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Preparation of Nano-porous aerogels by supercritical drying

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Abstract. Nano-porous silica aerogels are synthesized by two steps by the supercritical condition. By synthesized process, tetra-ethyoxysilane is used as raw material, isopropanol and H₂O which is distilled after ion exchange was used as solvent, HCl and NH4OH are used as hydrolysis and condensation catalysts, glycerol is used as drying control chemical agent. Silica aerogels are obtained by supercritical drying condition after aging, surface modification and exchanging solvent. The effect of water, PH, temperature, and so on, are analysed at supercritical drying condition. The resulting aerogels are characterized by means of X-ray diffraction and scanning electron microscopy. It is found that the aerogels made by this method have high porosity, specific surface area and the structure is sponge with narrow particle and pore size distribution.

1. Introduction

There are many siliceous materials for the obtainment of SiO_2 aerogels by sol-gel method. The earliest choice of Kistler is sodium silicate, but removing impurity ions is a difficult problem^[1-3]. Later, the use of tetra-methoxysilane (TMOS) or tetra-ethoxysilane (TEOS)^[4] is widely used. In order to reduce costs, In order to reduce cost, Silica sol and E-40 (polyethoxydisiloxanes) are used by some scholars. Methanol, acetone and ethanol are used as organic solvents. However, due to the toxicity of methanol and the poor co solubility of acetone and water, ethanol is most commonly used^[5,6]. At present, tetraethoxysilane (TEOS) is widely used as raw materials for obtaining SiO₂ aerogels on the domestic and foreign scholars study. The synthetic methods are divided into one-step process and two-step process ^[7,8]:

One-step process is to directly mix TEOS and water, ethanol and catalyst at proper molar ratio, then seal them in an oven at 60°C, and TEOS will form disordered and branched nano scale pore SiO₂ continuous network——SiO₂ aerogels in sol-gel process. The catalyst uses hydrochloric acid or ammonia water to adjust the pH value of the solution. In different catalytic conditions, the time of aerogels formation and the structure of the aerogels network will be very different.

The procedure of the two step process is as follows: first, under acidic conditions, the SiO₂ precursor is partially hydrolyzed and partially polycondensated by the reaction of TEOS with insufficient water (molar ratio of water / TEOS<2). Then, under alkaline conditions, sufficient amount of water and proper amount of ethanol are added to form the silica aerogels through hydrolysis polycondensation reaction. Solvent ethanol does not participate in the reaction. It acts as a diluent to regulate the density of the network and ultimately regulate the density of the silica aerogels.

In this paper, tetra-ethyoxysilane is used as raw material, isopropanol and H_2O which is distilled after ion exchange was used as solvent, HCl and NH₄OH are used as hydrolysis and condensation catalysts, glycerol is used as drying control chemical agent. SiO₂ aerogels are obtained by supercritical drying condition. On this basis, the microstructure, morphology, pore size distribution and specific surface area of the synthesized aerogels are analyzed.

2. Experimental methods

2.1. Preparation of SiO₂ aerogels

In this experiment, silica aerogels is obtained by two-step process at room temperature. First, weigh tetraethyl orthosilicate, distilled water and anhydrous ethanol lower than the stoichiometric ratio, put them into the container according to the proportion, add hydrochloric acid as catalyst, measure the pH value of the solution after slightly stirring, and stir with a magnetic stirrer for 2 hours. Then, distilled water is added to make up the water needed. At the same time, ammonia water is added to adjust the pH value. After mixing, the magnetic stirrer is used to stir for 1 hour and then pour it into the mold needed. After a certain time, the silica sol loses fluidity and forms an ethanol gel.

After aging, it is put into high-pressure autoclave for supercritical drying. When the temperature and pressure reached a certain value, drying it at constant temperature and pressure for about 3 hours, the ethanol supercritical fluid is slowly released by opening the vent valve of the autoclave. In the process of outgassing, pay attention to keep the temperature higher than the supercritical temperature of ethanol. After the degassing, the autoclave was naturally cooled to room temperature, and then the sample was taken out for testing.

2.2. X-ray diffraction analysis method

Phase analysis is carried out by using Japanese X-ray diffractometer D/max2500. Among them, the current is 250mA, the voltage is 40kV, Cu target, 2θ is in the range of $5 \sim 90^{\circ}$, the scanning rate is 80 / min, and the incident wavelength is λ .

2.3. Scanning electron microscope (SEM) analysis method

The microstructure of the samples was analyzed by s-3700n scanning electron microscope (SEM). The samples need to be sprayed with gold before testing. The acceleration voltage is 25 kV, and the surface morphology of the samples is observed under the magnification of 50000 times.

3. Experimental results and discussion

3.1. Effect of preparation conditions on gel time

(1) The effect of water consumption on gel time

In this experiment, we used the same amount of each reagent except water, that is, TEOS was 27.94ml, C₂H₅OH was 99.4ml, HCl was 0.1ml, ammonia was 0.25ml, and the whole process was completed at room temperature. The effect of water on gel time was studied by adding different distilled water at different times. Fig. 2 is the change trend of gel time with the dosage of distilled water.(Gel time is the time to gel at room temperature until the sol is tilted 45 degrees in the container.)





Fig. 1 Relationship of distilled water dosage and gel time

Fig. 2 Relationship of pH value and gel time

From the analysis of the change curve of Fig. 1, it can be known that in the preparation process, the gel time is shortened with the increase of distilled water, but when the water is added to 18ML, the gel time is the shortest. After that, the gel time prolong with the increase of water volume.

It is found by experiments that the gel produced by excessive water is difficult to dry in gel because of excessive water remaining in the pore space network of the gel, resulting in larger shrinkage of the aerogels generated after drying. The gel obtained by excessive water is milky white with poor transparency, and the final aerogels have poor comprehensive properties. The gel obtained with appropriate amount of water has higher transparency.

Considering various factors, it is determined that the molar ratio of water to TEOS is 3-8.

(2) The effect of pH value on gel time.

When preparing SiO_2 aerogels, the catalysts used are hydrochloric acid and ammonia water. Ammonia water, as the second catalyst, not only regulates the pH value of the sol, but also has great influence on the gel time. Fig. 2 shows the effect of pH value on gel time after adding dilute ammonia water. The experimental results show that the SiO_2 aerogel obtained from neutral or slightly alkaline catalytic conditions has better toughness.

(3) The effect of temperature on gel time

Temperature is a very important factor in the preparation of gelatin. If the temperature is not selected properly, it will directly affect the gelation time and aerogel. As shown in Fig. 3.



Fig. 3Analytical relationship of temperature and gel time

It can be seen from Fig. 3 that the gel time decreases sharply with the increase of temperature, and the higher the hydrolysis temperature, the shorter the gel time. The gel time is only tens of minutes at about 70°C, while the gel time is more than 10 hours at ten degrees Celsius.

The gel is unstable and easy to sink at 80°C. However, the excessive temperature will cause a large amount of volatilization of the solvent (the boiling point of ethanol is 78.4°C).

Although the gelation time will be greatly shortened at high temperature, it is not conducive to the control of the final gel density. The aerogels prepared are densely packed with dense structure and seriously affect their adiabatic effect as super insulation materials. Therefore, the temperature should not be higher than 60 °C. During the experiment, it is also found that if the gel temperature difference is large, the gel will crack and destroy its spatial network structure.

(4) The effect of aging time on aerogels

The hydrolysis and crosslinking polymerization of TEOS is a slow process, and with the decrease of water content, the rate of hydrolysis will become slower and slower, so the subsequent polymerization and crosslinking will inevitably lag behind. On the surface of the gel, the gel is already glued, but the internal process is still in progress. The network between -OH and -OH continues to form a network. Aging provides enough time for cross-linking hydrolysis and makes it firm and enhances its final strength ^[9,10]. At the same time, the water contained in the pore space of the gel before drying must be removed. That is to say, the gel must be rinsed several times with absolute ethanol at a certain time interval until the water in the hole is replaced by absolute ethanol, and the time needed is related to the thickness of the gel prepared. The gel obtained by this way is the real sense of the gel.

In this experiment, the specific operation in aging is to immerse the gel in absolute ethanol solution, replace the solution every 12 hours, and then prolong it for 2~4 days at room temperature. In the aging process, it is important to note that the sample must have sufficient sealing conditions to avoid ethanol volatilization as far as possible, avoid accidental contact with the air and cause the collapse of the aerogel porosity by ethanol volatilization, and avoid the relatively high content of water in the aging soaking solution.

3.2. The effect of ethanol on supercritical test of SiO_2 aerogel

(1) The effect of ethanol on gel time

This experiment focused on the effect of ethanol on gelation, and the effect of ethanol dosage on gelation rate was studied. The amount of ethanol is different (the amount of other reagents is the same, TEOS is 27.94m1, water is 8.92ml, HCl is 0.1ml, ammonia is 0.25ml). The effect of the amount of ethanol on the gel time is shown in Fig. 3.

As can be seen from Fig. 4, when other conditions are same, the gel time prolongs with the increase of ethanol dosage. Because ethanol has dilution effect on the sol formed, and ethanol is generated in the process of hydrolysis and condensation of TEOS. To a certain extent, it inhibits the reaction, reducing the reaction rate and prolonging the time required to reach the gel point. Meanwhile, the density of the aerogels decreased, the structure became more loose and the mechanical strength decreased, so the greater the amount of ethanol, the more obvious the effect.

Ethanol can enhance the mutual solubility of TEOS and H_2O , but from the reaction process, ethanol does not directly participate in the hydrolysis polycondensation reaction. Ethanol only fills some space in the gel network, thus regulating the size of the cavity of the gel network. When drying to the critical point, the liquid always evaporates from the larger hole first, so the tension in the large hole is relaxed. While the tension in the small hole still exists, so the small hole shrinks greatly and causes cracking. Therefore, adjusting the amount of ethanol can increase the pore size and reduce the capillary tension. At the same time, the increase of pore size can also increase the permeability, thus reducing the drying stress in the drying process. Since aerogels can basically maintain their network structure in the gel state, the density of the desired aerogels can be adjusted by changing the amount of ethanol. Although the use of excess water has a similar effect, too much water will completely soluble with TEOS and sink at the bottom of the container.



(2) The effect of ethanol on bulk density, porosity and thermal conductivity

The effect of ethanol dosage on bulk density, porosity and thermal conductivity of SiO_2 aerogels is shown in Fig. 5-7.

From the analysis of Fig.5 and Fig.6, it is known that with the increase of the amount of ethanol, the density of SiO_2 aerogels decreases and the porosity increases. The reason for this phenomenon is that ethanol plays an important role in the formation of SiO_2 aerogels. Besides playing the role of solvent, it also occupies the vacancy of stomata and regulates the density.

From Fig. 7, it can be found that the thermal conductivity at room temperature and normal pressure does not decrease with the increase of the amount of ethanol. The lowest value appears at EtOH/TEOS (molar ratio) of about 20, and the bulk density of the corresponding SiO_2 aerogel is about 100kg/m³. The main reason is that the gaseous heat conduction does not increase with the decrease of the bulk density of the aerogel, or the pore size decreases.



porosity of aerogels

ig. 7 Relationship of ethanol dosage and thermal conductivity of aerogels

*3.3. Phase analysis and microstructure analysis of SiO*₂ *aerogels* (1) Phase analysis

X-ray diffraction analysis was carried out on the typical sample with density of 100kg/m^3 . As shown in Fig. 8, there is no obvious characteristic diffraction peak in the whole spectrum, but there is a bulge around $2\theta = 23^\circ$ which means that the prepared sample is amorphous structure and is composed of disordered amorphous SiO₂.



Fig. 8 X-ray diffraction pattern of SiO₂ aerogels with a density of 100kg/m³

(2) The size measurement of skeleton particles

Small angle scattering tests were carried out on typical samples (density 100kg/m³) in order to identify the size and distribution of skeleton particles in aerogel network structure. According to the test results, the skeleton particle size of the sample is mainly below 16 nm, and the proportion of particles with particle size above 16 nm is very small, and the maximum particle size is only about 55 nm. In addition, the average particle size is 6.8nm.

(3) Pore size distribution test

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As a nano porous super thermal insulation material, it is necessary to make almost all the pores in the material at the nanometer level, that is less than 100nm, and it is better to make more than 80% of the pore size of the material less than 50nm, so that its thermal conductivity will be relatively low.

Since the free paths of the main components N_2 and O_2 in the air are about 70nm, only when most of the pore sizes are less than 50nm, the convection can be basically eliminated in the material and the convective heat transfer can be greatly reduced ^[11,12], which is the real nano porous super thermal insulation material. Therefore, the pore size distribution of a typical sample with a density of 100kg/m^3 was tested. The test results are shown in Fig.9, where the ordinate dV(d) is the differential of pore volume relative to pore diameter.



Fig. 9 Pore size distribution of SiO₂ aerogels

It can be seen from Fig. 9 that all pore sizes are below 80nm, and the size less than 50nm can reach 90%. Therefore, theoretically, the gas thermal conductivity should be low, and the total thermal conductivity will also decrease due to the decrease of gas thermal conductivity.

(4) Microstructure

Scanning electron microscopy (SEM) tests were carried out on the prepared samples (density of 100kg/m³) to directly observe the microstructure of the samples, such as particle size and pore size of skeleton particles, as shown in Fig. 10.



Fig. 10 SEM images of typical samples of SiO₂ aerogels

It can be seen from Fig.10 that the particle size of the skeleton particles is very uniform, and the particle sizes are between several nanometers and tens of nanometers. In addition, the pore size is also in the nanoscale, which is consistent with the results of the pore size distribution test.

3.4. Conclusion

Through the preparation of SiO₂ aerogels, the following conclusions can be drawn:

(1) Tetra-ethyoxysilane as precursor, ethanol and water mixture as solvent, hydrochloric acid and ammonia water as acid base catalyst, using two step process, through sol gel method, SiO_2 alcohol gel is easily obtained. The formulation of the gel is: EtOH/TEOS is prepared according to the preparation of aerogel density; H2O/TEOS=3 to 8 (mole ratio); pH is controlled at about 3~4 under acidic conditions; alkaline is controlled at about 7~8; the temperature is at room temperature or not higher than 60 degrees; aging time is 2~4 days at 20~30 temperature.

(2) In the range of equipment testing, the pore size of aerogels prepared by supercritical drying technology is within 80nm, and the pore size less than 50nm reaches 90%.

(3) Alkalinity of xonotlite itself is used as catalyst to promote SiO_2 sol to gel. In this way, two problems can be solved. First of all, the compound defect caused by too fast alkaline gel is avoided, followed by avoiding the pollution caused by ammonia water.

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