



Structure and thermal stability in hydrophobic Pluronic F127-modified silica aerogels



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ABSTRACT

Hydrophobic ambient pressure drying (APD) aerogels were prepared from hydrolysis of tetraethylorthosilicate (TEOS) in solutions with different concentrations of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (F127). APD was carried out after silylation of wet gels with 20% by volume of hexamethyldisilazane (HMDZ) in n-hexane. The samples were analyzed by small-angle X-ray scattering (SAXS) and nitrogen adsorption. The APD aerogels obtained in this process were submitted to heat treatment at 300, 500, 700 and 900 °C to study the pores stability. The samples were characterized by nitrogen adsorption. Wet gels are formed by mass-fractal domains, with fractal dimension close to 2.1 and characteristic size (ξ) spanning from about 9 nm (for the gel prepared without the addition of F127) up to values that exceed the maximum limit of the SAXS experimental setup, with increasing the concentration of F127. Nitrogen adsorption data showed that the pore volume (V_p) and the mean pore size (l_p) of the aerogels increased with increasing the concentration of F127. The drying process diminished the characteristic size ξ and increased the dimension D of the mass-fractal domains and the size (r_0) of the primary particles of the aerogels with respect to the wet gels. The characteristic size ξ of the mass-fractal of the aerogels was found significantly larger with increasing the concentrations of F127. Thermally treated aerogels exhibited a similar general behavior with temperature independent of the concentration of F127. The porosity was found fairly stable up to about 500 °C. The porosity started to be eliminated at 700 °C and it was found practically collapsed at 900 °C. The silylation layer on the silica surface of the present APD aerogels was promptly eliminated at about 350 °C yielding complete loss of hydrophobicity.

1. Introduction

Since the discovery of the amphiphilic properties and of the micelles formation in aqueous solution of the system copolymer tri-*block* poly(ethylene oxide) – poly(propylene oxide) – poly(ethylene oxide) [1,2], many scientific and technological advances have been achieved, using this and others similar surfactants in the preparation of the mesoporous silica, often resulting in interesting ordered pore structures [3,4]. In the preparation of composites, the copolymers block are an interesting class of structure modifier agents because the micelle structuration can determine the formation of the organized molds during the synthesis of the composites. These copolymers have advantage as their ordering way can be tailored by factors as solvent composition, molecular weight or copolymer architecture [3,4]. The use of the copolymer tri-*block* as impregnate structure agent in the silica polymerization process has allowed the preparation of ordered mesoporous silica with cubic arrangement and others forms [4–6].

Mesoporous silica shows interesting structural characteristics,

including high specific surface area and pore volume, making this material of great scientific and technological interest for applications in many knowledge areas. Applications in catalysis, separation, adsorption, immobilization of enzymes, transport and controlled release of drugs, and nanotechnology, as suitable matrices for preparation of nanoparticles of advanced materials, are naturally areas of interest [7–16].

The copolymer F127 when used as a structure modifier serves to produce pores in the silica gels, not only with an ordered porous structure, but with possibility of formation of various pore classes in the gel. This copolymer also allows one to obtain pores with characteristic size greater than those generated by surfactants of smaller molecular weight.

The sol-gel process allows one to obtain silica particles of different sizes through the variation of reaction parameters as temperature, pH, reactant concentration, type and concentration of catalyst, etc. The chemical nature of the particle surface can also be tailored in the sol-gel process. The sol-gel process of silicon alkoxides and the chemistry

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involved in the process lead to a more control of the purity of the final products.

The system silica/surfactant has attracted the attention of researchers in the material area due to the facility in obtaining mesoporous silica gels. This is due to the fact that the surfactant molecules form micelles in acids solutions, which can be cylindrical, spherical or lamellar, depending on the synthesis conditions [17], constituting a wide range of structural possibilities in the gel formation. In this work, copolymer F127 was used as an impregnate structure agent and HMDZ as a silylation agent in the obtaining of hydrophobic ambient pressure drying aerogels. The results were analyzed by small-angle X-ray scattering (SAXS), nitrogen adsorption and thermogravimetric analysis.

2. Material and methods

A starting F127 solution was prepared by dissolving 4.0 g of copolymer Pluronic F127 in 30 ml of water and 120 ml of HCl 2 M, under mechanical stirring for 20 h at ambient temperature. Sols of silica were prepared from hydrolysis of a fixed amount of 25 ml of TEOS and 8 ml of water mixed to different quantities of the F127 solution (0, 10, 20 and 30 ml) to yield silica sols with different concentrations of F127. The hydrolysis was carried out under mechanical stirring at 35 °C for 60 min in reflux conditions. The resultant sols were cast in sealed plastic containers for gelation followed by aging for 15 days at 40 °C to obtain very consolidate monolithic wet gels. The wet gels were washed in ethanol to remove the F127 to yield the washed wet samples named T0, T10, T20, and T30, associated respectively with the volumes 0, 10, 20 and 30 ml of the F127 solution used in the preparation of the gels. The wet gels T0, T10, T20, and T30 were studied by SAXS.

Aerogels were prepared by ambient pressure drying (APD), after silylation of the surface of the silica particles of the gels T0, T10, T20, and T30 with a solution of 20% v/v of the HMDZ (Sigma-Aldrich, 99%) in n-hexane. This procedure yields the set of APD aerogels AF0, AF10, AF20, and AF30, from the set T0, T10, T20, and T30, respectively. Samples of these aerogels were heated with a heating rate of 10 °C/min and kept for 4 h at 300, 500, 700 and 900 °C. The aerogels were degassed at 120 °C for 24 h prior to measurements of SAXS and nitrogen adsorption.

Small-angle X-ray scattering (SAXS) patterns was carried out using synchrotron radiation with a wavelength $\lambda = 0.1608$ nm at the SAXS beam line of the National Synchrotron Light Laboratory (LNLS), Campinas, Brazil. The beam was monochromatized by a silicon monochromator and collimated by a set of slits defining pinhole geometry. A 2D position sensitive X-ray detector was used to obtain isotropic SAXS intensity $I(q)$ as a function of the modulus $q = (4\pi/\lambda)\sin(\theta/2)$ of the scattering vector, where θ is the scattering angle. The coherent scattering data (the incoherent scattering is neglected at small angle) were corrected by sample attenuation and parasitic scattering (the scattering produced without the sample in the same experimental conditions). No additional background correction was carried out in the SAXS data of the wet gels (neither even of the aerogels) because the scattering from the silica particles is much more intense than the background produced by the solvent (essentially ethanol at this stage of the wet gels). The solvent background correction could be critical in polymeric organic systems (as soft resorcinol-formaldehyde polymer gels) [18] because the electronic density contrast between the organic polymeric matrix and the solvent is not too large.

Nitrogen adsorption isotherms were obtained at liquid nitrogen temperature (77 K), using a Micromeritics ASAP 2010 equipment. The specific surface area S_{BET} was determined using the BET method. The total pore volume per mass unit V_p was measured as the total volume of nitrogen adsorbed at a point close to the nitrogen saturation pressure. The mean pore size l_p was evaluated as $l_p = 4V_p/S_{\text{BET}}$. Thermogravimetric analysis was carried out in atmospheric conditions with a heating rate of 10 °C/min, using a Shimadzu Thermal Analyzer TA50 equipment.

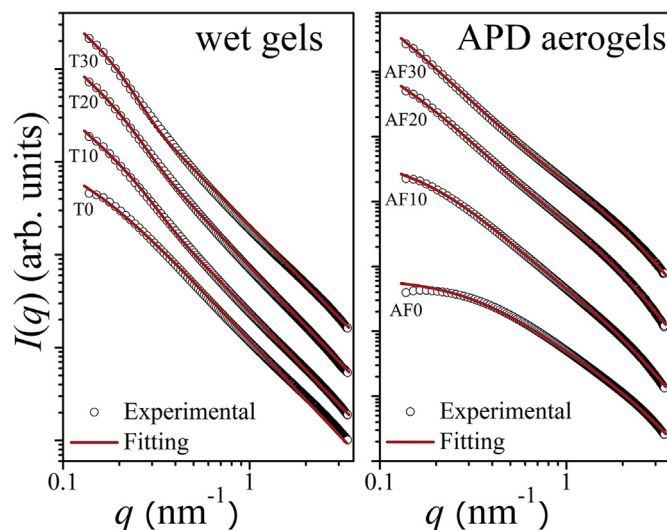


Fig. 1. (on the left) SAXS intensity of the wet gels prepared from hydrolysis of TEOS in different concentrations of the copolymer Pluronic F127. (on the right) SAXS intensity of the APD aerogels after silylation using HMDZ and ambient pressure drying (APD).

3. Results and discussion

3.1. Wet gels

Fig. 1 (on the left) shows the SAXS intensity $I(q)$ as a function of the modulus q of the scattering vector for the wet gels T0, T10, T20 and T30. The curve of the wet gel T0 can be associated with that produced by a system of mass-fractal clusters. The mass of a mass-fractal cluster scales with the length scale r as $m(r) \propto r^D$ in an interval $\xi \gg r \gg r_0$, where ξ is the characteristic length of the mass-fractal domain formed by primary particles of characteristic size r_0 , and D is the dimension of the mass-fractal structure, a value in the range $1 < D < 3$. The scattering intensity $I(q)$ from such a system is a power-law on the reciprocal space q , within the interval $\xi^{-1} \ll q \ll r_0^{-1}$, so that

$$I(q) \propto q^{-D}. \quad (1)$$

$I(q)$ deviates from the power-law of eq (1) at low- q , at about $q \sim 1/\xi$, due to the finite size ξ of the characteristic size of the cluster, and at high- q , at about $q \sim 1/r_0$, due to the finite size r_0 of the primary particle building up the mass-fractal structure [19]. The effects of the cut-offs at low- q ($\sim 1/\xi$) and high- q ($\sim 1/r_0$) have been treated by Freltof et al. [20] and Teixeira [21] and the results could be resumed in following equation

$$I(q) = A[1/(1 + r_0^2 q^2)^2][1 + B\Gamma(D + 1)\sin[(D-1)\arctan(q\xi)]/(1 + q^2\xi^2)^{(D-1)/2}(D-1)q\xi], \quad (2)$$

where A and B are constants, $[1/(1 + r_0^2 q^2)^2] = P(q)$ is Debye-Bueche form and represents the scattering from a isolate primary particle, and the last term in the brackets represents the interference function $S(q)$ between the scattering from all primary particles forming a cluster of characteristic size ξ and fractal dimension D .

The SAXS pattern of the sample T0 [Fig. 1 (on the left)] exhibits a crossover at low- q but no crossover at high- q , meaning that the characteristic size ξ of the cluster could be resolved but the characteristic size r_0 of the primary particle could not be resolved, since the high- q crossover ($\sim 1/r_0$) would be above $q_m \sim 3.34 \text{ nm}^{-1}$, being q_m the maximum experimentally accessible value for q in this experimental setup. When $r_0 \ll 1/q_m \sim 0.3 \text{ nm}$, the scattering from the primary particle $P(q)$ can be considered constant in the range $q_0 < q < q_m$, so that no crossover appears at high- q and the term 1 of the interference function $S(q)$ can be neglected in comparison with the second one, so eq

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