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Synthesis of spherical silica aerogel powder by emulsion polymerization technique

Sun Ki Hong, Mi Young Yoon and Hae Jin Hwang*

Division of Materials Science and Engineering, Inha University, Incheon 402-751, Korea

Spherical silica aerogel powders were fabricated via an emulsion polymerization method from a water glass. A water-in-oil emulsion, in which droplets of a silicic acid solution are emulsified with span 80 (surfactant) in n-hexane, was produced by a high power homogenizer. After gelation, the surface of the spherical silica hydrogels was modified using a TMCS (trimethylchlorosilane)/n-hexane solution followed by solvent exchange from water to n-hexane. Hydrophobic silica wet gel droplets were dried at 80 °C under ambient pressure. A perfect spherical silica aerogel powder between1 to 12 μ m in diameter was obtained and its size can be controlled by mixing speed. The tapping density, pore volume, and BET surface area of the silica aerogel powder were approximately 0.08 g · cm⁻³, 3.5 cm³ · g⁻¹ and 742 m² · g⁻¹, respectively.

Key words: Silica aerogel granule, Water glass, TMCS, Ambient pressure drying.

Introduction

A silica aerogel is an ultra-porous (more than 90% of porosity) material with wide-ranging applications. The unique properties includes low density, high surface area, low thermal conductivity, low dielectric constant, low index of refraction, and so on. Owing to these unique properties, such aerogels have been studied extensively for use as catalysts and thermal insulators, and in applications related to adsorption and drug delivery systems. [1-3]

The synthesis of the silica aerogel has been carried out mainly through the condensation of nano-sized colloidal silica particles produced by sol-gel processing in aqueous solutions containing alkoxide, alcohol and catalyst, followed by a supercritical drying process. However, the supercritical drying is dangerous, timeconsuming and expensive. To avoid the supercritical drying process, several efforts have been performed. [4-7] Schwertfeger et al reported that hydrophobic silica aerogels could be prepared without supercritical drying from water glass, trimethylchlorosilane (TMCS) and hexamethyldisiloxane (HMDSO). [8]

Silica aerogels have been produced in the form of a powder, monolith, blanket, and so on. [9, 10] From the point of view of wide applicability, the powder-type silica aerogel is the most promising and much attention has been focused on powder-, granule- and bead-type silica aerogels. [11-14] Recently, silica aerogel granules or beads from hydrogels or alcogels were mainly synthesized by breaking down the wet gel using a high power mixer or by dropping a silica sol into an aqueous

solution containing a gelation catalyst. However, these techniques make it difficult to obtain spherical aerogel granules or beads with a controlled particle size and microstructure. In this work, silica aerogel powders were synthesized via emulsion polymerization, in which droplets of monomer (silicic acid) are emulsified with surfactants in a continuous phase of hexane. After gelation of the silicic acid droplets, the surface of silica aerogel powders was modified and followed by an ambient pressure drying. Some physical properties and the microstructure of the silica aerogel powders were examined.

Experimental Procedure

A sodium silicate solution (water glass) was used as a precursor to prepare the silicic acid. Water glass solution (Young Il Chemical, Korea) was diluted with the distilled water to make an 8 wt% silicate solution. The solution was then passed through a column filled with an ion exchange resin (Amberlite, IR-120H, H. Rohm & Hass Co., PA). The obtained silicic acid solution and 4.0 ml (0.2 mol/L) of surfactant span 80 were added to n-hexane to prepare silicic acid droplets. The n-hexane containing silicic acid droplets was stirred for 5 min at speeds of 3200, 4000, 6000, 9000 and 14000 rpm using a homogenizer, (T25 D, IKA, Germany). A base catalyst (NH₄OH) was then used to bring the pH of the silicic acid to 6.0. The silica sol droplets were gelated at room temperature. The gelation process finished within 10 minutes.

The obtained hydrogel droplets were surface-modified in a 10% TMCS (Trimethylchlorosilane, Si(CH₃)₃Cl, 98% ACROS)/n-hexane solution for 10 hours at room temperature. The surface modification process was repeated 4-6 times. Finally, the wet gel droplets were

^{*}Corresponding author:

Tel:+82-32-860-7521

Fax: +82-32-862-4482 E-mail: hjhwang@inha.ac.kr

washed in n-hexane in order to remove the remaining surface modification agents and reaction products, such as hydrochloric acid. The wet gel droplets were dried at 80 °C in an electric oven under ambient pressure.

The density of the aerogel granules was determined using a tap density tester (TAP-2S, Logan Instruments Co., USA). The particle size and its distribution of the aerogel granules were measured by a scanning electron microscope (FE-SEM, S-4200, Hitachi, Japan). Fourier transform infrared (FT-IR) spectroscopy (FTS-165, Bio-Rad, USA) was used to confirm the surface chemical structure of the aerogels in the wave number range of 400 to 4000 cm⁻¹. The surface area was determined by BET analysis from the amount of N2 gas adsorbed at various partial pressures $(0.01 < p/p_0 < 1)$ (ASAP 2010, Micrometrics, USA). The pore size distributions were measured using the Barrette Joyner Halenda (BJH) cumulative pore volume method. The microstructure of the aerogels was observed by the FESEM.

Results and Discussion

Table 1 summarizes some physical properties of the aerogel powders obtained in this work. The tapping density, porosity, pore volume, pore diameter, and BET surface area of the samples were 0.08-0.09 gcm⁻³, 96%, $3.0-4.0 \text{ cm}^3\text{g}^{-1}$, 12-14 nm and $700 \text{ m}^2\text{g}^{-1}$, respectively. The aerogel powders showed very high pore volume and specific surface area. In addition, it appears that the mixing speed does not have an effect on the silica network structure.

Fig. 1(a) shows the viscosity change of silicic acid solutions with different pH values as a function of time. The pH value of the silicic acid solution that is passed through an ion exchange resin is approximately 2.2. When ammonia solution is added to the silicic acid solution, the viscosity does not change with time. It was observed that when the gelation occurs, the viscosity increases sharply. In addition, as shown in Fig. 1(b), the rate of change in the viscosity increases as the pH value increases. The gelation time was linearly decreased with increasing the pH value of the silicic acid solution. At pH = 2.2 (no ammonia solution

Table 1. Some physical properties of silica aerogel granules.

Sample	Mixing speed (rpm)	Tapping density (gcm ⁻³)	Porosity (%)	Pore volume (cm ³ g ⁻¹)	Average pore diameter (nm)	BET surface area (m ² g ⁻¹)
S 1	3,200	0.090	95.9	4.03	14.0	720
S2	4,000	0.084	96.2	3.37	11.9	733
S3	6,000	0.078	96.5	3.46	12.2	742
S4	9,000	0.068	96.9	3.16	11.9	713
S5	14,000	0.095	95.7	3.06	12.4	656

addition), the gelation time is estimated to be 11 h at 25 °C, while the gelation finished approximately within 100 seconds at pH = 5.5.

 N_2 adsorption and desorption isotherms are shown in Fig. 2. All the aerogel samples showed a typical Type IV adsorption-desorption isotherm. The N_2 gas adsorption



Fig. 1. (a) Viscosity vs. time curves and (b) the gelation time of the silicic acid solution as a function of pH value.



Fig. 2. (a) N_2 adsorption-desorption isotherms and (b) pore size distributions of silica aerogel powders.

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Fig. 3. FE-SEM images of silica aerogel powder: (a) S1, (b) S2, (c) S3, (d) S4, (e) S5.

occurred in the micropores at low pressure, followed by adsorption in the mesopores, with the capillary condensation occurring at the higher pressures, leading to hysteresis loops. This indicates that the silica aerogel granules are mesoporous. In addition, all aerogel samples showed a characteristic H1 hysteresis loop attributable to cylindrical pores and it was almost similar to that of supercritically-dried silica aerogels. [15, 16] It has been reported that aerogels show Type H1, H2 or its intermediate hysteresis loop, depending on their microstructure such as porosity, particle size, and threedimensional network structure. [10, 17]

Fig. 3 (a) ~ (e) shows the microstructure of the silica aerogel powder samples. The particle size decreased as the mixing speed increased: the particle sizes of S1 and S5 were 12.1 and 1.4 μ m, respectively. This result means that the size of silicic acid droplets dispersed in n-hexane can be controlled by the mixing speed. It can



Fig. 4. FT-IR spectra of silica aerogel powders: (a) S3, (b) S4 and (c) S5.

be expected that the higher mixing speed allows silicic acid droplets to be smaller, leading to smaller powder size. Irrespective of the mixing speed, all the samples exhibited a highly porous 3-dimentional silica network structure consisting of nano-sized silica particles. There was no distinct difference in the microstructure between the aerogels prepared from the solutions with different mixing speeds. In addition, the grain and pore structures were homogeneous. It was also found that the secondary particle size, which forms the powder, is estimated to be approximately a few nanometer.

Fig. 4 shows the FT-IR spectra of the aerogel granule samples. During the surface modification process, the surface Si-OH groups of the silica hydrogel droplets would react with Si-(CH₃)₃ groups of TMCS, resulting in hydrophobic Si-O-Si(CH₃)₃ surface groups and a reaction product, hydrochloric acid, HCl. The absorption bands at 1100, 1220, 800 and 460 cm⁻¹ are attributed to a Si-O-Si silica aerogel network structure. On the other hand, the bands around 2900, 1260 and 850 cm⁻¹ were assigned to the Si-CH₃ terminal, which originates from the TMCSmodified silica surface. [13, 18] The band intensity of the Si-CH₃ groups did not change in the aerogel powders with the different mixing speed. Another important feature can be observed in Fig. 4 is that there are no absorption peaks corresponding to the Si-OH bonds. This suggests that surface modification by the TMCS/n-hexane solution successfully proceeded through the wet gel droplets, and that their surfaces are completely hydrophobic.

Conclusion

Spherical silica aerogel powders were successfully fabricated through emulsion polymerization method. In order to produce stable silicic acid droplets which are dispersed in n-hexane, a surfactant, span 80 was used in this work. The irreversible coalescence between droplets during the gelation process was effectively prevented. The mixing speed is the most important step

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in the process of preparing silica aerogel granules with uniform size and microstructure. The obtained aerogel powders showed typical Type IV adsorption-desorption isotherm, suggesting that the surfactant does not affect the gelation process of the silicic acid solution. The aerogel granules exhibited a relatively low tapping density, high specific pore volume and high BET surface area.

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