CHAPTER 1

POROUS MATERIALS PROCESS, PROPERTIES AND APPLICATIONS

1.1 INTRODUCTION

In the recent years, nanomaterials have been a core focus of Nanoscience and Nanotechnology – which is an emerging multidisciplinary field of study attracting tremendous interest, investment and effort in research and development around the world. Nanoporous materials as a subset of nanostructured materials possess unique surface, structural, and bulk properties that highlight their importance in various fields such as ion exchange, separation, catalysis, sensor, bio-molecular isolation and purifications. Nanoporous materials are also of scientific and technological importance because of their voids of controllable dimensions on the atomic, molecular, and nanometer scales, enabling them to discriminate and interact with molecules and chemical clusters. They offer new opportunities in areas of inclusion chemistry, guest-host synthesis and molecular manipulations and reaction in the nanoscale for preparing nanoparticles, nanowires and other quantum nanostructures. Nanoscale is fascinating because it is on this scale that atoms and molecules interact and assemble into structures that possess unique properties, which are dependent on the size of the structures. It is at this scale that molecular interactions, processes and phenomena can be controlled and directed to form the desired geometries of the materials building blocks with desired properties (Lu and Zhao 2004). There is an increasing interest in understanding how the formation of porous materials
proceeds. Knowledge of this kind is important to provide the necessary means for controlling and directing the formation of porous materials. Structure, particle morphology, and size distribution are all material properties that need to be monitored for application purposes.

1.2 PORES AND POROUS MATERIAL

The presence of pores (holes) in a material can render itself all sorts of useful properties that the corresponding bulk material would not have. Generally porous materials have porosity (volume ratio of pore space to the total volume of the material) between 0.2 – 0.95. Pores are classified into two types: open pores which connect to the surface of the material, and closed pores which are isolated from the outside. In separation, catalysis, filtration or membranes, often penetrating open pores are required. Materials with closed pores are useful in sonic and thermal insulation, or lightweight structural applications.

The definition of pore size according to the International Union of Pure and Applied Chemistry (IUPAC) is that micropores are smaller than 2 nm in diameter, mesopores 2 to 50 nm and macropores larger than 50 nm. Nanoporous materials are subset of porous materials, typically having large porosities (greater than 0.4) and pore diameters between 1-100 nm. In the field of chemical functional porous materials, it is better to use the term “Nanoporous” consistently to refer to this class of porous materials having diameters between 1 and 100 nm. Nanoporous materials have specifically a high surface to volume ratio, with a high surface area and large porosity, and well ordered uniform pore structure.
1.2.1 Structural classification of porous materials

These materials are generally characterized into three categories


2. The two-dimensional (2D) mesostructured materials with hexagonal symmetry are the most easily produced, the classical products being SBA-12 and SBA-15 (Santa Barbara Amorphous). The deal models of basic structures are hexagonally closed packing cylindrical pore channels, belonging to the space group p6mm. Figure 1.1A shows hexagonally symmetric pore arrays.

3. Three-dimensional (3D) structure is classified into two types. These are 3D cubic bicontinuous and 3D cage-like cubic structures. Many 3D cubic silica mesostructures have been reported (Kresge et al 1992, Yanagisawa et al 1990). The first of these to be reported was the MCM-48 (Mobil Composition of Matter no 48) mesostructure, which has interesting and complicated pore channels. (Figure 1.1B). Subsequently, SBA-n, KIT-n (Korean Advanced Institute of Science and Technology) and AMS-n (Anionic surfactant templated) series silicates with cubic mesostructures were sequentially synthesized. Mesoporous silica materials like MCM-48 and KIT-6 have the cubic symmetry (Ia3d), and 3D bicontinuous mesochannels. The 3D cage-like cubic mesostructures SBA-1 and SBA-6 with Pm3n symmetry have been reported by Sakamoto et al (2000).
Figure 1.1 Pore models of mesostructures with symmetries of
(A) p6mm SBA-15 (B) Ia3d – MCM-48 & KIT-6
(C) Pm3n – SBA-1 & SBA-6 (D) Im3m – SBA-16
(E) Fm3m – KIT-5

1.3 TYPES OF MESOPOROUS MATERIALS

The mesoporous materials can be broadly classified into two types, siliceous and nonsiliceous, depending on their composition.

1.3.1 Siliceous or mesoporous silica materials

The first synthesis of ordered mesoporous materials were described in a patent literature. However, due to lack of analysis, the remarkable features of these materials were not recognized (Di Renzo et al 1997). Mobil oil corporation scientists obtained similar kind of material and they discovered remarkable features of this novel type of silica. At approximately the same time, Yanagisawa et al (1990) described an alternative but less versatile approach to the mesoporous materials. These novel materials were named FSM-16 (Folded Sheet Materials). These materials have higher thermal and hydrothermal stability than MCM-41 due to higher degree of condensation in the silica walls of the materials.
Figure 1.2  Schematic representation of possible formation mechanism of mesoporous silica

MCM-41 (Beck et al 1992, Kresge et al 1992) possesses honeycomb arrays of non-intersecting uniform sized one dimensional channel whose diameter is in the range of 1.5 – 10 nm which depends on the templates used, the addition of auxiliary organic compounds and the reaction parameters such as synthesis temperature, synthesis time or post synthetic hydrothermal treatment. The mesoporous silica materials have characteristic properties like large specific surface areas, ordered pore systems and well defined pore radius distributions. The well-known representative of mesoporous materials include the silica solids with MCM-41 (hexagonal arrangement of mesopores), MCM-48 (with a cubic arrangement of mesopores) and MCM-50 (with a lamellar arrangement of mesopores).

The original approach has been extended by a number of variations, for example, by the use of triblock copolymer templates under acidic conditions by which means the so-called SBA silica phases may be synthesized (Zhao et al 1998). The term template is used in zeolite synthesis to mean those molecules that have a definite structure-directing function in the construction of composite materials. Meanwhile, however, the meaning of this term has changed to such an extent that it is frequently used in the general sense of a structure-determining agent even when it relates to super molecular
aggregates and when several structural types can be produced by the same agent. A fundamental condition for this method is that an attractive interaction between the template and the silica precursor is produced to ensure inclusion of the structure directly or without phase separation. Mesoporous silicates such as MCM-41 and SBA-15 possess huge surface area (normally $\geq 1000 \text{ m}^2/\text{g}$), large pore size ($2 \text{ nm} \leq \text{size} \leq 20 \text{ nm}$) and ordered array of cylindrical mesopores with very regular pore morphology. Kleitz et al (2003) have reported the synthesis of noncrystalline ordered mesoporous silica KIT-6 (Korean Advanced Institute of Science and Technology no 6).

1.3.2 Non-siliceous mesoporous materials

Ordered non-siliceous mesostructured materials are of great interest because of their diversities in composites that lead to potential applications in catalysis, optics, electronics, magnetic and so on (Yang et al 2002). Since the first report of non-siliceous mesostructure by Huo et al in 1994, four strategies such as including surfactant (ligand)/inorganic self-assembly, true liquid crystal templating, nanocasting and nanocrystal templating, has been established for synthesizing these kinds of materials based on their chemical compositions and properties (Taguchi and Schuth 2005). Their use in diverse applications is directly related not only to their superior physical and chemical properties, such as electrical conductivity, thermal conductivity, chemical stability, and low density but also to their wide availability. The well-known species of non-siliceous mesoporous materials group are the mesoporous carbon materials, synthesized by using the pre-formed mesoporous silicates as hard templates. Many advances have been made in carbon technology in recent years, both through continued improvement of existing fabrication methods and through the development and introduction of new synthetic techniques. Successful synthesis of ordered mesoporous carbons, namely the CMK family, was reported by Ryoo and co-workers.
They have demonstrated that carbonization of sucrose, furfuryl alcohol, and acetylene can be performed inside the mesopores of MCM-48 (CMK-1, CMK-4), SBA-1 (CMK-2) and SBA-15 (CMK-3, CMK-5) so that well-ordered mesoporous carbons can be obtained after the complete removal of the template. The carbon materials with high surface area and ordered pore structure are of great technological interests. The mesoporous metal oxides, synthesized in the similar routes are also recently gaining importance in different applications as non-siliceous mesoporous materials.

![Schematic representation of possible formation mechanism of mesoporous carbon](image)

Figure 1.3  Schematic representation of possible formation mechanism of mesoporous carbon

These carbon materials normally have relatively broad pore-size distributions in both micropore and mesopore ranges. Activated carbons and carbon molecular sieves have been produced in large quantities, and are widely used in adsorption, separation, and catalysis applications.

1.4  MESOPOROUS CERAMICS

Ceramic materials are inorganic, non-metallic materials and things made from them may be crystalline or partly crystalline. They are formed by the action of heat and subsequent cooling. A ceramic material may be defined as any inorganic crystalline oxide material. Ceramic materials are brittle, hard and strong in compression, weak in shearing and tension. They withstand
chemical erosion that occurs in an acidic or caustic environment. Ceramics generally can withstand a very high temperature that ranges from 1000 °C to 1600 °C (1800 °F to 3000 °F). Exceptions include inorganic materials that do not have oxygen such as silicon carbide. But some of the materials that do have oxygen, that’s because of atmospheric oxygen.

Recently, increasing attention has been paid to the synthesis of porous ceramic materials with high specific surface area which can be used as a catalyst supports. Nanoporous ceramics with very high surface areas and large pore volumes have physical properties far different from the bulk solid materials. These materials exhibit potential applications in electric devices, (Connolly et al 2002) blue-emitting diodes, (Liao et al 1995) UV photodetectors, (Afanas’ev et al 2005) catalysis, (Keller et al 1999) biomaterials, (Rosenbloom et al 2004) and separations. The enhancement of these properties is attributed to the confined-space effect in nanospace. Therefore, mesoporous ceramics with ordered mesostructures and tunable compositions have attracted increasing interest in recent research. Several types of ceramic materials such as carbides, nitrides, silicates and borides are available for commercial applications. During the last three decades, rapid development of new processes of powder synthesis or shaping of parts, combined with a better knowledge of their mechanical, thermal and electric properties, have paved the way for their use as sintered materials, fibers, monocrystals or coatings. The need for new high performance ceramics for various economic sectors (mechanical engineering, aeronautics, electronics and nuclear) have been the driving force for their much diversified development. Thus, for example, silicon carbide powder, used for a very long time for its hardness as an abrasive, on sintering can be used as a structural ceramic for components operating at high temperatures. Boron carbide, which has a remarkable hardness, is used for high temperature thermo-electric conversion and also in the nuclear industry as a protective barrier and neutron speed reducer.
Advances in materials fabrication, including those enabled by nanotechnology, have required the integration of components and features with pore structures. Among the various ceramic materials that have found silicon carbides exhibit unique properties such as high thermal conductivity, excellent thermal stability, resistance toward oxidation, high mechanical strength and chemical inertness. These properties make them attractive for generation of high-temperature semiconducting devices, as hydrogen storage materials, as abradants, heater blocks, reinforced materials, optical materials and as catalyst support (Powell et al 2002, Pensl and Choyke 1993). Especially, because of the low oxidation resistance of carbon and poor hydrothermal stability of silica porous materials, SiC with a high surface area has been widely used as a catalyst support material at high temperatures in the catalysis field.

Well-ordered mesoporous SiC materials are essential for a number of these applications. Introducing a third component, such as oxygen, nitrogen, boron, titanium, aluminum, or zirconium, into the SiC network can yield various SiC based materials and efficiently improve their properties (Matsuura et al 2003, Samanta et al 2000, Weinmann et al 2000, Soraru et al 1999, Karmann et al 1992) For example, the oxidation resistance is enhanced in silicon oxycarbide (SiOC) and silicon carbonitride (SiCN) ceramics owing to the complex-covalent chemical bonds formed. The enhancement of different physical properties of the SiC materials has been attributed to the confined-space effect in nanospace. Therefore, mesoporous SiC-based ceramics (e.g., SiOC and SiCN) with ordered mesostructures and tunable compositions have attracted increasing interest in recent research.
Commercially available SiC (produced by the Acheson process) tends to have very low specific surface area (0.1-15 m$^2$/g) as a result of the extremely high temperatures (1800 - 2200 °C) of production, which leads to excessive sintering. A process by which high-surface-area, high-porosity SiC can be made is highly desirable. Numerous studies that report new approaches to produce high-surface-area SiC are available in the literatures. The application of SiC as a catalyst support has been demonstrated for several reactions including, hydride-sulfurization (Ledoux et al 1988), automotive exhaust-pipe reaction (Boutonnet-Kizling et al 1992), isomerization of linear saturated hydrocarbons (Pham-Huu et al 1999), selective oxidation of hydrogen sulfide into elemental sulfur (Keller et al 1999), and the selective oxidation of butane into maleic anhydride (Ledoux et al 2001). Surface area is thought to be an important consideration of hydrogen in the function of SiC as a catalyst support for these reasons.

1.6 PREPARATION TECHNIQUES

To date, several techniques have been used for synthesizing crystalline SiC material such as, chemical vapor deposition (CVD), spinning, nanocasting, autogenic-pressure reaction and sol-gel techniques. Many different pairs of silicon and carbon precursors have been used in such synthesis. On the basis of the types of reactions, the pairs of silicon and carbon precursors can be divided into the following categories.

1. Si carbonization, e.g., a mixture of milled Si and SiC powders and C$_3$H$_6$ (Li et al 2003), silicon – methane (Kim et al 2003, Ho et al 2004) and silicon – carbon nanotubes (Sung et al 2002).

polysilaethylene (Cheng et al 2005) and allylhydropoly (carbosilane) (Park et al 2004).


4. Reduction – carbonization such as SiCl$_4$ – Na – C (Hu et al 1999), Si-containing compounds and halocarbons (Huczko et al 2005).

Among these reactions, nanocasting and carbothermal techniques are widely used to form SiC with desired structures due to broad availability of silica-carbon precursors.

1.6.1 Carbothermal reduction process

Carbothermal reactions involving the use of fine carbons as a reactant in inert atmospheres at high temperatures has been extensively used since long for reduction metallic oxides as well as for beneficiation of several minerals. In particular, carbothermal reduction of natural silicate minerals to obtain silicon carbide or silicon nitride or their solid solutions with oxides.
The main advantage of this carbothermal process is the high crystallinity of the SiC materials. One can also expect lower oxygen content for carbothermal procedure because of carbon excess content as the lower specific surface areas.

1.6.2 Nanocasting

One of the easiest procedures to obtain mesoporous material is the use of templates. Inorganic materials with well-defined porosity are routinely synthesized by use of “templates”. The creation of periodically ordered, uniform pore systems in the submicrometer size range requires the aid of one or more chemical species, the porogen, to direct the formation of the inorganic phase in a suitable way. The desired material is formed with the porogenic species being incorporated into the solid structure, resulting in a composite from which the porogen is finally removed to yield the pore system. By strict terms, the porogen is called a “template” only if the relationship between its own structure or chemical nature and the resulting solid structure in the porous material is univocal, that is, if the choice of a specific porogenic species will lead to a unique pore structure which cannot be realized by a different porogen. In all other cases, the relationship between the porogen and the resulting structure is less well-defined, the term “structure director” is more adequate. However, the borderline between these two cases is of a diffuse nature, that is why “templates” is nowadays used quite frequently as a general expression for any species which is used to deliberately manipulate the structural or morphological features of the products.

There are several approaches of the template technique. We can refer to endotemplating and exotemplating to describe two types of templating procedure. Endotemplating occurs when the template is incorporated in the bulk as an isolated entity and exotemplating takes place when the template is
a structure that provides a scaffold to the synthesized material. In later macroscopic replica of the template can also be obtained, depending on the connectivity of porous structure of the template. A general principle of structure replication is very straightforward. A porous solid material is used as a rigid matrix (template); that is, pores are filled with one or more precursor species which react in situ to form the desired material. The matrix is finally removed to yield the product as its negative replica. In analogy to macroscopic procedures, this process is occasionally termed “casting” or “molding”, with the matrix (template) acting as the “casting mold” and the product (replica) being the “cast”. “Casting” on the nanometric length scale can consistently is termed as “nanocasting”.

Nanocasting is a highly versatile and promising technique for the preparation of ordered mesoporous materials (Yang et al 2005, Lu and Schuth 2006, Schuth 2003). In 1998, Goltner and coworkers first proposed the concept termed as nanocasting in mesoporous materials. They used a mesoporous silica monolith with the interconnective pore system as a confined hard template via two-step nanocasting to prepare mesoporous organic polymer networks with well-defined nanostructure. After that the hard templating and nanocasting process have attracted more and more attention and become one of the most important approaches for the synthesis of porous materials, especially mesoporous materials. Typically, mesoporous silica and carbons are used as hard templates (exotemplates) not only to prepare three-dimensional structure (Lu et al 2002, Ryoo et al 2001, Joo et al 2001) but also for the space confined synthesis of nanowires and nanoparticles (Krawiec et al 2006, Kockrick et al 2007). The application of nanocasting technique to the fabrication of inorganic compounds implies that the fabrication of these products takes place in nanospaces provided by the pores of a porous solid (hard template). This fact implies that growing is restricted
by walls of the pores. After synthesis of the material, the template framework is selectively removed and the inorganic product is obtained.

**Methodology:** Basically, the nanocasting route comprises three steps:

1. Infiltration of porosity of the template with a solution containing precursors of the inorganic compound.

2. Heat treatment under a controlled atmosphere of the impregnated template to convert infiltrated precursor into inorganic material.

3. Removal of the template framework, by dissolution (i.e. silica) or by oxidation at high temperatures (i.e. carbon).

Due to the fact that the synthesis takes place in a confined nanospace, sintering of the particles is restricted and preparation of high surface area materials (nanostructures or nanoparticles) is achieved. In this way, numerous inorganic compounds of high surface area can be obtained, although high temperatures are required to synthesize them. Moreover, this synthetic strategy clearly suggests that the structure of the synthesized inorganic compounds can be tailored depending on the pore characteristics of the selected template. Quite a number of reports address the preparation of ordered mesoporous oxides, carbons, and metals using nanocasting (Kleitz et al 2003, Rumplecker et al 2007), however, recently the synthesis of mesoporous or nanostructured carbides and nitrides are reported (Dibandjo et al 2007, Yant et al 2006, Krawiec et al 2006).

**Impregnation or Infiltration**

Infiltration is nothing but filling of pores. Hard templates such as ordered mesoporous silica materials filled with carbon source (sucrose or
PCS). Normally, impregnation process is to obtain fully polymerized and carbonized sucrose inside the pores of silica template. In the impregnation process, we are using sucrose solution and sulfuric acid, here sulfuric acid acts as a catalyst during carbonization at temperature of 1300-1400 °C.

**Pyrolysis**

The ceramization heat treatment is carried out under mechanical tension in neutral atmosphere (vacuum/N₂/Ar) up to temperatures of 1400 °C, according to the desired state of crystallization. During this stage, polycarbosilane or other carbon source precursor undergoes many structural transformations with ruptures of chemical bonds that are accompanied by variations in composition, mass and gaseous releases. We observe a release of matter corresponding to the elimination of volatile oligomers up to 500–550 °C, then, thermal decomposition occurs with the rupture of Si-H, C-H, Si-CH₂, Si-CH₃ bonds. This transformation of polycarbosilane starts with dehydrogeno-carbonation and dehydrogenation reactions. With the departure of hydrogen and alkanes, a three-dimensional lattice of Si-C bonds develops, the C/Si ratio tends to be 1 and C = C bonds appear in the structure. The fibers are then formed from β–SiC nanocrystals, carbon nanoparticles and an amorphous phase of SiOₓC_{4-x} type if the cross-linking has been carried out by controlled oxidation.

**Methods for removing templates**

The last step of nanocasting process is removal of hard template to obtain final nanocast replica. The mesoporous silica template is generally removed by either dilute hydrofluoric acid (HF) or hot sodium hydroxide (NaOH) solution depends on chemical stability of the target product. If both HF and NaOH solutions are applicable, the selection of which solution to use requires care. The silica template can be eliminated completely with dilute HF
solution at room temperature. However, HF itself is very toxic and harmful to the human body. Thus, an extremely strict protection measure is required during the use of HF. Dissolving the silica template with hot NaOH solution is much safer than HF. However, it generally requires two cycle steps to eliminate the silica template and the amount of residual silica in the final product is slightly higher than that obtained by using HF solution.

1.7 FORMATION MECHANISM OF SiC IN CARBON-SILICA NANOCOMPOSITES

When a SiO$_2$-C composition is heated in an inert atmosphere over a wide temperature range (Guterl et al 2004), the following carbothermal reduction and carbonization reaction could take place from a thermodynamic point of view:

\[
\begin{align*}
\text{SiO}_2(s) + C(s) & \rightarrow \text{SiO}(g) + \text{CO}(g) \quad (1.1) \\
\text{SiO}_2(s) + \text{CO}(g) & \rightarrow \text{SiO}(g) + \text{CO}_2(g) \quad (1.2) \\
\text{SiO}(g) + C(s) & \rightarrow \text{SiC}(s) + \text{CO}(g) \quad (1.3) \\
\text{SiO}(g) + 2\text{CO}(g) & \rightarrow \text{SiC}(s) + \text{CO}(g) \quad (1.4) \\
\text{CO}_2(g) + C(s) & \rightarrow 2\text{CO}(g) \quad (1.5)
\end{align*}
\]

The overall reaction is

\[
\text{SiO}_2(s) + 3C(s) \rightarrow \text{SiC}(s) + 2\text{CO}(g) \quad (1.6)
\]

During carbothermal reduction reaction, SiO$_2$ reacts with carbon, leaving to gaseous silicon monoxide (SiO). SiC is then produced by the reaction between SiO and C through equation (1.3) or between SiO and CO through equation (1.4). The equilibrium conditions at each step depend on the temperature and partials of the SiO ($p_{\text{SiO}}$) and CO ($p_{\text{CO}}$).
In some of the cases, when C/SiO$_2$ ratio is low, the rate of SiO production through equations (1.1) and (1.2) is very small. No SiC can be obtained in the lower ratio. When C/SiO$_2$ is raised to higher amount, the high carbon content in mesoporous pore walls gives higher partial pressures of SiO and CO. Flowing argon gas may carry away very little SiO and CO from the mesoporous C-SiO$_2$ samples because of small pore channels. SiC may nucleate through equation (1.2) throughout mesoporous precursors. As soon as SiC nuclei forms SiC nanofibers grow via gas-phase reaction between SiO and CO on the surface of mesoporous C-SiO$_2$ particles (Qian et al 2004) whereas SiC nanoparticles form inside the precursor particles since gas products generated from interpenetrating C-SiO$_2$ pore walls diffuse through mesoporous channels to accelerate the reaction kinetically. After nanoparticles form, internal mesopores of the precursors collapse, free space is thus generated, allowing gas phase reaction to form SiC nanofibers and nanoparticles.

While the mesoporous C-SiO$_2$ nanocomposites with low C/SiO$_2$ ratios were infiltrated with a small amount of carbon, the interface between C/SiO$_2$ pore walls and infiltrated carbon significantly enhances the local concentrations of SiO and CO and lowers the oxygen partial pressure. Locally concentrated SiO species readily react with carbon, resulting in a large number of SiC nuclei throughout the mesoporous C-SiO$_2$ nanocomposites and nanofibers form by the process similar to that described above.

In the case of dense C-SiO$_2$ nanocomposites with high C/SiO$_2$ ratio, the reaction between SiO$_2$ and carbon is suppressed inside the dense C-SiO$_2$ nanocomposites because there are no porous channels for diffusion of the gaseous products. The carbothermal reduction reaction takes place only starting from the surface of dense C-SiO$_2$ nanocomposites. Owing to diffusion limitation, the interpenetrating C-SiO$_2$ is slowly transformed into SiC
domains, and the consumption of carbon and silica facilitates the formation of pores on the surfaces. As the carbothermal reduction reaction proceeds, SiC pore walls develop at the interface between exterior porous SiC and interior C-SiO$_2$ due to concurrent gas transport and solid SiC formation. It is worth mentioning that, from a thermodynamic point of view, the driving force for SiC domain growth is quite small because of the relatively low reaction temperature (1300 °C) and the porous structure therefore remains almost unchanged once formed. The pore channels eventually develop uniformly throughout the dense C-SiO$_2$ nanocomposites, leading to mesoporous SiC.

1.8 ANALYSIS AND PHYSICOCHEMICAL CHARACTERIZATION METHODS FOR MESOPOROUS SOLIDS

In this section, necessary and useful techniques to characterize the pore system and structures of nanocast materials are briefly summarized. Since the periodicity of mesopore units is as large as 2-50 nm, the characterization techniques are a little different from those for atomic crystals. Three main techniques are often used, X-ray diffraction (XRD), electron microscopy and gas sorption measurements. Electron microscopy is generally used to distinguish pore structural topologies and determine the average pore-to-pore distance in a periodical phase. The pore structure in nanometers can be analyzed by electron microscopy, but only small domains of the sample can be analyzed in TEM images. Atomic lattice information can also be provided by the TEM technique. In the past, SEM was utilized to characterize surface features, nowadays it is being extended to pore and structural information. In the ensemble regime the adsorption behaviors of small molecules, usually N$_2$, provide information on the internal surface area, the pore volume, the distribution of pore size and to some extent the shape of the pores. Normally, no single technique is capable of providing complete
information of the specific structure of a nanocast solid. To obtain a comprehensive structure of a nanocast solid, a combination of several characterization methods are usually required, which provide important information about different physicochemical properties.

1.8.1 Powder X-ray diffraction (XRD)

It is well recognized that X-ray diffraction (XRD), based on wide-angle elastic scattering of X-rays, has been the most important tool to determine the structure of the materials characterized by long-range ordering. The X-ray diffraction patterns are obtained by the measurement of the angles at which an X-ray beam is diffracted by the sample. Bragg's equation relates the distance between two hkl planes (d) and the angle of diffraction (2θ) as:

\[ n\lambda = 2dsin\theta \]

where \( \lambda \) = wavelength of incident X-rays, \( n \) = an integer known as the order of reflection (h, k and l represent Miller indices of the respective planes). From the diffraction patterns, the uniqueness of structure, phase purity, degree of crystallinity and unit cell parameters of the crystalline materials can be determined. XRD patterns in a low angle range of 0.6-10° come from the periodicity of mesopores. Similarly, the patterns in a wide angle range of 10-80° can be used to determine atomic crystalline structures of nanocast materials. The identification of phase is based on the comparison of the set of reflections of the sample with that of pure reference phases distributed by International Center for Diffraction Data (ICDD). The mesopores are arranged in a fixed diameter and periodicity. Owing to a large cell parameter in a nanoscale and sometimes a low degree of regularity in mesoporous materials compared to single-crystals, often only a few Bragg peaks will come in XRD patterns. For measuring low-angle XRD patterns, the diffractometer should be adjusted to an appropriate condition. The most effective way is to choose a narrow slit, a low capacity factor of X-ray and a slow scanning speed. A narrow slit can not only reduce the damage on X-ray
irradiation, but also reduce noise and increase the resolution. However, an over-narrow slit would lower the intensity of the X-ray and attenuate the sample’s diffraction peak.

1.8.2 Fourier Transform Infrared (FTIR) spectroscopy

Fourier transform infrared spectroscopy deals with the vibration of chemical bonds in a molecule at various frequencies depending on the elements and types of bonds. After absorbing electromagnetic radiation the frequency of vibration of a bond increases leading to transition between ground state and several excited states. The energy of these transitions corresponds to the infrared region (4000–400 cm\(^{-1}\)) of the electromagnetic spectrum. The term Fourier Transform (FT) refers to a recent development in the manner in which the data are collected and converted from an interference pattern to an infrared absorption spectrum that is like a molecular "fingerprint". In the case of porous silicates, the FTIR spectra in 400–1300 cm\(^{-1}\) region provide information about the structural details including isomorphous substitution in framework, whereas the bands in 3000–4000 cm\(^{-1}\) region allow determining different Bronsted and Lewis acid sites (Freyhardt et al 1996) and silanol groups. Acidic and basic properties as well as their strength can also be estimated using carbon dioxide (CO\(_2\)), ammonia (NH\(_3\)), pyridine, triphenylphosphine (PPh\(_3\)) etc. as probe molecules and their quantitative estimation by FTIR (Ryczkowski 2001).

1.8.3 Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray spectroscopy (EDX)

Field Emission Scanning Electron Microscopy (FESEM) is an important tool for morphological characterization of mesoporous molecular sieve materials. A scanning electron microscope can generate an electron beam scanning back and forth over a solid sample. The interaction between
the beam and the sample produces different types of signals providing detailed information about the surface structure and morphology of the sample. When an electron from the beam encounters a nucleus in the sample, the resultant Coulombic attraction leads to a deflection in the electron’s path, known as Rutherford elastic scattering. A fraction of these electrons will be completely backscattered, reemerging from the incident surface of the sample. Since the scattering angle depends on the atomic number of the nucleus, the primary electrons arriving at a given detector position can be used to produce images containing topological and compositional information.

The high-energy incident electrons can also interact with the loosely bound conduction band electrons in the sample. However, the amount of energy given to these secondary electrons as a result of the interactions is small, and so they have a very limited range in the sample. Hence, only those secondary electrons that are produced within a very short distance from the surface are able to escape from the sample. As a result, high-resolution topographical images can be obtained in this detection mode.

**Energy Dispersive X-Ray Spectroscopy (EDS or EDX)**

It is a chemical microanalysis technique used in conjunction with scanning electron microscopy (SEM). The EDS technique detects X-rays emitted from the sample during bombardment by an electron beam to characterize the elemental composition of the analyzed volume. When the sample is bombarded by the SEMs electron beam, electrons are ejected from the atoms comprising the sample’s surface. The resulting electron vacancies are filled by electrons from a higher state, and an X-ray is emitted to balance the energy difference between the two electrons states. The X-ray energy is characteristic of the element from which it was emitted.
1.8.4 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) is typically used for high resolution imaging of thin solid sample for micro structural and compositional analysis. The technique involves: (i) irradiation of a very thin sample by a high energy electron beam, which is diffracted by the lattices of a crystalline or semi crystalline material and propagates along different directions, (ii) imaging and angular distribution analysis of the forward-scattered electrons (unlike SEM where back scattered electrons are detected), and (iii) energy analysis of the emitted X-rays. The topographic information obtained by TEM in the vicinity of atomic resolution can be utilized for structural characterization and identification of various phases of mesoporous materials, viz., hexagonal, cubic or lamellar. TEM also provides real space image on the atomic distribution in the bulk and surface of a nanocrystals.

1.8.5 Porosity measurement by $N_2$ adsorption

Despite of some theoretical limitations, the Brunauer-Emmett-Teller (BET) method continues to be the most widely used method for the evaluation of surface area, pore volumes and pore size distributions of porous solids from $N_2$ physisorption isotherm data. The BET equation can be represented as follows:

$$\frac{1}{n[P_o / P - 1]} = \frac{1}{n_m C} + \frac{(C - 1)}{n_m C (P / P_o)}$$

(1.7)

Where $n$ is the amount of gas adsorbed at a relative pressure $P_o$ and $n_m$ is the amount adsorbed constituting a monolayer surface coverage. The BET constant $C$ is related to the energy of adsorption in the first layer and consequently its value mirrors the adsorbent-adsorbate interactions. The total surface area ($S_t$) of the sample can be obtained using the following equation.
\[ S_t = n_m A_{cs} N \]  \hspace{1cm} (1.8)

\[ n_m = \frac{W_m}{M} \]  \hspace{1cm} (1.9)

\[ S_t = \frac{W_m N A_{cs}}{M} \]  \hspace{1cm} (1.10)

Where \( N \) is Avagadro’s number \( (6.023 \times 10^{23} \text{ molecules/mol}) \), \( M \) is the molecular weight of the adsorbate \( W_m \) is the weight of the adsorbate constituting a monolayer surface coverage, \( n_m \) is the amount absorbed constituting a monolayer surface coverage and \( A_{cs} \) is the molecular cross-sectional area of the adsorbate molecule. The specific surface area \( (S) \) of the solid can be calculated from the total surface area \( (S_t) \) and the sample weight \( (m) \) after degassing using the equation (1.11).

\[ S = \frac{S_t}{m} \]  \hspace{1cm} (1.11)

The total pore volume can be calculated by converting the volume of nitrogen adsorbed \( (V_{ads}) \) into the volume of liquid nitrogen \( (V_{liq}) \) by using the equation (1.12).

\[ V_{liq} = \frac{PV_{ads} V_m}{RT} \]  \hspace{1cm} (1.12)

in which \( P \) and \( T \) are ambient pressure and temperature respectively, \( V_m \) is the molar volume of the nitrogen \( (34.7 \text{ cm}^3/\text{mol}) \). Specific pore volume \( (V_p) \) can be calculated from equation (1.13).

\[ V_p = \frac{V_{liq}}{m} \]  \hspace{1cm} (1.13)
Where \( m \) is the weight of the adsorbent after degassing. Several computational procedures are available for the derivation of pore size distribution of mesoporous samples from physisorption isotherms. Most popular among them is the Barrett-Joyner-Halenda (BJH) model, which is based on speculative emptying of the pores by a stepwise reduction of \( P/P_0 \), and allowance being made for the contraction of the multilayer in those pores already emptied by the condensate. The mesopores size distribution is usually expressed as a plot of \( \Delta V_p/\Delta r_p \) versus \( r_p \), where \( V_p = \) mesopore volume, and \( r_p = \) pore radius. It is assumed that the mesopores volume is completely filled at high \( P/P_0 \).

1.8.6 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is a simple analytical technique that measures the weight loss (or weight gain) of a material as a function of temperature. As materials are heated, they can lose weight from simple processes such as drying or from chemical reactions that liberate gasses. Some materials can gain weight by reacting with the atmosphere in the testing environment. Since weight loss and gain are disruptive processes to the sample material or batch, knowledge of the magnitude and temperature range of those reactions are necessary in order to design adequate thermal ramps and holds during those critical reaction periods.

1.9 REVIEW

Quite a number of reports address the preparation of ordered mesoporous oxides, carbons, and metal using nanocasting, however, only recently the synthesis of mesoporous or nanostructured carbides and nitrides are reported. Recently, Vinu et al (2006) prepared mesoporous carbon and carbon nitrides with different pore diameters and morphologies using the hard templating approach by simply varying the pore diameter and the morphology of the templates. They reported that the pore diameter of the carbon or carbon
nitride can be done by simply varying either the pore diameter of the template by keeping the amount of the carbon or nitrogen precursor constant or varying the amount of carbon or nitrogen precursors in the mesochannels of the templates. On the other hand, the morphology of the materials was controlled by choosing the template with different morphology. The silicon carbide formation directly from silica and carbon requires high temperatures and in the first step proceeds via gaseous intermediates (SiO and CO), causing a collapse of the ordered mesoporous structure and lower specific surface areas (up to 260 m$^2$/g) (Lu et al 2005, Sonnenburg et al 2006). This process was recently studied and described in detail by Wang et al (2008) and Yao et al (2007), who also showed that only disordered (on the mesoscale) materials can be obtained via this method. Direct deposition of silicon carbide in silica matrix via Chemical Vapour Deposition (CVD) process and subsequent dissolving of silica in HF produces poorly ordered mesoporous SiC (Krawiecz and Kaskel 2006). The carbothermal reduction is widely used to form SiC with desired structures due to broad availability of silica-carbon precursors. SiC nanostructures such as nanofibers, nanoparticles and nanoporous monoliths have been produced by the carbothermal reduction reaction. In particular, SiC nanofibers are commonly observed on the surface of bulk silica-carbon precursors through the gas-phase reaction between SiO and CO intermediates (Qian et al 2004, Vix-Guterl et al 1999). Under flowing argon gas, SiC nanowires or nanofibers were grown from silica xerogel – carbon, in the absence of flowing argon, SiC nanoparticles were obtained from the same silica – carbon precursor (Meng et al 2000). However, the opposite effect was observed in the conversion of a freeze gel silica-carbon into SiC; porous SiC was produced from such a precursor in dynamic argon conditions, whereas SiC nanofibers were obtained in static conditions (Vix-Guterl et al 1999). The chemical reactivity of silica-carbon precursors may be another factor affecting the resulting SiC structure. SiC nanofibers were produced by infiltration of mesoporous silica (SBA-15) with sucrose and heat treatment
under flowing argon. Mixed SiC nanofibers and nanoparticles were produced from mesoporous C-SiO$_2$ nanocomposites, the proportion of nanofibers (or nanoparticles) was tunable by changing the C/SiO$_2$ ratio and using carbon infiltration (Yao et al 2007).

SiC whiskers are effective additives for reinforcement of various composite materials, mainly due to their high mechanical strength. The preparation of SiC whiskers is therefore important and has been achieved via various techniques, such as carbothermal reduction of silica or carbonaceous silica aerogels, decomposition of organic silicon compounds (Addamiano 1982), and reactions between silicon halides and carbon tetrachloride in the presence of hydrogen (Matojima and Hasegawa 1988). Tubular nanostructures have also been shown to be versatile catalyst supports in some reaction (Keller et al 2003). SiC nanorods with diameter 2-20 nm have been obtained by reacting carbon nanotubes with Si and I$_2$ at 1200 ºC. SiC nanorods have also been obtained from a solid carbon and silicon source on a Si substrate by hot filament chemical vapor deposition (HFCVD) (Zhou et al 1999). On the other hand, SiC nanotubes with medium surface area (30-60 m$^2$/g) have been obtained by reaction between carbon nanotubes and silica vapor via the shape memory synthesis method (Keller et al 2003).

Mesoporous SiC-based ceramics (e.g., SiOC and SiCN) with ordered mesostructures and tunable compositions have attracted increasing interest in recent research. With these demands, many approaches and combinations of approaches have been developed in both design and fabrication process. Nanoporous SiC-based materials are difficult to obtain because of their high formation temperatures. Disordered nanoporous silicon carbide ceramics can be fabricated by a solid-gas reaction of ordered mesoporous carbon replica with silicon vapor (Liu et al 2005) and a chemical vapor infiltration of dimethyldichlorosilane inside mesoporous silica followed
by the removal of silica (Krawiec et al 2004). To obtain an open and integrated mesoporous SiC framework, a sol-gel process from tetraethyl orthosilicate (TEOS) and phenolic resin in the absence of surfactants has been attempted (Jin and Guo 2003). However, the resulting products were disordered and the pore size distributions were broad. The surfactant-templating approach is normally used to synthesize highly ordered mesoporous oxides on the basis of the interactions between surfactants and precursors and between themselves. To date, only a few examples have been given for SiC-based materials from the surfactant-templating approach. Parmentier et al (2002) applied the nanocasting strategy for the fabrication of mesoporous SiC using bicontinuous MCM-48 with 3D structure whereas Lu et al (2005) demonstrated the preparation of mesoporous SiC by using SBA-15 as template and furfuryl alcohol as carbon precursor. Mesoporous SiOC materials have been prepared by directly treating mesostructured surfactant/organosilica/silica composites (Nghiem et al 2006) and periodic mesoporous organosilicas (PMOs) (Toury et al 2005) in an inert atmosphere. A casting-by-casting method also provides an approach to give mesoporous ceramics with open frameworks. Ordered mesoporous carbon replicas casted from mesoporous silicates are used as the hard templates. The final goal materials replicate the pore topologies of these carbons and have almost the same frameworks as the original mesoporous silica scaffolds. This concept avoids the interactions between precursors and surfactants. Therefore, it can widen the viable mesoporous components, especially for those that cannot be synthesized or difficult to synthesize by the surfactant templating approach. Recently, highly ordered mesoporous SiC materials with uniform pore sizes and ultralarge surface areas were synthesized by fully impregnating polycarbosilane inside the channels of mesoporous silicates, annealing the samples and then removing the hard templates of silicates (Shi et al 2006, Yant et al 2006, Krawiec et al 2006). This nanocasting strategy has proved to provide a general approach to the fabrication of mesoporous materials with
diverse components. To date, in all the cases, only the calcined form of mesoporous silica source was used as the silica source. However, a high temperature treatment is necessary for the preparation of both the calcined form of the mesoporous silica source and the mesoporous SiC which is neither economical nor the time and energy saving process. In addition, the formation of the Si-C framework requires the breakage of the strong Si-O-Si bonding in the calcined form of mesoporous silica and the reaction with the infiltrated nitrogen source which is quite complicated. This can be overcome by using the uncalcined form of mesoporous silica as a silica source for the fabrication of mesoporous SiC. Although there are few reported attempts to precisely control the pore diameter and the morphology of mesoporous carbons or carbon nitrides, however, to the best of our knowledge, there are no reports available in the literature on the preparation of mesoporous SiC or SiOC with tunable pore diameters and excellent surface morphology and uniform particle size.

1.10 SCOPE OF THE THESIS

The present work is aimed at the preparation and characterization of mesoporous SiC with high surface area with tunable pore diameter and SiC nano fibers. Ordered uncalcined mesoporous silica SBA-15 have been synthesized by hydrothermal process, here we have used the conventional stir mode as well as static mode of synthesize and a different process was followed for the removal of the structure directing block co-polymer. Block copolymers are well known which are used to synthesize mesoporous silica with large pore diameter.

Mesoporous and nanofiber SiC materials have been prepared by impregnation process using uncalcined mesoporous silica (SBA-15) as a template and sucrose as a carbon source at a reaction temperature of 1300 ºC at different period of time. It was seen that by varying the time duration,
heating rate and argon flow rate for carbothermal reduction, the morphology of silicon carbide readily modified. This study is motivated by the promising properties and possible uses expected from SiC materials that combine a well-defined mesoporous and nanofibers like structures. We demonstrate here a single step synthesis of highly crystalline mesoporous SiC materials with high specific surface areas and tunable pore diameter with controlled gas flow and heating rate. The structural characteristics of this material are found to be closely related to the mesoporous silica templates. We have observed that the mesoporous SiC materials prepared using conventional stir mode showed very high surface area. But the formation of porous structures is not uniform where as the SiC materials prepared with static mode SBA-15 is showing excellent surface area and good morphology with uniform structures. Our findings show that SiC nanofibers are obtained under high argon flow and high heating rate up to 1300 ºC and maintained for 8 h. Interestingly, on extending the reduction period to 12 h at 1300 ºC results in the formation of SiC nanofibers considerably more abundance.

Ordered mesoporous SiC and SiOC ceramics with hexagonal symmetry of pore arrangement were prepared via impregnation of uncalcined ordered mesoporous silica (SBA-15) templates with monodispersed rectangular shaped rod like particles with uniform length and width as template with polycarbosilane (PCS) as the carbon precursor. Different ratios of silica source to PCS are described here where different quantities of PCS were used for the SiC preparation. Highly crystalline SiC samples were obtained from low amount of PCS precursor, even upon pyrolysis at temperature as high as 1300 ºC. Mesoporosity of the SiC showed a decrease with increasing PCS content for both case of hydrothermal templates. The rough surface and high order of the nanowire arrays in the materials result from the strong interconnections of the SiC products. The synthesized mesoporous SiC ceramics exhibit a very high stability. The thermal and
structural properties of the material are studied thoroughly by various analytical techniques.

A three-dimensional bicontinuous cubic mesoporous SiC structure can be fabricated using uncalcined mesoporous silica KIT-6 as the mother silica. Here we have used sucrose and polycarbosilane as a carbon source. The SiC material prepared with sucrose had a less surface area and observed less mesoporosity. SiC products prepared with polycarbosilane had a good mesoporosity and the structure showed higher thermal stability than the 2D hexagonal mesoporous SiC, mostly because of the 3D network connections. The obtained mesoporous SiC ceramics are mainly composed of randomly oriented β-SiC crystallites after treatment at 1300 ºC. The high order and rough surface result from the strong interconnection of the SiC materials and are the main reasons for such high surface areas. Other thermal analysis showed that the mesoporous SiC ceramics have ultrahigh stability after heat treatment at 1300 ºC under argon atmosphere. 3D cubic mesoporous SiC showed superior thermal stability, as well as higher surface areas and large pore volumes.