CHAPTER 4

TEMPLATE SYNTHESIS OF THREE DIMENSIONAL CUBIC MESOPOROUS SiC WITH TUNABLE PORE SIZE

4.1 INTRODUCTION

The mesoporous materials known at present are usually composed of silica or aluminum silicate (Cicesla et al 1999). Owing to their lack of mechanical strength and thermal stability, these materials have not yet found applications in catalysis or other fields where rigorous conditions have to be used (Chang et al 1978). Therefore, it is necessary to develop routes for the synthesis of new mesoporous materials. Silicon carbide is a kind of covalent material with a tetrahedral structural unit similar to diamond. It has long been known for its many superior properties, such as excellent thermostability, high mechanical strength, excellent resistance to oxidation and corrosion, low coefficient of thermal expansion and high heat conductivity. These properties enable the use of silicon carbide as a catalyst support at rigorous conditions (Bao et al 2000, Okada et al 1994). Therefore, SiC has been used in many important fields. Several reports were published showing that this material effectively competes with conventional supports, such as alumina, silica or activated carbons, especially in exothermic reactions where heat conductivity of the support plays a crucial role (Phamhuu et al 1995, Kizling et al 1992, Cuong et al 1994). However, commercially available silicon carbide has a low specific surface area (< 25 m$^2$/g) and is not suitable as a catalyst support. Thus, new methods were developed for the preparation of the high surface
area materials. For example, Moene et al (1999) produced SiC of surface areas ranging from 20 to 80 m$^2$/g by reacting activated carbon with terachlorosilane and hydrogen in the presence of Ni. Puneet et al (2004) studied the formation of high surface area SiC using hydrolysis of phenyltrimethoxysilane precursors resulting in gel formation, followed by pyrolysis of the gel at 1500 ºC under vacuum. SiC with medium and high surface area in the range of 20-100 m$^2$/g was prepared in different size and shapes according to the shape memory synthesis developed by Ledoux and co-workers (1988). Jin et al (2003) prepared mesoporous SiC of surface areas 112 m$^2$/g by the sol-gel method using tetraethoxysilane (TEOS) as the silicon source and phenolic resin as the carbon source for preparing a binary carbonaceous silicon xerogel, and nickel nitrate was employed in the sol-gel process as a pore-adjusting reagent. Shi et al (2006) prepared SiC of surface area in the range of 430-720 m$^2$/g by mesoporous silica hard templates and commercial PCS precursors via a nanocasting process. In addition, there are many studies on the preparation of different kinds of SiC materials, such as nanoparticles, whiskers and nanowires (Wang et al 1994, Meng et al 1999, Hu et al 2000). In the present work the influence of nanocasting synthesis conditions for SiC/KIT-6 nano-composites on porosity and structure of porous high surface area SiC are discussed.

4.2 EXPERIMENTAL SECTION

4.2.1 Synthesis of KIT-6 Silica

The synthesis of mesoporous KIT-6 silica with cubic Ia3d symmetry was performed according to the literature procedure reported by Kim et al 2005 and a different process was followed for the removal of the structure directing block co-polymer. Typically, 4 g of Pluronic P123 was dissolved in 144 g of distilled water and 7.9 g of HCl solution (36 wt%) under vigorous stirring at 35 ºC. After complete dissolution, 4 g of n-butanol (99.4 wt%) was
added. Following further stirring for 1 h, 8.6 g of TEOS was added immediately. Subsequently the mixture was left stirring at 35 °C for 24 h and transferred into an autoclave, which was sealed and maintained at different hydrothermal temperatures such as 100, 130 and 150 °C for another 24 h under static conditions. The resulting solid product was filtered and dried at 100 °C overnight. After a brief ethanol wash, the final sample was dried at 100 °C.

4.2.2 Synthesis of SiC using Carbon-Silica Composite

Ordered mesoporous SiC materials were synthesized using the recipe described previously (Ryoo et al 1999, Lee et al 2008). Uncalcined KIT-6 and sucrose were used as the template and carbon precursor, respectively. In a typical synthesis of carbon-silica composite, 0.62 g of sucrose (95 wt%) and 0.0672 g of sulfuric acid (98 wt%) were dissolved in 3.5 g of distilled water. After 1 g of uncalcined KIT-6 silica was added, the mixture was heated at 100 °C for 6 h, and subsequently at 160 °C for another 6 h. The resulted composite was impregnated again with an aqueous solution consisting of 0.45 g of sucrose, 0.05 g of sulfuric acid and 3.5 g of distilled water. After the heat treatment at 100 °C and 160 °C, the composite was polymerized at 1300 °C for 5 h under Argon flow. Finally, the SiC materials were obtained by the removal of the silica template using 5 wt% HF solutions at room temperature and prepared samples were labeled as K-SiC-X where X denotes the synthesis temperature of the template.

4.2.3 Synthesis of SiC using PCS/Silica Composite

First, 0.5 and 1 g of PCS was dissolved separately in 5g of xylene then 1 g of mesoporous silica KIT-6 was mixed well. After the organic solvent xylene was evaporated, the products were dried in an oven at 100 °C overnight. The acquired PCS/silica composite was first heated at a rate of
5 °C/min to 300 °C under argon flow and then the temperature was maintained for 5 h. Further, heating process upto 700 °C was carried out at a rate of 2 °C/min for the cross linking and pyrolyzing of PCS. Lastly, the temperature was raised to the final value for crystallization at a heating rate of 5 °C/min and the temperature was kept for 5 h. The resulting SiC-silica composite was washed with 40 wt% aqueous hydrofluoric acid several times to remove the silica template. The same procedure has been done for the silica templates prepared at 130 and 150 °C. The samples were described as K-SiC-X-Y where X denotes the synthesis temperature of the template and Y denotes the amount of PCS added in 5 g of xylene.

4.3 RESULT AND DISCUSSION

4.3.1 Powder X-Ray Diffraction

Figure 4.1 illustrates the low angle X-ray diffraction (XRD) patterns of the sample KIT-6 with tailored pore sizes. The KIT-6 silica exhibits highly ordered 3D cubic Ia3d symmetry. Moreover, the high intensity peak of all KIT-6 samples only varied slightly towards lower angle side when the hydrothermal temperature of the silica host was increased from 100 to 150 °C. Low-angle XRD patterns of K-SiC samples are presented in Figure 4.2A. These K-SiC products with different pore sizes also exhibit cubic structure, which is similar to that of the KIT-6 silica template. But the sample prepared from 130 and 150 °C silica shows disorder mesostructure. The reason for the disordered structure of these samples was the lack of connectivity between the mesopores of silica template and subsequent collapse of the structure, after removal of silica.
Figure 4.1 Low angle XRD patterns of mesoporous silica KIT-6
Figure 4.2 (A) Low angle XRD patterns of the products obtained from mesoporous C/Si composites (B) Wide angle XRD patterns of the K-SiC samples
The wide angle XRD patterns of the resulting K-SiC samples are shown in Figure 4.2B. These materials show a broad peak between $2\theta = 10$-$30^\circ$ after the treatment at 1300 °C, indicating a certain amount of amorphous silica and carbon might have remained. However, the XRD reflections with high intensity in the $2\theta$ range from 30 to 80 ° are quite obvious, proving the formation of SiC. Reflection with strong intensity can be predominantly assigned to the $\beta$-phase of SiC. The small peak marked ‘S’ corresponds to the super lattice structure of stacking fault (Gogotsi et al 1996).

The low-angle XRD patterns of the samples K-SiC prepared from different amount of PCS are showing in Figure 4.3A. The XRD patterns of K-SiC samples prepared from PCS show significant difference as compared to the sample prepared from sucrose. Lower amount of PCS precursor (0.5 g) introduced into the pores of silica had higher relative intensity peak as compare to the higher amount of PCS (1g) used for SiC preparation. The lower diffraction peaks could be due to complete pore filling of the KIT-6 template by the SiC phase. Figure 4.3B shows the wide-angle XRD patterns of the K-SiC samples prepared from different quantity of PCS. The major peaks and their intensities at $2\theta$ values of 35.6°, 60.4°, and 71.5° correspond to carborundum ($\beta$-SiC) (PDF No. 75-0254). FWHM are wide for the SiC sample, indicating the smaller crystallite size. The presence of amorphous carbon is detected by the broad background in the XRD pattern for almost all the samples. However, the degree of silicon carbide crystallization in each sample was dependent on the silica template that was used for the preparation. Mesoporous silicon carbides prepared from templates hydrothermally treated at lower temperature (smaller pore diameter) was less crystalline. On the other hand, large pores of the high-temperature-treated silica allowed better crystallization. The same type of XRD pattern was obtained for the silicon
carbides prepared from high quantity of PCS precursor. But the sample prepared from lower amount of PCS results in good crystalline phase.

Figure 4.3(A) Low angle XRD patterns of K-SiC samples prepared from different amount of PCS
Figure 4.3(B) Wide angle XRD patterns of the K-SiC samples prepared from different quantity of PCS.
4.3.2 **Nitrogen physisorption.**

$N_2$ adsorption-desorption isotherms and the corresponding pore size distributions determined from the adsorption branches for K-SiC prepared from sucrose are shown in Figure 4.4. All samples represent type IV isotherms with a capillary condensation step, which is indicative of a uniformity of mesopore size. The measured surface area was in the range between 349.3 and 375.3 m$^2$/g and depends strongly on the properties of hard silica template and sucrose which was used for synthesis. The samples prepared from high-temperature-treated silica template (130 and 150 °C) are not having much difference in the surface area. This shows that the amount of sucrose used was not able to react properly with the mesopore system of the silica template. This is in good agreement with the previously discussed low angle X-ray diffraction data, which showed very poor mesostructured ordering of this sample. K-SiC samples prepared from low-temperature-treated KIT-6 have small pore diameter, in the mesopore range (2.94 nm) (Figure 4.4B). On the other hand, samples prepared from large pore templates (hydrothermally treated at higher temperature) show similar pore diameter (2.95 nm) (Figure 4.4B). The textural parameters of K-SiC samples are summarized in Table 4.1. Figure 4.5A and 4.5B shows the nitrogen physisorption isotherms and BJH pore size distribution of K-SiC materials prepared with PCS, respectively. According to the nitrogen physisorption measurement at 77 K, K-SiC materials prepared from different quantity of PCS have high specific surface areas in the range between 170.7 and 663.5 m$^2$/g (Table 4.1) which are higher than the K-SiC samples prepared from sucrose using the same silica template. The lowest specific surface area of 170.7 m$^2$/g was obtained for K-SiC-100-1.0. Furthermore, the pore size distributions were similar to that of the K-SiC prepared from sucrose with the same template. Also no secondary large mesoporous were observed.
Figure 4.4 Nitrogen adsorption-desorption isotherms and corresponding pore size distribution of K-SiC samples prepared from sucrose.
Figure 4.5(A) Nitrogen adsorption-desorption isotherms of K-SiC samples prepared from PCS precursor.
Figure 4.5(B) Pore size distribution of K-SiC samples prepared from PCS precursor
In our opinion, the pores are blocked with high amount of PCS precursor, seems more reasonable because X-ray diffraction patterns clearly indicate that very less structure formation. Moreover, the specific surface area is significantly higher for the sample prepared from low amount of PCS precursor.

Table 4.1 Textural properties of mesoporous SiC products prepared from different carbon precursors.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Carbon source</th>
<th>BET surface area (m²/g)</th>
<th>Pore Size (nm)</th>
<th>Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-SiC-100</td>
<td>Sucrose</td>
<td>349.3</td>
<td>2.94</td>
<td>0.327</td>
</tr>
<tr>
<td>K-SiC-130</td>
<td>Sucrose</td>
<td>365.6</td>
<td>3.02</td>
<td>0.512</td>
</tr>
<tr>
<td>K-SiC-150</td>
<td>Sucrose</td>
<td>375.3</td>
<td>2.95</td>
<td>0.632</td>
</tr>
<tr>
<td>K-SiC-100-0.5</td>
<td>PCS</td>
<td>368.4</td>
<td>3.75</td>
<td>0.348</td>
</tr>
<tr>
<td>K-SiC-130-0.5</td>
<td>PCS</td>
<td>623.6</td>
<td>2.93</td>
<td>0.511</td>
</tr>
<tr>
<td>K-SiC-150-0.5</td>
<td>PCS</td>
<td>663.5</td>
<td>3.34</td>
<td>0.707</td>
</tr>
<tr>
<td>K-SiC-100-1.0</td>
<td>PCS</td>
<td>170.7</td>
<td>2.90</td>
<td>0.140</td>
</tr>
<tr>
<td>K-SiC-130-1.0</td>
<td>PCS</td>
<td>296.1</td>
<td>3.32</td>
<td>0.344</td>
</tr>
<tr>
<td>K-SiC-150-1.0</td>
<td>PCS</td>
<td>590.0</td>
<td>3.06</td>
<td>0.712</td>
</tr>
</tbody>
</table>

Where 100, 130 and 150 represents the hydrothermal temperature of used silica host. 0.5 and 1 represents the amount of PCS used for sample preparation.
4.3.3 Scanning electron microscopy

Figure 4.6 presents the SEM micrographs of K-SiC samples prepared from sucrose. It can be seen that the appearances of K-SiC is very alike to the mesoporous carbon derivates, i.e., sample K-SiC-100 has foam-shaped appearance. Therefore, these K-SiC products prepared from sucrose show good retention of morphology of the original silica materials. Besides, the SEM images also show that the surfaces of these samples have porous structure. Liu et al (2005) studied that some minor difference between mesoporous carbon and mesoporous SiC. Firstly, the single particle size of SiC is larger than that of the carbon, and the intergranular texture of SiC materials seems looser than that of carbon. In addition, the SiC materials are less ordered than the carbon.

![Figure 4.6 SEM image of K-SiC-100 product prepared from sucrose](image)

Figure 4.6 SEM image of K-SiC-100 product prepared from sucrose

Figure 4.7 shows the SEM images of the achieved porous SiC with special morphology prepared from KIT-6 mesoporous silica template with PCS precursor. It is seen that all the samples mainly consist of irregular particles. The smooth surface of the silica/PCS composite was transformed
into a rough surface which is typical morphology for crystallized SiC. However, a careful look at the images reveals some minor difference between them, which is because of hydrothermal temperature of host silica and the amount used for SiC sample preparation. When we used low amount of PCS, the size of SiC sample is small and the intergranular texture of SiC materials seems looser. In addition, the SiC materials prepared from high amount of PCS is showing less order in the mesostructure. It is consistent with low-angle XRD analysis, showing less intensity diffraction peak (shown in Figure. 4.2) indicating the disordered pore structures of these SiC materials.

4.3.4 Transmission electron microscopy

TEM can serve as a unique technique for the studies of mesoporous materials, revealing the morphologies of particles and the local structures in a nanometer resolution. We obtained some extraordinary TEM images for mesoporous SiC prepared from KIT-6 with sucrose as well as PCS precursor (Figure 4.8). Almost all SiC samples are showing cubic mesoporous structure, it confirm that SiC replica was prepared using mesoporous silica KIT-6 as the template has a well ordered cubic Ia3d mesostructure. The samples prepared from 100 ºC silica with a low PCS content have maintained the integrity of the mesoporous structures are well compare to high PCS content after heat treatment at 1300 ºC for 5 h. The Selected-Area Electron Diffraction (SAED) pattern of all SiC samples displays three diffraction rings assigned to the 111, 220 and 311 planes, providing further evidence that the mesostructure is composed of β-SiC crystallites with random orientation.
Figure 4.7 SEM images of SiC products prepared with different amount of PCS (A) K-SiC-100-0.5 (B) K-SiC-150-0.5 (C) K-SiC-100-1.0 (D) K-SiC-150-1.0

Figure 4.8 TEM images of SiC products (A) K-SiC-100 prepared from sucrose (B) K-SiC-100-0.5 (C) K-SiC-100-1
4.3.5  Thermal Analysis

To find appropriate conditions for the heat treatment, TG analysis of K-SiC-150 was first carried out from room temperature to 1000 ºC at a ramp of 5 ºC/min under air flow. The TGA cure (Figure 4.9) shows four steps of weight change. The first minimum weight loss occurs below 330 ºC, corresponding to desorption and removal of water or other adsorbents. The second step is a weight increase of < 1% ranging from 330 to 525 ºC, owing to the oxidation of the SiC surface. The following large weight loss (10.5%) between 525 and 660 ºC is attributed to the combustion of amorphous carbons, including carbon template and the excess carbon from pyrolysis by products of sucrose. Finally, a fourth weight increases above 660 ºC is related to the further oxidation of the SiC frameworks. The residue weight is about 88.9%.

![Figure 4.9  TGA curve of a representative SiC material K-SiC-150](image-url)
Figure 4.10 TGA curve of the SiC products obtained from PCS precursor
(a) K-SiC-100-0.5 (b) K-SiC-100-1.0
Thermogravimetric analysis was carried out for the samples prepared from PCS precursor to study the weight loss/gain with an increase in temperature (Figure 4.10). It is observed from the TGA curve that there is almost no drastic gain or loss of weight in SiC sample at a temperature range of 25 to 1000 °C. Almost the same type of curve is obtained for both the samples (K-SiC-100-0.5 and K-SiC-100-1.0). This confirms that the purity of the SiC material prepared with PCS precursor is very high compared to the sample prepared with sucrose. The residue weight of the sample is about 99% for both the cases. But the percentage of oxidation is much higher in the case of K-SiC-100-0.5.

4.3.8 Composition analysis of K-SiC materials.

The Fourier Transform Infrared spectra (Figure 4.11 and 4.12) show that the silica matrix can be removed by HF etching without destroying the mesostructure of SiC replicas.

![Figure 4.11 FTIR spectrum of K-SiC-100 materials](image-url)
Figure 4.12 FTIR spectrum of representative mesoporous SiC
(a) K-SiC-100-0.5 and (b) K-SiC-100-1.0
The obtained FTIR spectra with one peak at 840-860 cm\(^{-1}\) resulting from Si-C bonds vibration for all samples, as well as smaller contribution of Si-O bonds in between 1120 and 1240 cm\(^{-1}\) (Merlemejean et al 1995). The relative intensity on Si-O peak was little high for K-SiC-100. On the other hand lowest Si-O peak intensity was observed for the crystalline K-SiC-100 -0.5 and K-SiC-100-1 samples, implying that a minor amount of silica remains after the carbothermal reduction reaction. For these samples TG measurements showed a small weight gain due to the surface oxidation of SiC into SiO\(_2\). Although for partial oxidation is expected, passivation with silica protects the SiC particles from partial oxidation and process kinetics becomes significantly slower. In case of K-SiC-100, a weight loss of 11.2% was observed due to the burning of the excess free carbon. Some additional bands are observed from the FTIR spectra for all samples. These new bands are ascribed to stretching and bending vibration of SiO\(_2\) species, which could be generated from the oxidation of SiC.

![Energy dispersive X-ray spectra of mesoporous K-SiC samples prepared from sucrose](image)

Figure 4.13 Energy dispersive X-ray spectra of mesoporous K-SiC samples prepared from sucrose
The elemental analysis showed the carbon content for SiC sample prepared from sucrose in the range of 55-60 wt%, which is higher than the theoretical value of 30 wt% for pure SiC, because percentage of oxygen is very low (8-10 wt%) (Krawiec and Kaskel 2006). The elemental analysis for the SiC products prepared from PCS precursor showed that the carbon content is less compared to the sample prepared from sucrose, but it is higher than the theoretical value. But these samples are having high oxygen content, TG measurements also showed weight gain due to the surface oxidation of SiC into SiO$_2$. EDX spectroscopy (Figure 4.13 and 4.14) reveals that all SiC products contain only silicon, carbon, and oxygen (Table 4.2). This is not surprising because, as reported previously, SiC ceramics derived from the pyrolysis of PCS and sucrose always contain excess carbon (Cao et al 2002).

**Table 4.2** Chemical composition of mesoporous SiC prepared from KIT-6 characterized by energy-dispersive X-ray (EDX) spectrum

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Carbon (wt%)</th>
<th>Silica (wt%)</th>
<th>Oxygen (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-SiC-100</td>
<td>60.91</td>
<td>30.31</td>
<td>8.77</td>
</tr>
<tr>
<td>K-SiC-150</td>
<td>55.18</td>
<td>34.21</td>
<td>10.61</td>
</tr>
<tr>
<td>K-SiC-100-0.5</td>
<td>41.82</td>
<td>29.70</td>
<td>28.48</td>
</tr>
<tr>
<td>K-SiC-150-0.5</td>
<td>45.01</td>
<td>31.52</td>
<td>23.46</td>
</tr>
<tr>
<td>K-SiC-100-1.0</td>
<td>37.28</td>
<td>36.25</td>
<td>26.47</td>
</tr>
<tr>
<td>K-SiC-150-1.0</td>
<td>37.56</td>
<td>34.52</td>
<td>27.61</td>
</tr>
</tbody>
</table>
Figure 4.14 EDX spectrum of mesoporous K-SiC material prepared from different amount of PCS precursor.
4.4 CONCLUSION

We have shown how different precursors and loadings of different carbon/KIT-6 nano-composites influence the textural properties of mesoporous silicon carbide prepared from them. High amount of PCS loadings cause deposition outside of KIT-6 channels and these SiC materials has low surface area and mesoporous volume. On the other hand, composites with lowest loading produce SiC materials with a high mesoporous volume but a broad pore size distribution and high surface area of 663 m$^2$/g. The crystalline $\beta$-SiC materials with good surface area and mesoporosity were successfully prepared by carbothermal reduction reaction, which involved a reaction between sucrose and mesoporous silica KIT-6. This SiC have maintained the crystallinity, but lost the mesoporous ordering. The properties of good surface area, mesoporosity and crystallinity may be closely related to low-temperature carbothermal reaction process. The elemental analysis and thermogravimetric analysis indicates the formation of silicon oxycarbide on the surface of SiC samples. The amount of free carbon deposited was examined using thermogravimetric measurements in air, and was found that the residual carbon was very less for the samples prepared from PCS precursor. Finally we have concluded that highly ordered mesoporous SiC with high specific surface areas, large pore volumes and different pore diameter have been successfully prepared using low amount of PCS as a precursor and mesoporous silica KIT-6 as hard templates.