Effect of Preparation Conditions of Ti Ion Species on Structural Properties of TiO₂ Pillared Mica

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TiO₂ pillared mica was prepared using Ti ion species as TiO₂ precursor. The titanium ion species were obtained by an addition of several titanium alkoxides to an aqueous solution of CH₃COOH, with different CH₃COOH/Ti ratios and temperatures. The structure and properties of the TiO₂ pillared mica was studied by X-ray diffraction, N₂ adsorption, FT-IR and TG-DTA. After calcined at 500°C, the BET surface area of samples varied between 250 and 460 m²/g. The sample prepared using titanium tetraethoxide as titanium source possessed well ordered structure and higher BET surface area. The basal spacing of TiO₂ pillared mica was increased with the decrease in CH₃COOH/Ti ratio and the increase in temperature of preparation of titanium ion species, while the degree of ordered structure of pillared mica was decreased.

Key Words : TiO₂ pillared mica, Titanium ion species, Acetic acid, Pillared structure, Titanium tetraethoxide, CH₃COOH/Ti ratio

1 INTRODUCTION

Pillared clays are two-dimensional zeolite-like materials prepared by exchanging cations located between layers of clays with bulky metal polyoxocations (polyoxocations) followed by calcination. The intercalated polycations increase the basal spacing of the clays and they are converted to metal oxide pillars by heat treatment that keep the clay layers apart. The increasing number of studies on pillared clays is in the field of applications such as heterogeneous catalysts, catalyst supports, adsorbents and environmental uses.

TiO₂ pillared clays have attracted much attention as potential materials for photocatalysts. TiO₂ has photo-induced strong oxidizing power and has been used practically as photocatalyst materials. TiO₂ pillared clays show higher adsorption ability than pure TiO₂ due to its large specific surface area, and this adsorption property accelerates photocatalytic reactions. In addition, the interlayer surface of pillared clays is generally hydrophobic, which is an advantage to adsorb and enrich diluted hydrophobic organic compounds in water¹⁾. Especially, utilization of fluorine mica as host clay results in higher photocatalytic activity toward highly hydrophobic and stable organic pollutant than a conventional pure TiO₂ photocatalyst^{2,3)}.

The physicochemical properties of the TiO₂ pillared clays depend on several synthesis parameters, including the concentration of the metal ion, the temperature, the method of preparation, and the nature of the host clay⁴⁾. Titania sol or titanium ion species, *i.e.* precursors of TiO₂ pillar, have been prepared by hydrolysis of TiCl₄ or titanium alkoxide with acid (HCl, CH₃COOH⁵⁾ etc.). Unlike the aluminum polycations, titanium ion species have no distinct metastable structure. Therefore, the preparation of TiO₂ pillared

clays with well-ordered structure, which is indispensable for shape selective ability, is difficult. Additionally, TiO₂ particles in pillared clays synthesized by a conventional method are amorphous or poorly crystallized anatase, which should exhibit lower activity than highly crystallized TiO₂ anatase. For the application of TiO₂ pillared clays as photocatalysts with high activity and shape selectivity, improvements in structural and textural properties is strongly required.

In this study, TiO₂ pillared mica samples were prepared by using synthetic fluoro-tetrasilicic mica as mother clay. Because of its large cation exchange capacity (CEC), it is expected that the amount and distribution of TiO₂ pillars introduced in interlayers of the mica can be widely controllable. Ti ion species as precursors of TiO₂ pillars were obtained by hydrolyzing several titanium alkoxides in aqueous solution of acetic acid, with different CH₃COOH/Ti ratios and temperatures. In particular, higher CH₃COOH/Ti ratio was employed compared with conventional method (usually CH₃COOH/Ti=24). It is expected that acetic acid acts as a hydrolysis agent of titanium alkoxides as well as a dispersing agent of mica particles. These properties of acetic acid may cause a good influence on intercalation of titanium ion species and on formation of well-ordered pillared structure at higher CH₃COOH/Ti ratio. Effect of preparation conditions of titanium ion species on the structural properties of TiO₂ pillared mica was investigated by detailed characterization using XRD, N₂ adsorption, FT-IR and TG-DTA.

2 EXPERIMENTAL

2.1 Preparation of TiO₂ pillared mica

Titanium tetraethoxide (Ti(O-Et)₄), titanium tetra-*i*-propoxide (Ti(O-*i*Pr)₄) and titanium tetra-*n*-butoxide (Ti(O-*n*Bu)₄) were used

Table 1 Preparation conditions of Ti ion species and physical properties of calcined TiO₂ pillared mica.

Ti precursor	CH ₃ COOH/Ti [-]	Temp. [°C]	<i>d</i> (001) [nm]	<i>S</i> (BET) [m ² /g]	Ti/Si [-]
Ti(O- <i>i</i> Pr) ₄	10	50	3.65	249	-
	25	50	2.98	281	-
	50	20	2.55	373	0.91
	50	30	2.39	354	0.96
	50	40	2.61	303	1.05
	50	50	2.88	292	1.34
	50	60	3.56	308	1.85
	50	75	-	-	3.42
	70	50	2.87	370	-
Ti(OEt) ₄	10	50	3.18	313	-
	25	50	3.20	319	-
	50	20	2.64	363	-
	50	50	2.90	459	-
	50	60	3.07	340	-
	70	50	2.96	388	-
Ti(O- <i>n</i> Bu) ₄	10	50	3.32	283	-
	37	50	2.88	256	-
	50	50	2.71	321	-
	70	50	2.79	425	-

Temp.: hydrolysis temperature of titanium alkoxides,
d(001): basal spacing, *S*(BET): specific surface area,
 Ti/Si: atomic ratio.

as Ti sources. A clear solution of titanium ion species was obtained by the addition of the Ti source to an aqueous solution of acetic acid (80 wt%) at 20, 30, 40, 50, 60 or 75°C for 1.5 h. Molar ratio of acetic acid to titanium alkoxide were varied from 10 to 70. Synthetic fluoro-tetrasilicic mica (NaMg_{2.5}Si₄O₁₀F₂, Topy Ind., Co.) was suspended in distilled water (1 wt%) and kept stirred at room temperature for 24 h to swell the mica. The solution of titanium ion species was added to the suspension of mica (Ti/mica=22 mmol/g, Ti/CEC=44), and the mixture was stirred for 3 h at room temperature. Then, the solid products were separated by a centrifugation at 3700 rpm, washed several times with distilled water, and dried in vacuum. Dried samples, *i.e.* the precursor of TiO₂ pillared mica, were calcined at 500°C in air for 2 h to yield TiO₂ pillared mica samples.

2.2 Characterization

X-ray diffraction patterns were recorded on a Rigaku RAD-C system, Rigaku Co., Ltd. using CuK α radiation. Basal spacing of TiO₂ pillared mica samples was calculated from (001) reflection. Nitrogen adsorption-desorption isotherms were measured at 77 K (BELSORP18, BEL JAPAN inc.). Specific surface area and pore size distribution were calculated from adsorption isotherm by B.E.T. method and MP method, respectively. Ti/Si atomic ratio

was determined by energy dispersive X-ray analysis (JEOL JSM-5900 LV). The FT-IR spectra were measured on a Spectrum 2000 (Perkin Elmer Japan Co., Ltd.) using KBr technique. TG-DTA measurements were carried out at a heating rate of 10°C/min using a Rigaku TG-DTA 8120.

3 RESULTS AND DISCUSSION

Preparation including intercalation of titanium ion species into interlayers of the mica was carried out under various conditions. Typical experimental conditions and physical properties of TiO₂ pillared mica samples calcined at 500°C are summarized in Table 1.

3.1 Effect of titanium alkoxide

The XRD patterns of parent mica, dried and calcined TiO₂ pillared mica samples prepared with different titanium alkoxide are shown in Figure 1. Three peaks were observed at $2\theta=2-8^\circ$ in each dried sample (Figure 1b-d). These peaks were assigned to (001), (002) and (003) reflections of layered mica intercalated with Ti ion species. This result indicates that the well-ordered layer structures were formed in intercalated samples. However, the difference in relative intensity of these three peaks were observed among these samples prepared using different titanium alkoxide precursors, implying that the amount, distribution and/or extent of dispersion of intercalated titanium ion species in interlayers of mica depend on the alkoxide species used in the preparation.

FT-IR spectra of parent mica and the precursors of TiO₂ pillared

Figure 1 XRD patterns of mica, the precursors of TiO₂ pillared mica and calcined samples with different titanium alkoxide (CH₃COOH/Ti=50, hydrolysis temperature: 50°C). The samples are a: parent mica, the precursors prepared with b: Ti(O-Et)₄, c: Ti(O-*i*Pr)₄, d: Ti(O-*n*Bu)₄, calcined samples prepared with e: Ti(O-Et)₄, f: Ti(O-*i*Pr)₄, g: Ti(O-*n*Bu)₄.

mica are shown in Figure 2. The broad bands between 3700 and 3000 cm⁻¹ are attributed to stretching vibration of silanol groups of external layers of mica, adsorbed water molecules, and titanium ion species of intercalated samples. The bands around 1001 cm⁻¹ and 473 cm⁻¹ are due to asymmetric stretching vibrations of SiO₂ tetrahedra and bending of Si-O vibration, respectively. Four new absorption bands *i.e.* 612, 654, 1450 and 1536 cm⁻¹ are appeared after the intercalation of titanium ion species. These bands indicate the hydrolysis of titanium alkoxides with acetic acid. The bands at 612 and 654 cm⁻¹ are attributed to the formation of Ti-O-Ti bond during condensation of Ti-acetate complex. The doublet bands in 1536 and 1450 cm⁻¹ are assigned to the asymmetric and symmetric stretching vibrations of the carboxylic group coordinated to Ti as a bidentate ligand⁶. At around 2900 cm⁻¹, trace band due to C-H stretching vibration which may be attributed to CH₃ group of acetic acid is observed. These features are almost the same for three precursors (Figure 2b-d). These results suggest that the coordination structure of titanium ion species are unaffected by titanium alkoxide precursors.

After the samples were calcined at 500°C, sharp (001) peak and broad (002) peak were observed, and (003) peak was disappeared (Figure 1e-g). TG-DTA curves of the precursor of TiO₂ pillared mica prepared using Ti(O-*i*Pr)₄ as a Ti source are shown in Figure 3. The main weight losses occurred in two steps, *i.e.* at 25-150°C and 150-425°C. The first weight loss (15.8 wt%) with an endothermic peak below 150°C is attributed to elimination of physically adsorbed water. The second one (13.6 wt%) with exothermic peak at around 380°C is ascribed to the decomposition and combustion of organic compounds which existed in interlayers of mica. Similar TG-DTA curves were obtained for the samples prepared from Ti(O-Et)₄ or Ti(O-*n*Bu)₄. These results indicate that thermal

decomposition of the organic compounds contained in the titanium ion species intercalated in mica occurs during calcination at 500°C and Ti ion species are converted to TiO₂ pillars. Almost all the TiO₂ particles may exist in interlayers of mica as pillars, since no clear peaks due to anatase and rutile were found in all the samples (Figure 1). The shift of (001) peak toward higher diffraction angles was found for TiO₂ pillared mica samples (Figure 1e-g) in

Figure 3 TG-DTA curves of the precursors of TiO₂ pillared mica prepared with Ti(O-*i*Pr)₄ (CH₃COOH/Ti=50, hydrolysis temperature: 50°C).

Figure 2 FT-IR spectra of parent mica, the precursors of TiO₂ pillared mica samples with different titanium alkoxide (CH₃COOH/Ti=50, hydrolysis temperature: 50°C). a: parent mica, the precursor prepared with b: Ti(O-Et)₄, c: Ti(O-*i*Pr)₄, d: Ti(O-*n*Bu)₄.

Figure 4 Nitrogen adsorption-desorption isotherms of TiO₂ pillared mica samples with different titanium alkoxide (CH₃COOH/Ti=50, hydrolysis temperature: 50°C). □: Ti(O-Et)₄, ○: Ti(O-*i*Pr)₄, ▲: Ti(O-*n*Bu)₄.

the order of $\text{Ti}(\text{O-Et})_4 < \text{Ti}(\text{O-}i\text{Pr})_4 < \text{Ti}(\text{O-}n\text{Bu})_4$. Additionally, the sample prepared with $\text{Ti}(\text{O-Et})_4$ (Figure 1e) exhibits most intense (001) reflection. Full width at half maximum of (001) peak is also narrower ($\text{Ti}(\text{O-Et})_4$; 0.589°) than other samples ($\text{Ti}(\text{O-}i\text{Pr})_4$; 0.644° , $\text{Ti}(\text{O-}n\text{Bu})_4$; 0.689°). The result indicates that the sample prepared with $\text{Ti}(\text{O-Et})_4$ gives well-ordered structure than other samples. This behavior may be caused by the difference in thermal stability of TiO_2 pillars.

Nitrogen adsorption-desorption isotherms of TiO_2 pillared mica samples calcined at 500°C are shown in Figure 4. Although the amount of nitrogen adsorbed were different from each other, every isotherm of the pillared mica seems to be the type IV characteristic to solids including both micro and meso pores (BDDT classification). Small adsorption-desorption hysteresis loop due to capillary condensation in mesopores was observed slightly. The sample prepared with $\text{Ti}(\text{O-Et})_4$ exhibits higher BET surface area ($459\text{ m}^2/\text{g}$, see Table 1) than other samples. This result also suggests that pillared structure of the sample is well-ordered, which agrees with most intense (001) reflection of the sample (Figure 1).

Castillo et al.⁷⁾ observed similar results with using HCl as hydrolysis agent and $\text{Ti}(\text{O-Et})_4$ as a source of titanium yielded the good textural and thermal stability for the preparation of TiO_2 pillared montmorillonite. They also suggested that the alkoxy groups affect the nature of the hydrolysis of titanium alkoxides and a more highly ramified titanium polymer ion could be obtained from titanium with large alkoxy groups. In this case, diffusion of titanium polymer ion in the interlayer space will be difficult, and which causes a poor distribution of the pillars of the titanium polymer between the layers of the clay. Since CH_3COOH slows down the hydrolysis of titanium alkoxides and CH_3COO^- groups are contained in titanium ion species, more ramified titanium polymers are likely formed. These situations may affect on the thermal stability of layered structure. In this study, as suggested above, more stable pillared structure was formed by using $\text{Ti}(\text{O-Et})_4$ as titanium ion source.

3.2 Effect of $\text{CH}_3\text{COOH}/\text{Ti}$ ratio

XRD patterns of calcined samples with different $\text{CH}_3\text{COOH}/\text{Ti}$ ratios are shown in Figure 5. These samples were prepared using $\text{Ti}(\text{O-}i\text{Pr})_4$ as precursor of titanium ion species. The (001) peaks found around $2\theta=3^\circ$ decreased in intensity and shifted toward lower diffraction angles with a decrease in the $\text{CH}_3\text{COOH}/\text{Ti}$ ratio. The basal spacing $d(001)$ value increased from 2.87 nm ($\text{CH}_3\text{COOH}/\text{Ti}=75$) to 3.65 nm ($\text{CH}_3\text{COOH}/\text{Ti}=10$) (Table 1). These results indicate that the TiO_2 pillar size was influenced by $\text{CH}_3\text{COOH}/\text{Ti}$ ratio, and that larger titanium ion species, the precursor of TiO_2 particles, were obtained under the conditions of smaller $\text{CH}_3\text{COOH}/\text{Ti}$ ratios. This behavior may be attributed to a difference in the degree of condensation of Ti species during hydrolysis of titanium alkoxide. However, the broadening of (001) peak was occurred, and a peak assigned to TiO_2 anatase ($2\theta=25.2^\circ$) were observed in the XRD pattern of the sample prepared under lower ratio of $\text{CH}_3\text{COOH}/\text{Ti}=10$. The decrease in specific surface area (Table 1) was also observed with a decrease in the $\text{CH}_3\text{COOH}/\text{Ti}$ ratio. Under a constant Ti/mica ratio, the formation of large titanium ion species during hydrolysis resulted in a decrease in the number of them. This may lead to the reduction in the amount of titanium ion species intercalated, and cause a poor thermal stability which is responsible for low specific surface area. Therefore, disordered structure of TiO_2 pillared mica and large TiO_2 particles

on external surface of mica were formed at $\text{CH}_3\text{COOH}/\text{Ti}=10$. Similar results were obtained for the samples prepared using $\text{Ti}(\text{O-Et})_4$ and $\text{Ti}(\text{O-}n\text{Bu})_4$.

3.3 Effect of hydrolysis temperature

XRD patterns of dried and calcined TiO_2 pillared mica samples synthesized using $\text{Ti}(\text{O-}i\text{Pr})_4$ at various hydrolysis temperatures are shown in Figure 6 and Figure 7, respectively. In Figure 6, sharp peaks assignable to (001), (002) and (003) reflections of layered structure were observed at $2\theta=2-8^\circ$ for the samples prepared at $20-50^\circ\text{C}$. In contrast, only broad peaks were found for the samples prepared using the Ti sols hydrolyzed at 60°C and 75°C . It is reasonable to expect that the rate of hydrolysis of titanium alkoxide is faster at higher temperatures, which results in a broad size distribution of titanium ion species. In that case, the titanium ion species tends to be intercalated irregularly into mica layers. After calcined at 500°C (Figure 7), two peaks due to (001) and (002) reflections were observed at $2\theta=2-7^\circ$ for the samples prepared at $20-60^\circ\text{C}$. However, intensity of (001) peaks for these samples decreased with an increase in the hydrolysis temperature. In addition, (001) peaks were shifted toward lower diffraction angles for the samples prepared at higher hydrolysis temperatures. Basal spacing increased from 2.39 nm (30°C) to 3.56 nm (60°C) (Table 1). Therefore, it is suggested that the size of TiO_2 pillars was influenced by the hydrolysis temperature, and that larger titanium ion species, the precursor of TiO_2 particles, were obtained at higher temperatures up to 60°C . However, the sample hydrolyzed at 75°C exhibited no distinct diffraction peaks of pillared structures, while a peak assigned to anatase was found at $2\theta=25.2^\circ$.

Ti/Si atomic ratios (Table 1) of calcined TiO_2 pillared mica samples were larger at higher hydrolysis temperatures, meaning a large amount of TiO_2 pillar (and/or titania anatase) was incorporated into mica layers at higher hydrolysis temperatures. From XRD results, as mentioned before, large particles of titanium ion species were intercalated in mica at higher hydrolysis

Figure 5 XRD patterns of TiO_2 pillared mica prepared with different $\text{CH}_3\text{COOH}/\text{Ti}$ ratio ($\text{Ti}(\text{O-}i\text{Pr})_4$, hydrolysis temperature: 50°C). $\text{CH}_3\text{COOH}/\text{Ti}$ ratio is a: 10, b: 25, c: 50, d: 75.

Figure 6 XRD patterns of the precursors of TiO₂ pillared mica with different hydrolysis temperature of Ti(O-*i*Pr)₄ (CH₃COOH/Ti=50). Hydrolyzed at a: 20°C, b: 30°C, c: 40°C, d: 50°C, e: 60°C, f: 75°C.

Figure 7 XRD patterns of TiO₂ pillared mica calcined at 500°C with different hydrolysis temperature of Ti(O-*i*Pr)₄ (CH₃COOH/Ti=50). Hydrolyzed at a: 20°C, b: 30°C, c: 40°C, d: 50°C, e: 60°C, f: 75°C.

temperatures. Thus, it is reasonable to consider that titanium ion species with large particle size as well as lower electric charge were generated when titanium alkoxides were hydrolyzed at higher temperatures. High Ti/Si atomic ratio observed at 75°C was responsible for anatase which generated at external surface of mica.

Thus, to prepare the well-ordered layer structure with large TiO₂ pillars, adequate combination of temperature, time and titanium alkoxide source is important.

The micropore size distribution of TiO₂ pillared mica prepared with Ti(O-Et)₄ is shown in Figure 8. All samples show a unimodal distribution. The center of micropore size distribution shifted from 0.7 nm to 1.0 nm with an increase in the hydrolysis temperature. However, other samples prepared with Ti(O-*i*Pr)₄ or Ti(O-*n*Bu)₄ exhibit almost no shift in the micropore size distribution. As mentioned above, the samples prepared with Ti(O-Et)₄ gave most stable pillared structure, which indicates homogeneous distribution of TiO₂ pillars in interlayer of mica. Therefore, it is likely that the pore size distribution of the TiO₂ pillared mica is controlled by preparation conditions of Ti ion species, *i.e.* hydrolysis temperature and CH₃COOH/Ti ratio, when Ti(O-Et)₄ is used as the titanium ion precursor.

4 CONCLUSION

Effects of preparation conditions of Ti ion species such as CH₃COOH/Ti ratio and hydrolysis temperature on the structural properties of TiO₂ pillared mica were studied. Thermally stable and well-ordered structure was formed by using Ti(O-Et)₄ as titanium ion source. It may be possible to control the pore size distribution of pillared mica using preparation method proposed in this study. The degree of condensation of Ti ion species during hydrolysis of titanium alkoxide was influenced by CH₃COOH/Ti ratio and hydrolysis temperature. Large Ti ion species were obtained at lower CH₃COOH/Ti ratio and higher hydrolysis temperature. Adequate combinations of these preparation parameters are required for the synthesis of TiO₂ pillared mica with large pillars and well-ordered layer structure.

Figure 8 Micropore size distribution of TiO₂ pillared mica with different hydrolysis temperature of Ti(O-Et)₄ (CH₃COOH/Ti=50). Hydrolyzed at a: 20°C, b: 50°C, c: 60°C.

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