

Preparation of Mesoporous SiCBN Ceramic Templated by Mesoporous Carbon

Quoc Dat Nghiem, Hyang Im Ryoo, and Dong-Pyo Kim[†]

School of Applied Chemistry and Biological Engineering, Chungnam National University, Daejeon 305-764, Korea

(Received July 6, 2007; Accepted July 18, 2007)

ABSTRACT

Well-ordered mesoporous SiCBN ceramics have been successfully synthesized by infiltrating a polymeric precursor, which was prepared from borazine and 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane via a hydroboration reaction, into a mesoporous carbon (CMK-3) as a hard template. This was followed by pyrolysis at 1400°C under nitrogen gas and subsequent oxidative removal of the carbon template without chemical etching. The prepared mesoporous SiCBN ceramic was characterized by a small-angle XRD, TEM, and BET surface area. The resulting mesoporous SiCBN ceramic revealed a BET surface area of 275 m²g⁻¹ and a pore volume of 0.8 cm³g with no crystallization.

Key words: Mesoporous ceramic, SiCBN ceramic, High temperature stability, CMK-3

1. Introduction

Mesoporous materials have attracted considerable attention in recent years due to their high specific surface area and narrow pore size distribution, which is very important in applications such as adsorbent large molecules and catalytic supports.¹⁾ Nanocasting into hard templates to replicate nanoscale structures has been widely used over the past two decades to synthesize various mesostructured materials.²⁾ Recently, a new series of ordered mesoporous carbons has been obtained using mesoporous silica materials as templates. This type of material with a high surface area and uniform pores promises to be suitable as adsorbents, catalyst supports, and materials for advanced electronics applications. The mesoporous carbon material (CMK-3), obtained from SBA-15 mesoporous silica, is a precise inverse replica retaining the structural symmetry of the silica template.^{3,4)} It is interesting to investigate the possibility of using mesoporous carbon as a template for mesoporous inorganic materials due to its well-ordered mesostructures and rigidity.⁴⁾

SiCBN ceramic materials have several interesting chemical and physical properties such as a high mechanical strength, oxidation resistance,^{5,6)} and an excellent thermal stability up to 2000°C without loss of mass and/or crystallization,^{7,8)} which makes them suitable for various applications such as catalyst supports,^{9,10)} high temperature semiconducting devices, and metal or polymer matrix compos-

ites.¹¹⁾ However, to date, there have been no reports regarding the synthesis of mesoporous SiCBN ceramics. It is anticipated that mesoporous SiCBN products will show excellent physical and chemical properties as demonstrated at the bulk SiCBN phase, which is promising for various applications in extreme conditions.

In this study, we report on the synthesis of well-ordered mesoporous SiCBN ceramics using poly (borosilazane) as a SiCBN ceramic precursor and mesoporous CMK-3 as a hard template. This method can avoid oxygen contamination in the production of mesoporous SiCBN ceramics because there is no oxygen composition in the carbon template. Moreover, this work is the first attempt to prepare ordered mesoporous SiCBN ceramics, which possess an identical mesostructure to that of mesoporous silica SBA-15.

2. Experimental

2.1. Synthesis of Mesoporous SiCBN Ceramics

All reactions were performed in a purified argon atmosphere using standard Schlenk techniques.¹²⁾ All glassware used were stored in a drying oven for several hours at 120°C prior to use. Tetrahydrofuran was dried using a sodium-benzophenone mixture under reflux. Borazine (B₃N₃H₆), a monomeric precursor for hydroboration, was synthesized as reported in our previous paper.¹³⁾ 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane was obtained from Fluka (Germany) and used without further purification. The mesoporous CMK-3 was synthesized following the procedures described elsewhere³⁾ and dried overnight at 120 °C in a vacuum prior to use.

Borazine (3 ml; 2.043 g, 26.25 mmol) was carefully dropp-

[†]Corresponding author: Dong-Pyo Kim
E-mail: dpkim@cnu.ac.kr
Tel : +82-42-821-6695 Fax : +82-42-823-6665

ed into a pre-cooled mixture of 2.5 ml (2.23 g, 8.75 mmol) 2,4,6-trimethyl-2,4,6-trivinylcyclosilazane dissolved in 5 ml tetrahydrofuran and 1 g of CMK-3 at ca. 0°C. The temperature of the mixture was kept below 5°C for 5 h and then gradually warmed to room temperature and maintained for 30 h. After curing at 70°C for 5 h, the tetrahydrofuran solvent was removed in a vacuum (0.023 Torr) at room temperature. Subsequently, the sample was pyrolyzed in nitrogen in temperatures up to 1400°C at a heating rate of 1°C/min; then it was maintained for 2 h and this resulted in a SiCBN/carbon composite. In order to remove the carbon template, the SiCBN composite was treated in air at 650°C for 2 h. The obtained template-free mesoporous SiCBN was designated as m-SiCBN.

2.2. Characterizations

Small-angle X-ray diffraction patterns were recorded on an MXLabo powder diffractometer equipped with CuK α radiation (40 kV, 20 mA) at the rate of 1.0 deg/min over the range of 0.2–6.0 (2 θ). High-resolution transmission electron microscope (HRTEM) images were taken at 200 kV (JEM 2100F, JEOL, Japan). The BET surface area and nitrogen adsorption-desorption isotherms were measured at 77 K using an ASAP2010 analyzer (Micromeritics, Japan) after evacuating at 473 K for 5 h. The pore size distribution was calculated using the BJH method. The evolution of the chemical structures was simultaneously investigated using a ^{29}Si NMR spectra performed using an FT Wide Bore (600 MHz) Unity NOVA 600 under cross polarization magic angle spinning (CP-MAS) conditions.

3. Results and Discussion

A well-ordered mesoporous SiCBN ceramic was synthesized by nanocasting poly (borosilazane) as a SiCBN precursor into mesoporous carbon, CMK-3, and then pyrolysis at 1400°C in an N $_2$ atmosphere. After the complete removal of the carbon template, the formation of mesoporous SiCBN ceramic was investigated using a small-angle X-ray diffraction (SA-XRD), and the result is shown in Fig. 1. In the SA-XRD pattern of m-SiCBN (Fig. 1(b)), a diffraction peak at 1.20° and a minor peak at 1.98° can be observed, corresponding to a d spacing of 7.3 nm. Also, the unit cell parameter a_0 can be calculated as 8.4 nm, on the base of $d_{100}=7.3$ nm and $a_0=2d_{100}/3^{1/2}$, which is 1.3 nm smaller than that of the CMK-3 carbon template (9.7 nm) due to structural shrinkage during the pyrolysis process.

High resolution TEM images of the carbon template and the mesoporous SiCBN ceramic product are shown in Fig. 2. The TEM image of m-SiCBN (Fig. 2(b)) reveals that the structure of m-SiCBN consists of a well-ordered hexagonal arrangement of cylindrical channels, which is similar to the structure of mesoporous silica SBA-15. Thus, it can be confirmed that, through the negative replication of the CMK-3

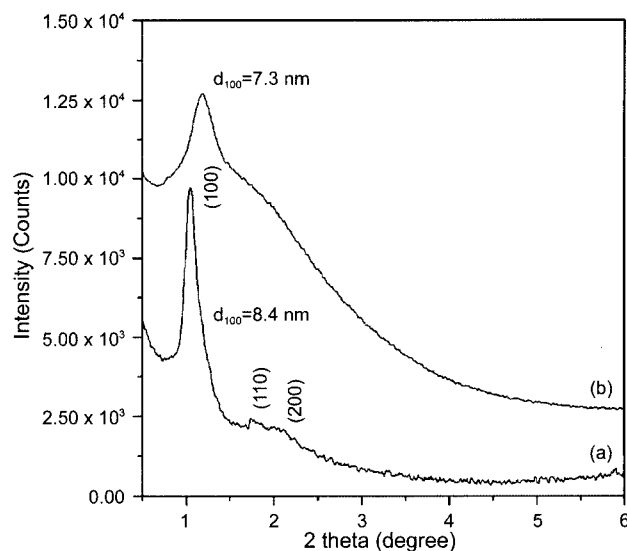


Fig. 1. Small-angle X-ray diffraction patterns of (a) the CMK-3 template and (b) mesoporous SiCBN ceramic after pyrolyzed at 1400°C in an N $_2$ atmosphere.

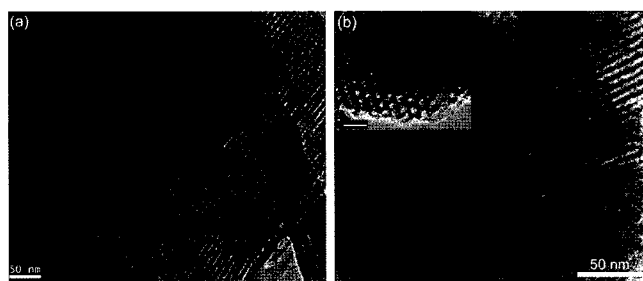


Fig. 2. TEM images of (a) CMK-3 and (b) the mesoporous SiCBN ceramic pyrolyzed at 1400°C.

template, the geometry of the initial silica template has been retained and the (100) reflection peak is observed in the SA-XRD pattern. Furthermore, the TEM image of m-SiCBN (Fig. 2(b)) shows that the m-SiCBN channel centers are separated by a distance of approximately 8 nm, which is in good agreement with the SA-XRD results.

The pore characteristics of m-SiCBN were investigated using the BET method, and N $_2$ adsorption-desorption isotherms and a BJH pore size distribution at 77 K were found, as shown in Fig. 3. These results are similar to that of the carbon template with an H $_2$ hysteresis loop at a relative pressure of approximately 0.6, which indicates that the sample possesses a mesostructure.¹⁴ Usually, the H $_2$ -type hysteresis loop is attributed to the presence of cage-like structures associated with effects such as large pores connected by smaller openings.¹⁵ The narrow pore size distribution centered at 5.6 nm indicates that the m-SiCBN material has uniform mesopore dimensions. The difference between the distance connecting two neighboring mesopores ($a_0=8.1$ nm) and their diameter (5.6 nm) corresponds to the m-SiCBN material's wall thickness of 4.1 nm, which is in good agreement with the pore size of the CMK-3 template. Moreover, the m-SiCBN material exhibits a BET sur-

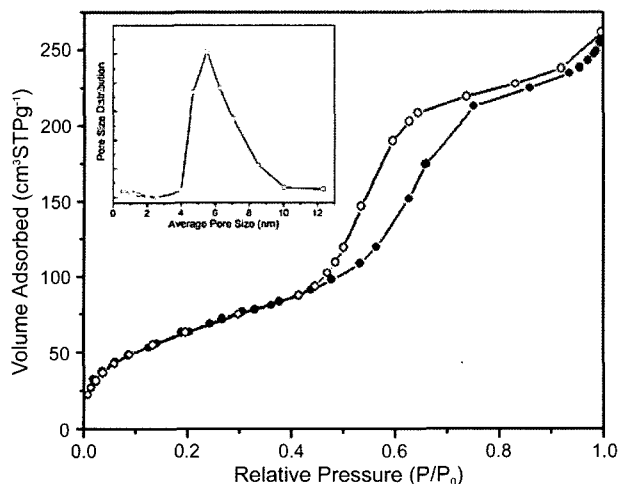


Fig. 3. N_2 adsorption (●) – desorption (○) isotherm and pore size distribution (inset) of the mesoporous SiCBN ceramic.

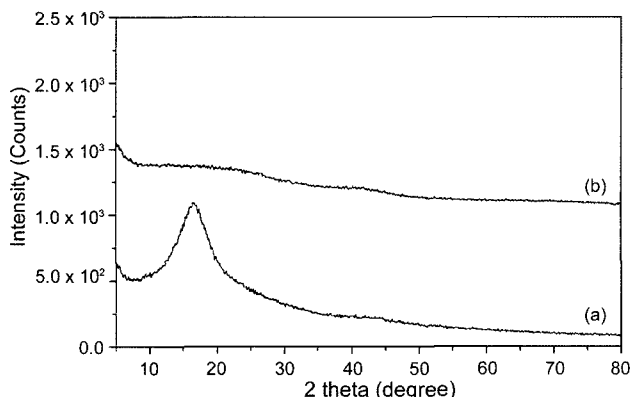


Fig. 4. Wide angle X-ray diffraction patterns of (a) the CMK-3 template and (b) the mesoporous SiCBN ceramic after pyrolyzed at 1400°C in an N_2 atmosphere.

face area of $275\text{ m}^2\text{g}^{-1}$ and a pore volume of $0.8\text{ cm}^3\text{g}^{-1}$.

In order to investigate the crystallization behavior, the mesoporous SiCBN ceramic was analyzed using a wide angle X-ray diffraction, as shown in Fig. 4. The pyrolyzed sample at 1400°C was fully amorphous, which demonstrates an unusual crystallization-resistance, and the mesoporous carbon was completely burned out. This is comparable with the bulk SiCBN ceramics that retain their amorphous phase up to 1600°C , as previously reported.⁵⁾ It is speculated that the presence of an atomic boron might retard the diffusion of other atoms and hinder the formation of a crystalline phase.^{7,8)} In addition, it is interesting that boron in the cyclic borazine might play a similar role to stabilize the amorphous state at high temperatures. Finally, the ^{29}Si CP-MAS NMR spectrum of the mesoporous SiCBN represents a superposition of the NMR line due to the three main structural components, namely $\text{SiC}_x\text{N}_{4-x}$ units with $x=0, 1$ or 2 . This indicates the heterogeneity of the local environment around the Si atoms in the amorphous material, regardless of the distribution of bond lengths and angles.

4. Conclusions

In summary, a well-ordered mesoporous SiC material with a high specific surface area of $275\text{ m}^2\text{g}^{-1}$ and a narrow pore size distribution centered at 5.6 nm has been prepared using CMK-3 carbon as a nanoporous template and poly (borosilazane) as a SiCBN precursor. The SA-XRD and TEM analysis clearly show that, as a replica of the CMK-3 carbon, the achieved SiCBN product processes ordered a hexagonal mesostructure as in the structure of SBA-15 silica. The well-ordered mesoporous SiCBN ceramic shows the same excellent physical and chemical properties as demonstrated in the bulk SiCBN phase, which is promising for various applications in extreme conditions.

Acknowledgements

This work was funded by the Center for Ultramicrochemical Process Systems (CUPS). We thank Korea Basic Science Institute (KBSI) for performing the TEM and NMR analysis and Korea Advanced Institute Science and Technology (KAIST) for the XRD measurements.

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