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In situ studies of order–disorder phenomena in the synthesis of mesoporous silica

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Abstract

The initial hydrolysis of a silicon alkoxide in the presence of a suitable structural directing agent (template) so as to form a mesoporous silica powder exhibiting long-range hexagonal ordering was monitored using *in situ* XRD (X-ray diffraction), SAXS (small angle X-ray scattering) and SANS (small angle neutron scattering). The non-ionic triblock copolymer P123 ($EO_{20}PO_{69}EO_{20}$) was employed as the organic templating agent and tetramethoxysilane (TMOS) was used as the silica source in the presence of a water/acid catalyst. The synthesis method described herein is based around a high volume concentration ratio of surfactant to TMOS. The formation of a long-range mesoscopically ordered organic–inorganic hybrid that could be subsequently calcined to form a hexagonally structured mesoporous oxide material was monitored over 6 days using the characteristic (100) reflection. It was seen that during this 'maturation' period the reaction is not progressive and SANS and SAXS data together with XRD experiments show that there is an initial kinetically rapid organic ordering process which provides a template for the formation of an ordered metastable organic–inorganic oxide phase which then becomes progressively more disordered before a final kinetically slow stable long-range ordered phase is formed. Discussions of the origin of the unexpected order–disorder phenomena are made.

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1. Introduction

A large amount of synthesis work has been carried out with the aim of producing high quality long-range ordered mesoporous materials since the pioneering work of Mobil scientists in the early 1990s. Several review papers have been written on the subject [1–4]. However, less effort has been devoted to understanding the details of the early stages of the formation mechanism and the kinetics of the processes involved. A number of different models or mechanisms for mesoporous material formation have been suggested (all of which may be valid in the particular conditions used). Amongst these models are: the 'liquid crystal templating' mechanism proposed by Kresge et al. [5], a 'charge density matching' mechanism proposed by Monnier et al. [6] and a mechanism suggested by Frasch et al. [7] where the key step is the formation of silica pre-polymers. Brinker [8] has discussed in depth the evaporation induced self-assembly process methods for the formation of mesoporous thin films. Cryogenic transmission

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electron microscopy [9], X-ray scattering [10], small angle neutron scattering [11,12] and electron paramagnetic resonance spectroscopy (EPR) [13] have been used to gain information about the kinetics of the formation of hexagonal mesoporous silica.

However, the work detailed to date has centered on the use of ionic surfactants as templates or, more correctly, structure directing agents (SDAs). Little work has been carried on the mechanism of formation of mesoporous silica materials in the presence of non-ionic amphiphiles and, in particular, materials prepared using high concentrations of the triblock SDAs in preparations similar to those used by Attard et al. [14] and Ryan et al. [15]. Boissiere et al. [16] have reported some findings from an investigation of a fluoride assisted two-step synthesis principally using non-ionic diblock surfactants ($C_x(EO)_y$ type) but some work on the non-ionic triblock copolymer (P123, $EO_{20}PO_{69}EO_{20}$) was also reported at this time. These authors showed that the association of hybrid units of organic polymer micelles and small silica oligimers gives well-structured seeds of the emerging meso-structured material within 10 min of the addition of fluoride ions. However, no details on the aggregation process of the P123-mediated synthesis were revealed. In a recent report by Ruthstein et al. [17], the formation of SBA-15 using EPR was followed. Little detail was provided in this work but it was shown that after 20 min of reaction, the EO chains have a different environment due to a new location within either in the micellar corona or the micropores. It was also shown that the hexagonal structure of the eventual product is present after 2 h of reaction. Flödstrom et al. [3,18] have also studied the system using various *in situ* techniques.

In the work described herein, the formation of mesoporous silica was followed using *in situ* XRD measurements supported by SANS and SAXS methods. X-ray diffraction and the non-coherent scattering methods provide complimentary information on the long-range and short range order of the materials. XRD has not been widely used to study time-resolved phenomena because of long data collection times but the availability of new instrumentation allows very rapid data acquisition and the *in situ* formation of meso-structured material to be followed in real time. These results showed that an increase in structural ordering is initially observed (for periods of up to 100 min) but following this a decrease in the ordering was noted. The results are discussed in detail and a model for the mechanism of meso-structured material proposed.

2. Experimental section

Mesoporous silica was prepared in similar method to that described by Attard et al. [14] and Ryan et al. [15]. Tetramethoxysilane (TMOS) was hydrolyzed in the presence of the polyethylene oxide (PEO) – polypropylene oxide (PPO) triblock copolymer surfactant P123 ($PEO_{20}PPO_{69}$-PEO_{20}) supplied by BASF, UK. Typically, P123 (5.00 g) was dissolved in TMOS (9.00 g, 0.059 mol) to which an aqueous solution of hydrochloric acid (5.0 g, 0.5 M unless otherwise stated) 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. A second experiment in which the methanol was not removed was performed in order to understand the importance of this procedure on the formation of mesoporous silica. Samples were calcined in air at 550 °C to yield a final mesoporous product.

Following the preparation, the sample was transferred to a XRD sample holder which consisted of a large 3 mm deep glass tray so that the incident X-ray beam footprint was centered only on the added material and not on any holder components. The ideal sample height was determined using a thin film silicon sample and X-ray reflectivity. The sample table height could then be set so that the focus point and the axis of rotation were at a depth of 1.5–2 mm within the sample. This ensured data were only collected from the sample and that shrinkage, etc. did not determine the quality of the data. *In situ* time-resolved studies were recorded on a Philips X'Pert diffractometer, equipped with a Cu K_α radiation source and accelerator detector. Each scan used took between 5 and 30 s. Incident and reflected Stöller slits of 0.2° were used with a programmable divergent slit to maintain a 10 mm footprint at the sample.

Synchrotron X-ray measurements were preformed at the Austrian SAXS beamline at the ELETTRA synchrotron (2 GeV electron storage ring), Trieste, Italy [19]. A linear position-sensitive Gabriel detector was used with a monochromatic incident X-ray beam of energy 8 keV. Samples as prepared above and then subjected to a vacuum evaporation treatment were transferred into a cell containing diamond windows through which the X-rays were passed. Data was taken in transmission and not reflection as used for XRD studies. The samples are essentially treated in the same way as those studied by XRD.

SANS experiments were carried out on the LOQ instrument at ISIS at the Rutherford Appleton Laboratory (RAL), UK. The absolute scattering cross-section $I(Q)$ (cm^{-1}) was measured as a function of the modulus of momentum transfer Q (A^{-1}) $= (4\pi/\lambda)\sin(\theta/2)$ where λ is the incident neutron wavelength (2.2–10 Å) and θ is the scattering angle (7°). All measurements were taken at 40 °C and a data collection time of 15 min.

Surface areas of the calcined mesoporous silicas synthesized were measured using nitrogen physisorption techniques [18] on a Micromeritics Gemini 2375 volumetric analyzer. Each sample was degassed for 12 h at 200 °C prior to the BET measurement. The average pore size distribution of the calcined silicas was calculated using the Barrett Joyner Halanda (BJH) method from a 30-point BET surface area plot. All the mesoporous silicas examined exhibited a Type IV adsorption isotherm typical of mesoporous solids. Adsorption isotherms were utilized in order to calculate the average pore diameters. A JEOL 5510 (0.5 nm resolution) electron microscope operating with a 180 kV accelerating