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An improved method for preparing monolithic aerogels based on methyltrimethoxysilane at ambient pressure Part I: Process development and macrostructures of the aerogels

Bi Xu [a,b], Jackie Y. Cai [a,*], Niall Finn [a], Zaisheng Cai [b]

[a] Division of Materials Science and Engineering, Commonwealth Scientific and Industrial Research Organisation (CSIRO), P.O. Box 21, Belmont, Victoria 3216, Australia
[b] College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, China

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ABSTRACT

In this paper, we introduced an improved method for producing methyltrimethoxysilane (MTMS) based aerogels at ambient pressure. The method developed is able to produce monolithic aerogels with low bulk densities over a range of the precursor concentrations at ambient pressure without the need for any solvent exchange and surface modification. This has been achieved through specifically tailored processing conditions according to the MeOH/MTMS molar ratios used. The effect of the key processing parameters on alcogel formation and macrostructures of the aerogels has been systematically investigated for achieving minimum volume shrinkage and bulk density. The specific process developed for MTMS based aerogel has not been reported in previous literature, and it is of significance in improving the practical feasibility of the aerogel fabrication.

1. Introduction

Aerogels derived from MTMS precursor exhibit attractive physical and mechanical properties. In addition to the general characteristics of silica aerogels (e.g. low bulk density, high surface area and porosity, low thermal and electrical conductivity), they are superhydrophobic and highly flexible [1]. At present, supercritical drying has been the predominant method for producing the aerogels [2–4]. Although the ambient pressure drying method is considered to be a desirable and more practical approach, it has been technically challenging due to the substantially higher capillary force generated during drying at ambient pressure, which may cause the gel structure to collapse. Our recent research has shown that the optimized alcogel (wet gel) preparation conditions (methanol/MTMS molar ratio at 35, gelation and ageing around 30 °C) that yielded high quality aerogel using the supercritical drying method [1] could not result in a similar quality aerogel with the ambient pressure drying method. Instead an aerogel with significantly higher bulk density and volume shrinkage (>50%) was obtained. This has clearly indicated that better network structure and higher network stability are required to withstand the high capillary force during drying under ambient pressure.

It has been reported that a good quality aerogel can be made through ambient pressure drying if solvent exchange and further surface modification processes are applied following the ageing stage [5–9]. However, this is a tedious and costly process. A simple and more practical method is therefore needed for any potential bulk production. In this study, we have systematically investigated the effect of key processing parameters on the alcogel formation and macrostructure of the aerogels dried under ambient pressure, and developed a new and simple method for fabricating MTMS based aerogels through an ambient pressure drying process without the need for any further solvent exchange and surface modification.

This paper is Part I of II, which mainly focuses on the new process development and macrostructures of the aerogels for achieving minimum volume shrinkage and bulk density under ambient pressure drying conditions, and provides general principles on how to manipulate the processing conditions to produce high quality monolithic aerogels with different MTMS precursor concentrations. The materials characterization, including the microstructures, physical and mechanical properties, and the relationships between the microstructures and material properties will be reported in Part II for further understanding of the development.

2. Experimental

All chemicals used including methanol (MeOH, 99.8% purity), MTMS (95% purity), oxalic acid, ammonium hydroxide were purchased from Aldrich and used as received. The alcogels were prepared via a two-step, acid–base catalyzed sol–gel process. In the first step, MTMS was mixed with MeOH at various MeOH/MTMS

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[*] Corresponding author. Tel.: +61 3 52464000; fax: +61 3 52464057.
E-mail address: Jackie.cai@csiro.au (J.Y. Cai).

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molar ratios from 20 to 39. The 0.01 M aqueous solution of oxalic acid (Solution A), as an acidic catalyst, was then added to the reaction media. The mixture was stirred at room temperature for 24 h to complete the hydrolysis process. In the second step, the 10 M aqueous solution of ammonium hydroxide (Solution B), acting as a basic catalyst, was added dropwise to the as-prepared sol while stirring. The molar ratios of MTMS/Solution A/Solution B were kept constant at 1:4:4. The prepared alcosol was transferred into glass test tubes, which were then made air-tight and placed at a certain temperature for the gelation to occur. The gelation temperatures (T_{gelation}) were varied from 30 °C to 60 °C. After gelation, more MeOH was added into each test tube and the alcogels were aged in MeOH for 48 h at the various ageing temperatures (T_{ageing}) from 30 °C to 60 °C. At last, the MeOH solvent was removed from the test tubes and the aged alcogels were dried under ambient pressure first at 50 °C for 24 h, then at 100 °C for 2 h and finally at 150 °C and 200 °C for 1.5 h each.

The bulk density of the aerogel was calculated from the mass to volume ratio of the sample. The mass of the sample was measured by an electron balance with a 0.01 mg accuracy. As the MTMS based aerogel was inherently superhydrophobic in nature with a specific density significantly lower than that of water, the bulk volume of the corresponding aerogel sample was measured by the method of water displacement. The aerogel sample was confined in a space of a known volume V_1, the volume of water needed to fill in the space was immediately recorded as V_2, and the aerogel's bulk volume was calculated by subtracting V_2 from V_1. The volume shrinkage of the aerogel dried at ambient pressure was determined from the difference in the volumes of the alcogel and the aerogel, expressed as a ratio to the alcogel volume.

3. Results and discussion

3.1. Theoretical background and considerations

Due to the hydrophobic methyl groups present in the siloxane backbone, and only three siloxane bonds available per silicon atom, the MTMS derived aerogels are hydrophobic and generally have a lower cross-linking density and higher deformability than those derived from the conventional tetraalkoxysilanes [10–11]. These special characteristics offer a greater potential for further engineering the fine structures of the gels for achieving low volume shrinkage by ambient pressure drying without the use of further solvent exchange and surface modification.

In general, the alcogel structure contains >90% by volume of fine pores containing alcohol. This alcohol must be removed to obtain an aerogel. When the radius of the pores in the alcogel is extremely small, the surface tension at the interface between the liquid and gas is extremely high. Alcogels with a relatively large pore radius may be favorable under ambient pressure drying conditions. However, pores that are too large weaken the alcogel's network structure and stability. To prevent damage to the gel structure from high interfacial forces (capillary force) during drying, generating suitable pore sizes and strengthening the porous network structures are critical points for obtaining high quality aerogels by ambient pressure drying.

It is known that MTMS precursor undergoes a series of hydrolysis and condensation reactions to form the polymethylsiloxane network structures, and these chemical reactions are responsible for the microstructures of the alcogels [12]. The reaction rates and reaction levels are primarily controlled by the precursor concentration (MeOH/MTMS molar ratio), gelation and ageing conditions (when the catalysts and water concentration are constant) [13].

Pore size is primarily determined by the concentration of the precursors and gelation conditions. Higher precursor concentration generally leads to a denser alcogel with smaller pore size. Under the same precursor concentration, faster gelation at a higher temperature involves accelerated chemical reactions and cluster aggregation, leading to relatively larger voids (or pores) in the gel [14], while slower gelation at a lower temperature gives rise to smaller voids (or pores). On the other hand, the siloxane network structure formed upon gelation need to be further developed and strengthened, so that during the ambient pressure drying process, the network structure is able to maintain the integrity of the network. This strengthening and stiffening effect is realized through ageing [12,13, 15–17], where many of the unreacted –OR and –OH groups continue to condense and form Si–O–Si bonds. More severe ageing conditions would impart a pronounced strengthening effect. Macroscopically, the ageing process is driven by the different degrees of solubility between small and large particles of the alcogel [13,18]. The smaller particles with higher solubility dissolve first and then reprecipitate onto large particles. Meanwhile, the concave part of the particle has a higher solubility than the necks with a negative curvature between particles; therefore neck growth is formed through the preferential dissolution and reprecipitation of the concave part of the silica particle onto the neck regions. Through this process, the microstructure of the alcogel is further modified and reinforced.

Based on the discussed considerations, this study therefore focuses on the development of suitable methods and conditions that are able to create desirable polymethylsiloxane network structures for obtaining a monolithic aerogel with minimum volume shrinkage and bulk density through ambient pressure drying. The effect of gelation and ageing temperatures on bulk density and volume shrinkage of the MTMS based areogels prepared at various MeOH/MTMS molar ratios have been extensively studied. Different approaches and processing conditions may be required at different MTMS precursor concentrations.

3.2. Aerogels prepared at MeOH/MTMS molar ratio = 30

The MTMS based alcogels were prepared by the two step sol–gel process as described earlier. Initially, the molar ratio of MeOH/MTMS was kept at 30 and gelation took place under a range of temperatures from 30 °C to 60 °C. Fig. 1 shows that gelation time reduces significantly with an increase in gelation temperature. This is because higher temperature promotes the hydrolysis and condensation reactions, leading to faster gelation.

It was also observed that at this molar ratio, the sols were completely transformed into macroscopically homogenous alcogels at

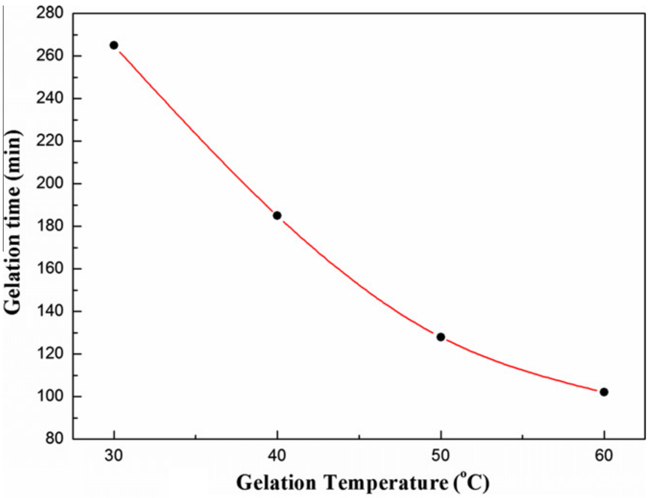

Fig. 1. Gelation time as a function of gelation temperature (at the MeOH/MTMS molar ratio = 30).