Microporous and Mesoporous Materials 158 (2012) 247–252

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

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

Structure and properties of polymethylsilsesquioxane aerogels synthesized with surfactant *n*-hexadecyltrimethylammonium chloride

Gen Hayase, Kazuyoshi Kanamori *, Kazuki Nakanishi

Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa, Sakyo-ku, Kyoto 606-8502, Japan

A R T I C L E I N F O

Article history:
Received 13 January 2012
Received in revised form 27 March 2012
Accepted 30 March 2012
Available online 6 April 2012

Keywords:
Polymethylsilsesquioxane
Sol–gel
Aerogels
Organic–inorganic hybrid

A B S T R A C T

Structure and physical properties of monolithic polymethylsilsesquioxane (PMSQ, $CH_3SiO_{1.5}$) aerogels have been systematically examined with varied starting compositions using a sol–gel system containing surfactant *n*-hexadecyltrimethylammonium chloride (CTAC). The precursor methyltrimethoxysilane (MTMS) undergoes hydrolysis and polycondensation under an acid–base two-step reaction to obtain uniform gels as a one-pot reaction. To compare the samples, each factor of starting composition, such as amount of CTAC, concentration of aqueous acetic acid solution, volume of solvent and amount of urea, is independently varied. With appropriate concentrations of surfactant CTAC, the aerogels with high light transmittance (at 550 nm) are obtained, owing to the effective suppression of macroscopic phase separation. Acid–base catalysts, acetic acid and urea also impose significant effects on the properties of obtained aerogels including their molecular-level structures. The aerogel with 91% of light transmittance was obtained under an optimized condition. The lowest density of the PMSQ aerogel in this system reaches 0.045 g cm^{-3}.

1. Introduction

Aerogels are prepared with various chemical compositions ranging from inorganic oxides such as silica and alumina, to organic cross-linked polymers such as resorcinol–formaldehyde (RF) resins [1–3]. Typical high-quality silica aerogels, which are generally prepared by the sol–gel process, possess high porosity (>90%) and small pore size (~50 nm) with the porous texture consisting of aggregates of silica nanoparticles (~10 nm). Owing to these structural features, a number of excellent properties are attained; high transparency, low refractive index, low thermal conductivity, and low dielectric constant. In particular, applications to (transparent) thermal insulators [4–6], catalyst supports [7,8], supercapacitors [9,10], and low-*k* materials [11] are widely concerned and much effort is made to fabricate aerogels with low-cost and efficient mass production processes. However, aerogels are inherently brittle due to the high porosity and to the weak linkage of the aggregated particles. To keep the delicate pore structure intact during the removal of solvent from the precursor wet gels, supercritical drying instead of simple evaporative drying is required, in which high pressure (and high temperature) is needed. This fatal drawback keeps aerogels away from the extended applications.

To improve the mechanical properties, much effort has been paid so far. Some researchers investigated the effect of extended aging in water, monomer solution, and mother solvent [12,13] to dry wet gels in milder (*i.e.* subcritical) conditions or even under ambient pressure and temperature. During the aging process, small primary particles with high positive curvature preferentially dissolve and re-precipitate onto the "neck" portion with high negative curvature in-between contacting particles. The resultant skeletal structure contains the smoothed linkage of particles, which increases the stiffness and strength of the original gel. Aging in monomer solution drastically enhances the mechanical properties by incorporating monomers from the aging solution into the as-prepared gel networks to increase the cross-linking density. Hybridization with organo-functional silanes or organic polymers is another promising way to increase the mechanical durability of aerogels [14–21]. Although sacrificing the transparency due to macroscopic phase separation of hydrophobic networks, organic–inorganic hybrid aerogels prepared from methyltrimethoxysilane (MTMS) [17] and MTMS/dimethyldimethoxysilane (DMDMS) coprecursors [21] show unusual flexibility.

Simultaneously, we have demonstrated that a modified two-step sol–gel process containing urea and surfactant prevents the occurrence of macroscopic phase separation, and transparent organic–inorganic hybrid aerogels are obtained utilizing MTMS as a single precursor [22–27]. The resultant ideal gel network is represented as polymethylsilsesquioxane (PMSQ, $CH_3SiO_{1.5}$). Urea is hydrolyzed into ammonia and carbon dioxide at 60 °C after the hydrolysis of MTMS which is catalyzed by dilute acetic acid, accelerates condensation and promotes homogeneous gelation by

---

* Corresponding author. Tel./fax: +81 75 753 7673.
E-mail address: kanamori@kuchem.kyoto-u.ac.jp (K. Kanamori).

1387-1811/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.micromeso.2012.03.049

raising solution pH. We used appropriate surfactants which effectively suppress phase separation by making the MTMS-derived condensates hydrophilic. In the case of nonionic surfactant, poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (EO_{106}–PO_{70}–EO_{106}, Pluronic F127) [29], it was deduced that MTMS-derived condensates were made hydrophilic through an attractive interaction between F127 and MTMS condensates. When cationic *n*-hexadecyltrimethylammonium salt (bromide CTAB or chloride CTAC) is employed, the MTMS condensates are more strongly made hydrophilic by weakly interacting with the hydrophobic chain of CTAB or CTAC. The resultant aerogels showed an unusual "spring-back" behavior which contains the compression of aerogel without cracking and the following perfect recovery when unloaded. Successful drying of wet gels without utilizing supercritical drying was also reported [22]. Low-density and transparent xerogels with comparable properties to corresponding aerogels thus obtained are promising for various applications such as to thermal insulators due to their potential for low-cost productions.

In the present paper, we show the control of pore structures and properties by systematically altering the starting composition. In particular, effects of changing concentrations of surfactant, urea and solvent are investigated. To minimize the effect of drying, all the gels have been processed by supercritical drying. The pore structure of aerogels is observed by field emission electron microscopy (FE-SEM). Properties including bulk density, light transmittance and compressive mechanical properties are also studied. The comprehensive information on relationships between starting compositions and physical properties is highly important to understand and design the pore properties of PMSQ aerogels/xerogels.

2. Experimental

2.1. Chemicals

Acetic acid, distilled water, urea, methanol, and 2-propanol were purchased from Hayashi Pure Chemical Ind., Ltd. (Japan). Surfactant *n*-hexadecyltrimethylammonium chloride (CTAC) was from Tokyo Chemical Ind. Co., Ltd. (Japan). Methyltrimethoxysilane (MTMS) was obtained from Shin-Etsu Chemical Co., Ltd. (Japan). All reagents were used as received.

2.2. Synthesis procedures

The sample notations are defined, for example, as C*w*A*x*-*y*U*z*, where *w*, *x*, *y* and *z* are weight of CTAC (in g), concentration of aqueous acetic acid (in mM), volume of aqueous acetic acid (in mL) and weight of urea (in g), respectively.

At the typical starting composition C0.4A5-10U3, 10 mL of 5 mM aqueous acetic acid, 0.40 g of surfactant CTAC and 3.0 g of urea were dissolved in a glass sample tube, and then 5 mL of MTMS was added with vigorous stirring. The molar ratio of this typical starting composition is MTMS:water:acetic acid:urea:CTAC = $1.0:1.6 \times 10:1.4 \times 10^{-3}:1.4:3.6 \times 10^{-2}$. The mixed solution was continuously stirred for 30 min at room temperature for acid-catalyzed hydrolysis, followed by base-catalyzed gelation and aging at 60 °C in a closed vessel for 4 d. The typical gelation time was about 3 h. The wet gels thus obtained were soaked in water/methanol (volume ratio 1:1) once, then methanol twice and 2-propanol three times each at 8 h duration to remove CTAC and other unreacted reagents. Alcogels obtained in this way were dried from supercritical carbon dioxide at 80 °C, 14.0 MPa for 10 h in a custom-built autoclave (Mitsubishi Materials Corp., Japan) to obtain aerogels.

2.3. Measurements

The pore structure was observed with an FE-SEM JSM-6700F (JEOL Ltd., Japan). Bulk density, ρ_b, was obtained by measuring the volume and weight of a carved gel. Porosity ε (%) was then determined as $\varepsilon = (1 - \rho_b/\rho_s) \times 100$, where ρ_s represents true density that was fixed to be 1.40 g cm^{-3} determined for a typical MTMS-derived aerogel by helium pycnometry. For light transmittance measurements, a UV–VIS spectrometer V-670 (JASCO Corp., Japan) equipped with an integrating sphere ISN-723 was employed. Direct-hemispherical transmittance was recorded, and obtained transmittance data at 550 nm were normalized into those of 10 mm-thick samples using the Lambert–Beer equation. The normalized total transmittance is denoted as *T*.

To assess the molecular structure of obtained PMSQ networks, FTIR measurement was performed with IRAffinity-1 (Shimadzu Corp., Japan) using an attenuated total reflection (ATR) attachment. A total of 100 scans were recorded with a resolution of 4 cm^{-1}. All samples were dried in vacuum at 80 °C for 1 d in advance of the measurement.

Mechanical properties of aerogels were measured by a material tester Autograph (Shimadzu Corp., Japan). Carved aerogels (typical length × width × height is $8 \times 8 \times 5$ mm^3) were compressed using a load cell of 5 kN. The measurements were performed by compressing up to 50% of its original height with a rate of 0.5 mm s^{-1} and then decompressing back to 0 N at the same rate. Young's modulus has been calculated using the slope of stress–strain curves between 0.1 and 0.2 MPa stress.

3. Results and discussion

3.1. Effects of CTAC

In many reaction conditions, MTMS does not form uniform gel networks in polar solvents, due to the high phase separation tendency resulted from the strong hydrophobicity of the methylsiloxane networks. To synthesize uniform monolithic aerogels, we have developed the method utilizing surfactant in starting compositions to suppress phase separation. In C*w*A5-10U3 system, we obtained transparent elastic aerogels with $w > 0.10$ g of CTAC (molar ratio [CTAC]/[MTMS] > 0.009), and relationships are presented between *w* and several properties as *T*, ρ_b and Young's modulus in Fig. 1. Light transmittance at 550 nm showed the maximum at $w = 0.40$ g with $T = 89\%$ (sample shown in Fig. 2(a)). Bulk density ρ_b of this aerogel was 0.138 g cm^{-3} and porosity, ε, was calculated as 90%. With increasing *w*, the light transmittance value *T* gradually decreased due to decreasing network homogeneity. Although monolithic aerogels can be obtained even with >4.00 g of CTAC ([CTAC]/[MTMS] > 0.36), translucency was low. In the cases of other surfactants, for example Pluronic F127, there is the upper limit of the amount of surfactant in the starting composition to obtain a monolithic gel. It is suggested that the interaction between CTAC and the MSQ condensates is weaker, and interruption of polycondensation hardly occurs. The attractive interaction may be predominantly based on the weak hydrophobic interaction between alkyl chains of CTAC and hydrophobic condensates.

With varying the amount of CTAC, microstructures (Fig. 3) as well as the physical properties of aerogels were changed. In C*w*A5-10U3 system, these changes can be explained by dividing into 4 regions about the *w* value. (1) In $w < 0.10$ ([CTAC]/[MTMS] < 0.009), macroscopic phase separation occurred because the amount of CTAC molecules is not enough to suppress the strong hydrophobicity of PMSQ networks. The resultant coarse structure is shown in Fig. 3(a). (2) In $0.10 < w < 0.60$ (0.009 < [CTAC]/[MTMS] < 0.054), the gel network became uniform