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Synthesis of monolithic aerogel-like alumina via the accumulation of mesoporous hollow microspheres

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ABSTRACT

Monolithic aerogel-like alumina was synthesized via the accumulation of mesoporous hollow microspheres through an epoxide-driven sol–gel method. The addition of propylene oxide to the solution controls the gelation process, while the aging time and H_2O/ethanol molar ratio in the initial component determine the morphology of the gel. The bulk density of the as-prepared sample was 0.133 g/cm^3, and the BET surface area was 505.6 m^2/g, which were very close to the values for the common alumina aerogel synthesized through the supercritical drying method. The microstructural evolution of the aerogel-like material as a function of aging time was carefully studied by SEM and TEM. The transition from solid particles to urchin-like mesoporous hollow microspheres can be explained as a self-templating process according to the Ostwald ripening mechanism. In addition, the samples were heat treated to 800 °C, 1000 °C and 1200 °C for 2 h. With an increase of the heat treatment temperature, the crystalline phases of the aerogel-like alumina varied from γ-phase alumina to θ-phase alumina. The microstructures as well as the physical properties, such as the thermal conductivity and elastic modulus, of samples heat-treated at different temperatures were also measured and revealed that the samples exhibited excellent stability against high temperature.

1. Introduction

Thermal insulation materials have attracted an enormous amount of attention for their potential applications in aerospace and energy conservation during the last decade [1–3]. However, some limitations still exist in traditional thermal insulation materials because these materials cannot meet the increasing requirements for their density, porosity and mechanical properties in some hi-tech areas. A monolithic aerogel is a synthetic porous ultralight material and is famous for its high specific surface area, high porosity, low density and extremely low thermal conductivity. Monolithic aerogels appear to be appropriate candidates for future thermal insulation materials. Thus far, monolithic-aerogel-based materials have been widely studied and are expected to be utilized in thermal insulation [4], catalysis [5], magnetics [6], electronics [7] and optics [8].

For a long time, monolithic aerogels were only fabricated using the supercritical drying (SCD) method [9] because this process was able to diminish the capillary force built up in the pore walls of the gels and avoid the collapse of most of the pore volume during the drying process under ambient conditions. However, complicated facilities and extreme conditions caused the SCD technique to become a dangerous, expensive, multi-step and time- and energy-consuming procedure, which greatly limited its applications in industrial production.

The weak high-temperature stability of the aerogels also limited their applications for thermal insulation. Alumina aerogels [10] undergo significant shrinkage and lose their extraordinary properties when heat-treated at high temperatures (>1000 °C) for a long time because of the severe sinter process caused by their high surface free energy. Consequently, it is very difficult for aerogels to be used at high temperature. It is necessary to find a new material with extraordinary physical properties and excellent high-temperature stability.

Recently, Gash and co-workers [11,12] demonstrated a new route to obtain crack-free monolithic porous aerogels of various metal oxides including Al_2O_3 using an inorganic metal salt as the precursor through the SCD method. Typically, epoxides were added to aqueous solutions of inorganic metal salts to initiate gelation through a ring-opening reaction and worked as an acid scavenger to gradually increase the solution pH. The uniform increase in the solution pH results in homogeneous gelation to produce a monolithic gel. This method would be very useful for designing various monolithic aerogels with different microstructures and functions. The high-surface-area alumina aerogels [3], monolithic

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Al_2O_3 with well-defined macropores and mesostructured skeletons [13] and monolithic alumina aerogel synthesized through ambient drying [14] were already synthesized through this method. However, some of them required SCD method and the weak high temperature stability still greatly limited their extensive applications.

In this paper, we demonstrate a new facile route to synthesize monolithic aerogel-like alumina with high-temperature stability via the accumulation of mesoporous hollow microspheres through ambient drying. Materials with hollow structures have been widely studied recently because of their unique structure. These materials can be useful in drug storage and release [15], catalysis [16], separation [17], and lithium-ion batteries [18]. Many papers have described the formation of hollow spherical materials: traditional template-based methods, including those using hard [15] and soft [19] templates, and self-templating methods [18], which have been widely used in obtaining a hollow structure without an extra template. Nevertheless, nearly all of the materials with hollow structures were presented as powders or films; bulk materials with a hollow structure have been rarely reported. At the same time, alumina aerogel has been synthesized through ambient drying. In this study, the monolithic porous alumina gel was accumulated with urchin-like hollow spheres; the gel was crack-free even when dried at a rapid rate under ambient pressure drying conditions. The as-dried monolithic porous alumina gel exhibited aerogel-like properties such as a low bulk density, high surface area, high porosity and low thermal conductivity, even though the microstructure was absolutely different from a traditional aerogel. In addition, the aerogel-like alumina also exhibited excellent physical property stabilities even after being heat-treated at high temperature (up to 1200 °C).

2. Experimental

2.1. Synthesis of aerogel-like alumina

Aluminum chloride hexahydrate (Aldrich) was used as the aluminum source, and a mixture of distilled water and ethanol (Sinopharm Chemical Reagent Co., Ltd.) was used as the solvent. Propylene oxide (Sinopharm Chemical Reagent Co., Ltd.) was added to initiate the condensation reaction. Isopropanol (Sinopharm Chemical Reagent Co., Ltd.) was used for the aging process. All of the reagents were used as received. Aluminum chloride hexahydrate (4.35 g, 18 mmol) was first dissolved in the mixture of distilled water and ethanol (using various H_2O/EtOH molar ratios: 1:0.48, 1:1.18, 1:0.2, the corresponding real volume rations of H_2O, EtOH is 4 ml, 5.5 ml; 2 ml, 7.5 ml; 6 ml, 2.5 ml). Propylene oxide (7 ml, 0.1 mol) was then rapidly added into the mixture solution, and stirring was continued for 20 s. The resultant homogeneous solution was sealed and maintained at 60 °C for gelation. As this reaction is an exothermic reaction and the solution would reach to about 60 °C just several second after the epoxide was added to the procurer. Then, the transparent solution turned into a translucent gel quite rapidly (in approximately 20 s). After gelation, the wet gel was aged with fivefold isopropanol for 2 days at 60 °C. Subsequently, the gel was dried by evaporation under ambient pressure condition. After the gel was completely dried, it was heat treated at various temperatures in air with a heating rate of 1 °C/min.

2.2. Characterization

FE-SEM (S-4800, Hitachi, Japan) was used to observe the morphology of the gel structure using a slight Pt coating on the sample. TEM analysis was performed in bright-field mode using a JEM-1200EX at 120 keV (JEOL Japan). The TEM samples were deposited onto carbon-coated, 3-mm diameter, copper electron microscope grids and dried in air. Nitrogen adsorption measurements (ASIC-2 Quantachrome Instruments USA) were performed to obtain the pore properties such as the BET-specific surface area and pore size distribution. The adsorption branch was used for the Barrett–Joyner–Halenda (BJH) calculation. Before measurement, the sample was outgassed under vacuum at 200 °C for 4 h. The bulk density was determined by measuring the rate of volume and weight of a rectangle sample. XRD analysis with Cu Kα (0.154 nm, X-98, Rigaku Japan) radiation was performed to identify the crystalline phases. All of the measurements were performed for the powder specimens prepared by grinding monolithic samples. Stress–strain curves were generated using a universal material tester (Zwieklroell Germany) with a load of 20 kN; the tests were performed in triplicate, and the speed was 1 mm/min. The elastic modulus was calculated based on the strain values between 100 and 500 N of stress. The thermal conductivities were measured using the hot-wire method (TC 3000 XIATECH China) at room temperature.

3. Results and discussion

3.1. Formation and characterization of aerogel-like alumina

The monolithic aerogel-like alumina was synthesized using a very convenient procedure based on the epoxide-driven method established by Gash [12,13]. In the previous work, epoxide was used as the gelation initiator to induce the gelation of a metal salt solution, acting as an irreversible proton scavenger through a ring-opening reaction. In this work, as we utilized a relatively high metal-ion concentration and propylene oxide/metal-ion molar rate, the transition from a clear solution to opaque gel was completed in a very short time (approximately 20 s). This approach is quite different from the traditional aerogel preparation with epoxide-driven sol–gel process [3], which requires a long gelation time for the complete reaction. An opaque monolithic aerogel-like material could be obtained after the wet gel was aged for 2 days and dried under ambient pressure conditions.

Fig. 1 presents a photograph of the as-dried monolithic aerogel-like alumina. Fig. 2 presents SEM images of alumina gels prepared using various H_2O/ethanol molar ratio. With an appropriate ratio of H_2O/ethanol (1:0.48), urchin-like hollow microspheres can be obtained, the diameter of these hollow microspheres was about $1 \sim 2$ μm (Fig. 2a); these hollow microspheres attached to each other and accumulated to form an opaque monolithic gel. When the H_2O/ethanol ratio was low (1:1.18), the gelation time became

Fig. 1. Photographs of monolithic aerogel-like alumina.