Studies of the Hydrous Niobium(V) Oxide Ion Exchanger. V. Effect of Heat Treatment on the Sodium Isotopic Exchange Rates between Hydrous Niobium(V) Oxide in Na^+ Form and Aqueous Solutions

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The effect of a heat treatment was studied on the sodium isotopic exchange rate between the hydrous niobium(V) oxide in the Na^+ form and aqueous solutions. The rate was controlled by the particle diffusion of sodium ions and increased with the heat-treatment temperature. The increase in the rate for the exchanger heat-treated at 200 °C was due to a decrease in the effective particle radius brought about by cracks which developed in the particles. A further increase in the rate at temperatures higher than 200 °C could be explained in terms of an increase in the Na^+-diffusion coefficient, which was produced by an increase in the pore size responsinble for the movement of sodium ions.

A radiochemical experiment was previously undertaken in order to measure the isotopic exchange rate of sodium ions between hydrous niobium(V) oxide in the Na^+ form and aqueous solutions of sodium salts, indicating that the rate in Na^+ solutions higher than 0.1 mol dm^{-3} was controlled by the particle diffusion.[1] On the other hand, this material may be useful for applications at high temperatures, since it is appreciably stable under heat treatment.[2] This aroused the interest of the present authors regarding a study of the effect of a heat treatment on the ion-exchange rate of this material. In addition, this study will greatly contribute to an understanding of the ion-exchange mechanism of hydrous niobium(V) oxide by clarifying the relation between the properties of the exchanger matrix and the ion-exchange rates.

The present paper describes the effect of a heat treatment in air on the isotopic exchange rates of sodium ions between the hydrous niobium(V) oxide and aqueous solutions, and discusses the important properties of the material which strongly governs the isotopic exchange rate.

Experimental

Sample Preparation. The hydrous niobium(V) oxide prepared by the previously recommended method was classified into four particle sizes by using Japan Industrial Standard sieves (mesh size; −48+60, −70+80, −100+120, −145+200) and then converted to the H^+ form.[1,3]

Two- to four-gram portions of the exchanger were heated in air to a constant weight at constant temperature (200, 350, and 450 °C). After being cooled, the exchanger was immersed in water overnight, followed by drying to a constant weight in a desiccator containing a saturated NH_4Cl solution (relative humidity, 79%).

The exchanger was then converted to the Na^+ form by treating it with a 0.05 mol dm^{-3} $Na_2B_4O_7$ buffer solution at pH 9.3. The buffer solution was used for preventing any part of the exchanger from dissolving, since the exchanger is chemically unstable in strong basic solutions. The particale size was again made uniform by using sieves, since the exchanger would be broken down during a heat treatment. The exchanger was then labeled with ^{22}Na by equilibrating it with a ^{22}Na-solution having the same chemical composition as the above-mentioned solution for 2d at room temperature. After having been washed with a 0.05 mol dm^{-3} $Na_2B_4O_7$ solution (free from ^{22}Na), the exchanger was used for a rate meassurement.

Properties of the Exchangers. The properties of each sample were all referred to the exchanger in the H^+ form dried in the desiccator. The average particle radius was estimated by approximating the particle shape by a sphere, from the particle-size distribution measured in an 83 wt% glycerol solution by using a Seishin Enterprise Micron-Photo-Sizer, Model SKC-2000S. The specific surface area of the sample, after heated at 110 °C to a constant weight, was determined by the BET method (N_2 adsorption at −196 °C) using a Yanagimoto Surface Area Measuring Apparatus (Model GSA-10). The pore-size distribution and the pore volume of each sample were calculated by Inkley's method from the adsorption isotherm of N_2 at −196 °C.[4] The density of the exchanger was measured in the usual manner by using a 25-cm^3 pycnometer. The exchange capacity of the sample for Na^+ ions was measured in a 0.05 mol dm^{-3} $Na_2B_4O_7$ solution (pH 9.3) by a column method. The water content was determined from the weight loss of the exchanger heated at 850 °C. 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.

Measurement of the Isotopic Exchange Rate. All the rate measurements were performed in a nitrogen atmosphere by using the same apparatus as described earlier.[5] The rate was measured in solution with the same compositions as those used for converting the exchanger to the Na^+ form. A portion less than 0.2 gram of the sample was placed in a cage and immersed in 200 cm^3 of a solution of a desired composition while the cage was being rotated. The solution had been adjusted in advance to a constant temperature (within ±0.1 °C). Aliquots of the solution (0.2 cm^3) were taken out at appropriate time intervals in order to measure the radioactivity with a well-type NaI(Tl)-scintillation counter (Aloka Model ARC-361). The time of contact of the exchanger with the solution was taken as the elapsed time between immersing the cage and withdrawing an aliquot of the solution. The fractional attainment of equilibrium, $F(t)=C_t/C_\infty$, was calculated from these results; here, C_t is the total radioactivity of the solution at time t and C_∞ at $t=\infty$. C_∞ was calculated using $C_\infty=C_iM/(\mathrm{M}+\mathrm{m})$, where C_i is the initial total radioactivity of the exchanger, and m and M the total amounts of Na^+ in the exchanger and in solution, respectively. Although the rate was measured by a batch method, the infinite solution-volume approximation was closely obeyed under the present experimental conditions: less than 0.2 g of the exchanger per 200 cm^3 of the solution.

Results and Discussion

Analysis of the Results. The exchange rate for the exchanger without heat treatment was confirmed to be controlled by the diffusion of ions in the spherical particles.[1] When the infinite solution volum approximation is obeyed, as is the case in the present experimental condition, Bt vs. t plots must give a straight line passing through the point of origin,and the slope of the line, i.e., B, is inversely proportional to the square of particle radius. Here,

$$B = \pi^2D/r^2, \tag{1}$$

where D is the self-diffusion coefficient of the ions in the exchanger and r refers to the radius of the particles. Bt can be calculated from the measured values of the fractional attainment of equilibrium ($F(t)$) by using the equation derived by Reichenberg:

$$Bt = 2\pi - \frac{\pi^2}{3}F(t) - 2\pi(1 - \frac{\pi}{3}F(t))^{1/2}. \tag{2}$$

This equation gives a fairly good approximation in the region where $F(t)$ is less than 0.85.[6] In putting the rate data in order, therefore, Bt values were plotted against t.

Effect of Heat Treatment on the Properties of the Exchanger. Table 1 shows some properties of the exchanger in the H^+ form heat-treated in air, together with those without heat treatment (designated sample as R.T.). These results were obtained for the sample of −145+200 mesh, but were essentially the same for those of differrent particle sizes.

When the samples were heated at 200 °C, the exchange capacity and the water content, respectively, decreased to about 60 and 70% of the original values, and then gradually decreased with temperature. The density increased with temperature, reaching a constant value at 350 °C. The specific surface area decreased with temprature, but the fractional pore volume was independent of the temperature of the heat treatment. Figure 1 shows distribution curves of the pore size as form of the frequency polygon, in which the percentage of the volume of pores of each size to the total pore volume is shown at intervals of 1 nm of the diameter. The distribution curves gradually shifted to the lager-pore side with increasing temperature during a heat treatment and became considerably broadened at 450 °C. The reason for the broad distribution curve for a sample heat-treated at 200 °C is not clear, but may be attributable to an incomplete relaxation of the distortion of the structure of the exchanger matrix, by considering an increase in the density of the exchanger at a heat treatment temperature between 200 and 350 °C.

Effect of Heat Treatment on the Exchange Rate. The Na^+-isotopic exchange rates for samples heat-treated at various temperatures, together with those for sample

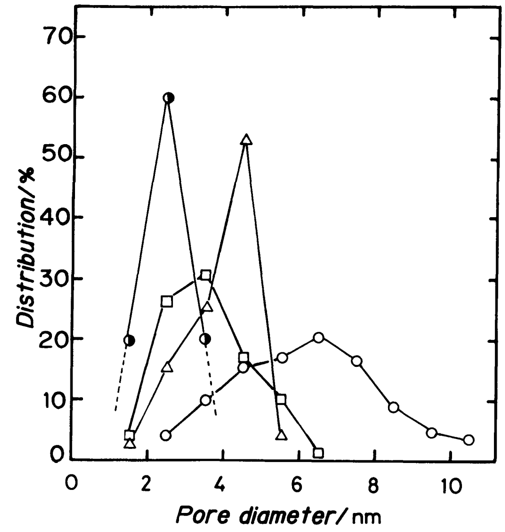

Fig. 1. Pore size distribution curves.
Temperature for heat treatment, ◑: R.T., □: 200 °C, △: 350 °C, ○: 450 °C. Particle size:−145+200 mesh.

Table 1. Properties of Exchangers[a]

Temp of treatment	Composition[c]	Density	Ion-exchange capacity[d]	Specific surface area	Pore volume
°C	mol$\mathrm{H_2O}$(mol$\mathrm{Nb_2O_5}$)$^{-1}$	g cm^{-3}	mol(mol$\mathrm{Nb_2O_5}$)$^{-1}$	m^2 cm^{-3}	ml cm^{-3}
R.T.[b]	6.45±0.06	2.39±0.05	0.665±0.008	758±20	0.50
200	4.61±0.05	2.70±0.05	0.401±0.004	610±18	0.63
350	4.03±0.05	2.95±0.05	0.297±0.003	519±17	0.54
450	3.59±0.04	2.91±0.05	0.205±0.003	329±15	0.63

a) Particle size: −145+200 mesh. b) Sample without heat treatment. c) The water content was determined from the weight loss at 850 °C. d) Exchange capacity for Na^+ at pH 9.3 (0.05 mol dm^{-3} $\mathrm{Na_2B_4O_7}$).

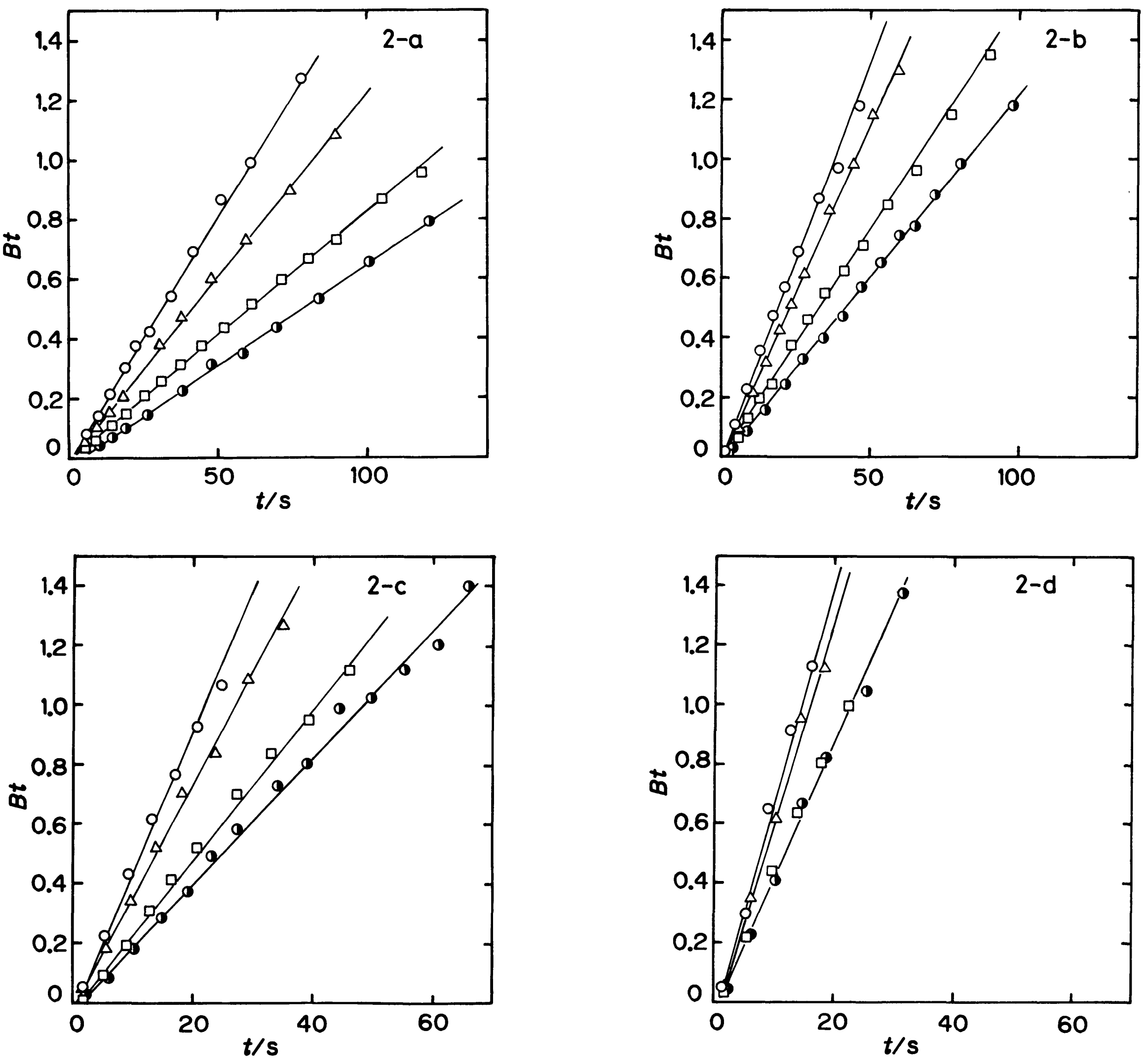

Fig. 2. Effect of heat treatment on the isotopic exchange rate.
Temperature, 5.1 °C; 0.10 mol dm^{-3} Na$^+$; temperature for heat treatment, ◑: R.T., □: 200 °C, △: 350 °C, ○: 450 °C. Particle size/mesh, 2-a:—48+60, 2-b:—70+80, 2-c:—100+120, 2-d:—145+200.

R.T., are shown in Figs. 2-a through 2-d. These figures indicate that the heat treatment enhanced the exchange rate in such different ways as to depend on the particle size; the rate increased monotonously with temperature in −48+60 mesh, but abruptly between 200 and 350 °C in −145+200 mesh. These figures also show that plots of *Bt* vs. *t* gave straight lines passing through the point of origin, irrespective of the heat-treatment temperature. Hence, the exchange rate is controlled by the rate of diffusion of sodium ions in the exchanger particles.

When this is true, the slopes of the straight lines (*B*) must be inversely proportional to the square of the particle radii (*r*). As is shown in Fig. 3, however, the exchangers which were heat-treated did not follow this relation, unlike sample R. T. This inconsistency may be ascribed to a dependence of the effective particle radius responsible for the diffusion of sodium ions or of the diffusion coefficient of Na$^+$ ions, on the apparent particle size. The latter is improbable for the following reason. As shown in Fig. 2, when the samples were heat-treated at 200 °C, an exchanger of small particle size (−145+200 mesh) showed the same rate as sample R. T. whereas the heat treatment appreciably increased the rate in the case of exchangers of large particle size. We can, therefore, conclude that the effective radius of the exchanger particles was decreased from the apparent radius estimated from the particle size distribution.

The decrease in the effective particle size is considered to be brought about by cracks developed during heating in the particles which are stressed due to a condensation of the hydroxyl groups. Naturally, the cracks build up more in large than in small particles; that is, the ratio of the effective to apparent radius becomes smaller when

Table 2. Particle Size of Samples Heat-Treated at 200°C

Particle size	Apparent particle radius (r)	B_0[a]	B'[b]	Effective[c] particle radius (r')	Volume[d] ratio
mesh	μm	$\times10^{-2}$ s^{-1}	$\times10^{-2}$ s^{-1}	μm	%
−48+60	145±4	0.67±0.02	0.84±0.04	130±5	72±4
−70+80	107±3	1.24±0.02	1.56±0.05	95±3	71±3
−100+120	74±2	2.13±0.09	2.54±0.11	68±3	77±5
−145+200	52±2	4.45±0.13	4.67±0.22	51±2	94±5

a) Slope of Bt vs. t plot for the sample R.T. b) Slope of Bt vs. t plot for the sample heated at 200 °C. c) Effective radius of the exchanger heated at 200 °C, determined by the equation: $r'=(B_0/B')^{1/2}r$. d) Ratio of the effective volume to the apparent volume determined from particle size distribution.

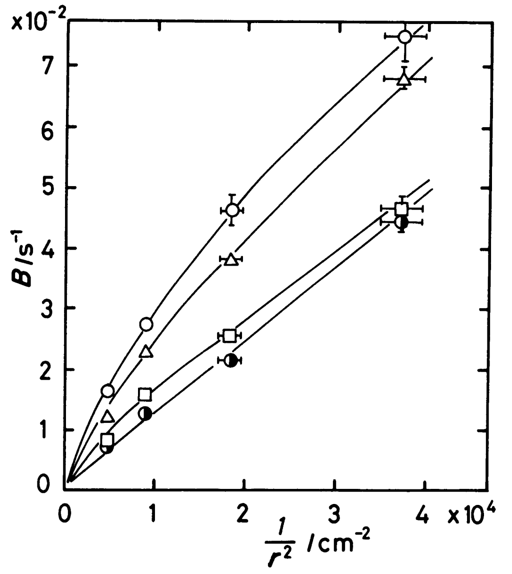

Fig. 3. Relationship between B and $1/r^2$. Temperature, 5.1 °C; 0.10 mol dm^{-3} Na$^+$; temperature for heat treatment, ◑: R.T., □: 200 °C, △: 350 °C, ○: 450 °C.

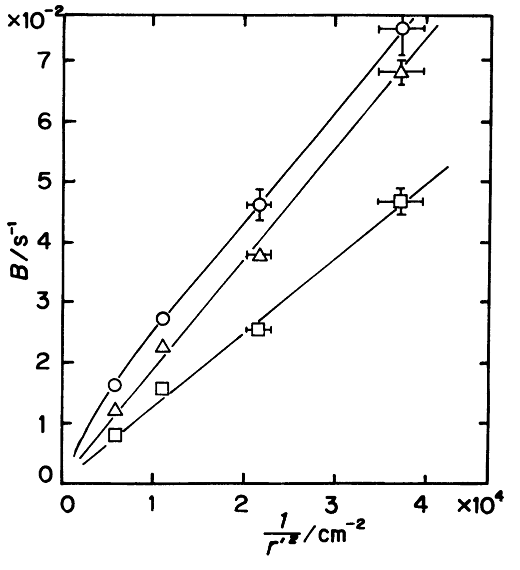

Fig. 4. Relationship between B and $1/r'^2$. Temperature, 5.1 °C; 0.10 mol dm^{-3} Na$^+$; temperature for heat treatment, □: 200 °C, △: 350 °C, ○: 450 °C.

the apparent radius is larger. Based on this view, by assuming a constant Na$^+$-diffusion coefficient, the effective particle radius (r') was calculated by using the equation $r'/r=(B_0/B')^{1/2}$, where B_0 and B', respectively, are the B values for samples without a heat treatment and those heat-treated at 200 °C; where r refers to the apparent particle radius of the exchanger. Table 2 shows the effective particle radii of exchangers heated at 200 °C of various apparent particle sizes. This table reveals that, although the effective radius of the exchanger particle of −145+200 mesh heated at 200 °C was nearly the same as its apparent radius, those of larger particles decreased considerably with heating at 200 °C.

By using the r' estimated for samples heat-treated at 200 °C (Table 2), B vs. $1/r'^2$ plots were made for samples heat-treated at higher temperatures, together with those for the samples heated at 200 °C for a comparison (Fig. 4). In the case where a sample was heated at 350 °C, the plot followed a straight line passing through the point of origin. Therefore, it is considered that cracking does not proceed further and that the effective particle radii are unchanged when the temperature for a heat treatment is raised from 200 to 350 °C. The larger slopes of the straight lines for the samples heated at 350 °C than at 200 °C indicate an increasing D with temperature on account of Eq. 1. At 450 °C, the factors contributing to an increase of the rate cannot be unequivocally determined, because a precise proportionality does not hold between B and $1/r'^2$, but may be a combination of the two factors mentioned above.

If we consider the situation microscopically, the hydrous niobium(V) oxide consists of two phases: the solid framework and the interstitial pore phase. Ions diffuse mainly through the pore phase, since a very large specific surface area of the samples (Table 1) indicates that the solid framework occupies only a small fraction of the exchanger particle. The diffusion is necessarily slower in the medium of the pore phase than in a homogeneous phase having the same medium as the pore phase. This is the situation for two reasons. First, the diffusion path is obstructed by the framework and is, thus, tortuous rather than straight. Secondly, the movement of the diffusing species in the pore phase may be reduced by friction or other interactions with the pore walls, together with a retarding effect of the electrostatic interaction between the ions and the exchange sites. The change of the Na^+-diffusion coefficient by heat treatment can be explained by one or combinations of these factors.

As was shown in Table 1, the fractional pore volume of the exchanger was unchanged upon heat treatment. Therefore, an increase in the diffusion coefficient in the exchanger with heating at 350 °C cannot be explained by a diminution in the tortuosity of the diffusing path or in the obstruction by the matrix. The retarding effect due to the electrostatic interaction between the ions and the exchange sites is also not effective, since changes of the exchange capacity for sodium ions and the electronic density on the fixed ionic groups of the exchanger have no influence on the exchange rate, as was described in a preceding report.(1) Collisions of ions and their friction with pore walls slow down the movement of the ions in the pore phase when the pores are not large enough compared to the size of the ions. From the large water content and fractional pore volume of the exchanger, sodium ions are considered to exist as hydrated ions in the exchangers. The diameter of hydrated sodium ions has been reported to be 1.2 to 1.4 nm.(7) Pores of dimeter smaller than 2.4 to 2.8 nm, therefore, strongly interrupt the movement of ions. On the other hand, such a retarding effect must be relaxed in pores lager than such a boundary value. As shown in Fig. 1, the peak, appearing in the vicinity of this boundary, of the distribution curve of the pore size in the exchanger heated at 200 °C shifted to the larger side of the boundary when the sample was heated at 350 °C. The large value of the Na^+-diffusion coefficient in the exchanger heated at 350 °C, therefore, is attributable to the large pore size, twice as large as the diameter of hydrated sodium ion, though some ambiguity remains concerning the effect of the broadness of the distribution curves. The further increase of the exchange rate for a sample heated at 450 °C may be partly due to a further increase in the diffusion coefficient produced by an increase in the pore diameter to 6.5 nm. Figure 5 shows the X-ray diffraction patterns of the samples, indicating an enhanced crystallization of the exchanger heated at 450 °C. If the retarding effect of pore walls on the diffusion of ions is small in a well-ordered exchanger matrix, the effective diffusion coefficient of ions may be increased by crystallization. As an example, Nancollas reported that the effective diffusion coefficient of sodium ions in hydrons thorium(IV) oxide was increased by the crystallization of the matrix.(8)

The effect of heating on the isotopic exchange rates of sodium ions for the hydrous niobium(V) oxide can be summarized as follows.

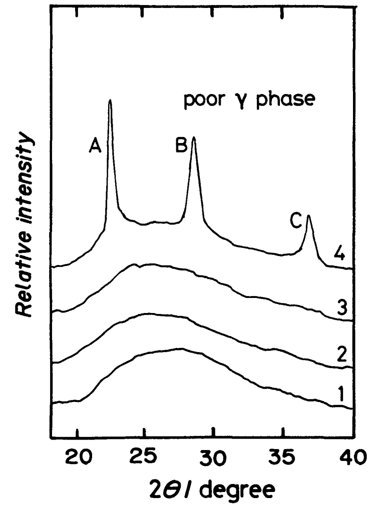

Fig. 5. X-Ray diffraction patterns.
Temperature of treatment, 1: R.T., 2: 200 °C, 3: 350 °C, 4: 450 °C. Interplaner distance/nm, A: 0.393, B: 0.315, C: 0.246.
γ-Niobium(V) oxide: low temperature phase of the compound reported by Brauer(9) and by Holtzberg et al.(10)

When an exchanger of large particle size is heated at 200 °C, the effective radius of the exchanger particle is decreased due to cracks which develop in the exchanger particles, resulting in an increased rate in the exchange reaction. A further increase in the exchange rate, when samples are heated at temperatures higher than 200 °C, can be explained in terms of an increase in the diffusion coefficient of sodium ions due to a reduction of the interactions between the ions and the pore walls, and the collisions of ions in the pores.

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