Preparation of Silicon Carbide-based Nanoporous Materials by Replica Technique

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We tried to prepare silicon carbide-based nanoporous materials using the replica method. The polycarbosilane (PCS) as the SiC precursor filled the mesopores of mesoporous silica as the template, and then calcination and subsequent removal of the silica matrix led to the mesoporous product with a BET specific surface area of $780\,\mathrm{m^2\,g^{-1}}$. The product had the $\mathrm{SiC_{\approx 1.9}O_{\approx 0.9}}$ composition and very low crystallinity, indicating a good resistivity to oxidative conditions.

Nanoporous materials are very effective for the adsorption of molecules and ions as an adsorbent, deodorant, or decolorant. Nanoporous carbons, such as activated carbons, have been widely utilized for this purpose and have a long history. However, activated carbons cannot be utilized in the air atmosphere at high temperature or oxidative media because the carbon matrix is easily oxidized. Silicon carbide (SiC) is known to be chemically stable, and has been employed as a ceramic material composite for gas turbines.[1] This suggests that nanoporous materials based on SiC, which has a comparable specific surface area ($>1000\,\mathrm{m^2\,g^{-1}}$) to activated carbons, should be very promising as an adsorbent or catalysis-supporting matrix under strongly oxidative conditions. Activated carbon is generally prepared by the gasification reaction (i.e. activation) of carbon with steam or CO_2 above 800 °C in order to form many micropores,[2] but the gasification technique is difficult to apply to SiC material, because of its high chemical stability.

Recently, the replica method has received great attention as a new preparation technique for nanoporous carbons, which is carried out not by a gasification process, but by using template materials such as zeolite[3] or mesoporous silica.[4] The replica technique can be applied for preparation of SiC-based nanoporous materials. Thus, Krawiec and Kaskel succeeded in realizing SiC-based nanoporous materials with a $700\,\mathrm{m^2\,g^{-1}}$ surface area, which was prepared by the CVD process of trimethyl silane as the SiC precursor on mesoporous silica.[5] However, this CVD process is not necessarily a facile and efficient. We have tired to use polycarbosilane (PCS) as the SiC precursor for the replica method (Figure 1) since 2005.[6]

PCS is known as a good precursor polymer through pyrolysis for SiC-based fibers.[7] The replica process using PCS does not need any polymerization and vapor deposition in its nanopores. Thus, two other groups also reported the SiC-based nanoporous materials by the similar method using PCS and laboratory-made mesoporous silica to ours.[8]

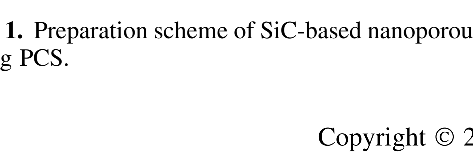

Figure 1. Preparation scheme of SiC-based nanoporous materials using PCS.

Here, we report SiC-based nanoporous materials using PCS and a commercially available mesoporous silica (Silfam-A, Nippon Chemical Inc., Japan) as the template. Silfam-A is a powder (average particle size is around 10 μm) having uniform cylindrical mesopores of 4 nm and BET specific surface area of around $1000\,\mathrm{m^2\,g^{-1}}$ (Mesopore volume: $1.1\,\mathrm{mL{\cdot}g^{-1}}$). This silica is thermally so stable as to maintain $800\,\mathrm{m^2\,g^{-1}}$ after 1000 °C heat treatment in N_2. PCS (type L, Nippon Carbon Co., Japan) was used as the SiC precursor, which has an 800 average molecular weight and 80 °C melting point. One gram Silfam-A was immersed in 30 mL of a tetrahydrofuran solution of PCS (20–50 wt %) under reduced pressure to allow the PCS to penetrate into the mesopores. The resulting suspension was filtered through a membrane filter with 5 μm pores in order to obtain the PCS-filled mesoporous silica. The calcination of the PCS-filled sample was carried out at 1000 °C for 1 h in a nitrogen atmosphere. Finally, the calcined product was washed with an HF solution (10 wt %) to remove the silica matrix and then rinsed with pure water. The final product was dried under vacuum at 200 °C. Only the PCS powder was heated in N_2 at 1000 °C for 1 h in the absence of the template to prepare the control sample.

The pore structure and the yield are summarized in Table 1. The BET specific area (S_{BET}) was obtained from the nitrogen adsorption isotherm at 77 K. The micropore volume (V_{micro}) or mesopore volume (V_{meso}) was calculated from the adsorption isotherms by the DH method or DR method, respectively. All products in Table 1 were meso/microporous materials from about 570 to $780\,\mathrm{m^2\,g^{-1}}$, which is much higher than the control one. A more concentrated THF solution produced a higher yield and higher BET specific surface area. For the 50 wt % solution,

Table 1. Preparation condition, BET specific surface area (S_{BET}), mesopore volume (V_{meso}), micropore volume (V_{micro}), and yield for the replica method product of PCS (RC series)

Sample name	Conc.[b] /wt %	S_{BET} /$\mathrm{m^2\,g^{-1}}$	V_{meso} /$\mathrm{mL{\cdot}g^{-1}}$	V_{micro} /$\mathrm{mL{\cdot}g^{-1}}$	Yield[c] /g
RC-20	20	570	0.43	0.28	0.17
RC-33	33	720	0.53	0.28	0.36
RC-43	43	760	0.56	0.31	0.43
RC-50	50	780	0.46	0.33	0.51
Control[a]	—	32	—	—	—

[a]Control: PCS calcination product at 1000 °C without the template. [b]Conc. means the concentration of PCS in the THF solution. [c]Yield is the amount of the product using the template of 1 g.

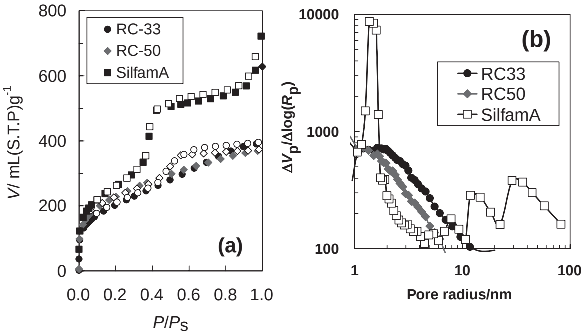

Figure 2. (a) Nitrogen adsorption/desorption isotherms and (b) pore size distribution curves in the mesopore region (DH method).

Table 2. Chemical composition characterized by EDS or XPS

Method	Sample	Si /atom %	C /atom %	O /atom %	F /atom %
EDS	RC-33	25	48	22	5
	Control	36	59	5	0
	β-SiC	49	49	2	—
XPS	RC-33	26	43	19	12
	Control	24	38	38	0

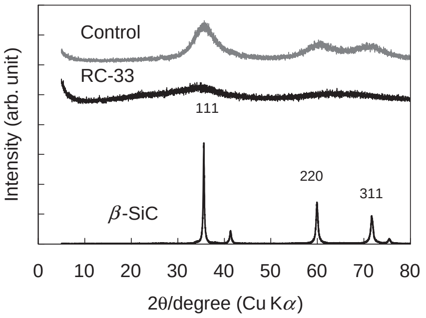

Figure 3. XRD profiles of RC-33, control sample, and β-SiC.

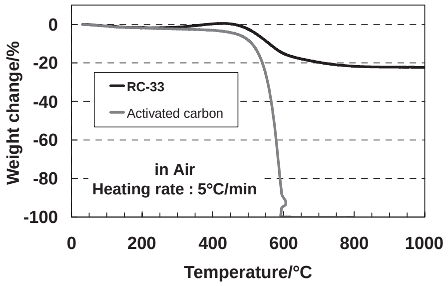

Figure 4. TG curve of RC-33 and activated carbon in air.

the highest yield and BET specific surface area were obtained. The maximum yield is expected to be ca. 0.5 g considering the mesopore volume (1.15 mL·g^{-1}) of Silfam-A, the density (1.1 g·cm^{-3}) of PCS, and the calcination yield of PCS at 1000 °C (ca. 40 wt %). This is in good agreement with the yield of RC-50. Therefore, it can be said that RC-50 was prepared under an ideal condition for PCS filling the pores of the template. Concentrated solutions of greater than 50 wt % were too viscous to remove the excess solution by the filtration.

The adsorption/desorption isotherms and pore size distribution curves are shown in Figure 2. The template shows a very sharp peak around 2 nm, but RC-33 and RC-50 had wide distributions. The highly uniform pore structure of Silfma-A was not present in the product. This might be due to the collapse of the mesopores during the calcination process or the removal step of the silica template. The absence of an ordered mesopore structure was also confirmed by small angle X-ray diffraction and transmission electron microscopy.

The chemical composition was characterized by energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). Based on the EDS results, β-SiC as the silicon carbide standard sample has the stoichiometry of Si:C = 1:1, while RC-33 is revealed to be a silicon oxycarbide, such as $SiC_{\approx 1.9}O_{\approx 0.9}$ which is almost in agreement with the XPS results. The carbon-rich nonstoichiometry is usually observed for the calcined PCS product.[9] The larger amount of elemental oxygen in RC-33 might originate from oxidation reactions of the product inside with air through the meso/micropores. XPS also detected the high fluorine content in RC33. This suggests a surface reaction with HF to form insoluble fluoride.

The X-ray diffraction (XRD) patterns (Figure 3) showed that RC-33 has a very low crystalline β-SiC matrix. It is a surprising result that the crystallinity of RC-33 was even lower when compared to the control sample. This suggests that the crystallite growth of he SiC component might be restricted by nanopores.

The thermal oxidation stability was evaluated by thermal gravimetry (TG). Figure 4 shows the TG curve in air for RC-33 and activated carbon (phenolic resin-based, S_{BET} : 2000 m^2 g^{-1}). The activated carbons burned out around 600 °C, while RC-33 showed only around a 20% loss at 1000 °C. A slight weight increase was observed around 400–500 °C for RC-33. This might be due to the surface oxidation. RC-33 also showed a higher stability in nitric acid compared with the activated carbons. RC-33 preserved ca. 75 wt % of its weight and its porosity (S_{BET} : ca. 900 m^2 g^{-1}) after a 14 mol·dm^{-3} HNO_3 immersion at 160 °C for 6 h, however, the activated carbons dissolved due to the oxidation reaction. Thus, the SiC-based nanoporous products made by the replica method can be considered as a stable adsorbent against oxidation.

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References

1 R. Naslain, *Compos. Sci. Technol.* **2004**, *64*, 155.
2 H. Marsh, F. Rodriguez-Reinoso, *Activated Carbon*, Elsevier, Amsterdam, **2006**, Chap. 5, p. 243.
3 Z. Ma, T. Kyotani, A. Tomita, *Chem. Commun.* **2000**, 2365.
4 R. Ryoo, S. H. Joo, S. Jun, *J. Phys. Chem. B* **1999**, *103*, 7743; J. Lee, S. Yoon, T. Hyeon, S. M. Oh, K. B. Kim, *Chem. Commun.* **1999**, 2177.
5 P. Krawiec, S. Kaskel, *J. Solid State Chem.* **2006**, *179*, 2281.
6 A. Oya, S. Shiraishi, Jpn. Kokai Tokkyo Koho JP2006327857, **2006**.
7 S. Yajima, K. Okamura, J. Hayashi, M. Omori, *J. Am. Ceram. Soc.* **1976**, *59*, 324; A. R. Bunsell, in *Fiber Fracture*, ed. by M. Elices, J. Llorca, Elsevier, Oxford, **2002**, p. 75.
8 P. Krawiec, D. Geiger, S. Kaskel, *Chem. Commun.* **2006**, 2469; Y. Shi, Y. Meng, D. Chen, S. Cheng, P. Chen, H. Yang, Y. Wan, D. Zhao, *Adv. Funct. Mater.* **2006**, *16*, 561.
9 M. Takeda, J. Sakamoto, Y. Imai, H. Ichikawa, *Compos. Sci. Technol.* **1999**, *59*, 813.

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