Microporous and Mesoporous Materials 218 (2015) 192–198

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Fast and one-pot synthesis of silica aerogels *via* a quasi-solvent-exchange-free ambient pressure drying process

Jin Wang [a], Yulu Zhang [a], Yong Wei [a], Xuetong Zhang [a, b, *]

[a] *Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, 215123, PR China*
[b] *School of Materials Science and Engineering, Beijing Institute of Technology, Beijing, 100081, PR China*

A R T I C L E I N F O

Article history:
Received 1 April 2015
Received in revised form
10 July 2015
Accepted 17 July 2015
Available online 26 July 2015

Keywords:
Silica aerogel
Solvent-exchange
Ambient pressure drying
Tetraethoxysilane
Condensed silica

A B S T R A C T

A very fast (less than 2 h) and one-pot synthetic strategy was developed for the synthesis of silica aerogels. Organic silica gel was first formed under basic condition by adding a predetermined amount of hexane to a freshly prepared silica sol. After aging at elevated temperature for several minutes, the organogel was mechanically crushed and vigorously stirred in a mixture of trimethylchlorosilane and hexane. Finally, silica aerogel was produced by drying the hydrophobized organogel at temperatures higher than 180 °C. The effects of gelation conditions, amount of modification agents, and drying temperatures on the physical properties of the silica aerogels were investigated. The N_2 adsorption and desorption measurements indicated that high BET surface areas (up to 725.8 m^2/g) could be obtained for the aerogels sintering at 350 °C, while that of the silica aerogels dried at 180 °C were relative lower (from 379.4 to 564.8 m^2/g based on the modification conditions). Similar trend was also found in the thermal conductivities of the aerogels, e.g., lower values of thermal conductivity (~0.025 W/mK) were obtained for the sintering samples, while that of the samples without sintering were relative higher (~0.034 W/mK). In summary, a fast ambient pressure drying method has been developed, which show a great potential to synthesize silica aerogels in the industrial scale.

1. Introduction

Aerogels are materials with unique properties such as high porosity (~98%), high specific surface area (up to 1200 $m^2\ g^{-1}$), low density (down to 0.003 g cm^{-3}), low thermal conductivity (~0.012 W m^{-1} K^{-1}), and ultra low dielectric constant (1.0–2.0). Due to these unusual characteristics, aerogels are found wide applications in thermal insulation, heat and energy storage, battery electrodes, catalyst supports, gas and humidity sensors, adsorbents, and drug delivery systems, etc. [1–6] Consequently, aerogels have received much interests in recent years from both academic and industrial fields. For instance, various novel aerogels such as conducting polymer aerogels (CPA), carbon nanotube aerogels (CNTA), graphene aerogels (GA), and their composite aerogels, were reported [7–15]. However, the functionalization of the conventional silica aerogels is lagged behind. Nevertheless, silica aerogels is one of the most promising aerogels for commercialization due to the recent developments in ambient pressure drying (APD) method and the scale up production of silica aerogels [16–20]. Moreover, silica aerogels offer the greatest potential for non-evacuated superinsulation systems, and the practical realization of scale up production of silica aerogels remains to be solved [21].

Up to now, there are basically three drying method to synthesize aerogels, namely the supercritical liquid drying (SCLD), the freeze-drying, and the APD. The SCLD method can produce high quality aerogels with few collapsing of the pore structures, but it is expensive and is hard to fabricate large dimensional aerogels. The freeze-drying process may damage the pore structures and results in macropores. To solve these problems, the APD method has been proposed in order to scale up the synthesis of aerogels in a cheaper and safer way. The APD process occurs *via* solvent-exchange with low surface tension solvents (LSTS) and surface modification of the wet gels [16–20], in which the silylated surfaces do not participate in condensation reactions as the gel is collapsed by the capillary tension during drying and springs back toward its original porous state after drying. However, solvent-exchange is a lengthy and tedious process, which usually takes several days or weeks

---

* Corresponding author. School of Materials Science and Engineering, Beijing Institute of Technology, Beijing, 100081, PR China.
E-mail address: zhangxtchina@yahoo.com (X. Zhang).

http://dx.doi.org/10.1016/j.micromeso.2015.07.019
1387-1811/

[22–25]. The reasons for solvent-exchange are mainly rely on two aspects: 1) exchange water and ethanol with LSTS in order to reduce capillary pressure; and 2) water should be exchanged with organic solvents so that the hydrophobic modification reagents, such as trimethylchlorosilane (TMCS), can reach to the pore surfaces. Though great efforts have been made in reducing the aging and solvent-exchange time for APD, it's normally takes 24 h [24–28].

In order to significantly reduce the fabrication time and the large assumption of LSTS, in this work, we developed an ultra fast strategy to synthesize high quality silica aerogels without solvent-exchanges steps, and the LSTS used in the hydrophobization step was drastically reduced (Scheme 1). The fabrication time was remarkably reduced to 2 h, and large quantity of solvents and modification agents could be saved due to the quasi-solvent-exchange-free process. The effects of synthetic conditions and drying temperatures on the structure and properties of the silica aerogels were investigated, and the results may be a meaningful guide for industrial scale production of high quality silica aerogels.

2. Experimental

2.1. Materials

TEOS (Aladdin Industrial Corporation) are used as received. Silica sol was prepared according to literature [28,29], the molar ratio of TEOS: water: ethanol is 1:1.3:2.5. Other reagents are of analytical pure and used as received.

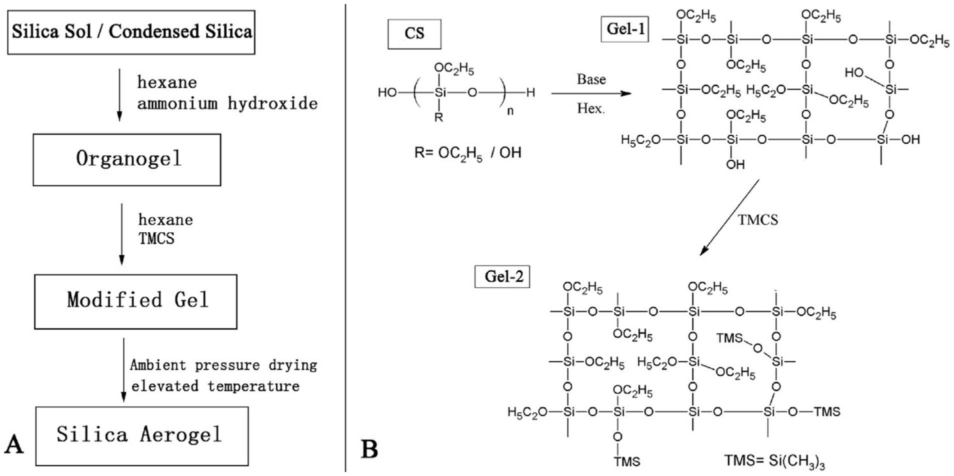
2.2. Synthesis of the silica aerogels by the fast and one-pot APD method

All the silica aerogels were synthesized *via* a one-pot APD process as described in Scheme 1A in this work. As an example, the synthesis of silica aerogel in entry 2 is as follow: 5 ml silica sol and 5 ml hexane were stirred for 5 min, then 1 ml ammonium hydroxide was added and the mixture gelled in 2 min. After aging at 50 °C for 15 min, the organogel was pulverized, in which 6 ml hexane and 0.5 ml TMCS were added and stirred for 40 min. Finally, the slush-like solid was dried at 180 °C for 30 min under ambient pressure and calcinated at 350 °C for 20 min to producing the silica aerogel. For entry 1, the only difference is that the silica aerogels were dried at 180 °C for 50 min without calcination. For entry 3 and entry 4, 1 ml TMCS was used while other reagents were the same as entry 2, entry 3 were dried at 180 °C for 50 min without calcination, while entry 4 were dried at 180 °C for 30 min under ambient pressure and calcinated at 350 °C for 20 min. The temperatures for aging and drying are preset and the gels are presented directly under desirable temperatures.

Entry 5 was dried by supercritical CO_2 liquid: 10 ml silica sol and 10 ml ethanol was stirred for 30 min and then 0.05 ml ammonium hydroxide was added into the mixture drop by drop. After gelation, the alcogel was aged in ethanol for 7 days before supercritical drying. A monolith and transparent silica aerogel was prepared, and the shrinkage is more than 50%. 10 ml ethanol was used because a same amount of hexane to silica sol was used. However, shrinkage was reduced (ca. 5%) when alcogel was formed when volume ratio of silica sol to ethanol is 5:1 (see Figure S1 the photo images and Figure S2 the N_2 adsorption–desorption isotherms curves of the silica aerogels in Supplementary material).

2.3. Characterizations

The pore size distributions and average pore diameters of the aerogels were analyzed by the BJH nitrogen adsorption and desorption method (ASAP 2020, Micromeritics, USA). The surface areas of the aerogels were determined by the Brunauer–Emmett–Teller (BET) method, based on the amount of N_2 adsorbed at pressures $0.05 < P/P_0 < 0.3$. The cumulative pore volume was measured at the point $P/P_0 = 0.99$. The FTIR spectra were measured on Thermo Scientific Nicolet iN10 spectrometer using a transmission mode. The thermal conductivity of the aerogel powders under room temperature were measured by using transient hot wire method (XIATECH TC3000, China), the data was collected for three times with 5 min interval of each measurement. The micro-structural studies of some selected aerogels were performed using field-emission scanning electron microscopy (Quanta 400 FEG). The samples were coated with Au nano-powder under current of 20 mA for 2 min. TEM measurement was carried on a Tecnai G2 F20 S-TWIN. Samples were prepared by dispersing aerogel powders in ethanol and dropped onto a copper grid, finally, it is dried under air for one week. The densities of the aerogels were calculated from the volume and weight of the aerogels powders, and that of entry 5 was calculated from the size and weight of the monolithic bodies.



Scheme 1. A flowchart showing experimental procedures for the synthesis of silica aerogels (A), and the proposed chemical structures of the gels (B).