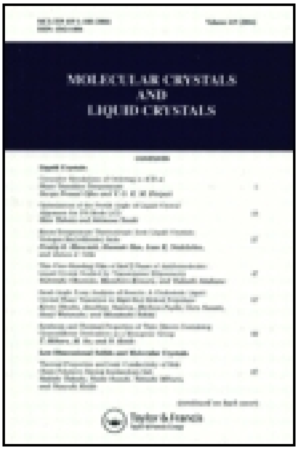

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One Pot Synthesis of Layered Tetratitanate-Organic Intercalation Compounds with the Aid of Macrocyclic Compounds

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One Pot Synthesis of Layered Tetratitanate-Organic Intercalation Compounds with the Aid of Macrocyclic Compounds

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We now report the preparation of alkylammonium-tetratitanate intercalation compounds with the aid of a macrocyclic compound, [2.2.2]-cryptand. The macrocyclic compound strongly interacts with the interlayer cation to promote the ion exchange reactions, which do not proceed in its absence. The formation of the intercalation compounds was confirmed by X-ray diffraction and elemental analysis. Since the present method is simple in operation, it is applicable to the preparation of a wide variety of inorganic-organic supramolecular systems.

Keywords: tetratitanate; macrocyclic compounds; ion exchange

INTRODUCTION

Intercalation of organic species into the interlayer spaces of layered solids is a way of producing inorganic-organic nanocomposites.[1,2] Although a wide variety of intercalation compounds have extensively been investigated, there is a demand for novel functional intercalation compounds. Layered titanates are attractive host materials partly due to their semiconducting properties. However, unlike the smectites, which is known to accommodate a wide variety of guest species,[3] the intercalating capabilities of layered titanates are low. For the introduction of bulky organic and inorganic species, so called "guest displacement method" has been used previously. [4]

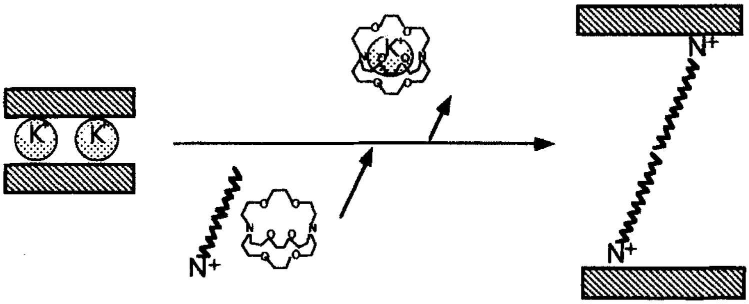

FIG.1 Schematic drawing for the cation exchange mechanism.

Recently, we have reported a novel synthetic way for the preparation of intercalation compounds, where macrocyclic compounds promote the ion exchange reactions (Figure 1).[5,6] In this paper, we report the synthesis of organoammonium-tetratitanate intercalation compounds in the presence of a macrocyclic compound, [2.2.2]-cryptand (abbreviated as C(222)). The present one pot synthesis utilizing the complexation of macrocyclic compounds with interlayer exchangeable cations is a novel and simple way for the introduction of bulky organic species into the interlayer spaces of layered solids with low intercalating capabilities.

EXPERIMENTAL SECTION

The organoammonium-tetratitanate intercalation compounds have been prepared as described in the previous communication;[5] $K_2Ti_4O_9 \cdot nH_2O$ was allowed to react with an solution containing organoammonium chlorides (abbreviated as C_n^+; where n denotes the carbon number of the alkyl chains) and C(222) at room temperature. After the reaction for a week, the products were corrected by centrifugation and dried under a reduced pressure at room temperature. The products were characterized by the X-ray diffraction, TG-DTA, FT-IR and CHN analysis.

RESULTS AND DISCUSSION

The XRD patterns of the products obtained when 1,4-dioxane was used as solvent are shown in Fig. 2. The *d(200)* peak shifted to a lower 2θ region from the original diffraction pattern (Fig. 2a) of $K_2Ti_4O_9 \cdot nH_2O$, where *d(200)* value is 0.87 nm. This observation shows the intercalation of C_n^+ and paraffin type arrangments of the C_n^+ in the interlayer space of tetratitanate. [5] The X-ray diffraction patterns of the products did not change when the reactions were carried out in the absence of C(222), confirming that the added C(222) played an important role for the ion exchange reactions.

The products were washed with 1,4-dioxane and the amounts of the adsorbed C_n^+ and the remained K^+ were determined by CHN analysis and ICP.(Table 1) The sum of C_n^+ and K^+ are not enough to fully compensate the negative charge of the $[Ti_4O_9]^{2-}$ layer, H_3O^+ ions are considered to occupy the interlayer space. On the other hand, the basal spacings of C_{18}^+-, C_{16}^+- and C_{14}^+-tetratitanates decreased by the washing, showing the deintercalation of C_n^+. The FT-IR spectra of the washed products showed absorption bands ascribable to C_n^+, supporting the intercalation of C_n^+.

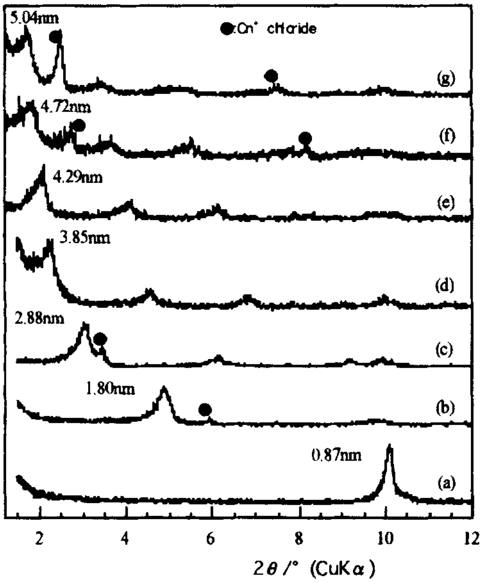

FIGURE 2: The X-ray diffraction patterns of (a) $K_2Ti_4O_9 \cdot nH_2O$ and (b-f) the C_n^+-Ti_4O_9 intercalation compounds; n=4 (b), 8 (c), 12 (d), 14 (e), 16 (f) and 18 (g).

TABLE I: The chemical composition of the washed products

C_n^+	a	B	c
C_4^+	0.97	0.11	0.92
C_8^+	0.98	0.11	0.91
C_{12}^+	0.96	0.12	0.92

a, b, c in $[C_n^+]_a\,[K^+]_b\,[H_3O^+]_c\,[Ti_4O_9]$

Since the direct ion exchange reaction of the organoammonium ions and $K_2Ti_4O_9 \cdot nH_2O$ was impossible, 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 using tetratitanic acid ($H_2Ti_4O_9 \cdot nH_2O$) and butylammonium-tetratitanate intercalation compound as intermediates.[7] Since the operation of the present reaction is simple if compared with those of the guest displacement method, the ion exchange reactions in the presence of macrocyclic compounds is an alternative way for the preparation of intercalation compounds.

There are also advantages in using an organic solvent as many organic cations will be soluble in the organic solvent and insoluble in water. In order to apply the reactions, methanol was used as the solvent. The molar ratio of C(222):K^+:C_n^+ for the reaction was 2:1:10, which was same when 1,4-dioxane was used as the solvent. Although the C_n^+–tetratitanate intercalation compounds (n=4, 8 and 16) with basal spacings similar to those in Figure 2 have been obtained,(the basal spacings were 1.89, 2.78, and 4.65 nm for C_4^+, C_8^+ , and C_{16}^+ -systems, respectively) the ion exchange with C_{18}^+ was unsuccessful. Additionally, in the preliminary experiment on the ion exchange reactions between sodium trititanate ($Na_2Ti_3O_7{\cdot}nH_2O$) and dodecylammonium chloride in the presence of 15-crown-5 ether, the reactions proceeded in water and did not in 1,4-dioxane. Thus, solvents apparently affect the ion exchange reactions to proceed.

In order to establish the present one pot synthesis for the preparation of intercalation compounds, further study on the ion exchange using various potentially ion exchangeable solids and appropriate macrocyclic compounds[8] are now underway in this laboratory and the results will be reported subsequently.

CONCLUSION

In summary, organoammonium-tetratitanate intercalation compounds have been prepared by one pot synthesis where macrocyclic compounds are thought to interact with the interlayer cations to promote the ion exchange reactions. 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.

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