Studies of the Hydrous Titanium Oxide Ion Exchanger. IV. The Effect of Radiation and Heat Treatment*

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The effects of ^{60}Co γ-ray irradiation and of heat treatment in air have been studied on the properties of the hydrous titanium oxide ion exchanger. The ion-exchange capacity of the sodium form did not change at all, while that of the hydrogen form decreased a little, by the exposure of 5.2×10^8 R. The color of the exchanger, initially white, turned yellow upon irradiation. This exchanger was stable against heat treatment up to around 80 °C; thereafter the exchange capacity gradually decreased with the temperature until 324 °C, where it was abruptly reduced to about a quarter of the initial value. The examination of the titration curves showed that the most acidic exchange site was weaker than less acidic sites against heat treatment. The structural formula of this hydrous titanium oxide ion exchanger has been suggested on the basis of the ion-exchange capacity, the thermal decomposition curves, and such auxiliary data as the X-ray diffraction and the infrared spectra.

In the field of nuclear chemical engineering, an ion exchanger is often exposed to an intense radiation and to a high temperature. Since most inorganic ion exchangers are expected to be superior to ion-exchange resins in these respects,[1] it is very important to study their radiation- and thermal stabilities. Moreover, these studies may be helpful in considering the structure of the exchanger. However, the radiation- and thermal stabilities of the hydrous titanium oxide ion exchanger have not yet been studied in detail. On the other hand, many propositions have been made concerning the structure of hydrous titanium oxide based on various circumstantial evidence.[4-11] However, neither the composition nor the ion-exchange properties, such as the ion-exchange capacity and the acid-base property, deduced from these structural formulas are compatible with those actually observed in the hydrous titanium ion exchanger prepared by the method previously proposed by the present authors.[2,3]

The present paper will describe the effect of ^{60}Co γ-ray irradiation and of heat treatment in air on the ion-exchange properties of the hydrous titanium oxide. Furthermore, the structural formula of the exchanger have been inferred from those results and from the data obtained by the previous studies.[2,3]

Experimental

Reagents and Apparatus. The hydrous titanium oxide ion exchanger was prepared by the method described previously[2] and then converted into H^+ or Na^+ forms. The other chemicals were of the highest purity grade and were obtained from Wako Pure Chemical Industries, Ltd.

γ-Ray irradiation was carried out using the ^{60}Co γ-ray irradiation facility of Tôhoku University. About 6 g of the exchanger in a desired ionic form was placed in a stoppered test tube with either 10 cm^3 of water or a 0.1 M NaOH (1 M= mol/dm^3) solution, or without them, and irradiated intermittently at an average exposure rate of 3.2×10^5 or 2.5×10^5 R/h (1 R=258 μC/kg).

The thermal analysis was undertaken with 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.

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

Heat Treatment. The exchanger in a desired ionic form was heated in air to a constant weight at a constant temperature. After cooling, the sample in the Na^+-form was converted into the H^+ form by immersing it in a 0.1 M HCl solution, while that in the H^+-form was immersed in water. Thereafter, they were both subjected to the humidifying operation described previously.[3]

The other experimental procedures were the same as those previously been described.[2,3]

Results and Discussion

Radiation Stability. Table 1 represents the effect of γ-irradiation on the properties of the exchanger, together with that of the ion-exchange resin, Dowex-50, for comparison. It took 1.5 y to reach a total exposure of 5.2×10^8 R. Even if the exchanger was not irradiated, the ion-exchange capacity decreased to about a half of the initial value when the exchanger in the hydrogen from was allowed to stand for 1.5 y. The decrease in the ion-exchange capacity is, thus, largely due to aging of the exchanger, and only slightly to the effect of the γ-rays. The ion-exchange capacity of the sodium form, however, did not change at all upon a γ-ray irradiation of up to 5.2×10^8 R. The amount of titanium dissolved in the supernatant solution during irradiation was 7.2×10^{-5} g. Since this value is compatible with the data concerning chemical stability described previously,[2] it can be said that γ-ray irradiation does not influence the solubility of the material. After irradiation, all the samples turned yellow except for the sample in the hydrogen form exposed up to 2.2×10^8 R. The yellow color of the exchanger in the hydrogen form disappeared when it was immersed in a 1.0 M sodium hydroxide solution, but appeared again by reconversion to the hydrogen form. In contrast, the yellow color

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Table 1. Effect of γ-irradiation on the properties of the exchanger[a)]

Sample No.	Exchanger (ionic form)	Environment	Exchange capacity[c)] meq. Na^+/g		Color of the exchanger after irradiation
			Irradiated	Unirradiated	
1	HTO(H^+)[b)]	Water	2.27±0.10	2.72±0.05	Yellow
2	HTO(H^+)	Air	2.64±0.07	2.85±0.08	Light creamy
3	HTO(Na^+)	0.1 M NaOH	4.31±0.00	4.30±0·10	Yellow
4	HTO(Na^+)	Air	4.68±0.07	4.61±0.05	Yellow
5	Dowex 50×8(H^+)	Water	4.37±0.05	4.71±0.13	Brown
6	Dowex 50×8(Na^+)	0.1 M NaOH	4.74±0.21	4.72±0.10	Brown
7	HTO(H^+)	Air	2.97	2.98	White
8	HTO(H^+)	Water	2.90	—	Yellow

a) Average exposure rate (R/h): No. 1—6; 2.5×10^5, No. 7—8; 3.2×10^5. Time of irradiation (h): No. 1—6; 2141, No. 7—8; 680. Time of standing: No. 16; 1.5 y, No. 78; 36 d. Exposure (R): No. 1—6; 5.2×10^8, No. 78; 2.2×10^8. b) Hydrous titanium oxide, c) No. 16: 1.0 M NaOH batch exchange capacity[3)], No. 7—8: 0.10 M NaOH column exchange capacity.[2)]

Table 2. Effect of the heat treatment of the H^+-form exchanger on the composition and the ion-exchange capacity

Sample No.	Temperature (°C)	Weight loss (wt%)	Composition, molar ratio of H_2O/Ti after		Exchange capacity[a)]		
			Heated	Humidified	meq. Na^+/g	eq. Na^+/mol Ti	mol H_2O/mol Ti
1	R.T.	—	1.892	1.892	4.54±0.22	0.517±0.025	0.258±0.012
2	80±0.5	23.50	0.303	1.536	4.78±0.27	0.514±0.029	0.257±0.014
3	122±1	24.74	0.241	1.426	4.42±0.25	0.466±0.026	0.233±0.013
4	159±1	26.32	0.165	1.269	3.92±0.27	0.402±0.027	0.201±0.013
5	324±2	29.06	0.038	0.996	1.33±0.24	0.130±0.023	0.065±0.011
6	623±7	29.39	0.023	0.111	0.54±0.21	0.044±0.017	0.022±0.008
7	830±10	29.91	0	—	—	—	—

a) 1.0 M NaOH batch exchange capacity.

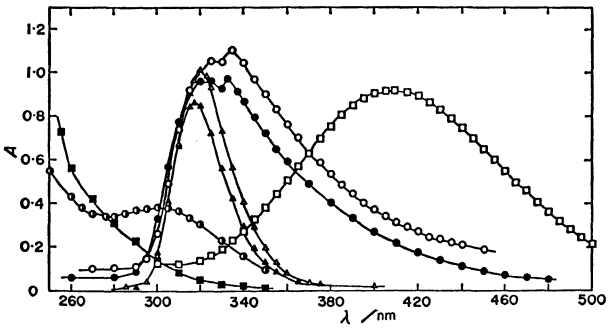

Fig. 1. Absorption spectra of the exchanger and the supernatant solution after irradiation.
●: Supernatant solution diluted by H_2O(Ti: 1.2×10^{-5} M), ○: Supernatant solution diluted by 1 M H_2SO_4 (Ti: 1.2×10^{-5} M), ▲: Exchanger, 5.9×10^{-2} M Ti/1 M H_2SO_4, △: Exchanger, $<5.9\times10^{-2}$ M Ti/1 M $HClO_4$, □: 1.25×10^{-3} M Ti(IV), 3.75×10^{-2} M H_2O_2 in 1 M H_2SO_4, ■: 200 ppm Ti(IV) in 1.8 M H_2SO_4 (Ref. 13), ◑: 10 ppm Fe(III) in 1.8 M H_2SO_4 (Ref. 13).

in the sodium form did not disappear when the sample was converted to the hydrogen form, but it almost disappeared when it was converted back to the sodium form again. Moreover, a sodium hydroxide solution wherein the sodium-form exchanger was immersed turned brownish yellow.

The change in color might be caused by the reaction of titanium with the radiolytic products of water. The absorption spectra were measured in order to identify the species responsible for yellow coloration (*cf.* Fig. 1). Sample No. 3 in Table 1 was dissolved with heating it in concentrated sulfuric or perchloric acid, followed by dilution to an acidity of 1 M. The absorption spectra of these solutions showed a single peak. Its position agreed approximately with one of the two peaks which appeared in the spectra of the solutions prepared by diluting the supernatant solution of the same sample with the respective acids. This observation leads to the conclusion that, besides the species formed in the exchanger, some other species are present in the supernatant solution. These absorption spectra differ from those of sulfuric acid—hydrogen peroxide and sulfuric acid solutions of titanium(IV) and of a sulfuric acid solution of iron(III)[13)], which may be present as an impurity. The peroxoc-omplex of titanium contained in solid titanium dioxide is reported to show the absorption band in the same position as in the sulfuric acid solution.[14)] Therefore, the species giving rise to the yellow color appearing in the irradiated hydrous titanium oxide and in the supernatant solution cannot be ascribed to the peroxo-complex. From these observations we can conclude that the sodium form is suitable for the preservation of the hydrous titanium oxide ion exchanger. Compared with Dowex-50, this ex-

Table 3. Effect of the heat treatment of the Na^+-form exchanger on the composition and the ion-exchange capacity[a)]

Sample No.	Temperature (°C)	Weight loss (wt%)	Composition[b)] mole ratio			Exchange capacity[c)] meq. Na^+/g
			H_2O/Ti	Na/Ti	H_2O/Na	
1	R.T.	—	1.634	0.517	3.16	4.54±0.22
2	80±0.5	14.53	0.622	0.517	1.20	4.73±0.22
3	122±1	18.12	0.372	0.517	0.719	4.59±0.32
4	159±1	19.19	0.297	0.517	0.574	3.04±0.20
5	324±2	23.95	≈0	0.517	≈0	0.93±0.27
6	623±7	24.80	≈0	0.517	≈0	0.26±0.25

a) The exchangers were subjected to conditioning and humidifying operation and converted to H^+-form. b) Immediately after heat treatment. c) 1.0 M NaOH batch exchange capacity.

changer is stable against radiation, at least to the same extent as the ion-exchange resin. Further studies are, however, required to reach a definite conclusion on the radiation stability; irradiation by γ-rays in much higher doses and by α- or β-rays emitted from isotopes adsorbed on the exchanger, and the identification of the yellow species.

Thermal Stability. The results for the hydrogen-form exchanger are shown in Table 2. It should be noted that the left of the three columns showing the exchange capacity represents the exchange capacity per 1 g of a humidified sample. The middle column shows the normalized exchange capacity per 1 mol of titanium. The right shows the amount of water per 1 mol of titanium that should be liberated by the condensation of the hydroxyl group which may act as an exchange site (bound water).

The exchange capacity did not change up to 80 °C; then it gradually decreased with the temperature, while at 324 °C it was suddenly reduced to a quarter of the original value. At 623 °C more than 90% of the exchange site was destroyed.

The amount of water contained in the exchanger immediately after the heat treatment (the fourth column in Table 2) at temperatures below 122 °C was more than that of the bound water, but the relation was reversed at a higher temperature. The latter relation indicates that the exchanger recovers bound water to a certain degree during the humidifying operation. However, no bound water was recovered for the sample heated at 623 °C.

Next, let us consider the relation between the water content after heat treatment and the water content of the exchanger subjected to the humidifying operation (the fifth column in Table 2). In the case of heat treatment in the range of 80—159 °C, the difference between these water contents, that is, the amount of water recovered by humidifying, is almost constant, 1.1—1.2 mol per mol of titanium. The exchanger heated at 623 °C recovered water only slightly.

The sudden decrease in both the exchange capacity and the degree of recovery of water at a heating temperature of 324 °C might be associated with the crystallization of the exchanger, because no X-ray diffraction pattern appeared until 324 °C, where two weak and broad peaks (d=3.52, 3.42 Å) appeared. (1 Å=0.1nm)

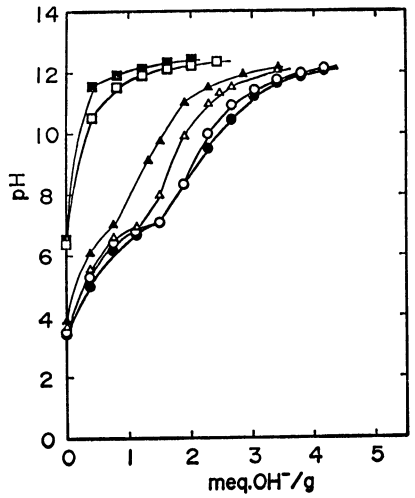

Fig. 2. Titration curves of the exchanger subjected to heat treatment in H^+-form.
I (Ionic strength); 0.10 M, ●: R. T. ○: 80 °C, △: 122 °C, ▲: 159 °C, □: 324 °C, ■: 623 °C.

When the heating temperature was raised to 623 °C, the diffraction line, d=3.52 Å, became sharper and many other lines appeared. This pattern is attributable to the mixture of anatase and brookite.

In order to examine the effect of heat treatment on the acid-base property of the exchanger, the titration curves were measured and found to be as shown in Fig. 2. For samples heated at a temperature not higher than 159 °C, the pH of the breaking point in the titration curves was independent of the temperature and the curves in the pH range higher than that point were parallel with each other. On the other hand, when the exchangers were heat-treated at 324 °C or higher, the curves started at pH 6.5, the point of breaking mentioned above. This means that the exchange site with the smallest pK_a value is responsible for the decrease in the capacity of the exchanger with heating at a temperature lower than 159 °C. The most acidic sites were completely destroyed at 324 °C, and the loss of less acidic sites began to occur at the same temperature. At 623 °C, almost all of the exchange sites were destroyed.

The effect of heat treatment on the sodium form is shown in Table 3 and Fig. 3. Obviously, the change

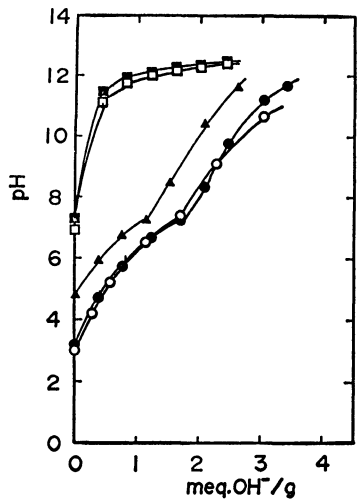

Fig. 3. Titration curves of the exchanger subjected to heat treatment in Na^+-form, followed by conditioning.
I; 0.10 M, ●: 80 °C, ○: 122 °C, ▲: 159 °C, □: 324 °C, ■: 623 °C.

in both the exchange capacity and the acid-base property with a rise in the temperature followed a tendency similar to that of the exchanger heat-treated in hydrogen form. On the other hand, a considerable difference in the release of water by heat treatment between the sodium and the hydrogen forms was observed; that is, at 80 °C the former left twice as much water behind as the latter, in which major part of the residual water was bound water. This cannot be understood by simply considering the hydrating power of the cations, because that of the sodium ion is weaker than that of the hydrogen ion; instead, it must be considered that the sodium ion hinders the release of water by exerting some special effect on the structure. X-Ray analysis exhibited no sign of crystallization until 850 °C, where the diffraction pattern attributable to rutile began to appear. These observations suggest a difference between the two ionic forms in the mechanism for the decrease in the exchange capacity with heat treatment. In the hydrogen form, the dehydrating condensation of hydroxyl groups plays an important role in both the loss in exchange capacity and the crystallization of the material, while, in the sodium form, the sodium ion forms a stable chemical bond with titanium dioxide and the exchange site loses its function as a result.

Structure. The structural formula of the hydrous titanium oxide ion exchanger can be deduced from the various properties described previously as well as by such supplementary data as DTA, TGA, the IR spectra, and X-ray diffraction.

The titration curves and the effect of heat treatment on them strongly suggest that the most acidic exchange site differs intrinsically from the others and accounts for a half of the total exchange capacity. The other, less acidic sites might be distinguished from each other by the change in the electronic structure caused by the adsorption of the sodium ion. When the exchange capacities corresponding to the first-, second-, and third plus fourth dissociable exchange sites are converted to the simplest integral ratio, it is 2 : 1 : 1. Considering this fact and the total exchange capacity of 0.5 eq./mol of titanium, the unit structure must contain 4 hydroxyl groups per 8 atoms of titanium.

Figure 4 shows the TGA and DTA curves of the exchanger in hydrogen form. The TGA curves indicate that the samples heat-treated at 159 °C and lower lost weight suddenly up to about 150 °C, and then gradually up to about 500 °C, where the weight became constant. In contrast, most of the water in the sample heat-treated at 324 °C was released below 80 °C. In the DTA curves, large endothermic peaks appearing in the temperature range lower than 150 °C sharpened as the temperature for heat treatment became higher. The position of the peak, initially at 100 °C, shifted to 75 °C when the exchanger was heat-treated at 80 °C. The shoulder observed in the peak became less pronounced with the rise in the temperature for heat treatment. When the sample was heated at 324 °C, it showed a sharp peak with a very small shoulder.

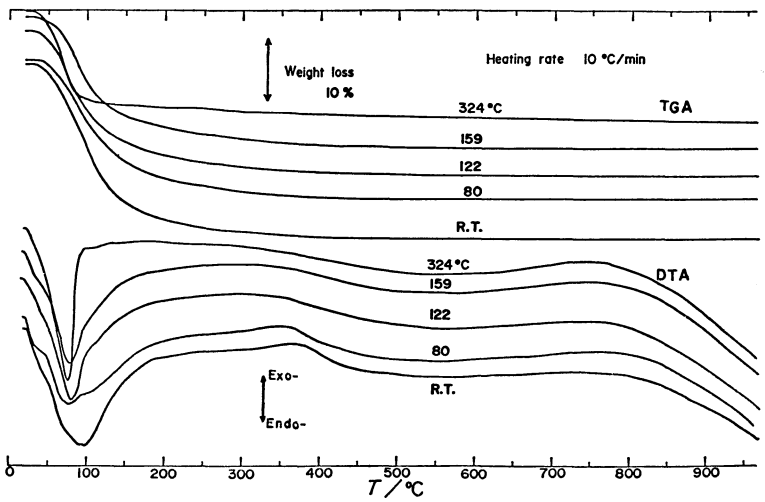

Fig. 4. TGA and DTA curves of the exchanger subjected to heat treatment in H^+-form.

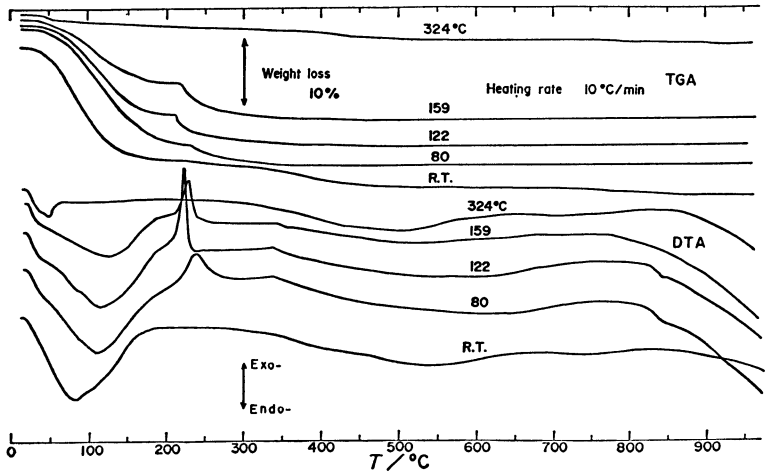

Fig. 5. TGA and DTA curves of the exchanger subjected to heat treatment in Na^+-form, followed by conditioning.

Apparently, the observation just described is compatible with the change in the exchange capacity and in the degree of the recovery of water with temperatures for heat treatment, if the peak near 75 °C is considered to correspond to the water recoverable by humidifying, and the shoulder, to the bound water.

The observations described above can be summarized as follows. When the exchanger in the hydrogen form is heated at 80 °C, the release of water is accompanied by the stabilization of the network structure. By the heat treatment at 122—159 °C the network structure remains essentially unchanged except for a slight modification. This stabilized network can accommodate an approximately constant amount of water. The release of the bound water becomes pronounced at temperatures higher than 324 °C and a partial crystallization occurs. Therby the exchange capacity decreases suddenly. At 623 °C the crystallization proceeds to an extreme end and the structure changes completely. Therefore, almost all the water, including the bound water lost by heat-treatment at 623 °C, is not recovered by the humidifying operation.

Figure 5 shows the DTA and TGA curves of the exchanger heat-treated as the sodium form. The TGA curve of the sodium form dried at room temperature consists of three steps: R.T.—170 °C, 350—450 °C, and 730—900 °C. The samples heat-treated at 80, 122, and 159 °C lost weight in two steps. The TGA curve observed for the sample subjected to heat treatment at 324 °C corresponds to the poor recovery of water. The slight weight loss above 730 °C, which is also observed for the exchanger dried at room temperature, is probably due to the decomposition of the sodium carbonate accidentally remaining in the exchanger after treatment with a 0.1 M hydrochloric acid solution. In the DTA curves, the endothermic peak corresponding to dehydration was displaced toward a temperature higher by about 30 °C by heat treatment at a temperature lower than 324 °C. After this shift, the position of the peak approximately agrees with that of the hydrogen form dried at room temperature. These samples also showed the exothermic peak in the range of 210—230 °C, where some weight loss was observed on the

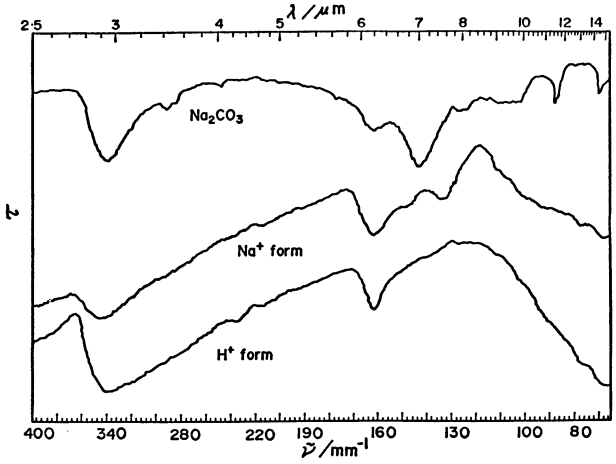

Fig. 6. IR spectra of the exchanger.

corresponding TGA curves. Because dehydration is an endothermic reaction, this peak cannot be accounted for by dehydration. This kind of exothermic peak has also been reported to be observed for the hydrous titanium oxide synthesized by the addition of ammonia water to a titanium tetrachloride solution.[10,12] Imoto *et al.*[10] ascribed the peak to the release of ammonia, while Vivien *et al.*[12] attributed it to crystallization. Since the present hydrous titanium oxide ion exchanger contains no ammonia, this exothermic peak cannot be attributed to the release of ammonia, but to the reaction which is responsible for the sudden decrease in the exchange capacity mentioned above.

Figure 6 shows the IR spectra of the exchanger in the hydrogen and the sodium forms dried at room temperature. The asymmetric absorption band observed near 3400 cm^{-1} is attributable to the sum of the contributions from water and hydroxyl-group bonding to titanium, the former at the lower, and the latter at the higher, wave number sides respectively.[12] The absorption band near 1625 cm^{-1} is due to the bending mode of water, and the absorption in the <1000 cm^{-1} range, the titanium–oxygen bond. The IR spectrum of the exchanger in the sodium form is similar to that of the exchanger in the hydrogen form except for the appear-

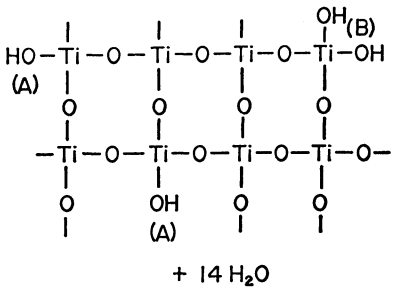

Fig. 7. Structural formula of the exchanger.

ance of the absorption band in 1380—1300 cm^{-1}. This absorption band disappeared when the samples was subjected to heat treatment at 825 °C. Further study is needed before this absorption band can be identified.

On the basis of the results concerning the properties of the exchanger presented above, the structural formula represented in Fig. 7 is inferred for the exchanger in the hydrogen form, though the arrangement of such a unit structure is not very regular because the X-ray diffraction pattern displays a nearly amorphous structure. Of the exchange sites in this model, (A) is the most acidic, and (B), the least acidic, ion-exchange group. The exchange site (A) is easily destroyed by condensation with the neighboring exchange site of the same kind. The appearance of anatase and brookite in the first crystallization step can also be understood by assuming this structure.

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