Preparation of silica aerogel using ionic liquids as solvents

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Received (in Bloomington, IN, USA) 3rd September 1999, Accepted 23rd December 1999

Ionic liquids have been used as effective solvents to synthesize aerogels; a long aging time can be used to produce stable aerogel structures without the need for supercritical drying processes.

Aerogels are a novel class of porous materials with wide-ranging applications. The unique properties include low density, high surface area, low thermal conductivity and low dielectric permittivity.[1–3] So far, the synthesis of silica-based aerogels has been accomplished mainly through the controlled condensation of small colloidal particles produced by sol–gel processing in alcoholic aqueous solutions, followed by a supercritical drying process. A highly desirable goal in aerogel synthesis is the elimination of the supercritical drying process, the most expensive and risky aspect of the process. For example, Guo and Guadalupe have succeeded in synthesizing a silica-based aerogel from a metastable lamellar composite through cooperative interaction between silica and surfactant species.[4] The surfactant molecules used to generate pores can be removed from the silica network through conventional solvent extraction. The porous structure is stable during this procedure, and no supercritical extraction is used. Here, we report a new aerogel synthesis methodology based on the use of ionic liquids as solvents. The structural features of the synthesized silica aerogel are characterized.

Ionic liquids are a unique class of solvents that have virtually no vapor pressure and possess versatile solvent properties.[5–7] Recently, they have been effectively demonstrated as a superior solvent for conducting many organic reactions. For example, Chauvin *et al.* have shown that oligomers of alkenes can be efficiently synthesized using ionic liquid solvents.[8,9] More recently, many new organic reactions in various ionic liquids have been carried out by Seddon's group.[10,11] Our interest is in exploring the ionic liquids as solvents to conduct inorganic polymeric reactions for synthesizing novel inorganic materials. Conventional sol–gel synthesis of aerogels involves hydrolysis and condensation of tetraalkylorthosilicates to form gels in alcoholic aqueous solutions. During the aging process, the solvents evaporate, causing gel shrinkage before formation of a stable sol–gel network. If the aging period is too long, the pore volume tends to be reduced to that of the corresponding xerogel. However, too short an aging time may cause instability of the gel network, which can result in its collapse after extraction of the solvent. Therefore, control of the aging time is critical to the success of the aerogel synthesis. Ionic liquids offer an attractive method for achieving longer aging times without shrinkage of the gel network. When used as the solvent for sol–gel processes, their negligible vapor pressure prevents solvent evaporation, and their high ionic strength increases the rate of aggregation. These and other effects allow hydrolysis and condensation to proceed to completion, accordingly producing a stable gel network before solvent extraction.[12] All the preceding assertions concerning the advantages of using ionic liquids as solvents for the aerogel synthesis, of course, rely on the solvation capability of ionic liquids to form homogeneous solutions with aerogel precursors.

Tetramethylorthosilicate (TMOS) is used as the sol–gel precursor. The room-temperature ionic liquid used in this work is 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl] amide ($EtMeIm^+Tf_2N^-$). This melt was synthesized as described in the literature.[13–15] Acid-catalyzed sol–gel processing was conducted: in a typical run,[16] 1 mL of TMOS, 2 ml of formic acid (Aldrich Chemical Co., 99%) and 1 mL of $EtMeIm^+Tf_2N^-$ were mixed. The sol–gel reaction can be described by eqn. (1).[17] The final mixture gelled overnight

$$2\ HC(O)OH + (CH_3O)_4Si \rightarrow SiO_2 + 2\ CH_3OH + 2\ HC(O)OCH_3 \quad (1)$$

and was cured at ambient temperature for three weeks. A transparent monolith glass was obtained. The entrapped ionic liquid was extracted by refluxing the above monolith in acetonitrile (Baker Chemical Co., HPLC grade) overnight. The extraction procedure did not result in any visible shrinkage of the gel. This may be attributed to the long curing time used to stabilize the aerogel network before the extraction. The C–H stretching vibrational IR features of the ionic liquid around 2900 cm^{-1} disappeared after extraction and vacuum drying. This indicates that all ionic liquid molecules were removed through extraction. Immersion of the aerogel in solvents with a high dielectric constant (*e.g.* water) can result in cracking of the aerogel monolith. However, the aerogel monolith is very stable in air.

The N_2 adsorption isotherm (Fig. 1) of the monolith glass after removal of the ionic liquid is identical to those of aerogels prepared using different solvent and supercritical extraction.[2,3] The surface area and pore volume calculated from Fig. 1 are 720 $m^2\ g^{-1}$ and 1.4 $cm^3\ g^{-1}$, respectively.[18] Further supports for the aerogel structure come from investigation by small-angle X-ray scattering (SAXS). Fig. 2 shows a typical SAXS curve of the aerogel prepared using the ionic liquid. The analysis of the SAXS data indicates that the aerogel is mass fractal with a fractal dimension of 1.4. This small fractal dimension indicates a highly porous sol–gel network and is consistent with the mass fractal dimension for the aerogel materials.[12] The constituent particles have a size distribution and the value of R_g (radius of gyration) ranges from 80 to 14 Å, based on Guinier analysis.

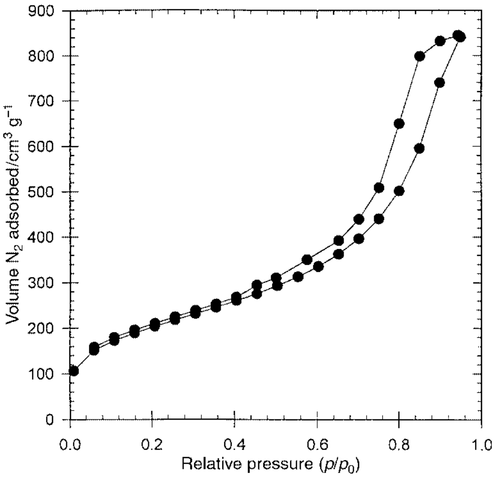
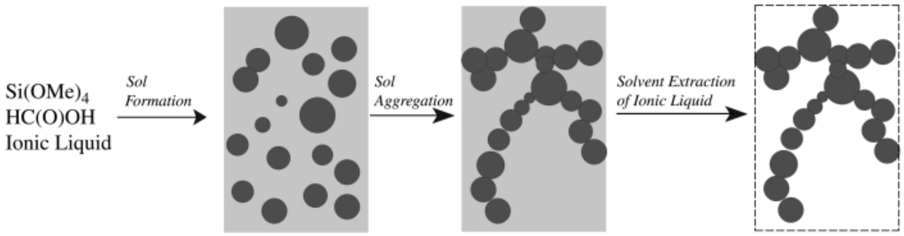


Fig. 1 Nitrogen adsorption–desorption isotherm.



Scheme 1

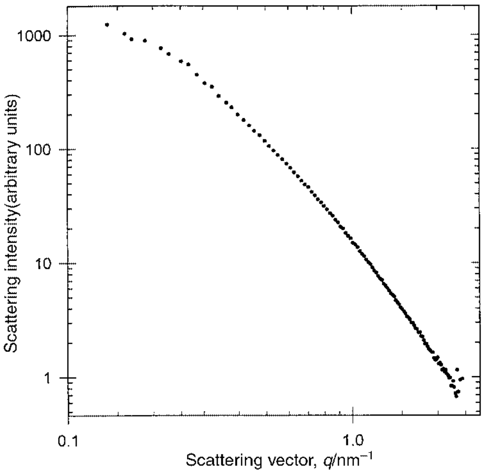


Fig. 2 Small-angle X-ray scattering curve for the aerogel.

Both the nitrogen adsorption and the SAXS data for our aerogel agree well with those obtained for the aerogels synthesized by conventional protocols.[1,3,13]

A possible mechanism for the aerogel formation in the ionic liquid is shown in Scheme 1. Formic acid initiates the formation of the sol particles, which effectively aggregate in the ionic liquid into a sol–gel network. Concurrently, the ionic liquid becomes entrapped in the growing covalent silica network, rather than being chemically bound to the inorganic matrix. A long aging time implemented before extraction of the non-volatile ionic liquid further enhances the stability of the aerogel network. No macroscopic phase separation between the gel and the ionic liquid solvent has been observed. The homogeneity is retained throughout the entire aging process. This indicates that the interaction between the sol particles and the ionic liquids is favored thermodynamically. The ionic liquid forms a homogeneous solution with sol–gel precursors. If other solvents (*e.g.* DMSO, water) are used in the sol–gel preparation, no appreciable pore volumes (< 0.1 cm^3 g^{-1}) are found. In fact, similar results have been reported in the literature concerning the doping of silica with organic liquids through sol–gel processes.[19]

In conclusion, the silica aerogel has been synthesized using an ionic liquid as a reaction solvent. This technique allows aerogel synthesis under mild chemical conditions and eliminates the risky supercritical drying process. We expect that this new methodology can find applications in synthesizing new aerogels and aerogel films for separation, catalysis, and insulation.

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp. We also thank reviewers for their valuable comments.

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Communication a907147d