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Studies of the Hydrous Titanium Oxide Ion Exchanger. V. The Stability of the Hydrogen Form in Air

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Synopsis. After being allowed to stand in air at room temperature, the exchanger in the hydrogen form showed an abrupt decrease in its ion-exchange capacity between 3 and 6 months after the preparation. This is attributable to the preferential destruction of the most acidic hydroxyl groups by dehydrating condensation.

In the previous paper,[1] it was pointed out that the hydrous titanium oxide in the hydrogen form lost about a half of its ion-exchange capacity when it was allowed to stand for 1.5 years after the preparation. Despite the importance of this observation from the practical point of view, the decrease in the ion-exchange capacity has not yet been stuied in detail as a function of the lapse of time. The present paper will describe the results of our study of this subject.

Experimental

Materials. The hydrous titanium oxide ion exchanger prepared by the method reported previously[1] was used after having been conditioned by the following procedure. The exchanger, sieved to obtain a desired particle size (100—200 mesh), was poured into a glass column, 10 mm in inside diameter and 20 cm high, with glass wool for column support. Then at least thirty times the column volume of 0.1 M (1 M=1 mol dm^{-3}) HCl, 0.1 M NaOH, and 0.1 M HCl were passed through, in this order, at a rate of about 1.0 cm^3/min. After each step, the column was washed with water until the effluent became neutral. The exchanger in the hydrogen form thus prepared was air-dried and stored in a desiccator containing a saturated NH_4Cl solution. A part of the exchanger was heated to a constant weight at 80 °C and stored in the same desiccator. As the result of the above treatment, two kinds of exchangers were obtained:

Sample A: Hydrogen form dried at room temperature,

Sample B: Hydrogen form subjected to thermal treatment at 80 °C.

Their composition and ion-exchange capacities are shown in Table 1.

Titration Curves. In 50 cm^3 of a solution (ionic strength: 0.10 M), 0.5 g of the sample was immersed for 5 d at room temperature, with intermittent shaking. This was followed by the pH measurement of the solution and by the determination of the sodium ions in the solution. The sodium ions were converted to pure sodium chloride and indirectly determined by titrating the chloride ions by means of the Fajans' method. To obtain a titration curve, this procedure was repeated for various solutions which had been prepared using the desired combinations of 0.1 M NaOH and 0.1 M NaCl. The ion-exchange capacity was calculated from the amount of sodium ions taken up from the 0.1 M NaOH solution.

Results and Discussion

The dependence of the ion-exchange capacity of Sample A on the standing period is shown in Fig. 1. The capacity first decreased slightly with the lapse of time for about 95 d after the preparation, this decrease amounted to 0.25 meq/g in this period. Thereafter, it decreased abruptly until about 180 d, at which point about a half of its original value was lost. Thereafter, the capacity continued to decrease gradually with the lapse of time. This phenomenon may be understood by considering that such a gelatinous material as hydrous titanium oxide is in the metastable state, which tends to be stabilized on standing. If this argument is true, the material which has been forced to age by thermal treatment will behave differently. Therefore, the exchanger treated thermally at 80 °C (Sample B) was also examined in a similar way. The reason for selecting this temperature for the thermal treatment is that the release of water is accompanied by a certain degree of stabilization of

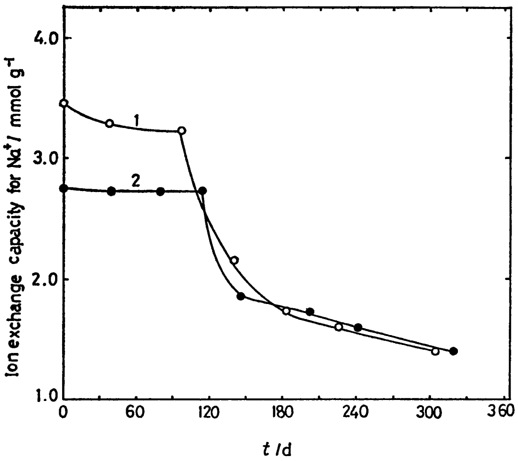

Fig. 1. Variation of ion-exchange capacity with time. ○: H$^+$ form, air-dried, ●: H$^+$ form, 80 °C heat-treatment.

Table 1. Ion-exchange capacity and the water content

Sample	Time of standing d	Composition, molar ratio of H_2O/Ti	Ion-exchange capacity for Na$^+$ mmol Na$^+$/g	 mmol Na$^+$/mmol Ti
A	0	2.08±0.10	3.47±0.05	0.407±0.007
	305	1.36±0.06	1.40±0.03	0.146±0.005
B	0	1.61±0.08	2.75±0.02	0.300±0.006
	310	1.09±0.07	1.38±0.03	0.138±0.004

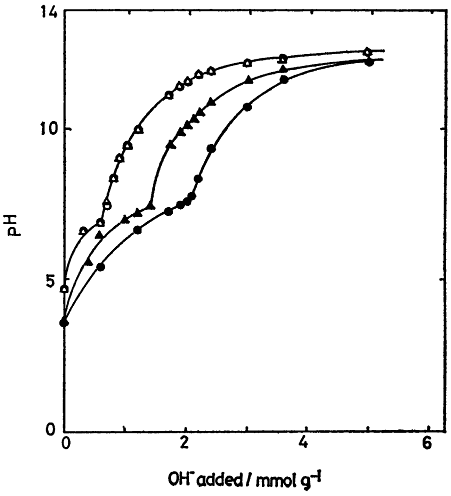

Fig. 2. Titration curve.
Exchanger of H^+ form and room temperature;
●: sample A, immediately after the preparation,
○: sample A, at 320 days after the preparation.
Exchanger of H^+ form and 80 °C heat-treatment;
▲: sample B, immediately after the preparation,
△: sample B, at 320 days after the preparation.

the network structure1) and that the material does not suffer so much loss in capacity as to become useless as an ion exchanger. A comparison of Curves 1 and 2 indicates that the capacity of Sample B decreased in the same way as that of Sample A. Besides, the capacities of Samples A and B reached the same value after standing for 180 d in spite of the difference in the initial values between the two samples. These facts suggest that the stabilization of the network structure does not play an important role in the stability of the exchange sites. In order to examine the effect on the acid-base property brought about by aging, the titration curves were measured for the samples stored for 320 d after the preparation, as is shown in Fig. 2. The titration curves for these samples were almost all the same. The breaking points in the curves were, however, observed at smaller amounts of OH^- for the aged samples than for the original ones. The titration curves in the pH range higher than that point ran parallel with each other. These findings strongly suggest that the most acidic exchange sites are liable to be destroyed upon standing. The preferential destruction of the most acidic sites was also observed when the exchanger was thermally treated in air.1) The change in the composition of the exchanger was then studied by estimating the content of water from the weight loss on ignition to TiO_2. Table 1 shows that an appreciable amount of water was lost from the exchanger which had been stored for a long time. Accordingly, in a study of this kind, the exchange capacity normalized per unit amount of titanium should be used instead of the capacity defined on the basis of the unit mass of the exchanger thus far used, because, when using the latter, we can not exactly compare the capacity based on the same amounts of the original materials. The normalized capacity is represented in the last column in Table 1. The results in Table 1 are compatible with the general relationship that an exchanger with a higher water content has a larger ion-exchange capacity.2–4) A sample which had been allowed to stand for 320 d was subjected to conditioning once again in order to examine the possibility of recovering the ion-exchange capacity. The reconditioning, however, was found not to be effective for that purpose. These facts clearly indicate that the destruction of the exchange site proceeds by means of an irreversible dehydrating condensation of the hydroxyl group with the loss of water. This change, however, was not accompanied by crystallization, because X-ray analysis exhibited no such diffraction pattern as appeared when the exchanger was thermally treated at 324 °C.1) From these considerations, we can conclude that the exchanger is subjected to a drastic change in its ion-exchange property when it is allowed to stand for three months in air and that this deterioration results basically from the same mechanism as that observed when the exchanger was thermally treated at a temperature below 159 °C.1)

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