Control of Pore Size in Mesoporous Silica by Incremental Surface Modification Using Tetramethyl Orthosilicate

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The pore size of mesoporous silica is precisely controlled by repeated surface treatment with tetramethyl orthosilicate (TMOS) and water. This surface treatment produces a silica monolayer by reaction between surface hydroxy groups and TMOS, and successive water treatment regenerates the surface silanol groups ready for further TMOS modification. This treatment method reduces the pore size of SBA-15 mesoporous silica incrementally by ca. 0.5 nm per treatment step, while preserving the original hexagonal pore structure.

Well-ordered mesoporous materials are expected to be useful as shape-selective heterogeneous catalysts for organic and polymer synthesis. The pore size of mesoporous silica has generally been controlled by changing the size of hydrophobic groups in the surfactant,[1,2] or by adding organic compounds such as 1,3,5-trimethylbenzene to the surfactant as a swelling agent.[3] However, it remains difficult using such direct methods to obtain a desired pore size precisely while maintaining the uniform ordering of mesopores. Niwa et al. reported that the size of the pore entrances in zeolite can be tuned by chemical vapor deposition (CVD) of a silicon alkoxide such as tetramethyl orthosilicate (TMOS) on the outer surface of zeolite particles.[4] Similar methods using organotrialkoxysilanes in liquid-phase reactions have also been employed to modify the internal surface of mesoporous silica, which has a larger pore metric than zeolite.[5,6] The internal modification of mesoporous silica is generally designed to stabilize functional groups by catalytically active sites. However, adequate control of the pore size in such modification has not yet to be achieved. In an attempt to gradually reduce the pore size of mesoporous silica, the reaction of surface silanol groups with TMOS in the liquid phase was investigated in this study with the purpose to generate the shape selectivity for polymerization. Treatment of the TMOS-treated mesoporous silica with water successfully regenerated the surface silanol groups, which could then be retreated with TMOS. Repetition of this process allows the pore size to be reduced incrementally by a constant amount per treatment cycle, providing precise and simple control of pore size.

Mesoporous silica SBA-15, a block copolymer-templated material with BET surface area of $704\,m^2\cdot g^{-1}$ and pore size of 7.3 nm, was first dried under evacuation at 250 °C for 2 h to remove adsorbed water. The precursor was then dispersed in anhydrous toluene with excess TMOS to the expected amount of hydroxy groups in SBA-15 followed by stirring at 80 °C for 6 h under an argon atmosphere to induce the first reaction (Figure 1). The modified solid was collected by filtration, thoroughly washed, and dried under ambient conditions. The dried solid and then stirred into a large quantity of water at 60 °C for 4 h for hydrolysis (Figure 1) and then filtered. This TMOS–water treatment reduces the pore size by the thickness of the silica monolayer formed, and repetition of this treatment

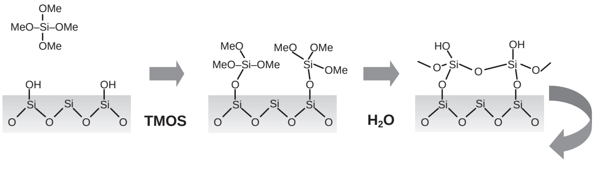

Figure 1. Schematic illustration of TMOS–water treatment process.

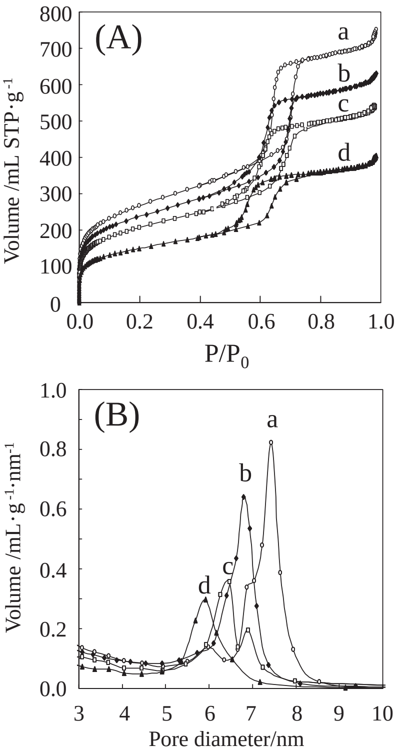

Figure 2. (A) N_2 adsorption–desorption isotherms and (B) BJH pore distributions of (a) original SBA-15, and (b)–(d) TMOS–water treated SBA-15 samples after (b) 1, (c) 2, and (d) 3 treatment steps.

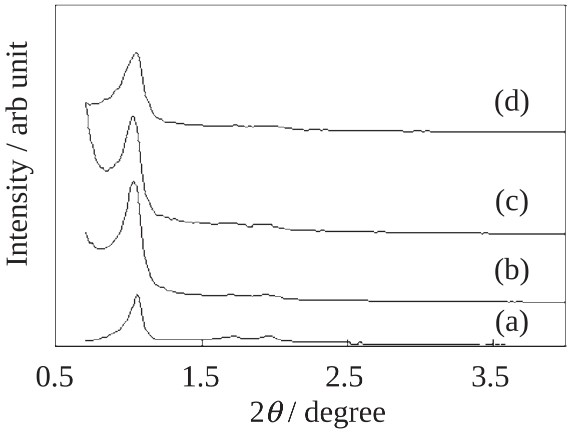

Figure 3. XRD patterns of (a) original SBA-15, and (b)–(d) TMOS–water treated SBA-15 samples after (b) 1, (c) 2, and (d) 3 treatment steps.

allows for the precise control of pore size.

Figure 2 shows nitrogen adsorption–desorption isotherms and the BJH pore-size distribution for SBA-15 samples before and after modification. All isotherms were analogs of the type-IV pattern with H1-type hysteresis typically observed for a two-dimensional mesoporous structure with hexagonal channels. The relative pressure in the hysteresis loops gradually decreased in a stepwise manner with repetition of the TMOS–water treatment, reflecting the decrease in pore size as observed in the BJH pore-size distribution estimated using adsorption branches (Figure 2B). The pore size of SBA-15 was found to decrease from the original size of 7.3 nm to 6.9, 6.5, and finally 6.0 nm with the repetition of TMOS–water treatment. Thus, the pore size is reduced by approximately 0.5 nm with each treatment cycle.

Powder X-ray diffraction (XRD) analysis confirmed the preservation of the original ordered structure throughout this TMOS–water treatment (Figure 3). All of the XRD patterns exhibit (100) diffraction peaks at the same position, demonstrating that the unit cell dimensions remained the same in all samples. Thus, the formation of a silica monolayer on the internal surfaces of the SBA-15 is confirmed to be responsible for the shrinkage of the mesopores. Transmission electron microscopy (TEM) images of the original and treated (3 times) SBA-15 samples (Figure 4) also clearly demonstrate that the ordered hexagonal structure is completely preserved.

Using MCM-41, the original pore size of 2.2 nm was reduced to 1.7 (1 step) and 1.4 nm (2 steps) by TMOS–water treatment, affording hexagonally ordered supermicroporous silica (1.0–2.0 nm).[7] However, as the second treatment only reduced the pore size by 0.3 nm, no further reduction in pore size can be expected by further repetition of TMOS–water treatment for MCM-41. This is likely to be due to the relatively poor and nonuniform access of TMOS into the narrow pores.

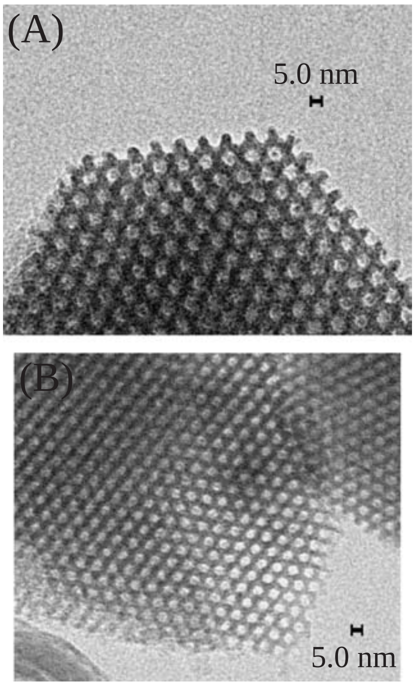

Figure 4. TEM images of (A) original SBA-15, and (B) SBA-15 after TMOS–water treatment (3 steps).

In summary, the pore size of mesoporous silica was shown to be precisely controllable in increments of ca. 0.5 nm by repeated reaction of surface silanol groups with TMOS in the liquid phase. This technique preserves the original hexagonal mesoporous structure, and has excellent potential for the tailored synthesis of shape-selective catalysts.

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