Titanium Hydroxide as a New Inorganic Fluoride Ion Exchanger

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新しい無機フッ化物イオン交換体としての $\text{Ti}(\text{OH})_4$ のイオン交換特性

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Although TiO_2 exhibits a small fluoride ion exchange capacity, it was found that titanium hydroxide, $\text{Ti}(\text{OH})_4$, can exchange fluoride ion with large saturation capacity of $1.60 \text{ m} \cdot \text{mol/g}$. Although the H_2PO_4^- interferes with the F^- exchange, the amount of F^- exchange of $\text{Ti}(\text{OH})_4$ was hardly changed by the coexistence of Cl^- , NO_3^- , and SO_4^{2-} . The capacity for F^- exchange was almost unchanged over 4 times repetition of ion-exchange and desorption and furthermore, the elution of Ti was negligibly small. Consequently, $\text{Ti}(\text{OH})_4$ is expected to be a new inorganic F^- exchanger for the removal of fluoride ion from wastewater.

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1. Introduction

Fluoride ion is extremely toxic to human body and a removal of fluoride ion in wastewater is an important subject from the viewpoint of environmental conservation. Wastewater containing high concentration of fluoride ion is mainly formed in the semiconductor manufacturing process at present. The allowance level in the wasted water becomes sever and is down to a concentration less than 0.8 from 15 mg/dm^3 in Japan at 2001. Also, it is set to few mg/dm^3 levels in many countries. At present, fluoride ion is removed by precipitation with calcium oxide to form CaF_2 .¹⁾ However, removal of fluoride ion is limited to 10 mg/dm^3 by the precipitation method from the solubility product. Comparing the precipitation method, ion-exchange method has many advantages such as simple operation process, small energy, and much higher removal level. In order to achieve a sub mg/dm^3 level of fluoride ion in wastewater, various compounds were investigated for the fluoride ion exchanger. In particular, it is reported that Al_2O_3 or Al_2O_3 based oxide has a fairly large capacity for fluoride ion adsorption.^{2)–3)} However, adsorption of fluoride ion on Al_2O_3 is too strong to desorb. On the other hand, it was reported that CeO_2 can exchange fluoride ion selectively and CeO_2 dispersing into polymer matrix is commercialized as a fluoride ion-exchanger (commercial name is read-F, Asahi Kasei Co., Ltd.).⁴⁾ However, CeO_2 is expensive and the process using CeO_2 based ion-exchanger also becomes expensive. Therefore, development of an inorganic ion-exchanger for fluoride ion with a reasonable price and a large capacity is strongly required. In this study, the ion-exchange property of titanium hydroxide for fluoride ion was investigated. Titanium oxide and the partially hydrated titanium oxide were investigated as an inorganic ion-exchange material for some toxic elements such as $\text{As}(\text{OH})_4^-$ and halogens.^{5)–7)} However, ion-exchange property of titanium tetrahydroxide, $\text{Ti}(\text{OH})_4$, is not studied as the fluoride ion exchange material.

2. Experimental

Titanium tetrahydroxide was obtained by precipitation in aqueous $\text{TiO}(\text{SO}_4)$ solution by the addition of aqueous ammonia solution. The obtained precipitates were dried in an oven at 343 K for 12 h . XRD measurement shows the ob-

tained titanium tetrahydroxide is amorphous, however, TG-DTA analysis suggests that the weight loss during heating up to 573 K was almost corresponded to that of $\text{Ti}(\text{OH})_4$. Therefore, it is considered that the obtained compound in this study is $\text{Ti}(\text{OH})_4$. NaF is used for the source of fluoride ion. The ion-exchange capacity of fluoride ion was measured by adding 1 g of sample into 500 ml of NaF aqueous solution containing $50 \text{ mg/dm}^3 \text{ F}^-$ at $\text{pH}=5.0$ which was kept constant by using $\text{CH}_3\text{COONa}-\text{CH}_3\text{COOH}$ solution. Change in F^- concentration was monitored by the F^- ion-selective electrode (Horiba, pH/ion meter, type F-23). Desorption of F^- was also monitored by the F^- selective electrode. Desorption of F^- was performed at $\text{pH}=12$ and the amount of F^- was measured with the selective electrode after adjusting pH to 8.0 by using CH_3COOH solution.

3. Results and discussion

Figure 1 shows the time dependence of F^- exchanged on TiO_2 (Rutile) and the prepared $\text{Ti}(\text{OH})_4$. It is clear that the removal of F^- was hardly occurred on TiO_2 , however, decrease in F^- is observed when $\text{Ti}(\text{OH})_4$ was added to the solution. Concentration of F^- gradually decreased with time and after 6 h , almost 40% of initial F^- was removed by ion-exchange with $\text{Ti}(\text{OH})_4$. After exposure to water at $\text{pH}=12$, almost the same amount (98%) of F^- adsorbed was desorbed. Therefore, it is clear that $\text{Ti}(\text{OH})_4$ exhibits F^- exchange property. Effects of drying temperature after precipitation upon F^- exchange capacity were also studied. The capacity for F^- exchange decreased with increasing temperature for the post-precipitation heat treatment and the largest capacity for F^- was obtained by calcination at 343 K . From XRD measurement, formation of TiO_2 was observed when the calcination temperature is higher than 573 K . Therefore, with increasing the calcination temperature, contents of TiO_2 , which exhibits poor F^- exchange capacity, increased resulting in a decrease in the F^- exchange capacity. Consequently, lower calcination temperature is preferable to F^- exchange capacity point of view. However, elution of Ti ion became significant with decreasing calcination temperature. Consequently, it is considered that the optimum post-precipitation heat treatment temperature for $\text{Ti}(\text{OH})_4$ is 473 K . From TG-DTA analysis data, weight loss of the sample from room temperature to 873 K is slight-

Fig. 1. Fluoride ion exchange property of Ti(OH)_4 and TiO_2 at room temperature.

Fig. 2. Cycle stability of F^- exchange capacity in Ti(OH)_4 . Ion-exchange was performed at $\text{pH}=5$ and desorption at $\text{pH}=12$.

ly larger than that of Ti(OH)_4 dehydration to TiO_2 . Therefore, it is considered that the large part of the sample after dry at 473 K is mainly Ti(OH)_4 and the content of TiO_2 seems to be small.

Figure 2 shows the cycle stability for fluoride exchange capacity on Ti(OH)_4 . It can be seen that Ti(OH)_4 obtained by the post-precipitation heat treatment at 473 K exhibits the stable capacity for F^- exchange and decrease in F^- exchange capacity was hardly observed over 6 times. On the other hand, reversibility in F^- exchange is also high and almost the same amount of F^- exchanged was desorbed at each cycles. The elution of Ti during F^- exchange and desorption was also measured by ICP. Small amount of Ti eluted at each desorption procedure. However, total amount of Ti eluted within 6 times F^- exchange and desorption corresponds to 0.8% in Ti(OH)_4 . Therefore, it can be said that

Fig. 3. Effects of coexisting anion on F^- exchange capacity of Ti(OH)_4 . Initial F^- ion: $2.63 \text{ m} \cdot \text{mol dm}^{-3}$, initial coexisting anion: $2.63 \text{ m} \cdot \text{mol dm}^{-3}$.

Ti(OH)_4 is stable during F^- exchange and desorption. It is also noted that the amount of adsorbed fluoride ion (ca. $0.6 \text{ m} \cdot \text{mol/g}$) at each ion-exchange procedure under the condition in Fig. 2 is 1.75% of that of OH^- , provided that the sample is Ti(OH)_4 . The amount of eluted Ti is smaller than that of exchanged F^- ion by an order of magnitude. Therefore, it can be excluded that F^- ion removed by the surface elution of Ti^{4+} to form titanium fluoride compound.

In wastewater, there are many ions coexisted and the high selectivity is also strongly required for F^- exchanger. In particular, sulfate ion coexists in the wastewater from the semiconductor manufacturing process. In this study, effects of the coexisting anion on F^- exchange capacity were investigated. For this measurement, ion exchange amount of each coexisting anion was also measured by using ion chromatographs. As shown in Fig. 3, no adsorption of Cl^- , NO_3^- was observed and small amount of SO_4^{2-} adsorption was observed. On the other hand, amount of ion-exchanged H_2PO_4^- is fairly large among the examined anions. However, the amount of H_2PO_4^- in the wastewater from the semiconductor manufacturing process is much smaller than that in Fig. 3. Therefore, it is considered that Ti(OH)_4 can selectively exchange fluoride ion.

Figure 4 shows the amount of F^- exchanged with Ti(OH)_4 as a function of pH after 12 h. It was seen that ion exchange with F^- occurs in pH range smaller than 6 and the amount of ion-exchanged F^- monotonically increased with decreasing the pH value. Therefore, higher ion-exchange capacity can be achieved at lower pH for Ti(OH)_4 . In Fig. 4, amount of ion-exchanged F^- on CeO_2 dispersed polymer (read-F, commercial fluoride ion-exchanger,) under the same condition is also shown for the comparison. Comparing with that of the commercial CeO_2 based ion-exchanger, the capacity of F^- exchange in Ti(OH)_4 is comparable and slightly higher at lower pH range. Amount of F^- exchange was measured at various initial F^- concentrations and it became clear that the saturated amount of F^- is $1.60 \text{ m} \cdot \text{mol g}^{-1}$. Since pH of the solution increased during ion-exchanging with F^- , it is considered that fluoride ion exchanges the surface OH^- in Ti(OH)_4 . This study reveals that Ti(OH)_4 is cheap, however, exhibits the excellent stability, selectivity, and large capacity for F^- ion exchange.

4. Conclusion

Although TiO_2 exhibits a small fluoride ion exchange capacity, it was found that titanium tetrahydroxide can ex-

Fig. 4. Amount of F^- exchange on $Ti(OH)_4$ and CeO_2 dispersed polymer as a function of pH. Initial F^- concentration was set to $2.63 \text{ m} \cdot \text{mol dm}^{-3}$.

change fluoride ion with large saturation capacity of $1.60 \text{ m} \cdot \text{mol g}^{-1}$. In addition, fluoride ion exchange on $Ti(OH)_4$ oc-

curs with high selectivity. $Ti(OH)_4$ is cheap and innocuous to environment. Therefore, it is considered that $Ti(OH)_4$ has a great possibility as an inorganic fluoride ion exchanger for wastewater treatment.

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