Pore size regulation of TiO_2 by use of a complex of titanium tetraisopropoxide and stearic acid

Satoshi Sato,* Satomi Oimatsu, Ryoji Takahashi, Toshiaki Sodesawa and Fumio Nozaki

Department of Applied Chemistry, Faculty of Engineering, Chiba University, Yayoi, Inage, Chiba 263, Japan

The pore size distribution of TiO_2 can be controlled by changing the molar ratio of stearic acid to titanium tetraisopropoxide.

Materials with a controlled pore size, in addition to high specific surface areas, are attractive for use as catalysts and catalyst supports. Mesoporous amorphous silicas such as MCM-41[1] and FSM-16[2] have been recently synthesized, and have specific surface areas > 1000 m^2 g^{-1} together with uniform mesopores. Interest in the synthesis of mesoporous materials are also focused on other oxides such as Al_2O_3, WO_3, and PbO.[3–7] Mesoporous aluminas with specific surface areas > 500 m^2 g^{-1} have been prepared from aluminium alkoxide in the presence of a surfactant.[6,7] On the other hand, the pore size distribution of alumina can be regulated by a pH-swing process.[8] In the process, the particle size of aluminium hydroxide was controlled by altering the pH of the solution containing aluminium hydroxide gel. Here we demonstrate the control of pore size of titania by using stearic acid as a pore regulating reagent.

A measured amount of stearic acid ($C_{17}H_{35}CO_2H$, STA) was dissolved in propan-1-ol at 50 °C and titanium tetraisopropoxide [$Ti(OPr)_4$] dissolved in propan-1-ol at room temp. was added to the STA solution at room temp. The molar ratios of $Ti(OPr)_4$, STA, and propan-1-ol were $1:X:26$, where X was varied from 0 to 2. After the mixed solution was stood at room temperature in an open container for at least 24 h, a white precipitate was formed. The solution was allowed to stand until no further precipitate was formed (up to 264 h). The precipitate was separated by decantation from the solution, and dried at 170 °C for 1 h. The dried sample was calcined at 400 °C for 4 h to obtain TiO_2. The pore size distribution of each TiO_2 sample was calculated from its N_2 adsorption isotherm at -196 °C according to a calcination method reported by Cranston and Inkray.[9]

Preliminarily, it was found that the addition of water to the starting solution decreased both the specific surface area and pore volume. Thus, we prepared samples without adding water to the solution. Since no STA was observed in the supernatant solution, almost all the added STA was included in the precipitate. When the samples were dried at 170 °C, the precipitates became yellow granules up to a molar ratio of STA/Ti (X) of 0.9, and melted above $X = 1.2$. Above $X = 0.2$, a white TiO_2 solid was obtained by calcining the dried sample at 400 °C, and the mass of the sample decreased. The mass decrease in the sample was nearly equal to the amount of added STA. For $X = 0.3$, the TiO_2 sample calcined at 400 °C had a specific surface area of 92 m^2 g^{-1}. For $X < 0.2$, however, carbon species remained in the samples calcined at 400 °C. The crystal structure, as confirmed by XRD, was anatase titania which at 500 °C, became a mixture of anatase and rutile (2.6 m^2 g^{-1}). At 600 °C, the crystal structure was completely converted to rutile and the specific surface area of the rutile titania was as low as 1 m^2 g^{-1}. Consequently, a calcination temperature of 400 °C was adopted.

The structural properties of the resulting TiO_2 altered with the amount of STA added in the starting solution (Figs. 1 and 2). At $X < 0.1$, specific surface areas of the samples were lower than 10 m^2 g^{-1}. A sample prepared without STA ($X = 0$) had a broad distribution of pore volume with a maximum at 5 nm, while the total volume was only 0.01 cm^3 g^{-1}. The specific surface area as well as the pore volume increased with increase in X up to 1.2 (Fig. 1), and the pore size distribution could be regulated; the pore diameter was shifted from 5 to 15 nm in the STA/Ti (X) range between 0.3 and 1.2 (Fig. 2). At $X > 1.2$, no change was observed in the structural properties including the pore size distribution. In the calculation of the pore size distribution of TiO_2 samples, cumulative surface areas calculated from the pore volume and the pore diameter were consistent with the specific surface areas obtained by the BET method. Therefore, the pore size distribution of TiO_2 is controlled by changing the molar ratio of STA to $Ti(OPr)_4$ in the range $0.3 < X < 1.2$.

For different X values, both the trend of the variation in structural properties and the behavior of the samples in the

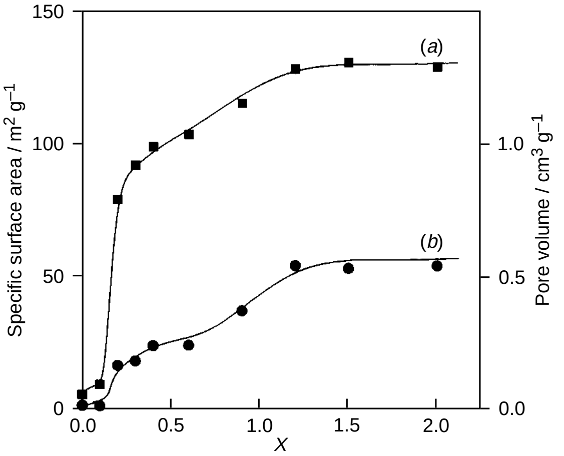

Fig. 1 Structural properties of TiO_2 prepared with different amounts of stearic acid. The molar ratios of $Ti(OPr)_4$, stearic acid, and propan-1-ol were $1:X:26$; (*a*) specific surface area, (*b*) pore volume.

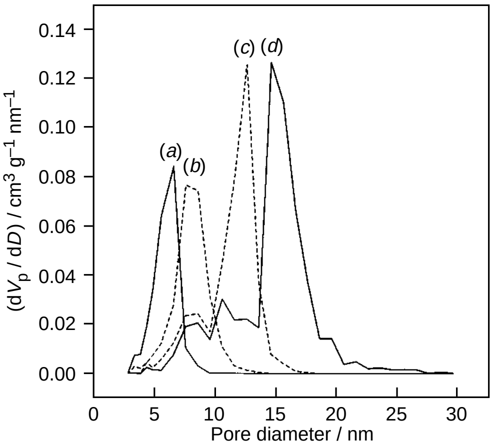

Fig. 2 Pore size distribution of TiO_2 prepared from a $Ti(OPr)_4$–STA complex. The molar ratios of $Ti(OPr)_4$, stearic acid, and propan-1-ol were $1:X:26$; (*a*) $X = 0.3$, (*b*) 0.6, (*c*) 0.9, (*d*), 1.2.

preparation process were clearly altered at X *ca*. 1. In the $Ti(OPr)_4$–$MeCO_2H$ system, two acetic acid molecules are known to coordinate with a titanium isopropoxide dimer to form a 2 : 2 complex.[10] In the $Ti(OPr)_4$–STA system, it is considered that the same type of complex is formed. In the IR spectrum of the precipitate dried at 170 °C, three characteristic absorption peaks were observed at 1450–1470, 1540–1560 and 1740 cm^{-1}. The broad peaks at 1450–1470 and 1540–1560 cm^{-1} are assigned as stretching vibrations of a bidentate carboxylate (CO_2^-) ligand, and the sharp peak at 1740 cm^{-1} as a stretching vibration of C=O in an ester bond of stearate. Because free STA was not detected in the sample dried at 170 °C, excess STA reacted with the solvent propan-1-ol to form *n*-propyl stearate.

For $X < 1.2$, the precipitates is a mixture of the $Ti(OPr)_4$–STA complex and titanium hydroxide contained residual alkoxide groups. For $X > 1.2$, the precipitate is a mixture of the $Ti(OPr)_4$–STA complex and *n*-propyl stearate. The results, for samples with $X > 1.2$, that the excess STA does not contribute to the formation of pore structure imply that the TiO_2 pores are formed upon decomposition of the $Ti(OPr)_4$–STA complex. In other words, an appropriate amount of STA acts as a template while excess of STA acts simply as a solvent. In conclusion, the pore size distribution of TiO_2 can be controlled by calcining the precipitate containing the $Ti(OPr)_4$–STA complex with different STA/Ti ratios.

Footnote and References

* E-mail: satoshi@planet.tc.chiba-u.ac.jp

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2 S. Inagaki, A. Koiwai, N. Suzuki, Y. Fukushima and K. Kuroda, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 1449.
3 Q. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schuth and G. D. Stucky, *Nature*, 1994, **368**, 317.
4 S. A. Bagshaw, E. Prouzet and T. J. Pinnavaia, *Science*, 1995, **269**, 1242.
5 U. Ciesla, D. Demuth, R. Leon, P. Petroff, G. Stucky, K. Unger and F. Schueth, *J. Chem. Soc., Chem. Commun.*, 1994, 1387.
6 F. Vaudry, S. Khodabandeh and M. E. Davis, *Chem. Mater.*, 1996, **8**, 1451.
7 S. A. Bagshaw and T. J. Pinnavaia, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1102.
8 T. Ono, Y. Ohguchi and O. Togari, *Preparation of Catalysts III, Third International Symposium on the Scientific Bases for the Preparation of Heterogeneous Catalysts*, Elsevier Science, Amsterdam, 1983, p. 631.
9 R. W. Cranston and F. A. Inkray, *Adv. Catal.*, 1954, **9**, 143.
10 C. J. Brinker and G. W. Scherer, *Sol–Gel Science, the Physics and Chemistry of Sol–Gel Processing*, Academic Press, New York, 1990, p. 55.

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