Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **13**: 249–256, 1992.

Preparation of an Intercalation Compound of Layered Titanic Acid $H_2Ti_4O_9$ with Methylene Blue

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(Received: 17 September 1991; in final form: 25 October 1991)

Abstract. Intercalation of methylene blue into layered titanic acid $H_2Ti_4O_9$ was examined by a guest exchange method using a propylammonium–$H_xTi_4O_9$ intercalation compound as the intermediate. Methylene blue cations were arranged in the interlayer space obliquely to the layer surface. The visible spectrum of the intercalation compound suggested that the methylene blue cations were in an associated state in the interlayer space of $H_2Ti_4O_9$. The intercalated methylene blue cations underwent a reversible electrochemical redox reaction in the dark, indicating that intercalation compounds of $H_2Ti_4O_9$ can be applied to a modified electrode.

Key words. Tetratitanate, methylene blue, intercalation.

1. Introduction

There are various layered materials which can form intercalation compounds, and the smectite group of clay minerals forms the most excellent host in respect of the intercalating capabilities. Many guest species have actually been incorporated in clay minerals [1]. Unusual properties of these intercalation compounds have also been reported, establishing the versatility of clay minerals [2]. By contrast intercalation compounds of other layered materials, with the exception of graphite, have not been investigated as extensively as the clay minerals. One of the disadvantageous points of these other materials is their low intercalating capability. However, it has been shown that these materials can take up many guest species, if appropriate techniques are used. In addition, intercalation compounds of these materials are expected to show unique properties which clay mineral intercalates cannot display.

Tetratitanic acid $H_2Ti_4O_9$ is a layered transition metal oxide with intercalating ability [3–5]. It can easily be prepared by an acid treatment of layered potassium tetratitanate $K_2Ti_4O_9$. $K_2Ti_4O_9$ consists of exchangeable interlayer K^+ions and the $[Ti_4O_9]^{2-}$ layers built up from TiO_6 octahedra connected to each other by the sharing of edges and corners [6]. A characteristic of $H_2Ti_4O_9$ is the property of semiconduction, which allows it to act as a photocatalyst for the splitting of water [7]. Thus, novel photofunctionalities can be achieved using the intercalation compounds of $H_2Ti_4O_9$ because the host lattice can act not only as a matrix but also as a photochemically active component. For example, we found that photoinduced host–guest electron transfer occurred in a methylviologen–$H_xTi_4O_9$ intercalation

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compound [8]. Although it is difficult to intercalate less basic compounds into $H_2Ti_4O_9$ [3], guest exchange methods have recently shown a way out of this difficulty [5, 8]: we have succeeded in intercalating a bulky porphyrin guest species into $H_2Ti_4O_9$ [9]. These observations support our contention that $H_2Ti_4O_9$ is a unique host matrix for functional molecules. However, the fundamental properties of $H_2Ti_4O_9$ as a matrix have not been clarified in detail. In order to utilize $H_2Ti_4O_9$ as a versatile matrix we need more investigations of the spectroscopic, electrochemical, and thermal properties of various guest species incorporated in its layered structure.

In the present study we caused $H_2Ti_4O_9$ to intercalate methylene blue (MB^+), which is a typical cationic dye. It has been reported that MB^+ is intercalated into the interlayers of clay minerals [10], and is adsorbed on the external surface of α-zirconium phosphate by cation exchange [11]. Furthermore, the absorption spectrum of MB^+ is known to change upon adsorption onto clay minerals (metachromasy), and the spectral change depends on the nature of the clay minerals [12–14]. Therefore, intercalation of MB^+ into $H_2Ti_4O_9$ is worthy of investigation. Moreover, the electrochemical redox behavior of MB^+ has been investigated in detail [15–19]. The electrochemical behavior of the intercalated MB^+ may be affected by host–guest interactions. Hence, we have conducted a preliminary examination of the electrochemical behavior of $MB^+–H_xTi_4O_9$ using an electrode modified with the intercalation compound.

2. Experimental

2.1. MATERIALS

Potassium tetratitanate, $K_2Ti_4O_9$, prepared by a flux method, was obtained from Ohtuka Chemical Co. $H_2Ti_4O_9$ was prepared by acid treatment of $K_2Ti_4O_9$; the structural formula was confirmed by powder X-ray diffraction (XRD) and chemical analysis [8]. K^+ ions in $K_2Ti_4O_9$ were removed (91%) after acid treatment. Methylene blue was purchased as the chloride (Wako Pure Chemical Industries Co., Guaranteed grade), and used without further purification.

2.2. SYNTHESIS OF THE INTERCALATION COMPOUND

We failed to prepare any $MB^+–H_xTi_4O_9$ intercalation compounds by direct reaction. Since $H_2Ti_4O_9$ is reported to incorporate basic compounds with $pK_a > 9$ [3], MB^+ ($pK_a = 0.5$ [14]) should be too weak a base to be intercalated into $H_2Ti_4O_9$. We therefore applied a guest exchange method using a propylammonium–$H_xTi_4O_9$ intercalation compound as the intermediate [8]. The propylammonium–$H_xTi_4O_9$ intercalation compound was synthesized by the reaction of $H_2Ti_4O_9$ with an aqueous propylamine solution [8]. The propylammonium–intercalate was then allowed to react with the excess amount of a $0.05\ \mathrm{mol\ dm^{-3}}$ MB^+ aqueous solution in a glass ampoule at 80°C for two weeks. After the reaction, the solid was separated by centrifugation and washed with methanol twenty times. The product was dried and stored under ambient conditions.

2.3. ANALYSES

All samples were characterized by XRD and infrared spectroscopy (IR). XRD patterns were obtained on a Rigaku RADI-C diffractometer (Ni-filtered CuK_α radiation). IR spectra were recorded on a Perkin Elmer FTIR-1640 spectrometer (KBr disk technique). Visible diffuse reflectance spectra were recorded on a Shimadzu UV-210A spectrometer equipped with an integrating sphere. The organic content of the samples were determined by conventional elemental (C, H, N) analyses.

2.4. ELECTROCHEMICAL MEASUREMENT

An SnO_2 glass electrode (ca. 1 cm^2) was coated with the powdered product. The powdered intercalation compound was suspended in an aqueous solution of poly(vinyl alcohol) (PVA) at sample/PVA ratio of 2 (by weight). The suspension was dropped onto the electrode and then the electrode was dried under ambient conditions. Cyclic voltammograms were obtained with a potentiostat (Hokuto Denko HA-303) combined with a function generator (Hokuto Denko HB-104). The reference electrode was an Ag/AgCl electrode and the counter electrode was a Pt wire. All experiments were carried out in nitrogen purged 0.1 mol dm^{-3} aqueous solution of Na_2SO_4 using a conventional three-electrode cell. A 100 W super high pressure mercury lamp (Ushio USH-102D) with a cut-off filter at 460 nm (Hoya Glass Co.) was used for visible light irradiation of the electrode.

3. Results and Discussion

3.1. FORMATION OF THE INTERCALATION COMPOUNDS

Figure 1 shows the XRD pattern of the reaction product, together with those of $H_2Ti_4O_9$ and the propylammonium–$H_xTi_4O_9$ intercalation compound. The position of the (200) peak corresponding to the basal spacing shifted to a lower 2θ angle and that of the (020) peak was almost the same as that of $H_2Ti_4O_9$. Therefore, the basal spacing was expanded by the reaction, while the layered structure of $H_2Ti_4O_9$ was retained. The basal spacing (the d_{200} value) of the product was 1.85 nm, being larger than those of $H_2Ti_4O_9$ (0.85 nm) and the propylammonium–$H_xTi_4O_9$ intercalation compound (1.52 nm). The IR spectrum of the product showed many characteristic bands assigned to MB^+ (e.g. 1605 cm^{-1}, C=N stretching of phenothiazine ring; 1487 cm^{-1}, C=C stretching of the ring; 1393 cm^{-1}, C—H bending of methyl group [13]), whereas the absorption bands due to propylammonium disappeared. The composition of the product was as follows: C, 14.8%; N, 3.3%; $[Ti_4O_9]^{2-}$, 61.3%. Thus, the C/N ratio is calculated as 5.2 while those of MB^+ and propylammonium ion are 5.3 and 3.0, respectively. These results confirmed that MB^+ ions were exchanged almost completely with pre-intercalated propylammonium ions. In addition, the amount of MB^+ is determined to be 0.4 mol MB^+ per $[Ti_4O_9]^{2-}$. The residual negative charge of the $[Ti_4O_9]^{2-}$ should be compensated by oxonium cations (or protons) because no other cationic species are present in the interlayer space.

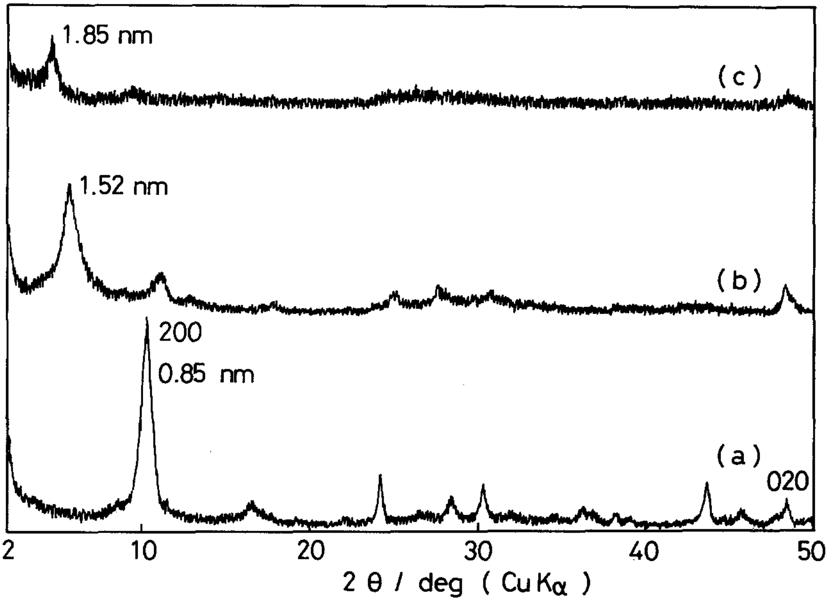

Fig. 1. XRD patterns of (a) $H_2Ti_4O_9$, (b) propylammonium–$H_xTi_4O_9$ intercalation compound, and (c) methylene blue–$H_xTi_4O_9$ intercalation compound.

The arrangement of MB^+ in the interlayer space was deduced from the basal spacing and the composition of the intercalation compound. Since the amount of MB^+ intercalated is 0.4 mol per $[Ti_4O_9]^{2-}$, the area of the $[Ti_4O_9]^{2-}$ layer surface occupied by one MB^+ molecule is calculated as 0.56 nm^2 from the specific area of the layered surface (0.225 nm^2 per $[Ti_4O_9]^{2-}$ unit [20]). However, the area of the molecular plane of an MB^+ ion is $1.70 \times 0.76 = 1.292$ nm^2 [10]. Thus, MB^+ should be arranged to make the layers denser by taking e.g. an inclined, a bilayer, or a trilayer arrangement. The Δd value, the increase in the basal spacing on intercalation, of the MB^+–$H_xTi_4O_9$ intercalation compound is calculated as 1.00 nm, and the thickness of an MB^+ molecule is 0.32 nm [10]. A flat bilayer arrangement is implausible because the Δd value is too large for the bilayer arrangement of MB^+. A trilayer arrangement is also unrealistic because the middle layer ions cannot be stable due to a lack of strong interactions with negatively charged host lattices. Therefore, the arrangement should be a monolayer. When MB^+ is arranged in a monolayer, the area of MB^+ projected onto the layer surface must be smaller than 0.56 nm^2 in order to accommodate 0.4 mol of MB^+ per $[Ti_4O_9]^{2-}$. If MB^+ is oriented in a perpendicular monolayer with its 0.76 nm side to the layer surface, the projected area of MB^+ is $1.70 \times 0.32 = 0.56$ nm^2. However, such an orientation should give a Δd value of 0.76 nm, which is smaller than the actual Δd value. Consequently, we infer an inclined monolayer arrangement of MB^+ with its 1.70 nm side to the layer surface. The maximum tilt angle is calculated from the Δd value to be 36°, which gives the projected area of 1.05 nm^2 per single molecule of MB^+. The MB^+ ions should be partly overlapped, one over another, with respect to the

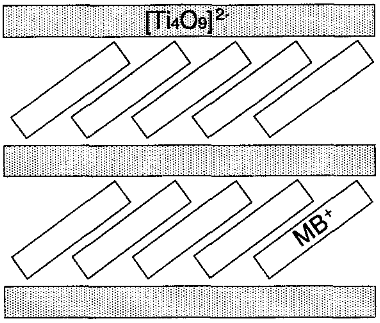

Fig. 2. Schematic representation of the arrangement of methylene blue cations in the interlayer space of $H_2Ti_4O_9$.

molecular plane, as shown in Figure 2. Such an arrangement has not been achieved in the previously reported MB^+–clay intercalation compounds because the charge density of the smectite group of clay minerals is not high enough to accommodate MB^+ ions with an inclined arrangement.

3.2. VISIBLE SPECTROSCOPY

A visible diffuse reflectance spectrum of the $MB^+–H_xTi_4O_9$ intercalation compound is shown in Figure 3c. A broad absorption band appears around 600 nm. The spectrum is quite different from that of MB^+ in an aqueous solution (Figure 3a), but resembles that of the MB^+ chloride salt (Figure 3b). This fact suggests that the intercalated MB^+ is in a state similar to the crystalline MB^+ chloride salt, in which MB^+ ions are considered to exist in an associated state $(MB^+)_n$ [21]. The spectral similarity supports the inclined arrangement of the MB^+ cations shown in Figure 2, which arrangement may cause the intermolecular association of the MB^+ cations through the successive partial facing of the phenothiazine rings one over another.

The visible spectrum of the intercalation compound is also different from those of MB^+ species on clay minerals reported previously [12–14]. This is due to the difference in the measuring conditions. Our spectrum was obtained by the diffuse reflectance method; the transmission spectra were observed for the clay minerals in suspensions. In our case it was impossible to measure the spectrum by the transmission method. Diffuse reflectance spectra tend to show broader peaks [22]., and, indeed, the spectrum obtained was broad. Therefore, it is difficult to obtain more detailed information, such as accurate peak positions, from Figure 3. Although the fluorescence spectrum is useful to obtain further information about the interlayer state of MB^+, we could not observe the fluorescence spectrum, probably due to the low fluorescence quantum yield of MB^+ [23].

3.3. ELECTROCHEMICAL BEHAVIOR

Figure 4a shows a typical cyclic voltammogram of the $MB^+–H_xTi_4O_9$ intercalation compound on an SnO_2 electrode in the dark. Although an MB^+–montmorillonite intercalation compound was reported to be electroinactive [19], the

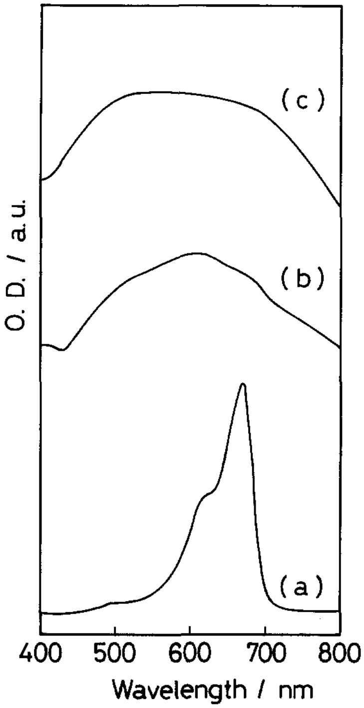

Fig. 3. Visible diffuse reflectance spectra of (a) an aqueous solution of methylene blue (1.1×10^{-5} mol dm^{-3}, transmission spectrum), (b) methylene blue chloride powders (diluted with a Toyo No. 2 filter paper) and (c) methylene blue–$H_xTi_4O_9$ intercalation compound (diluted with a Toyo No. 2 filter paper).

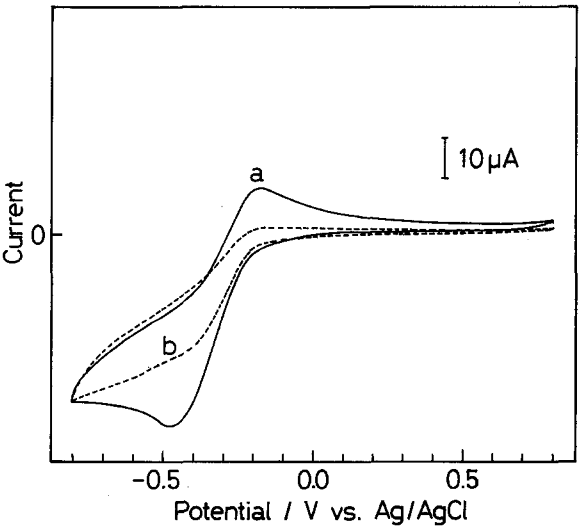

Fig. 4. Cyclic voltammograms of methylene blue–$H_xTi_4O_9$ intercalation compound (a) in the dark (solid line) and (b) under visible light irradiation (dotted line).

$MB^+-H_xTi_4O_9$ intercalation compound was electroactive. The observed pair of redox waves were due to the intercalated MB^+ because these waves were not observed in a cyclic voltammogram of $H_2Ti_4O_9$ on the SnO_2 electrode. This reaction should correspond to the redox reaction of MB^+ as follows [15–19]:

$$\underset{\text{methylene blue}}{MB^+} + 2e^- + H^+ \rightleftharpoons \underset{\text{leuco methylene blue}}{MBH}$$

The cyclic voltammogram changed drastically upon irradiation of the intercalation compound with visible light. Figure 4b shows a cyclic voltammogram of the intercalation compound under the irradiation. The pair of redox waves due to MB^+ disappeared, indicating that MB^+ became photoinactive due to the irradiation. Because the host lattice is not sensitive to the visible light, the electroinactivity should be due to a photoeffect on MB^+. Since the redox potential of excited MB^+ is more negative than -0.7 V (vs. SCE) [24], the excited MB^+ may not be reduced in the potential range which we used ($+0.8$–-0.8 V vs. Ag/AgCl).

4. Conclusion

A methylene blue–$H_xTi_4O_9$ intercalation compound was synthesized through a guest exchange method using a propylammonium–$H_xTi_4O_9$ compound as the intermediate. The densely charged host lattice arranged the guest species obliquely to the $[Ti_4O_9]^{2-}$ layers. The visible spectrum of the intercalation compound suggested that the interlayer MB^+ ions take an associated state. This fact proves that $H_2Ti_4O_9$ is a potential matrix for the organization of functional organic ions and that the organized guest ions can change their electronic state to exhibit novel photochemical/photophysical properties. The electrochemical activity of the present intercalation compound exemplifies a potential of intercalation compounds of $H_2Ti_4O_9$ for application as functional electrodes.

Acknowledgement

This work was partly supported by Izumi Science and Technology Foundation.

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