Preparation and Characterization of Integrated Bulk of Silica Aerogels

WEINA ZHANG[1,2], LIBO HAO[1], JILONG LU[1,*] and JIANWEI ZHU[3,*]

[1]College of Geo-exploration Science and Technology, Jilin University, Changchun 130026, Jilin Province, P.R. China
[2]College of Chemistry, Jilin Normal University, Siping 136000, Jilin Province, P.R. China
[3]College of Earth Sciences, Jilin University, Changchun 130061, Jilin Province, P.R. China

*Corresponding authors: Tel/Fax: +86 431 88502603; E-mail: lujl@jlu.edu.cn; zjw1095@sina.com

The integrated bulk of silica aerogels were synthesized by two step sol-gel process using tetraethoxysilane as precursor followed by supercritical drying technique. The X-ray diffraction, nitrogen adsorption-desorption method, differential thermal -thermogravimetric analysis, infrared spectroscopy and scanning electron microscopy analysis were used to observe the structure, the surface morphology and the chemical composites of the prepared silica aerogels. The results showed that the prepared silica aerogels had continual netted, amorphous and mesoporous microstructure with even spherical nanometer particles and porous channel. The density, averaged pore size and specific surface area of the prepared silica aerogels with high thermal stability were 0.12 g cm^{-3}, 14.9 nm and 925.7 m^2 g^{-1}, respectively.

Key Words: Silica aerogels, Integrated bulk, Supercritical drying, Characterization.

INTRODUCTION

Silica aerogels are amorphous transparent porous solid materials with a highly cross-linked three-dimension netted structure constituted with particles of colloid or polymer. Due to their unique structure the resulting silica aerogels have many outstanding properties[1-7] such as high porosity (up to 99.8 %), very low densities (0.03-0.6 g cm^{-3}), higer surface area (1000 m^{2}g^{-1}), in addition to, their Young's modulus is a factor 10^2-10^4 smaller than that of silica glass, due to this property they can be easily compressed. So, aerogels have an increasing interest in materials science research because of their unusual properties and wide industrial applications[8-12], such as, they can be used as materials of acoustic impedance in the acoustics, Cerenkov radiation detectors in high energy physics, photoluminescent materials in optics, batteries, capacitor electrodes and dielectric materials in electrics, materials of thermal protection in calorifics, an adsorbent in chemistry and other fields.

To obtain an aerogel, it is necessary to dry the gel, avoiding structural damage. This is feasible by the extraction of the solvent under supercritical conditions, traditionally[1,13]. However, limited practical applications of supercritical drying owing to its huge, expansive and dangerous apparatus make new ambient pressure drying technique develop rapidly[14-17]. While, bulk of pure silica aerogels can be obtained hardly because of capillary stress and associated drying shrinkage when drying at ambient pressure, which will cause the cracked

structure, uneven porous sizes and particular sizes, even lose all of outstanding properties, then limit its application. Moreover, vast waste liquid will be produced owing to the usage of large number of solvents, which can cause environmental pollution and large time will be cost when drying at ambient pressure. Therefore, further studies on supercritical drying technique are necessary for actual application of pure silica aerogels[18,19].

In this study, integrated bulk of pure silica aerogel was prepared from tetraethoxysilane precursors by supercritical drying technique, its structure and properties were characterized in detail *via* different analysis technique.

EXPERIMENTAL

Tetraethoxysilane (TEOS), ethanol (EtOH), oxalic acid, ammonia and propanetriol were all of analytical reagent grade or better, which purchased from Beijing Chemical Factory (Beijing, China). Ultrapure water of 18.2 MΩ·cm produced from the Milli-Q Plus system (Millipore, Bedford, MA, USA).

Silica alcogels were prepared by sol-gel method using tetraethoxysilane as resource of silica. The molar ratio of TEOS: EtOH: H$_2$O (oxalic acid): propanetriol was kept at 1:6.9:3.5:0.5, in which propanetriol was used as drying control chemical additives, the concentration of oxalic acid was 0.01 mol L^{-1}. When sol was produced after stirring several minutes and laying silently for 24 h, ammonia of 0.5 mol L^{-1} was added

with stirring continuously, the quantity of ammonia was two times of tetraethoxysilane. After gelation, a small quantity of ethanol was added to the gel to avoid shrinkage and cracks. The gel was placed in the stainless steel autoclave with ethanol according to the references[20]. Amounts of liquid CO_2 were introduced into the autoclave to replace the water and ethanol in the gels. When the solvents in the gels were replace completely by CO_2, then excess amounts of liquid CO_2 were introduced into the autoclave to achieve the critical pressure of the CO_2 (Pc, 8.5×10^6-9.5×10^6 Pa) as the temperature of the autoclave was slowly increased above the critical tempe-rature of the CO_2 (Tc, 35-38 ℃). After reaching a temperature and pressure well above the values of Tc and Pc in the autoclave, The samples were kept in the reactor (dried) for 3-4 h. Then the pressure was reduced and the reactor was brought to room temperature, the silica aerogels would be obtained.

The bulk density of the aerogel was measured from weight to volume ratio. Appearance of aerogels was observed by their photographs which obtained by a camera (model ES70, Samsung, Korea). Phase identification was performed *via* X-ray diffractometry (model D/MAX-2500, Rigaku, Japan), using nickel-filtered CuK_α radiation and a scanning speed of $2\theta = 8°$ per min, the working voltage and current were 40 KV and 30 mA, respectively. Meso- and microporous structures of the aerogels prepared in the present work were determined by nitrogen adsorption and desorption isotherms, which were obtained using a gas adsorption apparatus (model ASAP 2020, Micromeritics Instrument, USA) at 77.3 K, Surface areas were evaluated using the BET equation[21]. Pore size distribution and total pore volume of the materials were evaluated from the adsorption branch of nitrogen isotherms by using the Barrett-Joyner-Halenda (BJH) method. The thermal stability was evaluated by differential thermal analysis- thermogravimetric curves (model Pyris Diamond, PerkinElmer, USA), a-Al_2O_3 was used as reference materials at the rate of 10 ℃ min^{-1}. Infrared spectroscopy was performed with an Fourier transform infrared (FT-IR) spectroscopy (model VERTEX 70, Bruker, Germany) to confirm the surface chemical structure of the aerogels. The microstructure of the aerogels was observed using scanning electron microscope (model XL30ESEM-FEG, FEL Company, Holand), in which a working voltage of 20 KV was used.

RESULTS AND DISCUSSION

The obtained aerogel silica was cylindrical and translucent with regular shape that were 6.3 cm in diameter by 1.7 cm high and had certain rigidity without any crack. It was very light with the density of 0.12 g cm^{-3}. There was not obvious crystalline diffraction peak in X-ray diffraction patterns of obtained silica aerogel, which indicated that the sample was not crystalloid, but was amorphous with disordered structure.

Textural properties of silica aerogel: Nitrogen adsorption-desorption method was used to analyze the textural properties of silica aerogel. Figs. 1 and 2 showed the nitrogen adsorption-desorption isotherms and BJH pore size distribution of silica aerogel, respectively. As can be seen from Fig. 1, the adsorption isotherms were very similar to type-IV adsorption isotherms, which indicated the presence of mesopores[22]. The desorption

cycles of the isotherms showed a hysteresis loop which is gene-rally attributed to the capillary condensation occurring in the mesopores[23], which indicated that the prepared silica aerogel had characters of mesopores and was typical mesoporous material. It can be seen from Fig. 2 that the pore size distribution of silica aerogel sample was in the range of 2-60 nm with average pore diameter residing at 14.9 nm. And the specific surface areas, total pore volume were 925.7 m^2 g^{-1} and 4.4 cm^3 g^{-1} by measurement, respectively.
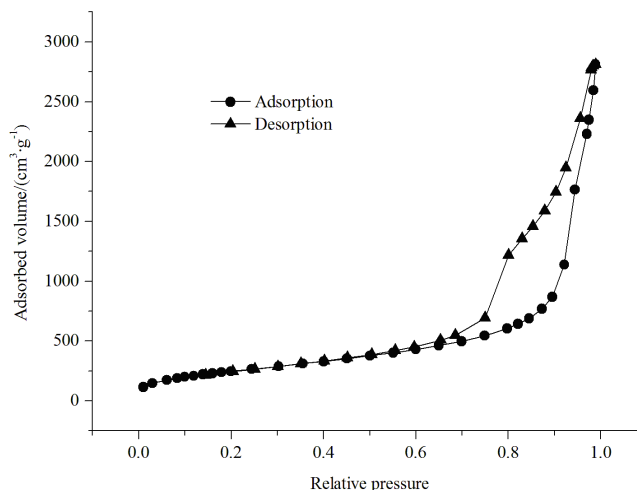

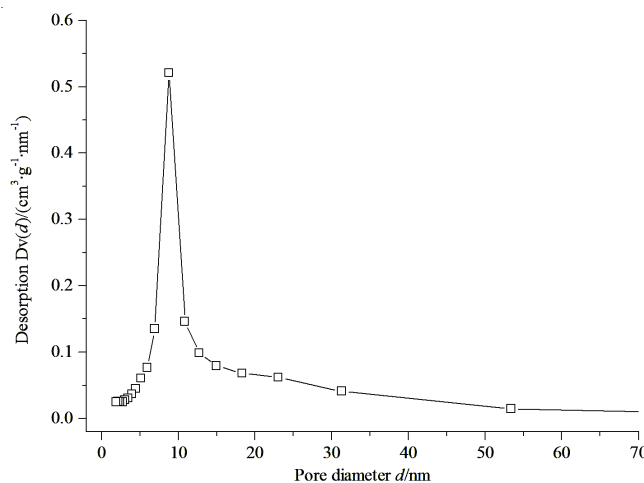Fig. 1. N_2 adsorption-desorption isotherms of silica aerogel

Fig. 2. Pore size distribution of silica aerogel

Thermal analysis of silica aerogel: Thermal analysis of prepared silica aerogel was evaluated by the differential thermal-thermogravimetric curves (DTA-TG, Fig. 3). Fig. 3 showed that the mass loss decreased gradually from around 40-1100 ℃, the total percentage of mass loss were 14.6 % and the mass loss was rapid before 200 ℃ due to evaporation of absorbent H_2O and rudimental alcohol. Subsequently, a further increase of temperature up to 260 ℃ caused the TG curve declined slowly, along with an exothermic peak in DTA curve corresponding to the oxidation of the surface hydroxyl groups and evaporation of structural water. And when the tempe-rature was higher than 600 ℃, the mass would keep constant and there was not any peak in DTA curve, which indicated the prepared silica aerogel had good thermal stability.
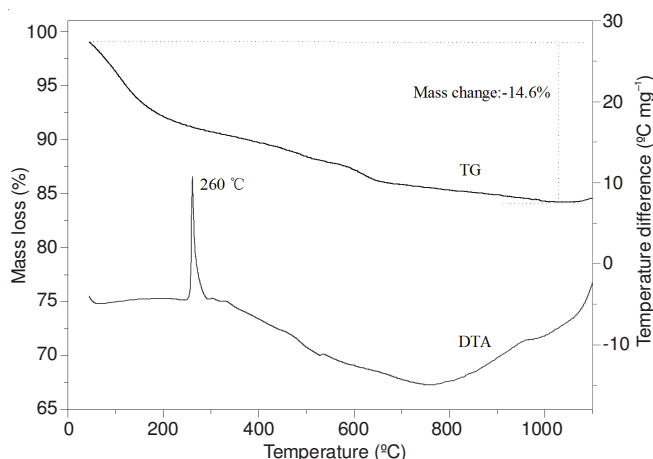
Fig. 3. Differential thermal-thermogravimetric analysis curves of silica aerogel

Fig. 5. Scanning electron microscopy photograph of silica aerogel

Infrared spectroscopy of silica aerogel: The IR investigation of the prepared material was shown in Fig. 4. The absorption peaks near 1086, 799 and 461 cm^{-1} were due to Si-O-Si vibrations[24], the intensities of these three peaks were strongest because the silica aerogel is an substance consisting mainly of silicon oxide. The peaks of 3440, 1626 and 980 cm^{-1} corresponded to the O-H adsorption bond, which was caused by physically adsorbed water, which indicated that the obtained silica aerogel was hydrophilic. The small peak at 3000 cm^{-1} correspond to Si-C$_2$H$_5$, which showed that little ethanol still existed in sample after drying, however, the main composition of the sample was SiO$_2$, which reached the prospective target.

Conclusion

Integrated bulk of silica aerogel was prepared by sol-gel method and supercritical drying technique using tetraethoxysilane as resource of silica. The obtained material was cylindrical, translucent and had low density (0.12 g cm^{-3}), high surface area (925.7 m^2 g^{-1}), even pore diameter (14.9 nm) and pore volume (4.4 cm^3 g^{-1}). The sample had continual netted microstructure constituted with even spherical nanometer particles and porous channel. The pore sizes and thermal analysis indicated it was typical amorphous mesoporous material with high thermal stability.
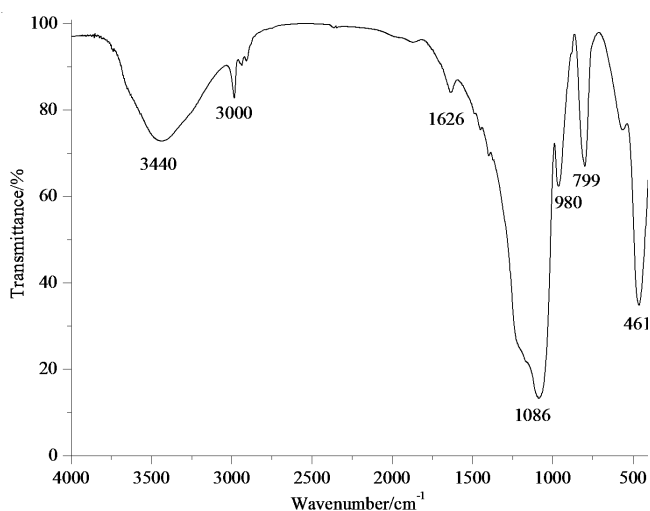
Fig. 4. Infrared spectroscopy of silica aerogel

Scanning electron microscopy (SEM) of silica aerogel: Fig. 5 showed the SEM morphology of prepared silica aerogel, it can be seen from which the prepared silica aerogel had loose porous network structure and uniform particle and pore sizes with average pore diameter in the range of 5-100 nm which was consistent with the result discussed in textural properties of silica aerogel. The particles had even size and existed as sphericity with the particle diameter in the range of 20-100 nm, which indicated that the prepared silica aerogel was typical porous nanometer material.
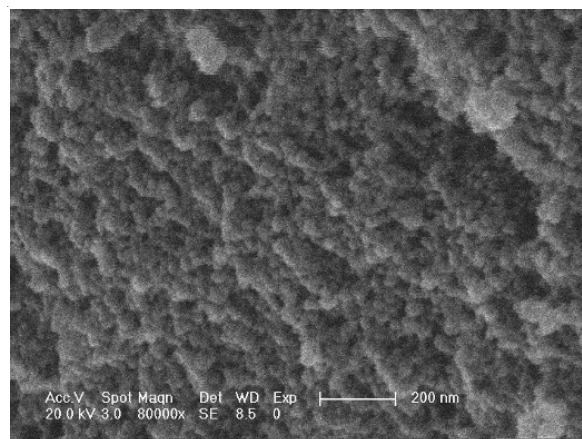
REFERENCES

1. S.S. Kistler, *Nature*, **127**, 741 (1931).
2. M. Gronauer and J. Fricke, *Acustica*, **59**, 177 (1986).
3. T.M. Tillotson and L.W. Hrubesh, *Mater. Res. Soc. Symp. Proc.*, **121**, 658 (1988).
4. K.I. Jensen, *J. Non-Cryst. Solids*, **145**, 237 (1992).
5. C.-Y. Kim and A.R. Jang, *Asian J. Chem.*, **24**, 4217 (2012).
6. J. Fricke and T. Tillotson, *Thin Solid Films*, **297**, 212 (1997).
7. M. Moner-Girona, A. Roig, E. Molins, E. Martínez and J. Esteve, *Appl. Phys. Lett.*, **75**, 653 (1999).
8. N. Hüsing and U. Schubert, *Angew. Chem. Int. Ed. Engl.*, **37**, 22 (1998).
9. L.W. Hrubesh, *J. Non-Cryst. Solids*, **225**, 335 (1998).
10. W.C. Ackerman, M. Vlachos, S.R. Rouanet and J. Fruendt, *J. Non-Cryst. Solids*, **285**, 264 (2001).
11. A.C. Pierre and G.M. Pajonk, *Chem. Rev.*, **102**, 4243 (2002).
12. G.S. Kim and S.H. Hyun, *J. Non-Cryst. Solids*, **320**, 125 (2003).
13. G.A. Nicolaon and S.J. Teichner, *Bull. Soc. Chim. Fr.*, **5**, 1900 (1968).
14. B.Unlusu, S.G. Sunol and A.K. Sunol, *J. Non-Cryst. Solids*, **279**, 110 (2001).
15. F. Shi, L.J. Wang and J.X. Liu, *Mater. Lett.*, **60**, 3718 (2006).
16. H.J. Liu, W. Sha, A.T. Cooper and M.H. Fan, *Colloids Surf. A*, **347**, 38 (2009).
17. Y.J. Oh and B.A. Nam, *Solid State Sci.*, **13**, 1579 (2011).
18. B.S.K. Gorle, I. Smirnova, M. Dragan, S. Dragan and W. Arlt, *J. Supercrit. Fluids*, **44**, 78 (2008).
19. D.M. Smith, G.W. Scherer and J.M. Anderson, *J. Non-Cryst. Solids*, **188**, 191 (1995).
20. M.J. van Bommel and A.B. de Haan, *J. Mater. Sci.*, **29**, 943 (1994).
21. S. Brunauer, P.H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).
22. J. Haber, A. Baiker, M. Nobbenhuis, J. Kiwi, R. Thampi and M. Gratzel, *Catal. Today*, **20**, 11 (1994).
23. S.D. Bhagat, Y.H. Kim, M.J. Moon, Y.S. Ahn and J.G. Yeo, *Solid State Sci.*, **9**, 628 (2007).
24. F. Shi, L.J. Wang and J.X. Liu, *Mater. Lett.*, **60**, 3718 (2006).