CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

New and distinct materials and chemistry prepared stepwise in a controlled manner provide an opportunity for the development of efficient catalytic molecularly organized surfaces on route to the ultimate catalyst technologies. Currently there is a need for alternative production technologies for fine chemical synthesis. Catalytic oxidation of hydrocarbons in general is employed in the manufacture of fine chemicals. In particular more than 60% of products synthesized by catalytic routes in the chemical industry are obtained by oxidation.

Catalytic oxidation is a key technology for converting petroleum-based feedstocks to useful chemicals of a high oxidation state such as alcohols, carbonyl compounds, and epoxides. Millions of tons of these compounds are annually produced worldwide and find applications in all areas of chemical industries, ranging from pharmaceutical to large-scale commodities. For economic and environmental reasons the oxidation processes of bulk chemical industries predominantly involve the use of molecular oxygen as the primary oxidant. Selective catalytic oxidation of organic compounds using eco-friendly and cheap oxidant such as molecular oxygen and easily recyclable catalyst is a challenging goal for the fine chemical industry. Their success depends largely on the use of metal catalysts.
to promote both the rate of reaction and the selectivity towards partial oxidation products.

1.1.1 Homogeneous catalysts for oxidation reactions

In earlier days, value added compounds have been synthesized by oxidation using powerful oxidizing agents like KMnO$_4$ and K$_2$Cr$_2$O$_7$ in stoichiometric quantities. However, this generates a large amount of reduced products of these materials. As a result the oxidation reactions involving catalytic amount of oxidizing agent have come into prominence.

The production of ethylene oxide from ethylene with molecular oxygen is catalyzed by silver salts (Lefort 1931). Terephthalic acid was synthesized from $p$-xylene using molecular oxygen in the presence of manganese and cobalt salts. Wacker oxidation of alkenes to carbonyl compounds is catalyzed by palladium salts. Later, Annie Liard et al (1997) attempted to carry out this reaction by using Xanthates as starting materials for the production of tetalone. A method for converting naphthalene to phthalic anhydride using sulphuric acid as the oxidizing agent using mercury salt as the catalyst was discovered by Sapper (1896). The above mentioned methods are examples of successful commercial oxidation processes. But traditional methods of many fine chemical oxidations involve stoichiometric quantities of toxic inorganic reagents such as permanganate and dichromate. These reactions generate large amount of inorganic salt-containing effluent along with the target products. Hence, the tedious process of effluent removal led to development of new catalyst which involves large production of the desired product as well as eliminating the waste matter. To achieve the above target, research is focused on the development of heterogeneous catalysis.
1.1.2 Heterogeneous catalysts for oxidation reactions

Layered silicate sheets (clays), layered metal oxides (sulfated zirconia and tungstated zirconia), and bulk metal oxides (spinel and MgO, heteropoly acids, porous solids (zeolites), mesoporous materials and activated carbon, are some of the well-known heterogeneous catalysts (Shaw et al 1998; Miyazaki et al 1999; Reetz et al 1998; Hermann et al 1999; Biffis et al 2001). General classifications of heterogeneous catalysts with corresponding applications are summarized in Table 1.1.

Table 1.1 Classification of heterogeneous catalysts

<table>
<thead>
<tr>
<th>Class of catalysts</th>
<th>Examples</th>
<th>Applications</th>
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<tbody>
<tr>
<td>Metals (supported-mono, bi-, multi-metallic, alloys, etc.)</td>
<td>Pt, Pd, Rh, Ni, Fe, Co, Cu and Ag on SiO₂, Al₂O₃. Activated carbon.</td>
<td>Hydrogenation, dehydrogenation, aromatization, oxidation.</td>
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<tr>
<td>Metal oxides (amorphous and crystalline) and mixed metal oxides (acidic or basic or redox)</td>
<td>MgO, CuO, SiO₂-Al₂O₃, zeolites, mesoporous metal oxides, AlPO₄, SAPO₄, oxides of Bi-Mo, Fe-Mo, perovskites, spinels, fluorites</td>
<td>Alkylation, acylation, cracking, isomerization, oxidation, disproportionation, dehydration-hydration, ammoniation, amination.</td>
</tr>
<tr>
<td>Metalsulfides (supported)</td>
<td>Co-Mo, Ni-Mo, Ni-W on Al₂O₃, SiO₂ or other supports.</td>
<td>Hydrodesulfurisation, hydrotreating, hydrogenation.</td>
</tr>
<tr>
<td>Metal salts</td>
<td>Zr₃(PO₄)₄, ZnS, LaPO₄, sulfates, carbonates</td>
<td>Etherification, amination.</td>
</tr>
<tr>
<td>Heteropolyacids (supported)</td>
<td>H₃PW₁₂O₴₀, H₃PMO₁₂O₴₀, H₄SiW₁₂O₴₀</td>
<td>Acid catalyzed reactions, oxidation condensation.</td>
</tr>
<tr>
<td>Clays and pillared clays, hydrotalcites.</td>
<td>Kaolinite, K-10 Montmorillonite, Al-pillared Montmorillonite</td>
<td>Acid-catalyzed reactions, cracking, alkylation, nitration.</td>
</tr>
<tr>
<td>Metal complexes (supported or encapsulated)</td>
<td>Metal porphyrins, salens and pthalocyanins</td>
<td>Selective oxidation.</td>
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1.1.3 Zeolites for oxidation reaction

The micro porous zeolite solid catalyst has shape selective properties. This is an additional benefit in fine chemicals synthesis. Furthermore, the modification of the solid catalysts by metals having redox functions along with their acidic or basic properties extends their catalytic scope to redox reactions. However, trivalent (B, Ga, Fe and As) (Taramasso et al 1979; Meyers et al 1985; McNicol, and Pott 1972; Bhaumik and Kumar 1995) and tetravalent (Ti, Ge, V, Sn and Zr) (Kumar and Ratnasamy 1993; Taramaso et al 1983; Thangaraj et al 1991; Ramasawamy et al 1993; Rakshe et al 1996) transition and non-transition metal ions have been incorporated in different zeolites (microporous materials). MFI appears to be the most preferred structure for heteroatom incorporation. Different architectural features of zeolites and related materials generate different types of shape-selectivity (product, reactant and transition state). Their relatively high stability towards thermal, hydrothermal and chemical treatments has also been well studied. This has lead to their use as catalysts for oil refining, petrochemistry and organic synthesis for the production of fine and specialty chemicals. Moreover, zeolites and related molecular sieves are regarded as ‘green catalysts’ due to prominent factors such as simplicity in operation, easy work-up, regeneration and reuse of the catalysts for several times.

Benzene to phenol oxidation over Fe-ZSM-5 catalyst was studied at temperature range 648–698K and near atmospheric pressure using a bench scale plug flow reactor with a feed gas concentration of 30–80 mol% benzene, 1.5–5.0 mol% N₂O, and 0–4.7 mol% phenol. Under these conditions, the selectivity of benzene was found to be 98%. It was assumed that benzene and phenol are in sorption equilibrium between the gas-phase and the zeolite micropore volume. Benzoquinone, hydroquinone, catechol, and carbon
oxides were the main by-products. Ivanov et al (2003); Akah Aaro et al (2007) have carried out the selective oxidation of NH₃ using Fe-ZSM-5. The oxidative activity of the catalysts was found to depend on the Al in Fe-H-[Al] ZSM-5. A catalyst without Al in H-[Fe]-ZSM-5 exhibited low activity during the selective catalytic oxidation (SCO) reaction suggesting that the presence of Al in the zeolite framework is of great importance. Also the presence of Al stabilizes the Fe active species in Fe-ZSM-5 catalyst. Yet another study on Fe-ZSM-5 revealed that framework Fe is more active and selective than extra framework Fe in the oxidation of phenol (Nguyen et al 2001) Zecchina et al reported contradicting results on Fe zeolites (2007). In another article, basic zeolites such as CsX and NaX zeolites were reported to be the promising catalysts for the catalytic oxidation of isopropanol/oxylene mixture. The strong adsorption of isopropanol, the main volatile organic compounds in the mixture, is reaction rate determining step in the oxidation reaction (Beauchet et al 2007).

Catalytic oxidation of o-xylene has been carried out over platinum loaded HBEA zeolite catalyst with framework Si/Al = 15 and 50 (Tsou et al 2003). The oxidation rate of o-xylene was found to increase with both platinum content and with Si/Al ratio. Further the catalyst performance was enhanced by pre-reduction of platinum under hydrogen flow showing that Pt⁰ were very active for xylene oxidation. Yoo Jin et al (1994) made stringent efforts to develop a process for selective synthesis of terephthaldehyde. In the gas-phase oxidation of xylene isomers over CVD Fe/Mo/DBH catalyst, it was found that a large reactivity gap exists between p- xylene and o-/m- xylene isomer and the reactivity of xylene isomers for oxidation was found to follow the order p- xylene > o-xylene > m- xylene. p- xylene was preferentially oxidized to terephthaldehyde and p-toluicdehyde from the xylene isomer mixture as well as from the commercially available xylene isomer feed containing ethylbenzene. Rest of the components remained almost intact. Coating the CVD Fe/Mo/DBH catalyst with tetramethyl-
orthosilicate enhanced the selectivity for the preferential oxidation of $p$-xylene over its isomers. Vinay Kumar and Prem Grover (1991) have studied the catalytic vapor-phase oxidation of $p$-xylene in an isothermal plug flow reactor using mixed oxides like V-Ce-O, V-Fe-O, V-Mg-O, V-Co-O, and V-P-O as catalysts. Among the catalysts investigated, only V-Fe-O and V-Ce-O exhibited sufficiently high activity. The activity of the various catalysts is in the following order: V-Fe-O > V-Ce-O > $V_2O_5$ > V-P-O > V-Mg-O > V-Co-O. Instead, V-Ce-O catalyst was found to be the more selective for $p$-tolualdehyde than V-Fe-O in the temperature range 325-425°C.

Pd supported on Na-ZSM-5 zeolite catalyst was tested for CO oxidation at low temperature (Yushui Bi and Gongxuan Lu 2003). It was reported that the activity of Pd/NaZSM-5 catalyst is strongly dependent on the preparation method and pretreatment conditions. High calcination temperature results in large Pd particle dimensions, which directly leads to the decrease of activity. High reaction temperature or high Pd loading results in high catalytic activity for CO oxidation, while pre-reduction of the catalyst by hydrogen causes low catalytic activity.

The catalytic activity and selectivity of a series of H-ZSM-5-supported manganese oxide catalysts with various manganese content, namely 1.0, 4.3, and 8.3 wt%, were evaluated for the oxidation of dichloromethane (DCM) and trichloroethylene (TCE) (Gutierrez-Ortiz et al 2003). Mn (4.3%)/H-ZSM-5 catalyst was found to be the best catalyst for the combustion of both single and double carbon chlorinated compounds, achieving > 95% conversion level at temperatures between 400 and 450°C. The major oxidation products were carbon monoxide, carbon dioxide, hydrogen chloride, and chlorine. It was also observed that high manganese loading led to increasing amount of carbon dioxide and chlorine.
1.1.4 ALPO’s for oxidation reactions

Success of the zeolites as oxidation catalysts led to the search for newer type of molecular sieves other than aluminosilicates. Since both phosphorus and aluminium in their usual oxidation states (5+ and 3+ respectively) form oxygen-sharing tetrahedra, attempts have been made to prepare aluminum phosphate molecular sieves. The first success in this direction was reported by Wilson et al (1982), wherein micro-pore sieves were prepared by hydrothermal treatment of a reactive aluminophosphate gel in the presence of an organic template. Structures of this type are made of alternating AlO$_4$ and PO$_4$ tetrahedra with shared oxygen between them. They form a variety of structures some of which are analogous to known zeolite structures. These are called ‘alpo’ and one structure ALPO$_4$-5 has the structure of the zeolite faujasite. The framework structure of ALPO$_4$-34 is similar to that of zeolite chabazite.

Number of studies has been made on oxidation reaction with various transition metal incorporated in ALPO molecular sieves. Lempers and Sheldon (1998) have studied the stability of the Cr in Cr substituted aluminophosphate-5 (Cr-ALPO-5), aluminophosphate-11 (Cr-ALPO-11), and silicalite-1 (CrS-1) during liquid phase oxidation reaction with tert-butyl hydroperoxide as oxidant. The results showed that this reaction did not take place in the micropores or at the outer surface of these catalysts but were homogeneously catalyzed by small amounts of leached chromium. The amount of chromium leached is related to the crystal size of the catalyst. In the case of the large CrAPO-5 crystals only 0.3% of chromium is leached during the reaction. Nevertheless, this very small amount is responsible for the observed catalyst activity. The necessity for catalyst filtration at the reaction temperature in catalyst recycling experiments is emphasized.
Selective oxidation of cyclohexane has been carried out using (Co, Cr) ALPO-5, (Co, V) ALPO-5 and (Cr, V) ALPO-5 molecular sieves in the presence of H₂O₂ (Weibin Fan et al 2006). The probability for framework incorporation of the transition metal ions decreased in the sequence: Co²⁺ > V⁴⁺ > Cr³⁺. Upon calcination, all V⁴⁺ ions were oxidized to V⁵⁺, while Cr³⁺ cations were oxidized to Cr⁵⁺ and Cr⁶⁺. Simultaneous incorporation of two types of transition metal ions in the AFI framework showed higher activity compared to single metal ion substituted analogues. (M, N)ALPO-5 (with M and N = Co²⁺, Cr³⁺ and V⁴⁺) molecular sieves are stable and retained their activity and selectivity at least for five repeated runs. The leached metal ions too played a significant role in catalyzing the oxidation of cyclohexane.

The incorporation of vanadium in the framework of aluminium phosphate materials has been achieved through structure directing template route. Vanadium (V⁴⁺/V⁵⁺) substituted AlPO’s have been shown to be promising oxidizing catalysts with 70 % TBHP and 30 % H₂O₂ as oxidizing agent. Cycloalkanes have been oxidized using divalent cobalt-substituted hexagonal mesoporous aluminophosphate molecular sieves as catalyst (Selvam and Mohapatra 2005). Wherein, cobalt-substituted hexagonal mesoporous aluminophosphate (Co-HMA) catalysts showed excellent activity for selective oxidation of cyclohexane under mild reaction conditions. The activity of CoHMA was found to be higher than those of the Co/MCM-41, CoAPO-5, and Co/S-1 catalysts. It was also demonstrated that Co-HMA can be used for the oxidation of bulky cycloalkanes such as cyclooctane and cyclododecane. These catalysts can be considered viable alternatives because of their easy recovery and recycling. Thus opening up a new avenue in the field of heterogeneous oxidation reactions.
MeAPO-11s (Me = Co, Mn, Cr and V) had better activity than corresponding MeAPO-5s and MeAPSO-34s for cyclohexane oxidation. Peng Tian et al (2004). CoAPO-11 exhibited the best activity and good selectivity for monofunctional oxidation products. Acidic molecular sieves had negative effect on the oxidation reaction. Both heterolytic and homolytic mechanisms existed in the decomposition of cyclohexyl hydroperoxide (CHHP) on CoAPO-11 and CrAPO-5. Kulkarni et al (1996) have carried out oxidation and ammoxidation of toluene and benzyl alcohol over silico-aluminophosphate and metal-silico-aluminophosphate catalysts. From the results of their studies it can be concluded that SAPO, VAPO and VSAPO catalysts, thermally stable or unstable molecular sieves, synthesized by hydrothermal method, are good and a new class of oxidation and ammoxidation catalysts. SAPO-37 containing structural chromium (III) and iron (III) ions were tested as catalysts in liquid phase oxidation of benzene and cyclohexane, using hydrogen peroxide and tert-butylhydroperoxide as oxidants. Only chromium (III) has been found good oxidation catalyst. In spite of the SAPO-37 framework stability under the reaction conditions, leaching of small quantities of chromium occurs and the observed catalytic reaction is mainly due to the chromium ions in solution (Estevam Vitorio Spinacé et al 1999).

Dong Chen Ji and Roger A Sheldon (1995) have synthesized CrALPO-5 catalyst and used for liquid phase oxidation of hydrocarbons using molecular oxygen in the presence of a small amount of alkylhydroperoxide as initiator. It was found that CrALPO-5 is an active, selective and recyclable heterogeneous catalyst for the oxidation reaction. The reaction was found to proceed via initial free radical autoxidation followed by an intermolecular, heterolytic decomposition of the formed alkyl hydroperoxide catalyzed by CrALPO-5. In another study (Haanepe and Van Hooff 1997) VAPO-5 and VAPO-11 have been synthesized with variable vanadium content for liquid
phase oxidation of allylic and secondary alcohols by tert-butyl hydroperoxide as oxidant. The activity of VAPO was low compared with a homogeneous vanadium catalyst. The only effect of the microporous structure is the observation of fast decomposition of the peroxide in case of VAPO-5. Only minor differences in activity and selectivity were found between different preparation methods. VAPOs with higher vanadium content are more active.

1.1.5 Clays for oxidation reactions

Hydrotalcite-like compounds (HTs), also known as layered double hydroxides, possess potential uses in various scientific areas including catalyzed organic synthesis (Vaccari 1999; Sels et al 2001; Cavanni et al 1991). The parent compound, a natural mineral called hydrotalcite (Miyata 1975), is a magnesium-aluminium hydroxycarbonate of formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3.4\text{H}_2\text{O}$. The structure of the above mentioned mineral is similar to that of brucite except that some $\text{Mg}^{2+}$ ions are substituted by $\text{Al}^{3+}$. Thus substitution produces layers bearing positive charges that are neutralized by carbonate ions present in the interlayer spacings. By replacing the magnesium, aluminium or both cations, and the carbonate, by other ions, a large family of compounds known as hydrotalcite-like (HT) or layered double hydroxides (LDHs) of general formula $[\text{M(II)}_{1-x}\text{M(III)}_x(\text{OH})_2]^{3+}$ $(\text{A}^{n-})_{x/n}$.mH$_2$O can be obtained where M(II) is a divalent cation such as Mg, Cu, Ni, Co or Zn, M(III) a trivalent cation such as Al, Fe, Cr, V, Mn, Ga or In (Cavanni et al 1991; Aramendia et al 1999; Aramendia et al 2000) and $\text{A}^{n-}$ the charge balancing anion, which can be an inorganic or organic species of widely variable nature (Cavanni et al 1991). HTs containing tetravalent metals are finding interesting uses in oxidation reactions.

Cesar Jiménez-Sanchidrián et al (2006) have carried out the Baeyer Villager oxidation using various Mg/Al, Mg/Al/Sn and Mg/Al/Zr
hydrotalcite-like compounds (HTs). The results showed that among the above mentioned catalysts the solids containing Mg/Al and Mg/Al/Sn and their calcination products (viz. Mg/Al and Mg/Al/Sn mixed oxides) are effective catalysts for the Baeyer Villager oxidation of cyclohexanone. The activity increased with increasing tin content. The active catalyst is the one containing the largest amount of tin. The catalyst retained full activity even after three reuses. Takahiro Nishimura et al (2000) have carried out the selective oxidation of alcohols using palladium (II)-supported hydrotalcite catalyst with molecular oxygen as an oxidant. These Palladium (II)-supported hydrotalcite was found to act as a reusable catalyst for the oxidation of alcohols to aldehydes and ketones in the presence of pyridine under atmospheric pressure of oxygen.

Tomonori Kawabata et al (2006) have carried out the oxidation of alcohols using nickel containing Mg-Al type hyrdotalcite-type anionic clay as catalysts with molecular oxygen as an oxidant. Substitution of Ni for the Mg site in Mg$_3$Al HT resulted in an active catalyst and the composition of Mg$_{2.5}$Ni$_{0.5}$Al HT exhibited better catalytic activity. The yield of benzaldehyde over the hydrotalcite catalyst increased significantly with increasing nickel content up to ca. 7.6 wt%, where atomically isolated and octahedrally coordinated Ni (II) sites were effective for the oxidation with molecular oxygen. The octahedrally coordinated Ni (II) cations incorporated inside the framework of hydrotalcite do not leach during the reaction and worked as a heterogeneous catalyst. It is considered that the Ni (II) site acted as the active site by activating molecular oxygen assisted by the Mg (II) as a base. Alcohol was also simultaneously activated by the Al (III) as an acid resulting in an enhancement of the activity of the Mg$_{2.5}$Ni$_{0.5}$Al HT heterogeneous catalyst for alcohol oxidation. Clean and selective Baeyer–Villiger oxidation of ketones was studied using Sn-exchanged hydrotalcites as catalysts using hydrogen peroxide (H$_2$O$_2$) as oxidant (Unnikrishnan R. Pillai
and Endalkachew Sahle-Demessie 2003). The study revealed that Sn-exchanged hydrotalcites are efficient and relatively cheap catalysts for the Baeyer–Villiger oxidation reaction. The mechanism of oxidation is tentatively explained as due to the activation of carbonyl group of ketone by Sn present in the interstitial positions of hydrotalcite followed by subsequent oxygen transfer from the active peroxide species to form lactone as the final product.

1.2 MESOPOROUS MOLECULAR SIEVES

Interest in expanding the pore sizes of zeolite type materials from micropore to mesopore (pore size >20 Å) region is ever growing response to the increasing demands with respect to both industrial and fundamental needs. Examples are treating heavy feeds, separating and selectively synthesizing large molecules and intra zeolite formation fabricating technology (Ozin and Gil 1989; Davis and Loba 1992). Zeo-type materials typically have a surface area greater than 700 m² g⁻¹. These are not truly crystalline like microporous zeolites and majority of the surface active sites are inside the pores and accessible only through apertures of well-defined dimensions (Zhao et al 1996).

In 1992, researchers at Mobil Corporation discovered the M41S family of silicate/aluminosilicates mesoporous molecular sieves with exceptionally large uniform pore structures. This has resulted in a worldwide resurgence in the area of mesoporous molecular sieves (Kresge et al 1992; Beck et al 1992). Three different mesophases in this family have been identified, i.e. lamellar (Dubois et al 1993), hexagonal (Beck et al 1992), and cubic phases (Vartulli et al 1994), in which the hexagonal mesophase, MCM-41, possesses highly regular arrays of uniform-sized channels whose diameters are in the range of 15-100 Å depending on the templates used, the
addition of auxiliary organic compounds (co-template) and the reaction parameters. The pores of this novel material are nearly regular, yet considerably larger than those present in crystalline materials such as zeolite thus offering new opportunities for applications in catalysis (Corma and Martinez 1995) and advanced composite materials (Huber et al 1994). Accordingly, MCM-41 has been investigated extensively because the other members in this family are either thermally unstable or difficult to obtain.

The purpose and advantages of synthesizing mesoporous materials is as follows:

i. The diffusional constraints with zeolites can be overcome.

ii. They possess very high surface area (>1000 m²/g) and pore size distribution (20-100 Å).

iii. They can be used as good host materials for guest species (i.e. heterogenization of homogeneous species or metal complexes on the walls).

iv. Easier to monitor the changes made with active species via surface area measurement and pore size distribution experiment.

1.2.1 Mechanisms of mesostructure formation of MCM-41

In order to explain the formation of mesoporous materials and to provide a rational basis for the various synthesis routes a number of models have been proposed. These models are predicted upon the presence of surfactants in a solution to guide the formation of the solubilised inorganic precursors. Surfactants contain a hydrophilic head group and a long
hydrophobic tail group within the same molecule and self organize in such a way as to minimize contact between incompatible ends. The type of interaction between surfactant and inorganic precursor results in various synthesis routes, formation models and the resulting classes of mesoporous materials.

The most outstanding feature of preparation of MCM-41, in contrast to the traditional single organic molecule or metal ion templating preparation is that the templates used are surfactants, having an alkyl chain length of greater than 16 carbon atoms. Therefore, the mechanisms responsible for the formation of MCM-41 from its precursors have attracted much attention. Two typical mechanisms have been proposed so far (Beck et al 1992 and Monnier et al 1993), accompanied by other modified routes (Inagaki et al 1994 and Steel et al 1994). It is well known that formation of the traditional zeolites and molecular sieves is templated by single molecules or ions. The crystallization is via silicate condensation around a tetra propyl ammonium cation. The initial ordered species may consist of an aggregate of water molecules or silicate moieties (Kerr 1996 and Feijen 1994). Subsequent growth proceeds because of nucleation by this initial structure or assembly of a number of such structures. But crystal growth is the result of initial silicate organization. In the case of MCM-41 formation, however, Beck et al (1992) initially proposed the liquid crystal templating mechanism.

1.2.2 Liquid Crystal Templating (LCT) Mechanism

In order to explain the synthesis mechanism, Mobil researchers proposed a liquid crystal templating (LCT) mechanism, based on the similarity between liquid crystalline surfactant assemblies (i.e. lyotropic phases) and M41S (Kresge et al 1992; Beck et al 1992a). The mesostructure
formation depends on the hydrocarbon chain length of the surfactant tail group (Beck et al 1994b), the effect of variation of the surfactant concentration and the additional organic swelling agents. The lowest concentration at which surfactant molecules aggregate to form spherical isotropic micelles is called critical micelle concentration (CMC1). Further increase in the surfactant concentration initiates aggregation of spherical micelles into cylindrical or rod-like micelles (CMC2). There are three main liquid crystalline phases with hexagonal, cubic and lamellar structures. The hexagonal phase is the result of hexagonal packing of cylindrical micelles, the lamellar phase corresponds to the formation of surfactant bi layers and the cubic phase may be regarded as a bi continuous structure. Two mechanistic pathways were postulated for the formation of M41S type materials:

(A) The structure is defined by the organization of surfactant molecules into lyotropic liquid crystal (LC) phase, which serves as template for the formation of MCM-41 structure. The first step of the synthesis is the formation of a micellar rod around the surfactant micelle which will produce a hexagonal array of rods, followed by incorporation of an inorganic array around the rod-like structures in the second step (Scheme 1.1).

(B) Highly sensitive liquid crystal structures formed in surfactant solutions may also interact with the silicate species directly which results in the ordering of the subsequent silicate surfactant micelles to form MCM-41 structure.

Hence, the negatively charged inorganic components preferentially interact with the positively charged ammonium head groups of the surfactants and condense into a solid. However, it was clearly shown that pathway A
(Figure 1.1) did not take place because the surfactant concentrations used were far below the critical micelle concentration (CMC2) required for hexagonal LC formation.

Figure 1.1 Liquid crystal templating mechanism proposed for the formation of MCM-41 (A) liquid crystal phase initiated and (B) silicate anion initiated

1.3 INTERACTION WITH WATER

The adsorption of water steam over MCM-41 characterized by a type VI isotherm reveals an initially repulsive character followed by a capillary condensation step of water, indicating that MCM-41 possesses both hydrophobic and hydrophilic properties (Llewellyn et al 1995). Three distinct stages were obtained in the TGA curves (Zhao et al 1996). The first weight loss at 25-150°C is associated with the desorption of physically adsorbed water and other gases; the second loss at 150-380°C is attributed to the decomposition and combustion of organic species, and the third loss at 380-800°C is related to the water loss due to condensation of silanol groups to form siloxane bonds (Chen et al 1993a). In addition, with the increase of the heteroatom content in MCM-41 framework, the amount of water desorbed increases and desorption of organic species decreases.
1.4 INTERACTION BETWEEN SURFACTANT AND SILICATE SPECIES

When a silica source is combined with an ionic surfactant like CTMABr in solution, the self-organization process involves surfactant/silicate self-assembly and the transformation of mesophase, shows the aggregation process driven by the silica species and these are very sensitive to pH, temperature, aging time, counter ions and the surfactant species. In the synthesis there are three kinds of charged species in solution: Silica species (I/I$^+$), cationic surfactant (S$^+$) and its counter ion (X$^-$). Their interactions depend on the silicate oligomeric species present because their charge density is different in the degree of oligomerisation. With strong interactions the silicate ions exchange on to the micellar interface and the concentrations results in a rapid condensation of the silicate species.

1.5 THERMAL AND HYDROTHERMAL STABILITY

For practical applications, the materials under consideration should display good thermal and hydrothermal stabilities. MCM-41 exhibits high thermal stability (~ 1173 K) in dry air or in air having a low water vapour pressure (Chen et al 1993b; Ryoo and Kim 1995; Cu et al 1999; Chen et al 1993a; Chen et al 1997; Kim et al 1995). In addition, it is relatively stable under acidic conditions. But it degrades readily in basic environments (Chen et al 1997). The latter is, however, expected as it is known that (amorphous) silica dissolves partially in water, especially at high pH (Iler 1979). On the other hand MCM-41 has a low hydrothermal stability in water, in aqueous solutions, and even in air saturated with water vapour (Zhao et al 1998; Chen et al 1997; Zhao et al 1998b; Kim et al 1999; Ryoo and Jun 1997; Koyano et al 1997). Furthermore, the structure collapses by mechanical compression through the hydrolysis of siloxane bonds in the presence of adsorbed water, as
is evident from the XRD patterns. However, the hydrothermal stability can be improved by increasing the hydrophobicity, i.e., by decreasing the number of silanol groups in the framework structure. For example, synthesis in the presence of various salts (Kim et al 1999; Ryoo and Jun 1997) or ion exchange (Kim et al 1995) after synthesis has been shown to stabilize MCM-41. In addition, post synthesis treatments with acid (Hitz and Prins 1997; On et al 1998; Edler and White 1999), modification by silylation (Koyano et al 1997), or removal of silanol groups by alumina (Mokaya and Jones 1996) have also been shown to improve both the chemical and mechanical stabilities. Recently, Igarashi et al (1999). reported increased stability of organically modified MCM-41 synthesized by a single-step procedure, in comparison to the unfunctionalized species.

On other hand, the so-called hydrothermal restructuring method is a convenient method for preparing large mesopore samples of MCM-41. It has been shown that pore size enlargement is accompanied by an improvement in pore size uniformity, a decrease in structural ordering, and a gradual decrease in specific surface area, as well as pore thickening. The restructuring of the as-synthesized material in the mother liquor (Khushalani et al 1995; Cheng et al 1996; Corma et al 1997; Sayari et al 1997) or water (Kruk et al 1999; Chen et al 1999) over longer crystallization times or at higher reaction temperatures (Sayari et al 1997; Cheng et al 1997; Khushalani et al 1995) result in expansion of pore size from 3 to 7 nm. However, the pore size distribution of the samples becomes broader. On the other hand, with an increase of the hydrothermal reaction temperature from 373 to \( \geq 438 \) K or with a prolonged reaction time at 443 K, MCM-41 transforms into the MCM-50 and/or ZSM-5 structures (Chen et al 1997). Addition of certain cations, such as tetraaerylammnonium or sodium ion, to the synthesis gel results in considerable improvement of the hydrothermal stability of MCM-41(Das et al 1999).
1.6 APPLICATIONS OF MESOPOROUS MATERIALS

The high surface area, well-defined regular pore shape, narrow pore size distribution, large pore volume, and tunable pore size, in conjunction with the high thermal, hydrothermal, chemical, and mechanical stability of MCM-41 are highly conducive for a number of important applications such as adsorption and separation, ion exchange, catalysis, and molecular hosts. In the past few years, the scientific community has witnessed a great deal of work and rapid expansion of the activities pertaining to this versatile material. We briefly describe below some of the important applications of MCM-41. Other developing applications include the separation of bulky molecules (Sano et al 1999), conversion of fly ash into M41S-type materials (Chang et al 1999), membranes (Zhao et al 1998; Uekawa and Kaneko 1998; Ogawa et al 1998), chromatography (Grun et al 1996; Grun et al 1997; Raimondo et al 1997), and electron-transfer materials (Corma et al 1994), as well as the sorption of methane (Menon and Komarneni 1998) and of hydrogen (Edler et al 1997).

1.6.1 Role as catalyst and support

Stringent environmental regulations, increasing public concern and legislation governing the disposal of hazardous wastes have become major issue of concern of the modern chemical industry. There are increasing restrictions on the use of traditional stoichiometric and conventional homogeneous catalytic processes because of their inherent problems such as cost, separation, handling, and waste disposal. This has accelerated the tendency to shift toward more viable alternatives such as heterogeneous catalysis, which offer the advantage of simple separation and easy recovery, reuse, waste reduction and elimination of hazardous chemicals in addition to their possible use in both liquid and gas-phase operations.
The development of eco-friendly, environmentally compatible, and recyclable solid (heterogeneous) catalysts for the production of fine chemicals and the synthesis of building blocks for pharmaceuticals and agrochemicals is becoming an area of growing interest. In this context, MCM-41 is considered promising for a variety of catalytic applications including photo catalysis and enzyme catalysis (Corma 1997; Corma and Kumar 1998; Sayari 1996; Sheldon et al 1998; Suzhuki et al 1999; Schuth 1995; Maschmeyer et al 1995; Xu and Langford 1997; Kloetstra and van Bekkum 1995; Selvam et al 1999; Kandavelu et al 2000; Sheldon 1996). Siliceous MCM-41 possesses a neutral framework which limits their applications in catalysis. Instead, they have great utility as adsorbents, molecular sieves, and supports. 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 (Kloetstra and van Bekkum 1995; Kim and Shin 1999; Badamali et al 2000; Sakthivel et al 2000; Corma et al 1994). Bronsted (solid) acid sites are generated by isomorphous substitution of trivalent cations of boron, aluminium, gallium, and iron for tetravalent silicon in the mesoporous matrix (Kloetstra and van Bekkum 1995; Badamali et al 2000; Sakthivel et al 2000; Corma et al 1994). They can function as mono functional acid catalysts. Once the acid sites are created they can be exchanged with alkali/alkaline-earth metal ions, thereby introducing mild basicity that will serve as catalysts for base-catalyzed reactions (Kloetstra et al 1997; Rao et al 1997; Rodriguez et al 1999). Likewise, the simultaneous incorporation of trivalent aluminium and tetravalent titanium in the silicate framework opens new possibilities for producing bi functional acid/oxide catalysts (Corma 1997; Corma 1998). On the other hand, the incorporation of tetravalent metal ions of titanium, vanadium, zirconium, and tin into the mesoporous matrix produces redox catalysts that are useful for selective oxidation as well as air pollution abatement (Corma 1997; Sayari 1996; Corma et al 1994; Tanev et al 1994; Mahalingam et al 1999). Extensions of this activity, viz., MCM-41 supported
mono and bimetallic catalysts, as well as certain catalytically active phases such as heteropoly acids, amines, transition metal complexes, metals, and metal oxides deposited novel catalyst systems have also been realized (Schuth 1995; Kozhevnikov et al 1995; Selvam et al 1999; Long and Yang 1998; Junges et al 1995). Furthermore, the use of MCM-41 as a support for a variety of applications that include hydrogenation (Schuth 1995), hydrocracking (Corma et al 1995), hydroxylation (Mahalingam et al 1999), nitric oxide reduction (Long and Yang 1998), carbon monoxide oxidation (Junges et al 1995), and polymerization reactions (Kozhevnikov et al 1995; Corma et al 1995; Reddy et al 1998) has been established. The effect of support (MCM-41, alumina-silica, and USY) on the catalytic activity of NiO-MoO₃ for hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and mild hydrocracking (MHC) was also investigated (Corma et al 1995; Basha et al 2006). A very high activity was observed on Ni, Mo-MCM-41 catalyst which was attributed to a combination of high surface area and large pore size that favors a high dispersion of the active species coupled with easy accessibility of the large feedstock molecules.

1.7 MODIFICATION OF MESOPOROUS MATERIALS

As synthesized mesoporous materials are catalytically inactive due to their framework neutrality. Modification of mesoporous materials can lead to the generation of acidic and basic properties and also leads to alteration of redox properties. So as to get desired catalytic activity for a particular reaction, the catalyst should be modified by the incorporation of metal or acidic or basic components. Such additives suppress undesirable side reactions by adjusting the acid base properties of the catalyst and also promote desirable reactions because of versatile active sites. The general procedures for the formation of metal incorporated ordered mesoporous
material can be either a direct method or a post synthesis modification of the mesoporous support.

The possibility of introducing heteroatom into the inert framework or walls of purely siliceous mesoporous materials by isomorphous substitution is an important route to modify the nature of framework and make them catalytically active through direct in situ method. Indeed the direct synthesis can be performed in two ways – one by the hydrothermal way in an autoclave and the other by using a reflux method at atmospheric pressure under stirred condition. In this method, the required amount of metal precursor salt dissolved in an appropriate solvent was added to the surfactant – silicate mixture and was aged for the desired time for incorporation of metals on the silica framework. The incorporation of trivalent metal ions such as Al, B, Ga and Fe (Ryoo et al 1997; Sayari et al 1995; Cheng et al 1996; Tuel and Gotier 1996) in the walls of silica network mesostructure produces framework negative charges that can be compensated by protons producing acid sites. As a result such materials are important from the point of view of acid catalysis. The incorporation of transition metals such as Ti, V, Cr and Mn (Tanev et al 1994; Reddy et al 1994; Ulagappan and Rao 1996; Zhao and Gold Farb 1995) is also important to prepare mesoporous catalysts with redox catalytic properties. M41S can be modified by various methods.

1.7.1 Heterogenesation of homogeneous catalysts

The presence of a high density of surface hydroxyl groups Zhao and Lu 1998; Zhao et al 1997; Jentys et al 1996; Chen et al 1995; Llewellyn et al 1995) in MCM-41 provides convenient anchoring sites on which certain homogeneous catalysts such as organic moieties, inorganic complexes and organometallic species can be grafted or immobilized (Maschmeyer et al 1995; Kim and Shin 1999; Rao et al 1997; Rodriguez et al 1999; Walker et al
1997; Zhou et al 1999; Shyu et al 1999) in order to heterogenise the homogeneous catalyst. This approach isolates the catalytically active sites at the molecular level leading to the so-called heterogenization of homogeneous catalysts. In such a situation, the mesopores allow for the fixation of active species that also restrict the reactants and enable reactions to take place within the cavities. The spatial freedom within the mesopores can be further hindered by the use of tethers (spacers) (Sheldon 1996; Zhou et al 1999) that deliberately restrict the freedom (of the reactants) in the vicinity of the active centre present at the extremity of the tether. This facilitates the freedom of the catalytically active sites to flutter in the molecular breeze during the process of catalytic conversion leading to high stereo selectivity of the products (Maschmeyer et al 1995; Kim and Shin 1999). Two approaches have generally been followed for grafting of the MCM-41 pore walls with organic functional compounds. They are post synthesis and co-condensation.

1.7.2 Acrid molecular sieves

Acidic properties can be created by incorporation of 3rd group cations. B, Al, Ga-substituted MCM-41 (B, Al, Ga-MCM-41) having large pores with acidic sites on the walls were used in catalytic cracking and alkylation. Use of MCM-41 as an acid catalyst for Friedel-Craft alkylation of 2,4-di-tert-butylphenol (bulky aromatic) with cinnamyl alcohol (Kloeststra et al 1995) and for the tetrahydropyranylation of alcohol and phenol (Armengol et al 1995) was reported. The advantages of MCM-41 were manifested in the above mentioned examples. Tertiary butylation of phenol has been studied over Me-MCM-41 and Me-MCM-48 (Me = Ga, Al, Fe or B). Ga incorporation into MCM-41 seems to exhibit high activity. (Selvam and Dapurkar 2004). In another study, tertiary butylation of toluene was reported with tertiary butyl alcohol over mesoporous Zn–Al–MCM-41 (Si/(Zn + Al) = 75, 151, 228, 304 and 380) molecular sieves and they found
that Zn–Al–MCM-41 (75) was the most active catalyst and it was suggested that more number of Bronsted acid sites available was responsible for the reaction (Selvaraj and Lee 2005).

1.7.3 Basic molecular sieves

If acidity is generated, the basicity of conjugate base can be increased by exchanging protons by alkaline ions. This mild basicity is useful for less demanding base catalyzed reactions. Na-MCM-41 and Cs-MCM-41 catalysts exhibit satisfactory performance in base catalysis (Kloetstra et al. 1995). For example, in the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate, 81% conversion of benzaldehyde and 75% selectivity to the desired product were obtained at 150 °C within 7 h and 90% conversion of benzaldehyde and ca.100% selectivity were observed at 100 °C within 3 h in water solvent. Amine-modified PE-MCM-41 (Pore Expanded-MCM-41) was synthesized and found to be a highly active, reusable, and truly heterogeneous catalyst for the Knoevenagel condensation (Dharani et al. 2007).

1.7.4 Redox molecular sieves

Molecular sieves containing redox active metals are used as active and selective catalysts for the oxidative transformations. The redox reactions are effective when carried out on framework modified ordered mesoporous materials, or materials which had been altered by grafting of active species. Ti-zeolites are effective catalysts in the oxidation of a variety of organic compounds. Ti containing mesoporous materials as well as those modified with transition metals, such as Zr, V, Cr, Mn and Fe was found to be promising oxidation catalysts (Taguchi and Schüth 2005). Ti(V,Cr)-MCM-41 materials exhibit excellent catalytic oxidation performance in the presence of
hydrogen peroxide or even the bulky oxidant TBHP (tertiarybutyl hydroperoxide), as reported by Tanev et al (1994) and Corma et al (1994).

1.8 REDOX MOLECULAR SIEVES FOR OXIDATION

Molecular sieves containing redox active metals are used as active and selective catalysts for oxidative transformation of organic molecules (Arends et al 1997). The advantage over soluble metal compounds which are used as homogeneous catalysts or as stoichiometric amounts is that the use of redox molecular sieves as heterogeneous catalysts avoids contamination of the effluents, which are becoming increasingly difficult to dispose. The versatility of redox molecular sieves over other heterogeneous catalysts is that it is possible to influence which substrate molecules approach the active site by choosing a suitable combination of molecular sieve and solvent (Sheldon 1991).

The molecular sieves can be viewed as a second solvent as it selectively extracts the substrate molecules from the bulk solvent. The substrate molecules that can be selectively extracted are determined by the size and hydrophobicity of the pores of molecular sieves and substrate. The properties of the molecular sieves such as pore dimensions, hydrophobicity, acidity and basicity can be tailored over a broad range allowing the preparation of highly sensitive catalysts and are effective with clean and economical oxygen donors such as 30% aqueous hydrogen peroxide (Arends et al 1997). Zeolites or zeotype molecular sieves consists of regular array of pores of molecular dimensions 4-13 Å. The incorporation of redox metals into such systems produces potential heterogeneous oxidation catalysts. Metal incorporated molecular sieves of MFI and MEL type structure have been investigated for selective oxidation reactions like epoxidation, hydroxylation, oxyfunctionalization of alkanes, ammoxidation and sulfoxidation (Arends et al
Although zeolites showed very high activity and selectivity they could be effective only in the oxidation of small molecules due to the small pore size of these materials (5.3 x 5.5 Å). As a result considerable amount of research is dedicated for the preparation of large pore metallosilicate molecular sieves resulted in structures like Ti-substituted beta zeolite with a beta structure (7.6 x 6.4 Å), enabling the epoxidation of long chain alkanes (Camblor et al 1992; Corma et al 1995; Blasco 1996). However, to catalyze oxidation of even bulkier substrates, development of mesoporous molecular sieves like MCM-41 with unique physical properties enhanced the incorporation of redox species by isomorphous substitution or by grafting or by anchoring. Mesoporous Ti-MCM-41 and Ti-HMS were found to be effective in the epoxidation of norbornene with TBHP and oxidation of 2,6-di-tert butyl phenols with aqueous H₂O₂ respectively (Tanev et al 1994; Corma et al 1994). Ti-grafted MCM-41 was found to be active for the selective epoxidation of cyclohexene and pinene using TBHP as oxidant. Vanadium substituted in the porous framework of MCM-41 was found to be highly active and selective for the partial oxidation of cyclododecane and 1-naphthol with H₂O₂ as oxidant (Reddy et al 1994; Parulescu and Su 2001; Sayari et al 1995; Wei et al 1999; Trukhan et al 2001). Likewise Cr incorporated mesoporous silicates were found active as oxidation catalysts (Ulagappan and Rao 1996). Although, the catalytic properties depends on the nature of metal sites and structure, sorption properties of molecules also produce some effects on its activity and further in the selectivity.

Wagner Alves Carvalho et al (1999) have carried out the oxidation of cyclohexane using Iron and copper immobilised on mesoporous MCM-41 molecular sieves as a catalyst. From the results, it was found that Fe(NC₃)Si-MCM-41 showed good catalytic activity for oxidation of cyclohexane and the activity of the catalysts decreases in the following order: Fe(NC₃)Si-MCM-41 > Fe-MCM-41 > Cu(NC₃)Si-MCM-41 > Cu-
MCM-41. However, when the catalysts are recycled, leaching of the metals is observed. The good catalytic activity found with Fe (NC$_3$) Si-MCM-41 can be attributed to the heterogenised iron complex. Ti and Al containing MCM-41 (Al-MCM-41 and Al-Ti-MCM-41) have been synthesized and tested for direct oxidation of propylene with molecular oxygen. Al-Ti-MCM-41 is more effective than Al-MCM-41, It was also found that MCM-22 with Si/Al ratio of 30 and Na/SiO$_2$ ratio of 0.18 are active for the reaction and a highest partial oxidation yield of 11.3% was obtained at 573 K. (Kazuhisa Murata et al 2003)

Ethyl benzene and diphenyl methane were subjected for oxidation using transition metals (M = Ti, V, Cr) incorporated MCM-41 (Jha et al 2006). The catalytic activities as well as the selectivity of the M-MCM-41 catalysts were explored in the one-step liquid-phase oxidation reaction of ethyl benzene and diphenyl methane. Experimental data showed that the oxidation activity is more when H$_2$O$_2$ as an oxidant, acetonitrile as solvent and V-MCM-41 as catalyst were used. However, the selectivity towards the desired keto derivatives (ethyl benzene to acetophenone and diphenyl methane to benzophenone) follows the order, Ti-MCM-41 > V-MCM-41 > Cr-MCM-41.

Oxidation of o-xylene to phthalic anhydride was studied (Selvaraj and Lee; 2005) using V-Mo-MCM-41. Among the various Si/ (V + Mo) ratio catalysts, V-Mo-MCM-41(46) catalyst showed high activity, due to the increased catalytic activity on the inner side pores of silica surface. Various Fe and V-MCM-41 (Template Ion Exchange (TIE), Fe and V-MCM-41 (Direct Hydrothermal (DHT) catalysts were prepared. The catalytic efficiency of the above mentioned catalysts was tested for the partial oxidation of methane (Qinghong Zhang et al (2005). The results showed that the V-MCM-41 prepared by the TIE method showed better catalytic performance than that prepared by the DHT method in the partial oxidation of methane to
formaldehyde with oxygen. However, Fe-MCM-41 prepared by the DHT method exhibited remarkable methane conversion and formaldehyde selectivity than that of the catalyst prepared by the TIE method.

Catalytic oxidation of toluene was carried out using Cr-substituted mesoporous molecular sieves with molecular oxygen as an oxidant (Subrahmanyam et al., 2003). They found that Mesoporous Cr-AlPO4 and Cr-MCM-48 catalysts were active for the vapour phase oxidation of toluene. Mesoporous Cr-AlPO4 is found to exhibit both acidic and redox properties and hence oxidation as well as dealkylation reactions are taking place in a concerted manner, whereas, the cubic silicate analogue acted as a pure redox catalyst. Cu²⁺-phthalocyanine and Co²⁺-perfluorophthalocyanine incorporated inside Y faujasite and mesoporous MCM-41 as heterogeneous catalysts were studied for oxidation of cyclohexane (Elvira Armengol et al, 1999). The results indicated that CoF₁₆PcMCM-41 was more active and selective than CoF₁₆PcY or unsupported CoF₁₆Pc. In contrast, the highest activity and selectivity were achieved on CuPc complex-Y zeolite.

Vanadium is introduced into MCM-41 by various methods such as direct hydrothermal (V-MCM-41), grafting (V/MCM-41), and immobilization methods (V–NH₂-MCM-41) and its effect has been studied for the one-step liquid-phase oxidation of naphthalene using aqueous H₂O₂ and TBHP as oxidants (Shylesh and Singh 2004). The progressive activity of the V-MCM-41 is greater than V/MCM-41 and V–NH₂-MCM-41 catalysts which may be due to the presence of tetrahedral-coordinated vanadium ions in the framework positions compared to the V–O–V bond formed for V/MCM-41 and the observed higher catalytic behavior of the V–NH₂-MCM-41 catalysts may result from active metal site isolations. The difference in the selectivity behavior of as-synthesized and calcined V-MCM-41 samples showed that apart from the active redox sites, the nature of hydrophilic–hydrophobic
interactions also plays an important role in selective oxidation reactions. Gas phase methanol oxidation (Sangyun Lim and Haller 1999) was studied over highly ordered V-MCM-41 and their study reveals that the main active sites for this reaction is weak Lewis acid sites, which has an isolated tetrahedral coordination of vanadium with surrounding oxygen anions and V-MCM-41 is a stable catalyst for vapour phase oxidation of methanol up to 350 C. Side-chain oxidation of ethylbenzene with tert-butyl hydroperoxide over mesoporous Mn-MCM-41 (Si/Mn = 29, 56, 73 and 104) was carried out by Vetrivel et al (2004). Among all the catalysts, Mn-MCM-41 (29) showed maximum activity and also it retained activity for three cycles of operation with α-phenyl ethanol and acetophenone as major products.

Bimetallic Ru-(Cr, Ni, or Cu) and La-(Co or Mn) incorporated MCM-41 molecular sieves were employed as a catalyst for liquid phase oxidation of styrene and benzene (Parvulescu et al 2004). It is very interesting to note that bimetallic Ru or La-based MCM-41 catalyst showed very high conversion of benzene to phenol but low conversion of styrene to benzaldehyde, which is contrary to the catalytic behavior of monometallic modified MCM-41 catalysts. It is shown that the activity and selectivity of bimetallic Ru, La-MCM-41 catalyst depends on the presence of the second metal and also on the reaction conditions.

Mahendiran et al (2007) have carried out vapour phase oxidation tetralin using Cr-MCM-41 (Si/Cr=25, 50, 75 and 100) and Cr-Fe-MCM-41 (Si/(Cr+Fe)=100) catalysts with molecular oxygen as an oxidant. Among all the catalysts under study, Cr-MCM-41 catalyst with Si/Cr = 25 exhibited maximum efficiency. The reaction is considered to occur in two steps: oxidation of tetralin to tetralol and oxidation of the latter to 1-tetralone, with the former process occurring over Cr$^{3+}$ and the latter over Cr$^{6+}$. 
Vanadium modified mesoporous silicates with a well ordered hexagonal and cubic structure was synthesized and oxidation of styrene and benzene was carried out by Parvulescu et al (2003). The results showed that all the materials obtained are active and selective for the oxidation of styrene to benzaldehyde and benzene to phenol when hydrogen peroxide is used as an oxidant. The activity in oxidation of alcohols is lower compared with that in oxidation of aromatic hydrocarbons. It is obvious that catalysts containing V species are more suitable for oxidation of aromatics and other metal ions should be incorporated in mesoporous materials to have high activity in oxidation of alcohols.

1.9 SCOPE OF THE PRESENT STUDY

The work described in this thesis is principally aimed at exploiting the advantageous properties of MCM-41 materials as supports for transition metals like Cr, V, Mn and Fe in the synthesis of fine chemicals using mono and bi metal incorporated MCM-41 by using CO₂ free air as an oxidant via eco-friendly catalytic processes. Literature survey has indicated that the transition metal incorporated MCM-41 have number of advantages over all other supports. Moreover the MCM-41 has a high surface area well defined regular pore shape, narrow pore size distribution, large pore volume, and tunable pore size in conjunction with the high thermal, hydrothermal, chemical, mechanical stability of MCM-41 are highly conductive for number of important applications in fine chemical industries and the vapour phase reaction can be easily carried out over these catalysts in the temperature range 523-673 K. Hence the present investigation includes the following objectives.

(i) Synthesis of mono metallic M-MCM-41 (M = Cr, V, Mn and Fe) with the Si/M atomic ratios of 25, 50, 75 and 100 and bi
metallic M-MCM-41 (M = Cr-Fe and V-Mn) by direct hydrothermal method (DHT).

(ii) Characterization of the above catalysts using ICP-AES, XRD, BET, FT-IR, DRUV-Vis, EPR, TPR, SEM and TEM techniques.

(iii) Synthesis of mono metallic M-HT and M-ZSM-5 (M = V and Mn) by high super saturation and hydrothermal methods respectively.

(iv) Synthesis of bi metallic M-HT (M=V-Mn) and M-ZSM-5 (M=V-Mn) by high super saturation and hydrothermal methods respectively.

(v) Study of vapour phase oxidation of hydrocarbons using CO₂ free air over various catalysts. Optimization of the reaction parameters such as effect of temperature, effect of flow rate, time-on-stream and weight hourly space velocity for better performance. Study of catalyst activity and selectivity for the following reactions.

- Vapour phase oxidation of tetralin over chromium and iron incorporated MCM-41 catalysts.
- Vapour phase oxidation of o-xylene and p-xylene over vanadium and manganese incorporated MCM-41 catalysts.

(vi) Study of the influence of support for vanadium and manganese catalysts on the above reactions.

(vii) Correlation of catalyst activity and selectivity with the physico-chemical characteristics.