Preparation of Mesoporous Titania Particles with Photocatalytic Activity under Visible-light Irradiation

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(Received September 8, 2005; CL-051157)

Novel visible light-responsive photocatalytic mesoporous titania particles were prepared using the sol–gel reaction of titanium oxysulfate sulfuric acid hydrate $TiOSO_4{\cdot}xH_2SO_4{\cdot}xH_2O$ in aqueous solution in the presence of lyotropic cetyltrimethylammonium bromide (CTAB) liquid crystal as template. The absorption threshold of the calcined particles shifted toward the longer wavelength side and they showed a photocatalytic activity in the oxidation of gaseous 2-propanol under visible light (>440 nm) irradiation.

Photocatalytic reactions based on the strong oxidizing and reducing power of titania (TiO_2)[1] are utilized in diverse applications including removal of toxic organic compounds, wet-type solar cells, and phototherapy of diseases. This power of the metal oxide is generated when it is excited by irradiation of light with energy higher than its band gap. The excitation of the oxide needs irradiation of ultraviolet light of wavelengths shorter than 400 nm since the band gap is about 3.2 eV. In recent years, introducing transition-metal ions[2] into or doping with nitrogen[3] or sulfur[4–6] atoms of titania has been found to shift the absorption threshold toward the longer wavelength side, thereby enabling the oxide to develop its photocatalytic activity under irradiation of visible light.

Meanwhile, mesoporous metal oxides[7] prepared in the presence of aggregates of surfactant molecules as template have a high specific surface area and an orderly pore structure and hence they are expected to be usable as adsorbent, catalyst carrier, etc. In particular, the preparation of mesoporous titania using titanium alkoxide as precursor is reported.[8] If mesoporous titania can be made visible light-responsive, it will then find many applications because of its high specific surface area and porosity. The present work aims to prepare visible light-responsive mesoporous titania using titanium oxysulfate as precursor.

Titanium oxysulfate sulfuric acid hydrate ($TiOSO_4{\cdot}xH_2SO_4{\cdot}xH_2O$) with a sulfur atom and cetyltrimethylammonium bromide (CTAB) with a nitrogen atom were used as titania precursor and lyotropic liquid crystal-forming cationic surfactant, respectively. The reaction substrate for evaluating the photocatalytic activity of titania was 2-propanol because the alcohol changes selectively to acetone in its photocatalytic reaction on the titania surface.

Titania particles were prepared in the following way. To 25 mL of aqueous 60 mM CTAB solution was added 25 mL of aqueous 400 mM $TiOSO_4$ solution and the mixture was stirred for 24 h at room temperature. The mixture was then filtered and the precipitates obtained were washed with ion-exchanged water, followed by drying for 10 h at 393 K to give mesoporous titania/surfactant composite particles. Mesoporous titania particles were obtained after the composite particles were calcined in air for 6 h at 723 K to remove the surfactant.

X-ray diffraction measurement was used to confirm the formation of mesoporous titania. The specific surface area of titania particles was determined by the nitrogen adsorption method. Evaluation of the photocatalytic activity of titania was conducted as follows. Into a 300 mL quartz cell was placed 0.1 g of titania particles pretreated according to the previous report[3] and the cell was sealed. IPA (0.4 µL) was introduced into the cell, which was then allowed to stand for 2 h in the dark to attain an adsorption equilibrium. Afterward, the cell was irradiated with visible light (>440 nm) obtained by passing the light emitted from a mercury-xenon lamp through an ultraviolet light cutting filter and the reactant and product were analyzed by gas chromatography.

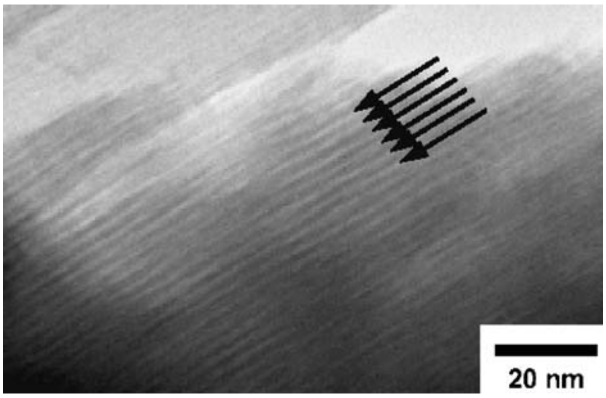

Figure 1. The TEM image of the mesoporous titania particles prepared using $TiOSO_4$ and CTAB as a titania precursor and template, respectively.

First, XRD measurement was performed on uncalcined titania/surfactant composite particles. The results indicated that mesoporous titania particles with orderly arranged pores in a hexagonal structure are obtained because diffraction peaks were observed at $2\theta = 2.1$, 3.6, and 4.2° in the low angle region. Figure 1 is a typical TEM image of the particles confirming that they have an orderly pore structure. The interpore distance calculated from the XRD data using the Bragg equation coincided with that estimated from the TEM data and gave a value of about 4.2 nm to the distance. On the other hand, no peak assigned to the crystal structure of titania was observed in the wide angle XRD pattern of uncalcined titania/surfactant composite particles.

Calcination (723 K, 6 h) was then performed on the composite particles to remove the surfactant as template. FT-IR measurements on the calcined particles confirmed complete removal of the surfactant. Although no diffraction peak was found in the low angle region of the XRD pattern for the calcined particles, several peaks arising from their anatase structure were observed

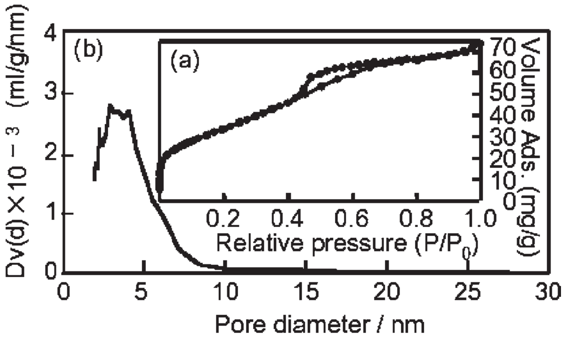

Figure 2. (a) The N_2 adsorption and desorption isotherms and (b) pore size distribution of the obtained titania particles after calcination at 723 K for 6 h.

in the wide angle region. These findings indicated a lowering in the order of pore structure with progressing titania crystallization. Nitrogen adsorption measurements for the particles revealed, however, that the adsorption and desorption isotherms exhibit a behavior characteristic of solids with mesopores (type IV, S-shaped isotherm) (Figure 2a) and show a hysteresis phenomenon that suggests the presence of cylindrical pores.[9] Estimation of specific surface area and pore size distribution showed that the particles have a large specific surface area of $125\,\mathrm{m^2/g}$ and pores with sizes around 4.5 nm (Figure 2b), a value identical with the interpore distance calculated using the Bragg equation for the uncalcined titania particles. Thus, all the findings mentioned so far demonstrate that calcined titania particles still keep their mesopore structure though their pore size and arrangement order are decreased.

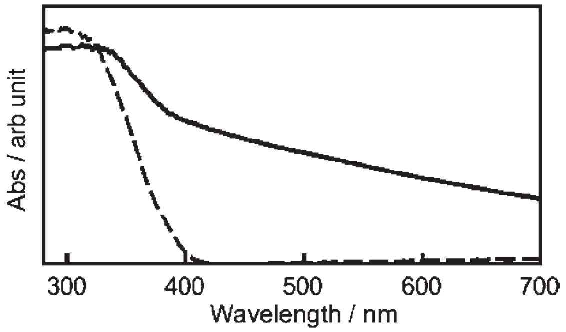

Figure 3. The reflectance UV–vis absorption spectra of mesoporous titania particles after calcination and commercial titania (P25). Solid line and broken line show mesoporous titania and commercial titania, respectively.

Figure 3 shows the UV–vis absorption spectra of calcined titania particles. The absorption threshold showed a red shift extending to the visible light region. The XPS spectrum of the particles exhibited two peaks at 169 and 161 eV, the former being due to the sulfur species (SO_2) adsorbed on the titania surface.[4,6] The rather broad latter peak is observed when oxygen atoms of the titania surface (110) are replaced by sulfur atoms and hence the above finding indicates the presence Ti–S bonds in the particles, thus verifying that the titania obtained in this work is doped with sulfur.[4,5] The reason for the observed shift of the absorption threshold is still under investigation because no coloring of titania particles was observed when they were calcined in the absence of surfactant or titanium alkoxide was used as titania precursor. Co-existing of nitrogen and sulfur atoms in the precursor solution may be essential for the development of photocatalytic activity under visible-light irradiation.

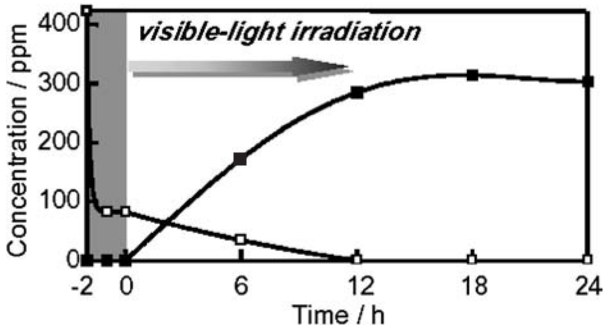

Figure 4. Changes with time in the concentrations of 2-propanol and acetone under visible-light irradiation upon mesoporous titania particles. The open square (□) and closed square (■) represent the concentration of 2-propanol and acetone, respectively.

The gas-phase oxidation of IPA was chosen to examine the photocatalytic activity of calcined titania particles under visible-light irradiation. Figure 4 shows the results of the examination. The initial decrease in IPA concentration observed even in the dark is brought about by the adsorption of the alcohol on the titania particle surface with a high specific surface area. Irradiation of visible light (>440 nm) after the attainment of an adsorption equilibrium caused the formation of acetone accompanying a decrease in IPA concentration. The photocatalytic activity of mesoporous titania under visible-light irradiation was 34 times higher than that of commercial titania (P25). Consequently, we have succeeded in preparing visible light-responsive mesoporous titania particles using the sol–gel reaction of $TiOSO_4$ as titania precursor in aqueous CTAB solution and calcining the reaction product in appropriate conditions.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

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Published on the web (Advance View) November 19, 2005; DOI 10.1246/cl.2005.1696