



Synthesis of silica aerogels microspheres prepared by ink jet printing and dried at ambient pressure without surface hydrophobization



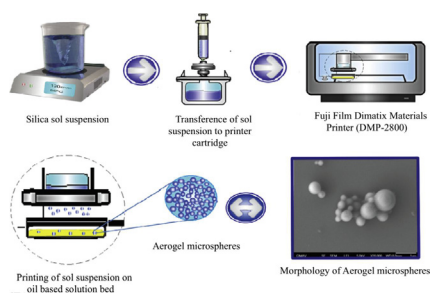
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HIGHLIGHTS

- SiO₂ aerogel was synthesized by ink jet printing and ambient pressure drying.
- Hydrophobization of aerogel precursor was not necessary for ambient pressure drying.
- Supercritical drying, nor modification step was necessary to obtain the SiO₂ aerogel.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 9 March 2015

Received in revised form

17 December 2015

Accepted 20 December 2015

Available online 11 January 2016

Keywords:

Amorphous materials

Sol–gel growth

Electron microscopy (SEM)

Aging

ABSTRACT

Silica aerogel microspheres were synthesized by sol–gel process via ambient pressure drying using tetraethylorthosilicate as precursor, and ink jet printing to shape the microspheres. Aerogels were synthesized with and without the surface hydrophobization step and at different volumetric ratios of sol precursor and a continuous oil phase, which was used to stabilize the spheres ejected by printer. By the first time, SiO₂ aerogel precursor was successfully ambient dried without modification step, keeping its integrity (cracks free) and with minimal size contraction, which was verified by comparison with the aerogel spheres obtained by the process of surface hydrophobization and drying.

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1. Introduction

Aerogels synthesis has been studied in recent decades due to its extraordinary characteristics and properties. More than 90% of its structure consists of air and the remaining 10% is formed by the solid part, which consist of a three-dimensional network of nanoparticles with diameter of approximately 3–15 nm conforming a structure with pore diameter of approximately 30–50 nm [1].

Common densities of aerogels are in the range of 0.12–0.3 g/cm³ [2,3], and they present high surface areas around 437–1200 m²/g, low thermal conductivities around 0.06 W/m-K [4], and porosity of 85%–99% [5,6]. Due to all these properties, aerogels present high potential for thermal [7], acoustic [8,9] and electrical insulation applications [10,11].

At present, different techniques have been developed to obtain aerogel spheres, like emulsion [12,13], dropping ball method [14,15] and spray. These techniques are typically based on supercritical pressure drying, which hindered the development of aerogels to be synthesized on large scales due to risks of having high temperatures and pressures in the presence of organic solvents. Some

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researchers used ambient pressure drying which is also called evaporative drying, obtaining thus materials called xerogels, where solvent exchange was necessary to reduce the capillary forces and be able to keep xerogel structure. Xerogels reach shrinkages of up to 75% with respect to original volume, and porosities are below to 50%, depending on the precursor used [16]. At present, researchers have synthesized aerogels using ambient pressure drying [2,3,6,10,15,17] in a process that requires the hydrophobization of surface to eliminate the problem of capillary forces induced by water and hydrophilic pore surface, getting good thermal and textural properties (porosity greater than 75% [16]). For ambient drying process, synthesis of aerogel spheres has a significant advantage, since solvent exchange step could be made fast (minimal diffusion problems), allowing thus a reduction time on their synthesis. Solvent exchanges are fundamental to modify the surface of the gel to obtain a hydrophobic surface, which is made by a silylating agent such as trimethylchlorosilane (TMCS). The purpose of the silylating agent is to change the nature of surface and expel the water occluded within the porous, preventing by this way the structure collapse due to capillary forces produced within the gel during the drying, minimizing the generation of fractures on the aerogel structure.

The aim of this work is to demonstrate that is possible to produce homogeneous microspheres of silica aerogels, free of fractures despite of use a drying step under ambient pressure and without hydrophobization of surface. This was possible through of an innovative technique using an ink jet printer; injecting sol drops of aerogel precursor over an oil phase. These results represent a breakthrough in the history of aerogel technology development.

2. Materials and methods

The synthesis was made by the sol–gel process. For this purpose it was used tetraethylorthosilicate (TEOS, Aldrich 98%), isopropyl alcohol (IPA, Lab Faga 99.5%), distilled water, hydrochloric acid (HCl, J. T. Baker 36–38%), ammonium hydroxide (NH₄OH, J.T. Baker 28–30%), n-heptane (Analytical 99.5%), trimethylchlorosilane (TMCS) and vegetable oil.

2.1. Aerogel synthesis

The synthesis was carried out at atmospheric conditions; the experimental method was made on four stages: synthesis, aging, surface modification (for comparative purposes) and drying. Two volumetric sol:oil solutions ratios were studied, 1:2 and 1:4.

Sol suspension was prepared using tetraethylorthosilicate (TEOS) precursor and hydrochloric acid as catalyst. A solution was prepared with 5 mL of TEOS, 4.6 mL of IPA, 0.003 mL HCl and 0.5 mL of distilled water, with pH = 3 (molar ratio of TEOS:IPA:H₂O:HCl = 1:2.75:1.22:1.8x10⁻³), which was stirred for 90 min at 60 °C. Three mL of sol solution were placed in a syringe and was passed through a filter to remove particles larger than 0.2 microns (Fig. 1) and transferred to ink jet printer cartridge.

A Fuji Film Dimatix Materials Printer (DMP- 2800) was used to develop this synthesis methodology. The cartridge has an injection capacity of 10 pL per drop, and nozzle diameter is 25 μm. As was mentioned, cartridge was filled with three mL of sol suspension and it was placed in the printer. The operation parameters to print the sol suspension were 21 V, injection frequency of 5 kHz and room temperature. Cartridge cleaning was made with isopropyl alcohol (IPA).

A second solution was added into vegetable oil with 0.52 ml of distilled water, 0.021 ml of NH₄OH and 1.1 ml of IPA (molar ratio H₂O:IPA:NH₄OH = 0.29:2.78: 8.12x10⁻³) with pH = 5. This oil solution was placed in a Petri dish and its function was as substrate,

thus the sol was printed over this solution.

The sol was ejected from cartridge printer into the oil solution on Petri dish forming microspheres; these microspheres were the precursor of aerogel particles. Microspheres into oil solution were stirred for 20 min to prevent agglomeration, thereafter suspension was aged on beaker (into oil solution) 3 h at 60 °C, to promote gelation. Microspheres settled on the bottom of beaker, and then the oil excess was removed with a syringe. After that, 7 mL of IPA were added and beaker was kept at ambient temperature for 12 h. The IPA was removed from the resultant gel, and it was washed for three times with n-heptane to remove residual oil, then 10 mL of n-heptane were added to suspend the gel particles.

For sample with hydrophobization treatment, the modification was made using TMCS as surface hydrophobizing agent by maintaining gel in contact with TMCS during 12 h. Resulting spheres were washed with n-heptane for three times, prior to the drying step.

Last step was the drying at atmospheric pressure and 50 °C for three hours, and thereafter oven temperature was changed to 200 °C and maintained by 3 h. In one case (aerogel synthesized without modification) the spheres were taken after IPA removal and n-heptane addition. Material with modification was dried after hydrophobization and n-heptane washing steps.

2.2. Characterization methods

Textural properties as surface area, adsorption–desorption isotherms, total pore volume and pore size distribution were determined by N₂ physical adsorption at 77 K in Quantachrome Autosorb model 1 equipment. The surface area was calculated using the method of Brunauer, Emmett and Teller (BET), whereas the pore size distribution was determined by the method of Barrette-Joynere-Halenda (BJH). The total pore volume was calculated at p/p₀ = 0.99. To determine surface area for micro and non-micropores, calculations were made by t-plot method with relative pressures below p/p₀ = 0.3. The morphology and particle size were studied by Field Emission Scanning Electron Microscopy (FESEM) in a Jeol JSM-7401 microscope. FTIR spectroscopy was made on GX Espectrum from Perkin Elmer to verify the anchorage of modifying agent to aerogel surface. For this analysis, aerogel spheres were crushed and mixed with KBr. Spectra were taken from 4000 to 500 cm⁻¹.

The bulk densities of silica aerogel spheres were estimated from their mass and volume. The volume was calculated by depositing silica spheres on a graduated cylinder and the mass of the silica aerogels spheres were measured with an analytical balance Sartorius BP 2215. The porosity of silica aerogel spheres was determined from bulk density (ρ_b) and skeletal density (ρ_s), which was measured by helium pycnometry (Ultrapycnometer 1000, from Quantachrome) [18,19].

$$\text{Porosity \%} = \left(1 - \left(\frac{\rho_b}{\rho_s}\right)\right) * 100$$

3. Results and discussion

In order to establish the best synthesis conditions, the effect of sol:oil volumetric ratio was studied at 1:2 and 1:4. It was observed that the increase of oil content allows a better dispersion of solids, forming homogeneous microspheres with low degree of agglomeration. For this purpose three samples prepared for each volume ratio were analyzed.

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