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Preparation of three-dimensional ordered macroporous SiCN ceramic using sacrificing template method

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Abstract

Three-dimensional (3D) long range well ordered macroporous SiCN ceramics were prepared by infiltrating sacrificial colloidal silica templates with the low molecular weight preceramic polymer, polysilazane. This was followed by a thermal curing step, pyrolysis at 1250 °C in a N_2 atmosphere, and finally the removal of the templates by etching with dilute HF. The produced macroporous SiCN ceramics showed high BET surface areas (pore volume) in the range 455 m^2/g (0.31 cm^3/g)–250 m^2/g (0.16 cm^3/g) with the pore sizes of 98–578 nm, which could be tailored by controlling the sizes of the sacrificial silica spheres in the range 112–650 nm. The sphere-inversed macropores were interconnected by 50 ± 30 nm windows and 3–5 nm mesopores embedded in the porous SiCN ceramic frameworks, which resulted in a trimodal pore size distribution. The surface of the achieved porous SiCN ceramic was then modified by Pt–Ru nanoparticle depositing under mild chemical conditions.

Keywords: Macroporous SiCN ceramic; Silica template; Pt–Ru nanoparticles; Catalyst supporter; Preceramic polymer

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1. Introduction

A variety of artificial morphologies and structures based on the sacrificing template method have been synthesized using the 'fixing' concept [1]. In this fabricating process, the target product materials are 'fixed' into the voids of a template, and after suitable treatment, the target composition with the designed morphologies and structures is finally replicated after removing the template. Based on the this procedure, the periodic sphere-inversed structure is attracting much attention and much work has currently been done, e.g. three-dimensional ordered macroporous (3DOM) silica [2,3], carbon [4], oxide ceramic [5,6], and polymers [7,8] with pore diameters (normally hundred of nanometers) comparable to optical wavelengths. This gives these periodic structures promising optical properties based on the Bragg diffraction and the formation of optical stop-bands [9]. In addition, this kind of material can also be used as support materials for advanced catalysts [10], chromatography [11], sensors [12], battery materials [6], purification of waste water [13] and optic–electronic devices [14]. In particular, the catalyst supported porous materials have been successfully applied in the mass transfer on the catalytic combustion [15,16], combustion in situ in underground reservoirs for enhanced oil recovery [17], efficient heat transfer devices [18] and the reduction of hazardous combustion products [19]. From this point of view, it could be anticipated that eventually non-oxide ceramics will be used as catalytic supports that operate under harsh conditions due to their high thermal, mechanical, and chemical stabilities. However, only a few reports have been issued on

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periodic nanostructured non-oxide ceramics [20], although the polymeric route to non-oxide ceramics, via wet fabrication and subsequent pyrolysis, offers a unique opportunity to manufacture conventional ceramic components, such as fibers, coatings, and composites [21]. Recently, we first reported on the liquid preceramic polymer-based fabrication of macroporous SiC containing a regular pore array [22]. However, the SiC product produced contained excess silicon, derived from polymethysilane (PMS), and was not stable over 600 °C due to silicon oxidation. Moreover, the use of a pyrophoric PMS precursor demanded careful handling during the fabrication process.

In this study, an alternative porous SiCN ceramic with a high surface area and a 3D ordered porosity was prepared straightforwardly using a colloidal silica template in combination with polysilazane, as a chemically stable precursor. The pore characteristics of the achieved porous SiCN ceramic were tailored using different size of sacrificial silica spheres. In particular, as a preliminary work of catalytic or electrode applications, Pt–Ru nanoparticles were deposited on the walls of the porous SiCN ceramic by borohydride reduction.

2. Experimental

In order to make sphere-inversed macroporous SiCN ceramic, monodisperse silica spheres were firstly synthesized using a sol–gel reaction [23]. Tetraethylorthosilicate (TEOS, 98%, Aldrich) was reacted in the mixture of anhydrous ethanol (99.9%, Aldrich), distilled water, and ammonia hydroxide (25.0–28.0%, Oriental Chem. Ind) as reported elsewhere [22]; all the reagents were used as supplied. The prepared colloidal silica spheres in the diameter range of 100–700 nm were then washed with ethanol for 3–5 times to remove impurities and dried in an oven at 70 °C for 7–8 h. The silica powder obtained was then packed to well order template by natural sedimentation, as previously described [22,4]. The sphere sizes were determined with SEM.

Polysilazane (PSZ, $-(\mathrm{HNCH_3SiC_2H_3})_x-(\mathrm{HNHSiCH_3})_y-$, $M_\mathrm{n} = 440$) was used to prepare the SiCN ceramic, as reported elsewhere [24]. The low viscous precursor, with no dilution, was infiltrated into the silica template, and the composite was placed in a quartz tube furnace to cure at 300 °C for 5 h. This was followed by heating up to 1250 °C at a heating rate of 2 °C/min in N_2 and kept there for 0.5 h. The ceramic composite then was dipped into 5% aqueous hydrofluoric acid (HF) solution for 6 h to etch out the silica spheres. The achieved porous product was thoroughly washed with distilled water until a neutral pH was obtained and dried finally in an oven at 110 °C overnight.

The achieved sphere-inversed macroporous SiCN ceramic was dipped into a $\mathrm{RuCl_3 \cdot \mathit{x}H_2O}$ (Alfa Aesar) and $\mathrm{H_2PtCl_6 \cdot 6H_2O}$ (Alfa Aesar) aqueous solution at a Pt/Ru mole ratio of 1 in 20 parts of H_2O, as previously described [25]. After 3 h, a 1 M $NaBH_4$ solution in distilled water was added to the solution and allowed to react for 6 h. The mixture was then filtered and washed with distilled water until a neutral pH was attained. The Pt–Ru treated porous SiCN was finally dried at 110 °C overnight.

The morphologies of the porous samples were examined by scanning electron microscopy (SEM, LEO1455VP) and transmission electron microscopy (TEM, F/20 Tecnai Philips). BET surface areas were determined from N_2 adsorption isotherms (BET, ASAP 2400, Micromeritics). The compositions of the pyrolytic products were investigated by powder X-ray diffraction (Siemens D5000, Cu Kα, radiation wavelength $\lambda = 0.154$ nm).

3. Results and discussion

Fig. 1 shows the representative SEM images of the various sphere-inversed porous SiCN ceramics with flat plane or deep-seated structures. It is generally observed that a highly ordered and interconnected 'honeycomb' pore structure was obtained, which replicated the long range and 3D close-packed silica template fabricated by natural sedimentation. As summarized in Table 1, macropore sizes of about 98–578 nm were approximately proportional to the sizes 112–650 nm of the original sacrificial silica sphere templates, which provides a means of tailoring the pore size of porous materials. The small windows of about 50 ± 30 nm are attributed to contact points between the initial neighboring silica spheres. Moreover, it is believed that the observed three windows per hemisphere provide existence of a previous closed-packed structure containing 12 spheres.

Typically, a 10–15% size difference was found between the silica spheres and the achieved pore size because the silica spheres and polymer shrink during the pyrolysis stage. However, this is a low level of shrinkage compared to 25–30% shrinkage of polymethylsilane (PMS)-derived macroporous SiC, as we reported earlier [22]. This shrinkage difference is caused by the higher ceramic yield of PSZ (ca. 80%) than that of PMS (ca. 45%). Furthermore, the pyrolysis of polymers in a confined space might enhance the ceramic yield by allowing gaseous products to redeposit on the framework. It should be noted that the weight change of the PSZ was subjected to three stages of thermal decomposition during pyrolysis process, the first step at 300–600 °C was associated with a 6 wt% loss, the second step at 600–800 °C and a 10 wt% loss, and the last step at 800–1250 °C with only a 3 wt% loss. In addition, the structural supporting effect of silica spheres must contribute to form the dense porous ceramic framework.