# Pore Expansion in Mesoporous Silicas Using Supercritical Carbon Dioxide

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*Received September 19, 2003. Revised Manuscript Received November 21, 2003*

In this paper we report the controlled expansion of pores within mesoporous silicas using supercritical carbon dioxide (sc-$CO_2$). Our method uses the tunable density of sc-$CO_2$ to induce the controlled swelling of the triblock copolymer surfactant templating agents, P123 ($PEO_{20}$-$PPO_{69}PEO_{20}$) and P85 ($PEO_{26}PPO_{39}PEO_{26}$). This swelling process ultimately leads to the control of pore diameters and hexagonal spacing within the mesoporous silicas. At pressures of approximately 482 bar, pore diameters of up to 100 Å can be achieved, representing a pore expansion of 54% compared to the conventionally formed mesoporous silicas. Powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), and nitrogen adsorption techniques were used to establish pore diameters, silica wall widths, and the hexagonal packing of the pores within the sc-$CO_2$ treated mesoporous silicas. The sc-$CO_2$ was shown not to effect the hexagonal ordering of the silica, a distinct advantage over conventional pore-swelling techniques.

## Introduction

Mesoporous materials have maintained the interest of the material science community since their discovery by researchers in the Mobil Corporation in 1992.[1,2] Their potential uses have been widely documented and they have found actual applications in molecular and protein separation,[3] catalysis,[4] and ultralow dielectric devices.[5] More recently, mesoporous materials have been used as hosts for a wide variety of metals,[6−8] metal oxides,[9,10] carbon nanotubes,[11] and quantum-confined nanowires.[9,12,13] In particular, Lyons et al.[14] reported that the optical properties of silicon nanowires encapsulated within mesoporous silicas can be tuned by controlling the pore size of the host matrix.

Many methods have been reported for controlling the periodic unit size and pore size of mesoporous materials.[15−17] The most commonly used technique is the introduction of a swelling agent into the structure-directing template. Commonly used swelling agents include the large organic hydrocarbons such as dodecane,[15] 1,3,5-trimethylbenzene,[18] triisopropylbenzene,[19] and tertiary amines.[16] The introduction of these agents has been shown to lead to pore expansion by up to 30%, but loss of long-range order of the mesoporous structure is commonly observed. Smarsly et al.[20] and Ryan et al.[21] recently reported a method of mixing surfactant blends to tailor the pore size of mesoporous silicas, showing Angström-level control over the pore size. However, the longest block copolymer surfactant chain used governs the largest pore size obtainable with this method.

Near critical and supercritical carbon dioxide (sc-$CO_2$) has emerged as an important solvent in industrial applications for the replacement of some organic solvents.[22] Several researchers[23−25] have recently exploited sc-$CO_2$ in the postsynthesis treatment of mesoporous

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10.1021/cm034882n CCC: $27.50 
Published on Web 01/10/2004

silica. They reported that modified $CO_2$ could be used to extract the surfactant template from the uncalcined mesoporous silica, thus facilitating in the recycling of the surfactant. In the polymer sciences, sc-$CO_2$ has found many uses for impregnation,[26] preparation,[27,28] and swelling.[29] Cooper et al.[30,31] have recently demonstrated the use of sc-$CO_2$ as a "pressure-adjustable" porogenic solvent in the production of porous poly(methacrylate) monoliths. Thus, properties such as surface area and pore diameters of porous polymers can be manipulated through $CO_2$ pressure changes. Johnston and co-workers[32] have also used $CO_2$ to swell thin films of poly(dimethylsiloxane) on silicon substrates. Film swelling was measured using in situ high-pressure ellipsometry techniques.

In this paper, we report for the first time pore size expansion in mesoporous silicas using sc-$CO_2$. The ordering of the mesoporous silica is shown to be unaffected by the presence of sc-$CO_2$, a distinct advantage over traditional pore-swelling techniques where unwanted modification and even extinction of pore ordering is commonly observed.[33]

## Experimental Section

Hexagonal mesoporous silicas were prepared using a method based on one described by Attard and Goltner,[34,35] that is, the hydrolysis of tetramethoxysilane (TMOS) in the presence of a poly(ethylene oxide) (PEO)−polypropylene oxide (PPO) triblock copolymer surfactant P123 ($PEO_{20}PPO_{69}PEO_{20}$) supplied by Uniquema, Belgium. In a typical synthesis P123 (5.0 g) was dissolved in TMOS (9.0 g, 0.0559 mol) to which an aqueous solution of HCl (5.0 g, 0.5 M) was added to give a surfactant concentration of 50 wt %. Methanol generated during the reaction was removed on a rotary film evaporator at 40 °C. The resulting viscous gel was then divided into two parts. One batch was loaded into a 50-mL stainless steel cell heated to 40 °C and was pressurized with $CO_2$ to the desired pressure using a 260-mL Isco syringe pump (Lincoln, NE). The pressures used were varied from 138 to 482 bar. The system was left to stand for 1 week. The second sample was aged at 40 °C (±2 °C) for 1 week in air. Both batches were subjected to identical thermal treatments (24 h at 450 °C). Powder X-ray diffraction (PXRD) profiles were recorded on a Philips X'Pert diffractometer, equipped with a Cu Kα radiation source and accelerator detector. Height and reflected stoller slits of 0.2° were used with a programmable divergent slit to maintain a 10-mm footprint at the sample. Sample heights were determined at $\theta = 2\theta = 0$ at the point when the sample reduced the beam intensity by 50%. Surface area of the calcined mesoporous silicas synthesized were measured using nitrogen Brunauer−Emmett−Teller (BET)[36] isotherms on a Micromeritics Gemini 2375 volumetric analyzer. Each sample was degassed for 12 h at 200 °C prior to a BET measurement. The average pore size distribution of the calcined silicas was calculated based on the Barrett−Joyner−Halanda (BJH) model[37] from a 30-point BET surface area plot. All the mesoporous silicas examined exhibited a Type IV adsorption isotherm typical of mesoporous solids.[38] In all cases, very little hysteresis was observed in adsorption and desorption isotherms. Desorption isotherms were used to calculate the pore diameters. An Hitachi H7000 (0.5-nm resolution) electron microscope operating with a 100-kV accelerating voltage was used for transmission electron microscopy (TEM). Samples were dispersed in chloroform, and a drop of the mixture was placed on a carbon-coated copper TEM grid.

**Warning:** High-pressure equipment such as that required for the experiments described in this paper should be equipped with a relief valve and/or a rupture disk to minimize the risk of personal injury.

## Results and Discussion

PXRD data of the treated (i.e., samples hydrolyzed under a pressurized $CO_2$ atmosphere) and untreated (i.e., hydrolyzed under normal conditions) silicas are depicted in Figure 1a. In each case, three peaks could be readily indexed to the ⟨100⟩, ⟨110⟩, and ⟨200⟩ hexagonal reflections common for mesoporous silicas.[39] The presence of these three well-defined peaks indicates that pore ordering is not extinguished due to the $CO_2$ expanding process. Figure 1b shows the position of the ⟨100⟩ peaks, from which pore-to-pore distances were calculated, plotted as a function of pressure. The inset in Figure 1 clearly shows how the hexagonal *d* spacing of the calcined silica varies as a function of $CO_2$ pressure. For example, the position of the intense ⟨100⟩ peak for mesoporous silica hydrolyzed in $CO_2$ at 206 bar reflects a *d* spacing of 124 Å compared to untreated silica, which has a *d* spacing of 110 Å. Figure 1c displays the TEM image of mesoporous silica treated with sc-$CO_2$ at 206 bar. The pore diameter (from BJH desorption isotherms) was calculated to be 77 Å (±1 Å). The micrograph displays excellent long-range ordering of the pores, once again indicating that pore ordering is retained. Typical ordering was of the order of at least 5 $\mu$m.

The variation in the pore diameter of mesoporous silica as a function of $CO_2$ pressure during the silica hydrolysis process is shown as the solid line in Figure 2a. As the $CO_2$ pressure increased, the pore diameter increases in an essentially linear fashion over the pressure range studied, that is, 138−482 bar. Untreated mesoporous silica templated from P123 displayed a mean pore diameter equal to 65 Å while the mesoporous silica hydrolyzed under a $CO_2$ pressure of 482 bar displays a mean pore diameter of 100 Å (±1 Å). The increase in pore diameter represents a pore expansion of 54%. To our knowledge, this represents the largest

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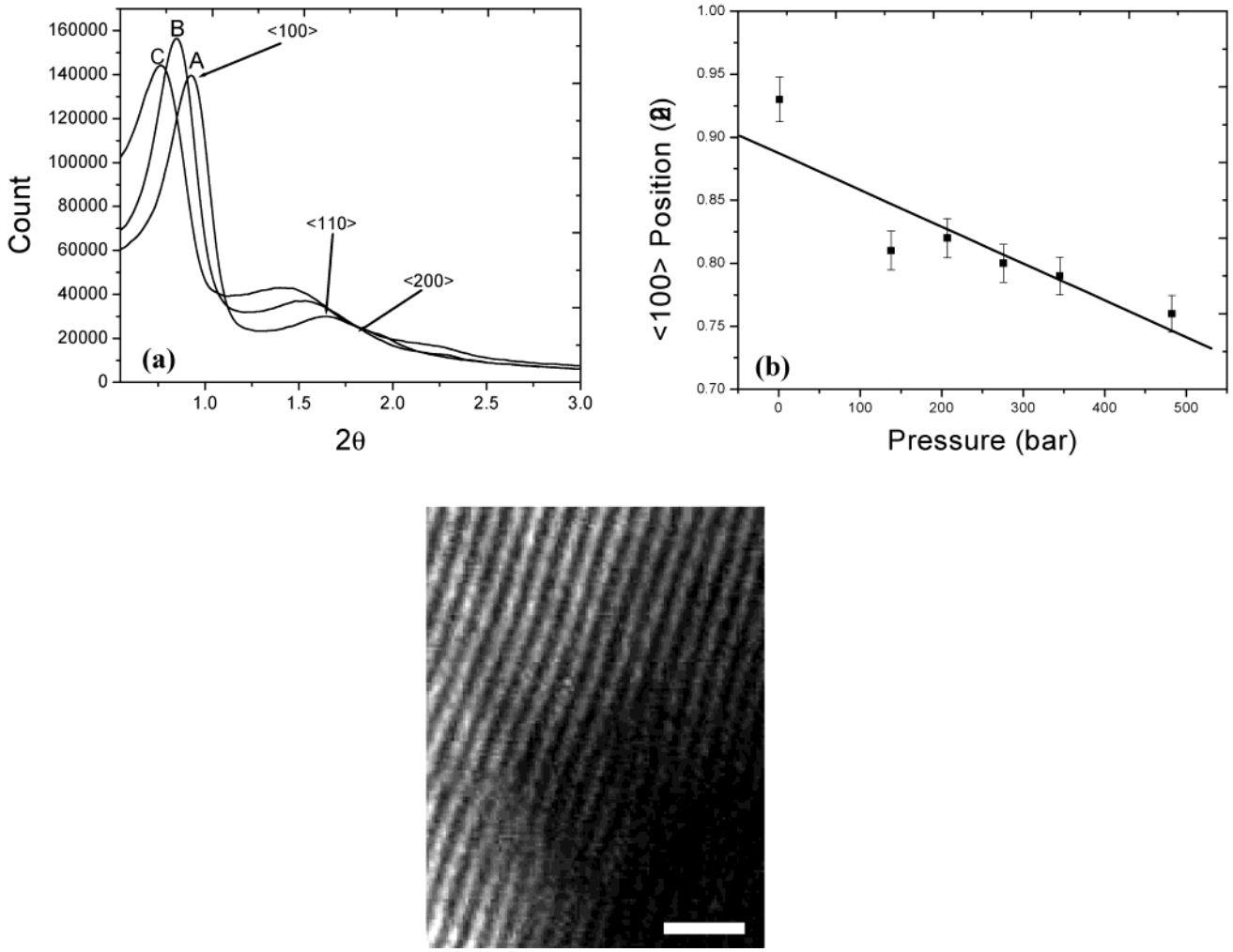


**Figure 1.** (a) PXRD graphs of treated (B and C) and untreated (A) samples (b) demonstrate the decrease in the ⟨100⟩ peak position with increasing pressure and (c) TEM micrograph of sample B (204 bar). Scale bar = 500 Å.

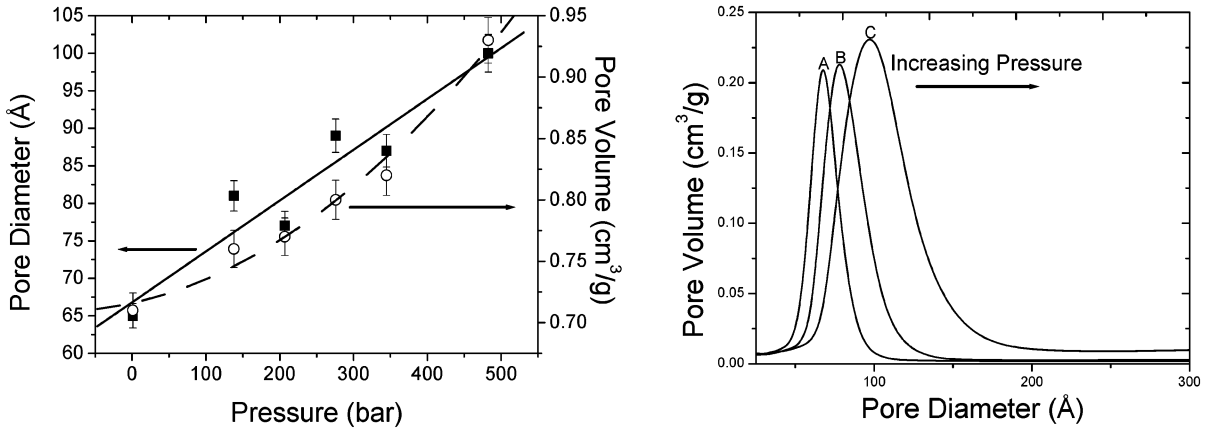


**Figure 2.** (a) Variations due to pressure increases: pore diameter (closed square, straight line) and pore volume (open circle, dashed line) and (b) the pore size distribution of treated and untreated samples: (A) 1 bar, (B) 206 bar, and (C) 482 bar.

pore expansion of hexagonal mesoporous silica using a swelling technique while still retaining pore order. Also represented in Figure 2a, as a dashed line, is the variation of pore volume with $CO_2$ pressure. As expected, an increase in the pore volume with increasing $CO_2$ pressure is observed. Figure 2b shows the BJH pore diameter profiles for treated and untreated mesoporous silica. All profiles illustrate narrow pore size distributions (typically of the order of 15 Å at half-height width). Table 1 gives a list of the physiochemical and textural properties of all treated and untreated mesoporous silicas. An interesting feature that is noticeable here is the thinning of the pore wall with increasing $CO_2$ pressure. The percentage micropore volume cannot be correlated simply to $CO_2$ pressure, suggesting that micropore volume is a function of the experimental procedure.

However, the most convincing evidence for retention of pore ordering can be seen in Figure 3. Distinctive Type IV nitrogen adsorption isotherms, characteristic

**Table 1. Physiochemical and Textural Properties of Mesoporous Silicas[a]**

| pressure (bar) | $\rho CO_2$ (g cm$^{-3}$) | ⟨100⟩ ($2\theta$) | pore (Å) | pore volume (cm$^3$ g$^{-1}$) | center (Å) | wall (Å) | micropore volume (cm$^3$ g$^{-1}$) | % micropore volume |
|---|---|---|---|---|---|---|---|---|
| 0.96 | 0 | 0.93 | 65 | 0.71 | 110 | 50 | 0.036 | 5.07 |
| 137.90 | 0.78 | 0.81 | 81 | 0.76 | 126 | 45 | 0.061 | 8.03 |
| 206.84 | 0.86 | 0.82 | 77 | 0.77 | 124 | 47 | 0.059 | 7.66 |
| 275.79 | 0.90 | 0.80 | 89 | 0.80 | 127 | 38 | 0.064 | 8.00 |
| 344.73 | 0.94 | 0.79 | 87 | 0.82 | 129 | 42 | 0.081 | 9.87 |
| 482.63 | 0.99 | 0.76 | 100 | 0.93 | 134 | 34 | 0.075 | 8.06 |

[a] Key: Values are based on measurements from three sample batches. Pore = mean pore diameter (±1 Å); center = mean center-to-center hexagonal pore spacing (±1 Å); wall = mean pore wall thickness (±1 Å); ⟨100⟩ = mean ⟨100⟩ peak position (±0.01° $2\theta$).

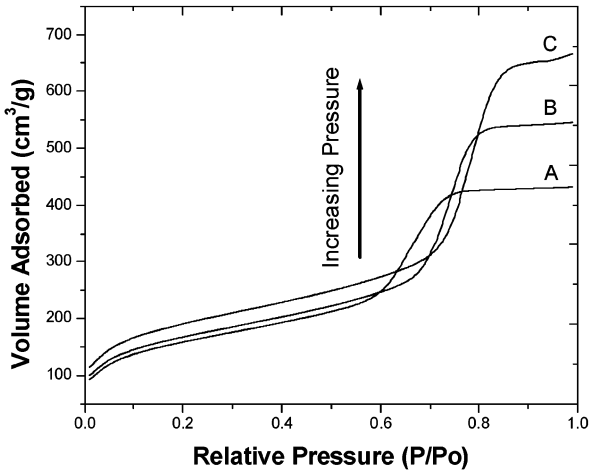


**Figure 3.** Nitrogen adsorption isotherms at 77.4 K for treated and untreated samples: (a) 1 bar, (b) 206 bar, and (c) 482 bar.

of a well-ordered hexagonal array of pores, is observed for treated samples. Qualitatively, the step in the isotherms reflects a narrow and uniform distribution of the pore size.

$CO_2$ swelling of block copolymers has been studied previously by Zhang and Lemert.[40] The authors reported a volume change of up to 25% for the polymers poly(methyl acrylate) and poly(styrene-methyl methacrylate) block copolymer at a pressure of approximately 110 bar. It was shown that the swelling of the polymers was density-dependent. While $CO_2$ is a very poor solvent for most high molecular weight polymers under readily achievable conditions (<100 °C and <1000 bar), the solubility of $CO_2$ in many polymers is substantial.[41] As the density of $CO_2$ increases, the sorption into the polymer increases, thereby swelling the polymer. In our case, swelling of the pores is also shown to be density-dependent; as the pressure of the $CO_2$ is increased, there is increased adsorption into the polymer core of the surfactant micelle, causing expansion and hence an increased pore diameter. The nature of the $CO_2$–surfactant interaction is currently under investigation and other triblock copolymer templates have also been subjected to this swelling technique. Mesoporous silica, templated from the triblock copolymer P85 ($PEO_{26}$-$PPO_{39}PEO_{26}$), shows similar trends in pore expansion when subjected to $CO_2$ swelling. The percentage expansion for mesoporous silica hydrolyzed under a pressure of 300 bar is approximately 20%.

## Conclusions

We have described a unique method for tailoring the pore size of hexagonal mesoporous silica using sc-$CO_2$ as a swelling agent during the silica hydrolysis process. In effect, our method involves an environmentally friendly route for tailoring mesoporous materials without the need for additional hydrocarbon swelling agents, or the use of complex surfactant systems. Additionally, unlike other swelling processes no loss of mesopore ordering was noticed for the expanded silica as determined by XRD and TEM analysis. This expansion method is a distinct advantage over the use of organic swelling agents. The ability to control the pore diameter of these mesoporous substrates increases their potential uses as molecular sieves for separations, catalysts, and nanowire hosts.

**Acknowledgment.** We acknowledge financial support from Enterprise Ireland. We wish to thank T.A.C. for useful discussions.

CM034882N

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