Na^+/H^+ Ion-exchange Process on Layered Hydrous Titanium Dioxide

Takayoshi Sasaki,* Mamoru Watanabe, Yū Komatsu, and Yoshinori Fujiki
National Institute for Research in Inorganic Materials, 1-1 Namiki, Sakura-mura, Niihari-gun, Ibaraki 305

(Received July 3, 1985)

The Na^+/H^+ ion-exchange on layered hydrous titanium dioxide, $H_2Ti_4O_9\cdot1.2$—$1.3H_2O$, has been studied from chemical and structural aspects. The ion-exchange reaction proceeded stepwise through two stages [0—50%, 50—72% conversion]. In stage I a discontinuous change in interlayer distance took place and the 1/2-exchanged phase with a widened interlayer distance appeared. The exchange in stage II proceeded *via* a solid solution and resulted in the 3/4-exchanged phase. The variation in unit cell dimensions indicates that these partially exchanged phases were formed by swelling the spacing of adjacent $[Ti_4O_9^{2-}]_n$ sheets. The structural and the thermoanalytical data can be interpreted on the basis of the structural model in which sodium ions and water molecules are arranged in a double row in the interlayer region.

Layered hydrous titanium dioxide, $H_2Ti_4O_9\cdot1.2$—$1.3H_2O$, has recently been prepared from potassium tetratitanate ($K_2Ti_4O_9$) by extracting interlayered potassium ions.[1—3] This material is attractive since it is one of the first hydrous metal oxides with a layer structure which act as inorganic ion exchangers. The material has a layer structure which consists of the host macroanion, $[Ti_4O_9^{2-}]_n$ sheets, and exchangeable protons (see Fig. 1).[4] Two types of exchangeable protons exist in the interlayer region; one oxonium ion and one hydroxylated proton per chemical formula. The unit cell has two equivalent interlayer spaces which are shifted by $b/2$ along the b axis. Each space contains two oxonium ions and two hydroxylated protons. This means that the material has four independent exchange sites. The authors have studied the K^+/H^+ ion-exchange process and obtained the satisfactory interpretation on the reaction mechanism which is consistent with the structural model described above:[4] Potassium ions replace the four exchange sites one by one. It is interesting and important to examine the exchange behavior of another ion to investigate whether the analogous explanation can be applied or not.

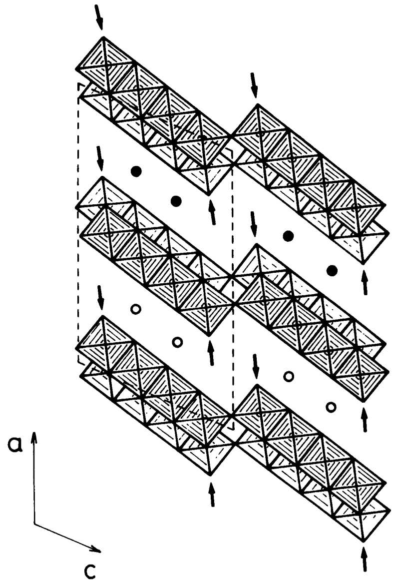

Fig. 1. Idealized representation of the crystal structure of layered hydrous titanium dioxide projected along (010). Arrows and circles show the possible positions of hydroxyl bonds and hydronium ions, respectively.

The ion-exchanged phases of layered hydrous titanium dioxide can be regarded as hydrated phases of alkali metal tetratitanate. Since these hydrated phases are chemically active, they are promising as catalyst carriers and starting or intermediate materials for further syntheses. There have been several reports on the hydrated phases which are obtained by hydrolyzing potassium tetratitanate.[1—3,5,6] This field is, however, in a state of confusion because the studies were not done systematically and they do not agree with each other. Moreover, no study has yet appeared on the hydrated phases of sodium tetratitanate. Thus it is significant to characterize the Na^+-exchanged phases from the viewpoint of clarifying the system of the hydrated phases of alkali metal tetratitanate.

This paper describes the Na^+/H^+ ion-exchange behavior on layered hydrous titanium dioxide and characterization of the Na^+-exchanged phases. The ion-exchange mechanism is discussed from chemical and structural aspects.

Experimental

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

Preparation of Layered Hydrous Titanium Dioxide. Potassium tetratitanate ($K_2Ti_4O_9$) was grown in a fibrous form by slowly cooling a mixture of K_2O-$3TiO_2$ in a K_2MoO_4 flux melt from 1150 °C to 950 °C.[7] Layered hydrous titanium dioxide was obtained by extracting interlayered potassium ions from potassium tetratitanate:

$$K_2Ti_4O_9(s) + 2H^+(aq) + 1.2\text{—}1.3H_2O(aq) \longrightarrow H_2Ti_4O_9\cdot1.2\text{—}1.3H_2O(s) + 2K^+(aq)$$

The potassium ion extraction was performed by a column technique; about 15 g of potassium tetratitanate in a column (2.5 cm i.d.) was treated with a 1 mol dm^{-3} HCl solution until the potassium ion concentration in the effluent decreased to be negligible. The resulting product was washed with water and was dried over a saturated NaCl solution (relative humidity: 70%) to a constant weight. The material used in this experiment had a composition of $H_2Ti_4O_9 \cdot 1.2H_2O$ (theoretical ion-exchange capacity: 5.57 mequiv g^{-1}) because the weight loss at 800 °C was 10.9%.

Titration Experiment. The titration experiment was carried out batchwise by shaking a weighed amount of the material with a 0.1 mol dm^{-3} (NaCl+NaOH) solution at 25 ± 0.5 °C. The solution to solid ratio was 0.1 $dm^3 g^{-1}$ and the ratio of NaCl/NaOH varied from 0.1 M/0.0 M to 0.0 M/0.1 M (1 M=1 mol dm^{-3}). After shaking for 4 d, an aliquat of the supernatant solution was pipetted and its sodium ion content as well as pH value was measured. The sodium ion uptake was calculated from the difference between initial and equilibrium concentrations of the solution. The solid was filtered off, washed with water and then dried over a saturated NaCl solution to a constant weight. The solid was characterized by chemical analysis, thermal analysis and powder X-ray diffractometry.

Apparatus. A TOA HM-20E digital pH meter was used to measure pH values of the solution. Sodium ion contents in the solution were determined by a Hitachi 180-80 atomic absorption spectrophotometer. X-Ray powder diffraction patterns were recorded by using a Philips PW-1130 type diffractometer with Ni-filtered Cu $K\alpha$ radiation (λ=1.5405 Å). Silicon or titanium dioxide (rutile) was used as an internal standard. The lattice constants were refined by the least-squares method.[8] The DTA-TG measurement was performed by using a Rigaku Denki M 8075 thermal analyzer at a heating rate of 10 °C min^{-1}.

Results and Discussion

Ion-exchange Process. Figure 2 shows the sodium ion titration curve. After an initial rising portion, the pH value increased rather gradually up to approximately 40% conversion. A pH jump was observed at 40—50% conversion and then the curve had a mild slope region again. At the uptake of 4.0 mequiv g^{-1}, the pH value increased steeply, indicating that the apparent capacity was approximately 3/4 of the theoretical limit.

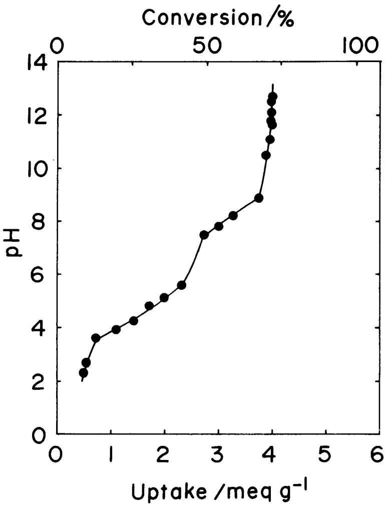

Fig. 2. Sodium ion titration curve. Exchanger: 0.2 g, Titrant: 20 cm^3 of 0.1 mol dm^{-3} (NaCl+NaOH) solution.

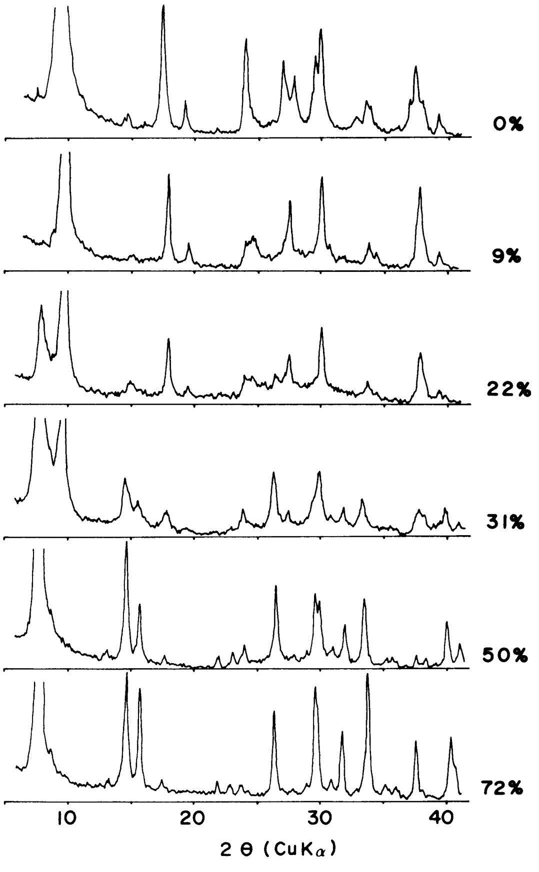

Fig. 3. X-Ray powder diffraction patterns of the sodium ion-exchanged solids at various loading levels. Numerals represent the percent uptake of sodium ion.

Figure 3 shows the X-ray powder diffraction patterns of the ion-exchanged solids at various loading levels which were obtained in the titration experiment. The X-ray patterns changed continuously up to the loading level of 0.5 mequiv g^{-1}. This means that layered hydrous titanium dioxide (designated as phase HH) can accommodate sodium ions by forming a solid solution in this region. This region corresponded to the initial rising portion of the titration curve. Beyond this loading level, two immiscible solid phases were present; one was the resulting phase of the solid solution and the other was the exchanged phase with a widened interlayer distance of 11.2 Å. The latter phase increased as the exchange proceeded, and was observed alone near 50% conversion. This phase was verified as the 1/2-exchanged phase since the chemical composition was determined to be $Na_{0.98}H_{1.02}Ti_4O_9 \cdot 3.3H_2O$ (termed phase Na1). Further exchange took place without an appreciable change in interlayer distance and water content. This indicates that sodium ions were taken into phase Na1 *via* a solid solution. The 3/4-exchanged phase (phase Na2) was formed at a result of this solid solution.

From the above results, the Na^+/H^+ ion-exchange process can be divided into two stages; stage I [0—50% conversion] and stage II [50—72%]. The ion-exchange reaction in each stage can be formulated as follows: stage I:

$$\underset{[9.1\ \text{Å}]}{H_2Ti_4O_9\cdot 1.2H_2O(s)} + Na^+(aq) + 2.1H_2O(aq) \longrightarrow \underset{[11.2\ \text{Å}]}{NaHTi_4O_9\cdot 3.3H_2O(s)} + H^+(aq)$$

stage II:

$$\underset{[11.2\ \text{Å}]}{NaHTi_4O_9\cdot 3.3H_2O(s)} + 0.4Na^+(aq) \longrightarrow \underset{[11.2\ \text{Å}]}{Na_{1.4}H_{0.6}Ti_4O_9\cdot 3.3H_2O(s)} + 0.4H^+(aq)$$

where numerals in brackets give the interlayer distance (d_{200}), and the subscripts "s" and "aq" represent solid and aqueous phases, respectively.

Figure 4 gives the approximate ratios of the above mentioned phases as a function of sodium ion uptake, which were estimated from the relative intensities of the (200) reflection.

Interpretation of the Ion-exchange Process. Analogously to the K^+/H^+ exchange process,[4] the Na^+/H^+ exchange proceeded in a stepwise fashion *via* several partially exchanged phases with different interlayer distances. Table 1 summarizes the salt forms of the solid phases that appeared in both processes. The two processes tended to be divided at $n/4$ of the theoretical ion-exchange capacity (n=1,2,3,4). This phenomenon is consistent with the structural model of phase HH in which four independent exchange sites exist. The Na^+/H^+ exchange process can be interpretted as follows: Two of the four sites are replaced simultaneously to form the 1/2-exchanged phase (stage I). The third site is occupied in stage II, which results in the 3/4-exchanged phase.

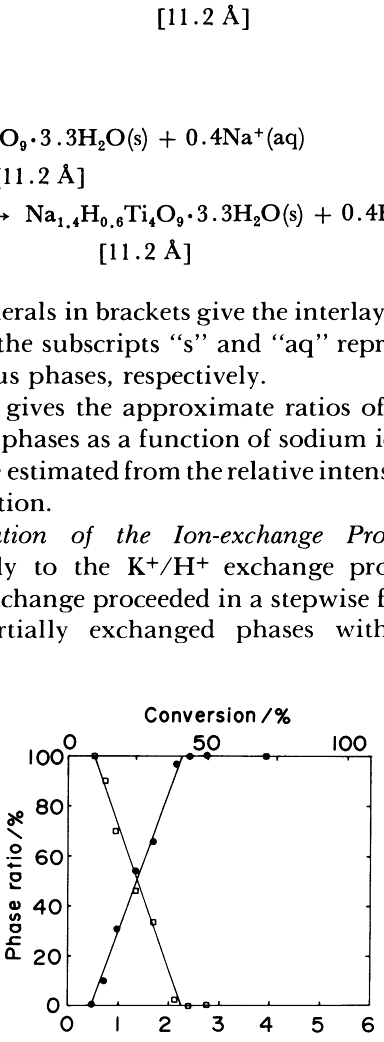

Fig. 4. Approximate ratios of the sodium ion-exchanged phases as a function of uptake.
□: Phase HH, ●: phase Na1, ■: phase Na2.

On the other hand, there are several differences between the Na^+/H^+ and K^+/H^+ exchange processes.

i) A complete exchange was not achieved for the Na^+/H^+ exchange.

ii) A 1/4-exchanged phase as well as a fully-exchanged one did not appear in the Na^+/H^+ exchange process.

iii) Phases Na1 and Na2 have larger interlayer distances than the corresponding K^+-exchanged phases.

Item i) may be due to the higher hydration energy of sodium ion than potassium ion:[9] A cation must give up a part or all of hydrated water when it enters into a host lattice. Therefore, a cation with a higher hydration energy is more difficult to be ion-exchanged.

Fact ii) may be explained by the idea that the ion-exchange behavior is rather dependent on the relative stability of the solid phases formed than the acidities of exchangeable protons.

Item iii) will be discussed in the next section.

Characterization of the Ion-exchanged Phases. The X-ray powder patterns of phases Na1 and Na2 could be indexed as a C base-centered monoclinic lattice. The X-ray data of phase Na1 is given in Table 2. The refined lattice constants are listed in Table 3 together with the values for phase HH.

Phase Na1 has the largely expanded a axis while the other three parameters were almost equal to those of phase HH. This means that phase Na1 was formed by swelling the interlayer spacing while the host framework of $[Ti_4O_9{}^{2-}]_n$ was remained unchanged.

Phase Na1 contains 1 mol of sodium ion and ≈3 mol of water per formula weight in the interlayer region. In contrast sodium tetratitanate ($Na_2Ti_4O_9$) accommodates 2 mol of interlayered sodium ion per formula weight. This means that phase Na1 accom-

TABLE 1. COMPARISON OF THE Na^+/H^+ AND K^+/H^+ ION-EXCHANGE PROCESSES

Conversion	Na^+/H^+ exchange		K^+/H^+ exchange[a)]	
	Salt form	d_{200}/Å	Salt form	d_{200}/Å
0	$\overline{\mathrm{HH}}\cdot 1.2H_2O$	9.1	$\overline{\mathrm{HH}}\cdot 1.2H_2O$	9.1
1/4	—	—	$\overline{K_{0.5}H_{1.5}}\cdot 0.6H_2O$	8.6
1/2	$\overline{\mathrm{NaH}}\cdot 3.3H_2O$	11.2	$\overline{\mathrm{KH}}\cdot 0.5H_2O$	9.0
≈3/4	$\overline{Na_{1.4}H_{0.6}}\cdot 3.3H_2O$	11.2	$\overline{K_{1.4}H_{0.6}}\cdot 1.2H_2O$	9.8
1	—	—	$\overline{\mathrm{KK}}\cdot 2.2H_2O$	10.9

a) Data taken from Ref. 4). b) d_{200}: Interlayer distance. c) $\overline{M_xH_{2-x}}\cdot nH_2O$ is the abbreviated form of $M_xH_{2-x}Ti_4O_9\cdot nH_2O$.

TABLE 2. X-RAY POWDER DIFFRACTION PATTERN FOR PHASE Na1

$h\ k\ l$	d_{calc}/Å	d_{obsd}/Å	Intensity
2 0 0	11.24	11.18	vs
2 0 $\bar{1}$	10.06	10.04	w
2 0 1	6.72	6.74	vw
4 0 $\bar{1}$	6.03	6.05	s
4 0 0	5.62	5.62	m
4 0 $\bar{2}$	5.03	5.03	vw
6 0 $\bar{1}$	4.05	4.05	vw
6 0 $\bar{2}$	3.868	3.866	vw
4 0 $\bar{3}$	3.842	3.842	vw
6 0 0	3.747	3.746	vw
1 1 0	3.711	3.713	w
3 1 0	3.363	3.362	s
4 0 2	3.360		
8 0 $\bar{2}$	3.016	3.014	s
8 0 $\bar{1}$	3.012		
5 1 $\bar{1}$	2.977	2.979	m
5 1 0	2.886	2.888	vw
8 0 0	2.810	2.807	m
4 0 3	2.660	2.662	s
1 1 3	2.542	2.541	vw
8 0 1	2.506	2.505	vw
10 0 $\bar{1}$	2.388	2.389	w
6 0 $\bar{5}$	2.346	2.346	vw
6 0 3	2.240	2.240	m
8 0 $\bar{5}$	2.201	2.201	w
10 0 1	2.056	2.055	vw
10 0 $\bar{5}$	2.012	2.012	m
12 0 $\bar{1}$	1.976	1.976	w
8 0 $\bar{6}$	1.921	1.920	m
0 2 0	1.881	1.881	m
12 0 0	1.873	1.873	vw
2 2 0	1.856	1.854	w
1 1 5	1.856		
0 2 1	1.855		

TABLE 3. LATTICE CONSTANTS OF THE SODIUM ION-EXCHANGED PHASES

phase	a/Å	b/Å	c/Å	β/°
HH[a)]	19.968(4)	3.746(1)	12.025(2)	114.01(1)
Na1	24.337(5)	3.763(1)	12.078(3)	112.52(2)
Na2	24.378(4)	3.781(1)	12.054(3)	113.10(1)

a) Data taken from Ref. 4). b) Numerals in parentheses give the estimated standard deviations in the last digit.

modates a double number of interlayered species compared with the case of sodium tetratitanate. Phase Na1 has a larger interlayer distance than sodium tetratitanate (d_{200}=8.38 Å)[10)] by 2.8 Å, which is equal to the diameter of a water molecule. We can propose the structural model to explain the above facts: Interlayered sodium ions and water molecules are arranged in a double row which lies on the levels at y=0 and 1/2, as shown in Fig. 5. Although there may be other possible structural models for phase Na1, the model in Fig. 5 is appropriate to explain the ion-exchange behavior and thermoanalytical data described later. For example, this model gives a good explanation for the fact iii). (The corresponding K^+-

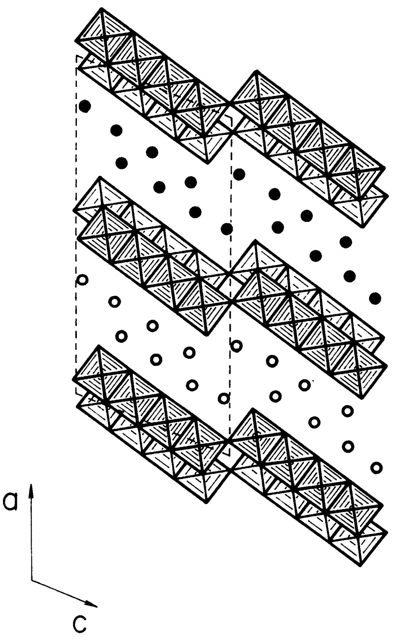

Fig. 5. Idealized structural model for phase Na1. (Projection along (010)).
●: y=1/2, ○: y=0.
Each circle is occupied at 25 and 75% by sodium ion and water molecule, respectively.

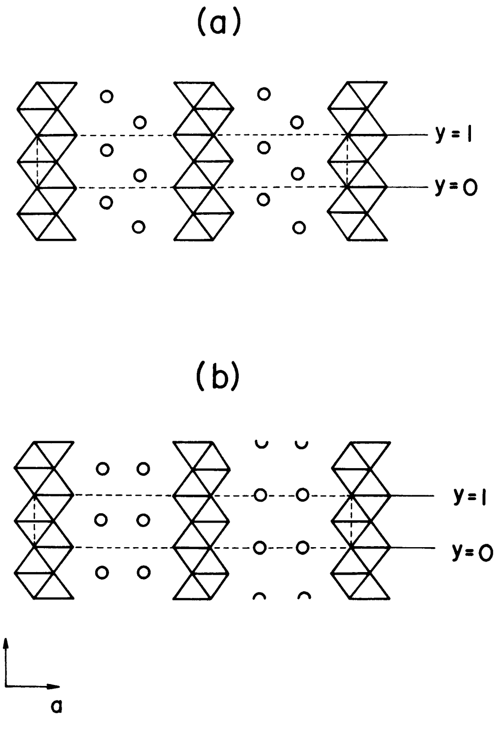

Fig. 6. Models for the arrangement of interlayered species. (Projection along (001)).
(a) Fully K^+-exchanged phase, (b) Phase Na1.
In the fully K^+-exchanged phase each circle is occupied evenly by potassium ion and water molecule, and in phase Na1 at 25 and 75% by sodium ion and water molecule, respectively.

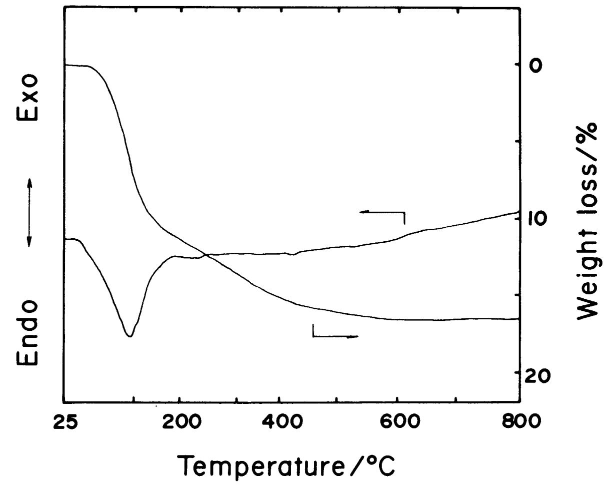

Fig. 7. DTA-TG curve of phase Na1. Heating rate: 10 °C min^{-1}.

exchanged phase has a single row arrangement.)[4]

The similar double row arrangement of interlayered species has been reported for the fully K^+-exchanged phase.[4] The double row is tilted with respect to the (010) plane in this case: Potassium ions and water molecules occupy the sites which are shifted above and below the levels at $y=0$ and $1/2$ (see Fig. 6). This tilt is considered to be due to the accommodation of relatively large interlayered species; potassium ions (ionic radius: 1.51 Å) and water molecules (1.40 Å).[11] On the contrary, phase Na1 can accommodate the interlayered species at the same y level since sodium ion is much smaller in size (1.16 Å)[11] than potassium ion.

The dehydration of phase Na1 took place apparently in two steps as shown in Fig. 7. The weight losses in each step were 10.0 and 6.5% and corresponded to the loss of 2.3 mol of hydrated water up to 100 °C and then 1.5 mol in the temperature range of 100—600 °C. When phase Na1 was heated at 100 °C, the interlayer spacing decreased to 8.4 Å. The resulting material easily rehydrated to restore the original state by being exposed to moisture in the air. Being heat-treated up to 600 °C, the material was decomposed into sodium hexatitanate ($Na_2Ti_6O_{13}$) and anatase (TiO_2).

In summary, the dehydration process can be written in the following scheme:

$$\begin{tikzcd}
 & \mathrm{NaHTi_4O_9\cdot 3.3H_2O} \arrow[d, shift right, "100^\circ\mathrm{C}"'] & {[11.2\ \text{Å}]} \\
\text{step I} & \mathrm{NaHTi_4O_9\cdot H_2O} \arrow[u, shift right, "\text{in the air}"'] \arrow[d, "100\text{—}600^\circ\mathrm{C}"'] & {[8.4\ \text{Å}]} \\
\text{step II} & \mathrm{1/2Na_2Ti_6O_{13}+TiO_2} &
\end{tikzcd}$$

The process can be understood on the basis of the structural model described above (see Fig. 8). In step I the double row arrangement of interlayered species is destroyed by evaporating 8 water molecules per unit cell (2 mol/formula weight). The resulting phase has a single row arrangement of sodium ions and water molecules. This inference is consistent with the shrinkage of interlayer distance, 2.8 Å, which is in good agreement with the size of a water molecule. The weight loss in step II corresponds to the removal of remaining interlayered water molecules and the condensation of the host framework. The layer structure cannot be maintained by such a dehydration.

The water content and interlayer distance of phase Na2 were almost equal to those of phase Na1. This fact implies that phase Na1 has some space in the interlayer region which can accommodate additional sodium ions.

The authors would like to express their gratitude to

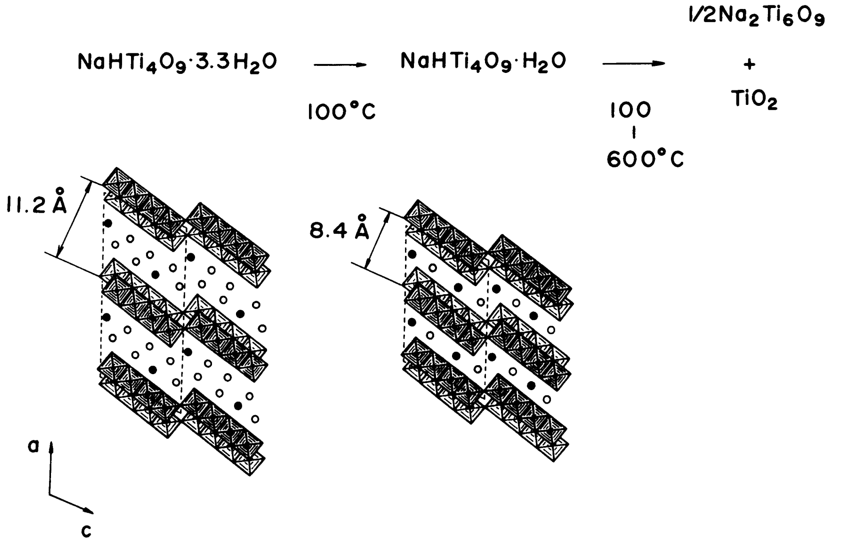

Fig. 8. Schematic explanation of the dehydration process of phase Na1. The closed circles and open ones denote sodium ions and water molecules, respectively. The configurations of the interlayered species are tentative.

Dr. Takefumi Mitsuhashi, National Institute for Research in Inorganic Materials, for his valuable discussion on the thermal analysis.

References

1) R. Marchand, L. Brohan, and M. Tournoux, *Mat. Res. Bull.*, **15**, 1129 (1980).

2) N. Ohta and Y. Fujiki, *Yogyo Kyokai Shi*, **88**, 1 (1980).

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

4) T. Sasaki, M. Watanabe, Y. Komatsu, and Y. Fujiki, *Inorg. Chem.*, **24**, 2265 (1985).

5) Y. Fujiki, F. Izumi, T. Ohsaka, and M. Watanabe, *Yogyo Kyokai Shi*, **85**, 475 (1977).

6) T. Shimizu, H. Yanagida, M. Hori, K. Hashimoto, and Y. Nishikawa, *Yogyo Kyokai Shi*, **87**, 565 (1979).

7) Y. Fujiki and N. Ohta, *Yogyo Kyokai Shi*, **88**, 111 (1980).

8) D. E. Appleman and H. T. Evans, *NTIS Document*, No. PB-216188 (1973).

9) H. F. Halliwell and S. C. Nyburg, *Trans. Faraday Soc.*, **59**, 1126 (1963).

10) M. Dion, Y. Piffard, and M. Tournoux, *J. Inorg. Nucl. Chem.*, **40**, 917 (1978).

11) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1973).