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Studies on the Hydrous Niobium(V) Oxide Ion Exchanger. I. A Method for Synthesis and Some Properties

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A comprehensive study of the preparation of hydrous niobium(V) oxide ion exchangers was made using three kinds of niobium solutions: (1) HCl, (2) C_2H_5OH, and (3) H_2SO_4. From a detailed examination of the dependency of the yield, the ion-exchange behavior toward Na^+, the chemical stability, and some other properties, regarding the method for precipitation, it was found that the pyrohydrolysis of the $NbCl_5$ solution was the best method, since the procedure was simple, rapid and reproducible, and the product had a comparatively good ion-exchange property. The product obtained from the H_2SO_4 solution had the largest ion-exchange capacity and was most stable in highly alkaline solutions, but the whole procedure was very tedious. The exchanger prepared from the ethanolic solution had a smaller ion-exchange capacity in a pH region higher than 8. The materials, thus obtained, had at least two kinds of weakly dissociable ion-exchange sites, and the ion-exchange capacity for alkali metal ions decreased in the order of $Li^+>Na^+>K^+$. The aging effect and the chemical stability were also examined.

As has been previously pointed out,[2] hydrous oxide ion exchangers based on various polyvalent metal ions have the serious disadvantage of giving inconsistent results to different investigators, because of the irreproducibility of the synthesis. With this point in mind, the present authours previously studied hydrous titanium(IV) oxide and hydrous tin(IV) oxide for establishing satisfactory synthesis methods.[1,2] Hydrous niobium(V) oxide is expected to have a large ion-exchange capacity (3.2 mequiv/g at pH 12) and to be stable in highly acidic or alkaline solutions.[3] Its ion-exchange properties, however, have not yet been investigated in detail. This material has been prepared using the following methods: (1) the neutralization of the acidic solutions of niobium salts, such as sulfate, chloride, and fluoride,[3–5] (2) the pyrohydrolysis of an $NbCl_5$ solution[6] and, (3) the hydrolysis of a potassium fluoroniobate solution or niobium(V) alkoxide solution.[7,8] These methods, however, are not always suited for synthesizing a large amount of a hydrous niobium(V) oxide. A detailed comparison of these methods must be experimentally made in order to choose the best method since a detailed description of the experimental conditions is lacking in the literature.

The present paper will describe the results of an investigation undertaken to establish the best conditions for the synthesis of the hydrous niobium(V) oxide ion exchanger, together with some of its properties, particularly those with direct bearing on the conditions of the synthesis.

Experimental

Reagents and Apparatus. Niobium(V) chloride and niobium(V) oxide, respectively, were supplied from Mitsuwa Kagaku Yakuhin Kaisha, Ltd. and Shinetsu Kagaku Kogyo Kaisha, Ltd. Hydrofluoric acid was obtained from Hirota Kagaku Kogyo Kaisha, Ltd., and sulfochlorophenol S from Dojindo laboratories. The other chemicals were of the highest purity grades supplied by Wako Pure Chemical Industries, Ltd.

The pH values were measured with a Toa Dempa model HM-6A pH meter. A thermogravimetric analysis was undertaken with a Shimadzu model DT-20B micro thermal analyzer, connected to a Shimadzu model TGC-20H thermal balance. The absorbance was measured with a Hitachi model 124 double-beam spectrophotometer with a 1-cm glass cell.

Synthesis of Hydrous Niobium(V) Oxide. A synthesis was tried for three systems: (a) $NbCl_5$–HCl, (b) $NbCl_5$–C_2H_5OH, and (c) Nb_2O_5–H_2SO_4, as shown in Fig. 1. The concentration of niobium was held constant for each system because of a technical difficulty to make a meaningful variation in the concentration of the niobium from the respective starting materials. In the HCl-system, the starting solution was produced by dissolving 25 g of niobium(V) chloride in 50 cm^3 of concentrated hydrochloric acid, followed by dilution to 1 dm^3 with distilled water. The niobium(V) ethoxide solution was produced by dissolving 25 g of niobium(V) chloride into 200 cm^3 of 99.5% ethanol, followed by dilution to 3 dm^3 with distilled water. In the H_2SO_4-system, the starting solution was obtained by fuming the hydrochloric acid solution or the hydrofluoric acid solution of niobium with 40 cm^3 of concentrated sulfuric acid; the hydrofluoric acid solution was made by dissolving 5 g of niobium(V) oxide in 50 cm^3 of hot 7 mol dm^{-3} hydrofluoric acid.

In the methods from (1) through (6), hydrous niobium(V) oxide was precipitated by pyrohydrolyzing the $NbCl_5$ solution, while in the methods from (7) through (11), the precipitate was obtained by hydrolyzing the $NbCl_5$ solution by the addition of alkaline solutions. In methods (8),(9), and (11), the obtained slurries were refluxed with the mother liquor. In the methods from (12) through (14), the hydrous oxide was precipitated by the dilution of the respective starting solution with distilled water.

After being separated from the mother liquor by a

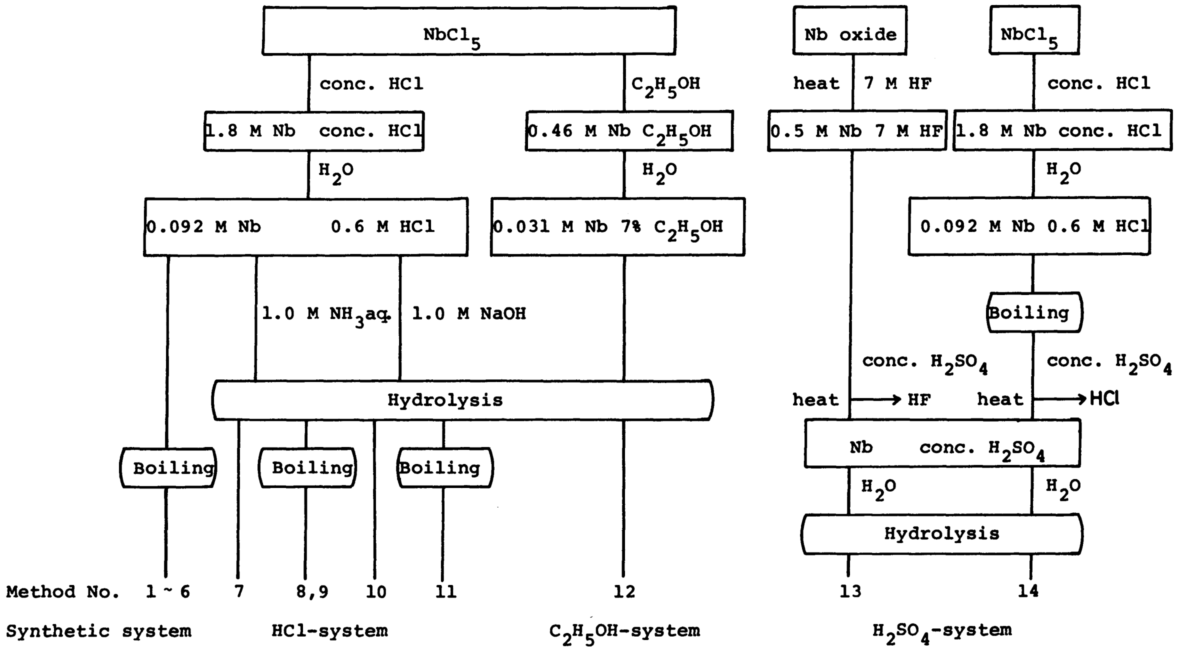

Fig. 1. Scheme of synthesis. (1 M = 1 mol dm^{-3})

combination of decantation and filtration through Toyo No. 1 filter paper under suction, the precipitate was uniformly dispersed into distilled water and filtered again after being completely sedimentated. This procedure was repeated until no chloride or sulfate ion was detected in the filtrate. Then, the precipitate was air-dried at room temperature. The resulting product was then immersed in distilled water to break it down into fine particles, which were subsequently dried again at room temperature. Particles were then ground in a porcelain mortar and sieved to obtain the required particle sizes.

Conditioning. The exchanger of a desired particle size (100—200 mesh) was washed with distilled water to remove any adherent powder. The slurry was poured into a glass tube with glass-wool plugging for column support, and then 0.1 mol dm^{-3} HCl was passed through the column until the pH of the effluent approached that of the influent. Then the column was washed with distilled water until the pH of the effluent became constant. The exchanger in the H^+ form thus prepared was air-dried and stored in a desiccator containing a saturated NaCl solution (relative humidity; 75% at 25 °C). The exchangers were used within 30 d after preparation, unless otherwise noted.

Specific Ion-exchange Capacity and Uptake Curves for Metal Ions. The exchanger (0.5 g) in the H^+ form was immersed into 50 cm^3 of different solutions, prepared by the desired mixed ratio of 0.1 mol dm^{-3} NaCl and 0.1 mol dm^{-3} NaOH, for 7 d at room temperature with intermittent shaking. This was followed by pH measurements and by the determination of the sodium ions. The sodium ions were converted to pure sodium chloride and indirectly determined by titrating the chloride ions. The amount of the ions taken up by the exchanger was evaluated from the difference between the initial and the final concentrations of the ions present in the solutions. The dissolved amount of the exchanger was evaluated from the amount of niobium in the supernatant solution which was determined spectrophotometrically by the sulfochlorophenol S method.[9] The limit of detection was 0.1 wt% of the exchanger used.

Analysis of Cl^- in the Exchanger. A sample of 0.5 g was dissolved by heating with 100 cm^3 of 9 mol dm^{-3} H_2SO_4 in a 500-cm^3 distilling flask, and the HCl evolving therefrom, carried by steam, was absorbed in a slightly alkaline solution and then determined spectrophotometrically using mercury(II) thiocyanate and ammonium iron(III) sulfate as coloring reagents. The limit of detection was 0.01 wt%.

Analysis of Water in the Exchanger. The water content was calculated from the weight loss at 850 °C in the TGA curves which were measured with 5 mg of sample in air at a heating rate of 10 °C min^{-1}.

Density. The apparent density of the exchangers was measured in the usual manner using a 25-cm^3 pycnometer.

Yield of the Exchangers. The yield was calculated on the basis of the recovery of niobium used.

Results and Discussion

Preparation of Hydrous Niobium(V) Oxide as an Ion Exchanger. The conditions for the precipitation, compositions and properties of the hydrous niobium(V) oxides are summarized in Table 1.

(I) Pyrohydrolysis of the Chloride Solution (the methods (1)—(6)): The semitransparent and gelatinous hydrous niobium(V) oxide was precipitated by heating 1 dm^3 of the hydrochloric acid solution of

Table 1. Comparison of various exchangers

Method No.[a)]	pH at precipitation	Boiling time / h	Composition	Ion-exchange capacity mmol Na^+/g		Yield	Density / g cm^{-3}
				pH 8.0	pH 10.0		
1	0.89	0.1	$Nb_2O_5 \cdot 5.3H_2O$	1.6	2.3	0.93	—
2	0.88	0.5	$Nb_2O_5 \cdot 4.7H_2O$	1.6	2.3	0.91	—
3	0.92	1	$Nb_2O_5 \cdot 4.7H_2O$	1.6	2.3	0.90	—
4	0.89	2	$Nb_2O_5 \cdot 4.7H_2O$	1.5	2.2	0.93	2.46±0.01
5	0.85	5	$Nb_2O_5 \cdot 4.6H_2O$	1.3	2.2	0.92	—
6	0.92	24	$Nb_2O_5 \cdot 4.1H_2O$	1.3	2.1	0.85	—
7	2.69	—	$Nb_2O_5 \cdot 6.7H_2O$	1.7	2.3	0.90	—
8	2.58	0.5	$Nb_2O_5 \cdot 6.4H_2O$	1.6	2.1	0.88	—
9	2.51	5	$Nb_2O_5 \cdot 5.5H_2O$	1.6	2.1	0.84	—
10	2.70	—	$Nb_2O_5 \cdot 5.6H_2O$	1.7	2.4	0.71	—
11	2.80	0.5	$Nb_2O_5 \cdot 4.4H_2O$	1.8	2.0	0.84	—
12	—	—	$Nb_2O_5 \cdot 5.7H_2O$	1.5	2.0	0.90	—
13	—	—	$Nb_2O_5 \cdot 4.9H_2O$	1.6	2.6	0.77	—
14	—	—	$Nb_2O_5 \cdot 4.3H_2O$	1.8	2.7	0.70	2.40±0.01

a) The method number corresponds to that in Fig. 1.

niobium in a 3-dm^3 round-bottom flask, equipped with a reflux condenser, for 0.1—24 h. When the precipitate was air-dried at room temperature, it turned into a light-creamy solid.

(II) Neutralization of the Chloride Solution (the methods (7)—(11)): The precipitate was made by hydrolyzing niobium ions in the hydrochloric acid solution with either a 1-mol dm^{-3} NaOH solution or 1-mol dm^{-3} NH_3 aq without refluxing the slurry (the methods (7) and (10)), the precipitate formed at a pH lower than 2.0 was partially lost during washing because of incomplete sedimentation. When the pH at the time of precipitation was higher than 5.0, the yield decreased due to the peptization during washing. When a NaOH solution was used for neutralization, a marked peptization occurred at a pH higher than 6.0 and, then, the yield fell to around zero at a pH higher than 9.0. On the other hand, when NH_3 aq was used, the yield always exceeded 50 per cent at any realizable pH value since the degree of peptization was slight. It can be concluded from the above observations that the desirable pH range at precipitation is 2.5 to 4.0. When the slurries were refluxed (the methods (8), (9), and (11)), the precipitate obtained at a pH as low as 1.0 to 2.0 did not peptize during washing, and the yield exceeded 80 per cent. The air-dried products obtained by the neutralization with NH_3 aq solution were the semitransparent and glassy solid, while those produced by the neutralization with NaOH solution were white, opaque, and brittle like chalk.

(III) Precipitation from Ethanolic Solution of $NbCl_5$: Three cubic decimetres of the starting solution were diluted with distilled water to make total volume 5 dm^3, and it was allowed to stand for 2 d at room temperature. Then, the gelation of the solution took place and, when the precipitate was air-dried, the glassy and semitransparent solid was obtained.

The amount of chloride ions included in the exchanger in the H^+ form synthesized from the HCl-system was below the detection limit (0.01 wt%).

(IV) Precipitation from Sulfuric Acid Solution: The sulfuric solution of niobium was diluted with distilled water to make a total volume of 2 dm^3 and stood for 1 d at room temperature to complete precipitation. The precipitate (air-dried at room temperature) was glassy solid; the solids obtained from methods (13) and (14) were pale purple and light brown, respectivery, in color. The yield in the H_2SO_4-system was appreciably lower than that in the other systems. This is attributable to the lengthy washing of the precipitate due to the difficulty to remove the sulfate ions included in the precipitate.

Ion-exchange Properties. Figure 2 shows the uptake curves for Na^+ of the exchangers prepared by the neutralization of $NbCl_5$ with alkaline solutions (the methods (7), (8), (10), and (11)). These materials were weakly acidic ion exchangers having at least two kinds of dissociable hydrogen atoms, since the inflection points existed in the curves at around pH 8. In the extremely high pH region, the specific ion-exchange capacity decreased with the pH. As will be shown later, this is attributed to the dissolution of a part of the exchanger. This observation was common to all exchangers prepared by any methods except those prepared from the H_2SO_4-system. The uptake curves of the exchangers prepared from methods (8) and (11) indicated that the boiling procedure reduced the ion-exchange capacity in the whole pH range by a total amount of 0.4 mmol Na^+ g^{-1}, instead, it stabilized the exchanger in alkaline solutions. The stabilization by aging, therefore, is accompanied by the degradation of some of the ion-exchange sites. Figure 3 compares the uptake curves of the exchangers obtained without using alkaline solutions. The ion-exchange capacities of the materials prepared by the pyrohydrolysis of the $NbCl_5$ solution (the methods (1), (3), and (6)) gradually decreased with the length of the boiling period and were slightly smaller than those of the exchangers prepared by the hydrolysis of the $NbCl_5$ solution with alkaline solutions. Furthermore, when the slurries were boiled for longer than 1 h, the degree of the decrease in the ion-exchange capacity in the highly alkaline region became very small, probably due to the stabilization of the exchanger in alkaline solutions. This figure also shown that the exchanger prepared from the H_2SO_4-system had the largest ion-exchange capacity throughout the pH range examined, and that it was most stable in alkaline solutions, since the ion-exchange capacity did not decrease in highly alkaline solutions. The ion-exchange capacities at a pH higher than 9 were appreciably smaller for the exchanger precipitated from the ethanolic solution of $NbCl_5$ than for the materials prepared by the pyrohydrolysis of $NbCl_5$ solution.

Water Content. The water contents in the exchangers are summarized in Table 1. It should be noted that the values in the table are not precise enough to determine the stoichiometry of the compounds since they were obtained during thermal nonequilibrium, the TGA method. However, they are useful for comparative purposes. Table 1 indicates that the water content differs greatly with the synthesis method, that is, 4.5—6.7 mol H_2O per mol Nb_2O_5. As a definite correlation between the water content and the ion-exchange capacity was not observed, it may be considered that a large part of the water does not take part in the ion-exchange reaction.

The exchangers prepared from the H_2SO_4-system have the best property as an ion exchanger, that is, they have the largest ion-exchange capacity and are most stable in alkaline solutions. The method, however, has a serious disadvantage due to a very complicated and lengthy procedure, whereas the synthesis by pyrohydrolysis is very simple. From a practical point of view, the advantages due to the simplicity and rapidity of the procedure in the latter method more than offset the demerits of smaller ion-exchange capacity. Efforts were then concentrated on determining the properties of the exchangers prepared from this system.

Physical Properties. Table 2 shows examples of the size distribution of the particles formed when a gel prepared from method (4) was immersed in water. It is evident from this table that a large part of the exchanger invariably possesses particles large enough for use in column operation. The density of the exchanger in the H^+ form was 2.46±0.01 g cm^{-3}.

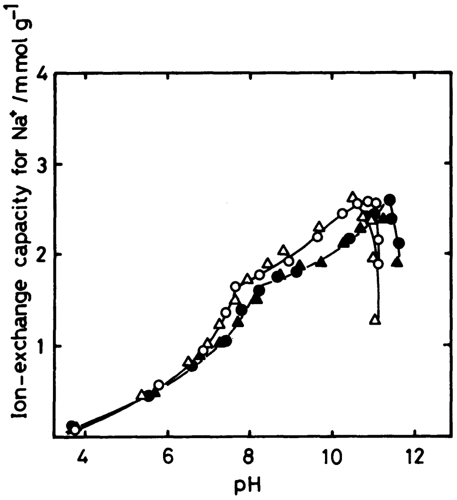

Fig. 2. Uptake curves of various exchangers for Na^+. Method number; ○: (7), ●: (8), △: (10), ▲: (11). The numbers are the same as those in Fig. 1.

TABLE 2. SIZE DISTRIBUTION OF THE EXCHANGER BEFORE GRINDING (THE METHOD (4) IN FIG. 1)

Batch number	Particle size(mesh)/wt%			
	≈42	42—100	100—200	200≈
1	87.7	10.5	1.2	0.2
2	86.4	11.8	1.2	0.6

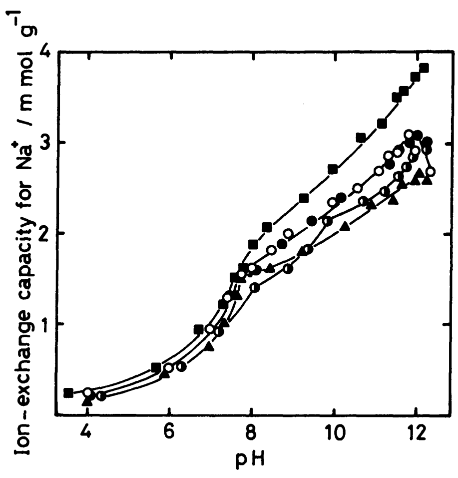

Fig. 3. Uptake curves of various exchangers for Na^+. Method number; ○: (1), ●: (3), ◑: (6), ▲: (12), ■: (14). The numbers are the same as those in Fig. 1.

Chemical Stability. To examine the chemical stability of the exchanger, the amount of niobium dissolved in various reagents was measured using the exchangers prepared by methods (3) and (14). The amount of niobium dissolved in the MOH–MCl solution (M=Li, Na, K) of ionic strength 0.1 is shown in Fig. 4, where the dotted line indicates the detection limit (0.1 wt%). The exchanger prepared from method (3) was stable up to a pH of 10.0, 10.5, or 10.8, respectively, for M=Li^+, Na^+, and K^+. This indicates that the kind of alkali metals in the solution greatly affects the stability of the exchanger. On the other hand, the exchanger prepared from method (14) was fairly stable in an alkaline solution; even at a pH as high as 11.9. Only 0.2 wt% of the exchanger was dissolved. As is shown in Table 3, the exchangers prepared from any method were unstable in a 0.1 mol dm^{-3} NaOH solution, but fairly stable in a 1 mol dm^{-3} NH_3 aq solution. To further examine the stability in various acids, measurements were made of the amount of niobium in typical mineral and organic acids. The results, also shown in Table 3, indicate that both exchangers were very stable against 1 mol dm^{-3} mineral acids but dissolved appreciably into organic acids, particularly into oxalic acid. This fact shows that the exchanger is easily attacked by acids with a strong tendency to complex Nb(V).

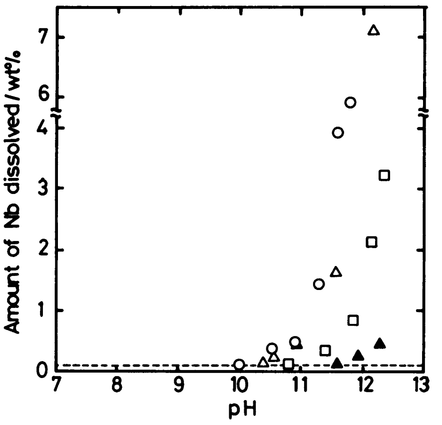

Fig. 4. Chemical stability against MOH-MCl mixed solution (M: Li, Na, K) at room temperature. Cation; ○: Li^+, △: Na^+, □: K^+. Exchanger; open mark: the method (3), filled mark: the method (14). The numbers are the same as those in Fig. 1.

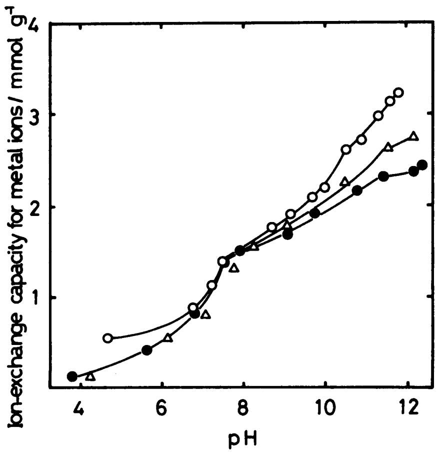

Fig. 5. Uptake curves for various alkali metal ions. Cation; ○: Li^+, △: Na^+, ●: K^+. Exchanger: The method (4) in Fig. 1.

Uptake Curves for Various Alkali Metal Ions. In order to compare the ion-exchange behavior of alkali metal ions, uptake curves were obtained for Li^+ and K^+, as is shown in Fig. 5. The ion-exchange capacities for these cations decreased in the order of $Li^+>Na^+>K^+$. This figure also shows that the pH of the inflection point in the curves was independent of the kinds of the exchanging cations and the difference of the ion-exchange capacities was mainly brought about in the pH range higher than that point. This observation can be understood by considering that the weakly dissociable sites are the hydroxyl groups which form olation bonds in the exchanger. When anhydrated cations are exchanged with H^+ from these hydroxyl groups, some of the olation bonds are severed, enhancing the tendency to dissolve into the solution; this tendency is compatible with the order of the ability of alkali metal ions to dissolve the exchanger.

Change in Capacities During Storage. As the hydrous oxide is thermodynamically metastable, the ion-exchange capacity is expected to decrease during storage; in fact hydrous titanium(IV) oxide in the H^+ form was reported to lose its cation-exchange capacity appreciably during storage in air.[10] Figure 6 shows the result for material prepared from method (4), which was stored for 300 d over a saturated NaCl

TABLE 3. CHEMICAL STABILITY AT ROOM TEMPERATURE[a)]

Solution		Amount of Nb dissolved/wt%	
Reagent	Concentration mol dm^{-3}	Method (3)	Method (14)
NaOH	0.10	41.4	88.3
NH_3 aq	1.0	0.5	0.2
HCl	1.0	<0.1	<0.1
H_2SO_4	0.56	<0.1	<0.1
HNO_3	0.94	<0.1	0.1
Tartaric acid	0.5	6.6	0.5
Oxalic acid	0.5	100	100
Citric acid	0.5	1.4	0.1

a) Exchanger: −100+200 mesh, H^+ form, 0.50 g. Solution: 50 cm^3. Contact time: 7 d.

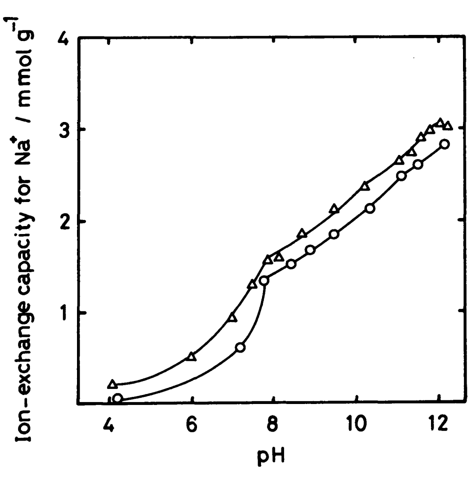

Fig. 6. Effect of storage time on the uptake curves of the method (4) exchanger for Na^+.
△: 30 d after the synthesis. ○: 300 d after the synthesis.

TABLE 4. REPRODUCIBILITY OF THE SYNTHESIS (THE METHOD (4))

Batch number	Composition	Ion-exchange capacity		Yield
		mmol Na^+/g		
		pH 8.0	pH 10.0	
1[a]	$Nb_2O_5 \cdot 4.7H_2O$	1.5	2.2	0.93
2[a]	$Nb_2O_5 \cdot 4.7H_2O$	1.5	2.2	0.95
3[b]	$Nb_2O_5 \cdot 5.2H_2O$	1.5	2.2	0.98
4[b]	$Nb_2O_5 \cdot 5.2H_2O$	1.5	2.2	0.97

a) Synthesis on the 5th of January in 1981. b) Synthesis on the 6th of October in 1980.

solution. This figure reveals that the ion-exchange capacity in a pH region lower than the inflection point decreased a little during storage. The stability in alkaline solutions was improved slightly. The storage, however, did not affect at all the stabilities of the exchanger in other reagents.

Recommended Synthetic Method. It is concluded that the exchanger precipitated from the concentrated sulfuric acid solution of niobium is best with respect to the ion-exchange capacity and the chemical stability. This method, however, is of no use in preparing a hydrous niobium(V) oxide as an ion exchanger because of the tedious procedure (due to the difficulty in preparing a sulfuric acid solution of niobium in high concentration and the lengthy washing of the precipitate). The method for the pyrohydrolysis of a $NbCl_5$ solution is considered practical since a large amount of pure hydrous niobium(V) oxide can be easily prepared without suffering much from the defects of low ion-exchange capacity and chemical unstability.

In the method regarding pyrohydrolysis, an increase in the boiling period improves the stability for highly alkaline solutions, but reduces the ion-exchange capacity of the product; hence, by a mutual concession between them, method (4), where the $NbCl_5$ solution was thermally hydrolyzed by boiling for 2 h, was chosen as the recommended procedure for synthesizing a hydrous niobium(V) oxide ion exchanger. Table 4 shows the reproducibility of the synthesis by this method. The variation of the water content may be ascribed to the sensitivity of the amount of occluded water to the conditions of the work environment (such as temperature and humidity) since the same water content was observed for exchangers prepared in different batches at a same time. The fluctuation in the yield is a natural consequence of the irregularity in the recovery of a precipitate at the time of repeated washing. As the ion-exchange capacities of the products agree well with each other, a synthesis using method (4) can be regarded as reproducible.

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