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A Study of Inorganic Ion Exchangers. IX.[1] The Synthesis of $Al_xZrH_{2-3x}(PO_4)_2 \cdot yH_2O$ and Its Characteristics

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Synopsis. To make a material with specific functions such as those of a catalyst, a layer-structure compound with the formula of $Al_xZrH_{2-3x}(PO_4)_2 \cdot yH_2O$ ($x \leqq 2/3$) was synthesized by a hydrothermal reaction between $ZrOCl_2 \cdot 8H_2O$ and $Al(H_2PO_4)_3$ at 200—270 °C. The product had a layer spacing of 7.75 Å, slightly longer than α-$Zr(HPO_4)_2 \cdot H_2O$ (7.62 Å), and fairly good thermal stability at 250—500 °C. However, the above objective was not attained by ion-exchange between various zirconium phosphates and an aqueous solution of aluminium chloride.

Inorganic layer-structure compounds with thermal stability have specific functions of ion-exchangers or catalysts. In this study, crystalline alminium zirconium phosphate, $Al_xZrH_{2-3x}(PO_4)_2$ ($x \leqq 2/3$), was synthesized by the hydrothermal reaction of zirconium(IV) chloride oxide with tris(dihydrogenphosphate) aluminium, and the properties of the product were examined. An attempt was also made to obtain such a material by means of ion exchange between various zirconium phosphates and aluminium chloride.

Experimental

The reaction product, $Al_xZrH_{2-3x}(PO_4)_2 \cdot yH_2O$, was synthesized by means of a hydrothermal reaction between $ZrOCl_2 \cdot 8H_2O$ and an $Al(H_2PO_4)_3$ aqueous solution (P_2O_5, 34.8%; Al_2O_3, 8.6%; specific gravity, 1.499; Nippon Chemical Co.) in an autoclave, according to the previously reported method.[1]

The formation of $Al_xZrH_{2-3x}(PO_4)_2$ was also examined by means of ion exchange between one gram of α-$Zr(HPO_4)_2 \cdot H_2O$. γ-$Zr(HPO_4)_2 \cdot 2H_2O$, or $Zr[(C_4H_9)_3NH]_xH_{2-3x}(PO_4)_2$[1] and 100 cm³ of M/10 (1 M=1 mol dm⁻³) $AlCl_3$. In this process, the pH change of the mother liquor was measured for 18 h at 20 °C, and the Al^{3+} ions adsorbed onto the zirconium phosphate were determined. The analysis of the above products was carried out as follows. The H_2O was estimated from the weight loss of the sample heated at 800 °C. After the heated product had been dissolved by alkali fusion, the ZrO_2, Al_2O_3, and P_2O_5 components were separated from each other and determined by means of gravimetric analysis. The reaction products were characterized by means of X-ray diffraction and thermal analysis (DTA, TG).

Results and Discussion

The conditions for the hydrothermal reaction of $ZrOCl_2$ with $Al(H_2PO_4)_3$ and the analytical data of the products are shown in Table 1.

The influence of the reaction temperatures was examined in Nos. 1—4 of Table 1. An amorphous product was formed in the mother liquor at temperatures lower than 150 °C. The crystallinity was augmented, and a crystalline product was obtained at 200 °C or higher.

The influence of the $Al(H_2PO_4)_3/ZrOCl_2$ (Al/Zr) mole ratios on the hydrothermal reaction was examined in Nos. 2, 5—7; the X-ray diffraction patterns of the reaction products are shown in Fig. 1.

At an Al/Zr mole ratio of 3 (No. 5), an amorphous product was formed, though the crystalline product was obtained with an increase in the mole ratio. However, the diffraction peaks (2θ; 20.6°, 26.3°) attributed to $Al_2(HPO_4)_3$ appeared in the X-ray diffraction pattern of the product at an Al/Zr mole ratio of 12 (No. 7). Thus, the reaction product is apparently intermingled with $Al_2(HPO_4)_3$. This is also evident from the increase in the Al_2O_3 content of the reaction product. Under suitable conditions (200—250 °C, Al/Zr=8) for the synthesis, the ZrO_2:P_2O_5 mole ratio of the reaction product was 1:1, and then the Al^{3+}-ion content was about 5%. The product composition can be written as $Al_{0.2-0.3}ZrH_{2-3(0.2-0.3)}(PO_4)_2 \cdot 0.7-1.4H_2O$.

The X-ray diffraction pattern of this product was quite similar to that of α-$Zr(HPO_4)_2 \cdot H_2O$, but the layer

TABLE 1. SYNTHESIS AND ANALYSIS OF $Al_xZrH_{2-3x}(PO_4)_2$

Reaction conditions								Reaction products				
No.	$ZrOCl_2$ $8H_2O$ (g)	Al $(H_2PO_4)_3$ (ml)	H_2O a) (ml)	Al:Zr:P Atomic ratio	Temp °C	Time h	Mother riquor (pH)	ZrO_2 (%)	P_2O_5 (%)	Al_2O_3 (%)	H_2O (%)	ZrO_2:P_2O_5:Al_2O_3:H_2O (mole ratio)
1	1.61	5.3	4.7	8:1:24	150	96	1.55	38.2	34.8	11.3	15.7	1.0:0.8:0.4:2.8
2	1.61	5.3	4.7	8:1:24	200	96	1.69	38.7	42.6	7.7	11.0	1.0:1.0:0.3:2.0
3	1.61	5.3	5.0	8:1:24	250	96	1.70	40.7	44.5	6.7	8.07	1.0:1.0:0.2:1.4
4	16.1	53	0.0	8:1:24	270	96	2.01	40.0	46.4	5.8	7.84	1.0:1.0:0.2:1.9
5	1.61	2.0	8.0	3:1:9	200	96	1.76	35.7	41.4	3.5	19.4	1.0:1.0:0.1:3.7
6	1.61	3.3	7.7	5:1:15	200	96	1.74	36.6	42.6	8.0	12.8	1.0:1.0:0.3:2.4
7	1.61	8.0	3.0	12:1:36	200	96	1.57	32.1	39.7	19.4	8.84	1.0:1.1:0.7:1.9
8	16.1	53	0.0	8:1:24	200	130	1.83	38.5	40.8	8.8	11.9	1.0:0.9:0.3:2.1
9	16.1	53	50	10.7:1:24	200	66	2.41	22.0	35.8	30.8	11.4	1.0:1.4:1.7:3.5
		+10.4(g)$Al(OH)_3$										
10	1.61	0.53	2.5	8:1:24	160	115	2.27	23.0	38.3	23.5	11.1	1.0:1.4:1.2:3.3
	+3.71(g)n−$(C_4H_9)_3N$							4.1$(C_4H_9)_3N$				:0.02:$(C_4H_9)_3N$

a) Aqueous solution of $Al(H_2PO_4)_3$ containing 34.8% of P_2O_5 and 8.6% of Al_2O_3.

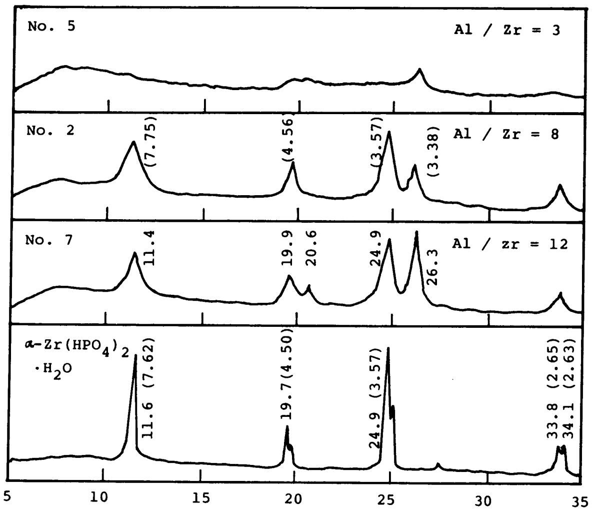

Fig. 1. X-Ray diffraction patterns of $Al_xZrH_{2-3x}(PO_4\cdot yH_2O$ and α-$Zr(HPO_4)_2\cdot H_2O$. Effect of $Al(H_2PO_4)_2$ mole/$ZrOCl_2$ mole (Al/Zr) on the synthesis Numerals on peaks indicate 2θ/degrees and lattice distances Cl/Å).

spacing of 7.75 Å, determined from the first d value (002) of the reaction product, was slightly longer than that of 7.62 Å for α-$Zr(HPO_4)_2\cdot H_2O$.

The results of adding $Al(OH)_3$ (No. 9), or $(C_4H_9)_3N$ (No. 10) to this reaction system were investigated. The pH of the reaction mixture containing $Al(OH)_3$ was slightly higher than that to which no addition was made, but the reaction product was possibly contaminated by metal ions dissolved by the corrosion of the autoclave. The X-ray diffraction patterns of the reaction products of Nos. 9 and 10 were shown to be intermingled with $Al_2(HPO_4)_3$ as a by-product. In Experiment No. 10, the crystalline zirconium phosphate connected to $(C_4H_9)_3N$ could not be obtained as a result of the formation of an oily tertiary amine phosphate.

The DTA and TG curves of $Al_xZrH_{2-3x}(PO_4)_2\cdot H_2O$ and α-$Zr(HPO_4)_2\cdot H_2O$ are shown in Fig. 2.

The thermal decomposition in the reaction product showed a behavior similar to that of α-$Zr(HPO_4)_2\cdot H_2O$. A broad endothermic peak attributed to the dehydration of the water of layer spacing appeared at 130—150 °C. The change in the weight of the heating product could not be detected on the TG curve at 250—500 °C. In this temperature range, the condensation was obstructed by aluminium ions present in the layer-spacing of the phosphate. The thermal stability of $Al_xZrH_{2-3x}(PO_4)_2\cdot yH_2O$ at 250—500 °C could also be observed from the X-ray diffraction pattern of the heated product.

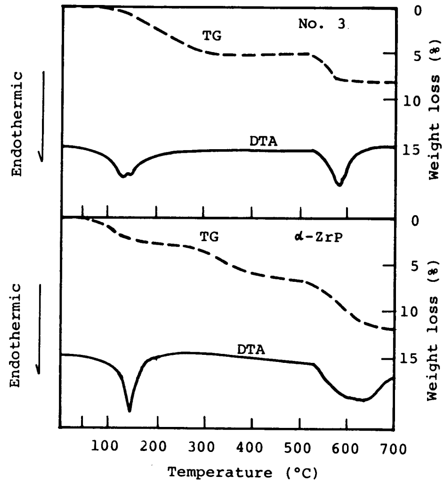

Fig. 2. DTA and TG curves of $Al_xZrH_{2-3x}(PO_4\cdot yH_2O$ and α-$Zr(HPO_4)_2\cdot H_2O$.

When a reaction between zirconium phosphate and aluminium ions occurs easily, the method of synthesizing $Al_xZrH_{2-3x}(PO_4)_2\cdot yH_2O$ directly becomes less necessary. Accordingly, the reactions of zirconium phosphates (α-$Zr(HPO_4)_2\cdot H_2O$, γ-$Zr(HPO_4)_2\cdot 2H_2O$ or $Zr[(C_4H_9)_3NH]_xH_{2-x}(PO_4)_2\cdot yH_2O$) with an aqueous solution of $AlCl_3$ were examined. The pH values were found to decrease from about 4.5 to 2.5, followed by the adsorption of Al^{3+} ions onto the solid phase by 1.66% in the case of the butyl amine salt (17.0 Å), 0.81% for γ-$Zr(HPO_4)_2\cdot 2H_2O$ (12.3 Å), and 0.24% for α-$Zr(HPO_4)_2\cdot H_2O$ (7.6 Å). The adsorbed Al^{3+} ions slightly increased in proportion to the layer-spacing of the phosphates. Thus, the direct synthesis is significant for the indicated purpose.

References

1) a) Presented at the 49th National Meeting of the Chemical Society of Japan, Tokyo, April, 1984; b) Part VIII of this series: E. Kobayashi and S. Shin, *Bull. Chem. Soc. Jpn.*, **57**, 465 (1983).