June, 1989] © *1989 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 62, 1837—1843 (1989)*

Studies of the Hydrous Silicon(IV)-Titanium(IV) Oxide Ion Exchanger. I. A Method of Synthesis and Some Properties

Hiromichi Yamazaki, Yasuhito Kanno, and Yasushi Inoue*
Department of Nuclear Engineering, Faculty of Engineering, Tohoku University, Aramaki, Sendai 980

(Received December 1, 1988)

Hydrous silicon(IV)-titanium(IV) oxide ion exchanger was prepared by using $TiCl_4$ and Na_2SiO_3 solutions. From a detailed examination of the dependency of the compositions and the acid-base properties of the products on the conditions for precipitation, a reproducible synthetic procedure was established. The exchangers with 37 to 67 mol% of titanium to metallic elements possess much larger ion-exchange capacities and are more stable to highly alkaline solutions than simple mixtures of hydrous silicon(IV) oxide and hydrous titanium(IV) oxide. The dependency of the ion-exchange capacity on the composition can be explained by the difference in the structure of the matrix as evidenced from the thermal analysis, X-ray diffraction, and infrared absorption studies.

Hydrous metal oxides are a group of promising materials for use in the processing of radioactive liquid wastes. This is on account of their unique ion-exchange selectivity produced by the metallic elements forming the materials.[1] However, amorphous hydrous metal oxides are liable to lose their ion-exchange capacity at high temperatures and their use is limited at elevated temperatures. On the other hand, it is conceivable that thermally stable hydrous metal oxides possessing various ion-exchange characteristics may be synthesized by combining more than two kinds of metallic elements.

Kaneko et al. investigated a silica-titania mixed oxide gel,[2,3] but did not clarify the relation between the ion-exchange properties of this material and those of simple hydrous metal oxides. In the investigation of this group of ion-exchange materials, it is indispensable to examine the synthetic conditions for establishing a reproducible method because of the difficulty in reproducible synthesis due to thermodynamical metastability of the materials.

The present paper deals with an investigation undertaken to establish the best conditions for the synthesis of hydrous silicon(IV)-titanium(IV) oxide ion exchanger, laying emphasis on the dependence of ion-exchange properties on the composition of the materials.

Experimental

Reagents and Apparatus. Sodium metasilicate and titanium(IV) chloride were of reagent grade supplied by Wako Pure Chemical Industries, Ltd., and their purities were checked before use. Hydrofluoric acid was obtained from Hirota Kagaku Kogyo Kaisha, Ltd. The other chemicals were of the highest purity grade supplied by Wako Pure Chemical Industries, Ltd.

Thermal analysis was undertaken using a Shimadzu micro thermal analyzer, Model DT-20B, connected to a thermal balance, Model TGC-20H, for thermogravimetric analysis (TGA), and a high-temperature sample holder, Model MDH-20B, for differential thermal analysis (DTA). The reference material for DTA was α-alumina. The measurement was performed in air at a heating rate of 10 °C min^{-1}. The infrared (IR) absorption spectra were measured with a Hitachi infrared spectrometer, Model 2650-50, using the KBr disk method. The specific surface areas of the samples were determined by the BET method (N_2 adsorption at -196 °C) using a Yanagimoto Surface Area Measuring Apparatus, Model GSA-10. Atomic absorption measurements were made with a Nippon Jarrell-Ash atomic-absorption and flame-emission spectrophotometer, Model AA-782. Spectrophotometric analysis was carried out with a Hitachi Model 557 double wavelength spectrophotometer with a 1 cm-glass cell. X-Ray diffraction patterns were obtained by means of Shimadzu X-ray diffraction unit, Model XD-3A, using Ni-filtered Cu $K\alpha$-radiation.

Synthesis of Ion Exchangers. The starting solution of $TiCl_4$ was prepared by dissolving a desired amount of unhydrated titanium(IV) chloride in distilled water, followed by dilution to a desired volume with either HCl solution or distilled water. The starting solution of Na_2SiO_3 was obtained by dissolving a desired amount of $Na_2SiO_3 \cdot 9H_2O$ in 1M NaOH solution (1 M=1 mol dm^{-3}), followed by dilution to a desired volume with either distilled water or NaOH solution. Hydrous silicon(IV)-titanium(IV) oxide was precipitated at various pH and different concentrations of metal ions by mixing an equal volume of the $TiCl_4$ and the Na_2SiO_3 solutions. After being separated from the mother liquor by decantation and filtration through Toyo No.1 filter paper under suction, the precipitate was uniformly dispersed into distilled water and filtered again after being sedimented. The precipitate was then dried at 70 °C or at room temperature. The product was immersed in distilled water to break it down into fine particles, which were subsequently dried at room temperature. The particles were then ground in a porcelain mortar and sieved to obtain required particle sizes (63 to 210 μm). Hydrous silicon(IV) oxide was precipitated by mixing an equal volume of 0.50 M Na_2SiO_3 solution in 1.0 M NaOH and 1.85 M HCl solution. Hydrous titanium(IV) oxide was precipitated at pH 7 by adding 0.98 M NaOH solution into 0.95 M $TiCl_4$ solution. These precipitates were washed in the same manner described above, until no Cl^- was detected in the filtrate, and then dried at room temperature.

Conditioning. The exchanger of a desired particle size was washed with distilled water to remove any adherent powder. The slurry was poured into a glass tube with glass-wool plugging for column support, and 0.05 M HCl was passed through the column until the pH of the effluent approached that of the influent. The column was then washed with distilled water until no Cl^- was detected in the effluent and its pH became constant (pH=5.5). The exchangers, thus prepared, were air-dried at room temperature and stored in a desiccator containing a saturated NH_4Cl solution (relative humidity; 79% at 25 °C).

Total Analysis of the Exchanger. A sample of 0.2 g was ignited at 850 °C, and the water content was calculated from the weight loss. The validity of the procedure had been confirmed thermogravimetrically. The oxide thus formed was dissolved in 1 cm^3 of concentrated H_2SO_4 and 2 cm^3 of 46% HF solutions. This solution was gently heated in order to vaporize SiF_4 and HF, followed by dilution to 50 cm^3 with 9 M H_2SO_4 solution. Titanium was assayed by a compleximetric titration: back titration using PAN(1-(2-pyridylazo)-2-naphthol) as an indicator. The amount of TiO_2 thus determined was subtracted from the mass of the calcined exchanger to obtain the amount of SiO_2.

Ion-Exchange Capacity. The ion-exchange capacity for Na^+ was measured as follows. The exchanger (0.10 g) in the H^+ form was immersed in 15 cm^3 of various solutions, prepared by the desired combinations of 0.10 M NaCl and 0.10 M NaOH solutions, for 7 d at room temperature with intermittent shaking. This was followed by pH measurements and by determination of the sodium ions. The sodium ions were converted to an equivalent amount of sodium chloride and indirectly determined by titrating the chloride ions (the Fajans' method). The amount of the ions taken up by the exchanger was evaluated from the difference between the initial and the final concentrations of the ions in the solutions.

Results and Discussion

(I) Synthesis of Hydrous Silicon(IV)-Titanium(IV) Oxides. In order to establish a reproducible synthetic method, the composition and the acid-base property of hydrous silicon(IV)-titanium(IV) oxides (hereafter called the composite exchanger) were studied as a function of the conditions for precipitation, as mentioned below.

(a) Effect of pH at Precipitation. As the solubility of Si^{4+} largely depends on the pH of the solution, in contrast to Ti^{4+} which is precipitated nearly quantitatively from solutions of pH higher than 1, the yield of silicon was examined as a function of pH. The hydrous metal oxides were precipitated at various pH by mixing 0.25 M $TiCl_4$ solution in HCl and 0.25 M Na_2SiO_3 solution in NaOH. Here, the concentrations of HCl and NaOH were adjusted to give the desired pH. After the precipitate had been completely sedimentated, the concentration of SiO_3^{2-} in the supernatant solution was determined spectrophotometrically, using 10% ammonium molybdate as a coloring reagent.[4] As seen in Fig. 1, the concentration of SiO_3^{2-} in the supernatant increases sharply on both sides of pH 7 to 9. Therefore, the pH at precipitation was controlled to be 7.6±0.3 in the subsequent experiments.

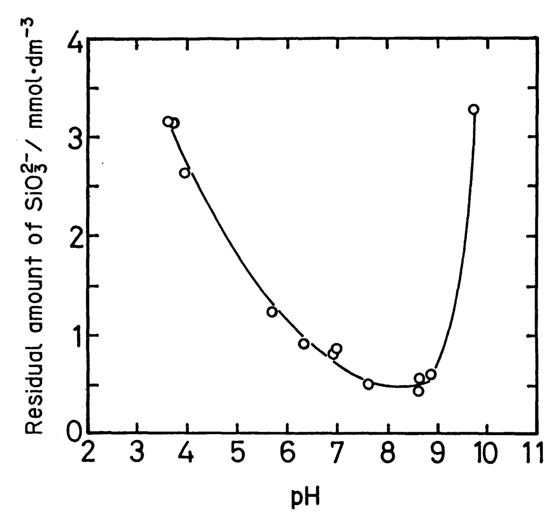

Fig. 1. Dependence of SiO_3^{2-} concentration in supernatant solution on pH at precipitation.

(b) Effect of the Methods of Mixing the Solutions. The ion-exchange capacity and physical strength were studied on the composite exchangers, which were prepared by the following three methods;

Method I: the Na_2SiO_3 solution was added to the $TiCl_4$ solution,

Method II: the $TiCl_4$ solution was added to the Na_2SiO_3 solution,

Method III: the $TiCl_4$ and the Na_2SiO_3 solutions were simultaneously poured into a beaker with vigorous stirring.

For each method, the rate of addition of the solutions was from 5 to 3000 $cm^3 min^{-1}$. After aging for 2 d, the precipitate was washed in a manner described in the experimental section, and then dried at 70 °C for 50 h. Irrespective of the addition rates, the composite exchangers prepared by methods I and II were glassy or chalky opaque particles large enough to be used for

Table 1. Effect of Addition Rates of Na_2SiO_3 Solution into $TiCl_4$ Solution on Ion-Exchange Capacity and Composition (Method II)

Addition rate	Ti-mol%	Water content	Ion-exchange capacity for Na^+ ions at pH 13
$cm^3 min^{-1}$	$\frac{mol\ TiO_2}{mol(SiO_2+TiO_2)} \times 100$	$\frac{mol\ H_2O}{mol(SiO_2+TiO_2)}$	$mmol\ g^{-1}$
3000	50±1	2.19±0.01	3.54±0.06
67	50±1	2.13±0.01	3.62±0.06
16	50±1	1.96±0.01	3.70±0.06
6	50±1	2.03±0.01	3.68±0.06

column operation. In method III, the physical strength of the particles was weak, except with the addition rate of 3000 $cm^3 min^{-1}$. As the precipitate could not be completely washed without suffering from peptization, it was washed only once to avoid wasteful loss. Table 1 shows the effect of the addition rate of the solution in method II on the ion-exchange capacity and the composition of the composite exchangers. The water content increased slightly with the addition rate, but the titanium content (titanium content refers to mol% of Ti/(Si+Ti)) and the ion-exchange capacity were not significantly affected by this factor.

(c) **Effect of Concentrations of the Solutions.** The hydrous metal oxides were precipitated by mixing the $TiCl_4$ solution and the Na_2SiO_3 solution in 1.0 M NaOH with varying concentration. The addition rates of the solutions were 5 $cm^3 min^{-1}$ for methods I and II, and 3000 $cm^3 min^{-1}$ for method III. Figure 2 shows the Na^+-uptake curves of the materials, indicating that the difference in the ion-exchange capacities is 0.4 $mmol\,g^{-1}$ (less than 5% of the total exchange capacity) at the largest. Thus, the acid-base properties of the exchangers are not significantly affected by the method of mixing, nor by the concentration of the solutions.

(d) **Effect of Titanium Content.** The exchange capacities for Na^+ at pH 13 were measured as a function of the titanium content in the exchangers which were precipitated by methods I and III under the best conditions of a constant total concentration of metal

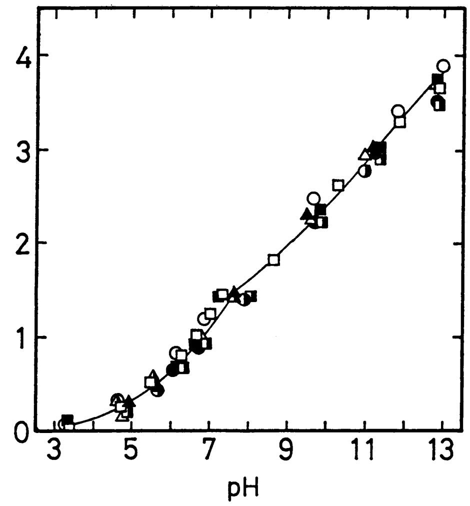

Fig. 2. Uptake curves for Na^+ ions (effect of concentrations of metal solutions used at precipitation).
Concentration of metal solution/M; ◑: 0.10, ○: 0.25, ●: 1.0 (Method I); ◭: 0.10, △: 0.25, ▲: 1.0 (Method II); ◨: 0.10, □: 0.25, ■: 1.0 (Method III).

Table 2. Synthetic Conditions and Compositions of the Exchangers

Sample No.	Method	Drying temp.	Ti-mol% in solution $\frac{mol\ Ti^{4+}}{mol(Si^{4+}+Ti^{4+})}\times100$	Ti-mol% in exchanger $\frac{mol\ TiO_2}{mol(SiO_2+TiO_2)}\times100$		Water content $\frac{mol\ H_2O}{mol(SiO_2+TiO_2)}$	
1	I	70 °C	35	37	±1	1.77	±0.02
2			40	42		1.62	
3			45	46		1.75	
4			50	51		1.80	
5			55	57		1.76	
6			60	62		1.64	
7			65	67		1.75	
8[a]			50	52		1.94	
9[a]			50	51		1.82	
10[a]			50	53		1.90	
11[a]			50	52		1.75	
12	III	Room temperature	11	10	±1	1.84	±0.02
13			11	10		1.75	
14			11	11		1.83	
15			32	34		2.04	
16			52	56		2.45	
17			52	57		2.61	
18			52	56		2.48	
19			72	76		2.51	
20			91	89		1.92	
21			91	90		1.97	
22			91	90		2.03	
23	Hydrous silicon(IV) oxide					$SiO_2\cdot1.27H_2O$	
24	Hydrous titanium(IV) oxide					$TiO_2\cdot2.35H_2O$	

a) Exchangers were prepared in a large amount by the recommended procedure.

ions (0.5 M). These conditions were realized by using desired combinations of 0.5 M $TiCl_4$ solutions in HCl and 0.5 M Na_2SiO_3 solutions in NaOH, where the concentrations of HCl and NaOH were suitably adjusted for providing pH 7.6 at precipitation. The gels thus prepared by method I were dried at 70 °C, while those by method III were dried at room temperature. As is shown in Table 2, the composite exchangers thus prepared have nearly the same titanium content as the solution mixed. The composite exchangers contained appreciably less water than the hydrous titanium(IV) oxide, but much more than the hydrous silicon(IV) oxide.

Figure 3 shows the ion-exchange capacities of the composite exchangers. For comparison, the exchange capacities were measured for simple mixtures of the hydrous silicon(IV) oxide and the hydrous titanium(IV) oxide (the mixed exchanger), as is shown in the same figure (dotted line). The measurement for the mixed exchangers was made at pH 12.2 instead of pH 13 because the dissolution of a part of the hydrous silicon(IV) oxide in the mixed exchangers limited the applicable maximum pH. The line shows that the ion-exchange capacities of the mixed exchangers are the algebraical sums of those of the component simple hydrous oxides. Based on this observation, we can estimate the hypothetical capacities at pH 13 of the mixed exchangers (a chain line). This figure indicates that the exchangers with 37 to 67 mol% titanium have nearly the same ion-exchange capacities, much larger than the mixed exchangers. The exchanger with 90 mol% titanium has a much smaller capacity than the mixed exchanger of the similar titanium content. This figure also indicates that the exchange capacities were not affected by the method of mixing the solutions or the drying temperature.

Figure 4 shows uptake curves for Na^+ of the exchangers with various titanium contents, along with those of the simple hydrous metal oxides. The decrease of the capacities of the exchanger with 10 mol% titanium in pH regions beyond 11.5, similar to the hydrous silicon(IV) oxide, is ascribed to the partial dissolution of the exchanger. This phenomenon is not observed in the other exchangers, which suggests the stabilization of the matrix in highly alkaline solution in spite of the large silicon content. The minimum pH at which sodium ions were adsorbed was significantly lower for the exchangers with 10 to 76 mol% titanium than for the simple hydrous oxides. These findings suggest the formation of a compound, basically different in properties from the hydrous silicon(IV) oxide and the hydrous titanium(IV) oxide.

(e) Effect of Drying Temperature. If no excessive decrease in the capacity occurs, heating is preferable for rapid drying of the hydrous oxide gel. From this standpoint, the acid-base property and the water content were compared between the exchangers dried at 70 °C (Nos. 8—11 in Table 2) and those at room temperature (Nos. 16—18 in Table 2). Although the water content is smaller in the materials dried at 70 °C than in those at room temperature, little difference in the Na^+ uptake curves was observed between them, when it was normalized to the number of moles of Na^+ taken up per mole of metals composing the materials. Hence, drying at 70 °C does not affect the acid-base property of the exchanger.

Recommended Procedure. The composite ex-

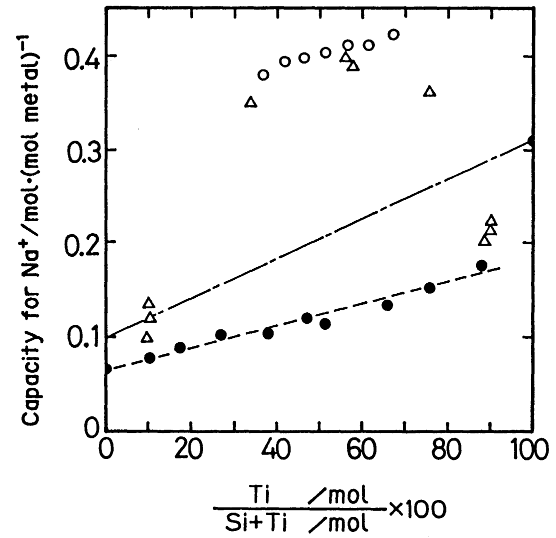

Fig. 3. Dependence of ion-exchange capacity on titanium content.
Exchangers; ○: Nos. 1—7 in Table 2, △: Nos. 12—22 in Table 2, ●: Mixture of $SiO_2 \cdot 1.27H_2O$ and $TiO_2 \cdot 2.35H_2O$, -.-.-: Estimated exchange capacity of the mixed exchanger at pH 13.

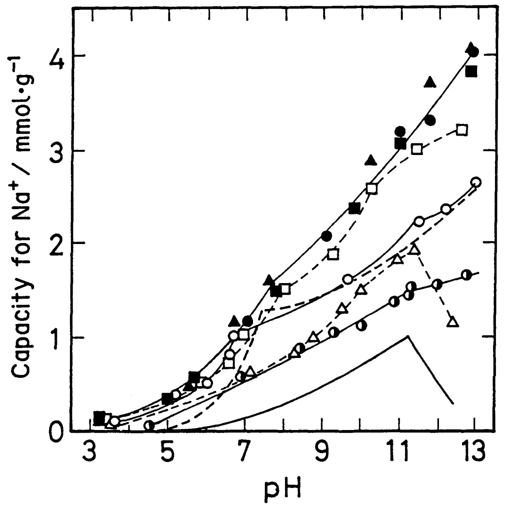

Fig. 4. Uptake curves for Na^+ ions (Effect of titanium content).
Exchangers; ■: No. 1, ▲: No. 4, ● : No. 7, △: No. 12, □: No. 15, ○: No. 19, ◑: No. 21, ——: No. 23, ------: No. 24. The numbers are the same as those in Table 2.

changers with 37 to 67 mol% titanium possess ion-exchange capacity larger than those with other compositions. In this study, the exchanger with 50 mol% titanium was selected as the best choice for easy control of the composition. Method I was chosen because it produced particles hard and large enough to be used for column operation. The concentrations of $TiCl_4$ and Na_2SiO_3 solutions were 0.5 M, which was as high as practicable to prepare a large amount of the exchanger in one batch. The recommended procedure is as follows: In 2 dm^3 of 0.5 M $TiCl_4$ solution, 2 dm^3 of 0.5 M Na_2SiO_3 solution in 1.0 M NaOH are added at a rate of 16 cm^3/min with vigorous stirring, followed by adjusting pH to 7.6 ± 0.3 by adding a small amount of concentrated HCl or NaOH solutions. After aging for 2 d, the precipitate thus formed is separated from the mother liquor by filtration under suction, and is then uniformly dispersed into 5 dm^3 of water. The precipitate is filtered again after being completely sedimentated, and is dried at 70 °C for 50 h. The resulting product is ground to a desired particle size, and is then converted to the H^+ form by the procedure described in the experimental section. As a result of four independent syntheses, the uptake curves and the compositions agreed well with each other, except for a little larger fluctuation of water content which is susceptible to the environmental conditions (Table 2). The synthetic procedure, therefore, is considered to be highly reproducible. The yield, calculated on the basis of the metallic element used, exceeded 99 percent.

(II) Structural Analysis of the Exchangers. In order to obtain structural information, (a) specific surface area, (b) infrared spectra, (c) thermal analytical curves, and (d) X-ray diffraction patterns were measured on the samples with various titanium content and the simple hydrous metal oxides. Their compositions are shown in Table 2.

(a) Specific Surface Area. Figure 5 shows the specific surface areas of the samples. It is nearly the same as that of the hydrous silicon oxide up to 57 mol% titanium content and decreased with titanium content; reaching to about one-half of the hydrous silicon oxide in the hydrous titanium oxide. As the ion-exchange capacity (Fig. 3) does not increase in keeping with the specific surface area, the uptake of Na^+ in the exchangers cannot be explained by the sorption only on the internal surface of the materials. The change in the ion-exchange capacities with the composition of the exchanger may be ascribed to the variation in the number of exchange sites in the whole sample.

(b) IR Spectra. Figure 6 shows IR spectra of the composite exchangers, along with the simple hydrous metal oxides. The asymmetric absorption band near 3400 cm^{-1} is attributable to the sum of the contributions from water and hydroxyl groups bonding to the metal in the materials; the former at the lower-, and the latter at the higher-wavenumber sides. The absorption band near 1630 cm^{-1} is due to the bending mode of water and the absorption in the wavenumber region below 1500 cm^{-1}, to the metal-oxygen bond in the matrix. The absorption peak due to the hydroxyl groups is larger for the exchanger with 57 mol% titanium than for the others. This result is compatible with the change in the ion-exchange capacities with the composition (Fig. 3), as the hydroxyl groups

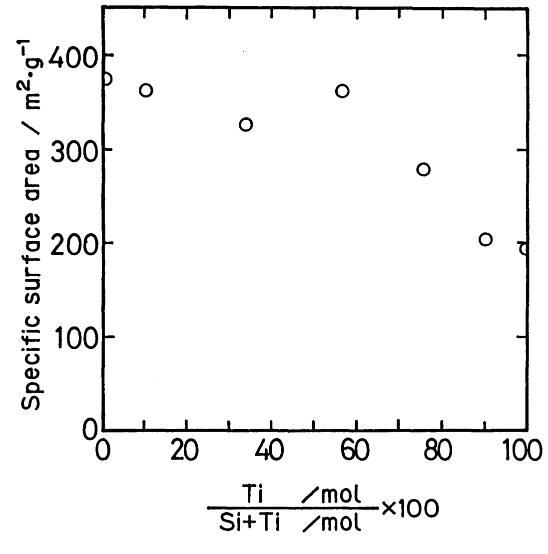

Fig. 5. Dependence of surface area of the exchangers on titanium content.

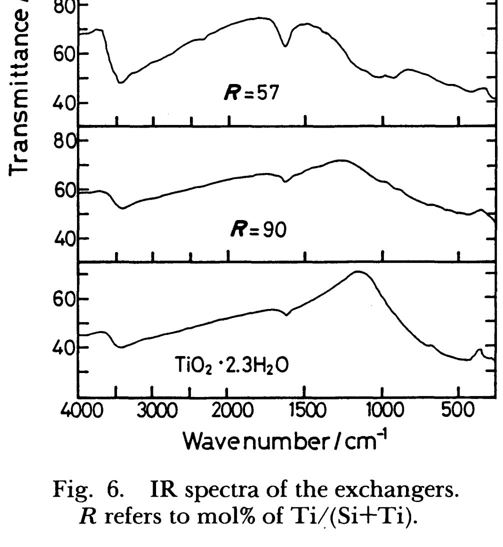

Fig. 6. IR spectra of the exchangers. *R* refers to mol% of Ti/(Si+Ti).

function as ion-exchange sites. In the wavenumber region below 1500 cm^{-1}, the exchangers with 10 and 90 mol% titanium, respectively, showed absorption spectra similar to hydrous silicon oxide and hydrous titanium oxide, while the spectrum of the exchanger with 57 mol% titanium differed from that of the simple hydrous metal oxides.

(c) Thermal Analysis. The TGA and the DTA curves were measured on the same samples as were used in the IR spectrum measurements. In the DTA curves, the large endothermic peak appearing in the range below 250 °C is due to loss of water. A combination of peaks at 90 °C and 125 °C indicates that the exchangers have at least two kinds of water having different binding energies. Figure 7 shows the percentile weight loss at various temperatures. As the fraction of water lost below 100 °C was smaller for the composite exchangers than for the simple hydrous metal oxides, the ratio of water of high binding energy to total is larger in the former than in the latter oxides. As had been discussed previously,[5–7] the water of lower binding energy is zeolitic or adherent, while the water of higher binding energy is present as either hydroxyl groups or water bound thereto. Accordingly, the large amount of bound water accounts for a large ion-exchange capacity of the exchanger with 57 mol% titanium, being compatible with the IR observations. The water lost during drying at 70 °C is mainly zeolitic or adherent and irrelevant to the ion-exchange capacity.

(d) X-Ray Analysis. Figure 8 shows X-ray diffraction patterns of the exchangers with various titanium contents. All exchangers have poor crystallinity. The broad peak at low angle, characteristic of the hydrous silicon oxide, shifts to higher angle and broadens further with the increase of titanium content up to 67 mol%. An increase in titanium content from 67 to 76 mol% results in a sudden change in the matrix; the X-ray diffraction pattern of the exchanger with 76 mol% titanium closely resembles that of the anatase form of the titanium oxide, as compared with the diffuse pattern of the composite exchanger with 67 mol% titanium. The peaks sharpen with titanium content, becoming most clear for the exchanger with 90 mol% titanium, indicating an enhanced crystallization of the matrix. The exchangers with 37 to 67 mol% titanium are amorphous because of the diffuse diffraction patterns.

From the observations described above, the change in the ion-exchange capacity with titanium content can be summarized as follows. The matrices of the exchangers with 37 to 67 mol% titanium are amorphous and contained a large number of hydroxyl groups compared to the exchangers with other compositions, so that these amorphous compounds have large ion-exchange capacity. While the exchanger with 10 mol% titanium possesses much more ion-exchange sites of higher acidity than those of the

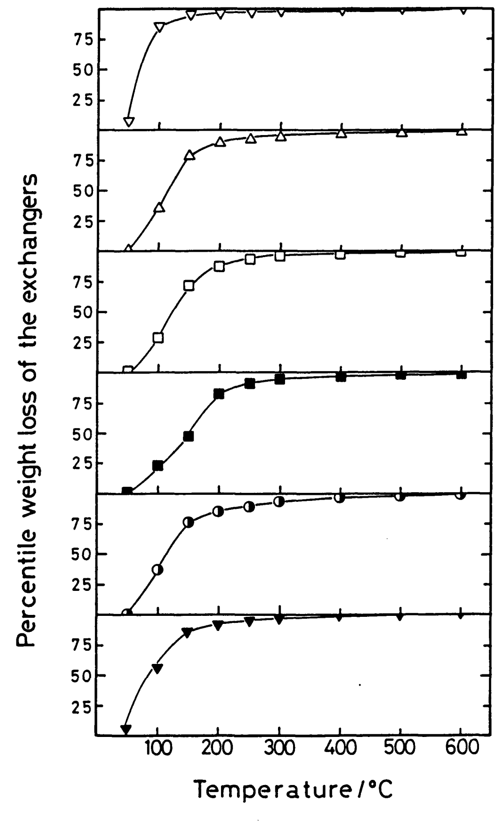

Fig. 7. Weight losses of the exchangers by heat treatment.
Exchangers; ▽: No. 23, △: No. 12, □: No. 17, ■: No. 8, ◑: No. 21, ▼: No. 24. The sample numbers are the same as those in Table 2.

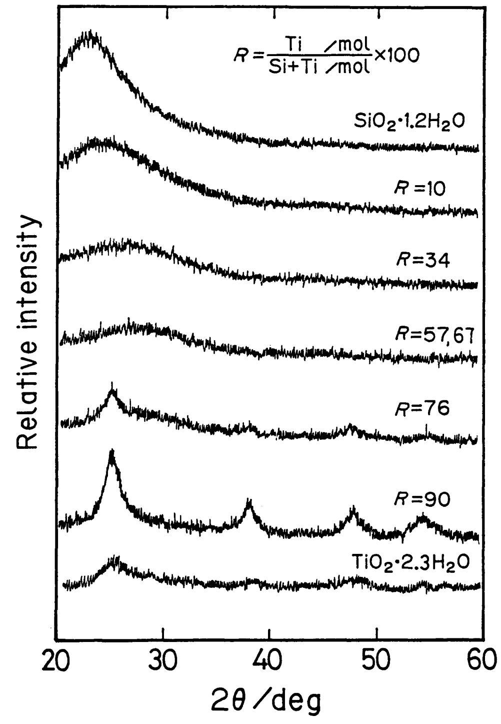

Fig. 8. X-Ray diffraction patterns of the exchangers.

hydrous silicon(IV) oxide, it is unstable to highly alkaline solutions because of the similarity in the structure to the hydrous silicon(IV) oxide. The smaller ion-exchange capacity of the exchanger with 90 mol% titanium than the hydrous titanium(IV) oxide is attributable to better crystallinity of the former than the latter.

This research was supported in part by a grant from Tohoku Radiological Science Center.

References

1) Y. Inoue and H. Yamazaki, *J. Nucl. Sci. Technol.*, **24**, 462 (1987).

2) S. Kaneko, S. Okuda, M. Nakamura, and Y. Kubo, *Chem. Lett.*, **1980**, 1621.

3) S. Kaneko and K. Tsukamoto, *Chem. Lett.*, **1983**, 1425; **1984**, 505.

4) JIS K-0101-1986 (1986).

5) Y. Inoue and M. Tsuji, *Bull. Chem. Soc. Jpn.*, **51**, 479 (1978).

6) Y. Inoue, H. Yamazaki, and H. Nakamizo, *Bull. Chem. Soc. Jpn.*, **58**, 1292 (1985).

7) Y. Inoue, H. Yamazaki, and Y. Matsuda, *Bull. Chem. Soc. Jpn.*, **58**, 3225 (1985).