Preparation and characterization of monolithic Al$_2$O$_3$–SiO$_2$ aerogel

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Al$_2$O$_3$–SiO$_2$ aerogel was prepared through mixed sol–gel process and ethanol supercritical drying technology using aluminum chloride hexahydrate (AlCl$_3$·6H$_2$O) and tetraethoxysilane (TEOS) as precursors. Under the condition of the propylene oxide used as gelation initiators, during the process, a kind of Al$_2$O$_3$–SiO$_2$ aerogel with porous and large specific surface area were achieved in our experiments. Structures and properties of Al$_2$O$_3$–SiO$_2$ aerogel are investigated by means of X-ray Diffraction, Nitrogen adsorption/desorption analysis, Scanning Electron Microscopy, Fourier Transform Infrared Spectroscope, and Thermogravimetry-Differential Thermal Analysis. The results showed that the Al$_2$O$_3$–SiO$_2$ aerogel with the mole ratio of Al/Si = 3/1 possessed better heat-insulation performance and high-temperature stability. And it possessed a porous network structure made up of leaf shape particles. At the same time, Al$_2$O$_3$–SiO$_2$ aerogel showed a low density of 0.071 g/cm$^3$ at room temperature, specific surface areas of 708 m$^2$/g at 600°C, as well as 255 m$^2$/g at 1200°C. The Al$_2$O$_3$–SiO$_2$ aerogel is the polycrystalline boehmite (γ-AlOOH) phase at room temperature. As the temperature growing, it transferred to γ-Al$_2$O$_3$ at 600°C, and mullite phase at 1200°C.

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Key-words : Al$_2$O$_3$–SiO$_2$ aerogel, Al/Si mole ratio, Mixed sol–gel, Supercritical drying, High-temperature stability

1. Introduction

Aerogel possesses many fantastic properties which are determined by the unique three-dimensional network and nano-porous structure, such as low density, low thermal conductivity, high specific surface area, a high porosity and so on. On account of these properties, aerogel has been applied in various fields, particularly in the field of thermal insulation. Al$_2$O$_3$–SiO$_2$ aerogel is an admirable material as a new type of super thermal insulation material because of its excellent thermal insulation properties. And it shows excellent resistance to elevated temperatures compared to SiO$_2$ aerogel, and good thermal stability compared to Al$_2$O$_3$ aerogel.

The Al$_2$O$_3$–SiO$_2$ aerogel is prepared through sol–gel process and supercritical drying technology. In sol–gel process, the Al$_2$O$_3$–SiO$_2$ mixed sol is obtained by mixing alumina sol and silica sol. In particular, alumina sol is mainly prepared by two kinds of precursors including hydrated aluminum salts [AlCl$_3$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O] and aluminum alkoxides (aluminum tri-sec-butoxide and aluminum isopropoxide). However, aluminum alkoxides have been limited due to their relatively high cost and chemical activity. It is difficult to control the hydrolysis and condensation process of aluminum alkoxides during the preparation of the mixed sol. Therefore, it would be desirable to adopt hydrated aluminum salts as the precursor. As described in the previous research, Itoh H, et al. added propylene oxide to mixed solution of hydrated aluminum salts and prepared transparent alumina gels. T. F. Baumann, et al. prepared alumina aerogel with high surface area and low density through the sol–gel process using hydrated aluminum salts as the precursor.

In this paper, monolithic Al$_2$O$_3$–SiO$_2$ aerogel is prepared by sol–gel process and ethanol supercritical drying technology using aluminum chloride hexahydrate (AlCl$_3$·6H$_2$O), tetraethoxysilane (TEOS) and propylene oxide as alumina source, silica source and gelation initiator respectively. This method achieved monolithic Al$_2$O$_3$–SiO$_2$ aerogel with outstanding performance. This work is expected to provide the effective reference to the industrial scale application of Al$_2$O$_3$–SiO$_2$ aerogel in the wide fields.

2. Experiment

2.1 Materials

Aluminium chloride hexahydrate (AlCl$_3$·6H$_2$O), tetraethoxysilane (TEOS) and propylene oxide (PO, ≥99.5%) were purchased from Sinopharm Group Chemical Reagent Co., Ltd., China. Anhydrous ethanol (EtOH) and hydrochloric acid (HCl) were from Beijing Chemical Reagent Corporation, China. These chemicals were all analytically pure. Deionized water was made by our machine.

2.2 Experimental procedure

The process routing of synthesizing Al$_2$O$_3$–SiO$_2$ aerogel is given in Fig. 1. The technological process involves three steps: (1) the synthesis of mixed sol; (2) the synthesis of wet gel and the process of aging treatment; (3) ethanol supercritical drying technology.

In the step 1, alumina sol and silica sol were prepared by stirring the mixture with the mole ratio of AlCl$_3$·6H$_2$O/EtOH/H$_2$O = 1/12/35 and TEOS/H$_2$O/EtOH/HCl = 1/4/6/7.5 × 10$^{-3}$ respectively. Then, mixed alumina sol and silica sol with mole ratio of Al/Si = 1/0, 1/1, 2/1, 3/1, 6/1 at 30℃ for 60 min to complete the hydrolysis.

In the step 2, in order to promote the condensation, propylene oxide was added to the mixed sol. The mixture was quickly...
stirred at 30°C for 15 min and sealed at room temperature to form the wet gel. In the process of aging treatment, the wet gel was soaked in anhydrous ethanol at 50°C to strengthen the network and swap out the redundant water and organic matter.

In the step 3, the wet gel was placed in an autoclave which was sealed and filled with anhydrous ethanol. In order to ensure safety requirements, the autoclave must be recharged with pure nitrogen gas to exhaust the oxygen. The absolute pressure was controlled in the range of 0.1 to 9.1 MPa. The temperature was increased to 270°C at a rate of 2°C/min. After the heat-preservation stage, the absolute pressure slowly reduced to 0.1 MPa. Finally, the samples were obtained at room temperature. The serial numbers of samples, 1Al–0Si, 1Al–1Si, 2Al–1Si, 3Al–1Si, 6Al–1Si, were corresponded to different mole ratio of Al/Si. In order to investigate the effect of calcination temperature on structural and textural properties of Al2O3–SiO2 aerogel, samples were calcined at 600, 800, 1000, 1200°C respectively for 2 h with a rate of 3°C/min.

2.3 Characterization

The microstructures of samples were observed by Scanning electron microscope (SEM, FEI QUANTA FEG250, USA). The crystalline phase of samples were analyzed by powder X-ray diffraction (XRD, Bruker D8 Advance, Germany) using a Rigaku D/MAX-IIIC diffractometer with the Cu Kα radiation at 40 kV and 20 mA, and the range of 2θ was from 10 to 80°. The FTIR spectra of samples were obtained by a Fourier transform infrared spectroscopy (FTIR, BIOCHROM S50, UK). The pore size and specific surface areas of samples were investigated by a Nitrogen adsorption/desorption analysis (Gemini VII 2390, USA). In order to know the thermal stability of samples, the TG–DTA curves were obtained by Thermogravimetry–differential thermal analysis (TG–DTA, Seiko Inst TG/DTA 7300) and investigated in nitrogen atmosphere at a heating rate of 10°C/min from room temperature to 1400°C.

3. Results and discussion

3.1 Structural characteristics

In the paper, supercritical drying technology can eliminate the surface tension between the gas phase and liquid phase, which can effectively reduce the shrinkage and crack, and enhance the monolithicity of aerogels.15) Figure 2 exhibits the photograph of monolithic Al2O3 aerogel and Al2O3–SiO2 aerogel. Comparing Figs. 2(a) and 2(b), the obtained Al2O3–SiO2 aerogel possesses high monolithicity. The effect of different Al/Si mole ratios on properties of Al2O3–SiO2 aerogel is provided in Table 1. With the increase of silicon content, the gelation time is extended. There are two factors which cause this phenomenon. The first is alumina phase forms gel faster than the silica phase, and the second is the less presence of PO.

The bulk density of aerogel can be approximately calculated by using the formula: \( \rho = \frac{M_{\text{aerogel}}}{V_{\text{gel wet}}} \), where the \( M_{\text{aerogel}} \) and \( V_{\text{gel wet}} \) are the mass of aerogel and the volume of wet gel respectively. And in the same volume of sol, the number of monomer in Si sol is more than Al sol. So the bulk density of samples increased with the increase of silicon content.

3.2 BET analysis

The specific surface areas, average pore size and pore volume were investigated by nitrogen adsorption/desorption techniques. Specific surface areas of samples at different calcination temperature are shown in Fig. 3. The specific surface area of 3Al–1Si is obviously higher than other samples. The addition of silica is effective in suppressing the phase transformation and maintaining the porous structure after heat treatment.7,16,17) The average pore size and pore volume of the as-prepared samples are provided in Table 2. With the increase of silicon content, average pore size firstly increase and then decrease, also the pore volume and specific surface area exist a directly proportional relationship. These results indicate the samples possess excellent thermal insulation performance. Three factors cause the excellent thermal insulation performance of Al2O3–SiO2 aerogel. The first one is the high porosity which leads to low solid thermal conductivity. The second one is the small pore size which is smaller than the mean free path (about 70 nm) of gas molecules (N2, O2). This can make the air molecules in the pores difficult to collide with each other.

Table 1. Effect of different Al/Si mole ratios on properties of Al2O3–SiO2 aerogel

| Simples  | 1Al–0Si | 6Al–1Si | 3Al–1Si | 2Al–1Si | 1Al–1Si |
|---------|---------|---------|---------|---------|---------|
| Gelation time/min | 30 | 40 | 45 | 60 | 80 |
| Density/(g cm−3) | 0.058 | 0.063 | 0.071 | 0.075 | 0.081 |
| Character of aerogel | White opaque monolith |
other, which results in low gas thermal conductivity. The third one is the little contribution of radiative thermal conductivity to the total thermal conductivity at room temperature. At high temperature, radiative thermal conductivity dominates the total thermal conductivity. And alumina aerogel can impede partial thermal radiation, which results in low total thermal conductivity at high temperature. According to the results of nitrogen adsorption/desorption techniques, the samples exhibit excellent thermal insulating properties.

3.3 TG–DTA analysis

The TG–DTA curves of the samples (1Al–0Si and 3Al–1Si) are shown in Fig. 4. In the process of calcination, weightlessness can be divided into two segments. The first is observed during room temperature to 200°C, and the weight loss of 1Al–0Si and 3Al–1Si is respectively 4.4 and 2.7%. At the same time, an endothermic peak is observed in the DTA curve. These results are mainly caused by evaporation of ethanol solvent and adsorbed water which are left in the network structure. The second is observed during 200 to 800°C, and the weight loss of 1Al–0Si and 3Al–1Si is respectively 12.2 and 11.6%. An endothermic peak is observed in DTA curve at 493°C [Fig. 4(a)] and 533°C [Fig. 4(b)]. These results are caused by the decomposition of residual organic matter and the crystal phase transformation. The γ-Al2O3 phase is formed through the dehydration reaction of polycrystalline boehmite, equation of the reaction: 2AlOOH = Al2O3 + 2H2O↑. After 800°C, the TG curves have not changed showing the samples exhibit the high-temperature stability. During 800 to 1400°C, no sharp exothermic is observed on the DTA curves. However, the DTA curves with growth trend are observed, which indicates the suppression of phase transformation. There are two main causes for this phenomenon: stabilization of the crystal structure of alumina by addition of silica, and low density.2)

3.4 XRD analysis

The XRD patterns of the samples (1Al–0Si and 3Al–1Si) calcined at different temperature are shown in Fig. 5. As can be seen from the XRD patterns, the dried samples possess distinct diffraction peaks which are characteristic of the polycrystalline boehmite (γ-AlOOH). Mizushima et al.20) point out that Al2O3 aerogel could form polycrystalline boehmite phase using supercritical fluid drying technique, and boehmite phase can effectively hinder the sintering to improve the high-temperature stability. During the heat treatment, condensation reaction between boehmite layers removes some oxygen atoms, which results in the phase transformation.2) After the calcination process at 600°C, the phase of samples was transformed into δ-Al2O3. We can see from Fig. 5(a) that the phase of 1Al–0Si was transformed into γ-Al2O3 at 800°C and θ-Al2O3 at 1000°C. When the temperature is at 1200°C, the phase is θ-Al2O3 and the intensity of the diffraction peaks increase. The results correspond to the TG–DTA analysis well. However, the broad and weak peaks which are observed on XRD patterns indicate poor crystallization of sample. In Fig. 5(b), when the temperature promoted to 1200°C, the strong diffraction peaks of 3Al–1Si are observed, which are characteristic of the mullite phase. Horiuchi T et al.19) pointed out that the mullite phase is compounded as the mole ratio of Al2O3/SiO2 = 2/1–3/2. Meanwhile, within 600–1000°C, the wide width bread peak is observed at 25° (2θ) that is characteristic of the amorphous SiO2.

Comparing 1Al–0Si and 3Al–1Si, the crystal transformation of aluminum structure is effectively delayed. This result is consistent with the TG–DTA analysis, which indicates the high-temperature stability of aerogels improves effectively.

3.5 FTIR analysis

FTIR spectra of 3Al–1Si are shown in Fig. 6. Boehmite and
silica are composed of AlO$_6$ octahedra and SiO$_4$ tetrahedra. All the Al–O and Si–O related vibrations are known to appear only in the 1200–400 cm$^{-1}$ region. The distinct peak at 1069 cm$^{-1}$ is characteristic of Si–O–Si vibration while the shoulders appearing at higher and lower side of this absorption band indicate the presence of Al–O–Si bonds through cross-condensation of boehmite and silica. The PO takes proton from hydrated aluminum, and undergoes irreversible ring-opening reaction by the nucleophilic attack of the chloride ion. This reaction process could reduce the pH of sol and promote the cross-condensation of boehmite and silica. The SiO$_2$ forces AlO$_3$ in boehmite to AlO$_4$ polyhedron. The peak at 730–760 cm$^{-1}$ is characteristic of AlO$_4$ polyhedron, and one at 620–630 cm$^{-1}$ is characteristic of AlO$_3$ polyhedron. The peak at 472 cm$^{-1}$ is characteristic of amorphous silica. The peak at 3351 cm$^{-1}$ is characteristic of –OH and H–O–H vibrations respectively. The peak at 3078 cm$^{-1}$ is attributed to C–H bond, which shows that residual organic substance is left in the network structure after drying. As can be seen from Fig. 6, the disappearing of the peaks which corresponds to the sample after heat treatment at 600°C certifies the phase transition.

3.6 Microstructure analysis

The SEM photographs of the samples (1Al–0Si and 3Al–1Si) with different heat treatment are shown in Figs. 7–9. The microstructure of 1Al–0Si is porous network structure formed by needles or rod-shaped particles seen, and 3Al–1Si is formed by leaf shape particles seen from Figs. 7(a) and 7(b) respectively. The particle size is small, and the porosity is high. During the heat treatment, the particle size of 1Al–0Si increases gradually with the increase of calcination temperature, the porosity decreases, and some micropores are collapsed, sintering phenomenon appears in the microstructure of 1Al–0Si, as shown in Fig. 8. However, the microstructure of 3Al–1Si has insignificant changes, as shown in Fig. 9, and some sintering phenomenon is observed in the microstructure of aerogels only when the temperature is 1200°C. But the porous structure remains relatively complete. These results indicate the better high-temperature stability of Al$_2$O$_3$–SiO$_2$ aerogel.

3.7 High-temperature stability analysis

In order to testify the high-temperature stability, the effects of heat treatment during different periods were investigated. The 3Al–1Si was calcined at 1200°C for 1, 2, 3, 4, 5 h respectively which are named T1, T2, T3, T4, T5. Figure 10 exhibits the photograph of samples (T1, T3, T5). The macro-morphology of samples has no obvious change. XRD patterns of the samples are shown in Fig. 11. The crystalline phases of T1 is γ-Al$_2$O$_3$, and T2 is γ-Al$_2$O$_3$ and mullite phase. However, the broad and weak peaks which are observed on XRD patterns indicate poor crystallization of sample. All the crystalline phases of T3, T4, and T5 are mullite phase. Specific surface areas of samples with different periods of heat treatment are shown in Fig. 12, and the average pore size and pore volume are shown in Table 3. During prolonged heat treatment, the specific area and pore volume show a gentle downward trend, and the average pore size shows a slow upward trend. These results indicate the 3Al–1Si possesses excellent high-temperature stability.

4. Conclusion

In this paper, Al$_2$O$_3$–SiO$_2$ aerogel was prepared through mixed sol–gel process and ethanol supercritical drying technology. The structure and properties of Al$_2$O$_3$–SiO$_2$ aerogel was investigated by BET, SEM, XRD, TG–DTA and FTIR. The results indicate...
Fig. 8. SEM photographs of Al$_2$O$_3$ aerogel (1Al–0Si) at different temperature: (a) Dried, (b) 600°C, (c) 800°C, (d) 1000°C, (e) 1200°C.

Fig. 9. SEM photographs of Al$_2$O$_3$–SiO$_2$ aerogel (3Al–1Si) at different temperature: (a) Dried, (b) 600°C, (c) 800°C, (d) 1000°C, (e) 1200°C.

Fig. 10. Photograph of samples (T1, T3, T5).
that the $\text{Al}_2\text{O}_3$–$\text{SiO}_2$ aerogel with the mole ratio of $\text{Al}/\text{Si} = 3/1$ possess better heat-insulation performance and high-temperature stability. It shows a low density of $0.071 \text{ g/cm}^3$ at room temperature, a specific surface area of $708 \text{ m}^2/\text{g}$ at $600^\circ\text{C}$ and $255 \text{ m}^2/\text{g}$ at $1200^\circ\text{C}$.

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