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A Study of Inorganic Ion Exchangers. VII.[1] The Synthesis of γ-$NH_4ZrH(PO_4)_2$ and Ion-exchange Properities of γ-$Zr(HPO_4)_2\cdot 2H_2O$

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The conditions for the synthesis of γ-$NH_4ZrH(PO_4)_2$ and the ion-exchange properties of γ-$Zr(HPO_4)_2\cdot 2H_2O$ were investigated. The influence of the mole ratio of MH_2PO_4 (M=Na, K, and NH_4) to $ZrOCl_2$ on the formation of γ-zirconium phosphate using NaH_2PO_4 as MH_2PO_4 was such that the γ-form was obtained not in the NaH_2PO_4/$ZrOCl_2$ mole ratio of 4, but in are of 8.3 or more. In case of the Na or K salt, a non-stoichiometric compound, $M_xZrH_{2-x}(PO_4)_2$, was obtained. When using the NH_4 salt, a stoichiometric compound was synthesized at 120—280 °C in accordance with the following equation: $ZrOCl_2+NH_4H_2PO_4 \longrightarrow NH_4ZrH(PO_4)_2+NH_4Cl+HCl+H_2O$. Using an autoclave lined with Hastelloy-B and equipped with a stirrer, the synthesis was carried out by a reaction at 150—160 °C for 18—54 h. γ-$Zr(HPO_4)_2\cdot 2H_2O$ was prepared from $NH_4ZrH(PO_4)_2$, and its ion-exchange capacity at pH 4.5 and selectivity quotient toward alkali metals and ammonium ions were measured. The measured values increased in the order of $Li^+ < Cs^+ < Na^+ < K^+ < NH_4^+$.

The crystalline phosphates of quadrivalent metals are generally prepared by reflux or a hydrothermal reaction of amorphous phosphate with phosphoric acid of a suitable concentration. The method for synthesizing γ-zirconium(IV) bis(hydrogenphosphate) dihydrate (γ-$Zr(HPO_4)_2\cdot 2H_2O$ or γ-zirconium phosphate) is somewhat different from the above process. Clearfield *et al.*[2] carried out the reflux of a zirconium phosphate gel in a mother liquor comprised of a concentrated NaH_2PO_4 and HCl solution. Yamanaka *et al.*[3] reported the region of the formation of $NaZrH(PO_4)_2$ and the structural model of γ-$Zr(HPO_4)_2\cdot 2H_2O$. They carried out a hydrothermal reaction of phosphate gel with a weakly acidified aqueous solution of sodium phosphate to obtain γ-zirconium phosphate, they found that the region of the formation of the γ-form was within the pH values of 1.5—4.0 at 180—230 °C.

In the present work, through the heating of a mixture of $ZrOCl_2\cdot 8H_2O$, MH_2PO_4 (M=Na, K, or NH_4) and water in a sealed glass tube, $MZrH(PO_4)$ was formed above 120 °C. Consequently, the mole ratios of MH_2PO_4 to $ZrOCl_2$ (M/Zr) and the reaction temperatures were investigated in order to determine whether or not the ammonium salt had a tendency to form a stoichiometric compound more easily than sodium and potassium salt; it was possible to directly synthesize $MZrH(PO_4)_2$ using an autoclave. In addition, the ion-exchange properties of γ-$Zr(HPO_4)_2\cdot 2H_2O$ toward Li^+, Na^+, K^+, Cs^+, and NH_4^+ were studied.

Experimental

Synthesis of $MZrH(PO_4)_2$. In a 20-cm³ hard glass tube were placed 1.61 g of $ZrOCl_2\cdot 8H_2O$, 2.4—9.5 g of MH_2PO_4 (M=Na, K, or NH_4) and 5 cm³ of water. The contents were thoroughly shaken, and the tube was sealed. From 2—4 such sealed tubes were prepared under various conditions (the type of MH_2PO_4 and mole ratio of M/Zr) and placed in a 200-cm³ stainless steel autoclave. To the autoclave was added 80 cm³ of water to prevent any rupture of the tubes. The contents of the tubes were heated to specified temperatures (120—280 °C), and the resulting products in the tubes were separated from the mother liquors, washed thoroughly with water, and dried at 20 °C in a relative humidity of 75%, or at 105 °C. On the other hand, 16.1 g of $ZrOCl_2\cdot 8H_2O$, 46 g of $NH_4H_2PO_4$ and 100 cm³ of water were directly charged in to a 300-cm³ autoclave lined with Hastalloy-B (Mitsubishi Kinzoku Co.). The mixture was made to react for 18—54 h with stirring (180 min⁻¹) at 120—165 °C. The product thus formed was repeatedly washed with water, separated by a centrifugal separator, and dried. γ-$Zr(HPO_4)_2\cdot 2H_2O$ was obtained by the ion-exchange treatment of γ-$NH_4ZrH(PO_4)_2$.

Analysis. The composition of the reaction products was analyzed according to a previously reported method.[4] The amount of H_2O was determined on the basis of the weight loss of the heated product at 800 °C (in the case of the $NH_4ZrH(PO_4)_2$, the amount of NH_3 was calculated from the weight loss on heating). The Na_2O and K_2O were measured according to the flame-photometering method. The NH_3 was determined by Kjeldahl's method. The empirical values of P_2O_5 and ZrO_2 in the reaction products of $MZrH(PO_4)_2$ synthesized in the present study were almost 1 : 1 in mole ratio. Accordingly, the amounts of the two components were also obtained by dividing the residual amount (R%) derived from the following equation by the proportion of the formula weight of P_2O_5 and ZrO_2:

$$100\% - H_2O\% - M_2O\% \ (\text{or } NH_4\%) = R\%.$$

X-Ray diffraction was then performed with a Shimadzu Seisakusho diffractometer under the conditions of Cu *Kα*, 30 kV P, and 20 mA.

Ion-exchange Capacity. The ion-exchange titration curves and ion-exchange values were obtained according to a previously reported method.[5]

Results and Discussion

Formation of γ-$MZrH(PO_4)_2$. In the previously reported reaction methods,[2,3] much more sodium phosphate was used than a soluble zirconium salt (M/Zr=20), and the adjustment of the pH value was necessary for the formation of γ-$MZrH(PO_4)_2$.

The Mole Ratios of $MH_2PO_4/ZrOCl_2$: Table 1 shows the synthesis conditions and analytical values of the γ-zirconium phosphate obtained by the reaction of $ZrOCl_2$ with NaH_2PO_4 or KH_2PO_4. Table 2 gives the same data for the γ-ammonium zirconium(IV) hydrogen bis(phosphate) obtained by the reaction of $ZrOCl_2$ with $NH_4H_2PO_4$.

In Expt No. 1 in Table 1, a mixture of NaH_2PO_4 and Na_2HPO_4 was used as the phosphate. The pH value of the mother liquid, 4.26, was thus somewhat higher[3]

Table 1. Synthesis and analysis of γ-$MZrH(PO_4)_2$ (M=Na, K)

	Reaction conditions							Reaction products					
No.	$ZrOCl_2 \cdot 8H_2O$ (g)	MH_2PO_4[a)] (M=Na, K) (g)	H_2O (ml)	M/Zr atomic ratio	Temp °C	Time h	Mother liquor (pH)	Dry (Temp/°C, R.H%)	ZrO_2 (%)	P_2O_5 (%)	M_2O (%)	H_2O (%)	$ZrO_2 : P_2O_5 : M_2O : H_2O$ (mole ratio)
1	3.22	2.40 (1.42)	50	2.0 (4.0)	250	96	4.26	105	44.6	51.4	2.2	1.8	1.0 : 1.0 : 0.1 : 0.3
2	1.61	2.40	10	4.0	250	96	2.32	105	42.9	49.5	2.3	5.3	1.0 : 1.0 : 0.1 : 0.8
3	1.61	5.00	10	8.3	250	96	2.61	20,0	40.6	46.8	5.4	7.1	1.0 : 1.0 : 0.3 : 1.2
4	1.61	10.0	10	16.6	250	96	2.88	20,0	40.2	46.2	5.8	7.8	1.0 : 1.0 : 0.3 : 1.3
5	1.61	5.44	5	8.0	120	96	3.12	20,75	32.8	38.2	10.7	18.0	1.0 : 1.0 : 0.4 : 3.1
6	1.61	5.44	5	8.0	200	96	2.57	20,0	40.3	46.3	5.1	8.4	1.0 : 1.0 : 0.2 : 1.4
7	1.61	5.44	5	8.0	250	96	3.38	105	42.4	48.9	3.9	4.8	1.0 : 1.0 : 0.1 : 0.8
8	1.61	5.44	5	8.0	280	96	2.61	105	39.2	45.2	10.7	4.9	1.0 : 1.0 : 0.4 : 0.8
($NaZrH(PO_4)_2$)									(40.38	46.51	10.16	2.95)	
($KZrH(PO_4)_2$)									(38.36	44.18	14.66	2.80)	

a) In Nos. 1—4, NaH_2PO_4, and in Nos. 5—8, KH_2PO_4 are used; the values in parentheses indicate the weight of Na_2HPO_4 used with NaH_2PO_4.

Table 2. Synthesis and analysis of γ-$NH_4ZrH(PO_4)_2$

	Reaction conditions							Reaction products					
No.	$ZrOCl_2 \cdot 8H_2O$ (g)	$NH_4H_2 \cdot PO_4$ (g)	H_2O (ml)	NH_4/Zr (mole ratio)	Temp °C	Time h	Mother liquor (pH)	Dry (Temp/°C, R.H%)	ZrO_2 (%)	P_2O_5 (%)	NH_3 (%)	H_2O (%)	$ZrO_2 : P_2O_5 : NH_3 : H_2O$ (mole ratio)
1	3.22	3.42	7	3.0	250	96	2.15	105	43.2	49.7	3.7	3.5	1.0 : 1.0 : 0.6 : 0.5
2	1.61	2.30	10	4.0	250	96	2.25	105	41.1	47.4	4.8	6.7	1.0 : 1.0 : 0.8 : 1.1
3	12.9	38.0	50	8.2	250	96	2.51	20,75	41.2	47.5	5.5	5.9	1.0 : 1.0 : 1.0 : 1.5
4	1.61	9.5	5	16.7	250	96	2.65	105	41.0	47.1	5.5	6.5	1.0 : 1.0 : 1.0 : 1.0
5	1.61	4.6	5	8.0	120	138	3.39	20,75	37.5	43.0	5.0	14.6	1.0 : 1.0 : 1.0 : 2.7
6	1.61	4.6	5	8.0	200	96	2.53	105	41.1	47.3	4.7	7.0	1.0 : 1.0 : 0.8 : 1.2
7	6.44	19.0	25	8.2	280	96	2.76	105	41.3	47.5	5.4	5.8	1.0 : 1.0 : 0.9 : 1.0
8	16.1	46.0	100	8.0	120	18	3.61	20,75	36.5	42.1	5.5	17.0	1.0 : 1.0 : 0.9 : 3.2
9	16.1	46.0	100	8.0	150	18	3.56	20,0	40.2	46.3	5.2	8.4	1.0 : 1.0 : 0.9 : 1.4
10	16.1	46.0	100	8.0	150	36	3.50	20,0	40.6	46.7	5.2	7.5	1.0 : 1.0 : 0.9 : 1.3
11	16.1	46.0	100	8.0	150	54	3.45	20,0	40.9	47.1	5.3	6.7	1.0 : 1.0 : 1.0 : 1.1
12	16.1	46.0	100	8.0	165	18	3.42	20,75	37.5	43.3	4.7	14.6	1.0 : 1.0 : 0.9 : 2.7
13	— ZrP							20,75	39.2	45.0	—	15.7	1.0 : 1.0 : — : 2.8
($NH_4ZrH(PO_4)_2$)									(41.05	47.27	5.66	6.00)	
($NH_4ZrH(PO_4)_2 \cdot 2H_2O$)									(36.66	42.22	5.06	16.06)	
($Zr(HPO_4)_2 \cdot 2H_2O$)									(38.61	44.47		16.92)	

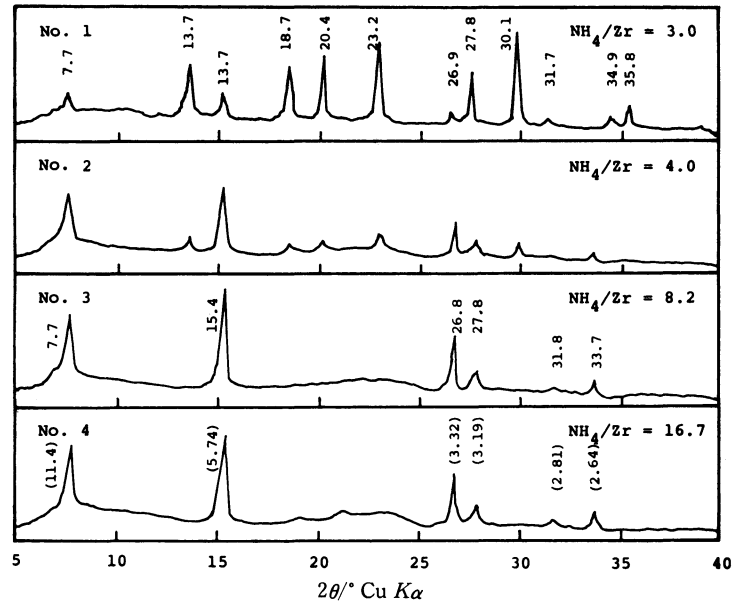

Fig. 1. X-Ray diffraction patterns of $(NH_4)_xZrH_{2-x}(PO_4)_2$. (Effect of NH_4HPO_4 mol/$ZrOCl_2$ mol (NH_4/Zr) on the synthesis.)
Numerals near peaks indicate 2θ degrees and lattice distances (Å).

in the formation of γ-zirconium phosphate. In fact, no diffraction peak characterizing the γ-$NaZrH(PO_4)_2$ was detected in the X-ray diffraction pattern. Neither was the diffraction peak characterizing the γ-form found in the X-ray diffraction pattern of the reaction product in the second experiment at a Na/Zr mole ratio of 4. Howevere in Expts No. 3 and 4 at M/Zr mole ratios of 8.3 and 16.6 respectively, the formation of γ-zirconium phosphate apparently took place, since peaks appeared at 11.7, 6.36, 4.57, 4.41, 3.91, 3.81, 3.17, 2.87, and 2.54 Å ($Å=10^{-10}$ m) in the X-ray diffraction patterns. It was found, therefore, that the amount of NaH_2PO_4 could be reduced to less than half of that previously reported.

The influence of the mole ratio of NH_4/Zr was investigated also when the ammonium salt was used. The results are shown in Expts No. 1—4 in Table 2, while the X-ray diffraction patterns of the reaction products are shown in Fig. 1.

As the mole ratio of NH_4/Zr increased, the diffraction peak at 11.3 Å (7.8°) characterizing γ-$NH_4ZrH(PO_4)_2$ was intensified. The mole ratio of NH_3 in the product from Expt No. 1 was 0.6 and the mole ratio of NH_4/Zr was small. With an increase in the mole ratio of M/Zr, however, that of NH_3 reached 1.0, and a stoichiometric compound, $NH_4ZrH(PO_4)_2$, was formed. In the case of the Na salt, the mole ratios of Na_2O in the reaction products were 0.3 or less, as is shown in Table 1, and products of an indefinite $Na_{0.2-0.6}ZrH_{1.8-1.4}(PO_4)_2$ composition were obtained.

In the processes previously reported, hydrochloric acid was added to the reaction solutions[2,3] or the solutions were adjusted to pH 2.[3] The pH value of an aqueous solution of MH_2PO_4 (M=Na, K, or NH_4) showed 4—4.5, and the pH value of an aqueous solution equilibrated with $MM'H(PO_4)_2$ (M'=Ti or Zr), obtained by the ion-exchange of $M'(HPO_4)_2$ and MOH, also showed 4—4.5.

The reaction giving rise to the formation of the γ-zirconium phosphates can be written as follows:

$$ZrOCl_2+2MH_2PO_4 \longrightarrow MZrH(PO_4)_2+MCl+HCl +H_2O.$$

In this reaction, since HCl is liberated into the aqueous solution, the pH values were expected to become less than 4. In fact, the pH values of the mother liquors following the termination of the reaction inevitably showed the expected pH values (2.5—3.5).

Reaction Temperature: The reactions between $ZrOCl_2$ and KH_2PO_4 in Expts No. 5—8 are shown in Table 1. As with the Na-product, the K-product was also low in M_2O (K_2O) content, and a product of an indefinite $K_{0.2-0.8}ZrH_{1.8-1.2}(PO_4)_2$ composition was obtained. No correlation was observed between the X-ray diffraction peak intensity of 11.0 Å characterizing the γ-potassium zirconium(IV) hydrogen bis(phosphate) and the reaction temperature. As has been described above, the ease with which the crystalline γ-zirconium phosphates were produced as stoichiometric compounds reacting $ZrOCl_2 \cdot 8H_2O$ with MH_2PO_4 is considered to be in the order of the NH_4-product Na-product K-product.

The reaction temperatures were investigated for the NH_4-products; the results from Expts No. 5, 6, 3, and 7 are shown in Table 2. The mole ratios of NH_3 in the products ranged from 0.8—1.0 at 120—280 °C, and products of approximately a $NH_4ZrH(PO_4)_2$ composition were obtained. In the X-ray diffraction patterns of the NH_4 salt, the diffraction-peak intensity of 11.3 Å characterizing γ-$NH_4ZrH(PO_4)_2$ increased with an elevation of the reaction temperature.

Synthesis in the Autoclave. For the purpose of developing an industrial method for synthesizing γ-zirconium phosphates as compounds with a layer structure, the reaction between $ZrOCl_2$, $NH_4H_2PO_4$ and water was carried out in autoclave equipped with a stirrer and lined with Hastelloy-B (Ni: 67, Mo: 28, and Fe: 5%).

Table 3. Ion-exchange properties of γ-zirconium(IV) bis(hydrogenphosphate) in solutions to alkali metal and ammonium ions

Ion	Equilibrium capacity at pH 4.5 Q^A/mequiv g^{-1}	Saturation capacity at pH 4.5 Q°/mequiv g^{-1}	Selectivity quotient K_H^M	Mole fraction Q^A/Q°	Absorption quantity A/%	Distribution coefficient K_D/ml g^{-1}
Li	0.36	1.80	0.04	0.20	14.4	8.42
Na	0.74	2.40	0.19	0.31	29.6	21.0
K	1.50	2.40	2.51	0.63	60.0	75.0
Cs	1.02	2.60	0.45	0.39	40.8	34.4
NH_4	1.69	2.70	3.26	0.62	66.8	100.5

Selectivity quotient: $K_H^M = \frac{(M^+)I}{(H^+)I} \cdot \frac{(H^+)S}{(M^+)S} = \frac{Q^A}{Q^\circ - Q^A} \cdot \frac{Q^A}{C - Q^A}$. Absorption quantity : $Q^A/C\ 100 = A$. Distribution coefficient: $K_D = A/I \cdot S(100-A)$. C: Initial quantity of MCl (2.5 mequiv). S: MCl solution (25 ml). I: Ion-exchanger (0.5 g).

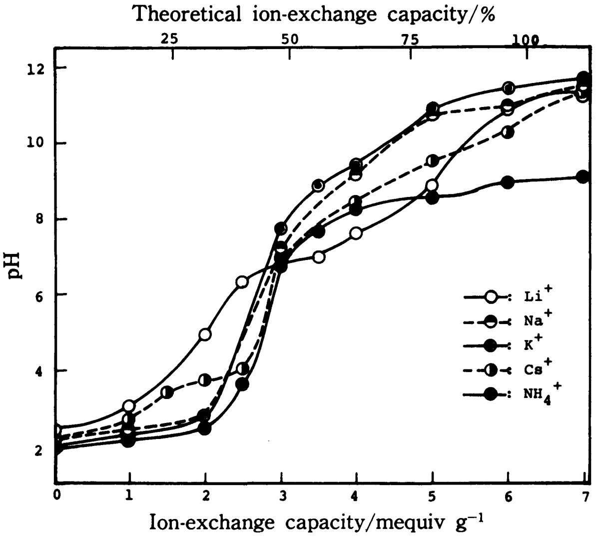

Fig. 2. Alkali metal and ammonium ion-exchange titration curves of γ-$Zr(HPO_4)_2 \cdot 2H_2O$.

The results are shown in Table 2.

The reaction temperature was maintained within 120—165 °C to prevent the corrosion of the metallic vessel. The reaction time of the contents under agitation could be significantly shortened compared to that required for a stationary state. Judging from the X-ray diffraction patterns of the products, a crystalline product was obtained after a reaction period of 18 h. The crystallization of the products (Nos. 9, 10, and 11) was brought to completion with an additional reaction time. When γ-zirconium phosphates are synthesized in the autoclave and the container is attacked above 180 °C, there is a chance that the reaction product may react with metal ions. Thus, a reaction temperature of about 150 °C was considered the most appropriate.

Ion-exchange Properties. Since γ-$Zr(HPO_4)_2 \cdot 2H_2O$ is present to a greater extent in the interlayer spacing (12.2 Å), it is considered void of selectivity as an ion-exchanger. With regard to the inorganic ion-exchange properties of this compound, therefore, there is no literature available except for one report by Clearfield *et al.*[2] They converted the γ-form into the β-form as a complete anhydride, and obtained ion-exchange titration curves of Cs^+, Na^+, and Ba^{2+} using the β-form. In the present study, ion-exchange titration curves of γ-$Zr(HPO_4)_2 \cdot 2H_2O$ toward alkali metal (Li, Na, K, Cs) and ammonium ions were measured in order to reconsider γ-$Zr(HPO_4)_2 \cdot 2H_2O$ as an ion-exchanger. The results are shown in Fig. 2. In the titration curves, the ion-exchange capacity up to pH 4.5 was arbitrarily defined as the saturation ion-exchange capacity (Q°).[5] On the other hand, an equilibrium ion-exchange capacity (Q^A) up to pH 4.5 was also obtained using the method of the previous report.[5] Table 3 showns the values for the selectivity quotient (K_H^M), the adsorption quantity (A), and the distribution coefficient (K_D) calculated from both ion-exchange capacities. In the ion-exchange titration curves of Fig. 2, the theoretical value for a 100% ion exchange of the two hydrogens in γ-$Zr(HPO_4)_2 \cdot 2H_2O$ corresponds to 6.25 mequiv/g. When the two hydrogens are theoretically 100%-ion-exchanged with Li^+, Na^+, K^+, or Cs^+, the pH values of the aqueous solution are each about 11. γ-$Zr(HPO_4)_2 \cdot 2H_2O$ tends to be attacked in such an alkaline solution. On the other hand, the pH value of the solution is 8.9 in the case of ion-exchange with NH_4^+; thus, there is little fear of γ-$Zr(HPO_4)_2 \cdot 2H_2O$ being attacked. An analysis of the ion-exchanger, however, indicated that about 65% of the ion-exchange was actually carried out. The values of Q^A, Q°, K_H^M, A, and K_D at pH 4.5 were, respectively, in the order of $Li^+ < Cs^+ < Na^+ < K^+ < NH_4^+$. That is, Li^+, with a smaller radius, was hydrated to the greatest extent, causing it to appear to have a large radius; thus, the ion-exchange quantity of the hydrated ion was small. Cs^+ was not hydrated, but was itself larger than Na^+, K^+, or NH_4^+. Consequently, the ion-exchange quantity of this ion was less than those of the other ions. NH_4^+ was not so high in selective ion-exchange compared with alkali metal ions, but was highest with respect to ion-exchange capacity. This point is of interest in consideration of the fact that NH_4^+ salt more easily forms stoichiometric compounds than the Na and K salts in the synthesis of γ-zirconium phosphates.

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