Rapid synthesis of Super Insulation silica aerogel composites strengthened with mullite fibers

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Keywords: Sodium silicate; Silica aerogel; Mullite fibers; Mechanical property; Thermal conductivity; **Abstract.** In this study, we tried to synthesize super insulation and hydrophobic silica aerogel doped with mullite fibers (10wt %), by using cost effective processing from sodium silicate. Before dried under ambient pressure, the surfaces of the gels were modified using trimethylchlorosilane (TMCS) via one-step solvent exchange and surface modification. And the proper molar ratio of TMCS to pore water is 0.02. The obtained aerogel doped with fibers exhibited excellent physical properties with less than 10% volume shrinkage, extremely high specific surface area (762 m²/g) and super hydrophobicity (contact angle of~145°). In addition, DMA and Hot-Disk results indicated that composite aerogels also with excellent performance in multitudinous physical properties, such as excellent heat insulation (0.0225 W/ (m K)) and better mechanical property (12.5 MPa). Thermal conductivity coefficients of silica aerogel monoliths changed from 0.0225 to 0.0393 W/ (m K) as temperature increased to 500°C, revealed an excellent heat insulation effect during thermal process.

Introduction

Silica aerogels are translucent and thermal insulating material consisting of nanoparticle building blocks, networked together to form an open, highly porous structure. They are consisting of over 95% air and <5% skeleton and possessing extremely lower density ($0.003g/cm^3-0.5g/cm^3$ range), high surface area (500-1200 m²/g), ultra-low dielectric constant (k=1.0-2.0), low index of refraction (~1.05) [1].Due to these excellent properties, silica aerogels have attracted much attention for they have potential to be applied in many fields. Silica aerogels can serve as thermal super-insulators in solar energy systems, refrigerators, internal confinement fusion (ICF) targets for thermonuclear fusion reactions, and catalytic supports [2, 3].

However, the practical applications have been hindered seriously due to the inherent fragility and low strength of silica aerogels. Fiber reinforcement can significantly improve the integrity and strength of composite aerogel. Diversified fibers including cellulose fiber, nonwoven polypropylene fiber, silica fiber or glass fiber, ceramic fiber, and carbon fiber have been used to reinforce silica aerogel matrix [4]. To considerate the thermal properties of composite aerogels, fibers by selected are the key point. Mullite fibers, stable compounds with chemical formula $3Al_2O_3-2SiO_2$, are kind of materials with good thermostability, low thermal conductivity, and good flame retardant.

For solving the fragility and achieving good mechanical and thermal insulting properties of sodium silicate based silica aerogel prepared by the TMCS modification, mullite fiber was introduced to reinforce silica aerogel using the same preparation route. The amount of fiber added, the way through which fiber incorporated into aerogel matrix, and their effects in control structure and property were investigated. Possible insulation mechanism of ambient pressure dried sodium silicate based fibers reinforced silica aerogel monoliths synthesized by the one-step solvent exchange and surface modification is discussed.

Experimental procedure

Silica aerogels were prepared by a single-step sol-gel process followed by ambient pressure drying. Start with the forty milliliters of water glass (molar ratio $SiO_2:Na_2O = 3.1$) was diluted to be a 1:5 (volume ratio) silicate solution by dispersing in 200 ml deionized water. And then, the silica hydrogel

was obtained through the hydrolysis and polycondensation of water glass as a silica source. To avoid the effect of NaCl, a strong acidic cation resin (732# resin, SCRC, China) of the sulphonated polystyrene type was selected to remove sodium ions in the sodium silicate solution. The collected silica sol had a pH ranging 3-4. Then 0.5 mol/L aqueous NH₄OH solution was added to modify the pH of the solution to 6, and composite materials mixed by mullite fibers were fabricated into alveolate gridding so as to supporting the skeleton of hydrogel. The gelation occurred and porous network formed. Deionized water was added to age the gel for 12 h, the gel followed by the solvent exchange and surface modification process at stirring of 30 r/min. Ethanol was used to exchange water within the pores of hydrogel twice within 12 h and the ethanol was replaced by n-hexane twice in 6 h. All of the age and exchange process was carried out in 45 °C water bath. The surface modification of the gel was carried out by adding the silylating mixture of TMCS: hexane in the volume ratio of 15% under condition of 45 °C water bath in 12 h. The optimized volume ratio of TMCS/hexane was determined to be 1:4. Then the silylated gel was dried in ambient pressure at 100 °C for 2 h and finally dried at 150 °C for 3 h to get composite aerogel.

For comparison the pure silica aerogel was also prepared using the same synthesis procedure as that of the composite silica aerogel without adding fibers. Fig.1 shows the photographs of pure silica aerogel and doped with fibers. The samples shape are very good, almost no shrinkage and no cracking.

Characterizations

The apparent density of aerogels was calculated using a known volume of aerogel and dividing by its mass. The microstructures and morphology of aerogel were characterized by scanning electron microscopy (SEM, Philips XL-30FEG). The textural properties were investigated by the standard N_2 gas adsorption method using a surface area analyzer (Quanta chrome Autosorb-1 MP, USA). The complex modulus was measured by a three-point bending test on a Dynamic Mechanical Analyzer Model (DMA8000, USA) (sample: $9.5 \times 8.2 \times 7.1 \text{ mm}^3$). The thermal conductivities of aerogels at desired temperatures were determined by the transient plane heat source method (Hot-Disk, TPS2500, Sweden).







Fig.2. SEM photograph of pure silica aerogel (a) and doped with fibers (b).

Results

SEM-images of pure silica aerogel (a) and composite aerogel are shown in Fig.2. The uniformed three-dimensional loose networks consisting of nano-sized particles and pores were observed from pure silica aerogel (Fig. 2a). It is obvious that the mullite fibers acted as a supporting skeleton that could increase the mechanical properties of the silica aerogels. The silica aerogels doped with fibers still maintain a spongy porous structure and high porosity. The pore and skeleton sizes of the silica aerogels are mostly under 50nm (Fig. 2b).



Fig. 3 Isotherms of composite aerogel.



Fig. 4 Pore size distribution of composite aerogel.

Figs.3 and 4 show N_2 adsorption-desorption isotherms and pore size distribution of composite aerogels. From Fig. 3 it seems that composite aerogels exhibit type-IV isotherm, characteristics of mesoporous structure and the shape of hysteresis loop is of type H2 suggesting the existence of spherical pores [5]. The BET specific surface area of composite aerogel is up to 762 m²/g, the average pore size is 37 nm calculated from the BJH desorption isotherm.

Furthermore, the pore size distribution of composite aerogels is provided in Fig. 4. The aerogels showed a pronounced peak in the mesoporous region (2-50nm) [6]. This confirms that the aerogel structure is preserved by ambient pressure drying.

The mechanical property of composite aerogel monoliths was measured using dynamic mechanical analysis (DMA). From the Fig.5 known that storage modulus of pure silica aerogel and doped with fibers were 3.7MPa and 12.5MPa at room temperature (24°C), respectively. The curve slightly increased when the temperature increased to 200°C. At nearby 200°C, storage modulus of composite aerogel was 13.6 MPa. In the range of 100-200°C, which owing to the polymerization of more surface Si-OH groups. As a consequence, the external stress relatively evenly distributes over the whole composite without inducing material failure, hence the flexibility of composite aerogels is improved.



Fig.5 DMA on a monolith in a three-point bending mode.



Fig.6 The thermal conductivities of composite aerogels.

Fig. 6 presents thermal conductivity of composite aerogel ranging from 0.0225 W/ (m K) to 0.0393 W/ (m K) and increasing slightly with the temperature from 25 to 500 °C at a muffle furnace (Vecstar-LF2, U.K.) which connected to the hot-disk apparatus. Because of the composite structure of composite aerogels that the three dimensional nanostructure wraps the fiber skeleton, impairing the heat transfer across the fibers, an excellent thermal insulation property was obtained. With the temperature increasing, more heat transfer passageways are provided so that the thermal conductivity increases slightly. Compared to the aerogel doped with fibers, the pure aerogel possess a lower thermal conductivity of 0.0211 W/ (m K) at room temperature, but higher at 500 °C. It is evident that mullite fibers contribute to the thermal conductivity of silica aerogels, denoted as total thermal conductivity.

Conclusions

The highly integrated shape-controllable ambient pressure dried sodium silicate based silica aerogel monoliths incorporated with 10wt% mullite fibers exhibited the densities of 0.115g/cm³ with mechanical property of 12.5 MPa at room temperature. Through the one-step solvent exchange and surface modification, the silica fiber and silica precursor were simultaneously modified by TMCS, which assisted the fiber to be well dispersed and then incorporated into the three-dimensional silica network. Accordingly, excellent integrity with controllable shape, good mechanical and thermal insulating properties could be achieved. Furthermore, the thermal conductivity of the monoliths at desired temperatures was analyzed by the transient plane heat source method. When the temperature flowed from 25 to 500°C, thermal conductivity coefficients of silica aerogels changed from 0.0225 to 0.0393 W/ (m K), revealed an excellent heat insulation effect in high-temperature area.

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