

Preparation and photocatalytic activity of titania particulate film with mesostructured silica as binder

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Abstract

TiO₂ (titania) particulate films with mesostructured silica (SiO₂) as binder were prepared by drying glass substrate coated with an aqueous mixture of titania particles, tetramethoxysilane (TMOS) and cetyltrimethylammonium bromide (CTAB) at appropriate temperature. X-ray diffraction (XRD) and IR absorption measurements on the obtained films revealed the formation of titania particles/silica composite thin film. XRD patterns at low angle region on these films indicated silica binder has well-ordered lamellar type mesostructure. These films show characteristic properties on both high absorption ability and photocatalytic activity to oxidative degradation of gaseous 2-propanol.

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1. Introduction

Thin films of fine TiO₂ (titania) particles on a substrate (particulate thin films) have recently attracted much attention as promising materials for photocatalyst bearing both a high photocatalytic activity derived from titania particles and easiness of handling derived from titania thin films prepared by the sol–gel method. However, these titania particulate thin films have a disadvantage that their mechanical strength is not sufficient. Recently, we succeeded in preparing titania particles/silica composite films by sintering the titania particles deposited on a glass substrate with alkoxysilane as binder [1]. These titania particulate films with silica binder showed both high mechanical strength and photocatalytic activity against oxidative degradation of gaseous 2-propanol.

In the meantime, mesoporous materials [2–6] with surfactant molecular assemblies as templates have highly ordered pore

structure with high specific surface area and, therefore have gathered increasing attention in applications such as adsorbents. Although there have been many reports about preparation of mesoporous metal oxide particles [7–11], the solvent evaporation method [12,13] has recently been developed to prepare mesoporous metal oxide thin films [14]. If mesostructure can be provided to silica used as a binder of titania particulate films, photocatalytic activity can be expected due to improved absorption ability (increased specific surface area). The present work aims to prepare titania particles/mesostructured silica composite thin films with high specific surface area by solvent evaporation method.

2. Experimental

2.1. Materials

P-25 (70% anatase, 30% rutile, Nippon-Aerosil Co. Ltd., primary particle size 30 nm) was used as supplied as a titania particle photocatalyst. Cetyltrimethylammonium bromide (CTAB) (Aldrich) was used as a surfactant to form lamellar liquid crystal template. Tetramethoxysilane (Si(OCH₃)₄, TMOS) (Shinetsu Silicon Chemicals) was used as purchased as a precursor of silica

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working as binder of titania particles. The substrate used was a glass substrate (Micro Slide Glass, Matsunami Glass Ind., Ltd.) and the water for the reaction with TMOS was distilled water for injection (JP, pH 5.7, Ohtsuka Pharmaceutical Co. Ltd.). Titania particles/silica composite film to investigate photocatalytic activity was prepared on a glass substrate (18 mm × 18 mm; Matsunami Cover Glass, Matsunami Glass Ind., Ltd.). Adjustment of pH of water was made using reagent grade hydrochloric acid (Wako Pure Chemicals Ind.).

2.2. Methods

2.2.1. Preparation of titania particles/mesoporous silica composite film

About 1 g TMOS and hydrochloric acid aqueous solution at pH 3.0 were mixed (the molar ratio of TMOS: H₂O was 1: 2) and stirred for 2 h at 0 °C and TMOS was partially hydrolyzed. To this solution was added CTAB aqueous solution (the molar ratio of TMOS:CTAB was 2.5:1) and titania particles. This mixture was stirred for 30 min at room temperature. Titania particles/mesoporous silica composite films were obtained by spincoating this suspension on a glass substrate at various condition (3000–6000 rpm) and drying in air at various temperature (100–200 °C).

2.2.2. Analysis of composite film

The crystallinity of the thin film prepared and the formation of mesopore were evaluated by X-ray diffraction (XRD) measurement (X'pert-MPD, Philips; CuK α radiation) and transmission electron microscopy (TEM) observation (JEL-1200EX, JEOL). Identification of the film was also performed spectroscopically using a FT/IR spectrophotometer (FT/IR 410, JAS) with KBr disk method. The sample for FT/IR measurement was prepared by grinding the thin film scraped from the substrate in a mortar and tableting the ground solid with KBr.

2.2.3. Measurement of photocatalytic activity

Evaluation of the photocatalytic activity of the composite film was performed according to following method [1]. Composite film was located in 300 ml quartz cell. After injecting 2-propanol gas to the cell, the sample was kept in the dark to attain adsorption equilibrium. Then, time-course measurement of concentration of 2-propanol and acetone was carried out under UV-light irradiation (intensity: 2.3 mW cm⁻²) with a gas chromatograph (GC-8A, Shimadzu Co). The column, filler and detector used were a 3-m-long glass column, Sorbitol (GL Science) and a hydrogen flame ionization detector, respectively. The light-irradiating apparatus and light source used were a UV-fiber spot irradiator (San-Ei Supercure 203 S, San-Ei Electric) and a 200 W mercury–xenon lamp.

3. Results and discussion

3.1. Qualitative analysis of the particulate film

Fig. 1 shows the XRD pattern of the film which was prepared by spincoating TiO₂ particles (0.5 wt.%) suspended in a

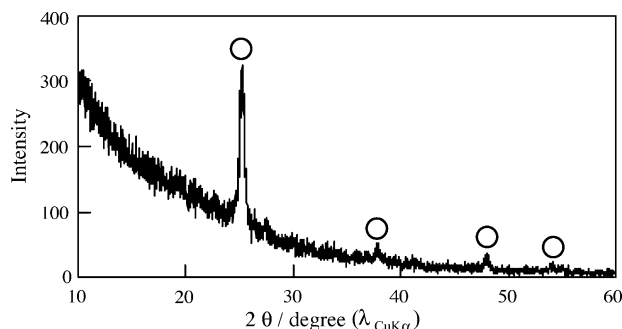


Fig. 1. X-ray diffraction pattern of the film prepared by spincoating an aqueous mixture of 0.5 wt.% titania particles, 300 mM CTAB and 750 mM TMOS by coating with 3000 rpm and drying at 100 °C for 2 h. A diffraction peak at $2\theta = 25^\circ$ (○) corresponds to anatase crystalline structure.

CTAB/TMOS aqueous solution at 3000 rpm and dried for 2 h at 160 °C. The peaks assigned to anatase-type titania nearby 25, 38, 48 and 55° were observed. This verified the loading of titania particles on the glass substrate. The peaks assigned to silica were not appreciably observed. Therefore, FT/IR measurement was carried out to confirm the silica formation. Fig. 2 shows the result of FT/IR measurement. Here, signal derived from glass substrate was never detected in this measurement because the measurement was performed with the solid scraped from the substrate. Peaks due to the Si–O stretching vibration of silica nearby 1100 cm⁻¹ [15,16] and the C–H stretching vibration of CTAB nearby 2900 cm⁻¹ pointed by arrows in Fig. 2 [15,17] were observed, respectively, indicating silica and CTAB are loaded on the glass substrate. These findings demonstrate that the thin film obtained was a composed of titania particles, silica and CTAB.

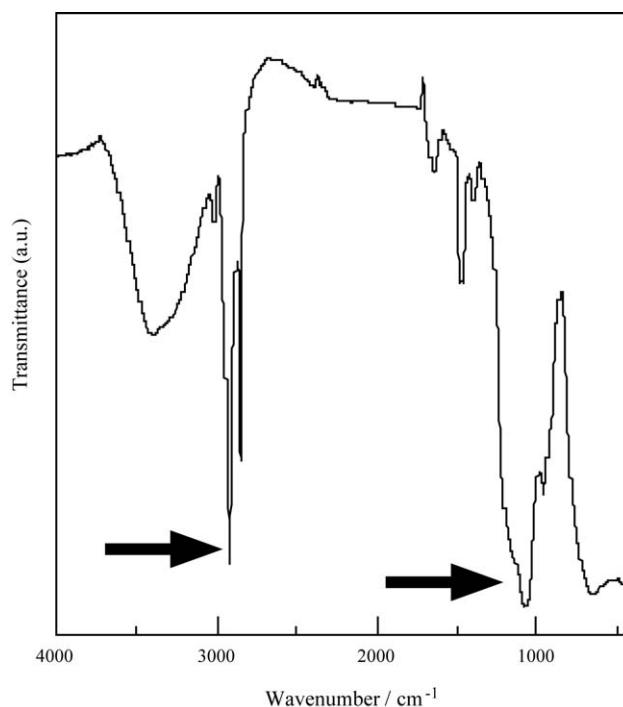


Fig. 2. Infrared spectrum of the composite film. The film preparation condition is same as Fig. 1.

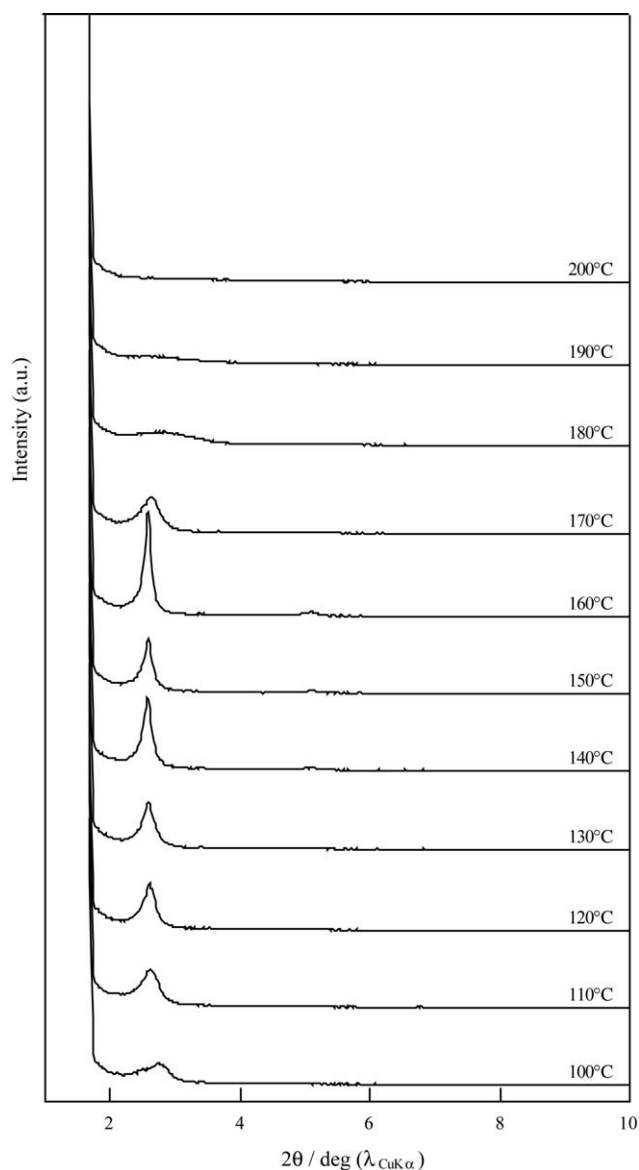


Fig. 3. X-ray diffraction patterns of the composite films prepared by drying treatment at various temperature. The amount of TiO_2 : 0.5 wt.%. The spincoating rate: 3000 rpm.

3.2. Influence of drying temperature on the thin film formation

The influence of drying treatment (drying temperature) after spincoating, on the mesostructure formation was studied in terms of X-ray diffraction measurements. Thin films were prepared with the 0.5 wt.% titania amount and spincoating condition at 3000 rpm. Drying temperature was changed from 100 to 200 °C by 10 °C. Fig. 3 shows XRD patterns of obtained films at small angle region. The XRD patterns had sharp diffraction peaks (nearby $2\theta = 2.5, 5.0$) assigned to lamellar structure [18,19]. The distance between pores estimated by Bragg's equation was about 3.5 nm. These results indicate that silica binder has lamellar type mesostructure. The order of mesostructure becomes higher with increasing drying temperature up to 160 °C, however, it gradually becomes lower above 170 °C. In the film formation process,

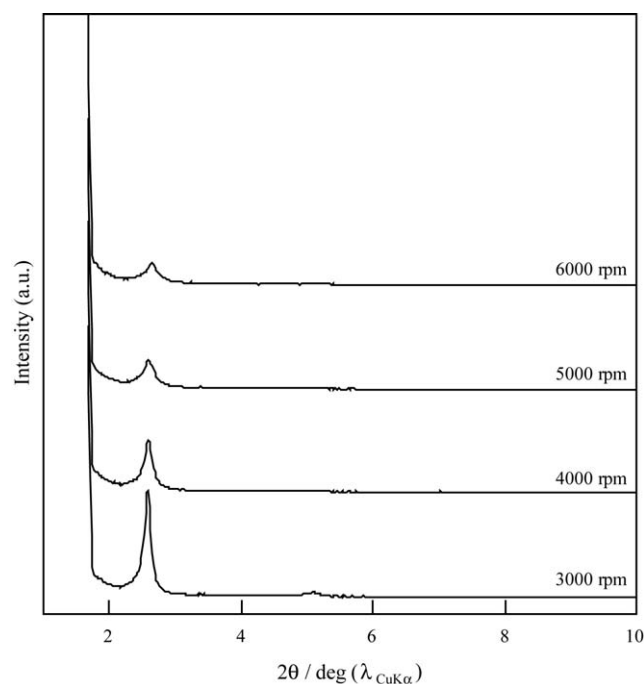


Fig. 4. X-ray diffraction patterns of the composite film prepared by spincoating with various spinning conditions. The amount of TiO_2 : 0.5 wt.%. Drying temperature: 160 °C.

surfactants form lamellar liquid crystalline structure by condensation during the drying treatment process. Mesostructured silica then formed by the sol-gel reaction of TMOS with this lamellar structure as a reaction template. Consequently, drying temperature has a significant influence on the formation and the order of mesostructure.

3.3. Influence of the spincoating condition on the thin film formation

Fig. 4 shows the results of XRD measurements. Here, the titania particles/silica composite films were prepared with 0.5 wt.% titania particles. Also, drying temperature was fixed at 160 °C because the mesostructure with the highest uniformity was obtained at this temperature as shown in Fig. 3. Films prepared with lower rate of spincoating have mesostructure with better uniformity. These results reveal that the rate of spincoating, in other words, the amount of precursor suspension on the glass substrate give the influence on the mesostructure formation.

Hence, drying temperature and the quantity of precursor suspension on the substrate affect the formation process of mesostructure. This suggests that the solvent evaporation rate is an important factor to give the mesostructure with high regularity. Fig. 5 shows the schematic illustration of process of mesostructured silica formation with the present method. Surfactants (CTAB) form micelles in an aqueous solution before drying process. Negatively charged TMOS molecules adsorb on positively charged micelle and then form silica oligomer. The formation of liquid crystalline structure (lamellar structure) by CTAB molecules is essential during sol-gel reaction of TMOS to form silica binder having mesostructure. In case

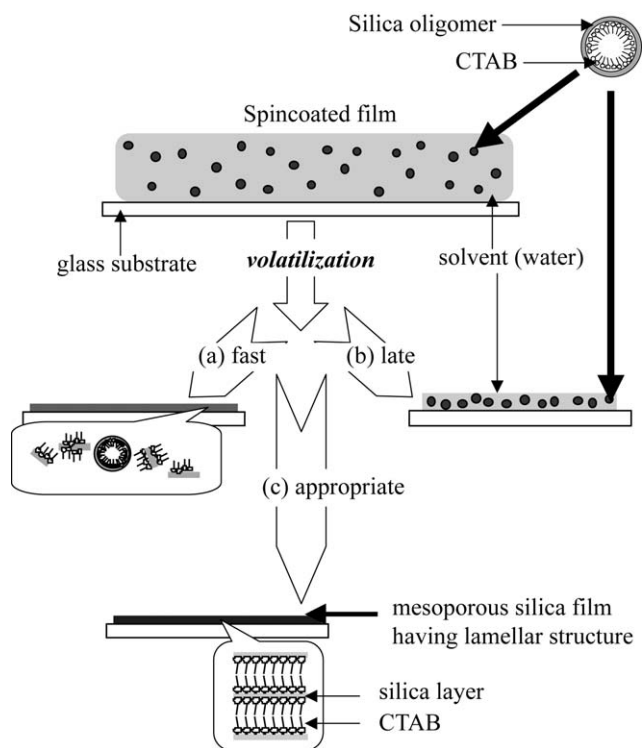


Fig. 5. The formation process of titania particles/mesoporous silica composite film. (a) In case the volatilization rate of solvent is too fast; (b) too late; (c) in case the rate of solvent volatilization and silica polycondensation are balanced.

the volatilization rate of solvent (water) is too fast, solvent is vaporized before CTAB form lamellar structure and obtained silica does not have well-ordered mesostructure. Meanwhile, when the solvent evaporation rate is too late, formed silica does not have well-ordered mesostructure since sol-gel reaction proceeds before CTAB forms lamellar structure by condensation. Only when the rates between volatilization of solvent and polycondensation reaction of silica precursor are comparable, mesostructured silica binder having lamellar structure is obtained.

3.4. Influence of titania particle amount on the mesostructure formation

The influence of loading amount of titania particles on the mesostructure formation was studied. Titania amount in the suspension varied from 0.5 to 8.0 wt.%. The drying temperature and the spincoating condition also varied from 100 to 200 °C by 10 °C step and from 3000 to 6000 rpm by 1000 rpm step, respectively. Table 1 summarizes the effect of the preparation condition on the mesostructure formation. Highly ordered mesostructure was obtained when the suspensions containing from 1.0 to 5.0 wt.% titania particles were loaded on the substrate and dried at temperature from 140 to 160 °C for 2 h. When the amount of titania particles is above 6.0 wt.%, thin films did not have well-ordered mesostructure. If we use a large amount of titania particles, CTAB molecules mainly adsorbed on the surface of the particles in the process of solvent volatilization and they are not able to work as reaction template. The optimal

Table 1
The effect of the preparation condition on the mesopore formation

(a)	The amount of titania / wt%					
	0.5	1.0	2.0	5.0	6.0	8.0
100	○	○	○	○	○	△
110	○	○	○	○	○	△
120	○	○	○	○	○	△
130	○	○	○	○	○	△
140	⊙	⊙	⊙	○	○	△
150	⊙	⊙	⊙	○	○	△
160	⊙	⊙	⊙	○	○	×
170	○	⊙	△	○	△	×
180	△	△	△	×	×	×
190	△	△	△	×	×	×
200	×	×	×	×	×	×

(b)	The amount of titania / wt%					
	0.5	1.0	2.0	5.0	6.0	8.0
100	○	○	○	○	○	○
110	○	○	○	○	○	○
120	○	○	○	○	○	○
130	○	○	○	○	○	○
140	○	⊙	○	⊙	○	○
150	○	⊙	⊙	⊙	○	○
160	⊙	⊙	⊙	○	○	×
170	○	⊙	○	○	○	×
180	△	△	×	×	×	×
190	△	△	×	×	×	×
200	×	×	×	×	×	×

(c)	The amount of titania / wt%					
	0.5	1.0	2.0	5.0	6.0	8.0
100	○	○	○	○	○	×
110	○	○	○	○	○	×
120	○	○	○	○	○	○
130	○	○	○	○	○	○
140	○	○	○	○	○	○
150	○	⊙	⊙	○	○	○
160	○	⊙	⊙	⊙	○	○
170	○	○	○	⊙	○	○
180	○	○	○	△	×	×
190	△	○	△	×	×	×
200	×	×	×	×	×	×

(d)	The amount of titania / wt%					
	0.5	1.0	2.0	5.0	6.0	8.0
100	○	○	○	○	○	×
110	○	○	○	○	○	×
120	○	○	○	○	○	△
130	○	○	○	○	○	△
140	○	⊙	○	○	○	△
150	○	⊙	○	○	○	△
160	○	⊙	⊙	⊙	○	△
170	○	⊙	⊙	⊙	○	△
180	○	○	○	△	△	×
190	○	△	×	△	△	×
200	×	×	×	×	×	×

(a) spincoating at 3000 rpm; (b) 4000 rpm; (c) 5000 rpm; (d) 6000 rpm. (⊙): XRD patterns have the secondary diffraction peak ○: only primary peak △: broad peak nearby $2\theta = 2.5^\circ$ ×: no peak assigned to mesopore structure.



Fig. 6. A transmission electron micrograph of the titania/mesoporous silica composite film prepared by optimal condition. The amount of TiO_2 : 5.0 wt.%. Spincoating rate: 5000 rpm. Drying temperature: 160°C .

amount of titania loading was around 5.0 wt.%. From the results mentioned above, the optimal condition for the film preparation was determined as follows. The concentration of titania particles, the spincoating condition and drying temperature were 5.0 wt.%, 5000 rpm and 160°C , respectively.

Fig. 6 shows the TEM image of the titania particle/mesoporous silica composite film prepared by the optimal condition. The formation of a well-ordered mesostructure was confirmed. The distance of pores estimated from TEM image was in good agreement with the calculated value from XRD results using Bragg's equation. These results confirmed that the titania particulate film with mesoporous sil-

ica as binder is prepared using the present solvent evaporation method.

3.5. The photocatalytic activity of titania particles/mesoporous silica composite film

Finally, the investigation of photocatalytic activity of the titania particles/mesoporous silica composite film was carried out by using the oxidative degradation of 2-propanol to form acetone. As a pretreatment, UV-light irradiation to the composite film without 2-propanol was carried out for photodegradation of CTAB adsorbed on the titania surface. Pretreatment was carried out for 12 h at 10 mW cm^{-2} in the absence of reactants. Fig. 7 shows the photocatalytic activity of (a) titania particles/non-porous silica composite film and (b) titania particles/mesoporous silica composite film. Although the concentration of 2-propanol did not decrease in the dark for the particulate film with non-porous silica binder (a), a decrease in 2-propanol concentration was observed for the titania particles/mesoporous silica composite film (b). This result indicated that the introduction of mesostructure to silica binder lead high adsorption ability toward 2-propanol due to an increase of their specific surface area. UV light was then irradiated after the adsorption of 2-propanol attained an equilibrium state. While photo-irradiated titania particulate film with non-porous silica binder oxidized 2-propanol and generated acetone efficiently, a decrease of 2-propanol concentration and an increase of acetone concentration were not observed for the titania particulate film with mesoporous silica binder, probably due to the coverage of titania surface by CTAB used as reaction template for silica synthesis. Photo-oxidation of surfactant on titania surface was then attempted through pretreatment with UV-light irradiation for 12 h at 10 mW/cm^2 in the absence of reactant. Evaluation of the photocatalytic activity was then performed on the pretreated film. This pre-irradiation of UV light was found to enhance the rate of photodecomposition of 2-propanol and photogeneration of acetone, though the photocatalytic activity was lower

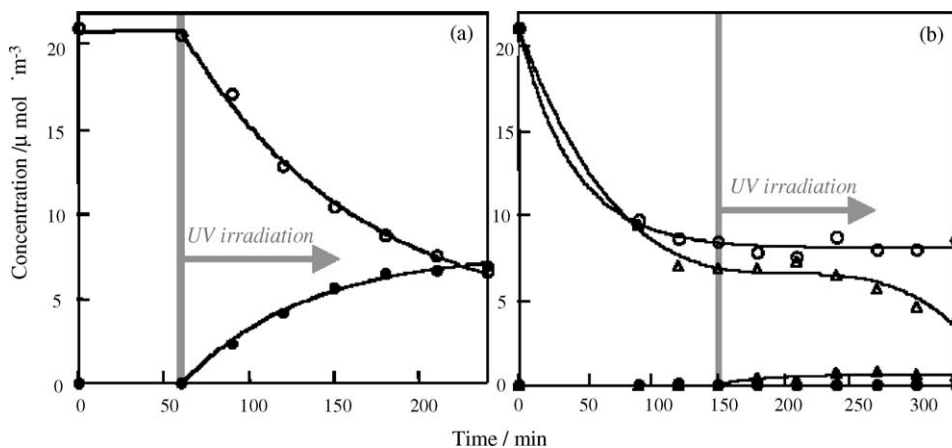


Fig. 7. Changes with time in the concentrations of 2-propanol and acetone under UV-light irradiation upon titania particulate film with non-porous silica binder (a) and titania particles/mesoporous silica composite film (b). The open symbols (\circ, Δ) and closed symbols (\bullet, \blacktriangle) represent the concentration of 2-propanol and acetone, respectively. The circles (\circ, \bullet) and triangles (Δ, \blacktriangle) in (b) represent the concentration changes with time upon titania particles/mesoporous silica composite film without and with the pretreatment with UV-light irradiation for 12 h at 10 mW cm^{-2} .

than that of the titania particulate film with non-porous silica binder. Titania particles/non-porous silica binder composite film was pretreated with concentrated NaOH aqueous solution for removal of silica coating the titania surface [1]. This treatment enables the titania particulate film with mesostructured silica binder to have higher photocatalytic activity.

The kinetics of gaseous degradation of 2-propanol by photocatalytic reaction can be generally fitted to the Langmuir–Hinshelwood (LH) equation. However, that for the thin films obtained in this study and in our previous report [1] could not be fitted to this equation. Photocatalytic reaction of titania normally proceed after adsorption of reactions agent on its surface. However, our film has separated adsorption site (mesostructured silica) and reaction site (titania particles) and 2-propanol molecules adsorbed on the silica surface have to migrate to the titania surface to undergo the oxidative degradation. In addition, the effective surface area being able to participate in the photo-oxidation of 2-propanol is considered to increase after UV irradiation due to photolysis of the surfactant contained in the mesostructured silica binder. These are the reason why the 2-propanol degradation on our titania particulate films with mesostructured silica binder do not obey LH equation.

4. Summary

- Titania particles/mesostructured silica composite films were able to be prepared by drying glass substrate coated with a mixed solution of titania particles, TMOS and CTAB at appropriate temperature.
- XRD measurement and FT/IR measurement indicated that the obtained films were composed of titania particles, CTAB and silica.
- The results obtained by low angle XRD measurements and TEM observation showed that silica binder has mesostructure with lamellar structure.
- Titania particles/mesostructured silica composite film had both high adsorption ability due to large specific surface area and photocatalytic activity derived from anatase titania particles.

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