Nonsupercritical Synthesis of Microporous Gels

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ABSTRACT: In this work, the development of microporous gels using a novel degradation process not involving supercritical fluids is proposed. Photosensitive organic–inorganic hybrid sols in an alcoholic solution based on TEOS and an organic modified alcoxysilane were gelled by photopolymerization, and then dried at ambient pressure before sintering at 550°C. The result was a microporous gel with porosity higher than 90%. Chemical, physical, thermal, and mechanical characterizations were carried out on the microporous gel obtained by the nonsupercritical drying procedure. These results demonstrated the physical properties comparable with those of aerogels obtained by supercritical drying can be obtained. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2563–2568, 2008

Key words: silica; density; aerogel; photopolymerization; sol–gel

INTRODUCTION

Silica aerogels are usually made of at least 75% of air, and the remaining part by a SiO_2 network.[1] In some cases, the composition of aerogels can reach 99% of air and only 1% SiO_2. It is not surprising if aerogels present the lowest density and thermal conductivity among the known solid materials. These characteristics make this material an optimal candidate for several applications such as thermal insulation at high temperature, acoustic insulation, or heterogeneous catalysis. The standard procedure for aerogel fabrications goes through a supercritical drying of a wet-silica gel.[2] This expensive process involves high temperature and pressure requiring long production time; for these reasons, costs are high, and large scale production is still not developed.[3–7] Actually bulk aerogels part can be only obtained by supercritical drying. In this process the wet gel is heated above the supercritical temperature of the solvent, usually methanol or more frequently CO_2,[8–11] to reduce surface tension.[12] If drying is not made in supercritical condition, the high shrinkage gives a xerogel, with high density due to the shrinking related to interfacial tension between the liquid and the solid phase.

Low density silica xerogels ($\rho \cong 0.22$ g/cm³) can be obtained by the addition of reactive organic monomers to a silica network and changing aging parameters such as time and pH of liquid phase.

The reaction of the monomers increase the strength and the stiffness of the alcogel.[5] Silica xerogels with low density and porosity of the order of 90% can be synthesized at room pressure using trimethyl-chloro-silane (TMCS), toxic and highly reactive with air, and applying a proper heat treatment to the wet gel. This procedure leads to pore characteristics, and a microstructure of similar to those of hypercritical aerogels.[13] Sol–gel processes were also employed for the synthesis of hybrid organic–inorganic materials promoting an intimate mixture of organic polymers and inorganic glasses.[14,15] The resulting hybrid is often characterized by a reduced shrinkage after gelling and eventually after drying thanks to simultaneous presence of inorganic and organic networks.

In our original approach, to avoid shrinking during the drying phase at ambient pressure without the use of supercritical fluids, organic–inorganic hybrid sols in an alcoholic solution were gelled by photopolymerization. A polymer gel was crosslinked in the interstitial spaces of the silica gel, acting as a scaffold supporting the silica structure. Then the organic residue is burned out resulting in a microporous structure with a porosity of 90%.

EXPERIMENTAL

Microporous gel synthesis

Supercritical aerogels (sup-sample) were obtained for reference purposes. A silica sol was prepared from tetraethoxysilane (TEOS 98%) dissolved in ethanol. TEOS, ethanol, H_2O, and HCl were mixed and stirred at room temperature until complete hydrolization of the TEOS. Molar ratio of TEOS,

TABLE I
Composition of Silica Sols Used as Precursors

Processing	Sub-sample 1	Sub-sample 2	Sup-sample
Molar ratio: H_2O/(TEOS+MEMO[a])	20	20	4[b]
Molar ratio: HCl/(TEOS+MEMO[a])	0.01	0.01	0.01[c]
Molar ratio: CABOSIL/(TEOS+MEMO[a])	–	2	–

[a] MEMO: 3-(trimethoxysilyl)propylmethacrylate.
[b] Molar ratio: H_2O/TEOS.
[c] Molar ratio: HCl/TEOS.

H_2O, and HCl were 1 : 4 : 0.01. The compositions used for the gel synthesis are shown in Table I. A pH-METER CRISON BASIC 20 was used to evaluate sol acidity; the instrument reading is expressed in pH although the value is not representative of proton concentration in water. After hydrolysis, sol pH was 3.2, and it was raised to pH = 4.5 adding a solution of water and ammonia (eight parts of water and two parts of ammonia). The sol was then cast into a polypropylene mold. After gelation, the sol has been washed 10 times with acetone and placed in an autoclave. The role of the acetone was to replace alcohol and water present into the pores. Subsequently, autoclave has been cooled down to 10°C and filled with liquid CO_2 until a pressure of 50 bar is reached. After ∼ 5 min, a washing procedure was performed by introducing again CO_2 in the autoclave chamber, which diluted the one present inside. After the washing step, the autoclave was filled again with CO_2, the cooling system was turned off and the heating system turned on, until the chamber reach a temperature of 40°C and a pressure of 100 bar. Finally, the chamber was emptied by a slow release of the fluid. The time necessary to drain the chamber was ∼ 5 h before sample is removed.

Microporous gel by the nonsupercritical drying process (Sub-sample 1) were prepared starting from TEOS (Aldrich) dissolved in ethanol. The solution was prepared and mixed at room temperature; after complete hydrolization of the TEOS, 3-(trimethoxysilyl)propylmethacrylate (commercialized with the name MEMO from DOW) was added to the solution. A molar ratio of TEOS, MEMO, H_2O, and HCl of 1 : 1 : 40 : 0.02 was used as reported in Table I. 61+/−1 g of ethanol were added to reach 100 g of solution. After the hydrolysis, the pH of the resulting solution was 2.6, and it has been raised to pH = 7.6, adding a solution of water and ammonia in the proportions of eight parts of water and two parts of ammonia. Then 1-idrossi-cicloesil-fenil-chetone (commercialized with the name IRGACURE 184 from CIBA) as photoinitiator was added (5 wt % of the MEMO) to activate the radical polymerization of the methacrylate group of MEMO. The sol was sonicated for 10 min, to allow a perfect IRGACURE 184

solubilization. In the following step, the sol was exposed to UV-light until gelation is observed. Gelation is usually associated to a divergence of viscosity and a morphological modification leading to a white aspect from a transparent solution (Fig. 1). The haze at gelation is associated with a phase separation between the solvent and the polymer network. The beaker containing the gel was introduced in an oven for the following drying step at 60°C and ambient pressure.

After drying, a heat treatment was carried out with the aim to burn out the organic fraction of the gel. To prevent gel cracking, a very gentle heating procedure was adopted: temperature of the sample was slowly raised (0.2°C/min) to 550°C and hold at that temperature for 60 min. The bulk density of the nonsupercritical microporous gel before the heat treatment was equal to 0.215 g/cm^3; after the heat treatment it became equal to 0.231 g/cm^3. The density of the supercritical aerogel was equal to 0.237 g/cm^3. These value are in the range indicated in the literature for an aerogel.[16]

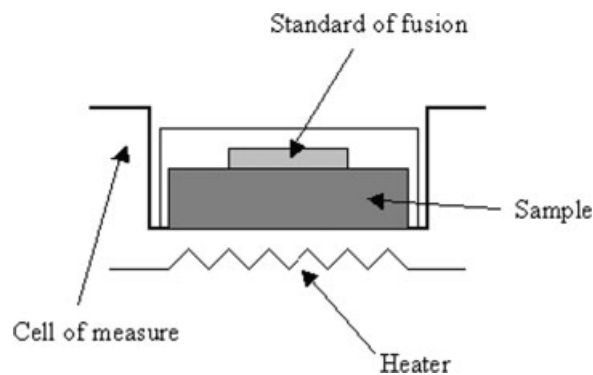**Figure 1** Image of a nonsupercritical microporous gel sample.

Figure 2 Sketch of the measure apparatus.

Figure 4 Weight loss of the nonsupercritical dry-microporous gel sample as a function of the temperature.

Microporous gel characterization

Weight loss as a function of temperature was studied by a thermogravimetric analyzer (TGA Netzsch STA406). A total weight loss at 1100°C of 71% was registered for the nonsupercritical sample before heat treatment. The larger contribution to such loss was attributed to the burn out of the organic phase. The microstructural characterization has been carried out through infrared spectroscopy (FT IR Jasco FT/IR-430). FT IR analysis was performed on three different samples: a supercritical aerogel sample, a nonsupercritical microporous gel sample before heat treatment at 550°C, and finally a nonsupercritical microporous gel sample heated up to 550°C.

Thermal conductivity of the samples was studied by a differential scanning calorimetry (DSC Perkin–Elmer DSC-7). Thermal conductivity (K) was obtained from the following equation:[17]

$$K = \frac{\Delta H_f \cdot s}{\Delta t_f \cdot A \cdot \Delta T}$$

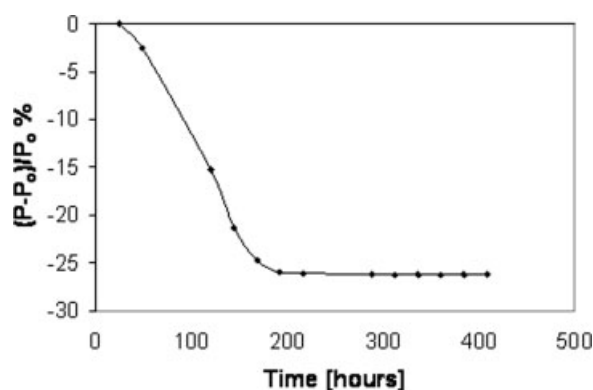where ΔH_f is the heat of fusion of a neat indium standard sample used for DSC calibration, s is the thickness of the aerogel placed under the sample of indium, Δt_f is the time elapsing between the beginning and the maximum of the fusion peak, A is the area of the sample of aerogel, and ΔT is the temperature difference throughout the sample measured as the difference between the oven temperature and the melting temperature of the indium standard. Different tests have been carried out on each aerogel sample. A quartz sample with a known thermal conductivity value was used for instrument calibration. Then a series of tests were carried out with different amounts of indium operating at different heating rates range (2–10°C/min). The experimental setup for the measurement of K by DCS is shown in Figure 2.

The coefficient of thermal expansion were obtained by thermomechanical analysis (by TMA Perkin–Elmer TMA-7). Mechanical properties in compression were carried out using the compression device of a parallel plate rheometer (ARES TA instruments).

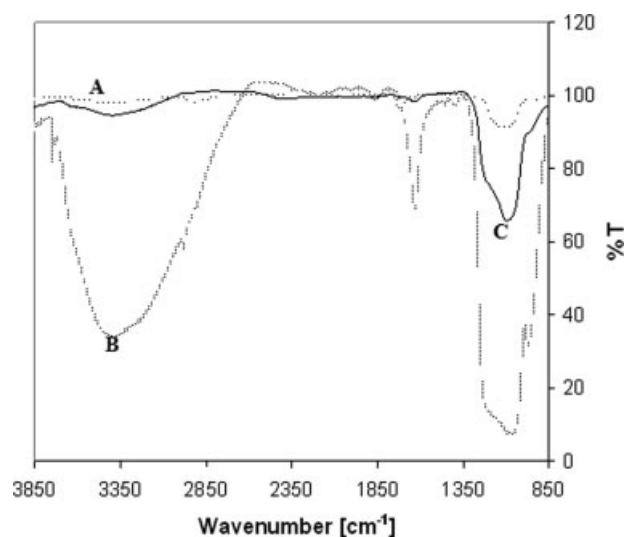Brunauer, Emmett, and Teller method (BET) and Barrett, Joyner, and Halenda method (BJH) analysis

Figure 3 Weight-loss % of the nonsupercritical microporous gel sample during the desiccation at 60°C.

Figure 5 FT IR spectra for the three samples: (A) nonsupercritical; (B) supercritical; and (C) nonsupercritical with heat treatment at 550°C.

TABLE II
Properties of the Three Different Samples

	Sub-sample 1 (nonsupercritical microporous gel)	Sub-sample 2 (nonsupercritical microporous gel obtained adding silica fumed)	Sup-sample (supercritical aerogel)
Density (g/cm^3)	0.231	0.261	0.237
Thermal conductivity (W/mK)	0.0298	0.0178	0.0286
Coefficient of thermal expansion (K^{-1})	6.1×10^{-6}	–	6.5×10^{-6}
Young modulus (N/m^2)	1.67×10^6	–	–
Superficial area (m^2/g)	33.3	210	>600

were carried out by means of a Quantachrome, Nova 1200 for the calculation of the surface area, and for the evaluation of pore dimensions, their distribution and shape. BJH analysis evidenced the presence of micropores. Horvath-Kawazoe (H-K) analysis of the adsorption isotherm in the region of the low relative pressures led to the distribution of micropores.

RESULTS AND DISCUSSION

After UV exposure the gelled sample was dried at 60°C and ambient pressure. The weight loss due to the evaporation of alcohol and water is shown by the thermogravimetric analysis in Figure 3. A 70% total weight loss was registered for the nonsupercritical dry-microporous sample after a further heating at 1100°C (Fig. 4). As shown in Figure 4 a two-step process is observed: at low temperature the weight change is associated with the loss of condensation water, at high temperature to the burn of the organic fraction.

The FT IR analysis (Fig. 5) shows a sharp band of absorption at about 3400 cm^{-1}, which was attributed to the stretching of the OH groups present on the material's surface linked to silicon, and of the OH

groups associated to the presence of water. Another sharp band was detected at about 1100 cm^{-1} and was attributed to the presence of siloxane groups (Si—O—Si).

As shown in Figure 5 the microporous sample, obtained without the supercritical drying and without heat treatment at 550°C, exhibited a band of absorption at 2930 cm^{-1}, associated to the stretching of —CH surface groups; such groups belonging to MEMO disappear after the heat treatment at 550°C. Another band of absorption, observed in the same sample at 1460 cm^{-1}, is associated to the bending vibrations of the same —CH groups.

DSC was used to measure the thermal conductivity of the sample obtained by not supercritical drying method (Sub-sample 1), of a sample prepared introducing CABOSIL M-5 fumed silica (200 wt % of the SiO$_2$ in solution) in the nonsupercritical procedure (Sub-sample 2) and for a sample obtained by supercritical method (sup sample). The lowest thermal conductivity is observed for the sample with CABOSIL M-5, as shown in Table II.

A coefficient of thermal expansion equal to 6.1×10^{-6} K^{-1} for the nonsupercritical sample was calculated as the slope of the regression line relative to the section in expansion of the curve (as showed in Fig. 6). A coefficient of thermal expansion equal to
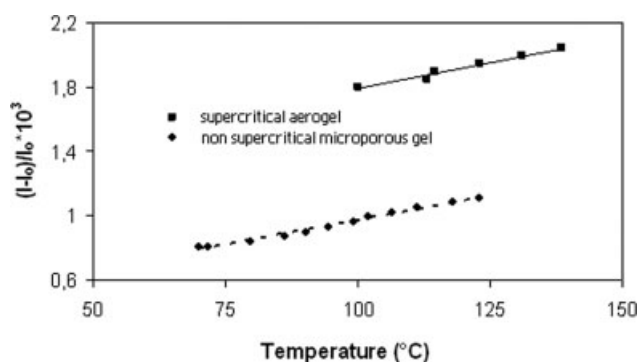

Figure 6 Linear regression of the expansion segment of the TMA curve for the nonsupercritical microporous gel and supercritical aerogel.
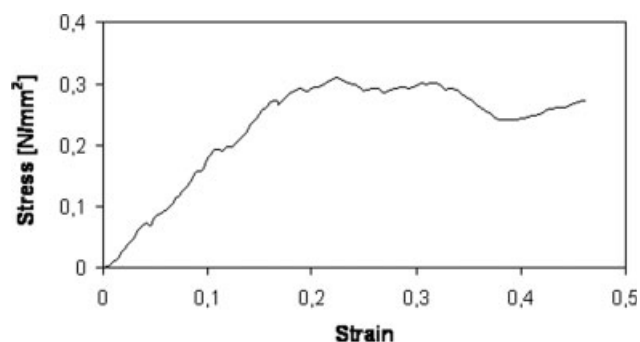

Figure 7 Compression stress–strain plot obtained on a nonsupercritical sample.

6.5×10^{-6} K^{-1} is measured for the microporous gel sample obtained by the supercritical drying method. This value is comparable with that reported in literature[18] (up to 6×10^{-6} K^{-1}). The thermal expansion coefficient was measured in a narrow temperature range since above 140°C both samples shrinks as a consequence of limited sintering.

The results of a compression test are shown in Figure 7. The Young's modulus is evaluated as the slope of the regression line of the initial linear part of the curve. The Young's modulus for the nonsupercritical sample is 1.67×10^6 [N/m^2] while the compression strength is $\sigma_U = 305$ KPa. Typical values of compression modulus of supercritical aerogels are in the range 10^6–10^7 N/m^2.[19]

The BET analysis indicates a surface area equal to 33.3 m^2/g for the nonsupercritical sample. This value is very low and is associated with the significant presence of micropores. To increase this value silica fumed M-5 from Cabosil, characterized by a high surface area, was added (200 wt % of the SiO$_2$ in solution). The sol sonicated for $\sim$ 15 min, leading to a good dispersion of CABOSIL M-5. The sample with silica fumed (Sub-sample 2) followed the same thermal treatment of the one obtained without CABOSIL M-5. The density of this microporous gel with silica fume was 0.261 g/cm^3, and its surface area is 210 m^2/g. Also this value is in the range reported in the literature for an aerogel. The supercritical aerogel was characterized by a value of 600 m^2/g. The isotherm obtained from BJH analysis shows a sharp increase of the adsorbed gas volume for low values of relative pressure, related to the absorption into micropores. Distribution of the pores is shown in Figure 8 for the nonsupercritical sample obtained with the silica fumed.

Elaboration of data reported in Figure 9, relatives to H-K analysis, results in a microporous structure with a maximum of the distribution of the dimensions of the pores of 5.8 Å.
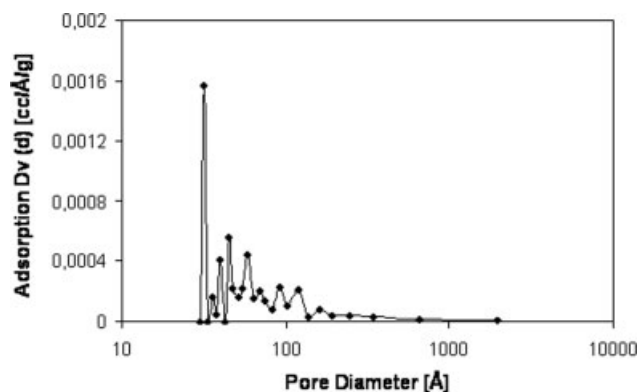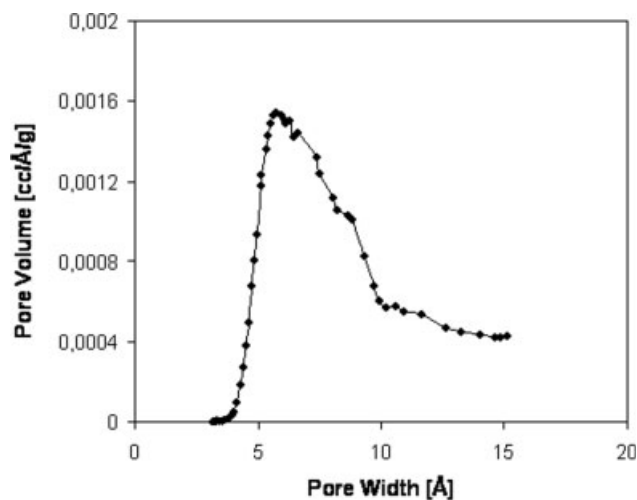

Figure 9 Pore-size distribution for the nonsupercritical microporous gel sample obtained through the H-K method.

CONCLUSIONS

A novel technique was developed for the synthesis of microporous gels, both in bulk form and in powder, by means of a gelling and drying procedure, which does not involves the use of supercritical fluids. A significant reduction of process complexity and time was achieved, associated with a significant reduction of the final product cost. The key idea is given by polymerizing a methacryl terminated siloxane monomer in the interstitial spaces of the silica gel. This polimeric phase acts as a structural support in the early stages of the synthesis procedure. The organic phase is then removed by a thermal treatment in air at 550°C, leading to a microporous silica gel. A chemical, physical, thermal, and mechanical characterization was carried out. Values similar to the one reported in literature for silica aerogel obtained by supercritical drying were observed. However, the surface area of supercritical aerogels is higher than those obtained in the nonsupercritical process.

Figure 8 Distribution of the pores for the nonsupercritical microporous gel sample: mesopores and macropores are detected.

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