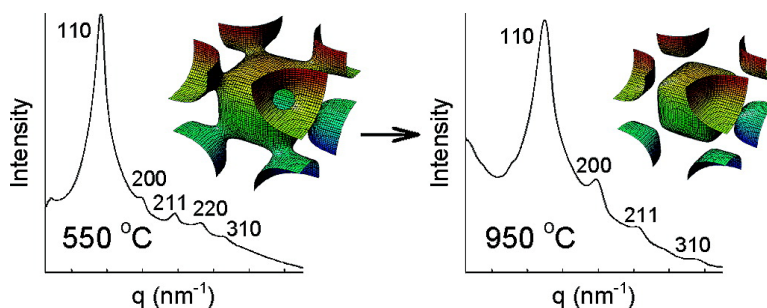


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Thermally Induced Transition between Open and Closed Spherical Pores in Ordered Mesoporous Silicas

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Mesoporous materials are highly promising in electronics industry as low-dielectric-constant (low- k) on-chip insulating media.^{1–3} In these applications, materials with closed (isolated) pores are preferred.^{1,3} The synthesis of ordered mesoporous silicas and organosilicas with closed spherical mesopores of diameters 5–30 nm has been reported using poly(ethylene oxide)-polystyrene (PEO-PS) copolymer micelles as templates (porogens).^{3–6} Herein, it is demonstrated that the formation of closed mesopores can be achieved through a simple thermal treatment in widely known ordered mesoporous silicas (OMSs) templated by readily available poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) Pluronic block copolymers (e.g., Pluronic F127).^{7–10} Our results indicated that the thermal closure is likely to be a general property of copolymer-templated OMSs with spherical mesopores, provided that the pore entrance size is significantly smaller than the pore cage diameter.

Recently, the synthesis of large-pore FDU-12 (LP-FDU-12) silica¹¹ with $Fm\bar{3}m$ (face-centered cubic, fcc) structure of connected spherical mesopores was reported. Our subsequent study showed¹² that LP-FDU-12 synthesized exclusively at low temperature (e.g., 15 °C), and some samples obtained after heating of the synthesis mixture at 100 °C, exhibited low, sometimes negligible, N₂ adsorption capacity at –196 °C after the removal of copolymer template via calcination for 5 h at 550 °C under air (see Figure 1). At first, the lack of accessible porosity seemed to indicate a collapse of the mesopore structure during calcination, but such a collapse was unlikely on the basis of earlier studies of thermal stability of OMSs.^{13,14} Therefore, the existence of closed pores was envisioned and subsequently confirmed as follows. The decrease in calcination temperature to 450 °C afforded silica with pore size of ~15 nm and appreciable adsorption capacity, whereas the increase to 640 °C reduced the adsorption capacity to virtually zero (see Figure 1 and Supporting Table S1), revealing a strong dependence of adsorption properties on the calcination temperature. Despite the differences in the adsorption capacity, all the samples exhibited similarly intense, well-resolved small-angle X-ray scattering (SAXS) patterns that can be indexed on the $Fm\bar{3}m$ lattice (see Figure 2). Since in the case of OMSs, SAXS patterns arise from periodic arrangements of mesopores, it is clear that the pore structure did not collapse at 550–640 °C, despite the fact that it became largely or completely inaccessible to N₂, which implies the pore entrance size below 0.35 nm.¹⁵ Transmission electron microscopy (TEM) images confirmed the retention of ordered pore structure for the sample calcined at 640 °C (see Supporting Information Figure S1). The fact that the unit-cell size appreciably decreased with the increase in calcination temperature (see Supporting Information Table S1) suggests that elevated calcination temperatures led to

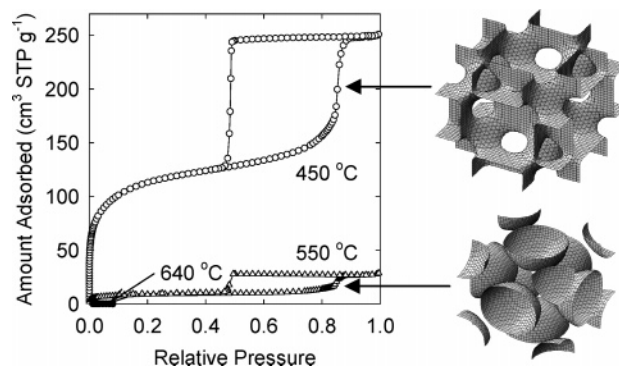


Figure 1. N₂ adsorption isotherms at –196 °C for LP-FDU-12 silicas of fcc structure with open mesopores (after calcination at 450 °C) and closed mesopores (after calcination at 550–640 °C). The sample was synthesized at 14 °C and heated in the synthesis mixture at 100 °C for 1 d.

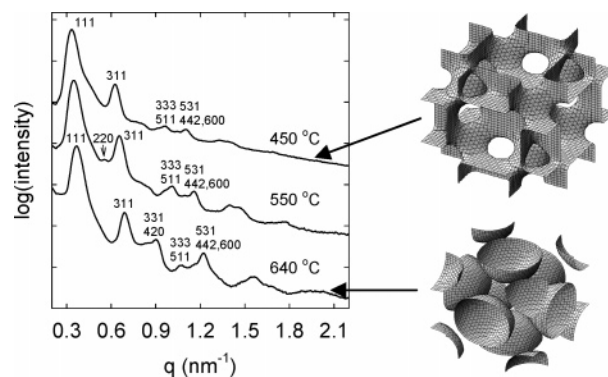


Figure 2. Small-angle X-ray scattering patterns for LP-FDU-12 silicas of fcc structure with open mesopores (after calcination at 450 °C) and closed mesopores (after calcination at 550–640 °C).

the fusion of the pore entrances, or at least, to reduction of their diameter below 0.35 nm, rendering effectively isolated spherical mesopores. Pore blocking experiments with organosilanes¹⁵ indicated that LP-FDU-12 calcined at 450 °C exhibited pore entrances (i.e., passages between adjacent mesopores) of diameters (in the narrowest point) primarily below 1.9 nm. The length of the entrances can be estimated as ~6 nm (see Supporting Information). A combination of prominent structural shrinkage with small diameter and appreciable length of pore entrances was likely to facilitate the transition between open and closed (isolated) pores.

Our study of LP-FDU-12 gave us a reason to expect that the thermally induced transition between open and closed mesopores is a general feature of OMSs with spherical pores¹⁶ connected with one another through entrances of sufficiently small size (relative to the pore cage size). To verify this contention, our study was extended on SBA-16 silica with $Im\bar{3}m$ symmetry (body-centered

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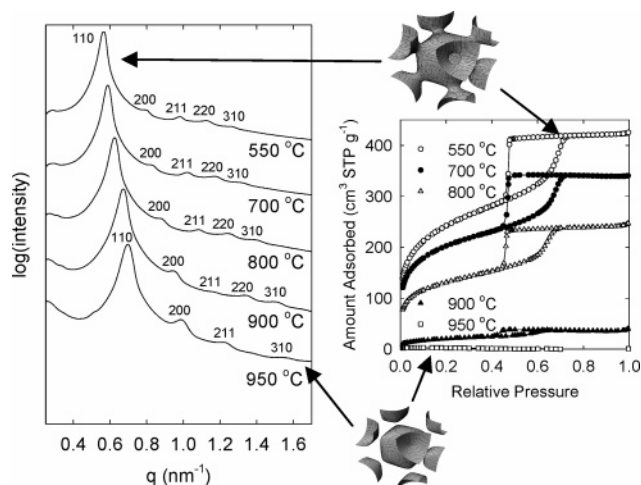


Figure 3. Small-angle X-ray scattering patterns (left) and nitrogen adsorption isotherms at $-196\text{ }^{\circ}\text{C}$ (right) for SBA-16 silicas of bcc structure with open mesopores (after calcination at $550\text{--}800\text{ }^{\circ}\text{C}$) and closed mesopores (after calcination at $900\text{--}950\text{ }^{\circ}\text{C}$).

cubic, bcc, structure),⁸ which is the most extensively studied copolymer-templated OMS with spherical pores.¹⁷ The synthesis of SBA-16 was carried out as reported by Kleitz et al.^{18,19} and the hydrothermal treatment for 1 day at $100\text{ }^{\circ}\text{C}$ was performed to achieve an appreciable adsorption capacity without overly increasing the pore entrance size.²⁰ SAXS patterns and N_2 adsorption isotherms for SBA-16 calcined in air at temperatures from 550 to $950\text{ }^{\circ}\text{C}$ for 5 h are shown in Figure 3. The SAXS patterns had similar intensity independently of the calcination temperature and could be indexed on $Im\bar{3}m$ lattice. The shrinkage upon calcination was prominent (up to 27% for calcination at $950\text{ }^{\circ}\text{C}$). The pore size of samples calcined at $550\text{--}800\text{ }^{\circ}\text{C}$ decreased with temperature (following the unit-cell size changes, as expected), but in all cases, the adsorption capacity was appreciable (see Figure 3 and Table S1). The gas uptake was significantly lowered by calcination at $900\text{ }^{\circ}\text{C}$ and eventually reduced to nearly zero after heating at $950\text{ }^{\circ}\text{C}$. Clearly, the pore closure commenced at $900\text{ }^{\circ}\text{C}$, and was completed at $950\text{ }^{\circ}\text{C}$, leaving the highly ordered porous structure intact (as confirmed by TEM, see Figures S2, S3). Like LP-FDU-12, SBA-16 has thick walls (pore entrance length of $\sim 4\text{ nm}$, see Supporting Information), which may facilitate the pore closure.

Our results indicate that the thermal transition between open and effectively closed (isolated) spherical mesopores is a common phenomenon for block-copolymer-templated OMSs with different structures. It resembles the thermally induced closure of connections between cylindrical mesopores observed for SBA-15 silicas.²¹ Requirements for the formation of isolated spherical pores via the surfactant templating remain to be fully elucidated, but they are likely to include (i) a large degree of shrinkage upon calcination, (ii) a small entrance size relative to the cage diameter, and (iii) an appreciable length of pore entrance passages. The formation of closed mesopores in silicas and organosilicas templated by PEO-PS copolymers was reported earlier^{3–6} and related to the shrinkage of PS domains that would cause a retraction of PEO chains from the pore walls with concomitant pore closure.³ Our study suggests that the pore closure is a more general phenomenon. In particular, we observed the thermally induced pore closure of cage-like pores for copolymer-templated²² periodic mesoporous organosilicas (PMOs)^{23–25} with organic groups in the framework (see Figures S4, S5, and pertinent discussion). It is yet to be seen

whether this structural transition occurs in oligomeric-templated⁸ and alkylammonium-surfactant-templated²⁶ silicas and organosilicas²³ with spherical mesopores. Another important issue to be explored is the control of the pore closure temperature via the adjustment of synthesis conditions. The results reported herein and their envisioned extensions open new opportunities in development of closed-pore materials that will meet the stringent processing demands for low- k materials in electronics.

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Supporting Information Available: Five figures showing TEM images, SAXS patterns, and N_2 adsorption isotherms; one table with structural data; description of synthesis of methylene PMO; supplementary discussion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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