Swelling Behaviors of an Organosilylated Lithium Potassium Titanate in Organic Solvents

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An organically modified layered titanate, prepared by the reaction of $K_{0.8}Ti_{1.73}Li_{0.27}O_4$ with *n*-octadecyltrimethoxysilane, was dispersed in benzene, chloroform, toluene, *n*-decane, *n*-octanol, and ethyl acetate to form colloidal suspensions.

Layered transition metal oxides are class of solids with semiconducting and ion-exchange properties. These solids have been found to swell in aqueous solutions containing such bases as tetrabutylammonium hydroxide and propylamine.[1] Although the characterizations and applications of the aqueous suspensions have actively been investigated,[1b,c,2] the swelling mechanism is not still understood well. Additionally, the presence of the bases on the surfaces is undesirable for a certain kind of applications.

Recently, we have reported the preparation of an organically modified layered titanate by the interlayer silylation of $K_2Ti_4O_9 \cdot nH_2O$ with an organosilane and its swelling in an organic solvent.[3] This was the first successful report on the preparation of the organic suspension of a layered titanate.[3] The silylation is possible for various hosts and a wide variety of organosilanes, so that systematic study on the preparations and properties of various silylated derivatives is worth conducting.

Herein, the silylation of $K_{0.8}Ti_{1.73}Li_{0.27}O_4$ (designated as KTLO) with *n*-octadecyltrimethoxysilane and the swelling behavior of the resulting silylated derivative are investigated. KTLO possesses a lepidocrocite-type layered structure, which is similar to that of $H_xTi_{2-x/4}\square_{x/4}O_4 \cdot H_2O$ (□: vacancy) whose swelling in aqueous solutions has been extensively studied.[1a,2,4] Because of the lower layer charge density if compared with other layered transition metal oxides,[5] KTLO is expected to swell more easily as suggested by a fact that swelling abilities of smectites correlates to electrostatic interaction between layers.[6] Moreover, KTLO is characterized by the versatilities in particle sizes[7] and compositions which correlate layer charge densities.[8] Accordingly, systematic study on the swelling behaviors of various organosilylated derivatives in organic solvents will be possible.

The silylation of the KTLO, which was synthesized by a solid-state reaction,[9] was conducted by using the octylammonium-exchanged form (designated as C_8N^+–TLO) as the intermediate. This strategy has been originally developed for the silylation of layered silicates[10] and used for that of $K_2Ti_4O_9 \cdot nH_2O$.[3] The C_8N^+–TLO was prepared by cation-exchange reaction of KTLO with an aqueous mixture of propylamine and octylamine.[3] The basal spacing, d_{020} value, of 2.8 nm (0.78 nm for the KTLO, Figure 1b), as well as the IR (data not shown), ICP-AES, and CHN elemental analysis (Table 1) indicated the successful formation of the C_8N^+–TLO. The silylated derivative (designated as C_{18}TMS–TLO) was prepared by dispersing the C_8N^+–TLO (0.25 g) in a toluene (50 mL) solution of *n*-octadecyltrimethoxysilane (27.6 mL) and refluxing the mixture at 100 °C for 48 h. The product was collected by centrifugation at 4000 rpm for 20 min and washed with acetone.

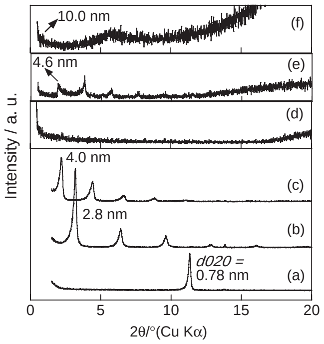

Figure 1. XRD patterns of (a) KTLO (b) C_8N^+–TLO (c) C_{18}TMS–TLO and the C_{18}TMS–TLO (d) chloroform (e) ethyl acetate (f) *n*-octanol slurries with a concentration of 1.9×10^{-2} mol dm^{-3} of TLO.

Table 1. Chemical compositions of the products

	C	N	K	Li	Si	Ti	N/TLO	Si/TLO
	mass%						molar ration	
C_8N^+–TLO	27.7	4.0	0.32	0.63	—	27.6	0.86	—
C_{18}TMS–TLO	37.2	0.47	0.20	0.46	4.4	19.5	0.14	0.67

The XRD pattern of the C_{18}TMS–TLO is shown in Figure 1c. The d_{020} value increased upon the silylation to 4.0 from 2.8 nm for the C_8N^+–TLO. The IR spectrum (data not shown) showed the absorption bands due to octadecylsilyl groups, such as SiO–C and Si–O–Si stretching vibration at 1150–1000 cm^{-1}.[11] The presence of an absorption band at 971 cm^{-1}, which is ascribable to Si–O–Ti stretching vibration,[12] indicates that the octadecylsilyl groups were attached onto the TLO sheets through Si–O–Ti bonds. From the Si and Ti contents, the amount of the attached octadecylsilyl groups was determined to be 0.67 mol per TLO. The presence of N in the C_{18}TMS–TLO showed that a part of C_8N^+ was remained after the silylation. Taking the d_{020} value and the size of octadecyltrimethoxysilane (ca. 2.6 nm) into account, the arrangement of the attached octadecylsilyl groups is thought to be a paraffin-type coverage, which is the same as that of the octadecylsilylated $K_2Ti_4O_9 \cdot nH_2O$ (designated as $C_{18}TMS–Ti_4O_9$).[3] If the packing of the octadecylsilyl groups is a hexagonal closest one, the surface coverages with the octadecylsilyl groups for the C_{18}TMS–TLO and the $C_{18}TMS–Ti_4O_9$ are calculated from the compositions[3] and lattice constants of the parent titanates[9,13] to be 3.0 and 2.2 group/nm^2, respectively.[14] This difference in the surface coverage may correlate to the variation in the following swelling behavior.

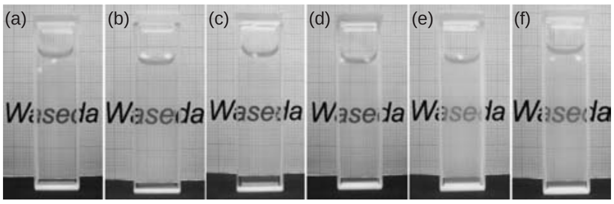

Figure 2. Photographs of (a) chloroform (b) benzene (c) toluene (d) *n*-decane (e) *n*-octanol and (f) ethyl acetate suspensions of C_{18}TMS–TLO.

The C_{18}TMS–TLO was dispersed in benzene, chloroform, toluene, *n*-decane, *n*-octanol, and ethyl acetate (Figure 2).[15] UV–vis. absorption spectra of these suspensions were characterized by the facts that the well-developed absorption peaks appeared at around 270 nm near absorption onsets and they obeyed Beer–Lambert law.[16] Similar spectroscopic features have also been reported for the aqueous suspensions prepared by swelling of a layered protonic titanate, $H_xTi_{2-x/4}\square_{x/4}O_4 \cdot H_2O$ ($\square$: vacancy)[4] and for the organic suspension of the C_{18}TMS–Ti_4O_9.[3] The XRD pattern of the chloroform slurry showed that the d_{020} diffraction peak was not detectable (Figure 1d) and those of the ethyl acetate and *n*-octanol slurries showed the expansion of the basal spacing (Figures 1e and 1f). These results indicate that the present C_{18}TMS–TLO incorporates organic solvents into the organically modified interlayer space to swell. The affinity of the modified titanate sheets and solvents may affect the degree of the swelling, though more quantitative discussion is difficult at present. The difference in the expansion of the basal spacing may affect the light transmittance in the swollen particles, so that the difference in the transparency of the suspensions was observed (Figure 2). The refractive index matching between particle (or titanate sheet)–solvent phase interface may be an another reason for the difference. The refractive index of the TLO sheets is 2.00 at 600 nm[17] and those of the solvents are 1.501, 1.446, 1.497, 1.411, 1.431, and 1.372 for benzene, chloroform, toluene, *n*-decane, *n*-octanol, and ethyl acetate, respectively.

The UV–vis. absorption spectrum and the photograph of the chloroform suspension of the C_{18}TMS–TLO are shown in Figure 3 together with those of the C_{18}TMS–Ti_4O_9 with the same titania concentration. The C_{18}TMS–TLO suspension was more transparent even though particles sizes of both the silylated derivatives (C_{18}TMS–TLO: 0.5–4 μm, C_{18}TMS–Ti_4O_9: 1–3.5 μm) were comparable. Similar tendency in the transparency was observed for the C_{18}TMS–TLO and the C_{18}TMS–Ti_4O_9 suspensions with other organic solvents. The XRD pattern of the C_{18}TMS–Ti_4O_9 chloroform slurry showed only the expansion of the basal spacing to 7.0 from 4.2 nm of the powder, and those of the ethyl acetate and *n*-octanol slurries showed that even the expansion of the basal spacing was not observed. From these results, the expandability of the interlayer space of the C_{18}TMS–TLO is thought to be higher than that of the C_{18}TMS–Ti_4O_9, because of the higher surface coverage and partly because of the lower layer charge density. The reason for the difference in the absorbance of both suspensions is not clear at present. The molar extinction coefficient of the C_{18}TMS–TLO chloroform suspension (ca. 12000) is equivalent to that of the $H_xTi_{2-x/4}\square_{x/4}O_4 \cdot H_2O$ aqueous suspension.[4]

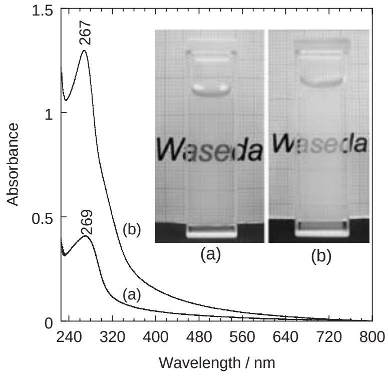

Figure 3. UV–vis. absorption spectra of the chloroform suspensions of C_{18}TMS–TLO and (b) C_{18}TMS–Ti_4O_9 at same titania concentration (4.0×10^{-4} mol dm^{-3}). Inset: photographs of the corresponding suspensions.

In summary, we have synthesized the organically derivatized $K_{0.8}Ti_{1.73}Li_{0.27}O_4$ using the octylammonium-exchanged form as the intermediate. The silylated derivative was found to swell in organic solvents. The swelling behavior varied with the surface coverage. The difference in the layer charge density was also though to affect the swelling behaviors.

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14 Calculated as $0.67/2ac$ for C_{18}TMS–TLO and $1.0/bc$ for C_{18}TMS–Ti_4O_9 where *a*, *b*, and *c* are lattice constants of the parent titanates. Compositions of *ac* and *bc* unit cells are Ti_4O_9 and TLO, respectively.
15 The C_{18}TMS–TLO was dispersed in organic solvents (0.06 g dm^{-3} or 4.0×10^{-4} mol dm^{-3} of TLO) within glass ampoules and ultrasonicated for 1 h followed by stirring for 5 days at room temperature.
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