Chapter 1

(INTRODUCTION)
INTRODUCTION

1.1 SCOPE OF THE THESIS

The present work was undertaken with the following objectives:

(1) To synthesise and characterise ZSM-5 (MFI) type zeolites and study their activity and selectivity to hydrocarbons in the conversion of ethanol.

(2) To study the influence of temperature, pressure, WHSV, SiO$_2$/Al$_2$O$_3$ ratio, dilution of the feed and dilution of the catalyst on the product distribution in conversion of ethanol.

(3) To synthesise and characterise zeolite LTL, and to introduce platinum and palladium metal for comparing the activity and selectivity of the zeolite supported metals in hydrogenation of phenol to those of platinum and palladium catalysts supported on alumina.

(4) To study influence of temperature, feed rate, pressure, metal content and nature of metal, reaction medium and poison on product distribution in hydrogenation of phenol.

(5) To study deactivation of the catalysts with reaction time.

The principal aim of the study was to arrive at some conclusion regarding the suitability of the catalysts with respect to the two chosen hydrocarbon transformation reactions—ethanol conversion and phenol hydrogenation.
1.2 ZEOLITE SYNTHESIS, STRUCTURE, CHARACTERIZATION AND CATALYSIS

A zeolite may be described as a hydrated alumino-silicate or more appropriately as a silico-aluminate, having a definite crystal pattern with the unit cell formula —

\[ M_{x/n}[(AlO_2)_x(SiO_2)_y]WH_2O \]

Where M is a metal ion and x, y and n are integers. The bracketted portion describes the framework composition and the values of x and y are such that \( y/x \) is usually greater than 1 and they represent the number of tetrahedra in the zeolite, W being the number of water molecules.

The natural zeolites and their properties were known more than 200 years ago but their unique properties came to receive increasing attention only in 1940s. More than 90 percent of all catalytic cracking reactions, yielding hundreds of useful hydrocarbons are now-a-days done over zeolites. With the advent of X-ray crystallography, it soon became possible to synthesis several of these zeolites for use in various commercial applications. Some of these synthesized zeolites are analogs of zeolite minerals while others are not found in nature. In this way, zeolites type A, X, Y, mordenite, etc. were synthesized and characterized\(^1-3\). The earliest uses of these zeolites were for adsorption and drying of gases, separation of gases and ion exchange. Soon their importance as catalysts for reactions was realized. They were thus first employed\(^4,5\) as cracking catalysts in 1964. The selectivity and activity of the synthetic zeolites donot change much with time and temperature. The man made zeolites are also immensely suitable for a number of other
industrially important reactions, such as isomerization, hydrogenation, oxidation, polymerization, selective reforming, alkylation etc. Zeolites in the early period have been reviewed by Milton\textsuperscript{6}. The recent reviews\textsuperscript{7-14} illustrate the various principles of synthesis, identification and applications of zeolites.

The discovery of high silica zeolites in late 1960s and early 1970s has paved the way for enormous success in use of zeolites as catalysts. One of the important zeolites, ZSM-5 was discovered by Argauer and Landolf\textsuperscript{15} in 1972.

'Pentasil zeolites' — this generic name has been used to refer to ZSM-5 type zeolites. The other members of the pentasil family are ZSM-8, ZSM-11 and silicalite. Silicalite\textsuperscript{16} contains no aluminium.

1.2.1 Zeolite synthesis

(i) General approach:

Synthetic zeolites have been first put to extensive commercial use by the Mobil Oil Corporation, USA and most of the methods of synthesis of different zeolites appear as patents by Mobil scientists. The synthesis essentially consists of a nucleation controlled process occurring from molecularly inhomogeneous, alkaline aqueous gels. The composition of the reaction mixture\textsuperscript{17} is defined by a set of mole ratios —

\[
\text{SiO}_2/\text{Al}_2\text{O}_3, \text{H}_2\text{O}/\text{SiO}_2, \text{OH}^-/\text{SiO}_2, \text{M}^+/\text{SiO}_2
\]

where \( \text{M}^+ \) is commonly \( \text{Na}^+ \) ion, but can also be other alkali, alkaline earth or ammonium ions. In recent years the highly shape selective ZSM-5
type zeolites have been prepared by addition of quarternary ammonium salts, amines or other polar substances. The composition is thus determined also by the mole ratio: $R^+_4 N^+/SiO_2$.

The specific role of each of the ratio in determining the composition of the zeolite has been discussed by Rollmann which can be summarized as given in Table 1.1.

The reactants essentially consist of sources of oxides of silicon and aluminium. Commercially available silicon and aluminium source materials may be used for synthesis of zeolites. These include sodium silicate, silica gel, silica sol, sodium aluminate, aluminium sulphate, aluminium turnings, alumina etc. Clays can also be used as the source material.

The four component system $Na_2O - Al_2O_3 - SiO_2 - H_2O$, provided by the sources of oxides, has been effected by hydrothermal action. The system, being thermodynamically unstable, provides several metastable phases. Each of these phases considered to represent a zeolite phase. It is therefore possible to have several zeolite phases depending upon the composition of the reactant mixture, the nature and period of hydrothermal treatment. Some general conditions favouring the synthesis of zeolites are enlisted below:

1. Reactive starting materials such as freshly prepared co-precipitated gels or amorphous solids.
2. Relatively high pH introduced in the form of an alkali metal hydroxide or other strong base.
Table 1.1 Reaction Mixture, Composition and their Primary Influence on Zeolite Synthesis

<table>
<thead>
<tr>
<th>Mole Ratio</th>
<th>Primary influence</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$/Al$_2$O$_3$</td>
<td>Framework composition</td>
</tr>
<tr>
<td>H$_2$O/SiO$_2$</td>
<td>Rate, crystallization mechanism</td>
</tr>
<tr>
<td>OH$^-$/SiO$_2$</td>
<td>Silicate molecular weight and OH$^-$ concentration</td>
</tr>
<tr>
<td>Na$^+$/SiO$_2$</td>
<td>Structure, cation distribution</td>
</tr>
<tr>
<td>R$_4$N$^+$/SiO$_2$</td>
<td>Framework aluminium content</td>
</tr>
</tbody>
</table>
(3) Low temperature hydrothermal conditions with concurrent low autogeneous pressure at saturated water vapour pressure.

(4) A high degree of supersaturation of the components of the gel leading to nucleation of a large number of crystals.

Prior to 1960 inorganic bases were used to supply the necessary alkalinity to the system. Organic bases were introduced first to the system by Barrer and Denny, Barrer et al., and later by Kerr. This was one of the major events in zeolite chemistry and catalysis. This enabled synthesis of more siliceous materials culminating in the discovery of ZSM-5. Szostak has described in details the methods of synthesis and identification of molecular sieve zeolites.

(ii) Synthesis of ZSM-5 zeolite:

The first preparation of ZSM-5 structure was reported in 1972. HZSM-5 was synthesised similarly by Chen et al. and also studied extensively by Dai et al.

The synthesis system for ZSM-5 is \((\text{TPA})_2O\cdot M_2O \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O\), where TPA stands for tetrapropyl ammonium ion and M for an alkali metal cation.

The synthesis of ZSM-5 is carried out by mixing aqueous solutions containing the organic cation and oxides of sodium, aluminium and silicon. The required oxides are supplied by choosing appropriate reagents from among sodium silicate, sodium aluminate, aluminium salts, alumina, silica hydrosol, silicic acid, sodium hydroxide and tetrapropyl ammonium hydroxide or bromide.
Rollmann et al. has described a range of composition of reaction mixtures in terms of mole ratios of oxides which is given below:

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Broad range</th>
<th>Preferred</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH−/SiO₂</td>
<td>10⁻⁸ - 1.0</td>
<td>0.01 - 0.2</td>
</tr>
<tr>
<td>Na⁺/SiO₂</td>
<td>0.1 - 1.5</td>
<td>0.1 - 0.6</td>
</tr>
<tr>
<td>Pr₄N/SiO₂</td>
<td>0.01 - 0.6</td>
<td>0.02 - 0.2</td>
</tr>
<tr>
<td>H₂O/SiO₂</td>
<td>5 - 200</td>
<td>15 - 50</td>
</tr>
<tr>
<td>Si/Al</td>
<td>6.2 - ∞</td>
<td>10 - 1000</td>
</tr>
<tr>
<td>Al/Na</td>
<td>1.6 - 0</td>
<td>1.0 - 0.003</td>
</tr>
<tr>
<td>Na₂O/(TPA)₂O</td>
<td>0.17 - 150</td>
<td>5 - 30</td>
</tr>
</tbody>
</table>

A typical temperature range for hydrothermal treatment is given as 373-473 K with a reaction period from 6 hrs to 60 days.

Nucleation and crystal growth these two stages are considered to occur during crystallization of ZSM-5. The period and mechanism of these stages are immensely affected by the synthesis variables and conditions used. Various experimental techniques are used to monitor the different steps of nucleation and crystallization. XRD, IR, DTA, NMR, SEM and thermogravimetry are some of these techniques.

Several workers have investigated the kinetics of crystallization under different experimental conditions. Activation energy for nucleation and for crystallization in certain synthesis system has also been determined. It has been shown that with other synthesis variables remaining constant, the rate of nucleation and crystallization can be increased by increasing temperature.
1.2.2 Structure and characterization of ZSM-5

(i) Major structural features:

ZSM-5 zeolites consist of a novel configuration of linked tetrahedra which are bound together in groups consisting of 8-five membered rings. These rings are attached to each other through oxygen atoms forming chains, which are interconnected to form planes. The planes are linked with one another to give a three dimensional structure. The ZSM-5 structure contains two intersecting channel systems (Fig. 1.1), defined by 10 membered ring openings. One of them is sinusoidal, running parallel to the (001) plane and the other straight and parallel to (010) plane.

The straight channel has elliptical opening having diameter 5.2 - 5.8 Å and sinusoidal channel has near circular opening having a diameter 5.4 - 5.6 Å. Silicalite which contains no aluminium has been shown to have a similar structure.

The pore structure of ZSM-5 type zeolite has pore dimension intermediate between those of the so-called 'large pore' zeolites (eg. faujasite, dia 7.4 Å) and small pore zeolites (eg. zeolite type A, erionite 3.8 Å x 5.2 Å). This is an important feature of ZSM-5 structure which is likely to be responsible for its shape selective catalytic properties.

The unit cell representation for ZSM-5 is given by the formula
Fig. 1.1 'Hollow tube' representation of the two pore systems (sinusoidal and straight) of ZSM-5.
\[
\text{Na}_n \text{Al}_n \text{Si}^{(96-n)}_n \text{O}_{192} \cdot 16\text{H}_2\text{O}
\]

where \(n\) is generally less than 27. ZSM-5 zeolites have a larger Si/Al ratio in comparison to X or Y zeolites (Si/Al = 2.4) and this gives the zeolite better thermal, hydrothermal and acid stability.

The number of aluminium atoms per unit cell, \(N_{\text{Al}}\), can be obtained using the relation \(N_{\text{Al}} = \frac{96}{(1+R)}\) from the crystallographic formula as defined above with \(R\) representing Si/Al ratio per unit cell.

The zeolite as-synthesised exhibits orthorhombic symmetry with lattice constants \(a=20.1\text{Å}, b=19.9\text{Å}\) and \(c=13.4\text{Å}\). However, transformation to monoclinic symmetry has been observed upon high temperature calcination and ion exchange.

(ii) Properties related to structures:

(a) Sorption — ZSM-5 zeolite can absorb only small and medium size molecules because of its intermediate size of pore opening. Larger molecules like o-xylene, m-xylene and 1,2,4 trimethylbenzene are absorbed slowly indicating steric hindrance. Pentamethylbenzene and 1,3,5 trimethylbenzene (7.8Å) are essentially excluded. The sorption studies can therefore give valuable information regarding pore size of the zeolites.

(b) Diffusivity and catalytic properties— The dimensions of benzene and p-xylene are comparable to the channel dimension of ZSM-5 indicating that these molecules can easily diffuse through the ZSM-5 structure and therefore, they will be highly mobile on the ZSM-5 surface. It
is found that the diffusivity of p-xylene is three orders of magnitude greater than that of o- and m-xylene. The easy diffusivity and mobile nature of benzene and its homologues on ZSM-5 zeolites is expected to have significant influence on the performance of these zeolites as catalysts for aromatic hydrocarbon transformations. This will be further discussed at a later stage.

1.2.3 Characterization techniques

Several experimental techniques are employed to monitor various chemical reactions occurring during synthesis of zeolites and characterize the final product. Some of these techniques are discussed below.

(i) X-Ray Diffraction (XRD):

X-ray diffraction is the most convenient method for identification of the zeolites and also to understand the kinetics and mechanism of zeolites crystallization. Variations in the lattice parameters and framework symmetry, collapse of crystal structure and presence of alien phases are also detected by XRD measurements.

XRD measurements have also been used to quantitatively estimate alumina content of ZSM-5 zeolites.
(ii) Infrared Spectroscopy (IRS)

IR spectroscopy is considered to be complementary to XRD. The zeolites have characteristic framework vibrations. The fundamental vibrations of (Al, Si)O₄ tetrahedra are in the mid-infrared region (1300–200 cm⁻¹) and these have been used in conjunction with XRD to identify the zeolite structure. It is found that the main (Si, Al)–O band occurs at about 1100 cm⁻¹ and is related to the Si/Al ratio in the zeolite framework. Progress in the crystallization during synthesis and also progressive incorporation of organic cation into the zeolite lattice can also be studied by IR spectroscopy.

The IR technique is useful in hydroxyl group characterization. Topsøe et al. has shown that OH groups characterized by absorption band at 3600 cm⁻¹ and 3700 cm⁻¹ correspond to strong and weak Brönsted acid sites respectively in zeolites. Ward, Datka et al. and Kiricsi and Forster have discussed the application of infra red spectroscopy for zeolite characterization. A comparative infra red study of zeolite acidity by using ammonia, methylamine, and n-butylamine has been reported by Ghosh and Curthoys.

(iii) Nuclear Magnetic Resonance (NMR):

²⁹SiNMR has been used to provide information as to the number, concentration and structure of the constituent species. It has also been used to study differences in number, nature and distribution of detectable species in solution. The position of the ²⁹SiNMR resonance is not only dependent on the number of tetrahedral(T) atoms in the
first cationic sphere of Si but also on the actual geometry of T-O-T linkage. Earlier Barrer and Ibbitson\textsuperscript{60} have shown the use of $^{13}$C NMR technique to study adsorbate-adsorbent interaction.

$^{27}$Al NMR has also been used to investigate mechanism of zeolite precipitation\textsuperscript{61}. J.V. Prasad et al.\textsuperscript{62} have shown that the $^{27}$Al and $^{29}$Si MAS NMR studies can be employed to differentiate Si/Al ratio, framework tetrahedral content and the crystal size. Viswanathan\textsuperscript{63} has reviewed the use of $^{129}$Xe NMR study of xenon adsorbed on zeolites to determine certain properties of zeolites and metal zeolites.

(iv) Temperature programmed desorption (TPD):

To characterize and estimate acid sites in zeolites, TPD is an useful technique. This has been reviewed by Tanabe\textsuperscript{64}, Jacobs\textsuperscript{65} and Szostak\textsuperscript{12}.

Many dynamic experiments have been conducted with ammonia as a probe molecule\textsuperscript{66–74}. Anderson et al.\textsuperscript{75} reported results on TPD of ammonia on ZSM–5 and silicalite and suggested that TPD maximum observed at 780 K is the probable site for hydrocarbon conversion processes. These studies and the study of Borade et al.\textsuperscript{76} showed three adsorption maxima in the TPD spectrum of ammonia on HZSM–5. The amount of ammonia released above 753K was considered by Jacob et al.\textsuperscript{77} to represent the very strong sites on HZSM–5.

Acidic properties of fresh and partially deactivated catalysts have been studied by Topsøe et al.\textsuperscript{46}. These results have been verified by Sawane et al.\textsuperscript{78}. 

73 65 69
(v) Thermogravimetry — Differential Thermal Analysis (TG — DTA):

TG—DTA has been utilized to study the synthesis mechanism\(^79\) as well as thermal behaviour of final synthesised products\(^80\). TG—DTA curves indicate various physico-chemical changes occurring during thermal treatment of the zeolite such as dehydration of adsorbed water, decomposition of occluded organic cations, dehydroxylation at higher temperature to produce Lewis acid sites and in certain cases, location of water molecules in hydrated zeolites\(^81\).

TG—DTA studies also show that stability of zeolites increases with \(\text{SiO}_2/\text{Al}_2\text{O}_3\) ratio and that the crystal structure of ZSM-5 changes from orthorhombic to monoclinic by calcination\(^83\). Although silicalite is stable in air up to 1373 K, it is converted to amorphous silica at that temperature\(^16\).

(vi) Microcalorimetry:

The use of microcalorimetric techniques has been extensively reviewed recently by Martinez and Dumesic\(^84\). Previously, several authors\(^85-89\) have shown the use of this technique to characterize the strength and distribution of acid sites in zeolites.

Besides these techniques cited above other techniques such as XPS and ESR\(^90,91\), XPS-XES\(^92\), UV visible\(^93\), Far IR spectroscopy have also been successfully used for characterization of zeolites.
Sorption Measurement:

Size and shape of pores in the zeolites can be approximately estimated from sorption measurement studies and these results are generally compared with those obtained from X-ray crystallographic measurement. Adsorption of molecules which have free access to the voids can be used to measure the void volume in the zeolites. Adsorption capacities have been reported for selected organics (such as n-hexane, n-heptane, toluene, benzene, o and p-xylene) in ZSM-5 by several authors. From these studies it has been possible to show the ease of accessibility of different hydrocarbon molecules to different channels during adsorption and diffusion. Barrer et al. have made elaborate studies on sorption of various gases and vapours on synthetic zeolites.

1.2.4 Shape selectivity in zeolites

Highly crystalline nature and regular channel structure are among the principal features for which zeolites can be used as shape selective molecular sieve catalysts. Weisz and Frilette were the first to use the concept of 'Molecular shape-selective catalysis' to explain the difference in catalytic properties shown by conventional silica-alumina catalyst and zeolite type A and X. Later various authors have described this concept in the light of various types of selectivities observed in zeolite based reactions.

In case of ZSM-5, the sinusoidal channel system has near circular pore (5.4Å x 5.6Å) and the linear, elliptical pore openings
The total length of the pore system has been calculated to be 8.8Å as per unit cell, to which the elliptical channel system contributes 5.9Å\textsuperscript{95}. These two pore systems actually control the access of the molecules to the channel interactions where the active sites are probably located\textsuperscript{96}.

Shape selectivity operates by either reactant shape selectivity, product shape selectivity, or transition state selectivity. These type of selectivities\textsuperscript{104} are depicted in Fig 1.2.

Some of the reactant molecules cannot enter into and diffuse effectively inside the zeolite crystal. This limitation is responsible for 'reactant shape selectivity'. On the other hand slowly diffusing product molecules cannot escape easily from the crystal and undergo secondary reactions. This gives rise to 'product shape selectivity'. 'Restricted transition state selectivity' results from kinetic effect arising from the local environment around the active site. Reactant shape selectivity is important in cracking and hydrocracking reactions of hydrocarbons over ZSM-5\textsuperscript{105,106}. Product selectivity effects are found in selective formation of p-xylene\textsuperscript{107}, and in conversion of methanol to hydrocarbons\textsuperscript{108} while effect of transition state selectivity is manifested in the isomerization of isobutane over HZSM-5 zeolite\textsuperscript{109}. This reaction has been shown to take place by bimolecular transition state mechanism over a variety of acidic catalysts to give propane and pentanes while the same reaction does not take place by bimolecular mechanism over HZSM-5 inspite of the presence of stronger acid sites in this zeolite. Product distribution is also affected by the following effects.
Fig. 1.2 The three types of selectivity: reactant, product and transition state selectivity.
(i) Molecular Traffic Control (MTC):

As already discussed, two types of intersecting channels are found in ZSM-5. One type of the pore systems (sinusoidal, circular) is supposed to allow preferentially the entry of the reactant molecules while the other type (straight, elliptical) favours the exit of the bulkier product molecules. This gives rise to molecular traffic control effect which was initially proposed by Derouane and Gabelica to explain the absence of 'counter diffusion' effects in the conversion of methanol to hydrocarbons. Hydrocarbon adsorption measurement experiment of Derouane also explains this effect clearly.

The high activity of ZSM-5 for alkylation of benzene with ethylene is also explained by the presence of molecular traffic control effect in ZSM-5. On the other hand greater activity of HZSM-11 for alkylation of toluene with methanol is supposed to be due to the absence of this effect in HZSM-11 which has only one kind of intersecting channel.

(ii) Diffusion of molecules:

The activity of the catalysts for reaction and selectivity of the products are also greatly determined by diffusion capability of the molecules. For example, molecules with high diffusivity in the catalyst may react faster. Also the faster rate of diffusion of a product may increase its selectivity among the products, whereas those with lower diffusivity may undergo secondary reactions. On the other hand the diffusivity of molecules depends strongly on the size and shape of the
molecules which is to be comparable with those of the pores of zeolite
system\textsuperscript{110}.

(iii) Deactivation of ZSM-5 zeolites:

The unique structural features of ZSM-5 are regarded as the main
cause for high resistance of it to coking and ageing compared to large
pore zeolites. The formation of bulky molecules are minimized or
prevented by product selectivity, transient state selectivity and
molecular traffic control effects via steric and spatial restrictions.

Rollmann\textsuperscript{112} studied the various reactions over zeolites of
different pore structures and concluded that intra-crystalline coking is
a shape selective reaction directly related to zeolite pore structure.
Walsh et al.\textsuperscript{113} had shown that the differences in coke yield for ZSM-5
(10 membered) and Y-type zeolite (12-membered) for the same reaction
were due to structural constraints influencing the coke-formation
reactions.

According to Dejaifve et al.\textsuperscript{114} coking in HZSM-5 is a surface
phenomenon which is likely to deactivate the catalyst and modify the
product distribution pattern by partially blocking the pore opening. The
high SiO$_2$/Al$_2$O$_3$ ratio of HZSM-5 is also partly responsible for its
resistance to coking and ageing.

1.2.5 Catalytic reactions over ZSM-5

The performance of ZSM-5 zeolite as a catalyst for several
reactions has been studied after the discovery of this zeolite and the
realization of its superior shape selective properties. Below are given some of these reactions.

(a) Conversion of ethanol and methanol and other oxygenated compounds to hydrocarbons.

(b) Aromatic reactions like (i) isomerization of xylene (ii) alkylation of aromatics, and (iii) disproportionation of toluene.

(c) Other hydrocarbon reactions like cracking, hydrocracking, dewaxing etc.

Some of the industrially important reactions based on shape-selective zeolites are presented in Table 1.2.

(i) Conversion of methanol and ethanol over HZSM-5:

Conversion of methanol is one of the important reactions studied over ZSM-5 zeolites from industrial and academic point of view. In the earlier studies of this reaction, production of \(C_2-C_5\) olefins was reported as the first reaction sequence. According to them, in the final steps of the reaction path, the \(C_2-C_5\) olefins got converted to paraffins, aromatics, cycloparaffins and \(C_6^+\) olefins.

The effect of different process parameters such as temperature, WHSV, \(\text{SiO}_2/\text{Al}_2\text{O}_3\) ratio and pressure on the product distribution was studied to optimize the different conditions for production of olefins and aromatics. Olefins formation can be decoupled from aromatization via a combination of high temperature and low catalyst activity. Ethylene was the primary hydrocarbon produced from methanol at low conversion. With increasing conversion olefin
<table>
<thead>
<tr>
<th>Process</th>
<th>Objective</th>
<th>Major chemicals/process characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selectoforming</td>
<td>Octane number increase in gasoline, LPG</td>
<td>Selective n-paraffins cracking</td>
</tr>
<tr>
<td></td>
<td>Production</td>
<td></td>
</tr>
<tr>
<td>M-forming</td>
<td>High yield; Octane number increase in gasoline</td>
<td>Cracking depending on degree of branching; aromatic alkylation by cracked fragments</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dewaxing</td>
<td>Light fuel from heavy fuel oil; lube oils with low temperature pour point.</td>
<td>Cracking of high molecular weight n- and mono methyl paraffins.</td>
</tr>
<tr>
<td>Xylene isomerization</td>
<td>High yield para-xylene production</td>
<td></td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>High yield ethyl benzene production eliminate AlCl₃ handling</td>
<td>High throughput long cycle life; suppression of side reactions</td>
</tr>
<tr>
<td>Toluene disproportionation</td>
<td>Benzene and xylene from toluene</td>
<td></td>
</tr>
<tr>
<td>Methanol to gasoline</td>
<td>Methanol (from coal or natural gas) conversion to high grade gasoline</td>
<td>Synthesis of hydrocarbons only, restricted to gasoline range (C₄ to C₁₀) including aromatics</td>
</tr>
</tbody>
</table>
distribution was found to be governed by kinetics, due to autocatalysis and competitive sorption of water. On the other hand, the extent of aromatization and distribution of aromatic hydrocarbons in the conversion of methanol over HZSM-5 was found to be very much dependent on the Si/Al ratio, and degree of $H^+$ exchange. Relatively high aluminium content in HZSM-5 framework and increasing degree of $H^+$ exchange enhanced the aromatization activity of the zeolite.

The methanol to hydrocarbon reaction was also studied over different ZSM-5 zeolites modified with other elements such as phosphorous and magnesium, zinc and gallium, and also by zinc oxide and magnesium oxide.

Several mechanisms have been proposed to explain the formation of initial C–C bond in the methanol conversion reaction. Once the primary olefins (namely ethylene and propylene) are produced in the reaction, these give higher olefins by alkylation with methanol or dimethylether (formed from methanol) and oligomerization by the Brönsted acid sites. Subsequently once a higher olefin is formed a series of consecutive steps of oligomerization, isomerization, cracking, cyclization and hydride transfer start to operate to form different paraffins, aromatics and cycloparaffins by carbenium ion mechanism. Similar product distribution was observed for all C$_1$–C$_6$ alcohols which indicates that a common reaction path must be followed as given below:

\[
\text{Alcohol} \rightarrow \text{Olefins} \rightarrow \text{Oligomers} \rightarrow \text{Paraffins} \\
\text{Aromatics} \\
\text{Cycloparaffins} \\
\text{Coke}
\]
Conversion of ethanol has also been studied by several authors with the prospect of finding important processes in chemical and petrochemical industries for the production of benzene, toluene and xylene (BTX), high grade gasoline and other hydrocarbons. Ethanol can be easily produced from a renewable agricultural source like biomass. In countries like India and Brazil, alcohol (ethanol) is produced by fermentation of molasses, a bye-product of sugar industry.

Ethanol and methanol conversion over ZSM-5 catalyst has generated tremendous academic interest for providing a satisfactory reaction mechanism to account for the various products.

The initial step in the formation of aromatics is a 'concerted' cycloaddition of an olefin and a carbenium ion. The growth of the hydrocarbon chain has been shown to occur by a C1 step addition showing the existence of cracking during the enlargement of the hydrocarbon. The details of the mechanism of conversion of ethanol to various hydrocarbons will be discussed later. Conversion of olefins and other alcohols over ZSM-5 has also been studied with different objectives.

(ii) Some other reactions over ZSM-5:

Some other industrially important processes such as alkylation of benzene, disproportionation and alkylation of toluene and isomerization of xylenes have been found to be more efficient over ZSM-5 zeolites than conventional silica alumina catalysts.
1.3 SUPPORTED METAL CATALYSTS

1.3.1 Introduction to metal catalyst

Metallic catalysts always contain the metal more or less in high state of dispersion. Dispersion helps to maximise the surface area available for a given mass of metal. The transition metals are of the greatest importance as catalysts. The availability of incomplete d-orbitals in them has been ascribed to be the main reason for the high activity of group VIII metals. Incomplete d-orbitals give rise to co-ordinate type bond leading to reversible chemisorption and catalysis. For example, a nickel atom in the (001) face of the face centered crystal has a co-ordination number equal to eight instead of twelve in the bulk of the crystal which facilitates adsorption of a gas molecule by co-ordinate type bond. For example, dissociative adsorption of H–H or R–H is favoured by the spin free Ni\(^{5+}\) configuration. Catalytic hydrogenation and dehydrogenation activity of transition metals results from high density of such "free valencies"\(^{144}\). The relative activities of transition metal films in the hydrogenation of ethylene and their relation to the crystal parameters of the metals was studied by Beeck\(^{145}\). The percentage d-character of the metallic bond has often been correlated in an empirical way with catalytic or adsorption data. On an orbital model, it presumably reflects the linear extension of a hybrid dsp orbital in space. A valence bond approach has also been described by Altmann et al.\(^{146}\).

The correlation between activities of group VIII metals and their d-character have also been obtained on supported metals by several
Although the electronic theory of catalysis seems to explain significantly the catalytic activity of the transition metals, yet it can not be considered as completely satisfactory. Electronic as well as geometric factors play a role in determining the catalytic activity of metals.

1.3.2 The Supports

A large number of support materials can be used to conform to the wide range of conditions under which supported metal catalysts are used. These are mainly particulate or granular, although fibrous materials are also used. Recently monolithic porous ceramic has become an important support. Berkman et al.\textsuperscript{151}, and Innes\textsuperscript{152} have given very good reviews of catalyst supports.

One of the most important criteria for a substance to be a support is that the surface atoms must have a markedly different environment to those in the bulk. Although theoretically any solid can be used as a catalyst support for dispersed metal, however, in practice the range of materials in common use is restricted to silica, alumina, silica alumina, the zeolites and carbon which overshadow the rest. Alumina and zeolites, which are used in this study as support materials, are discussed below:
(i) **Alumina** :

(a) **Structural features**

There are various structural modifications of alumina. Of these \( \tau \)- and \( \psi \)-are the two catalytically useful forms, the former being more active than the later. Dehydration of bayerite and boehmite respectively gives \( \tau \)- and \( \psi \)-forms at temperature not exceeding 873K. Knozinger and Ratnaswamy has reviewed the surface models and characterization of surface sites of catalytic aluminas.

Lippens et al. has extensively studied the crystallographic structure of aluminas. Both \( \tau \)- and \( \psi \)-aluminas possess defect spinel lattices which are slightly tetragonally distorted, this distortion being more pronounced in the \( \psi \)-phase. The differences in catalytic activity of the two forms may be due to the differences in the structures which are summarized below.

(1) Preferentially exposed faces might be the (111) faces in case of \( \tau \)-alumina and the (110) or (100) faces in the case of \( \psi \)-alumina. \( \psi \)-alumina obtained from gelatinous boehmite exposes the (100) plane predominantly, while the one obtained from well crystallized boehmite exposes the (110) plane.

(2) \( \psi \)-alumina has a uniform pore size distribution with most (90%) of the pore volume being made up of pores of width 20\( \AA \) to 40\( \AA \), while a significant contribution (37%) for pore volume in \( \tau \)-alumina comes from pores less than 20\( \AA \), and about 30% contribution is from 20\( \AA \) to 30\( \AA \) pores.
(3) For γ-alumina the mean thickness of the solid lamellas separating the narrow pores is of the order of 16 Å whereas the corresponding value for η-alumina is 600 Å.

(b) Active centres

(1) Acid sites — The catalyzing activities of alumina and mixed oxides have been explained mostly on the basis of acid sites present on the surface of these catalysts. These acid centres could be protonic (Brönsted) and nonprotonic (Lewis).

Incompletely co-ordinated aluminium atoms are considered to be the cause of Lewis acidity in dehydrated alumina which may be formed as follows:

\[
\begin{align*}
\text{OH} & \quad \text{Al} & \quad \text{OH} \\
0 & \quad \text{Al} & \quad \text{Al} & \quad \text{OH} & \quad \text{Al} & \quad \text{OH} & \quad \text{H}_2\text{O}
\end{align*}
\]

These Lewis sites are converted into Brönsted sites, by adsorption of moisture:

\[
\begin{align*}
\text{OH} & \quad \text{Al} & \quad \text{OH} & \quad \text{Al} & \quad \text{OH} & \quad \text{Al} & \quad \text{OH} & \quad \text{H}_2\text{O}
\end{align*}
\]

The model for the two acid sites can be given as follows:

\[
\begin{align*}
0 & \quad \text{Al} & \quad 0 & \quad \text{Al} & \quad 0 & \quad \text{Al} & \quad 0 & \quad \text{Al} & \quad \text{OH}
\end{align*}
\]

Lewis

Brönsted
The impregnation of potassium and sodium\textsuperscript{157} into alumina, and silica alumina has been found to lower the activity of the oxides in isomerization and cracking reactions due to poisoning of the acid sites.

The poisoning of the acid centres of these catalysts, has been confirmed by activity studies using Hammett indicators\textsuperscript{158}.

(2) Basic sites — The basic sites on the surface of alumina and sodium poisoned catalysts have also been recognized. According to Pines et al.\textsuperscript{159} both acid and basic sites are responsible for dehydration of alcohols. Sodium or other alkali metals impregnated in silica and alumina show promise as basic catalysts, the basic sites being considered as the oxide ions and cation vacancies on their surface. The catalytic properties of these catalysts towards hydrocarbons are similar to organo-sodium compounds in a homogenous liquid phase reaction\textsuperscript{144}.

(ii) Zeolites :

In this work, zeolite LTL was also used as a support. Some salient features of this zeolite are discussed below:

Zeolite LTL belongs to the class of intermediate silica\textsuperscript{160} and large pore\textsuperscript{161} zeolites. The alumino silicate framework of zeolite LTL is based on polyhedral cages formed by five six-membered and six four-membered rings\textsuperscript{162}. The main channels consisting of alternate cancrinite (or E) cages and hexagonal prisms form columns that run parallel to the C-axis (Fig 1.3). The main channel is circumscribed by 12-membered rings. A typical unit cell composition of dehydrated zeolite LTL is —
Fig. 1.3 Structure of zeolite LTL (a) framework structure (b) structure of zeolite LTL as viewed along the c-axis.
Studies on the catalytic activity of zeolite LTL are very few. Hopkins observed that the effect of activation temperature on activity for heptane cracking for samples of ammonium LTL zeolite (66% exchange) and ammonium Y–zeolite (74% exchange) is similar. Franco-Parra et al. studied the effects of the degree of exchange of potassium, activation temperature, and silicon to aluminium ratio on the activity, acidity and stability of calcined ammonium LTL zeolites. An IR study of ammonium LTL zeolites in the hydroxyl stretching region produced results which could not be interpreted in a conclusive manner. The thermal stability of different ion exchanged zeolite LTL was studied by Franco Parra et al., Weeks et al. and Y. Ono et al.

1.3.3 Supported metal catalyst and metal support interaction

(1) Supported metal catalysts:

Supported metal catalysts are usually called bifunctional catalysts. The metal and the support in these catalysts contribute to the two types of active centres. This is the reason why they are capable of catalyzing two different reactions simultaneously. The metal usually contributes to the hydrogenation and dehydrogenation activities, while the support takes part in isomerization, dehydration, and cracking reactions. On the other hand simple oxides like alumina, chromia, titania, zirconia and zinc oxide can also exhibit dual functional properties though to varying extent. For example, ethyl alcohol is both dehydrogenated (9%) and dehydrated (91%) over chromia (623 K/1atm);
the same reactions also take place over zinc oxide but to different extents (dehydrogenation 95%, dehydration 5%). The following are considered to be the advantages arising from using a metal or metals supported on a medium of high surface area —

(1) Very large specific metal surface area is obtained because metals get well dispersed over the support.

(2) Dispersion of metal on support makes the metal highly resistant to sintering.

(3) The catalysts may be obtained in any suitable physical form.

(4) There is a possibility of some supports of interacting electronically with the metal leading to its activation or deactivation. This can always be used advantageously.

(ii) Metal-Support interaction:

The first specific suggestion of how the catalytic properties of a metal might be influenced by a support was proposed by Adadurov in 1935\textsuperscript{167}.

Now-a-days, work on metal support interaction has become very important in the context of the effect of support on the dispersion and activity of the metal in catalytic reactions. Different aspects of these interactions have been reviewed by several authors,\textsuperscript{168-171} the following being proposed as models —
(a) Inductive models for Metal-Support interaction

According to this model (Schwab in late 1950s and Solymosi), the most important properties of an interacting support were the type and strength of its conductivity, since this governed the flow of electrons into or out of the metal with consequent perturbation on the metal catalytic properties. Despite many limitations, Solymosi and Schwab succeeded in systematically relating catalytic properties to Fermi Level equilibration between the catalytically active phase and the substrate.

The highly unusual chemisorptive properties of titania-supported group VIII metals have been proposed as due to Strong Metal Support Interaction (SMSI). Recently Badyal et al. have examined similar SMSI effects also for the TiO$_2$/Ru/SiO$_2$ system. Another model known as the Surface Transition Metal Cation (STMC) model has also been put forward to explain catalytic properties of supported metals vis-a-vis metal-support interaction. This model has been shown to be consistent with the known properties of transition metal oxide surfaces towards oxygen and other electrophilic adsorbates.

(b) Other types of support effects and metal support interaction

Besides the two inductive models mentioned above other types of support effects may be considered as discussed by Boudart and Dje'gaMariadasson. For example, (i) support may interact with a metal by inducing structural changes, (ii) different supports have been found to favour the formation of particles of different sizes resulting shifts in catalytic activity or selectivity by changing the
concentration of edge or corner sites, (iii) the reducibility of a metal may also be strongly affected by interaction with an oxide support\textsuperscript{180-182}.

(c) Metal Zeolite interaction

Metals supported on zeolites are usually in a highly dispersed state which makes identification and modification of this metal by the support much more difficult\textsuperscript{170}. The electronic and physical structures of small metal particles are often different from those of the bulk metal. Again because of their size, the metal crystallites may interact more easily with the constituents of the support. Both particle size effect and metal support interaction might be expected to result in unusual adsorption properties. Gallezot\textsuperscript{183} has reviewed the numerous publications dealing with the adsorption and catalytic properties of zeolite supported platinum and palladium. IR studies of Goodwin\textsuperscript{184} and Naccache et al.\textsuperscript{185} have shown that interaction of small metal crystallites with zeolite structures can also result in changes in their adsorption properties.

It has now been established that metal support interaction does occur and this interaction is responsible for lowering the free energy of the system, thus altering the behaviour of the metal in a variety of ways. However correlation between metal-support interaction and catalytic action has remained an open question.
(iii) Dispersion, sintering and redispersion of metal:

During preparation of the supported metal catalysts, metals get dispersed over large internal surface areas of metal oxides as small crystallites. The results obtained by various authors on the dispersion of platinum over aluminas of varying surface area and structure, have remarkable similarities. These authors have shown a near complete dispersion of the metal over all the alumina catalysts. The catalytic activities also are not very different for the fresh catalysts. ESCA analysis revealed that in all cases the principal platinum species is not Pt (IV) but rather Pt (II). Modest amount of the surface platinum in the oxidised system may be in the Pt (IV) and Pt (0) states.

While during preparation of the catalyst a large number of small crystallites are formed, during heating and particularly during the catalytic reaction the crystallites are likely to undergo sintering, thus decreasing surface area of the metal exposed to the chemical atmosphere, and a consequent decrease in the free energy of the system. Under suitable conditions the surface area of the metal can be made to increase. This is known as redispersion. The physiochemical interaction between crystallites, substrate and atmosphere plays a dominant role in the free energy of dispersion of small particles. The parameters which influence the extent of sintering are time, temperature, gas phase composition, presence of other species on the substrate surface and the properties of the substrate and metal. The role of interactions and surface phenomena in sintering and redispersion
of supported metal catalysts have been reviewed by Ruckenstein\textsuperscript{190}. It is seen therefore that sintering not only changes the exposed surface area, but it can also affect the selectivity of the catalyst.

1.3.4 Hydrogenation of phenol over supported metal catalysts.

Hydrogenation of phenol is an industrially important reaction. Of the various products formed in the reaction, cyclohexanol and cyclohexanone are the two important chemicals both of which are utilized in the manufacture of a large number of industrially important products. Cyclohexanol itself can be selectively converted to cyclohexanone\textsuperscript{191}. Cyclohexanone, on the other hand, is the starting chemical for production of nylon 6 and nylon 6,6. Nylon 6 can be manufactured by a ring opening polymerization of ε-caprolactam. ε-caprolactam is a cyclic amide which is easily prepared by the Beckmann rearrangement of cyclohexanoneoxime, which in turn can be made from cyclohexanone.

\[
\begin{align*}
\text{Cyclohexanone} & \xrightarrow{\text{NH}_2\text{OH}} \text{Cyclohexanoneoxime} \\
\text{Cyclohexanoneoxime} & \xrightarrow{\text{H}^+} \text{Caprolactum} \\
\text{Caprolactum} & \xrightarrow{\text{Polymerization}} \text{Nylon 6}
\end{align*}
\]
Nylon 6,6 is manufactured by polymerization of adipic acid and hexamethylenediamine. Adipic acid is obtained by air oxidation of cyclohexane via cyclohexanone.

\[
\begin{align*}
\text{Cyclohexanone} & \quad \xrightarrow{\text{dil. HNO}_3} \quad \text{Adipic acid} \\
\end{align*}
\]

Adipic acid can also be converted to hexamethylenediamine.

Nylon 6 and nylon 6,6 are used for synthetic fibre and tyre industries and home furnishings.

Cyclohexanol is also used as a solvent and as a building block in the synthesis of many organic compounds such as pharmaceutical, insecticides etc.

Depending upon the type of catalyst and conditions of the reactions, phenol hydrogenation gives cyclohexanol, cyclohexanone, cyclohexane, benzene and cyclohexene.

Hydrogenation and hydrogenolysis reactions of phenol can be visualised as follows:
Cyclohexanone has been isolated as an intermediate during the course of the reaction under certain conditions with specific catalysts. Coussemant et al. proposed the following mechanism on the basis of the study of the reaction over Raney nickel catalyst —
Following conclusions are drawn from the analysis of this reaction\textsuperscript{194,195} that —

(a) The activation energy for reduction of the Ketone is 6.5 kcal per mole between temperature 113 and 117°C, while that for phenol to cyclohexanone over the same catalyst under the same condition is 8.5 kcal per mole.

(b) The ratio $k_2/k_1$ is 1.95 at 174°C and 3.0 at 113°C which suggest that yield of cyclohexanone increases with increasing temperature.

(c) Phenol is converted to cyclohexanol directly without the intervention of the ketone.

(d) Slow reaction between phenol and cyclohexanol to cyclohexanone makes full analysis of the system more complicated.

Smith and Stump\textsuperscript{196} gave the following mechanism for hydrogenation of phenol over Adams platinum catalyst and 5% Rh-alumina catalyst.
The tautomerization of cyclohexene-1-ol to cyclohexanone takes place readily due to the greater stability of cyclohexanone by 18 kcal/mole.

Similar mechanism have been suggested by Takagi et al.\textsuperscript{197,198} for hydrogenation of o-, m-, and p-cresols over rhodium hydroxide based catalysts in the liquid phase. Production of large amount (47-70\%) of methylcyclohexanones indicates, according to them, that the stereochemistry of cresols does not affect the steps which lead to the formation of the ketones.
Step 2 is slower than step 1 resulting in accumulation of the ketones in the product. Hydrogenation of phenol and cresols have been extensively studied in the liquid phase, mostly at high pressure over Raney nickel and Adams platinum catalysts. Metals like Ir, Pd, Rh and Ru have also been used in the liquid phase catalysis of the reaction, the catalysts being either 'blacks' or supported on carbon. Hydrogenation in the vapour phase has not widely been reported though a few results for nickel supported cerium oxide and a very few results for platinum and palladium alumina are known. The hydrogenation of phenol in the vapour phase over palladium and platinum supported on zeolite LTL has not been reported yet.
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