

# Synthesis and Catalytic Activity of Surfactant-Templated Nanoporous TiO<sub>2</sub>

Shinsuke NAGAMINE\*, Shinsuke TAKAHASHI\*\* and Eiji SASAOKA\*\*

(Received October 23, 2002)

Nanoporous TiO<sub>2</sub> were synthesized via hydrolysis of titanium tetraisopropoxide (TTIP) in HCl acidic conditions using sodium dodecylsulfate (SDS) as a templating agent. The order of the nanostructure of samples before calcination was improved with increasing the SDS/TTIP molar ratio. The calcined samples presented uniform mesopore structure with the average diameter of 4 - 5 nm and considerably large surface areas over 200 m<sup>2</sup>/g, although the periodicity of the nanostructure was exceedingly reduced by the removal of the template. The prepared TiO<sub>2</sub> exhibited exceedingly higher activities on the catalytic oxidation of benzene compared to the commercial TiO<sub>2</sub>, probably due to the difference of their pore structures.

**Key words:** *template, titania, lamellar nanostructure, nanopore structure, catalyst*

## 1 INTRODUCTION

On the design of a catalyst or a catalyst support, the control of its pore structure is one of the most important problems. Since the reaction is caused on the surface of catalyst, a large surface area accessible for reactant molecules is required. In this viewpoint, the presence of mesopores where molecules can smoothly diffuse is advantageous for catalytic reactions. Recently, nanoporous solids with controlled pore sizes and high surface areas have been synthesized using the surfactant micellar structures as structure-directors (Kresge, et al., 1992, Ogawa, 1996, Tanev and Pinnavaia, 1996).

In this study, the authors have attempted to prepare nanoporous TiO<sub>2</sub>, which is widely used as a photocatalyst or a catalyst support, with the help of surfactant as a template. The nanoporous TiO<sub>2</sub> were previously synthesized using the ligand-assisted hydrolysis of titanium alkoxide templated by alkylphosphate (Antonelli and Ying, 1995, Putnam, et al, 1997) or using nonionic alkylamine (Antonelli, 1999). Here we consider that anionic surfactants are suitable for

the template to give a nanostructure to TiO<sub>2</sub> because of its tendency to be positively charged in acidic conditions.

In this study, nanostructured TiO<sub>2</sub> templated by an anionic surfactant sodium dodecylsulfate (SDS) were synthesized via the hydrolysis of titanium tetraisopropoxide (TTIP). The dependence of nanostructure on the molar ratio of SDS to TTIP was investigated. The prepared TiO<sub>2</sub> were applied to the catalytic oxidation of benzene, the emission of which to atmosphere is restrained recently. The activities of the samples were compared with that of a commercial TiO<sub>2</sub> and their dependence on the pore structures were discussed.

## 2 EXPERIMENTAL SECTION

SDS, TTIP, and HCl aqueous solution were provided by Wako Chemical Co. Ltd., Japan. The surfactant-templated TiO<sub>2</sub> were prepared by the following procedure. An adjusted amount of SDS was fully dissolved into 20 ml of HCl aqueous solution (1.0 mol/l). 5.68 g of TTIP was added to the solution, resulting in the immediate formation of white precipitates. The molar composition of each component was TTIP: 1.0, SDS: 0 - 1.0, H<sub>2</sub>O: 55.6, and HCl: 1.0. The resultant white precipitates were immersed in 40 ml of ion-exchanged water and kept at 323 K for 1h to

---

\* Graduate School of Natural Science and technology, Okayama University.

\*\* Department of Environmental Chemistry and Materials, Faculty of Environmental Science and technology, Okayama University.

remove sodium ions. At this stage, the sample prepared at SDS/TTIP = 0 turned to a transparent gel, while the others are still white solids. The same treatment was repeated once again and then the solids were dried at 323 K for 1 - 2 days. The dried solids were calcined at 723 K in air for 3 h to remove the surfactant.

The nanostructures of the prepared TiO<sub>2</sub> were characterized using the powder X-ray diffraction (XRD, Shimadzu XRD-6100, Cu/K $\alpha$  radiation,  $\lambda = 0.154$  nm, operated at 30 kV and 30 mA). The pore structures of the calcined samples were characterized by the nitrogen adsorption measurements (Micromeritics Gemini 2375) at 77 K after outgassing the samples at 573 K for 2 h in nitrogen.

The catalytic oxidation of benzene was carried out using a packed-bed tubular reactor at reaction temperatures ranging from 448 to 623 K under the atmospheric pressure. The weight and particle size of packed catalysts were 0.50 g and 1 mm, respectively. The inlet gas composed of benzene (50 ppm) and air (balance) was fed into the reactor at 250 cm<sup>3</sup>-STP/min. The outlet gas was analyzed by a gas chromatograph (Shimadzu GC-9A) equipped with a hydrogen flame ionization detector (FID) after mixed with an adjusted amount of methane as a reference to give a standard peak on the chromatogram. The concentration of benzene in the outlet gas was determined by the ratio of the peak areas of benzene to methane.

### 3 RESULTS AND DISCUSSION

The nanostructures were characterized by XRD for samples both before and after calcination, and typical

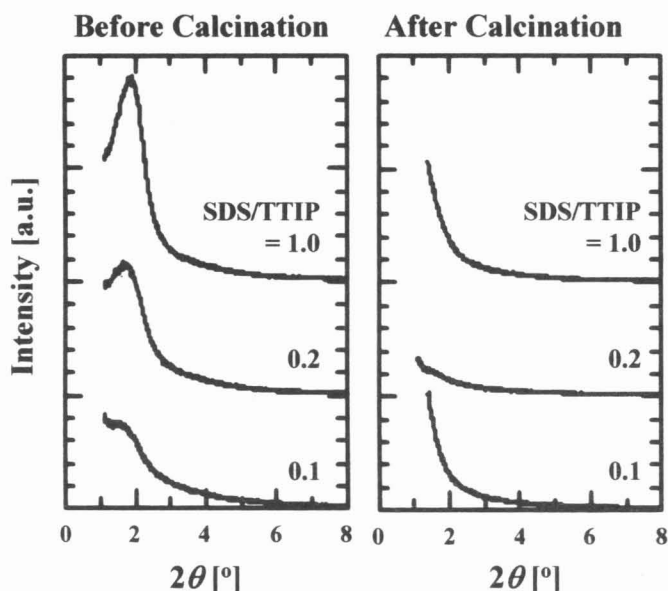


Fig. 1. Powder XRD patterns of samples prepared at various SDS/TTIP molar ratios.

results are presented in Fig. 1 for various SDS/TTIP molar ratios. At the SDS/TTIP of 0.1, no obvious diffraction peak but only a shoulder is observed. At the SDS/TTIP over 0.2, a single diffraction peak exists at  $2\theta = 1.6 - 1.7^\circ$  in the pattern before calcination, exhibiting the presence of an ordered nanostructure with  $d$  value of 4.6 - 5.2 nm. The intensity and sharpness of the diffraction peak are enhanced with the increased SDS/TTIP molar ratio. It is reasonable that a more ordered nanostructure is formed at a higher surfactant concentration. The peak shifts to the higher diffraction angle with increasing the SDS/TTIP ratio, indicating the decrease in spatial periodic length of the nanostructure. This tendency probably results from the reduction of thickness of TiO<sub>2</sub> wall due to the reduced amount of TiO<sub>2</sub> per SDS molecule. However, this diffraction peak disappears after calcination, indicating that the ordered nanostructure is severely damaged by calcination. This result suggests the formation of the lamellar nanostructure supported by surfactant molecular bilayers between the discrete TiO<sub>2</sub> sheet-like structures, which is similar to the results as to the alkylphosphate-templated TiO<sub>2</sub> by Putnam et al (1997). The retention of the nanostructure through the calcination is the most significant problem and being studied at present.

The XRD measurements in the range of  $2\theta = 5 - 80^\circ$  showed that the samples were comprised of the anatase crystal structure. The crystallite sizes were calculated from the full-width at half maximum (FWHM) of the (101) diffraction peaks by Scherrer method. As to the calcined samples, the crystallite size without the addition of SDS was 12.6 nm, while the sizes in the presence of SDS ranged in 4.5 - 5.0 nm and decreased with the increased SDS/TTIP molar ratio. The reduction of crystallite size with the SDS/TTIP ratio suggests that SDS has an effect to suppress the growth of TiO<sub>2</sub> particle.

The nanostructure after calcination was directly observed by TEM and an image is presented in Fig. 2.

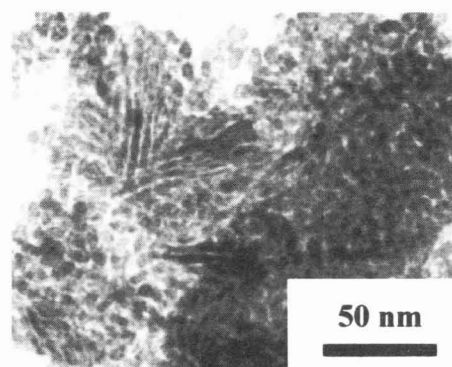


Fig. 2. TEM image of a calcined sample prepared at the SDS / TTIP molar ratio of 1.0.

Partly, a few sheet-like structures are aligned in order, which are the traces of the SDS-templated nanostructure existing before calcination. However, most part of the sample is formed by aggregated nano-sized particles. This result suggests the collapse of the ordered nanostructure by calcination and is in accordance with the disappearance of the diffraction peak in the XRD pattern.

The pore structures of the calcined samples were investigated by nitrogen adsorption measurements. Examples of nitrogen adsorption / desorption isotherms at the SDS/TTIP molar ratios of 0 and 0.2 are shown in Fig. 3. The desorption isotherms show the steep change in the adsorbed volume at a certain  $p/p_0$  depending on the SDS/TTIP ratio. These results indicate the presence of uniform-sized mesopores, in spite of the reduction of the order of nanostructure. Note that even the sample without SDS (SDS/TTIP = 0) shows a peak at the diameter of ca. 8 nm in the pore size distribution. This uniform mesopore structure, which is formed without any templating structure, is probably derived from the spaces between the nano-particles as shown in Fig. 2. The pore size distributions calculated from the desorption isotherms by Dollimore-Heal method are shown together. The peak diameters are 4 – 5 nm and decrease with the increased SDS/TTIP molar ratio up to 0.2. The BET surface area reaches to the maximum value of 230 m<sup>2</sup>/g at SDS/TTIP = 0.2 and considerably larger compared to the surface area of 60 m<sup>2</sup>/g evaluated for the sample prepared without SDS.

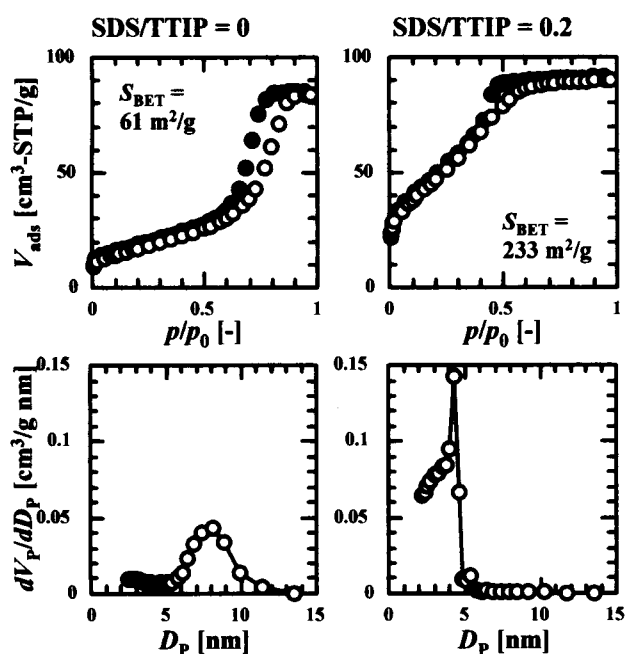


Fig. 3. Nitrogen adsorption (open circles) / desorption (filled circles) isotherms and Dollimore-Heal pore size distributions of calcined samples.

The TiO<sub>2</sub> prepared at two different SDS/TTIP molar ratios of 0.1 and 0.2 were applied to the catalytic oxidation of benzene. The conversions of benzene are shown as the function of reaction temperatures in Fig. 4. For comparison, a series of results from a commercial TiO<sub>2</sub> is also presented. The conversions of benzene increase with the reaction temperature and exceed 90 % over 598 K for both prepared TiO<sub>2</sub> and the activity is almost independent of the SDS/TTIP molar ratio. The TiO<sub>2</sub> prepared in this work exhibit much higher activities compared to that of commercial TiO<sub>2</sub> at all the examined temperatures. The molecular size of benzene is ca. 0.6 nm in width and therefore surfaces of nanometer-sized pores accessible for the benzene molecules are expected to efficiently contribute to the oxidation of benzene. The prepared TiO<sub>2</sub> possess larger surface areas originating from the nanometer-sized pores than the commercial one, resulting in the higher catalytic activities on the oxidation of benzene.

#### 4 CONCLUSION

Nanostructured TiO<sub>2</sub> were prepared by hydrolysis of TTIP in HCl acidic conditions using SDS as a templating agent and the dependence of the nanostructure on the molar ratios of SDS to TTIP was investigated. The order of the nanostructure increased with the increases in the SDS/TTIP molar ratios. However, the ordered nanostructure collapsed by the removal of SDS by calcination at 723 K, suggesting the presence of lamellar structure supported by SDS molecular bilayers. The samples had anatase crystal structure and the crystallite size decreased with the increased SDS/TTIP ratio. The calcined samples showed high BET surface areas of 230 m<sup>2</sup>/g at the largest and mesopore structures with uniform pore size depending on the SDS/TTIP molar ratios.

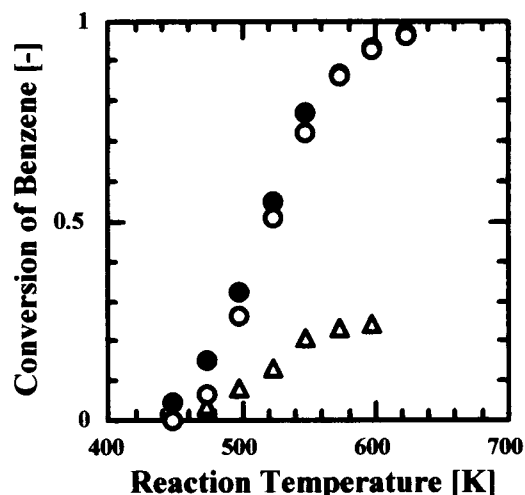


Fig. 4. Dependence of conversion of benzene on the reaction temperature for the oxidation of benzene catalyzed by TiO<sub>2</sub>.

These mesopore structures, which appeared even without SDS, are supposed to originate from the spaces between nano-sized particles attracted around the SDS molecular assemblies. The retention of the nanostructure through the removal of template is the most important problem to be solved.

The catalytic activity of the prepared TiO<sub>2</sub> was revealed to be much higher than that of commercial TiO<sub>2</sub> when they were applied to the oxidation of benzene. This result was probably due to the large surface area of nanometer-sized pores which allowed the easy access of the benzene molecules.

#### REFERENCES

- Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C., & Beck, J. S. (1992): Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism, *Nature*, **359**, pp. 710-712.
- Tanev, P. T., & Pinnavaia, T. J. (1996): Biomimetic templating of porous lamellar silicas by vesicular surfactant assemblies, *Science*, **271**, pp. 1267-1269.
- Ogawa, M. (1996): A simple sol-gel route for the preparation of silica-surfactant mesostructured materials, *Chemical Communication*, pp. 1149-1150.
- Antonelli, D. M., & Ying, J. Y. (1995): Synthesis of hexagonally packed mesoporous TiO<sub>2</sub> by a modified sol-gel method, *Angewandte Chemie International Edition in English*, **34**, pp. 2014-2017.
- Putnam, R. L., Nakagawa, N., McGrath, K. M., Yao, N., Aksay, I. A., Gruner, S. M., & Navrotsky, A. (1997): Titanium dioxide-surfactant mesophases and Ti-TMS1, *Chemistry of Materials*, **9**, pp. 2690-2693.
- Antonelli, D. M. (1999): Synthesis of phosphorus-free mesoporous titania via templating with amine surfactants, *Microporous and Mesoporous Materials*, **30**, pp. 315-319.