Bull. Chem. Soc. Jpn., *58*, 1292—1298 (1985) [Vol. 58, No. 4

Studies of the Hydrous Tin(IV) Oxide Ion Exchanger. IV. The Effect of Heat Treatment

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(Received November 1, 1984)

The effects of heat treatments in air or water at high pressure have been studied regarding the properties of a hydrous tin(IV) oxide ion exchanger. The exchanger in a H^+ form was stable against heat treatments in both air and water up to around 80 °C; thereafter the exchange capacity progressively decreased with temperature until 300 °C, at which point it was reduced to about a quarter of the initial value. The exchanger began to crystallize at 300 °C, and formed nearly-complete cassiterite crystals at 500 °C (where the capacity disappeared). In contrast, the exchanger in a Na^+ form was more stable against heat treatment than the H^+ form; at 400 °C, the Na^+ form retained 40 per cent of the initial exchange capacity. An examination of the uptake curves showed that more acidic exchange sites were stronger than less acidic sites against heat treatment. The existence of three kinds of water in the exchanger (adherent, zeolitic, and bound) has been suggested on the basis of the ion-exchange capacity, the thermal-analysis curves, and the recovery of water brought about by humidifying.

In a previous paper, the acid-base property, the ion-exchange selectivity for various cations and other important properties were studied on an hydrous tin(IV) oxide ion exchanger prepared by a method previously proposed by the present authors.[1] The study on the effect of heating regarding ion-exchange properties is also important since most inorganic ion exchangers are expected to be superior to ion-exchange resins regarding thermal stability. As hydrous tin(IV) oxide has an amorphous structure, this investigation may be helpful in considering the structure of this exchanger by adding some strong circumstantial evidence. As to the effect of thermal treatment, there have been many studies regarding the composition and the physical properties,[2–7] while there have been few reports on the ion-exchange properties.

The present paper describes the effect of heat treatment in both air and water with regards to the composition and ion-exchange properties of hydrous tin(IV) oxide. Furthermore, a classification of various water forms present in the exchanger is discussed.

Experimental

Reagents and Apparatus. The hydrous tin(IV) oxide ion exchanger was prepared by a method described previously[1] and then converted into a H^+ or Na^+ form. The other chemicals were of the highest purity (Wako Pure Chemical Industries, Ltd.).

A thermal analysis was undertaken using a Shimadzu micro thermal analyzer, Model DT-20B, connected to a thermal balance, Model TGC-20H, for thermogravimetric analysis (TGA), and a high-temperature sample holder, Model MDH-20, for differential thermal analysis (DTA). The reference material for DTA was α-alumina. The measurement was performed in air at a heating rate of 10 °C/min.

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. The diffraction angle was calibrated using silicon powder.

The infrared (IR) absorption spectra were measured with a Nihon Bunko infrared spectrometer, Model IR-G, using the KBr disk method. The wave number was calibrated using polystyrene.

Heat Treatment. About 7 g of the exchanger in a desired ionic form was heated in air to a constant weight at a constant temperature (controlled with an accuracy of 1% by using an automatic temperature controller; Chino Workers, Ltd.). After cooling, a sample in the Na^+ form was converted into the H^+ form by conditioning with a 0.1-mol dm^{-3} HCl solution; that in the H^+ form was immersed in water. Thereafter, they were both subjected to the humidifying operation described previously.[1]

The hydrothermal treatment was carried out in a Sakashita autoclave, Model SR-100 (inner volume, 1 dm^3), by controlling the temperature whthin an accuracy of 5 °C. In this autoclave, 5 g of the exchanger in the H^+ form was immersed in 400 cm^3 of distilled water; this was treated at temperatures from 100 to 250 °C for 6 h under a pressure of 100 atm, which was regulated by pressurized N_2 gas. After cooling, a portion of the sample was conditioned with 0.1 mol dm^{-3} HCl. The rest was washed with only water. Thereafter, they were both subjected to the humidifying operation.

The other experimental procedures were the same as those described previously.[1]

Results and Discussion

Thermal Stability of the Exchanger in the H^+ Form. The results for the H^+ form exchanger are shown in Table 1. It should be noted that values at the left of the two columns (showing the exchange capacity) were those normalized to the capacity per 1 mole of tin. The right-hand values (marked C) show the amount of water per 1 mole of tin that is liberated by the condensation of the hydroxyl groups (which may act as ion-exchange sites). In the case of the exchanger without heat treatment (designated as sample R. T.), the dissolution of a part of the exchanger in strong basic solutions limits the maximum cation-exchange capacity to the value at pH 11.3.

The maximum cation-exchange capacity did not change up to 80 °C, and then it decreased with temperature; at 500 °C it was reduced to a tenth of the value of the sample R. T. The amount of water contained in the exchanger immediately after the heat treatment (marked A) at 80 °C was reduced to 37% of the original value; then, it gradually decreased with

TABLE 1. EFFECT OF HEAT TREATMENT OF H^+ -FORM EXCHANGER ON THE COMPOSITION AND THE ION-EXCHANGE CAPACITY

No.	Temp of treatment °C	Weight loss wt%	Composition $A^{1)}$ mol H_2O/mol Sn	Composition $B^{2)}$ mol H_2O/mol Sn	Recovery of water (B-A) mol H_2O/mol Sn	Exchange capacity$^{3)}$ mol Na^+/mol Sn	Exchange capacity$^{3)}$ C mol H_2O/mol Sn	C/A
1	R.T.	—	2.15±0.02	2.15±0.02	—	0.230±0.003$^{4)}$	0.115±0.002	—
2	80	12.85	0.80±0.02	1.64±0.01	0.84±0.03	0.227±0.003	0.113±0.002	0.14±0.01
3	150	15.14	0.56±0.02	1.45±0.01	0.89±0.03	0.166±0.003	0.083±0.002	0.15±0.01
4	200	16.59	0.40±0.02	1.29±0.01	0.89±0.03	0.138±0.003	0.069±0.002	0.17±0.01
5	300	18.17	0.24±0.02	1.00±0.01	0.76±0.03	0.066±0.003	0.033±0.002	0.14±0.02
6	400	19.56	0.096±0.02	0.66±0.01	0.56±0.03	0.030±0.003	0.015±0.002	0.16±0.05
7	500	20.34	0.010±0.02	0.11±0.01	0.10±0.03	0.023±0.003	0.012±0.002	1.2±0.6
8	850	20.43	0	≈0	≈0	≈0	≈0	—

1): Immediately after heat treatment. 2): Immersed in water, dried over saturated NH_4Cl. 3): 0.1 mol dm^{-3} NaOH batch exchange capacity. 4): Exchange capacity at pH 11.3.

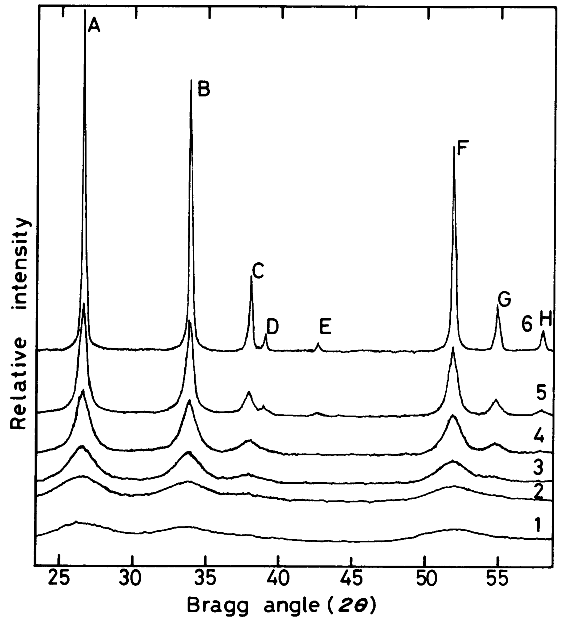

Fig. 1. X-Ray diffraction pattern of H^+-form exchanger.
Temperature of treatment; 1: R.T., 2: 200 °C, 3: 300 °C, 4: 400 °C, 5: 500 °C, 6: 600 °C. Interplanar distance/nm; A: 0.335, B: 0.264, C: 0.237, D: 0.231, E: 0.212, F: 0.176, G: 0.167 H: 0.159.

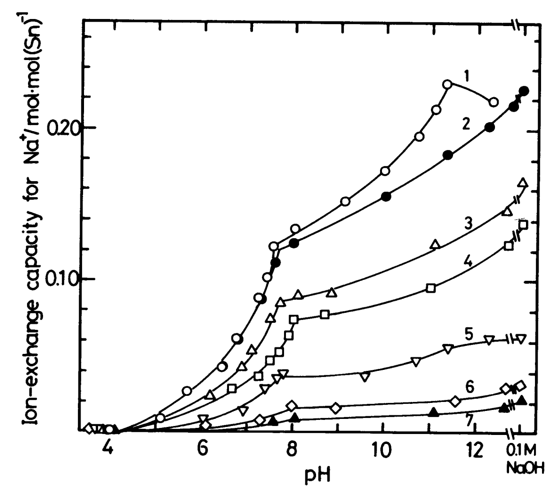

Fig. 2. Uptake curves for Na^+ (Heat treatment in H^+ form, followed by humidiation).
Temperature of treatment; 1: R.T., 2: 80 °C, 3: 150 °C, 4: 200 °C, 5: 300 °C, 6: 400 °C, 7: 500 °C.

temperature, and finally reached zero at 500 °C. The ratio of the water originated from the exchange sites (OH groups) to the total water remaining in the exchanger immediately after the heat treatment, C/A, did not change up to 400 °C, while at 500 °C it suddenly increased to around unity. Hence it is considered that the water molecules remaining in the exchanger immediately after the heat treatment were liberated cooperatively with the condensation of the OH groups, so that the water molecules might be fixed in the exchanger by OH groups through some kind of interaction such as a hydrogen bond (bound water). This bound water was completely liberated at 500 °C.

Next, let us consider the relation between the water content immediately after the heat treatment (marked A) and that of the exchanger subjected to the humidifying operation (marked B). For the exchangers heated up to 300 °C, the amount of water recovered by humidifying was nearly constant, while for samples heated over 400 °C it decreased suddenly; the exchanger heated at 500 °C recovered water only slightly. Figure 1 shows the X-ray diffraction patterns of the samples subjected to the humidifying operation. The samples heated up to 300 °C, together with the sample R. T., show three weak broad peaks (d=0.335, 0.264, 0.176 nm) and, hence, have poor crystallinity. The peaks sharpened with increasing temperature, indicating an enhanced crystallization. When a sample was heated at 500 °C, it reflected most of the peaks characteristic of cassiterite. At 850 °C, the exchanger completely crystallized as cassiterite. Therefore, the sudden decrease of water recovery at a temperature above 400 °C may be associated with the crystallization of the exchanger. This brings about a decrease in the space which can hold water molecules.

In order to examine the effect of a heat treatment on the acid-base property of the exchanger, the uptake curves for Na^+ and Cl^- were measured as a function of pH. Figure 2 shows the change in the cation-exchange behavior. For the sample heated at 80 °C, the exchange capacity in a pH range higher than the breaking point in the curve decreased slightly, while in a pH range lower than that point, the curve was the same as that of the sample R. T. When the exchangers were heat-treated at 150 °C or higher, the capacity decreased in the whole pH range with the temperature; the main part of the exchange capacity remaining after the heat treatment as 300 °C was in a pH region lower than the breaking point. The exchange sites were almost completely destroyed at 500 °C. The uptake curves for Cl^- are shown in Fig. 3, which reveals that the highest pH of anion uptake was lowered with the increase in temperature. This means that basic exchange sites are liable to be destroyed. From the above observations it is considered that the resistance to thermal decomposition is greater for more acidic rather than for less acidic ion-exchange sites.

Figure 4 shows the TGA and the DTA curves for the exchangers in the H^+ form. The TGA curve of the sample heat-treated at 80 °C was similar to that of the sample R. T. except the amount of the water released below 150 °C; the sample lost weight suddenly up to around 150 °C and then, gradually, up to about 650 °C, where the weight became constant. In contrast, the weight of the sample heat-treated at 300 °C decreased sharply below 80 °C, then became constant between 150 and 300 °C, and gradually decreased again up to 650 °C. In the DTA curves, large endothermic peaks appearing in the range lower than 200 °C sharpened as the temperature for heat treatment became higher. The position of the peak, observed at 70 °C for the samples heated below 200 °C, shifted to 40 °C and its area became very small when the sample was heated at 500 °C. Apparently, this observation is compatible with the change in the exchange capacity and in the degree of the recovery of water with the temperature for heat treatment, 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-temperature sides, respectively, of the peak for the samples heat-treated at temperatures below 200 °C are attributable to the bound water liberated by the condensation of the hydroxyl groups and to the adherent water in the exchanger matrix. Mikhail *et al.* observed a small broad exothermic peak at 470 °C,[2] and Durand and Masdupuy observed a large sharp exothermic peak at 300 °C and three small ones at 400, 500, and 620 °C.[8] The DTA curves were measured at varying heating rates, but these high-temperature peaks were not observed in the present experiment.

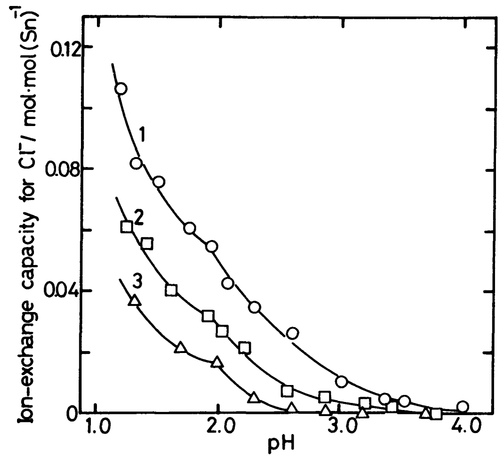

Fig. 3. Uptake curves for Cl^- (Heat treatment in H^+ form, followed by humidiation).
Temperature of treatment; 1: R.T., 2: 150 °C, 3: 300 °C.

Figure 5 shows the IR spectra of the exchangers in the H^+ form heat-treated at different temperatures. The asymmetric absorption band near 3400 cm^{-1} is attributable to the sum of the contribution from water and hydroxyl-group bonding to tin; the former at the lower, and the latter at the higher, wave-number sides. The absorption band near 1630 cm^{-1} is due

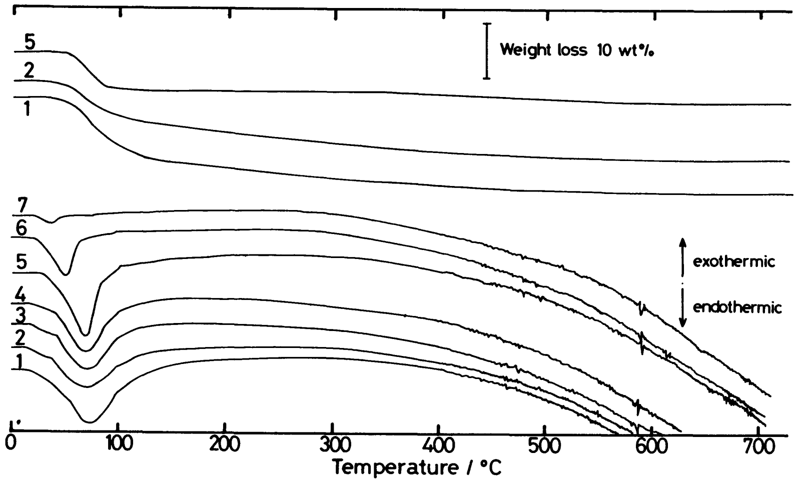

Fig. 4. TGA and DTA curves (Heat treatment in H^+ form, followed by humidiation).
Temperature of treatment; 1: R.T., 2: 80 °C, 3: 150 °C, 4: 200 °C, 5: 300 °C, 6: 400 °C, 7: 500 °C.

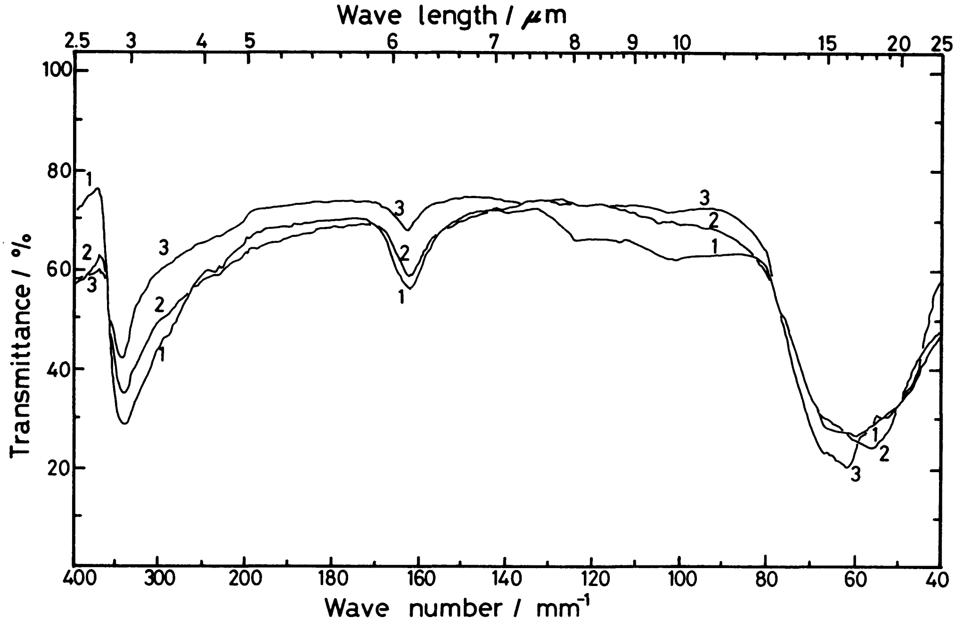

Fig. 5. IR spectra of hydrous tin(IV) oxide (Heat treatment in H^+ form). Temperature of treatment; 1: R.T., 2: 300 °C, 3: 500 °C.

TABLE 2. EFFECT OF HEAT TREATMENT OF Na^+ -FORM EXCHANGER ON THE COMPOSITION AND THE ION-EXCHANGE CAPACITY

No.	Temp of treatment °C	Weight loss wt%	Composition A[1] Molar ratio of H_2O/Sn	Composition A[1] Molar ratio of Na/Sn	Composition B[2] Molar ratio of H_2O/Sn	Composition B[2] Molar ratio of Na/Sn	Exchange capacity mol Na^+/mol Sn	Exchange capacity pH
1	R.T	—	1.794±0.013	0.233±0.002	2.13±0.02	$<1\times10^{-3}$	0.230±0.003	11.3
2	150	11.60	0.594±0.008	0.233±0.002	1.13±0.03	5.1×10^{-3}	0.169±0.003	11.3
3	200	12.96	0.405±0.006	0.233±0.002	1.05±0.03	6.8×10^{-3}	0.130±0.003	11.0
4	300	14.77	0.215±0.008	0.233±0.002	0.92±0.03	1.3×10^{-2}	0.111±0.003	11.1
5	400	15.65	0.122±0.009	0.233±0.002	0.89±0.03	3.2×10^{-2}	0.099±0.003	11.4

1): Immediately after heat treatment. 2): Converted to H^+ form. 3): After volatilization of tin with Br_2/HBr, measured by the atomic absorption spectrophotometric method.

to the bending mode of water and the absorption in the <900 cm^{-1} range, to Sn–O band.[9,10] The comparison of the spectra for the exchangers heat-treated at different temperatures shows that the water and hydroxyl bands were weaken with increasing temperature, while the Sn–O band was intensified. Accordingly, it is considered that the exchanger dried at room temperature contains a Sn–O band, a OH group, and water. Thus the formula of the exchanger may be written as $SnO_{2-x}(OH)_{2x}\cdot nH_2O$ in analogy with the formula proposed by Vivien *et al.*[9]

The observations described above can be summarized as follows. When the exchanger in the H^+ form is heated to 80 °C, the release of adherent water is accompanied by the stabilization of a network structure. By the heat treatment at temperatures between 150 and 300 °C the irreversible release of the bound water proceeds gradually and, thereby, the exchange capacity decreases with the increasing temperature of the treatment. However, the network structure remains essentially unchanged and the stabilized matrix can accommodate an approximately constant amount of a zeolitic water when humidified. The further release of the bound water at temperatures higher than 300 °C leads to the partial crystallization of the exchanger. At 500 °C the crystallization proceeds to an extreme and the structure changes completely. Therefore, almost all the water is not recovered by the humidifying operation.

Thermal Stability of the Exchanger in the Na^+ Form in Air. The effect of the heat treatment on the Na^+ form is shown in Table 2. The water content of the exchangers immediately after heat treatment (composition A) appears to be nearly the same as that of the exchangers heat-treated in the H^+ form as shown in Table 1. To make the comparison valid, however, the values for the Na^+ form should be corrected by adding 0.115±0.002 mol H_2O/mol Sn, which corresponds to the amount of the hydroxyl groups fixed by sodium ions. Thus, the water content of the exchanger heat-treated is larger in the Na^+ form than in the H^+ form, and it is considered that Na^+ in the exchanger hinders the release of water by heat treatment. Next, let us consider the composition of the samples converted to the H^+ form after being heat-treated in the Na^+ form (composition B). The composition of the exchanger without heat treatment became that of the original exchanger in the H^+ form. This observation is compatible with the reversibility of the exchange reaction between Na^+ and H^+, as reported previously.[1] The decrease of the water content with increasing temperature for heat treatment showed a tendency similar to the exchanger heat-treated in the H^+ form except for the exchanger heat-treated at 400 °C, which recovered nearly the same amount of water as the exchanger heat-treated at 300 °C.

On the other hand, the decrease of the exchange capacity was less for the Na^+- than for the H^+ form; even at 400 °C, the former still had exchange capacity five times as large as the latter. This tendency can be seen from Fig. 6, which shows the acid-base property of the exchangers heat-treated in the Na^+ form; the exchange groups in the Na^+ form appears resistant to the heat treatment especially at such high temperature as 400 °C.

Figure 7 shows the DTA and the TGA curves of the exchanger heat-treated in the Na^+ form. These curves show general features similar to those for the exchangers heat-treated in the H^+ form. The amount of water released up to 150 °C, however, was less for the Na^+- than for the H^+ form, which is a natural result of the difference of water content of the exchangers between the H^+ and Na^+ form. Furthermore, the curves for the samples heat-treated at 300 and 400 °C do not differ from each other. It was consequently concluded that the sodium ion in the exchanger retards the release of water at temperatures beyond 300 °C.

Figure 8 shows the X-ray diffraction patterns of the

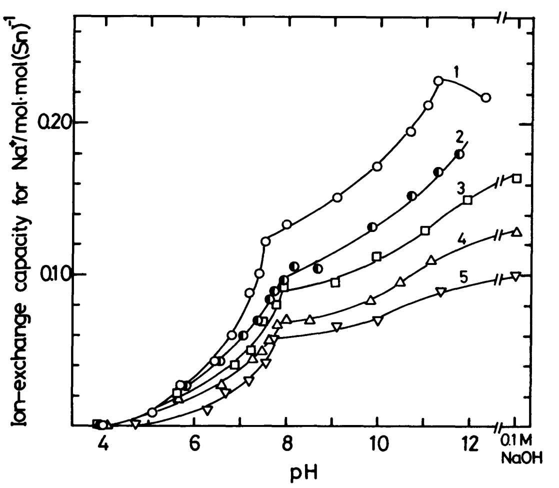

Fig. 6. Uptake curves for Na^+ (Heat treatment in Na^+ form, followed by conditioning to H^+ form).
Temperature of treatment; 1: R.T., 2: 150 °C, 3: 200 °C, 4: 300 °C, 5: 400 °C.

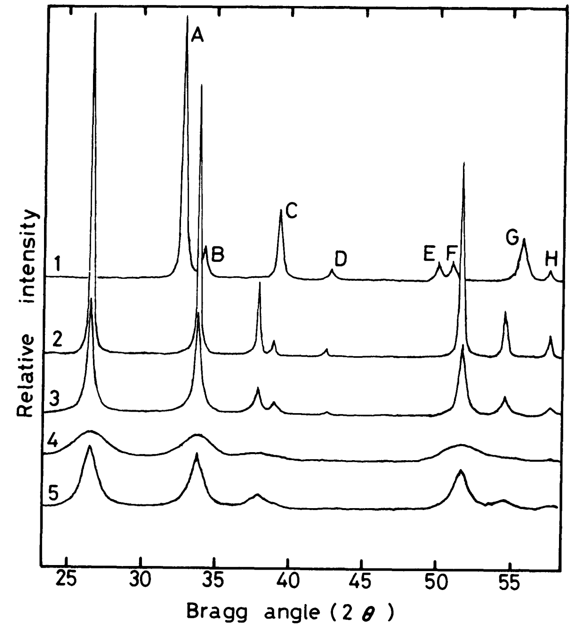

Fig. 8. X-Ray diffraction pattern of Na^+-form exchanger.
Sample 1: Na_2SnO_3 ($Na_2SnO_3 \cdot 3H_2O$, 850 °C), 2: SnO_2 (H^+ form, 850 °C), 3: Na^+ form, 850 °C, 4: Na^+ form, 400 °C, 5: H^+ form, 400 °C. Temperature: Temp. of heat treatment.

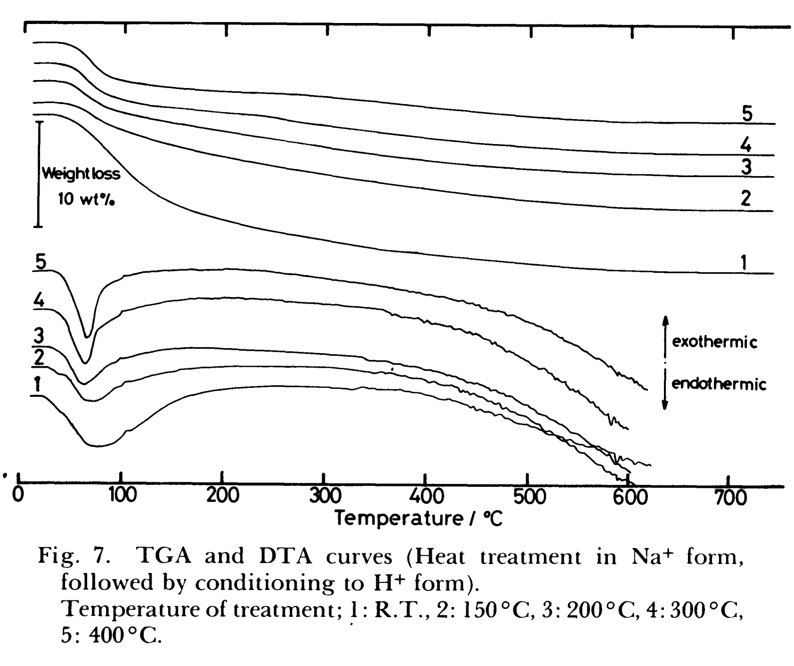

Fig. 7. TGA and DTA curves (Heat treatment in Na^+ form, followed by conditioning to H^+ form).
Temperature of treatment; 1: R.T., 2: 150 °C, 3: 200 °C, 4: 300 °C, 5: 400 °C.

samples heat-treated as the Na^+ form. It is apperent from a comparison with the H^+ form that the exchangers in the Na^+ form do not crystallize as disodium tin(IV) trioxide but as cassiterite. In addition, the broadness of the peaks indicates that the rate of the crystallization is slower for the Na^+- than for the H^+ form.

The observations described above can be summarized as follows. Although the substitution of the hydrogen ions by sodium ions is considered to stabilize the exchanger against the condensation of hydroxyl groups by a heat treatment, the matrix of the exchanger changes into a thermally stable phase by the irreversible release of water, ultimately to crystallize into cassiterite. Accordingly, the water content and the ion-exchange capacity of the exchanger decrease with the heat treatment temperature. However, the sodium ions in the exchange sites retard the change and stabilize the exchanger considerably. The difference in the thermal stability of the exchangers between the H^+- and the Na^+ form became prominent in a temperature range higher than 300 °C.

Thermal Stability in Water. The effect of a hydrothermal treatment on the properties of the exchanger in the H^+ form was studied under a pressure of 100 atm as is shown in Table 3 and Fig. 9. The symbols A and B, respectively, in Table 3 indicate the exchangers subjected to only the humidifying operation and to both the conditioning and humidifying operations. Obviously, the change in the uptake curves for sodium ions with temperature followed a tendency similar to that of the exchanger heat-treated in air. The degree of crystallization (examined by the X-ray analysis) also shows a similarity to the exchanger heated in air. On the other hand, decreases of water content with thermal treatment were less in water than in air.

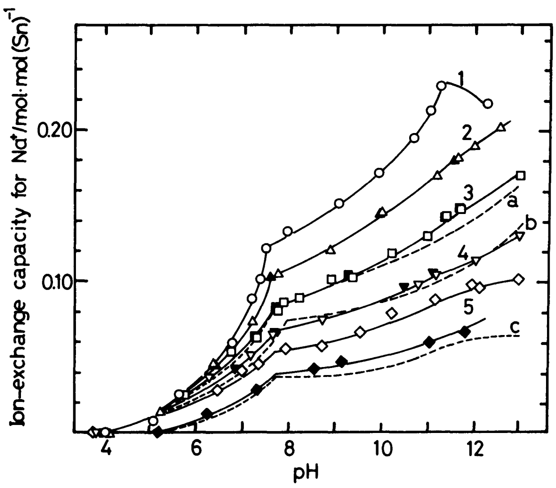

Fig. 9. Uptake curves for Na^+ (Hydrothermal treatment in H^+ form).
Temperature of treatment; 1: R.T., 2: 104°C, 3: 150°C, 4: 206°C, 5: 251°C. Solid mark: Without conditioning. ----: Heat treatment in air, temperature of treatment/°C; a: 150, b: 200, c: 300.

Figure 10 shows the TGA and the DTA curves of the exchangers treated hydrothermally. These curves indicate the similar behavior of dehydration to the sample heat-treated in air. The amount of water released (up to 100 °C) was, however, larger with a hydrothermal treatment than with a heat treatment in air. For the exchanger heat-treated in air, most of the adherent water and the zeolitic water were lost below 100 °C and the release of the bound water occurred mainly at temperatures higher than 80 °C. Accordingly, the amount of the adherent and the zeolitic water was not reduced by the hydrothermal treatment in spite of the irreversible release of the bound water.

The conditioning did not affect the composition and the exchange capacity except for the sample heat treated at 250 °C; the conditioning increased the water content and the exchange capacity by an amount 0.2 mol H_2O/mol Sn and 0.03 mol Na^+/mol Sn, respectively. The reason for this observation is not clear, but may be due to a slight increase in the recovery of bound water, which can be seen from the increase in the area of endothermic peak higher than 72 °C.

The observations described above can be summarized as follows. When the exchanger in a hydrogen form is heat treated in water at 100 atm, the matrix crystallizes to cassiterite along with the loss of the bound water which cannot be recovered only by the humidifying operation, and the exchange capacity decreases by an amount about the same as in the case of heat treatment in air. The amount of the adherent and the zeolitic water is maintained at the original value. Thus, the loss of water is smaller in this case than in the case of heat treatment in air.

The authors wish to express their thanks to Professor Wataru Suëtaka and to Yoshio Matsumoto, Depart-

TABLE 3. EFFECT OF HYDROTHERMAL TREATMENT OF H^+-FORM EXCHANGER ON THE COMPOSITION AND THE ION-EXCHANGE CAPACITY

No.	Conditions of treatment			Composition		Exchange capacity			
	Pressure kgw/cm²	Temperature °C	Time h	A[1)] mol H_2O/mol Sn	B[2)] mol H_2O/mol Sn	A mol Na^+/mol Sn	pH	B mol Na^+/mol Sn	pH
1	1	R.T.	—	2.16±0.02	—	0.230±0.003	11.3	—	
2	94	104±4	6	2.14±0.02	2.15±0.02	0.192±0.003	11.6	0.190±0.003	11.6
3	102	150±3	6	2.05±0.02	2.07±0.02	0.148±0.003	11.5	0.146±0.003	11.4
4	92	206±5	6	1.90±0.02	1.86±0.02	0.104±0.003	11.2	0.106±0.003	11.2
5	98	251±2	6	1.60±0.02	1.40±0.02	0.097±0.003	11.9	0.067±0.003	11.8

1): Conditioned by 0.1 mol dm^{-3} HCl. 2): Without conditioning.

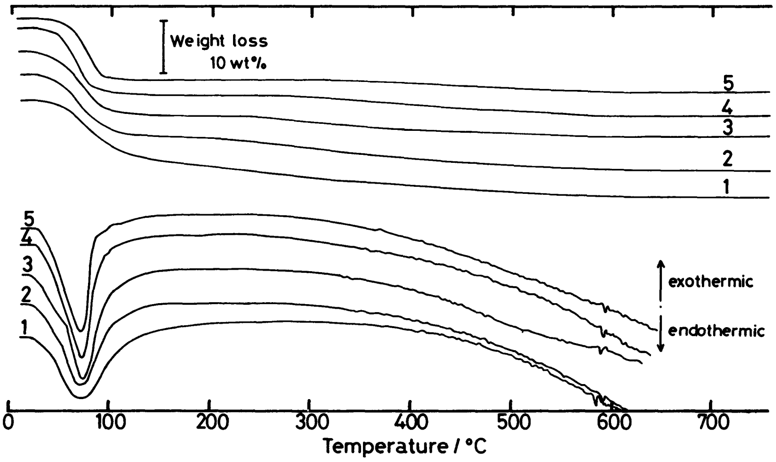

Fig. 10. TGA and DTA curves (Hydrothermal treatment in H$^+$ form, followed by conditioning with 0.1 mol dm^{-3} HCl). Temperature of treatment; 1: R.T., 2: 104 °C, 3: 150 °C, 4: 206 °C, 5: 251 °C.

ment of Metal Processing and Mechanical Metallurgy, Faculty of Engineering, Tohoku University, for their valuable suggestions on the measurement of IR spectra.

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