Pore-size control in the sol–gel synthesis of mesoporous silicon carbide

XIANG-YUN GUO*, GUO-QIANG JIN
State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Taiyuan 030001, China
E-mail: xyguo@sxicc.ac.cn

Chemical reactions operating at high temperatures and extreme conditions usually require catalyst and separation materials possessing good thermal and chemical stability [1]. Silicon carbide materials are potential candidates for such applications due to their excellent thermal and chemical stability [2, 3]. As a prospective catalyst support, it should have a high specific surface area and suitable pore structure [4]; however, SiC materials currently lack these qualities. Because the materials are often produced at very high temperatures usually above 1000 °C, it is very difficult to control SiC crystal growth to form porous structures. Despite these limitations, many researchers are devoted to developing novel routes for the synthesis of porous SiC materials with high surface areas [5–8].

In reported works, Ledoux and coworkers developed a shape-memory synthesis method to prepare porous SiC [4, 5, 9]. In the method, porous carbon was employed as a starting template, and gaseous silicon monoxide was flowed through the starting carbon. The porous SiC was produced by the reaction of SiO and the carbon template. In another method, Vix-Guterl *et al.* employed porous SiO_2 as a starting template and then infiltrated carbon into the porous template [6, 10]. The porous SiC was produced via the carbothermal reduction of SiO_2. The two methods above are effective for the preparation of porous SiC, but both of them require two steps to obtain the desired product. Other routes are also employed for the preparation of porous SiC [11–13]; however, the surface area and pore size cannot be directly controlled in these methods.

The sol–gel process is a promising technique for fabricating and tailoring nanostructured materials [14, 15]. The technique has been used to prepare nanostructured SiC materials [16–18]. In our previous works, a carbonaceous silica sol–gel from tetraethoxysilane (TEOS) and phenolic resin was used to synthesize SiC nanowires and mesoporous SiC [17, 18]. In this letter, we propose a method to control the specific surface area and pore size of mesoporous SiC by employing different amounts of nickel nitrate in the sol–gel process.

A typical sol–gel process for synthesis of the mesoporous SiC is described as follows. Twelve grams of phenolic resin (condensation polymer from formaldehyde and phenol, softening point 80–90 °C) and 0.8 g nickel were dissolved in 35 ml ethanol. Subsequently, 50 ml TEOS (AR grade) and 8 ml oxalic acid aqueous solution (3.4% wt.%) were added to the ethanol solution. 0.8 ml hexamethylenetetramine aqueous solution (35 wt.%) was added to enhance gelation after the mixture had been stirred at room temperature for 48 hr. Finally, the gel was aged and dried at 100 °C for 24 hr to get a xerogel. The SiC product was produced by heating the xerogel at 1250 °C for 20 hr in an argon environment (flow rate 40 cm^3 min^{-1}).

From the above process, a light green SiC sample was obtained after removal of residual carbon, silica, and other impurities. The sample is β-SiC according to X-ray powder diffraction (XRD). A Micromeritics ASAP-2000 porosimeter, using N_2 as adsorptive, was employed to measure the surface area and pore size of the sample, as shown in Fig. 1. From the figure the N_2 adsorption-desorption isotherms exhibit two abrupt changes when the relative pressure is about 0.4 and 0.8, respectively. The changes suggest that the sample has two kinds of pores. The pore size distribution from the BJH method confirms that one has a size about 3.5 nm and the other about 15 nm [19]. Both pore sizes fall into the defined size range of mesopores, from 2 to 50 nm.

The nickel employed in the sol–gel preparation plays an important role in the SiC synthesis. As previously reported [16, 17], the usual product from the above sol–gel process was SiC whiskers when no nickel is employed. However, a small quantity of nickel nitrate changes the morphology of SiC product. Furthermore, the specific surface area and pore size of the SiC product can be controlled by adjusting the Ni/Si molar ratio in the xerogel. In the typical synthesis, the Ni/Si ratio is 0.0123 and the SiC sample is specified as SiC-[Ni]-0.0123, where the square brackets indicate that nickel had been employed and the number represents the molar ratio. A series of SiC samples were synthesized through the sol–gel route by employing different concentrations of nickel, and their surface areas and pore sizes are summarized in Table I. From Table I, the surface area increases with increasing Ni/Si ratio, and approaches a maximum of 204 m^2/g when the ratio is 0.0123. Above this ratio, the specific surface area begins to decrease. The pore size and volume also display similar dependence on the Ni/Si ratio.

By scanning electron microscope (SEM) and transmission electron microscope (TEM) observations, the sample without nickel is completely whiskery and the second one consists of whiskery and porous SiC. Samples 3, 4 and 5 mostly are mesoporous SiC, and they have continuously increased pore diameters. The TEM images of samples 3 and 4 are shown in Fig. 2. Sample 6 is composed of porous and granular SiC, and the last

---

[*] Author to whom all correspondence should be addressed.

0022–2461

TABLE I Pore parameters of silicon carbide samples. The pore size here is the location of the main peaks in the BJH pore distribution

	BET surface area/m^2 g^{-1}	Pore size (nm)	Pore volume (cm^3 g^{-1})
1. SiC-[Ni]-0	48	45	0.108
2. SiC-[Ni]-0.0077	47	45 (4)	0.134
3. SiC-[Ni]-0.0123	204	3.5 (15)	0.343
4. SiC-[Ni]-0.0154	112	10	0.286
5. SiC-[Ni]-0.0185	64	30	0.175
6. SiC-[Ni]-0.0308	42	40	0.144
7. SiC-[Ni]-0.154	5	>100	0.01

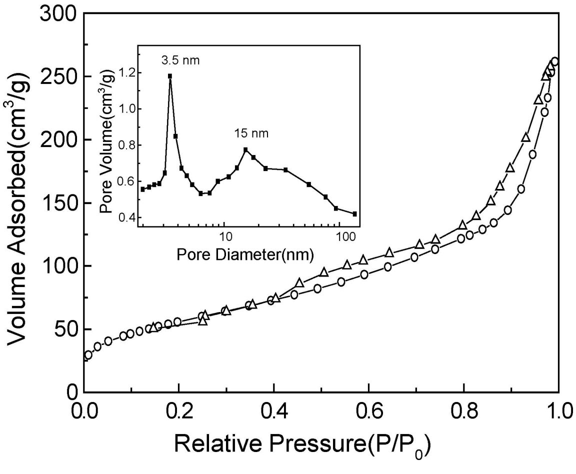

Figure 1 Nitrogen adsorption-desorption isotherms of the purified SiC sample (SiC-[Ni]-0.0123). The inset picture displays the corresponding pore-size distribution from the BJH method.

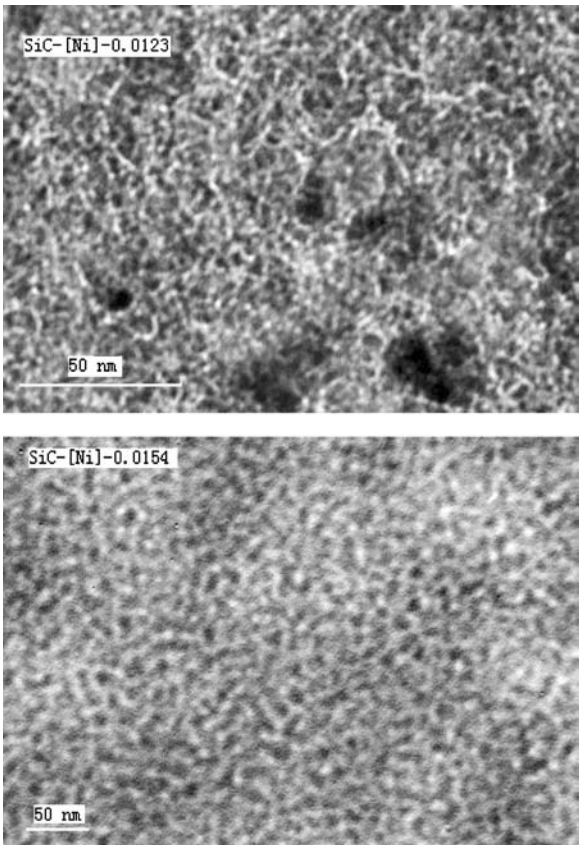

Figure 2 TEM images of two mesoporous SiC samples. The top displays two kinds of pores and the bottom shows a uniform pore structure.

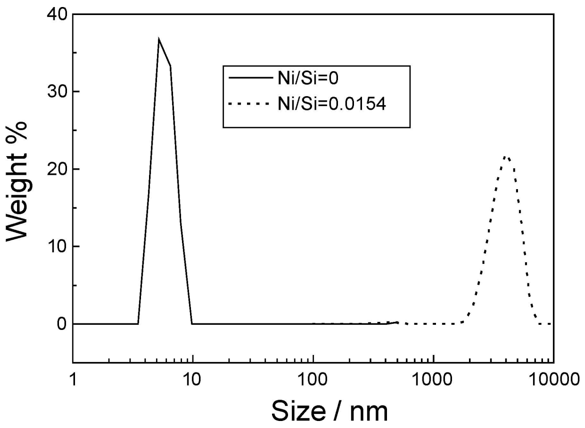

Figure 3 The granularity analysis (Coulter N4 Plus) results of two sols with and without nickel.

one mainly consists of SiC grains with sizes ranging from 50 to 200 nm.

The role of nickel in the preparation is rather complicated. At first, charged nickel ions in the sol–gel process may result in the self-organization of primary colloidal particles. The self-organization usually generates large secondary grains consisting of phenolic resin and embeded silica particles. The granularity analysis results show that the primary colloidal particles have sizes smaller than 10 nm while the secondary grains have sizes larger than 1000 nm, as shown in Fig. 3. The secondary grains can produce a great deal of SiO_2/C interfaces after carbonization. The SiC produced at the interfaces through carbothermal reduction forms a mesoporous framework. On the other hand, nickel may still act as a catalyst in the SiC formation as reported in literature [5, 7]. Melted nickel particles react with silica and produce various nickel silicide active phases including Ni_2Si,

$$SiO_2 + 2Ni + 2C \rightarrow Ni_2Si + 2CO \qquad (1)$$

Subsequently the melted alloy drops roll on interfaces and react with carbon,

$$Ni_2Si + C \rightarrow SiC + 2Ni \qquad (2)$$

The nickel generated from reaction (2) again participates in reaction (1). Several nickel silicide active phases can be detected from XRD patterns of unpurified SiC rough products. However superfluous nickel can cause sintering of the mesoporous SiC, which usually results in collapse of the porous framework. Simultaneously, largened alloy drops can dissolve more SiC. The dissolved SiC can be recrystallized out and form spherical particles when the system temperature decreases [20, 21]. These lead to the very low surface area of sample 7.

In conclusion, we present here a method to control the surface area and pore size of mesoporous SiC in the sol–gel preparation. The key of the method is to aggregate the primary colloidal particles with suitable size though employing different amount of nickel nitrate.

Acknowledgment

The work was supported by a "Hundred Talents" project from Chinese Academy of Sciences.

References

1. M. A. VANNICE, Y. L. CHAO and R. M. FRIEDMAN, *Appl. Catal.* **20** (1986) 91.
2. R. MOENE, P. A. M. TIJSEN, M. MAKKEE and J. A. MOULIJN, *Appl. Catal. A: General* **184** (1999) 127.
3. C. MÉTHIVIER, B. BÉGUIN, M. BRUN, J. MASSARDIER and J. BERTOLINI, *J. Catal.* **173** (1998) 374.
4. N. KELLER, C. PHAM-HUU, M. J. LEDOUX and C. EHRET, *Appl. Catal. A: General* **187** (1999) 255.
5. M. J. LEDOUX, S. HANTZER, C. PHAM-HUU, J. GUILLE and M. P. DESANEAUX, *J. Catal.* **114** (1988) 176.
6. C. VIX-GUTERL, B. MCENANEY and P. EHRBURGER, *J. Eur. Ceram. Soc.* **19** (1999) 427.
7. R. MOENE, M. MAKKEE and J. A. MOULIJN, *Appl. Catal. A: General* **167** (1998) 321.
8. R. J. LEDNOR and R. DE RUITER, in "Inorganic and Metal-Containing Polymeric Materials," edited by J. E. Sheets, C. E. Carraher, C. U. Pittman, M. Zeldin and B. Currel (Plenum, New York, 1990) p. 187.
9. J. M. NHUT, R. VIEIRA, L. PESANT, J. P. TESSONNNIER, N. KELLER, G. EHRET, C. PHAM-HUU and M. J. LEDOUX, *Catal. Today* **76** (2002) 11.
10. J. PARMENTIER, J. PATARIN, J. DENTZER and C. VIX-GUTERL, *Ceram. Int.* **28**, (2002) 1.
11. G. Z. SHEN, D. CHEN, K. B. TANG, Y. T. QIAN and S. Y. ZHANG, *Chem. Phys. Lett.* **375** (2003) 177.
12. T. L. RITTENHOUSE, P. W. BOHN and I. ADESIDA, *Solid State Comm.* **126** (2003) 245.
13. Q. LIU, H. J. WU, R. LEWIS, G. E. MACIEL and L. V. INTERRANTE, *Chem. Mater.* **11** (1999) 2038.
14. A. IMHOF and D. J. DINE, *Nature* **389** (1997) 948.
15. M. KLOTZ, A. AYRAL, C. GUIZARD and L. COT, *Bull. Korean Chem. Soc.* **22** (1999) 879.
16. X. K. LI, L. LIU, Y. X. ZHANG, S. D. SHEN, S. GE and L. C. LING, *Carbon* **39** (2001) 159.
17. G.-Q. JIN, P. LIANG and X.-Y. GUO, *J. Mater. Sci. Lett.* **22** (2003) 767.
18. G.-Q. JIN and X.-Y. GUO, *Microporous Mesoporous Mater.* **60** (2003) 207.
19. E. P. BARRET, G. JOYNER and P. P. HALENDA, *J. Amer. Chem. Soc.* **73** (1951) 373.
20. L. STOBIERSKI and A. GUBERNAT, *Ceram. Int.* **29** (2003) 355.
21. D. N. YOON and W. J. HUPPMANN, *Acta Metall.* **27** (1979) 973.

Received 6 January
and accepted 20 July 2004