Synthesis of Mesoporous TiO_2 Spheres under Static Condition

Lianzhou Wang,* Shinji Tomura, Masaki Maeda, Fumihiko Ohashi, Keiichi Inukai, and Masaya Suzuki
Ceramic Technology Department, National Industrial Research Institute of Nagoya, 1-1 Hirate, Kita-ku, Nagoya 462-8510

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Mesoporous TiO_2 with well-defined spherical morphologies has been synthesized under quiescent condition via the template-assisted slow hydrolysis of titanium alkoxide in environmental humidity.

Considerable efforts have been devoted to the morphological control of novel mesoporous silica M41S since its first report in 1992.[1–5] Various shapes of mesoporous silica, such as films, fibers, spheres, spirals, gyroids, etc., have been successfully synthesized by using supramolecular template method.[6–12] The rich diversity of morphologies in mesoporous silica materials may trigger new developments in catalysis, separation, biomedical, electronics, nano-technology, etc.[5] Meanwhile, some strategies have been made on the extension of mesoporous transition metal oxides other than those of siliceous solids. Porous TiO_2 is well-known for its potential applications[13] in photoelectronics, catalysts, semiconductors, and of course, attracted increasing interests in designing its mesoporous structures via the template-assisted approaches.[14–17] However, up to now, there is still no example to give a particular morphology of mesoporous structured TiO_2 similar to those of mesoporous silica. In the present work, we describe an approach to prepare well-defined TiO_2 spheres containing mesoporosity ranging from sub-micrometer to micrometer.

In the synthesis, neutral surfactant dodecylamine was employed as template to combine with titanium tetraisopropoxide ($Ti(OPr)_4$) precursor. It is known that the hydrolysis and condensation rates of $Ti(OPr)_4$ are much faster than those of silicon alkoxides; thus, it should be more difficult to control the combination and morphologies of organic–inorganic hybrids in the synthesis of TiO_2 materials. Herein, the synthesis principle is based on the natural outgrowth of inorganic–organic hybrids in static 1-propanol solvent via the slow hydrolysis of $Ti(OPr)_4$ promoted by atmospherical humidity.

In a typical preparation, 0.7 g of $Ti(OPr)_4$ (2.46 mmol) and 0.5 g of dodecylamine (2.70 mmol) were mixed with 20 mL 1-propanol and further stirred for 15 min, and then the solution was left in an open container without stirring at room temperature for 48 h. The resulting precipitates were separated by decantation from the solution and dried at room temperature overnight to get as-made sample. Removal of the surfactant was conducted as follows: 0.3 g of as-made sample was dispersed into 40 mL of ethanol which contained 1 mL of concentrated HCl and further stirred for 2 h; then the sample was recovered by centrifugal separation; finally, the material was calcined at 400 °C for 3 h to obtain mesoporous TiO_2 spheres.

The X-ray powder diffraction patterns of samples were carried out on a Rigaku RINT 2000 diffractometer. Thermo-gravimetric Analysis (TG-DTA) was performed on a Seiko RTG-320U instrument with a heating rate of 2 °C /min in air. The morphologies of materials were observed on a Hitachi S-3500N SEM instrument. The N_2 adsorption–desorption isotherm, BET surface area and BJH pore size distribution of sample were determined using a Sorptomatic 1900 analyzer.

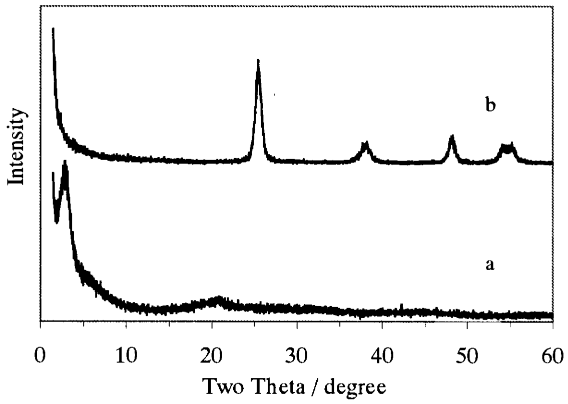

Figure 1. X-Ray powder diffraction patterns of (a) as-made and (b) calcined TiO_2 samples.

Powder XRD pattern of as-made sample (Figure 1a) shows a single intense diffraction peak at low 2θ angle (d = ca. 3.1 nm), which can be often observed in the materials with non-ordered mesopores.[18,19] A weak broad peak at around 20–22° can also be identified, indicating the framework of material is amorphous. After calcination at 400 °C, the XRD pattern of material shows the characteristic of anatase structure and no signal at low angle is distinguished (Figure 1b). Figure 2 gives the SEM picture of calcined TiO_2 spheres. The morphologies of sample are well-defined spherical forms and have smooth surfaces. The particle sizes range from hundreds of nanometers up to several microme-

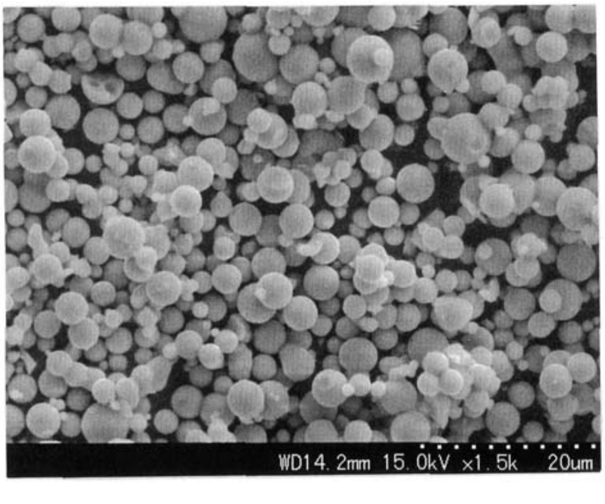

Figure 2. SEM image of calcined mesoporous TiO_2 spheres.

ters. There are not detectable changes between the shapes of the as-made (not shown) and calcined spheres, indicating the spherical forms remain intact after the acidified extraction and calcination procedures.

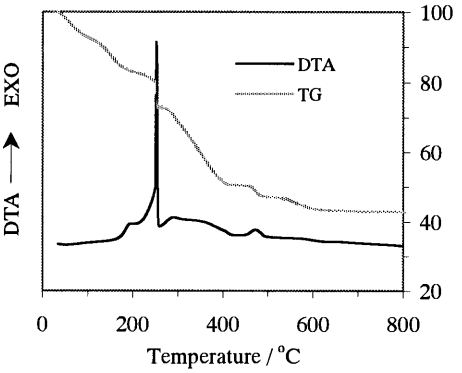

Figure 3. TG-DTA curve of TiO_2 spheres.

The TG-DTA curve (Figure 3) of as-made spheres show that the total weight loss of material is about 57 wt%. The loss of surfactant in the range of 200–400 °C is the major event during the whole thermal process, accompanied with a sharp exothermic signal at 245 °C in DTA curve. The surfactant is very difficult to be completely removed only by using calcination but without acidified ethanol extraction procedure. Therefore, the extraction processing is necessary for the surfactant removal. TG-DTA result of sample after extraction shows that most of surfactants have been extracted, however, the peak intensity of low angle XRD pattern decreased than that of as-made sample, indicating that the surfactant extraction can disturb the pore structures of material. The N_2 isotherm of calcined sample (Figure 4) exhibit type IV-like isotherm with a sharp inflection of N_2 adsorbed volume at $P/P_0 = 0.55$ (type H2 hysteresis loop), indicating the existence of mesoporosity in the materials. The BJH pore size distribution based on the adsorption branch of isotherm is relative narrow with an average pore diameter at ca. 5.4 nm. The BET surface area and specific pore volume of material are about 115 m^2/g and 0.19 cm^3/g, respectively.

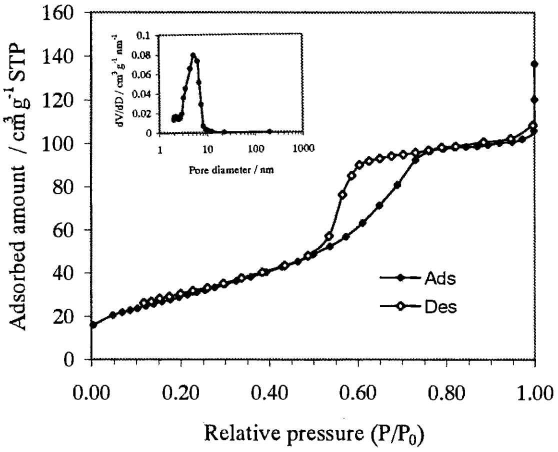

Figure 4. Nitrogen adsorption isotherm and its BJH differential pore size distribution (inserted) of calcined mesoporous TiO_2 spheres.

In the experiments, we also found that the TiO_2 materials synthesized by employing stirring or by dropping water gave only the particles without any specific shapes, indicating that static treatment plays a key role in the formation of spherical TiO_2. The molar ratio of $Ti(OPr)_4$ to surfactant dodecylamine (Ti/S) is another factor to influence the morphologies of products. The spherical shapes of TiO_2 are favorable under low concentration of $Ti(OPr)_4$ in reaction system. Higher concentration of $Ti(OPr)_4$ in the solution (Ti/S > 1) will lead to two-ply precipitations: the under-layer attached to the container has the monolithic structures of several millimeter size, however, the above layer shows to be spherical powder. Both of these products have the mesoporous characteristics. Therefore, the main contribution of surfactant should be the formation of mesoporous structures rather than the evolution of spherical morphologies.

In summary, well-defined mesoporous TiO_2 spheres has been obtained through the slow self-assembly of $Ti(OPr)_4$ and surfactant under quiescent condition. The pathway may provide another example in the morphological control of diverse mesoporous materials.

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