



Studies of the mechanical and extreme hydrothermal properties of periodic mesoporous silica and aluminosilica materials



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ABSTRACT

In order to assess the suitability of mesoporous materials for applications in energy harvesting/storage processes occurring under extreme conditions, their mechanical, thermal and hydrothermal properties need to be fully investigated. In this study, the bulk mechanical and extreme hydrothermal properties of periodic mesoporous SBA-15 type silica and SBA-15 type aluminosilica (Al-SBA-15) were investigated using *in situ* small angle x-ray scattering (SAXS). *In situ* SAXS measurements were made on dry mesoporous SBA-15 silica and Al-SBA-15 aluminosilica samples as a function of pressure (at room temperature) to ~12 GPa and on the same mesoporous materials under extreme hydrothermal conditions (to 255 °C and ~114 MPa) using the diamond anvil cell (DAC). The analyses of the high-pressure SAXS data indicate that the mesoporous Al-SBA-15 aluminosilica has substantially greater bulk mechanical stability (isothermal bulk modulus $\kappa = 34.7(4.5)$ GPa) than the mesoporous SBA-15 silica ($\kappa = 12.0(3.0)$ GPa). Our molecular dynamics (MD) simulations are able to accurately model the bulk mechanical stability properties of mesoporous SBA-15 silica but underestimate the same properties of Al-SBA-15 aluminosilica. Analysis of the *in situ* SAXS data measured under extreme hydrothermal conditions indicates swelling of the pore walls due to water incorporation that is more significant in mesoporous Al-SBA-15 aluminosilica (~2x) than in SBA-15 silica. In addition, the Al-SBA-15 aluminosilica clearly exhibits superior hydrothermal stability compared to SBA-15 silica under the extreme experimental temperature and pressure conditions.

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1. Introduction

Periodic mesoporous sieves are attractive materials for an ever-growing array of industrial and commercial applications due in part to their inherent high surface area and controllable pore size. The high surface-to-volume ratio in these materials and meso-scale (2 nm < diameter < 50 nm) pores make them useful for heterogeneous catalysis, ion exchange, gas sensing and alternate energy applications [1–5]. The remarkable growth in the discovery of a wide variety of materials having well-ordered pores on the meso-

scale is in large measure owed to the first developments made in the synthesis of mesoporous silica materials. The first mesoporous silica having well controlled pore size was synthesized by Yanagisawa et al. [6] by the introduction of a surfactant into the intercalation channels of a layered polysilicate kanemite. Soon after, Kresge et al. [7] were the first to use the method of liquid crystal templating for the synthesis of well-ordered mesoporous MCM-41 type silica having uniform pore size. The first synthesis of a periodically ordered mesoporous silica having larger pore size (from ~5 to 30 nm) and thicker pore walls, dubbed SBA-15, was accomplished by Stucky and coworkers [8]. The SBA-15 and other types of mesoporous silicate materials are useful for their functionality properties and hydrophobic characteristics. In order to improve upon the catalytic properties, aluminum was incorporated directly in the synthesis of SBA-15 to produce a mesoporous Al-SBA-15 aluminosilica having a two dimensional hexagonal pore structure

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by Yue et al. [9] The improved catalysis in Al-SBA-15 is owed to the substitution of Al for Si on the pore surfaces leading to the formation of both Brønsted and Lewis acid sites [10]. In contrast to SBA-15 silica, Al-SBA-15 aluminosilica is more hydrophilic and thus has a tendency to preferentially adsorb and remove water from organic matter.

For energy and industrial applications that involve extreme operating conditions, it is vital that the mechanical, thermal, and hydrothermal stability properties of periodic mesoporous silica and aluminosilica materials are well understood. Examples of energy applications under extreme conditions include petrochemical refinement in pressurized steam at 800–850 °C, biomass gasification in supercritical water (critical point: 374 °C and 22.064 MPa), and high-temperature fuel cells. There are very few studies of the mechanical response of ordered mesoporous materials under high pressure (to GPa range) conditions. A few select types of ordered mesoporous silica materials possessing 3D pore structure have been shown to exhibit a high degree of mechanical stability under quasi-hydrostatic pressure [11,12]; the authors are not aware of such studies made on mesoporous aluminosilica in the past. The majority of previous studies of the hydrothermal stability of mesoporous silica and aluminosilica materials have been limited predominantly to experiments made in boiling water or non-pressurized steam conditions which yield useful data but are not representative of the extreme conditions in near- and supercritical aqueous-based solutions or in pressurized high-temperature steam. Using *in situ* small angle x-ray scattering (SAXS), Mayanovic et al. [11] found that the pore structure of FDU-12 type mesoporous silica becomes irreversibly disordered upon exposure to water at 300 °C and 160 MPa. Conversely, exposure to boiling water experiments have shown that mesoporous aluminosilica materials have somewhat better promise for being stable under extreme hydrothermal conditions [13,14]. Similarly, Wang et al. discovered from boiling water experiments that structural incorporation of Al atoms into the pore wall surfaces of MCM-48 silica improved its hydrothermal stability [15]. Nevertheless, the correlations between the chemical composition, the atomic-scale structure and the pore structure in governing the mechanical, (hydro)thermal, and other physicochemical properties of mesoporous materials are poorly understood. In the first-of-its kind study presented herein, we examine the mechanical stability under high pressures and the stability under extreme hydrothermal conditions (to 255 °C and 114 MPa) of SBA-15 type mesoporous silica and of SBA-15 type mesoporous aluminosilica (Al-SBA-15). Preliminary results from our study were presented elsewhere [16]. By use of *in situ* SAXS measurements, molecular dynamics (MD) simulations modeling and additional characterization, herein we present a detailed investigation of how the chemical composition, for a given pore structure (2D-dimensional *p6mm* hexagonal), pore architecture, and atomic-scale (disordered) structure combine to govern the mechanical and hydrothermal stability properties of SBA-15 silica and Al-SBA-15 aluminosilica.

2. Materials and methods

2.1. Synthesis of mesoporous materials

Commercially available triblock copolymer Pluronic P123 (EO₂₀PO₇₀EO₂₀; BASF) was used as a structure directing agent and tetraethyl orthosilicate (TEOS; Sigma-Aldrich) was used as a silica source to synthesize the mesoporous SBA-15 silica according to procedures described in the literature [8,17]. First, 1.0 g of Pluronic P123 was dissolved in 38.0 ml of 1.6 M HCl aqueous solution. Next,

the solution was magnetically stirred at 35 °C to complete dissolution of the polymer. Subsequently, 2.2 g of TEOS was added to the mixture and stirred thoroughly for 1 day. The aqueous solution/mixture was hydrothermally treated at 100 °C for 1 day. The resulting SBA-15 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).

The mesoporous Al-SBA-15 aluminosilica was synthesized using the pH adjusting method outlined previously [18–20]. A measure of 0.8 g of Pluronic P123 (EO₂₀PO₇₀EO₂₀) block copolymer was dissolved in 25 ml of 2 M HCl solution and magnetically stirred at 40 °C to complete dissolution. Next, 1.7 g of tetraethoxysilane (Gelest) was added to the solution and stirred for 4 h, after which 1.36 g of Al₂(SO₄)₃·xH₂O, x~14–18, (Alfa Aesar) were added and the mixture was stirred for 1 day at 40 °C. Subsequently, the mixture was hydrothermally treated at 100 °C for 2 days. After the hydrothermal treatment, the pH of the mixture was adjusted to about 7.5 using drops of concentrated NH₄OH solution. The mixture was further treated hydrothermally (at 100 °C) for 2 days. After the second hydrothermal treatment, the material was centrifuged and then washed with deionized water and subsequently allowed to dry. In the final step, removal of the surfactant was accomplished by calcination of the final product in air at 550 °C (at a heating rate of 2 °C per minute) for 5 h.

2.2. *In situ* SAXS measurements

The SAXS measurements were made at the B1 beam line, at the Cornell High Energy Synchrotron Source (CHESS). The high energy x-rays (25.5 keV) were collimated to a beam size of ~100 μm in diameter. For pressure measurements, a Re gasket with diameter ~200 μm was placed on top of the culet face of the bottom anvil of the diamond anvil cell (DAC), loaded with a sample and then sealed by pressing the top anvil and secured with tightening screws. The loading of the samples was made in an argon environment and a small piece of ruby crystal was placed with the sample for the high pressure portion of the experiment. The shift in the B2 fluorescence line of ruby was used to gauge the pressure of the sample in the DAC. The fluorescence measured from the ruby crystal in the sample chamber indicated that the conditions were quasi-hydrostatic during the experiment made under pressure. As shown in (Fig. 1a), the x-rays were incident on the sample parallel to the compression axis of the DAC. The x-rays scattered from the sample were imaged using a MAR345 image plate detector (Fig. 1b) placed at ~1134.6 mm downstream from the sample. The SAXS images were processed using Fit2d software [21] to produce the intensity (I) of SAXS vs Q data, where $Q = 4\pi\sin\theta/\lambda$, 2θ is scattering angle, and λ (0.48608 Å) is the incident wavelength. For hydrothermal experiments, the sample was loaded along with HPLC grade water (pH = 7) in the sample volume defined by the hole in the Re gasket (~300 μm) and anvils in the DAC (see Fig. 1c). Each sample was loaded in the sample chamber of the cell so as to contain an appropriately sized small vapor bubble. The liquid-vapor homogenization temperature (T_h), used to determine the fluid density of the aqueous fluid, was recorded for each sample by watching the disappearance of the vapor bubble in the sample using a microscope. Upon heating above T_h, the pressure follows an isochore that is determined by the fluid density, sample temperature and the T_h value. The estimated pressures were calculated using the equation of state of water [22] and the T_h and temperature values. The SBA-15 silica and Al-SBA-15 aluminosilica samples were held under hydrothermal conditions for ~4.5 h and ~3.33 h,

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