Syntesis of silica xerogel

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Syntesis of silica xerogel: *Silica xerogel was prepared from sodium silicate by sol-gel process followed by ambient pressure drying. Sodium silicate was neutralized with citric acid to form silica gel. To prepare xerogel, first the pore water of the gel was exchanged by ethanol and then surface modification was done by aging alcogel in tetraethylorthosilicate (TEOS)/ethanol solution. Before drying, TEOS/ethanol solvent was exchanged with n-heptane. Capillary stress and shrinkages were greatly reduced due to the low surface tension of n-heptane. The prepared xerogel was a opaque and crack-free solid, with bulk density of 0.67 g.cm*$^{-3}$*, porosity of about 80%. The nature of surface modification and thermal stability of the aerogel was studied by FTIR and DSC/TG respectively.*

Key words:*aerogel,xerogel, TEOS*

INTRODUCTION

Silica aerogels are the lightest and extremely porous manmade solids ever known.[1] Because of their fascinating properties the aerogels find potential applications in superthermal insulators, catalyst supports and dielectric materials.[2–4] Aerogels are usually prepared by supercritical drying of wet silica gels.[5–7] Supercritical drying process can avoid capillary stress and associated drying shrinkage, which are usually prerequisite of obtaining aerogel structure. However, supercritical drying process is so energy intensive and dangerous that real practice and commercialization of the process is difficult. An alternative cost-effective process is very important for commercial success of the aerogel.

The ambient pressure drying technique is one of the alternative cost-effective processes of aerogel synthesis.[8–10] In order to obtain highly porous aerogel structure, elimination of capillary stress during ambient pressure drying is very important.[11] Liquid evaporation from wet gel during drying creates a capillary tension (due to the liquid-vapour interface) and that tension is balanced by the compressive stress on the solid network, causing shrinkage of the gel.[9] Strengthening of gel network, surface modification and solvent exchange of the wet gel are necessary to suppress such type of capillary tension and shrinkage during ambient pressure drying.[12,13] The gel should be aged in silane solution [14] to increase the strength and stiffness of it. Finally, pore liquid must be replaced by low surface tension solvent to reduce capillary stress and associated drying shrinkage.

The conventional method of silica xerogel preparation is sol-gel process using organic silicon monomer, such as tetramethylorthosilicate (TMOS), tetraethylorthosilicate (TEOS) or polyethoxydisiloxane (PEDS) as precursors.[7] Derived products are a cheap approach have better properties and method uses a cheap source of silica (sodium silicate).

EXPERIMENTAL

Wet gels were prepared from commercial sodium silicate precursor of specific gravity 1.05 diluted from specific gravity of 1.39 (Na_2SiO_3, Marvin-Ltd, Bulgaria, $Na_2O:SiO_2$ = 1:3.13) using citric acid ($C_6H_8O_7.H_2O$) as catalyst keeping molar ratio of $Na_2SiO_3:H_2O$ constant at 1:150. The sols were prepared by adding acid dropwise in sodium silicate solution while stirring and were kept for gelation at 50^{o}C in a temperature controlled oven to form a gel. The formed gels were aged for 3 h at 50^{o}C to give strength to the gel network. To study the effect of acid, the monolithic gels were first cut into very small pieces then washed with 50 ml water four times so that the sodium salt trapped in the pores of gel will come out and once with methanol in 24 h respectively. Subsequently, the silica gel was soaked in a solution of 20 vol% H_2O/ethanol for 24 h at 50^{o}C followed by aging with ethanol at same condition.

The ethanol treated gel was aged in a solution of 70 vol% TEOS/ethanol for 24 h at 70°C. The gel was washed with n-heptane for several times to remove TEOS/ethanol solution from the gel. Then, it was aged inside n-heptane at 50°C for 24 h with 4 times renewal of fresh n-heptane. Finally, modified gels were aged for another 24 h inside n-heptane at room temperature before air drying. The gel was dried in 24 h interval at 50, 90, 120 and 150°C with partially covered condition.

Bulk density and apparent porosity of silica xerogel was measured by Archimedes principle using kerosene liquid. Fourier transform infrared spectroscopy (FTIR) was employed to investigate the chemical bonding state of surface modifying agent with xerogels. The thermal behaviour of the dried gel was examined using DSC/TG analysis.

RESULTS AND DISCUSSION

The strength and stiffness of the wet silica gel was enhanced by aging it in TEOS/ethanol solution. Prior to this aging, the gel was thoroughly washed with ethanol.

The strength and stiffness of gel may also increase by ethanol washing due to dissolution of silica from the particles and reprecipitation into the necks between the particles. However, it has been reported that the increase in strength and stiffness by such washing was not sufficient to avoid shrinkage during drying and hence, further aging in TEOS solution was necessary. TEOS – aging causes silica to precipitate from the aging solution on to the silica network. Precipitation of silica gives an increase in the density of the wet gel and corresponding strengthening and stiffening of the gel network. During aging hydrolysis of TEOS and condensation of silica gel occurs. The two reactions are stated below as reaction (1) and (2), respectively. Residual pore water and water by-product of condensation reaction (2) may be responsible for hydrolysis of TEOS. TEOS can also take part in condensation reaction with Si-OH group of gel structure (reaction-3) :

Hydrolysis :

$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH \text{ ....(1)}$$

Condensation :

$$Si(OH)_4 + (OH)_4Si \rightarrow (OH)_3Si{-}O{-}Si(OH)_3 + H_2O \text{.................(2)}$$

$$\equiv Si(OC_2H_5) + HO{-}Si\equiv \rightarrow \equiv Si{-}O{-}Si\equiv + C_2H_5{-}OH \text{...................(3)}$$

After surface modification, TEOS/alcohol solution was replaced by n-heptane to prohibit cracks formation during drying of the gel. Capillary stresses and associated drying shrinkage of gel were reduced due to the low surface tension of n-heptane.

Fig. 1 – Silica xerogel prepared from sodium silicate by ambient pressure drying process

The silica xerogel prepared from sodium silicate was a opaque porous solid with an appearance as shown in Fig. 1. Bulk density and apparent porosity of the xerogel were 0.67 g.cm^{-3} and 80% respectively.

Figure 2 shows FTIR spectra of the xerogel heated at different temperatures. There are characteristic bands of silica xerogel at ~1098, ~804 and ~471 cm^{-1}. The ~1098 cm^{-1} band is associated with the Si-O-Si asymmetric bond stretching vibration while the band at ~804 cm^{-1} is assigned to a network Si-O-Si symmetric bond stretching vibration. The bands at ~471 cm^{-1} are associated with a network Si-O-Si bond bending vibration. The bands at ~960 cm^{-1} are associated with stretching mode Si-OH typical of gel structure. The intensity of this band indeed decreases with increasing temperature due to polycondensation and dehydroxylation of gel. The bands at ~3440 and ~1630 cm^{-1} are associated with the –OH absorption band which is caused by physically adsorbed water. The intensity of those bands decreases with increasing temperature. The small absorption peaks at ~2927 and ~2856 cm^{-1} may be associated with –OC_2H_5 terminal group. Those peaks were absent in the xerogel which were heat treated above 400°C.

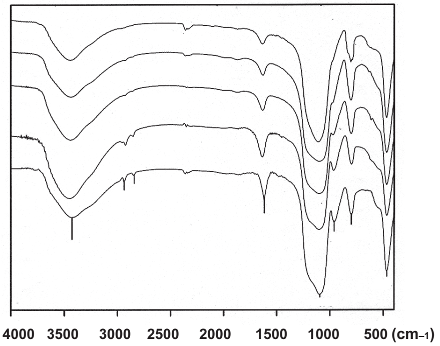

Fig. 2 – FTIR spectra of silica xerogel heated at different temperatures

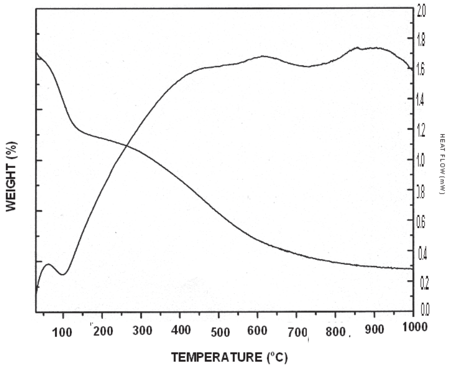

Fig. 3– DSC/TG curve of air-dried silica xerogel

Figure 3 shows the DSC/TG curve of silica xerogel. There is a sharp weight loss up to a temperature of 150°C due to the evaporation of residual water from the xerogel. Further, the significant weight loss observed in the temperature range of 300-700°C can be attributed to the progressive poly-condensation and dehydration of xerogel as stated above.

CONCLUSIONS

The present paper demonstrated a cost-effective process for the production of silica xerogel using sodium silicate precursor via ambient pressure drying. The surface modification and strengthening of wet gel was obtained by aging it in TEOS/ethanol solution. Low surface tension liquid n-heptane was used to suppress capillary stresses and associated shrinkage during ambient pressure drying of the gel. Using this route, it was possible to obtain the silica xerogel with low density (0.67 g.cm^{-3}), and high porosity (80%). The process of xerogel production from by sodium silicate ambient pressure drying method is very important from the industrial point of view and it will significantly widen the commercial exploitation of the silica xerogel.

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This paper has been reviewed