Heat-Treatment of Crystalline Hydrated Titania Fibers and Ion-Exchange Properties for Alkaline Earth Metal Ions in Aqueous Solutions

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The distribution coefficients for alkaline earth metal ions on heat-treated crystalline hydrated titania fibers were determined as a function of pH at 25°C. The exchange behavior of these ions was well explained by their ion-exchange reaction with hydrogen-ion in the fibers. The ion-exchange ability of these fibers was not affected when these fibers were heat-treated between 25°C and about 70°C, but the value of distribution coefficients decreased when the heat-treatment temperature exceeds 80°C. This behavior is related to the change in the interlayer distance of crystalline hydrated titania.

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結晶質チタニア水和物繊維の熱処理と水溶液中のアルカリ土類 金属イオンに対するイオン交換特性

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熱処理した結晶質チタニア水和物繊維に対するアルカリ土類金属イオンの 25°C における分配係数を pH に対する関数として求めた。これらのイオンの吸着挙動は、繊維中の水素イオンとのイオン交換反応としてよく説明される。またこれらの繊維の吸着能力に及ぼす熱処理の影響は 70°C 以下の熱処理温度ではほとんどみられないが、80°C 又はそれ以上の温度では減少の傾向がみられた。このことは、熱処理における層間距離の変化と良く対応している。(1984 年 2 月 9 日受付)

Key-words : Heat-treated crystalline hydrated titania fiber, Adsorption of alkaline earth metal ions on inorganic ion-exchanger, Ion-exchange equilibria of alkaline earth metal ions in hydrochloric acid solutions

1. Introduction

The treatment of radioactive wastes has been studied by using various adsorbents¹⁾⁻³⁾. The authors have also studied the adsorption properties of crystalline hydrated titania fibers from the viewpoint of the treatment of high-level liquid radiowastes. We have reported that the titania fibers adsorbed alkali metal ions^{4), 5)}, alkaline earth metal ions^{6), 7)}, and divalent transition metal ions⁸⁾ in weak acid solutions and the ion-exchange equilibria at 25°C were measured. It was found that the fibers ion-exchanged cations in the order

of $\text{Cs}^+ > \text{Rb}^+ \simeq \text{K}^+ \gg \text{Na}^+ > \text{Li}^+$ for alkali metal ions, $\text{Ba}^{2+} \gg \text{Sr}^{2+} > \text{Ca}^{2+} \gg \text{Mg}^{2+}$ for alkaline earth metal ions, and $\text{Cu}^{2+} \gg \text{Zn}^{2+} > \text{Mn}^{2+} \simeq \text{Co}^{2+} > \text{Ni}^{2+}$ for divalent transition metal ions. These selectivity series for these cations are the same orders as that of increased ionic radii of these cation series except for divalent transition metal ions.

The ion-exchange reaction of alkaline earth metal ions on this fiber may decrease when the fibers are treated at high temperature, because hydrogen-ions in crystalline hydrated titania fibers are ion-exchanged with cations when these

cations are entered in the fibers. It is very interesting to know the relationship between the adsorption properties and heat-resisting character of crystalline hydrated titania fibers. In the present paper, the ion-exchange of barium, strontium, calcium, and magnesium on the heat-treated crystalline hydrated titania fibers was studied under the conditions similar to those of the previous work⁷⁾. After the fibers were heat-treated at 80°C, the ion-exchange equilibria between these cations and hydrogen-ions are measured at 25°C in order to obtain further information.

2. Experimental

Titanium dioxide used was of 99.9% purity. All the other reagents were of an analytical grade. The aqueous solutions of alkaline earth metal ions were prepared using their chloride salts. Crystalline potassium tetratitanate fibers, $K_2Ti_4O_9$, have been synthesized by the method reported previously⁹⁾. The fibers of about 10g were filled in a pyrex glass column (inner diameter : 25mm), and washed with about 20l of distilled and deionized water to eliminate a K_2MoO_4 flux. To obtain crystalline hydrated titania fibers, 1 mol·l⁻¹ hydrochloric acid was passed through this column until the detection limit of potassium ion in the effluent by an atomic absorption method was reached. The heat-treated fibers, which were used as ion-exchanger, were prepared by heating of the crystalline hydrated titania fibers at 50°C, 60°C, 70°C, 80°C, 90°C, and 100°C for one hour.

Ion-exchange reactions were made at 25°C. The measurements of the ion-exchange equilibria were carried out in a similar way as in the previous study⁷⁾. The X-ray powder diffractogram was obtained by using a Rigaku Denki Diffractometer

with Cu $K\alpha$ radiation. A Hitachi Polarized Zeeman Atomic Absorption Spectrophotometer (Model 180-80) was used to determine the cation contents in the solution. The pH of the solution was measured with a TOA pH meter (Model HM-20E).

3. Results and discussion

In order to achieve the ion-exchange equilibria of alkaline earth metal ions, an agitation for ten days was necessary. The extraction of potassium from potassium tetratitanate fibers is represented by the following equation :

Figure 1(a) shows the weight loss of the hydrated fibers as a function of the heat-treated temperature. Figure 1(b) shows the value of d_{200} spacing obtained from the strongest peak in X-ray powder diffractogram as a function of the heat-treated temperature. The shape of this curve resembles to that of the curve in Fig. 1(a).

From the data in Fig. 1(a), the heat-treated fibers hold interlayer water up to the temperature of about 50°C, but a part of the water in the fibers is released under the conditions above 50°C. By this dehydration, the interlayer distance may shrink. This fact is well explained by the data of the d -spacing obtained from the strongest peak, d_{200} spacing, in X-ray powder diffractogram showed good coincidence with the data previously reported¹⁰⁾. It is known that hydrated titania fibers are crystalline materials having a layer structure which resembles the layer structure of potassium tetratitanate¹⁰⁾. This indicates that crystalline potassium tetratitanate fibers are changed to crystalline hydrated titania fibers by passing through the concentrated hydrochloric

Fig. 1. (a) The weight loss of the fibers as a function of the heat-treated temperature. Heating time : One hour. (b) The values of d_{200} spacing obtained from the strongest reflection peak in X-ray powder diffractogram as a function of the heat-treated temperature.

acid solution as Eq. (1). This equation means that protons may replace potassium ions to form hydroxyl group by being attached to oxide ions in $[\text{TiO}_6]$ octahedra forming a layer structure. The strongest reflection peak for the (200) plane of the fibers was observed at about 10° of 2θ value, and related with the interlayer distance: the larger the value of 2θ , the smaller the interlayer distance.

Fig. 2. The ion-exchanged amount of alkaline earth metal ions as a function of the heat-treated temperature of adsorbent at 25°C . The ion-exchanger (0.1g) is heat-treated $\text{H}_2\text{Ti}_4\text{O}_9 \cdot n\text{H}_2\text{O}$ (the weights were measured before heating). The aqueous solution (10 cm^3) is contained $1 \times 10^{-4} \text{ mol} \cdot \text{l}^{-1}$ of each alkaline earth metal ion at initial. $[\text{M}^{2+}]_i$: Initial concentration of alkaline earth metal ions in the aqueous phase. $[\text{M}^{2+}]_f$: Final concentration of alkaline earth metal ions in the aqueous phase. Ba^{2+} (○), Sr^{2+} (●), Ca^{2+} (◐), and Mg^{2+} (◑).

Figure 2 gives the ion-exchanged amount of alkaline earth metal ions as a function of the heat-treated temperature of adsorbent at 25°C . In these experiments, each of the initial cation concentration in the aqueous phase was always kept at $1 \times 10^{-4} \text{ mol} \cdot \text{l}^{-1}$. When the fibers were heat-treated up to the temperature of 70°C , the distribution ratio of these cations was always nearly constant. On the other hand, it was decreased when the fibers were heat-treated at 80°C or above. The cation exchange reaction on crystalline hydrated titania fibers can be expressed as the following equation,

Here, the subscripts "s" and "aq" denote the solid phase and aqueous one, respectively. When these cations are incorporated in the hydrated fibers,

they may occupy the same sites as those of potassium ions in the layer of $\text{K}_2\text{Ti}_4\text{O}_9$. Consequently, the ion-exchanged amount of these cations on these fibers may decrease with shrinking interlayer distance.

The distribution coefficient Kd was calculated as:

$$Kd = \frac{\text{mole of } \text{M}^{2+} \text{ per 1 g of solid}}{\text{mole of } \text{M}^{2+} \text{ per 1 cm}^3 \text{ of solution}} \quad (3)$$

Here, the weight of the solid was measured in the air-dried state.

The ion-exchange behavior of these cations on heat-treated fibers in Fig. 2 resembles to these results in Fig. 1(a) and Fig. 1(b). Though the weight loss and the shrinkage of the interlayer distance of the fibers had already been started at heating up to the temperature of 50°C , the values of distribution coefficient did not decrease at the temperature region between 50°C and 70°C . This fact may explain that the interlayer distance of the crystal was restored to the state of fiber of no heat-treatment when the fibers were contacted with the aqueous phase, and the shrinkage was not reversible under the temperature condition at 80°C or above. The distribution coefficient of alkaline earth metal ions for crystalline hydrated titania fibers is higher than that for the fibers heated at 80°C . This means that the former can ion-exchange larger amount of these cations than

Fig. 3. Distribution coefficient (Eq. (3)) of alkaline earth metal ions as a function of pH in aqueous phase at 25°C . The ion-exchanger (0.1g) is heat-treated $\text{H}_2\text{Ti}_4\text{O}_9 \cdot n\text{H}_2\text{O}$ at 80°C (the weights were measured before heating). The aqueous solution is hydrochloric acid solution (10 cm^3) containing $1 \times 10^{-4} \text{ mol} \cdot \text{l}^{-1}$ of each alkaline earth metal ion at initial. Ba^{2+} (○), Sr^{2+} (●), and Ca^{2+} (◐). Broken lines indicate the data of alkaline earth metal ions in Ref. 7).

Table 1. Values of $\log Kd$ of alkaline earth metal ions on crystalline hydrated titania and calculated separation factors for adjacent ions (pH=3).

Ion-exchanger	Ba ²⁺	Sr ²⁺	Ca ²⁺	Mg ²⁺
H ₂ Ti ₄ O ₉ ·nH ₂ O $\log Kd_1$	3.96	1.72	1.01	-1.24
($\log sf$)	(2.24)	(0.71)	(2.25)	
Heat-treated $\log Kd_2$	2.65	1.06	0.62	
H ₂ Ti ₄ O ₉ ·nH ₂ O ($\log sf$)	(1.59)	(0.44)		
$\log Kd_1 - \log Kd_2$	1.31	0.66	0.39	

the latter because of the larger interlayer distance.

Figure 3 gives the $\log Kd$ values of barium, strontium, and calcium as a function of pH in the aqueous phase. The slope of the $\log Kd$ vs. pH plot showed about +2 for these cations under the substantially constant concentration of the hydrogen-ion in the solid. This indicates that the adsorption of alkaline earth metal ions on crystalline hydrated titania fibers is well fitted with the ion-exchange reaction in Eq. (2). The values of distribution coefficient and separation factor calculated from these data are given in Table 1.

The results in Fig.3 and Table 1 can be summarized as follows:

i) The amount of ion-exchange on the heat-treated fibers at a certain pH is in the order of Ba²⁺ > Sr²⁺ > Ca²⁺ (The amount of ion-exchange of magnesium on the fibers was very poor even in the neutral water. Then we omitted the experiment for the ion-exchange of magnesium on the fibers). This order agrees with that obtained in the previous study⁷⁾, which is parallel with the increased ionic radii. ii) The Kd values of the alkaline earth metal ions are smaller than those obtained by original crystalline hydrated titania fibers. iii) The influence of the heat-treatment on the Kd is in the order of Ba²⁺ > Sr²⁺ > Ca²⁺. This order indicates that these cations having large ionic radii are more disturbed than those having

small ionic radii. The results may be explained as follows. When the fibers were shrinked by the heat-treatment at high temperature, the interlayer free-space was decreased. Then, the diffusion of the interlayer metal ions may be restricted by the layer structure having the narrow interlayer distance. The influence of this steric effect on large metal ions is greater than that on small metal ions.

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