Preparation of Silica Aerogel by Ambient Pressure Drying Process using Rice Husk Ash as Raw Material

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[MS received June 10, 2008; revised copy received April 14, 2009]

Silica aerogel was prepared from rice husk ash by sol-gel process followed by ambient pressure drying. Silica was extracted from ash as sodium silicate by boiling it in sodium hydroxide solution. Sodium silicate was neutralized with nitric acid to form silica gel. To prepare aerogel, 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 aerogel was a light and crack-free solid, with bulk density of 0.67 g.cm^{-3}, porosity of about 80%, total pore volume of 3.1 cm^3.g^{-1} and specific surface area of about 273 m^2.g^{-1}. The nature of surface modification and thermal stability of the aerogel was studied by FTIR and DSC/TG respectively.

[Keywords : Silica aerogel, Rice husk ash, Ambient pressure drying]

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 super-thermal 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 aerogel preparation is sol-gel process using organic silicon monomer, such as tetramethylorthosilicate (TMOS), tetraethylorthosilicate (TEOS) or polyethoxydisiloxane (PEDS) as precursors.[7] However, such organic precursors are so expensive that aerogel production in an industrial scale is not economically viable. Rice husk ash (RHA) can be a cheap raw material for silica aerogel production because amorphous silica content of the ash can easily be dissolved in sodium hydroxide solution. RHA has long been used to synthesize silica gel.[15–19] There are few reports on the synthesis of silica aerogel using RHA. Tang and Wang[7] have prepared the aerogel using RHA by supercritical carbon dioxide drying. In the present study, we report upon our efforts to synthesize silica aerogel through ambient pressure drying using rice husk ash as the silica source.

Experimental

The flow chart of silica aerogel preparation from rice husk ash is illustrated in Fig. 1. Properly cleaned rice husk was burned at 700°C for 6 h to get rice husk ash. 5 g of the ash was mixed with 50 mL 1 mol.L^{-1} NaOH aqueous solution. The mixture was refluxed for 1 h. Most of the ash was dissolved in NaOH solution. The solution was filtered to remove the undissolved residues. The sodium silicate solution was neutralized using 1 mol.L^{-1} HNO$_3$ solution to form silica gel at pH 6. The prepared gel was aged at room temperature for 24 h under sealed condition. The aged gel was washed using de-ionized water to remove sodium nitrate. The extent of Na removal was measured by analyzing Na-content of dried gel using EDX. The sodium content of the dry gel was about 0.02% as shown in Fig. 2. Subsequently, the silica gel was soaked in a solution of 20 vol% H$_2$O/ethanol for 24 h at

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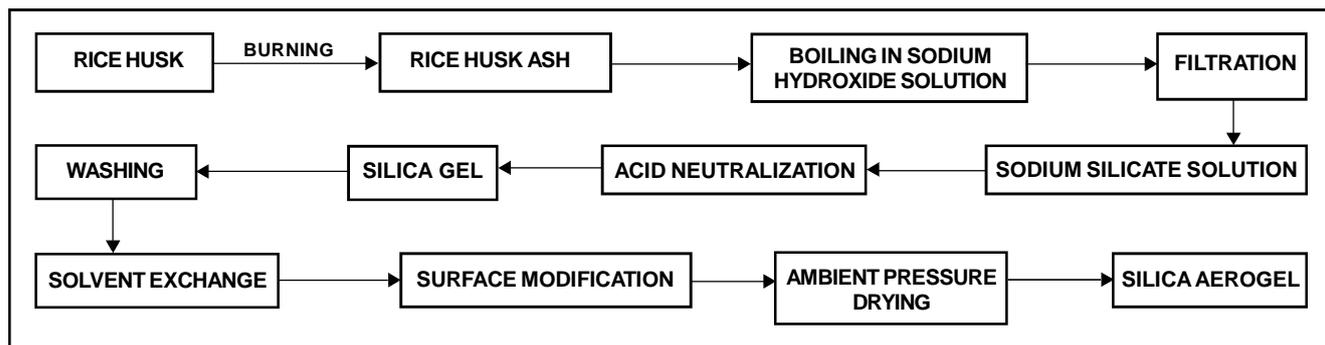
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Fig.1 – Flowchart of silica aerogel preparation from rice husk ash

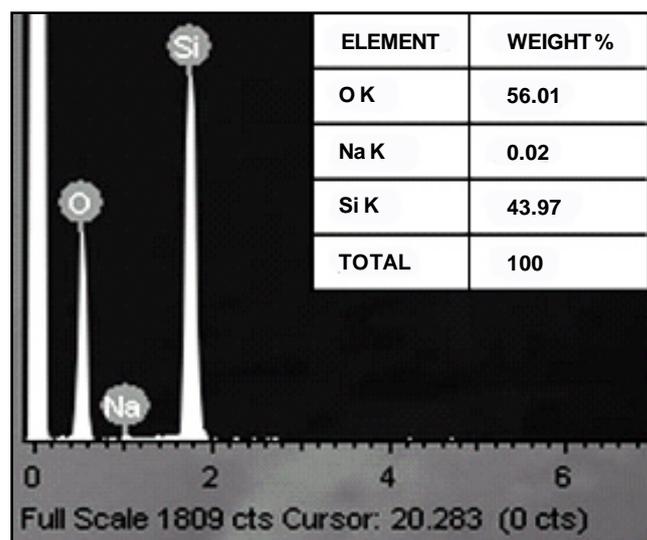| ELEMENT	WEIGHT %
O K	56.01
Na K	0.02
Si K	43.97
TOTAL	100

Fig. 2 – EDX spectra and elemental analysis of dry silica gel

50^oC 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^oC. 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^oC 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^oC with partially covered condition.

Bulk density and apparent porosity of silica aerogel was measured by Archimedes principle using kerosene liquid. Fourier transform infrared spectroscopy (FTIR, Spectrum RX-1, Perkin Elmer) was employed to investigate the chemical bonding state of surface modifying agent with aerogels. The specific surface area and pore size distribution of aerogel were determined by Brunauer-Emmett-Teller (BET) method using Autosorb-1, Quantachrome surface area analyzer. The thermal behaviour of the dried gel was examined using DSC/TG analysis (DSC/TG, Netsch STA 449 C Jupitor).

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.[20, 21] 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.[14] TEOS-aging causes silica to precipitate from the aging solution onto 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.[14] 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 :

$$Si(OC_2H_5)_4 + 4H_2O \longrightarrow Si(OH)_4 + 4C_2H_5OH \quad ..(1)$$

Condensation :

$$Si(OH)_4 + (OH)_4Si \longrightarrow (OH)_3Si–O–Si(OH)_3 + H_2O ..(2)$$

$$\equiv Si(OC_2H_5) + HO–Si\equiv \longrightarrow \equiv Si–O–Si\equiv + C_2H_5–OH \quad ..(3)$$

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.

The silica aerogel prepared from rice husk ash was a light, semi-translucent porous solid with an appearance as shown in Fig. 3. Bulk density and apparent porosity of the aerogel were 0.67 g.cm^{-3} and 80% respectively.

Figure 4 shows FTIR spectra of the aerogel heated at different temperatures. There are characteristic bands of silica aerogel at ~1098, ~804 and ~471 cm^{-1}. The ~1098 cm^{-1} band is associated with the Si-O-Si asymmetric bond stretching vibration[22] 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 poly-condensation and dehydroxylation of gel.[23] The bands at ~3440 and ~1630 cm^{-1} are associated with the –OH absorption band which is caused by physically adsorbed water.[10] The intensity of those bands decreases with increasing temperature. The small absorption peaks at ~2927 and ~2856 cm^{-1} may be associated with –OC$_2$H$_5$ terminal group.[24] Those peaks were absent in the aerogel which were heat treated above 400°C.

Figure 5 shows the DSC/TG curve of silica aerogel. Similar results of the weight loss for aerogel was observed by Folgar et al.[25] There is a sharp weight loss up t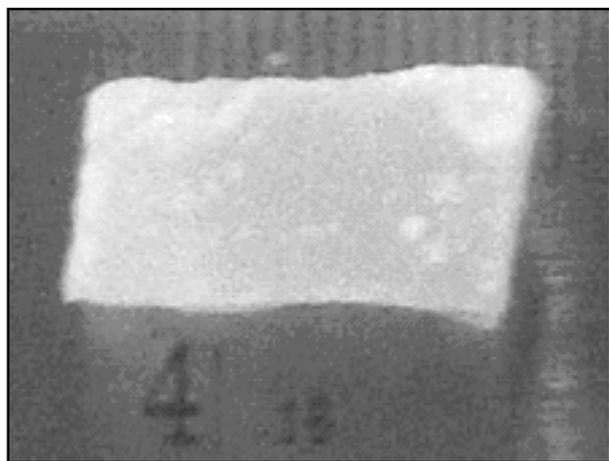o a temperature of 150°C due to the evaporation of residual water from the aerogel. Further, the significant weight loss observed in the temperature range of 300°-700°C can be attributed to the progressive poly-condensation and dehydration of aerogel as stated above.

Figure 6 shows the nitrogen adsorption-desorption isotherm of silica aerogel. BET surface area and total pore volume of the aerogel were 273 m^2.g^{-1} and 3.1 cm^3.g^{-1} respectively. The aerogel exhibited type-IV adsorption isotherm, which indicates the presence of mesopores.[10] Pore size distribution of the aerogel is shown in Fig. 7. The pores were in the range of 10-40 nm, i.e. in the mesoporous range.

Conclusions

The present paper demonstrated a cost-effective process for the production of silica aerogel using rice husk

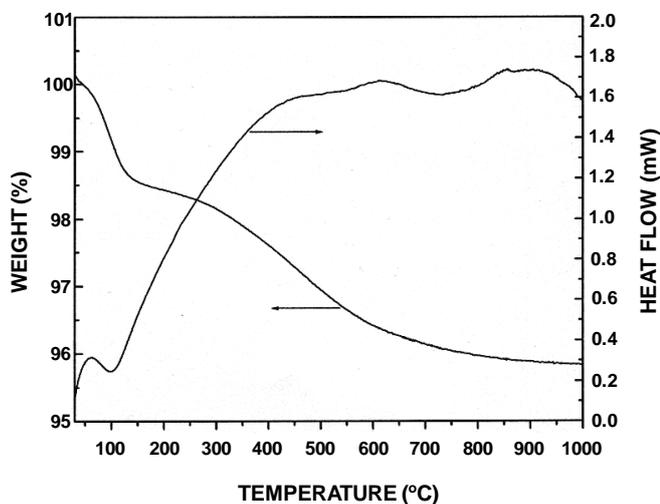**Fig. 3 – Silica aerogel prepared from rice husk ash by ambient pressure drying process**

Fig. 5 – DSC/TG curve of air-dried silica aerogel derived from rice husk ash

Fig. 4 – FTIR spectra of silica aerogel heated at different temperatures
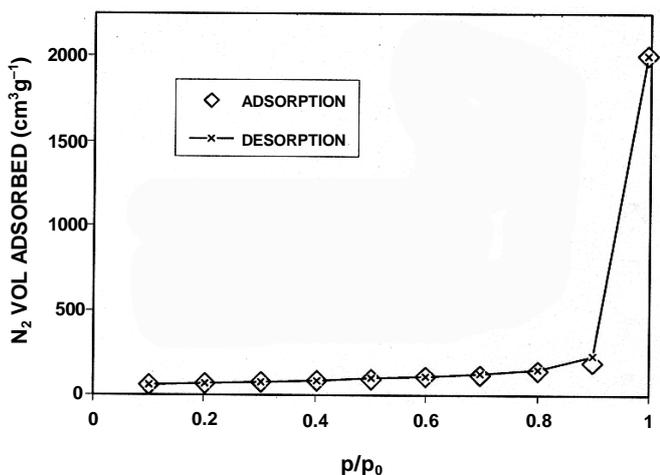

Fig. 6 – Nitrogen adsorption-desorption isotherm of silica aerogel derived from rice husk ash
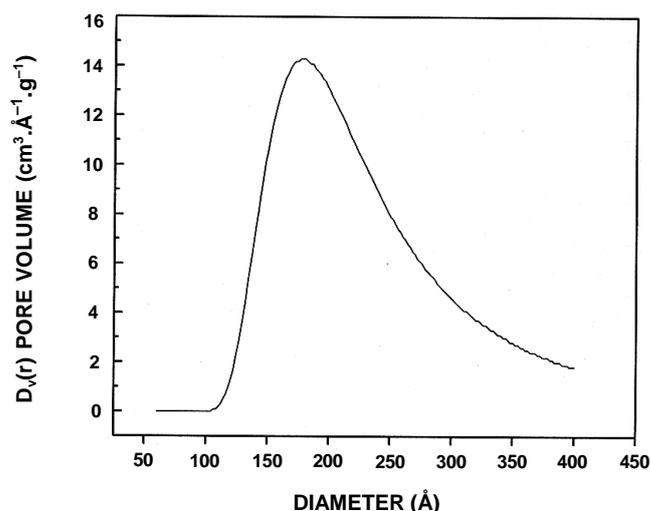
Fig. 7 – Pore size distribution of silica aerogel derived from rice husk ash

ash 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 aerogel with low density (0.67 g.cm^{-3}), high porosity (80%) and a specific surface area of 273 m^2.g^{-1}. The process of aerogel production from rice husk ash by ambient pressure drying method is very important from the industrial point of view and it will significantly widen the commercial exploitation of the silica aerogel.

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