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Preparation of monolith SiC aerogel with high surface area and large pore volume and the structural evolution during the preparation

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Abstract

Resorcinol–formaldehyde/silica composite (RF/SiO_2) aerogel was synthesized by sol–gel process followed by supercritical drying (SCD). Monolithic SiC aerogel was obtained from RF/SiO_2 aerogel after carbothermal reduction. The evolution of physical property, crystal structure, morphology and pore structure from RF/SiO_2 to SiC aerogel was investigated by different methods, such as X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and N_2 adsorption/desorption. The as-synthesized SiC aerogel presented typical mesoporous structure and possessed high porosity (91.8%), high surface area (328 m^2/g) and large pore volume (2.28 cm^3/g). Carbothermal reduction mechanism was also discussed based on the experiment and characterization results.

Keywords: Sol–gel; Supercritical drying; Silicon carbide; Carbothermal reduction; Microstructure

1. Introduction

Silicon carbide (SiC) has high hardness, good thermal shock resistance, high thermal conductivity and stability, low thermal expansion coefficient, superior chemical inertness and large band gap [1–4]. Therefore, it is considered as a promising material in many fields, such as reinforcement, catalysis, high-power and high-frequency electronics, photoelectric, anti-radiation, membrane supports for hydrogen separation and wave-absorbing devices [5–10]. It has been widely reported that mesoporous SiC can be successfully prepared by carbothermal reduction of binary carbonaceous silica composites. However, the resulting products are usually particles, fibers and whiskers [11–14]. Monolithic materials with compact framework and porous microstructure have advantages for many applications. For example, porous monoliths used in flow through catalytic or separation systems give lower back-pressure, higher permeability and better performance compared to packed columns which are prepared by particles. Furthermore, monolithic aerogels can provide higher surface area and larger pore volume than their state-of-art counterparts. These advantages, accompanied with excellent pore structure and good thermal and chemical stability of monolithic SiC aerogel can lead to novel applications [15]. Monolith SiC aerogel has been successfully prepared via magnesiothermic reduction and carbothermal reduction [16–18]. However, the pore volumes and surface areas are relatively low. Herein, we proposed a method to prepare monolithic SiC aerogel with higher surface area and larger pore volume from resorcinol–formaldehyde/silica composite (RF/SiO_2) aerogel. The structural evolution during thermal treatment was studied systematically.

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2. Experimental

2.1. Sample preparation

Silica sol and carbonaceous sol (RF sol) were prepared separately. Resorcinol (R) and anhydrous sodium carbonate (Na_2CO_3, a catalyst to prompt the reaction between R and F) were dissolved in the mixture of deionized water (W), formaldehyde (F, weight fraction of 37% in aqueous solution) and ethanol (EtOH) with a molar ratio of R:F:EtOH:W:Na_2CO_3=1:2:3.43:2:0.01. RF sol was obtained after stirring for 30 min at 50 °C. Tetraethoxysilane (TEOS) was diluted in the mixture of EtOH, W and hydrochloric acid (HCl), with TEOS:EtOH:W:HCl prepared at a molar ratio of 1:10.3:2:0.002. After stirring for 30 min at 30 °C, the RF sol was poured into silica sol, with a molar ratio of R:TEOS=1:2. Subsequently, binary sol was made by regulating the pH value of compound to 9.4 ± 0.1 by ammonium hydroxide (25% w/w aqueous solution). The binary sol was poured into a polypropylene mold (40 mm of inner diameter). After gelation within 3 h under room temperature (25 °C), RF/SiO_2 gel was aged at 60 °C for 24 h and simultaneously washed with ethanol every 8 h to remove water and residual chemicals. Alcogel was dried by supercritical drying to form RF/SiO_2 aerogel. Thermal treatment of RF/SiO_2 aerogel was performed in a tube furnace (72 mm inner diameters of tube). The temperature was first raised to 800 °C with a rate of 1 °C/min under flowing argon (150 ml/min), and maintained at that level for 3 h. Subsequently, the flow rate was lowered to 70 ml/min and the temperature was raised further to 1500 °C with a rate of 2 °C/min and it was maintained at that level for 5 h to produce carbon/silicon carbide composite (C/SiC) aerogel. At the end of that period, the temperature was lowered to 550 °C, argon was changed to air (200 ml/min), excess free carbon was burned off by maintaining the temperature at that level for 3 h to obtain monolithic SiC aerogel.

2.2. Characterizations

Apparent density (ρ_a) was calculated from the weight and the physical dimensions of the samples. Skeletal density (ρ_s) was determined by using a Micromeritics AcuuPyc II 1340 instrument. Porosity was determined by $1-\rho_a/\rho_s$. The microstructure was surveyed by using LEO-1530VP scanning electron microscope (SEM). The phase composition was evaluated by ARL ARLX′TRA X-ray diffraction (XRD) using a Cu-Kα radiation. Transmission electron microscope (TEM) was conducted by using a JEOL JEM-2010 electron microscope. N_2 adsorption/desorption tests were performed by using a Quantachrome Autosorb-iQ instrument. The specific surface area was calculated by Brunaur–Emmett–Teller (BET) model. The pore-size distribution was derived by using the non-local density functional theory (NLDFT) model. The pore volume was estimated from the adsorbed amount at a relative pressure P/P_0 of 0.99. Thermogravimetric analysis (TGA) was performed by using a NETZSCH STA449C thermogravimetric analyzer under a constant air flow of 30 ml/min at a heating rate of 10 °C/min.

3. Results and discussion

Fig. 1 shows the formation of RF RF/SiO_2 aerogel and its transformation to monolithic SiC aerogel. RF gel forms much slower than silica gel. The reaction between R and F to form RF gel at room temperature takes place very slowly. A multiple stage heating process and catalysts are used to accelerate the gelation. Generally, the reaction is conducted with base catalyst (such as Na_2CO_3) under a temperature around 80–90 °C for a few days or weeks [19–21]. However, silica gel can form in a short period at much lower temperature with base catalysis or acid/base catalysis [22,23]. Therefore, the RF gel forms later on will surround the silica gel.

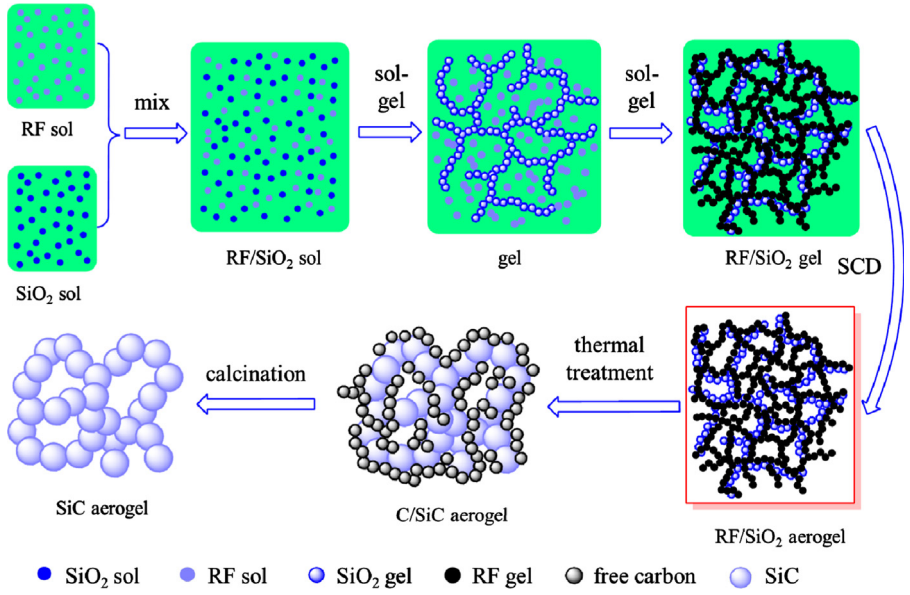

Fig. 1. Formation of RF/SiO_2 aerogel and its transformation to SiC aerogel.