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Ion-Exchange Properties and Thermal Stability of Hydrous Titanium(IV)-Zirconium(IV) Oxide Ion Exchanger

Hiromichi Yamazaki, Yasushi Inoue,* Naoki Kikuchi, and Hiroshi Kurihara
Department of Nuclear Engineering, Faculty of Engineering, Tohoku
University, Aramaki, Aoba-ku, Sendai 980

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Ion-exchange properties and thermal stability were studied for hydrous Ti^{IV}-Zr^{IV} oxide ion exchangers with various contents of titanium. The cation-exchange capacity increased with the titanium content in the exchanger, along with a decrease in the anion-exchange capacity. Though the affinity for representative metal ions increases with the acidity of the exchange sites, no such simple relation holds for transition metal ions. Exchangers with 30 to 70 mol% Ti (the mol% of Ti to Ti+Zr) do not suffer from drastic changes in both the water content and crystallinity upon heating to 500 °C; they are much more heat-resistant than component simple hydrous metal oxides. Though the total cation-exchange capacity decreases with increasing temperature during a heat treatment, only a minute amount of the acidic sites dissociating at a pH lower than the isoelectric point of the exchangers with $\leqslant$70 mol% Ti increases upon heating. The effect of a heat treatment on the distribution coefficients of cations has been explained by these observations.

Hydrous metal oxides are sorbents with an ion-exchange selectivity peculiar to the metallic elements forming the materials.[1] However, they are thermodynamically metastable and liable to lose their ion-exchange capacity at high temperature. Tanabe et al. reported that binary metal oxides have a marked higher acidity than do component simple oxides.[2-4] It is conceivable that thermally stable hydrous metal oxides possessing a large ion-exchange capacity can be synthesized by combining more than two kinds of metallic elements. There have been few studies concerning the relation between the ion-exchange properties of binary and simple hydrous metal oxides. For this reason hydrous Si-Ti^{IV} oxides with various titanium contents were synthesized, and both their ion-exchange properties and thermal stability investigated. As a result, a hydrous Ti^{IV} oxide modified with Si, which has a higher ionic potential than does Ti^{IV}, had a larger ion-exchang capacity and was thermally more stable than simple hydrous Ti^{IV} oxide.[5]

In the present study a hydrous Ti^{IV} oxide modified with Zr^{IV}, which has a lower ionic potential than does Ti^{IV}, was investigated in order to clarify the effect of modifiers on the ion-exchange property and thermal stability of the materials.

Experimental

Reagents and Apparatus. Titanium(IV) chloride and zirconium(IV) chloride oxide octahydrate were supplied by Wako Pure Chemical Industries Ltd., and their purity was checked before use. A thermogravimetric analysis (TGA) and a differential thermal analysis (DTA) were undertaken with a Seiko micro thermal analyzer (Model SSC5020-TG/DTA300) at a heating rate of 10 °C min^{-1}. All the other apparatuses were the same as those described previously.[5]

Ion-Exchangers. A 1 M $TiCl_4$ aqueous solution and a 1 M $ZrOCl_2$ aqueous solution (1 M=1 mol dm^{-3}) were prepared by dissolving unhydrated titanium(IV) chloride and zirconium chloride oxide octahydrate in distilled water. They were mixed to make a solution with the desired molar ratio of Ti to Ti+Zr (the mixture). Hydrous Ti^{IV}-Zr^{IV} oxide was then precipitated by pouring the mixture into 1 M NaOH. The pH at precipitation was controlled within 13.0±0.1 by varying the volume ratio of the NaOH solution to the mixture. After being washed with distilled water the precipitate was filtered and dried at 70 °C. 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 the required particle size (63 to 210 mm). Hydrous Ti^{IV} and Zr^{IV} oxides were precipitated at pH 13 in the same manner as described above.

The exchanger of a desired particle size was converted to the H$^+$ form by treating it with 0.05 M HCl by the procedure described previously[5] 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 0.5 g was ignited at 850 °C; the water content was calculated from the weight loss. A part (0.1 g) of the oxide, thus formed, was decomposed by a mixture of concentrated H_2SO_4 (4 cm^3) and $(NH_4)_2SO_4$ (2.5 g) by heating, followed by dilution to 50 cm^3 with 4 M H_2SO_4. The titanium in this solution was assayed by extraction-spectrophotometry; the absorbance of the titanium-thiocyanate complex extracted from a 9 M H_2SO_4 solution by trioctylphosphine oxide in cyclohexane was measured.[6] The amount of TiO_2, thus determined, was subtracted from the mass of the calcined exchanger to obtain the amount of ZrO_2.

Titration Curves. One tenth gram of each exchanger in the H$^+$ form was immersed in 25 cm^3 of 0.1 M NaOH for 24 h at 25 °C; the solution pH was then measured. After every addition of a small amount of 1 M NaOH or HCl, the solution pH was measured after standing for 24 h to obtain a titration curve.

Uptake Curves. One tenth gram of each exchanger in the H$^+$ form was immersed in 15 cm^3 of various solutions prepared by the desired combinations of 0.1 M NaCl, and 0.1

M NaOH or 0.1 M HCl, for 7 d at 25 °C with intermittent shaking. This was followed by pH measurements and a determination of the Na^+ and Cl^-. The chloride concentration was determine by the Fajans' method after the solution had been neutralized. The sodium ions were converted to an equivalent amount of sodium chloride by evaporating the solution with HCl, and indirectly determined by titrating the Cl^-. The amount of ions taken up by the exchanger was evaluated from the difference between the initial and final concentrations of the respective ions in the solutions.

Distribution Coefficients. The distribution coefficients, K_d, were determined in the following way. The exchanger was contacted at 25 °C with a solution containing metal ions to be examined until their concentration in the supernatant solution became constant (8 to 18 d). The ratio of the solution volume (cm^3) to the amount of exchanger (g) was always kept constant at 100. The initial concentration of metal ions was 1×10^{-4} M (except carrier free ^{241}Am) and the ionic strength was adjusted to 0.1 M by using an $NaNO_3$ solution. The pH and metal ion concentration in the supernatant solution were then measured. The K_d, expressed in $cm^3\,g^{-1}$, was obtained from a calculation performed in the usual manner. Analyses of Cs, Sr, Ba, Mn, Fe, Co, Zn, Eu, and Am, respectively, were carried out radiometrically using ^{137}Cs, ^{85}Sr, ^{133}Ba, ^{54}Mn, ^{59}Fe, ^{60}Co, ^{65}Zn, ^{152}Eu, and ^{241}Am as tracers. Uranyl(VI) ions were analyzed spectrophotometrically using 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol,[7] while the concentration of the other cations was determined by means of atomic absorption spectrophotometry.

Heat Treatment. About 5 g of each exchanger in the H^+ form were heated in air to a constant weight at a constant temperature (150, 300, and 500 °C). After being cooled over P_2O_5, the sample was weighed and then left immersed in water overnight. The sample separated from water was allowed to stand to a constant weight in a desiccator containing a saturated NH_4Cl solution (humidification). The water recovery of the heat-treated sample was calculated according to the difference in the water content between samples cooled over P_2O_5 immediately after the treatment and those subjected to humidification.

Results and Discussion

(I) Synthesis of the Exchangers. The effect of the conditions at precipitation on the yield and the acid-base property of the exchangers was first examined. It was found that exchangers with a variety of acid-base property can be synthesized by controlling the molar ratio of Ti to Ti+Zr in mixed solutions. The cation-exchange capacity of an exchanger of high titanium content increased with pH at precipitation. The total concentration of Ti plus Zr in the solution, the kind of alkali used (NaOH or NH_3), and the mixing method had little effect on the acid-base property of the exchangers. By applying the method described in Experimental, which was established by taking the yield and the convenience of the procedure into consideration, exchangers with various composition were synthesized. As is shown in Table 1, the exchangers, thus prepared, have nearly the same titanium content as that in the mixed solutions. The water content of the exchangers tends to decrease with an increase in the titanium content. Independent triplicate preparation was carried out for each of the exchangers with 50 and 90 mol% Ti (the molar percent of Ti to Ti+Zr is used to distinguish the exchangers with titanium content in the text and the molar ratio *R* in the figures) in order to examine the reproducibility of the synthesis. The uptake curve (Fig. 1) and the composition of the three samples agree well with each other, except for a small fluctuation in the water content, which is susceptible to environmental conditions (Table 1). The synthetic procedure, therefore, is considered to be reproducible.

The X-ray diffraction patterns of the binary and simple hydrous metal oxides showed that all of the samples were amorphous at room temperature. Being heated at 850 °C, the exchangers showed diffraction peaks: The exchanger with 90 mol% Ti crystal-

Table 1. Composition of the Exchangers

Sample No.	Ti-mol% in solution	pH at precipitation	Ti-mol% in exchanger	Water content
	$\frac{TiO_2/mol}{(TiO_2+ZrO_2)/mol}\times100$		$\frac{TiO_2/mol}{(TiO_2+ZrO_2)/mol}\times100$	$\frac{H_2O/mol}{(TiO_2+ZrO_2)/mol}$
1	10±1	13.06	10±1	2.44±0.01
2	30±1	13.07	30±1	2.59±0.01
3	50±1	13.04	49±1	2.16±0.01
4	50±1	13.06	49±1	2.12±0.01
5	50±1	13.05	50±1	2.14±0.01
6	70±1	13.10	70±1	1.99±0.02
7	90±1	13.10	91±1	1.33±0.01
8	90±1	13.05	91±1	1.46±0.02
9	90±1	13.00	90±1	1.28±0.01
10	Hydrous TiO_2	12.95		1.43±0.01
11	Hydrous ZrO_2	13.08		2.44±0.02

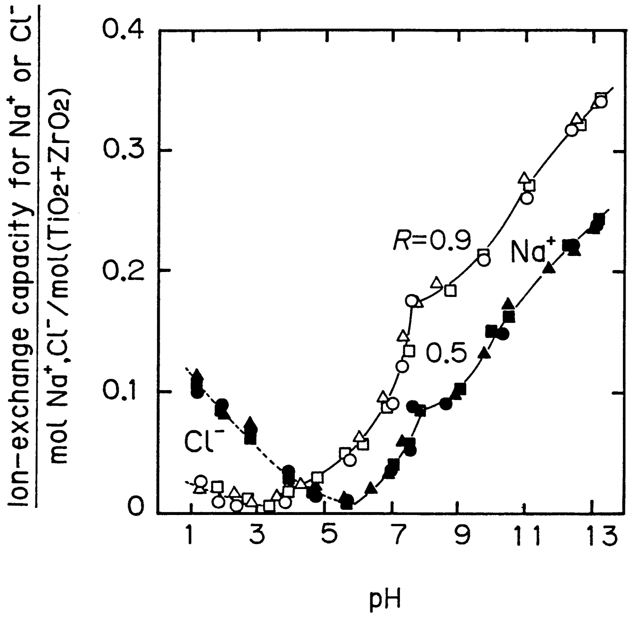


Fig. 1. Uptake curves of Na^+ or Cl^- (reproducibility of synthesis).
Ionic strength of solution: 0.1 M (HCl-NaCl-NaOH).
Exchanger, ▲: No. 3; ●: No. 4; ■: No. 5 (50 mol% Ti). △: No. 7; ○: No. 8; □: No. 9 (90 mol% Ti).

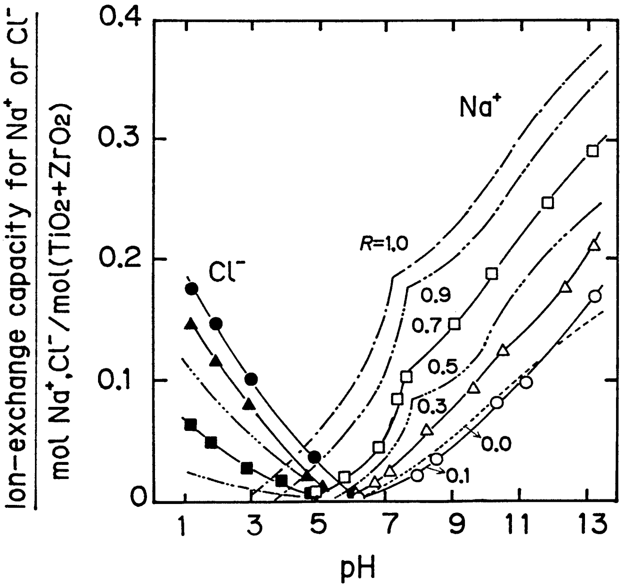


Fig. 2. Uptake curves of Na^+ or Cl^- (acid-base property as a function of titanium content).
Ionic strength of solution: 0.1 M (HCl-NaCl-NaOH).
Exchanger, ○: No. 1; △: No. 2; ——···——: No. 3—5; □: No. 6; —··—: No. 7—9; —·—: No. 10; ------: No. 11. Open and Closed symbols show Na^+ and Cl^- uptake, respectively.

lized to anatase TiO_2; the hydrous $\mathrm{Ti^{IV}}$ oxide crystallized to the rutile form. Though the diffraction patterns of the orthorhombic $(Ti, Zr)O_2$ were observed in exchangers with 50 and 70 mol% Ti,[8] no pattern characteristic of the titanium-containing phase was found in exchangers with ⩽30 mol% Ti; an exchanger with 30 mol% Ti crystallized to a mixture of cubic and orthorhombic ZrO_2, and that with 10 mol% Ti and the hydrous $\mathrm{Zr^{IV}}$ oxide crystallized to monoclinic ZrO_2.

(II) Ion-Exchange Property. (a) Acid-Base Property of the Exchangers: Figure 2 shows uptake curves of Na^+ and Cl^- on exchangers with various titanium contents, along with those on simple hydrous metal oxides. This figure reveals that all exchangers, except for the hydrous $\mathrm{Ti^{IV}}$ oxide, are amphoteric, and that an increase in the zirconium content reduces the cation-exchange while increasing the anion-exchange capacity. The acid-base property of hydrous $\mathrm{Ti^{IV}}$-$\mathrm{Zr^{IV}}$ oxides might reflect that of the component simple hydrous metal oxides; the hydrous $\mathrm{Ti^{IV}}$ oxide is weakly acidic and the hydrous $\mathrm{Zr^{IV}}$ oxide is an amphoteric ion exchanger with an isoelectric point at pH 6.5, having an anion-exchange capacity larger than the cation-exchange capacity.[9,10] In exchangers with ⩾30 mol% Ti, the increase in the titanium content shifted the pH, at which the sorption of Na^+ commenced, to the acidic side and increased the cation-exchange capacity in the region of pH lower than the inflection point of the uptake curves. The acidity was almost constant in exchangers with ⩽30 mol% Ti, which crystallized to the form of $\mathrm{Zr^{IV}}$ oxides.

It is apparent from these results that both the acidity and number of OH groups in hydrous $\mathrm{Ti^{IV}}$ oxide decrease upon modifying the material with hydrous $\mathrm{Zr^{IV}}$ oxide. As has been previously reported, the hydrous Si-$\mathrm{Ti^{IV}}$ oxides with 37 to 67 mol% Ti possess a cation-exchange capacity that is much larger than a simple mixture of hydrous Si and $\mathrm{Ti^{IV}}$ oxides.[5] These facts would suggest that the cation-exchange capacity of hydrous metal oxides can be improved by modifying them with a metal element having a larger ionic potential.

(b) Selectivity for Cations: In order to examine the relation between the cation-exchange selectivity and the composition of the exchangers, the K_d's for various cations were measured as a function of pH. The pH's at which the K_d's reach 100 are shown in Table 2, as an indicator of the cation-exchange selectivity of the materials.

The pH's for representative metal ions increased with a decrease in the titanium content, while those for transition metal ions did not depend largely on the composition of the exchangers. In exchangers with ⩽70 mol% Ti, the affinity was markedly higher for a transition than for representative metal ions, while in those with ⩾90 mol% Ti such a relation is unclear. The selectivity series for alkali metal or alkaline earth metal ions appears to increase with the ionic potential of hydrated cations. This conforms

Table 2. Cation-Exchange Selectivities of the Exchangers[a]

Cation	pH at which K_d reaches 100						
	No. 10[b]	No. 9	No. 6	No. 5	No. 2	No. 1	No. 11
Li^+	6.3	7.7	9.6	x[c]	x	x	x
K^+	5.9	6.5	7.9	x	x	x	x
Cs^+	1.8	4.1	6.5	7.8	x	x	x
Mg^{2+}	—	5.8	—	7.4	—	7.6	—
Ca^{2+}	—	5.3	—	6.5	—	7.2	—
Sr^{2+}	4.0	5.1	5.4	6.2	6.6	7.0	7.0
Ba^{2+}	3.3	4.2	4.8	5.7	6.5	6.7	6.7
Mn^{2+}	4.0	4.5	5.0	5.7	6.0	6.3	—
Co^{2+}	3.9	4.9	4.9	5.6	5.8	6.0	6.0
Zn^{2+}	3.4	4.3	4.5	4.9	5.1	5.3	5.3
Cu^{2+}	2.8	3.4	3.6	3.8	4.0	4.2	4.2
Fe^{3+}	—	2.4	2.2	2.2	2.2	2.4	2.4
Eu^{3+}	2.5	3.6	3.6	4.0	4.3	4.5	4.5
Am^{3+}[d]	2.1	3.1	3.0	3.6	3.7	4.2	4.2
UO_2^{2+}	2.1	3.4	2.7	2.7	2.9	3.3	3.4

a) Conditions, Initial concentration of metal ion: 1×10^{-4} M; volume of solution/amount of exchanger: 100 $cm^3\,g^{-1}$; ionic strength of solution: 0.1 M (HNO_3-$NaNO_3$-NaOH); Temperature: 25±1 °C. b) The numbers are the same as those in Table 1. c) The K_d is smaller than 100 in the region of pH>10. d) Tracer concentration.

to ion-hydration theory, which claims that the strength of the electrostatic interaction between hydrated cations and fixed anionic sites determines the selectivity of a strongly acidic resin.[11] On the other hand, such a simple relation does not hold for transition metal ions. Irrespective of the compositions of the exchangers, the affinity series for bipositive transition metal ions follows the Irving-Williams series: Mn<Fe<Co<Ni<Cu<Zn.[12] This order arise in part from an increase in the acidic strength of metal ions as Lewis acids. In addition, UO_2^{2+} had an affinity higher than that expected value due to the ionic charge. It may therefore be considered that in the ion-exchange reaction of transition metal ions the formation of covalent bonds between anionic sites in the exchanger and metal ions plays an important role in determining the selectivity of the exchanger, along with the remote Coulombic interaction.

These findings are consistent with the decrease in the acidity of the exchange sites with the titanium content in the exchangers (Fig. 2). Due to the higher acidity of the sites, an exchanger with a higher titanium content is preferable for the sorption of representative metal ions, since their ion-exchange reactions are governed by an electrostatic interaction between the ions and dissociated sites in the exchangers. The decrease in the acidity of exchange sites lowers the electrostatic interactions between ions and sites, but increases the ability to form a covalent bond between them. By presuming that the former effect is not completely offset by the latter, we can understand the small positive dependence of K_d on the titanium content in the ion-exchange reaction of transition metal ions. Since the acidity of the exchange sites in the hydrous Ti^{IV}-Zr^{IV} oxides depends on the titanium content, exchangers possessing a variety of selectivity series can be obtained by varying the compositions of the materials.

Table 3. Effect of Heat Treatment on the Water Content of the Exchangers

Exchanger[b]	Water content/mol H_2O (mol(TiO_2+ZrO_2))$^{-1}$						
	Room temperature	150 °C[a]		300 °C		500 °C	
		A	B	A	B	A	B
No. 1	2.44	0.39	1.72	0	0.98	0	0.55
No. 2	2.59	0.47	2.04	0.16	1.68	0	1.25
No. 3—5	2.12—2.14	0.31	1.82	0.06	1.58	0	1.22
No. 6	1.99	0.27	1.80	0.04	1.54	0	1.25
No. 7—9	1.28—1.46	0.27	1.12	0.04	0.98	0.05	0.51
No. 10	1.43	0.22	1.18	0.10	0.74	0.02	0.18
No. 11	2.44	0.39	1.72	0.02	0.98	0	0.55

A: Water content in the exchangers immediately after heat treatment. B: Water content in the exchangers subjected to humidification. a) Temperature for heat treatment. b) The numbers are the same as those in Table 1.

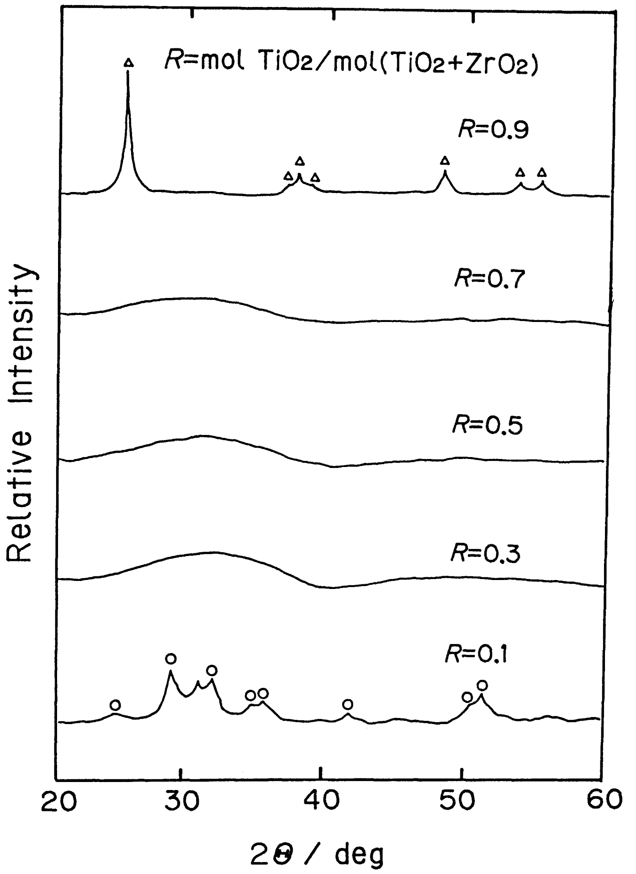


Fig. 3. X-Ray diffraction patterns of the exchangers heated at 500 °C.
○: Peaks corresponding to monoclinic ZrO_2. △: Peaks corresponding to anatase TiO_2. Ni filtered Cu $K\alpha$-radiation was used.

(III) Effect of Heat Treatment. (a) Water Content: Table 3 shows the relation between the temperature for a heat treatment and the water content of the exchanger immediately after the treatment or being subjected to humidification. Irrespective of the titanium content, the amount of water contained in the exchangers immediately after a heat treatmen at 150 °C was reduced to <20% of the original values; it then decreased to almost zero at 300 °C. On the other hand, the water content of exchangers subjected to humidification varied with the titanium content. For exchangers with 30 to 70 mol% Ti heated at 500 °C, about 1.3 mol of water per 1 mol of the metallic elements were recovered, indicating that 50 to 65% of water lost by heating was recovered by humidification. When exchangers with a composition close to that of the simple hydrous metal oxides were heated at 500 °C, more than 75% of water originally present was released irreversibly.

As shown in Fig. 3, the X-ray diffraction patterns of exchangers with 30 to 70 mol% Ti, display an amorphous structure which did not change, even when heated at 500 °C. Heat-treated exchangers with 10 and 90 mol% Ti, respectively, showed peaks characteristic of monoclinic ZrO_2 and anatase TiO_2. These results indicate that the heat treatment hardly changed the structure of exchangers with 30 to 70 mol% Ti, but easily crystallized exchangers with a composition

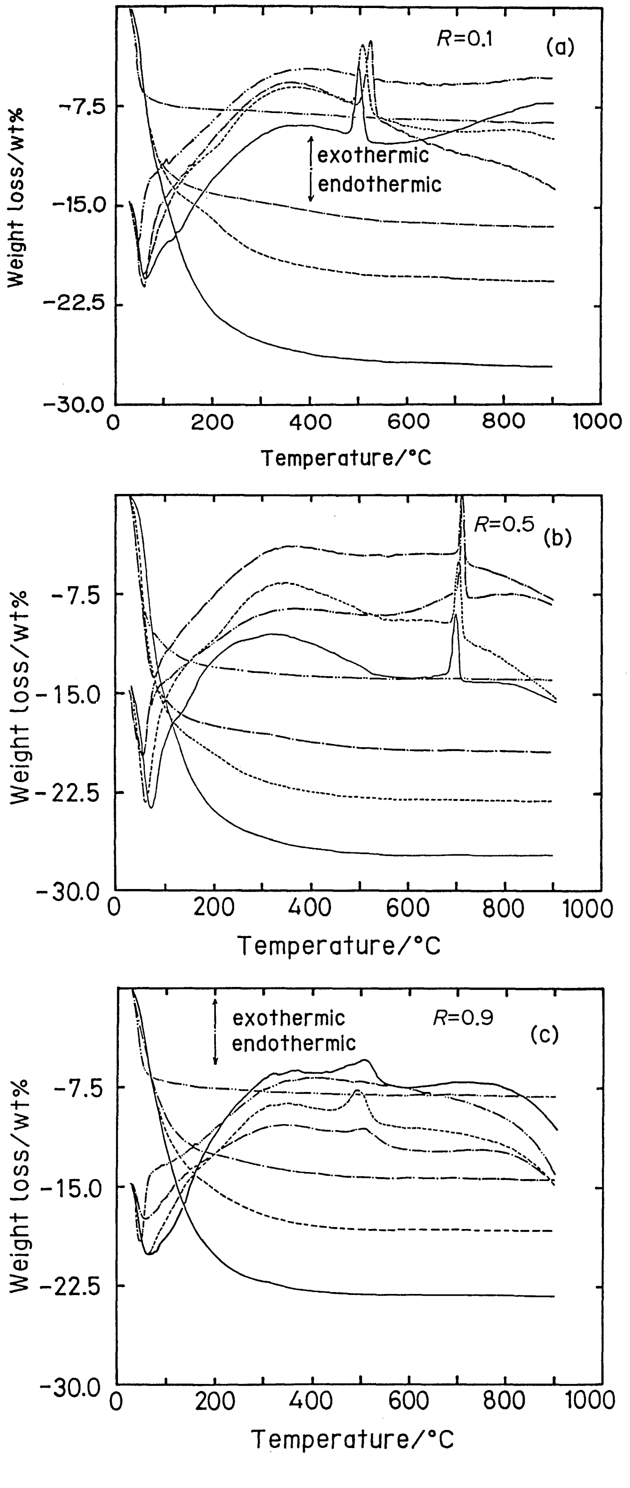


Fig. 4. TGA and DTA curves of the exchangers subjected to humidification.
Exchangers, (a): No. 1; (b): No. 3—5; (c): No. 7—9. Temperature for heat treatment, ——: R.T.; ----: 150 °C; — - —: 300 °C; — -- —: 500 °C.

close to that of simple hydrous metal oxides.

The DTA and TGA measurements were made for the heat-treated and a humidified exchangers, along with samples without a heat treatment, as shown in Fig. 4. In the DTA curves, a large endothermic peak with a shoulder appearing in the range below 200 °C is due to a loss of water. A large exothermic peak observed at 450 °C or higher is assigned to the crystallization of exchangers as judged from X-ray data. Exchangers with 30 to 70 mol% Ti crystallized at 660 to 715 °C, while those with a composition close to that of simple hydrous oxides crystallized at a temperature below 520 °C. The large difference in the crystallization temperature reflects the difference in the structures of the exchanger matrices. The shoulder at the high-temperature side of the large endothermic peak indicates that the exchanger has at least two kinds of water having different binding energies. The large endothermic peaks at around 75 °C sharpened and the area under the shoulders decreased as the heat-treatment temperature became higher. When simple hydrous metal oxides and exchangers with 10 and 90 mol% Ti were heated at 500 °C, the water lost in regions with a temperature higher than 100 °C decreased to negligibly small amount, as can be seen from the TGA curves. Exchangers with 30 to 70 mol% Ti, heated at 500 °C, still had a small amount of water of high binding energy.

As discussed previously, 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.[13–15] Accordingly, the water recoverable by humidification is considered to correspond mainly to a certain kind of zeolitic water, while the hydroxyl groups and the bound water are lost irreversibly from a heated exchanger. The irreversible loss of water of high binding energy is smaller in exchangers with 30 to 70 mol% Ti than in those with composition close to the simple hydrous metal oxides.

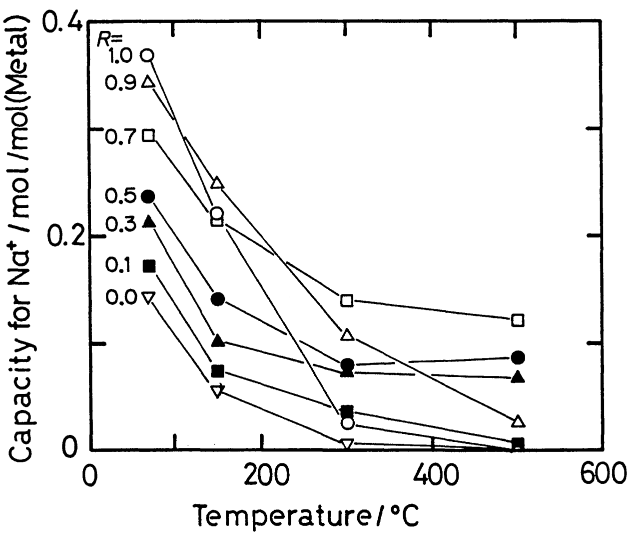


Fig. 5. Effect of heat treatment on the ion-exchange capacities for Na$^+$.
Exchanger, ■: No. 1; ▲: No. 2; ●: No. 3—5; □: No. 6; △: No. 7—9; O: No. 10; ▽: No. 11.

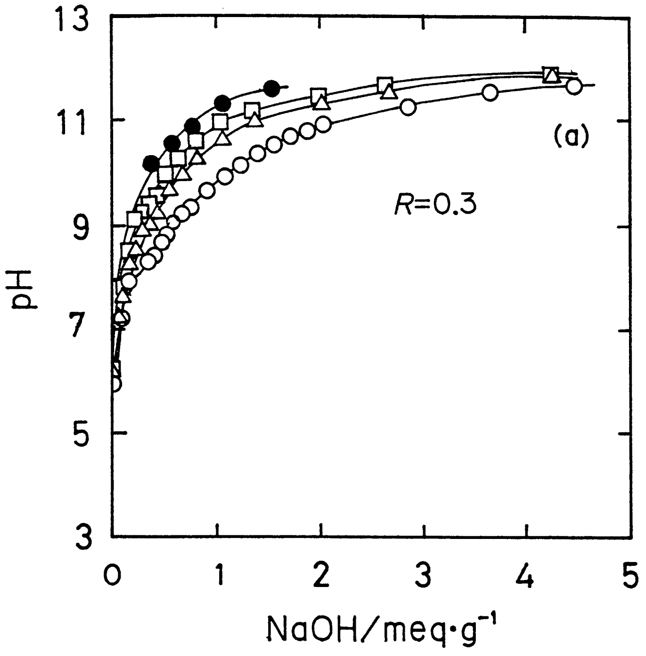
(b) Acid-Base Property: To examine the dependence of the thermal stability on the titanium content, the ion-exchange capacity of Na$^+$ was measured at pH 13 on samples with or without a heat treatment (Fig. 5). When simple hydrous metal oxides and an exchanger with 10 mol% Ti were heated at 300 °C, the capacity decreased to about ≤10% of the original values. Exchangers with 30 to 70 mol% Ti retaind larger capacity at the same temperature; an exchanger with 70 mol% Ti had the largest residual capacity. Even when heated at 500 °C, they did not lose their capacity further, which indicates that they were thermally more stable than the component hydrous metal oxides. These findings are compatible with the results of thermal analysis, which indicates that OH groups in exchangers with 30 to 70 mol% Ti once lost by heating, were recovered to a certain degree during humidification. The recovery of the exchange sites may be due to the matrices of these exchangers which are thermally more stable than those of simple hydrous metal oxides (Fig. 3).

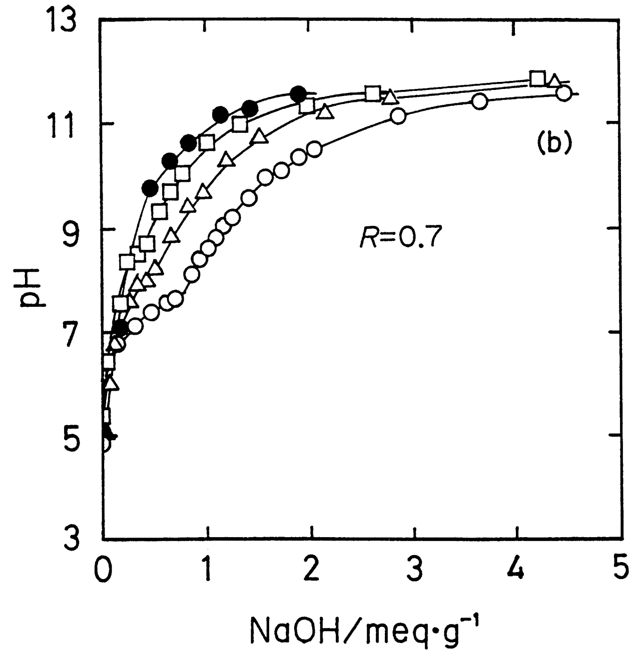
In order to examine the effect of a heat treatment on the acid-base properties of exchangers, the pH-titration curves were measured for samples both with or without a heat treatment. Some results are shown in Fig. 6. In hydrous Ti^{IV} oxide[16] and an exchanger with 90 mol% Ti, the pH at which the sorption of Na$^+$ commenced, greatly shifted to the alkaline side upon heating. This indicates that the acidity of the exchange sites is decreased by a heat treatment. On the other hand, the acidity of the exchange sites in exchangers with ⩽70 mol% Ti was not affected by heating. Regardless of the composition, the exchange capacity at a pH lower than the inflection point decreased with the temperature for a heat treatment, while, in the higher pH region, the curves of samples with a given titanium content were parallel with each other. This observation indicates that a heat treatment destroys mainly the exchange sites with higher acidity.

In hydrous Ti^{IV}-Zr^{IV} oxide, the destruction of the exchange sites by heat treatment occurs mainly at more acidic sites, as in the hydrous Si-Ti^{IV} oxide.[5] The degree of the decrease in the exchange capacity by heat treatment is larger in exchangers with a higher titanium content. Hence, we can give an excellent thermal stability to hydrous Ti^{IV} oxide by modifying it with hydrous Si or Zr^{IV} oxide. The optimum titanium content for the thermal stability depends on the kind of modifiers.

(c) Distribution Coefficients: The distribution coefficients, K_d, of Cs$^+$, Sr^{2+}, Co^{2+}, Eu^{2+}, and UO$_2^{2+}$ on heat-treated exchangers with various titanium contents were measured at various pH's. Heat treatments did not alter the dependency of the K_d's on the pH, indicating that the stoichiometric relation governing the ion-exchange reaction does not change with a heat treatment.

Figures 7-a to 7-e show plots of the K_d's of Cs^+ and Sr^{2+} at pH 6, of Co^{2+} at pH 5.5, of Eu^{3+} at pH 3.5, and of UO_2^{2+} at pH 2.5 against the temperature for a heat treatment. The K_d's of Cs^+ and Sr^{2+} decreased with increasing temperature for the treatment, with the extent higher on the exchangers with $\geqslant$70 mol% Ti than on those with smaller titanium content (Figs. 7-a to 7-b). On an exchanger with 90 mol% Ti and hydrous Ti^{IV} oxide, the K_d's of Co^{2+} decreased consistently with temperature, while remaining nearly constant on exchangers with 50 and 70 mol% Ti or even increased somewhat on exchangers with 10 and 30 mol% Ti between 150 and 300 °C (Fig. 7-c). On hydrous Ti^{IV} oxide, the K_d's of Eu^{3+} decreased greatly





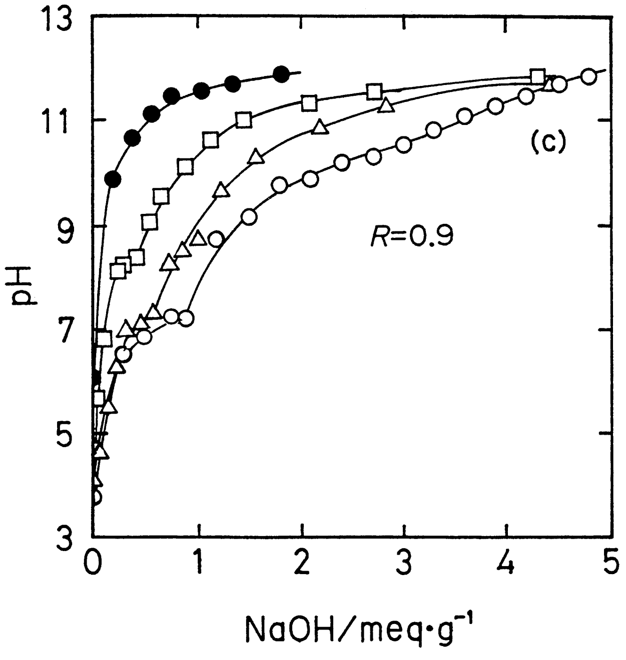
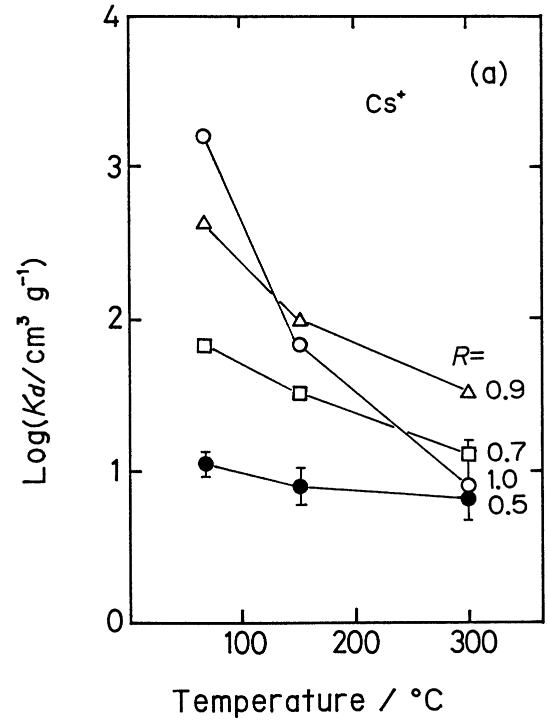


Fig. 6. Titration curves of heat-treated exchangers. Exchangers, (a): No. 2; (b): No. 6; (c): No. 7—9. Temperature for heat treatment, ○: R.T.; △: 150 °C; □: 300 °C; ●: 500 °C.



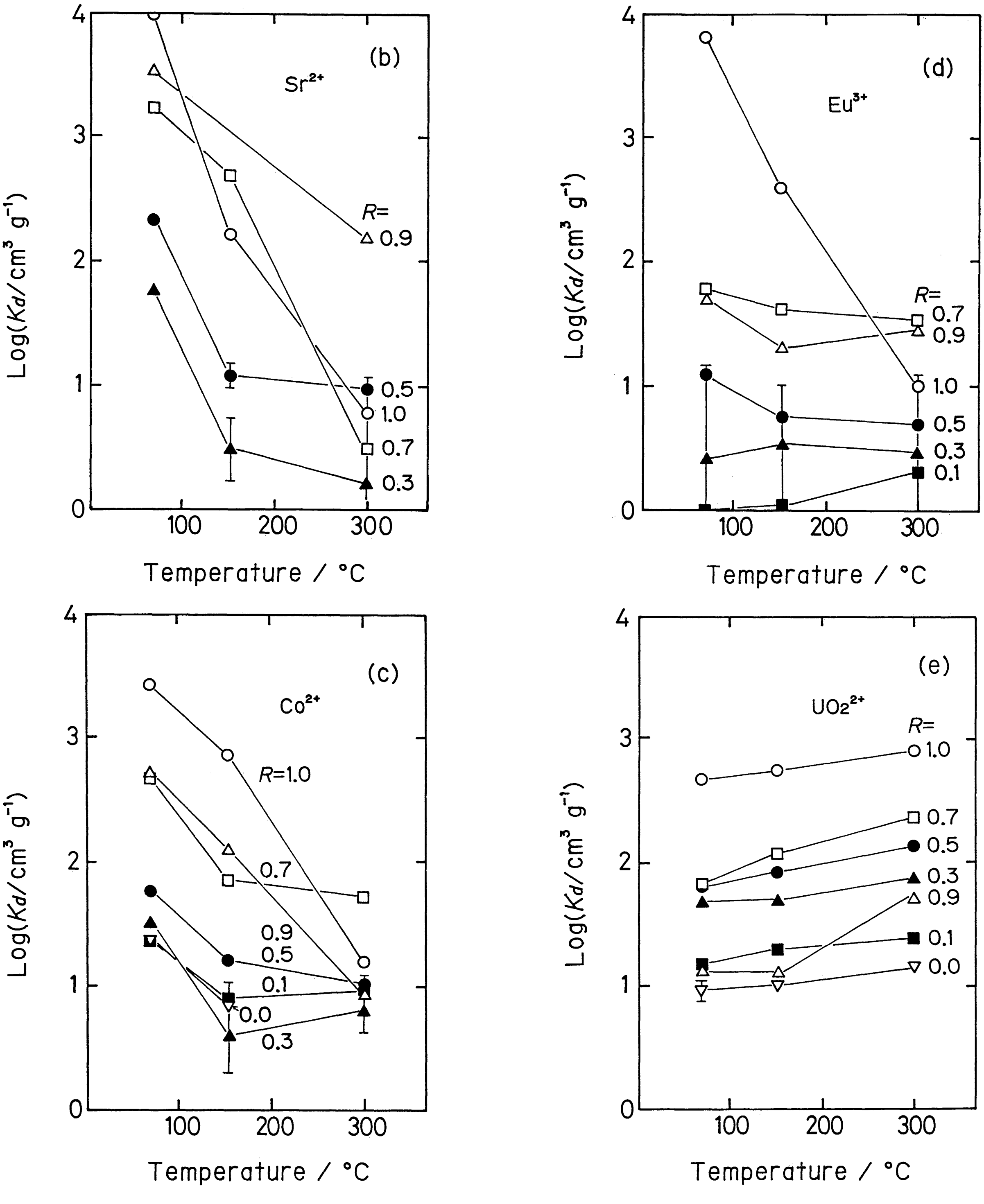


Fig. 7. Effect of heat treatment on the distribution coefficients of cations.
Cations, (a): Cs^+; (b): Sr^{2+}; (c): Co^{2+}; (d): Eu^{3+}; (e): UO_2^{2+}.
Exchanger, ■: No. 1; ▲: No. 2; ●: No. 3—5; □: No. 6; △: No. 7—9; ○: No. 10; ▽: No. 11.

with increasing temperature for a heat treatment, while on exchangers with 30 to 90 mol% Ti, they changed a little, and even somewhat increased on an exchanger with 10 mol% Ti by a heat treatment. The K_d's of UO_2^{2+} increased with the heat-treatment temperature, irrespective of the composition of the exchangers. The degree of the increase was somewhat larger on exchangers with 50 to 90 mol% Ti than on those with other compositions. These findings suggest that the exchangers after a heat treatment tend to retain their high affinity to cations, which can be sorbed from solution with a pH lower than the isoelectric point of the materials.

In order to understand these observations, the effect

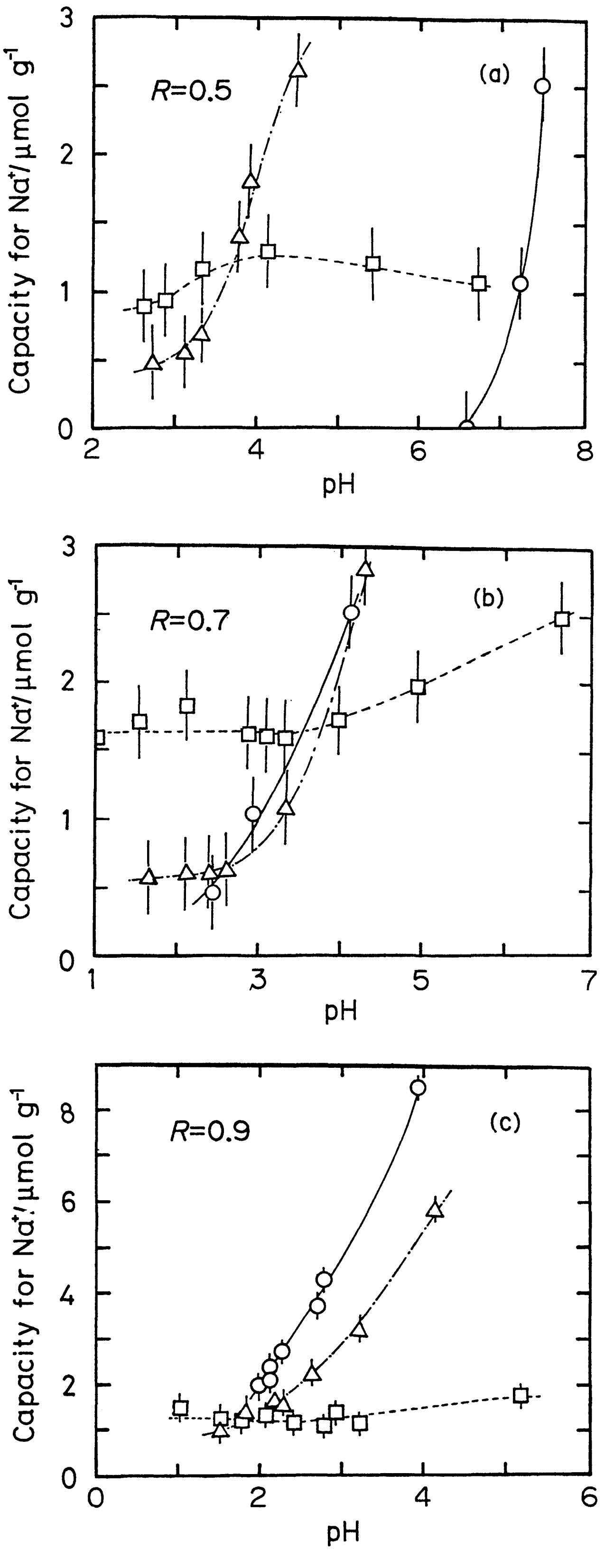


Fig. 8. Effect of heat treatment on a small amount of strongly acidic exchange sites.
Exchangers, (a): No. 3—5; (b): No. 6; (c): No. 7—9.
Temperature for heat treatment, O: R.T.; Δ: 150 °C; □: 300 °C.
Solution: 2×10^{-4} M HNO_3-NaOH. Solution volume/Exchanger mass: 20 cm^3/0.2 g.

of a heat treatment on a small amount of the most acidic sites in the exchangers was examined by measuring the Na^+-uptake curve in Na^+-solutions of such low initial concentration as 2×10^{-4} M (Figs. 8-a to 8-c). In a pH range higher than 2, the amount of Na^+ sorbed on an exchanger with 90 mol% Ti and hydrous Ti^{IV} oxide decreased with increasing temperature, while at lower pH, it depended little on the temperature (Fig. 8-c). The curve of an exchanger with 70 mol% Ti was not affected by a heat treatment at 150 °C, but changed appreciably with a heat treatment at 300 °C; the amount of Na^+ sorbed was almost independent of the pH; thus, at a pH lower than 3.5 it was larger than the values for an exchanger without a heat treatment (Fig. 8-b). When exchangers with $\leqslant 50$ mol% Ti were heat-treated, the pH at which the sorption of Na^+ commenced largely shifted to the acidic side and the sorption capacity in the region of pH <4 increased with temperature for a heat treatment (Fig. 8-a).

From the above-mentioned observations, the effect of a heat treatment on the distribution coefficients can be understood as follows. Although the total cation-exchange capacity decreases with increasing temperature, a heat treatment brings about a small increase in strongly acidic exchange sites, which can dissociate at a pH lower than the isoelectric point of exchangers with $\leqslant 70$ mol% Ti. This is the reason why the distribution coefficients of cations with high affinity increase with a heat treatment. On the other hand, cations with low affinity are sorbed on exchangers by exchanging with hydrogens on abundant ion-exchange sites less acidic than the isoelectric point. The number of these sites determines the total cation-exchange capacity. A heat treatment, therefore, brings about a decrease in the distribution coefficients of cations with low affinity, in keeping with a decrease in the total cation exchange capacity.

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