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Studies of Hydrous Tin(IV) Oxide Ion-exchangers. I. A Method for Synthesis and Some Properties

Yasushi Inoue* and Hiromichi Yamazaki
Department of Nuclear Engineering, Faculty of Engineering, Tohoku University, Aramaki, Sendai 980

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A comprehensive study of the preparation of hydrous tin(IV) oxide ion-exchangers was made by using eight systems: (1)$Na_2[Sn(OH)_6]$–H_2SO_4, (2)$Na_2[Sn(OH)_6]$–H_2SO_4(boiling), (3)$Na_2[Sn(OH)_6]$–HCl, (4)$Na_2[Sn(OH)_6]$–CH_3COOH, (5)$SnCl_4$–NaOH, (6)$SnCl_4$–NH_3aq, (7)$SnCl_4$–NH_3aq(boiling), and (8)$SnCl_4$–pyrohydrolysis. From a detailed examination of the dependency of the yield, the ion-exchange behavior toward Na^+ and Cl^- ions, the composition, and some other properties on the conditions for precipitation, it was found that the ion-exchange characteristics are similar among materials produced from the systems from (1) through (7) if we neglect some aging effect of boiling, while the difficulty of synthesis differs according to the systems. The materials obtained from the (8) system, however, showed titration curves different from those for the exchanges obtained from the other systems and had less cation-exchange capacity for Na^+ by 20 per cent. From these results, it is concluded that the simplicity of the synthetic procedures in the most important criterion for choosing the best conditions for preparing the exchanger.

Many hydrous oxides for use as ion-exchange materials have been investigated because of their unique characteristics of selectivity and the simplicity of preparation. They have, however, the serious disadvantage of giving inconsistent results to different investigators. This may be due to irreproducibility of the synthesis. Nevertheless, many authors do not describe the details of the investigations concerning synthesis. To promote further investigation of this group of ion-exchange materials, it is indispensable to reexamine the synthetic conditions for establishing reproducible methods. With this point in mind, one of the present authors previously successfully studied hydrous titanium(IV) oxide in establishing a satisfactory method of synthesis.[1] Several studies have been carried out on hydrous tin(IV) oxide[3–9] since the work of Kraus *et al.*, who first reported the amphoteric ion-exchange property of this material.[2] In this case, also, different compositions and ion-exchange properties were reported by each investigator. This induced us to undertake a thorough study of the synthesis of hydrous tin(IV) oxide.

This paper will describe the results of one investigation to establish the best conditions for the synthesis by varying such factors as the starting materials, the methods of hydrolysis, the pH values of precipitation, and the concentrations of the hydrolyzing reagents, as well as aging.

Experimental

Reagents and Apparatus. $Na_2[Sn(OH)_6]$ was purified by recrystallization.[10] The other chemicals were of the highest purity grade and were used without further purification. The pH values were measured with a Toa Dempa model HM-5BS pH meter. The atomic absorption measurements were made with a Nippon Jarrell-Ash model AA-782 atomic-absorption and a flame-emission spectrophotometer, while the other absorption measurements were carried out with a Hitachi model 124 double-beam spectrophotometer.

Synthesis of Hydrous Tin(IV) Oxide. The synthetic systems adopted in the present investigation are shown schematically in Fig. 1. In the systems from (1) through (3), hydrous tin(IV) oxide was precipitated by hydrolyzing a $Na_2[Sn(OH)_6]$ solution by the addition of different acids, while in the (4) and (5) systems, the precipitate was made by hydrolyzing $SnCl_4$ solution by the addition of alkaline solutions. In some cases the slurries thus obtained were refluxed for five hours; the methods of precipitation of the (7) and (8) systems are similar to those of the (1) and (5) systems respectively. In the (6) system, the oxide was precipitated by the pyrohydrolysis of the $SnCl_4$ solution.

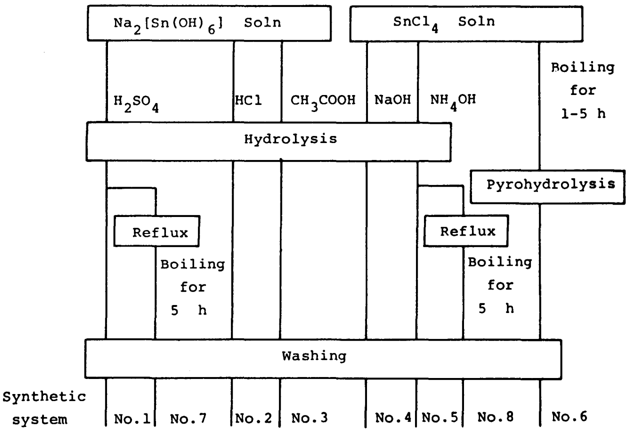

Fig. 1. Method of synthesis.

After precipitation had been completed, the precipitate was washed and dried by the following procedure unless otherwise noted. After being separated from the mother liquor by a 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 impurity was detected in the filtrate. Then the precipitate was sufficiently 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. At this stage the yield was calculated. 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 water to remove any adherent powder. The slurry was poured into a glass tube, 10 mm in inside diameter and 15 cm high, with glass-wool plugging for column support. Then, 0.1 M (1 M = 1 mol dm^{-3}) HCl was passed through the column until the pH of the effluent approached that of the influent at a flow rate of about 1 cm^3 min^{-1}. Then the column was washed with water until the effluent showed a constant pH value (about 5). The exchanger in H^+ form thus prepared was air-dried and stored in a desiccator containing a saturated NH_4Cl solution (relative humidity, 79% at 25 °C).

Specific Ion-exchange Capacity and Titration Curves. A quarter gram of the exchanger in H^+ form was immersed in 30 cm^3 of various solutions, prepared by the desired combination of 0.1 M NaCl, and 0.1 M NaOH or 0.1 M HCl, for 4 d at room temperature with intermittent shaking. This was followed by pH measurements and by the determination of the sodium or chloride ions. The chloride concentrations were determined by the Fajans' method after the solution had been neutralized. 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 final concentrations of the respective ions present in the solution. The amount of the exchanger dissolved was also evaluated from the amount of tin dissolved in the supernatant solution spectrophotometrically by the phenylfluorone method.[11)] The limit of detection was 0.05 wt% of the exchanger used.

Total Analysis of the Exchanger. *Na^+ and SO_4^{2-}*: A half gram of the exchanger was dissolved in hydrobromic acid containing 10% bromine. The Na^+ concentration in this solution was determined atomic absorption-spectrophotometrically, while the absence of SO_4^{2-} ions was checked by adding a $BaCl_2$ solution. The limit of detection was 0.01 wt% for Na^+ and 0.005 wt% for SO_4^{2-}.

Cl^-: A sample of 0.5 g was dissolved by heating with 100 cm^3 of 9 M 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 spectrophoto-metrically, using mercury(II) thiocyanate and ammonium iron(III) sulfate as coloring reagents. The limit of detection was 0.02 wt%.

Water: A sample of 0.25 g was ignited at 850 °C, and the water content was calculated from the weight loss. The validity of the procedure had been confirmed thermogravimetrically.

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

Results and Discussion

Precipitation Behavior in Various Synthetic Systems. It is required for practical purposes that a large amount of pure hydrous tin(IV) oxide can be prepared readily in a high yield; especially, the precipitation conditions should be such that the precipitate can be easily washed without peptization. For this reason, the yield evaluated from only the solubility loss is impractical; the yield should include all losses resulting from the whole synthetic processes. With this in view, we examined the relation between the yield and the conditions of precipitation for the synthetic systems shown in Fig. 1.

In this experiment, the solution of tin and a solution of acid or base of a suitable concentration were mixed together to make a total volume of 50 cm^3. The precipitate thus formed was then treated by the method described in the Experimental section. The yield was measured on the basis of the recovery of tin. Figure 2 shows the results for the (2) system. In this figure, the concentrations of tin and hydrochloric acid in the mixed solution were taken as the abscissa and the ordinate respectively. The area of the figure was distinguished into four regions based on the overall yield.

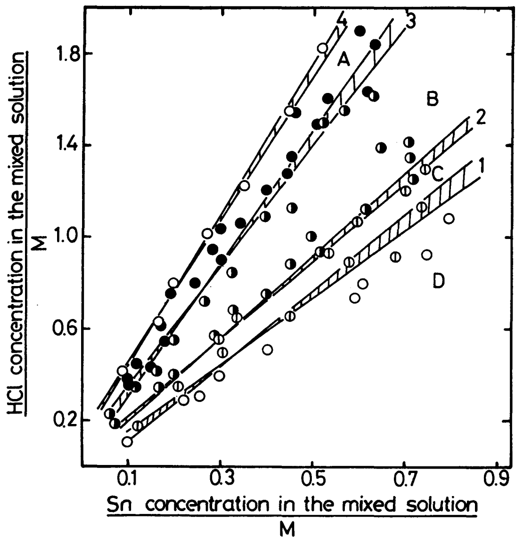

Fig. 2. Dependence of the yield of hydrous tin(IV) oxide on the conditions for precipitation (system (2)). Yield; ○: zero, ⦶: <0.2, ◑: <0.6, ●: >0.8. Molar ratio ([HCl]/[Sn^{4+}]); 1: 1.5—1.7, 2: 1.7—1.8, 3: 2.7—3.0, 4: 3.3—3.4. For A, B, C, and D, see text.

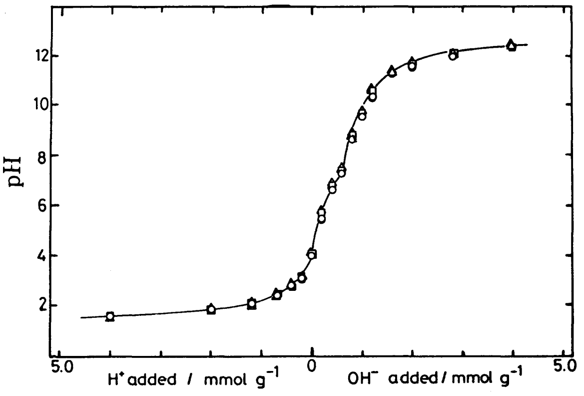

Fig. 3. Titration curves.
○: System (1) (pH=3.8), ●: system (2) (pH=3.8), □: system (3) (pH=4.6), △: system (4) (pH=3.5), ▲: system (5) (pH=3.5), ( ) shows the pH value at precipitation.

Region A: The precipitate could be washed without peptization until no impurity was detected in the filtrate, and the yield exceeded 80%. Thus, this is the optimum region.

Region B: The precipitate peptized during washing, and the yield was 20—80%.

Region C: The precipitate peptized at an early stage of washing, and the yield fell below 20%.

Region D: No precipitate was formed at all. Figures similar to Fig. 2 were made for every synthetic system; the results are summarized in Table 1. The appraisal of the synthetic system is made by a comparison of the area of Region A, because the experimental conditions can be more easily set up for a system having the larger

Table 1. Summary of the precipitation behavior

	Synthetic system	Sn concn[a] M	Molar ratio[b]	pH[c]
Experimental conditions	(1)	0.08—0.8	0.4—3.8	0.4—12
	(2)	0.08—0.8	1.2—3.8	0.4—12
	(3)	0.08—0.8	1.2—6.0	3.7—12
	(4)	0.05—0.5	2.0—6.0	0.5—12
	(5)	0.05—0.5	2.0—6.0	0.5—10
	(6)	9.3×10^{-3}—0.2	—	—
Region-A	(1)	0.08—0.8	>0.96∼1.0	<3.5∼4.0
	(2)	0.08—0.8	2.5∼3.0—3.3∼3.4	0.4∼0.5—0.7∼1.0
	(3)	—	—	—
	(4)	0.05—0.3	3.0∼3.5—4.5∼4.8	0.8∼1.1—4.4∼4.7
	(5)	0.05—0.5	3.0∼3.5—4.2∼4.5	0.9∼1.1—4.5∼4.7
	(6)	<0.10	—	—
Region-B	(1)	0.08—0.8	0.90∼0.95—0.96∼1.0	3.5∼4.0—4.5∼6.5
	(2)	0.08—0.8	1.7∼1.8—2.5∼3.0	0.7∼1.0—6.0∼7.0
	(3)	0.08—0.8	2.2<	<5.0∼6.0
	(4)	0.3 —0.5	3.0∼3.5—4.5∼4.8	0.8∼1.1—4.4∼4.7
	(5)	0.05—0.5	4.2∼4.5—4.7	4.5∼4.7—7.0∼7.2
Region-C	(1)	0.08—0.8	0.6∼0.7—0.90∼0.95	4.5∼6.5—10.5∼11.5
	(2)	0.08—0.8	1.5∼1.6—1.7∼1.8	6.0∼7.0—10.0∼11.5
	(3)	0.08—0.8	1.5∼1.7—2.2	5.0∼6.0—10.0∼11.5
	(4)	0.05—0.5	4.5∼4.8<	4.4∼4.7<
	(5)	0.05—0.5	4.7<	7.0<
Region-D	(1)	0.08—0.8	<0.6∼0.7	>10.5∼11.5
	(2)	0.08—0.8	<1.5∼1.6	>10.5∼11.5
	(3)	0.08—0.8	<1.5∼1.7	>10.0∼11.7
	(4)	0.05—0.5	<3.0∼3.3	<0.8
	(5)	0.05—0.5	<3.0∼3.5	<0.9∼1.1

a) The concentration in the mixed solution. b) [Acid] or [alkali]/[tin]. c) The pH range at precipitation when the Sn concn and molar ratio were in the range shown in the left columns.

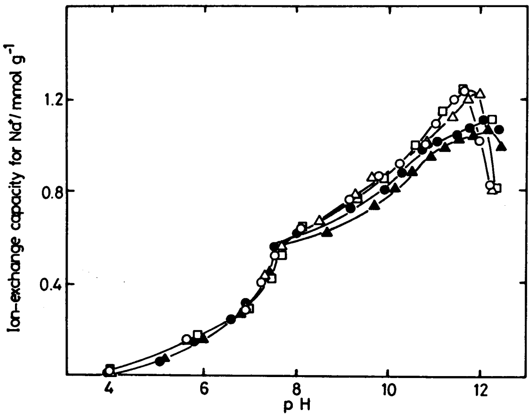

Fig. 4. Uptake curves of various exchangers for Na^+ ions. ○: System (1) ([Sn]=0.28 M, pH=3.8), □: system (4) ([Sn]=0.19 M, pH=3.0), △: system (5) ([Sn]=0.23 M, pH=3.1), ●: system (7) ([Sn]=0.26 M, pH=3.5), ▲: system (8) ([Sn]=0.26 M, pH=3.1), ( ) shows the conditions for precipitation.

area of this region. Table 1 reveals that the (1) and (5) systems have A regions relatively large compared with other systems. The (1) system, however, has a defect in that it must be washed nearly three times as much as other systems before any impurities are removed. This makes the whole procedure unduly long. On the other hand, the area of Region A is small in the (2) and (4) systems due to the peptization of the precipitate; in the latter system, the concentration of tin is limited to the rather low value of 0.3 M since the peptization increases its prominence with an increase in the concentration. In the (6) system, Region A is found only in a concentration less than 0.1 M. Region A does not exist in the (3) system.

Ion-exchange Properties. The titration curves for the exchangers prepared from the systems from (1) through (5) are shown in Fig. 3. This indicates that no variations in the titration curves are observed between different systems and that the exchangers have at least two dissociable hydrogen atoms, since the inflection points exist in the curves at pH 7.5—8.0. Figure 4 shows the uptake curves for sodium ions as a function of the pH. These curves correspond to those in Fig. 3 except in the extremely high pH region, where the specific ion-exchange capacity decreases with the pH. This observation is attributable to the dissolution of a part of the exchanger, which was verified by analyzing the amount of tin dissolved in the supernatant solution; about 8 wt% of the exchanger was dissolved at pH 12.3. Figure 4 also shows that the exchanger possesses the maximum cation-exchange capacity of 1.17—1.25 mmol Na^+/g.

The anion-exchange property is not clearly observed in the titration curves. The uptake curves for chloride ions (Fig. 5), however, do indicate anion exchanges

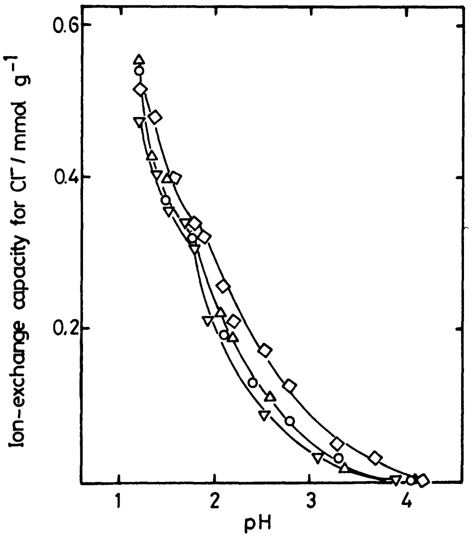

Fig. 5. Uptake curves of various exchangers for Cl^- ions. ○: System (1) ([Sn]=0.28 M, pH=3.8), △: system (5) ([Sn]=0.23 M, pH=3.1), ▽: system (8) ([Sn]=0.26 M, pH=3.1), ◇: system (6) ([Sn]=0.048 M, pH=1.2), ( ) shows the conditions for precipitation.

which occurs in two steps, an inflection point being at about 0.3 mmol Cl^-/g. The anion-exchange capacity is 0.56—0.60 mmol Cl^-/g at pH 1.2.

Sharygin[7] and Jaffrezic-Renault[8,9] reported the multiple cation-exchange behavior. They observed a maximum cation-exchange capacity similar to ours, but two inflection points in the titration curves showing three cation-exchange stages. On the other hand, anion-exchange capacity, 0.3—0.7 mmol/g, for the chloride ion in the vicinity of pH 1 was reported, but the multiple steps were not observed for anion exchange.[2,3,5,9] The reason for the contradiction between the published data and the present results is not clear, but it may be the difference in the details of the experimental procedure. In any event, this material is an amphoteric ion-exchanger possessing at least two weakly dissociable ion-exchange sites. The isoelectric point exists close to pH 4, as can be seen from Figs. 4 and 5. Hereafter, we will concentrate our discussion mainly on the cation-exchange properties because of the large ion-exchange capacity and the convenience of experimentation. For convenience, the cation exchange in the pH region lower than the inflection point will be referred as the first stage, and that in the higher pH region, as the second stage.

The uptake curves of the exchangers prepared from the (7) and (8) systems are shown in Fig. 4, which indicates that the boiling does not affect the first stage, but diminishes the ion-exchange capacity of the second stage by a total amount of 0.15 mmol/g. These findings suggest that the weak dissociable exchange sites are liable to be destroyed by aging. In these exchangers, the degree of the decrease in the ion-exchange capacity in the highly alkaline region becomes small, probably because of the stabilization of the exchanger against alkaline solutions; actually, all kinds of exchangers were dissolved only as much as 2 wt% at pH 12.5. It is, therefore, considered that the stabilization by aging is accompanied by the degradation of some of the weakly acidic sites. It is concluded that the hydrolysis by neutralization, with the exception of the decrease in the cation-exchange capacity by aging, leads to the exchangers having essentially the same ion-exchange characteristics regardless of the systems employed. The (1) and (5) systems being thus found to be most promising on account of the ease with which the precipitating conditions can be set up, efforts were then concentrated on elecidating the relation between the synthetic conditions (the effect of pH and the concentration of tin) and exchange properties with these systems in detail.

Table 2. The effect of pH at precipitation on ion-exchange capacity and water content (system (5))

Synthetic conditions Molar ratio $[NH_3aq][Sn]^{-1}$	$pH^{a)}$	Composition $\frac{mol\ H_2O}{mol\ SnO_2}$	Ion-exchange capacity for Na^+ pH	mmol g^{-1}
3.7	1.2	2.01±0.02	7.6	0.56
			11.6	1.22
4.0	2.6	2.23±0.01	7.5	0.57
			11.6	1.24
$4.0^{b)}$	2.6	2.19±0.01	7.6	0.64
			11.8	1.19
4.4	4.7	2.30±0.01	7.6	0.62
			11.6	1.25
4.7	7.7	2.29±0.02	7.8	0.80
			11.6	1.39
$4.7^{b)}$	7.4	2.09±0.02	7.7	0.71
			11.7	1.30
7.0	9.4	2.33±0.01	8.0	0.82
			11.6	1.34

a) pH at precipitation. b) Washed.

The effect of the pH at precipitation was examined for the (1) and (5) systems. For the (1) system, this effect was not observed to any appreciable extent on the titration-and uptake curves. The effect of the pH was, however, observed for the (5) system. The experiments carried out to examine this effect are presented in Table 2. The uptake curves are shown in Fig. 6, which reveals nearly the same curves for all the exchangers precipitated at pH values lower than 2.6. For those precipitated at a pH higher than 2.6, however, the ion-exchange capacity increases with the pH at the precipitation. Table 2 also shows the interesting fact that the water content of the exchanger increases with the pH at the precipitation. In order to examine the aging effect of washing, the uptake curves of the (5) system were compared for samples with or without washing. It is revealed from this comparison that the washing results in a slight lowering of the ion-exchange capacity in the region of high pH values. As is shown in Table 2, the water content also decreases by washing.

The effect of the concentration of tin in the mixed solution was then studied at the conditions shown in Table 3. The concentration of tin did not appreciably affect the titration curves, but it did influence the

TABLE 3. THE EFFECT OF TIN CONCENTRATION ON THE PHYSICAL PROPERTIES (SYSTEM (1))

Synthetic conditions			Physical properties						
Sn^{4+} concn	Molar ratio	pH$^{a)}$	Glassy luster	Distribution of particle size (mesh)/wt%$^{b)}$					Density of H^+ form
M	$[H_2SO_4][Sn]^{-1}$			−65	65—100	100—200	200—350	350—	g cm^{-3}
0.10	1.0	3.8	o	98	1.0	0.8	0.1	0.1	3.23±0.06
0.28	1.0	3.8	o	98	1.0	0.5	0.3	0.2	3.31±0.06
0.53	1.0	3.8	x	85	6.5	4.5	1.8	2.2	3.06±0.06

a) pH at precipitation. b) The distribution of grain size when the air-dried materials were immersed in water.

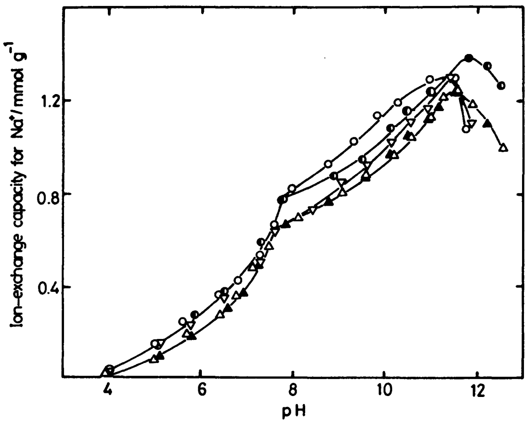

Fig. 6. Effect of pH at precipitation on the uptake curves of the system (5) exchanger for Na^+ ions.
pH at precipitation; ▲: 1.2, △: 2.6, ▽: 4.7, ◐: 7.8, ○: 9.4.

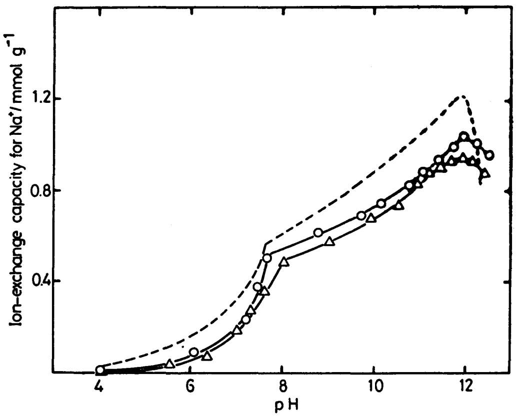

Fig. 7. Uptake curves of the system (6) exchanger for Na^+ ions.
○: Boiled for 1 h, △: Boiled for 5 h, ----: system (5).

physical properties; the exchangers precipitated from the solution of a high concentration of tin (0.53 M), possess no glassy luster and a low density (3.06±0.06 g/cm^3), in contrast with those precipitated from the dilute solution of tin, which have densities of 3.26—3.31 (g/cm^3) and a large, glassy grain. Table 3 shows an example of the size distribution of the exchanger before grinding in a porcelain mortar. It is evident from this table that the distribution of particle size extends to a smaller range with materials obtained from a tin solution of a higher concentration. Similar results were obtained for other systems. Thus, the concentration of tin at the precipitation affects the physical properties, but not the ion exchange.

Figure 7 shows the uptake curves of the exchangers prepared by hydrolyzing a 4.8×10^{-2} M $SnCl_4$ solution by boiling for one or five hours with refluxing (the (6) system). The ion-exchange capacities of these materials are smaller than those of others by 0.05—0.1 mmol/g at the first stage and 0.2—0.3 mmol/g at the second stage. Hence, the numbers of exchange sites of this exchanger are small throughout the pH range examined as compared with those precipitated by neutralization. As the drop of the ion-exchange capacity at pH values higher than 11 is slight, the stability against an alkaline solution appears to be improved to some extent. Actually, the amount of the exchanger dissolved in the solution with a pH of 12.8 was only 1 wt%. The smaller ion-exchange capacity at the first stage in addition to the second suggests the formation of an exchanger with distinctive characteristics.

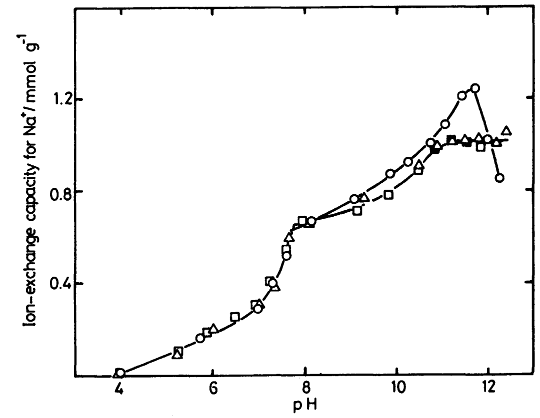

Fig. 8. Effect of storage time on the uptake curves of the system (1) exchanger for Na^+ ions.
○: Immediately after the synthesis, ([Sn]=0.53 M), △: 430 d after the synthesis, ([Sn]=0.28 M), □: 450 d after the synthesis, ([Sn]=0.43 M).

Stability in Air. Inoue and Yamazaki reported that the hydrous titanium(IV) oxide in the H^+ form lost its cation-exchange capacity appreciably during storage in air.[12] As the exchanger in the present study is the same type of compound as hydrous titanium(IV) oxide and is subjected to some aging effect by boiling with the mother solution, the ion-exchange capacity is expected to decrease during storage. Figure 8 shows the results for the materials prepared from the (1) system, which was stored over a saturated NH_4Cl solution. The ion-exchange capacity decreased by 0.1—0.2 mmol/g in the second stage 15 months after the prepara-

Table 4. Summary of synthesis

System[a]	Synthetic conditions		Composition of H^+ form			Density $\frac{}{\text{g cm}^{-1}}$	Acidity[d]	Ion-exchange capacity for Na^+ ion	
	$\frac{Sn^{4+} \text{ concn}^{b)}}{M}$	pH[c]	$\frac{Na^+}{wt\%}$	$\frac{Cl^- \text{ or } SO_4^{2-}}{wt\%}$	$\frac{H_2O \text{ (mol)}}{SnO_2 \text{ (mol)}}$			pH	mmol g^{-1}
(1)	0.10	3.8	1.2×10^{-2}	L.D.[g]	—	—	3.97	11.5	1.14 ± 0.03
(1)	0.28	3.8	L.D.	—	2.43 ± 0.01	3.23 ± 0.07	4.00	11.1	1.10 ± 0.02
(1)	0.53	3.7	1.3×10^{-2}	L.D.	2.41 ± 0.01	3.06 ± 0.06	4.00	11.5	1.24 ± 0.03
(2)	0.10	3.5	L.D.	L.D.	2.29 ± 0.02	3.31 ± 0.06	4.00	10.6	1.02 ± 0.02
(3)	0.10	4.6	—	—	1.97 ± 0.02	—	4.08	10.9	0.96 ± 0.02
(4)	0.19	3.0	2.2×10^{-2}	—	2.12 ± 0.02	—	4.07	11.6	1.25 ± 0.02
(5)	0.23	3.1	—	4.7×10^{-2}	2.18 ± 0.02	3.36 ± 0.06	4.03	11.3	1.18 ± 0.02
(6)[e]	0.048	1.2	—	L.D.	1.94 ± 0.02	—	4.11	11.7	0.99 ± 0.02
(6)[f]	0.048	1.2	—	2.7×10^{-2}	1.93 ± 0.02	3.53 ± 0.06	4.13	11.9	0.92 ± 0.02
(7)	0.26	3.5	L.D.	—	1.94 ± 0.02	3.58 ± 0.07	3.90	11.8	1.08 ± 0.02
(8)	0.26	3.1	—	—	1.90 ± 0.02	3.61 ± 0.06	3.94	11.6	1.01 ± 0.02

a) The numbers are the same as those in Fig. 1. b) The concentration in the mixed solution. c) pH at precipitation. d) The equilibrium pH of the supernatant solution when the exchangers are immersed in 0.1 M NaCl. e) Boiled for 1 h. f) Boiled for 5 h. g) Limit of detection, SO_4^{2-}: 5×10^{-3} wt%, Cl^-: 1.5×10^{-2} wt%, Na^+: 1×10^{-2} wt%.

tion. This aging effect is similar to that by boiling, but it is not as abrupt as in hydrous titanium(IV) oxide. The result is compatible with Fuller's observation that the capacity for Cu(II) decreased by 0.18 mmol/g after 200 d of preparation.[5]

Composition and Other Properties. The purity, water content, density, and acidity (the equilibrium pH of the supernatant solution when the exchangers are immersed in 0.1 M NaCl) were measured. The results are summarized in Table 4, along with the ion-exchange capacity for Na^+ ions at pH 11. The amount of impurities was below or near the limit of detection.

As to the water content, a variety of papers have been published. According to Donaldson and Fuller, 17% of the water was contained in the exchanger prepared by a method similar to that used in our (1) system.[5] Sautereau *et al.* reported that the composition of α-stannic acid, prepared by a method similar to that used in (5) system, was $SnO_2\cdot1.78H_2O$.[13] Durand and Masdupuy obtained an exchanger whose composition was $H_2[Sn(OH)_6]$ by adding aqueous ammonia to a solution of $SnCl_4$ to make pH 5—6.[14] Abe and Ito obtained the composition of $SnO_2\cdot1.8H_2O$ for α-stannic acid.[3] Mikhail *et al.* obtained an exchanger whose composition was $SnO_2\cdot1.66H_2O$.[15] Goodman and Gregg prepared hydrous tin(IV) oxide with the composition of $SnO_2\cdot1.0$—$1.3H_2O$ by hydrolyzing tin(IV) ethoxide and by drying the precipitate at 25 °C.[16] Weiser and Milligan regarded the stannic acid as a hydration product of tin(IV) oxide rather than of tin(IV) hydroxide.[17] Based on this view, it is considered that the water content of the exchanger changes continuously with aging. Thiessen and Koerner reported a variety of compositions for hydrous tin(IV) oxide, that is, $2SnO_2\cdot5H_2O$, $SnO_2\cdot2H_2O$, $4SnO_2\cdot7H_2O$, and $SnO_2\cdot H_2O$.[18] As has been pointed out above, there exist discrepancies in water content between the results reported by different authors, even when the exchangers were prepared by substantially the same method. The reason for this may be the difference in the details of the conditions for precipitating and drying the precipitate. When we look over Table 4, we find the compositions of the exchangers in the vicinity of $SnO_2\cdot2H_2O$, although the exchangers prepared by neutralizing $Na_2[Sn(OH)_6]$ by acids contained a little more water. Furthermore, the exchangers containing a larger amount of water tend to have higher ion-exchange capacities.

From the values of acidity listed in Table 4, it can be deduced that the exchange sites of the first stage are more basic for the exchanger prepared by pyrohydrolysis than for that aged by boiling.

The density (3.23—3.40 g cm^{-3}) was nearly the same, irrespective of the method of precipitation, although the exchangers precipitated from the concentrated solution of tin had small densities and the densification occurred by heating. The fact that the water content decreases with the density suggests the extrusion of water by the densification.

Recommended Procedure. Since the ion-exchange behavior is not so much affected by the conditions of preparation, the simplicity and the rapidity of the procedure are a matter of utmost concern in choosing the best conditions for the preparation. Thus, the (1) and (5) systems are most appropriate. If we compare these two systems, the first is inferior to the second in that washing is very lengthy, while superior in that the starting materials are less expensive. The selection, therefore, should be made based on the judgment of which is more significant, the time or the cost spent in preparing the material.

References

1) Y. Inoue and M. Tsuji, *J. Nucl. Sci. Technol.*, **13**, 85 (1976); *Bull. Chem. Soc. Jpn.*, **49**, 111 (1976).

2) K. A. Kraus, H. O. Philips, T. A. Carlson, and J. S. Johnson, *Prog. Int. Conf. on Peaceful Use of Atomic Energy*, **28**, 3 (1958).

3) M. Abe and T. Ito, *Nippon Kagaku Zasshi*, **86**, 1259 (1965).

4) E. Merz, *Z. Electrochem.*, **63**, 288 (1959).

5) J. D. Donaldson and M. J. Fuller, *J. Inorg. Nucl. Chem.*,

30, 1083, 2841 (1968); **32**, 1703 (1970).

6) P. C. Ho, F. Nelson, and K. A. Kraus, *J. Chromatogr.*, **147**, 263 (1978).

7) L. M. Sharygin, *Radiokhimiya*, **20**, 414 (1979).

8) N. Jaffrezic-Renault, *J. Inorg. Nucl. Chem.*, **40**, 539 (1978).

9) N. Jaffrezic-Renault, *Radiochem. Radioanal. Lett.*, **37**, 257 (1979).

10) R. L. Williams and R. J. Pace, *J. Chem. Soc.*, **1957**, 4143.

11) M. Ishibashi, T. Shigematsu, Y. Yamamoto, and Y. Inoue, *Bunseki Kagaku*, **7**, 473 (1958).

12) Y. Inoue and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, **53**, 811 (1980).

13) J. Sautereau, M. Baverez, and J. M. Bloch, *Bull. Soc. Chim. Fr.*, **1977**, 207.

14) S. Durand and E. Masdupuy, *Bull. Soc. Chim. Fr.*, **1974** 1844.

15) R. S. Mikhail, S. A. Selim, and F. I. Zeidan, *J. Appl. Chem. Biotechnol.*, **26**, 191 (1976).

16) J. F. Goodman and S. J. Gregg, *J. Chem. Soc.*, **1960**, 1162.

17) H. B. Weiser and W. O. Milligan, *J. Phys. Chem.*, **36**, 3030 (1932).

18) P. A. Thiessen and O. Koerner, *Z. Anorg. Allg. Chem.*, **195**, 83 (1931).