

Preparation, Structure, and Ion-Exchange Properties of $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$

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A sodium titanate, $\text{Na}_4\text{Ti}_9\text{O}_{14} \cdot x\text{H}_2\text{O}$, was synthesized at low temperatures (90–280°C) by a reaction of either anatase or titanium isopropoxide with NaOH. $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ is a layered compound with an interlayer distance of 6.9 Å in the anhydrous form, ≈ 8.6 Å in the metastable "semihydrous" form, and 10.0 Å in the fully hydrated form. Regardless of its hydration state, this sodium titanate has an ion-exchange capacity of 4.74 meq/g of $\text{Na}_4\text{Ti}_9\text{O}_{20}$, and all the Na^+ ions are exchangeable. When heated to 700°C, $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ decomposes to a mixture of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$. © 1988 Academic Press, Inc.

Introduction

In the late 1970's a new sodium titanate product was prepared and reported to be especially effective for use in the separation of radioactive nuclides from nuclear waste solutions (1). The preparation method consisted of mixing sodium hydroxide, in methanol solution, with titanium isopropoxide and precipitating the sodium titanate by adding water. This compound was found to exhibit high selectivities as an ion exchanger for strontium ion and the actinides (2, 3). Lynch *et al.* (1) proposed the formula $\text{NaTi}_2\text{O}_5\text{H}$ for this compound. However, its structure and composition were not characterized with a high degree of certainty.

Most of the known sodium titanates belong to either of the following series: $\text{Na}_2\text{Ti}_n\text{O}_{2n+1}$ or $\text{Na}_4\text{Ti}_n\text{O}_{2n+2}$. Of the former se-

ries all the members with $n = 1-9$ have been reported (4-11). Compounds with n odd ($n = 1, 3,$ and 5) have been reported for the latter series (12-14). Many of these sodium titanates are layered compounds. The layers are constructed of TiO_6 octahedra sharing edges with Na^+ ions located between the layers. In some of the layered compounds the Na^+ ions are readily exchangeable. Most of the sodium titanates have been synthesized from mixtures of Na_2CO_3 and TiO_2 by high temperature solid-state reactions, but the highest member, $\text{Na}_2\text{Ti}_9\text{O}_{19}$, has been obtained only by a hydrothermal method at temperatures above 400°C.

An extensive literature can be found for the ion-exchange properties of hydrous titanium oxide (15, 16). Due to the amorphous nature of the exchanger, however, the ion-exchange mechanism is not entirely known. For the crystalline titanates the literature is limited, but ion-exchange properties have been reported for $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{K}_2\text{Ti}_2\text{O}_5$, Na_2

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Ti_4O_9 , and $\text{K}_2\text{Ti}_4\text{O}_9$ (17–20). The purpose of this study is to better define the structure and ion-exchange behavior of the low temperature sodium titanate, reported by Lynch to be $\text{NaTi}_2\text{O}_5\text{H}$, and possibly relate it to the known families of titanates.

Experimental

Preparation

A broad spectrum of preparative methods were employed based upon two sources of titanium: titanium(IV) isopropoxide and anatase.

Preparation from titanium isopropoxide. Titanium isopropoxide (Alfa Products, 95%) was used without further purification. Sodium titanate was synthesized from titanium isopropoxide (referred to a TiIP) by two methods:

(a) Sol-gel method: TiIP was diluted with methanol in a ratio 1 : 1 and a 10% solution of NaOH in methanol was added. The sodium to titanium ratio in the starting materials was varied in the range 2/9–3/1. An alcohol-soluble intermediate was formed and the solution remained clear. Sodium titanate was precipitated by exposing the solution to the atmosphere so that moisture was taken up while at the same time solvent evaporated. The ensuing hydrolysis resulted in the formation of a gel. The gel was air-dried and then treated hydrothermally in water for 20 hr at temperatures of 160–320°C and autogenous pressures corresponding to values resulting from approximately 50% filling of the liners: at 300°C it was approximately 150 bar and at 250°C about 40 bar. In most of the reactions the volume of the liners was 15 ml, but in some cases it was 150 ml.

(b) Hydrous titanium oxide (referred to as HTiO) was precipitated by treating 50 ml of TiIP with 20 ml of water at ambient temperature. This compound was then dried at 110°C and treated hydrothermally in NaOH

solutions of different concentrations. A sample of the HTiO was heated to 800°C, and its titanium content was calculated by taking into account that the heated product was TiO_2 .

Preparation from anatase. The anatase-type hydrous titanium oxide used was an industrial intermediate from the sulfate process for the preparation of pigment-grade titanium dioxide. Two to five grams of this oxide was dried at 100°C, slurried with 20–50 ml of water, and heated to boiling. Different amounts of 10 M NaOH solution were added and the slurry was stirred while boiling for 2–3 hr. Portions of the products were then treated hydrothermally for 20 hr in their mother liquor at temperatures of 200–300°C. Hydrothermal treatments were carried out in order to increase crystallinity and to determine the formation range of the sodium titanate. The treatments were carried out in Teflon-lined steel bombs. After 20 hr of hydrothermal treatment, the products were recovered by filtration, washed free of NaOH with deionized water, and dried at 100°C.

Determination of Composition

Sodium and titanium contents in the products were determined by neutron activation analysis (NAA) at the Texas A&M University Nuclear Reactor. Samples, approximately 50 mg in size, were irradiated and the resulting ^{24}Na and ^{51}Ti nuclide activities were determined with a Ge(Li) detector and a multichannel analyzer using $\text{Na}_2\text{Ti}_3\text{O}_7$ as a standard.

X-ray Diffraction Studies

X-ray diffraction patterns of the dried powders were obtained with a Seifert-Scintag PAD-II automated powder diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at a scanning rate of 2°/min.

Determination of Water Contents

Water content of the products was determined in most cases by heating samples to 700–800°C and calculating the water content from the weight loss. For some products the water content was determined by trace gas analysis with a Cahn RG thermal balance using a heating rate of 4°/min.

Electron Microscopic Studies

Two sodium titanate products were studied by electron microscopy. The first was prepared hydrothermally at 250°C from HTiO, and the second was prepared from TiIP by the sol-gel method followed by a hydrothermal treatment at 250°C. A JEOL JSM-35CF scanning electron microscope (SEM) was used operating at 15 keV and 10⁴ magnification. A Zeiss 10C transmission electron microscope (TEM) was used to obtain micrograph images. The TEM was operated at 60 keV and the camera constant was 4.50 cm Å.

Determination of Titration Curves

Sodium titanate was titrated with HCl by shaking 0.2-g samples of the exchanger with 20 ml of solution containing 0–20 ml 0.10 M HCl. After 5 days equilibration, the solid was separated with a 0.45- μ m Millipore filter. The pH of the filtrate, as well as its sodium ion concentration, were determined by atomic absorption spectroscopy (Perkin-Elmer 306 and Jarrell-Ash 810). For the back titration, sodium titanate was converted to the H⁺ form by several consecutive equilibrations with 0.1 M HCl solution. Samples (0.2 g) of the H⁺-form titanate were shaken with 20 ml of 0.1 M (NaOH + NaCl) solution in which the ratio of NaOH to NaCl was progressively increased. The same equilibration times and analytical procedures were used to determine uptakes as in the forward titration. All uptake values given are based upon the dry weight of exchanger.

Results and Discussion

Composition of the Sodium Titanate

Sodium titanate, prepared from anatase by boiling for 3 hr in a NaOH solution for which the molar Na to Ti ratio was 2:1, gave a product whose X-ray diffraction pattern consisted of very broad reflections at $\approx 10^\circ$, $\approx 24^\circ$, $\approx 28^\circ$, and $\approx 48^\circ$. The first reflection was the strongest. The pattern did not match those of any of the known sodium titanates or titanium oxides. Neutron activation analysis for two samples yielded a ratio of Ti to Na of 2.31 ± 0.05 .

When sodium titanate was hydrothermally prepared from anatase, with the Na to Ti reactant ratio of 2:1 at 200–300°C, the peaks in the pattern were sharper with the broadness decreasing with increasing temperatures. The relatively high intensity of the first peak, which corresponds to the interlayer distance, appeared to result from preferred orientation of the crystallites. The X-ray pattern of this solid prepared at 300°C, but dried at 110°C, is shown in Fig. 1 as curve b.

Analysis of three of these hydrothermally prepared samples in the temperature range 200–300°C gave a molar Ti to Na ratio of 2.16 ± 0.03 (determined by NAA). Five sodium titanates, prepared hydrothermally from TiIP at 150–250°C with the molar Na

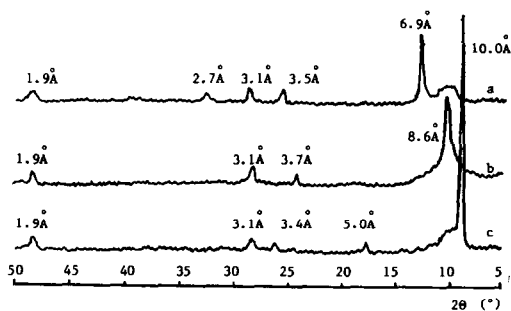


FIG. 1. X-ray diffraction patterns of $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ with different water contents. (a) Anhydrous phase; (b) semihydrated phase; (c) fully hydrated phase.

TABLE I
ANALYTICAL DATA FOR SODIUM TITANATE
PREPARED AT LOW TEMPERATURE

Source of titanium	Ti/Na ratio in reactants	Reaction temperature (°C)	Reaction time (hr)	Ti/Na ratio in product
Anatase	0.87	100	3	2.35
Anatase	0.87	100	3	2.28
Anatase	0.5	200	20	2.14
Anatase	0.5	250	20	2.20
Anatase	0.5	300	20	2.15
TiIP	1.33	150	20	2.19
TiIP	1.33	200	20	2.26
TiIP	1.33	250	40	2.28
TiIP	1.0	250	40	2.32
TiIP	1.0	250	20	2.21

to Ti ratio 3:4 and 1:1, gave the same X-ray pattern and the products had the molar Ti to Na ratio 2.25 ± 0.05 . One sodium titanate product prepared from TiIP at room temperature gave a ratio of 2.41. Based on these composition measurements (Table I) a formula of $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ was deduced for the sodium titanate under study. For a formula weight for the anhydrous $\text{Na}_4\text{Ti}_9\text{O}_{20}$ of 842.86, the theoretical ion-exchange capacity is 4.74 meq/g.

Reaction Diagram

Reference to Table I shows that an excess of sodium was required to form $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$, and the magnitude of this excess was dependent on the source of titanium. When hydrous titanium oxide was precipitated from TiIP with water and then treated hydrothermally with NaOH at 280°C, $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ was obtained with a reactant mix in which the Na to Ti ratio was 1:1. However, when anatase was used, the same ratio of reactants gave anatase as the only product at 200–250°C, but at 300°C the product was a Na_xTiO_2 bronze (21). A ratio of 2:1 was required in this case to get the desired product.

The only way to prepare an entirely homogeneous precursor with respect to Ti and Na is the sol-gel technique. This technique enables one to make the preparation independent of the solubility of the titanium compound used. The reaction diagram obtained by treating sol-gel precursors hydrothermally with different Na to Ti ratios is given in Table II.

TABLE II
PRODUCTS OBTAINED FROM TITANIUM ISOPROPOXIDE AND NaOH BY THE SOL-GEL METHOD FOLLOWED BY HYDROTHERMAL TREATMENT OF THE GEL^a

T (°C)	Na/Ti ratio in the starting materials (mole)						
	2/9	4/9	3/4	1/1	4/3	2/1	3/1
320	Anatase ≧ Na_xTiO_2	Brookite + Na_xTiO_2	Na_xTiO_2	Na_xTiO_2	Na_xTiO_2 > $\text{Na}_4\text{Ti}_9\text{O}_{20}$	Na_xTiO_2	?
280	Anatase ≧Brookite	Brookite ≧ $\text{Na}_4\text{Ti}_9\text{O}_{20}$ ≧ Na_xTiO_2	Na_xTiO_2 > $\text{Na}_4\text{Ti}_9\text{O}_{20}$	$\text{Na}_4\text{Ti}_9\text{O}_{20}$ + Na_xTiO_2	$\text{Na}_4\text{Ti}_9\text{O}_{20}$	$\text{Na}_4\text{Ti}_9\text{O}_{20}$	$\text{Na}_4\text{Ti}_9\text{O}_{20}$
240	Anatase ≧Brookite	Brookite > $\text{Na}_4\text{Ti}_9\text{O}_{20}$	$\text{Na}_4\text{Ti}_9\text{O}_{20}$	$\text{Na}_4\text{Ti}_9\text{O}_{20}$	$\text{Na}_4\text{Ti}_9\text{O}_{20}$	$\text{Na}_4\text{Ti}_9\text{O}_{20}$	$\text{Na}_4\text{Ti}_9\text{O}_{20}$
200	Anatase ≧Brookite	Brookite > $\text{Na}_4\text{Ti}_9\text{O}_{20}$	$\text{Na}_4\text{Ti}_9\text{O}_{20}$	$\text{Na}_4\text{Ti}_9\text{O}_{20}$	$\text{Na}_4\text{Ti}_9\text{O}_{20}$	$\text{Na}_4\text{Ti}_9\text{O}_{20}$	$\text{Na}_4\text{Ti}_9\text{O}_{20}$
160	Anatase	$\text{Na}_4\text{Ti}_9\text{O}_{20}$	$\text{Na}_4\text{Ti}_9\text{O}_{20}$	$\text{Na}_4\text{Ti}_9\text{O}_{20}$	$\text{Na}_4\text{Ti}_9\text{O}_{20}$	$\text{Na}_4\text{Ti}_9\text{O}_{20}$	$\text{Na}_4\text{Ti}_9\text{O}_{20}$

Note. +, Products formed in the same amount range; >, latter product is minor product; ≧, latter product is found only in very small amounts.

^a The $\text{Na}_4\text{Ti}_9\text{O}_{20}$ listed in the table was always obtained in a hydrated condition with $d_{001} \approx 8$ Å.

$\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ formed in a wide range of Na to Ti ratios at temperatures $\leq 280^\circ\text{C}$. In the low sodium range titanium dioxide was the main product. At 320°C the Na_xTiO_2 bronze, which is formed by partial reduction of titanium ions from +4 valence to +3 valence, resulted. Our findings differ from those presented by Wefers (5), Keesmann (22), and Watanabe (23), whose results also differ from each other. The main differences in the reaction conditions were the raw materials used and the reaction times. In our study, summarized in Table II, sol-gel precursors were used. The other workers used amorphous hydrous titanium oxide, which they treated hydrothermally with NaOH. Another, perhaps more important, factor is the reaction time. In this study it was usually 20 hr but in those of Keesmann and Watanabe it was ten times longer. We therefore repeated Watanabe's experiment using a Na to Ti ratio of 3:4 with durations of 20 hr and 10 days. The former gave $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ and the latter an unknown product with a d -spacing of 9.8 Å in addition to $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$. When a sol-gel precursor with the same Na to Ti ratio was treated hydrothermally for 10 days, the products were $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ and TiO_2 instead of pure $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ as was obtained under a reaction time of 20 hr.

X-ray Diffraction Studies

The x-ray diffraction pattern shown in Fig. 1 is not detailed enough to enable us to solve the crystal structure of $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$. In most of the syntheses the phase with d -spacing ≈ 8.6 Å was found (see Fig. 1). Other preparations yielded a phase with a spacing at 10.0 Å and some of the ≈ 8.6 -Å compounds turned into the 10.0-Å phase on standing in air for a couple of days. When the 10.0-Å phase was heated to 500°C and the diffraction pattern determined immediately, a 6.9-Å phase was obtained. This phase, when allowed to stand in air, reab-

sorbed water and the interlayer distance expanded through the ≈ 8.6 -Å phase to the 10.0-Å phase. Based on these results we conclude that $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ is a layered compound whose interlayer distance is dependent on the water content. The 6.9-Å phase is an anhydrous form, the ≈ 8.6 -Å phase a metastable semihydrous form, and the 10.0-Å phase a fully hydrated form of $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ (Fig. 1). When heated to 500°C , the ≈ 8.6 -Å phase did not show a sharp peak at 6.9 Å, but rather a broad one centered around 7.2 Å. On standing in air, or contact with water, it hydrates to form first the 8.6-Å phase and then the 10.0-Å phase. The latter one is probably a more organized product with higher water content as judged from the X-ray pattern. The water content varied from 10–20% of the weight but was difficult to determine precisely. This percentage range corresponds to 0.5–1 mole of water per mole of titanium.

Electron Microscopic and Diffraction Studies

Electron microscope images revealed that $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ is crystalline and the crystals are needle shaped. The length of the needles prepared hydrothermally is in the range 0.5–2 μm and their thickness is 0.05–0.2 μm . Figure 2A shows the SEM micrograph of a sodium titanate product prepared hydrothermally at 250°C from HTiO. Another product, prepared from TiIP by the sol-gel method followed by hydrothermal treatment at 250°C , gave shorter and thicker crystals as shown in Fig. 2B, but higher proportions of amorphous material. Thus lower temperatures and less heating time yields larger portions of X-ray amorphous material along with the fine crystals. Electron diffraction photographs of both samples, as well as a number of others, were obtained. In those cases where only refluxing at 90 – 100°C was used, concentric rings were obtained, and these gave the same d -spacings as the powder

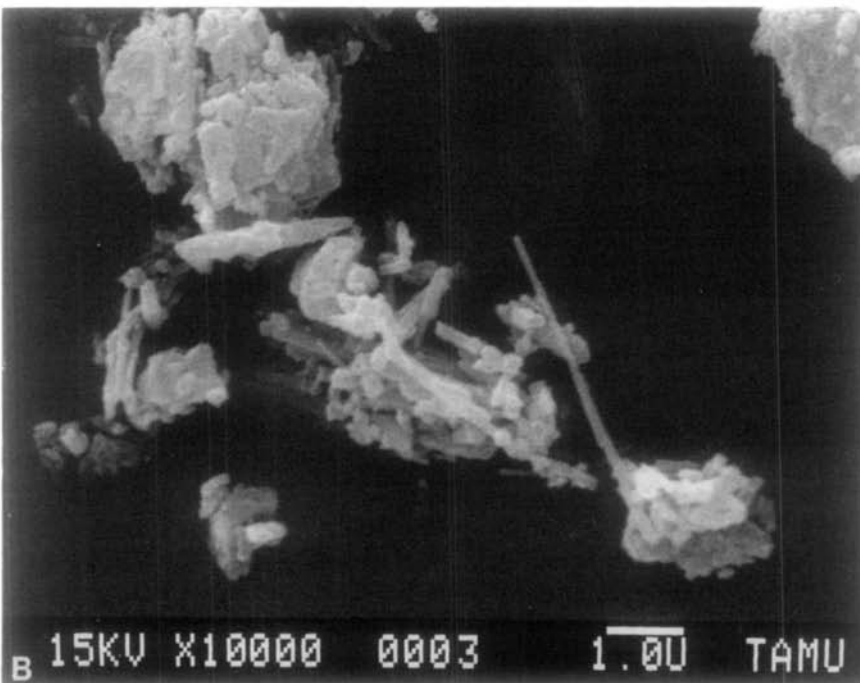
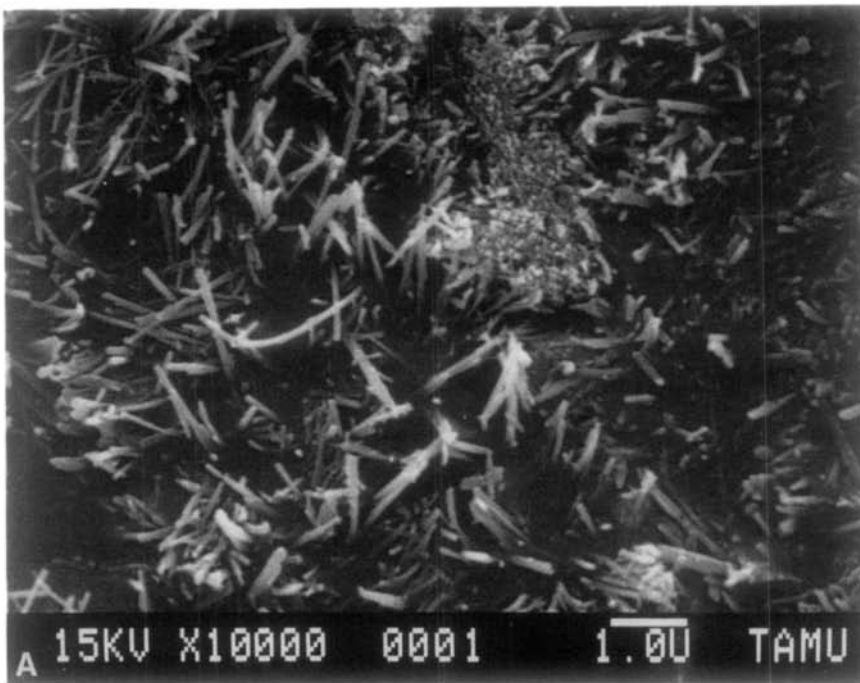


FIG. 2. Micrographs from $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ determined by scanning electron microscope (magnification $10^4\times$) and from (A) HTiO and (B) TiO_2 gel.

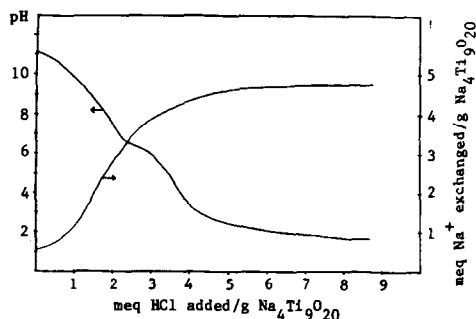


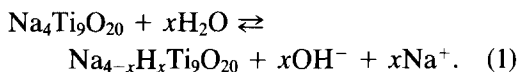
FIG. 3. Titration of $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ (prepared hydrothermally from anatase at 300°C) with 0.1 M HCl.

pattern, i.e., 8.6, 3.7, 3.1, and 1.9 \AA . Electron diffraction patterns from the flat face of well-defined crystals yielded two prominent spacings—3.65 and 1.55 \AA . However, the spots were not sharp but streaked along the layer lines indicating severe disorder. In a short time beam damage was observed, probably due to Na^+ movement toward surfaces negatively charged by the electron beam. Because of the beam damage and the absence of a tilting stage further diffraction studies were not pursued at this time.

Titration Curves

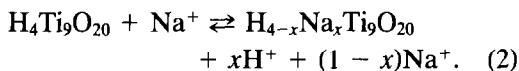
The sodium nonatitanate in water (100 mg) attains an equilibrium pH of ≈ 11 indicative of partial exchange of H_3O^+ for Na^+ . Titration of $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ with 0.1 M HCl showed that it is dibasic (Fig. 3). The inflection points were observed at pH 8–9 and pH 4–5 with the half exchange point at about pH 6. Sodium released from the exchanger after addition of 8.7 meq H^+ per gram of $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ was 4.90 meq/g which was reasonably close to the theoretical ion-exchange capacity, 4.74 meq/g.

As indicated above, when $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ is shaken with water, the pH becomes 11.0–11.2. This means that $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ is hydrolyzed according to the following reaction:



When 1 g of solid is used per 100 ml of solution, as in these experiments, x can be estimated to be 0.08–0.12 based on the pH change from 6 to 11.0–11.2. The amount of sodium in the solution, however, was 3.7–5.6 times higher than the value obtained from Eq. (1). This is probably caused by the dissociation of the exchanger or excess Na^+ on the surface which was not washed out. Partial hydrolysis naturally takes place in the washing procedure also. The degree of hydrolysis caused by washing has not been estimated. Back titration of the H^+ form, $\text{H}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$, also showed difunctionality (Fig. 4). The exchange reaction to produce the sodium form was complete at pH 12 and the amount absorbed was close to the theoretical capacity of $\text{H}_4\text{Ti}_9\text{O}_{20}$, 5.30 meq/g.

When $\text{H}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ was equilibrated with 0.1 M NaCl solution the pH was 3.0. This means that without NaOH addition the following reaction takes place:



According to the pH change from 6.0 to 3.0, x is 0.08 and according to the Na^+ absorbed

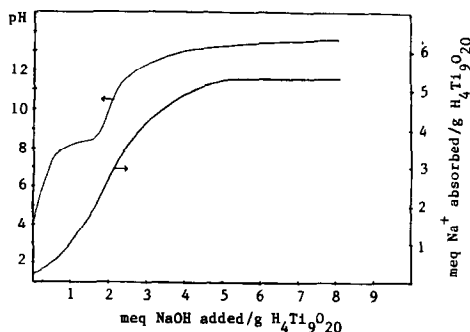


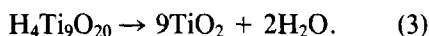
FIG. 4. Titration of the H^+ form of $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ (prepared hydrothermally from anatase at 300°C) with 0.1 M (NaOH + NaCl) solution.

at this point, 0.20 meq/g, x is 0.15, or twice as large.

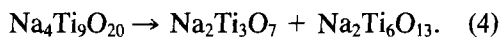
When $\text{H}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ was shaken with pure deionized water the pH fell from 6.0 to 3.5–4.0. This means that only 1–2% was dissociated in these circumstances.

Thermal Decomposition

Heating $\text{H}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ to 700°C resulted in the formation of TiO_2 according to the following equation:



However, on heating $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ to 700°C, the following decomposition reaction took place:



Tri- and hexatitanates are the only products at 700°C and above. Before the decomposition, $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ at 600°C forms an unidentified, poorly crystalline phase with reflections at 7.4, 3.6, 3.1, 2.7, 2.0, and 1.9 Å in its X-ray diffraction pattern.

Conclusions

Most sodium titanates are prepared at elevated temperatures by a solid-state reaction of the oxides. However, in aqueous media and at temperatures below 280°C, a sodium titanate $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ is formed in a wide range of Na to Ti ratios of the starting materials. $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ behaves as a layered compound, the inter-layer distance being dependent on the water content. It decomposes to $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$ at temperatures above 600°C. $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$ is an ion exchanger, all the Na^+ ions being exchangeable. The theoretical ion-exchange capacity is 4.74 meq/g of anhydrous exchanger and accords with the experimentally observed values of 4.9 meq/g for the sodium form and 5.35 meq/g in the hydrogen form.

Compounds with the corresponding stoichiometry have been reported for $\text{Cs}_4\text{Ti}_9\text{O}_{20}$

(24) and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ (25). No structural details were given for the former compound. The latter was reported to consist of hollandite-type lamellae alternating with BaTiO_3 -like units. No information for an isomorphous structure of $\text{Na}_4\text{Ti}_9\text{O}_{20}$ was available. However, these nonatitanates are formed at very high temperatures and undoubtedly have different structures from the sodium titanate described in this paper. The nonatitanate reported by Watanabe *et al.* (11) probably has a three-dimensional framework. If a layered variety were prepared, it would exhibit roughly half the exchange capacity of our titanate.

Based on the results given above, the formula proposed by Lynch *et al.* (1), $\text{NaTi}_2\text{O}_5\text{H}$, for the low temperature sodium titanate, seems unreasonable. The existence of hydrogen ions in the product prepared at high pH is not logical especially since a pH above 11 is obtained when the compound is slurried in water. The above cited formula is in error because the authors substituted a proton for one-fourth of a titanium atom.

Acknowledgments

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