



Inverse silicon carbide replica of porous glasses



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ABSTRACT

Porous glasses are used for the first time as template in a nanocasting approach to synthesize nanoporous silicon carbide. By varying the structural parameters of the glasses, the properties of the resulting silicon carbides can be controlled. Furthermore, the template and the replicate thereof are distinguished by a three-dimensional, continuous pore network. Pore sizes of the SiC DUT-88 (DUT = Dresden University of Technology) are varied in the nanoscale (10–50 nm) and specific surface areas of up to 477 m² g⁻¹ are reached after precursor-ceramic conversion at 1300 °C. Even beads of nanoporous silicon carbide can be synthesized if shaped porous glass templates several hundred microns in diameter are used. The results demonstrate how to control the silicon carbide structures in a very appropriate and extended way. Such nanoporous silicon carbide materials are promising components for application as e.g. filter, membrane or catalyst supports.

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1. Introduction

The nanocasting approach is one powerful opportunity generating porous materials. Hard matter therein acts as template molding a precursor into the desired nanoscaled shape and after transformation to the aimed product and removal of the filler a porous material can be obtained. Exo- or endotemplates are applicable [1,2].

One template class that has been investigated extensively for synthesizing nanoporous silicon carbide is silicon dioxide [3–10]. The application of liquid phase infiltration was essential to accomplish the syntheses of replicates and ordered structures [3,5,6,8,10,11]. Nevertheless, the template structure controls directly the pore character of the resulting SiC and e.g. in case of mesoporous silica (e.g. SBA-15 and KIT-6) their properties only can be tailored in a narrow range resulting in a strict limitation of obtainable pore size and wall thickness. Porous glasses derived from phase-separated alkali borosilicate glasses have a SiO₂ content of usually more than 96 wt.% and hence, can be considered as siliceous if used as template in the nanocasting process. The properties of porous glasses can be adjusted in a relatively wide range. It was shown that pore sizes ranging from 1 nm to 1000 nm and pore volumes between 0.1 and 1.1 cm³ g⁻¹ are realizable. Those structural parameters are influenced by the initial glass composition, the heat treatment conditions and the leaching

procedure. Furthermore, porous glasses are distinguished by a continuous three-dimensional, sponge-like pore network. Moreover, the preparation of hierarchical porous glasses and monolithic structures (e.g. beads, membranes, tubes and rings) is possible.[12–15] Due to those tunable parameters, porous glasses are investigated for application in e.g. the fields of membrane technology [16,17], as component for optical chemosensors [18], as materials for confinement effect studies [19,20] or as catalyst supports [21–23]. The integration of porous glass with its versatile controllable structure parameters as template in the nanocasting approach was already described in literature and e.g. an inverse replica made of cerium dioxide as catalyst support was obtained [24]. Furthermore, there are some investigations concerning the application of silicon carbide as catalyst support where it could be shown that it is favorable against common supports like alumina and silica [25–37]. Therefore, the use of porous glasses with their variable structure parameters in the nanocasting approach to silicon carbide could result in materials with interesting features and characteristics in the same way as the templates are tunable. The application of the resulting ceramics as e.g. catalyst support [25–37] or filtration and membrane material [38,39] is feasible.

In the following, the implementation of porous glasses to the hard-template silicon carbide synthesis method (= nanocasting) using a polymeric ceramic precursor and a liquid infiltration strategy is described. Besides, the replication of the continuous nanoscaled pore structure, the opportunity of the particle shape conservation by using glass beads was investigated. The results could show the possibility transferring porous glass property varieties to silicon carbide and hence, numerous pore sizes, porosities as well as monolithic structures with controllable characteristics

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are likely reachable. In our opinion, the control of structure parameters in a wide range is fundamental to investigate silicon carbide as e.g. catalyst support in a more appropriate way as well as monolithic structures are desirable.

2. Experimental

2.1. Chemicals

Aqueous hydrochloric acid (37%, VWR), NaOH pellets (Fisher Scientific), sodium borosilicate glass beads and granules (VitraBio GmbH Steinach), allylhydridopolycarbosilane SMP-10 (Starfire Systems), aqueous hydrofluoric acid (40%, Merck), *n*-heptane ($\geq 95\%$, Sigma–Aldrich). All the chemicals (except sodium borosilicate glasses) were of analytical grade and were used without further purification.

2.2. Synthesis of porous glasses

Sodium borosilicate glass beads or granules, respectively, with a composition of 70 wt.% SiO₂, 23 wt.% B₂O₃ and 7 wt.% Na₂O were used as starting materials. The particle fraction was 160–200 μm . To initiate the phase separation, the glass was thermally treated at various temperatures (Table 1). Subsequently, the glass was rapidly cooled to below 500 °C to avoid a further phase separation. The extraction of the sodium-rich borate phase was performed at 80 °C with 3 N hydrochloric acid for 18 h. The liquid–solid-ratio of aqueous HCl to glass was 15:1. The colloidal silica deposits remaining in the pore system after acidic leaching were removed by a treatment with 0.5 N sodium hydroxide solution at room temperature for 2 h. In all leaching steps the glass was kept in suspension by stirring to ensure a complete extraction [12]. In dependence of the applied annealing temperature, the samples are denoted PG10S, PG30 and PG60. Therefore, the number reflects the approximated pore size as determined by mercury intrusion (Table 1) and S stands for sphere due to the bead morphology of the glass used.

2.3. Synthesis of nanoporous silicon carbide

The porous glasses PG10S, PG30 and PG60 were infiltrated with the liquid silicon carbide precursor (SMP-10) applying the nanocasting procedure. The siliceous material acts as mold during the polymer-carbide transformation while pyrolysis. In case of the large pore samples without specific shape, an incipient wetness analogous method described earlier was used [10]. As can be seen from SEM (Fig. A.1) the PG10S spheres have a kind of peel which is only slightly porous due to the shaping. Hence, incipient wetness does not work and an adaption is necessary. For PG10S, wet infiltration was applied using *n*-heptane as solvent which was removed with rotary evaporator. The precursor was impregnated in two steps of 60%, firstly, and 40%, secondly. According to the total pore volume of the glasses 0.5 g SMP-10 ($\rho = 0.998 \text{ g cm}^{-3}$) was used for

1.0 g silica template. In case of wet infiltration precursor was dissolved in 15 mL *n*-heptane per step. Pyrolysis was performed in a horizontal tubular alumina furnace in argon flow. After flushing, samples were heated to 300 °C with 120 K/h and held at this temperature for 5 h. Afterwards 700 °C were reached with a temperature ramp of 30 K/h and finally, temperature was raised to 1300 °C applying a heating rate of 150 K/h and holding for 2 h. After cooling down, composites were etched with approximately 120 mL diluted HF solution (equal amounts of 40 wt% HF solution, ethanol and water) for 24 h. Finally, silicon carbides denoted as DUT-88(XXY) (DUT = Dresden University of Technology; XX = approximated pore size of the porous glass template; Y = S for spherical shaped template, in other cases it is missed) were obtained by filtration, washing with 600 mL ethanol and drying in air at 80 °C.

2.4. Characterization

Scanning electron microscopy was performed for all porous glasses and DUT-88 samples after sputtering with gold using a DSM982 (Zeiss). The mercury porosimetry was carried out on a POREMASTER 60 apparatus by Quantachrome. A contact angle of 141.3° was used for mercury. The cumulative pore volume V_{cum} of the samples represents the total volume of mercury taken up by the sample at the given pressure. The corresponding pore diameter was calculated applying the Washburn equation and a cylindrical pore model. The total pore volume from mercury intrusion $V_{\text{P,Hg}}$ was defined as the cumulative pore volume V_{cum} at the highest applied pressure. The samples were examined by nitrogen physisorption measurements using a Quadrasorb (Quantachrome) at 77 K after activation at 150 °C in vacuum over night. For determination of specific surface areas S_{BET} the BET method was applied in the relative pressure range p/p_0 from 0.05 to 0.3. The pore diameter $d_{\text{p,nitrogen}}$ was determined by BJH method using the desorption branch of the isotherm. The total pore volume $V_{\text{p,nitrogen}}$ was quantified for a relative pressure p/p_0 of 0.98. Digital images of the spherical shaped beads of PG10S and the corresponding DUT-88(10S) were recorded using an optical microscope. Powder X-ray diffraction (XRD) was performed with an X'Pert apparatus by PANalytical in Bragg–Brentano geometry and applying CuK₂₁ radiation ($\lambda = 0.15405 \text{ nm}$).

3. Results and discussion

3.1. Porous glass templates

The SEM pictures, as shown in Fig. 1, reveal the nanoporous character of the samples and the increasing pore size from PG10S over PG30 to PG60 and hence, the raise of pore diameter with annealing temperature $T_{\text{separation}}$. The porosities of the porous glass samples are about 50%. Furthermore, the continuous porosity as typical for porous glasses is visualized in the SEM pictures [12]. Mercury intrusion as well as nitrogen physisorption allowed deter-

Table 1
Mercury porosimetry and nitrogen physisorption results of the prepared porous glass samples.

Sample	$T_{\text{separation}}$ (°C) ^a	S_{BET} (m ² g ⁻¹) ^b	$d_{\text{P,Hg}}$ (nm) ^c	$d_{\text{p,nitrogen}}$ (nm) ^d	$V_{\text{P,Hg}}$ (cm ³ g ⁻¹) ^e	$V_{\text{p,nitrogen}}$ (cm ³ g ⁻¹) ^f
PG10S	550	110	10.8	11.7	0.39	0.38
PG30	570	57	27.5	32.7	0.48	0.46
PG60	625	22	55.0	–	0.41	0.04

^a Temperature for 24 h annealing procedure.

^b Specific surface area determined by multi-point BET method.

^c Pore diameter determined from mercury intrusion.

^d Pore diameter determined from nitrogen physisorption (77 K).

^e Pore volume determined from mercury intrusion for pores between 7 nm and 100 nm in diameter.

^f Pore volume determined from nitrogen physisorption (77 K).

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