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A Study of Inorganic Ion Exchangers. XI. The Hydrothermal Reactions of $ZrOCl_2$ and $M(H_2PO_4)_2$ (M=Mg, Ca, Sr, Ba)

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The possibility of the hydrothermal synthesis of layered zirconium phosphates containing various alkaline earth metals (abbreviated as ZrMP; M=Mg, Ca, Sr, Ba) has been studied from $ZrOCl_2$ and $M(HPO_4)_2$, and their characteristics have been investigated. The optimum conditions for the synthesis of a highly crystalline product were as follows; the molar ratio of the starting materials of $Ca(H_2PO_4)_2$ and $ZrOCl_2$ was Ca/Zr=3, and the temperature of the hydrothermal reaction was in the range of 200—270 °C. By the hydrothermal reaction of $ZrOCl_2$ and $Mg(H_2PO_4)_2$, a new compound of $ZrMg_{0.5}H(PO_4)_2 \cdot H_2O$ with a layer-spacing of 11.94 Å was obtained. Layered phosphate (ZrMP) was not obtained by the hydrothermal reaction of $ZrOCl_2$ and $Ba(H_2PO_4)_2$. The temperature range of the inter-layer dehydration of the layered phosphates (ZrMgP, ZrCaP, and ZrSrP) was similar to that of α-zirconium(IV) bis(hydrogenphosphate) (α-ZrP); i.e. the water in the interlayer was lost at 130—240 °C, and dehydro-condensation took place at a higher temperature above 340 °C. Zirconium phosphate containing Mg^{2+} or Ba^{2+} was not obtained by the ion exchange of the protons in α-ZrP with the alkaline earth metal cations (M^{2+}) in MCl_2, while Ca^{2+} and Sr^{2+} were exchanged with the protons. These alkaline earth metal ions except for Ba^{2+} were easily exchanged with H^+ in α-ZrP, when NaOH was added. The layer-spacing of the Mg^{2+}-exchanged zirconium phosphate was 9.6 Å, which was different from that of the hydrothermal product. The layer distances of Ca^{2+}- or Sr^{2+}-exchanged products were similar to those of the hydrothermal products.

Layered tetravalent metal phosphates are widely used as inorganic ion-exchangers of great importance. Much attention has been paid recently for the layered compounds with different molecules and ions as catalysts for various reactions.[1)]

As reported previously,[2)] α-zirconium phosphates containing tertiary amines or aluminum ions between the layers have been synthesized hydrothermally, and used as catalysts for methanol conversion. However, a thermally stable layered phosphate having a wide inter-layer distance was not obtained.

This paper reports whether layered zirconium phosphates containing alkaline earth metal ions (abbreviated as ZrMP; $M^{2+}=Mg^{2+}$, Ca^{2+}, Sr^{2+}, Ba^{2+}) may be hydrothermally synthesized, and discusses the difference between the hydrothermal products and the layered compounds obtained by ion-exchange of H^+ in α-zirconium(IV) bis(hydrogenphosphate) (abbreviated as α-ZrP) with alkaline earth metal ions.

Experimental

Hydrothermal Reactions of $ZrOCl_2$ and $M(H_2PO_4)_2$ (M=Mg, Ca, Sr, Ba). A glass tube (20 cm^3) was filled with the appropriate amount of $ZrOCl_2 \cdot 8H_2O$, $M(H_2PO_4)_2$, H_2O, and NaCl or $Ca(OH)_2$ as listed in Table 1. After stirring the mixture thoroughly, the tube was sealed, and autoclaved (200—270 °C; 93—106 h). The hydrothermal products were separated from the mother liquor by centrifugation, and were washed with distilled water. The products were dried in a desiccator at 75% relative humidity.

Ion Exchange of H^+ in $Zr(HPO_4)_2$ with M^{2+} in MCl_2 (M=Mg, Ca, Sr, Ba). 100 cm^3 of an aqueous solution of MCl_2 (0.1 mol dm^{-3}) was added to 1.00 g of α-$Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP) and stirred overnight at room temperature. The precipitate was washed and separated by centrifugation. 50 cm^3 of an aqueous solution of MCl_2 (0.2 mol dm^{-3}) was added to 1.00 g of α-ZrP and stirred. Thirty cm^3 of an aqueous solution of NaOH (0.1 mol dm^{-3}) was slowly added to the mixture with vigorous stirring. The precipitate was washed and separated as described above.

Chemical Analysis. The composition of the products was determined as follows.[3)] The amount of H_2O was determined on the basis of the weight loss of the samples heated up to 800 °C.

The heated product was fused with 2.0 g of flux (Na_2CO_3:K_2CO_3=1 : 1) at 1000 °C. After cooling, the fused product was dissolved in distilled water at 100 °C, and 6 mol dm^{-3} HCl was added in order to dissolve the solid completely. Zirconium hydroxide was precipitated by adding 6 mol dm^{-3} NH_3 aq to the solution, and separated by filtration. After igniting the precipitate, a gravimetric method was employed for the determination as ZrO_2.

The phosphate ion in the filtrate was determined absorptiometrically, by the JIS K-0102 method.

The alkaline earth metals in the products were determined by atomic absorption after dissolving it.

Instrumental Analysis. The X-ray diffraction (XRD) was performed with Cu*Kα* radiation (30 kV, 20 mA), by using an X-ray diffractometer (Rigaku, Geigerflex RAD). A scanning electron microscope (Shimadzu, ASM-SX) was employed for observation of the surfaces of the hydrothermal products. Surface areas of the products were determined by adsorption of argon at liquid nitrogen temperature using a fully-automatic surface area analyzer (Shimadzu, Micromeritics 2200). A micro-thermal analyzer, with 100 μV of DTA sensitivity and ±20 mg of TG sensitivity was used for the thermal analysis.

Results and Discussion

Hydrothermal Reaction of $ZrOCl_2$ and $Ca(H_2PO_4)_2$. The conditions of the hydrothermal reaction of zirconium(IV) oxychloride and various alkaline earth metal salts of bis(dihydrogenorthophosphate), as well as the analytical data of the products, are listed in Table 1.

Effects of Reaction Temperature. By varying the

Table 1. Hydrothermal Reactions of $ZrOCl_2$ with $M(H_2PO_4)_2$ (M=Mg, Ca, Sr, Ba), and Analysis of the Products

	Reaction condition								Reaction product						
No.	$ZrOCl_2\cdot 8H_2O$ g	$M(H_2PO_4)_2$[a] g	Additive[b] g	H_2O cm^3	Zr : M : P : Na (Atomic ratio)	Temp °C	Time h	Mother liquor pH	Yield g	ZrO_2 %	P_2O_5 %	MO %	H_2O %	Na_2O_2 %	ZrO_2 : P_2O_5 : MO : H_2O : Na_2O (Molar ratio)
1	8.05	18.9		30	1 : 3 : 6	200	96	2.5	7.60	41.1	42.7	2.0	13.9		1.1 : 1.0 : 0.1 : 2.6
2	1.61	3.78		10	1 : 3 : 6	250	106	2.7	1.43	39.7	42.8	1.1	13.1		1.1 : 1.0 : 0.1 : 2.4
3	16.1	37.8		40	1 : 3 : 6	270	96	2.7	17.0	41.5	41.4	2.7	14.2		1.1 : 1.0 : 0.2 : 2.7
4	1.61	1.89		10	1 : 1.5 : 3	250	106	2.4	1.36	39.9	42.2	1.5	14.6		1.1 : 1.0 : 0.1 : 2.7
5	1.61	5.61		10	1 : 4.5 : 9	250	106	2.6	1.68	42.7	42.7	2.9	13.5		1.2 : 1.0 : 0.2 : 2.5
6	1.61	3.78	0.584	10	1 : 3 : 6 : 2	250	106	2.5	1.35	41.5	43.8	1.3	10.9	0.58	1.1 : 1.0 : 0.1 : 2.0 : 0.03
7	1.61	3.78	0.740	10	1 : 5 : 6	250	93	3.3	3.05	57.9	31.8	6.2	8.0		2.1 : 1.0 : 0.5 : 2.0
8	8.05	18.75(cm^3)		35	1 : 3 : 6	250	96	1.7	7.60	48.8	34.2	5.1	12.0		1.6 : 1.0 : 0.5 : 2.8
9	1.61	3.75(cm^3)	0.584	10	1 : 3 : 6 : 2	250	93	1.8	1.18	48.8	33.9	5.4	13.1	0.40	1.7 : 1.0 : 0.6 : 3.1 : 0.03
10	1.61	4.22		10	1 : 3 : 6	250	93	3.4	2.70	32.3	34.3	19.8	13.6		1.1 : 1.0 : 0.8 : 3.1
11	4.83	12.7	1.75	30	1 : 3 : 6 : 2	250	96	2.6	5.80	44.9	28.2	21.1	5.9	0.07	1.8 : 1.0 : 1.0 : 1.7 : 0.01
12	1.61	4.97		10	1 : 3 : 6	250	93	3.1	3.47	41.8	28.3	25.1	4.8		1.7 : 1.0 : 0.8 : 1.4
13	3.22	9.93	1.17	30	1 : 3 : 6 : 2	250	96	3.2	7.00	34.0	37.6	24.8	3.1	0.46	1.0 : 1.0 : 0.6 : 0.6 : 0.03

a) M=Ca for No. 1—7; M=Mg (4 mol dm^{-3} $Mg(H_2PO_4)_2$) for Nos. 8 and 9; M=Sr for Nos. 10 and 11; M=Ba for Nos. 12 and 13. b) NaCl for Nos. 6, 9, 11, and 13; $Ca(OH)_2$ for No. 7.

reaction temperature, it was found that the products were amorphous below 150 °C, but that highly crystalline products were obtained above 200 °C. The X-ray diffraction intensity of the products increased in the order of No. 1 (200 °C)<No. 2 (250 °C)<No. 3 (270 °C) in Table 1.

The average content of P_2O_5 in these products was about 42% and was almost the same as that of α-zirconium(IV) bis(hydrogenphosphate) (42.09%). About 40% of the ZrO_2 content in the product was a little higher than that of α-zirconium(IV) bis(hydrogenphosphate) (α-Zrp). The CaO content was in the range of 1.1—2.7%, corresponding to about 0.1 mol of P_2O_5. The average H_2O content was 13.7%, which was slightly higher than that (10.68%) of α-ZrP.

Effects of $Ca(H_2PO_4)_2/ZrOCl_2$ Molar Ratio (Ca/Zr). The Ca/Zr molar ratios in the hydrothermal products of Nos. 4, 2, and 5 are listed in Table 1, and the XRD patterns of these samples are shown in Fig. 1. The XRD patterns of the products were almost the same as those of α-ZrP, except for a new peak at 2θ=8.7—8.9°. The new peak suggests the partial expansion of the layer distance of the products by the intercalation of Ca^{2+} between the layers. The crystallinity of the pro-

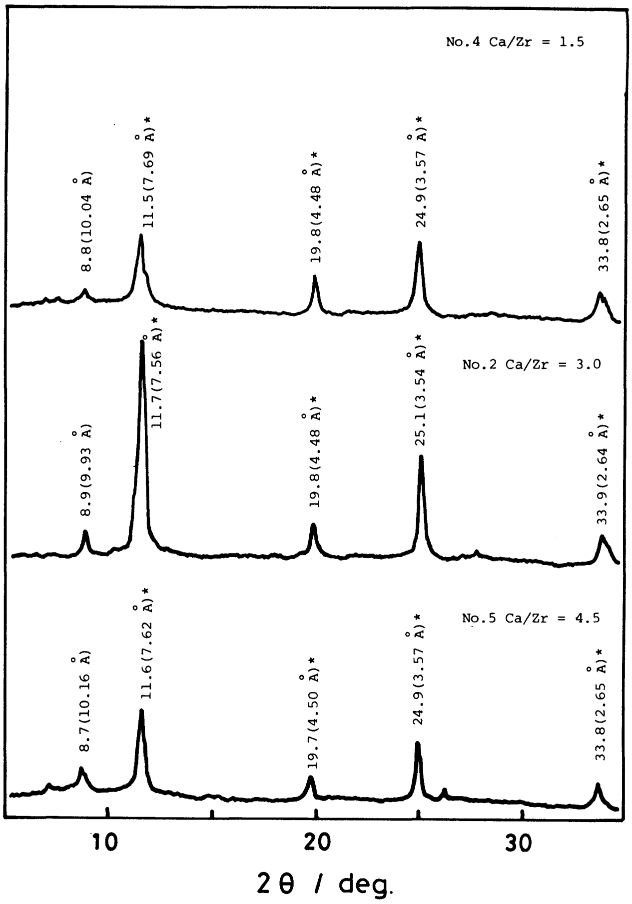

Fig. 1. X-Ray diffraction patterns of reaction products of $ZrOCl_2$ with $Ca(H_2PO_4)_2$ (Influence of molar ratio of $Ca(H_2PO_4)_2/ZrOCl_2$ (Ca/Zr)). Numerals on peaks indicate 2θ/degrees and lattice distances. *: The diffraction peaks of α-ZrP.

duct No. 4 (Ca/Zr=1.5) was low, suggesting an insufficient amount of phosphate in the starting materials. When the Ca/Zr ratio was 4.5 (No. 5), the XRD intensity was low. The crystallization of the product was assumed to be prevented by the excess amount of Ca in the starting materials. Therefore, the molar ratio of Ca/Zr=3.0 (No. 2) was optimal for the crystallization of the hydrothermal product (ZrCaP).

Effects of Additives. On the hydrothermal reaction of $ZrOCl_2$ and $Ca(H_2PO_4)_2$, appropriate amount of NaCl and $Ca(OH)_2$ were added. The XRD patterns of the products are shown in Fig. 2.

It is known that the layer distance is expanded up to 11.8 Å by the ion exchange of H^+ in α-ZrP with Na^+, and then Mg^{2+} is easily introduced between the layers after the expansion.[4,5] Expecting a similur effect, addition of NaCl was carried out in this investigation. The first *d*-value of the product No. 6 (NaCl addition) was 9.93 Å. The XRD pattern was not changed remarkably by the addition. Additional weak peaks in the XRD pattern were observed at 13.9, 19.5, 23.9, 28.1, and 31.1° by the NaCl addition. These new peaks did not belong to those of α-ZrP in the Na^+ form.

In order to obtain a product having a high content of Ca^{2+}, $Ca(OH)_2$ was added (No. 7). As shown in Table 1, the pH of the mother liquor was a little higher (pH=3.3) than the solution without $Ca(OH)_2$ (pH=2.5—2.7). The reaction product contained higher amounts of ZrO_2 and CaO than the others (Nos. 1—3). It was suspected from this result that the product was a mixture of zirconium(IV) hydroxide, calcium hydrogenphosphate ($CaHPO_4$) and zirconium phosphates.

Hydrothermal Reaction of $ZrOCl_2$ and $Mg(H_2PO_4)_2$. The hydrothermal synthesis of Mg-salts was examined under the optimal conditions similar to the case of Ca (Nos. 2, 6, and 7). The XRD patterns of the products (Nos. 8 and 9 in Table 1) were shown in Fig. 3. The chemical analysis of the samples suggests that the composition of the products corresponded to $ZrMg_{0.5}H(PO_4)_2 \cdot H_2O + 1/2[Zr(OH)_4 \cdot H_2O]$. When NaCl was added (No. 9), the product contained only a slight amount of Na. The XRD pattern was similar to that of No. 8. These results showed that the addition of NaCl had no effect on the crystal form of the product. The first *d*-value was 11.94 Å, and was larger than that of α-ZrP (7.56 Å). As mentioned below, the XRD pattern showed many additional peaks, suggesting that the product was a mixture of zirconium(IV) hydroxide, magnesium phosphates and layered zirconium(IV)

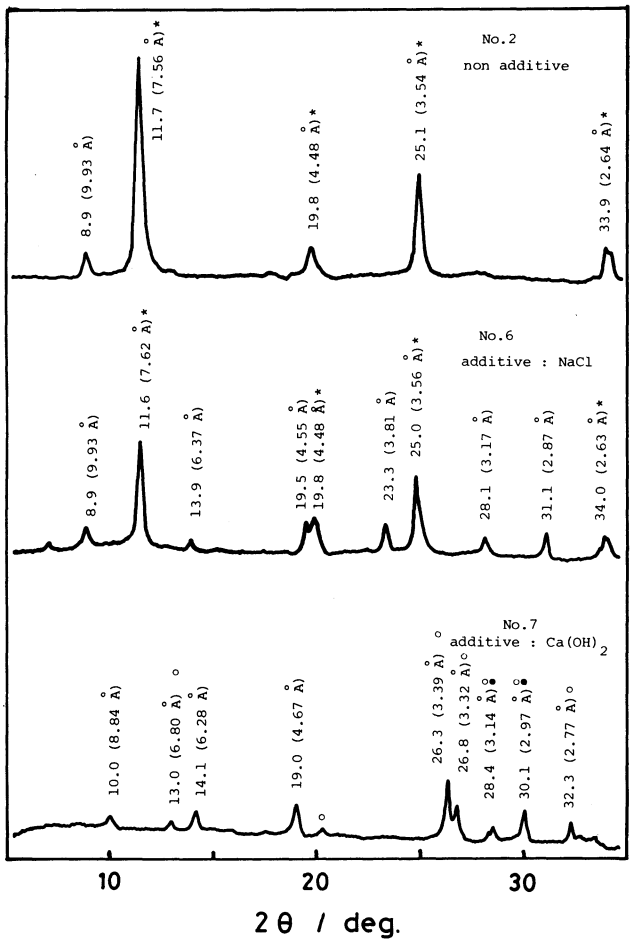

Fig. 2. X-Ray diffraction patterns of reaction products of $ZrOCl_2$ and $Ca(H_2PO_4)_2$ (Influence of additives on the synthesis). Numerals on peaks indicate 2*θ*/degrees and lattice distances. *: The diffraction peaks of α-ZrP, ○: the diffraction peaks of $CaHPO_4$, ●: the diffraction peaks of ZrO_2.

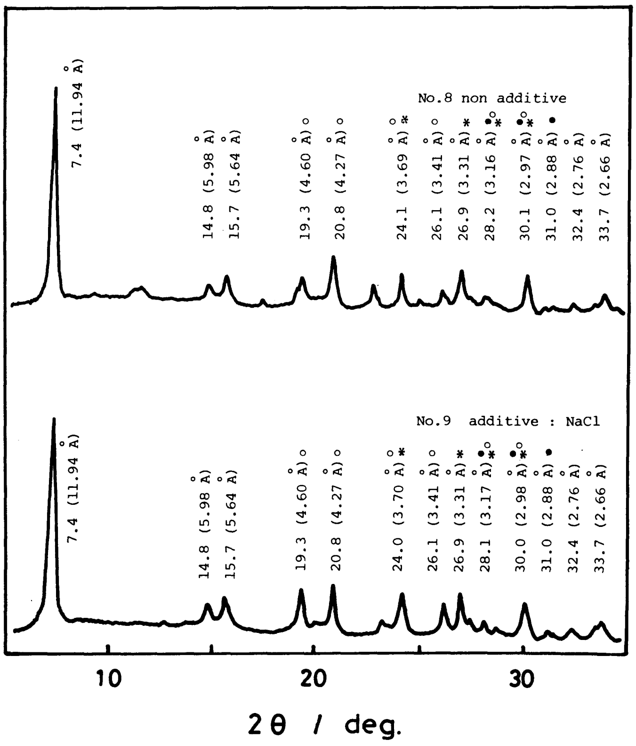

Fig. 3. X-Ray diffraction patterns of reaction products of $ZrOCl_2$ with $Mg(H_2PO_4)_2$. Numerals on peaks indicate 2*θ*/degrees and lattice distances. *: The diffraction peaks of ZrP_2O_7, ○: the diffraction peaks of $Mg_3(PO_4)_2$, $Mg(PO_3)_2$, $Mg_2P_2O_7$, ●: the diffraction peaks of ZrO_2.

phosphate containing Mg^{2+} (ZrMgP).

Hydrothermal Reaction of $ZrOCl_2$ and $Sr(H_2PO_4)_2$. The Sr-containing products are listed in Table 1, and the XRD patterns are shown in Fig. 4. The chemical analysis showed that the ZrO_2 content was lower than α-ZrP by about 10%, and that the SrO content was up to about 20%. The first *d*-value was 10.39 Å in the XRD pattern, suggesting that the product was a mixture of strontium hydrogenphosphate ($SrHPO_4$) and layered zirconium(IV) phosphate containing Sr^{2+} between the layers (d=10.2 Å).[7] This is supported by the fact that a part of the product was dissolved by treatment with HCl to leave zirconium(IV) bis(hydrogenphosphate). The reaction product No. 11 (NaCl addition) contained larger amount of ZrO_2 than No. 10. The first *d*-value was 9.02 Å, suggesting a wide layer spacing, but the product was easily dissolved in 1 mol dm^{-3} HCl solution. Therefore, it cannot be layered zirconium phosphate, since zirconium phosphate should be stable in acidic conditions in general.

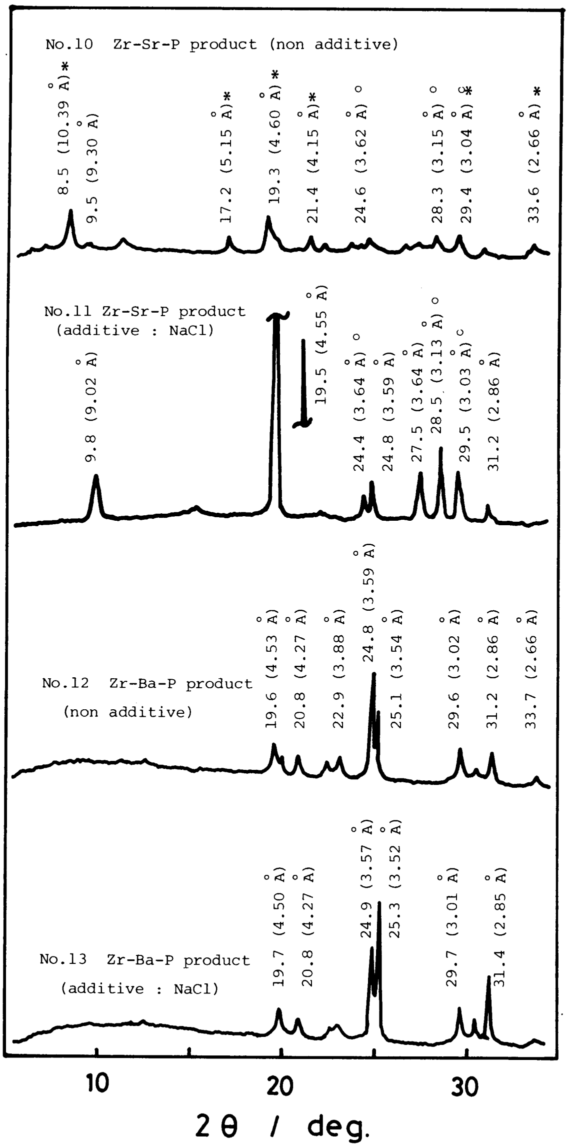

Fig. 4. X-Ray diffraction patterns of reaction products of $ZrOCl_2$ with $Sr(H_2PO_4)_2$ and $ZrOCl_2$ with $Ba(H_2PO_4)_2$. Numerals on peaks indicate 2θ/degrees and lattice distances. *: The diffraction peaks of α-ZrP containing Sr^{2+} between the layers, O: the diffraction peaks of $SrHPO_4$.

Hydrothermal Reaction of $ZrOCl_2$ and $Ba(H_2PO_4)_2$. The Ba-salts are listed in Table 1 (Nos. 12 and 13), and the XRD patterns are shown in Fig. 4. The BaO contents of the salts were as high as 25%. The peaks corresponding to α-ZrP were not found in the XRD patterns. The salts were easily dissolved in HCl solution. These results suggest that layered zirconium phosphate did not form in this reaction.

Treatment of Hydrothermal Products with Hydrochloric Acid. As mentioned above, when 1.00 g of the hydrothermal products were treated with 1 mol dm^{-3} HCl solution (100 cm^3), the products containing Mg, Ca, or Sr were partially dissolved and the weight was reduced to 0.76, 0.82, and 0.50 g, respectively. The Ba-salt was completely dissolved by this treatment. The XRD pattern of the Mg-salt treated with HCl is shown in Fig. 5. The XRD pattern of α-ZrP is also shown as the reference. The Mg-salt was turned into α-ZrP by this treatment. The by-products were dissolved in HCl solution, and the alkaline earth cations between the layers of the main products were exchanged with protons by this treatment.

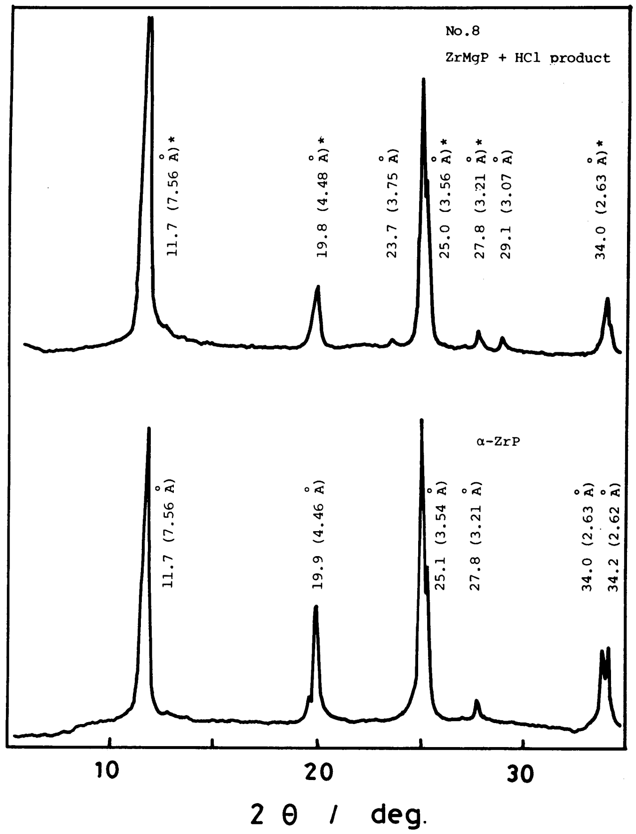

Fig. 5. X-Ray diffraction patterns of HCl-treated products of ZrMgP (No. 8) and α-$Zr(HPO_4)_2\cdot H_2O$ (α-ZrP). Numerals on peaks indicate 2θ/degrees and lattice distances. *: The diffraction peaks of α-ZrP.

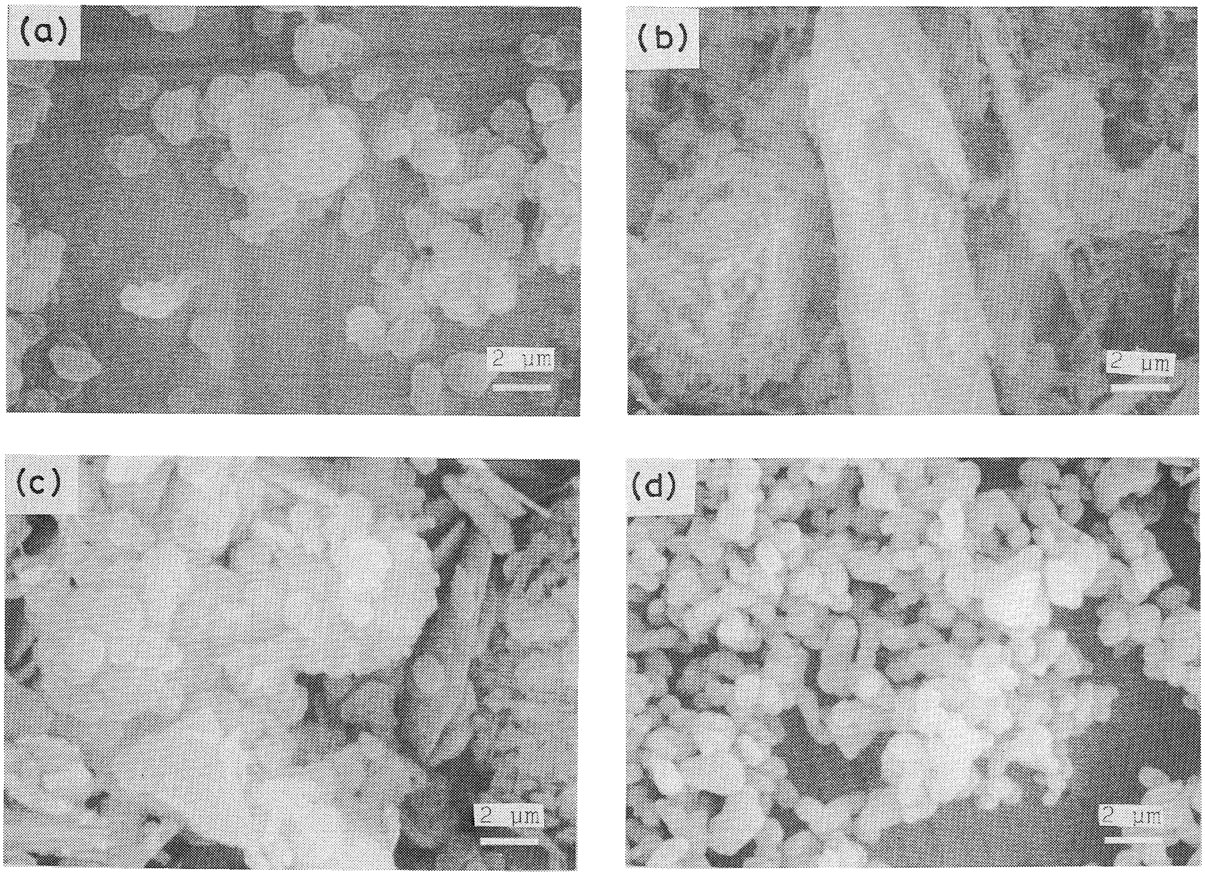

Fig. 6. Scanning electron micrographs of (a) reaction product No. 2, (b) reaction product No. 8, (c) reaction product No. 8 treated with HCl, and (d) α-$Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP).

SEM Results. A few products were observed by a scanning electron microscope (SEM), and are shown in Fig. 6. The scale below right of each picture denotes 2 µm.

The product No. 2 containing Ca (a) had a hexagonal plate shape, with a diameter of about 1 µm. The surface area was estimated by BET method at 9.4 $m^2 g^{-1}$, which was smaller than that of α-ZrP (14 $m^2 g^{-1}$) or γ-ZrP (22 $m^2 g^{-1}$).

The shape of the product No. 8 containing Mg (b) was hexagonal plate. But the crystals seemed to be columns because they were associated and the large crystals were surrounded by small needles. The surface area of the product was estimated at 11 $m^2 g^{-1}$.

After the HCl treatment, the product No. 8 changed into large hexagonal plate crystals (c). The shape resembled that of α-ZrP (d). The crystallinity of the HCl-treated product was high, but the crystals were associated.

Thermal Analyses. The DTA and TG curves of the products are shown in Fig. 7 with those of α-ZrP. The endothermic peaks at 130—245 °C in DTA of the products containing Ca (No. 2) or Mg (No. 8), as well as α-ZrP, corresponded to the desorption of water from the interlayers. The endothermic peak of the Sr-containing product (No. 10) at 100 °C was not due to the dehydration between the layers of zirconium(IV) phosphate containing Sr, but to dehydration of other compounds. The dehydro-condensation between the layers of the phosphates gradually occurred above 340 °C, and the TG curves were similar to that of α-ZrP.

Ion Exchange of H^+ in α-ZrP with M^{2+} ($M=Mg^{2+}$, Ca^{2+}, Sr^{2+}, Ba^{2+}). All of the hydrothermal products obtained by the reaction of $ZrOCl_2$ and $M(H_2PO_4)_2$, except for the case of M=Ba, were turned into α-ZrP by the HCl treatment. Thus, it was investigated whether the same compounds as the hydrothermal products could be obtained by the ion exchange of H^+ in α-ZrP with M^{2+} or not. The ion exchange has already been investigated by Alberti et al.[6] and Clearfield et al.[7] They reported that Na^+ acts as a catalyst for the reactions.[4,5] In this paper, ion exchange of the proton in α-ZrP with M^{2+} was compared (1) in the absence and (2) presence of NaOH. The ion exchange conditions and the analytical data are listed in Table 2. The pH of the reaction solution was acidic in each case. The pH decreased in spite of the addition of NaOH, indicating that the ion exchange was accelerated by the addition. The XRD patterns of the ion-exchanged products are shown in Fig. 8. The XRD profile of (a) was almost the same as that of α-ZrP, indicating that ion exchange did not occur. In the case of (b), the peak corresponding to the basal spacing of α-ZrP at

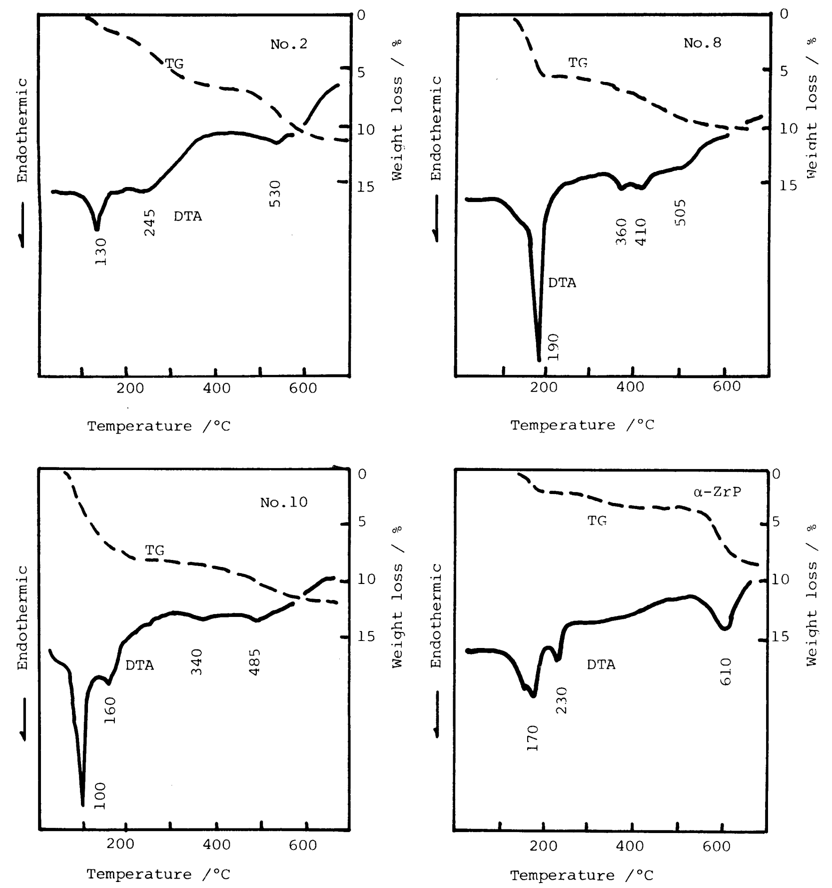

Fig. 7. DTA (——) and TG (----) curves of reaction products of $ZrOCl_2$ and $M(H_2PO)_2$ (M=Mg, Ca, Sr), and α-$Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP). No.2: Reaction product of $ZrOCl_2$ and $Ca(H_2PO_4)_2$, No.8: reaction product of $ZrOCl_2$ and $Mg(H_2PO_4)_2$, No.10: reaction product of $ZrOCl_2$ and $Sr(H_2PO_4)_2$.

Table 2. Ion Exchange of H^+ in α-$Zr(HPO_4)_2$ with M^{2+} (M=Mg, Ca, Sr, Ba), and Analysis of the Products

	Ion exchange condition					Reaction product						
No.	α-ZrP[a] g	$MCl_2 \cdot xH_2O$[b] g	NaOH[c] cm³	H_2O g	Mother liquor pH	Yield g	ZrO_2 %	P_2O_5 %	MO %	H_2O %	Na_2O %	ZrO_2 : P_2O_5 : MO : H_2O : Na_2O (molar ratio)
1	1.00	2.03		100	3.83	0.76	40.5	46.6	0.41	12.5		1.0 : 1.0 : 0.02 : 2.1
2	1.00	2.03	30	70	2.94	0.98	35.2	40.5	4.89	18.5	1.00	1.0 : 1.0 : 0.26 : 3.6 : 0.06
3	1.00	1.47		100	2.36	0.94	38.8	44.7	1.87	14.7		1.0 : 1.0 : 0.18 : 2.6
4	1.00	1.47	30	70	2.53	1.06	34.3	39.6	6.90	19.1	0.07	1.0 : 1.0 : 0.73 : 3.8 : 0.004
5	1.00	2.66		100	2.20	1.01	38.6	44.5	2.89	14.0		1.0 : 1.0 : 0.09 : 2.5
6	1.00	2.66	30	70	2.43	1.25	31.6	36.4	13.1	19.0	0.00	1.0 : 1.0 : 0.49 : 4.1 : 0.00
7	1.00	2.44		100	2.86	0.94	41.0	47.2	0.69	11.2		1.0 : 1.0 : 0.01 : 1.9
8	1.00	2.44	30	70	2.36	1.20	33.5	38.6	16.7	11.1	0.11	1.0 : 1.0 : 0.40 : 2.3 : 0.01

a) α-$Zr(HPO_4)_2 \cdot H_2O$. b) $MgCl_2 \cdot 6H_2O$ for Nos. 1 and 2; $CaCl_2 \cdot 2H_2O$ for Nos. 3 and 4; $SrCl_2 \cdot 6H_2O$ for Nos. 5 and 6; $BaCl_2 \cdot 2H_2O$ for Nos. 7 and 8. c) 0.1 mol dm^{-3}.

$2\theta=11.7°$ (7.5 Å) decreased, and a new peak appeared at $2\theta=9.2°$ (9.60 Å). In this reaction, it was considered that the proton in α-ZrP was first exchanged with Na^+ and then with Mg^{2+}. However, the chemical analysis showed that the Na content of the product was negligible. The product was a mixture of α-ZrP and a Mg^{2+}-exchanged compound having the same layer-spacing as $ZrMg_{0.75-1}H_{0.5-0}(PO_4)_2 \cdot H_2O$ (9.64 Å).[7] The layer-spacing was a little smaller than that of reported compounds $ZrMg_{0.5}H(PO_4)_2 \cdot 3H_2O$ (9.9 Å)[8] and $ZrMg_{0.72}H_{0.56}(PO_4)_2 \cdot 4H_2O$ (9.85 Å).[4] The Mg^{2+}-exchanged compound had a different layer-spacing from the hydrothermal product (11.94 Å), as mentioned above.

In the XRD profiles of (c) and (d), the peak intensity corresponding to the basal spacing of α-ZrP (7.56 Å) decreased, and a new peak appeared at $2\theta=8.9°$ (9.93 Å). The intensity of the new peak increased on

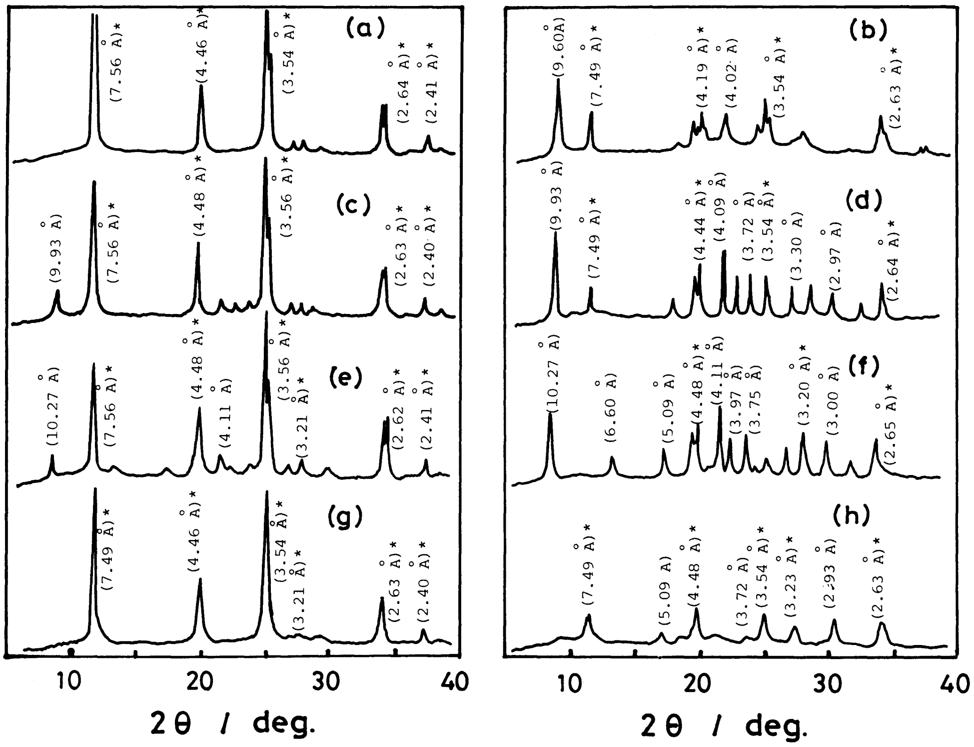

Fig. 8. X-Ray diffraction patterns of ion exchange products of α-ZrP with MCl_2 (M=Mg, Ca, Sr, Ba). Numerals on peaks indicate lattice distances. (a): α-ZrP+$MgCl_2$, (b): α-ZrP+$MgCl_2$+NaOH, (c): α-ZrP+$CaCl_2$, (d): α-ZrP+$CaCl_2$+NaOH, (e): α-ZrP+$SrCl_2$, (f): α-ZrP+$SrCl_2$+NaOH, (g): α-ZrP+$BaCl_2$, (h): α-ZrP+$BaCl_2$+NaOH.

the addition of NaOH (d). This fact clearly implies that the layer distance (9.93 Å) of the ion-exchanged product with Ca^{2+} was similar to that of the corresponding reported compounds, $ZrCa_{0.5-0.65}H_{1-1.7}(PO_4)_2 \cdot 3H_2O$ (9.4 Å)[7] or $ZrCa_{0.8-1.0}H_{0.3-0}(PO_4)_2 \cdot 4H_2O$ (9.64 Å),[7] and the distance was in accord with that of $ZrCa_{0.63}H_{0.74}(PO_4)_2 \cdot H_2O$ (9.98 Å)[6] within the experimental error, and perfectly agreed with that of the hydrothermal product. The composition of (d) compound (NaOH addition) was determined to be $ZrCa_{0.75}H_{0.5}(PO_4)_2 \cdot 3H_2O$.

The XRD pattern of (e) showed that the proton in α-ZrP was exchaned with Sr^{2+} only slightly. By the addition of NaOH (f), the peak corresponding to the basal spacing of α-ZrP disappeared in the XRD profile, and changed into the peak of the ion-exchanged product (10.27 Å). The value was in good accord with those of the hydrothermal product (10.39 Å) mentioned above and the reported compound $ZrSrH(PO_4)_2 \cdot 3.6H_2O$ (10.2 Å)[8] within the experimental error.

The XRD profile of the reaction product of α-ZrP and $BaCl_2$ (g) was almost the same as that of α-ZrP, suggesting that ion exchange did not occur. In the XRD pattern of (h), the peak intensity decreased and new peaks appeared at 2θ=17.4, 21.4, 23.9, and 30.5°. The peak corresponding to the basal spacing was not clear. As for such a compound, $ZrBa_{0.8-1}H_{0.4-1}(PO_4)_2 \cdot 2H_2O$ has been reported.[7]

References

1) G. Alberti and U. Costantino, *J. Mol. Catal.*, **27**, 235 (1984); A. Clearfield, *ibid.*, **27**, 251 (1984); K. Segawa, and M. Kinoshita, *Shokubai*, **27**, 244 (1985).

2) E. Kobayashi, *Bull. Chem. Soc. Jpn.*, **56**, 3756 (1983); E. Kobayashi and S. Shin, *ibid.*, **57**, 465 (1984); E. Kobayashi, *ibid.*, **57**, 3003 (1985).

3) E. Kobayashi, *Bull. Chem. Soc. Jpn.*, **48**, 3114 (1975).

4) G. Alberti, U. Costantino, and J. P. Gupta, *J. Inorg. Nucl. Chem.*, **36**, 2109 (1974).

5) G. Alberti, R. Bertrami, and U. Costantino, *J. Inorg. Nucl. Chem.*, **38**, 1729 (1976).

6) G. Alberti, U. Costantino, and M. Pelliccioni, *J. Inorg. Nucl. Chem.*, **35**, 1327 (1973).

7) A. Clearfield and H. Hagiwara, *J. Inorg. Nucl. Chem.*, **40**, 907 (1978).

8) G. Alberti, R. Bertrami, M. Casciola, U. Costantino, and J. P. Gupta, *J. Inorg. Nucl. Chem.*, **38**, 843 (1976).