken up, and the precipitate was separated centrifugally. This procedure was repeated several times, and the product finally dried at 50—60 °C for 24 h.

Analysis. The components of the product, P_2O_5, TiO_2, and H_2O, were determined by previously reported methods.[1] The quantity of H_2SO_4 in the mother liquor was determined gravimetrically as barium sulfate. The X-ray diffraction patterns were obtained using a Rigaku-Denki model 2001 diffractometer with Ni-filtered Cu $K\alpha$ radiation, with 20 kVP and 15 mA, or 30 kVP and 20 mA.

Results and Discussion

Reaction of Amorphous Titanium(IV) Phosphate with H_3PO_4–H_2SO_4 Solution. The effects of sulfuric acid on the formation of titanium(IV) bis(hydrogenphosphate) have been investigated by using amorphous titanium(IV) phosphate as the starting material. The conditions of synthesis and the results of analysis are summarized in Table 1.

Proportion of Titanium Compound with Mother Liquor. When the quantity of amorphous titanium(IV) phosphate is small compared with the volume of mother liquor, the reflux is smooth; this production is, however, commercially unprofitable. When a large amount of the titanium compound is refluxed with the mother liquor, the operation is not smooth, and the growth of the crystal of titanium(IV) bis(hydrogenphosphate) is obstructed. As may be seen from Table 1 (Nos. 1—4), the quantity of amorphous titanium(IV) phosphate mixed with H_3PO_4 as the mother liquor was varied. The X-ray diffraction patterns of the products thus obtained are shown in Fig. 1. It is evident that the crystallinities of the products increase in the order Nos. 1, 2, and 3. The ratios (R) of the volume of mother liquor to the

TABLE 1. SYNTHESIZING CONDITIONS OF TITANIUM(IV) BIS(HYDROGENPHOSPHATE) BY THE ADDITION OF SULFURIC ACID, AND ANALYTICAL DATA

No.	Reaction conditions[a)]							Reaction product				
		Mother liquor										
	Amorphous titanium-(IV) phosphate (g)	H_3PO_4 (mol/l)	H_2SO_4 (mol/l)	$\frac{H_2SO_4}{H_3PO_4}$	Volume (ml)	Temp (°C)	Time (h)	TiO_2 (%)	P_2O_5 (%)	H_2O (%)	TiO_2: P_2O_5: H_2O (Mole ratio)	Estimated formula
1	20.0	15.1	0	0.00	300	175	12	32.7	57.0	10.3	1.02:1.00:1.43	$Ti(HPO_4)_2 \cdot 1/2H_2O$
2	4.0	15.1	0	0.00	96	175	12	32.5	56.9	10.6	1.02:1.00:1.47	$Ti(HPO_4)_2 \cdot 1/2H_2O$
3	3.0	15.1	0	0.00	96	175	12	32.0	58.1	10.9	0.98:1.00:1.48	$Ti(HPO_4)_2 \cdot 1/2H_2O$
4	2.0	14.9	0	0.00	97	175	12	31.6	58.0	10.4	0.97:1.00:1.41	$Ti(HPO_4)_2 \cdot 1/2H_2O$
5	3.0	12.9	1.8	0.14	101	175	12	31.6	57.4	11.0	0.98:1.00:1.51	$Ti(HPO_4)_2 \cdot 1/2H_2O$
6	3.0	12.4	5.1	0.41	96	175	12	32.5	57.2	10.4	1.01:1.00:1.43	$Ti(HPO_4)_2 \cdot 1/2H_2O$
7	3.0	9.1	7.5	0.82	88	175	12	31.7	57.1	11.2	0.99:1.00:1.54	$Ti(HPO_4)_2 \cdot 1/2H_2O$
8	3.0	12.1	1.7	0.14	108	140	15	30.9	54.8	14.5	1.00:1.00:2.08	$Ti(HPO_4)_2 \cdot H_2O$
9	3.0	12.8	1.8	0.14	102	148	15	30.7	54.7	14.6	1.01:1.00:2.11	$Ti(HPO_4)_2 \cdot H_2O$
10	3.0	14.3	2.0	0.14	91	155	12	32.2	56.8	11.1	1.01:1.00:1.54	$Ti(HPO_4)_2 \cdot 1/2H_2O$
11	3.0	16.5	2.3	0.14	79	160	12	32.3	57.0	10.7	1.01:1.00:1.48	$Ti(HPO_4)_2 \cdot 1/2H_2O$
12	3.0	9.9	4.1	0.41	110	148	12	31.5	54.5	14.0	1.03:1.00:2.03	$Ti(HPO_4)_2 \cdot H_2O$
13	3.0	10.4	4.3	0.41	105	155	12	33.6	57.8	8.7	1.03:1.00:1.18	$Ti(HPO_4)_2 \cdot$ 0—$1/2H_2O$
14	3.0	7.3	6.0	0.82	120	148	12	32.2	54.9	13.0	1.04:1.00:1.86	$Ti(HPO_4)_2 \cdot$ 1/2—$1H_2O$
15	3.0	7.7	6.4	0.83	113	155	12	33.2	55.8	11.0	1.06:1.00:1.56	$Ti(HPO_4)_2 \cdot 1/2H_2O$
16	25.0	13.0	1.8	0.14	880	160	24	32.4	56.2	11.4	1.02:1.00:1.60	$Ti(HPO_4)_2 \cdot 1/2H_2O$
17	25.0	13.0	1.8	0.14	880	160	50	32.0	56.4	10.1	1.01:1.00:1.43	$Ti(HPO_4)_2 \cdot 1/2H_2O$
								42.7	33.8	23.3	2.24:1.00:5.42	

a) The mixture of amorphous titanium(IV) phosphate and mother liquor was refluxed at boiling point.

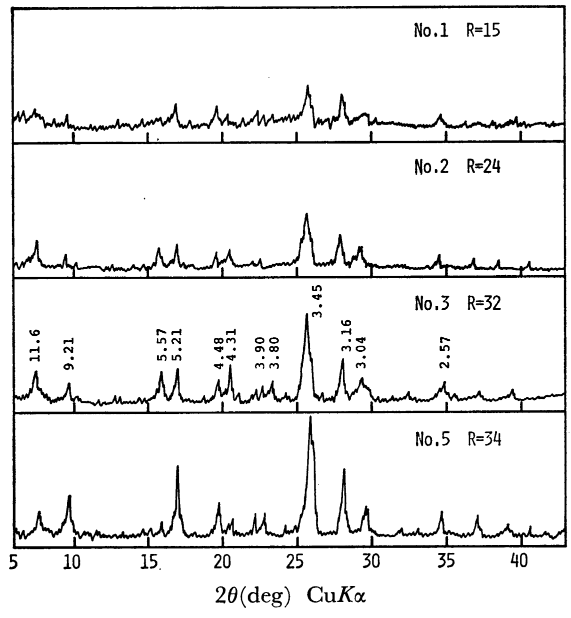

Fig. 1. X-Ray diffraction patterns of $Ti(HPO_4)_2 \cdot 1/2H_2O$. Effect of amount of amorphous titanium(IV) phosphate to mother liquor.
R: Mother liquor(ml)/amorphous titanium(IV) phosphate(8). Nos. 1, 2, and 3: H_3PO_4 used as mother liquor, No. 5: H_3PO_4–H_2SO_4 mixed solution used as mother liquor. Numerals near peaks indicate corresponding *d* values.

weight of titanium compound were found suitable within 32 to 50 (ml/g). In No. 5 the H_3PO_4–H_2SO_4 solution was used as the mother liquor, and the crystallinity of product improved more than in the case of only H_3PO_4.

Effect of Concentration of H_2SO_4. The effect of concentration of H_2SO_4 added to the mother liquor was examined (Nos. 5—7). The initial volume ratios of 18 M H_2SO_4 to 14.5 M H_3PO_4 were 1: 9, 2.5: 7.5, and 4: 6 in Nos. 5, 6, and 7, respectively. In these cases, the concentrations of H_3PO_4 and H_2SO_4 in the mother liquor after reflux are shown in Table 1. In the product X-ray diffraction patterns, the intensities decreased slightly with increase in H_2SO_4. However, the compositions of products and X-ray diffraction patterns were all the same with those of $Ti(HPO_4)_2 \cdot 1/2H_2O$. Therefore, an obstacle to the formation of the hemihydrate did not appear until a volume ratio of 4: 6 was reached. But the existence of a different phosphate was recognized from the X-ray diffraction pattern and analytical data (TiO_2: 35.2%, P_2O_5: 35.6%, SO_3: 19.5%, H_2O: 8.5%) of the product formed in the case of a volume ratio 9: 1 of H_2SO_4 to H_3PO_4.

Effect of Reaction Temperature. As previously reported, $Ti(HPO_4)_2 \cdot 1/2H_2O$ was formed by refluxing amorphous titanium(IV) phosphate with H_3PO_4 containing more than 64% P_2O_5 at above 170 °C.[1)] $Ti(HPO_4)_2 \cdot H_2O$ was also formed as the solid phase in equilibrium with the mother liquor containing 13—64% P_2O_5. Variations in the mixing ratio of H_2SO_4 to H_3PO_4 and the refluxing temperature were conducted (Nos. 5 and 8—15). From the results of analysis and the X-ray diffraction data, the species of titanium phosphate are shown in Fig. 2. As seen from the figure a mother liquor consisting of only phosphoric acid

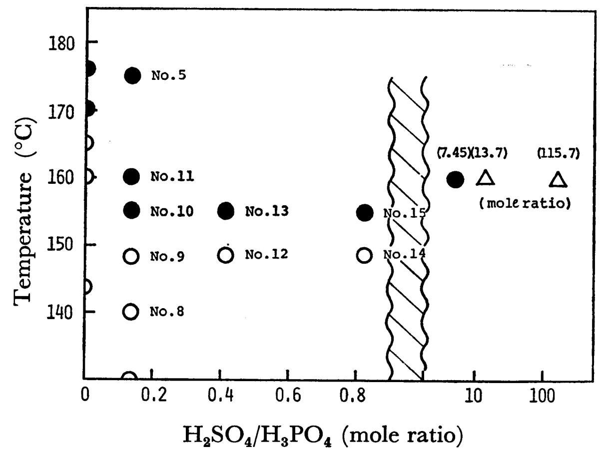

Fig. 2. Effects of sulfuric acid in mother liquor and reaction temperature on formed salts.
●: $Ti(HPO_4)_2\cdot 1/2H_2O$, ○: $Ti(HPO_4)_2\cdot H_2O$, △: unknown salt.

produced a border in the formation of the monohydrate and the hemihydrate between 160 and 170 °C. When the mole ratio of H_2SO_4 to H_3PO_4 exceeded 0.14, a borderline appeared in the range of 148—155 °C, *i.e.* the reaction temperature for formation of the hemihydrate was lowered by about 15 °C by the addition of H_2SO_4. Since the fraction of water in the mother liquor decreased by the addition of 18 M H_2SO_4, the water required for the formation of the monohydrate was not sufficient, and the resulting hemihydrate was formed as the stable solid phase in equilibrium with the mother liquor. It is possible that the sulfuric acid in the heated mother liquor dehydrated the water of crystallization.

Determination of Reaction Time. The effects of reaction time in the synthesis of $Ti(HPO_4)_2\cdot 1/2H_2O$ have been examined (Nos. 11(12h), 16(24h), and 17(50h)). With the H_3PO_4–H_2SO_4 solution as mother liquor, the X-ray diffraction patterns showed the crystallinity of product improved until a reaction time of 24 h. The reaction time in the synthesis of the monohydrate has been reported to be 50[6] and 200 h.[7] Therefore, in terms of hemihydrate formation as an ion exchanger and the commercialization of the process the reaction time has been set at 50 h.

Synthesis of $Ti(HPO_4)_2\cdot 0$—$1/2H_2O$ Using the Sulfuric Acid Solution of $TiOSO_4$. The synthesizing conditions of titanium(IV) bis(hydrogenphosphate) and their analytical results are summarized in Table 2.

The reaction between $TiOSO_4$ and H_3PO_4 is shown in the following equation

$$TiOSO_4 + 2H_3PO_4 \longrightarrow Ti(HPO_4)_2\cdot H_2O + H_2SO_4.$$

Titanium(IV) bis(hydrogenphosphate) crystallizes in the mother liquor, and then sulfuric acid is newly formed. When the $TiOSO_4$–H_2SO_4 solution was used as the starting material, a gelatinous product of undefined composition was initially produced. To avoid aggregation of the gel, the $TiOSO_4$–H_2SO_4 solution was added little by little to the stirred H_3PO_4–H_2SO_4 solution. A second method was to stir the reaction mixture without refluxing in a mother liquor having the boilling point higher than the appointed reaction temperature. This method is called the precipitate method compared with the previous one, the refluxing method. In No. 18, which used a mother liquor of boilling point 160 °C, the monohydrate was formed by the precipitate method at 100 °C. The diameter of the product thus obtained was 10—30 μ, and appeared larger than that of the product formed by the refluxing method. Upon investigation through a microscope the product was shown to be an aggregation of fine particles. This aggregation gradually separated into fine particles as the temperature of the mother liquor rose. In Nos. 19—21 (precipitate method) and Nos. 22—25 (refluxing method) the monohydrate, hemihydrate and anhydride were obtained as fine particles with a diameter of about 1—3 μ. The X-ray diffraction patterns of $Ti(HPO_4)_2\cdot H_2O$ formed by the precipitate method and $Ti(HPO_4)_2\cdot 0$—$1/2H_2O$ formed by the refluxing method are shown in Fig. 3.

The X-ray diffraction patterns of the products obtained using the sulfuric acid solution of $TiOSO_4$ at

Table 2. Synthesizing conditions of titanium(IV) bis(hydrogenphosphate) using $TiOSO_4$–H_2SO_4 solution or $TiO_2\cdot H_2O$, and analytical data

No.	Reaction conditions: Raw material: $TiOSO_4$[a] (ml)	Raw material: $TiO_2\cdot H_2O$ (g)	Mother liquor: H_3PO_4 (mol/l)	Mother liquor: H_2SO_4 (mol/l)	Mother liquor: Volume (ml)	Temp (°C)	Time (h)	Method[b]	Reaction product: TiO_2 (%)	P_2O_5 (%)	H_2O (%)	$TiO_2:P_2O_5:H_2O$ (Mole ratio)	Estimated formula
18	20	—	8.60	2.82	600	100	50	PPT	31.4	57.4	13.6	0.97:1.00:1.87	$Ti(HPO_4)_2\cdot H_2O$
19	30	—	6.76	3.08	900	135	50	PPT	32.1	54.4	14.5	1.05:1.00:2.10	$Ti(HPO_4)_2\cdot H_2O$
20	30	—	8.03	3.40	900	150	50	PPT	31.2	54.6	14.2	1.01:1.00:2.05	$Ti(HPO_4)_2\cdot H_2O$
21	30	—	8.03	3.40	900	160	50	PPT	32.6	57.7	9.0	1.01:1.00:1.23	$Ti(HPO_4)_2\cdot$ 0—$1/2H_2O$
22	20	—	8.60	2.82	600	163	50	REF	32.4	57.5	8.85	1.01:1.00:1.22	$Ti(HPO_4)_2\cdot$ 0—$1/2H_2O$
23	30	—	10.9	3.06	900	165	50	REF	32.4	60.7	7.6	0.95:1.00:0.99	$Ti(HPO_4)_2$
24	—	9.18	8.31	1.59	900	140	50	REF	29.9	54.9	14.5	0.97:1.00:2.08	$Ti(HPO_4)_2\cdot H_2O$
25	—	9.18	9.26	3.83	900	168	50	REF	32.8	56.8	8.2	1.02:1.00:1.14	$Ti(HPO_4)_2$

a) Solution containing 250 g TiO_2 and 1044 g/l H_2SO_4. b) PPT: precipitate method, REF: refluxing method.

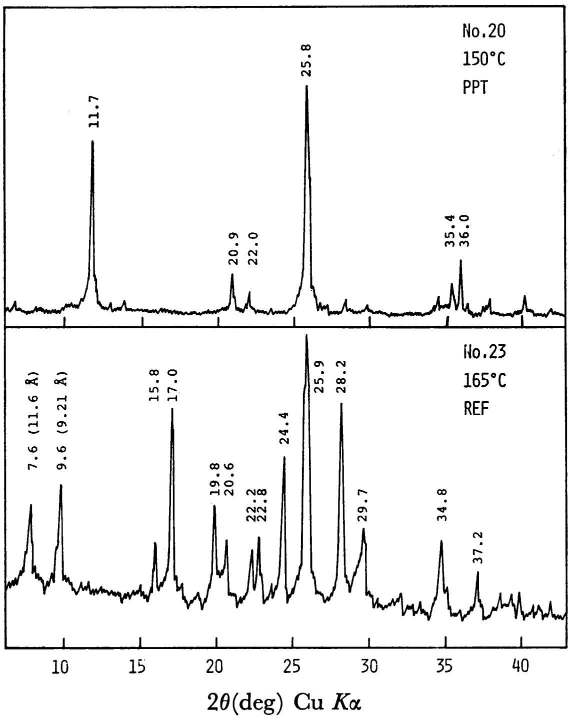

Fig. 3. X-Ray diffraction patterns of $Ti(HPO_4)_2 \cdot H_2O$ (No. 20) and $Ti(HPO_4)_2 \cdot 0$—$1/2H_2O$ (No. 23). No. 20: 15 mA, 20 kVP, No. 23: 20 mA, 30 kVP.

above 160 °C were almost the same with those of the hemihydrate obtained using amorphous titanium(IV) phosphate. However, from the results of analysis, the compositions of product were shown by $Ti(HPO_4)_2 \cdot 0$—$1/2H_2O$, and the products (Nos. 23, 25) corresponding to the anhydride were also formed at times. In the X-ray diffraction pattern of $Ti(HPO_4)_2 \cdot 0$—$1/2H_2O$ the intensity was lower than that of the monohydrate, two characteristic diffraction lines appearing at 11.6 and 9.21 Å. The lines also differed slightly in the 2θ values. It may be assumed from these X-ray diffraction patterns that $Ti(HPO_4)_2 \cdot 0$—$1/2H_2O$ is not a pure crystallite, but consists of two or more species. Generally, it is considered that the diffusion of phosphoric acid on the solid of titanium(IV) oxide monohydrate ($TiO_2 \cdot H_2O$) is the rate determining step. The powders of $TiO_2 \cdot H_2O$ were clearly dissolved with sulfuric acid, and therefore, the rate of formation of $Ti(HPO_4)_2 \cdot 0$—$1/2H_2O$ would be accelerated using a H_3PO_4–H_2SO_4 solution as compared with the pure phosphoric acid solution. The refluxing method, in which the suspended TiO_2–H_2O actively reacts with the mother liquor, is more suitable than the precipitate method.

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