

An HREM Study of Channel Structures in Mesoporous Silica SBA-15 and Platinum Wires Produced in the Channels

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The molecular sieve, mesoporous silica SBA-15, is synthesized using poly(alkylene oxide)-type nonionic amphiphilic triblock copolymers as structure-directing agents under acidic conditions.^[1, 2] The pore diameter of SBA-15 can be controlled uniformly over the range 6–12 nm,^[3] which exceeds the typical pore size limit for well-ordered MCM-41.^[4] The SBA-15 material attracts attention because of its large mesopores (typically 8 nm), which are suitable as hosts for nanoparticles or protein molecules, and of its thicker wall (larger unit-cell constant) than MCM-41. The synthesis, functionalization, characterization, and applications of SBA-15 have been targets of very active recent research.

The SBA-15 material is most easily characterized by X-ray powder diffraction (XRD) patterns and transmission electron microscopy (TEM) images and shows a characteristic 2-D hexagonal structure. The same 2-D hexagonal symmetry, $p6mm$, of SBA-15 and MCM-41 may lead us to assume that both of these materials are constructed with honeycomb-like 1-D channels. However, recent studies pointed out that the two mesoporous materials could have different channel connectivities. Nitrogen adsorption isotherms indicated the presence of pores with diameters less than 3.4 nm in SBA-15, in addition to 2-D ordered mesopores,^[5–7] while such pores were not found in MCM-41. Recently, Ryoo and co-workers developed a method to infiltrate pores of SBA-15 and MCM-41 with carbon or platinum, in order to synthesize “negatives” of the mesoporous systems.^[8]

In the case of the SBA-15 material, the carbon or platinum negatives retained the 2-D hexagonal structures, which exhibited very similar XRD patterns to that of SBA-15 even after complete dissolution of the silica frameworks with HF.^[9] The result indicated that the main channels in SBA-15 were interconnected through smaller pores located in the channel walls.^[10] On the other hand, disordered assemblies of separate carbon or platinum nanowires, which were synthesized in and isolated from MCM-41, indicated that the MCM-41 channels were separated by pore walls.^[11, 12]

Recently, the SBA-15 channel structure has been a matter of growing interest in light of many new possibilities of the extra-large mesoporous molecular sieves. However, and in spite of the evidence for 3-D channel connectivity, the detailed pore structure of SBA-15 has yet not been elucidated. In the present work, therefore, we investigated the pore structure of SBA-15 through high-resolution electron microscope (HREM) observation of platinum wires that were produced within and then isolated from the channels. The aim of the present study is twofold: To investigate the pore structure through the observation of the platinum negatives and to study the structure of new platinum complex at the atomic scale. This is possible because platinum forms a crystalline phase with well-defined interatomic distances and follows the pore shape to form inverse platinum negatives of the pores. Platinum is so stable under electron beams that we can take HREM images at the atomic scale. The HREM images show that the main mesoporous channels are corrugated. More importantly, these channels are interconnected to each other through mesopores about 3.5 nm in diameter that penetrate the silica walls in a disordered way and this means that the channels must exhibit modulations in their diameter.

Figures 1a and 1b show TEM images with the incident electron beam parallel and perpendicular to the direction of main channels of calcined SBA-15 respectively; the inset (Figure 1c) is the electron diffraction (ED) pattern of calcined SBA-15 taken from the c -direction. It can be calculated that the lattice parameter of SBA-15 is about 9.8 nm from this ED pattern (10.5 nm from its powder XRD pattern^[13]). The channels exhibit a well-ordered hexagonal structure similar to that of MCM-41. However, the pore diameter is about 7.7 nm, which is much larger than those of MCM-41.

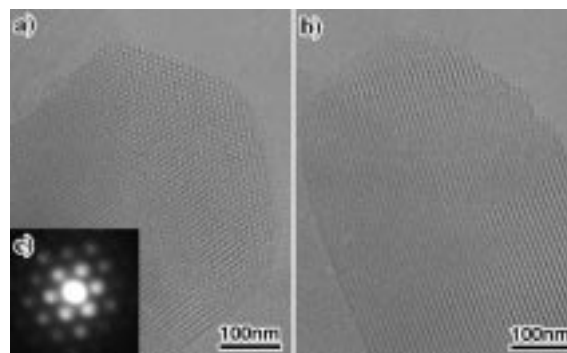


Figure 1. TEM images of calcined SBA-15 with the incident electron beam a) parallel and b) perpendicular to the direction of main channels. c) The electron diffraction pattern taken from the c -direction.

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Platinum wires were synthesized within the channels of calcined SBA-15. Figures 2a and 2b are taken with the incident electron beam parallel and perpendicular to the direction of the channels respectively. The black dots and stripes, indicated by the arrows, are the platinum wires. The wires clearly form inside the channels of SBA-15. The bright contrast areas are the channels of SBA-15, which are not filled with the wires. These images also show that filling with platinum wires does not destroy the channels of SBA-15.

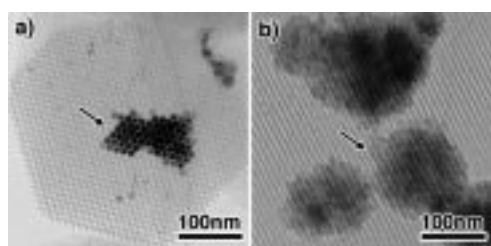


Figure 2. TEM images of Pt wires synthesized within the channels of calcined SBA-15, taken with the incident electron beam a) parallel and b) perpendicular to the direction of the channels.

Figures 3a and 3b show the energy-dispersive X-ray (EDX) spectra before and after the dissolution of the silica wall of SBA-15. After removal of silica walls with HF solution, the silicon peak is much weaker and illustrates that there is almost no silica left.

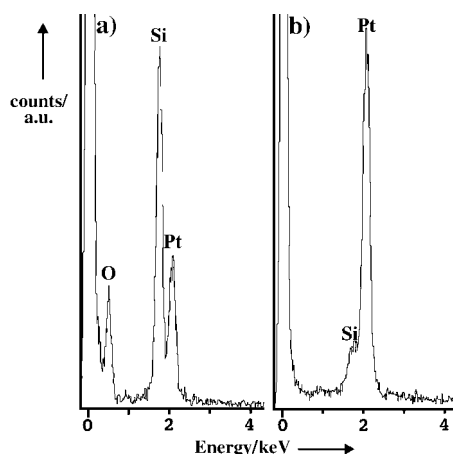


Figure 3. EDX patterns a) before and b) after dissolution of the silica walls of SBA-15.

Platinum wires extracted from SBA-15 are stable and accurately retain the form of mesopores; the structure of silica SBA-15 could be clearly understood through the investigation of its platinum negatives. TEM images showing the platinum wires after dissolution of the silica from SBA-15, viewed with the incident electron beam parallel and perpendicular to the length direction of the wires, are shown in Figures 4a and 4b. The platinum “wires” did not disperse into isolated wires upon

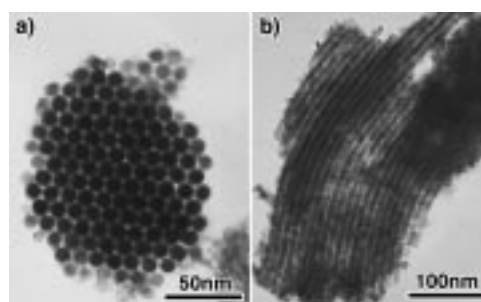


Figure 4. TEM images of the Pt wires extracted from the SBA-15, taken with the incident electron beam a) parallel and b) perpendicular to the length direction of Pt wires.

dissolution of the silica and sonic treatment. This phenomenon is completely different from that of MCM-41,^[12] in which the platinum nanowires dispersed into isolated wires. It can thus be inferred that the platinum wires are interconnected. From the EDX results, it is concluded that this connection could not be due to the silica network of SBA-15.

Figure 5 shows an HREM image of the platinum wires extracted from the pores. Although platinum wires manufactured in the channels of calcined SBA-15 are single crystals, similar to the

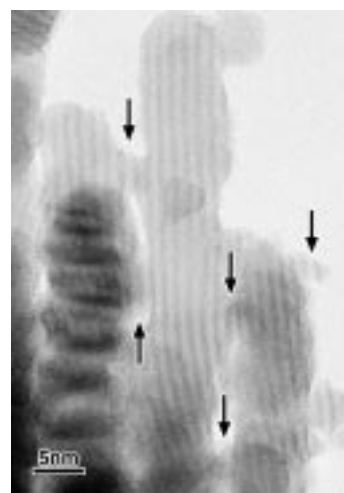


Figure 5. HREM image of the Pt wires extracted from the SBA-15.

single-crystalline platinum nanowire manufactured in the calcined MCM-41,^[12] two different aspects from the platinum nanowires from MCM-41 are clearly observed in the image: a) The projections of the surfaces of the platinum wires are not straight but curve smoothly and b) there are bridges and small protuberances on the surfaces of the wires between adjacent wires (highlighted by the arrows in Figure 5). The crystal orientations of two adjacent platinum wires and the small platinum bridge that connects those two wires are the same. That is, the two adjacent wires with the small bridge between them are, as a whole, a single crystal. This is very strong evidence for the existence of small pores that interconnect the channels in SBA-15. It can be concluded from the observations that there are

small catenoid-shaped platinum domains interconnecting the main channels in calcined SBA-15. However, the small bridges are arranged in a random way with average diameter about 3.5 nm. The pore structure of calcined SBA-15 is therefore not two-dimensional but instead three-dimensional.

The variation of the channel diameter is not surprising to give the hyperbolic geometry of the pore wall induced by the interwire connection, shown schematically in Figure 6. In order to

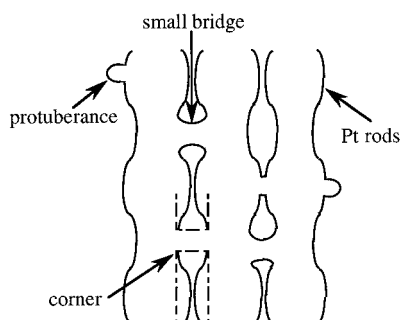


Figure 6. Schematic drawing of Pt wires extracted from the SBA-15 which are the negatives of the channel system of SBA-15.

maintain uniform Gaussian curvature for the wall after connecting the main channel, channel dimensions vary along their length: Formation of interconnected channels of uniform diameter and zero Gaussian curvature would result in "corners" at the interconnection sites (the dotted line in Figure 6) and high local (hyperbolic) curvature. In order to smooth such curvature inhomogeneities, the channels must exhibit modulations in their diameter. Preservation of those modulations in the platinum product indicates the effective templating of the SBA-15 material by the precursor liquid-crystalline mesostructure, whose stability is dominated by the bending energy of the amphiphilic film, to favor uniform curvatures.

The possibility of this topology has been inferred theoretically from analysis of the change in pore dimensions with volume in mesoporous hexagonal materials through a swelling analysis.^[14] In the case of SBA-15 materials, the data are too scattered to apply this analysis with confidence. However, the observations presented here confirm the possibility of a continuation of topologies, from 1-D channels to fully interconnected 3-D channels (for example in MCM-48).

Experimental Section

A high-quality SBA-15 sample was prepared using the triblock copolymer Pluronic P123 (EO₂₀PO₇₀EO₂₀, BASF) as the surfactant and tetraethyl orthosilicate (TEOS; 98%, Acros) as the silica source following the synthesis procedure reported by Zhao et al.,^[2] except for the modifications of the starting composition and stirring mode. The initial composition was P123 (10 g), TEOS (0.10 mol), HCl (0.60 mol), and H₂O (20 mol). The starting mixture was prepared by dissolving the P123 polymer (0.5 g) in distilled water containing HCl (19.0 mL, 1.6 M) at 308 K. TEOS (1.1 g) was added after the P123

polymer dissolved and the mixture thus obtained was stirred for a few minutes until TEOS itself had just dissolved completely. This mixture was then placed in an oven for 24 h at 308 K. Loosely crosslinked SBA-15 particles (their structure was damaged if filtered) precipitated during this reaction period at 308 K. The silica framework was further crosslinked by heating the reaction mixture for 24 h at 373 K before filtration, in order to prevent loss of the ordered structure upon subsequent filtration. The product was then filtered without washing, dried in an oven at 393 K, washed with ethanol (95%) in order to extract the surfactant, and finally calcined in air under static conditions at 823 K.

In a typical experiment to prepare the Pt negative, the calcined SBA-15 silica sample (0.2 g) was supported with tetraammineplatinum(II) nitrate [Pt(NH₃)₄(NO₃)₂] (0.16 g) by repeating alternation of the impregnation of aqueous solution and drying at 373 K four times. The SBA-15 sample was heated under a H₂ flow after supporting the Pt compound, while the temperature was increased from room temperature to 573 K over 4 h and maintained at 573 K for 2 h using a U-tube reactor equipped with two fritted disks. The SBA-15 sample was then put in a vacuum for 30 min at 573 K prior to the exposure to air at room temperature. The evacuation was carried out in order to remove the chemisorbed hydrogen that might cause sintering of the negative by the heat of reaction with atmospheric O₂. The silica framework of this sample was dissolved completely with HF (10%). The Pt residue was filtered and washed with distilled water. An ethanol dispersion of this Pt sample was dropped onto TEM grid, and the solvent was dried at room temperature.

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