



Synthesis of Non-oxide Porous Ceramics Using Random Copolymers as Precursors

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In this paper, we reported a novel method for synthesis of non-oxide porous ceramics by using random copolymers as precursors. A silazane oligomer and styrene monomer were used as starting materials, which were copolymerized at 120 °C to form random polysilazane–polystyrene copolymers. The copolymers were then pyrolyzed at 500 °C to obtain porous ceramics by completely decomposing polystyrene (PS) and converting polysilazane (PSZ) into non-oxide Si–C–N ceramics. The obtained material contained a bi-model pore-structure consisting of both micro-sized and nano-sized pores with very high surface area of more than 500 m²/g. We also demonstrated that the pore structure and surface area of the materials can be tailored by changing the ratio of the two blocks. Current results suggest a promising simple method for making multi-scaled porous non-oxide materials.

KEY WORDS: Non-oxide porous ceramics; Polymer-derived ceramics; Random copolymer

1. Introduction

Non-oxide porous ceramics have attracted increasing interests in recent years^[1–5]. This new class of materials exhibit many advantages over their oxide counterparts, including low density, better chemical inertness and high thermal stability^[6,7], thus promising for applications in extreme environments, such as solid–liquid separation, gas and liquid filtration, purification, catalysts supports, sound and shock absorption, and thermal insulation^[8]. Previously, non-oxide porous ceramics were primarily synthesized by using “conventional” ceramic materials via following techniques: replica, sacrificial template, direct foaming techniques, freeze–drying and sol–gel method^[1,9,10]. While a variety of porous materials have been prepared, these techniques are limited in terms of the complex fabrication processes and the lack of flexibility in pore structure manipulations.

Recently, non-oxide porous ceramics have also been synthesized by thermal decomposition of polymeric precursors (so-called polymer-derived ceramics, PDCs). The technique can easily achieve multi-scaled porous structures even in one step. For example, nano-scaled pores can be self-formed during the decomposition of the chemical bonds such as C–H, Si–H, and N–H in polymer precursors^[11,12]; the mesopores can be obtained by designing the molecular structure of the preceramic polymer^[13,14]; and the large-scaled pores can be realized by using template technique^[14–16]. In addition to the flexible processing, polymer-derived ceramics also exhibited a set of unique structural and functional properties^[17–25], which makes porous PDC very promising for widespread applications.

In this paper, we report a new facile approach to prepare non-oxide porous Si–C–N ceramics by using random copolymers as precursors. The basic idea of the technique is illustrated in Fig. 1. It includes following basic steps: (i) synthesizing copolymers containing polysilazane blocks which can be converted to non-oxide ceramics and polystyrene blocks which will be completely decomposed to form pores; (ii) cross-linking the copolymer to form preceramic precursor; and (iii) pyrolyzed the precursor to form porous ceramics. By this technique, the inner structure, size and distribution of the pores can be designed and controlled by tailoring the amount and size of the two blocks.

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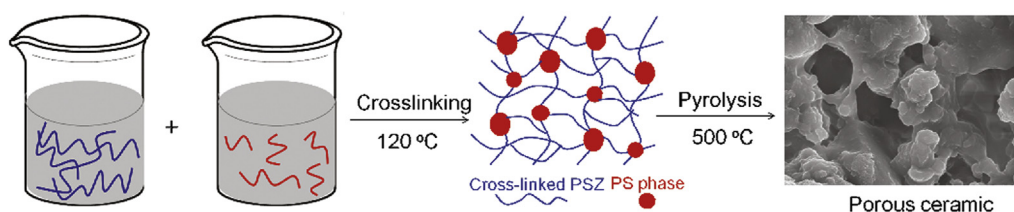


Fig. 1 Schematic illustration of the proposed synthesis procedure for non-oxide porous ceramics by using random block copolymer as the precursor.

2. Experimental

2.1. Starting materials

A liquid-phased polysilazane (PSZ) was purchased from Institute of Chemistry, Chinese Academy of Sciences, Beijing, China. Styrene (purity, 98.0%), toluene (purity, 99.5%) and *n*-hexane (purity, 97.0%) were obtained from Xingyue Chemical Co. Ltd., Tianjin, China. Azodiisobutyronitrile (AIBN, 99%) was provided by J&K Scientific Ltd., Beijing, China. Tetrahydrofuran (THF, analytically pure grade) was obtained from Aladdin Chemistry Co. Ltd., Shanghai, China. The chemicals were used as-received without further treatment, except that THF was distilled under reflux using sodium/benzophenone followed by drying under vacuum of 2 kPa (20 mbar) at 40 °C for 24 h.

2.2. Synthesis of copolymer

PSZ, styrene, AIBN and anhydrous toluene were filled into a flame-dried flask equipped with a Teflon stir bar, septum, and high-vacuum stopcock at room temperature under an inert argon atmosphere. The flask was then heated to 120 °C in an oil bath for 4 h to form PSZ–PS copolymer. The obtained copolymer was dissolved in THF, and then was slowly added to excess *n*-hexane to precipitate. After three times of dissolve-precipitation process, the copolymer was separated from the solution. The residual solvent in the filtered polymer was removed at room temperature for 24 h in a vacuum oven. The produced copolymer was white powders with a yield of 35%–40%. Two kinds of copolymers were prepared with the ratios of PSZ to styrene of 2:1 and 3:5, respectively, and labeled as PSZ–co–PS (2:1) and PSZ–co–PS (3:5).

2.3. Pyrolysis

The pyrolysis process was carried out at 500 °C in an alumina tube furnace (GSL-1600X, Hefei Kejing Materials Technology Co., Ltd., Hefei, China) with the protection of flowing high-purity argon. The heating and cooling rate was 2 °C/min and the holding time was 2 h. The open porosities and the densities of the resultant ceramics were measured by Archimedes drainage method.

2.4. Characterization

The resultant porous ceramics were characterized by scanning electron microscopy (SEM, JEOL 6700F, Tokyo, Japan) and energy dispersive spectroscopy (EDS). The bonding structure of the copolymers was measured by Fourier transform infrared spectroscopy (FTIR, Nicolet, Beijing Second Optical Instrument

Factory, Beijing, China) with KBr tablets; nuclear magnetic resonance spectroscopy (NMR, INOVA-400, Varian, Inc., USA) was carried out using CDCl_3 as solvent and tetramethylsilan (TMS) as internal standard. The thermal properties of the obtained copolymers were studied by using thermogravimetric analysis (TGA, Q50, TA Instrument, USA) in a platinum crucible up to 800 °C under an argon atmosphere with a flow rate of 40 mL/min and a heating rate of 10 °C/min, and using differential scanning calorimeter (DSC, MD2910, TA Company, USA). The molecular weight and its distribution of the synthesized copolymers were investigated by gel permeation chromatography (GPC, Waters, USA) using THF as solvent. Simultaneous thermal analysis of TGA and DSC coupled with mass spectrometry was performed using a simultaneous thermoanalyzer (STA 449 F3) coupled with a quadrupole mass spectrometer (QMS 403 C Aëolos, Netzsch Group, Germany) in the temperature range of 40–1400 °C with a heating rate of 10 °C/min under argon atmosphere with a flow rate of 50 mL/min. The Brunauer–Emmett–Teller (BET) surface area and pore size were measured by surface area and porosimetry analyzer (Gold APP Instrument Corporation, Beijing, China).

3. Results and Discussion

The formation of the copolymers was first analyzed by FTIR spectrometry. It is seen (Fig. 2(a)) that both copolymers contain peaks corresponding to N–H bond, Si–H group, Si–N–Si bond and Si–CH₃ group stretching at 3377, 2127, 800 and 1255 cm^{-1} , respectively. However, peaks corresponding to the C=C in raw materials of polysilazane and styrene disappear in the copolymers. It is indicated that the two substances have cross-linked together by the vinyl polymerization. The concentration of PSZ and PS in the copolymers can be estimated from the relative intensity of the representative peaks. Here, Si–CH₃ signal and benzene ring single were used for PSZ block and PS block, respectively. It was found that the ratios of $I_{\text{Si-CH}_3}/I_{\text{benzene ring}}$ are 0.74 and 0.83 for PSZ–co–PS (3:5) and PSZ–co–PS (2:1), respectively, suggesting that the former contains more PS than the later. This is consistent with our original design.

Further characterization of the copolymers was carried out by using ¹H NMR (Fig. 2(b)). It is seen that the benzene ring protons, Si–CH₃ groups and silicon hydrogen bonds (Si–H) were observed at chemical shifts of 7.08×10^{-6} – 7.18×10^{-6} , 0 and 4×10^{-6} , respectively. The peak for C=C around 5.6×10^{-6} – 6.2×10^{-6} was not found, confirming that the polymerization reaction happened between the vinyl in PSZ and styrene. The peak at 1.6×10^{-6} was assigned to –CH₂– protons, which was derived from the polymerization of vinyl in polysilazane. By using the silicon hydrogen bond (Si–H) at the chemical shift of 4.15×10^{-6} as an internal reference, it is found

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