  Bull. Chem. Soc. Jpn., 58, 3225—3228 (1985)

Studies of the Hydrous Niobium(V) Oxide Ion Exchanger. III. The Effect of Heat Treatment

Yasushi INOUE,* Hiromichi YAMAZAKI, and Yuzo MATSUDA
Department of Nuclear Engineering, Faculty of Engineering, Tohoku University, Aramaki, Sendai 980
(Received March 18, 1985)

The effects of heat treatments in air have been studied regarding the properties of a hydrous niobium(V) oxide ion exchanger in H^+ form. The exchanger lost 17 per cent of the initial ion-exchange capacity when it was heat-treated at 110 °C; thereafter the exchange capacity decreased progressively with temperature until 400 °C, at which point it retained about a half of the initial value. The exchanger began to crystallize into γ-phase at a temperature between 450 to 500 °C where the capacity disappeared. The γ-phase transformed to α-phase at a temperature above 800 °C. An examination of the uptake curves showed that less-acidic exchange sites were more resistant than more-acidic sites to 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 water recovery brought about by humidifying.

Previous papers in this series described detailed studies regarding the synthesis, the acid-base properties, and the ion-exchange selectivity for various cations of a hydrous niobium(V) oxide ion exchanger.[1,2] The study on the effect of heat treatment 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 the hydrous niobium(V) oxide has an amorphous structure, this investigation may be helpful in considering the structure of the compounds by adding some strong circumstantial evidence: The relation between the ion-exchange capacity and the thermal behavior of water in the compound. As to the effect of thermal treatment, there have been many studies regarding the composition and the physical properties,[3-8] while there have been few reports on the ion-exchange properties.

The present paper describes the effect of heat treatment in air with regards to the composition and the ion-exchange properties of hydrous niobium(V) oxide. Furthermore, a classification of various water forms present in the exchanger is discussed, and the thermal stability of the material is compared with other hydrous oxides.

Experimental

Reagents and Apparatus. The hydrous niobium(V) oxide ion exchanger was prepared by pyrohydrolyzing a $NbCl_5$ solution, as has been previously described.[1,2] A thermal analysis was undertaken using a Shimadzu micro thermal analyzer, Model DT-20 B, connected to a thermal balance, Model TGC-20 H, 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^{-1}.

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.

Heat Treatment. About 8 g of the exchanger in H^+ form was heated in air to a constant weight at a constant temperature, which was controlled within an accuracy of 1% using an automatic temperature controller (Chino Workers, Ltd.). After cooling, the sample was immersed in water overnight, followed by the humidifying operation described previously.[1,2]

The other experimental procedures were the same as those described in the preceeding papers.

Results and Discussion

Effect of Heat Treatment on the Composition of Hydrous Niobium(V) Oxide. Figure 1 shows the relation between the water content immediately after the heat treatment (open mark) and that of the exchanger subjected to the humidifying operation

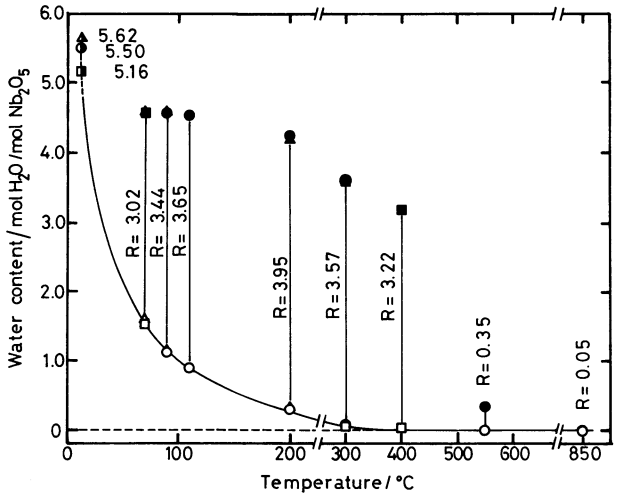

Fig. 1. Change in composition.
▲◑◧: Sample R.T. Open marks: Immediately after heat treatment. Filled marks: Immersed in water, dried over saturated NaCl solution. R: Water recovery.

(filled mark). It should be noted that the water content was normalized to the number of moles of water per 1 mole of Nb_2O_5. In the case of the exchanger without heat treatment (designated as sample R.T.), there existed a fluctuation in the water content by an amount of 0.5 mol H_2O/mol Nb_2O_5. This fluctuation is insignificant in considering the effect of the heat treatment since the heat treatment, even at a temperature as low as 70 °C, led to the same composition irrespective of the original values. 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 reached zero at 400 °C. This result is compatible with Lapitskii's observation that the water content of 6.93 mol H_2O/mol Nb_2O_5 at room temperature decreased to 1.79 mol H_2O/mol Nb_2O_5 at 110 °C and to almost zero at 400 °C, in spite of the difference in the experimental conditions.[4]

The following relation holds between the water content immediately after the heat treatment and that of the exchanger subjected to the humidifying operation. For the exchangers heated up to 400 °C, 3 to 4 mol of water per 1 mol of Nb_2O_5 were recovered, while for the samples heated over 550 °C, water was only slightly recovered by humidifying. Figure 2 shows the X-ray diffraction patterns of the samples subjected to the humidifying operation. The samples heated up to 400 °C, together with the sample R.T., have poor crystallinity. Over the range of 450—500 °C many peaks characteristic of γ-niobium(V) oxide, the low temperature phase of the compound reported by Brauer[3] and by Holtzberg *et al.*,[5] appeared and sharpened with increasing temperature, indicating an enhanced crystallization; the material crystallized completely in the γ-phase at a temperature between 600 to 650 °C. When the crystals were heated at a temperature above 800 °C, they were transformed to the α-phase. 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 accommodate water molecules.

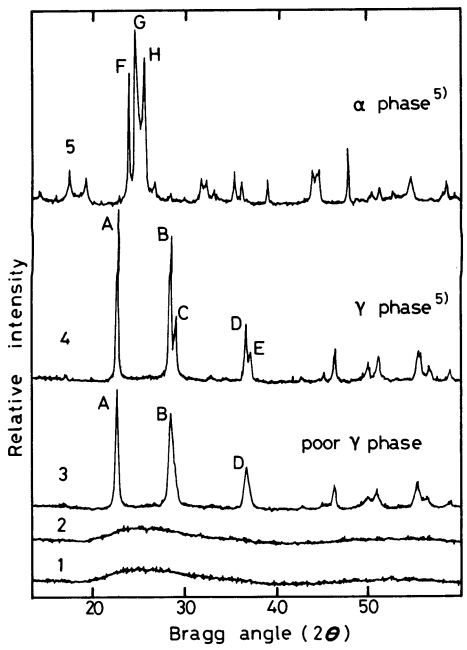

Fig. 2. X-Ray diffraction patterns.
Temperature of treatment; 1: R.T., 2: 400 °C, 3: 550 °C, 4: 650 °C, 5: 850 °C. Temperature range of transition; Poor γ-phase : 450—500 °C, γ-phase: 600—650 °C, α-phase: 800—850 °C.
Interplaner distance/nm; A: 0.393, B: 0.315, C: 0.309, D: 0.246, E: 0.243, F: 0.375, G: 0.364, H: 0.350.

Change in the Ion-exchange Capacity. In order to examine the effect of the heat treatment on the acid-base property of the exchanger, the uptake curves for Na^+ were measured as a function of the pH. The results are shown in Fig. 3. In the case of the exchangers heated up to 400 °C, the dissolution of a part of the exchanger in strong basic solutions limits the maximum cation-exchange capacity to the value at around pH 10.5. For the samples heated up to 110 °C, the decreases in the ion-exchange capacity were 0.06 and 0.13 mol Na^+/mol Nb_2O_5, respectively, at pH 7.6 (breaking point in the curve) and at pH 10; hence, nearly the same amount of exchange sites was destroyed in the pH ranges of either side of the breaking point. When the exchangers were heat-treated at 200 °C or higher, the capacity in a pH range lower than the breaking point decreased with

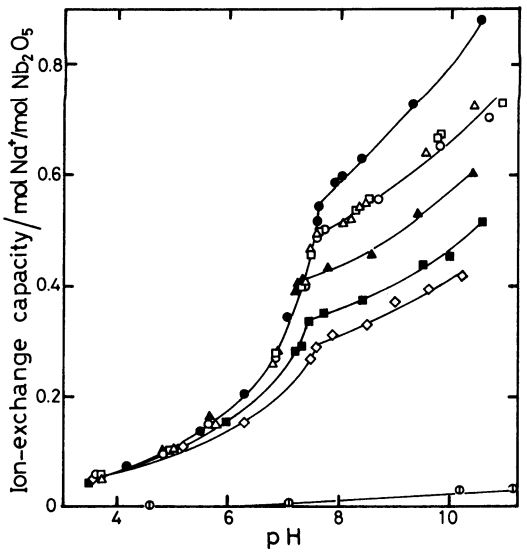

Fig. 3. Uptake curves for sodium ions.
Temperature of treatment; ●: R.T., △: 70 °C, □: 90 °C, ○: 110 °C, ▲: 200 °C, ■: 300 °C, ◇: 400 °C, ⓘ: 550 °C.

Table 1. Changes in ion-exchange capacity and water content

Temp of treatment °C	Difference in A[1] exchange capacity mol Na^+/mol Nb_2O_5	Difference in A/2[2] water content mol H_2O/mol Nb_2O_5	Difference in B[3] water content mol H_2O/mol Nb_2O_5	2B/A
70	0.14±0.01	0.07 ±0.01	0.60±0.04	9±2
200	0.24±0.01	0.12 ±0.01	1.27±0.04	11±1
300	0.34±0.01	0.17 ±0.01	1.58±0.04	9±1
400	0.39±0.01	0.19_5±0.01	1.93±0.04	9±1

1) Ion-exchange capacity at pH 10.0; difference between sample R.T. and sample thermally treated. 2) Difference in capacity was converted into that in water content. 3) Difference in water content between sample R.T. and heat-treated sample subjected to the humidifying operation.

the temperature, while in a pH range higher than that point, the curves were parallel to those for the samples heated at a temperature lower than 110 °C; the main part of the exchange sites, destroyed by the heat treatment at a temperature higher than 110 °C, was in the pH region lower than the breaking point. The exchange sites were completely destroyed at 550 °C. The sample heated at 850 °C exhibited no uptake of Na^+ throughout the pH region examined. From the above observations it is considered that the resistance to thermal decomposition is greater for less-acidic than for more-acidic ion-exchange sites.

Table 1 shows the relation between the decrease in ion-exchange capacity at pH 10 and that in the water content of the heat-treated samples subjected to the humidifying operation. Symbols A and B, respectively, are referred to the difference in the exchange capacity and in the water content between the sample R.T. and the heat-treated exchanger. As one mole of water should be liberated by a condensation of two moles of the OH groups which may act as ion-exchange sites, half of the difference in the ion-exchange capacity (A) is equivalent to a decrease of the water content due to the condensation of the exchange sites (A/2). As is shown in the right column in Table 1, the ratio of the loss of total water to the loss of water that originated from the exchange sites (OH groups), by heat treatment, 2B/A, did not change up to 400 °C. Hence, a constant amount of water molecules is considered to be fixed in the exchanger by OH groups through some kind of interaction such as a hydrogen bond (bound water); the irreversible condensation of the OH groups, which cannot be recovered by the humidifying operation, is accompanied by the irreversible release of water.

Thermal Analysis of the Samples. Figure 4 shows the TGA and DTA curves for the samples subjected to the humidifying operation. The TGA curves of the samples heat-treated up to 400 °C are similar to those of the sample R.T.; the sample lost weight abruptly up to around 100 °C and then,

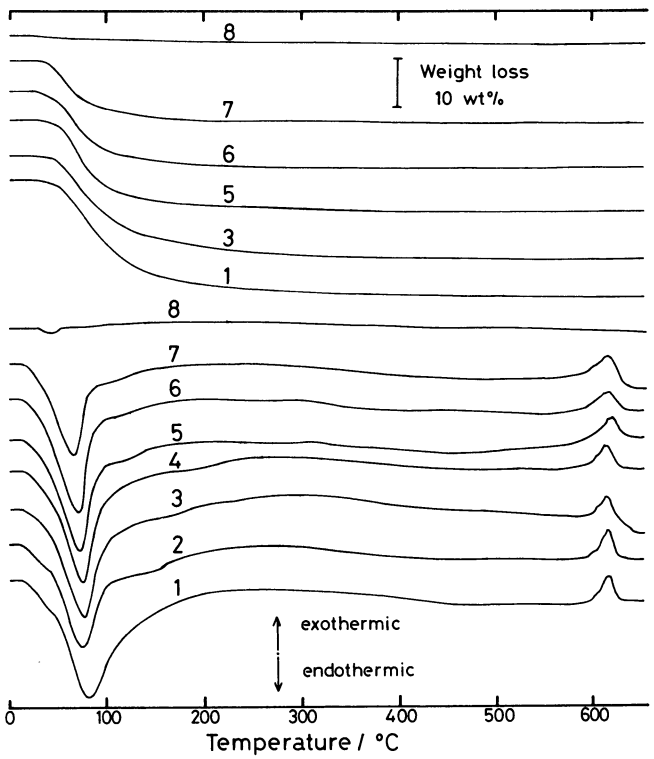

Fig. 4. TGA and DTA curves (Heat treatment, followed by humidiation).
Temperature of treatment; 1: R.T., 2: 70 °C, 3: 90 °C, 4: 110 °C, 5: 200 °C, 6: 300 °C, 7: 400 °C, 8: 550 °C.

gradually, up to about 600 °C, where the weight became constant. In contrast, the sample heated at 550 °C showed little weight loss up to 600 °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 to 80 °C for the samples heated below 400 °C, shifted to 45 °C and its area became very small when the sample was heated at 550 °C. Apparently, this observation is compatible with the changes in both the exchange capacity and

Table 2. Effect of heating time on the composition of sample

Heat treatment		Composition	
Temperature	Time	A	B
°C	h	mol H_2O/mol Nb_2O_5	
200	12	0.28±0.01	4.23±0.03
	72	0.26±0.01	4.15±0.03
400	12	0.02±0.01	3.22±0.03
	72	0.02±0.01	3.19±0.03

A: Immediately after heat treatment. B: Immersed into water, dried over sat. NaCl.

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 the 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. For the samples heat-treated below 400 °C, a small exothermic peak was observed at 605 °C; this peak can be assigned to crystallization. This temperature for crystallization is higher, by 100 °C, than that expected from the results in Fig. 2. This may be due to thermally non-equilibrium conditions in DTA measurements; incidentally, the exothermic peak shifted from 610 °C to 574 °C when the heating rate was decreased from 15 °C/min to 2 °C/min. Two exothermic peaks were observed at 375 °C and 545 °C by Sathyanarayana and Patel[6] and at 470 °C and 609 °C by Lapitskii.[4] In the present experiment, however, no exothermic peak was observed in the temperature region below 500 °C.

It is considered from above observations that the samples heated at temperatures up to 400 °C, keep the network structure essentially unchanged and, thereby, recover nearly a constant amount of the zeolitic water and some amount of the bound water, when humidified. When the exchanger is heat-treated at 550 °C or higher, the crystallization proceeds to an extreme and thereby almost all the water is not recovered by humidifying.

Effect of Heating Time. The thermal equilibrium is not always attained even when the exchanger is thermally treated until no weight loss is observed. To make clear this point, the effect of the heating time on the properties of the material was investigated at 200 °C and 400 °C. Table 2 shows that the composition of the exchangers (both immediately after the heat treatment and after the humidifying operation) is independent of the length of the heating period. There existed no difference in the uptake curves for Na^+, the thermal analysis curves, and the X-ray diffraction patterns between the samples heated for 12 h and those for 72 h. The materials, therefore, reach to thermal eqilibrium within 12 h.

Thermal Stability of the Exchanger. The thermal stability of hydrous niobium(V) oxide can be summarized as follows. The amount of water contained in the exchanger immediately after the heat treatment decreases with increasing temperature and becomes zero at 400 °C. The structure of the samples heated up to 400 °C, however, remains essentially unchanged, and the stabilized matrix can accomodate an approximately constant amount of a zeolitic water and some bound water when humidified. This brings about the recovery of a large part of the exchange sites; less acidic sites are more stable to thermal decomposition than more acidic sites. The ion-exchange capacity is halved when the exchanger is heat-treated at 400 °C. When the exchanger is heat-treated at temperatures above 500 °C, the crystallization of the matrix proceeds to an extreme and the structure changes completely. In this case, almost all the water is not recovered by the humidifying operation and, thereby, the sample has no ion-exchange capacity for Na^+ even in strong alkaline solution.

If the thermal stability of the exchangers is compared with hydrous titanium(IV) oxide[9] and hydrous tin(IV) oxide,[10] which have previously been investigated by the present authors, niobium(V) oxide is superior to these two hydrous oxides; hydrous titanium(IV) oxide, hydrous tin(IV) oxide, and niobium(V) oxide, respectively, keep 25, 29 and 57% of the original ion-exchange capacities for Na^+ when they are heat-treated at 300 °C.

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