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Cation Exchange Properties of Tetratitanic Acid with Interlayer Protons and of Titania with Surface Hydroxyl Protons*

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Cation exchange properties of tetratitanic acid with interlayer protons were measured and compared to those of titania with surface hydroxyl protons using the Frumkin equation. Tetratitanic acid showed larger ion-exchange capacity and much higher activity than titania. The characteristics of exchangeable protons and intercalated cations are discussed to explain the different ion-exchange properties. The interlayer protons of tetratitanic acid can be regarded as acid functional groups of an oxoacid of Ti^{IV}, and acid functional groups dissociate much more easily than the surface hydroxyl groups on titania that are formed by hydration. The cations intercalated into tetratitanate are sandwiched between opposing titanate layers with negative charges and are better stabilized than the cations adsorbed on the outer surfaces of titania owing to better neutralization of cationic charges.

Keywords
layered tetratitanic acid
hydroxyl group
interlayer
ion exchange
Frumkin equation

INTRODUCTION

Layered titanic acids, stacked 2-D oxoacids of titanium(IV), are, like titanium(IV) dioxides, difficult to dissolve in water and show ion exchange properties for cations in external solutions. Their ion exchange capacities are very large due to internal layer surfaces and cation intercalates are chemically and thermally stable. The proposed applications of these titanate properties include removal and immobilization of radioactive nuclides from high-level radioactive liquid waste, and a proton-cation exchange mechanism has been proposed.[1,2] The ion exchange and thermal behavior of titanates have been shown to depend on the lattice structure.[3] To increase cation selectivity, intercalation kinetics[4] and the effect of introduction of alkylammonium ions, large cations, into the interlayer[5] have also been studied, as well as the semiconductive and optical properties of these compounds.[6]

Figure 1 shows the layer lattice of alkali metal tetratitanate ($M_2Ti_4O_9$). A linear linked set of four TiO_6 octahedra sharing edges is a structural unit, and in the plane of the page these units are linked together by sharing corners and extend stepwise in a staggered arrangement. In the direction normal to the page, the rows linked to the top rows by sharing edges are displaced in the up and left or down and right directions by half the TiO_6 octahedron, the following rows are positioned immediately below these, and there is a succession of layers perpendicular to the page.[7] There are two types of interlayer distances, one large and the other small. Alkali metal ions are situated in the wide interlayers to counterbalance the layer negative charges, but in the interlayers

* Dedicated to Professor Nikola Kallay on the occasion of his 65th birthday.

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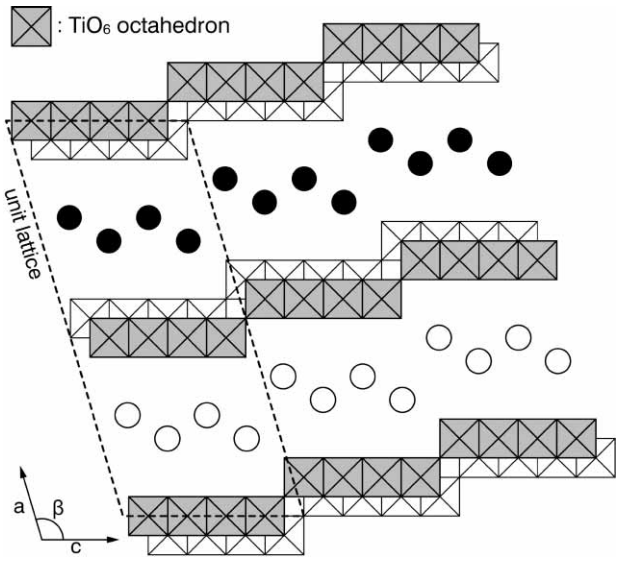

Figure 1. Layered tetratitanate lattices (a-c plane) with alkali metal ions (●) in the top row, and (○) in the second row.

with small distances there are no cations for neutralization, causing structural instability. As a result, tetratitanate is more flexible than other titanates and it may intercalate water molecules, hydrated metal ions, and cations with large molecular sizes, like alkylammonium ions, expanding the interlayer distances.[3–5]

Tetratitanic acid ($H_2Ti_4O_9$) can be made by replacing alkali metal ions of tetratitanates with protons; conversely, exchanging interlayer protons with cations in solution is also possible, as described above. The interlayer protons and cations are placed in nanospaces created by intercalation of cations and water molecules. Nanospaces are thought to show special activities owing to the overlap of molecular potentials[8] and it would be interesting to know how the cation exchange properties of tetratitanic acid differ from those of other compounds with only outer surfaces. Titania, the titanium(IV) dioxide, also shows cation exchange properties owing to surface hydroxyl protons[9,10] and provides a reference for cation exchange properties of layered titanate. The authors have shown elsewhere[11] that tetratitanic acid has a higher affinity for alkali metal ions than titania. In this paper, the characteristics of exchangeable protons and incorporated cations in the interlayer are discussed to explain the superior ion exchange properties of tetratitanic acid.

EXPERIMENTAL

Preparation of Tetratitanic Acid

As a raw material for tetratitanic acid, potassium tetratitanate was prepared according to the following procedure: Potassium carbonate (K_2CO_3) and anatase (TiO_2) were mixed in a 1:4 mole ratio with acetone, and the mixture was calcined at 800 °C for 20 hours. The product was ground and mixed, and calcined again. The obtained potassium tetratitanate was washed with distilled water and dried in vacuum at 40 °C to obtain hydrated potassium tetratitanate. Five grams of potassium tetratitanate hydrate were dispersed in 1 dm^3 of a 1 mol dm^{-3} hydrochloric acid solution and stirred for 24 hours. The hydrochloric acid solution was three times replaced with a new solution to ensure a complete exchange of interlayer potassium ions with protons. Tetratitanates and tetratitanic acid showed very low solubility in water even in acidic solutions like titanium(IV) oxide. The suspension was filtered, and the filtrate was washed with distilled water until the pH of the supernatant solution became the same as that of the distilled water, and no potassium ions were detected by flame analysis. The product was dried in vacuum at 40 °C to obtain hydrated tetratitanic acid. The crystal structure of potassium tetratitanates and tetratitanic acid hydrate were identified by XRD.

Ion Exchange Experiments

Portions of tetratitanic acid hydrate (0.1 g) were dispersed in 200 cm^3 of 0.1 mol dm^{-3} alkali metal (Na or K) chloride solutions through which nitrogen was bubbled to prevent contamination with carbon dioxide from the air. Alkali metal hydroxides (4×10^{-4} mol / 200 cm^3) were added to the suspensions to attain a pH around 10 where alkali metal ions are intercalated by exchange with interlayer protons. Different amounts of hydrochloric acid solutions were added to the respective suspensions (batchwise titration); the solution pH first decreased and then increased owing to the proton uptake accompanied by deintercalation of cations, and pH monitoring was continued for 5 days until equilibrium was reached. The amount of cations intercalated was determined by comparing the titration curves for the suspension and for the blank solution without tetratitanic acid. As described elsewhere,[9,10] the difference in the amount of hydrochloric acid added at the same pH gives the amount of protons released (equivalent to the amount of cations incorporated) by the ion exchange. The ion exchange capacity of tetratitanic acid was obtained from saturated amounts of the sodium ions intercalated; 2 or 4 g of tetratitanic acid was dispersed in 20 cm^3 of 1.93 or 3.89 mol dm^{-3} NaOH solution, and the sodium ion concentration in solution was determined by flame photometry. Changes in the crystal structure in the course of ion exchange were followed by XRD.

RESULTS AND DISCUSSION

Formation of Tetratitanic Acid

Figure 2 shows the crystal structures of (a) potassium tetratitanate prepared as the starting material for tetratitanic acid, (b) the hydration product of (a), and (c) tetratitanic acid obtained by replacing interlayer potassium ions with protons. The diffraction peaks of (a) coincided with those reported for potassium tetratitanate ($K_2Ti_4O_9$),[7] and the respective peaks could be indexed as a monoclinic system with spacings of C2/m. Hydrated potassium tetrati-

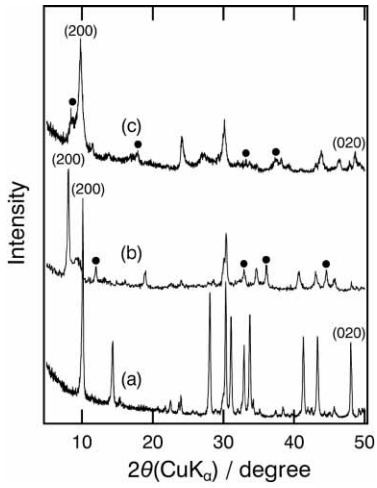

Figure 2. XRD patterns of (a) potassium tetratitanate, (b) hydration product of (a), and (c) hydrated titanic acid. Peaks that are not possible with a C base-centered lattice are indicated (●).

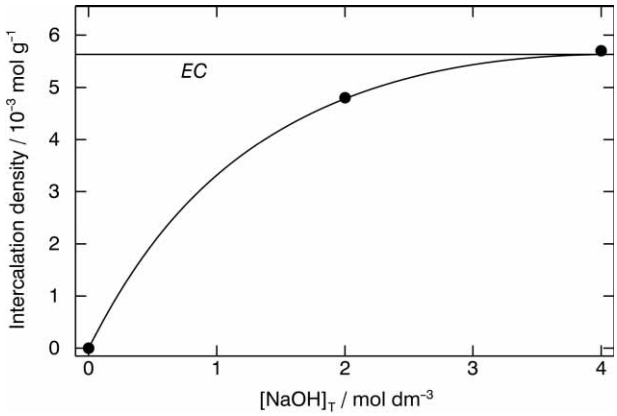

Figure 3. Amount of sodium ions intercalated into tetratitanic acid (intercalation density) as a function of the concentration of sodium hydroxide added.

tanate (b) is also monoclinic, but the XRD pattern shows peaks that are not possible with a C base-centered lattice (indicated by ●) and the crystal symmetry decreased to a simple lattice. However, the peaks representing the layer structure, such as the (020) plane within a layer and the (200) plane for the interlayer distance, are still present, and the host structure maintains the C base-centered lattice. The peak for the (200) plane of potassium tetratitanate shown in (a) shifts to a lower angle of 2θ by hydration as shown in (b), indicating an increase in the interlayer distance, possibly due to hydration of interlayer potassium ions. The diffraction pattern of hydrated tetratitanic acid (c) coincided with that reported for tetratitanic acid monohydrate ($H_2Ti_4O_9 \cdot H_2O$).[3] The XRD pattern of tetratitanic acid monohydrate (c) also shows peaks that are not possible with the C base-centered lattice (indicated by ●), but the (200) and (020) peaks indicate that this compound has a layered structure. The peak position for the (200) plane of tetratitanic acid monohydrate (c) is about the same as that of anhydrous potassium tetratitanate (a). This indicates that the interlayer distances of these compounds are similar. The crystallographic diameter of potassium ions is nearly equal to that of the water molecule, and the result here indicates that the layered structure of tetratitanic acid is supported by water molecules in the interlayer.

*Ion Exchange Capacity (*EC*) of Tetratitanic Acid*

Figure 3 shows the amount of sodium ions intercalated into 1 g of tetratitanic acid monohydrate, defined as the »intercalation density (mol g^{-1})«, as a function of the concentration of sodium hydroxide added to the solution, $[NaOH]_T$. At a concentration of around 4 mol dm^{-3}, the intercalation density reaches the value of 5.63×10^{-3} mol g^{-1} calculated from the amount of the two interlayer protons. It is apparent that the two interlayer protons are fully exchanged with sodium ions at the high concentration of sodium hydroxide, and this saturated intercalation density (mol g^{-1}) was taken as the ion exchange capacity (*EC*) of this compound.

Titania, the Ti^{IV} dioxide, is similar to titanic acid, a layered oxoacid of Ti^{IV}, in that both are oxides of Ti^{IV}. Metal oxides in general have cation exchange properties owing to their surface hydroxyl protons. Here, only outer surfaces are available for ion exchange and the quantity related to the extent of adsorption is expressed by the term »surface density (mol m^{-2})«. The determined surface density of hydroxyl groups on titania was 1.80×10^{-5} mol m^{-2}, and half of this is the surface density of cation exchange sites.[9,10] The determined specific surface area of this oxide was 2.60 m^2 g^{-1},[9,10] and the cation exchange capacity (*EC*) of titania expressed in the same unit as the intercalation density was calculated to be: 2.34×10^{-5} mol g^{-1}. The *EC* of tetratitanic acid obtained above (5.63×10^{-3} mol g^{-1}) is more than two orders of magnitude larger than that of titania. This much larger *EC* of tetratitanic acid could be due to the presence of layer surfaces inside particles, while in titania only the outer surfaces of particles are available for ion exchange.

Intercalation of Na^+ and K^+ Ions as a Function of pH

Figure 4 shows the amounts of intercalated Na^+ and K^+ ions per gram of tetratitanic acid (intercalation density) against pH. Intercalation densities of both Na^+ and K^+ ions increase similarly over a wide pH range. The increase in pH by 6 (from 4 to 10), a 6 orders of magnitude decrease in the proton concentration, results in only a 3 to 4 times increase in intercalation densities, indicating suppression with the progress of intercalation. Sasaki *et al.*[1,2] reported that the titration curves for the intercalation of cesium and rubidium ions change stepwise with pH due to the different reactivities of the four different protons in the unit

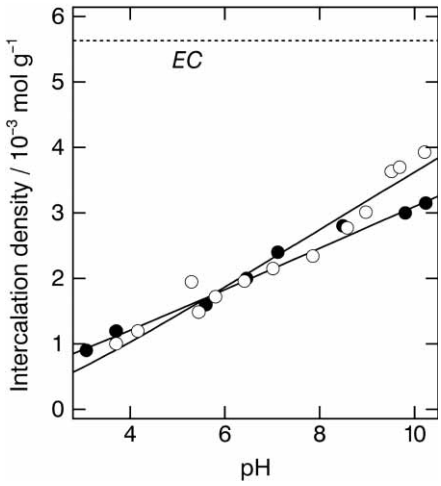

Figure 4. Amounts of sodium (O) and potassium (●) ions intercalated into tetratitanic acid (intercalation density) as a function of pH. Points – experimental; curves – calculated.

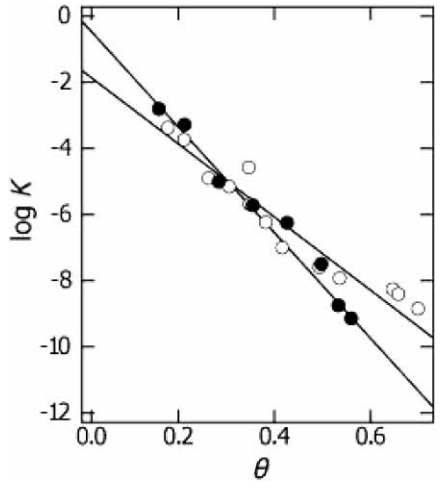

Figure 5. Relationship between log *K* and θ for sodium (O) and potassium (●) ions intercalated into tetratitanic acid.

lattice, but here the amounts of intercalated ions change gradually and smoothly with pH.

Reversibility of ion exchange is apparent, since the tetratitanic acid prepared by replacing potassium ions of tetratitanate with protons intercalates alkali metal ions replacing interlayer protons.

Evaluation of Intercalation Properties by Modeling with the Frumkin Isotherm

The interlayer protons of tetratitanic acid available for ion exchange have been suggested to exist as hydronium ions formed by protonating intercalated water molecules.[1–5] However, the lattice oxide ions would have stronger basic properties than the interlayer water molecules and the lattice oxide ions may be protonated to become the layer acid hydroxyl groups as interlayer protons. As a result, the layers are electrically neutral tetratitanic acid, and the neutral layers would be held together by bridges of interlayer water molecules with hydrogen bonds. This may be evidenced by the unstable lattice of tetratitanic acid that dehydrates at the relatively low temperature of 100 °C to transform into $H_2Ti_8O_{17}$ by condensation.[3] In contrast, titanates with alkali metal ions in the interlayer exhibit very strong heat resistive properties owing to the stable crystal lattices constructed by electrostatic bonds.

If a layer with an exchangeable interlayer proton is designated as RH, the exchange of the interlayer proton with an alkali metal ion (M^+) can be described by:

$$RH + M^+ \leftrightarrow R^- \bullet M^+ + H^+ \quad (1)$$

The material balance equation with respect to the ion exchange sites is:

$$EC = \{RH\} + \{R^- \bullet M^+\} = 5.63\times10^{-3} \text{ mol } g^{-1} \quad (2)$$

where the braces stand for the amount of species per unit mass of solid (mol g^{-1}) with the dimension of the intercalation density defined above.

The coverage θ of the layer surface by adsorbed ions is given by:

$$\theta = \{R^- \bullet M^+\} / EC \quad (3)$$

The equilibrium concentration ratio K of reaction (1) is:

$$K = \frac{\{R^- \bullet M^+\}[H^+]}{\{RH\}[M^+]} \quad (4)$$

where K is dimensionless because the units for the respective species are canceled out in the ratio. If K is a constant, Eq. (4) shows that the 6 orders of magnitude decrease in the proton concentration results in a 6 orders of magnitude increase in the $\{R^- \bullet M^+\} / (\{RH\}[M^+])$ ratio, a very large increase in the amount of intercalated cations $\{R^- \bullet M^+\}$. However, as described above, the increase in intercalation density is much smaller, and the cause of suppression may be electrostatic repulsion and/or steric hindrance between intercalated cations (lateral interactions).

Various electrical double layer (EDL) models have been developed for ion adsorption with electrostatic lateral interacions.[12,13] These models assume well-defined, uniform surfaces, so as to enable deriving mathematical equations with parameters that embody system properties. However, tetratitanic acid, a layered compound, has internal layer surfaces that are very difficult to define in terms of EDL dimensions, shapes and flatness. As a result, a mechanistic approach to developing a model would be difficult to justify. If a ready-made EDL model is applied to this compound and convergence is attained, then

because of the discrepancy between the model and reality, the model parameter values would not have the physical significance originally assigned to them.

It has been shown that the experimental data here can be well described by the Frumkin isotherm:[11]

$$K^\circ = K \exp(A \cdot \theta) \quad (5)$$

where K° is an intrinsic equilibrium constant and A is a constant for suppression of the reaction by lateral interactions. Parameter A is not restricted to particular surface characteristics with respect to double layer thickness, flatness, *etc.*, and it is not restricted to either electric or steric interaction. Apparently, parameter A does not take the form of an electric term, but to a system where the constant capacitance model applies, the Frumkin isotherm also applies, and parameter A could correspond to the EDL capacitance.[14] The linear form of Eq. (5) is:

$$\log K = \log K^\circ - (A \log e)\, \theta \quad (6)$$

where e is the base of natural log.

From the measured data in Figure 4, the concentration ratio K was calculated and log K was plotted against coverage θ in Figure 5. It is apparent that there are linear relations between log K and θ, indicating a good fit of the model to the data. The values of K° and A can be obtained from the intercepts and the slopes of the log K *vs.* θ lines, respectively, and Table I lists the values of K° and A for potassium and sodium ions with tetratitanic acid. The curves in Figure 4 were drawn based on calculations with the K° and A values. Comparison of the measured data points and the calculated curves gives an indication of the suitability of the model for the data. Here, potassium ions have a higher affinity (K°) and a stronger suppressive lateral interaction (A) than sodium ions. This indicates that potassium ions in the interlayer have stronger electrostatic properties than sodium ions.

The intercalation of sodium or potassium ions from aqueous solutions resulted in a shift of the (200) peak to a smaller 2θ angle, indicating an increase in the interlayer distance, as described in the section *Formation of Tetratitanic Acid*. The crystallographic diameters of sodium and potassium ions are smaller than or about the same as those of the water molecules that are replaced by these cations and the intercalated cations are likely to be more or less hydrated. Sodium ions with a smaller crystallographic diameter are more strongly hydrated than potassium ions, and the hydrated interlayer potassium ions would be smaller than the hydrated interlayer sodium ions, resulting in higher electric charge density. This can be the reason why potassium ions have higher affinity for layer negative sites and are subject to a more significant repulsive interaction with neighboring ions of the same kind.

TABLE I. Values of K° and A for potassium and sodium ions with tetratitanic acid (TTA) and titania (TiO_2)

Ions / Adsorbents	K°	A
K^+ / TTA	7.12×10^{-1}	36.7
Na^+ / TTA	2.28×10^{-2}	25.4
Na^+ / TiO_2 (Ref. 9,10)	7.94×10^{-7}	24.5

Titania, the Ti^{IV} dioxide, has been shown to adsorb cations by releasing protons of surface hydroxyl groups that are formed by hydration.[9,10] The concentration of surface species defined as the amount of species per unit surface area (surface density, mol m^{-2}) was measured as a function of pH, and equally the concentration ratio K was obtained. The unit of surface density is different from intercalation density, but the concentration ratio K here is also dimensionless, like tetratitanic acid. It was shown that the cation adsorption on titania obeys the Frumkin isotherm, giving a good linear plot of log K *vs.* θ similar to Figure 5, as Table I includes the reported values of K° and A for sodium ions with titania.[9,10] Comparison of tetratitanic acid and titania shows that the suppressive lateral interaction constants A are about the same, but that the intrinsic equilibrium constant K° in case of tetratitanic acid is more than four orders of magnitude larger than in case of titania (Table I).

Different affinities of the two compounds indicate that the cations intercalated into tetratitanic acid are better stabilized than those adsorbed on the outer surfaces of titania and/or that the layer hydroxyl groups of tetratitanic acid dissociate protons much more strongly than the surface hydroxyl groups on titania. For proton dissociation, the two types of hydroxyl groups can be differentiated as follows: the surface hydroxyl groups on titania are hydration products and protons are released by the dissociation of attached water molecules affected by the oxide. Such dissociation would largely depend on the properties of water itself and reflect the properties of the substrate compound only indirectly or secondarily. The layer hydroxyl groups of tetratitanic acid are the acid functional groups of an oxoacid of titanium(IV), the negative charges that hold protons are permanent structural charges due to the non-stoichiometric arrangement of titanium(IV) and oxide(II) ions in the lattice, and their dissociation depends directly on the acid properties of this compound. As a result, the layer hydroxyl groups of tetratitanic acid can dissociate much more completely than the surface hydroxyl groups on titania. As regards the stability of adsorbed cations, the interlayer of tetratitanic acid and the outer surface of titania can be differentiated as follows: within an interlayer, intercalated ions are sandwiched by opposing layers as $R^- \bullet M^+ \bullet R^-$, while on an outer surface, ions are adsorbed as $R^- \bullet M^+$. Electrically, the intercalated cations are neutralized more symmetrically by

the charged sites than the cations adsorbed on the outer surface. In general, this would provide an explanation for why the interlayer has a higher affinity than the outer surface.

REFERENCES

1. T. Sasaki, M. Watanabe, Y. Komatsu, and Y. Fujiki, *Inorg. Chem.* **24** (1985) 2265–2271.
2. T. Sasaki, Y. Komatsu, and Y. Fujiki, *Inorg. Chem.* **28** (1989) 2776–2779.
3. H. Izawa, S. Kikkawa, and M. Koizumi, *J. Phys. Chem*. **86** (1982) 5023–5026.
4. H. Izawa, S. Kikkawa, and M. Koizumi, *J. Solid State Chem*. **60** (1985) 264–267.
5. H. Izawa, S. Kikkawa, and M. Koizumi, *J. Solid State Chem*. **69** (1987) 336–342.
6. T. Sasaki and M. Watanabe, *J. Phys. Chem*. *B* **101** (1997) 10159–10161.
7. M. Dion, Y. Piffard, and M. Tournox, *J. Inorg. Nucl. Chem*. **40** (1978) 917–918.
8. K. Kaneko, *Hyomen Kagaku* **21** (2000) 2–9.
9. H. Tamura, N. Katayama, and R. Furuichi, *Environ. Sci. Technol*. **30** (1996) 1198–1204.
10. H. Tamura, *J. Colloid Interface Sci*. **279** (2004) 1–22.
11. H. Tamura, K.Nakamura, and S. Kikkawa, *Electrochemistry* **70** (2002) 530–535.
12. U. Singh and G. Uehara, *Electrochemistry of the Double Layer: Principles and Applications to Soils*, in: D. L. Sparks (Ed.), *Soil Physical Chemistry*, Second Edition, Boca Raton, FL, 1999, pp. 1–46.
13. J. M. Zachara and J. C. Westall, *Chemical Modeling of Ion Adsorption in Soils*, in: D. L. Sparks (Ed.), *Soil Physical Chemistry*, Second Edition, Boca Raton, FL, 1999, pp. 47–95.
14. W. Stumm, *Chemistry of the Solid-Water Interface*, Wiley-Interscience, New York, 1992, p. 97.

SAŽETAK

Svojstva izmjene kationa tetratitanske kiseline s međuslojnim protonima i svojstva izmjene titanijeva oksida s površinskim hidroksilnim protonima

Hiroki Tamura, Kyosuke Nakamura i Shinichi Kikkawa

Mjerena su svojstva izmjene kationa tetratitanske kiseline s međuslojnim protonima i rezultati su, pomoću Frumkinove jednadžbe, uspoređeni s rezultatima dobivenima za svojstva izmjene kationa titanijeva oksida s površinskim hidroksilnim protonima. Tetratitanska kiselina pokazala je veći kapacitet ionske izmjene i znatno veću aktivnost od titanijeva oksida. Kako bi se objasnila različita svojstva ionske izmjene, raspravljena su svojstva izmjenjivih protona i interkalarnih kationa. Međuslojni protoni tetratitanske kiseline mogu se promatrati kao kisele funkcionalne skupine oksokiseline titanija(IV), a takve kisele funkcionalne skupine znatno lakše disociraju nego površinske hidoksilne skupine na titanijevu oksidu koje nastaju hidratacijom. Kationi interkalirani u tetratitanate smješteni su između titanatnih slojeva s negativnim nabojem i bolje su stabilizirani nego kationi adsorbirani na vanjsku površinu TiO_2 zbog bolje neutralizacije kationskih naboja.