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Sorption of Ammonia/Ammonium Ion on Crystalline Hydrous Titanium Dioxide Fibers

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The sorption of ammonia/ammonium ion has been studied on crystalline hydrous titanium dioxide fibers with a layer structure, which are prepared from potassium tetratitanate ($K_2Ti_4O_9$). From the measurement of the distribution coefficient, it was found that this material strongly preferred ammonium ion to sodium ion. The results of the pH titration curves indicated that this material showed a wide range of acidities toward ammonia/ammonium ion and had 2.63 mequiv/g of an apparent capacity which was about a half of the theoretical ion-exchange capacity. The characterizations of the ammonium adsorbed solid phase at various loading levels were carried out by measuring the X-ray powder diffractograms and the water contents. From these studies, it was concluded that the sorption-desorption reaction of ammonia/ammonium ion on this material took place almost reversibly in three stages.

Recently Fujiki *et al.* have prepared a crystalline hydrous titanium dioxide with a fibrous form from potassium tetratitanate ($K_2Ti_4O_9$).[1,2] This material, which was named "crystalline hydrous titanium dioxide fibers," has been attractive because it has a layer structure and is supposed to be highly selective for some metal ions. We have studied the sorption of the microquantities of alkali metals, alkaline earth metals and divalent transition metals and determined their order of selectivity.[3–5] Considerably large differences of the affinities were observed between these metal ions, and some mutual separations of these metals were achieved on the column of this material.[4,5] We have also proposed that this material can be used advantageously to immobilize the dangerous nuclides such as cesium and strontium in a high-level radioactive waste solution.[6,7]

On the other hand, much attention has been paid to the problem of removal of ammonia/ammonium ion from an aqueous solution during the last decade. Some kinds of ion-exchangers such as zirconium phosphate are being employed to remove ammonia/ammonium ion from human blood, *e.g.* artificial kidney machine.[8,9] The sorption of ammonia/ammonium ion on crystalline hydrous titanium dioxide fibers, however, has not been studied yet, although they are promising for such a practical use because they are suitable for column operations because of their fibrous form. The sorption on this material is expected to be different from that on zirconium phosphate because there are some differences in the layer arrangement or the characteristics of the exchangeable protons. Thus it is interesting and important, from both fundamental and practical viewpoints, to study the sorption of ammonia/ammonium ion on crystalline hydrous titanium dioxide fibers.

In this paper, the sorption of ammonia/ammonium ion on crystalline hydrous titanium dioxide fibers is studied and the mechanism and characteristics of the sorption are also discussed.

Experimental

Reagents. Titanium dioxide used was of 99.98% purity. All the other chemicals were of analytical grade. Distilled, deionized water was used throughout the experiments.

Preparation of Crystalline Hydrous Titanium Dioxide Fibers. Crystalline hydrous titanium dioxide fibers were prepared as described previously;[5] potassium tetratitanate ($K_2Ti_4O_9$) fibers were grown by slow-cooling a K_2MoO_4 flux melt containing a mixture of K_2CO_3 and TiO_2 (1:3 molar ratio). The obtained fibers were placed in a column and converted into a hydrogen form by passing through 1 mol dm^{-3} hydrochloric acid as given by Eq. 1.

$$K_2Ti_4O_9 + 2H^+ + nH_2O \longrightarrow H_2Ti_4O_9 \cdot nH_2O + 2K^+. \tag{1}$$

After the concentration of potassium ion in the effluent became negligible, the resulting product was washed with water and dried in the air to a constant weight. The chemical formula of this material can be written as $H_2Ti_4O_9 \cdot 1.3H_2O$ taking into account the fact that the weight loss at 800 °C was 11.49%. The theoretical ion-exchange capacity is calculated to be 5.53 mequiv/g.

Distribution Coefficients. Distribution coefficients of ammonium ion were obtained by shaking 0.2 g of the material with 0.02 dm^3 of 1×10^{-3} mol dm^{-3} NH_4Cl solution at 25±0.5 °C. The pH value of the solution was controlled with hydrochloric acid. After the equilibrium was attained, the supernatant solutions were analyzed for their pH values and ammonium ion contents. The ammonium ion contents were determined by means of a TOA AE-235 ammonium ion selective electrode. The distribution coefficients were calculated by using

$$K_d = \frac{\text{moles of ammonium ion per 1 g of the material}}{\text{moles of ammonium ion per 1 cm}^3\text{ of the solution}}\ (\text{cm}^3/\text{g}).$$

The concentrations of ammonium ion in the material were calculated from the differences between initial and final concentrations of solutions.

pH Titration Curve. The titrations for ammonia/ammonium ion were carried out batchwise; in the forward titration, 0.5 g of the material was shaken with 0.05 dm^3 of 0.1 mol dm^{-3} ($NH_4Cl+NH_3H_2O$) solution at 25±0.5 °C until the equilibrium was attained. The ratio of NH_4Cl/NH_3H_2O was varied from 0.1 M/0.0 M to 0.0 M/0.1 M (1 M=1 mol dm^{-3}). After the pH value at equilibrium was measured, the ammonium content in the solution was determined by the standard acidimetric titration in the presence of formaldehyde. The solid was filtered off, washed and dried in the air at room temperature. The ammonium content in the solid was determined by the Kjeldahl method.

In the backward titration, 0.5032 g of the end product in the forward titration was treated with 0.05 dm^3 of 0.1 mol dm^{-3} ($NH_4Cl+HCl$) solution. Other procedures were similar to those in the forward titration. The pH titration curve for potassium ion was obtained in a similar way by using 0.1 mol dm^{-3} ($KCl+KOH$) solution.

Apparatus. The pH values of the solution were measured by a TOA HM-20E digital pH meter. X-Ray powder diffractograms were obtained by a Philips X-ray diffractometer with Cu $K\alpha$ radiation.

Results and Discussion

Distribution Coefficients. In order to determine the equilibration time, 0.2 g of the material was shaken with 0.02 dm^3 of 1×10^{-3} mol dm^{-3} NH_4Cl solution (pH=2.0) at 25±0.5 °C. Figure 1 shows the percent uptake of ammonium ion as a function of time. It was confirmed that 2 d shaking was enough to attain the equilibrium. Thus all the experiments were carried out by shaking the fibers with solutions for 3 d.

Figure 2 shows the pH dependence of distribution coefficients (K_d) of ammonium ion. The dashed lines denote the data of alkali metals obtained previously under similar experimental conditions.[3] The linear relationship was observed between log K_d and pH with a slope of +1. This fact indicated that the sorption of ammonium ion took place by an ideal ion-exchange reaction as given by Eq. 2.

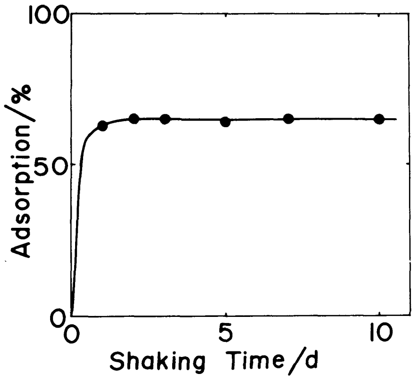

Fig. 1. Time dependence of the sorption of ammonium ion.
Exchanger: 0.2 g, solution: 0.02 dm^3 of 1×10^{-3} mol dm^{-3} NH_4Cl (pH=2.0).

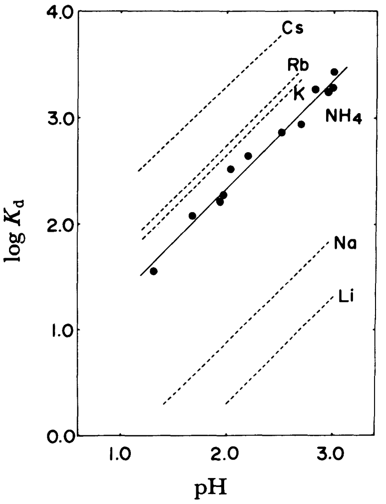

Fig. 2. pH dependence of distribution coefficients of ammonium ion.
Exchanger: 0.2 g, solution: 0.02 dm^3 of 1×10^{-3} mol dm^{-3} NH_4Cl.

$$xNH_4^+(aq) + H_2Ti_4O_9\cdot nH_2O(s) \rightleftharpoons (NH_4)_xH_{2-x}Ti_4O_9\cdot n'H_2O(s) + xH^+(aq) \quad (0<x<0.04), \qquad (2)$$

where the subscripts "aq" and "s" represent aqueous and solid phases, respectively.

The order of selectivity was found to be Cs>Rb>K>NH_4>Na>Li. In the case of alkali metals, this order was parallel to their ionic radii. Since the ionic size of ammonium ion is almost the same as that of potassium ion, the affinities of these two ions are expected to be almost equal with each other, which is actually true from Fig. 2.

Table 1 gives the distribution coefficients and separation factors of ammonium ion and alkali metal ions at a pH value of 2.0. A large value of separation factor was observed between ammonium ion and sodium ion. This fact will be one of advantages when this material is employed to remove ammonium ion from a solution which contains a large amount of sodium ion.

TABLE 1. DISTRIBUTION COEFFICIENTS (K_d) AND SEPARATION FACTORS (α_A^B) OF AMMONIUM ION AND ALKALI METAL IONS AT pH=2.0

Ion	Cs	Rb	K	NH_4	Na	Li
K_d	2460	563	458	225	8.0	2.1
α_A^B		4.4	1.2	2.0	28.1	3.8

$\alpha_A^B = K_d{}^B/K_d{}^A$ for neighboring ions. Data for alkali metal ions are from Ref. 3.

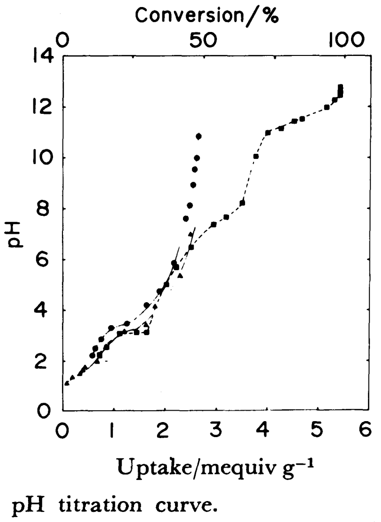

Fig. 3. pH titration curve.
—●— Ammonia/ammonium ion (forward); exchanger: 0.5 g, solution: 0.05 dm^3 of 0.1 mol dm^{-3} ($NH_4Cl+NH_3H_2O$), —▲— ammonia/ammonium ion (backward); exchanger (ammonium form): 0.5032 g, solution: 0.05 dm^3 of 0.1 mol dm^{-3} ($NH_4Cl+HCl$), —■— potassium ion (forward); exchanger: 0.2 g, solution: 0.02 dm^3 of 0.1 mol dm^{-3} ($KCl+KOH$).

pH Titration Curve. pH titration curves for ammonia/ammonium ion (forward and backward) are shown in Fig. 3. pH titration curve for potassium ion is also shown for comparison. The exchangeable protons in crystalline hydrous titanium dioxide fibers had a wide range of acidities toward ammonia/ammonium ion. The inflection point was observed at 25—30% conversion, which indicated that 25—30% of the exchangeable protons were more acidic than the others. The backward titration curve had a similar curvature to the forward one except for a slight difference. The apparent capacity for ammonia/ammonium ion was 2.63 mequiv/g which was about a half of the theoretical ion-exchange capacity of this material, whereas almost complete exchange was achieved with potassium ion.

Characterization of Ammonium-Adsorbed Solid Phase. Figure 4 shows the X-ray powder diffractograms of the material at various loading levels of ammonium in the forward titration. In most of the ion-exchange processes of inorganic ion-exchangers with a layer structure, two immiscible phases are observed; one is an unexchanged phase and the other is an exchanged phase with a different interlayer distance from that of the unexchanged phase.[10,11] In this work, however, X-ray diffractograms changed continuously, which indicated that ammonia/ammonium ion is taken into crystalline hydrous titanium dioxide fibers without phase transition.

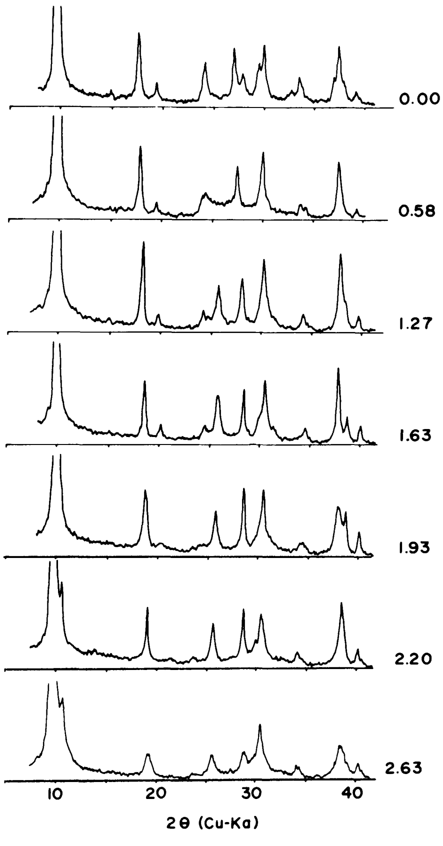

Fig. 4. Schematic diagrams of X-ray powder diffractograms of the ammonium adsorbed phase in forward titration. Numerals represent the uptake of ammonia/ammonium ion (mequiv/g).

Figure 5 shows the *d*-spacing of the strongest reflection, which appeared near the 2*θ* value of 10° in the X-ray diffractograms, as a function of ammonium loading. This reflection is from (200) plane and is attributable to the interlayer of the material.[12] Its spacing was determined by using potassium hexatitanate ($K_2Ti_6O_{13}$) as an internal standard.

Figure 6 shows the water content of the ammonium-adsorbed solid phase as a function of loading. The weight loss was determined by heating the ammonium-adsorbed solid phase at 800 °C for 1 h. The water content was calculated from the weight loss by assuming the decomposition given by Eq. 3.

$$(NH_4)_xH_{2-x}Ti_4O_9\cdot nH_2O(s) \longrightarrow 4TiO_2(s) + xNH_3(g) + (n+1)H_2O(g) \quad (3)$$

where subscripts "s" and "g" represent solid and gas phases, respectively.

Figure 7 shows the *d*-spacing of the (200) reflection at various loadings of ammonium in the backward titration. The *d*-spacings coincided roughly with those of

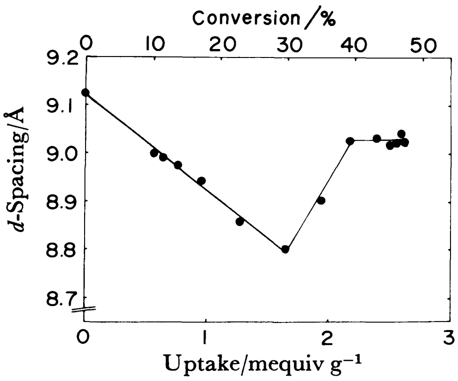

Fig. 5. *d*-Spacing of the (200) reflection as a function of loading in forward titration.

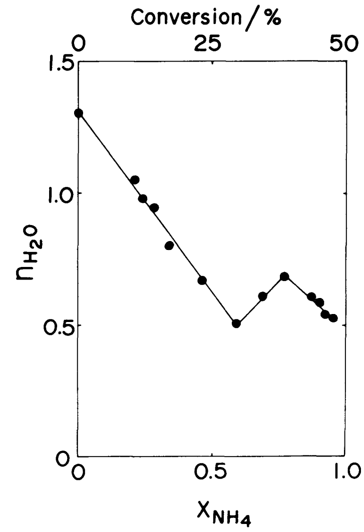

Fig. 6. Water content of the ammonium adsorbed solid phase in forward titration.
x_{NH_4} and n_{H_2O} correspond to the subscripts in the chemical formula of the ammonium adsorbed solid phase, $(NH_4)_xH_{2-x}Ti_4O_9\cdot nH_2O$.

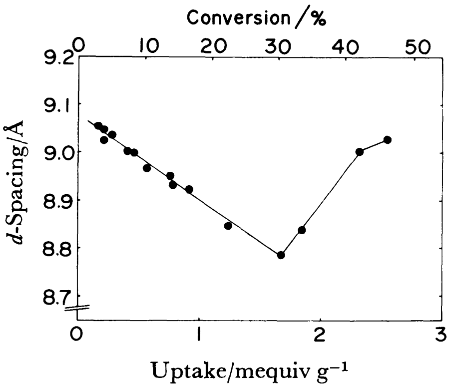

Fig. 7. *d*-Spacing of the (200) reflection as a function of loading in backward titration.

the material in the forward titration, which indicated that the sorption-desorption reaction took place almost reversibly. A slight difference between the forward and backward titration curves may be due to the loss of crystallinity of the material used in the backward titration which was the end product in the forward titration.

Mechanism of the Sorption of Ammonia/Ammonium Ion. There are two possible explanations for the sorption of ammonia/ammonium ion; one is an NH_4^+/H^+ exchange reaction and the other is a direct addition of NH_3 to the protons in the exchanger giving ammonium ion. Alberti and his co-workers have reached a conclusion after detailed investigations that the sorption on crystalline zirconium phosphate took place by the direct addition of NH_3.[12] In the case of crystalline hydrous titanium dioxide fibers, the sorption can be explained by the NH_4^+/H^+ exchange in the pH range of 1.0 to 3.0 from distribution coefficients shown in Fig. 2. However it is difficult to determine which way of the sorption process was predominant in the higher pH region from the result of pH titration curve.

As described above, about a half of the exchangable protons was replaced by ammonia/ammonium ion. The plots of the interlayer distance and the water content of the ammonium-adsorbed solid phase showed two distinct turning points at 30 and 40% conversion. These facts suggested that the ammonia/ammonium ion uptake took place in three stages; stage I [0—30% conversion], stage II [30—40% conversion] and stage III [40—48% conversion].

In stage I, ammonia/ammonium ion uptake proceeded accompanying the continuous decrease in interlayer distance and water content. This phenomenon can be explained as follows; the ammonium ion adsorbed between the layers can make a hydrogen-bond with an unexchanged hydroxyl group in an adjacent layer. As the ammonium loading increased, the number of hydrogen-bond increased, which induced the continuous decrease in interlayer distance. The water content also decreased linearly. The value of $\mathrm{d}\,n_{H_2O}/\mathrm{d}\,x_{NH_4}$ was 1.33 which was approximately equal to the number of water molecules per formula weight of the material. From these facts, it is suggested that the ammonia/ammonium ion was taken into the lattice by forming a hydrogen-bond and expelling the water around the sorption site.

In stage II, the ammonia/ammonium ion uptake gave rise to increase in interlayer distance and water content. In the X-ray powder diffractograms, a new tiny shoulder appeared beside the (200) reflection as seen in Fig. 4. It seems that ammonia/ammonium ion uptake beyond 30% of the conversion caused a slight distortion of the lattice of the material. If this is true, the sorption in this stage will require more energy than in stage I and the sorption will proceed in the higher pH region. This expectation is actually the case as shown in Fig. 3.

In stage III, no definite change was observed in the X-ray powder diffractograms, which suggested that the ammonium ion already adsorbed between the layers may act like a "pillar" and the material can accomodate additional ammonia/ammonium ion without an appreciable change in interlayer distance.

In conclusion, the sorption process can be summarized by the following three equation:

stage I $H_2Ti_4O_9\cdot 1.3H_2O + 0.6NH_3(NH_4^+)$
[9.1 Å]
$\longrightarrow (NH_4)_{0.6}H_{1.4}Ti_4O_9\cdot 0.5H_2O + 0.8H_2O$
[8.8 Å]
$+ (0.6H^+)$

stage II $(NH_4)_{0.6}H_{1.4}Ti_4O_9\cdot 0.5H_2O + 0.2NH_3(NH_4^+)$
[8.8 Å]
$+ 0.2H_2O \longrightarrow (NH_4)_{0.8}H_{1.2}Ti_4O_9\cdot 0.7H_2O$
[9.0 Å]
$+ (0.2H^+)$

stage III $(NH_4)_{0.8}H_{1.2}Ti_4O_9\cdot 0.7H_2O + 0.15NH_3(NH_4^+)$
[9.0 Å]
$\longrightarrow (NH_4)_{0.95}H_{1.05}Ti_4O_9\cdot 0.5H_2O + 0.2H_2O$
[9.0 Å]
$+ (0.15H^+)$,

where numerals in brackets correspond to the *d*-spacings of the (200) reflection.

Only a half of the exchangeable protons can be replaced by ammonia/ammonium ion. This phenomenon cannot be attributed to the steric effect, because almost all of the exchangeable protons were exchanged by potassium ions whose size is approximately equal to that of ammonium ion. This fact can also be explained by the hydrogen-bond formation of the ammonium ion between the layers. The stable pair of ammonium ion and an unexchanged hydroxyl group, which is hydrogen-bonded with each other, may be a good explanation for the fact that the apparent capacity was about a half of the theoretical ion-exchange capacity.

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