

# Control of the microporosity within the pore walls of ordered mesoporous silica SBA-15

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**Microporosity within the pore walls of ordered mesoporous silica SBA-15 was confirmed by physisorption; the micropore volume could be systematically controlled by varying the synthesis temperature and the TEOS/surfactant ratio.**

Mesoporous molecular sieves, such as MCM-41<sup>1</sup> and FSM-16,<sup>2</sup> have attracted much attention as catalysts and adsorbents owing to their large pore dimensions compared to microporous zeolites. It is, however, difficult to obtain mesoporous materials exhibiting specific catalysis and adsorption properties such as the uniform acidity and the strong adsorption properties characteristic of zeolites, owing to the amorphous pore walls and large pore dimensions. Although some efforts have been made to crystallize the pore walls of mesoporous materials in order to endow them with a specific functionality,<sup>3–5</sup> it is well known that crystallization of thin pore walls (1–6 nm) is not easy. The generation of microporosity within the amorphous pore walls of mesoporous materials is a promising strategy for endowing them with a specific functionality. Such a material possessing a bimodal pore system, *i.e.* one in which micropores exist within the walls of mesopores, is an ideal porous material for catalysts and adsorbents, because molecules are first transported through mesopore channels and then strongly adsorbed in the micropores. The synthesis of a material with micro- and meso-porous properties would be of great interest. Although there have been some reports suggesting microporosity within the pore walls of MCM-41<sup>6,7</sup> and SBA-15,<sup>8,9</sup> a systematic study for confirmation and control of the microporosity within the pore walls of an ordered mesoporous material has not been reported. Here, we report that the micropore volume of SBA-15 can be controlled systematically by the synthesis temperature and the Si/surfactant ratio in the starting mixture, and micropores are certainly established within the pore wall of SBA-15 material.

A triblock copolymer, Pluronic P104 (BASF), EO<sub>17</sub>PO<sub>58</sub>EO<sub>17</sub> (EO = –CH<sub>2</sub>CH<sub>2</sub>O–, PO = –CH<sub>2</sub>CH(CH<sub>3</sub>)O–), was used as a structure-directing agent for the synthesis of mesoporous materials. In a typical preparation, 0.8 g of P104 was dissolved in 53 cm<sup>3</sup> of deionized water at 45 °C, and then 10 cm<sup>3</sup> of an aqueous 36% HCl solution was added to the solution. After 2.1–5.6 g of TEOS had been added to the

solution, the mixtures was maintained at 45 °C for 8 h with vigorous stirring, followed by heating at 80–100 °C for 8 h under static conditions. The solid products were filtered off and then washed with deionized water repeatedly. After drying at 45 °C overnight, the powders were calcined at 550 °C for 6 h in air. The chemical composition of the reaction mixtures was 0.18 mmol P104: 0.010–0.027 mol TEOS: 0.12 mol HCl: 3.3 mol H<sub>2</sub>O. The SBA-15 materials reported previously<sup>10,11</sup> were synthesized with a higher concentration of a surfactant (33.7 g L<sup>–1</sup>) than the concentration (15.2 g L<sup>–1</sup>) used in this study. Triblock copolymer P104 has not been previously used for the synthesis of an SBA-15 material. The X-ray diffraction patterns of the products had 2–4 peaks in the low angle region ( $2\theta(\text{Cu-K}\alpha) = 0.7\text{--}3.5^\circ$ ) indicating the formation of ordered mesoporous materials with hexagonal (*p6mm*) symmetry. Table 1 lists the lattice constants, BJH pore diameters, BET surface areas and pore wall thicknesses of the mesoporous products prepared with different TEOS/P104 ratios and synthesis temperatures.

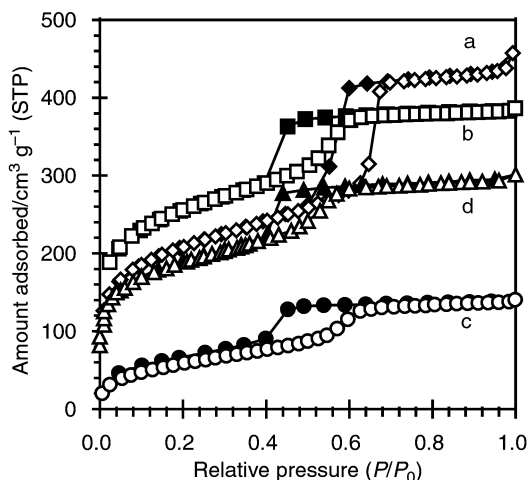
The adsorption isotherms of the mesoporous materials synthesized under various conditions using the triblock copolymer surfactant exhibited sharp increases in adsorption at  $P/P_0 < 0.1$  and  $P/P_0 = 0.4\text{--}0.7$  as shown in Fig. 1(a) and (b). The MS-1 material (Fig. 1(a)) showed a type IV isotherm according to the IUPAC classification,<sup>12</sup> which is typically observed for conventional mesoporous materials such as MCM-41<sup>1</sup> and SBA-15.<sup>10</sup> The first increase in adsorption at  $P/P_0 < 0.1$  is due to multilayer adsorption on the surface while the second increase at  $P/P_0 = 0.5\text{--}0.7$  arises from capillary condensation in the mesopores with nitrogen multilayers adsorbed on the inner surface.<sup>12</sup> The ratio of the first to second feature is higher for MS-6 (Fig. 1(b)) than for MS-1. This suggests that the MS-6 material not only has mesopores but also micropores, since a microporous material shows a type I isotherm,<sup>12</sup> which exhibits a sharp increase in adsorption at  $P/P_0 < 0.1$  and a plateau at  $P/P_0 > 0.1$ .

A comparative plot of the nitrogen adsorption isotherm<sup>7,12</sup> was used to confirm the microporosity and to estimate the micropore volume in the mesoporous materials, similarly to previous reports.<sup>8,9</sup> The t-plots were obtained by using a

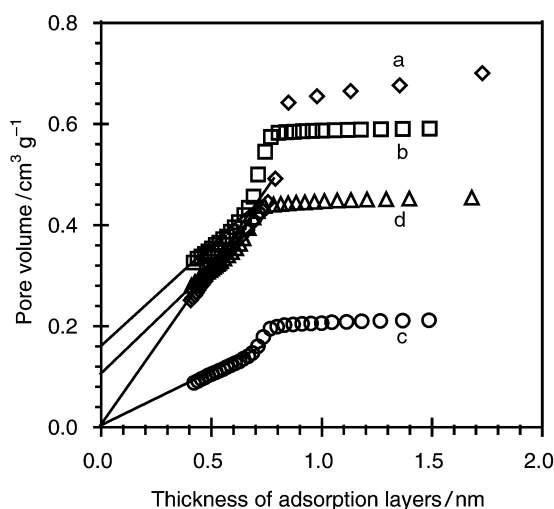
**Table 1** Physical properties of ordered mesoporous silicas prepared using different TEOS/P104 ratios and temperatures

Sample	TEOS/P104 molar ratio	Synthesis temperature/°C	Lattice constant <sup>a</sup> /nm	Pore diameter <sup>b</sup> /nm	Surface area <sup>c</sup> /m <sup>2</sup> g <sup>–1</sup>	Pore-wall thickness <sup>d</sup> /nm	Micropore volume <sup>e</sup> /cm <sup>3</sup> g <sup>–1</sup>
MS-1	60	100	10.4	6.4	646	4.0	~0
MS-2	60	80	9.9	5.8	565	4.1	0.07
MS-3	90	80	10.7	5.4	506	5.3	0.10
MS-4	120	100	10.4	5.8	619	4.6	0.08
MS-5	120	90	10.0	5.0	734	5.0	0.13
MS-6	120	80	10.8	4.7	401	6.2	0.15
MS-7	150	80	11.3	4.9	436	6.5	0.19
MS-6 <sup>f</sup>	120	80	10.7	5.0	249	5.7	~0
MS-6 <sup>g</sup>	120	80	10.3	5.1	410	5.2	0.11

<sup>a</sup>  $2d_{100}/1.732$ . <sup>b</sup> Calculated from the adsorption branch of the N<sub>2</sub> isotherm. <sup>c</sup> Calculated by the BET method. <sup>d</sup> Lattice constant–pore diameter. <sup>e</sup> Calculated by the t-plot method. <sup>f</sup> As-synthesized form of MS-6. <sup>g</sup> Surfactant-depleted MS-6 material after solvent extraction.



**Fig. 1** Nitrogen adsorption-desorption isotherms for mesoporous materials prepared under different conditions: (a) MS-1, (b) MS-6, (c) as-synthesized form of MS-6 and (d) surfactant-depleted MS-6 material after solvent extraction.



**Fig. 2** *t*-Plots of nitrogen adsorption isotherms for mesoporous materials: (a) MS-1, (b) MS-6, (c) as-synthesized form of MS-6 and (d) surfactant-depleted MS-6 material after solvent extraction.

reference isotherm obtained for a non-porous silica described in a previous report.<sup>13</sup> The *t*-plots for MS-1 and MS-6 are shown in Fig. 2(a) and (b).

The *t*-plot for MS-1 gave a straight line at  $t = 0.40\text{--}0.75$  nm ( $t$  = thickness of adsorbed layer) and the extrapolation line went through the origin, indicating that the MS-1 material has no micropores. Although the MS-6 material also showed a straight line in the same *t*-value region in the *t*-plot, the extrapolation line cut the *y*-axis at  $0.15\text{ cm}^3\text{ g}^{-1}$ . This indicates that the MS-6 material has a micropore volume of  $0.15\text{ cm}^3\text{ g}^{-1}$  with a pore radius of  $<0.4$  nm. A *t*-plot calculation with the same reference isotherm as for the nitrogen adsorption isotherm of the SBA-15 described in the previous report<sup>10</sup> revealed the absence of microporosity.

The microporosity in the mesoporous materials changed systematically with variation of the synthesis temperature and the TEOS/P104 ratio, as shown in Table 1. Microporosity was not observed for the mesoporous material (MS-1) prepared with a TEOS/P104 molar ratio of 60 and a temperature of  $100\text{ }^\circ\text{C}$ . A decrease in the temperature from  $100$  to  $80\text{ }^\circ\text{C}$  with a constant TEOS/P104 molar ratio of 120 increased the micropore volume from  $0.08$  to  $0.15\text{ cm}^3\text{ g}^{-1}$ . An increase in the TEOS/P104 molar ratio from 60 to 150 with a constant temperature of  $80\text{ }^\circ\text{C}$  also increased the micropore volume from  $0.10$  to  $0.19\text{ cm}^3\text{ g}^{-1}$ . These are the first results on the systematic control of

microporosity for SBA-15. The increase in microporosity was accompanied by enlargement of the pore-wall thickness (Table 1). The density of micropores in the walls, obtained by dividing the micropore volume by the pore-wall volume, increased with enlargement of the pore walls. The generation of microporosity can be explained by penetration of hydrophilic poly(ethylene oxide) chains of triblock copolymer in the silica wall, as reported by Kruk *et al.*<sup>9</sup> who also suggested that the micropore volume should decrease at elevated temperatures, owing to dehydration of ethylene oxide blocks.<sup>9</sup> The result obtained in this study clearly shows this relationship between the micropore volume and the synthesis temperature. An increase in TEOS/surfactant ratio in the starting mixture is also found to be an effective method to increase the micropore volume of SBA-15. The TEOS/surfactant ratio affects the siloxane network structure in the pore walls, and thereby results in changes of microporosity. There are many variations in the siloxane network structure in a silica gel, which give different pore sizes and porosity.<sup>14</sup> The systematic change of the micropore volume and pore-wall thickness of the mesoporous materials also indicates the existence of micropores within the mesopore walls.

The nitrogen adsorption isotherm and *t*-plot for the as-synthesized MS-6 material are shown in Fig. 1(c) and Fig. 2(c), respectively. They indicate that the as-synthesized MS-6 material contains surfactant in the mesopore spaces (73% occupation of the mesopore space) with no microporosity. The as-synthesized MS-6 material (1 g) was treated with an ethanol solution ( $30\text{ cm}^3$ ) at room temperature three times to remove the surfactant. The treated MS-6 material showed a micropore volume of  $0.11\text{ cm}^3\text{ g}^{-1}$ , which was confirmed by the *t*-plot (Fig. 2(d)) of the nitrogen adsorption isotherm (Fig. 1(d)). The removal of the surfactant from the mesopore spaces made it possible for nitrogen molecules to gain access to the micropores within the mesopore walls. This strongly suggests that micropores exist within the mesopore walls, and that MS-6 is not a physical mixture of mesoporous and microporous materials.

In conclusion, *t*-plot analysis of nitrogen adsorption isotherms strongly suggests the formation of micropores within the mesopore walls of mesoporous materials. The microporosity can be controlled *via* the synthesis conditions. A novel porous material possessing an ideal bimodal pore system should exhibit high performance catalysis and adsorption properties.

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