CHAPTER 3

PREPARATION OF HIGHLY ORDERED MESOPOROUS SiC and SiOC USING POLYCARBOSILANE (PCS)

3.1 INTRODUCTION

The preparation of various porous and non-porous materials with controlled morphology and defined properties is actively studied in the modern material science. Non-oxide and oxide ceramics, such as silicon carbide (SiC), silicon nitrides, silicon (oxy) carbide (SiOC), and boron nitrides have been investigated intensively in various research areas because of their unique mechanical and functional characteristics (Klemm et al 2003, Watari et al 2001, Dibandjo et al 2005). Among these, the non-oxide and oxide ceramics that have found commercial applications like Silicon carbide and silicon (oxy) carbide are the most widely used materials. The attractive properties of SiC, such as its high tensile strength, and youngs modulus at elevated temperatures, stiffness, relatively low weight, good corrosion and erosion resistance, and chemical inertness make it an effective catalyst supports for many reactions under drastic conditions. The demand for high surface area and uniform porosity in this application makes the preparation of mesoporous ceramics as an attractive challenge (Krawiec et al 2004, Nicolas et al 2005). Therefore, many efforts have been devoted to prepare porous silicon carbide with high surface area and there have been a very few reports on fabricating ordered mesoporous ceramic structures with high surface area. Methods used to produce SiC powders can be classified into two
categories (1) carbothermal reduction of silica and (2) pyrolysis and crystallization of preceramic precursors, such as polysilazene, polysilane, polycarbosilane (PCS), and polymethylsilane. The parameters of the polymeric precursor, such as chemical composition and network architecture, associated with the residual porosity of the resulting ceramic phase, usually affect the crystallization behavior of amorphous ceramic matrix (Krawiec et al 2008). In addition, increase in the number of elemental constituents in the ceramic matrix contributes to improve thermal stability against crystallization (Shi et al 2006). Polycarbosilane is now recognized as one of the important precursors in the commercial production of SiC materials. Recently, highly ordered mesoporous SiC materials with tunable pore sizes and high surface areas were synthesized by impregnating polycarboxysilane (PCS) inside the channels of mesoporous silicates, pyrolysising the samples, and then removing the hard templates of silicates (Shi et al 2006 and Yant et al 2006). This nanocasting strategy has proved to provide a general approach to the fabrication of mesoporous materials with diverse components. Herein we report for the first time on the preparation of highly ordered mesoporous SiC using uncalcined mesoporous silica template with monodispersed rectangular shaped rod like particles with uniform length and width as template and PCS as the carbon precursor. We also demonstrate here for the first time that the pore size mesoporous SiC can be controlled by simply changing the synthesis temperature of the mesoporous silica template.

3.2 MATERIAL SYNTHESIS

Mesoporous silica SBA-15 was prepared according to the procedures reported previously (Vinu et al 2003, Sayari et al 2004), the conventional stir mode of synthesis as well as static mode of synthesis was used and a different process was followed for the removal of the structure directing block co-polymer. Detailed procedure has been given in Chapter 2.
The samples were aged at the usual hydrothermal temperatures (100, 130 and 150 ºC). Uncalcined SBA-15 was stirred with ethanol for removing part of triblock copolymer P123. The white solid precipitates were recovered by filtration and these samples were used for the preparation of mesoporous SiC. In a typical synthesis procedure, 1g of uncalcined SBA-15 was infiltrated with the appropriate amount of polycarboxysilane precursor (PCS precursor with molecular weight 800 was procured from Aldrich). At first, different quantity of PCS was dissolved separately in 5 g of xylene. 1g of mesoporous silica template (SBA-15) was added to the prepared solution (for static mode SBA-15, three different quantities of PCS (0.5, 1 and 1.5 g) was used and for stir mode SBA-15, two different quantities of PCS (0.5 and 1 g) were used). After the evaporation of xylene at the room temperature, the products were dried at 100 ºC for 6 h in a hot-air oven. The PCS infiltrated SBA-15 was placed in an alumina boat which was kept inside the tubular furnace under an argon atmosphere with a flow rate of 200 ml/min and was then subjected to heat treatment according to the following temperature program: Room temperature (RT) to 300 ºC at a rate of 5 ºC/min, and then the temperature was maintained for 5 h. A further heating process to 700 ºC was carried out at a rate of 2 ºC/min for the cross linking and pyrolyzing of PCS. After reaching 700 ºC, the sample was heated to 1300 ºC for crystallization at 5 ºC/min and the temperature was maintained for 5 h. The chamber was then cooled down to room temperature under an argon atmosphere. The resulting SiC/Silica composite sample was treated with a 40 wt% aqueous solution of HF, shaken for 10-15 min to remove excess silica. The solution was then filtered and washed with an ethanol and dried at 100 ºC for 6 h. A set of samples was prepared by adding different amount of PCS in xylene in uncalcined SBA-15 prepared at different temperature and the samples were labeled as 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. In the same manner, samples prepared from stir mode SBA-15 were labeled as S-SiC-X-Y.
3.3 RESULTS AND DISCUSSION

Mesoporous Silicon carbide samples were prepared using uncalcined SBA-15 templates (Table 3.1). Advantage of the preparation method has been explained in Chapter 2. In both the cases three different SBA-15 templates, hydrothermally treated at 100, 130, and 150 ºC were used and impregnation process of PCS infiltration into the mesopore system were employed. Such choice of hydrothermal treatment temperature gives corresponding silica materials with different pore sizes. The impregnation process is the method to introduce PCS into mesoporous silica, where SBA-15 sample is added to a solution of PCS in xylene, and the solvent was evaporated. All materials were prepared using the same heating program with the temperature reaching up to 1300 ºC.

3.3.1 Low and High angle XRD

Figure 3.1, 3.2 and 3.3 shows the low angle as well as high angle X-ray diffraction (XRD) patterns of mesoporous silicon carbide prepared from static mode SBA-15 and Figure 3.4 and 3.5 shows the low and wide angle XRD patterns of mesoporous SiC sample prepared from stir mode SBA-15. The samples show an intense peak at lower angle which reveals the mesoporous nature of the samples. However, a significant difference in the intensity and the shape of the peak is observed for the samples prepared at different amount of PCS. The intensity of the peak is increased with decreasing the amount of PCS loading in the synthesis mixture. The sample SiC-100-0.5 displayed a sharp peak together with a broad 110 reflection when the PCS loading of 0.5 g was used in the synthesis mixture, revealing the presence of highly ordered 2-D hexagonal mesoporous structure. On the other hand, only a broad peak was observed for the sample SiC-100-1.5, which was prepared using the PCS amount of 1.5 g, due to the agglomeration of the PCS on the external surface of the sample during the infiltration process.
Similar results trend was also obtained even when we used the templates prepared at different temperature. These data reveal that the amount of PCS play a critical role in controlling the mesoporous structure of the samples. It was previously reported by Shi et al. (2006) that high amount of PCS, 1.32 g per 1 g of the template is necessary to obtain the SiC materials with well ordered mesoporous structure.

However, in this case, well ordered mesoporous SiC can be obtained even with a PCS amount of 0.5 g. This is mainly due to the fact that the pore volume of the uncalcined template is very small as the pores are partially occupied by the surfactant molecules. When a small amount of PCS is added in the uncalcined sample, PCS molecules can freely go and occupy the empty pore space, and are sandwiched between the surfactant molecule and the silica wall of the nanocomposite before thermal treatment at high temperature. In addition, the carbon atoms from the surfactant molecule, which are struck in the confined matrix, can take part in the reaction and ease the reaction between the silica and the carbon. These factors are responsible for the formation of well ordered structure when a small amount of PCS was used.

It should be noted that this process will not only save the time and the amount of carbon sources but also, at the end, can offer the well ordered mesoporous SiC with well ordered pore structure. On the other hand, when high amount of PCS is added in the template, serious agglomeration of the PCS on the external surface of the template may be expected. In addition, the small pore volume of the uncalcined sample does not permit to take huge amount of the PCS in the pore channels, resulting in a decrease in the structural order. From these results, one can come to the conclusion that PCS amount of 0.5 g is enough for the formation of the well ordered mesoporous SiC from the uncalcined sample. S-SiC samples also showing excellent thermal stability in inert atmosphere. The obtained XRD pattern of S-SiC samples were related to the SiC samples prepared from static mode SBA-15.
The wide angle XRD patterns indicate that the samples were all crystalline $\beta$-SiC. All the samples show three diffraction peaks at higher angle that can be indexed as 111, 220, and 311 planes, in agreement with the carborundum ($\beta$-SiC), according to the standard (JCPDS card number 29-1129), confirming the formation of highly crystalline SiC. It should be noted that the intensity of the higher angle peaks varies significantly with the amount of the addition of the PCS in the synthesis mixture. Sample prepared with a low amount of PCS shows a high intense peaks whereas peaks with less intensity is observed for the sample prepared with a high amount of PCS. As explained before, the addition of the large quantity of the PCS in the porous structure favors the agglomeration of the PCS on the external surface which, we believe, may hinder the reaction between the silica template and the carbon source, resulting the SiC sample with less crystallinity. Since the same reaction condition including the constant reaction temperature of 1300 °C and the reaction time of 5 h was used for the preparation of all the samples, one can conclude that the amount of PCS addition in the synthesis mixture plays a significant role in controlling the crystallinity of the final product. It is interesting to note that the full width half maxima of all the samples is quite wide, revealing the smaller crystallite size of the SiC matrix which are indeed formed as the walls of the mesoporous materials. In all the samples, a broad low intensity peak centered at 2θ value of 21° is observed. This may be attributed to either the molecularly disordered starting product or amorphous carbon which may come from the unreacted PCS or the surfactant molecules. As the intensity of the peak is very less, it can be assumed that only a little amount of impurity is present in all the samples after the high temperature and the HF treatment.
Figure 3.1 Low and Wide angle XRD patterns of mesoporous SiC samples derived from static mode silica template treated hydrothermally at 100 °C
Figure 3.2 Low and Wide angle XRD patterns of mesoporous SiC samples derived from static mode silica template treated hydrothermally at 130 °C
Figure 3.3 Low and Wide angle XRD patterns of mesoporous SiC samples derived from static mode silica template treated hydrothermally at 150 °C
Figure 3.4 Low and Wide angle XRD patterns of S-SiC-0.5g with different hydrothermal temperature of silica template
Figure 3.5 Low and Wide angle XRD patterns of S-SiC-1g with different hydrothermal temperature of silica template
3.3.2 Nitrogen Physisorption Measurements

Figure 3.6, 3.7 and 3.8 shows the N$_2$ adsorption - desorption isotherms plots for the nitrogen sorption (at 77 K) and pore size distribution of the SiC samples synthesized from static mode SBA-15. Figure 3.9 and 3.10 shows the nitrogen adsorption-desorption isotherms and corresponding pore size distributions of the samples S-SiC and data of the surface area and pore volume are listed in Table 3.1. All ordered SiC materials showed characteristic type IV nitrogen adsorption isotherms with a distinct capillary condense and hysteresis loop indicate that the SiC materials prepared by this method have a good mesoporous nature. However, the capillary condensation step in the isotherms of the samples SiC-100-1.0 and SiC-100-1.5 is neither sharp nor clear, indicating the disordered mesoporous nature in the samples. This is mainly due to the limited pore volume space of the uncalcined mesoporous silica template which results in the agglomeration of the PCS on the external surface when high amount of PCS is used. This result is quite consistent with the data obtained from the low angle XRD pattern for the same samples. On the other hand, the capillary condensation step in the isotherms of SiC-150-1.0 and SiC-150-1.5 is sharp, revealing the uniform pore size in these samples and the importance of using the template with the large pore diameter. It should also be noted that the amount of nitrogen adsorbed at lower relative pressure which gives the quantity of the specific surface area, is significantly higher for the samples prepared using the template SBA-15-150 than that for the samples prepared by using SBA-15-100 as template. However, the specific surface area and the specific pore volume of the sample decrease with increasing the addition of PCS in the synthesis mixture, irrespective of pore diameter of the templates used. Among the samples prepared, SiC-150-0.5 showed the highest specific surface area and specific pore volume. The measured specific surface area and the specific pore volume of the samples were in the range between 285.2 and 564.4 m$^2$/g, and
0.236 and 0.732 cm$^3$/g respectively. These results reveal that low amount of PCS and the template prepared at the reaction temperature of 150 °C is the best condition to obtain the well ordered mesoporous SiC with excellent textural characteristics.

One of the most important findings in the work is the fine control of the pore diameter of the mesoporous SiC which has been never reported in the literature. With an increase in the synthesis temperature of the template from 100 to 150 °C, the capillary condensation step shifts to higher relative pressure, indicating a rise in the pore size of the final product. The pore diameter increases from 3.0 nm for SiC-100-0.5 to 4.4 nm for SiC-150-0.5. However, a huge reduction in the pore diameter of the sample is observed when the amount of PCS addition in the synthesis mixture is increased from 0.5 to 1.5. The pore diameter of SiC-150-0.5 is 4.4 nm which is decreased to 2.95 nm for SiC-150-1.5. This huge reduction could be related with the collapse of the mesostructure in the sample prepared using high amount of PCS. These data suggest that not only the specific surface area and the specific pore volume but also the pore size of the final product is significantly influenced by the amount of addition of PCS in the synthesis mixture and the synthesis temperature of the template. The interesting point is that, with a low amount of PCS in the starting mixture, a highly ordered mesoporous SiC can be prepared with a high surface area and a large pore volume. Nitrogen sorption isotherms of S-SiC ceramics also showed typical type-IV curves, indicative of uniform mesopores. The BET surface area, pore size, and total pore volume were mainly in the range of (490.8-564.4 m$^2$/g), (2.93-4.40 nm), and (0.43-0.66 cm$^3$/g), respectively. It must be noted that there is no much difference in the surface areas and pore size values for both the case of SiC samples.
Table 3.1  Textural properties of mesoporous SiC products prepared under different conditions

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC-100-0.5</td>
<td>438.2</td>
<td>0.5894</td>
<td>3.00</td>
</tr>
<tr>
<td>SiC-100-1.0</td>
<td>309.0</td>
<td>0.2631</td>
<td>3.09</td>
</tr>
<tr>
<td>SiC-100-1.5</td>
<td>285.2</td>
<td>0.2359</td>
<td>2.99</td>
</tr>
<tr>
<td>S-SiC-100-0.5</td>
<td>524.6</td>
<td>0.5029</td>
<td>2.93</td>
</tr>
<tr>
<td>S-SiC-100-1.0</td>
<td>490.8</td>
<td>0.4640</td>
<td>2.94</td>
</tr>
<tr>
<td>SiC-130-0.5</td>
<td>552.6</td>
<td>0.4930</td>
<td>2.92</td>
</tr>
<tr>
<td>SiC-130-1.0</td>
<td>509.2</td>
<td>0.3157</td>
<td>2.93</td>
</tr>
<tr>
<td>SiC-130-1.5</td>
<td>407.7</td>
<td>0.4116</td>
<td>2.93</td>
</tr>
<tr>
<td>S-SiC-130-0.5</td>
<td>555.5</td>
<td>0.4335</td>
<td>2.93</td>
</tr>
<tr>
<td>S-SiC-130-1.0</td>
<td>502.3</td>
<td>0.5312</td>
<td>2.94</td>
</tr>
<tr>
<td>SiC-150-0.5</td>
<td>564.4</td>
<td>0.7324</td>
<td>4.40</td>
</tr>
<tr>
<td>SiC-150-1.0</td>
<td>529.9</td>
<td>0.5926</td>
<td>4.30</td>
</tr>
<tr>
<td>SiC-150-1.5</td>
<td>421.5</td>
<td>0.3732</td>
<td>2.95</td>
</tr>
<tr>
<td>S-SiC-150-0.5</td>
<td>564.4</td>
<td>0.6628</td>
<td>4.40</td>
</tr>
<tr>
<td>S-SiC-150-1.0</td>
<td>529.4</td>
<td>0.6619</td>
<td>4.51</td>
</tr>
</tbody>
</table>
Figure 3.6 Nitrogen sorption isotherms and pore size distribution of mesoporous SiC ceramics derived from static SBA-15-100
Figure 3.7  Nitrogen - sorption isotherms and pore size distribution of mesoporous SiC ceramics derived from static SBA-15-130
Figure 3.8  Nitrogen - sorption isotherms and pore size distribution of mesoporous SiC ceramics derived from static SBA-15-150
Figure 3.9  Nitrogen adsorption - desorption isotherms and pore size distribution of S-SiC samples prepared from stir mode SBA-15 with different hydrothermal temperature and 0.5g PCS
Figure 3.10  Nitrogen adsorption - desorption isotherms and pore size distribution of S-SiC samples prepared from stir mode SBA-15 with different hydrothermal temperature and 1g PCS
3.3.3 Scanning electron microscopy

It is quite interesting to see the morphology of the final mesoporous SiC prepared from the different template with the addition of different quantity of PCS in the synthesis mixture. As explained in the introduction, the template used for the preparation of mesoporous SiC exhibits well ordered morphology with the uniform sized nanorods and a rectangular shape. Figure 3.11 shows the HRSEM images of mesoporous SiC samples prepared using SBA-15-100 and SBA-15-150. As can be seen in Figure 3.11, well-ordered morphology with uniform size rectangular shaped nanorods, similar to the morphology of the parent template, is observed for all the samples. However, small agglomerated particles are seen on the external surface of the mesoporous SiC prepared with a high amount of PCS. Interestingly, similar agglomerated particles are not seen on the surface of the mesoporous SiC prepared from SBA-15-150 using high amount of PCS. These results support our claim that the template with a small pore diameter (SBA-15-100) favors the agglomeration of the particles when high amount of PCS is used.

A linear array of mesopores with a regular interval along the particle can also be seen in the HRSEM images for SiC-100-0.5 and SiC-150-0.5. Normally it is very difficult to observe the mesoporosity and the pore structural order of the samples by HRSEM. As our instrument has the ability to observe the samples in nanoscale, we were lucky enough to see the mesoporosity in the SiC-100-0.5 and SiC-150-0.5. Another interesting observation in the HRSEM images of samples prepared from the SBA-15-S-100 and SBA-15-S-150 is the difference in the size of the particles. As can be seen in the HRSEM images, the particle size of the SiC-100-X is much smaller than that of the SiC-150-X. It is quite clear from these images that the variation of the amount of PCS addition in the synthesis mixture does not alter the particle size at all. We assume that the synthesis temperature of
the template controls the particle size of the template which is directly transferred into the final mesoporous SiC. These results reveal that the textural parameters, morphology including the size of the particles and the mesostructural order can be controlled by choosing the appropriate mesoporous silica template prepared at different temperature.

Figure 3.11 SEM images of ordered mesoporous SiC products
(A) SiC-100-0.5  (B) SiC-100-1.0  (C) SiC-100-1.5
(D) SiC-150-0.5  (E) SiC-150-1  (F) SiC-150-1.5

Figure 3.12 shows the SEM images of S-SiC samples. It can be seen that the appearance of S-SiC sample size are not uniform. These S-SiC products show undesirable morphology and also show that the surface of these samples all has porous structure. However, a careful look at the images reveals some difference between them. Firstly, the single particle size of S-SiC-150-1.0 is larger than that of the S-SiC-150-0.5 and the intergranular texture of S-SiC materials seems looser than that of parent silica. In addition, the S-SiC materials are less ordered than the SiC samples prepared from static
mode SBA-15. For example, Figure 3.11 shows that SiC sample has ordered and parallel pore structure, but no clearly ordered structures can be identified for S-SiC samples (Figure 3.12).

![SEM images of representative S-SiC materials](image)

**Figure 3.12** SEM images of representative S-SiC materials  
(A) S-SiC-100-0.5 (B) S-SiC-100-1 (C) S-SiC-150-0.5 (D) S-SiC-150-1

### 3.3.4 Transmission electron microscopy

The mesostructural order of the prepared mesoporous SiC was also observed by the high resolution transmission electron microscope. Figure 3.13 shows the representative high and low resolution TEM images of SiC-100-0.5, SiC-100-1.0, SiC-150-0.5 and SiC-150-1.5 samples. As can be seen from the HRTEM images, a rod like morphology of the template is retained in all the samples. The HRTEM images of the SiC-100-0.5 and SiC-150-0.5 samples also clearly show the well-ordered linear arrays of
mesopores which are arranged in a regular interval, revealing the presence of mesoporosity in all the samples. However, when we look at the same samples with a high resolution, disordered mesoporous structure is observed in some part of the samples SiC-150-1.0 and SiC-100-1.0, which is quite consistent with the data and the conclusion derived from the XRD and porosity measurements for the same samples. It is also confirmed by the HRTEM images that the length of the rod like particles with a rectangular shape of SiC-150-0.5 is longer than that of SiC-100-0.5 which is again supported with the data obtained from HRSEM measurements. The selected-area electron diffraction (SAED) patterns of mesoporous SiC, which is placed in the corner of the HRTEM image, display three diffraction rings assigned to the 111, 220, and 311 planes, which is an indication of the highly crystalline nature of the samples and provides further evidence that the mesostructure was composed of β-SiC crystallites with random orientation. Typical TEM images of representative S-SiC samples (S-SiC-150-0.5 and S-SiC-150-1) are shown in Figure 3.14. The structures of the mesoporous S-SiC samples were exact inverse replicas of their silica templates but slightly disorder mesostructures compare to SiC samples prepared from static mode SBA-15. Since the pores of both the templates were effectively filled with the polymer, followed by a subsequent series of curing, pyrolysis and etching step, it turned out that the obtained mesoporous SiC products retained the structural symmetry of silica templates. The void channels of SBA-15 were converted into SiC ceramic walls, whereas the silica walls of SBA-15 were removed to form hollow channels of mesoporous SiC.
Figure 3.13  The representative high and low resolution TEM images of representative SiC samples (A) SiC-100-0.5 (B) SiC-100-1.0 (C) SiC-100-0.5 (D) SiC-150-0.5 (E) SiC-150-1.5 (F) SiC-100-1.0 (Insets show the corresponding SAED patterns)
3.3.5 Thermal stability of SiC materials

The representative Thermogravimetric Analysis (TGA) curve of the ordered mesoporous SiC measured in air (Figure. 3.15) indicates that there are three significant weight-change steps. During the first step of the sample prepared from low quantity PCS (SiC-100-0.5), which occurs from 25 to 308 °C, a small weight loss of 4.1% occurs, corresponding to the loss of water
absorbed on the surface. The second weight loss of 0.42 %, which occurs between 310 and 640 °C, which could be ascribed to the combustion of residual carbon. This confirms that the percentage of residual carbon is very negligible. In the third step, a gradual weight increases from 640 °C is seen. This is probably related to the oxidation of SiC. We could observe similar kind of curve for the sample SiC-150-0.5. For the samples prepared from high quantity PCS, a small weight loss occurred during the first step. The weight loss of 6.23% which occurs from 310 to 700 °C in step two, which could be ascribed to the combustion of residual carbon. From this TGA analysis we could confirm that the residual carbon is increased because of the quantity of PCS. The thermal behaviors for S-SiC samples are shown in Figure 3.16. These TGA curves reveals similar kind of results but in the first weight loss is too high (6.3 – 7%) that because of water absorbed on the surface and there is no much weight loss in the second step and oxidation of this samples are very high. These results were consistent with the Si/C ratio in the mesoporous SiC samples, implying that very less amount of residual carbon present is burnt in air and a small amount of oxygen is simultaneously introduced.
Figure 3.15(A) TG analysis curve of SiC-100-0.5 sample

Figure 3.15(B) TG analysis curve of SiC-150-0.5 sample
Figure 3.15(C) TG analysis curve of SiC-100-1.5 sample

Figure 3.15(D) TG analysis curve of SiC-150-1.5 sample
Figure 3.16(A) TG analysis curve of S-SiC-100-0.5 sample

Figure 3.16(B) TG analysis curve of S-SiC-150-0.5 sample
3.3.6 Chemical compositions

The Fourier-Transform infrared (FTIR) spectra (Figure 3.17 and 3.18) shows that the silica matrixes can be removed by HF etching without destroying the ordered mesostructure of the SiC samples. The FTIR spectra of SiC-100-0.5 and SiC-100-1.5 samples display a strong band at around 850 cm\(^{-1}\) which is associated with the Si-C bond, further confirming the existence of silicon carbide after the removal of mesoporous silica. Another peak at around 1097 cm\(^{-1}\) caused by Si-O-Si bonds is also observed, implying that a certain amount of oxygen remains after HF etching and may be located in the surface of the SiC samples. Intense bands for the samples SiC-150-0.5 and SiC-150-1.5 at a frequency centered at 857 cm\(^{-1}\) were observed. This indicates that the Si-C bond and another small absorbance band at around 1110 cm\(^{-1}\) are attributed to Si-O-Si bond. The absorbance band at around 3450 and 1637 cm\(^{-1}\) are attributed to the presence of moisture.

The FTIR spectrum of the pyrolyzed S-SiC samples are given in Figure 3.18. For the sample S-SiC-100-0.5, the peak around 854 cm\(^{-1}\) is assigned to Si-C linkage while peak at 1099 cm\(^{-1}\) is attributed to Si-O-Si which is due to the trace of silica. Similar kind of result also obtained for the sample S-SiC-100-1.0. It is noticeable that the oxygen absorbance capacity is very less for the SiC samples prepared from static mode SBA-15 templates hydrothermally treated in the temperature of 150 °C. We could observe that the sample prepared from 150 °C silica (stir mode SBA-15) with high amount of PCS shows very less Si-C bond that we have confirmed with wide-angle XRD. We have confirmed that the percentage of oxygen present in the SiC samples using Energy-dispersive X-ray spectroscopy (EDX). Figure 3.19(A) shows the EDX spectrum of SiC-100-0.5, SiC-100-1.5, SiC-150-0.5 and SiC-150-1.5. Figure 3.19(B) shows the EDX spectrum of S-SiC-100-1.0 and
S-SiC-150-1.0. The spectrums reveal the presence of silicon, carbon and oxygen in SiC with different compositions and are tabulated in Table (3.2).

Figure 3.17 FTIR spectra of SiC-100-0.5, SiC-100-1.5, SiC-150-0.5, SiC-150-1.5 samples
Figure 3.18 FTIR spectra of S-SiC-100-0.5, S-SiC-100-1.0, S-SiC-150-0.5, S-SiC-150-1.0 samples
Figure 3.19(A) EDX spectra of representative SiC samples (a) SiC-100-0.5 (b) SiC-100-1.5 (c) SiC-150-0.5 (d) SiC-150-1.5

Figure 3.19(B) EDX spectrum of representative SiC samples
(a) S-SiC-100-1.0 (b) S-SiC-150-1.0
Both FTIR and EDX spectra confirmed that the oxygen content is decreased for SiC samples, when the hydrothermal temperatures of the templates were changed from 100 to 150 °C. But in the case of S-SiC samples percentage of carbon is high compared to silicon and formation of silicon carbide is also less which could be confirmed with FTIR.

Table 3.2 Chemical composition of mesoporous SiC Characterized by EDX

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Carbon (Wt%)</th>
<th>Oxygen (Wt%)</th>
<th>Silicon (Wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC-100-0.5</td>
<td>33.12</td>
<td>25.60</td>
<td>41.69</td>
</tr>
<tr>
<td>SiC-100-1.5</td>
<td>37.82</td>
<td>19.84</td>
<td>42.35</td>
</tr>
<tr>
<td>SiC-150-0.5</td>
<td>29.51</td>
<td>19.39</td>
<td>51.09</td>
</tr>
<tr>
<td>SiC-150-1.5</td>
<td>32.31</td>
<td>17.57</td>
<td>50.13</td>
</tr>
<tr>
<td>S-SiC-100-1.0</td>
<td>62.64</td>
<td>18.22</td>
<td>19.14</td>
</tr>
<tr>
<td>S-SiC-150-1.0</td>
<td>44.15</td>
<td>23.14</td>
<td>32.70</td>
</tr>
</tbody>
</table>

3.4 CONCLUSION

In summary, we demonstrated for the first time that, mesoporous SiC with highly ordered mesoporous structure and monodispersed rectangular shaped rod like particles with uniform length and width, has been successfully synthesized using uncalcined mesoporous silica template prepared from static mode SBA-15 as well as stir mode SBA-15 templates hydrothermally treated in the temperature range between 100 and 150 °C. A new single step nano casting method has been used to prepare ordered mesoporous SiC samples. We also demonstrated that the presence of the surfactant molecules in the
uncalcined template which is sandwiched between the silica wall and the PCS precursors provides the extra carbon and enhances the reaction between the carbon and the silica sources to obtain high purity mesoporous SiC. We also proposed a new method of controlling the pore diameter of mesoporous SiC by simply changing the synthesis temperature of the mesoporous silica template. The pore diameter of the materials can be tuned from 3.0 to 4.4 nm with increasing the synthesis temperature of the template. All the materials possess high surface area and specific pore volume and uniform pore size distribution. The phase purity of the sample was also confirmed by the FT-IR spectroscopy. However, no significant changes were observed when we used static mode SBA-15 and stir mode SBA-15. But the chemical composition cures reveals that the formation of SiC is less in the case of the sample prepared from stir mode SBA-15. We believe that this method is quite novel and avoids the unnecessary calcination step for the preparation of the template which reduces the cost of the process significantly. We also strongly hope that this method can be applied for the fabrication of various other mesoporous non-siliceous materials and could pave the way for creating novel materials and ease the commercialization of the process.