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SiO_2 aerogels prepared by ambient pressure drying with ternary azeotropes as components of pore fluid

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ABSTRACT

Silica aerogels were synthesized by two-step sol–gel polymerization of tetraethoxysilane (TEOS) in alcohol and using ambient pressure drying with ternary azeotropes as components of pore fluid. The structure and physical properties of these aerogels were investigated by several experimental methods, such as scanning electron microscopy (SEM), thermo-gravimetric and differential scanning calorimetry (TG–DSC), Fourier transform infrared spectroscopy (FTIR), specific surface area analyzer and pore size analyzer. The results indicated that silica aerogels are coherent, hydrophobic and nano-porous solid. The high specific surface was 838.6 m^2/g.

1. Introduction

Silica aerogels have unique properties, which have been used as efficient candidates for a wide variety of applications, such as catalysts, catalyst supports, efficient thermal insulation, Cherenkov sensors, integrated circuit, condenser, and cosmic dust collectors, while these excellent properties are closely related to their preparing process [1–9]. Traditionally, silica aerogels were prepared by supercritical drying method, but supercritical drying needs autoclave, which is a complex process, high cost, and dangerous. However, silica aerogels prepared by ambient pressure drying reduce the risk and costs, so there are broad application prospects in preparing aerogels.

Many researchers have devoted to the research of ambient pressure drying [10–13]. The current ambient pressure drying methods mainly based on using low surface tension of solvents to replace large surface tension solvents, and surface modification in the control of drying speed. These methods are aimed at weakening reaction performance and hydrophily of gel backbone network surface so that gels after ambient pressure drying can still keep the original network structure and pore structure of the aerogels. Some surface modification agents are used commonly, for example, trimethylchlorosilane (TMCS), trimethylethoxysilane (TMES), six methyl two silazane (HMDS), six methyl two silicon ether (HMDSO), and fluorinated alkyl siloxane [14–18]. Studies were performed in silica gels synthesized with isopropanol followed by evaporative drying quantitatively as reported by A. Bisson [19], with the last drying phase controlled by vapor diffusion in the gel nanostructure. Under the control of using trimethylchlorosilane (TMCS) solution as surface modification agents and isopropanol as solvent, the affinity between solid phase and liquid phase was obviously improved.

In this paper, SiO_2 aerogels were synthesized by ambient pressure drying process, using TEOS as silicon raw material, ethanol (EtOH) and H_2O as solvent, trimethylchlorosilane (TMCS) as surface modification agents, and H_2O/n-butanol/n-hexane ternary as azeotropic solution. The structure and morphology of the aerogels were investigated by SEM, TG/DSC, FTIR and BET techniques. The theory of azeotropic triple solution method was also discussed.

2. Experimental

2.1. Preparation

The typical mole ratios of ethyl were TEOS:EtOH:deionized water = 1:4:6. After the mixture was continuously stirred for 15 min, muriatic acid (0.5 mol/L) was added drop by drop with vigorous stirring. Then the mixture was adjusted to pH 3.0–3.5. With vigorous stirring for 45 min, $NH_3 \cdot H_2O$ (0.05 mol/L) was added drop by drop and continuously stirred for 10 min. Then the gel generated was placed in a mother liquid at room temperature and aged for more than 12 h. The obtained condensed substances were called alcogels.

2.2. The surface modification of alcogels (solvent replacement) and drying

The surface modification and drying of alcogels were as follows.

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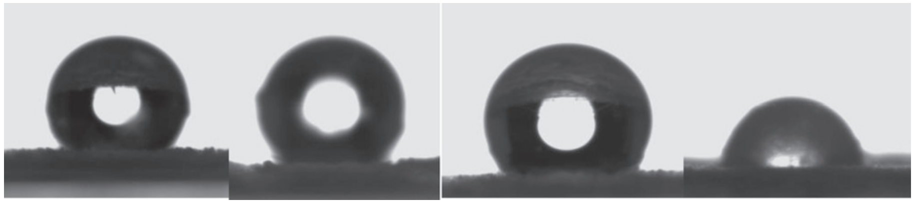

Fig. 1. Photograph of water droplet on the modified silica aerogels (where a–d are respectively the photographs water droplet on the modified silica aerogels at different heat treatment temperatures).

(1) Take out a certain rigidity of alcohol gel after aging and pour into a beaker with ethanol and soak for 1 h, then drop out the solution.
(2) Dip alcogels in n-butanol two times (every 24 h) at 50 °C in order to make all the waters in the alcohol gels replaced by n-butanol. Then drop out the solution.
(3) Add n-butanol solution of TMCS, then place at 50 °C constantly for 24 h in order to make sure the surface modification of alcogels.
(4) Add n-butanol solution, then place at 50 °C constantly for 12 h.
(5) Use n-butanol solution of n-hexane (the volume ratio is 1:3) to clean the surface of the wet gels. Then place in the oven at 50 °C for 12 h. Then use again n-butanol solution of n-hexane (the volume ratio is 1:1), clean the surface of the wet gels and place in the oven at 50 °C for 12 h.
(6) Then use the n-hexane solution to clean the surface of the wet gels. Then place in the oven at 50 °C for 12 h.
(7) Finally, place the gels in the oven at 50 °C for 12 h. Then dry for 1 h at 80 °C and obtain the silicon aerogels.

In the test aerogels were prepared by two methods, one of which was ambient pressure process and another was in an autoclave sealed, but the process of two methods was similar.

2.3. Characterization

Organic groups were investigated by a Fourier transform infrared spectroscope (FTIR, Vector33, Germany). Static contact angles of the silicon aerogels were measured by Contact Angle Meter (Dataphysics OCA 15, Germany). TG–DSC curves were measured with thermal analyzer (NETZSCH STA 449 C). The morphology and particle size of samples were characterized by scanning electron microscope (SEM). Surface area measurements and pore diameter distribution were made on Micromeritics NOVA Station B Analyzer using the BET nitrogen adsorption/desorption technique.

3. Results and discussion

3.1. Hydrophobicity

The hydrophobicity of silica aerogels was characterized by measuring contact angles. The contact angles between water drops and aerogel surface can be calculated from the following formula [20]:

$$\theta = 2\tan^{-1}(2\,h/w) \quad (1)$$

where h and w is respectively the height and width of water drop contact with aerogels' surface.

Different contact angles of SiO_2 aerogels after heat treatment at different temperatures are shown in Fig. 1. The contact angle of subpanel *a* is 129° without heat treatment, showing favorable hydrophobic property. After 200 °C heat treatment hydrophobic properties of SiO_2 aerogels improved, and the contact angle is 134° as shown in subpanel *b*. After 300 °C heat treatment the contact angle is 127° as shown in subpanel *c*. Samples after 400 °C heat treatment exhibits hydrophilic property, and the contact angle is 73° as shown in subpanel *d*.

Si–CH_3 groups exist in the samples without heat treatment, showing hydrophobic property. After 200 °C heat treatment, part of the adsorbed waters decompose, and Si–CH_3 groups don't change, so the hydrophobic performance improves. Si–CH_3 groups in the samples after 300 °C heat treatment begin to be oxidized. But only a few Si–CH_3 groups may be oxidized, so the hydrophobic performance degenerates not so obviously. When the temperature of heat treatment was 400 °C, a large number of Si–CH_3 groups decompose, and the hydrophobic performance of aerogels declines rapidly. The higher the temperature is, the poorer the hydrophobicity is. When the temperature of heat treatment is 500 °C, the —CH_3 groups completely decompose, and aerogels exhibit full hydrophobic performance.

Hydrophobic SiO_2 aerogels were grinded into powder in a mortar. Then a drop of water droplet was put onto the powder and rolled. Because of the favorable hydrophobic performance of the aerogels, water droplet would be wrapped by SiO_2 gel powder, becoming an internal

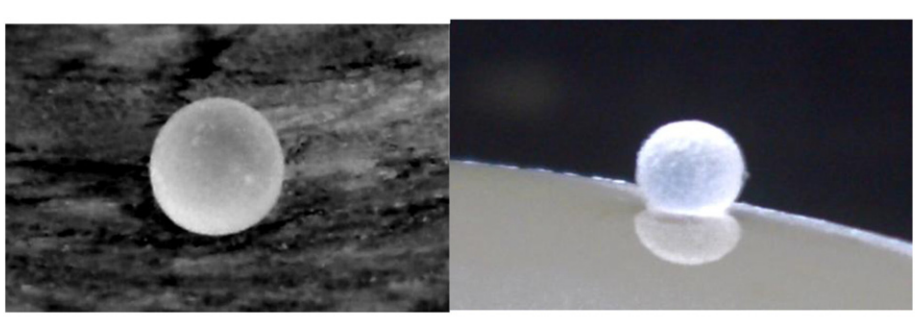

Fig. 2. The photographs of a droplet of water (water marble) coated with the hydrophobic aerogel powder.