30 *Chem. Mater.* **1999,** *11,* 30−32

Intercalation of Alkylammonium Cations into a Layered Titanate in the Presence of Macrocyclic Compounds

Makoto Ogawa*,[†,‡] and Yoshinao Takizawa[‡]

PRESTO, Japan Science and Technology Corporation, Japan, and Institute of Earth Science, Waseda University, Nishiwaseda 1-6-1, Tokyo 169-8050, Japan

Received September 24, 1998
Revised Manuscript Received November 9, 1998

We now report a novel way of preparing tetratitanate−organic intercalation compounds in the presence of a macrocyclic compound, [2.2.2]-cryptand [abbreviated as C(222)], and a crown ether, 18-crown-6. It is well-known that such macrocyclic compounds selectively and strongly bind cations of appropriate sizes.[1] The added C(222) and 18-crown-6 promoted the ion exchange reactions between potassium tetratitanate ($K_2Ti_4O_9 \cdot nH_2O$) and alkylammonium chlorides to give alkylammonium−tetratitanate intercalation compounds, which are not available by the conventional ion exchange method. The reaction is a new application of macrocyclic compounds in inorganic−organic supramolecular chemistry.

Intercalation of guest species into the interlayer spaces of layered solids is a way of producing inorganic−organic nanocomposites with specific functions controlled by their microstructures.[2] Among possible layered solids, layered titanates are attractive host materials owing to their semiconducting properties. Since they can be regarded as an aggregate of nanostructured particles of titanium oxide, their application as a building unit of novel supramolecular systems is worth investigating.[3] Their ion exchange,[4] photocatalytic,[5] and luminescence[6] properties have been reported so far. Unlike the smectite group of layered clay minerals, which is known to accommodate a wide variety of guest species in its interlayer spaces to form intercalation compounds,[7] the intercalating capabilities of titanates are low. For the introduction of bulky organic species such as cationic dyes,[8] the so-called "guest displacement method" has been used previously. The present one-pot synthesis utilizing the complexation of macrocyclic compounds with interlayer exchangeable cations is a novel and simple way to introduce bulky organic species into the interlayer spaces of layered solids with low intercalating capabilities.

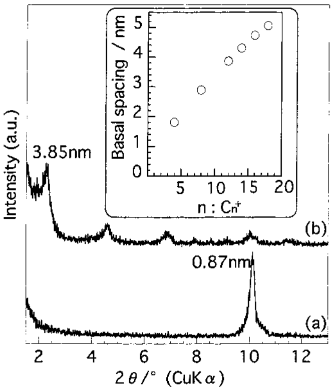

Figure 1. X-ray diffraction patterns of (a) $K_2Ti_4O_9 \cdot nH_2O$ and (b) the C_{12}^+−tetratitanate. (inset) The variation of the basal spacings of the C_n^+−tetratitanate intercalation compounds as a function of alkyl chain length.

Since the intercalation of organoammonium ions into the ion exchangeable layered solids has extensively been investigated from both fundamental and practical viewpoints,[9] alkylammonium ions were used as cationic guest species in the present study. For example, organoammonium−titanates have been used as intermediates for the preparation of pillared titanates[10] and organic dye intercalated materials.[8]

The organoammonium−tetratitanate intercalation compounds have been prepared as follows: $K_2Ti_4O_9 \cdot nH_2O$ was allowed to react with an 1,4-dioxane solution containing organoammonium chlorides (abbreviated as C_n^+; where n denotes the carbon number of the alkyl chains) and C(222) at room temperature. The molar ratio of C_n^+:C(222):$K_2Ti_4O_9 \cdot nH_2O$ was 20:4:1 and the concentration of C(222) in 1,4-dioxane was 0.1 mol L^{-1}. After reaction for 1 week, the products were collected by centrifugation and dried under a reduced pressure at room temperature.

The X-ray diffraction pattern of the product obtained when C_{12}^+ was used as the guest species is shown in Figure 1b. The $d(200)$ diffraction peak shifted to a lower 2θ region [$d(200) = 3.85$ nm] from the original diffrac-

---

[†] Japan Science and Technology Corp.

[‡] Waseda University.

(1) Gokel, G. *Crown Ethers and Cryptands*; The Royal Society of Chemistry: Cambridge, 1994.

(2) (a) Müller-Warmuth, W., Schöllhorn, R., Eds. *Progress in Intercalation Research*; Kluwer Academic Publishers: Dordrecht, 1994. (b) Alberti, G.; Bein, T., Eds. *Comprehensive supramolecular chemistry;* Pergamon: Oxford, 1996; Vol. 7. (c) Ogawa, M.; Kuroda, K. *Chem. Rev.* **1995**, *95*, 399−438.

(3) (a) Keller, S. W.; Kim, H.-N.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, *116*, 8817−8812. (b) Sasaki, T.; Watanabe, M.; Hashizume, H.; Yamada, H.; Nakazawa, H. *J. Am. Chem. Soc.* **1996**, *118*, 8329−8335. (c) Sasaki, T.; Nakano, S.; Yamauchi, S.; Watanabe, M. *Chem. Mater.* **1997**, *9*, 602−608.

(4) (a) Izawa, H.; Kikkawa, S.; Koizumi, M. *J. Phys. Chem.* **1982**, *86*, 5023−5026, (b) Izawa, H.; Kikkawa, S.; Koizumi, M. *Polyhedron* **1983**, *2*, 741−744, (c) Sasaki, T.; Watanabe, M.; Komatsu, Y.; Fujiki, Y. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3500−3505, (d) Sasaki, T.; Watanabe, M.; Komatsu, Y.; Fujiki, Y. *Inorg. Chem.* **1985**, *24*, 2265−2271, (e) Sasaki, T.; Komatsu, Y.; Fujiki, Y. *Inorg. Chem.* **1989**, *28*, 2776−2779.

(5) (a) Shibata, M.; Kudo, A.; Tanaka, A.; Domen, K.; Maruya, K.; Onishi, T. *Chem. Lett.* **1987**, 1017. (b) Kim, Y. I.; Atherton, S. J.; Brigham, E. S.; Mallouk, T. E. *J. Phys. Chem.* **1993**, *97*, 11802−11810.

(6) Kudo, A.; Sakata, T. *J. Mater. Chem.* **1993**, *3*, 1081−1082.

(7) Theng, B. K. G. *The Chemistry of Clay-Organic Reactions;* Adam Hilger: London, 1970.

(8) (a) Miyata, H.; Sugahara, Y.; Kuroda, K.; Kato, C. *J. Chem. Soc., Faraday Trans.1* **1988**, *84*, 2677−2682. (b) Nakato, T.; Iwata, Y.; Kuroda, K.; Kaneko, M.; Kato, C. *J. Chem. Soc., Dalton Trans.* **1993**, 1405−1409. (c) Nakato, T.; Iwata, Y.; Kuroda, K.; Kato, C. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1992**, *13*, 249−256.

(9) (a) Ogawa, M.; Kuroda, K. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2593−2618, (b) Lagaly, G. *Solid State Ionics* **1986**, *22*, 43. (c) Lagaly, G.; Beneke, K.*Colloid Polym. Sci.* **1991**, *269*, 1198. (d) Clearfield, A. pp 223−271 in ref 2a. (e) Clearfield, A. *Chem. Rev.* **1988**, *88*, 125.

(10) (a) Landis, M. E.; Aufdembrink, B. A.; Chu, P.; Johnson, I. D.; Kirker, G. W.; Rubin, M. K. *J. Am. Chem. Soc.* **1991**, *113*, 3819−3190. (b) Hou, W.; Yan, Q.; Peng, B.; Fu, X. *J. Mater. Chem.* **1995**, *5*, 109−114. (c) Cheng, S.; Wang, T.-C. *Inorg. Chem.* **1989**, *28*, 1283−1289.

10.1021/cm980671k CCC: $18.00

Table 1. Composition of the Products Determined by Elemental Analysis (C, H, N)

C_n^+	C (wt %)	N (wt %)	m in $[C_n^+]_m[Ti_4O_9]$
C_4^+	11.1	2.7	1.0
C_8^+	19.6	2.8	1.0
C_{12}^+	25.2	2.4	1.0

tion pattern (Figure 1a) of $K_2Ti_4O_9{\cdot}nH_2O$, where the $d(200)$ value is 0.87 nm. This observation shows the expansion of the interlayer space caused by the reaction. When C_n^+ with different alkyl chain lengths was employed, products with different $d(200)$ values were obtained. The basal spacings of the products are summarized in the Figure 1 inset as a function of the alkyl chain length of the C_n^+. There is a linear relationship between the $d(200)$ values and n, indicating the intercalation of C_n^+ by the cation exchange mechanism.

From the relationship between the basal spacing and n, the intercalated C_n^+ ions are thought to form paraffin type aggregates in the interlayer space of tetratitanate. Supposing that the alkyl chains are in an all-trans configuration, the alkyl chains of the intercalated C_n^+ are inclined to the titanate layer at ca. 65 °C.

The amounts of the adsorbed C_n^+ were determined for the products washed with 1,4-dioxane. The results of the C, H, N analysis of the washed products are shown in Table 1. When C_n^+ with $n = 4$, 8, and 12 were used, the basal spacings of the products did not change significantly upon washing. This fact indicates that the interlayer microstructures were not affected by the washing. The adsorbed amounts of C_n^+ are determined for the C_4^+, C_8^+, and C_{12}^+ systems to be ca. 1.0 mol per $[Ti_4O_9]^{2-}$. The C/N ratios of the products are consistent with those of C_n^+, showing the absence of C(222) in the washed products. The infrared spectra of the washed products showed absorption bands characteristic to C_n^+ such as CH stretching vibration at 2918 and 2850 cm^{-1}, confirming the formation of the C_n^+–tetratitanate intercalation compounds.

On the other hand, the basal spacings of C_{18}^+–, C_{16}^+–, and C_{14}^+–tetratitanates decreased, showing the deintercalation of C_n^+ during the washing. Efforts are being made to avoid the deintercalation of C_n^+ during the washing.

Since the direct ion exchange reaction of the organoammonium ions and $K_2Ti_4O_9{\cdot}nH_2O$ did not occur, the intercalation of long chain alkylammonium ions into the interlayer space of $K_2Ti_4O_9{\cdot}nH_2O$ has been conducted by means of the guest displacement method, as schematically shown in Figure 2(3).[11] A tetratitanic acid ($H_2Ti_4O_9{\cdot}nH_2O$) was prepared by acid treatment of $K_2Ti_4O_9{\cdot}nH_2O$ and allowed to react with an aqueous solution of n-butylamine. The butylammonium–tetratitanate intercalation compound thus obtained was used as the intermediate for the introduction of bulkier organic cations. It is also possible to accomplish the two-step reaction (Figure 2(3)) in one pot in an acidic organoammonium solution. The basal spacings and the adsorbed amounts of C_n^+ of the C_n^+–tetratitanates prepared in the present study are consistent with those reported for the products prepared by the guest displacement method, indicating that the microstructures of the products are similar, irrespective of the reaction methods. Thus, the ion exchange reaction in the presence of C(222) has proved to be an alternative way for the preparation of organo–titanate intercalation compounds.

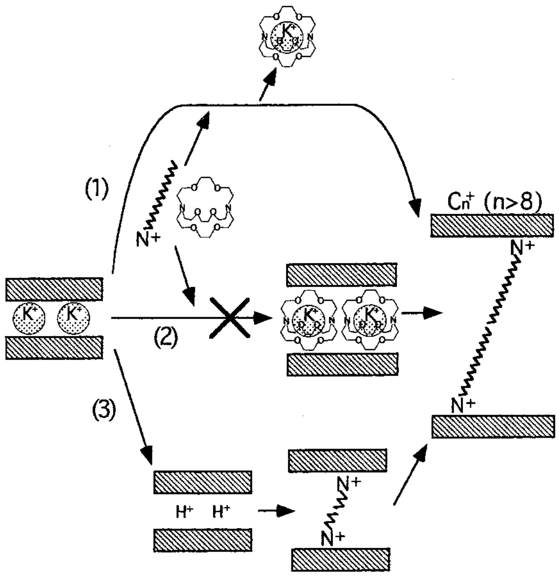

Figure 2. Schematic drawing of the cation exchange reaction.

Although the C_n^+–tetratitanates intercalation compounds ($n = 4$ and 12) have been obtained when C(222) was replaced by 18-crown-6, the yields are much lower compared with those when C(222) was employed. This difference in the reactivity was ascribable to the difference in the potassium binding strength of C(222) and 18-crown-6.[1]

There are two possible mechanisms for the present ion exchange reaction, as schematically shown in Figure 2: (1) C(222) molecules form complex ions with the potassium ions deintercalated from the interlayer space and organoammonium cations are intercalated into the interlayer space to compensate the charge balance and (2) C(222) molecules are first intercalated into the interlayer space of $K_2Ti_4O_9{\cdot}nH_2O$ to form a intercalation compound. Subsequently, the complex ions formed in the interlayer space are exchanged with organoammonium cations.

To understand the reaction mechanism, the intercalation of C(222) into the interlayer space of $K_2Ti_4O_9{\cdot}nH_2O$ was attempted. The intercalation of crown ethers and cryptands into the interlayer spaces of smectites has been reported so far, because the resulting intercalation compounds may act as solid-electrolytes and ion selective membranes.[12] Additionally, we have successfully introduced 18-crown-6 into layered silicates, K-kenyaite and K-fluorotetrasilicic mica, which show a relatively low intercalating capability if compared with smectites.[13] The interactions between the ligands and the

---

(11) Choy, J.-Y.; Han, Y.-S.; Park, N.-M.; Kim, H.; Kim, S.-W. *Synth. Met.* **1995**, *71*, 2053–2054.

(12) Ruiz-Hitzky E.; Casal, B. *Nature* **1978**, *276*, 596–597. Casal, B.; Ruiz-Hitzky, E.; Serratosa, J. M. *J. Chem. Soc., Faraday Trans., 1* **1984**, *80*, 2225–2232, Ruiz-Hitzky E.; Casal, B. *Clay Miner.* **1986**, *21*, 1–7, Ruiz-Hitzky E.; Casal, B. In *Chemical Reactions in Organic and Inorganic Constrained Systems;* Setton, R., Ed.; Reidel: Dordrecht, 1986; pp 179–189. Casal, B.; Aranda, P.; Sanz, J.; Ruiz-Hitzky, E. *Clay Miner.* **1994**, *29*, 191–203, Aranda, P.; Casal, B.; Fripiat, J. J.; Ruiz-Hitzky, E. *Langmuir* **1994**, *10*, 1207–1212,

(13) Ogawa, M.; Kadomoto, H.; Kuroda, K.; Kato, C. *Clay Sci.* **1997**, *10*, 185–194.

interlayer exchangeable cations have been proved to play an important role for the reactions. However, C(222) did not intercalate into the interlayer space of $K_2Ti_4O_9 \cdot nH_2O$ by the reaction between $K_2Ti_4O_9 \cdot nH_2O$ and C(222) in a 1,4-dioxane solution of C(222) (C(222)/K = 2) at room temperature for up to 20 days. This fact indicates that the ion exchange between potassium ions and organoammonium ions in the presence of C(222) occurred by mechanism 1, as schematically shown in Figure 2.

In our separate study on the solid-state formation of organoammonium−montmorillonite intercalation compounds, we have found that the counteranions affect the ion exchange reactions and proposed that the driving force for the solid−solid reactions is the difference between the free energies of the products and the reactants.[14] In the present system, the complexation of potassium ion with C(222) and the solubility of the formed complex in 1,4-dioxane led the successful ion exchange reaction.

In summary, a novel synthetic method for the preparation of organoammonium−tetratitanate intercalation compounds has been reported. Macrocyclic ligands strongly interact with the interlayer cations to promote the ion exchange reactions, which do not proceed in their absence. Beside the scientific importance of the reaction mechanism, the application of the present method to the preparation of a wide variety of inorganic−organic supramolecular systems is promising, since macrocyclic ligands with variable guest binding selectivities and layered solids with a wide variety of structures and properties are known. There are also advantages in using an organic solvent, as many organic cations are soluble in an organic solvent and insoluble in water.

CM980671K

---

(14) (a) Ogawa, M.; Handa, T.; Kuroda, K.; Kato, C. *Chem. Lett.* **1990,** 71−74, (b) Ogawa, M.; Hagiwara, A.; Handa, T.; Kuroda, K.; Kato, C. *J. Porous Mater.* **1995**, *1*, 85−89.