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Studies on the Preparation and Thermal Stability of SiO_2 Aerogels Doped with Fibrous Bructite and TiO_2 Opacifier

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The reinforced silica aerogel and composite silica aerogel doped with fibrous bructite and titanium dioxide opacifier had been prepared by sol-gel method and supercritical drying technique, using tetraethoxysilane as precursor. The thermal stability and micromorphology of the reinforced silica aerogel and composite silica aerogel had been studied by the differential thermal analysis, thermogravimetric analysis and scanning electron microscopy and these properties had been compared with pure silica aerogel. The results showed that the weight loss of silica aerogels increased a little and the thermal stability decreased slightly after fiber and TiO_2 power were doped. But the porous netted structure of obtained reinforced and composite silica aerogels were very even and ordered, which will be enough to satisfy the demands of the super heat insulation and heat preservation of materials in the fields of avigation, spaceflight, civilian technology and industry.

Key Words: Silica aerogels, Fibrous bructite, Composite silica aerogels, Thermal stability.

INTRODUCTION

Silica aerogels are new unique non-crystal materials with high porosity that is *ca.* 90-99 % air by volume and low density (< 30 kg/m^3) which were called as the lightest solid material in world. They have special three-dimension netted structure, this structure is responsible for giving aerogel materials claim to the lowest known density, index of refraction, thermal conductivity, electrical and acoustical conductivities of any solid material, except that they have surface area as high as 106 m^2/kg[1-4]. Due to this unusual combination of properties in the same material, aerogels find several industrial applications such as Cerenkov radiation detectors in high energy physics, containers for liquid rocket propellants and perfumes, windows for thermal protection, acoustic insulating systems, automobile exhaust catalytic supports, comet dust collectors and heat-storage devices for automobiles[5-11]. So, the studies of silica aerogels have been more and more extensive. But the pure silica aerogels have big drawbacks such as low intensity, big brittleness and bad toughness, their nano-scale structure is easily destroyed by the extraneous load which restricts their application. So the emphases of study are focusing on the intensity, brittleness and toughness of aerogels to prevent the collapse of the porous structure. Many works have been studied about the aspects. Wang *et al.*[12] had studied the thermal conductivity and mechanical property of the monolithic silica aerogels doped with TiO_2 powder and ceramic fibers. Wang *et al.*[13] had prepared hydrophobic silica aerogels heat insulation composites reinforced by mullite fiber. SiO_2-Aerogel/short silica fiber porous skeleton composite SiO_2 had been fabricated and their properties had been studied by Wang *et al.*[14]. Mechanical properties of fiber-reinforced aerogel were investigated by Yang and compression tests were performed at both room and evaluated temperature[15]. But there are no investigation on the thermal stability of reinforced composite silica aerogels doped with fibrous bructite and TiO_2 opacifier simultaneously and the comparison with which of pure silica aerogel.

In this paper, fibrous bructite was selected as the enforced material of silica aerogels, the thermal conductibity of silica aerogels can not be affected because of its low heat conduction coefficient and high melting point[16]. The composite silica aerogel was prepared by adding TiO_2 fine powder, which was used as an opacifier to reduce the radiative heat transport at higher temperature[17]. The discrimination of the thermal stability between enforced composite silica aerogels and pure silica aerogel had been studied simultaneously.

EXPERIMENTAL

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

Preparation of alcogel: According to our previous works[18,19], pure silica alcogels were prepared by hydrolysis and polycondensation. On the basis of this method, in the process of polycondensation, the fibrous bructite which had been dispersed evenly by dispersant sodium dodecylsulfate was added synchronously to alcosols with the ammonia, then alcogels of reinforced silica aerogels by fiber were obtained. When the TiO_2 powders were added synchronously to alcosols with the fibrous bructite, then alcogels of composite silica aerogels were obtained.

Preparation of aerogels: After gelation, a small quantity of ethanol was added to the alcogels to avoid shrinkage and cracks. All the gels were aged at the ambient temperature for 2 days. Silica aerogels were obtained by supercritical drying of the alcogels in an autoclave of capacity 100 mL (Parr Instrument Company, USA) according to the references[20]. Amounts of liquid CO_2 were introduced into the autoclave to replace the water and ethanol in the alcogels. When the solvent in the alcogels 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 temperature of the CO_2 (Tc, 35-38 ºC). 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 further 1 h. Then the pressure was reduced and the reactor was brought to room temperature, the silica aerogels will be obtained.

Methods of characterization: Appearance of aerogels was observed by their photographs which obtained by a camera (ES70, Samsung, Korea).The thermal stability was evaluated by differential thermal analysis-thermogravimetric curves (Pyris Diamond, PerkinElmer, USA), α-Al_2O_3 was used as reference materials at the rate of 10 ºC /min. The microstructure of the aerogels was observed using scanning electron microscope (XL30ESEM-FEG, FEL Company, Holand), in which a working voltage of 20 KV was used.

RESULTS AND DISCUSSION

Photographs of samples: Photographs of the monolithic silica aerogel samples were shown in Fig. 1, as can be seen from Fig. 1(a), the pure cylindrical silica aerogel was translucent with regular shape that are 6.3 cm in diameter by 1.7 cm high; Fig. 1(b) was reinforced silica aerogel doped with fibrous bructite, the shape was also cylindrical with the 3.6 cm in diameter by 4.1 cm high, which showed ivory-white and had good plasticity without any crack; Fig. 1(c) was composite silica aerogel doped with titanium dioxide opacifier, whose appearance looked similar with reinforced silica aerogels doped with fibrous bructite, but it was cuboid with the 1.5 cm in length and width by 1 cm high.

Fig. 1. Photographs of silica aerogels samples

Thermogravimetric analysis of samples: Fig. 2 showed the thermogravimetric analysis of prepared aerogel samples. The weight loss decreased gradually from around 45-1020 ºC for three aerogel samples and the percentage of weight loss were 14.7, 18.2 and 18.6 % for pure silica aerogel, reinforced silica aerogel doped with fibrous bructite and composite silica aerogel doped with titanium dioxide opacifier, respectively. Doped silica aerogels had higher percentage of weight loss than pure silica aerogel, this is perhaps because of the impurities of fibrous bructite and titanium dioxide opacifier. Moreover, the volatilization and decomposition of giblets of sodium dodecylsulfate which used as dispersant could affect the weight loss.

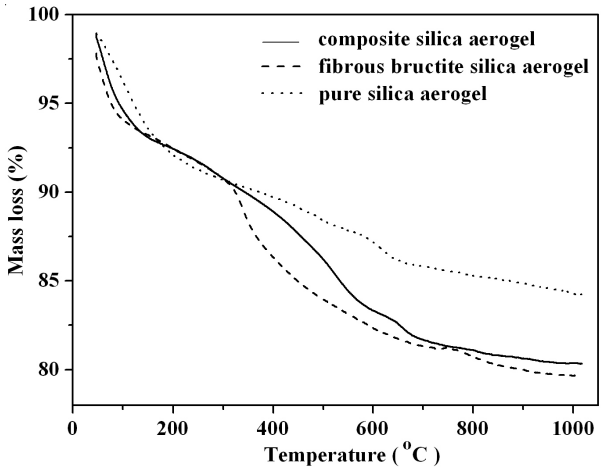

Fig. 2. TGA curves of silica aerogels samples

The increase in weight loss of pure silica aerogel was rapid before 450 ºC due to evaporation of trapped H_2O and alcoholic groups, produced from the condensation reactions of Si-OH and $Si(OC_2H_5)$ groups. After 450 ºC the TG curve declined slowly. When the temperature was higher than 600 ºC, the percentage of weight loss did not reduce because of the structural water evaporating completely. But the weight loss of doped silica aerogels both decreased sharply, except for the reasons of evaporation of trapped H_2O and alcohol like the pure silica aerogel and the effect of impurity which mentioned above, there is an important reason that dehydration of fibrous bructite at the temperature of 400-500 ºC theoretically, however, the structural water of fibrous bructite lose at 750 ºC in actual experiment, which showed an inflexion in TG curves. This would be explained by the low conductivity of the silica aerogels, which caused the temperature lower inside of the silica aerogels than their outside. Moreover, infrared resistance of fibrous bructite could reduce the heat transport of infrared radiation. Thus, the structural water of fibrous bructite evaporated at the temperature of 750 ºC.

Differential thermal analysis of samples: Differential thermal analysis of samples had been illustrated in Fig. 3, an strong exothermic peak was produced at around 260 ºC and 340 ºC for pure silica aerogel and reinforced silica aerogel doped with fibrous bructite, respectively, which corresponds to oxidation of the surface hydroxyl groups and evaporation of trapped H_2O and alcohol. There was a temperature lag of 80 ºC for fibrous reinforced silica aerogel comparing with pure silica aerogel, which would be indicated that the conductivity of the fibrous reinforced silica aerogel was lower than that of pure silica aerogel. The reason had been stated before, the added fibrous bructite in fibrous reinforced silica aerogels could resist infrared radiation, which leaded to low conductivity at high temperature. But these peaks did not relate to phase transition.

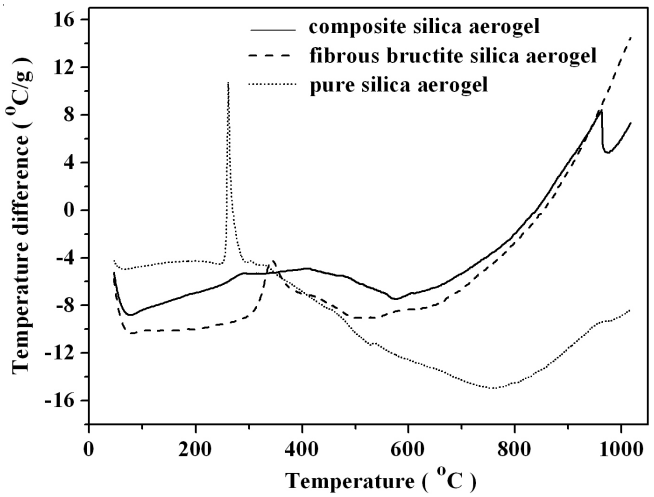

Fig. 3. DTA curves of silica aerogels samples

For composite silica aerogel, the DTA curve was not as good as both other silica aerogels, the reason perhaps was that the particle size of added TiO_2 fine powder was uneven (20 nm - 10 μm), which were greater than pore diameter (average pore diameter 15 nm) of silica aerogels. Thus, the integrality of gel framework was broken which leading to the decrease of thermal stability. However, as can be been from Fig. 3, the DTA cures of these three silica aerogels samples increased rapidly after the temperature of 700 ºC, which would be enough to satisfy the demands of the super heat insulation and heat preservation of materials in the fields of avigation, spaceflight, civilian technology and industry.

Scanning electron microscopy of samples: The scanning electron microscopy (SEM) observations were shown in Fig. 4, which indicated that both the prepared pure and reinforced composite silica aerogels had uniform particle and pore sizes with average pore diameter in the range of 5-30 nm. The fiber in reinforced silica aerogels doped with fibrous bructite had hanged together with the matrix of silica aerogel and formed porous netted structure.

Conclusion

The pure, reinforced and composite silica aerogels doped with fibrous bructite and titanium dioxide opacifier had been prepared by sol-gel method and supercritical drying technique. Monolithic silica aerogel samples had good shapes and intensity without any crack. The thermal stability and micromorphology of different silica aerogel samples had been compared by the TG, DTA and SEM. The three silica aerogels all had good thermal stability and continuous porous netted structure with average pore diameter in the range of 5-30 nm. Though the weight loss of doped silica aerogels had slight decrease than that of pure silica aerogel, it is enough to satisfy the demands of the super heat insulation and heat preservation of materials in actual industry. The prepared enforced composite silica aerogels may be a promising materials and broaden the application of silica aerogels.

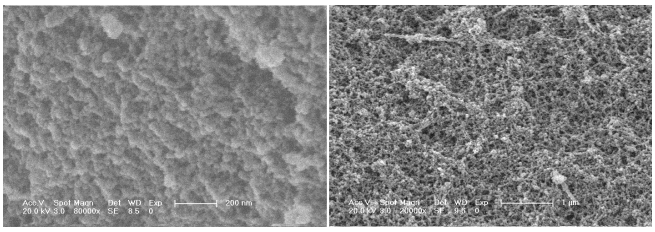

Fig. 4. SEM photographs of pure silica aerogel (left) and reinforced silica aerogel doped with fibrous bructite (right)

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