CHAPTER 1

INTRODUCTION

1.1 GENERAL

Chemical synthesis which involves the conversion of raw materials into useful chemicals and products may be a catalytic or non-catalytic process. However, catalyst based chemical synthesis accounts for 60% of today’s chemical products and 90% of current chemical processes. The food that we eat and the medicines we take, many of the fabrics and building materials that keep us warm, and almost all fuels that transport us by road, sea or air are produced by heterogeneously catalysed reactions. In every catalytic process, lowering of energy requirements, products selectivity and reduced number of unit operations are the major advantages. Thereby catalytic processes are important to run energy efficient and waste minimisation processes. Hence, catalysis has become the heart of modern chemical industry. A good catalyst must possess both high activity and long term stability. But its single most important attribute is its selectivity, which reflects its ability to direct conversion of the reactant(s) along one specific pathway.

1.2 HETEROGENEOUS CATALYSIS

Heterogeneous catalysis is perennially relevant, endlessly fascinating and continues to be hard to make out (Thomas and Thomas 1997).
Heterogeneous catalysts are of crucial importance to the petrochemical industry. Catalytic reforming, cracking, alkylation, isomerisation and conversion of methanol into olefins are some of the most important processes aided by heterogeneous catalysts. One of the major problems related to the use of heterogeneous catalysts is the loss of catalyst activity and/or selectivity with time on stream. The changes produced by catalyst deactivation play a significant role although disadvantageous for a large number of important industrial processes. There is no scientific approach which allows catalyst deactivation to be entirely eliminated (Petrov and Kumbilieva 2006). Hughes (1984) reported catalyst deactivation phenomena due to (i) poisoning of catalysts by impurities present in the reaction mixture, (ii) sintering of the catalyst and (iii) strong adsorption of initial reactants, products or intermediates that arise in the succession of elementary steps involved in the reaction mechanism. Heterogeneous catalysis is a key phenomenon in many fields of modern technology. Many heterogeneous catalysts have been employed in the treatment of environmental pollution (Ertl et al 1999), production of fine chemicals and energy storage and conversion (Ertl et al 1997, Thomas and Thomas 1997).

1.2.1 Biocatalysts

Enzymes are the ubiquitous components of living cells, where they catalyse and regulate reactions of essential biochemical pathways. In common with all catalysts they accelerate the attainment of chemical equilibria but cannot mediate a thermodynamically unfavourable reaction. They are generally specific. They catalyse only one reaction of one particular reactant (substrate). Usually the enzyme and its substrate have complementary structures and can bond together to form a complex that is more reactive.
The functional groups in the enzyme stabilise the transition state of the reaction or lower the activation energy. The majority of enzymatic transformations that have been used for the industrial synthesis of optically active compounds have involved hydrolytic processes which, in general, are kinetic resolutions. The use of protease, chymotrypsin (CHT) catalyse the enantioselective hydrolysis of an ester (Cohen and Khedouri 1961).

\[
\begin{align*}
\text{EtOOC} & \quad \text{HN} \quad \text{C} \quad \text{CH}_3 \quad \text{COOEt} \\
\text{HN} \quad \text{C} \quad \text{CH}_3 \quad \text{COOEt} & \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{HOOC} \quad \text{HN} \quad \text{C} \quad \text{CH}_3 \quad \text{COOEt}
\end{align*}
\]

1.2.2 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>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>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 and Cr-silicates)</td>
<td>Medium and large pores</td>
<td>0.5-0.8</td>
</tr>
<tr>
<td>Phosphate based molecular sieves</td>
<td>Aluminophosphates (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>

### 1.3 Zeolites

Zeolites are complex, hydrated, microporous, crystalline aluminosilicates which form a network of AlO$_4$ and SiO$_4$ tetrahedra linked by shared oxygen atoms. The negative charge of AlO$_4$ tetrahedra is balanced by the inclusion of protons or alkali metal ions. Their general formula is $M_{x/n}((\text{AlO}_2)_{x}(\text{SiO}_2)_{y})z\text{H}_2\text{O}$ where M is an extra-framework cation that balances the anionic charge of the framework. Since 1960 zeolites have been applied in an increasing number of catalytic processes. The interstitial spaces or channels formed by the crystalline network enable zeolites to be used as
molecular sieves in separation processes. Their high surface area provided by their open structure makes them to have very good sorption properties. Their open structure permits in turn accommodating a wide variety of cations such as Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\) and other ions to balance the framework negative charge. These ions are loosely held and so can be readily exchanged for others in a contact solution. If such cations are exchanged by protons, then the zeolites become solid acids with catalytic properties. It is because of these properties zeolites have become an important group of inorganic materials finding extensive applications in industries as sorbents, ion-exchangers and catalysts (Corma 1995).

Up to now, 136 different structures have been reported, of which about 40 are naturally occurring, and the rest has been synthesised in laboratory. The naturally occurring zeolites are of limited value because (i) they always contain undesired impurity phase, (ii) their chemical composition varies from one deposit to another and even from one stratum to another in the same deposit and (iii) nature did not optimise their properties for catalytic applications.

It was only with the advent of synthetic zeolites that this class of porous materials began to play a role in catalysis. A land mark event was the introduction of synthetic faujasites (zeolites X and Y) on an industrial scale in fluid catalytic cracking of heavy petroleum distillates, which is the most important chemical processes world wide. In the period after 1962, zeolite catalysts rapidly conquered additional processes in the fields 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, disproportionation of toluene into benzene and xylenes and isomerisation of xylenes. It is well known that zeolites are usually used as solid acid catalysts...
(Corma 1995). In the beginning of 1990s, zeolites were used as base catalysts in their ion-exchanged and impregnated forms (Weitkamp et al 2001).

Altogether catalysis is the single most important application of zeolites in terms of financial market size with an estimated market value around 1 billion US dollars per year (Naber et al 1994). The main advantages of zeolites compared to conventional solid acids include

1. well-defined crystalline structures differing in channel diameters, geometry and dimensionality,
2. high surface area,
3. a precisely defined inner void volume,
4. ability to adsorb and transform molecules in the inner volume,
5. isomorphous substitution of some trivalent cations into the silicate framework enabling tuning of the strength and concentration of the acid sites,
6. shape selectivity, given by the ratio of the kinetic diameters of the reactants, intermediates and products to the dimensions of the channels,
7. environmental tolerance and
8. thermal and hydrothermal stability.

1.3.1 Classification of Zeolites

Zeolites are classified on the basis of their (i) chemical composition based on SiO$_2$/Al$_2$O$_3$ ratio (Table 1.2) and (ii) pore diameter and pore opening (Table 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 opening

<table>
<thead>
<tr>
<th>Type of molecular size</th>
<th>Structure type code</th>
<th>Largest pore dimension (nm)</th>
<th>Number of Si/Al tetrahedral in pore cross-section</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small pore</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zeolite A</td>
<td>LTA</td>
<td>0.41 (circular)</td>
<td>8</td>
</tr>
<tr>
<td>Erionite</td>
<td>ERI</td>
<td>0.36 x 0.51</td>
<td>8</td>
</tr>
<tr>
<td>Medium pore</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZSM-5</td>
<td>MFI</td>
<td>0.53 x 0.56</td>
<td>10</td>
</tr>
<tr>
<td>ZSM-11</td>
<td>MEL</td>
<td>0.53 x 0.54</td>
<td>10</td>
</tr>
<tr>
<td>Large pore</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zeolite X and Y (faujasite)</td>
<td>FAU</td>
<td>0.74 (circular)</td>
<td>12</td>
</tr>
<tr>
<td>Mordenite</td>
<td>MOR</td>
<td>0.65 x 0.70</td>
<td>12</td>
</tr>
</tbody>
</table>

1.4 STRUCTURE OF ZEOLITES

Basically, zeolites look like sponges but with a very regular structure and pore sizes which are typically of molecular dimensions. Two of the more important zeolites are depicted in Figure 1.1, namely, mordenite and silicalite-1. The regularly shaped channels in these zeolites can be clearly seen. The different zeolites differ in pore diameter, pore size and the way these pores are interconnected. Mordenite has one-dimensional pore system consisting of channels with a diameter of about 7 Å while the pores of silicalite-1 form a three-dimensional network of straight and zig-zag channels (shown schematically in Figure 1.2) with a diameter around 5.5 Å.
1.5 SHAPE SELECTIVE CATALYSIS

Small, uniform intracrystalline cavities and pores characterise zeolite catalysts. If the overwhelming majority of the catalytic sites are
confined within this pore structure and if the pores are small, the fate of reactant molecules and the probability of forming product molecules are determined mostly by molecular dimension and configuration. Only molecules whose dimensions are less than the critical size can enter the pores, have access to internal catalytic sites and react there. Furthermore, only molecules which can leave appear in the final product. Bulkier molecules will react or bulkier products will form only on the relatively few catalytic sites on the external surface of the zeolite crystals. Shape selective catalysis was first reported by Weisz and Frilette (1960) and subsequently many applications appeared in the literature. Csicsery (1984) reviewed shape selective catalysis in zeolites, and Derouane (1980) discussed shape selective catalysis with ZSM-5 zeolites. Shape selective alkylation of naphthalene to methylnaphthalene on ZSM-5 zeolite catalysts was reported by Fraenkel et al (1986).

1.5.1 Types of Shape Selectivity

Reactant selectivity is observed when only one part of the reactant molecules can pass through the catalyst pores. The remaining molecules are too large to diffuse through the pores. The cage or window effect is a special case of reactant selectivity in which certain molecules react at a rate different from most other molecules because their length matches the length of a sieve cavity.

Product selectivity occur when, among all the product species formed within the pores, only those with the proper dimensions can diffuse out and appear as observed products. Bulky products, if formed, are either converted to less bulky molecules or eventually deactivate the catalyst by blocking the pores.
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 a reactant nor potential product molecule is prevented from diffusing through the pores and reactions requiring smaller transition states proceed unhindered. Figure 1.3 represents the three types of selectivities.

Figure 1.3 Schematic representation of the types of shape selectivity
1.6 APPLICATIONS OF ZEOLITES

Compensating cations present in the non-framework position of zeolites are labile and may be exchanged for other cations. Systematic investigation of the aqueous ion-exchange with zeolites has been reported by Barrer (1950). Ames (1960) reported high capacity and selectivity for processing radioactive wastes, and their long term storage owing to the stability of zeolites under the ionising radiation at elevated temperatures. As zeolites have inbuilt pore system, approaching molecular size, they can discriminate molecules based on size. This leads to the term molecular sieve coined by McBain (1932). The molecular sieving property of zeolites is used in industrial separation.

Zeolites can perform filtering, odour removal and gas absorption tasks. The most well known use for zeolites is in water softeners. Calcium in water can cause it to be ‘hard’ and capable of forming scum and other problems. Zeolites charged with much less damaging sodium ions can allow hard water to pass through its structure and exchange calcium for sodium ions. This process is reversible. In a similar way zeolites can absorb ions and molecules and thus act as a filter for odour control, toxin removal and as a chemical sieve. Zeolites can have water in their structures which can be driven off by heat keeping the basic structure intact. Other solutions can be pushed through the structure and thus they can act as delivery systems for the new fluid. This process has applications in medicine, livestock feeds and other types of research. Zeolites added to livestock feed have been shown to absorb toxins that are damaging and even fatal to the growth of animals, while the basic structure of the zeolite is biologically neutral. Aquarium hobbyists are seeing more zeolite products in pet stores as zeolites make excellent remover of ammonia and other toxins. Most municipal water supplies are processed through zeolites before public consumption.
Zeolite catalysts have become widely used in the processing of petroleum and in the production of various petrochemicals. Reactions such as cracking, hydrocracking, alkylation, dealkylation, trans-alkylation, isomerisation, polymerisation, addition, disproportionation and other acid catalysed reactions can be performed with the aid of zeolites. Both natural and synthetic zeolites are known to be active for reactions of these kinds.

1.7 ZSM-5 ZEOLITE

Among the zeolites the medium pore ZSM-5 is important as it is extensively used in industries. The following section is a concise account of structure of ZSM-5, synthesis and catalytic applications and the topics selected for the study are also cited in appropriate places.

1.7.1 Structure of ZSM-5

ZSM-5 (Zeolite Socony Mobil-5) is a catalyst first made by Argauer and Landolt (1972). It is a type of zeolite built from the pentasil unit (Figure 1.4). 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 67 °C while for Si/Al < 80, the transition takes place below 27 °C. The substitution of an Al$^{3+}$ for a Si$^{4+}$ requires a proton to compensate the negative charge created by aluminium in the framework. This additional proton gives Brönsted acidity, which gives the catalytic activity. ZSM-5 has two types of channels, both of which have 10-membered ring openings (Figure 1.3). 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 1996).
It has been suggested (Dědeček et al 2000) that aluminium tetrahedra in ZSM-5 zeolite are predominantly (70-80%) located in the channel intersections of diameter 9 Å. Generally the synthesis of ZSM-5 is carried out with tetrapropylammonium compounds. The corresponding cations are located in the channel intersection and thus after their decomposition protonic sites are formed in such places. It was reported (Dĕdeček et al 2002) that synthesis of ZSM-5 without tetrapropylammonium cations with only sodium ions as counter ions also led to similar distribution of aluminium. Therefore, it can be assumed that the active sites are situated predominantly in the channel intersection in ZSM-5. So, the major portion of catalytic transformations in ZSM-5 occurs mainly in the channel intersections.

1.8 SYNTHESIS OF ZSM-5

In most cases, the synthesis of ZSM-5 is achieved by hydrothermal synthesis. The crystallisation process and final products are sensitively dependent on the composition of source materials, temperature, time, template agents and other initial conditions of the reaction system.

1.8.1 Template Free Synthesis of ZSM-5

Grose and Flanigen (1981) first reported the synthesis of organic-free ZSM-5 with and without seeds after 68-72 h of reaction at
200 °C. Shiralkar and Clearfield (1989) investigated the compositional constraints in the synthesis of pentasil molecular sieves, including aluminosilicate zeolites, without organic templates from the gel composition aSiO$_2$ : Al$_2$O$_3$ : bNa$_2$O : 1500 H$_2$O, in the temperature range 150-190 °C, where a = 20–∞, b = 4.5–10. When a < 30, the system crystallised into mordenite as a major phase along with traces of ZSM-5. At SiO$_2$/Al$_2$O$_3$ ≥ 60, the contribution from α-quartz increased coexisting with ZSM-5 and mordenite. Some hydrous silicon (IV) oxide was also present as an impurity phase. Almost 100% pure α-quartz was obtained when the gel contained no added alumina. At a composition of a = 40 and b = 4.5-6.0, pure ZSM-5 crystallised with the occlusion of Na$^+$ in excess of charge compensation in the zeolite framework. As the Na$_2$O content was increased in the gel, ZSM-5 product was found to be lower in framework silica-alumina ratio probably due to greater solubility of silica.

Schwieger et al (1989) also reported the synthesis of organic free ZSM-5 using narrow SiO$_2$/Al$_2$O$_3$ molar ratio of 30-50 and reaction time of 36-72 h. Li et al (2003) synthesised template-free nanosized ZSM-5 seeds from commercially available ZSM-5 powder. By use of these seeds, thin and hydrophilic ZSM-5 zeolite membranes were prepared on the outer surface of a porous α-alumina tube in a clear solution free from organic template. The membranes showed high thermal stability to withstand pretreatment at 400 °C. Kim et al (2004) synthesised MFI type high silica ZSM-5 with well-defined crystal morphology in the absence of organic template within a short reaction time under stirring at 200 rpm and 190 °C. The results clearly showed the structure directing as well as a charge balancing role of Na$^+$. 

Nanosized ZSM-5 zeolite was successfully synthesised by Cheng et al (2008a) at 180 °C for 24 h after stirring for 5 h and aging of 24 h in the synthesis mixture with the molar composition of
$12\text{Na}_2\text{O} : 100\text{SiO}_2 : 2\text{Al}_2\text{O}_3 : 2500\text{H}_2\text{O}$. Na$^+$ cation was reported to play the structure directing role in place of organic template. Synthesis temperature, time, concentration, agitation and aging were important to prepare nanosized ZSM-5 zeolite. ZSM-5 was synthesised by template-free method using sodium silicate as a silica source and the content of Na$_2$O in mother liquid was controlled by H$_2$SO$_4$ (Kang et al 2009). The effect of Na$_2$SO$_4$ generated by added H$_2$SO$_4$, hydrothermal crystallisation was carried out with two types of mother liquids having low and high Na$_2$SO$_4$ content at 170 °C. High crystalline, isometrical shaped and uniform 1-2 μm sized ZSM-5 with relative crystallinity around 100% could be obtained successfully from the mother liquids having the molar range of (11-21)Na$_2$O : (21.4-11.4)Na$_2$SO$_4$ : 100SiO$_2$ : 2Al$_2$O$_3$ : 4000H$_2$O.

### 1.8.2 Templated Synthesis of ZSM-5

The properties of ZSM-5 zeolite crystallised from the reaction mixture of $10\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 60\text{SiO}_2 : 3000\text{H}_2\text{O} : 10\text{organic}$ (organic = tetrapropylammonium bromide, hexane-1,6-diol, hexane-1,6-diamine or piperazine) at 150 °C were compared with those of organic free ZSM-5 by Araya and Lowe (1986). It was shown that organic species had a marked effect on the composition and excess cation content of the product. Tetrapropylammonium ion was considered to be a true structure directing template, and piperazine and hexane-1,6-diol acted as hydrophobic void fillers and hexane-1,6-diamine held an intermediate position.

Ali et al (2003) prepared the hydrogel from sodium silicate and aluminium sulphate with silicon-to-aluminium molar ratios (Si/Al) in the range 15-100 and transformed into ZSM-5 zeolite using tetrapropylammonium bromide template at pH 10. The crystallisation of gel having Si/Al molar ratio of 10 was achieved with difficulty and represented lower limit of Si/Al ratio, while the gel with Si/Al molar ratio of 9 could not
be crystallised even after several attempts. The catalytic activity of synthesised zeolites was evaluated at 70, 80, 90 and 100 °C in a flow reactor. For the reaction of methanol and isobutene to produce methyl tert-butyl ether, the activity increased with decreasing Si/Al molar ratio of the zeolite and with increasing reaction temperature. These zeolites were found to have methyl tert-butyl ether selectivity in the range of 90-98% that decreased with increase in reaction temperature.

Nayak and Moffat (1990) synthesised ZSM-5 zeolites of various silicon-to-aluminium (Si/Al) ratios with tetrapropylammonium bromide as templating agent and one sample (Si/Al = 36) prepared by use of ammonia in place of tetrapropylammonium bromide. Cracking activity of 1-hexene, 1-heptene and 1-octene was tested. The activities and selectivities were found to be similar for the catalysts prepared with the two templating agents. In addition, the cracking activity was shown to decrease with increasing Si/Al while the activity per aluminium atom increased with decrease in the aluminium content of the zeolite up to Si/Al ratio of approximately 1000. The ease of alkenes cracking was found to be in the order: octenes > heptenes > hexenes. The cracking of alkenes resulted mainly in the production of C₃, C₄ and C₅ alkenes.

Fouad et al (2006) synthesised nanosized ZSM-5 zeolite from precursor mixtures containing different templates, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide and tetrabutylammonium hydroxide and different template/silica mole ratios viz., 0.215, 0.322, 0.43 and 0.537. Physico-chemical investigations showed that the products obtained by different type of templates and different template/silica mole ratios were ZSM-5 phase. The as-synthesised ZSM-5 sample prepared by using tetrapropyl ammonium hydroxide template and 0.215 template/silica mole ratio at 230 °C for 45 h had the highest
crystallinity. It was found that the average crystallite size increased in the following order: tetramethyl < tetrabutyl < tetraethyl < tetrapropyl and surface area increased in the following order: TMAOH < TEAOH < TBAOH < TPAOH.

1.8.3 Synthesis of HZSM-5 in Fluoride Medium

Though ZSM-5 has been largely exploited catalyst in industries, in order to further extend its contribution to catalysis new synthesis routes that offer controlled morphology, surface acidity, crystallinity, large particle size and high surface area are always important. An unprecedented discovery in zeolite synthesis is the replacement of hydroxide ion mineraliser by fluoride. The latter facilitates synthesis of zeolites even in acidic medium (Flanigen and Patton 1978). Synthesis of microporous aluminosilicates, aluminophosphates and gallophosphates in fluoride medium was reported by Guth et al (1984), Guth et al (1989), Guth et al (1992) and Kessler et al (1994). Several advantages have been reported for fluoride mediated synthesis. Fluoride medium construct crystals of large size with fewer defects and high surface area (Guth et al 1986, Mostowicz et al 1994, Nigro et al 1997, Schüth and Schmidt 2002). Fluoride favours fewer metastable phases that facilitate formation of a desired zeolite structure (Axon and Klinowski 1990, Guth et al 1992, Camblor et al 1999). Fluoride aids direct formation of NH₄⁺ZSM-5 in acidic medium, which can be directly calcined to HZSM-5 without resorting to ion-exchange of Na-form to get H-form. But there are disadvantages like occlusion of fluoride inside the cages (George and Catlow 1995, Camblor et al 1999, Fyfe et al 2001) which reduces the acidity of proton (Louis and Kiwi-Minsker 2004) and reduced transport of aluminium from the gel to the framework due to formation of AlFₓ⁻ species (Gougeon et al 2001).
Aiello et al (1999) studied the influence of NH$_4^+$, Na$^+$, K$^+$ and Cs$^+$ on the transport of aluminium from the gel to the framework during the synthesis of HZSM-5 in fluoride medium. It was reported that potassium is the most effective one for aluminium transport and ammonium the least effective one. Even though the alkali ions facilitate aluminium transport to framework during synthesis, it retains alkali ions as charge-compensating ion for framework negative charge. It is a major disadvantage as it demands the hectic ion-exchange of the product zeolite after synthesis just like synthesis in alkaline medium. This problem was taken as first priority in this study to find solution.

As reduced aluminium transport is due to complexation of aluminium by fluoride ions, incorporation of an additional co-complexant to aluminium to compete with fluoride in the gel medium was thought to be a cognizant solution to solve such problem in comparison to the use of alkali ions. In order to verify complexation before application, a potentiometric titration between phosphoric acid, and phosphoric acid and aluminium sulphate versus potassium hydroxide was conducted.

To put it in a nutshell the main purpose of this study was

(i) to solve the problem of aluminium transport from the synthesis gel to the framework during the synthesis of HZSM-5 in fluoride medium using phosphate as a co-complexant,

(ii) to establish that HZSM-5 synthesised in fluoride medium is better than that synthesised in alkaline medium for p-selective activity particularly in tert-butylation of ethylbenzene and ethylation of ethylbenzene, as the fluoride medium affords ZSM-5 crystals of large dimensions and
(iii) to establish that HZSM-5 synthesised in fluoride medium is better than that synthesised in alkaline medium to crack naphtha to light olefins, as the fluoride medium plant only weak and medium acid sites. These acid sites do not re-adsorb much pre-formed olefins and convert them into aromatics.

1.8.4 Synthesis of ZSM-5 from Environmental Waste

ZSM-5 zeolite was also synthesised from lignite fly ash. Charoenpanich et al (2004) synthesised ZSM-5 with varying SiO$_2$/Al$_2$O$_3$ mole ratio (20-100) in the presence of tetrapropylammonium bromide. Their results revealed that SiO$_2$/Al$_2$O$_3$ mole ratio in the raw fly ash is too low to synthesise ZSM-5 zeolite (SiO$_2$/Al$_2$O$_3$ mole ratio = 2.8) while a maximum yield of 43 wt% was obtained with SiO$_2$/Al$_2$O$_3$ mole ratio of 40. Mainly cubic crystals, accompanying with some flake-like structure was observed. As the SiO$_2$/Al$_2$O$_3$ mole ratio increased from 20 to 40, the cubic crystals of ZSM-5 zeolite are increased in size from 5 to 8 $\mu$m. However, the opposite trend was observed when SiO$_2$/Al$_2$O$_3$ mole ratio is higher than 40. The smallest size of about 1 $\mu$m was found at SiO$_2$/Al$_2$O$_3$ mole ratio of 100.

Rice husk (RH) consists of about 40% cellulose, 30% lignin group and 20% silica. When RH is burnt, approximately one fifth of the original weight is obtained as a by-product. Rice husk ash (RHA) contains over 80% silica and a small proportion of impurities such as K$_2$O, Na$_2$O and Fe$_2$O$_3$ which can be removed by acid leaching. RH is a by-product of milling process of rice. It accounts for about one fifth of the annual gross rice production. Production of rice is dominated in Asia, where rice is the only food crop that can be grown during the rainy season in the waterlogged tropical areas. With such a large availability of raw materials it becomes economical to extract silica from RHA. Hence, RH is an excellent source of silica (Vempati et al 1995, Chandrasekhar et al 2003). This silica has been
expected to be an excellent source of pure silicon, silicon carbide and silicon
nitride powders (Rahman and Riley 1989, Krishnarao 1993) and the silica
extracted from rice husk ash by a suitable alkali solution has been found to be
highly reactive for some zeolite synthesis (Bajpai et al 1981, Dalai et al 1985,

The silica in RH is amorphous and transforms to crystalline when it
is heated at high temperatures. The transformation temperature is affected by
its chemical purity and particle size. The international agency for research on
cancer (IARC) announced in 1997 that crystalline silica forms quartz and
cristobalite, belong to Group 1 of hazardous materials which is the same
group as asbestos. Accordingly, respirable crystalline silica is recognised as a
material that can cause respiratory and other tissue damage including cancer.
To protect the environment and decrease the amount of RHA waste products
it is required to have a contained storage for an appropriate utilisation of the
ash. It has been known that SiO\(_2\) in industrial waste RHA can exist in both
amorphous and crystalline (mostly cristobalite) forms depending on its heat
treatment history. In addition to environmental and operative safety concerns,
to be economically able to compete with established commercial ZSM-5
production, a simple and low cost production route has to be employed.
Apart from the use of a low temperature hydrothermal reaction under
autogeneous pressure of the aqueous suspension, using a low cost but
abundant and renewable source of SiO\(_2\) with high potential, i.e., fine grain,
high porosity, large surface area, high purity and in an amorphous form, is
promising since the crystallisation time can be greatly reduced and a high
yield attained.

A simple synthetic route was demonstrated by the efficient
ash (RHA) was utilised as an alternative silica source for the synthesis of
ZSM-5. The reaction of RHA with the organic template tetrapropylammonium bromide at low temperature and under atmospheric pressure led to successful transformation of crystalline ash to ZSM-5. Porosimetry measurements revealed that from a non/macroporous material with a specific surface area of 28 m$^2$g$^{-1}$, microporous material was obtained with a high specific surface area of 397 m$^2$g$^{-1}$. ZSM-5 with Si/Al = 40 and 80 has been synthesised by Mohamed et al (2008) using RHA in the presence of tetrapropylammonium bromide. Both samples exhibited texturing composed of micro-mesoporous character of high surface areas. The SEM image of ZSM-5(Si/Al = 80) revealed platelets with some fibers (needle-like) indicating their nano dimensions.

Panpa and Jinawath (2009) synthesised ZSM-5 zeolite and silicalite with a wide range of SiO$_2$/Al$_2$O$_3$ molar ratios (30-2075) by hydrothermal treatment (150 °C) of the precursor gels (pH 11) under autogeneous pressure in a short reaction time (4-24 h). They reported that the gels with a low range of SiO$_2$/Al$_2$O$_3$ molar ratios (<80) produced an amorphous phase to poorly crystalline ZSM-5 zeolite. Those with a medium range (80-200) favored well crystalline ZSM-5 production with a large surface area whilst those with a high range of SiO$_2$/Al$_2$O$_3$ molar ratios (>200) yielded silicalite. The increase in Na$_2$O content, which was derived from the addition of NaAlO$_2$ to attain the desired SiO$_2$/Al$_2$O$_3$ molar ratio of the gel, did not significantly enhance the crystallisation rate, crystallinity or yield of products. On the contrary, these properties were greatly affected by the increase in SiO$_2$/Al$_2$O$_3$ molar ratio. In the present study it was planned to examine CO$_2$ sorption on NaZSM-5 prepared using RHA as the silicon source. The influence of ceria impregnated in NaZSM-5 on CO$_2$ sorption was also studied.
1.9 CATALYTIC APPLICATIONS OF ZSM-5

ZSM-5 is one of the most important zeolites due to its application in many fields like separation of gases or liquids (van Bekkum et al 1994, Dyer 1988), synthesis of fine chemicals (Hölderich and van Bekkum 1991), one step phenol production (Hölderich and van Bekkum 1991, Häfele et al 1997, Louis et al 2001), in space research (Ghobarkar et al 1999) and essentially as a solid acid catalyst (Chen 2001, Corma 1995, Mota et al 1997).

It has gained increasing importance as high potential catalyst in a number of commercially important processes (Guth et al 1986). It showed high resistance to deactivation by coke deposition than other commercial zeolites, which has been related to absence of large cavities in the pore structure and its low concentration of acid sites (Nigro et al 1997, Mostowicz et al 1994). A brief account of catalytic applications is delineated below.

1.9.1 Trans-alkylation

Mordenite and faujasite Y, both of which belong to zeolite family with a 12-membered ring pore structure are the only two zeolites that have been largely studied for trans-alkylation of toluene and trimethylbenzene (Csicsery 1971, Yashima et al 1972, Inoue and Sato 1981, Wu and Leu 1983, Barakat et al 1987, Mikhail et al 1987, Chao and Leu 1989).

Trans-alkylation of toluene with C$_9$ aromatic hydrocarbons over ZSM-5 with varying SiO$_2$ : Al$_2$O$_3$ ratios (30-800) as well as over Ni-HZSM-5 catalyst was studied by Meshram et al (1984). As SiO$_2$:Al$_2$O$_3$ ratio increased, the rate of trans-alkylation decreased. Among the C$_9$ aromatics that were present in the feed, the ethyl toluenes were extensively de-ethylated to toluene. The shape-selective characteristics of ZSM-5 were revealed through
the relative order of reactivity of three trimethylbenzene isomers 1,2,4 > 1,2,3 > 1,3,5. Trans-alkylation of C₉ aromatics with toluene to xylenes occurred mainly on the external surface of the ZSM-5 crystals. The disproportionation of toluene to yield benzene and xylene, however, took place predominantly in the pore system. Cheng et al (2009) employed nanosized ZSM-5 and micron-sized ZSM-5 for trans-alkylation of benzene with 1,2,4-trimethylbenzene. The catalytic activity of the former was higher than the latter.

1.9.2 Disproportionation of Toluene

The process of toluene disproportionation over ZSM-5 developed by Mobil was reported to be able to effectively upgrade toluene into benzene and xylenes (Grandio et al 1972). Yashima et al (1972) studied transalkylation over zeolites Y and mordenite and showed that among various types of cations in the zeolites the hydrogen form exhibits the greatest activity. By controlling the hydrogen ion exchanged level of NaY, Chao and Leu (1989) demonstrated similar results.

Selective toluene disproportionation was studied over ZSM-5 modified with P, Si and Cs compounds (Uguina et al 1993). For P and Si modified samples, p-xylene proportion in the primary product was 100% due to the diffusional control on the internal xylene isomerisation. The number and strength of the acid sites were reduced by three modifiers but a relationship between p-selectivity and the decrease of the acid strength was not observed. The most p-selective samples were those modified with Si due to the deposition of this agent on the external surface of zeolite crystals avoiding the primary product isomerisation.

Selective toluene disproportionation to benzene and xylenes was investigated over HZSM-5 and modified HZSM-5 zeolites by
Meshram (1987). The zeolites were modified with nickel, magnesium, phosphorus and boron. Two types of active sites were identified, one promoting disproportionation and the other cracking and dealkylation of toluene. The latter sites were suppressed by the modifiers. Kaeding et al (1981) reported that toluene disproportionated to produce benzene and xylene rich in the p-isomer (70-90%) over ZSM-5 zeolites which were modified with phosphorus, boron or magnesium compounds. A mechanism was proposed where oxides of these elements present in the zeolites reduce the dimensions of pore openings and channels sufficiently to favor formation and outward diffusion of p-xylene, the isomer with the smallest minimum dimension.

Kunieda et al (1999) reported selective formation of p-xylene in the disproportionation of toluene over 20 kinds of synthesised ZSM-5. Based upon the total characterisation and its comparison with the selectivity, it was found that the selectivity in disproportionation could be correlated with not only diffusion rate but also the external solid acidity. Unusual low or high selectivity was caused by high external surface acidity or by slow diffusion rate respectively.

1.9.3 Disproportionation of Ethylbenzene

Zhu et al (2006) reported shape-selective disproportionation of ethylbenzene to p-diethylbenzene over ZSM-5 modified by chemical liquid deposition and MgO. MgO modification improved p-diethylbenzene selectivity (p-DEB to DEB) up to 98.6% with appreciable ethylbenzene conversion of 28.1%, and it greatly reduced the side reaction of ethylbenzene dealkylation.

The shape selectivity of H-ZSM-5 in the disproportionation of ethylbenzene was investigated by Melson and Schüth (1997) using a set of
samples with the same Si/Al ratio of 35 but different particle sizes in the range from 0.1 to 80 µm. The external acidity was measured using 2,6-dimethylpyridine. Over large crystals (80 µm) with a very low external acidity only p-diethylbenzene is formed. With decreasing crystal size and thus an increasing number of external acid sites, first the m-isomer, and only for very small crystals (100 nm) also the o-isomer, are observed as the reaction products. The catalyst efficiency decreases from around 1 for the smallest crystals down to about 0.1 for the 80 µm material. The measured external acidity is much higher than expected from the Si/Al ratio and the crystal size. This is because of the fact of surface roughness and the presence of cracks and enrichment of aluminium in the crystal rim. The disproportionation of ethylbenzene most probably proceeded shape-selectively to p-diethylbenzene in the pore system of ZSM-5. The p-diethylbenzene is then isomerised on the external surface of the crystals via 1,2-alkyl-shift reactions first to the m-isomer and subsequently to o-diethylbenzene.

1.9.4 Isomerisation

Li and Jun (1996) studied xylene isomerisation over HZSM-5, MgO-HZSM-5 and CaO-HZSM-5 zeolites using pulse microreactor-chromatograph technique and the dynamic modeling method. The rate constants, activation energies and activation entropies for each step in the reaction network on the catalysts were obtained. The results indicated that strong acidity can favour the conversion of m- and o-xylene while the isomerisation of p-xylene not only takes place on strong acidic sites but also on the weak acidic sites.

1.9.5 Dealkylation

Benzene is produced during the dealkylation of C\textsuperscript{7} aromatics and during disproportionation reactions of toluene and xylenes over zeolites.
Benzene, produced by disproportionation of toluene, for example, contained higher \((C_8^+)\) alkylaromatics such as xylenes. By modifying ZSM-5 with a metal or metal oxide permitted selective dealkylation of 1,4-dialkylbenzene maintaining yield and purity of olefins formed (Sato et al 1987).

1.9.6 Upgradation of Residual Oil

The upgrading of residual oil into light alkenes has attracted increasing interest since the market demand for ethylene and propylene is steadily increasing (Xiao et al 1995). This situation promoted the development of a novel technology, residual oil catalytic cracking. This process is carried out at high temperature \((680 \, ^\circ\text{C})\) and the catalysts required to have good thermal and hydrothermal stability. ZSM-5 is used as a catalyst additive in gas oil cracking and plays a key role in enhancing the gasoline octane rating (Triantafillidis et al 1999).

1.9.7 Additive to Fluidised Catalytic Cracking Catalyst

The addition of ZSM-5 to fluidised catalytic cracking (FCC) units in petroleum refineries is widely practiced as a means of increasing gasoline octane and for producing additional light olefins (Buchanan et al 2001). ZSM-5 is an important additive to FCC catalyst to improve FCC naphtha octane. It is generally accepted that the presence of low amount of ZSM-5 increased the octane number primarily by favouring catalytic cracking and isomerisation of low octane compound to more lighter and branched products (Madon 1991, Buchanan et al 1996).

It is generally accepted that the acid strength required for cracking and isomerisation of alkenes is in the order cracking \(\approx\) oligomerisation \(>\) skeletal isomerisation \(>>\) double bond isomerisation.
(Corma and Wojciechowski 1982). According to this, strong acid sites will promote the undesired oligomerisation-cracking while weak acid sites will be more selective towards skeletal isomerisation. An important point to mention at this stage is that HZSM-5 synthesised in fluoride medium in the present study carries weak and medium acid sites without strong acid sites. Hence, it is expected to exhibit significant influence on cracking of naphtha and on the yield of olefins by suppressing oligomerisation.

Methanol to hydrocarbon process over acid zeolites has received significant industrial attention since its discovery in the late 1970s (Chang 1984). In the last two decades the main focus of this research has been on the methanol to olefin part of the reaction due to increasing demand for light olefins (Chen et al 2005). The methanol to light olefin process is an acid catalysed reaction, of which SAPO-34 and ZSM-5 are the most common catalysts (Stöcker 1999).

### 1.9.8 Synthesis of Fine Chemicals

Catalytic applications of ZSM-5 in the synthesis of fine chemicals such as 2'-hydroxychalcone and flavanone was reported by Saravanamurugan et al (2004). van de Water et al (2004) reported that in the acylation of anisole with acetic anhydride over germanium incorporated ZSM-5 zeolite, a conversion of 21-23% was obtained. The selectivity towards the p-product (p-methoxyacetophenone) was >99% illustrating that the reaction predominantly takes place inside the zeolite micropore. Small size ZSM-5 crystals exhibit higher activity in the acylation of anisole with acetic anhydride due to the increased external surface (Selvin et al 2008). In the acylation of phenol with acetic anhydride over ZSM-5 catalyst, the yield of C-acylated product, o-hydroxyacetophenone (o-HAP) decreased with increase in Si/A1 ratio while the yield of the O-acylated product, phenyl acetate increased. Padró and Apesteguía (2005) studied acylation of phenol with...
acetic acid over Al-MCM-41, HY, Hβ and HZSM-5. Phenyl acetate, o-HAP and p-HAP were obtained as major products with trace amount of p-acetoxyacetophenone. HZSM-5 and HY zeolite exhibited high selectivity to o-HAP while formation of p-HAP was only 0.2% on HZSM-5 and 8.9% on HY. o-HAP is obtained via both direct C-acylation of phenol and acylation of phenyl acetate intermediate formed from O-acylation of phenol.

In addition, ZSM-5 zeolite is employed as catalyst in the cyclisation of diketone. In acid catalysed cyclisation of acetonylacetone, HZSM-5 with Si/Al = 300 yielded 2,5-dimethylfuran (>97%) while in the presence of a base 3-methyl-2-cyclopenten-1-one (>89%) was obtained at 350 °C (Dessau 1990).

1.9.8.1 Para-selective alkylation of aromatics

Selective formation of p-dialkyl aromatics in isomerisation, disproportionation, alkylation and transalkylation of aromatics within the zeolite pore may occur when some of the products cannot leave the zeolite channel. A representative p-dialkyl substituted benzene is p-xylene as it is the raw material in the manufacture of terephthallic acid used in the manufacture of synthetic fibers such as Dacron. Production of p-xylene may be performed by methylation of toluene or by toluene disproportionation over a catalyst under conversion conditions. But such methods result in the production of a mixture of three xylene isomers, o-, m- and p-xylenes. Depending upon the degree of selectivity of the catalyst and reaction conditions different percentage of p-xylene is formed.

It has been tried to enhance the p-selectivity in alkylation of aromatics through various methods (Sayed and Védrine 1986, Wang et al 1989). Lowering the effective pore size of zeolite, enhancement of the diffusional constrain, suppression of non-shape selective sites located on
the external zeolite surface and control of the catalyst acid strength are a few methods. Silylation has been considered as the most effective method among the various modifications to give high p-selectivity to alkylation. Čejka et al (1996) used silylated H-ZSM-5 in toluene alkylation, which improved conversion and selectivity.

Shape-selective catalysis over zeolites is a promising way to synthesise symmetrically substituted isomers of dialkyl aromatics. It occurs to form the least bulky isomer because of steric restriction to formation of bulky transition state and to diffusion of products by the pores. Types of zeolite, adjustment of pore radii, acidity, and/or deactivation of external acid sites are key factors for the enhancement of shape selectivity (Csicsery 1984, Venuto 1994, Chen et al 1996, Čejka and Wichterlová 2002, Perego and Ingallina 2004). Improvement of the selectivity of 4,4′-dimethylbiphenyl in the methylation of 4-methylbiphenyl over alkaline earth metal modified H-ZSM-5 was reported by Guo et al (2003, 2004). Mobil group proposed that the high p-selectivity of modified H-ZSM-5 in the alkylation is due to “product selectivity”, i.e., the intracrystalline diffusivity of p-isomer is higher than both the o- and m-isomers (Chen et al 1979, Kaeding et al 1981, Kaeding 1985). It was reported that the p-isomer was produced selectively inside the ZSM-5 pores in the ethylation of toluene with ethanol but isomerisation of p-isomer occurred on the external acid sites (Paparatto et al 1987).

Yashima et al (1981) proposed that the primary product in the alkylation of alkyl benzene is the p-isomer due to restricted transition state selectivity inside ZSM-5 pores and the other isomers are produced through subsequent isomerisation of already produced p-isomer (Kim et al 1988, 1989, 1991, 1992, 1993, Namba et al 1984). These findings prompted many researchers to deactivate the external acid sites or the enhancement of shape
selectivity in these reactions. Mobil research group proposed that p-selectivity was improved by the modification of H-ZSM-5 with magnesia and phosphorus oxide and that the selective coking of H-ZSM-5 zeolites increased the selectivity of p-xylene in the disproportionation of toluene and other alkyl benzene (Chen et al 1979, Chen et al 1996, Kaeding et al 1981, Kaeding 1985). Yashima et al (1981) described that the isomerisation of p-isomer was retarded by deactivation of external acid sites with the addition of 2,4-dimethyl quinoline in the ethylation of ethylbenzene and in the disproportionation of toluene (Namba et al 1984, Kim et al 1989). Modification of H-ZSM-5 with silicon alkoxide and silane alkoxide improved the shape selectivity in the methylation of toluene (Niwa et al 1986, Hibino et al 1991, Niwa et al 1999).

Ethylation of ethylbenzene to p-diethylbenzene is also important as its dehydrogenated product, p-divinylbenzene, is important in the production of cross-linked polystyrene (Kaeding et al 1987, Rajesh et al 2002, Nandhini et al 2006). It is also a desorbent for the separation of p-xylene from C8 aromatic mixture by absorption process (Kulprathipanaj 1996). Hence, selective ethylation of ethylbenzene has been a topic of high level research interest in petrochemical laboratories. Ethanol, ethylene and diethyl carbonate are the most commonly employed ethylating agents (Kim et al 1988, Wichterlová and Čejka 1992, Nandhini et al 2005). p-tert-Butyl ethylbenzene is also important as its dehydrogenated product, p-tert-butyl vinylbenzene, is important to form poly-p-tert-butyl ethylbenzene with enhanced plasticity over the parent polystyrene (Burress 1986). Based on the above facts p-selective alkylation of aromatics becomes important.

In addition to the methods mentioned above for p-selective alkylation, increase in crystal size is also shown to be important for shape selective alkylation (Chen et al 1996). In this context ZSM-5 synthesised in
fluoride medium might be commented to be good for p-selective alkylation as the medium give crystals of large dimensions. So, it also became one of the main objectives to study p-selectivity in the tert-butylation of ethylbenzene and ethylation of ethylbenzene over ZSM-5 synthesised in fluoride medium.

1.9.9 Cracking of Naphtha to Light Olefins

Olefins of carbon numbers two to five are called light olefins. There is a high demand for them as they are the building blocks for clean fuel alkylates, octane enhancing oxygenates and polymers (Buchanan 2000). The commonly employed feedstocks for them are methane, LPG, gas oil, crude oil and ethanol but conventional naphtha is the most attractive one because it can take advantage of the existing facilities that are used for steam cracking. In addition it is also very cheap. So currently light olefins are manufactured from naphtha by thermal cracking, also called steam cracking. But the process is not energy efficient, as it has been carried out at about 750 ºC. There is also huge evolution of CO$_2$. In addition, it is difficult to control the composition of olefins formed during cracking. Because of such problems, there is huge demand for alternative process like catalytic cracking of naphtha which could be an eco-friendly one.

Zeolites have been the mostly studied catalysts for cracking of naphtha to light olefins. n-Alkanes have been the commonly employed probes to unravel the complexity of cracking. Based on the product distribution two mechanisms have been suggested (Figure 1.5). In the first monomolecular mechanism, the olefin is protonated by the zeolite to form a carbenium ion which then cracks to olefins by beta scission. But paraffins are protonated to form a penta coordinated transition state which then cleaves to form methane and a carbenium ion. The carbenium ion then cracks in the usual manner to olefins.
Monomolecular mechanism

\[
\text{Alkanes} + \text{Alkanes} \rightarrow \text{Paraffins} + \text{Hydride ions}
\]

Bimolecular mechanism

\[
\text{Alkanes} + \text{Alkanes} \rightarrow \text{Paraffins} + \text{Hydride ions}
\]

**Figure 1.5 Mechanism involved in naphtha cracking**

This monomolecular mechanism is favoured at low reactant pressure, low conversion and high temperature. It is featured by simple product distribution. In the bimolecular mechanism ethyl, propyl and other primary carbenium ions abstract hydride ions from the feed alkanes to form paraffins. Sequential abstraction of hydride ion from naphthenes results in aromatics. In addition, hydride transfer can occur between a feed and the zeolite. The bimolecular mechanism is favoured by high reactant pressure, high conversion and low temperature. It is featured by complicated product distribution. Though the former mechanism yields olefins, the latter provides routes for paraffins and aromatics in addition to olefins. It appears therefore the olefin yield is controlled by hydrogen transfer reactions. In addition, they also have strong influence on the catalyst stability (Scherzer 1989). Hence, suppression of such reactions becomes an additional part of research currently in naphtha catalytic cracking.

As hydrogen transfer reactions require large space, large pore HY zeolite is proved to have high hydrogen transfer index. Hence, zeolites of 10-membered ring pore such as ZSM-5, ZSM-11, ZSM-22, ZSM-48, ZSM-23, 12-MRP, ZSM-12, etc are suggested to suppress hydrogen transfer. Low density of acid sites is again better to suppress hydrogen transfer (Sedran 1994), yet it also has been postulated that controlling issue is the catalyst affinity for olefin adsorption (Corma et al 1989). Ion-exchange of zeolites with large metal ions is also suggested to be beneficial, as it reduces
pore volume and so also bimolecular hydrogen transfer. Olefins are actually required for the bimolecular reaction and they are believed to be formed via unimolecular reaction. Conditions that favour a large olefin concentration in the catalyst bed such as longer residence time and an increased level of conversion, result increase contribution to the bimolecular mechanism to the overall catalytic reaction. If the olefin concentration is very small or if the reaction is carried out at high temperatures so that adsorption of olefins is small, the cracking will be dominated by unimolecular reactions. Conversely, at moderate olefin concentrations and at lower temperatures it has been suggested that the fraction of Brönsted acid sites complexed with olefins approaches unity and the rate of cracking is dominated by bimolecular reactions. In general it is accepted that a carbenium ion adsorbed on the catalyst surface takes a hydride ion from a nearby donor molecule-this defines the reaction as bimolecular, to desorb saturated, while the donor, which adsorbs as a carbenium ion, may repeat the process, desorb dehydrogenated after donating a proton back to the catalyst, or suffer beta cracking to yield an olefin and a smaller carbenium ion on the surface (Corma et al 1990). The major products obtained in the cracking of naphtha is presented in Table 1.4.

Medium pore zeolite ZSM-5, for example, is good for suppressing bimolecular reaction in naphtha cracking, as it cannot provide enough space for it. Since, the rate of bimolecular reaction depends on the concentration of chemisorbed carbenium ions, the latter also requires significant suppression. In addition to other factors, decreasing the strength of acid sites is also advantageous, as the re-adsorption of pre-formed olefin can be suppressed. Actually in the present study HZSM-5 zeolite synthesised in fluoride medium is observed to exhibit weak and medium sites without strong acid sites. So it is another objective in this study to carry out naphtha cracking over HZSM-5 synthesised in fluoride medium to verify whether there is enhancement in the yield of olefins.
Table 1.4 Major products obtained in the cracking of naphtha

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention time</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methylpentane</td>
<td>24.223</td>
<td>2.7</td>
</tr>
<tr>
<td>3-Methylpentane</td>
<td>25.378</td>
<td>2.3</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>26.819</td>
<td>7.1</td>
</tr>
<tr>
<td>Methyl cyclopentane</td>
<td>29.584</td>
<td>2.2</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>33.438</td>
<td>1.7</td>
</tr>
<tr>
<td>2-Methylhexane</td>
<td>34.188</td>
<td>3.0</td>
</tr>
<tr>
<td>3-Methyl hexane</td>
<td>35.394</td>
<td>3.7</td>
</tr>
<tr>
<td>trans-1,2-Dimethyl cyclopentane</td>
<td>37.282</td>
<td>1.3</td>
</tr>
<tr>
<td>cis-3-Heptene</td>
<td>38.953</td>
<td>10.5</td>
</tr>
<tr>
<td>Methyl cyclohexane</td>
<td>42.705</td>
<td>4.6</td>
</tr>
<tr>
<td>2,2,3-Trimethyl pentane/2,4-Dimethyl pentane</td>
<td>44.593/44.735</td>
<td>1.4/1.4</td>
</tr>
<tr>
<td>Toluene</td>
<td>49.108</td>
<td>3.9</td>
</tr>
<tr>
<td>2-Methylheptane</td>
<td>51.367</td>
<td>3.8</td>
</tr>
<tr>
<td>4-Methylheptane</td>
<td>51.660</td>
<td>1.1</td>
</tr>
<tr>
<td>3,4-Dimethylhexane</td>
<td>52.943/53.166</td>
<td>3.1/3.1</td>
</tr>
<tr>
<td>1-cis-2-cis-4-Trimethyl cyclopentane</td>
<td>53.827</td>
<td>1.3</td>
</tr>
<tr>
<td>n-Octane</td>
<td>58.291</td>
<td>8.6</td>
</tr>
<tr>
<td>Propyl cyclopentane</td>
<td>63.917</td>
<td>1.4</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>67.510</td>
<td>1.7</td>
</tr>
<tr>
<td>m-Xylene/p-Xylene</td>
<td>69.054/69.236</td>
<td>4.3/4.3</td>
</tr>
<tr>
<td>2-Methyl octane</td>
<td>70.014/70.296</td>
<td>1.9/1.9</td>
</tr>
<tr>
<td>3-Methyl octane</td>
<td>71.510</td>
<td>1.6</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>72.998</td>
<td>1.5</td>
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<tr>
<td>n-Nonane</td>
<td>76.183</td>
<td>4.0</td>
</tr>
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</table>
1.9.10 CO\textsubscript{2} Adsorption

Carbon dioxide is a fatal green house gas (GHG) and its accumulation into the atmosphere leads to climatic change which is followed by destruction of earth’s ecological system. For the global energy requirement we solely depend on fossil fuel, which emits large amount of CO\textsubscript{2} into air. Hence it is a vital task to the scientific community to mitigate the emission CO\textsubscript{2} before it is reaching its higher concentration or finding new renewable energy source. The permanent sequestration of CO\textsubscript{2} in deep sea and coal field may be effective. But the recent literature proved even though this method gives permanent solution for CO\textsubscript{2} removal, they also have some serious adverse effect like cracking of earth crust due to continuous gas permeation and pressure in coal field and increase in pH in deep sea which ultimately leads to the destruction of eco-system. Hence, there is growing interest in reducing green house gas emissions from fossil fuel combustion and maintaining the future viability of coal-fired power generation. One approach is to capture and then sequester CO\textsubscript{2}. Thus the development of high capacity CO\textsubscript{2}-selective adsorbents that can be used in pressure swing adsorption (PSA) processes is one way forward (Knowles et al 2005).

Amine functionalised high surface area inorganic supports were used for adsorption of CO\textsubscript{2}. Formation of ammonium carbamates under anhydrous condition and ammonium bicarbonate and carbonate species in the presence of water (Figure 1.6) was also reported (Leal et al 1992, Leal et al 1995, Delaney et al 2002, Chang et al 2003).
Carbon dioxide, by virtue of its relatively high polarisability and quadrupole energy gets readily adsorbed on zeolites at room temperature (Bonelli et al 2000). Even though several technologies have been developed to separate and capture the industrial emissions of CO$_2$, adsorption/desorption using natural and synthetic zeolites (Rao and Rubin 2002) are important.

1.9.10.1 Mechanism of CO$_2$ adsorption

Adsorption of CO$_2$ in cationic zeolites was reported to form mono- and bidentate carbonate due to interaction of CO$_2$ with the bridging oxygen (Angell and Howell 1969, Jacobs et al 1973, Gallei and Stumpf 1976, Doskocil and Davis 1999). Gallei and Stumpf (1976) described the formation of monodentate carbonate as shown in Figure 1.7. CO$_2$ is initially polarised by interaction with Ca$^{2+}$ ions. The interaction between polarised CO$_2$ and bridging oxygen results in the rupturing of Al–O bond (Gallei and Stumpf 1976, Angell and Howell 1969).

Figure 1.6 Surface reaction of tethered amine groups with CO$_2$

Khelifa et al (1999) and Khelifa et al (2001) observed decrease of CO$_2$ adsorption affinity when Na$^+$ cations of an X-type zeolite were exchanged by M$^{2+}$ cations (Mg$^{2+}$, Sr$^{2+}$, Zn$^{2+}$, Cu$^{2+}$). However, there was an increase of CO$_2$ adsorption affinity when the degree of Na$^+$ exchange increased. Khelifa et al (2004) showed that CO$_2$ adsorption on the zeolites X exchanged with Ni$^{2+}$ and Cr$^{3+}$ decreased compared to that of zeolite NaX due to decrease of adsorbate-adsorbent interaction. Calleja et al (1998) and
Harlick and Tezel (2003) indicated that CO₂ adsorption capacity of H-ZSM-5 decreased with increase in Si/Al ratio. Yamazaki et al (1993) reported that CO₂ adsorption on alkali ion-exchanged ZSM-5 decreased with increase in size of the cation. Based on the reports of CO₂ adsorption on ZSM-5, it was planned in the present study to test CO₂ adsorption by impregnating ceria in NaZSM-5. Finely divided ceria could also polarise CO₂ and enhance its adsorption.

1.10 SCOPE AND OBJECTIVES OF THE PRESENT INVESTIGATION

The scope of the present investigation is

- Hydrothermal synthesis of HZSM-5(Si/Al = 25) in fluoride medium with different F/Si ratios at neutral pH using tetraethylorthosilicate and sodium aluminate as the sources for silicon and aluminium respectively and tetrapropylammonium bromide as the structure directing agent.

- Characterisation of the material by XRD and comparison of them with commercial HZSM-5(Si/Al = 25).

- Optimisation of fluoride content in the synthesis gel for high crystallinity.

- Hydrothermal synthesis of HZSM-5(Si/Al = 25) in fluoride medium with phosphoric acid as co-complexant to fluoride in the pH between 4 and 6 using tetraethylorthosilicate and aluminium sulphate as the sources for silicon and aluminium respectively and tetrapropylammonium bromide as the structure directing agent.
• Characterisation of the material by XRD, EDS and BET.

• Potentiometric titration of phosphoric acid versus potassium hydroxide, and Al\(^{3+}\) and phosphoric acid versus potassium hydroxide to establish complexation between Al\(^{3+}\) and phosphoric acid during the synthesis of ZSM-5 in fluoride medium.

• Hydrothermal synthesis of HZSM-5(Si/Al = 25) in fluoride medium in the pH range between 4 and 6 using tetraethylorthosilicate, LUDOX-ammonium stabilised colloidal silica (AS silica), LUDOX-sodium stabilised silica (HS silica), fumed silica and sodium silicate as the sources for silicon. Aluminium sulphate as the source for aluminium and tetrapropylammonium bromide as the structure directing agent in the presence of phosphoric acid.

• Characterisation of the materials by XRD and comparison of the results with that of commercial HZSM-5(Si/Al = 25) and thereby selection of the right source for silica.

• Bulk synthesis of HZSM-5 with Si/Al = 25, 50 and 75 hydrothermally in fluoride medium in the pH range between 4 and 6 using tetraethylorthosilicate and aluminium sulphate as the sources for silicon and aluminium respectively and tetrapropylammonium bromide as the structure directing agent in the presence of phosphoric acid.

• Characterisation of the materials by XRD, SEM, EDS, TPD (ammonia), \(^{27}\)Al MAS-NMR, \(^{29}\)Si MAS-NMR, FT-IR and BET surface area techniques.
- Study of tert-butylation of ethylbenzene over HZSM-5(Si/Al = 25, 50 and 75) in the vapour phase using tert-butyl alcohol as the alkylation agent.

- Study of the effect of temperature and feed ratio, and optimisation of the parameters for high conversion and product selectivity.

- Study of the effect of time on stream on conversion and product selectivity and comparison of the activity of the catalysts.

- Ethylation of ethylbenzene over HZSM-5(Si/Al = 25, 50 and 75) in the vapour phase using ethanol as the alkylation agent.

- Study of the influence of temperature, feed ratio, WHSV and optimisation of the parameters for high conversion and selectivity of products.

- Cracking of naphtha to light olefins over synthesised HZSM-5(Si/Al = 25, 50 and 75) and commercial HZSM-5(Si/Al = 25) and comparison of the results.

- Synthesis of NaZSM-5 in alkaline medium using rice husk ash as the silicon source and aluminium sulphate as the source of aluminium in the presence of tetrapropylammonium bromide as the structure directing agent. Impregnation of NaZSM-5 with ceria using cerium nitrate hexahydrate.

- Characterisation of the materials using XRD, SEM, TPD (CO$_2$), DRS-UV-Vis, XPS, TGA and BET surface area techniques.

- Study of the sorption of CO$_2$ on NaZSM-5 and ceria impregnated NaZSM-5 and comparison of the results.