



Preparation and properties of TiO₂/montmorillonite composites

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ABSTRACT

TiO₂/montmorillonite composites were prepared by reaction of montmorillonite with a TiO₂ sol formed by hydrolyzing titanium iso-propoxide, at 50–80 °C. The composites showed expanding and broadening of the basal reflections of montmorillonite indicating a partial intercalation of the smaller colloidal TiO₂ particles and increased disorder. The reaction temperature affected largely the amount of TiO₂ hydrolyzed and the resulting pore sizes. Both properties increased with increasing reaction temperature; the TiO₂ content from 24.2 to 46.6 mass% and the average pore size from 2 to 20 nm. The colloidal TiO₂ particles consisted of anatase up to 1000 °C without transforming into rutile. The growth of the TiO₂ particles was suppressed by the montmorillonite particles. Adsorption of methylene blue (MB) was higher in the composite prepared at 80 °C than in that at 50 °C because of the larger pore size. Photocatalytic decomposition of 1,4-dioxane by the composites was higher than for pure anatase due to the synergy effect of adsorption for 1,4-dioxane and photodecomposed intermediates by montmorillonite and its photodecomposition by TiO₂.

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1. Introduction

Montmorillonite is widely used as the host materials for synthesizing various kinds of intercalation compounds and composites. Yamanaka et al. (1992) intercalated positively charged colloidal TiO₂/SiO₂ core-shell particles into montmorillonite and prepared mesoporous materials with 2–3 nm pore size. Montmorillonites have higher chemical durability in acid solution than several other clay minerals (Okada et al., 2006; Bergaya et al., 2006). Thus, intercalation of other various colloidal particles such as TiO₂, ZrO₂, Fe₂O₃, etc may be performed in an acid solution without detrimental collapsing of the host layered structure. Although pillared clays are interesting porous materials because of the unique slit shaped pores and high thermal stability (Yamaguchi et al., 2003), heat treatment tends to deteriorate various attractive chemical functions of the intercalated guest molecules.

Among various colloidal guest particles, TiO₂ is attractive owing to its photocatalytic properties. TiO₂ is a semiconductor with a band gap energy of about 3.0 eV. Although the position of conduction band of TiO₂ is only slightly lower than lower limit of water reducing to form electron, the position of valence band is much higher than upper limit of water oxidizing to form positive hole. Thus, TiO₂ shows very strong oxidizing ability under irradiating UV at ≤380 nm, being able to photodecompose most organic compounds (Mills and Hunt, 1997; Fujishima et al., 2000). By intercalating colloidal TiO₂ particles into montmorillonite, synergy effects of adsorption of organic molecules in

the interlayer spaces of montmorillonite and its enhanced photocatalytic decomposition by colloidal TiO₂ particles are suggested by the high surface area of TiO₂ and high possibility of their contacting with the adsorbates due to the restricted spaces of interlayers. Dispersing of colloidal TiO₂ particles in the interlayer space or on the external surfaces of montmorillonite may stabilize the anatase phase even at higher temperatures (Okada et al., 2001).

In this study, TiO₂/montmorillonite composites were prepared by reaction of montmorillonite with colloidal TiO₂ particles formed by hydrolysis of Ti-alkoxide. Thermal stability, adsorption of methylene blue (MB) and photocatalytic decomposition of 1,4-dioxane were investigated.

2. Experimental

2.1. Samples

Sodium-montmorillonite from Aderazawa, Yamagata, Japan (Kunipia-F, Kunimine Co.) and titanium tetra iso-propoxide (TTIP, Ti(OⁱC₃H₇)₄), Wako Pure Chemicals were used as the starting materials. The chemical composition of montmorillonite determined by X-ray fluorescence (RIX 2000, Rigaku) is listed in Table 1 and the cation exchange capacity (CEC_{Clay}) was 1.15 meq/g.

The montmorillonite was dispersed in 100 ml of distilled water (1 mass%) and stored during slowly stirring. The TiO₂ sol was prepared by adding TTIP dropwise 1 N HCl solution with reaching up to the molar ratio Ti/H⁺ = 4 and stirring for 3 h at room temperature. The TiO₂ sol was added drop by drop to the montmorillonite dispersion adjusted at various temperatures from 20° to 90 °C with vigorous stirring up to the ratio of Ti/CEC_{Clay} = 40 and was stirred for 3 h. The

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Table 1
Chemical compositions (mass%) of the samples.

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	CaO	TiO ₂	Cl
Montmorillonite	64.4	25.4	2.3	3.8	3.5	0.7	–	–
Composite 50 °C	51.1	19.5	1.7	2.9	–	–	24.2	0.1
Composite 80 °C	36.0	13.8	1.0	2.0	–	–	46.6	0.1

pH after the reaction was about 1.1 and did not change largely. The samples were centrifuged and washed several times until Cl[−] was absent (AgNO₃). The solids separated by centrifugation were dried at 60 °C overnight. In order to check the influence of acid solution for the montmorillonite structure, montmorillonite was treated similarly in 1 N HCl solution at 70 °C without adding TTIP.

2.2. Characterization

The crystalline phases in the samples were identified by powder XRD (XRD-6100, Shimadzu) with monochromated Cu K α radiation. The crystallite sizes of the anatase were calculated by Scherrer's equation for the (101) reflection at about $2\theta = 25^\circ$. The morphology of the composites was observed in a TEM (H-9000, Hitachi) at an accelerated voltage of 300 kV.

The porous properties were investigated by determining the N₂ adsorption–desorption isotherms at 77 K (Autosorb-1, Quantachrome). The sample was preheated at 180 °C for >3 h under vacuum before the measurement. The S_{BET} values were calculated by the Brunauer–Emmet–Teller (BET) method (Brunauer et al., 1938) from the linear part of BET plot according to IUPAC recommendations (Sing et al., 1985) using the adsorption isotherm (relative pressure (P/P_0) = 0.08–0.30). The pore size distributions were calculated from the desorption isotherms by the Barrett–Joyner–Halenda (BJH) method (Barrett et al., 1951) and the total pore volume was obtained from the maximum adsorption at P/P_0 of 0.999.

2.3. Thermal stability, MB adsorption

The thermal stability of the composite synthesized at 75 °C (composite 75 °C) was examined by heating at various temperatures for 1 h.

Adsorption of methylene blue (MB) by the composites was tested by the batch method. 20 mg of the powdered sample was irradiated

Table 2
Various data of the composite samples.

Sample	Temperature [°C]	S_{BET} [m ² /g]	Pore volume [ml/g]	Pore size [nm]	D_{an} (101) [nm]
Composite 20 °C	20	152	0.18	2	3.7
Composite 50 °C	50	238	0.27	4	4.6
Composite 60 °C	60	240	0.31	6	5.1
Composite 75 °C	75	251	0.3	5	5.4
Composite 80 °C	80	207	0.4	20	6.5
Composite 90 °C	90	213	0.32	6.6	4.9

with UV at an intensity of 1.0 mW/cm² for 20 h to remove organic surface contaminants. The sample was then dispersed in 100 ml of 50 μM MB solution, dispersed ultrasonically for 5 min. Equilibrium MB concentration in the separated solution after a fixed reaction time was determined spectrometrically at 664 nm (a Hiram Rika Model 6B absorptiometer). All the experiments were performed in the dark.

The photocatalytic activity of the samples were tested by the decomposition of 1,4-dioxane (C₄H₈O₂) under UV irradiation. 20 mg of the powdered sample were pre-treated similarly as above, then mixed with 100 ml of 50 ppm (0.568 mM) 1,4-dioxane solution in the dark, dispersed ultrasonically for 5 min and stirred for 2 h. This solution was UV-irradiated using a Hg–Xe lamp at an intensity of 125 mW/cm² at 365 nm. The concentration of 1,4-dioxane, intermediate ethylene glycol diformate (EGDF) and ethylene glycol monoformate (EGMF) in the separated solution after a fixed reaction time were determined by gas chromatography (GC-14A, Shimadzu). The detailed measurement conditions were reported elsewhere (Nakajima et al., 2004).

3. Results and discussion

3.1. Characterization of composites

The XRD pattern of montmorillonite (Fig. 1) showed a very sharp and strong (001) reflection due to the preferred orientation by the platy shaped particle. A small reflection of quartz was observed at about $2\theta = 27^\circ$. The XRD pattern of the acid treated montmorillonite showed broadening of basal reflections, indicating smaller numbers of layer stackings after acid attack. The composites showed basal spacings increased by 0.2–0.3 nm and pronounced broadening of the (001) reflections. The basal spacing increase was smaller than that reported by Yamanaka et al. (1992). This implies that the intercalation

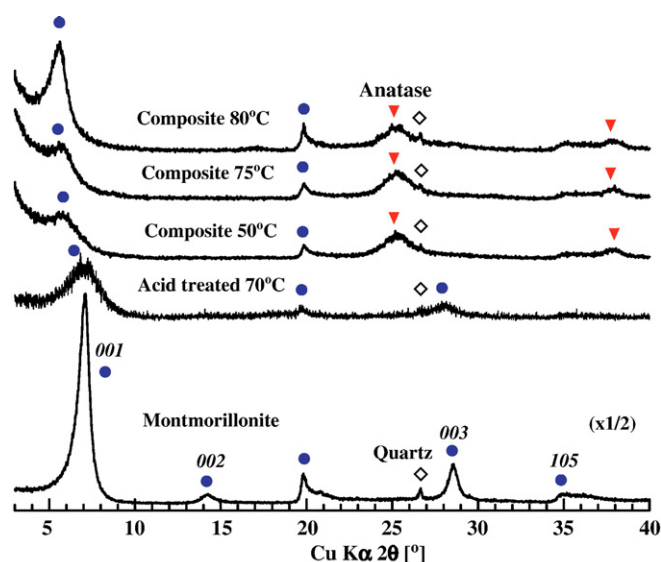


Fig. 1. XRD patterns of the montmorillonite and composites prepared at 50 °C etc.

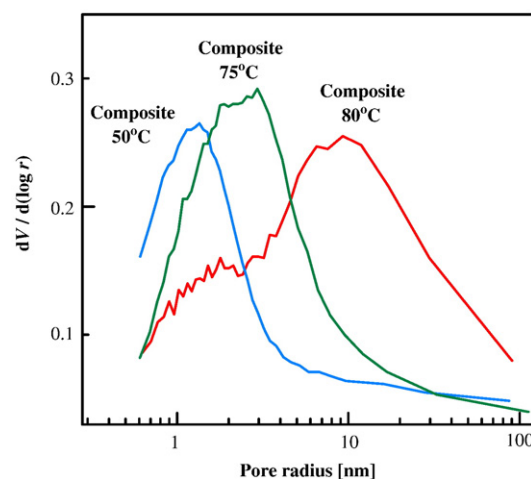


Fig. 2. Pore size distributions of the composites prepared at 50 °C etc.

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