CHAPTER 1

INTRODUCTION

1.1 IMPORTANCE OF CATALYSIS

Catalytic technologies have played a vital role in the economic development of chemical industries in the twentieth century with a total contribution of 20% of world Gross National Product (GNP). In the twenty first century, it is expected to drive towards cleaner technologies brought about by public, legislative and corporate pressure to provide new and exciting opportunities for catalysis and catalytic processes. More than 90% of chemical industries involving products such as food, fuels, polymers, textiles, pharma, agrochemicals, etc. make use of catalysts. Unfortunately, the traditional chemical industries, certainly until 1980s, were hazardous and polluting one. These industries generate stoichiometric amount of waste causing pollution of both air and water. The most famous are Bhopal catastrophe in 1984 where 3,000 people were killed and more than 40,000 injured. The grounding of Exxon Valdez in the Prince William Sound in Alaska in 1989 still affects the marine ecosystem nearly 20 years later. Apart from immediate health and environmental hazards, there is also problem of resource management (Rothenberg 2008). The chemical industries during the past 200 years drew heavily on resources. The concept of green chemistry was initiated in 1990s and it deals in designing chemical products and processes that generate and use fewer (or preferably no) hazardous substances. Majority of fine, specialty and pharmaceutical chemicals manufacturing processes still rely on homogeneous reagents and catalysts.
1.2 HETEROGENEOUS CATALYSIS

Both homogeneous and heterogeneous catalysts find wide applications in the fields of oil refining, petrochemicals and chemicals production. Heterogeneous catalysts generally offer advantages such as easy handling of requirements, simplicity and versatility of process engineering, catalyst regeneration, decreasing reactor and plant corrosion problems and environmentally safe disposal. These catalysts can also be designed to give higher activity and selectivity and longer catalyst life. The advantage of heterogeneous catalysis was first appreciated in petroleum refining and bulk chemical industries. Heterogeneous catalysts not only minimise the production of waste but also exhibit activity and selectivity comparable or superior to the existing homogeneous route (Wilson and Clark 2000). Large number of solid acid catalysts such as zeolites, oxides, complex oxides, ion-exchange resins and phosphates are employed for industrial applications. In particular, the contribution of zeolites to industrial application is appreciated to be the greatest.

There is a vast scope for the introduction of solid acid catalysts in the synthesis of fine chemicals and pharmaceutical intermediates. In fine chemical operations, the E-factors are of the order of 5-50 kg waste per kg product compared with values of <1-5 for bulk chemicals and ~0.1 for refinery operations (Sheldon 2000). There are number of reasons for the fact that fine chemical industries have been slower to embrace the benefits of heterogeneous catalysis. The increasing complexity of the reactions demands design of heterogeneous catalysts. In particular, the molecules of fine chemicals, generally bulky, more poly-functional and less stable than those of petrochemicals, impose requirements for activity under milder conditions and higher selectivity on catalysts. These are now met by many novel catalytic
materials. In the area of enantioselective catalysis especially, the engineering of specific sites on appropriate solid surfaces is becoming feasible.

1.3 DIFFERENT HETEROGENEOUS CATALYSTS

1.3.1 Biocatalysts

Enzymes are the most common and efficient catalysts found in nature. Most of the chemical reactions that occur in the human body and in other living things are high energy reactions that would occur slowly, if at all, without catalyst provided by enzymes. Enzymes are generally specific catalyst. They catalyse only one reaction of one particular reactant (called substrate). Usually the enzyme and its substrate have complementary structures and can bond together to form a complex that is more reactive due to the presence of functional groups in the enzyme, which stabilise the transition state of the reaction or lower the activation energy. The toxicity of certain substances (e.g., carbon monoxide and the nerve gases) is due to their inhibition of life sustaining catalytic reactions in the body.

1.3.2 Metals and Metal Oxides Catalysts

Finely divided metals are often used as catalysts and they adsorb reactants onto their surfaces, where the reactions occur more readily. Finely divided metals or metal oxides catalyse hydrogenation reactions, e.g., the formation of hard cooking fats from vegetable oils. Commercial preparation of sulfuric acid and nitric acid also depends on such surface catalysis. The other commonly used surface catalysts in addition to platinum are copper, iron, nickel, palladium, rhodium, ruthenium, etc. Metal oxides (amorphous and crystalline), mixed metal oxides and supported metal oxides are also widely used as catalysts. Semiconductor oxides such as TiO$_2$, ZnO, WO$_3$, SnO$_2$, etc. are used as photocatalysts in various photochemical reactions.
1.3.3 Porous Materials

Porous inorganic solid acid catalysts such as zeolites, zeotypes and mesoporous materials have the advantages of being tunable, recyclable and easily amenable for separation from liquid reaction mixtures. Proper surface area, chemical composition, channel geometry and pore size distribution are the necessary parameters to provide a catalyst with appropriate active sites and accessibility for desired reactants and products selectivity. Pore size parameters of solid acid catalysts are responsible for the active site accessibility and hence activity. According to the IUPAC definition, porous inorganic materials can be grouped into three major classes based on their pore diameter (Ramaswamy 2000) (Table 1.1).
Table 1.1 Classification of porous materials

<table>
<thead>
<tr>
<th>Class of materials</th>
<th>Examples</th>
<th>Pore structure</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Microporous materials</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zeolites (aluminosilicates)</td>
<td>Faujasites (X, Y), Beta, MOR, ZSM-5, etc.</td>
<td>Small, medium and large pores, 2 and 3-dimensional</td>
<td>0.3-0.7</td>
</tr>
<tr>
<td>Silica molecular sieves</td>
<td>Silicalites, metallosilicates (Ti, V, Sn, Cr-silicates)</td>
<td>Medium and large pores</td>
<td>0.5-0.8</td>
</tr>
<tr>
<td>Phosphate based molecular sieves</td>
<td>Aluminophosphate (AlPOs) and silicoaluminophosphates (SAPOs)</td>
<td>Medium and large pores</td>
<td>0.5-1.0</td>
</tr>
<tr>
<td>Clays and pillared clays</td>
<td>Smectite, K-10 intercalated with metal oxides and pillared interlayered clays (PILCs)</td>
<td>2-Dimensional</td>
<td>&gt;1.0</td>
</tr>
<tr>
<td>2. Mesoporous materials</td>
<td>MCM-41, MCM-48, SBA-15, SBA-1, etc.</td>
<td>1 and 3-Dimensional</td>
<td>2-50</td>
</tr>
<tr>
<td>3. Macroporous materials</td>
<td>Porous gels, porous glasses, etc.</td>
<td>-</td>
<td>&gt;50</td>
</tr>
</tbody>
</table>

Even though mesoporous materials have several advantages, zeolites are the most exploited heterogeneous catalyst in most of the chemical industries. Zeolites have the following special features that make them especially interesting for heterogeneous catalysis (Corma 2003 and Bhatia 1990).

i) They have exchangeable cations that allow introduction of cations with various catalytic properties.

ii) If these cationic sites are exchanged with $H^+$, they can have very high number of strong acid sites.
iii) They have high surface area.

iv) Their pore diameters are less than 10 Å.

v) They have pores with one or more discrete sizes.

Properties (iv) and (v) account for their molecular sieving properties.

1.4 ZEOLITES

Zeolites occur in nature and have been known for almost 250 years as aluminosilicate minerals. Examples are faujasite, mordenite, offretite, ferrierite, erionite and chabazite. Naturally occurring zeolites are rarely phase pure, and are contaminated to varying degrees by other minerals (e.g. Fe$^{2+}$, SO$_4^{2-}$, quartz, other zeolites and amorphous glass). For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential (Weitkamp 2000).

Zeolites are a group of hydrated, microporous, crystalline aluminosilicates containing exchangeable cations of Group IA and IIA elements (e.g. Na$^+$, K$^+$, Mg$^{2+}$ and Ca$^{2+}$) which reversibly adsorb and desorb water. Zeolites have framework structure encloses cavities (or pores) occupied by cations and water molecules, both of which have considerable freedom of movement, permitting ion-exchange and reversible dehydration. They possess highly regular structure of pores and channels that allow some molecules to pass through and cause others to be either excluded or broken down. Zeolites are found to be characterised by the following properties (Tomlinson 1998):

i) low density and high void volume when dehydrated

ii) high hydration degree
iii) generally stable crystal structure when dehydrated
iv) cation exchange properties
v) sorption properties (gases and vapours)
vi) catalytic properties
vii) less or no corrosion
viii) no waste or disposal problems
ix) easy set-up of continuous processes in fixed bed reactions
x) high hydrothermal stability
xi) uniform molecular channels in dehydrated crystals

Synthetic faujasites (zeolites X and Y) were the first zeolite used in industrial scale in fluid catalytic cracking (FCC) of heavy petroleum distillates (Weitkamp 2000). The new zeolitic catalysts are not only orders of magnitude more active than the previously used amorphous silica-alumina catalysts but they also brought significant increase in the yield of gasoline, the most valuable product from FCC plants. The cost of petroleum refining worldwide would be higher by at least 10 billion US dollars per year, if zeolite catalysts are not available today. Zeolite catalysts rapidly conquered additional processes in the field of petroleum refining and basic petrochemistry. The most important processes are hydrocracking of heavy petroleum distillates (Scherzer and Gruia 1996), octane number enhancement of light gasoline by isomerisation (Sie et al 1997), synthesis of ethylbenzene (precursor of styrene and polystyrene) (Dwyer 1981), disproportionation of toluene into benzene and xylenes and isomerisation of xylenes (precursor for terephthalic acid) (Chen et al 1989).

The application of zeolite catalysts is still limited in the manufacture of fine chemicals even though their potential is considered to be very high in
this area (Venuto 1994 and Davis 1998). The single most important application of zeolites is in catalysis in terms of financial market size (not in terms of tonnage) with an estimated market volume around 1 billion US dollars per year.

1.4.1 Composition of Zeolites

Zeolites with rigid three dimensional network structure are composed of tetrahedral units TO$_4$ of SiO$_4$, partially substituted by units of AlO$_4^-$ with charge compensating cations (mostly group IA or group IIA) maintaining charge imbalance between Si$^{4+}$ and Al$^{3+}$ species. The TO$_4$ tetrahedra (T = Si and Al) are interconnected in an orderly fashion so as to form an open structure with uniform pore channels, void volumes and cavities which are unique to zeolites. The TO$_4$ tetrahedra can be arranged in many ways to form different porous crystal structures with a condition that two AlO$_4^-$ tetrahedra are never in adjoining positions, but are separated by at least one SiO$_4$ tetrahedron. Thus, zeolites may be represented by an empirical formula (Jacobs 1977)

$$M_{m/n}[(AlO_2)_x(SiO_2)_y]zH_2O$$

where M represents the non-framework metal cation with valence n and z is the number of moles of water contained in the pores, (x+y) is the number of tetrahedra per crystallographic unit cell and x/y is the framework silicon/aluminium ratio (Si/Al). According to the Löwenstein’s rule (Löwenstein 1954), silicon to aluminium ratio (Si/Al) is equal or greater than one, which forbids neighbouring AlO$_4^-$ tetrahedra due to local charge restrictions. Most of the physical and chemical properties of zeolites are essentially determined by the aluminium content in their framework. Moreover, a number of chemical elements other than silicon and aluminium
can be incorporated into the zeolite lattice structure (i.e. isomorphously substituted zeolites).

All commercially useful zeolites owe their value to one or more of the three properties viz., adsorption, ion-exchange and catalysis. This depends upon the exact shape, size and charge distribution of the lattice structure of the zeolite. Zeolites have the ability to act as catalysts for chemical reactions, which take place within the internal cavities. The important class of reactions is the one that catalysed by hydrogen exchanged zeolites, whose framework bound protons give rise to very high acidity. This is exploited in many organic reactions including crude oil cracking, isomerisation and fuel synthesis. Zeolites can also serve as oxidation or reduction catalysts, often after metals have been incorporated into the framework.

1.4.2 Classification of Zeolites

Zeolites are classified on the basis of their (i) chemical composition (based on Si/Al ratio) (Flanigen et al 1976) and (ii) pore openings (Tsai et al 1999) as shown in Tables 1.2 and 1.3.

**Table 1.2 Classification of zeolites based on the chemical composition**

<table>
<thead>
<tr>
<th>Class of zeolites</th>
<th>Si/Al ratio</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low silica</td>
<td>2 to 3</td>
<td>A, X</td>
</tr>
<tr>
<td>Medium silica</td>
<td>4 to 10</td>
<td>Y, L, MOR, Omega</td>
</tr>
<tr>
<td>High silica</td>
<td>&gt;10</td>
<td>ZSM-5, ZSM-11</td>
</tr>
</tbody>
</table>
Table 1.3 Classification of zeolites based on the pore openings

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Number of rings</th>
<th>Pore opening (Å)</th>
<th>Pore/channel structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Erionite</td>
<td>8</td>
<td>3.6 × 5.1</td>
<td>Intersecting</td>
</tr>
<tr>
<td>10-Membered ring</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZSM-5</td>
<td>10</td>
<td>5.1 × 5.6</td>
<td>Intersecting</td>
</tr>
<tr>
<td>ZSM-11</td>
<td>10</td>
<td>5.3 × 5.4</td>
<td>Intersecting</td>
</tr>
<tr>
<td>ZSM-23</td>
<td>10</td>
<td>4.5 × 5.2</td>
<td>Unidimensional</td>
</tr>
<tr>
<td>Dual pore system</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferrierite (ZSM-35, FU-9)</td>
<td>10, 8</td>
<td>4.2 × 5.4</td>
<td>Unidimensional</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.5 × 4.8</td>
<td>Intersecting</td>
</tr>
<tr>
<td>MCM-22</td>
<td>12</td>
<td>7.1</td>
<td>Capped by six rings</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>Elliptical</td>
<td>2-Dimensional</td>
</tr>
<tr>
<td>Mordenite</td>
<td>12</td>
<td>6.5 × 7.0</td>
<td>Unidimensional</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>2.6 × 5.7</td>
<td>Intersecting</td>
</tr>
<tr>
<td>Omega (ZSM-4)</td>
<td>12</td>
<td>7.4</td>
<td>Unidimensional</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>3.4 × 5.6</td>
<td>Unidimensional</td>
</tr>
<tr>
<td>12-Membered ring</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZSM-12</td>
<td>12</td>
<td>5.5 × 5.9</td>
<td>Unidimensional</td>
</tr>
<tr>
<td>Beta</td>
<td>12</td>
<td>7.6 × 6.4</td>
<td>Intersecting</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>5.5 × 5.5</td>
<td></td>
</tr>
<tr>
<td>Faujasite (X, Y)</td>
<td>12</td>
<td>7.4</td>
<td>Intersecting</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>7.4 × 6.5</td>
<td>Intersecting</td>
</tr>
</tbody>
</table>

1.4.3 Structure of Zeolites

The salient feature of zeolites is that their frameworks are made up of TO₄ tetrahedra called primary or basic building units. Larger finite units with three to sixteen tetrahedra, called secondary building units (SBU), are often used to describe the zeolite framework. These tetrahedra are made up of
silicon atoms in the middle and oxygen atoms at the corners and are then linked together by their corners to form a rich variety of structures. The framework structure may contain linked cages, cavities or channels, which are of the right size to allow small molecules to enter i.e., the limiting pore sizes are roughly between 3 and 10 Å in diameter.

The extraordinary properties of zeolites are caused by their crystal lattice. Instead of using the unit cell of the respective zeolite for description, which is only specific for the zeolite type, secondary building units consisting of different arrangements of tetrahedra (primary building units) are used (Figure 1.1). Different SBUs can be used for the classification of zeolites. The main crystallographic characteristics of zeolites are the channel and cage systems. Zeolite channels are classified according to the number of oxygen or T atoms forming the window together with the geometrical dimensions of the two dimensional channel opening. As per definition, the minimum T atoms necessary to build up a channel is six but even a four membered ring is actually a gateway to a channel. Up to 20-membered rings exist as channel openings as in the case of cloverite structure. The cross section of the opening need not be necessarily ring shaped, it can be elliptical, drop shaped or asymmetrically shaped openings. One, two and three dimensional channel systems are directed to main crystallographic directions of zeolite structures and are distinguished by their connectivity.

Different kinds of arrangements of three dimensional channel systems can exist viz., tetrahedrally (FAU), octahedrally (PHI), hexahedrally (ANA), trigonal, hexagonal, etc. Even channel systems set in each other do exist (Ghobarkar et al 1999). Actually the sizes of channel openings are dependent on water content and/or cation species present in the channel system. Zeolite cages are as important for zeolite specific properties as the channel systems. A proper definition of cages has to include the fact that the
channels themselves are also cages of infinite length. Cages can be defined as voids bigger in diameter than normal channel systems. They are accessible only through the channel system. The simplest cages are formed at the crossing of two channel systems. Molecules bigger than those accessible to the channel system fit into these cages. In some zeolites like FAU, supercages exist at the crossing of the channel systems and they are formed by tetrahedral crossing of channel systems (Weitkamp 2000).

Figure 1.1 Structure of Y zeolite and ZSM-5 with their micropore systems and dimensions

1.4.3.1 Structure of Y zeolite

Zeolite Y (Figure 1.2 (a)) is of utmost important in heterogeneous catalysis. It is the most active component in fluid catalytic cracking (Venuto and Habib 1979 and Ballmoos et al 1997). Its pore system is relatively spacious and consists of spherical cages, referred to super cages, with a diameter of 1.3 nm connected tetrahedrally with four neighbouring cages through windows with a diameter of 0.74 nm formed by 12 TO₄ tetrahedra. Zeolite Y is classified as cubic, which possesses three dimensional, 12-membered ring pore system (Weitkamp 2000 and Baerlocher et al 2001).
1.4.3.2  Structure of mordenite (MOR)

Mordenite (Figure 1.2 (b)) is a zeolite with a dual pore system, which normally possesses interconnecting pore channels with two different pore opening sizes. The pore structure of mordenite is two dimensional. One of the channel is 12-ring (7.0 × 6.5 Å) while the other is a complex 8-ring (2.6 × 5.37 Å and 3.7 × 4.8 Å) which are interconnected (Tsai et al 1999 and Baerlocher et al 2001).

![Figure 1.2 Structure of (a) zeolite Y and (b) mordenite](image)

1.4.3.3  Structure of zeolite beta (β)

Zeolite beta (Figure 1.3 (a)) is a disordered intergrowth of two isomorphs, which are permeated by three dimensional network of 12-membered ring channels with two different types of pores. The dimensions of pore opening in the linear channel are 5.7 × 7.5 Å and the tortuous channel system, consists of interactions of two linear channels of approximate dimensions, 5.6 × 6.5 Å. Zeolite β belongs to a family of zeolites which has a tetragonal and monoclinic system. Both frameworks result from the same
centro symmetrical tertiary building units arranged in layers. There is a high density of stacking faults in the zeolite structure because successive layers are interconnected either in a left or right handed fashion. It is the only large pore zeolite which possesses chiral pore intersections (Halgeri and Das 1999 and Baerlocher et al 2001).

1.4.3.4 Structure of ZSM-5

ZSM-5 (Figure 1.3 (b)) is a type of zeolite built from the pentasil unit. It contains intersecting system of ten membered ring pores, one is straight and another one is sinusoidal. H-ZSM-5 shows a reversible phase transition from monoclinic to orthorhombic symmetry at a temperature, which is composition dependant. For H-ZSM-5 with Si/Al = 300, it occurs at 340 K while for Si/Al < 80, the transition takes place below 300 K. The substitution of an Al\textsuperscript{3+} for a Si\textsuperscript{4+} requires a proton to compensate the negative charge created by aluminium in the framework. This additional proton gives Brönsted acidity, which causes the activity. ZSM-5 has two types of channels, both of which have ten membered ring openings. One channel system is sinusoidal and has a nearly circular (5.4 × 5.6 Å) cross section. The other channel system has elliptical openings (5.2 × 5.8 Å). These are straight and perpendicular to the first system. The cavity at the intersection of the channels is about 9 Å in diameter. It is the only zeolite with high silica to alumina ratio (Scherzer and Gruia 1996a and Baerlocher et al 2001).
ZSM-5 is another example of zeolite, which has gained huge importance in heterogeneous catalysis. They possess important characteristic properties including high activity, high tolerance to coking and high hydrothermal stability. The discovery of ZSM-5 led to many important refining and petrochemical processes such as dewaxing, methanol to gasoline and olefin oligomerisation and catalytic cracking of petroleum. This is one of the most versatile catalysts in methanol to gasoline (MTG) process, hydrocarbon interconversion and m-xylene to p-xylene. It is used industrially in the synthesis of ethylbenzene, isomerisation of xylenes and disproportionation of toluene. It is often looked upon as a prototype of shape selective catalysts (Weitkamp 2000).

This unique two-dimensional pore structure allows a molecule to move from one point to anywhere else in the catalyst (Csicsery 1984) (Figure 1.4). For the MTG process, the pores created by 10-oxygen rings are essential for the formation of desirable products of gasoline, along with zig-zag pores intersecting them. The 8-oxygen ring zeolite will not produce molecules with C6 or more carbons. Molecules of these sizes will not fit into
small pores of the zeolites. The 12-oxygen ring zeolite produce large amounts of C11 and C12 compounds, which are undesirable products for gasoline. Some of the zeolites used in chemical and fuel industries are shown in Table 1.4 (Bhatia 1990).

![Figure 1.4 Schematic pore structure of ZSM-5](image)

Table 1.4 Use of zeolites in chemical and fuel industries

<table>
<thead>
<tr>
<th>Process</th>
<th>Wt %</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic cracking</td>
<td>90</td>
<td>REY, HY</td>
</tr>
<tr>
<td>Hydrocracking</td>
<td>9</td>
<td>HY, mordenite</td>
</tr>
<tr>
<td>Organic chemicals</td>
<td>&lt;1</td>
<td>ZSM-5, REY</td>
</tr>
<tr>
<td>Inorganic chemicals</td>
<td>&lt;1</td>
<td>Mordenite</td>
</tr>
</tbody>
</table>

1.4.4 Shape Selectivity in Zeolites

Underpinning all these types of reaction is the unique microporous nature of zeolites, where the shape and size of a particular pore system exerts steric influence on the reaction, controlling the access of reactants and products. Thus, zeolites are often said to act as shape selective catalysts. Increasingly, attention has focused on fine tuning the properties of zeolite
catalysts in order to carry out specific synthesis of high value chemicals such as pharmaceuticals and cosmetics. Shape selectivities can be distinguished depending on the pore size, which limits the entrance of reacting molecule, departure of the product molecule, or formation of certain transition states. Reactant selectivity occurs when only part of the reactant molecules are small enough to diffuse through the catalyst pores (Csicsery 1984) (Figure 1.5).

![Figure 1.5 Schematic diagram of reactant shape selectivity](image)

An example of reactant selectivity is alcohol dehydration, which requires weak acid sites. Activities were compared over CaA and CaX. Over non-shape selective catalysts, secondary alcohols require much lower temperature because they are easier to dehydrate than primary alcohols. Over CaX all these alcohols have very high conversion, but over CaA the secondary alcohol does not react at all. Isobutyl alcohol has very low dehydration rate (Csicsery 1984).

Product selectivity occurs when some of the products formed within the pores are too bulky to diffuse out as expected products. They are either converted to less bulky molecules (e.g. by equilibration) or eventually deactivate the catalyst by blocking the pores (Csicsery 1984) (Figure 1.6).
Product selectivity is illustrated by iso/normal ratios of butanes and pentanes formed. Over silica-alumina these ratios for the cracked products are quite high viz., 1.4 with butanes and 10 with pentanes. However, isobutane or isopentane is not practically formed over the shape selective CaA, which has a pore opening of slightly below 5 Å. Isobutane that forms internally has to isomerise first to normal butane before it can diffuse out (Csicsery 1984).

Restricted transition state selectivity occurs when certain reactions are prevented because the corresponding transition state would require more space than available in the cavities. Neither reactant nor potential product molecules are prevented from diffusing through the pores. Reactions requiring small transition states proceed unhindered (Csicsery 1984) (Figure 1.7).
In the restricted transition state selectivity towards transalkylation of m-xylene over HMOR (shown in Figure 1.7), the transition state clearly shows an alkyl group in this reaction protruding downward, making this transition state too wide for the pores of mordenite. Thus, 1,2,4-isomer can form whereas 1,3,5-isomer cannot diffuse through the pores of mordenite. Mordenite is similar to a bundle of macaroni aligned parallel to each other. It has one-dimensional pore structure with pore diameter ~7 Å. Very strongly acidic MOR can be prepared and quite large molecules even symmetrical trialkylbenzenes (7-8 Å wide) can pass through the pores. However, if one of them stops, the whole pore is blocked. Therefore, activities generally decline with time unless hydrogenation activity is present.

Molecular traffic control may occur in zeolites with more than one type of pore system. Reactant molecules may preferentially enter the catalyst through one of the pore systems while the products diffuse out by the other. Counter diffusion is thus minimised in such case (Csicsery 1984) (Figure 1.8).

Figure 1.8 Molecular traffic control in (a) ZSM-5 and (b) mordenite
1.4.5 Brönsted and Lewis Acid Sites in Zeolites

Extremely selective reactions can be made to occur over zeolites. In the past, zeolites were mainly used in hydrocarbon transformations in processes occurring through acid catalysis (e.g. cracking). Indeed, the density and strength of Brönsted acid sites make zeolites very active for difficult reactions. These characteristics make them potentially interesting for certain reactions of functional compounds which at present are carried out with very strong acid solutions. However, most of the transformations of functional compounds require catalysts with moderate acid strength, acid sites plus basic sites (bi-functional acid-base catalysis) or even basic sites alone. Zeolites are potential catalysts for these reactions since their acid-base properties can be tailored during their synthesis or by a large variety of post-synthesis treatments.

The reactivity and selectivity of zeolites depend on the nature, concentration and distribution of active sites in the matrix. Thus, there is a direct relationship between the catalytic property of a zeolite and its active sites, which are acidic in nature. When trivalent Al substitutes tetravalent Si, a net negative charge on the framework is created, which has to be compensated by cations. These cations are exchangeable and thus any cation that fits into the channel or pore system can be introduced to neutralise the negative lattice charge. If the cation is a proton, it forms a bridging hydroxyl by covalent bonding to the bridging oxygen. This bridging hydroxyl group is a possible proton donor and consequently a Brönsted acid site. These charge balancing cations are generally group IA and IIA elements of the periodic table or large organic quaternary amine cations, which are employed as template in the synthesis medium. Direct proton exchange of these cations with mineral acids should be avoided as framework aluminium gets leached out, thereby decreasing the number of Brönsted acid sites and resulting structural
instability of the zeolites. The cationic form of synthesised zeolites is exchanged with ammonia solution, thereby leaving the H\(^+\) ions to counter balance the anionic framework. Brönsted acidity depends on the Si/Al ratio of zeolites. As the Si/Al ratio decreases, the number of Brönsted acid sites increase with decrease in the strength of individual sites, which is of utmost importance in acid catalysis. Hence, each aluminium atom in the framework induces potential Brönsted acid sites. The generation of Brönsted and Lewis acid sites in zeolites during calcination is depicted in Scheme 1.1 (Uytterhoeven et al 1965).
Scheme 1.1  Schematic representation of Brönsted and Lewis acid sites in zeolites
Lewis acidity arises due to trigonally coordinated aluminium. These aluminium centers act as electron pair acceptors. Lewis acid sites also arise from the formation of extra framework aluminium associated with bond breaking process. However, the acid strength in zeolites is generally defined in terms of Brönsted acid sites.

1.5 CATALYTIC APPLICATIONS OF ZEOLITES

Zeolites find applications in fine chemical synthesis through alkylation, acylation, isomerisation, dehydration, dehydrogenation, halogenation, hydrogenation, etc. (Hölderich et al 1988). Among the zeolites, HY, ZSM-5, MOR and BEA are widely used as catalysts. Zeolite Y has been mainly used for the fluid catalytic cracking and hydrocracking reactions. Mordenite is used in the isomerisation of light alkenes for octane enhancement of gasoline.

Zeolite catalysed Friedel Crafts alkylation reactions have received considerable attention because many products of these reactions are used as starting materials for the synthesis of polymers, perfumes, flavours and pharmaceuticals. Zeolites are well exploited for alkylation of different substrates like benzene, ethylbenzene, toluene, phenol, anisole, naphthalene, biphenyl, aniline, quinoline, thiophene, pyridine, thianthrene, chlorobenzene, etc. with different alkylation agents such as ethylene, propylene, dodecene, methanol, ethanol, dimethyl carbonate, isopropyl alcohol and n-propyl alcohol (Venuto 1994). The diversity of substrates and alkylation agents exemplified the broad spectrum of application of zeolites in alkylation reactions.

Alkylation of benzene with propane (Bigey and Su 2004) over gallium modified ZSM-5 improved the catalytic activity and influenced the selectivity. The effect of oxidative and reductive treatments has been shown
that the catalytic activity and selectivity to toluene was enhanced due to increase in gallium dispersion. The coke deposition probably occurred in the zeolite channel resulting from condensed polyaromatics. Wichterlová and Čejka (1994) studied alkylation of toluene with isopropyl alcohol over large pore zeolites Y, mordenite and ZSM-5. It has been shown that isopropyltoluenes are formed in the first alkylation step followed by a bimolecular reaction with toluene molecules leading to n-propyltoluenes. The bimolecular isomerisation reaction takes place only in the three dimensional channel system of H-ZSM-5 and H-Y, enabling the transition complex formation, which is enhanced by the channel geometry of H-ZSM-5.

Zeolite Y, mordenite, ZSM-5 and other large pore zeolites (Haag and Chen 1987) are predominantly used for transalkylation and disproportionation of toluene to xylene, which are the key raw materials for the production of polyesters, plasticisers and engineering plastics (Jeanneret 1997). Llopis et al (2004) studied the alkylation of toluene with methanol, ethanol, propanol and isopropyl alcohol over ZSM-5, NU-87, SSZ-33 and β zeolites. The selectivity to mono alkylated products is larger with ZSM-5 than with NU-87 due to larger pore restrictions existing in the former for the formation and diffusion of di-alkylated and tri-alkylated products.

The adjustment of pore radii and acidity and/or deactivation of external acid sites of zeolites are the key factors for enhancement of shape selectivity. Sugi et al (2004) found that among the large pore zeolites H-mordenite (H-MOR) exhibited the highest shape selectivity for the formation of 4,4’-diisopropylbiphenyl in the isopropylation of biphenyl. But modification with cerium enhanced the selectivity of 4,4’-diisopropylbiphenyl which is ascribed to the decrease of external acid sites, active in non-regioselective alkylation and isomerisation (Tawada et al 2000).
The effect of light rare earth elements modification including La, Ce, Pr, Nd, Sm, Eu and Gd on the catalytic performance of H-ZSM-5 in the catalytic cracking of mixed alkanes was investigated by Xiaoning et al (2007). The presence of rare earth metal on H-ZSM-5 not only modified the acidic properties of H-ZSM-5, including the amount of acid sites and acid type, but also altered the basic properties, which in turn promoted the catalytic performance of H-ZSM-5 in the catalytic cracking of butane. The existence of empty f orbital is favourable for the formation of Lewis acid site consequently led to the enhancement of total acid site amount, especially the amount of Lewis acid. This could affect the catalytic performance of butane cracking. Ce/ZSM-5 gave the highest yield of total olefins and Nd/ZSM-5 gave the highest yield of propene.

Song et al (2007) reported that molybdenum modified H-ZSM-5 catalyst showed rather high methane conversion and selectivity of aromatics by effectively inhibiting the formation of coke during methane dehydroaromatisation. ZSM-5 modified by the incorporation of either zinc or gallium displayed catalytic performance in the conversion of light alkanes to aromatics, which depend on the crystallinity of zeolite and the method used for zinc or gallium incorporation (Nicolaides et al 2004). Zinc appeared to enhance both activity and BTX (benzene, toluene and xylenes) selectivity, relative to ZSM-5, in contrast to gallium, which affected only BTX selectivity.

Dealuminated Y zeolite modified with InO⁺ has been studied in the reactions of toluene and ethyl benzene disproportionation (Mavrodinova et al 2004). The catalysts with Brönsted acid sites directed methyl transfer upon toluene disproportionation. In contrast, predominant Lewis sites initially enhanced the activity followed by deactivation at the expense of rapid process of accumulation of strongly held reaction products and intermediates.
Further condensation led to catalyst aging rapidly if the concentration of Lewis acid sites is high.

Beckmann rearrangement has been examined over several medium pore (ZSM-5, ZSM-11) and large pore zeolites (Y and beta) as well as montmorillonite and pillared interlayer clays. The lower the aluminium content, the higher the selectivity to caprolactam. Yashima et al (1997) examined Beckmann rearrangement over H-ZSM-5, silicalite-1, silica gel, H-mordenite, H-ferrierite, CaA, NaA and clinoptilolite. They concluded that weak acidic sites showed high selectivity to caprolactam and observed multitude of side reactions like ring opening, decomposition and polymerisation on stronger acid sites. Testova et al (1996) used mordenite, erionite, ZSM-5, ZSM-11, beta and Y-zeolites for their experiments. It was found that acidic sites were strong enough to protonate NH₃ and pyridine that are not favourable for Beckmann rearrangement. Weak acidic centers were shown to be highly selective to caprolactam.

Dahlhoff et al (2001) reported that MCM-22 possessing large outer surface area and its special structure influenced Beckmann rearrangement. The entrance of 12-membered ring super cages consists of 10-membered ring and hence it could be possible that 12-membered ring super cages may not only accessible but could further take part in the reaction producing by-products. The use of MCM-22 catalyst in a fluidised bed seemed unlikely due to presumably strong attrition problems of this special structure.

Hölderich (1989), Hölderich et al (1997), Hölderich and Heitmann (1997), Sato (1997) and Dahlhoff et al (2001a) reviewed vapour phase Beckmann rearrangement over different catalysts. Beckmann rearrangement of cyclohexanone oxime to caprolactam over ZSM-5 showed the importance of weak acidic sites, large outer surface and pore structure accessible only through 10-membered ring channels. They found vicinal silanol groups and
more specifically silanol nests that are the active sites on the catalyst surface rather than strong acidic sites. Furthermore, those sites have to be well dispersed on the surface as well as in isolated and equidistant positions. Such features can only be obtained in the case of zeolites and not in the case of silica.

Beckmann rearrangement of cyclohexanone oxime to caprolactam over Al-beta and B-beta significantly improved the overall catalytic performance by chemical modification (Heitmann et al. 1999). The vicinal hydrogen bonded hydroxyls on Al-beta zeolite showed favourable strength for the rearrangement of oxime, which is in agreement with ZSM-5. This trend was supported in the examination of B-beta. In contrast to the ZSM-5 structure, it is possible to form caprolactam inside the elliptic pores of beta zeolites but the chances for migration of lactam out of the pores are comparatively low. Upon calcination in air, most of the boron was extracted from the framework resulting in the formation of silanol nests and vicinal silanols. These hydroxyl groups were responsible for the high selectivities. Removal of boron from the catalyst resulted significant decrease in activity and selectivity. In the case of B-ZSM-5 (Heitmann et al. 2000), in addition to silanol nest, strong evidence was found for positive influence of boron oxide species on both conversion and in the service time of the catalyst. Upon removal of boron oxide by an acid or basic treatment or deactivation by hydration, the conversion decreased. If boron oxide species were left on the surface or reactivated, as in the case of water absorption, increase of conversion was obtained.
1.6 OTHER APPLICATIONS OF ZEOLITES

1.6.1 Adsorption

The most fundamental consideration regarding adsorption of chemical species by zeolites is molecular sieving. Species with kinetic diameter, which makes them too large to pass through a zeolite pore, are effectively "sieved". This "sieve" effect can be utilised to produce sharp separation of molecules by size and shape. The particular affinity a species has for an internal zeolite cavity depends on electronic consideration. The strong electrostatic field within a zeolite cavity results strong interaction with polar molecules such as water. Non-polar molecules are also strongly adsorbed due to the polarising power of these electric field. Thus, excellent separation can be achieved by zeolites even when no steric hindrance occurs.

The shape selective properties of zeolites are also the basis for their use in molecular adsorption. The ability to adsorb preferentially certain molecules while excluding others has opened up a wide range of molecular sieving applications. Different types of molecules enter the zeolite, but some diffuse through the channels more quickly, leaving others stuck behind, as in the purification of $p$-xylene by silicalite. Cation containing zeolites are extensively used as desiccants due to their high affinity for water and find application in gas separation where molecules are differentiated because of their electrostatic interactions with metal ions. Conversely, hydrophobic zeolites preferentially absorb organic solvents. Zeolites can thus separate molecules based on the differences in size, shape and polarity.

1.6.2 Ion-exchange

Since cations are free to migrate in and out of zeolite structures, they are often used to exchange their cations for those of surrounding fluids.
The preference of a given zeolite among available cations can be due to ion sieving or due to competition between zeolite phase and aqueous phase for the cations that are present. Sodium zeolite A is among the most efficient remover of cations causing hardness to water. The loosely bound nature of extra framework metal ions (such as NaA zeolite) means that they are often readily exchanged for other types of metal in aqueous solution. This is exploited in a major way in water softening where alkali metals such as sodium or potassium prefer to exchange out of the zeolite by hardness causing calcium and magnesium ions from the water.

1.7 MODIFICATION OF ZEOLITES

Modification of zeolites is important for the synthesis of specialty and fine chemicals. Generally, modification of zeolites has been done by passivating the external acid sites to suppress isomerisation whereas narrowing the pore size to enhance the selectivity. Since the number and strength of acid sites play a crucial role in controlling the catalytic activities, the properties of catalysts are carefully tuned for the desired catalytic process. The acid-base properties of zeolites depend on the aluminium content in the framework. The adjustment of acidity may be realised by proper Si/Al molar ratio, other elements replacing framework constituents or modification of the zeolite. Dealumination, the removal of framework aluminium from the zeolite lattice, is a well known procedure for stabilising zeolites and creating mesopores which helps to overcome diffusional problems in the zeolite micropores. Silylation passivates the external surface and thus reduces the non-selective surface reactions. Zeolites could be modified using organometallic complexes by chemical vapour deposition method. By altering the reaction conditions and using large organometallic complexes, it is possible to modify only the external surface hydroxyl groups without altering the internal properties of zeolites.
1.7.1 Modification by Dealumination

Dealumination, the removal of framework aluminium atoms without destroying the micropore structure, is one of the most useful and widely used modifications. Dealumination methods such as thermal, hydrothermal or mineral acid treatment and their mechanisms have been investigated in depth to obtain zeolites with higher stabilities and stronger acidities. Dealumination by steaming, silicon tetrachloride treatment, reaction with chelating agents like EDTA, acetylacetone, ammonium hexafluorosilicate, oxalic acid, etc. and leaching with HCl are some of the post-synthesis methods used to control the acidity of zeolites (Jacobs et al 1984). But steaming is the most common dealumination technique used to prepare industrially important catalysts of high activity, selectivity and stability (Scherzer 1984). Mild steaming is found to enhance greatly the acidity of H-ZSM-5 zeolite (Haag and Lago 1981). The enhancement of acidity is manifested in reactions like paraffin isomerisation, paraffin cracking and toluene disproportionation.

Lago et al (1986) reported generation of sites with enhanced activity up on mild steaming of H-ZSM-5 while severe steaming was found to reduce the activity. Infrared spectroscopy of ZSM-5 samples after mild treatment with aqueous HF showed a decrease in the number of strong Brönsted acid sites and an increase in the number of Lewis acid sites (Ghosh and Kydd 1990). Loeffler et al (1990) studied the nature of different -OH groups in dealuminated H-ZSM-5 and they identified five different types of acid sites due to the formation of non-framework aluminium. Dealumination of Pd/H-ZSM-5 by HCl treatment was found to increase the strong acid site density resulting an increase in isobutane yield in n-butane isomerisation. But there is no clear change in the surface area or pore volume on dealumination (Cañizares et al 1998). Similarly, the activity of H-ZSM-5 for phenol hydroxylation was found to increase after hydrothermal dealumination.
that was attributed to the creation of Lewis acid extra framework alumina (Motz et al 1998).

Kumar et al (2000) studied the effectiveness of dealumination with reagents like HCl, acetylacetone (AA) and ammonium hexafluorosilicate (AHFS). Acetylacetone is the most effective reagent while ammonium hexafluorosilicate is the least effective for aluminium leaching. Increase in the crystallinity and BET surface area were observed after dealumination in the order: H-ZSM-5 (untreated) < H-ZSM-5(AHFS) < H-ZSM-5(HCl) < H-ZSM-5(AA). Even though there is only a slight change in the overall area, the surface area of mesopores was found to increase considerably in the same order, though the micropore area decreased slightly in the reverse order. The overall surface area increased in the same order as that of increase in crystallinity, which was attributed to aluminium leaching as well as creation of mesopores. Nesterenko et al (2006) reported that dealumination of mordenite led to creation of secondary micro/mesopore structure, providing easier transport for alkylaromatic compounds inside the pores and higher acid sites accessibility. Both factors led to significant improvement in the catalytic activity, stability and selectivity.

Oumi et al (2002) investigated dealumination behaviour of ZSM-5 zeolite by steaming treatment, namely, dealumination. BEA zeolite could be very easily dealuminated by HCl treatment. However, HCl treatment did not dealuminate highly siliceous MOR, ZSM-5 and FER zeolites. Therefore, dealumination was carried out by a combination of calcination in air and HCl treatment. The bulk Si/Al ratio of dealuminated MOR zeolite was strongly dependent on the calcination temperature and period. Hydrolysis of Si-O-Al bonds in the zeolite framework may be promoted by calcination in air. The bulk Si/Al ratio of ZSM-5 and FER zeolites did not change during the treatment. Müller et al (2000) reported similar results and suggested that the
number of T atoms in the four membered ring of the framework structure has an influence in the stability towards dealumination because the tension in the smaller rings is larger. The more number of aluminium atoms in an environment with tension, the easier it is to dealuminate the zeolite. The extent of dealumination decreased in the same order as the number of T sites in four membered ring: BEA > MOR > ZSM-5 > FER.

1.7.2 Modification by Surface Passivation

Silylation of H-ZSM-5 led to increase in Brönsted acid sites and decrease in Lewis acid sites but no such changes took place in the excessively dealuminated H-ZSM-5. It is proposed that aluminium species in partially dealuminated state but still attached to the framework, by one or two points, are reinserted totally into the framework positions by silylation. These aluminium sites are covered by deposited silica extra layers and resulted internal Brönsted acid sites. Such catalysts become highly para selective without loosing activity due to alteration in pore mouth opening and the SiO₂ deposition passivates the external surface acidity.

Modification using organometallic complex (Sn(Bu)₃) reduces the density of acid sites on the external surface of H-ZSM-5. The number of MoOₓ species deposited at such external surfaces during the exchange process increases benzene selectivity for methane aromatisation (Wu et al 2005). Yoo et al (1999) studied tert-butylaation of catechol with tert-butyl alcohol over ZSM-5, Na-ZSM-5 and H-ZSM-5 modified by silylation with tetraethylorthosilicate or poisoned with bulky amine (tributylamine). Among the catalysts, H-ZSM-5 appeared to be the most efficient catalyst for the selective formation of 4-tert-butyl catechol. The conversion increased with increase in the concentration and strength of acid sites. But its selectivity is influenced by the size of zeolite pore aperture. The selectivity to 4-tert-butyl catechol has been improved by removing the external acidic sites through
silylation and poisoning using large molecules that are bigger than the pore size of zeolites.

Bhat et al (1995) studied the effect of ZSM-5 extrudates in the ethylation of ethylbenzene with ethanol. Attempts have been made to enhance the para selectivity of this zeolite with and without binder by chemical vapour deposition of silica towards the combined effect of extrusion and silylation on \( p \)-diethylbenzene selectivity. Silylation resulted narrowing of pore opening with silica deposited on external surface leaving the internal structure unaffected. High Si/A1 ratio (500) exhibited the highest selectivity with least silica deposition. Shaikh et al (1999) studied the silylation of H-ZSM-5 by chemical vapour deposition using tetraethylorthosilicate as silylating agent and used the silylated material for disproportionation of ethylbenzene. As a result of silylation, \( p \)-diethylbenzene with almost 100% selectivity was obtained.

The effect of different silicon compounds as modifying agents on the catalytic activity of ZSM-5 zeolite was attempted in the ethylation of toluene (Wang et al 1989), n-hexane cracking (Handreck and Smith 1990) and selective toluene disproportionation (Uguina et al 1992). Bhat and Halgeri (1993) have modified ZSM-5 zeolite by chemical vapour deposition of tetraethylorthosilicate and used it for ethylbenzene alkylation with ethanol. The chemical vapour deposition method changed neither the channel size nor the acidity. The deposited silica narrowed the pore opening size and at the same time deactivated the external surface due to coating of inert silica on the external surface (Niwa et al 1986). As a result, the shape selective property of the zeolite is enhanced to a great extent. Bhat et al (1996) established the relationship between morphology, crystal size and catalytic activity of the external surface inactivated H-ZSM-5 for the alkylation of toluene with ethanol. The external surface inactivated H-ZSM-5 showed enhanced para
selectivity up to 99%. The extent of modification was higher for H-ZSM-5 with smaller crystallite size, while it was lower for twinned elongated prismatic crystals. The covering of these crystals by foreign particles enhanced the extent of inactivation needed to achieve desired high para selectivity.

Corbin et al (1990) reported the poisoning of external surface acid centers of H-ZSM-5 with trimethylphosphite for methanol amination. As a result, the selectivity of dimethylamine increased but the activity decreased. Čejka et al (1996) studied the para selectivity of H-ZSM-5 in toluene alkylation with methanol and ethylene. Surface silylation of H-ZSM-5 with tetraethylorthosilicate led to blocking of Si-OH-Al groups on the external surface and substantial decrease in the transport rate of \( p \)-ethyltoluene compared to H-ZSM-5. Substantial enhancement of para selectivity has been found after surface silylation of H-ZSM-5 as a result of pore entrance narrowing rather than annihilation of external acid sites.

1.7.3 Modification by Metal Cations

The acidity of zeolites can be modified with alkali, transition and rare earth metal cations by isomorphous substitution or ion-exchange or impregnation method. The generation of new Brönsted and Lewis acid sites was observed when NaY zeolite was ion-exchanged with rare earth metal ions like La, Nd, Sm, Gd and Dy. The Brönsted acidity of ion-exchanged catalysts is in the order: GdNaY < SmNaY < NdNaY < LaNaY, which is in the same order of ionic radius of the rare earth metal ions (Sousa-Aguiar et al 1998). This is also coincided with the results of Li et al (2003). Berndt et al (1996) observed higher activity for \( \text{Zn}^{2+} \) ion-exchanged H-ZSM-5 than unmodified and \( \text{Zn}^{2+} \) impregnated H-ZSM-5 zeolites in the conversion of propane to aromatics. It was suggested that the high activity of \( \text{Zn}^{2+} \) ion-exchanged H-ZSM-5 zeolite is due to its greater number of strong Lewis acid sites.
Choudary et al (2002) studied benzylation of benzene over H-ZSM-5, isomorphously substituted Fe, Ga and GaAl-ZSM-5 and Zn, Fe, Ga and In impregnated H-ZSM-5. The impregnated catalysts showed higher activity due to the presence of non-framework Zn, Fe, Ga and In oxide species in combination with zeolitic protons. The activity of metal substituted ZSM-5 is much lower than that of impregnated ZSM-5 due to low concentration of non-framework Fe or Ga in the zeolite channels. Wichterlová et al (1996) studied the alkylation of benzene and toluene with isopropyl alcohol over large pore zeolites Y, beta, mordenite and ZSM-12 and medium pore ZSM-5 with isomorphously substituted Fe in the framework. It is observed that open three dimensional (beta or Y) or unidimensional (mordenite or ZSM-12) molecular sieve structures are preferable for cumene synthesis. ZSM-5 with isomorphously substituted Fe is more favoured for \( p \)-cymene synthesis.

Narayanan and Sultana (1998) studied the alkylation of aniline over HX, HY, H-ZSM-5, H-mordenite and solid state ion-exchanged vanadium zeolites. Three dimensional and mildly acidic zeolites (ZSM-5, Y or X) are more active than wide pore unidimensional and strongly acidic H-mordenite. Vanadium addition certainly improved the activity by (i) blocking the strong acid sites and (ii) creating \( \text{V}^{4+} \) species due to vanadium-zeolite interaction, which act as active sites for alkylation. Su and Barthomeuf (1995) studied the alkylation of aniline over Li, Na, K, Rb and Cs modified Y zeolites and they concluded that N-alkylation is favoured on the basic sites and C-alkylation on the cationic acid sites. Yuvaraj et al (1999) studied the vapour phase ethylation of aniline over alkali and alkaline earth metal (Li, Na, K, Cs, Mg, Ca and Sr) exchanged zeolites Y and \( \beta \). N-alkylation is much higher than C-alkylation over all the zeolites. Diethyl carbonate is a better N-alkylating agent than ethanol. Among the catalysts, K\( \beta \) is a good N-mono-alkylating catalyst with 41% aniline conversion and 100% selectivity at 473 K.
A wide variety of heterogeneous catalysts such as rare earth exchanged Y zeolites (Venuto et al 1966), ZSM-5 (Young 1981 and Ming-Yuan et al 1988), CaNaY (Bakhshi-zad 1980) and MCM-22 (Le et al 1990) have been investigated for the alkylation of benzene with higher n-alkenes in the manufacture of linear alkylbenzene (LAB). Sivasanker and Thangaraj (1992) studied the alkylation of benzene with an industrial mixture of higher alkenes for the production of LAB over β-zeolite and mordenite. Almeida et al (1994) evaluated the applicability of medium and large pore zeolites such as ZSM-5 and HY in the alkylation of benzene with 1-dodecene. Y-zeolite exhibited 97-98% selectivity to LAB while H-ZSM-5 showed very low activity due to its small pore size. The channel system of H-ZSM-5 does not provide enough space for the formation of bulky intermediate, which would result from the electrophilic attack of benzene ring with secondary dodecylcarbenium ion.

ZSM-5 modified by impregnation with silicon and magnesium compounds (SiMg/ZSM-5) has been investigated for xylene isomerisation. The precursor used for silicon modification was dimethylsilicone polymer, which cannot penetrate into the zeolite channel system due to its large molecular size. Hence, it is deposited on the external surface and deactivated the non-selective acid sites. But the precursor used in the case of magnesium modification, magnesium acetate tetrahydrate, was located inside the zeolite pore leading to enhancement of diffusional limitations. p-Xylene is the only isomer diffused out of the channel system. Hence, xylene isomerisation over acid sites remained on the external zeolite surface after both modifications (Uguina et al 1993).

NaY ion-exchanged with Cu$^{2+}$, Co$^{2+}$ and Pb$^{2+}$ were investigated for cyclohexane oxidation. It was observed that exchange capacity decreased in the sequence: Pb$^{2+} >$ Cu$^{2+} >$ Co$^{2+}$. But the order of activity was found to be
CuY > CoY > PbY. It was found that conversion increased with increase of empty active sites. The formation of cyclohexanol is favoured initially but subsequently cyclohexanol is converted to cyclohexanone (Sökmen and Sevin 2003). Jong and Cheng (1995) prepared cobalt containing ZSM-5 by incorporation (Co-ZSM-5) and impregnation (Co/ZSM-5) for the hydrogenation of carbon monoxide. The structure of Co-ZSM-5 was partially destroyed after high temperature reduction due to the removal of framework cobalt. On the other hand, Co/ZSM-5 did not affect the zeolitic structure. As the cobalt loading in Co-ZSM-5 increased, the amount of extra framework cobalt oxide formed was also increased and well dispersed in the pore. The catalytic activity was found to be directly proportional to the amount of CoO present, which was formed during pretreatment.

1.8 MODIFICATION OF ZSM-5 WITH PHOSPHORUS COMPOUND

The catalytic activity and selectivity of ZSM-5 can be enhanced by incorporation of group VA elements especially phosphorus, which provided the catalyst with greater number of acid sites but lesser strength than the parent zeolite in addition to pore size modification. Modification of H-ZSM-5 by impregnation with phosphoric or boric acid is found to be indispensable because of its promising catalytic properties in many reactions such as conversion of methanol to hydrocarbons (MTH), n-hexane cracking, disproportionation of toluene, alkylation of toluene with methanol, xylene isomerisation and conversion of methyl chloride to ethylene and propylene. Generally, phosphorus modification has been done by post-synthesis method (wet impregnation) with various phosphorus agents. Phosphoric acid is the most versatile modifying agent. Other reagents include ammonium dihydrogen phosphate, trimethylphosphate and trimethylphosphine.


Sun et al (1993) examined the activity of Mg-ZSM-5 and P,Mg-ZSM-5 for the conversion of CH3Cl to ethylene and propylene. They found that Mg-ZSM-5 was the most active catalyst and exhibited the
longest life time. This catalyst was reasonably selective for the production of light olefins with propylene selectivity as high as 40 wt%. Rumplmayr and Lercher (1990) have demonstrated that phosphorus treatment with trimethylphosphine removed the strong Brönsted acidity and reduced the activity as well. P,Mg-ZSM-5 was unable to convert the light olefins to paraffins and aromatics without the presence of strong Brönsted acidity. Dehertog and Froment (1991) have noticed that the addition of trimethylphosphite to H-ZSM-5 decreased the activity of CH₃OH conversion.

Modification of H-ZSM-5 with phosphoric acid has become a common technique to alter the activity and/or selectivity. The effect of post-synthesis modification on the hydroxyl groups of H-ZSM-5 was investigated using modifiers such as phosphoric acid, trimethylphosphine and trimethylphosphite. The concentration of weak acid sites was found to increase after phosphoric acid and trimethylphosphite treatment and did not vary after trimethylphosphine treatment. The enhanced para selectivity in the alkylation of toluene with methanol over P-ZSM-5 suggested that phosphorus reagent interacted with acid sites of zeolite and attached to the zeolite via framework oxygen atoms. This partially blocked the pore openings and therefore restricted the diffusion of m- and o-xylene (Kaeding and Butter 1980). Vapour phase methylation of toluene with methanol and isopropylation of toluene with 2-propanol was studied over H₃PO₄ modified and unmodified ZSM-5 (Ghiaci et al 2007). H₃PO₄ modified ZSM-5 enhanced the selectivity of p-xylene probably due to deposition of phosphoric acid on the entrance of pores and inside the pores of zeolite. The large fraction of loaded phosphoric acid led to narrowing of pore openings of the zeolite, which probably suppressed further penetration of oligomers of phosphoric acid into the pores of zeolite.
The performance of phosphorus modified H-ZSM-5 was investigated in the cracking of n-hexane and found that the introduction of phosphorus in H-ZSM-5 would increase selectivity to propylene and butenes as well as hydrothermal stability of framework aluminium. In phosphorus zeolite interaction framework aluminium pairs are stabilised by extra framework cationic species formed by protonation of orthophosphoric acid (Blasco et al 2006, Caeiro et al 2006, Xue et al 2007 and Zhao et al 2007). When phosphorus is added in excess of the optimum amount, more framework aluminium is stabilised but the acidity and activity decrease significantly. Introduction of phosphorus into H-ZSM-5 greatly enhanced the selectivity of light olefins especially propylene, thus increased the total yield of olefins in the catalytic cracking of mixed C4 alkanes (Jiang et al 2008). The presence of phosphate in ZSM-5 during steaming lead to stabilisation of the zeolite towards dealumination and retained a larger number of active Brönsted acid sites (Degnan et al 2000). Cordoso et al (2005) reported phosphoric acid modified ZSM-5 calcined at 600 ºC slightly decreases the surface aluminium. However steaming resulted in enrichment of aluminium on the surface due to the migration of extra framework aluminium.

Védrine et al (1982), Nunan et al (1984) and Abubakar et al (2006) have broadened this approach for three modifying agents viz., orthophosphoric acid, trimethylphosphine and trimethylphosphite. Phosphorus modified ZSM-5 affected the acid sites on the outer surface, which increased the relative fraction of strong Brönsted acid sites in the channels. However, Kaeding and Butter (1980) and Chandawar et al (1982) suggested uniform distribution of the modifying agent over the catalyst. At low loadings, the phosphorus compound blocked the sites for reactions that are not subjected to shape selectivity control. Tynjälä and Pakkenen (1998) and Tynjälä et al (1998a) have studied the structure and the acidic properties of H-ZSM-5 zeolite modified with trimethylphosphite. The modifications
resulted in the total elimination of strong Brönsted acid sites accompanied by the formation of new type of acid sites with decreased acid strength. They have studied the conversion of primary and secondary C1-C4 alcohols over these catalysts and concluded that the conversion of methanol to dimethyl ether and then to carbon monoxide takes place even on the weak acid sites, but that the conversion of dimethyl ether to hydrocarbons requires stronger acidity. In the case of higher alcohols the production of ethers decreased significantly probably due to the steric constraints caused by the channels, and therefore the dehydration of alcohols to corresponding alkenes became dominant.

Lercher et al (1985) and Lercher and Rumplmayr (1986) reported the effects of increasing amount of phosphoric acid and trimethylphosphine on the acid-base properties of H-ZSM-5. It was found that the density of strong acid sites decreased with increasing amount of phosphorus loading. The density of weak acid sites increased for phosphoric acid modified ZSM-5 and remained constant for trimethylphosphine modified samples. It was found that in phosphoric acid modified catalyst the P-OH group of phosphoric acid covered by bridged hydroxyl groups. But in the case of trimethylphosphine modified ZSM-5, the decrease in the density of strong Brönsted acid sites caused by strong adsorption of trimethylphosphine on the bridged hydroxyl groups. Trimethylphosphine only blocked strong Brönsted acid sites without affecting the concentration of weak acid sites. Fries rearrangement of phenyl acetate was conducted on the externally modified H$_3$PO$_4$/ZSM-5 and compared with unmodified ZSM-5 (Ghiaci et al 2006). Moderate conversion, high para selectivity and low formation of by-products were observed with phosphoric acid modified ZSM-5. Lu et al (2003) attempted phosphoric acid or boric acid modification with steam treatment of H-ZSM-5. Heptane cracking activity of phosphorus or boron modified sample is lower than that of parent ZSM-5. The activity of steam treated P-ZSM-5 is higher
than that of phosphorus modified ZSM-5 while the activity of steam treated B-ZSM-5 is remarkably enhanced compared to B-ZSM-5.

1.9 SCOPE AND OBJECTIVES OF THE PRESENT INVESTIGATION

The merits of solid acids especially zeolites over soluble acidic catalysts, such as reduction of salt and waste production, replacement of hazardous acids and prevention of plant corrosion, have been proved in refining and petrochemical industries. The increasing involvement of acidic zeolites in the synthesis of intermediates and fine chemicals deserves special mention. Their attractiveness most likely result from the variety of structures and pore dimensions which lead to shape selectivity, tunable acidity and easy regeneration.

ZSM-5 zeolite has been extensively investigated as active catalyst for a variety of chemical reactions. The ability of this type of zeolite for catalysis is based on its acidity combined with special feature of the pore structure. The catalytic behaviour of ZSM-5, expressed in terms of activity, selectivity and stability, is usually assumed to be connected with sites involving tetrahedral aluminium ions in substitutional positions in the framework of silica. Therefore, the value of acidity is related to the number of aluminium ions within the zeolite framework that can be adjusted by proper choice of synthesis conditions to achieve the requirements of a reaction of interest. The acidity can be modified by the introduction of a further chemical component into the zeolite system. Apart from metal cations and boron, phosphorus has been used successfully to improve the desired catalytic properties of ZSM-5. The impregnation of phosphoric acid in ZSM-5 exerts an effect, which is similar to that obtained by thermal and hydrothermal treatments. The number of Brönsted acid sites decreased but dealumination did not happen. The recorded decrease of Brönsted acidity is due to reversible
interaction between orthophosphoric acid and part of the acid bridged hydroxyl groups of the zeolite framework. Phosphorus obviously exerts certain influence that protects aluminium in the framework.

The salient features of ZSM-5 such as medium pore diameter that prevents simultaneous entry of many molecules inside the pores and widely scattered distribution of weak acid sites that discourage rapid catalyst deactivation instigated the reduction in pore size by the modification of H-ZSM-5 with orthophosphoric acid. Such modified ZSM-5 may find specialty in catalytic applications. The focus is also emphasised on the characterisation of modified ZSM-5 and evaluation of their catalytic performance in the alkylation of ethylbenzene and Beckmann rearrangement.

The scope of the present investigation are:

i) Characterisation of the commercial H-ZSM-5 by XRD, TG-DTG, BET surface area, FT-IR spectroscopy and TPD of ammonia.

ii) Modification of H-ZSM-5 with orthophosphoric acid of different loadings (8%, 10% and 12%) by wet impregnation method.

iii) Characterisation of the modified materials using XRD, TG-DTG, BET surface area, FT-IR spectroscopy, TPD of ammonia, $^{27}$Al-MAS-NMR and $^{31}$P-MAS-NMR.

iv) Catalytic evaluation of H-ZSM-5, 8% P-ZSM-5, 10% P-ZSM-5 and 12% P-ZSM-5 in the vapour phase ethylation of ethylbenzene using diethyl carbonate as alkylation agent.
v) Optimisation of reaction parameters such as temperature, feed ratio and WHSV to obtain high selectivity of 1,4-diethylbenzene at maximum ethylbenzene conversion.

vi) Study of the vapour phase tert-butylation of ethylbenzene with tert-butyl alcohol and optimisation of reaction parameters such as temperature, feed ratio and WHSV to obtain high selectivity of 4-tert-butylethylbenzene.

vii) Beckmann rearrangement of cyclohexanone oxime in the liquid phase in the presence of modified and unmodified ZSM-5 and optimisation of reaction variables to get high selectivity of caprolactam.

viii) Correlation of the activity and selectivity of the catalysts with the physico-chemical characteristics in the above reactions.

ix) Study of the sustainability of the catalysts by performing time on stream study.