



Synthesis and characterization of silica aerogels dried under ambient pressure bed on water glass



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ARTICLE INFO

Article history:

Received 7 October 2014

Received in revised form 6 December 2014

Accepted 7 December 2014

Available online 18 December 2014

Keywords:

Water glass;

Sol–gel process;

Silica aerogel;

Ambient pressure;

DMF

ABSTRACT

In this paper, we report the experimental results on the synthesis of water glass based silica aerogels, which were dried under ambient pressure. Water glass was hydrolyzed and condensed in water using HCl as the catalyst. To minimize shrinkage during drying process, N,N-dimethylformamide (DMF), acting as drying control chemical additive (DCCA), was introduced. Before the ambient pressure drying, solvent exchange and surface modification were completed. In order to get hydrophobic aerogel, trimethylchlorosilane (TMCS) was used to modify the hydrophilic hydrogel surface. Here a large amount of TMCS can be saved compared with that in single step solvent exchange/surface modification method. The effects of DMF on the physical and textural properties of the resulting aerogels were investigated. When the molar ratio of Si in water glass to DMF is 2.23, the synthesized silica aerogels have better properties. Characterized by FT-IR, SEM, BET, etc., the resulting aerogels have well-developed mesoporous structure (mean pore size of ~15 nm) with super hydrophobicity (contact angle of 161°) and excellent absorption capacity of organic liquids.

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1. Introduction

Silica aerogels are low density, translucent and thermal insulating material consisting of nanoparticle building blocks, networked together to form an open, highly porous structure. They have a large surface area (500–1500 m²/g), high porosity (80–99%) and low bulk density (0.03–0.35 g/cm³). Due to these unusual properties, aerogels have attracted much attention for they have large potential to be applied in many fields. Silica aerogels modified with methyl (–CH₃) groups can function very well in the sorption of organics, and their adsorption capacities are 10 times higher than those of activated carbon [1–3]. Silica aerogel beads (micron-sized) can easily be filled into hollow spaces and provide high thermal resistance. Further, silica aerogels can serve as thermal super-insulators in solar energy systems, refrigerators, thermal flasks [4–6], internal confinement fusion (ICF) targets for thermonuclear fusion reactions [7], very efficient catalysts and catalytic supports [8,9]. The extremely low density and high surface area of monolithic aerogels provide an opportunity to improve the performance of various metal-oxide-based devices, including gas and bio-sensors, batteries, heterogeneous catalysis devices, and low dielectric constant materials for integrated circuits (low-k dielectrics) [10–13]. Despite these advantages, aerogels are still not routinely found in our daily life, because they are fragile, collapse easily and difficult to prepare in a large-scale industrial production setting.

Silica aerogels are produced by removing the entrapped solvent from the wet gel while maintaining the integrity and high porosity of the gel. Supercritical fluid drying and ambient pressure drying are the most commonly used drying methods. Several researchers have used supercritical organic solvents for drying [3,10,11,14–18] to synthesize silica aerogel. Generally, fluids under supercritical pressures have almost zero surface tension. And this avoids the collapse and shrinkage caused by the surface tension force associated with the removal of the fluid. However, supercritical drying, involving high pressures (5–10 MPa), requires more power and high quality of manufacturing equipments.

Some researchers have prepared silica aerogel using tetraethoxysilane (TEOS) under ambient pressure [19–21]. However TEOS is a rather expensive organic reagent as precursor. To reduce the preparation cost of silica aerogel, water glass has been chosen as a much cheaper precursor. Based on water glass, aerogels have been synthesized by researchers through sol–gel process to form a gel under ambient pressure drying [22–26]. Sodium ion should be removed from the water glass solution to improve the optical transmission of the final aerogel product [26]. The pore size distribution (PSD) is a key factor that judges and decides the quality of silica aerogels. And the DCCA was studied to have the influence on PSD of silica aerogels [27]. Several researchers have investigated the DCCA's effect with different agents [28–33] in recent years.

In this work, to obtain a well distributed pore structure, DMF, acted as DCCA, has been introduced and its effect on the properties of water glass based silica aerogel was studied, which has not been investigated before. The aerogels with low density, low shrinkage and high porosity have been obtained by adding appropriate DMF. The pore size distribution became

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uniform. Besides, much less amount of TMCS was used to completely modify the gel compared with previous research [34].

2. Experimental procedure

2.1. Sample preparation

Silica aerogels were prepared by a single-step sol-gel process followed by ambient pressure drying. The precursor used for preparation of hydrogels was water glass (wt: 34%, QDSS (Qingdao Dongyue Sodium Silicate CO., Ltd, China), $\text{Na}_2\text{O}:\text{SiO}_2 = 1:3.33$). Other agents including hydrochloric acid (HCl), DMF, ethanol (EtOH), n-hexane and trimethylchlorosilane (TMCS) were purchased from SCRC (Sinopharm Chemical Reagent CO., Ltd, China).

Water glass was diluted with deionized water. The hydrolysis was carried out with the participation of HCl (5 M), before which DMF was added to the solution. The sol was stirred for 1 min in room temperature and the pH is about 6.2. The hydrolysis reaction led to the formation of silicic acid with the probable byproduct of NaCl. The gelation occurred within 15 min.

To age and remove the sodium, the gel was soaked with enough deionized water in a beaker, which was put in 45 °C water bath in 10 h. The water was removed by filtration. Ethanol was added into the gel to exchange water within the pores of hydrogel twice in 12 h and the ethanol was replaced by n-hexane in 6 h. The whole exchange process was carried out in 45 °C water bath and the solvent was removed by filtration.

The surface chemical modification of the gel was carried out by adding the silylating mixture of TMCS: hexane with the volume ratio of 15% to the gel under the condition of 45 °C water bath in 12 h.

Then the silylated gel was dried in ambient pressure at 60 °C for 2 h and finally dried at 100 °C to get aerogel. The aerogel was weighted every 2 h to make sure that the aerogel was dried completely.

2.2. Characterization

The bulk density of the aerogel sample was calculated by measuring its mass to volume ratio. The porosity of the aerogels was calculated using the following formula:

$$\text{porosity} = \left(1 - \frac{\rho_a}{\rho_s}\right) \times 100\% \quad (1)$$

where ρ_a is the bulk density of aerogel and ρ_s is the skeleton density of the silica aerogels. Generally the value of ρ_s is 2.2 g/cm³. The content of sodium in the aerogel was measured by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

The contact angle measurements were performed using a KSV (Helsinki, Finland) CAM 200 contact angle goniometer at ~20 °C. The thermal stability of aerogel sample was studied by the thermal gravimetric and differential thermal analysis (TG-DTA) using SDT Q600 (TA Instruments, USA). TG-DTA can also help to determine the oxidation temperature of -CH₃ group contained in the aerogel, that is, the temperature up to which the silica aerogel samples retain its hydrophobicity. The hydrophobic nano-porous silica aerogels with a weight of 6 mg were heat-treated in air, from room temperature (25 °C) up to 800 °C, with a controlled heating rate of 10 °C·min⁻¹.

The microstructure and morphology of the aerogels were studied using Field Emission Scanning Electron Microscope (FESEM) (SIRION 200, FEI, USA). The specific surface areas were determined by nitrogen sorption isotherms with standard Brunauer-Emmett-Teller (BET) analysis (Tristar II 3020 M, Micromeritics Instrument Corporation, USA). The cumulative pore volume was calculated from the N₂ adsorption-desorption profiles. The average pore diameters and pore size distributions (PSD) were estimated by the Barrett-Joyner-Halenda (BJH) method (Tristar II 3020 M, Micromeritics Instrument Corporation, USA). The surface chemical modification of aerogels was studied using Fourier Transform Infrared

Spectroscopy (FT-IR) (Nicolet 8700, Thermo Fisher Scientific, USA), which gave information about various chemical bonds, such as O-H, C-H, and Si-O-Si. For this purpose, the silica aerogels were ground into refined powders, mixed with KBr and pressed to form a sample pellet for FT-IR measurements.

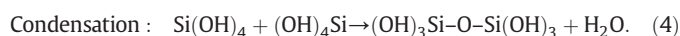
To measure the absorption capacity of the silica aerogels, the samples were immersed into various types of solvents/oils. The absorption process was very fast and generally reached equilibrium within a few minutes. Then the soaked samples were taken out and weighed after the aerogel surface was blotted using a filter paper to remove excess surface solvent/oil [35]. The absorption capacity (Q) was calculated from the mass gain using Eq. (2),

$$Q(\%) = \frac{(W - W_0)}{\rho_L V_0} \times 100\% \quad (2)$$

where W_0 and W are the weights of aerogels before and after absorption respectively, V_0 is the aerogel volume, and ρ_L is the density of absorbed solvent/oil. The weight measurements of the aerogels with absorbed oil were carried out quickly to avoid evaporation of the solvent/oil.

3. Results and discussion

Silica hydrogels were prepared by a single-step sol-gel process of deionized water (DI·H₂O) diluted water glass in the presence of acid (hydrochloric acid) catalyst, as shown in the following reactions:



When the liquid contained in the pores of hydrogel vaporised, the capillary pressure which can lead to pore collapse is occurred. It can be calculated with the following equation:

$$p = 2\sigma\cos\theta/r \quad (5)$$

where p is capillary pressure, σ is surface tension of solvent, θ is contact angle and r represents the capillary radius. To minimize the capillary pressure, the solvent exchange and surface modification process is necessary. Through comparison (Table 1), ethanol and n-hexane were chosen to be the exchange solvents, respectively. TMCS was the surface silylation reagent and the chemical reaction in the surface modification process is as follows:



After gelation, measured by ICP-AES, the weight content of sodium in the hydrogel is 1.24%, while it sharply decreased to 0.02% after the DI·H₂O washing process. So the DI·H₂O washing is an effective way to remove the sodium in the hydrogel. To determine the volume ratio of the solvent DI water to water glass, a series of experiments setting the volume ratio from 1 to 5 with increment of 1 were conducted, in which enough TMCS was added to the system to modify the gel. The porosity is presented in Fig. 1. It is clear that when the volume ratio is 3, the obtained aerogels have the highest porosity. And thus the volume ratio of DI water to water glass is fixed 3.

Table 1
Surface tension of several solvents at 20 °C [36].

Solvent	Surface tension (10 ⁻³ N·m ⁻¹)
Isopropanol	21.7
n-Hexane	18.4
Acetone	23.7
Ethanol	22.8
Ethylene glycol	48.4
Water	72.7

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