

## Studies of the Hydrous Zirconium(IV) Oxide Ion Exchanger. I. Ion-Exchange Properties and Effect of Heat Treatment

Yasushi INOUE\* and Hiromichi YAMAZAKI

Department of Nuclear Engineering, Faculty of Engineering, Tohoku University,  
Aramaki, Sendai 980

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A satisfactory method was established for synthesizing a hydrous zirconium(IV) oxide ion exchanger; also, its ion-exchange properties and thermal stability were studied. The exchanger was synthesized reproducibly by hydrolyzing a  $\text{ZrOCl}_2$  solution at pH 9.3 with the addition of  $\text{NH}_3$  aq. This material was an amphoteric ion exchanger possessing an isoelectric point close to pH 6.5. The order of affinity for the cations was, transition metal > alkaline earth metal > alkali metal. Transition metal ions form a coordinate bond with OH groups in the exchanger. The OH groups, which were easily condensed by a heat treatment, were not restored even when the samples subjected to thermal treatment were immersed in water: Thirty percent of the initial ion-exchange capacity was lost when the exchanger was heat-treated at a temperature as low as 70 °C, and the exchange sites were completely destroyed between 400 and 550 °C.

Hydrous oxides based on various polyvalent metal ions have been investigated because of their unique selectivity characteristics and the simplicity of preparation. They have, however, a serious disadvantage in that they give inconsistent results to different workers because of the irreproducibility of the synthesis. To promote a further investigation of this group of ion-exchange materials, it is indispensable to reexamine the synthetic conditions for establishing reproducible methods. With this point in mind, the present authors previously established satisfactory methods for synthesizing such hydrous oxides as  $\text{TiO}_2 \cdot 2.1 \text{H}_2\text{O}$ ,  $\text{SnO}_2 \cdot 2.2 \text{H}_2\text{O}$ , and  $\text{Nb}_2\text{O}_5 \cdot 5.3 \text{H}_2\text{O}$ ; they also studied the ion-exchange selectivity, the thermal stability and other important properties of these materials.<sup>1-3)</sup>

Hydrous zirconium(IV) oxide is also an important material of this group of inorganic ion exchangers and there is much left to be studied during a series of these investigations. Since the work of Kraus et al., who first reported that hydrous zirconium(IV) oxide was an amphoteric ion exchanger possessing a large anion-exchange capacity, emphasis has been placed on its anion-exchange property. There are, however, a few reports on the cation-exchange properties of hydrous zirconium(IV) oxide. In addition, the effect of a heat treatment on the ion-exchange properties of the material has not yet been investigated, although inorganic ion exchangers are generally expected to be superior to ion-exchange resins regarding thermal stability.

The present paper deals with a study undertaken to establish a reproducible synthetic method for producing hydrous zirconium(IV) oxide, together with its ion-exchange properties and thermal stability. Among various methods for synthesizing hydrous zirconium(IV) oxides,<sup>4-9)</sup> the hydrolysis of a  $\text{ZrOCl}_2$  solution by alkaline solutions was adopted, because of its applicability to the synthesis of a large amount of the hydrous zirconium(IV) oxide. A recommended

procedure was established after examining the effects of such factors as the concentration of the  $\text{ZrOCl}_2$  solution, the kind of alkaline solutions used, and the pH value during precipitation on the yield as well as the composition and acid-base property of the product. After the reproducibility of the procedure was confirmed, the distribution coefficients of various cations were measured as functions of the pH and temperature in order to study the cation-exchange mechanism. Furthermore, the thermal stability was studied by examining the effect of a heat treatment on the composition and the ion-exchange property of the material.

### Experimental

**Reagents and Apparatus.** All chemicals were of the highest purity grade supplied by Wako Pure Chemical Industries, Ltd. The specific surface area was determined by the BET method ( $\text{N}_2$  adsorption at -196 °C) using a Yanagimoto Surface Area Measuring Apparatus, Model GSA-10. All the other equipment was the same as that described previously.<sup>1-3)</sup>

**Synthesis.** The desired amount of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  was dissolved in distilled water to make 1 dm<sup>3</sup>. The solution was hydrolyzed by adding (drop by drop) either an  $\text{NH}_3$  or an  $\text{NaOH}$  solution of the molar concentration, 2.5-times that of the zirconium solution, up to a desired molar ratio between hydroxide and zirconium ions. After being separated from the mother liquor by a combination of decantation and filtration through Toyo No. 1 filter paper under suction, the precipitate was uniformly dispersed into 5 dm<sup>3</sup> of distilled water and again filtered after being sedimentated. This procedure was repeated until no chloride ions were detected in the filtrate. Then, the precipitate was air-dried at room temperature. The resulting product was then immersed in water in order to break it down into fine particles, which were subsequently again dried at room temperature. At this stage the yield was calculated based on the zirconium recovery. Particles larger than those desired, if any, were ground in a porcelain mortar and sieved in order to obtain the required particle size (-100+200 mesh).

The exchanger was converted to the free acidic form (the H form) by the following column method. In the case of the exchangers precipitated at a pH lower than 7, which may adsorb  $\text{Cl}^-$  ions,  $0.05 \text{ mol dm}^{-3}$  NaOH was passed through an exchanger column in order to remove  $\text{Cl}^-$  ions until the pH of the effluent approached that of the influent. Then, the column was washed with distilled water until no  $\text{Na}^+$  ions were detected in the effluent and its pH became nearly constant ( $\text{pH}=6.2\text{--}6.5$ ). In the case of the exchangers precipitated in the alkaline region, which may adsorb  $\text{NH}_4^+$  or  $\text{Na}^+$  ions,  $0.05 \text{ mol dm}^{-3}$  HCl was passed through the column; the column was then washed until no  $\text{Cl}^-$  ions were detected in the effluent and its pH became nearly constant ( $\text{pH}=6.2\text{--}6.5$ ). As shown in Fig. 1, the constant pH value of the effluent corresponds to the isoelectric point of the exchanger. The exchangers, thus prepared, were air-dried at room temperature and allowed to humidify to a constant weight in a desiccator containing a saturated  $\text{NH}_4\text{Cl}$  solution (relative humidity: 79% at  $25^\circ\text{C}$ ). Table 1 shows the synthetic conditions, yields and compositions of the exchangers.

**Ion-Exchange Capacity.** The exchanger ( $0.20 \text{ g}$ ) in the H form was immersed in  $20 \text{ cm}^3$  of various solutions, prepared by the desired combination of  $0.1 \text{ mol dm}^{-3}$  NaCl, and  $0.1 \text{ mol dm}^{-3}$  NaOH or  $0.1 \text{ mol dm}^{-3}$  HCl, for 6 d at room temperature with intermittent shaking. This was followed by a pH measurement and by a determination of the  $\text{Na}^+$  and  $\text{Cl}^-$  ions. The chloride concentration was determined by the Fajans' method after the solution had been neutralized. The sodium ions were converted to an equivalent amount of sodium chloride and were indirectly determined by titrating the chloride ions. The amount of ions taken up by the exchanger was evaluated from the difference between the initial and the final concentrations of the respective ions present in the solution. The dissolved amount of the exchanger was evaluated from the amount of zirconium in the supernatant solution determined spectrophotometrically by the arsenazo III method.<sup>11)</sup> The limit of detection was  $0.009 \text{ wt\%}$  of the exchanger used.

**Analysis of Chloride Ions in the Exchanger.** A half gram of the sample was dissolved by heating with  $100 \text{ cm}^3$  of

$9 \text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  in a  $500\text{-cm}^3$  distilling flask, and the HCl evolving therefrom, carried by steam, was absorbed in a slightly alkaline solution and then determined spectrophotometrically using mercury(II) thiocyanate and ammonium iron(III) sulfate as coloring reagents.<sup>10)</sup> The limit of detection was  $0.009 \text{ wt\%}$  of the exchanger used.

**Analysis of Sodium Ions in the Exchanger.** One tenth gram of the sample was dissolved by heating with  $10 \text{ cm}^3$  of  $6 \text{ mol dm}^{-3}$  HCl. After cooling,  $6 \text{ mol dm}^{-3}$ ,  $\text{NH}_3 \text{ aq}$  was added, and the precipitate was filtered and washed with  $0.05 \text{ mol dm}^{-3}$  HCl. A negligible amount of  $\text{Na}^+$  ions was lost by occlusion in the precipitate in this procedure (less than  $2 \text{ wt\%}$  of the  $\text{Na}^+$  ion to be determined). The filtrate and the washings were collected in a volumetric flask and then diluted to the mark. The concentration of  $\text{Na}^+$  ions in this solution was determined by means of atomic absorption spectrophotometry. The limit of detection was  $0.007 \text{ wt\%}$  of the exchanger used.

**Analysis of Water in the Exchanger.** A quarter gram of the sample was ignited at  $800^\circ\text{C}$ , and the water content was calculated from the weight loss. The validity of the procedure had been confirmed thermogravimetrically.

**Density.** The apparent density of the exchangers was measured in the usual manner using a  $25\text{-cm}^3$  pycnometer.

**Distribution Coefficients.** The distribution coefficients,  $K_d$ , were determined in the following way. A  $0.12\text{-g}$  portion of the exchanger in the H form was immersed in  $7 \text{ cm}^3$  of the solution with a suitable pH value, adjusted by using a desired combination of  $0.11 \text{ mol dm}^{-3}$  NaCl, and  $0.11 \text{ mol dm}^{-3}$  HCl or  $0.11 \text{ mol dm}^{-3}$  NaOH, for 2 d at room temperature. A  $1\text{-cm}^3$  portion of the solution containing the metal ion to be examined was added to the slurry to make the concentration of the cation in the test solution  $1 \times 10^{-4} \text{ mol dm}^{-3}$  and the ionic strength  $0.10 \text{ mol dm}^{-3}$ . The mixture was then allowed to stand until the concentration of the cation in the supernatant solution became nearly constant (about 6 to 20 d). The pH and the concentration of the cation in the supernatant solution were then measured. The  $K_d$  values were calculated by means of the following equation:

Table 1. Synthetic Conditions and Compositions of the Exchangers

Batch No.	Concn of reagents/mol dm <sup>-3</sup>			Volume ratio		pH at ppt.	Peptization	Appearance	Yield	Composition mol H <sub>2</sub> O/mol ZrO <sub>2</sub>
	ZrOCl <sub>2</sub>	NH <sub>3</sub> aq	NaOH	Alkaline soln.						
				Zr(IV) soln.						
1	0.2		0.50	0.64	5.22	Yes	Glass	0.48	4.22±0.04	
2	0.2		0.50	0.72	7.09	Yes	Glass	0.62	4.16±0.04	
3	0.2		0.50	0.80	11.15	Slightly	Glass	0.88	4.10±0.04	
4	0.2	0.54		0.59	5.23	Yes	Glass	0.49	4.11±0.04	
5	0.2	0.54		0.67	7.16	Yes	Glass	0.69	4.16±0.04	
6	0.2	0.54		1.1	9.28	No	Glass	0.93	4.10±0.04	
7	0.05	0.10		1.4	9.24	No	Glass	0.93	3.78±0.04	
8	1	2.4		1.3	9.31	Slightly	Chalk	0.80	4.04±0.04	
9	0.2	0.56		0.96	9.15	No	Glass	0.93	3.78±0.04	
10	0.2	0.56		1.1	9.30	No	Glass	0.93	3.89±0.04	
11	0.2	0.56		1.4	9.60	No	Glass	0.94	3.99±0.04	
12	0.2	0.56 <sup>a)</sup>		1.1	9.30	No	Glass	0.90	3.97±0.04	

a) The rate of addition of alkaline solution:  $35 \text{ cm}^3 \text{ min}^{-1}$ , in the other cases  $10 \text{ cm}^3 \text{ min}^{-1}$ .

$$K_d = \frac{I-F}{F} \cdot \frac{V}{m} (\text{cm}^3 \text{g}^{-1}),$$

where  $I$  and  $F$ , respectively, are the initial and final concentrations of the metal ions in the solution,  $V$  the volume of the solution in  $\text{cm}^3$  and  $m$  the weight of the exchanger in grams.

The metal ions were added as their chlorides, except  $\text{Fe}^{3+}$ ,  $\text{Th}^{4+}$  and  $\text{UO}_2^{2+}$ , for which the corresponding nitrates were used. The analyses of Cs, Sr, Ba, Mn, Fe, Co, Ce, Eu, and Am were carried out radiometrically using  $^{137}\text{Cs}$ ,  $^{85}\text{Sr}$ ,  $^{133}\text{Ba}$ ,  $^{54}\text{Mn}$ ,  $^{60}\text{Co}$ ,  $^{144}\text{Ce}$ ,  $^{152}\text{Eu}$ , and  $^{241}\text{Am}$ , respectively as tracers. Their radioactive purity was confirmed by means of  $\gamma$ -ray spectrometry. Thorium(IV) and uranium(VI), respectively, were analyzed spectrophotometrically using arsenazo III<sup>11</sup> and 2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol<sup>12</sup> as coloring reagents, while the concentrations of the other cations were determined by means of atomic-absorption spectrophotometry.

**Heat Treatment.** About 5 g of the exchanger in the H form was heated in air to a constant weight at a constant temperature, which was controlled within an accuracy of 1% by using an automatic temperature controller (Chino Workers, Ltd.). After being cooled to room temperature over  $\text{P}_2\text{O}_5$ , the sample was weighed and then immersed in water overnight. The sample was then separated from water and allowed to stand to a constant weight in a desiccator containing a saturated  $\text{NH}_4\text{Cl}$  solution (humidifying operation). The water-recovery of the heat-treated samples was calculated from the difference in water content between samples cooled over  $\text{P}_2\text{O}_5$  immediately after the heat treatment and subjected to a humidifying operation.

The other experimental procedures were the same as those described previously.<sup>1-3)</sup>

## Results and Discussion

**Synthesis of Hydrous Zirconium(IV) Oxide.** It is required for practical purposes that a large amount of pure hydrous zirconium(IV) oxide having reproducible and good ion-exchange properties can be easily prepared; in conformity with this line, we examined the effect of synthetic conditions on the yields and the acid-base properties of the products.

The effect of the pH during precipitation ( $\text{OH}^-/\text{Zr}^{4+}$  molar ratio) and of the kind of alkali used on the uptake curves for  $\text{Na}^+$  ions are shown in Fig. 1. This figure indicates that the products are amphoteric ion exchangers possessing larger ion-exchange capacities for anions than for cations and have an isoelectric point close to pH 6.5. The ion-exchange capacity is slightly smaller for the products precipitated from alkaline solutions than for those from acidic or neutral solutions. It is, however, considered that the ion-exchange behavior is not very much affected by the kind of alkali used and the pH during precipitation, since the maximum difference in the ion-exchange capacity is only  $0.15 \text{ mmol g}^{-1}$ . In contrast, the yield was significantly affected by these factors, as is shown in Table 1. The decrease in the

yield is due mainly to the peptization of the precipitate during washing. Only the precipitate formed at around pH 9 by adding  $\text{NH}_3$  aq can be washed without sufferings from peptization, and affords an excellent yield exceeding 90%. Efforts were then concentrated on examining the properties of the exchanger precipitated under these conditions.

In order to prepare a large amount of the exchanger in one batch, it is preferred to use a concentration of zirconium during precipitation that is as high as possible. The uptake curves of the exchangers prepared from different concentrations of zirconium (batch (6)—(8) in Table 1) are compared in Fig. 2; this

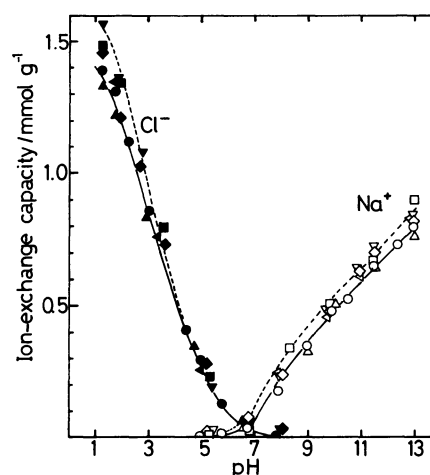


Fig. 1. Uptake curves of various exchangers for  $\text{Na}^+$  and  $\text{Cl}^-$  (Effects of alkali used and pH at precipitation). Exchangers;  $\triangleleft$ : No. 1,  $\diamond$ : No. 2,  $\triangle$ : No. 3 ( $\text{NaOH}$  system).  $\nabla$ : No. 4,  $\square$ : No. 5,  $\circ$ : No. 6 ( $\text{NH}_3$  system). The numbers are the same as those in Table 1.

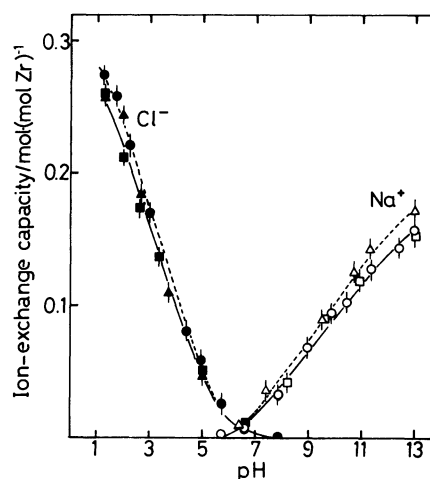


Fig. 2. Uptake curves of various exchangers for  $\text{Na}^+$  and  $\text{Cl}^-$  (Effect of Zr-concentration at precipitation). Exchangers;  $\circ$ : No. 6,  $\square$ : No. 7,  $\triangle$ : No. 8. The numbers are the same as those in Table 1.

indicates that the concentration did not appreciably affect the ion-exchange property. However, the concentration of zirconium did influence the yield and the physical properties of the product; the exchangers precipitated from the solution with a high concentration of zirconium ( $1 \text{ mol dm}^{-3}$ ) had poor physical strength (brittle chalk), while those precipitated from a dilute solution of zirconium had a large, glassy grains. The yield decreased with increasing concentration of zirconium due to the accentuating degree of peptization during washing. Thus,  $0.2 \text{ mol dm}^{-3}$  of zirconium concentration was selected for preparing the exchanger.

While the water content of the products slightly increased with the volume of  $\text{NH}_3 \text{ aq}$  added (less than 5%), the ion-exchange capacity remained unchanged within the limit of the experimental error, as is shown in Table 1 (batch (9)–(11)). Furthermore, the rate of addition of  $\text{NH}_3 \text{ aq}$  was not found to affect the composition and ion-exchange properties of the products. Therefore, no exact control of the procedure is necessary; thus, the present method for preparing hydrous zirconium(IV) oxide is considered to be fairly reproducible.

From these results, the synthetic conditions of batch (10) in Table 1 was selected as being the best method for reproducibly synthesizing a hydrous zirconium(IV) oxide ion exchanger. The contents of both  $\text{Na}^+$  and  $\text{Cl}^-$  ions as impurities were below the limit of detection (0.007 wt%). Thus, the conditioning is effective for converting the exchanger into the H form. The composition of the product was  $\text{ZrO}_2 \cdot (3.8\text{--}$

$4.1)\text{H}_2\text{O}$ , in agreement with that of fully-hydrolyzed zirconium(IV) hydroxide,  $\text{Zr}_4(\text{OH})_{16}(\text{H}_2\text{O})_8$ , which was reported by H. Th. Rijntjen in the study of the hydrolysis of  $\text{ZrOCl}_2$  solution.<sup>13</sup> The solubilities of the exchanger in  $0.1 \text{ mol dm}^{-3}$   $\text{NaOH}$ - and  $\text{HCl}$  solutions were determined to be 0.01 and 0.07 wt%, respectively; this assures the applicability of the exchanger in pH region.

**Selectivity for Cations.** Figure 3 shows the pH-dependency of the  $K_d$  values for the representative elements. As can be seen from this figure, the affinity of the exchanger is much greater for alkaline earth metal ions than for alkali metal ions; this indicates that the electrostatic interaction between counter ions and ion-exchange sites is an important factor in governing the selectivity of the hydrous zirconium(IV) oxide. The higher  $K_d$  values for  $\text{Li}^+$  than for  $\text{Cs}^+$  may suggest that removal of the solvated water molecules from counter ions. However, there is no difference in the affinity between alkaline earth metal ions.

Figure 4 shows the pH-dependency of the  $K_d$  values for transition metal ions. The affinity of the exchanger was much greater for the transition metal ions than for the representative elements. The order of selectivity for the transition metals,  $\text{Fe}^{3+} \gg \text{UO}_2^{2+} > \text{Th}^{4+} \gg \text{Am}^{3+} > \text{Eu}^{3+} > \text{Ce}^{3+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+}$ , indicates the general trend that the exchanger exhibits a preference for transition metal ions with a larger ionic charge and a smaller crystalline radius. The distribution coefficients for  $\text{Th}^{4+}$ , which are smaller than would be expected from the ionic charge, are

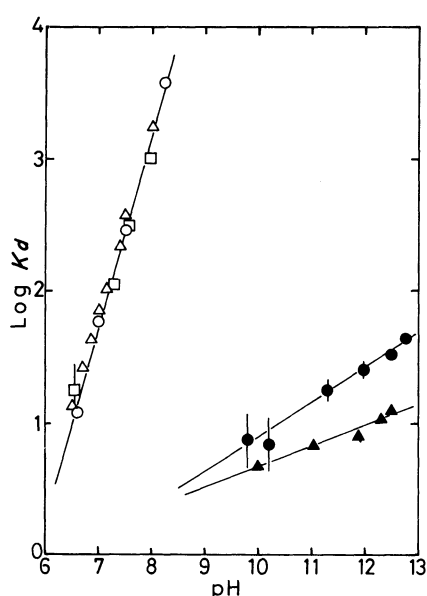


Fig. 3.  $\text{Log } K_d$  for several representative metal ions. Ionic strength:  $0.10 \text{ mol dm}^{-3}$  ( $\text{NaCl}$ – $\text{NaOH}$ ) at room temperature. Initial concentration of cation:  $1 \times 10^{-4} \text{ mol dm}^{-3}$ . Cations;  $\bullet$ :  $\text{Li}^+$ ,  $\blacktriangle$ :  $\text{Cs}^+$ ,  $\square$ :  $\text{Mg}^{2+}$ ,  $\circ$ :  $\text{Sr}^{2+}$ ,  $\triangle$ :  $\text{Ba}^{2+}$ .

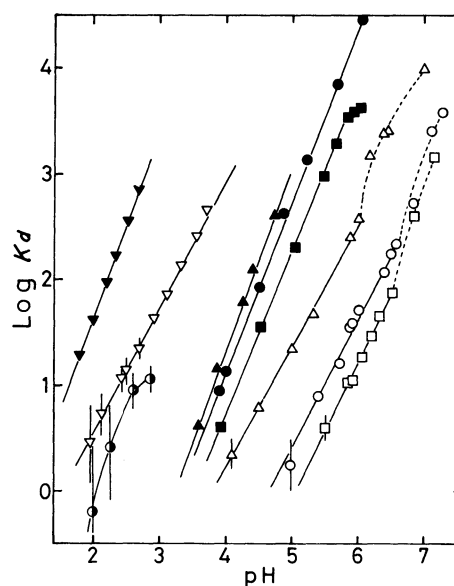


Fig. 4.  $\text{Log } K_d$  for several transition metal ions. Ionic strength:  $0.10 \text{ mol dm}^{-3}$  ( $\text{HCl}$ – $\text{NaCl}$ ) at room temperature. Initial concentration of cations:  $1 \times 10^{-4} \text{ mol dm}^{-3}$  ( $\text{Am}^{3+}$ : Tracer scale). Cations;  $\square$ :  $\text{Mn}^{2+}$ ,  $\circ$ :  $\text{Co}^{2+}$ ,  $\triangle$ :  $\text{Zn}^{2+}$ ,  $\blacktriangledown$ :  $\text{Fe}^{3+}$ ,  $\blacksquare$ :  $\text{Ce}^{3+}$ ,  $\bullet$ :  $\text{Eu}^{3+}$ ,  $\bullet$ :  $\text{Th}^{4+}$ ,  $\nabla$ :  $\text{UO}_2^{2+}$ ,  $\blacktriangle$ :  $\text{Am}^{3+}$ .

attributable to the hydrolysis of ions in the pH region effective for sorption ( $\text{pH} > 2$ ). On the other hand,  $K_d$  values for  $\text{UO}_2^{2+}$  ions, which are higher than expected from the ionic charge, may be due to the peculiarity of the structure of  $\text{UO}_2^{2+}$  ions; the effective charge on a uranium atom is higher than the formal charge of the ions. With these exceptions, the electrostatic force may be considered as being an important factor in determining the selectivity of the hydrous zirconium(IV) oxide for the transition metals.

In order to obtain further information on the important factors affecting the selectivity for the transition metals, the  $K_d$  values at pH 4 were compared with their first hydrolysis constants<sup>14)</sup> and the first stability constants of their acetato complexes.<sup>15)</sup> The results are shown in Table 2, where the

Table 2. Interaction between Cations and Exchange Sites

Metal ion	Log $K_d$ (at pH 4)	A <sup>1)</sup>	B <sup>2)</sup>
$\text{UO}_2^{2+}$	2.9	-5.8	2.61
$\text{Fe}^{3+}$	5.1	-2.19	3.36
$\text{Eu}^{3+}$	1.2	-7.8	2.13
$\text{Ce}^{3+}$	0.69	-8.3	1.91
$\text{Zn}^{2+}$	0.22	-9.0	1.3
$\text{Co}^{2+}$	-0.73	-9.7	1.1
$\text{Mn}^{2+}$	-1.2	-10.6	0.8
		$R=0.99$	
		$R=0.98$	

1)  $A = \log K_{11}(\text{OH}^-)$ : First hydrolysis constant.<sup>14)</sup> 2)  $B = \log K_{11}(\text{CH}_3\text{COO}^-)$ : First stability constant (equilibrium quotient at 25°C and ionic strength 0.1)<sup>15)</sup> R: Correlation coefficient.

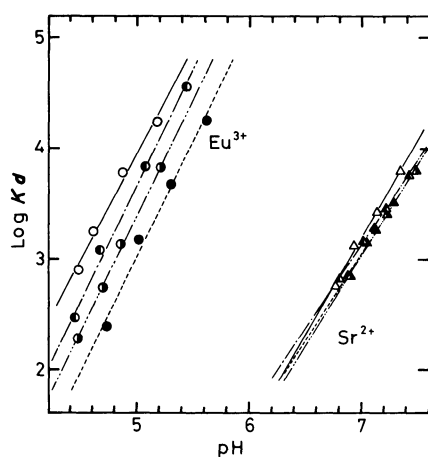


Fig. 5. Temperature dependence of  $K_d$  values for  $\text{Sr}^{2+}$  and  $\text{Eu}^{3+}$  ions.

Initial concentration of metal ions:  $1 \times 10^{-6} \text{ mol dm}^{-3}$ . Ionic strength:  $0.10 \text{ mol dm}^{-3}$  ( $\text{HCl-NaCl-NaOH}$ ). Temperature/°C;  $\bullet$ : 14.8,  $\Delta$ : 25.2,  $\blacktriangle$ : 34.5,  $\triangle$ : 44.8.

$K_d$  values which could not be obtained experimentally were estimated from an extrapolation of the log  $K_d$  vs. pH plot to pH 4 (Fig. 4). This table indicates that the  $K_d$  values is very strongly related to the hydrolysis constants ( $R=0.99$ ) and the stability constants ( $R=0.98$ ). Figure 5 shows the temperature-dependence of  $K_d$  values for  $\text{Sr}^{2+}$  and  $\text{Eu}^{3+}$  ions. The values for  $\text{Sr}^{2+}$  ions depended little on the temperature, while those for  $\text{Eu}^{3+}$  ions increase with temperature, indicating an endothermic reaction. From the slope of the linear plot of the logarithm of  $K_d$  against  $1/T$ , the standard enthalpy change of the latter reaction was found from a calculation to be  $55 \pm 6 \text{ kJ mol}^{-1}$ ; this is considerably larger than the values ( $< 10 \text{ kJ mol}^{-1}$ ) associated with the exchange of the dissociated ions in the exchanger and the counter ions in solutions. From these results, we concluded that the formation of a coordination bond between anionic sites in the exchanger and counter cations plays a part in determining the selectivity of the exchanger, along with the remote coulombic interaction. This consideration is in line with the fact that the affinity with the exchanger was greater for transition metals than for representative elements, since the former is stronger than the latter as Lewis acids.

**Thermal Stability.** Figure 6 shows the effect of a heat treatment of the hydrous zirconium(IV) oxide on the composition and the specific surface area. It should be noted that the water content was normalized to the number of moles of water per 1 mole of  $\text{ZrO}_2$ . The amount of water contained in the exchanger immediately after the heat treatment at 70°C was reduced to about 30% of the original value; then, it gradually decreased with temperature, and finally fell to zero at 400°C. When the exchangers heated at temperatures up to 400°C were subjected to the humidifying operation, a roughly constant amount of water, viz. 0.85 to 1.4 mole per 1 mole of  $\text{ZrO}_2$ , was recovered, while the samples heated over 550°C

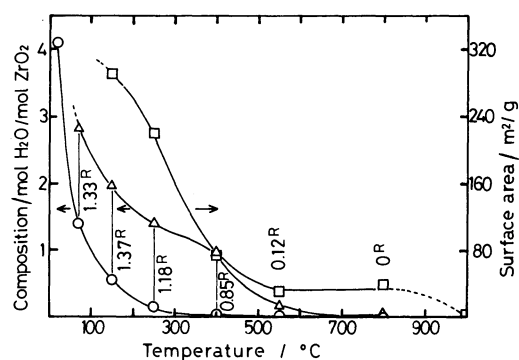


Fig. 6. Change in composition and surface area.

Water content;  $\circ$ : Immediately after heat treatment,  $\Delta$ : Heat-treated, followed by humidifying operation. R: Water recovery.  $\square$ : Specific surface area of heat-treated sample.

recovered a negligible amount of water. The amount of water recovery as a result of humidifying the exchangers heat-treated even at a temperature as low as 70 °C fell short of the full recovery by 1.4 mole of water per 1 mole of  $\text{ZrO}_2$ . The surface area decreased sharply with increasing temperature up to 550 °C, where the surface area became nearly constant ( $40 \text{ m}^2 \text{ g}^{-1}$ ). As is shown in Table 3, the density of the samples immediately after the heat treatment increased with temperature, approaching to a constant value of  $5.53 \pm 0.08 \text{ g cm}^{-3}$  at 550 °C. This value corresponds to the density of tetragonal  $\text{ZrO}_2$ ,  $5.60 \text{ g cm}^{-3}$  within the limit of experimental error.

In order to examine the effect of the heat treatment on the acid-base property of the exchanger, the ion-exchange capacities for  $\text{Na}^+$  or  $\text{Cl}^-$  ions were measured as a function of the pH (Fig. 7). The ion-

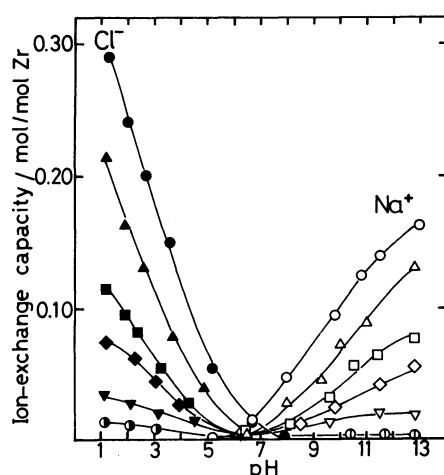


Fig. 7. Uptake curves for  $\text{Cl}^-$  and  $\text{Na}^+$  ions (Effect of thermal treatment).

Temperature of treatment/°C; ○: R. T., △: 70, □: 150, ◇: 250, ▽: 400, ⊙: 550.

exchange capacities for both ions decreased even at a temperature as low as 70 °C, and were reduced to about 30 % of the original value when the exchanger was heated at 250 °C. The sample heated at 550 °C exhibited a very small exchange capacity for only  $\text{Cl}^-$  ions. Therefore, the exchange sites of the hydrous zirconium(IV) oxide is susceptible to thermal decomposition.

Figure 8 shows DTA curves for the samples subjected to the humidifying operation. The large endothermic peaks appearing in the range lower than 200 °C sharpened and became smaller in area as the temperature of the heat treatment became higher. The position of the peak, observed at 80 °C for the sample without heat treatment, shifted to the lower-temperature side upon increasing the temperature of the heat-treatment (gradually up to 400 °C, and then abruptly). When the exchanger was heat-treated at 550 °C, the peak shifted to 40 °C and developed a very small area. Apparently, this observation is compatible with changes in both the exchange capacity and the degree of water recovery with the heat-treatment temperature, if the peak is considered to correspond mainly to the release of water recoverable by humidifying, that is, a certain kind of zeolitic water. The shoulders observed at the high- and low-

Table 3. Density of the Samples Immediately after the Heat Treatment

Temperature of treatment °C	Density $\text{g cm}^{-3}$
150	$4.30 \pm 0.07$
250	$5.15 \pm 0.06$
550	$5.53 \pm 0.08$
700	$5.53 \pm 0.06$

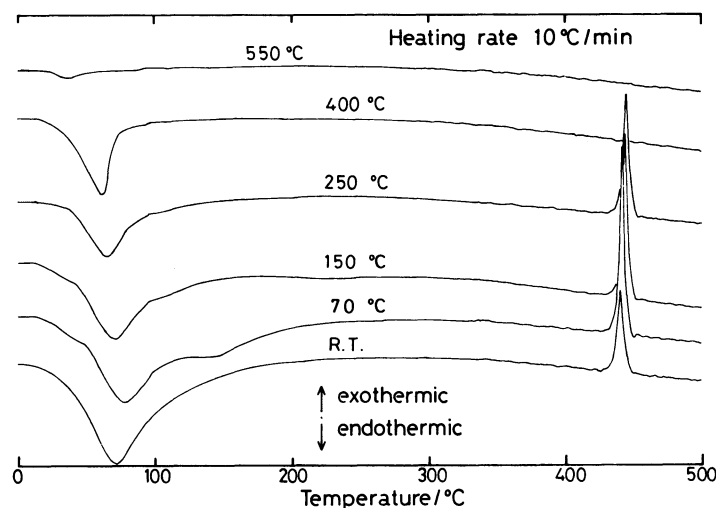


Fig. 8. DTA curves of the samples subjected to the humidification.

temperature sides, respectively, of the peak for the samples heated at temperature below 150 °C are attributable to the bound water liberated by the condensation of the hydroxyl groups and to the adherent water in the exchanger matrix. As the area under the shoulder decreased with increasing temperature of the treatment, both bound and adherent water are considered to be released irreversibly. A large exothermic peak observed at 430 °C for samples heated at a temperature below 400 °C may be assigned to the crystallization of the exchanger as judged from the change in the degree of recovery of water, in the density and in the exchange capacity of the samples. Rijnten obtained a similar thermogram for hydrous zirconium(IV) oxide prepared by a similar method to the present study. In his report, the exothermic peak at 405 °C was attributed to crystallization into monoclinic  $\text{ZrO}_2$ , which eventually transformed into a mixture of tetragonal and monoclinic  $\text{ZrO}_2$  at 800 °C.<sup>13</sup> In the present experiment, however, X-ray studies made on the samples heated at 550 and 800 °C, showed no diffraction peak in spite of prolonged heating for 72 h; a few peaks, indicating the formation of a mixture of tetragonal and monoclinic  $\text{ZrO}_2$ , appeared only when the sample was heated at 1000 °C for 72 h. With the appearance of such peaks, the surface area of the sample suddenly decreased to about 5 m<sup>2</sup> g<sup>-1</sup>.

From the above observations, the thermal stability of the hydrous zirconium(IV) oxide can be summarized as follows. When the exchanger is heat-treated at a low temperature, a disordered network structure, formed at precipitation, is stabilized by irreversibly releasing adherent water and a portion of structural water. Then, the stabilized matrix can accommodate an approximately constant amount of water which can be recovered by humidification. With the stabilization of the network structure, the water molecules formed by the condensation of a part of the OH groups in the exchanger together with the water molecules bound to these groups are released irreversibly, even at low temperatures, causing a

decrease in the ion-exchange capacity. The crystallization occurring at temperatures between 400 to 550 °C brings about densification as well as a decrease in the surface area and in the interstitial space which can accommodate water molecules. Thus, almost all the water is not recovered by the humidifying operation and the ion-exchange capacity completely disappears.

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