

Structure and diffuse-boundary in hydrophobic and sodium dodecyl sulfate-modified silica aerogels



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ARTICLE INFO

Article history:

Received 23 June 2015

Received in revised form

29 October 2015

Accepted 6 November 2015

Available online 18 November 2015

Keywords:

Diffuse-boundary

APD aerogels

Silylation

SAXS

Nitrogen adsorption

ABSTRACT

Small-angle X-ray scattering (SAXS) and nitrogen adsorption were used to study ambient pressure drying (APD) silica aerogels prepared from hydrolysis of tetraethoxysilane (TEOS) with additions of sodium dodecyl sulfate (SDS). The surfactant-extracted precursor wet gels have presented mass-fractal structure with typical fractal dimension 2.25 in a SAXS characteristic length scale from ~10 nm to ~0.35 nm. Hydrophobic APD aerogels with typical specific surface of 800 m²/g and bulk density of 0.20 g/cm³ were obtained after silylation of the precursor wet gels with a mixture of hexamethyldisiloxane (HMDSO) and trimethylchlorosilane (TMCS). The pore volume and the mean pore size of the APD aerogels increased with increasing the SDS quantity. APD aerogels presented most of the mass-fractal characteristics of the precursor wet gels at large length scales. The radius of gyration of the clusters of the APD aerogels (typically 17 nm) increased with increasing the SDS quantity, while the radius of the silica primary particles (typically 2.0 nm) increased at first with the addition of SDS (with respect to the sample without SDS) and decreased regularly afterward with increasing the SDS quantity. The primary particles presented yet some internal inhomogeneity and a diffuse-boundary interface with thickness of about 0.7 nm, according to a linear-gradient model for the diffuse boundary.

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1. Introduction

Silica aerogels exhibit interesting structural properties often associated with low density and high specific surface [1], which make them be considered largely for scientific and technological applications in several areas of the knowledge as catalysis [2], adsorption [3], separation [4], sensing [5], thermal isolation [6], drug delivery [7], enzyme immobilization [8], and nanotechnology [9].

Drying is the most critical step in the obtaining of aerogels from the sol–gel process [10,11]. Conventional drying often causes collapse of the silica network due to capillary forces associated with the liquid surface tension. Supercritical extraction of the liquid phase of the wet gels (supercritical drying) often yields aerogels with structure not so far from that of the original wet gels, at least at large length scales. Supercritical drying (SCD) aerogels may be limited for application in some areas because they were hydrophilic

(as they have OH end groups) and the structure of the aerogels could collapse even in moderate humid atmosphere with time [12,13]. Ambient pressure drying (APD), after a proper silylation pre-treatment on the silica surface, is an alternative method to prepare high-porosity hydrophobic aerogels [12–14], which diversifies the applicability of aerogels in several areas, since the hydrophobic surface of the APD aerogels prevents the structure deterioration in humid environments.

The process of obtaining hydrophobic APD aerogels requires a pre-treatment on the silica surface, named silylation, modifying the characteristic of the surface from hydrophilic to hydrophobic. Hexamethyldisiloxane (HMDSO) and trimethylchlorosilane (TMCS) are typical chemical silylating agents often used for this purpose [13]. Silylation replaces –H from hydrophilic Si–OH groups on the silica surface for stable hydrophobic –SiR₃ groups. Silylation also prevents the collapse of the silica network on drying provoked by capillary forces [11,13]. It would not be possible to dry the wet gel before the silylation if the aim is to obtain a sparse silica network as that of the aerogels, because of the collapsing of the silica network on drying occurring in the production of xerogels.

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Surfactants can form micelles and structural organization in a reactant silicate medium so they have been used as structure modifiers for a variety of mesoporous silica [15–18]. Particularly, sodium dodecyl sulfate (SDS) is an anionic surfactant which has been used in a few cases for this purpose [19–24]. In a previous work [23], a fixed quantity of SDS was used with varied quantities of an oil phase to produce hydrophobic APD silica aerogels. In a more recent work [24], we have obtained SCD aerogels in an autoclave, starting from a set of precursor wet gels prepared using varied quantities of SDS in the hydrolysis step of the process. It was concluded that the surface of the silica particles develops a surface-fractal characteristic with the supercritical process. In this work, the same set of precursor wet gels prepared with varied SDS quantities was used to produce hydrophobic APD aerogels, using a mixture of HMDSO and TMCS as silylating agent. The surface of the silica particles in the present APD aerogels showed completely different characteristics from that of the previous SCD aerogels, with the developing of a diffuse-boundary in the interface silica-pore, likely due to the attaching of hydrophobic groups on the silica surface. An original modified analytical approach was employed by incorporating the diffuse-boundary effect in the mass-fractal model characterizing the precursor wet gels, which was able to describe the SAXS curves in the whole q -domain (q being the modulus of the scattering vector), yielding complete characterization of the mass-fractal structure and the thickness of the diffuse-boundary of the present APD aerogels. The procedure certainly will be of interest for several researchers dealing with surface science. Interesting structural properties of the hydrophobic APD aerogels were yet inferred by combining small-angle X-ray scattering (SAXS) and nitrogen adsorption.

2. Material and methods

The APD aerogels were prepared from a set of silica wet gels prepared from acid hydrolysis of tetraethoxysilane (TEOS) in several water solutions of SDS. The water solutions of SDS were prepared with relative concentrations C_R (with respect to the SDS critical micelle concentration $\sim 8.2 \times 10^{-3}$ M) varying to $C_R = 0, 1, 25, 50, 75$ and 100 . The hydrolysis of TEOS was carried out into the SDS solutions (after additions of ethanol and HCl) at 45°C , so the TEOS/water/ethanol/HCl molar ratio was $1:26.5:0.78:0.070$ while the SDS/TEOS molar ratio varied to $0, 0.0035, 0.0875, 0.175, 0.26$ and 0.35 . The hydrolyzed solutions were kept in sealed containers at 40°C for gelation (which occurred in a few hours) and aging (for 5 days) to obtain monolithic wet gels. The wet gels were yet washed with water, ethanol, and n -hexane to remove the surfactant, non-reacted residues, and byproducts of hydrolysis.

APD aerogels were prepared after silylation of the wet gels by immersion in a solution of HMDSO and TMCS (the silylating agents) in isopropyl alcohol (IPA) and n -hexane as a solvent mixture [13]. The HMDSO/TMCS/IPA/ n -hexane molar ratio of the silylating solution was $1:1:1:1$. The silylation was carried out under mechanical stirring at ambient temperature for 5 days, being the silylating solution renewed at each 24 h. The excess of the silylation agents was removed by washing in n -hexane. The silylated gels were allowed to dry under ambient pressure for 3 days at 40°C to obtain hydrophobic APD aerogels samples. The APD aerogels were yet degassed at 120°C in vacuum conditions ($\sim 3 \times 10^{-3}$ mmHg) for about 24 h before they were studied by nitrogen adsorption and SAXS.

The SAXS experiments were carried out using synchrotron radiation with a wavelength $\lambda = 0.1608$ nm at the SAXS beamline of the National Synchrotron Light Laboratory (LNLS), Campinas, Brazil, using a pinhole geometry for the X-ray beam collimation. A 2D position sensitive X-ray detector was used to obtain high precision

data for the isotropic SAXS intensity $I(q)$ as a function of the modulus of the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle. The experimental SAXS data were measured from $q_0 = 0.1379$ nm $^{-1}$ up to $q_m = 3.3480$ nm $^{-1}$ with resolution of about 4×10^{-4} nm $^{-1}$. The data were corrected by sample attenuation and parasitic scattering (the scattering produced without the sample) and normalized with respect to the beam intensity. No additional background subtraction was carried out in the corrected and normalized SAXS data, neither for the present APD aerogels nor for the original wet gels studied earlier. The scattering intensity data were analyzed as obtained in relative units, without normalization to any standard to have absolute units.

Nitrogen adsorption isotherms were obtained at liquid nitrogen temperature (77 K) by using an ASAP 2010 Micromeritics apparatus. The data were analyzed for the BET specific surface, the total pore volume (as the nitrogen adsorbed volume at a point close to the nitrogen saturation pressure, $p/p_0 \sim 0.984$), and the mean pore size.

3. Results and discussion

3.1. SAXS

Fig. 1 shows the curves of the SAXS intensity $I(q)$ for the hydrophobic APD aerogels in direct comparison with those of the original precursor wet gels. A little-modified but basically the same

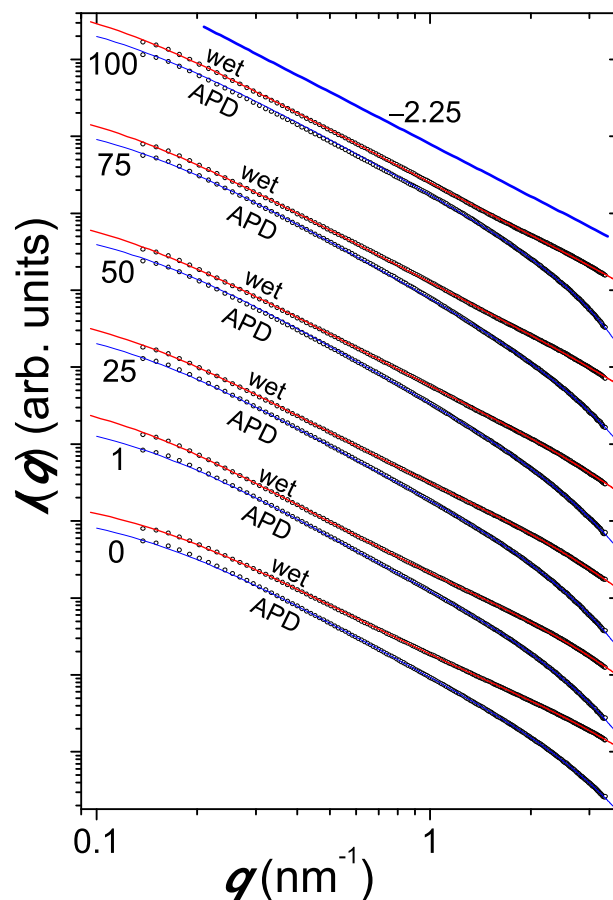


Fig. 1. SAXS patterns for the APD aerogels compared to those of the precursor wet gels. Numbers represent the SDS relative concentration C_R used in the preparation of the gels. The curves were vertically shifted for the sake of clarity. The full lines were drawn from fitting processes of the models (see the text) to the experimental data (points). A straight line with slope equal to -2.25 was drawn as a reference.

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