



Mechanical and hydrothermal stability of mesoporous materials at extreme conditions



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ABSTRACT

In situ SAXS measurements were made on periodic mesoporous carbon and silica-based materials as a function of pressure and temperature and in water to supercritical conditions. Our data show that periodic mesoporous silica-based materials exhibit substantial mechanical strength. The pore structure, size and related mesoscale properties appear to directly impact the mechanical response of silica-based materials to high pressures and temperatures. Our results indicate that hydrolysis does not seem to be responsible for the mechanical collapse of the pore structure of silica-based mesoporous materials under high pressure conditions. SBA-15 type mesoporous carbon exhibits excellent hydrothermal stability under extreme conditions. The mesostructure of FDU-12 silica is irreversibly disordered after extreme hydrothermal exposure in a manner consistent with H₂O dissociation reactions causing topological alteration of the silicate network.

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1. Introduction

Periodic mesoporous materials show promise for chemical and energy applications due to their large surface area and pore volume, molecular shape and size selectivity, and tunable adsorption properties [1–7]. A critical requirement of porous materials for use in heterogeneous catalysis involving cracking of petrochemicals, supercritical water biomass gasification and other extreme-environment energy applications, is sufficient thermal, hydrothermal and mechanical stability. The development of silica-based materials having periodic pores on the mesoscale (2–50 nm pore size) has generated considerable interest in the synthesis of highly stable mesoporous catalysts having superior mass transport properties compared to microporous zeolites (<2 nm pore size) [1,8]. However, because of the amorphous pore walls, periodic mesoporous silica materials do not exhibit the hydrothermal stability that is required for such applications. This has motivated interest in the development of hydrothermally stable periodic mesoporous materials for catalytic applications.

Nominal improvement of hydrothermal stability of silica-based periodic mesoporous materials to low temperatures and pressures

(≤ 100 °C and 0.1 MPa) has been achieved using zeolite seed supports [9], aluminosilicates in place of silicates [10], silylation [11] and low-temperature hydrothermal treatment of the pore walls [12,13]. The low-temperature hydrothermal stability of SBA-15 mesoporous silica was also improved using carbon coating of the pore walls [14]. The most promising efforts at developing silica-based mesostructured materials having exceptional hydrothermal stability involve using high pressures and temperatures [15,16]. Whereas this method was successful in causing crystallization of pore walls while preserving pore structure, the role of the mesostructure in requiring lower temperature conditions for amorphous-to-crystalline phase conversion in mesoporous vs bulk materials has yet to be elucidated.

Previous studies of the hydrothermal stability of periodic mesoporous materials (solely silica-based) are limited to low temperatures (≤ 100 °C) and are ex situ in nature, i.e., made prior to and after hydrothermal treatment. Because the physical and chemical properties of supercritical water are dramatically different (e.g., the solubility of organics is substantially higher) than those of water under ambient conditions, in situ studies are vital for developing insight into the mechanisms responsible for maintaining hydrothermal stability of periodic mesoporous materials to extreme conditions. In addition to potential uses in extreme hydrothermal environments, silica-based periodic mesoporous materials

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show promise for applications where the desired properties include having light weight and high mechanical stability. In situ small-angle X-ray scattering (SAXS) measurements made under high pressures (to 12 GPa) revealed that MCM-41 silica and MCM-41 silica/surfactant composite exhibit high mechanical stability [17,18]. The authors conjectured that the periodic nanoscale architecture and hydrolysis of siloxane bonds have a direct bearing on the mechanical stability properties of mesoporous materials. However, these hypotheses have yet to be fully tested. Synchrotron SAXS is ideally suited for such studies because it enables monitoring of the meso-structure of the pores of mesoporous materials in a diamond anvil cell under high pressures and temperatures or in extreme hydrothermal environments. Here we present a first comprehensive in situ synchrotron SAXS study of mesoporous silica-based and carbon materials under high pressure and temperature conditions, with and without the presence of water.

2. Experimental

2.1. Synthesis of periodic mesoporous FDU-12 silica

Commercially available triblock copolymer Pluronic F127 (BASF) and tetraethyl orthosilicate (Sigma–Aldrich) were used in the synthesis of the mesoporous materials. Synthesis of periodic mesoporous FDU-12 silica was made using Pluronic F127 (EO₁₀₆PO₇₀EO₁₀₆) as a structure directing agent and tetraethyl orthosilicate (TEOS) as a silica source according to procedures described in the literature [19]. In the first step of FDU-12 synthesis, 0.5 g of Pluronic F127 was dissolved in 30 ml of 2.0 M HCl aqueous solution. This was followed by magnetic stirring until complete dissolution of the polymer was achieved in the solution at 15 °C. In the next step of synthesis, 0.60 g of mesitylene and 2.5 g of KCl were added and, after waiting for 2 h, 2.08 g of TEOS was added to the mixture. The mixture was then stirred thoroughly for 1 day. The aqueous solution/mixture was hydrothermally treated at 100 °C for 1 day. The resulting FDU-12 material was subsequently collected by centrifuging and then washed with deionized water and dried in air. The as-synthesized dried material was then calcined at 550 °C for 5 h under air (heating rate 2 °C/min). A representative TEM image of the as-synthesized FDU-12 material (i.e., before calcination) is shown in (Appendix A Supplementary Fig. S1a).

2.2. Synthesis of periodic mesoporous SBA-16/carbon composite

The periodic mesoporous silica SBA-16 silica was synthesized using Pluronic F127 block copolymer as a structure directing agent and TEOS as a silica source according to procedures outlined elsewhere [20]. A quantity of 1.00 g of F127 was thoroughly dissolved in an aqueous solution prepared from 48 g of distilled water and 2.1 g of HCl (35 wt.%) by magnetic stirring at 45 °C. This was followed by adding 3.1 g of butanol to the reaction mixture. One hour after adding butanol, 4.8 g of TEOS was added to the reaction mixture which was then stirred for 1 day. Next, the reaction mixture was hydrothermally treated for 1 day at 100 °C. The resulting material was collected using a centrifuge, washed with deionized water, and then dried in air. The as-synthesized dried material was then calcined at 550 °C for 5 h under air (heating rate 2 °C/min). The calcined SBA-16 silica was used to synthesize SBA-16/C nanocomposite. This resin was finally carbonized. Ground mesophase pitch (Mitsubishi Gas and Chemical) was sonicated with calcined SBA-16 silica dispersed in ethanol. The whole mixture was then stirred at ~40 °C overnight to remove the solvent completely. The solid mixture was then heated from room temperature to 500 °C (heating rate 5 °C/min) and kept for 8 h under nitrogen

atmosphere. Then, the temperature was raised to 850 °C (heating rate 5 °C/min) for 4 h to obtain a SBA-16/C nanocomposite. The carbon filler in SBA-16/C is an amorphous material with sp² hybridized carbon atoms. A representative TEM image of the as-synthesized SBA-16/C nanocomposite is shown in (Appendix A Supplementary Fig. S1b).

2.3. Synthesis of SBA-15 type periodic mesoporous carbon

The SBA-15 type periodic mesoporous carbon was synthesized using Pluronic F127 block copolymer as a structure directing agent and resorcinol and formaldehyde as a carbon source following published procedures [21]. A quantity of 1.0 g of Pluronic F127 and 1.0 g of resorcinol were dissolved in absolute ethanol (4.5 ml) in a plastic vial followed by magnetic stirring at room temperature. After 1 h, 4.5 ml of 3.0 M HCl solution was added to the reaction mixture. To this mixture, 1.3 g of formaldehyde (37 wt.%) solution was added after 1 h followed by stirring for 10 min. Then, the whole reaction mixture was centrifuged to collect the polymeric gel and the supernatant was discarded. A 1:1 mixture of ethanol and tetrahydrofuran (2 ml) was added to the polymeric gel followed by stirring for 30 min. The gel mixture was then aged overnight under ambient conditions and then cured at 100 °C for 2 days. Finally, the material was carbonized under nitrogen atmosphere by heating from room temperature to 400 °C (heating rate 1 °C/min) for 2 h, followed by raising the temperature to 850 °C (heating rate 5 °C/min) for 3 h to obtain mesoporous carbon. A representative TEM image of the as-synthesized SBA-15 type carbon is shown in (Appendix A Supplementary Fig. S1c).

2.4. In situ SAXS measurements

The in situ SAXS measurements were made at the Cornell's High Energy Synchrotron Source, beam line B1. A monochromatic X-ray beam, with energy of 23.22 keV, was collimated using an aluminum collimator to ~100 μm spot size at the sample. The SAXS images were collected using a large area Mar345 detector having a maximum detectable 2θ of ~2°. The Mar345 detector has a total pixel count of 3450 × 3450, with each pixel extending over an area of 100 μm × 100 μm. The detector was situated approximately 2.3 m downstream away from the sample. The 2D diffraction images from the Mar345 detectors were integrated using Fit2D software [22] yielding intensity vs. 2θ (chi) plots. The unit cell parameters of the pore structure of the mesostructured silica and carbon samples were obtained using the chi plots. Ag-behanate was used to calibrate the SAXS images.

2.4.1. In situ SAXS measurements at high pressures

For high-pressure SAXS measurements, each of the mesoporous samples was loaded into a diamond anvil cell (DAC), having anvils with 400 μm diameter culet faces, under atmospheric conditions. The Re gaskets used in the DAC, having a hole with a starting inner diameter 200 μm, were pre-indented prior to loading of each sample. Samples were loaded in the DAC with a small ruby crystal pressure calibrant for pressure determination. For measurements made under elevated temperature and high pressure conditions, type K chromel–alumel thermocouples positioned directly on the diamond anvils of the externally heated DAC were used to measure the sample temperature within an accuracy of ±1–2 °C. A Raman spectroscopy setup using a 532 nm green laser excitation source was used and the resulting shift in the characteristic fluorescence lines of ruby were utilized to ascertain the pressure of the sample. The sample pressure was measured before each series of SAXS images was acquired.

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