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Simple Synthesis Route to Monodispersed SBA-15 Silica Rods

Abdelhamid Sayari,* Bao-Hang Han, and Yong Yang

Centre for Catalysis Research and Innovation (CCRI), Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

Received April 13, 2004; E-mail: abdel.sayari@science.uottawa.ca

Triggered by the discovery of the so-called M41S family of ordered mesoporous silicas,[1] a new research field dealing with periodic mesoporous materials was developed. Among the wide variety of silica mesophases, MCM-41[1] and SBA-15[2] have been the most extensively investigated. Though both of them exhibit two-dimensional hexagonal structures (*p*6*mm*), they have some notable differences: (i) SBA-15 is endowed with larger pores and thicker pore walls than MCM-41;[2] (ii) MCM-41 is purely mesoporous in nature, whereas typical SBA-15 silica contains a significant amount of micropores within the pore walls;[3] and (iii) while the channels of MCM-41 are not connected to each other, those of SBA-15 are interconnected via micropores[3b] or secondary mesopores.[4] In addition to the nature of the pore system, i.e., pore size, shape, and connectivity, depending on the targeted application, the morphology of the mesophase may be particularly important. Simple morphologies with short, unhindered path lengths such as small spheres and crystal-like particles as well as short, straight rods are beneficial for applications limited by intraparticle diffusion processes such as catalysis, separation, guest molecule encapsulation and internal surface modification. Thus, not surprisingly, extensive work was devoted to the morphological control of mesoporous silicas[5−8] and organosilicates.[9] Most approaches were based on changes in synthesis conditions, including the silica source, the nature of the surfactants, cosurfactants, cosolvents, and additives, and the overall composition of the synthesis mixture.

As far as SBA-15 is concerned, the most common morphology consists of bundles of fibers several tens of micrometers in length obtained by coupling short rodlike particles.[2,5,6d] More exotic particles having doughnut-, rope-, egg-sausage-, gyroid-, and discoidlike shapes have been obtained by Zhao et al.[6a] using organic additives and inorganic salts. More recently, an interesting morphology consisting of discrete 1−2 μm rodlike particles has been obtained in high yield in the presence of large amounts of KCl relative to tetraethyl orthosilicate TEOS (KCl/TEOS = 1.5).[8] Similar SBA-15 particles were found to occur in the presence of sodium silicate, but under a "very narrow range of synthesis conditions" (cit.).[10] This method was adversely affected by temperature variations as small as 5 °C. Moreover, monodispersed rods could be synthesized only at 30 °C, leading to material with ca. 5 nm pores. Though the formation of rodlike particles was first attributed to the presence of salt,[8] the occurrence of such particles may actually be due to a large extent to the fact that the synthesis was carried out without stirring. Indeed, earlier work showed that the use of salt (NH_4F) under stirring afforded not SBA-15 rods but wheatlike fibers.[6d]

Moreover, despite its severe restrictions, Kosuge et al.'s method[10] demonstrated the importance of static conditions in the synthesis of SBA-15 short rods. However, they used sodium silicate, which in the presence of HCl acts as both a silica source and inorganic salt ($NaCl/SiO_2$ = ca. 0.7).[10,11] Here, we present a simple, flexible, reproducible, high-yielding (ca. 100%) synthesis of hexagonally facetted SBA-15 straight rods with uniform sizes (ca. 1.5 × 0.4 μm) under static conditions without using salts. This method afforded rodlike particles with temperature-dependent pore sizes ranging from 5.8 to 12.5 nm but with similar external dimensions.

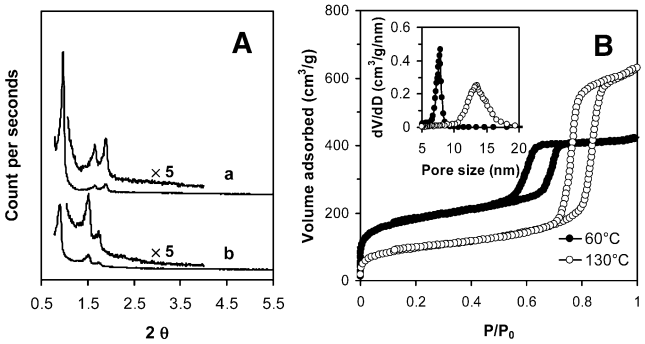

Figure 1. (A) XRD patterns for samples prepared at (a) 60 °C and (b) 130 °C and (B) the corresponding nitrogen adsorption−desorption isotherms and pore size distributions.

Table 1. Structural Properties of Samples Prepared at Different Temperatures

T (°C)[a]	d_{100} (nm)[b]	S_{BET} (m^2/g)[c]	V_t (cm^3/g)[d]	w (nm)[e]	b (nm)[f]
35	8.3	560	0.38	5.8	3.78
60	8.5	530	0.61	7.6	2.10
80	9.0	786	0.77	8.5	1.89
100	10.6	865	1.12	10.4	1.84
130	11.8	352	0.98	12.5	1.12

[a] Temperature of the second synthesis stage. [b] (100) interplanar distance. [c] BET (Brunauer, Emmett, and Teller) specific surface area. [d] Total pore volume calculated as the amount of nitrogen adsorbed at the relative pressure of ca. 0.99. [e] Pore diameter. [f] Pore wall thickness $b = d_{100}(2/3^{1/2}) - w$.

The preparation procedure was as follows: 4.0 g of triblock copolymer Pluronic P123 was added to a mixture of 30 g of water and 120 g of 2 M HCl aqueous solution in a Teflon-lined container, which was stirred at 35 °C usually overnight. Then, 8.50 g of TEOS was added to this solution under vigorous stirring. After 5 min of stirring, the mixture was kept under static conditions at 35 °C for 20 h, followed by 24 h at different temperatures. The solid products were collected by filtration, washed with water, dried, and calcined at 550 °C in flowing air.

All samples exhibited XRD patterns consistent with the occurrence of two-dimensional hexagonal symmetry. Representative diffractograms are shown in Figure 1A. The corresponding nitrogen adsorption−desorption isotherms (Figure 1B) are typical of ordered mesoporous materials with narrow pore size distributions (Figure 1B, inset). The structural properties of samples prepared at different temperatures are collected in Table 1. The effect of temperature on the pore size is consistent with literature data.[4b,8] The increase in pore size was accompanied by an increase in the unit cell dimension ($a = d_{100}(2/3^{1/2})$) from 9.58 to 13.62 nm and a decrease in the pore wall thickness from 3.78 to 1.12 nm. Similar thinning

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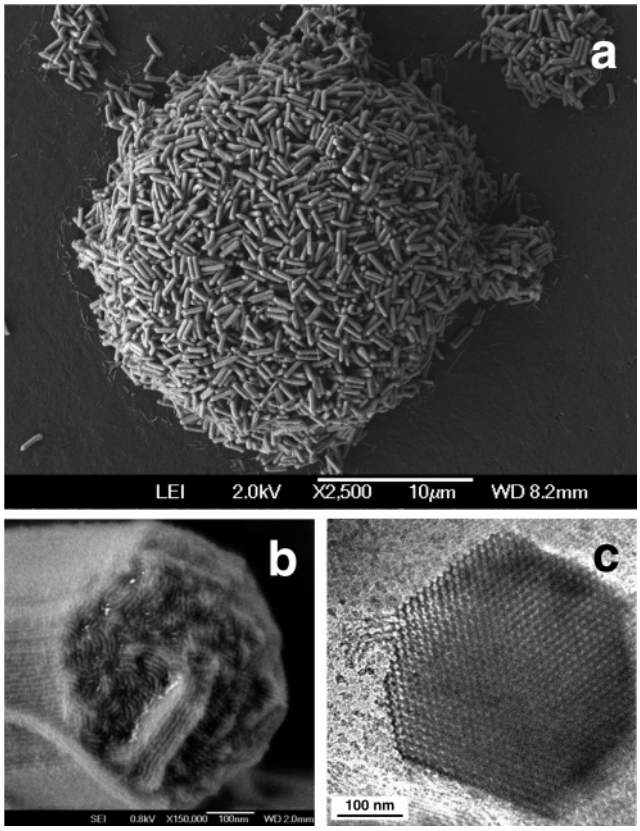

Figure 2. Low- (a) and high-magnification (b) SEM images for material made at 100 °C. (c) TEM image.

of the pore walls as the synthesis temperature is increased was observed earlier by Galarneau et al.[4b] who argued that at low temperature, because of molecular repulsion, the micelles which have ca. 1 nm protruding poly(ethylene oxide) chains remain 3−4 nm apart. Thus, the silica mesophase prepared at 35 °C would have thick pore walls, microporosity, and small but not interconnected channels. At higher temperature, water becomes a less effective solvent, and the micelles increase in size, leading to a silica mesophase with thinner pore walls and larger interconnected channels.

All samples prepared at temperatures between 35 and 130 °C were comprised of almost 100% monodispersed rodlike particles 0.4−0.5 μm in diameter and 1−1.5 μm in length. Figure 2a shows a representative low-magnification SEM image of calcined SBA-15 silica prepared at 100 °C. Additional SEM images for materials prepared at different temperatures are provided as Supporting Information (Figure S-1). The high-magnification image (Figure 2b) indicates that such particles are hexagonally facetted. Moreover, the external surface perpendicular to the *c* direction shows that numerous channels are actually connected through curved bridges.[12] The TEM image (Figure 2c) offers direct evidence that the channels are hexagonally packed and run parallel to the *c* direction. With regards to the temperature of the first step, it has to be relatively low in the range of 30−60 °C. Single-step synthesis in this temperature range also gave rise to monodispersed rods with increasing pore sizes from ca. 5 to 9 nm. However, materials prepared at the lowest temperature 30−35 °C exhibited poor structural properties (Figure S-2). Finally, regardless of salt addition, stirring gave rise to fibrous materials (Figure S-3). The absence of shear flow and the slower rate of precipitation under static conditions are possible key factors in the formation of rodlike particles. Addition of salts such as NaCl had little effect on the morphology of the particles. However, it reduced drastically the microporosity and, thus, the surface area.[11]

This work shows that in order to prepare short monodispersed SBA-15 rods, (i) the absence of stirring is essential, (ii) the temperature of the first stage should not exceed 60 °C, and (iii) addition of inorganic salts is not required.

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Supporting Information Available: SEM images for SBA-15 synthesized (i) at different temperatures under static conditions and (ii) under stirring with and without added salt (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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