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Preparation and characterization of silica aerogels from by-product silicon tetrachloride under ambient pressure drying

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ABSTRACT

The by-product silicon tetrachloride ($SiCl_4$) was usually obtained from polysilicon industry and was a cheaper alternative precursor. An economic method to produce silica aerogel using silicon tetrachloride under ambient pressure drying was presented in this work, which can also solve the pollution problem during the by-product silicon tetrachloride treatment process. The prepared aerogel samples were characterized by scanning electron microscopy, Brunauer-Emmett-Teller analysis, thermal conductivity analysis, contact angle test, Fourier transform infrared spectroscopy and thermogravimetric analysis. It was found that the molar ratio of $H_2O/SiCl_4$ could affect the properties of aerogels seriously. The density and thermal conductivity first decreased and then increased as the molar ratio increased from 13 to 32. The porosity showed an opposite trend with the density. Silica aerogel with high specific surface area (856.7 m^2/g), low density (0.077 m^3/g) and low thermal conductivity (0.0213 W/m·k) were obtained at the optimal conditions when the molar ratio was 25. The resulting aerogel is also mesoporous material with super hydrophobicity and have a huge application in thermal insulation field.

1. Introduction

Silica aerogel is unique porous material which is made up > 95% air and < 5% skeletons [1–3]. It has many fascinating properties of high optical transparency (> 90%), extremely low density (0.03–0.5 g/cm^3), high specific surface area (~1000 m^2/g) and low thermal conductivity (~0.02 W/m·k) [4–6]. Therefore, aerogels have attracted much attention in thermal and acoustic insulation [7], adsorption and catalyst supports [8], containers for liquid rocket propellants [9], etc. So far, the main precursor involved in the research is silicate ester or sodium silicate. Jyolti L. Gurav et al. used TEOS precursor to synthesize hydrophobic and low density silica aerogels followed by ambient pressure drying [10]. C. J. Lee developed a new modified ambient drying process for synthesizing silica aerogels cost-effectively from water glass [11]. While, silicon source like silicate ester is expensive, and silica aerogels have to undergo tedious solvent-exchange and surface-modification under ambient pressure drying, which is harmful to humans and environment.

With the rapid development of the global photovoltaic industry, the polysilicon industry is developing rapidly. The development of solar photovoltaic industry is an important direction for ensuring energy supply and building a low-carbon society. The production of polysilicon usually used modified Siemens method. This method produces 1 t of polysilicon, which will produce about 10–15 t of by-product $SiCl_4$. Corrosive by-product silicon tetrachloride causes serious environment pollution and restricts the development of polysilicon industry chain. $SiCl_4$ is a highly hazardous chemical that cannot be handled by ordinary methods. Recently, the treatment methods are mainly high temperature, high pressure hydrolysis, hydrogenation, purification, etc. [12]. Hot hydrogenation is currently the main process for the treatment of $SiCl_4$. However, the conversion rate of $SiCl_4$ is low and the energy consumption is high. The catalytic hydrogenation is based on the thermal hydrogenation, and the mixture of $SiCl_4$ and H_2 is passed through the catalyst bed to perform the reaction. However, the purity requirements of the raw materials $SiCl_4$ and H_2 are relatively high and the catalyst is easily deactivated. These methods are costly and low in productivity. It is important to explore a low-cost, high efficiency processing technology of $SiCl_4$. Therefore, this paper proposes $SiCl_4$ as silicon source for aerogel preparation, which is another feasible way.

$SiCl_4$ is prone to hydrolysis and release large amounts of hydrochloric acid. Until now the research on the preparation of aerogels using silicon tetrachloride as a precursor have rarely been reported. J.R. Heley et al. prepared fine silica powder by hydrolysis of Silicon tetrachloride using ammonia solution followed by supercritical drying [13]. But there are still some problems to be solved. Supercritical drying method is difficult for large-scale commercialization because it requires

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intensive energy and high-cost facility. On the other hand, $SiCl_4$ hydrolyzes rapidly and the reaction is violent. Precipitates were inevitable in most studies. It affects the homogeneity of the gel and further influence the performance of aerogels.

In order to solve the problem of precipitates, $SiCl_4$ reacts with anhydrous ethanol first and then deionized water is added to decrease the reaction rate and reduce the volatilization of hydrochloric acid. The present work focuses on producing silica aerogels based on surface modification of SiCl4, followed by ambient pressure drying to replace supercritical drying. In addition, the mixture of hexamethyldisiloxane/trimethylchlorosilane (HMDSO/TMCS) was used for surface modification that can avoid tedious solvent exchange in conventional modification methods [14]. Producing silica aerogels using SiCl4 can not only solve environmental problems, but also create wealth. $SiCl_4$ hydrolysis reaction goes quickly and the rapid preparation can greatly shorten the preparation cycle.

2. Experimental

2.1. Sample preparation

The whole process can be divided into five steps: (1) reaction, (2) gelation, (3) ageing, (4) surface modification, (5) ambient pressure drying. The precursor used for preparation was silicon tetrachloride (AR, ≥99.5%, Aladdin, USA). Other agents including anhydrous ethanol (EtOH), trimethylchlorosilane (TMCS) and hexamethyldisiloxane (HMDSO) were all of analytical grade and purchased from SCRC (Sinopharm Chemical Reagent Co., Ltd., China). Deionized water was used throughout the experiment.

$SiCl_4$ was added dropwise to the vigorously stirred anhydrous ethanol in the beaker. Then varying amount of deionized water was added to the beaker by using a pipette. Since the reaction was violent and exothermic, the whole process was carried out in the ice-water bath to avoid heat concentration. A lot of white fumes of hydrochloric acid were given off, so it is necessary to wear personal protection and operate in the fume cupboard. The molar of $SiCl_4$: Ethanol was fixed at 1:15.8. The molar ratio of deionized water/$SiCl_4$ was defined as X, and the values of X are 13, 19, 25, 28 and 32, respectively. The specific amount of reagents was given in Table 1. The molar ratio of $H_2O/SiCl_4$ between 13 and 32 is a reasonable range. The value < 13 or > 32 could cause great volume shrinkage and influence the properties of aerogels. The resultant sols were stirred for about 10 min. Then the beakers were sealed with Polyethylene plastic film and gelled at room temperature. The gelation time increased dramatically with the increasing of water content. When X is 13, the gelation time is about 25 min. But the gelation is > 6 h when X is 32. After gelation, samples were aged at room temperature for a week to strengthen the skeleton structure. The surface modification of the gel was carried out by adding the mixture of HMDSO/TMCS with the molar ratio of 1 which can avoid tedious solvent-exchange.

Finally, the silylated gel was dried at ambient pressure at 80, 100 and 120 °C for 8 h respectively, to get the hydrophobic silica aerogel.

2.2. Methods of characterization

The tap density of the aerogel was calculated by measuring its mass to volume ratio. The mass was measured by the electronic balance (Sartorius SQP). Due to the fragility of the sample, the volume can be obtained by tapping apparatus after the graduated cylinder filled with powders and tapped with the fixed speed. The porosity of the aerogels was calculated using the formula:

$$P(\%) = \left[1 - \frac{\rho_b}{\rho_s}\right] \quad (1)$$

where ρ_b is the tap density and ρ_s is the skeletal density of the silica aerogel which is usually 2.2 g/cm^3.

The hydrophobicity of the aerogel was quantified by measuring the contact angle (θ) with the help of contact angle instrument (SL200K, USA). The water droplet of 2.4 mm diameter was placed on the three different places of aerogel surface and the average value was taken. The value was measured through a traveling microscope using the following formula:

$$\theta = 2\tan^{-1}\left(\frac{2h}{w}\right) \quad (2)$$

where h is the height and w is the base width of the water drop. The microstructure of the aerogels was studied by using Field Emission Scanning Electron Microscope (FESEM, SIRION200, FEI). Transmission electron microscopy (JEM-2100F, JEOL, Japan) was conducted with an energy dispersive X-ray spectrometer (EDS) to investigate the morphology and elemental composition of the sample. Thermal conductivity (λ) is an important parameter to determine insulation materials. It was measured by the transient hot wire method in a vacuum container (TC3000E, Xiaxi technology, China). The crystalline data for aerogels were acquired by X-ray diffraction (XRD, Philips X'pert PRO SUPER X-ray diffractometer).

The specific surface areas and pore size distributions (PSD) were estimated by Brunauer-Emmett-Teller (BET) analysis and Barrett-Joyner-Halenda (BJH) method (Tristar II 3020 M, Micromeritics Instrument Corporation, USA), respectively. TG-DTA (SDT Q600, TA) was employed to test the thermal stability with a heating rate of 10 °C/min from room temperature to 800 °C in the air. Fourier transform infrared spectroscopy (FTIR, Nicolet 8700, Thermo Fisher Scientific, USA) was employed to get the information about various chemical bonds of aerogels which reflected the effect of surface modification. The samples were ground into powders, mixed with KBr and pressed to form sample pellet for measurement. The X-ray photoelectron spectroscopy (XPS) test was conducted by ESCALAB MK II (VG Co., Ltd., England) in vacuum condition. In the experiment, three specimens were tested and the average values plus standard error were regarded as the final test results. Error bars are used to indicate the error or uncertainty in the measurement. The error bars can be calculated by subtracting the average value from the maximum value and the average value minus the minimum value.

Table 1
Properties of aerogel samples with various X values.

	$SiCl_4$/mL	H_2O/mL	Molar ratio of $H_2O/SiCl_4$	BET surface area(m^2/g)[a]	Pore volume (cm^3/g)[a]	Average pore size(nm)[a]
S1	10	20	13	838.6 ± 8.60	3.21 ± 0.15	11.02 ± 0.31
S2	10	30	19	839.9 ± 8.72	3.27 ± 0.18	10.88 ± 0.39
S3	10	40	25	856.7 ± 8.92	3.35 ± 0.21	9.12 ± 0.28
S4	10	45	28	768.4 ± 8.16	2.91 ± 0.11	8.88 ± 0.30
S5	10	50	32	785.1 ± 8.06	2.74 ± 0.13	8.52 ± 0.26

[a] All the parameters were given in the average of three measurements.

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