CHEMISTRY LETTERS, pp. 1775-1778, 1985.

LITHIUM ION TITRATION OF LAYERED TITANIC ACID, $H_2Ti_3O_7$

Hajime IZAWA,[+] Fumio YASUDA, Shinichi KIKKAWA,[*] and Mitsue KOIZUMI
The Institute of Scientific and Industrial Research, Osaka University,
Osaka 567
[+]Research Laboratory, Osaka Cement Co. Ltd., Minamiokajima, Osaka 551

A lithium ion titration curve of $H_2Ti_3O_7$ was measured with pH value of solution in equilibrium with the exchanger. There might be two different exchangeable sites in the interlayer region of $H_2Ti_3O_7$. A new metastable phase, $Li_2Ti_6O_{13}$, was obtained by a dehydration of the Li^+-exchanged product in the temperature range of 300-500 °C.

$H_2Ti_3O_7$, an alkali extracted product from $Na_2Ti_3O_7$, has a layered crystal structure and behaves as a cation-exchanger in alkaline solution.1) Recently a preference for lithium was found out among alkali ions on exchange reactions.2) Lithium will be an important natural resources in lithium battery manufacturing and also in nuclear fusion technology in near future. The title compound could work as an ion-exchanger below 150 °C in water and the cycling of absorption and desorption was possible at least 30 times.3) However, the amount of lithium taken up into the titanic acid was about half of the total number of the interlayered ions in these studies. The reason for the half exchange has not been clear. Measurement of pH of the solution in equilibrium with the exchanger can give a preciser information about its exchange reaction.

In the present manuscript, a lithium ion titration of $H_2Ti_3O_7$ was performed by measuring pH value of solution in equilibrium with the exchanger. The exchanged products were characterized using X-ray powder diffractometry (hereafter denote as XRD) and DTA-TG.

$Na_2Ti_3O_7$ 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 h. The product was heated for another 20 h after grinding to complete the reaction. $H_2Ti_3O_7$ was obtained by removing Na^+ in

$Na_2Ti_3O_7$(ca. 10 g) in 500 cm^3 of 0.5 M HCl at 30 °C for 3 d. 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 lithium titration was investigated on $H_2Ti_3O_7$ whose average particle size was 1.3 µm. The samples(ca. 500 mg) were equilibrated with 40 cm^3 of aqueous solution of 0.1 M (LiCl+LiOH) having various mixing ratios in polyethylene bottles for 3 d at 60 °C, and then pH value of the solution was measured. The products were washed with distilled water and dried in vacuum at 30 °C. The exchanged products were dissolved in a mixed solution containing 15 times of $(NH_4)_2SO_4$ and 50 times of H_2SO_4 in weight at about 230 °C. The amounts of lithium were determined by atomic absorption. Those of titanium were determined by colorimetry using 4,4'-methylenediantipyrine. Dehydration processes and water contents of the products were estimated by DTA-TG. The dehydrated products were characterized by XRD.

Reaction rates of cation-exchange for lithium were very rapid.$^{2)}$ The amount of lithium was about 45% of total exchangeable cations in the sample soaked in 0.1 M LiOH solution for 1 h at 60 °C. The value was 63% in 3 d and 57% in 10 d. The reaction could be assumed to attain an equilibrium in 3 d under these conditions. The lithium titration curve, as a function of pH value of the solution, is shown in Fig.1. The theoretical ion-exchange capacity of $H_2Ti_3O_7$ is 7.76 mequiv./g. The titration curve suggested that the ion-exchange reaction occurred in two stages. The pH values of solutions were 6-8 in the range between 0 and 3.0 mequiv./g. After a half amount of proton was exchanged to lithium, the pH value began to increase up to about 11. The residual protons seemed to be attracted stronger by $(Ti_3O_7)^{2-}$ layers. The pH values did not increase so much in the range of 5.5 to 8.0 mequiv./g, and then began to increase again above the theoretical ion-exchange capacity.

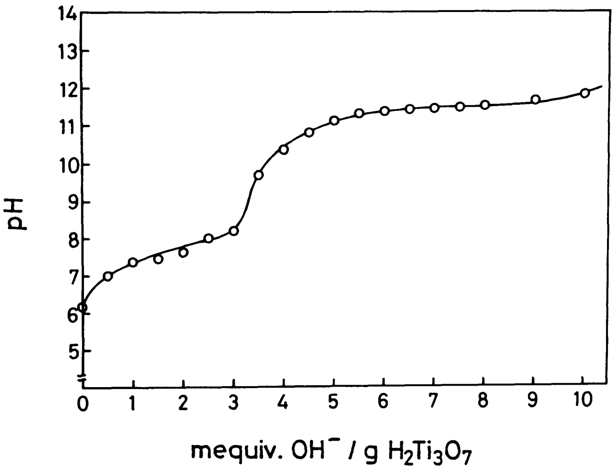

Fig. 1. Titration curve of $H_2Ti_3O_7$ with lithium ion.

There might be two different exchangeable sites in the interlayer region of $H_2Ti_3O_7$. One can be easily exchangeable and another is a little difficult. And a removal of the exchanged lithium from the latter site is relatively easy even in washing with water of the exchanged product. This might be the reason why the amount of lithium was ca. 50% of total ion-exchange capacity.[2,3) X-Ray structural analysis of $Na_2Ti_3O_7$ showed two kinds of sites for the interlayer sodium.[4) All atoms in $Na_2Ti_3O_7$ are in general positions 2e for $P2_1/m$. The positions Na1 and Na2 in the structure are respectively in (x=0.682, y=0.250, z=0.595) and in (x=0.508, y=0.250, z=0.154). These two crystallographic sites probably correspond to those found in the present titration.

XRD patterns of the products exchanged with lithium ions higher than 8 mequiv. OH^-/g $H_2Ti_3O_7$ were identical with those of $Li_2Ti_3O_7$ if the products were not washed with water. $Li_2Ti_3O_7$ was recently obtained by the ion-exchange of $Na_2Ti_3O_7$ in an excess amount of molten $LiNO_3$.[5) Its DTA-TG was performed up to 800 °C. $Li_2Ti_3O_7$ changed to a metastable phase(U-1 phase), which might be $Li_2Ti_6O_{13}$, at 450 °C evaporating Li_2O and then decomposed to a mixture of spinel $Li_{1.33}Ti_{1.66}O_4$(ASTM 26-1198) and anatase TiO_2 at 620 °C. This U-1 phase had a similar XRD pattern to that of $Na_2Ti_6O_{13}$ as shown in Table 1.

XRD of the product taken out just after the first step of exchange reaction was analogous to that of $Li_{0.95}H_{1.05}(Ti_3O_7)$.[3) Its DTA-TG curves are shown in Fig.2. Three apparent endothermic peaks were observed in the temperature ranges of 300-410, 410-500, and 640-800 °C. Another endothermic reaction might occur in the range of 500-640 °C. Very small depression could be found in this temperature range on the DTA curve. The sample heated to 500 °C was a mixture of anatase and an unknown phase(U-2 phase). This U-2 phase had a few XRD peaks as shown in Table 1. The peaks agreed with some of the peaks of U-1 phase having large intensity. The observed weight loss in the temperature range of 300-500 °C was 3.3%. The weight of one molar water corresponds to 3.4% of the weight of two molar $LiH(Ti_3O_7)$. The former two endothermic peaks with one step weight loss seemed to correspond to the formation of $Li_2Ti_6O_{13}$. The sample heated to 640 °C was a mixture of

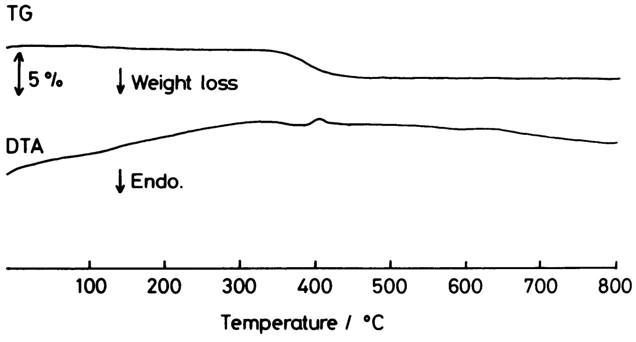

Fig.2. DTA-TG of $Li_{0.95}Ti_{1.05}(Ti_3O_7)$.

Table 1. X-Ray powder diffraction data for U-1 and U-2 phases were compared with the Guinier powder pattern of $Na_2Ti_6O_{13}$ 6)

U-1 phase		U-2 phase		$Na_2Ti_6O_{13}$		
d/nm	I/I_0	d/nm	I/I_0	d/nm	hkl	intensity
0.763	14			0.747	200	s
0.636	10			0.627	20$\bar{1}$	ms
0.537	61	0.537	72	0.3727	400	vw
0.379	8			0.3633	110	s
0.365	8			0.3327	111	vw
0.336	100	0.339	70	0.2993	310	ms
0.297	47	0.297	60	0.2965	20$\bar{3}$	ms
0.269	4			0.2927	31$\bar{1}$	ms
0.238$^{a)}$	67	0.238	100$^{a)}$	0.2781	112	mw
0.233$^{a)}$	11			0.2763	311	w
0.204	44	0.205	30	0.2677	402	m
0.192	13			0.2501	60$\bar{1}$	mw
0.188$^{a)}$	57	0.188	98$^{a)}$	0.2365	11$\bar{3}$	vw
0.177	8			0.2087	40$\bar{4}$	ms
0.167$^{a)}$	25			0.2047	602	ms
				0.1873	020	s

a) These XRD peaks overlapped with those of anatase.

anatase and $Li_{1.33}Ti_{1.66}O_4$. The latter reaction completed at 640 °C. The sample heated to 800 °C was a mixture of anatase, rutile and $Li_{1.33}Ti_{1.66}O_4$. Anatase changed to rutile in the temperature range of 640-800 °C.

References

1) H. Izawa, S. Kikkawa, and M. Koizumi, J. Phys. Chem., 86, 5023(1982).

2) H. Izawa, S. Kikkawa, and M. Koizumi, J. Solid State Chem., in press.

3) H. Izawa, S. Kikkawa, and M. Koizumi, Yogyo Kyokai Shi, submitted for publication.

4) S. Andersson and A. D. Wadsley, Acta Crystallogr., 14, 1245(1961).

5) S. Kikkawa, F. Yasuda, and M. Koizumi, Mater. Res. Bull., in press.

6) S. Andersson and A. D. Wadsley, Acta Crystallogr., 15, 194(1962).

(Received August 24, 1985)