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Cation Exchange Selectivity of Layered Titanates, $H_2Ti_3O_7$

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Introduction

Ion selectivities on exchange reactions have been observed on crystals having zeolite-like cavities due to sieving effects (*1*). Such cavities are in relatively rigid structures. On the other hand, the interlayer distance of layered compounds changes during the ion-exchange process. It expands when the interlayer ions are replaced by the larger ones. The larger ions require much more energy to diffuse into the interior of the crystal than the smaller ones. The difference in the rate of diffusion might be applied to separate a specific kind of ion in solution.

$Na_2Ti_3O_7$ has a layered crystal structure among a series of $A_2O \cdot nTiO_2$ compounds. It is monoclinic having lattice parameters $a = 8.571$ Å, $b = 3.804$ Å, $c = 9.135$ Å, $\beta = 101.57°$ (*2*). The basic framework of $Na_2Ti_3O_7$ is built up by three TiO_6 octahedra sharing edges at one level. These units are joined to similar blocks by additional edge-sharing to form zigzag strings extending in the *b* direction. The strings are linked by sharing corners of octahedra to form staggered sheets.

The isomorphism of the tetratitanates $M_2Ti_4O_9$ with M = Li, Na, K, Rb, Cs, Ag, which were prepared by ion exchange of $Tl_2Ti_4O_9$ in molten salts of the respective metal chlorides, has already been demonstrated (*3*). The tetratitanates also have a layered crystal structure. The hydrolysis of $K_2Ti_4O_9$ has been investigated by several research groups (*4–6*). There was no report on $Na_2Ti_3O_7$ concerning ion exchange. The present authors have reported that the interlayer ions are exchangeable and that their HCl-treated products are $H_2Ti_3O_7$ and $H_2Ti_4O_9 \cdot H_2O$ (*7*). The reversibility of ion exchange was first confirmed in our previous manuscript.

This paper deals with the cation preference of $H_2Ti_3O_7$ on exchange. The uptake of alkali was investigated in aqueous mixed solutions of NaCl and NaOH against pH. The reaction rates were investigated in alkali hydroxide aqueous solutions. Large differences were observed between alkalies with a sharp preference for lithium.

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Experimental

$Na_2Ti_3O_7$ was prepared by heating a mixture of Na_2CO_3 and TiO_2 in a molar ratio of 1 : 3 at 800°C for 20 hr and then for another 20 hr after grinding. The hydrolysis of $Na_2Ti_3O_7$ (ca. 750 mg) was performed in 200 cm^3 of 0.5 *M* HCl at 60°C for 3 days. The acid solution was changed everyday in order to remove alkali completely from the compounds. The products were washed with distilled water and dried in vacuum at 30°C.

The pH dependences of the exchange reactions were investigated on $H_2Ti_3O_7$ whose average particle size was 1.3 μm. The samples (ca. 500 mg) were soaked in 40 cm^3 of aqueous mixed solution of NaCl and NaOH having various ratios in polyethylene bottles. The solutions were prepared from CO_2-free water and their total alkali concentrations were 0.1 *M*. The bottles were filled with nitrogen gas and sealed. The duration of each treatment was 3 days at 60°C. The bottles were shaken on a shaking machine during the reaction to keep the reaction homogeneous. The products were washed with distilled water, and dried in vacuum at 30°C. The products were characterized by X-ray powder diffraction. The amounts of alkali and titanium were determined by atomic absorption. The dehydration processes and water contents of the products were estimated by DTA–TG.

The reaction rate of $H_2Ti_3O_7$ was also studied in aqueous solutions of 0.1 *M* LiOH, NaOH, and KOH at 60°C. Then cation preference of $H_2Ti_3O_7$ (ca. 500 mg) was studied in 160 cm^3 of 0.1 *M* total alkali concentration containing equal amounts of LiOH, NaOH, KOH, and CsOH.

Results and Discussion

pH dependence. Cation exchange was investigated on $H_2Ti_3O_7$ in solutions having various pH values. Molar percents of alkali ions in the products were calculated for total amounts of exchangeable ions. The values were plotted against the solution pH as shown in Fig. 1. The amount of sodium was less than 20% in the products prepared from $H_2Ti_3O_7$ below pH = 10, rapidly increased with pH in the region of pH $\geqq$ 11, and attained the value of 54% above pH = 12. The exchange reactions seem to require high pH values of solutions. $H_2Ti_3O_7$, therefore, behaves as a weak Brönsted acid, and the acid–base interaction is a driving force for the reaction. It takes more than 3 days to saturate $H_2Ti_3O_7$ with alkali as will be described below.

The exchanged products showed sharp X-ray diffraction patterns indexed as monoclinic and isomorphous with $H_2Ti_3O_7$. The lattice parameter *a*, reflecting the interlayer distance, varied from the product to product. The other parameters, *b*, *c*, and β, did not alter so much with each ion-exchange treatment. The *a* parameters and the chemi-

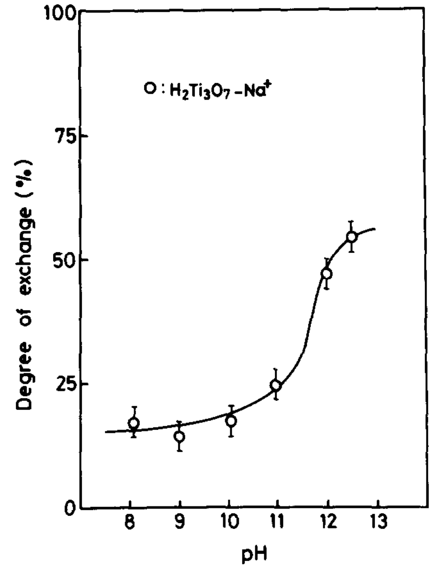

FIG. 1. Effect of pH values on the cation exchange of $H_2Ti_3O_7$ with sodium metal ions. The degree of exchange in the figure means the molar percentages of sodium in the products for the total amount of interlayered ions.

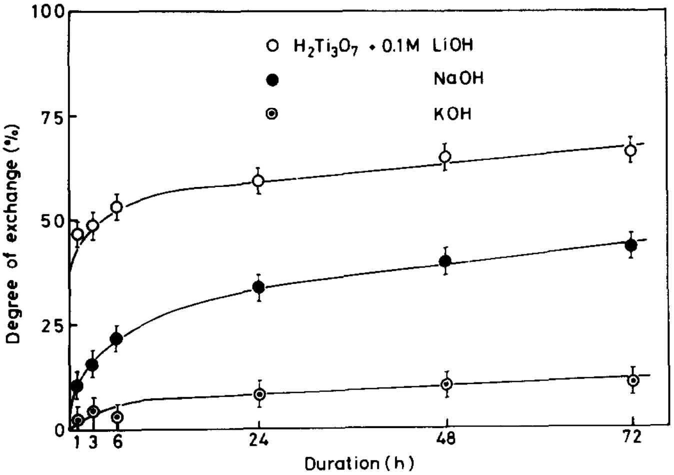

FIG. 2. Exchange reactions of $H_2Ti_3O_7$ in solutions of 0.1 *M* LiOH, NaOH, and KOH.

cal compositions were 8.08 Å, $Na_{0.04}H_{1.96}(Ti_3O_7)$, and 8.27 Å, $Na_{0.86}H_{1.14}(Ti_3O_7)$, respectively, for the products obtained in 0.1 *M* NaCl and NaOH solutions. The value is 8.57 Å for $Na_2Ti_3O_7$. It can be linearly related to the amount of sodium in the compound and continuously expands with the uptake of sodium. This result suggests that the size of the interlayer ion is critical for the exchange reaction. $H_2Ti_3O_7$ was recovered by the HCl treatment on each cation-exchanged compound. Thus the structural reversibility of the exchange reaction was confirmed and there was no irreversible reconstruction of the layers in the course of the exchange process.

Reaction rate. Reaction rates were investigated in solutions of 0.1 *M* LiOH, NaOH, and KOH, where the pH of the solutions were greater than 12. The reaction rate of $H_2Ti_3O_7$ was strongly influenced by the kinds of alkali metals represented in Fig. 2. Li^+ was exchanged into $H_2Ti_3O_7$ most quickly. The amount of Li^+ was about 45% of total exchangeable cation in the sample soaked in 0.1 *M* LiOH solution for 1 hr. The value increased with duration and was 63% at 3 days. In NaOH solution, Na^+ content was 11% at 1 hr of duration and increased to 43% in 3 days. Exchange of K^+ was very slow, and only 11% of K^+ was attained in 3 days. The rate of the exchange reaction seems to be related to the ionic radii of the alkali metals. The reaction rate decreased in the order $Li^+ > Na^+ > K^+$. The interlayer cations of the trititanate were not hydrated even if the samples were in equilibrium with solution of 0.1 *M* *A*OH. The *a* lattice parameters of exchanged products under equilibrium with electrolyte were the same as those of the dried anhydrous samples. The neighboring $(Ti_3O_7)^{2-}$ layers stack along the *c* axis with exactly the same configuration so that the interlayer distance is not much different anywhere (*7*). Thus the smaller cation can diffuse faster in the interlayer space of trititanate than the larger one expanding the interlayer distance. The same experiments were peformed on $H_2Ti_4O_9 \cdot H_2O$. The reaction rate was only slightly different between three alkalies probably due to the presence of interlayer water.

Cation preference. The cation exchange of $H_2Ti_3O_7$ was studied in 0.1 *M* mixed solution prepared from equal amounts of LiOH, NaOH, KOH, and CsOH. Molar ratios of Li : Na : K : Cs in the products were

TABLE I

LITHIUM ACCUMULATION ON THE EXCHANGE REACTION OF $H_2Ti_3O_7$

Run	Molar ratios of alkali ions In the original solution Li : Na : K	In the product Li : Na : K
1	1.00 : 1.00 : 1.80	1.00 : 0.60 : 0.06
2	1.00 : 3.00 : 4.00	1.00 : 1.34 : 0.11
3	1.00 : 5.00 : 7.03	1.00 : 1.59 : 0.15
4	1.00 : 10.00 : 14.38	1.00 : 1.99 : 0.10

1.00 : 0.34 : 0.04 : 0.01 in trititanate due to the difference in the reaction rate observed in the previous section. $H_2Ti_3O_7$ prefers to absorb smaller cations into its interlayer regions. The smaller cations diffuse faster in the tight interlayer of trititanate.

The ion exchange of $H_2Ti_3O_7$ was performed in the mixed solution of LiCl, NaCl, and KCl. KOH was added to raise the pH of the original mixed solution to 12.5. The relative amount of Li against Na and K is much higher in the exchanged products than in the original solution as shown in Table I. Lithium might be accumulated by the repeated cycling of the ion exchange and the acid treatment.

Acknowledgments

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