Aerosol-assisted Rapid Fabrication of Well-dispersed and Highly Doped Titanium-containing Mesoporous Silica Microspheres

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Ti-containing mesoporous silica microspheres with high Ti content are prepared by a spray-drying method. Ti species are well-dispersed and highly doped in the silicate frameworks without collapse of mesoporous structures.

Ordered mesoporous silica has attracted enthusiastic interests as one of the key materials in nanotechnology since 1990.[1] Such mesoporous materials having high surface area, large pore volume, and uniform pore size show excellent performances in separation and catalysis.[2] Incorporation of other metal species in the silica walls is vital for the development of mesoporous catalysts, because pure silica is limited for use in various catalytic reactions owing to the lack of acid sites.

Synthetic pathways of mesoporous metallosilicates are mainly classified into grafting[3] and cocondensation routes.[4] In the former pathway, mesopore surfaces of pure silica materials are modified with metal precursors. However, the metal species are not diffused inside the entire mesopores and thus not distributed homogeneously. The latter enables the metal species to be introduced into the silicate frameworks in one-pot. The loading metal species are more homogenously distributed than those fixed by the grafting route. In most cases, however, deformation (or collapse) of ordered mesoporous structures and/or formation of by-products (e.g., bulk metal oxides) have often been observed with the increase in the amount of loading metal species.

In this communication, we demonstrate a facile aerosol-assisted fabrication of well-dispersed and highly doped Ti-containing mesoporous silica microspheres. In the aerosol-assisted fabrication, the initial stoichiometry of nonvolatile inorganic species in precursor solutions is strictly retained in final products.[5] Therefore, this process can allow a wide range of compositional control of the final products. Here, we focused on the preparation of Ti-containing mesoporous silica microspheres, because of their interesting and useful catalytic properties.[2a,2b] By utilizing the aerosol-assisted fabrication, high Ti contents (20 atom % at the highest) into silica frameworks were successfully achieved without collapse of mesoporous structures. The highly doped Ti species were uniformly distributed without phase separation or by-product formation.

In the experimentals, a precursor solution was prepared by cocondensation of tetraethoxysilane (TEOS) and titanium tetra-*n*-butoxide. TEOS (4.15 g) was added to ethanol (4.58 g) containing Pluronic F127 (1.58 g, $EO_{106}PO_{70}EO_{106}$) and then was hydrolyzed with 3.6 wt % HCl solution (1.43 g) for 30 min. The hydrolyzed solution was mixed with titanium tetra-*n*-butoxide (1.41 g) diluted with ethanol (10 g) and stirred continuously for 30 min. The molar ratio of TEOS to titanium tetra-*n*-butoxide was 4:1. The total amount of the precursor solution was adjusted to 300 mL by adding ethanol. The aerosol generator used in this study is a laboratory-made apparatus based on a Spray Dryer GA32 (Yamato Scientific Co.).[6] Droplets of the precursor solution were generated from a two-flow spray nozzle with inside and outside diameters of 406 and 1270 µm, respectively. The droplets were carried by an air flow (250 °C) and dried in a heating zone. A white powder was collected by a cyclone separator. The obtained particles were heated at 550 °C in flowing nitrogen and then calcined at 550 °C in flowing oxygen to remove the template.

The low angle XRD pattern and the TEM image of the calcined sample are shown in Figure 1. A broad diffraction peak was observed at $d =$ ca. 9.5 nm, indicating that the calcined sample possessed a periodic mesostructure. From the TEM image of fine particles (Figure 1, inset image), mesoporous structures can be observed; pore–pore distance was measured to be about 10 nm (See Supporting Figure S1).[7] The N_2 adsorption–desorption isotherm of the calcined sample shows a type IV behavior with a H_1 hysteresis loop. The pore size distribution measured by the BJH method was 7–8 nm. The surface area was calculated to be about 230 m^2/g by the BET method.

Figure 2 shows the SEM and EDS mapping images of the calcined sample. The spherical particles from 0.2 to 5 µm were observable over the entire area (Figure S2).[7] In our aerosol generator apparatus, the droplets generated from the spray nozzle assemble with each other in the heating zone, resulting in the particles size being widely distributed.[6] The SEM image corresponds clearly to the images of the EDS mappings of Si, Ti,

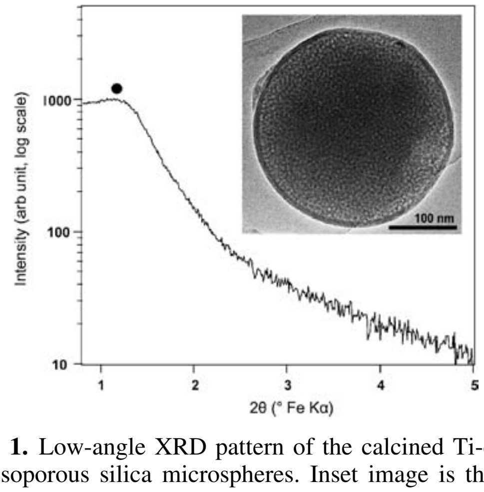

Figure 1. Low-angle XRD pattern of the calcined Ti-containing mesoporous silica microspheres. Inset image is the corresponding TEM image.

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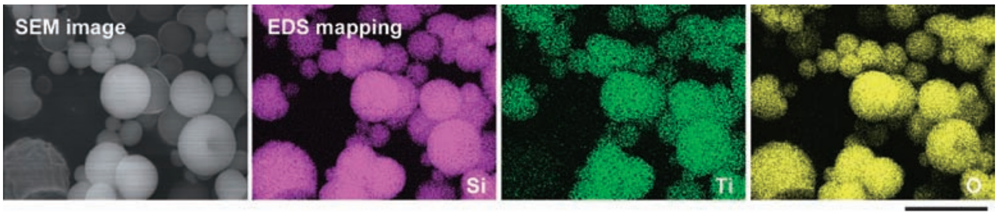

Figure 2. SEM and EDS mapping (Si, Ti, and O) images of the calcined Ti-containing mesoporous silica microspheres. Scale bar is 5 µm.

and O. It was proved that Ti and Si atoms were well dispersed throughout the microspheres without phase separation at micrometer scale. From the EDS spectrum, the composition was measured to be about Si:Ti = 80:20 (Figure S3).[7] The initial stoichiometry in the precursor solution was strictly retained in the final product.

For further understanding of the environment of Ti sites in the silicate framework, UV–vis spectroscopic measurements were performed. The UV–vis spectra of the as-prepared and calcined samples are shown in Figure 3. The adsorption band in the spectra was not dramatically changed. In each case, the broad bands were observed in the range from 210 to 300 nm. The main peak area observed at around 250 nm is attributed to the low-energy charge-transfer transition associated with Ti^{4+} sites in tetrahedral coordination.[4c,8a] Shoulder peaks observed at around 280 nm are related to Ti sites in pentahedral and octahedral coordination with adsorbed water molecules[8b] or partially condensed hexagonally coordinated Ti species belonging to a silicon-rich amorphous phase.[8c] Another important point was that bands at around 330 nm due to bulk titania were not observed at all.[8d] Consequently, most of the Ti atoms are present as four-coordinated species in the silicate framework and are thought to be catalytically active.

For the investigation of catalytic activity due to the TiO_4 units, epoxidation of cyclohexene was carried out by using *tert*-butylhydroperoxide (TBHP) as an oxidant. Cyclohexene (0.82 g) in chloroform (7.39 g) and the mesoporous catalyst (0.2 g) were mixed in a vial, and then TBHP solution (1.28 g, 5.0–6.0 M in decane) was added to the mixture. The mixture was heated and refluxed (at around 56 °C) under stirring to proceed the epoxidation reaction. After 1 h, the catalyst was separated by filtering, and the resultant solution was analyzed by using gas chromatography. It was discovered that oxidation of alkenes was catalyzed by TiO_4 units in microporous crystalline titanosilicates such as TS-1[9] but not by extra-framework TiO_6 units. Here, oxidation of cyclohexene was certainly proceeded over the Ti-containing mesoporous silica spheres. Cyclohexene oxide and cyclohexanediol were obtained as main products, and the total yield was calculated to be about 27%. The catalytic activity is not as high as that over conventional Ti-MCM-41,[2] because both the TiO_4 and TiO_6 species are present in the spheres as shown in Figure 3.

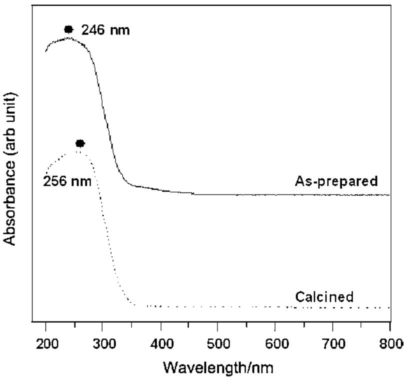

Figure 3. UV–vis spectra of the as-prepared and calcined Ti-containing mesoporous silica.

In conclusion, we prepared Ti-containing mesoporous silica microspheres with high Ti content via one-pot aerosol-assisted fabrication. By using a number of metal alkoxides, various types of metal-containing mesoporous silica microspheres can be designed for catalysts, adsorbents, fillers, and other future applications. This method provides a productive route and can be readily scaled up in industry.

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