CHAPTER 1

NANOPOROUS MATERIALS

1.1 INTRODUCTION

In recent years, nanomaterials have been a core focus of nanoscience and nanotechnology - which is an ever-growing multidisciplinary field of study attracting tremendous interest, investment and effort in research and development around the world. Nanoporous materials, a subset of nanostructured materials possess unique surface, structural and bulk properties that underline their important uses in various fields such as ion exchange, separation, catalysis, sensor, biological molecular isolation and purifications. Nanoporous materials are also of scientific and technological importance because of their vast ability to adsorb and interact with atoms, ions and molecules on their large interior surfaces and in the nanometer sized pore spaces. They offer new opportunities in areas of inclusion chemistry, guest-host synthesis and molecular manipulations and reaction in the nanoscale for making nanoparticles, nanowires and other quantum nanostructures.

1.2 NANOTECHNOLOGY AND NANOMATERIALS

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 desirable properties. Nanoscale phenomena and objects have, of course, been
utilized for some time. Small metal or metal oxide crystallites supported on a ceramic material, for example, are mostly nanoscale particles that have been used to crack crude oil into fuels for many years. However, what distinguishes cutting-edge nanoscience is the degree of understanding, deliberate control, and precision that new nanostructuring techniques afford. Instead of discovering new materials by trial-and-error, we can now design them systematically. Nanostructured materials may possess nanoscale crystallites, long-range ordered or disordered structures or pore space.

1.3 POROUS MATERIALS

Porous materials have attracted the attention of researchers due to commercial interest in their use as adsorbents, catalysts, catalyst supports and adsorption of large bio-molecules owing to their high specific surface area, large pore volume and pore diameter. Depending upon the predominant pore size, the porous materials are classified by IUPAC into three classes: (1) Solids that contain pores with diameter in the size range of 0.2 - 2.0 nm, which are considered as microporous materials; Zeolites, zeotype materials and activated carbons are examples of microporous materials. (2) Solids that contain pores with diameter in the size range of 2.0 - 50.0 nm, which are considered as mesoporous materials; examples of mesoporous materials include M41S, mesoporous aluminophosphates, aerogels and pillar-layered structures. (3) Materials containing pore size exceeding 50.0 nm are called macroporous, such as silica-gel, active charcoal and CPG (Controlled Porous Glass).

1.3.1 Mesoporous Materials for Sensor Application

Mesoporous silicas, especially those exhibiting ordered pore systems and uniform pore diameters, have shown great potential for sensing applications. The nanostructured mesoporous materials are suitable for

The adsorption of proteins from solution onto solid surfaces has attracted much attention due to its application in many areas. In the medical and food industries, it is essential to remove adsorbed proteins since even a small amount of deposited proteins may give rise to the subsequent adsorption of fibrous proteins leading to adverse biological consequences. Porous carbonaceous materials are also important in many areas including water and air purification, gas separation, catalysis, chromatography and energy storage. These applications prompted us to prepare new modified mesoporous materials and study their properties.

1.4 MESOPOROUS MOLECULAR SIEVES

1.4.1 Origin of Mesoporous Molecular Sieves

Chiola et al (1971) patented the synthesis of low density silica materials which were prepared by the ammoniacal hydrolysis of tetraethylorthosilicate in the presence of cationic surfactant, alkyltrimethylammonium bromide. Unfortunately these results were ignored or lacked attention because of the incomplete characterisation. Renzo et al (1997) reproduced the low density silica, described in the above patents which lead to the formation of solids having properties similar to MCM-41 (Mobil composition of Matter No.41), the ordered mesoporous silica, which was rediscovered by Mobil Oil Corporation (Kresge et al 1992). Yanagisawa et al (1990) reported the synthesis of mesoporous materials through intercalation
of cetyltrimethylammonium cations into the layered polysilicate kanemite (idealized formula NaHSi$_2$O$_5$·3H$_2$O) followed by calcination to remove the organic moiety. 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. (Inagaki et al 1993) reported that the pore diameter of FSM-16 can also be controlled by varying the alkyl chain length of the cationic surfactant.

1.4.2 Mesoporous Materials via Non-ionic Surfactants

The method for the production of periodic mesoporous material is based on the use of surfactant molecules as structure directing agents (SDAs). Surfactants (surface active agents) are molecules with hydrophobic and hydrophilic areas. Three of the most often used templates PEG (Figure 1.1(a)) and Pluronic P123 were used in this work. Non-ionic Pluronic P123 is a tri-block copolymer with two hydrophilic polyethylene oxide blocks and one hydrophobic polypropylene oxide block (Figure 1.1(b)). In solution, surfactants self-organize into micelles and eventually into liquid crystal phases, depending on stoichiometry (Coleman et al 2001).

![PEG](a) PEG

![Pluronic P123](b) Pluronic P123

*Figure 1.1 (a) PEG (b) Non-ionic tri-block copolymer Pluronic P123*
The advantage of using neutral or non-ionic surfactants over ionic route is the possibility of recovery of the surfactants. Tanev and Pinnavia developed the neutral templating route for mesoporous materials which is based on H-bonding and self assembly between the neutral amine surfactants and neutral inorganic precursor and the material was called HMS (hexagonal mesoporous silica) (Tanev et al 1995).

1.4.3 Mesoporous Oxides

Even though it has been realized initially that non-silica based materials can also be prepared by the same mechanistic ideas, the first successful attempt to prepare mesoporous titania was made only in 1993 (Monnier et al 1993). However, the removal of surfactant caused collapse of the mesostructure. With modified synthetic approach, mesoporous titania was prepared in 1995 (Antonelli et al 1995). However, the field of non-siliceous ordered mesoporous materials has received considerably less attention compared to that of mesostructured silica. Through a number of alternative surfactant assisted synthetic approaches, essentially non-silicate mesoporous metal oxides were achieved using low molecular weight surfactants, e.g. titania (Antonelli et al 1995; Jin-Yu et al 2001; Muller et al 2000), niobia (Stone et al 1998), alumina (Bagshaw et al 1996), tin oxide (Ulagappan et al 1996b), ceria (Yang et al 1998), and zirconia (Yang et al 1998), vanadium oxide (Yang et al 1998), aluminophosphates and vanadophosphates (Tiemann et al 2001a). All the above materials are mesoporous in assynthesized form but after removal of the surfactant, the mesoporous network collapsed. Attempts have been made to synthesize transition metal oxides in mesoporous form by optimizing the interaction between surfactant and inorganic precursor. The strategy adopted for non-ionic surfactants mesophases has been extended to prepare a variety of mesoporous metal oxides such as SnO₂ (Ulagappan et al 1996b) and TiO₂, (Antonelli et al 1995). Mesoporous tin
oxide and titania has been synthesised by using non-ionic surfactant templating method. Among the mesoporous transition metal oxides, synthesis of mesoporous tin oxide and titania is of particular interest.

1.4.4 Mesoporous Materials via Polymeric Template Route

Zhao et al (1998) have disclosed the synthesis of a two-dimensional hexagonal material with large surface area, large pore size (5 to 15 nm) and thick walls (3-5.3 nm) named as SBA-15 by using a triblock copolymer viz., EO$_{20}$ PO$_{70}$ EO$_{20}$ (Pluronic P123) as the structure directing agent. SBA-15 was synthesised in highly acidic media and follows $S^0$H$^+$X$^-$I$^+$ mechanism (explained in the next section). It exhibits XRD pattern which has one intense peak (100) and three or more higher order small peaks (110, 200, 210 etc.) at 2θ value below 10, which can be indexed according to the $p6mm$ space group. These materials possess higher hydrothermal stability compared to MCM-41. Yu et al (2000) have reported the synthesis of a highly ordered and ultra hydrothermally stable caged cubic mesoporous silica (FDU-1 Fudan University No. 1, $Im3m$ space group) by using more hydrophobic poly (butylene oxide) containing triblock copolymer (PEO-PBO-PEO) as the structure directing agent.

1.5 POSSIBLE SYNTHESIS MECHANISM

Several researchers have proposed different synthesis mechanism to rationalise the formation of mesostructures and to allow for the rational design of new surfactant templated materials. The structure of mesoporous materials is controlled by the different phases of the surfactant molecules in aqueous solution. Surfactants are large organic molecules with a long hydrophobic tail of variable length and a hydrophilic head group and will self organise in such a way as to minimise contact between the incompatible ends. The type of interaction between the surfactant and the inorganic precursor
will be seen as the significant difference between the various synthesis routes, the formation models and the resulting classes of mesoporous materials.

1.5.1 Phase Transformations of Surfactant Molecules in Aqueous Solution

In aqueous solution surfactant molecules manifest themselves as very active components with variable structure as a function of concentration (Fig. 1.2). At low concentrations, surfactants exist as monomolecules. With increasing concentration, surfactant molecules aggregate to form micelles in order to decrease the system entropy. The initial concentration threshold at which monoatomic molecules aggregate to form isotropic micelles is called cmc (critical micellar concentration). As the concentration process continues, hexagonal close packed arrays appear producing the hexagonal phases (Lawrence et al 1994). The next step in the process is the coalescence of the adjacent, mutually parallel cylinders to produce the lamellar phase. In some cases, the cubic phase is generally believed to consist of complex, interwoven networks of rod-shaped aggregates (Fromherz 1981).

![Phase sequence of the surfactant – water system with increasing concentration](image)

**Figure 1.2** Phase sequence of the surfactant – water system with increasing concentration
The phase transformation of surfactant molecules in aqueous solution depends on its physical properties such as concentration, hydrophobic chain length, hydrophilic head group and counter ions present in the aqueous media (Myers et al 1992). Further, the environmental parameters such as pH, temperature, ionic strength and other organic additives influence the phase transformation of surfactant molecule. The cmc decreases with increasing chain length of surfactant, valency of the counter ions and ion strength of the solution. On the other hand, it increases with increasing counter ion radius, pH and temperature of the surfactant solution.

1.5.2 Mechanism of Formation of KIT-6 Molecular Sieves

Mesoporous silicas with three-dimensional porous networks are thought to have advantages over materials having one-dimensional arrays of pores, mainly because materials with three-dimensional pore structure are more resistant to pore blocking, have better mass transfer of the reactant molecules in the pore channels, and provide more adsorption sites. Recently, Ryoo et al reported three-dimensional large-pore mesoporous silica with cubic Ia3d symmetry (KIT-6), which has well-ordered pore structure with high surface area, large pore volume, and large, tunable pore diameters. KIT-6 was synthesized by utilizing an ethylene oxide (EO) propylene oxide (PO) triblock copolymer (EO$_{20}$PO$_{70}$EO$_{20}$)/butanol mixture as structure-directing agent in a highly acidic medium (Kim et al (2005)). The materials are of interest for their three-dimensional structures with large pore diameters. The pore diameter of KIT-6 is similar to that of SBA-15 but larger than that of MCM-48. The pore diameter of the materials can also be tuned by simply changing the synthesis temperature. Although the structure and textural parameters of the KIT-6 materials are superior to those of MCM-48, no detailed study has been performed on immobilization of biomolecules on these materials. Here we report on the preparation and characterization of
KIT-6 materials with different pore diameters by using pluronic P123 surfactant in a highly acidic medium at different synthesis temperatures. The KIT-6 measurements were confirmed by physiochemical methods such as XRD, N\textsubscript{2} absorption, and UV-vis spectroscopy.

1.5.3 Mechanism of Formation of SBA-15 Molecular Sieves

SBA-15 was synthesised by using a nonionic poly(alkylene oxide) block copolymers as the structure directing agent (Zhao et al (1998)). Solubilisation of these surfactant in aqueous media is due to the association of water molecules with the alkylene oxide moieties through hydrogen bonding. It can be increased by using highly concentrated acid where hydronium ions instead of water molecules are associated with the alkylene oxygen atoms, thus adding long range columbic interactions to the co-assembly process of the mesophase. If the synthesis is carried out below the isoelectric point of silica (pH = 2), cationic silica species will be present as precursors and the assembly might be expected to proceed through an intermediate of form S\textsuperscript{0}H\textsuperscript{+}X\textsuperscript{−} (nonionic polymeric surfactant, (S\textsuperscript{0}), halogen anions (X) and the protonated inorganic SiO\textsubscript{2} species (I\textsuperscript{+}). Zhao et al (1998) followed the S\textsuperscript{0}H\textsuperscript{+}X\textsuperscript{−} I\textsuperscript{+} mechanistic pathway for the synthesis of SBA-15 mesoporous silica in acidic medium.

First alkoxy silane species are hydrolysed

\[
\text{Si(OEt)}_4 + n\text{H}_3\text{O}^+ \xrightarrow{\text{Hydrolysis}} \text{Si(OEt)}_{4-n}(\text{OH}_2^+)n + n\text{EtOH} \quad \text{pH} < 2
\]

This is followed by partial oligomerisation of the silica species. In strong acidic media, the EO moieties of the surfactant in strong acid media are associated with hydronium ions

\[
\text{REO}_m + y\text{HX} \xrightarrow{\text{H}_2\text{O}} \text{REO}_{m-y}[(\text{EO}).\text{H}_3\text{O}^+]_{y}y\text{X}^-
\]
where \( R = \text{alkyl or poly(propylene oxide)} \) and \( X^- = \text{Cl}^- \). They also proposed that these charge-associated EO units and the cationic silica species are assembled together by the combination of electrostatic, hydrogen bonding and van der Waals interactions of \( \text{REO}_{m-y}[(\text{EO}).\text{H}_3\text{O}^+]_{y...3}X^-...1^+ \) which can be designated as \((S^0\text{H}^+)(\text{X}^-\text{I}^+)\). Coordination sphere expansion around the silicon atom by anion (e.g., \( \text{Cl}^- \)) coordination of the form \( \text{X}^-\text{Si-OH}_2^+ \) may also play an important role. During the hydrolysis and condensation of the silica species, an intermediate hexagonal mesophase is obtained (SBA-15). Further condensation of the silica species and organisation of the surfactant and inorganic species result in the formation of the lowest energy silica-surfactant mesophase structure allowed by the solidifying inorganic network.

### 1.6 HETEROATOM SUBSTITUTION IN SBA-15 MOLECULAR SIEVES

Pure silica SBA-15 possess neutral framework, which limits their applications in catalysis and separation applications. In order to provide solids with potential catalytic applications, it is possible to modify the nature of the framework by incorporation of heteroelements. When trivalent cations like \( \text{Al}^{3+}, \text{B}^{3+}, \text{Ga}^{3+}, \text{Fe}^{3+} \) substitute silicon in the walls of the mesoporous silica, the framework possesses negative charges that can be compensated by protons and these solids can be used in acid-catalysed reactions. When other cations like \( \text{Ti}^{4+}, \text{V}^{4+}, \text{Sn}^{4+}, \text{Zr}^{4+} \) are introduced, the electro-neutrality is maintained and the corresponding mesoporous materials are used in specific reactions like oxidations. There are, however, large difference between substituted zeolites and mesoporous silicas. The later can be regarded as mesoporous organized mixed oxides, which means that their physical and catalytic properties will not differ greatly from those of mixed oxides. In particular, while in most of the zeolitic structures all active sites are within the channels and accessible to guest molecules, a large proportion of these sites in
mesoporous silicas are located inside the walls and are thus not accessible. This will effectively occur when the metal precursor is introduced together with the silica source during synthesis. However, this can be circumvented by grafting active species in the inner surface of the mesopores of pure silica materials. In this case, all catalytic sites are accessible and it was reported that these materials are more active than samples prepared by direct synthesis (Oldroyd et al 1996).

Incorporation of Titanium, Manganese, cobalt, Zinc, Tin into SBA-15 is very difficult due to the sensitive synthesis parameters and highly acidic synthesis media (SBA-15). It has been shown that Ti, Mn, Co, Sn and Zn atom can also be incorporated into the framework of SBA-15 via post synthesis procedures by reacting SBA-15 with tetraisopropyl titanate and Manganese acetate Cobalt acetate Tin cholride and Zinc acetate followed by calcination. The Si/Ti+Mn,Si/Ti+Co,Si/Ti+Sn and Si/Ti+Zn ratios in the resulting materials are in close agreement with the composition in the post synthesis mixtures over a range of 40-10, indicating that aluminium is mostly incorporated into silica SBA-15 (Luan et al 1999). Titanium substituted mesoporous molecular sieves have received considerable attention over the past years due to their remarkable activity in oxidation reactions at low temperature with dilute H₂O₂ solutions (Camblor et al 1993; Tuel 1995a, 1995b; Dart et al 1996). The co-ordination and nature of titanium in the mesoporous silicates have been studied using a variety of spectroscopic techniques. UV-Vis spectroscopy is one of the most commonly used techniques to access the local environment of Ti in the silicates (Klein et al 1996). A few researchers have tried to incorporate Ti into SBA-15 molecular sieves via post synthetic grafting, microwave and direct synthesis method (Morey et al 2000; Newalkar et al 2001; Wu et al 2002). Very recently, Zhang
et al (2002) reported the direct synthesis of Ti substituted SBA-15 which shows high activity in the epoxidation of styrene.

1.7 SCOPE OF THE PRESENT INVESTIGATION

Mesoporous molecular sieves by the researchers at Mobil about a decade ago opened a new and rapidly growing field of research interest. These materials have large internal surface area and narrow pore size distributions. They are potentially interesting candidates for many industrial applications such as catalysis and adsorption. Due to their pore size in the mesopore region, they allow faster mass transport of reactants or products in catalytic reactions and can be used for adsorption of bigger molecules like proteins, vitamins etc., (Takahashi et al and Yiu et al 2001). Further studies led to the discovery of several other types of mesoporous silicas with high specific surface area, high specific pore volume and pores in the mesopores range with a narrow pore size distribution. Envisaging potential industrial applications as catalysts or adsorbents, mesoporous molecular sieves is of tremendous interest since the powders obtained by hydrothermal synthesis. Materials with uniform and tunable pore size are expected to play an important role in a number of applications that range from catalysis to molecular separations and sorption of bulky molecules (Corma et al 1994a), and to the fabrication of semiconductors, semiconductor nanowires and low dielectric devices (Tanev et al 1996; Brunisma et al 1997).

Pure silica mesoporous molecular sieves possess neutral frameworks, which limits their application in catalysis and adsorption. In order to prepare solids with potential for catalytic applications, it is necessary to modify the nature of the amorphous walls by incorporation of heteroelements. When trivalent cations such as Al$^{3+}$, B$^{3+}$ substitute for silicon in the walls of mesoporous silica, the framework possesses negative charges
that can be balanced by protons and hence Brønsted acid sites are created. Therefore, the resulting solids can be used in acid-catalysed reactions. When transition metal ions viz., Ti$^{4+}$, Mn$^{3+}$, Co$^{3+}$, Sn$^{2+}$ and Zn$^{2+}$ are introduced, the synthesised catalysts can be employed in oxidation reactions. Recently, researchers have turned their attention to incorporate heteroatom in the new mesoporous materials like KIT-6 and SBA-15.

The objectives of the present investigation are envisaged below

- Syntheses of tin oxide mesoporous materials under microwave assisted synthesis conditions using PEG as surfactant.
- Syntheses of titanium oxide mesoporous materials under microwave assisted synthesis conditions using P123 as surfactant.
- Syntheses of transition metal ions incorporated (Cu and Mo)-KIT-6 materials under hydrothermal synthesis conditions using P123 as surfactant.
- Syntheses of transition metal ions incorporated (Ti, Co, Mn and Sn)-SBA-15 Bimetallic materials under hydrothermal synthesis conditions using P123 as surfactant.
- Physico-chemical characterization of the synthesized materials by low angle XRD, N$_2$ adsorption, UV-Vis DRS, ICP-OES and electron microscopy.

In view of the above, new heteroatom incorporated mesoporous materials such as KIT-6 and SBA-15 were carried out. The structural properties of the mesoporous molecular sieves were studied and the results are presented in the thesis.