Preparation of Al$_2$O$_3$-SiO$_2$ Aerogel by Supercritical Drying

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Abstract. Al$_2$O$_3$-SiO$_2$ aerogel was prepared through sol-gel process and ethanol supercritical drying technology using aluminum chloride hexahydrate (AlCl$_3$•6H$_2$O) and tetraethoxysilane (TEOS) as precursors. Structures and properties of Al$_2$O$_3$-SiO$_2$ aerogel were investigated by means of BET, XRD, SEM, FTIR, TG-DTA. At room temperature, the specific surface area of Al$_2$O$_3$-SiO$_2$ aerogel was 574 m$^2$•g$^{-1}$, and the average pore size was 26.34nm. The three-dimensional network skeleton was composed of leaf shape particles. Al$_2$O$_3$-SiO$_2$ aerogel went through the transformation process of $\gamma$-AlOOH + amorphous SiO$_2$ $\rightarrow$ $\gamma$-Al$_2$O$_3$ + amorphous SiO$_2$ $\rightarrow$ Mullite (3Al$_2$O$_3$•2SiO$_2$) when heat treatment temperature increased from room temperature to 1200$^\circ$C. At 1200$^\circ$C, the specific surface area was 162 m$^2$•g$^{-1}$, the average pore size was 59.91nm. It was indicated that Al$_2$O$_3$-SiO$_2$ aerogel possessed excellent high temperature stability and heat insulation performance.

1. Introduction

Aerogel is porous nanomaterials with high specific surface area and low bulk density. Due to its unique nano-structure, aerogel has broad application prospects in aerospace, catalysis, environmental protection and other fields, and its preparation technology has become a new field of chemical engineering research. Sol-gel method is a common method to synthesize aerogel, which includes three processes: sol preparation, gel preparation and gel drying. Gel drying is the most important process in the whole process. Traditional drying methods have some adverse effects on the synthesis of aerogel, such as the thickening of the basic particles of the material, the substantial decrease of specific surface area, and the large reduction of pores. The supercritical fluid drying technology developed in recent years doesn’t produce these kinds of adverse effects[1-6].

Currently, SiO$_2$ aerogel is widely studied and applied. But the high temperature stability of SiO$_2$ aerogel is poor, the long-term use of temperature is not higher than 800$^\circ$C, thus SiO$_2$ aerogel is difficult to use in a higher temperature environment. It is an important research direction to seek high temperature resistance aerogel heat insulation composites. Al$_2$O$_3$ aerogel has a high temperature resistance, but its thermal conductivity is much higher than that of SiO$_2$ aerogel. Therefore, Al$_2$O$_3$-SiO$_2$ aerogel is an ideal heat-resistant material at present. Al$_2$O$_3$-SiO$_2$ aerogel after 1000$^\circ$C treatment will still be able to better maintain its nano porous structure. Al$_2$O$_3$-SiO$_2$ aerogel has excellent performance advantages, which not only makes up for the lower service temperature of SiO$_2$ aerogel, but also improves the heat insulation performance of materials on the basis of Al$_2$O$_3$ aerogel. Therefore, Al$_2$O$_3$-SiO$_2$ aerogel has high application value[7-9].

In this paper, aluminum chloride hexahydrate (AlCl$_3$•6H$_2$O) is selected as the aluminum source, tetraethoxysilane (TEOS) is selected as the silicon source, and the mixture solution (volume ratio 1/1) of anhydrous ethanol (EtOH) and water (H$_2$O) is selected as the solvent. In the sol-gel process,
propane oxide (PO) is selected as the gel additive to synthesize stable Al₂O₃-SiO₂ aerogel. After supercritical drying treatment, Al₂O₃-SiO₂ aerogel with low density and high porosity is synthesized. BET, XRD, SEM, FTIR, TG-DTA and other methods were used to characterize the structures and properties of Al₂O₃-SiO₂ aerogel.

2. Experimental

The alumina sol and silica sol were synthesized by stirring the starting raw materials with the mole ratio of AlCl₃•6H₂O/H₂O/EtOH=1/30/20 and TEOS/H₂O/EtOH/HCl=1/4/8/7.5×10⁻³, respectively. And mix alumina sol and silica sol at 50°C for 60 min to prepare hybrid sol. In the gel treatment, epoxy propane as gelation initiator was added to the mixture. The mixture was quickly stirred at ambient temperature for 15 min and sealed to form the wet gel. In aging treatment, the wet gel was soaked in ethanol in order to strengthen the network and swap out the redundant water and epoxy propane. Finally, Al₂O₃-SiO₂ aerogel was obtained by supercritical drying technology. The Al₂O₃-SiO₂ aerogel was calcined at ambient temperature, 600°C, 800°C, 1000°C and 1200°C for 1h, which are named Y25, Y600, Y800, Y1000 and Y1200 respectively.

![Figure 1. The photo of Al₂O₃-SiO₂ aerogel.](image)

3. Result and Discussion

3.1. Basic properties of Al₂O₃-SiO₂ aerogel

Figure 1 is the photo of the synthesized Al₂O₃-SiO₂ aerogel. As can be seen from figure 1, the synthesized Al₂O₃-SiO₂ aerogel sample is a white opaque block with low density and good lumpiness. There is a little shrinkage and cracking phenomenon, this phenomenon is due to the gel formation process and aging process, the overall volume of shrinkage, after drying treatment, defect amplification, there are obvious cracks. The density formula \(\rho = \frac{m_{\text{aerogel}}}{V_{\text{wet-gel}}}\) is adopted for calculation, and the density of Al₂O₃-SiO₂ aerogel is 0.102g·cm⁻³, which has a certain structural strength and can withstand a certain pressure. After a series of tests, the Al₂O₃-SiO₂ aerogel sample is polycrystalline boehmite phase and amorphous SiO₂ after drying treatment, with a specific surface area of 542 m²·g⁻¹, average pore diameter of 27.35nm and pore volume of 2.68 cm³·g⁻¹.

3.2. The microscopic morphology analysis of Al₂O₃-SiO₂ aerogel

In order to observe the microscopic morphology of Al₂O₃-SiO₂ aerogel and analyze the influence of heat treatment on the microscopic morphology of the samples, the Al₂O₃-SiO₂ aerogel samples after
heat treatment at different temperatures are tested by scanning electron microscopy (SEM). The test results are shown in figure 2.

As can be seen from figure 2, Al$_2$O$_3$-SiO$_2$ aerogel is composed of vane-like or rod-like particles overlapped with each other to form a three-dimensional network skeleton structure with high porosity and uniform pore distribution. After heat treatment at 600°C, microscopic structure of the sample Y$_{600}$ is more clear, pore structure is more complete, this is mainly because of residual organic matter in discharge, after heat treatment to dehydroxylation reaction further, phase composition of the polycrystalline boehmite phase dehydration gradually into $\gamma$-Al$_2$O$_3$ phase, structure is more clear. After 800°C heat treatment, there is no change in the phase of the sample composition, microstructure of the sample Y$_{800}$ does not change significantly. After 1000°C heat treatment, the phase composition of the sample does not change, but the particle size in the microstructure of the sample Y$_{1000}$ increases, still maintaining a relatively complete porous network structure, no sintering phenomenon, showing good high temperature stability. After 1000°C heat treatment, the sample appears mullite phase, microstructure of the sample Y$_{1200}$ show partial sintering phenomenon, the small pores disappear, the large pores increase, the specific surface area decreases dramatically, and the average pore diameter increases. However, the three-dimensional network structure is still maintained to maintain certain performance advantages.

According to the SEM analysis results of Al$_2$O$_3$-SiO$_2$ aerogel samples after heat treatment at different temperatures, the structure of Al$_2$O$_3$-SiO$_2$ aerogel appears sintering phenomenon with partial property attenuation. However, it still has a certain three-dimensional network structure, indicating that Al$_2$O$_3$-SiO$_2$ aerogel has good high temperature stability and high temperature resistance.

3.3. XRD analysis of Al$_2$O$_3$-SiO$_2$ aerogel
In order to investigate the phase composition of Al$_2$O$_3$-SiO$_2$ aerogel and determine the effect of heat treatment temperature on the sample phase. The sample Y$_{25}$, Y$_{600}$, Y$_{800}$, Y$_{1000}$ and Y$_{1200}$ are analyzed by X-ray diffraction, the test results are shown in figure 3.
Figure 3. XRD spectra of Al$_2$O$_3$-SiO$_2$ aerogel after heat treatment at different temperatures.

reason is that the existence of SiO$_2$ inhibits the phase transition process of Al$_2$O$_3$. The phase transition process of Al$_2$O$_3$ is the reduction of hydroxyl groups by Al$_2$O$_3$, and the introduction of SiO$_2$ sol-gel process, some Si-OH replace Al-OH on the surface of sol particles, which even react with groups on the surface of particles to generate Si-O-Si or Si-O-Al structure, thus inhibiting the phase transition process of Al$_2$O$_3$. After 1200°C heat treatment, the phase composition of sample Y$_{1200}$ have the emergence of mullite phase. It is shown that at this temperature, solid phase reaction occurred between SiO$_2$ and Al$_2$O$_3$, resulting in the formation of mullite phase, which prevents the production of $\alpha$-Al$_2$O$_3$, and reduces the sharp decrease of specific surface area and performance attenuation caused by the change of phase compositions. XRD analysis results show that Al$_2$O$_3$-SiO$_2$ aerogel has excellent high temperature stability.

3.4. Nitrogen adsorption-desorption analysis of Al$_2$O$_3$-SiO$_2$ aerogel

In order to analyze the pore structure parameters of aerogel, nitrogen adsorption-desorption test is required, which mainly includes specific surface area, pore diameter distribution and pore volume test. Nitrogen adsorption-desorption test is mainly based on the adsorption characteristics of gas on the surface of solid materials. Under certain conditions of temperature and pressure, the surface structure of aerogel has reversible adsorption on nitrogen molecules, and there is an equilibrium adsorption amount corresponding to the pressure. By measuring the equilibrium adsorption amount, the pore structure parameters are calculated.

Nitrogen adsorption-desorption test results of sample Y$_{25}$ are shown in figure 4. It can be seen from figure that the nitrogen adsorption-desorption isotherm of Al$_2$O$_3$-SiO$_2$ aerogel belongs to the IV isotherm in IUPAC classification and the H1 hysteretic loop, indicating that sample Y$_{25}$ is a cylindrical mesoporous material. When the relative pressure is within the range of 0.05 to 0.8, the nitrogen adsorption grows slowly, in this stage, the adsorption mode of gas molecules is monolayer adsorption. When the relative pressure is within the range of 0.8 to 0.91, the growth rate of nitrogen adsorption is accelerated, in this stage, the adsorption mode of gas molecules is multi-layer adsorption. When the relative pressure within the scope of 0.92 to 0.995, growth rate of nitrogen adsorption quantity increases sharply, in this stage, the adsorption of gas molecules way for capillary condensation, this range is narrow, reflects the sample pore size distribution is relatively concentrated, which changes in the relative pressure after 0.90, show that particle pore structure of aerogels for accumulation.

The pore diameter distribution curve of sample Y$_{25}$ is shown in figure 4.
As can be seen from figure 5, the pore size distribution of sample Y_{25} is concentrated in the range of 20nm to 50nm, and the pore size distribution is relatively concentrated, the sample is mesoporous material. The results of pore diameter distribution curve are consistent with those of nitrogen adsorption-desorption isotherm.

According to the test, the specific surface area of sample Y_{25} is 542 m^{2}\cdot g^{-1}, the average pore diameter is 27.35nm, and the pore volume is 2.68 cm^{3}\cdot g^{-1}. After heat treatment, the pore structure parameters of the samples change, and the test results are shown in table 1.
Table 1. Pore structure parameters of samples.

| Sample | Specific surface area (m²·g⁻¹) | Average pore diameter (nm) | Pore volume (cm³·g⁻¹) |
|--------|---------------------------------|---------------------------|-----------------------|
| Y₂₅    | 542                             | 27.35                     | 2.68                  |
| Y₆₀₀   | 587                             | 29.76                     | 2.82                  |
| Y₈₀₀   | 473                             | 35.57                     | 1.75                  |
| Y₁₀₀₀  | 328                             | 43.28                     | 1.21                  |
| Y₁₂₀₀  | 132                             | 59.91                     | 0.65                  |

Can be seen from the data in Table 1, after 600°C heat treatment, the specific surface area of the sample Y₆₀₀ increases slightly, this is mainly because of the heat treatment process to remove the excess water and organic matter in the structure, promoted the part to take off the hydroxy reaction, make the structure more complete, more uniform pore distribution, resulting in the increase of the specific surface area. After 1000°C heat treatment, specific surface area of the sample Y₁₀₀₀ is 352 m²·g⁻¹, the average pore size is 42.58 nm. After 1200°C heat treatment, specific surface area of sample Y₁₂₀₀ is 162 m²·g⁻¹, the average pore size is 56.29 nm. The results show that Al₂O₃-SiO₂ aerogel still has good pore structure, heat insulation and high temperature resistance after heat treatment.

4. Conclusion

We have synthesized Al₂O₃-SiO₂ aerogel composite by hybrid sol-gel process, ethanol supercritical drying technology using aluminum chloride hexahydrate (AlCl₃·6H₂O) and tetraethoxysilane (TEOS) as raw materials. The investigation results showed that Al₂O₃-SiO₂ aerogel possessed excellent heat-insulation performance and high-temperature stability property.

References

[1] Joseph B E 2004 U.S. Patent 6,689,470, 2004-2-10
[2] Zhou Y, Tong R, LI X et al. 2009 Fire Science and Technology 10 20
[3] Riegler N 1996 U.S. Patent 5,529,624,1996-6-25
[4] Zhou X, Zheng F, Li H et al. 2010 Energy and Buildings 42 (7) 1070
[5] Keysar S, Shter G E, Hazan Y et al. 1997 Chemistry of Materials 9 2464
[6] Saito Y, Takei T, Hayashi S et al. 1998 American Ceramic Society 81 2197
[7] Poco J F, Satcher J H, Hrubesh L W 2001 J. Non-Crystalline Solids 285 57
[8] Baumann T F, Gash A E, Chinn S C, et al. 2005 Chemistry of Materials 17 395
[9] Hirashima H, Kojima C, Imai H 1997 Sol-Gel Science and Technology 8 843