CHAPTER 1

INTRODUCTION

1.1 GENERAL BACKGROUND

Development in science, engineering and technology are rapid within which progress has been made in the field of catalysis from its origin. The most successful industrial sectors are petroleum, chemicals production, energy generation and food production, and all of these industries rely heavily on catalysis. Importance of catalysis is well understood as more than 90% of all industrial chemical processes are benefited by the use of catalytic materials worldwide. The basic phenomenon of catalysis is the ability to increase the rate of a chemical reaction, or more specifically the rate at which equilibrium is attained. This is achieved by employing a catalyst under milder operating conditions, and compared to the uncatalyzed reaction. The catalyst is not consumed during the chemical reaction, and therefore it is a species that effects change. Catalysts are of crucial importance not only due to its capacity to facilitate chemical reactions, but also due to its tendency to improve the selectivity of catalyzed transformations. Increasing the selectivity reduces by-product formation, resulting in chemical processes of superior performance. By focusing on the years to come, engineers and scientists from chemistry, materials science, physics, biology and biochemistry has begin to pool their resources and outline appropriate strategies towards the improvement of designing novel catalytic systems that are suitable for implementation of more efficient and greener manufacturing processes.
1.2 ORIGIN OF CATALYSIS

Catalytic processes have been used by mankind for some thousands of years, but left unnoticed for example in fermentation, soap making and beavering of bread that involves catalysis. The introduction to concept of catalysis was first summarized by Swedish chemist Jons Jakob Berzelius in 1835. He proposed the existence of a new force which he called the “catalytic force” and he called “catalysis” the decomposition of bodies by this force. Dehydrogenation of alcohols over metallic catalysts had been carried out before 1800 by Joseph Priestley, the discoverer of oxygen, and by the Dutch chemist Martinus van Marum. Russian chemist Gottlieb Sigismund Constantin Kirchhof studied the behavior of starch in boiling water using sulphuric acid in 1812. In 1813 Louis Jacques Thenard discovered that ammonia is decomposed into nitrogen and hydrogen when passed over various red-hot metals and ten years later with Pierre Dulong, he found the activity of various metals over decomposition of ammonia. The first rational theory of catalysis was explained by Charles Bernard Desormes and Nicolas Clement for the homogeneous catalytic effect of nitrogen oxides in the lead chamber process for the manufacture of sulphuric acid.

Other early chemists involved in catalysis were Alexander Mitscherlich who referred to contact processes and Johann Wolfgang Döbereiner who spoke of contact action based on hydrogen and a platinum sponge became a huge commercial success in the 1820s. The beginning of industrial catalysis originated for the sulphuric acid production in 1831 and proceeded till 1875. In the 1880s, Wilhelm Ostwald at Leipzig University started a systematic investigation into reactions that were catalyzed by the presence of acids and bases, and found that chemical reactions occur at finite rates and that these rates can be used to determine the strengths of acids and bases. For this work, Ostwald was awarded the 1909 Nobel Prize in
Chemistry. The above mentioned history of catalysis has been reviewed by A. J. B. Robertson (1975). Contributions from many researchers in explaining the catalytic mechanism in their respective processes is still to some extent a mystery and it is notable that large-scale processes are based on catalysts which from a theoretical point of view can hardly be described. Catalysis over a century and more after many discoveries still remains a challenge to the chemist.

In general, there are two types of classification of catalysts such as homogeneous and heterogeneous depending on physical form in which they are used. Heterogeneous reaction involves the presence of catalyst in a different phase from the reactants and in homogeneous reaction; the catalyst is in the same phase as the reactants. Typically homogeneous catalysts are dissolved in a solvent with the substrates. For example, hydrolysis of sugarcane solution in the presence of dilute sulphuric acid.

\[
\text{C}_{12}\text{H}_{22}\text{O}_{11} \text{(aq)} + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4} \text{C}_6\text{H}_{12}\text{O}_6 \text{(aq)} + \text{C}_6\text{H}_{12}\text{O}_6 \text{(aq)} \quad (1.1)
\]

\[
\text{(Glucose)} \quad \text{(Fructose)}
\]

The main advantage of using a heterogeneous catalyst is the relative ease of catalyst separation from the product stream that aids in the creation of continuous chemical processes. Additionally, heterogeneous catalysts are typically more tolerant of extreme operating conditions than their homogeneous analogues. Different possible mechanisms for reactions on surfaces are known, depending on how the adsorption takes place. For example, in Haber’s process iron is used as catalyst for the manufacture of NH₃ from N₂ and H₂.

\[
\text{N}_2 + 3\text{H}_2 \xrightarrow{\text{Fe}} 2\text{NH}_3 \quad (1.2)
\]
Heterogeneous catalysis is of paramount importance in many areas of the chemical and energy industries. Heterogeneous catalysis has attracted Nobel prizes for Fritz Haber and Carl Bosch in 1918, Irving Langmuir in 1932, and Gerhard Ertl in 2007. In the 21st century, heterogeneous catalysis, which uses small metal particles supported on solid surfaces, became the basis for much of the chemical industry. This field takes prominent position in producing the feed stock for making the synthetic materials that we use every day, from fuels to fertilizers. New experimental techniques have brought fresh insights into this form of catalysis, and now it seems that there are more similarities between enzymes and heterogeneous catalysts. Existing catalyst technologies and trends focus in research for end-of-pipe clean up of pollutant emissions.

1.3 CATALYSIS FOR GREEN CHEMISTRY

It is very important and urgent that the G20 (Group of Twenty) takes on a global governance role in promoting a green recovery. Recent green stimulus of various nations has been surveyed by Edward Barbier, a professor of economics (Barbier 2010). The importance of greening our current global economic-recovery efforts have been highlighted. With that scope, green chemistry is a vital proposal and referred to as sustainable chemistry which involves the design and development of various chemical processes and products that reduce or eliminate the use or generation of hazardous substances. Generally, green chemistry is governed by twelve principles (Anastas and Warner 1998) that are to be followed by a chemist.

Catalysis plays an inevitable role in maintaining the green economy level since most of the industrial products are induced by catalysts. For many years these processes were focused on the basis of product yield without considering the effect of waste and toxicity of by-products and other
intermediates formed during the course of the reaction (Sheldon 1997). Heterogeneous catalysis serves as good alternative for the significant progress of cleaner technologies. Solid acid catalysts are environmentally friendly catalysts for a number of organic reactions (Wilson and Clark 2000) and those came into existence to avoid the use of conventional mineral acids that cause serious damage to the environment. The use of heterogenisation of catalysts and reagents as a method for achieving clean synthesis can lead to considerable reductions in waste produced in organic chemical manufacturing processes. Moreover, solid catalysts are potential in the manufacture of important fine chemicals through liquid phase transformations (Clark and Macquarrie 1997). Owing to the increasingly strict environmental system, researchers have paid more attention to solid acid catalysts to search for stable and eco-friendly catalysts. Multifunctional solids often are catalytically active, e.g. zeolites, alumina and certain forms of graphitic carbon. Among the solid acids, heteropoly acids, sulfated metal oxides, metal oxide impregnated clays, transition metal incorporated mesoporous materials have attracted considerable attention because they are more environmentally benign, and more active and selective for the transformation of hydrocarbons. The chemical modification of mesoporous solids can be used to make a range of catalysts, including solid acids and bases, and stable metal complexes for selective reactions (Clark 2001).

1.3.1 E-Factor

Increasing importance of ecological aspects in industrial transformations demands the design of environmental and ecological processes. Monitoring the environmental accessibility of chemical processes are been done by a specific term called E-Factor. To maintain the environmental factor, synthetic methods have to be planned to maximize the incorporation of all materials used in the process into the final product.
Table 1.1 represents E-Factors obtained across various segments of the chemical industry.

**Table 1.1 E factors in various segment of chemical industry**

<table>
<thead>
<tr>
<th>Industry segment</th>
<th>Product tonnage(^a)</th>
<th>E (kg waste/kg product)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil refining</td>
<td>(10^6 - 10^8)</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Bulk chemicals</td>
<td>(10^4 - 10^6)</td>
<td>&lt; 1 (\rightarrow) 5</td>
</tr>
<tr>
<td>Fine chemicals</td>
<td>(10^2 - 10^3)</td>
<td>5 (\rightarrow) &gt; 50</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>(10 - 10^3)</td>
<td>25 (\rightarrow) &gt; 100</td>
</tr>
</tbody>
</table>

\(^a\)Represents annual production volume of a product at one site (lower end of range) or world-wide (upper end of range)

The simple ratio is units of waste divided by units of product tells us that the lower the E-factor, the less waste is produced. E-factor is defined as kgs waste generated per kg of product (Equation 1.1). Take for example; the E-Factor of the pharmaceutical industry is in the range of 25 to 100 plus kgs. This means that 1 kg pharmaceutical product produced generates 25 kgs to 100 plus kgs of waste. Today, across the world, more than 1 billion kgs of drugs are being manufactured. This gives us an indication of the magnitude waste the pharmaceutical industry generates.

\[
\text{E Factor} = \frac{\text{kg of secondary products}}{\text{kg of desired product}} \quad (1.3)
\]

The substantially higher E factors in fine chemicals and pharmaceuticals compared with bulk chemicals is a reflection of the more widespread use of stoichiometric reagent and multi-step synthesis in the
former steps. Thus, replacement of stoichiometric protocols in those sectors by catalytic methods will help to reduce the E factors in these sectors and thus will help to achieve the objective of green chemistry. Now main research focus is on the use and generation of substance that possess little or no toxicity to human health and the environment. Energy requirements of chemical processes have to be recognized for their environmental and economic impacts and should be minimized.

1.4 SIGNIFICANCE OF HETEROGENEOUS CATALYSIS

Eco-friendly and commercially viable catalyst systems are in demand for selective organic substrates to corresponding value added products. Shortcomings of homogeneous catalytic processes (e.g., short lifetime, lower structural and thermal stability, and difficulties in catalyst separation and recovery) as well as concerns about product purity provoked a turn around research towards heterogeneous catalysis. Heterogeneous catalysis has had a major impact on chemical and fuel production, environmental protection and remediation, and processing of consumer products and advanced materials. In recent years, this field has gained much importance in laboratories and industries because of its good catalytic activity, non-toxicity, low cost and wide range of applications in organic synthesis. With homogeneous catalysts, we have more precise control over the local molecular structure. Unlike heterogeneous catalysts, the reaction sites can be uniform and, thus, are more selective for the desired products of a catalytic reaction. In this case, there are several problems to overcome to achieve a good reaction. First, anchoring or incorporation or impregnation of the metal catalyst or homogeneous forms to the support and get it to stay attached. Second, once attached, it must be convinced to remain intact and behave as it did before. Overall, design of heterogeneous system intends to achieve a separable, active and stable catalyst.
Vastly processed acid/base catalytic systems are based on promoting the reactions with economic sense in industries and now many reactions have been run over heterogeneous type catalysts under simple conditions in the liquid phase as well as in the vapour phase with feasible environmental sense. Heterogeneous catalysis moves under this notion and has been widely investigated on solid acid catalysts such as inorganic supports, including porous materials, metals and layered compounds. Generally, this type of catalysts offer several advantage such as short reaction times, mild reaction conditions, high selectivity and the ease of work-up procedure. There are increasing restrictions on the use of traditional stoichiometric and conventional homogeneous catalytic processes because of their inherent problems. This has accelerated the tendency to shift toward more viable alternatives which offers the advantages of simple separation and easy recovery, reuse, waste reduction, and elimination of hazardous chemicals, in addition to their use in both liquid- and gas-phase operations. Modified forms of porous materials possess these advantages and can play a key role in the development of environmentally benign processes in chemical industry as well as in the production of chemicals from biomass.

1.5 POROUS MATERIALS

Porous inorganic solids have found great utility as catalysts and sorption media because of their large internal surface area, i.e. the presence of voids of controllable dimensions at the atomic, molecular, and nanometer scales. International Union of Pure and Applied Chemistry (IUPAC) classifies porous materials into three categories: microporous with pores of less than 2 nm in diameter, mesoporous having pores between 2 and 50 nm, and macroporous with pores greater than 50 nm (Sing et al 1985) as given in Table 1.2. The term nanoporous materials have been used for those porous
materials with pore diameters of less than 100 nm. The main challenges in research of nanoporous materials include the understanding of structure-property relations and tailor-design of nanostructures for specific applications. A substantial progress has been made in the control of the pore shape and sizes and active sites activity and distribution.

**Table 1.2 Classification of porous materials**

<table>
<thead>
<tr>
<th>Class</th>
<th>Pore diameter (Å)</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microporous</td>
<td>&lt;20</td>
<td>Zeolites, VPI-5, microporous AlPOs and SAPOs, pillared clays, etc.,</td>
</tr>
<tr>
<td>Mesoporous</td>
<td>20-500</td>
<td>MCM-41, MCM-48, MCM-50, mesoporous metal oxides, mesoporous carbon, mesoporous AlPOs, SAPOs, SBA-1, SBA-15, KIT-5, KIT-6, etc.,</td>
</tr>
<tr>
<td>Macroporous</td>
<td>&gt;500</td>
<td>Porous gels, porous glasses, etc.,</td>
</tr>
</tbody>
</table>

### 1.5.1 Zeolites

Zeolites are crystalline minerals that are broadly present in nature and have been known to mankind for almost 250 years. It was the Swedish mineralogist Axel Fredrick Cronstedt in 1756 who discovered that the natural occurring mineral, nowadays known as stilbite, lost large amounts of steam upon heating. Therefore he named the material ‘zeolite’ which emerges from the classical Greek, where (zeo) means ‘to boil’ and (lithos) means ‘stone’. Since then the nomenclature of this kind of porous material seems to be ambiguous. The success of synthetic crystalline aluminosilicates, in particular the emergence of the new family of aluminophosphates (Wilson et al 1982)
and silicoaluminophosphates (Lok et al 1984), made the concept of zeolite and molecular sieves more intricate. In a broad sense, zeolites are molecular sieves. Strictly speaking, zeolites are crystalline aluminosilicates with molecular sieve properties inside which are organized by small channels or pores (Newsam 1986). Zeolite structures consist of silicon cations (Si\(^{4+}\)) and aluminum cations (Al\(^{3+}\)) that are surrounded by four oxygen anions (O\(^{2-}\)). Each oxygen anion connects two cations and this yields a macromolecular three-dimensional framework, with net neutral SiO\(_2\) and negatively charged AlO\(_2\) - tetrahedral building blocks with Bronsted and Lewis acid sites. The negative charge arises from the difference in formal valency between the silicon and aluminum cations, and will be located on one of the oxygen anions connected to an aluminum cation. Commonly, the negative charge is compensated by additional non-framework cations like sodium (Na\(^+\)), which is generally present after the synthesis of the zeolite.

The most known zeolites are silicalite-1, ZSM-5, zeolite Beta and zeolites X, Y, and A. The incorporation of small amounts of transition metals into zeolitic frameworks influences their properties and generates their redox activity. They can impart shape selectivity for both the reactants and products when involved in the chemical reactions and processes (Corma 1995). Their intricate channel structure allows the zeolites to present different types of shape selectivity which can be used to direct a given catalytic reaction toward the desired product avoiding undesired side reactions.

In catalysis, the medium-and large-pore zeolites have found particular applications. The geometry and dimensionality of the zeolite channels are decisive in shape-selective adsorption and catalysis on zeolites. This phenomenon arises from the well-defined sterically constrained inner environment of zeolites, in which the reactants interact and diffuse into or out of the zeolite pores. Three principal types of molecular sieve shape selectivity
have been defined: (a) reactant selectivity allows or prevents penetration of reactant molecules into zeolite channels; (b) restricted transition-state selectivity prevents the formation of bulky reaction intermediates; and (c) product selectivity preferably enables smaller products to easily diffuse from the channels compared with larger molecules, which are held in the zeolite interior. Zeolites are extremely successful as catalysts for oil refining, petrochemistry, and organic synthesis in the production of fine and specialist chemicals (Clerici 2000, Corma and Martinez 2005, Degnan 2000 and Marcilly 2000) particularly when dealing with molecules having kinetic diameters below 10 Å. In many cases the low effective diffusivity in zeolite crystals limits the reaction rate and yields rather high values for the diffusional time constant. Due to the relatively small size of the pore of zeolite and zeotype materials, much effort has been devoted to the development of new materials with pores larger than 1.5 nm (Corma 2006). The absence of such materials significantly limits the possibilities of upgrading of crude oil and transformations of numerous bulky compounds, particularly in the field of fine chemicals and chemical specialties.

Numerous strategies for preparation of new materials that combine the advantages of mesoporous materials with those of zeolites have been developed. The first mesoporous zeolite single crystal (ZSM-5) was synthesized by Jacobsen et al. and since that time a particular attention has been devoted to characterization of this material (Jacobsen et al 2000 and Boisen et al 2003). Despite these catalytically desirable properties of zeolites they become inadequate when reactants with sizes above the dimensions of the pores have to be processed. In this case the rational approach to overcome such a limitation would be to maintain the porous structure, which is responsible for the benefits described above, but to increase their diameter to bring them into the mesoporous region. The strategy used to do this was based on the fact that most of the organic templates used to synthesize zeolites
1.5.2 Need for Mesoporous Materials

As discussed above, zeolites are limited to pore sizes of ~15 Å and their applications are limited by the relatively small pore openings; therefore, pore enlargement is one of the main aspects in zeolite chemistry. Materials characteristics similar to zeolites but with larger pores would be very useful in many applications. It was recognized that a need in the area of synthesizing ordered mesoporous materials would complement to the requirements, whose magnitude are generally investigated. The only restrictions imposed were that the pores must be ordered, accessible, and have free diameters of less than 50 nm (generally accepted range for microporous and mesoporous materials). However, compared with conventional zeolites, these mesostructured materials have relatively low acidity and hydrothermal stability, which severely hinders their practical applications in catalytic reactions for the petroleum industry. To improve the hydrothermal stability of mesoporous materials, considerable efforts have been put into this area and some encouraging results have been reported in literature. A chance of overcoming diffusion limitation in zeolite micropores is the generation of mesopores, i.e. pores with a diameter between 2 and 50 nm (Karger and Ruthven (1992)).

In general, the mesoporous heterogeneous catalysts exhibit several advantages compared with the homogeneous catalysts due to their importance in practical productions of chemicals from the viewpoints of the so-called “zero-emission” or “green” chemistry and ease of separation from the reaction mixture. Mesoporous materials of M41S family possess various physico-chemical properties such as:

affect the gel chemistry and act as void fillers in the growing porous solids. Great synthetic efforts led to the preparation of mesoporous molecular sieves of various compositions, structures and pore sizes.
- High surface area (>1000 m²/g)
- Tunable pore size (20 to 100 Å)
- Large pore volumes (>0.6 cm³ g⁻¹)
- Thermal stability up to 800°C in dry atmosphere
- Higher Hydrothermal stability

In addition mesoporous materials were found to have well-defined pore shapes (hexagonal/cylindrical), narrow distribution of pore sizes, negligible pore networking or pore blocking effects, very high degree of pore ordering over micrometer length scales, exceptional sorption capacity, large amount of internal hydroxyl (silanol) groups (40-60%), ease of modification of the surface properties, enhanced catalytic selectivity in certain reactions and good chemical and mechanical stability. These prominent properties attracted much attention in catalysis and nanoscience. They are likely to offer improved reaction selectivity in the conversion of larger substrate molecules in their well-defined channels with narrow pore-size distribution. The larger pore dimensions and the acidity of metal or acid functionalised mesoporous materials serves as good catalysts for fine chemical synthesis. Focus was brought on the comparison of their catalytic properties towards organic synthesis. In addition, they were also compared with the catalytic activities of microporous zeolites and commercial catalysts. Apart from catalysis, mesoporous materials find its importance in synthesizing many other metal based mesostructures with excellent properties.

1.6 M41S FAMILY

Recent developments in materials chemistry has led to the discovery of the M41S family of mesoporous molecular sieves offering pore sizes in the range 20-100 Å (Kresge et al 1992). This family of materials
generically called M41S involves the formation of mesoporous silicate and aluminosilicate molecular sieves with liquid crystal templates and have large channels from 1.5 to 10 nm ordered in a hexagonal, cubic and lamellar array. These three different mesophases of M41S family are shown in Figure 1.1 (Biz and Occelli 1998).

![Hexagonal MCM-41, Cubic MCM-48, Lamellar MCM-50](image)

**Figure 1.1** Mesophase structure of M41S family

The members of the M41S family were synthesized using the organic-template-assisted synthesis approach, in which, instead of individual organic molecules typically used in zeolite synthesis, self-assembled molecular aggregates or supramolecular assemblies were used as structure-directing agents (Roth and Vartuli 2005). The molecular sieves with well-defined pores up to about 30 nm in diameter broke down pore-size constraints of zeolites and zeolite-like materials. The high surface areas, tunable pore sizes, and variable wall composition are desirable properties that made these materials centre of interest in heterogeneous catalysis applications.

1.6.1 **Synthesis Methodologies**

The design, synthesis and modification of mesoporous silica materials are challenging and many synthesis methods have been proposed to
control the textural properties. The system with a two dimensional hexagonal array of pores, known as MCM-41, is the most important member of the M41S family, with p6mm symmetry space group. The typical synthesis involves the addition of acid or alkali to aqueous solution containing silica or silica-metal source (e.g., sodium silicate, fumed silica, or tetraethylorthosilicate as the silica source) for the formation of gel (pH 8-11). Then the solution of micelle-forming surfactant (e.g., long-chain quaternary ammonium halides) is added under constant stirring. A variety of self organized surfactant molecules were employed for the synthesis (e.g., \( \text{C}_n\text{H}_{2n+1}(\text{CH}_3)_3\text{N}^+ \) (\( n = 8-22 \)) or \( \text{C}_n\text{H}_{2n+1}-\text{C}_5\text{H}_5\text{N}^+ \) (\( n = 12 \) or 16)) which have a hydrophilic (water-soluble) head group and a hydrophobic (water insoluble) tail group. Over the extended period of time, the silica condenses to form a siloxane framework. Then the resultant gel is hydrothermally treated (between 70 and 150 °C) for fixed period of time followed by filtration, drying and calcination at appropriate temperature.

Many alternative synthesis procedures were adopted for the preparation of MCM-41 in order to obtain highly ordered structures with good desirable textural properties. The synthesis conditions were performed by varying the temperature, time, acid/base medium, silica-surfactant ratio and by changing the silica or surfactant source. Synthesis of mesoporous silica in alkaline medium was first reported by Kresge et al (1992). Huo et al (1994) reported the modified synthesis of periodic surfactant/inorganic composite Materials. Mesoporous siliceous MCM-41 (Edler and White 1995, Steoguchi et al 1997 and Voegtlín et al 1997) and metallosilicate MCM-41 has also been synthesised at room temperature (Chatterjee et al 1998, Chatterjee et al 1999 and Chatterjee et al 2000). The compound showed similar characteristics to hydrothermally synthesised materials. They have also reported the
characterisation of V-MCM-41 and Ga-MCM-41 synthesised at room temperature. The structure of mesoporous materials can be altered by varying the surfactant/SiO$_2$ ratio (Beck et al 1993). It was observed that the final phase of formation of the material is affected by many different factors such as surfactant/silica ratio, surfactant concentration (Koyano and Tatsumi 1996), surfactant chain length (Ulagappan and Rao 1996), synthesis temperature, source of silica, presence of extraneous cations such as Na$^+$, and post synthesis hydrothermal treatment (Huo et al 1996 and Stucky et al 1997). Microwave assisted preparation of high quality hexagonal mesoporous materials with good thermal stability and smaller crystal size were done by heating precursor gels in the microwave at 150ºC for 1 h or even less (Wu and Bein 1996). Huo et al (1994a) reported the synthesis of mesoporous silica under acidic conditions and Tanev and Pinnavia (1995) proposed the synthesis by using neutral inorganic species as template. Mesoporous materials obtained from neutral templating mechanism are named as ‘hexagonal mesoporous silica’ (HMS).

1.6.2 Mechanism for the Formation of M41S Materials

Several models have been proposed to explain the mechanistic route of mesostructure formation. At basic level, all these models suggest that, surfactant supramolecular assemblies provides template structure and this finally leads to the formation of pore structure in the inorganic matrix. Considering different mode of interaction of inorganic precursors with surfactants, several models have been proposed. In general, mesoporous materials are formed by four different mechanisms, viz., liquid crystal templating (LCT), co-operative selfassembly (CSA), folded sheets (FS) and Neutral templating (NT).
All the proposed mechanisms mainly includes three principle stages: (i) the molecular level, which involves the interaction between the organic and the inorganic precursors and the silica polymerization process; (ii) the mesoscopic scale, which involves the development of the micellar structure and the onset of the long-range order; and finally (iii) the macroscale which is related to the shape/morphology of the final material. The mechanism initially involves the adsorption of silicate ions at the micellar interface and this leads to the ordered phase. This ordered phase results by two considerations such as; a) the process changes the morphology of the micelles followed by condensation of silicate covered micelles into ordered or disordered phase and b) the process (silicate adsorption) does not change the morphology of the micelles but rather reduces the intermicellar repulsion (Firouzi et al 1995). This causes aggregation into larger particles and precipitation of a disordered phase, which then may rearrange to form an ordered phase.

1.6.2.1 Liquid crystal template mechanism

A liquid crystal templating mechanism (LCT) in which surfactant liquid crystal structures serves as organic templates has been proposed for the formation of M41S materials (Kresge et al 1992). Related mechanisms have been proposed for a number of systems in which inorganic structures of widely varying morphologies are deposited in the presence of preformed micellar arrays or micellar structures, as, for example, in the biochemical formation of bones and shells from 40 different materials (Heuer et al 1992).

The formation process involves two possible mechanistic pathways (Figure 1.2) (Beck et al 1992): (1) the liquid crystal mesophases may form prior to the addition of silicate species; (2) the silicate species added to the reaction mixture may influence the ordering of the isotropic rod-like micelles
to the desired liquid crystal phase, i.e., hexagonal mesophase. Therefore, the mesophase formed is structurally and morphologically directed by the existing liquid crystal micelles and/or mesophases. The behaviour of the surfactant in binary surfactant/water systems is the key for the controlled preparation of silica mesostructures. The LCT mechanism has been further confirmed by subsequent reports (Chen et al 1993, Beck et al 1992b and Vartuli et al 1994). Vartuli et al (1994) studied the effect of surfactant/silica molar ratio on the resultant phases in a simple system containing alkali metal, tetraethylorthosilicate, water, and CTAOH at 100°C. They found that as the surfactant/silica molar ratio increased from 0.5 to 2, the siliceous products obtained could be classified into four separate groups: MCM-41 (hexagonal), MCM-48 (cubic), thermally unstable lamellar phase, and the cubic octamer [(CTMA)SiO$_{2.5}$]$_8$. This was agreement with the behavior of surfactants in solution as proposed in previous works by Myers (1992) (Figure 1.3).

**Figure 1.2** Schematic model of liquid crystal templating mechanism via two possible pathways

Chen et al. (1993a) employed various techniques like XRD, $^{29}$Si NMR, in situ $^{14}$N NMR, and thermogravimetric analysis (TGA) to
confirm the mechanism. Hexagonal liquid crystalline mesophases were not detected either in the synthesis gel or in the surfactant solution used as template. This was confirmed by a later study (Steel et al 1994) and the LCT mechanism seems to be plausible for the formation of mesoporous silicates of MCM-41 type which was evident with the existence of crystalline mesophases during the process.

Figure 1.3 Phase sequence of surfactant-water binary system

1.6.2.2 Charge density and folded sheet mechanism

The phase transformation involved in the formation of hexagonal phase was explained by Monnier et al (1993) on the basis of charge density concept (Figure 1.4). It was observed that MCM-41 can be synthesized at low surfactant concentration (1 wt.%) and they proposed that the formation of surfactant-silica composite involves three steps;

i) Oligomeric silicate poly-anions act as multidentate ligands resulting in the interaction of surfactant-silica interface with lamellar phase
ii) Polymerization of silicates occurs at the interface by the reduction of negative charge at the interface region.

iii) Finally the charge density matching leads to the formation of surfactant-silica composite which in turn transforms to the hexagonal phase.

Figure 1.4  Hexagonal mesophase obtained by charge density matching mechanism

An alternative synthesis pathway was described by Yanagisawa et al (1990) for preparing mesoporous silicate from a layered silicate, kanemite, which consists of single layers of SiO$_4$ tetrahedra. This material was designated as FSM-16 (Folded Sheet Mesoporous Materials). The preparation was similar to MCM-41 using a layered silicate as silica source. For this model a ‘‘folded sheet’’ mechanism was proposed (Inagaki et al 1993) according to which the layered organic-inorganic composites are formed by intercalation of the layered silicate using surfactants. Figure 1.5 (Inagaki et al 1993) depicts the schematic model representing the "folded sheets" mechanism. The transformation to the hexagonal phase occurs during the hydrothermal treatment by condensation of the silanol groups. Even though MCM-41 and FSM-16 are similar; they possess slightly different properties in adsorption and surface chemistry.
1.6.3 SBA-n Materials

Although a majority of the studies have focused on MCM-41, there has been continued interest in developing new mesophases. A number of reviews have appeared on various aspects of different mesoporous materials. Among them, large pore size materials such as the SBA-family (SBA-11, SBA-12, SBA-15 and SBA-16) were synthesized in acidic medium using non-ionic surfactants having polyethylene oxide (PEO) units. Extensive research studies led to the synthesis of many framework structures such as SBA-1, SBA-2 and SBA-3 by employing cationic surfactants; they are mediated by $S^0H^+X^-I^+$ or by $S^+X^-I^+$ type mechanism, where $S^0$ is non-ionic surfactant; $S^+$ is cationic surfactant, $X^-$ is anion and $I^+$ is silicate species. $X^-$ mediation decreases the interaction between silicate species and the template as the template removal does not affect the structure of the material. The hexagonal mesoporous SBA-15 is one of the most important ordered mesoporous silica synthesized after MCM-41. The synthesis of SBA-15 was reported by Zhao et al (1998), Zhao et al 1998a and Clerc et al (2000) and these materials exhibits a significant amount of disordered micropores and small mesopores. The volume and size of these complementary pores were found to be dependent to some extent on the synthesis/aging temperature (Kruk et al 2000). SBA-15 materials were synthesized in acidic media to produce highly ordered, two-dimensional hexagonal (space group $p6mm$)
mesoporous silica. It has attracted considerable attention because of its high structure regularity, thick inorganic walls, and excellent thermal and hydrothermal stability, its low-cost and nontoxic template, and because the synthesis method is simple and reproducible. In addition, one of the interesting properties of SBA-15 is the coexistence of meso- and micropores. The source of the microporosity has been ascribed to PEO chains that are trapped in the silica network during the synthesis and are removed by calcination, leaving open micropores (Ryoo et al 2000, Imperor-Celrc et al 2000 and Ruthstein 2003).

### 1.6.4 KIT-6 Materials

Very large pore silica with bicontinuous body-centered (Ia3d) cubic symmetry was first reported by Kleitz et al (2003) and the material was designated as KIT-6 (KAIST). In contrast to MCM-48, these two intertwined systems of relatively large channels in KIT-6 can also be connected through irregular micropores present in the mesopore walls analogous to those in SBA-15. The structure of Ia3d cubic phase in KIT-6 silica is shown in Figure 1.6 (Alfredsson and Anderson 1996).

![Figure 1.6 Structure of KIT-6 silica (Ia3d Cubic Phase)](image-url)
Mesoporous materials consisting of interconnected large cage-type pores (>5 nm), organized in a three-dimensional network, are expected to be superior to hexagonal structures with one-dimensional channels for applications involving selectively tuned diffusion, immobilization of large molecules, or host–guest interactions in nanostructured materials (Alfredsson et al 1996 and Sakamoto et al 2004). However, mesoporous materials with cubic symmetry are usually more difficult to prepare than the 2D hexagonal counterparts, and they can be obtained only in a narrow range of synthesis mixture compositions (Alfredsson et al 1996 and Voort et al 2002). The bicontinuous body-centered (Ia3d) cubic mesostructured silica with large pores can be obtained using additives such as inorganic salts and anionic surfactants with or without a swelling agent. Ryoo and co-workers reported a simple synthesis route to high-quality cubic Ia3d silica, using Pluronic P123 and n-butanol at low acid conditions (Kleitz et al 2003, Kleitz et al 2003a and Kim et al 2005). The advantage of this synthesis is its high reproducibility and the relatively large range of compositions that produce the ordered cubic phase. For a number of synthesis procedures of the bicontinuous cubic phase, it was reported that variation in the relative amounts of additives can lead to a transition from 2D hexagonal to cubic material (Chen et al 2005, Chen et al 2006 and Kleitz et al 2003). A typical synthesis of KIT-6 by Kleitz et al (2003) involves the use of P123 (Pluronic 123, a triblock co-polymer) as the template and butanol as co-solvent under acidic conditions (conc. HCl) with the use of TEOS as silica source. The formation of cubic phase could be better explained in monitoring each step involved in the synthesis.

1.6.4.1 Mechanism for the Formation of Ia3d Cubic Mesoporous Silica

(KIT-6)

KIT-6 mesoporous materials with Ia3d symmetry are synthesized via a surfactant-assisted formation process which can proceed either in
concentrated or in dilute surfactant solutions. The meso-structures with block copolymers were initially reported by Zhao et al (1998). These have the attractive properties of larger pore diameters, thicker walls, and higher stability than the M41S family of structures. Block copolymers are used in the synthesis of many of the SBA materials. Also diblock copolymer (EO<sub>m</sub>MA<sub>n</sub>) Poly(ethylene oxide)-b-poly(methyl acrylate) prepared via an atom transfer radical polymerization (ATRP) approach was used as a template to synthesize Ia3d mesostructured silica with thick walls under acidic conditions (Chan et al 2002). Triblock copolymers (Pluronics) are found to be adaptable in these syntheses as these polymers have a central polypropylene block surrounded by polyethylene blocks ((EO)<sub>x</sub>-(PO)<sub>y</sub>-(EO)<sub>x</sub>). Also for the SBA materials it is the hexagonal form that has attracted the largest interest. Pluronics show an anomalous temperature behavior, which is manifested as an increase in the hydrophobicity of the polymer as the temperature is raised. In an aqueous solution, this will eventually lead to association of the polymers and phase separation.

The synthesis conditions in mesoporous silica formation vary depending on the chain lengths of the different polymer blocks of the Pluronics. Also, the chain lengths dictate the conditions for the type of meso-structure that will form (Kipkemboi et al 2001). An important synthesis parameter is the temperature, largely due to the temperature sensitivity of the polymers. A raise in temperature can for certain Pluronics alter the behaviour to such an extent that the resulting silica will have a different structure. This has been shown to occur for Pluronic P123 and P103, which normally will assist in forming a 2D hexagonal structure but at higher temperature will direct the structure toward a multi-lamellar vesicle-like phase (Flodstrom and Alfredsson 2003). Based on these studies, variety of meso-scale structures was developed by changing the surfactant source, temperature, time, acid concentration, addition of inorganic salt etc.
The mechanism of cubic KIT-6 structure is interesting because of their fascinating formation system. Only few reported the mechanism of this type of materials. Ruthstein et al (2008) summarized the observations to explain the process in detail. Considering the basic formation mechanism of mesoporous materials, the KIT-6 formation was studied under various circumstances. Synthesis of KIT-6 at different time intervals (Kim et al 2005) helped in understanding the process and the SAXS measurements showed that the cubic phase is formed via a transformation from a lamellar phase. This was later supported by Ruthstein et al (2008) and their results claimed that the formation of the cubic phase occurs through a formation of mesophase with a lower curvature, lamellar or hexagonal bicontinuous cubic phase which is formed through an intermediate structure with a higher curvature.

Role of butanol is important in the synthesis of KIT-6 material. Butanol is known to act as a co-solute in block copolymer-water systems, which combines with the block copolymer and stabilizes apolar–polar interfaces, determining the micellar interfacial curvature. The investigations by Kim et al (2005) suggested that the cubic phase is formed at a certain low acid concentration and a certain range of butanol concentration. The experiments were carried out at a fixed amount of TEOS by increasing the amount of butanol and resulted in a transition from 2D hexagonal to Ia3d cubic mesophase, and further increase in butanol leads to a distorted phase. In addition, at fixed butanol and TEOS concentrations, an increase in the acid amount yields a transition from cubic to hexagonal phase.
Overall studies obtained from various characterizations like SAXS, EPR measurements, ESEEM (Electron Spin-Echo Envelope Modulation) measurements and cryo-TEM with time study concluded and arrived to explain a different mechanistic pathway. Further studies were carried out by Ruthstein et al (2008) which revealed that addition of butanol to a reaction mixture of SBA-15 generates the Ia3d cubic phase after the formation of the hexagonal arrangement before the whole polymerization of silica. The significance of butanol in the phase transformation from hexagonal to cubic is evident with this observation. Also the results showed that the amount of acid is not critical, and even at high acid concentration as in the SBA-15 synthesis, the cubic phase forms. However, the rate of silica hydrolysis and condensation and the rate of formation of the hexagonal phase are induced by the amount of acid (Ruthstein et al 2006). It was suggested that butanol was not essential in the earlier stages of the reaction and the role of butanol was
crucial after the formation of the hexagonal phase. Precipitation occurs after the addition of TEOS and the intermediate formation of spheroidal micelles or short thread-like micelles (TLM) was observed with free fracture replication (FFR) rather than cryo-TEM technique. Reaction time was the important factor in predicting the possible mechanism and at certain time intervals; SAXS was performed for the phase identification. The overall process involves the following conclusions; the addition of butanol results in swelling of TLMs and causes hydration as the flow of water molecules is rapid to the corona (PEO chain). Five main stages were resolved on the addition of TEOS (Ruthstein et al (2008)); (1) 0-50 min: initially spheroidal micelles are present, and condensation of the silica oligomers takes place at the micellar/water interface and within the corona, causing a depletion of water. (2) 50-140 min: water depletion, appearance and aggregation of TLMs take place during this period. (3) 140-160 min: Precipitation occurs and the core of the aggregated TLMs becomes more hydrophobic. The size of the aggregates reduces, while the size of the PEO increases. (4) 160-350 min: depletion of water and butanol from the corona is large and the core size increases. The aggregated TLMs transformed into a hexagonal structure. (5) 6-24 h: Transition from hexagonal to cubic phase occurs during this time without any changes on the molecular level.

Omer et al (2009) investigated the last stage of the formation of the cubic material, namely the transformation from the hexagonal phase by cryo-electron microscopy techniques. The suggested mechanism of KIT-6 formation is represented in Figure 1.7 (Omer et al 2009). It was shown that the main role of the butanol is in curvature lowering after the formation of the hexagonal phase (Omer et al 2009). First, a hexagonal phase is formed, that further evolves into a perforated lamellar phase through cylinder merging. The final bicontinuous cubic structure evolves within the layers. The studies included the prediction of another minor mechanism involving the direct
transition between the hexagonal to the final cubic phase through cylinder branching.

1.7 MODIFICATION OF MESOPOROUS MATERIALS

Siliceous mesoporous materials possess neutral framework, which limits their applications in catalysis, but they have great utility as adsorbents, molecular sieves, and supports. Ion-exchange, catalytic and adsorptive properties of molecular sieve materials originate from acid sites which arise from the presence of accessible hydroxyl groups associated with tetrahedral framework aluminium in a silica matrix (Corma et al 1994 and Luca et al 1996). Silicon is tetrahedrally bonded (Si\(^{4+}\)) to four bridging ‘O’ atoms, and consequently cannot show cation exchange properties. On the other hand, the siliceous materials can easily be modified by incorporation of hetero ions into the silicate framework, thereby creating catalytically active sites (Figure 1.7a and Figure 1.7b). More number of acid sites can be generated by isomorphous substitution of trivalent cations of boron, aluminum, gallium, and iron for tetravalent silicon in the mesoporous matrix.

1.7.1 Transition Metal Supported Mesoporous Materials

Modified mesoporous silica can be achieved either by direct synthesis or by post-modification. Much effort has been devoted to the introduction of various metals into silica frameworks starting with MCM-41. Typically, different metals (M = Al, Fe, Zn, Sn, Ga, La, Ti etc.) are incorporated into the framework of a silicate material by “direct synthesis” procedure in which an aluminium precursor is added into the gel prior to hydrothermal synthesis. This direct synthesis method often requires specialized synthesis conditions depending on the respective structures of the
materials. The nature of the acid sites and structure of porous materials are shown in Figure 1.8a and Figure 1.8b respectively.

![Figure 1.8a Nature of acid sites in porous solid silica](image)

Other types of mesoporous materials like SBA-15 and KIT-6 are hydrothermally synthesized in strong acidic media. Since most aluminium sources dissolve in strong acids, precipitation to incorporate framework aluminium into SBA-15 or KIT-6 by direct synthesis seems unlikely under strong acidic conditions. Under such acidic conditions, free aluminium species (Al\(^{3+}\)) only exist in cationic form and thus cannot enter the framework of SBA-15 by conventional synthesis. There is an easy dissociation of Al–O–Si bond under acidic hydrothermal condition and the remarkable difference between the hydrolysis rates of silicon and aluminium alkoxides makes it much more difficult for direct synthesis of Al-SBA-15. Condensation of silicon and aluminium alkoxides becomes much harder due to these effects. Selvam et al (2010) reviewed various strategies adopted for the aluminium incorporation in SBA materials.
Grafting method or post synthesis method is opted for the incorporation of metals over such silica supports. Earlier studies have shown that aluminium can be effectively incorporated into mesoporous siliceous MCM-41 materials via various post-synthesis procedures by grafting aluminium onto MCM-41 wall surfaces with anhydrous AlCl₃ (Ryoo et al 1997) or aluminium isopropoxide in non-aqueous solution, (Mokaya et al 1997) or with sodium aluminate in aqueous solution (Hamdan et al (1996)) followed by calcination. All of these sources were used for the alumination of SBA-15 by Luan et al (1999). The authors claimed that the materials produced via these post-synthesis procedures have superior structural integrity, acidity and catalytic activity to those of materials having aluminium incorporated during synthesis. By post-modification, it is possible to sophisticatedly design and synthesize custom-tailored materials. For example, post-silylation can drastically improve the hydrothermal stability and

Figure 1.8b  Structure of pure silicates and metallosilicates
mechanical stability of mesoporous materials due to enhanced surface hydrophobicity.

1.7.2 Heteropoly Acid Supported MCM-41

A heteropoly acid is a class of acid made up of a particular combination of hydrogen and oxygen with certain metals and non-metals. This type of acid is frequently used as a re-usable acid catalyst in chemical reactions. Keggin with the use of X-ray diffraction experimentally determined the structure of $\text{H}_3[\text{PW}_{12}\text{O}_{40}]\cdot5\text{H}_2\text{O}$ (Keggin 1934). The Keggin structure accounts for both the hydrated and dehydrated $\alpha$-Keggin anions without a need for significant structural change. This structure contained 12WO$_6$ octahedra linked by edge and corner sharing, with the hetero atom occupying a tetrahedral hole in the centre as shown in Figure 1.9 (http://en.wikipedia.org/wiki/Heteropoly_acid Oct 2012). Later, Dawson (1953) reported the next two structures (now frequently referred to as the Wells-Dawson structure) of 18:2 heteroploy anion [$\text{P}_2\text{W}_{18}\text{O}_{62}$]$^6$. Heteropoly acids are much stronger than the oxoacids of constituent elements and ordinary mineral acids.
Figure 1.9  Heteropolyanion with the Keggin structure, PW$_{12}$O$_{40}^{3-}$.

Heterogeneous acid catalysis by HPAs has the potential of a great economic reward and green benefits. The acidity of HPAs is stronger than that of the conventional solid acid catalysts (e.g., acidic oxides and zeolites), decreasing in the order: $\text{H}_3\text{PW}_{12}\text{O}_{40} > \text{H}_4\text{SiW}_{12}\text{O}_{40} > \text{H}_3\text{PMo}_{12}\text{O}_{40} > \text{H}_4\text{SiMo}_{12}\text{O}_{40}$ (Okuhara et al 1996, Kozhevnikov 1998 and Kozhevnikov 2002). In organic media, the stepwise dissociation is often observable, and the acid strength measured in acetone has been found to show the following order: $\text{PW}_{12} > \text{PW}_{11}V > \text{PMo}_{12} \approx \text{SiW}_{12} > \text{PMo}_{11}V \approx \text{SiMo}_{12} >> \text{HCl, HNO}_3$ (Kozhevnikov and Matveev 1983). Small surface area ($<10 \text{ m}^2/\text{g}$) of these nonporous heteropoly acid materials is to some extent less effective for reactions involving large molecules. The solution to this predicament may be to impregnate heteropoly acid onto a solid support material with a large surface area. Many types of supports have been chosen for effective impregnation of heteropoly acid and those includes silica, alumina, resin, active carbon, clays, and microporous zeolites (Nowinska et al 1991,
Cheng et al 1988, Rao et al 1989 and Mastikhin 1995. Their non-uniform pore size and relatively small surface area limit their potential for catalyzing bulky molecules because of diffusion problems. In particular, incorporation of HPA into zeolite pores to obtain shape selective catalysts has long been a challenge. However, conventional zeolites are not suitable for this because their pores are too small to adsorb large (12 Å) HPW molecules (Kozhevnikov 1998). The supports also influence the acidity and catalytic activity of HPAs. It has been found that the basic solids like MgO (Misono et al 1987, Izumi et al 1983) and Al$_2$O$_3$ (Pizzio et al 1999) tend to decompose the HPAs, causing a significant decrease in their catalytic activities.

Mesoporous silica materials possessing large surface area (typically 1000 m$^2$/g) and uniform large pore size overcome the limitations caused by other carriers as the silica is the most often used support since it is relatively inert towards HPAs. Among those, M41S materials are excellent supports for preparing bifunctional catalysts and for expanding the catalytic capability of traditional acidic materials for specific applications. Mesoporous silica molecular sieves are considered to be ideal supports for HPAs compared with zeolites. The pores are large enough for HPA molecules to enter their mesoporous channels. Loading of HPAs on mesoporous silica not only allows transfer of HPA-catalysed reactions from homogeneous to heterogeneous systems to avoid the difficulty in catalyst separation, but also effectively increases the surface area of HPAs. Kozhevnikov et al (1995) prepared HPWA supported on a novel mesoporous molecular sieve MCM-41. They observed that HPW retains the Keggin structure on MCM-41 surface at an HPW loading above 20 wt. %. HPWA forms finely dispersed species on the MCM-41 surface and there is no HPWA crystal phase seen at HPWA loadings as high as 50 wt. %. Other mesoporous supports, including SBA-15, were also used for this purpose and the formation and catalytic performances
of SBA-15 supported solid heteropoly acid/zirconia have been studied by Dhanashri et al 2005, Dhanashri et al 2007).

The deposition of HPW on mesoporous silica is an efficient way to decrease the abundance of surface hydroxyls to a large extent. Xia et al (2002a) explained the structure, acidity and catalytic activity of HPW/MCM-41 materials. The work revealed that the dispersion and interaction of HPW over Si-MCM-41 resulted in the decrease in the relative coverage of surface hydroxyls, from 100% for Si–MCM-41 to 29.0% for pure HPW as shown in Figure 1.10 (Xia et al 2002a). It was observed that continuous increasing HPW loading further enhanced the hydrophobicity property of the HPW/MCM-41 materials.

![Figure 1.10 Dispersion and interaction of H$_3$PW$_{12}$O$_{40}$ over Si-MCM-41](image)

Heteropoly acid supported mesoporous materials have been used mainly in catalysis towards the synthesis of fine chemicals. It is considered to be important that on recycling the catalysts leaching of the heteropoly acid is suspected leading to relative loss in activity. 12-Phosphotungstic acid simply impregnated onto porous carriers leads to severe leaching of active species in a polar reaction medium. Thus, efforts have been made to prepare the water-tolerant supported heteropoly acid catalysts. Alumina grafted silica supported PW showed no leaching in methanol solution was reported by Rao et al. (2004). Pizzio et al (2003) revealed that PW supported on Si-MCM-41 and
functionalized SiMCM-41 exhibited low or negligible solubility in the mixture of ethanol and water. Izumi et al (1995) and Kukovecz et al (2002) found the occlusion of PW in the pore of silica by a sol–gel procedure prevented its leaching; Sulikowski et al encapsulated PW in the supercage of Y zeolite by a “ship-in-the-bottle” method and the catalyst acted as the solid acid in the liquid phase (2003).

Recently, important advances in the improvement in acidity and stability of mesoporous materials have been made through the modification considering the nature of the supports (2 dimensional or 3 dimensional pore system). Particularly important fact is that the reliability and activity of the modified materials, which is exactly that required for the manipulation of fine chemicals. It is becoming possible to design solid catalysts whose physical characteristics can be altered for the intended application. While much effort has been currently expended on acid modified larger pore materials with significant success, research has not yet reached the point where large-scale applications are imminent. Nevertheless, the choice of novel solid catalysts will almost certainly be significant in the near future.

1.8 APPLICATIONS OF MESOPOROUS MATERIALS

Mesoporous materials have been extensively used in the field of catalysis and adsorption studies and highlighted applications are discussed in this section. Since the discovery of the M41S family, a number of attempts have been made to synthesize mesoporous materials that exhibit better catalytic properties and that are more readily available. Catalytic activity of MCM-41 impregnated with Cr for olefin oligomerization to produce lube oil additives was patented by Pelrine et al (1992). Beck et al (1992a) performed comparative studies on reduction of NO with Ti,V/MCM-41, Ti,V/SiO₂ Ti,V/MCM-41 catalyst exhibits a higher NOₓ conversion than the silica-based
catalyst. Catalytic activity of Ti(V,Cr)-MCM-41 materials over oxidation reactions has been studied by Tanev et al (1994) and Corma et al (1994a). The catalytic activity of Cr-MCM-41 catalyst over hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and mild hydrocracking (MHC) was investigated by Corma et al (1995b). Initially alkali containing MCM-41 materials was shown as active for base and acid catalyzed reactions by Kloetstra and van-Bekkum (1995). Friedel-Crafts alkylation of 2,4-di-t-butyl phenol with cinnamyl alcohol was reported by Armengol et al (1995). It was observed that the activity of MCM-41 was higher than that of commercial zeolite and sulphuric acid catalysts over the alkylation. Also, it was noted that bulky organic compounds could also diffuse through mesopores and created more expectations of developing novel catalytic mesoporous materials. Catalytic properties and applications of MCM-41 based materials in organic reactions gained importance and were reviewed by Corma et al (1997).

Apart from metal supported mesoporous materials, heteropoly acid impregnated MCM-41 materials were developed. Heterogeneously active forms of heteropoly acid catalysts exhibited good catalytic activity over many industrially important reactions. Kozhevnikov et al 1995a and Shen et al (2004) performed liquid-phase alkylation of phenol over HPW/MCM-41. Liquid phase esterification of 1-propanol with hexanoic acid and gas-phase esterification of acetic acid with 1-butanol using \( \text{H}_3\text{PW}_{12}\text{O}_{40} \) and \( \text{H}_4\text{SiW}_{12}\text{O}_{40} \) supported MCM-41 catalysts were performed by Verhoef et al (1999). Recent review on the applications of mesoporous silica-supported heteropolyacids emphasized the importance of the use of such solid acid materials in organic reactions (Ren et al 2010). Taguchi and Schuth (2005), Ciesla and Schuth (1999) reviewed the synthesis and applications of ordered mesoporous materials which showed the wide range of applicability of the materials. S. Bhattacharyya et al (2006) summarized and presented an overview of selected applications of MCM-41 in various fields. These works paved the way for
finding the applications of other types of mesoporous materials (MCM-48, SBA-15, KIT-5, KIT-6 etc.) in catalysis.

For most applications, the nature of the pore system and also the access of the pore system from the surface are highly important. Among various mesoporous supports, KIT-6 possess two enantiomeric pore systems, separated by a minimal surface composed of silica. In recent times, research focus on KIT-6 materials gained much potential and the use of such materials created great expectations to explore. KIT-6 materials served as good supports for palladium complexes and their catalytic activity over industrially important Suzuki-Miyaura coupling reaction was studied (Nohair et al 2008). KIT-6 aluminosilicates (Al-KIT-6) in particular is a potential catalyst and have been used for selective O-acylation of phenol with acetic acid in vapour phase by A. Prabhu et al (2009). KIT-6 supported cobalt catalyst displayed better methane selectivity in Fischer–Tropsch Synthesis (Gnanamani et al 2010). Ti-KIT-6 catalysts exhibited superior activity with certain epoxidation reactions was reported by Vinu et al (2008).

Catalytic performance of Ni,Mo catalysts supported on hierarchically porous Beta-KIT-6 material was performed over hydrodesulfurization of dibenzothiophene by Zhang et al (2010). Soni et al illustrated that KIT-6 was effective support for Mo, CoMo and NiMo catalysts and the catalytic activity was higher on (HDS) of thiophene and (HDN) of cyclohexene. This was attributed to 3-D mesopore connectivity resulting in better catalyst dispersion, higher reducibility of Mo, and faster diffusion of reactants and products in case of KIT-6 supported catalysts. The formation of nickel phosphide was studied on mesoporous silica (SBA-15 and KIT-6) and zeolite (mMFI) supported catalysts by Koranyi et al (2009). The results revealed SBA-15 and KIT-6 supported nickel phosphide catalysts provided prominent intrinsic parallel hydrotreating activities of
dibenzothiophene hydrodesulfurization and o-methyl aniline hydrodenitrogenation.

Jermy et al (2009) showed a high level of conversion of cyclohexane when oxidized over V-KIT-6 with good product selectivity. The study described that the catalytic effect is due to the presence of tetrahedral vanadium with weak and medium Bronsted acid sites in the material. Tsoncheva et al (2009) studied and compared the catalytic effect of cobalt impregnated on various supports like SBA-15, KIT-5 and KIT-6. The interconnectivity of the mesopores and the uniformity of the channel dimensions also had an influence on the catalytic activity on the oxidation of ethyl acetate, implying that mass-transfer effects, especially in the case of supports with cage-like mesopores.

KIT-6 materials have not only been used as catalysts but they are also used as hard templates for the synthesis of meso-structured materials. The cubic Ia3d structure helps in directing the guest species (metal ions, carbon substrates etc.) to novel meso-structures. Zhang et al (2009) reported the synthesis of mesoporous Ag-TiO$_2$ using KIT-6 as template. High surface area and large number of ordered pore channels facilitated the adsorption and transportation of dye molecules, leading to higher photocatalytic activity. Djinovic et al (2009) used KIT-6 as hard template for the synthesis of ordered CuO–CeO$_2$ mixed oxides. These methods revealed very high surface area being in the range of 147-166 m$^2$/g, depending on CuO content and calcination temperature. The employed preparation technique resulted in abundance of acidic sites on the surface of investigated mixed oxides.

Three-dimensional (3D) structure of KIT-6 facilitates the mass transfer kinetics in adsorption-based applications and is beneficial for obtaining the carbon replicas and other mesostructures. 3D interconnected
system of KIT-6 with larger pore sizes (Al-KIT-6) was used as a template with furfuryl alcohol (FA) for the production of bicontinuous ordered mesoporous carbon (OMCs) and the systematic study explains the effect of pore volume on the capacitance for OMCs synthesized using KIT-6 (Li et al. 2010). Mesoporous chromia with ordered three-dimensional (3D) hexagonal polycrystalline structures were fabricated by Xia et al. (2009) through a novel solvent-free route using KIT-6 as the hard template. According to the results of the temperature-programmed reduction and X-ray photoelectron spectroscopy investigations, it was apparent that the coexistence of multiple chromium species promotes the low-temperature reducibility of chromia. The excellent performance of meso-structured chromia on complete oxidation of toluene and ethyl acetate was because of good 3D mesoporosity and low-temperature reducibility as well as the high surface area of the chromia. All these applications shows that like MCM-41 materials, KIT-6 materials would serve as potential supports in various fields.

Experimental and theoretical studies of mesoporous catalysts are based on combination of various physico-chemical techniques such as XRD, nitrogen sorption analysis, FT-IR, Thermogravimetry (TGA) and Differential thermal analysis (DTA), acidity measurements include ammonia TPD and pyridine FTIR and electron microscopy studies such as Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Each technique is unique by itself and provides important information for the understanding of different structural features of a particular microporous or mesoporous material. Understanding of both the structure of these materials and also the formation mechanism facilitates in obtaining new materials as per the requirements of the desired application. Recent trends in research focus on the applications of novel mesoporous materials as solid acid catalysts in organic synthesis and towards the conversion of biomass to fuels and useful chemicals that are vital to current and future energy needs.
1.9 SCOPE AND OBJECTIVE OF THE PRESENT INVESTIGATION

The potential use of porous solid acid catalysts in fine chemical production and biomass conversion is enormous. The use of such heterogeneous catalysts is known to suppress side reactions resulting in better selectivity and product yield. Thus the cost and energy has been saved to a certain extent for the downstream separation and purification of the product. It also avoids the complex neutralization and separation steps needed to recover the homogeneous catalysts from the reaction mixture.

In general, acid-catalysed condensation, addition and cyclization reactions are some of the important reaction steps employed for building large and complex molecules involving heterocyclic compounds that characterise many of the fine chemicals and pharmaceutical products. On the other hand, catalytic conversion of biomass sugars to fuels and useful chemicals is essential to current and future energy needs. Basic chemical transformations that enable this conversion involve many undetectable steps leading to various hydrocarbons. There has been enormous progress in recent research on the catalytic conversion of carbohydrates to useful industrial chemicals such as 5-hydroxymethylfurfural, levulinic acid and furfural. Design and synthesis of more resourceful catalysts for these basic chemical transformations still remains a challenge. As said earlier, among the large number of Bronsted and Lewis catalysts used in organic synthesis, heteropoly acids and other metal salts (stannous chloride, aluminium chloride etc.) have been explored for their specific catalytic activity. Even though these homogeneous catalysts show good catalytic performance, problems related to corrosion, handling, recovery, and reuse of the catalyst set up are limitations of its use. Neutral solid supports (such as silica or alumina) activated with metal salts have received considerable attention in heterogeneous organic reactions in different
areas of organic synthesis. Creating sequential one-pot combinations of multi-
component reactions (MCRs) and multi-catalysis cascade (MCC) reactions is a challenging task that has already emerged as a new technology in synthetic organic chemistry. The results are dependent on the reaction conditions: solvent, temperature, catalyst, concentration, the kind of starting materials and functional groups. Such considerations are of particular importance in connection with the design and discovery of novel MCRs. So in the present study, each catalyst type used were particularly selective for certain MCRs listed in the following scope. Also for some of the reactions, in addition to catalysts, an effective system or method like ultrasonic influence was required in order to obtain better yields. The combination of catalysts was chosen based on the practical performance of the solid acid materials and the reaction system.

The main objective of the present work involves the synthesis of solid acid mesoporous materials and their application towards certain organic reactions. Hence the results presented in the thesis demonstrate the synthesis of HPWA/MCM-41, Sn-MCM-41 and Al-KIT-6 mesoporous materials. The mesoporous materials were used as solid acid catalysts for various organic transformations to synthesise xanthenediones, pyrazolo pyridines, benzopyrans, pyrazole phthalazine diones and 5-hydroxymethyl furfural. The present investigation involves the following objectives:

- Synthesis of phoshphotungstic acid (10, 20 and 30 wt. %) supported Si-MCM-41 by wet impregnation method.
- Synthesis of tin incorporated mesoporous molecular sieves (Sn-MCM-41) of various ratios (Si/Sn = 150, 170 and 190) by direct hydrothermal method.
• Synthesis of aluminium containing KIT-6 mesoporous silicates (Al-KIT-6) of various ratios (Si/Al = 25, 50, 75 and 100) by post synthesis grafting method.

• Characterisation of the above materials by various physicochemical techniques namely; Inductively coupled plasma-optical emission spectroscopy (ICP-OES), X-ray diffraction (XRD), \( \text{N}_2 \) adsorption-desorption measurements, Fourier transform infrared (FT-IR) spectroscopy, Diffuse reflectance ultraviolet spectroscopy (DRUV-Vis), \( ^{29}\text{Si} \) magic angle spinning nuclear magnetic resonance spectroscopy, \( ^{31}\text{P} \) magic angle spinning nuclear magnetic resonance spectroscopy, \( ^{119}\text{Sn} \) magic angle spinning nuclear magnetic resonance spectroscopy, \( ^{27}\text{Al} \) magic angle spinning nuclear magnetic resonance spectroscopy, Scanning electron microscopy (SEM), Energy dispersive analysis of X-rays (EDAX), High resolution transmission electron microscopy (HR-TEM).

• Synthesis of xanthenedione derivatives using phosphotungstic acid supported MCM-41 (HPWA/MCM-41) catalysts under liquid phase condition.

• Synthesis of pyrazolopyridine derivatives using HPWA/MCM-41 catalysts under ultrasonic condition.

• Synthesis of benzopyrans over Sn-MCM-41 catalysts under liquid phase condition.

• Synthesis of pyrazolo phthalazinediones over Al-KIT-6 catalysts under liquid phase condition.

• Dehydration of D-Glucose to 5-Hydroxy methyl furfural over Al-KIT-6 catalysts under autogenous pressure condition.