



Effects of processing conditions on silica aerogel during aging: Role of solvent, time and temperature



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ARTICLE INFO

Article history:

Received 21 May 2013

Received in revised form 30 June 2013

Available online xxxx

Keywords:

Aerogel;

Alcogel;

FTIR;

BET;

Compression strength and modulus

ABSTRACT

Effective parameters that enhanced mechanical properties of silica aerogel during aging were investigated. Silica aerogel was made by tetraethyl orthosilicate (TEOS), water, methanol and ammonium fluoride (NH_4F) as catalyst using a one-step method. Aging on the samples were performed under three different solvents including n-hexane, methanol and water for different time periods and also different temperatures. Subsequently, solvent exchange with n-hexane, modification under trimethyl chlorosilane (TMCS) solution and the ambient pressure drying (APD) were applied on all samples. The Fourier transform infrared spectroscopy (FTIR), Brunauer, Emmett and Teller (BET) method and compression tests were carried out on the produced samples. Both the compression strength and compression modulus of the gel increased with increasing of the time and temperature of aging. Those samples aged under water showed higher mechanical properties. On the contrary, the specific compression strength and modulus of samples aged in water were declined drastically.

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1. Introduction

When a sol reaches the gel point, it is thought that the reactions of the silicon alkoxide groups are complete and the alcogel has gained the desired results. However, the gel point is a statistical event indicating the time when the silica species take the container shape. At this point the silica backbone of the gel contains a significant number of unreacted alkoxide groups. In fact, gelation is a spectacular event, when a solution suddenly loses its fluidity and acquires an elastic solid shape [1–5]. The final properties of the silica aerogel are strongly influenced by the structure developed during aging. The chemical reactions that lead to gelation continue long after the sol changes into gel [6–9]. Since aging enhances the alcogel backbone, it reduces the subsequent drying shrinkage [10]. When the solid phase of alcogel is partly soluble in the pore solvent, elimination of the pores, reduction in surface area and phase separation may occur. During drying, the small pores of the gel develop high capillary pressures that result in shrinkage. The differential shrinkage between exterior and interior surfaces of the pores causes warping and cracking. To prevent such phenomenon, very slow drying is required [11]. In order to overcome this drawback, attempts have been made to synthesize the aerogel by APD method. This method is commercially attractive as a safer process compared to the supercritical drying method as it does not involve very high temperature and pressure [12]. Fracture usually takes place when shrinkage stops and the liquid/vapor surface meniscus happens [1]. On the other hand, aging in a solution in which the solid phase is slightly soluble can

cause coarsening. Moreover dissolution and re-precipitation cause neck among the particles and the aged gel becomes stiffer and shrinks less when dries [13]. A wide variety of chemical and physical changes can occur after gelation even when evaporation is prevented. Those changes are categorized as polymerization, syneresis shrinkage and phase separation. Polymerization increases the oxygen–Si chemical bonds. Syneresis shrinkage coincides with solvent extraction and phase separation decreases surface area [1,6].

Scherer et al. [1–5] suggested that the oxygen–Si bonds would increase with time and temperature. Furthermore, the re-esterification reaction would be suppressed and hydrolysis and condensation reactions accelerated. Since the chemical reaction is faster at higher temperatures, aging can be accelerated by hydrothermal treatment. As a result, less shrinkage may develop before the network stiffens. Moreover, hydrothermal aging increases the modulus and viscosity of the wet gels where stiffened gel causes less shrinkage during the drying process.

Zhao et al. [14] showed that pore size and pore volume of silica aerogel aged in autoclave at 100 °C were almost twice of the samples that were aged in ethanol at room temperature. They suggested that high aging temperature and pressure promoted the dissolution and reprecipitation process of silica. They also have reported that esterification process of silanols enhanced the backbone strength of silica gel.

In the present research the influences of aging time and temperature and aging solvents are investigated. Subsequently, solvent exchange with n-hexane, modification under TMCS solution and APD are performed for all samples. The FTIR technique is used to examine the reaction progress and completion. The BET test is used to indicate porosity, surface area and pore diameter. Compression strength and modulus, density, shrinkage and permeability of samples are also found out. Using

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Table 1
Designation of samples based on aging time and temperature.

Sample	Aging temperature (°C)	Aging time (h)	Solvent
1	25	12	n-Hexane
2	25	24	n-Hexane
3	25	24	Methanol
4	50	12	Methanol
5	50	24	Methanol
6	50	48	Methanol
7	50	72	Methanol
8	50	144	Methanol
9	50	240	Methanol
10	50	24	Water
11	75	12	Water
12	75	24	Water

those data, the roles of time, temperature and solvents are studied on the final properties of silica aerogel.

2. Experimental procedures

2.1. Materials

TEOS, methanol, n-hexane (Merck chemicals) and deionized water were used as received. Stable 0.4% w/w NH_4F (Merck chemicals) in deionized water and 10% w/w TMCS (Merck chemicals) in n-hexane solution were prepared by dissolving the mentioned materials in the solvent and stirring for 1 h at the ambient conditions.

2.2. Sample preparation

Twelve samples of silica gels were prepared via a one-step procedure employing ammonium fluoride as catalyst. Silica aerogel were made, using a one-step method, from TEOS, water, ethanol and NH_4F in a molar ratio of 1:4:8:2 $\times 10^{-3}$ respectively. After vigorous stirring the obtained sol was cast into PE mold with 46 mm in diameter and 9.2 mm in height and allowed to gel at room temperature. After aged for 1 h in the mold, silica wet gels were transferred into an oven. Each sample was kept in the oven under certain temperature and for certain time as described in Table 1.

Subsequently, three times solvent exchanges were carried out with 50 cm^3 of n-hexane at 25 °C for every 24 h. Finally, modifications with 50 cm^3 of TMCS solution at 25 °C for 24 h and APD at 80 °C for 5 h were performed on all samples.

2.3. Characterization

Bulk densities of the dried gels were calculated directly from their mass to volume ratio.

FTIR spectra of aerogel samples were recorded by Bruker Equinox 55LS 101 series, Germany instrument at a resolution of 4 cm^{-1} and veraging 50 scans. This test was performed to confirm the existence of Si–O–Si and Si– CH_3 bonds in the wave number range of 400 to 4000 cm^{-1} .

The elastic modulus of the samples was measured through compression test technique using a Gotech universal testing machine with a 100 kg load cell at the strain rate of 0.3 mm/min according to ASTM D 695.

BET test was also carried out to determine surface areas of aerogels by N_2 adsorption at 77 K with Belsorp-mini, BEL Co., Japan. The samples were preheated in a nitrogen flow for 3 h at 200 °C to remove all the volatile materials. The specific surface area was determined using the BET equation with an accuracy of $\pm 10 \text{ m}^2/\text{g}$. The total pore volume was calculated at $P/P_0 = 0.99$. The pore size distribution was obtained using the Barrette–Joynere–Halenda (BJH) method.

3. Results and discussion

Although material types and their ratios are fundamental, the key feature of aerogel manufacturing is process conditions specially aging and drying. Using identical formulation, similar surface modification and APD method of drying for all samples, the aerogel synthesis variables decrease to three main factors including time, temperature and the solvent used for aging. Fig. 1 shows the silica aerogel production procedure.

To confirm the formulation and reaction of all stages such as hydrolysis, condensation, surface modification and drying, FTIR test for samples was carried out. Since the sol formulation and surface modification of the specimens are similar, the functional groups and their related peaks in FTIR spectra are exactly alike as expected. Fig. 2 illustrates the FTIR spectrum of sample 1 as a representative.

According to previous reports [11,15,16,31,32] peaks at 758 and 843 cm^{-1} can be assigned to Si– CH_3 bond. The peaks at 460, 800, and 1061 cm^{-1} are due to Si–O–Si bending modes, symmetric Si–O–Si stretching vibration and asymmetric Si–O–Si stretching vibration, respectively. The intense and broad peak appearing at 1061 cm^{-1} and the shoulder around 1200 cm^{-1} are assigned respectively to the transversal optical (TO) and longitudinal optical (LO) modes of the Si–O–Si asymmetric stretching vibrations. The peak at 1742 cm^{-1} corresponds to Si–O– C_2H_5 and finally Si–OH coincides with alcoholic OH at 3499 cm^{-1} . Compared to the other peaks, the area under the peaks at 758 and 1061 which are due to Si– CH_3 and Si–O–Si is extremely high and the peaks corresponding to OH and Si–O– C_2H_5 are negligible. The negligible O–H peak indicates that surface modification is quite complete and an appropriate formulation has been chosen. Available surface reacts to produce Si–O–Si bonds by condensation. Formation of Si–O–Si bonds collapses the pore network of the wet gel to some extent [17]. Surface reactions occurred homogeneously throughout the wet gel by diffusion along its open pore structure and these reactions were terminated with either hydroxyl (OH) or alkoxy (OR) groups converted to stable SiCH_3 groups which prevent further condensation reactions [18].

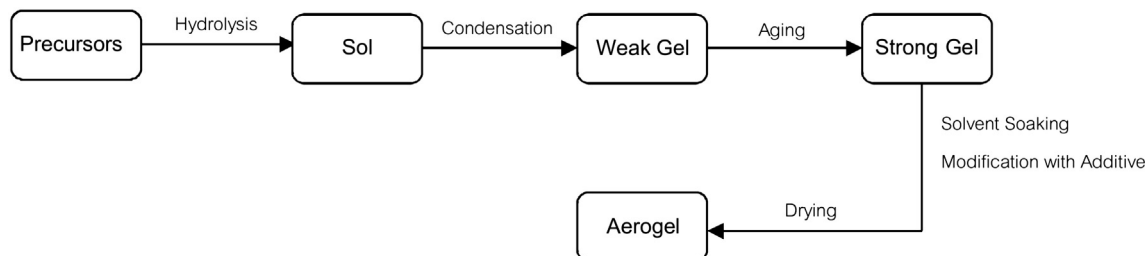


Fig. 1. Highlighted steps and related variables during aerogel synthesis procedure.

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