Effect of Heat Treatment of Hydrous Metal Oxides on Their Cation-Exchange Selectivity

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The effect of a heat treatment on the ion-exchange selectivity of hydrous metal oxides was studied by measuring the distribution coefficients of Cs^+, Ba^{2+}, Co^{2+}, and Eu^{3+} on hydrous oxides of Ti^{IV}, Sn^{IV}, Zr^{IV}, and Nb^{V}. The distribution coefficients decreased with increasing temperature for the heat treatment, except on hydrous Nb^{V} oxide, in which the reverse effect was observed (except for Cs^+). The decrease in the hydrous Sn^{IV} and Zr^{IV} oxides is ascribed to a decrease in their ion-exchange capacity. In the case of hydrous Ti^{IV} and Nb^{V} oxides, the distribution coefficients were strongly affected by a change in the acidity of the most dissociable OH groups by the heat treatment. The selectivity of the exchangers has no direct correlation with the change in the porosity, the specific surface area and the density of the materials by the heat treatment.

Hydrous metal oxides are a group of promising materials used for processing radioactive liquid wastes because each of them has a unique ion-exchange selectivity series which is specific to the metallic element forming the material. They have, however, a significant disadvantage regarding the liability to lose their ion-exchange capacity upon heat treatment, accompanying a change in their specific surface area and crystallinity.[1] Although the ion-exchange selectivity is another important property as sorbents, there exist a few studies concerning the effect of a heat treatment on this property. It was reported that hydrous Th^{IV} oxide heated at 400 °C did not sorb cations at all, while hydrous Ti^{IV} oxide retained its affinity toward transition metal ions.[2] The ion-exchange selectivity series of hydrous Fe^{III} oxide for either cations or anions varied with increasing temperature.[3,4] At present, however, we cannot understand the reason for the change in the ion-exchange selectivity of hydrous metal oxides upon heat treatment.

The present authors previously established reproducible methods for synthesizing hydrous oxides of Ti^{IV}, Sn^{IV}, Nb^{V}, and Zr^{IV}, and investigated their ion-exchange properties.[5] This paper deals with the relation between the effect of heat treatment of these materials on their ion-exchange selectivity for Cs^+, Ba^{2+}, Co^{2+}, and Eu^{3+}, and such properties as ion-exchange capacity, acidity of exchange sites, density, specific surface area, and crystallinity.

Experimental

Reagents and Apparatus. Titanium(IV) chloride was of reagent grade and supplied by Wako Pure Chemical Industries, Ltd.; its purity was checked before use. Niobium(V) chloride of the highest purity grade was obtained from Mitsuwa Kagaku Yakuhin, Ltd. The other chemicals were of the highest purity grade supplied by Wako Pure Chemical Industries, Ltd.

A well-type NaI(Tl) scintillation counter (Fuji Denki, Model NDE-14001) was employed for the measurement of the γ-radioactivity. The specific surface area of samples, after being heated at 100 °C to a constant weight, was determined by the BET method (N_2 adsorption at −196 °C). The pore size distribution and the pore volume of the exchangers were calculated by Inkley's method from the adsorption isotherm of N_2 at −196 °C.[6] X-Ray diffraction patterns were obtained by means of a Shimadzu X-ray diffraction unit (Model XD-3A) using Ni-filtered Cu $K\alpha$-radiation.

Ion Exchangers. Hydrous metal oxides other than hydrous Ti^{IV} oxides were prepared by methods described previously.[7-9] Hydrous Ti^{IV} oxide was precipitated at pH 7 by adding a 0.98 mol dm^{-3} NaOH aqueous solution into a 0.95 mol dm^{-3} $TiCl_4$ aqueous solution. The precipitate was washed with water until no Cl^- could be detected in the filtrate, and dried at room temperature. The resulting cake was ground in a porcelain mortar, sieved to obtain the desired particle size (63 to 210 μm), and then converted to the H^+ form by treating it in a column with a 0.05 mol dm^{-3} HCl aqueous solution. The column was washed with water until no Cl^- could be detected in the effluent. Finally, the exchanger was air-dried and stored in a desiccator containing a saturated NH_4Cl aqueous solution (relative humidity, 79% at 25 °C). Each hydrous metal oxide was heat-treated as follows. About 5 g of an exchanger in the H^+ form were heated in air to a constant weight at a constant temperature, which was controlled within an accuracy of 1%. After being cooled, the exchanger was immersed in water overnight, followed by drying to a constant weight over a saturated NH_4Cl aqueous solution (humidification). The water content of the sample was evaluated from the weight loss when the humidified exchanger was heated at 850 °C. The density was measured in the usual manner by using a 25 cm^3 pycnometer.

Distribution Coefficients. The distribution coefficients, K_d, were determined in the following way, unless otherwise noted. One tenth gram of an exchanger in the H^+ form was immersed for 4 d at 40 °C in 7 cm^3 of a solution with a suitable pH, which was adjusted by using a combination of 0.133 mol dm^{-3} NaCl, and 0.133 mol dm^{-3} HCl or NaOH. One cubic centimeter of a solution containing metal ions to be examined was then added to the slurry to make their concentration 1×10^{-4} mol dm^{-3}. The mixture was allowed to stand at 40 °C until the concentration of the cation in the supernatant solution became constant (8 to 15 d). The K_d, expressed in $cm^3\,g^{-1}$, was calculated in the usual manner. The analysis of Cs, Ba, Co, and Eu was carried out radiometrically using ^{137}Cs, ^{133}Ba, ^{60}Co, and ^{152}Eu respectively as tracers.

Ion-Exchange Capacity. The exchanger (0.15 g) in the H^+ form was immersed in 15 cm^3 of 0.1 mol dm^{-3} sodium or cobalt solution for 8 d at 20±1 °C, with intermittent shaking. This was followed by a pH measurement and a determination of the cations. A sodium solution with a suitable pH was prepared by a desired combination of 0.1 mol dm^{-3} NaCl and 0.1 mol dm^{-3} NaOH. The pH of the cobalt solution was adjusted by using a small amount of NaOH–MES (2-(*N*-morpholino) ethanesulfonic acid) buffer solution. Sodium ions were converted to an equivalent amount of sodium chloride and indirectly determined by titrating the chloride ions, using Fajans' method. Cobalt ions were assayed by compleximetric titration with a 0.01 mol EDTA aqueous solution, using Murexide as an indicator.

Results and Discussion

(1)Distribution Coefficients. The K_d values on the four hydrous metal oxides with or without heat treatment were measured for Cs^+, Ba^{2+}, Co^{2+}, and Eu^{3+}. Figure 1 is an example of log K_d vs. pH plots. The heat treatment did not alter the dependence of K_d on the pH, indicating that the stoichiometric relation governing the exchange reaction does not change with the treatment.

The K_d values at constant pH are plotted against the temperature for the heat treatment (Figs. 2-a to 2-d). The K_d values, except those on hydrous Nb^V oxide, decreased with increasing temperature; the decrease was larger for hydrous Ti^{IV} oxide than for hydrous Sn^{IV} and Zr^{IV} oxides. In the case of hydrous Nb^V oxide, the tendency differs according to the ions sorbed, that is, the K_d values for Cs^+ decreased, while those for Co^{2+}, Eu^{3+}, and Ba^{2+} increased with the heat treatment; the increase in the values for the former two ions was appreciable at 200 °C. These results indicate that the effect of a thermal treratment on the affinity of cations depends on the nature of both the exchangers and the cations to be sorbed. As has been shown in preceding papers,[9–11)] transition metal ions are sorbed on hydrous metal oxides by a bond partially covalent in character along with a remote Coulombic interaction. However, Figs. 2-a to 2-d show no clear difference between the reprsentative metal and the transition metal ions regarding the effect of the heat treatment on the affinities for the hydrous metal oxides.

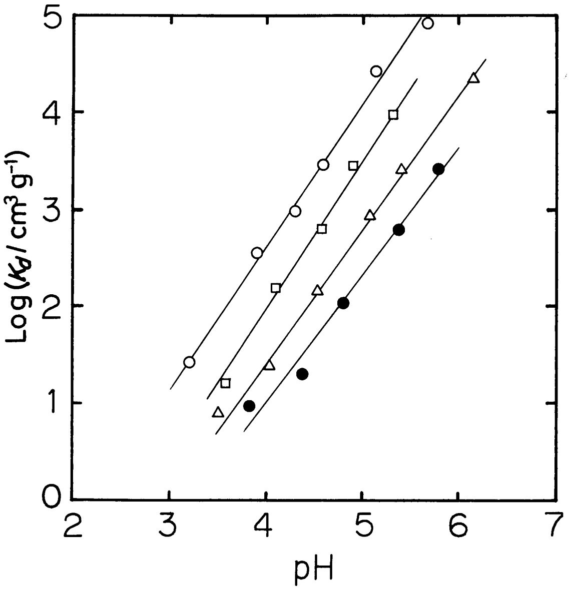

Fig. 1. Log K_d of hydrous Ti^{IV} oxide for Co^{2+} as a function of pH. Heat treatment of the exchanger; ○: R.T., □: 80 °C, △: 140 °C, ●: 220 °C.

(2)Ion-Exchange Capacity and Some Other Properties. To understand the reason for the change in ion-exchange selectivity of hydrous metal oxides by heat treatment, the effect of the heating temperature was examined on the ion-exchange capacity, the acidity of the exchange sites and some physical properties of the exchanger matrix.

(a)Ion-Exchange Capacity: Figures 3-a to 3-d show the pH-dependence of ion-exchange capacities for Na^+ on the exchangers with or without heat treatment. These figures indicate that the hydrous metal oxides have several kinds of OH groups with different acidities; in the hydrous oxides of Ti^{IV}, Sn^{IV}, and Nb^V, the existence of exchange sites having acidities appreciably different from each other can be observed as the appearance of inflection points at a pH around 7.5. In the hydrous Ti^{IV} oxides, a large fraction of the decrease in the total exchange capacity was observed in a pH region lower than the inflection point. Furthermore, the pH at which the sorption of Na^+ commenced (hereafter called the lowest pH for Na^+) shifted monotonously to the alkaline side upon heat treatment. These facts indicate an appreciable decrease of the acidity of exchange sites by heat treatment. The hydrous Nb^V oxide is the most stable against a heat treatment among the four hydrous metal oxides; even when the exchanger was heated at 400 °C, it retained about half of the original exchange capacity at pH 10. The lowest pH for Na^+ shifted somewhat to the acid side upon heat treatment. Accordingly, the acidity of the highest acidic OH groups is considered to be increased by the treatment. In the case of hydrous Sn^{IV} and Zr^{IV} oxides, the exchange capacity decreased with temperature over the entire pH range, though the lowest pH for Na^+ did not shift. Hence, a heat treatment uniformly destructs all OH groups, but does not affect the acidity of the exchange sites.

Figure 4 shows the Co^{2+}-uptake curves of the exchangers with or without a heat treatment. The lowest pH's for Co^{2+} are lower compared with the uptake of Na^+ (Figs. 3-a to 3-d), which indicates a

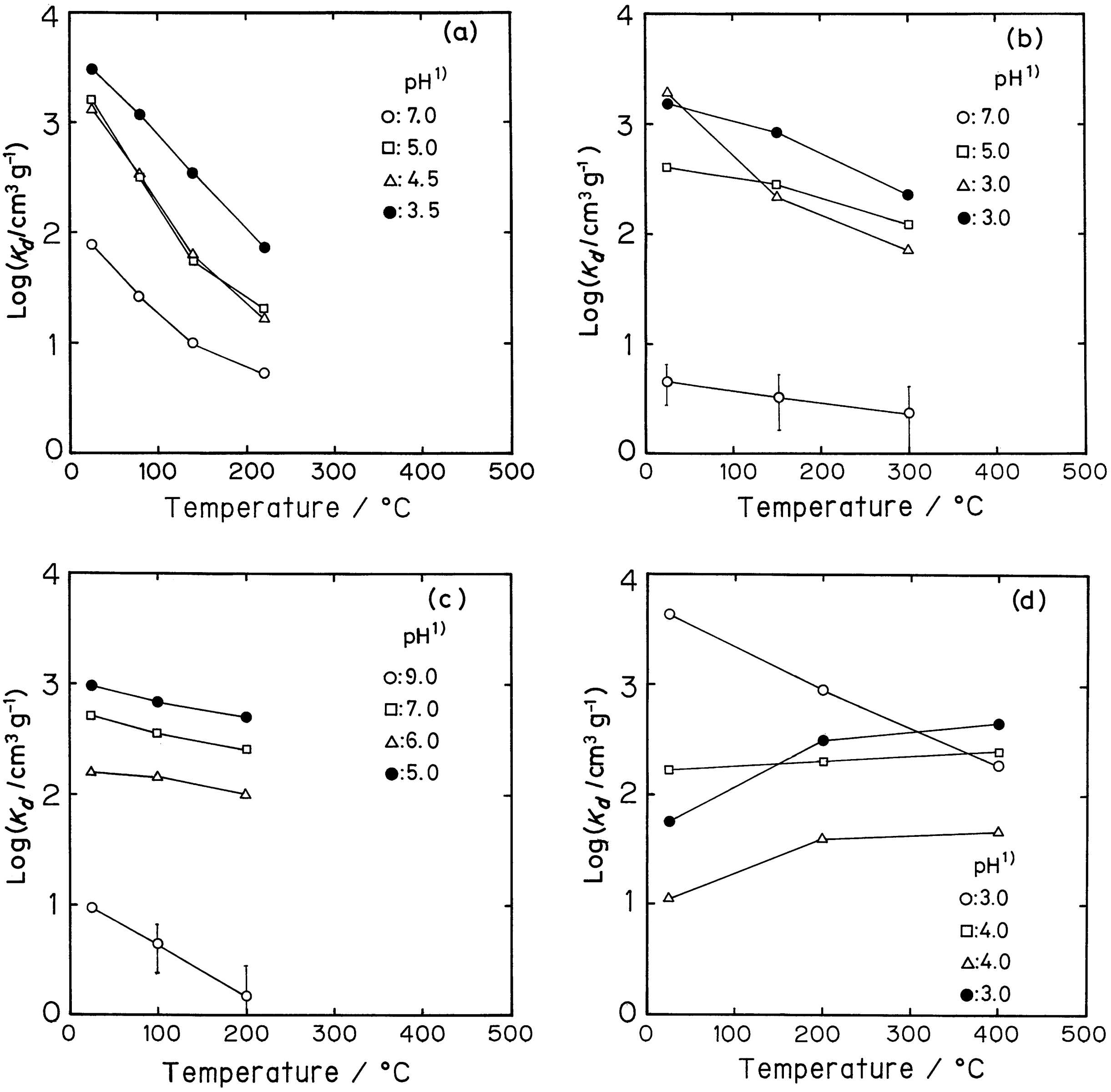

Fig. 2. Change in K_d values of the exchangers by heat treatment. (a): Hydrous Ti^{IV} oxide, (b): Hydrous Sn^{IV} oxide, (c): Hydrous Zr^{IV} oxide, (d): Hydrous Nb^{V} oxide. Cations; ○: Cs$^+$, □: Ba^{2+}, △: Co^{2+}, ●: Eu^{3+}. 1): pH at which K_d's are measured.

stronger interaction of exchange sites to Co^{2+} than to Na$^+$. In every exchanger the uptake curves for Co^{2+} change in much the same fashion as those for Na$^+$. This fact suggests that the changes in both the number and acidity of the exchange sites by heat treatment exert a similar influence on the adsorbability of the materials, irrespective of the nature of the cations to be sorbed.

(b)X-Ray Diffraction Patterns: Figure 5 shows the X-ray diffraction patterns of hydrous Ti^{IV} oxide with or without a heat treatment. The sample without a heat treatment has poor crystallinity, but a sample heated at 80 °C showed some peaks characteristic of anatase, which were intensified with increasing temperature. This result suggests that a heat treratment over 80 °C changes the structure of the exchanger matrix. The other hydrous oxides without a heat treatment also have poor crystallinity. The crystallinity of hydrous Nb^{V} oxide was almost unchanged with heat treatment at 400 °C, and that of hydrous Sn^{IV} and Zr^{IV} oxides, heated at 300 and 200 °C respectively, improved very slightly. The change of the X-ray measurement, corresponds well to that of the ion-exchange capacity; the change in both the number and acidity of the exchange sites by a heat treatment is largest in hydrous Ti^{IV} oxide with a thermally

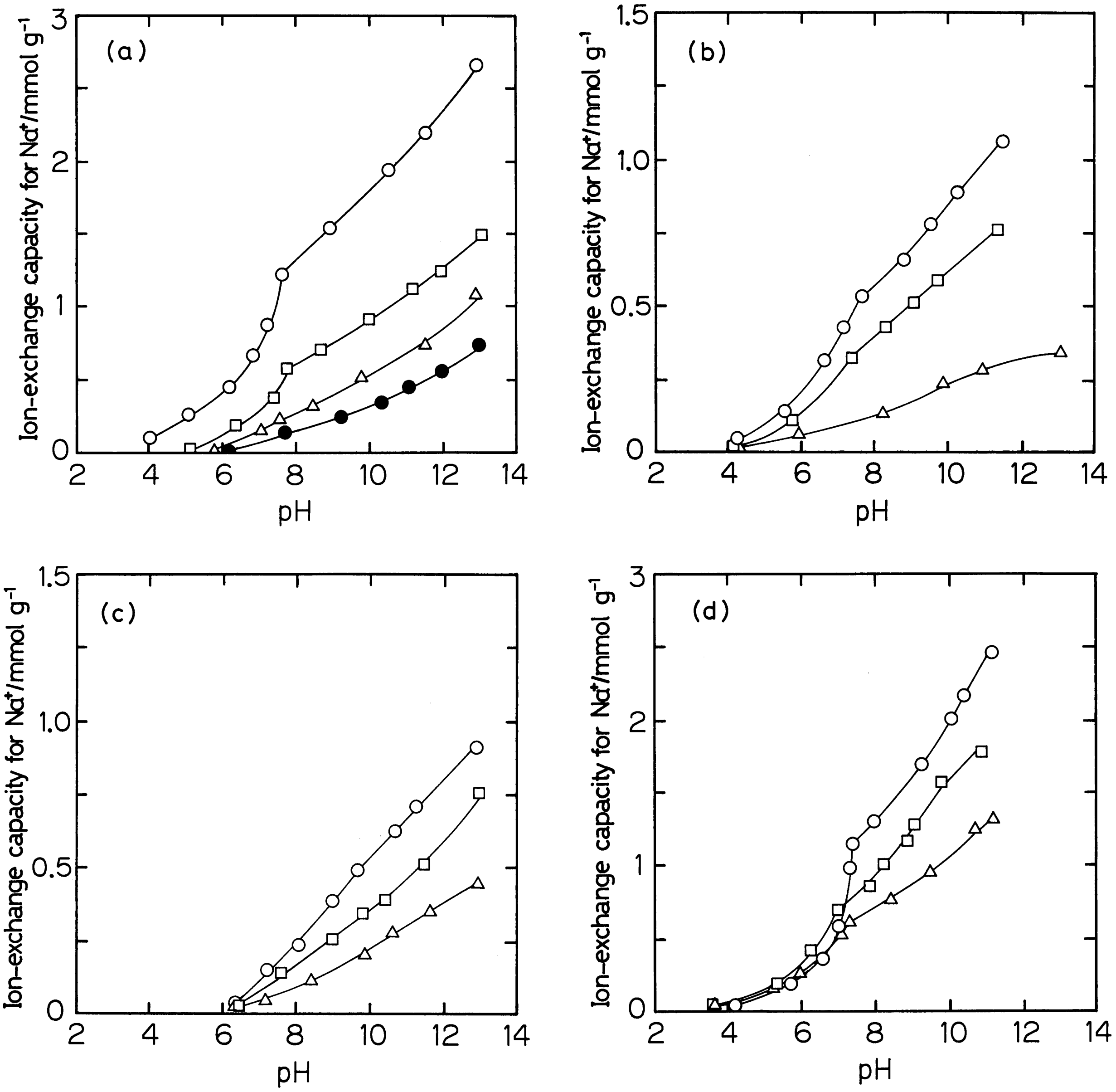

Fig. 3. Uptake curves of the exchangers for Na+. (a): Hydrous Ti^{IV} oxide. Temperature of treatment; ○: R.T., □: 80 °C, △: 140 °C, ●: 220 °C. (b): Hydrous Sn^{IV} oxide. Temperature of treatment; ○: R.T., □: 150 °C, △: 300 °C. (c): Hydrous Zr^{IV} oxide. Temperature of treatment; ○: R.T., □: 100 °C, △: 200 °C. (d): Hydrous Nb^{V} oxide. Temperature of treatment; ○: R.T., □: 200 °C, △: 400 °C.

unstable matrix, but smallest in hydrous Nb^{V} oxide with thermally stable matrix.

(c)Some Physical Properties: The water content, density, specific surface area, and fractional pore volume of four hydrous metal oxides with or without heat treatment are shown in Table 1. In any hydrous metal oxides, the specific surface area and the water content decreased monotonously, while the density increased, with increasing temperature. The fractional pore volume was unchanged by heat treatment. Although not shown in this paper, the distribution of the pore diameter gradually shifted to the larger pore side and broadened with a heat treatment. The change in the pore size distribution was most prominent in hydrous Nb^{V} oxide. These observations indicate that the heat treatment varies the micro structure, while maintaining the principal structure of the matrix.

(3)Correlation between Ion-Exchange Selectivity and Some Properties of the Hydrous Metal Oxides. The dependence of the K_d values for cations on the temperature for heat treatment is brought about by a complex combination of changes in their properties.

It is, therefore, very difficult to clearly understand the reason for the change in the K_d values with a heat treatment. In this section, we attempt to extract the important properties responsible for the change in the K_d values.

Although the fractional pore volume of exchangers does not change with a heat treatment (Table 1), the K_d values change appreciably with the treatment. The fractional pore volume is irrelevant to the affinity of cations toward the exchangers. The tendency of decreasing the specific surface areas of the four exchangers with increasing temperature for heat treatment is similar to each other. Hence, the decrease of the specific surface area cannot explain the different degree of change in K_d values by a heat treatment between the exchangers, especially the increase of the K_d's of hydrous Nb^V oxide for Ba^{2+}, Co^{2+}, and Eu^{3+}. The order of the decrease in the specific volume of the exchangers (the reciprocal of density) by heat treatment is hydrous Sn^{IV} oxide > hydrous Zr^{IV} oxide >

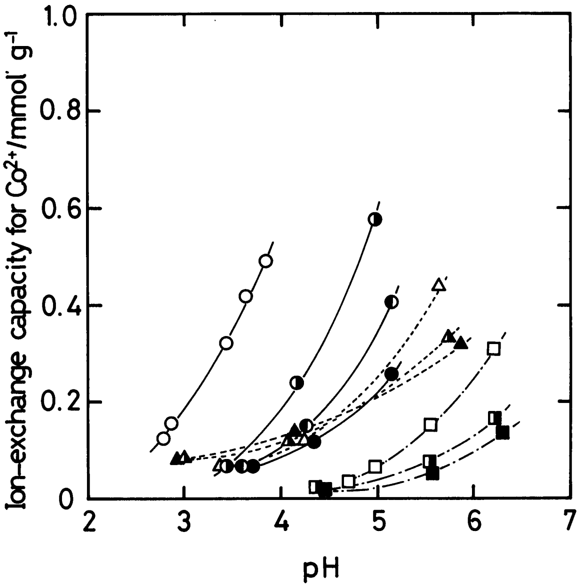

Fig. 4. Uptake curves of the exchangers for Co^{2+}. Heat treatment of hydrous Ti^{IV} oxide; ○: R.T., ◑: 80 °C, ◐: 140 °C, ●: 220 °C. Heat treatment of hydrous Zr^{IV} oxide; □: R.T., ◨: 100 °C, ■: 220 °C. Heat treatment of hydrous Nb^V oxide; △: R.T., ◭: 200 °C, ▲: 400 °C.

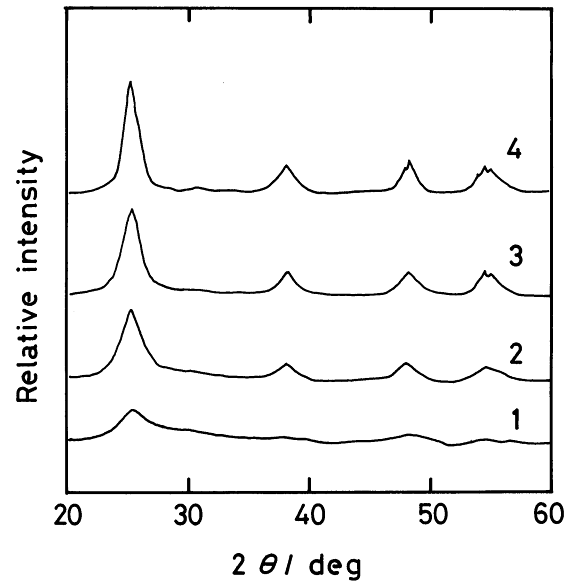

Fig. 5. X-Ray diffraction patterns. Exchanger: Hydrous Ti^{IV} oxide. Temperature of treatment; 1: R.T., 2: 80 °C, 3: 140 °C, 4: 220 °C.

Table 1. Some Physical Properties of the Exchangers

Temperature for treatment	Water content	Density	Surface area	Pore volume
	mol H_2O (mol metal)$^{-1}$	g cm^{-3}	m^2 g^{-1}	cm^3 g^{-1}
Hydrous Ti^{IV} oxide				
R. T.	2.16±0.02	2.02±0.04	292±10	0.24±0.02
80 °C	1.40	2.36	245	0.20
140 °C	1.36	2.57	209	0.21
220 °C	1.31	2.72	154	0.22
Hydrous Sn^{IV} oxide				
R. T.	2.27±0.02	2.37±0.04	178±8	0.08±0.01
150 °C	1.58	3.88	164	0.07
300 °C	1.20	4.34	105	0.08
Hydrous Zr^{IV} oxide				
R. T.	3.59±0.03	2.68±0.04	290±10	0.12±0.01
100 °C	2.34	2.94	247	0.14
200 °C	1.57	3.60	202	0.12
Hydrous Nb^V oxide				
R. T.	5.17±0.03	2.46±0.04	262±10	0.18±0.02
200 °C	4.19	2.75	180	0.17
400 °C	3.63	2.93	133	0.16

hydrous Ti^{IV} oxide > hydrous Nb^{V} oxide. This order is not in accord with that of the decrease in K_d values. Hence, the changes in the surface area and in the density of the exchangers by a heat treatment have no direct bearing on the change in the K_d values.

As was reported in preceding papers, the K_d's decreased with an increasing concentration of metal ions in the surrounding solution when their amount cannot be ignored as compared with the ion-exchange capacity of samples.[10,11] In such a case, the K_d values depend on the ratio of the mass of the exchanger to the volume of the surrounding solution (V/m-ratio). This phenomenon is called here the loading effect. Since the ion-exchange capacities of hydroous metal oxides were decreased upon heat treatment, the decrease in the K_d's measured at a constant V/m-ratio by a heat treatment may be due to the loading effect. To eliminate this effect, the K_d's for Eu^{3+} at a tracer concentration (initial concentration=1×10^{-9} mol dm^{-3}) were measured by using exchangers with or without a heat treatment(Figs.6-a to 6-d). In hydrous Sn^{IV} and Zr^{IV} oxides, the K_d values did not change with the heat treatment. Hence, the smaller K_d of Eu^{3+} on the heated exchangers measured at an initial concentration of 1×10^{-4} mol dm^{-3} (Figs.2-a to 2-d) is ascribed to the loading effect; that is, the affinity of exchange sites of these two hydrous oxides toward cations remains essentially constant and the decrease in K_d for metal ions in high concentration is merely due to the low available exchange capacity of the heated materials.

In the case of hydrous Ti^{IV} and Nb^{V} oxides, on the other hand, the K_d values for Eu^{3+} changed with the

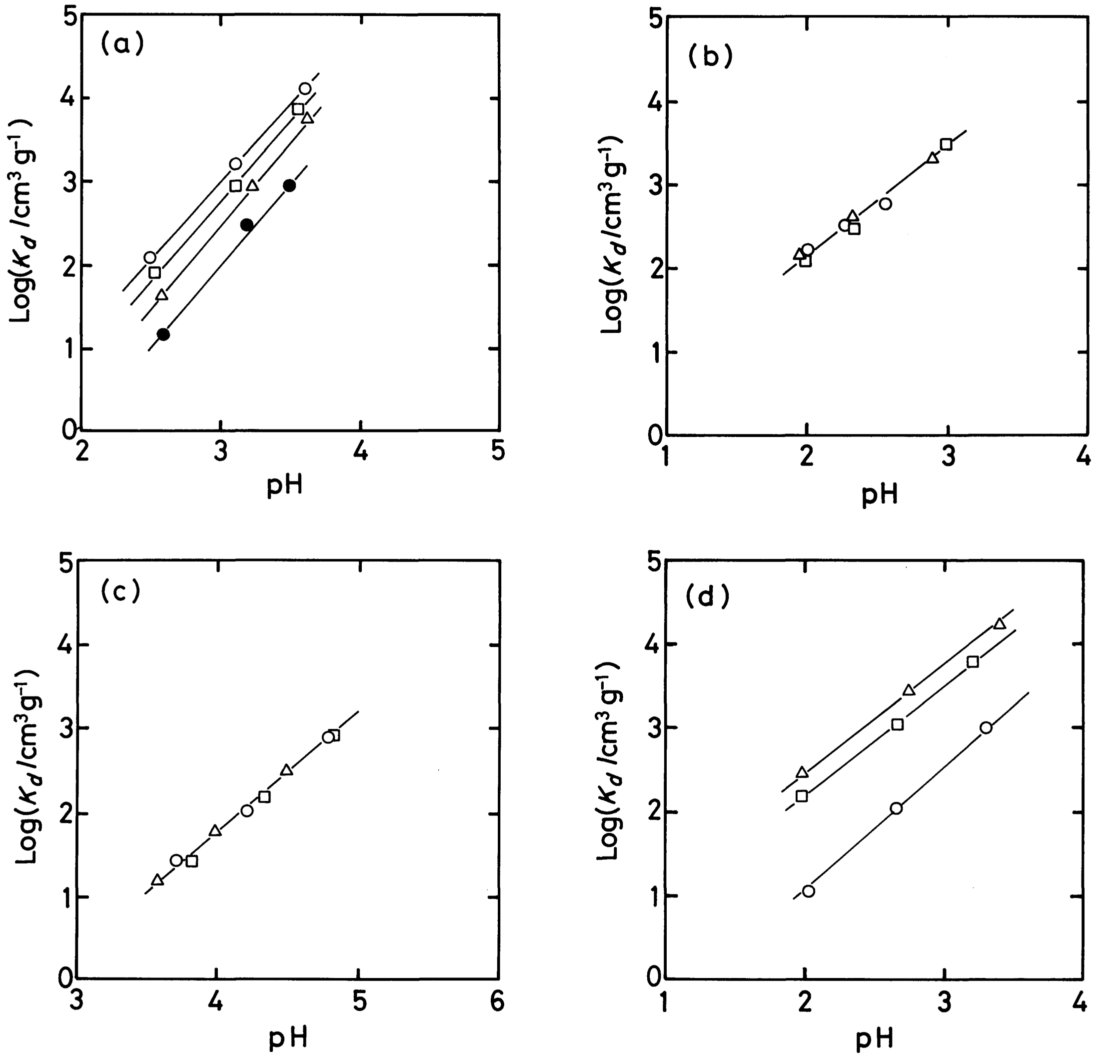

Fig. 6. K_d values of the exchangers for Eu^{3+} in tracer concentration. (a): Hydrous Ti^{IV} oxide. Temperature of treatment; ○: R.T., □: 80 °C, △: 140 °C, ●: 220 °C. (b): Hydrous Sn^{IV} oxide. Temperature of treatment; ○: R.T., □: 150 °C, △: 300 °C. (c): Hydrous Zr^{IV} oxide. Temperature of treatment; ○: R.T., □: 100 °C, △: 200 °C. (d): Hydrous Nb^{V} oxide. Temperature of treatment; ○: R.T., □: 200 °C, △: 400 °C.

temperature of the heat treatment, even when they were measured at a tracer concentration. In the exchangers explainable by the loading effect, the acidity of the exchange sites does not change upon a heat treatment. When hydrous metal oxides have some kinds of exchange sites with different acidity, the most acidic sites are considered to be prior to the other sites in the sorption of metal ions. Thus, an exchanger with large exchange capacity of higher acidic sites generally shows higher K_d values. Accordingly, the change in the acidity of the exchange sites, as well as their numbers, in exchangers upon a heat treatment affects the affinity of heated materials toward metal ions. Based on this view, we can understand, at least qualitatively, the behavior of the hydrous Nb^V and Ti^{IV} oxides, as follows. An increase in acidity, without any change in the number of the most acidic sites in hydrous Nb^V oxide by heating at 200 °C (Figs. 3-d and 4) increases the K_d values for Ba^{2+}, Co^{2+}, and Eu^{3+}. Since the acidity does not change between heating temperatures 200 and 400 °C, no change in the K_d values occurs between these temperatures. Referring to Figs. 3-a and 4, we can understand the behavior of hydrous Ti^{IV} oxide in a similar way.

As discussed above, the effect of a heat treatment of hydrous metal oxides on their cation-exchange selectivity can be explained mainly by the loading effect due to a decrease in the ion-exchange capacity and by a change in the acidity of exchange sites, which participate in the affinity of the exchanger towared cations to be sorbed. We cannot, however, account for the behavior of heated hydrous Nb^V oxide to Cs^+ in terms of this view.

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