

## Rapid Crystallization of High Quality Cubic Silica SBA-16 Nanoporous Material

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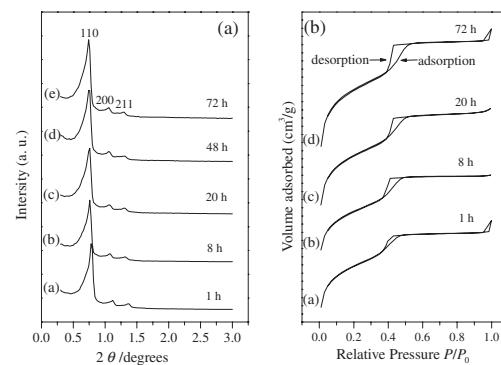
High quality cubic SBA-16 can be synthesized rapidly at room temperature in 1 h using low surfactant concentrations and has 65% of micropore volume and 5.3 nm of wall thickness on average. The structure integrity of SBA-16 is very sensitive to the acid concentration in gel because of the necessity of moderate hydrogen-bonding and electrostatic interaction between silicates and surfactants.

Mesoporous materials with larger pore sizes and better stability as compared to the M41S materials were synthesized with nonionic poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymers (Pluronic,  $EO_xPO_xEO_y$ ) by Stucky et al. in 1998.<sup>1</sup> These novel mesoporous silicas denote SBA-*n* materials, and these materials formed exhibit 2- and 3-dimensional hexagonal (SBA-2, 12, 3, 15)<sup>1-3</sup> and cubic (SBA-1, 6, 16) pore architectures.<sup>4</sup> The cubic phase mesoporous materials SBA-16 ( $Im\bar{3}m$ ) possesses 3-D channel system and uniformly sized pore structure of large cage-like structure with a cubic symmetry. Because of the large cage, high surface area, high thermal stability and, especially, 3-D channel connectivity, SBA-16 is considered to be suitable for a promising candidate for applications in catalytic<sup>5</sup> and separation technologies, e.g., supercritical fluids chromatography (SFC).<sup>6</sup> Morishige et al.<sup>7</sup> used SBA-16 as a model absorbent to study the adsorption/desorption behavior of ink-bottle pore. Stucky et al.<sup>1</sup> first reported a novel cubic cage-structure mesoporous silica SBA-16 prepared at room temperature for 20 h and 80 °C for 2 days, but no detailed data of synthesized parameters and properties were reported. In 2002, Voort et al.<sup>5</sup> gave an important and critical report for the synthesis of SBA-16 at 25–65 °C for 4 h to 20 h with stirring and then 65–100 °C for 15–48 h. Here, we report the rapid synthesis of cubic SBA-16 with high quality at low surfactant concentrations and room temperature for 1 h or more. Resulting products show well-defined XRD patterns, TEM image of cubic  $Im\bar{3}m$  symmetry, regular sphere morphology and 65% of micropore volume on average. The structure integrity of SBA-16 is very sensitive to the acid concentration.

The cubic mesoporous material SBA-16 was synthesized using the surfactant source of Pluronic F127 ( $EO_{106}PO_{70}EP_{106}$ ) and silica source of tetraethyl orthosilicate (TEOS). SBA-16 was prepared as following. The surfactant was dissolved in 2 M HCl solution at room temperature about 25–30 °C for 2 h and then the silica source was added into this solution with stirring for 1 to 72 h. The final gel of composition is  $1 SiO_2 : 0.0044 F127 : 5 HCl : 150 H_2O$ . The XRD patterns of samples were recorded using beam line BL17A of the National Synchrotron Radiation Research Center (NSRRC), Taiwan, with a wavelength of 1.3263 Å.

XRD patterns of calcined SBA-16 prepared by using different acid concentrations (1.8 to 2.6 M) at room temperature are

shown in supplements. The structure integrity of SBA-16 is much sensitive to the acid concentration of the initial gel mixture as compared to the synthesis of SBA-15, which can be synthesized at acid concentrations from 2 to 0.005 M in our groups. (see supplements) Optimal acid concentration for the preparation of SBA-16 is between 2.0 and 2.4 M. It seems that the structure-directed assembly of 3-D SBA-16 depends strongly on the electrostatic or H-bonding interaction between silica and EO (ethylene oxide) part of surfactant. It results in the difficulty to build up the 3-D cubic structure of SBA-16 if strong electrostatic or H-bonding interaction between silicas and surfactants is absent or too much; that is the acid concentration of gel is smaller than 2.0 M or larger than 2.4 M, respectively.



**Figure 1.** (a) XRD patterns of calcined SBA-16 prepared using different reaction time at room temperature. (a) 1, (b) 8, (c) 20, (d) 48, and (e) 72 h; and (b) N<sub>2</sub> adsorption/desorption isotherms of samples prepared for different reaction time. (a) 1, (b) 8, (c) 20, and (d) 72 h.

Figure 1a shows the XRD patterns of calcined SBA-16 at room temperature for different synthesis time from 1 to 72 h. Three well-resolved diffraction peaks can be indexed to (110), (200), (211) reflections corresponding to a cubic  $Im\bar{3}m$  structure,<sup>8</sup> not hexagonal structure. It illustrates the rapid assembly of cubic SBA-16 architecture between surfactant and silica so that high quality cubic SBA-16 can be synthesized at room temperature in 1 h using low surfactant concentrations of 2 wt %. The surfactant concentration affects not only assembling time but also product quality of SBA-16 architecture. If 3–5 wt % of F127 surfactant according to the recipe of Stucky et al. was used, our calcined products have XRD patterns with a broad (200) reflection and mostly TEM images with worm-like pore. The product quality is inferior to that of Stucky et al. but it is similar to those of Morishige et al.<sup>7</sup> and Voort et al.<sup>5</sup> Rapid assembly of cubic SBA-16 organic–inorganic composite is probably related to long hydrophilic and interactive surface of the EO part in  $EO_{106}PO_{70}EP_{106}$  surfactant. The long EO moiety of  $EO_{106}PO_{70}EP_{106}$  serves for a large and reactive balcony for sili-

ca condensation, which attracts the cationic silica oligomer and catalyzes effectively silica polymerization on the surface of micelle. The silicated surfactants further assemble and form a 3-D cubic architecture of SBA-16 at moderate electrostatic or H-bonding interaction between silica and surfactants affected by acid concentration. Cubic unit cells of SBA-16 increase slightly from 13.77 to 14.5 nm as a result of increasing crystallization time from 1 to 72 h at room temperature (Figure 2a and Table 1).

**Table 1.** Physical properties of SBA-16 prepared at different conditions

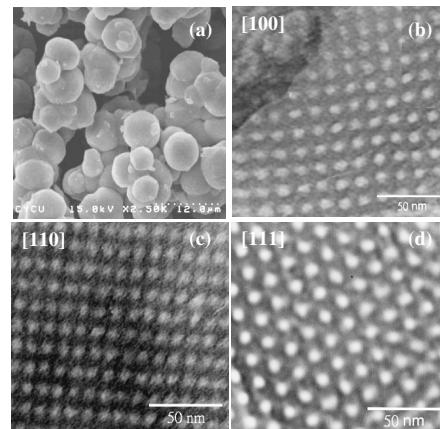
| [H <sup>+</sup> ]<br>/M | Reaction<br>Time/h | $a_0$<br>/nm | $D_p$<br>/nm | W<br>/nm | $V_t$<br>/cm <sup>3</sup> g <sup>-1</sup> | $V_\mu$<br>/cm <sup>3</sup> g <sup>-1</sup> | $S_{BET}$<br>/m <sup>2</sup> g <sup>-1</sup> |
|-------------------------|--------------------|--------------|--------------|----------|---|---|--|
| 1.2                     | 20                 | 14.92        | 3.8          | 5.1      | 0.28                                      | 0.17  | 480  |
| 2.6                     | 20                 | 14.52        | 3.2          | 5.3      | 0.23                                      | 0.14  | 413  |
| 2.0                     | 1                  | 13.77        | 3.3          | 5.3      | 0.22                                      | 0.14  | 401  |
| 2.0                     | 8                  | 14.13        | 3.5          | 5.2      | 0.23                                      | 0.14  | 406  |
| 2.0                     | 20                 | 14.52        | 3.8          | 5.4      | 0.27                                      | 0.18  | 482  |
| 2.0                     | 72                 | 14.52        | 3.8          | 5.3      | 0.29                                      | 0.19  | 516  |

$a_0$ : Cubic unit cell parameter,  $D_p$ : Pore diameter ( $a_0 = \sqrt{2} \times d_{110}$ ), W: Wall thickness calculated from the model of spherical cavity,<sup>2</sup>  $V_t$ : Total pore volume,  $V_\mu$ : Micropore volume calculated from *t*-plot method,  $S_{BET}$ : BET surface area.

The adsorption/desorption isotherms for calcined SBA-16 in Figure 1b is the type IV according to the IUPAC classification, characteristic of mesoporous materials with a narrow pore size distribution. Pore size of SBA-16 enlarges gradually from 3.3 to 3.8 nm as a result of increasing crystallization time from 1 to 72 h at room temperature (Figure 1a and Table 1). The pore wall thickness of cubic phase SBA-16 is calculated from a simple formula<sup>6</sup>  $W = \sqrt{3}a_0/2 - D_{me}$  where  $D_p$  and  $a_0$  are the mesopore diameter and cubic unit cell parameter, respectively. Ultra-thick wall thickness of 5.3 nm for SBA-16 may lead to higher thermal and hydrothermal stability of calcined SBA-16 than those of other cubic mesoporous molecular sieves. After treatment of MCM-48 and SBA-16 in boiling water for one day, the structure of MCM-48 is collapsed but most mesostructure of SBA-16 is maintained. It is worthy for further study from the standpoint of the transport assistance in catalysis because there are 61–67% micropore volume calculated from *t*-plot analysis for all samples prepared at different reaction times and acid concentrations, which have never achieved by other mesoporous sieves. The micropore originates from the penetration of the EO chain of the triblock copolymer into the silica wall, thus creating intrawall porosity, and connecting the different mesoporous cavities. The large EO chain in EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub> has high hydrophilicity to interact with and perforate into silica wall and could be responsible for the significant microporosity of SBA-16. This result also shows the relationship between the microporosity and the EO ratio in structure of multiblock copolymer.

The scanning electron micrograph of SBA-16 in Figure 2a shows the spherical morphology with the average particle size of 6  $\mu$ m in diameter. It is noticed that samples with low crystallinity or structure observed by their XRD patterns have the morphology of irregular block. Our products with 3-D channel and moderate particle size of 6  $\mu$ m could be excellent candidates for applications of catalysis and separation. TEM image of thin

section for calcined SBA-16 shows the pore structure along the cubic (110), (100), (111) planes in Figures 2b–2d and the direct evidence of good quality for SBA-16.<sup>8</sup> It can be observed that the part of SBA-16 channel is wormlike (not shown) because of long EO part and the polydispersion of molecular weights and structure for surfactant.



**Figure 2.** (a) SEM images of calcined SBA-16 sample. TEM section images of calcined SBA-16 samples along (b) [100], (c) [110], (d) [111] direction.

This study shows that high quality cubic SBA-16 can be synthesized rapidly at room temperature in 1 h or more under the gel with low surfactant concentrations. High quality SBA-16 can be evidenced by their well-defined XRD patterns, TEM pore image of SBA-16 section, narrow pore size distribution and regular sphere morphology of SBA-16. Ultra-thick wall thickness of 5.3 nm for SBA-16 may lead to higher thermal and hydrothermal stability of calcined SBA-16. Resulted products with 3-D channel, 65% of micropore volume and moderate particle size of 6  $\mu$ m could be excellent candidates for applications of catalysis and separation.

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## References

- 1 D. Zhao, Q. Hau, J. Feng, B. F. Chmelka, and G. D. Stucky, *J. Am. Chem. Soc.*, **120**, 6024 (1998).
- 2 P. I. Ravikovich and A. V. Neimark, *Langmuir*, **18**, 1550 (2002).
- 3 M. C. Liu, H. S. Sheu, and S. F. Cheng, *Chem. Commun.*, **2002**, 2854.
- 4 D. Das, C. M. Tsai, and S. Cheng, *Chem. Commun.*, **1999**, 473.
- 5 P. V. D. Voort, M. Benjelloun, and E. F. Vansant, *J. Phys. Chem. B*, **106**, 9027 (2002).
- 6 K. Schumacher, P. I. Ravikovich, A. D. Chesne, A. V. Neimark, and K. K. Unger, *Langmuir*, **16**, 4648 (2000).
- 7 K. Morishige, N. Tateishi, and S. Fukuma, *J. Phys. Chem. B*, **107**, 5177 (2003).
- 8 Y. Sakamoto, M. Kaneda, O. Terasaki, D. Zhao, J. M. Kim, G. Stucky, H. J. Shin, and R. Ryoo, *Nature*, **408**, 449 (2000).