CHAPTER 1

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1.1 Growth of zeolite chemistry

Zeolites are crystalline aluminosilicates having the unit cell formula [1]

\[ M^{n+} \frac{x}{n} [(AlO_2)_x (SiO_2)_y] wH_2O \]

Where \( M \) is the exchangeable cation with charge \( n^+ \) (generally from Groups I and II metal ions) and \( x, y \) and \( n \) are integers. The bracketed portion describes the framework composition and the value of \( X \) and \( Y \) are such that \( Y/X \) is usually greater than 1 and they represent the number of tetrahedra in the zeolite. \( W \) is the number of water molecules in the zeolite. The primary building block of zeolite structure is the SiO\(_4\) and AlO\(_4\) tetrahedra [2,3] in which silica and alumina tetrahedra are linked through oxygens to form a rigid three dimensional framework. The water molecules occupy spaces between the tetrahedra. The prominent feature of the zeolite structure is the presence of cavities, channels and pores, resulting in very large surface area making them very effective as catalysts [3-6]. Zeolites are classified according to morphological characteristics [5,7], effective pore diameter [5], chemical composition and natural occurrence.
Although natural zeolites and their properties were known more than 200 years ago, their unique properties came to receive increasing attention only in 1950’s. The earliest uses of zeolites were for adsorption and drying of gases, separation of gases and ion exchange. With the advent of X-ray crystallography, it is soon possible to synthesize several of these for use in commercial applications. Since 1950, approximately 150 synthetic zeolites have been made while the number of natural zeolites remained at around 37. Zeolite catalysts have been introduced in a number of industrial processes, especially in Petroleum refining and the manufacture of organic commodity chemicals [8,9]. Synthetic zeolites can be tailor-made today to suit production of specialised chemicals. This has greatly enhanced the utility of the zeolites [10].

1.2 General features of zeolite — synthesis

The synthesis of the first zeolite involved the use of only inorganic reagents in analogy to the natural materials. The early synthesis product as well as the natural zeolites exhibit the common characteristics of low framework Si/Al ratio, high ion exchange capacity and high affinities towards water. A systematic study on zeolite synthesis from silica-rich reaction mixtures containing ammonium ions led Kerr and co-workers [11,12] to discover zeolite ZK-4 (Si/Al
ratio of 1.7) and zeolite Beta (Si/Al ratios 5 to 100). These breakthroughs were followed rapidly by the synthesis of many other high silica zeolites from reaction mixtures containing organic cations. The most important of these, the ZSM-5 (Zeolites Secony Mobil Number 5) was discovered by Argauer and Landolt[13] in 1972. Typical examples of some synthetic zeolites and their characteristics are reported in Table 1.1.

Table 1.1 Characteristic Properties of some Synthetic Zeolites

<table>
<thead>
<tr>
<th>Zeolite Type</th>
<th>SiO₂/Al₂O₃ Ratio</th>
<th>Cation (in assynthesized material)</th>
<th>Pore diameter (Å)</th>
<th>Crystal Structure</th>
<th>Adsorption capacities for H₂O (Wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>2.5 - 3</td>
<td>Na⁺, Ca²⁺</td>
<td>8 - 10</td>
<td>Body Centered Cubic</td>
<td>36.0</td>
</tr>
<tr>
<td>Y</td>
<td>3 - 6</td>
<td>Na⁺</td>
<td>10</td>
<td>do</td>
<td>35.0</td>
</tr>
<tr>
<td>L</td>
<td>5 - 7</td>
<td>K⁺ (Na)⁺</td>
<td>7.1-7.8</td>
<td>Hexagonal</td>
<td>12.0</td>
</tr>
<tr>
<td>ZSM -5</td>
<td>10-infinity</td>
<td>Na⁺ TPA</td>
<td>5.1x5.6</td>
<td>Orthorhombic</td>
<td>10.0</td>
</tr>
<tr>
<td>ZSM -11</td>
<td>-do-</td>
<td>Na⁺ TBA</td>
<td>5.1x5.5</td>
<td>Tetragonal</td>
<td>10.0</td>
</tr>
<tr>
<td>ZSM -12</td>
<td>100-600</td>
<td>Na⁺ TEA</td>
<td>5.6x6.1</td>
<td>Monoclinic</td>
<td>9.0</td>
</tr>
<tr>
<td>ZSM -34</td>
<td>22 - 40</td>
<td>Na⁺ TMA</td>
<td>6.4</td>
<td>Hexagonal</td>
<td>22.0</td>
</tr>
<tr>
<td>Silicalite (Aluminium free)</td>
<td></td>
<td>TBA</td>
<td>5.1x5.6</td>
<td>Orthorhombic</td>
<td>2.4</td>
</tr>
</tbody>
</table>

TMA, TEA, TPA, TBA, are tetra methyl, tetra ethyl, tetra propyl and tetra ethyl ammonium ions respectively.

For the synthesis of high-silica zeolites, in most instances, two solutions are prepared. Solution A contains
the organosilicate and solution B is prepared by dissolving successively in water the inorganic base(S) and the aluminium salt [14]. Solution A is prepared by adding the organic molecules(or its solution) to the silicate solution for all silica sources except Aerosil. Solution B is added slowly to A with vigorous stirring and the pH is subsequently adjusted by drop wise addition of a mineral acid. The gel thus obtained is autoclaved and heated at a temperature range of 373 - 473 K for a period lasting from 6 h to 60 days. The synthesis efficiency is defined as the weight percentage of SiO₂+Al₂O₃ that is recovered after the whole operation compared with the SiO₂ + Al₂O₃ in the gel. The phase purity of synthesised zeolites is checked by comparing the peaks in the X-ray diffractograms (XRD) with those given in literature. A number of independent reaction variables are responsible for the synthesis of zeolites. Barrer[15] has reviewed these variables and these are summarized in Table 1.2

Some general conditions for the synthesis are the following [3]

(i) Reactive starting materials such as freshly prepared co-precipitated gels or amorphous solids.

(ii) Relatively high pH introduction in the form of an alkali metal hydroxide or other strong base.

(iii) Low temperature hydrothermal conditions with concurrent low autogenous pressure at saturated water vapour pressure.
(iv) A high degree of supersaturation of the components of the gel leading to nucleation of a large number of crystals.

Some recent reviews illustrate the various methods for Synthesis [5,7,14,16] of zeolites.

Table 1.2 Reaction variables in zeolite synthesis

* Pressure
* Temperature
* Reactant composition
* Synthesis time
* Role of $\text{OH}^-$
* Cations as structure directing agents
* Role of organic bases
* Role of other salts or added anions
* Ageing or ripening period of reaction mixture prior to hydrothermal synthesis
* Whether mixture is stirred; stirring rate
* Physical and chemical nature of reactants
* Order of addition of reactants
* Effect of seed crystals on synthesis.

1.3 Pentasil zeolite-ZSM-5

The generic name pentasil zeolite has been used to refer to ZSM-5 type of zeolite. ZSM-5 can be prepared with Si/Al ratio of 10 up to infinity. The first patent in which the
preparation of ZSM - 5 was claimed by Argauer and Landolt[3] on November 14, 1972 is given in Table 1.3.

Table 1.3 Synthesis of ZSM-5 according to the original Argauer and Landolt patent:

<table>
<thead>
<tr>
<th>Example</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Molar composition of the gel</strong> [Al$_2$O$_3=1$]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(TPA)$_2$O</td>
<td>9.0</td>
<td>17.1</td>
<td>17.1</td>
<td>17.1</td>
<td>17.1</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>1.2</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>29.1</td>
<td>27.7</td>
<td>27.7</td>
<td>27.7</td>
<td>27.7</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>481</td>
<td>453</td>
<td>453</td>
<td>453</td>
<td>453</td>
</tr>
<tr>
<td><strong>Crystallization conditions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>423</td>
<td>423</td>
<td>423</td>
<td>398</td>
<td>448</td>
</tr>
<tr>
<td>Time (days)</td>
<td>6.0</td>
<td>5.0</td>
<td>8.0</td>
<td>5.5</td>
<td>5.0</td>
</tr>
<tr>
<td><strong>Molar composition of the crystalline product (Al$_2$O$_3=1$) on an inorganic basis</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.50</td>
<td>0.89</td>
<td>0.86</td>
<td>1.31</td>
<td>0.83</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>32.5</td>
<td>32.1</td>
<td>35.5</td>
<td>45.0</td>
<td>37.0</td>
</tr>
<tr>
<td><strong>Nature of product, based on X-ray diffraction</strong></td>
<td>ZSM-5</td>
<td>ZSM-5</td>
<td>ZSM-5</td>
<td>ZSM-5</td>
<td>ZSM-5</td>
</tr>
</tbody>
</table>

The synthesis system for ZSM-5 is (TPA)$_2$O - M$_2$O - Al$_2$O$_3$ - SiO$_2$ - H$_2$O, where TPA stands for Tetrapropyl Ammonium cation and M for an alkali metal cation. The synthesis is carried out by mixing aqueous solutions
containing the organic cation and oxides of sodium, aluminium and silicon. These oxides are supplied by choosing appropriate reagents from among sodium silicate, sodium aluminate, aluminium salts, alumina, silica hydrosol, silicic acid, sodium hydroxide and tetra propyl ammonium hydroxide or bromide. The influence of the concentration of the different components in a typical gel [14] for the synthesis of ZSM-5 zeolites are

(i) The SiO₂/Al₂O₃ ratio of the gel  
(ii) The TPA/SiO₂ ratio of the gel  
(iii) The degree of dilution or the H₂O/SiO₂ ratio  
(iv) The M/SiO₂ ratio  
(v) The OH/SiO₂ ratio  
(vi) The nature of the silica source.

A range of composition of reaction mixtures in terms of mole ratios of oxides described in a patent is given below [17].

<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>0.10 - 1.5</td>
<td>0.10 - 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 -- α</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 373-473K with a period lasting from 6h to 60
days[18]. The as-synthesised material contains the TPA$^+$ ions which are entrapped in the channels. The channel system becomes accessible upon removal of template ions by means of calcination. Crystallization of ZSM-5 occurs in two stages—nucleation and crystal growth, and period and mechanism of these stages are strongly influenced by the synthesis variables and conditions used. Several experimental techniques are used to monitor the various events during nucleation and crystallization. X-ray diffraction, infrared spectroscopy, and scanning electron micrograph are some of these.

Several workers have studied the kinetics of crystallization under different experimental conditions. Activation energy for nucleation and for crystallization in certain synthesis systems has been determined [19-21]. It has been shown that with other synthesis variables remaining constant, the rate of nucleation and crystallization can be increased by increasing temperature [21], SiO$_2$/Al$_2$O$_3$ ratio[22] or (TPA)$_2$O/SiO$_2$ ratio [23]. The crystal structure of ZSM-5 was described by Kakotailo et al. [24] which consists of a novel configuration of linked tetrahedra which are bound together in groups consisting of five membered rings. The latter are then attached to each other through oxygen to form chains which are then connected to form planes (Fig 1.1, a and b). These planes are then linked to give a 3-dimensional structure having the following features:
a) CHARACTERISTIC CONFIGURATION OF ZSM-5

b) LINKAGE OF ZSM-5

c) SKELETAL DIAGRAM OF 010 FACE

d) SKELETAL DIAGRAM OF 100 FACE

e) CHANNEL STRUCTURE OF ZSM-5 ZEOLITE

FIG. 1.1 STRUCTURE OF ZSM-5 ZEOLITE
The structure contains two intersecting channel systems, defined by 10 membered ring openings. One of them is sinusoidal running parallel to the (001) plane and the other a straight channel parallel to (010) plane. The planes and the channel systems are shown in Fig 1.1 (c,d & e). Sinusoidal channel has near circular opening having a diameter 5.4-5.6Å and the straight channel has an elliptical opening of diameter 5.2-5.8Å. It can thus be seen that the pore dimensions are intermediate between those of the so-called 'large pore' zeolites (e.g. faujasite, dia 7.4 Å, zeolite Y, dia 8.0 Å) and small pore zeolite (e.g. zeolite type A - erionite - 3.8 x 5.2 Å). Very large pore zeolites, such as MCM-41, with pores of size 16 to 100 Å and with ring sizes larger than 12 membered rings have been recently synthesized [25-27].

The crystallographic unit cell of ZSM-5 has the composition represented by the formula [13]

$$Na_n Al_n Si_{(96-n)} O_{192} 16H_2O$$

Where n is generally less than 27. This value is less than that for X and Y type of zeolites (Si/Al = 2.4) and gives the zeolite better thermal, hydrothermal and acid stability. The crystallographic formula, as defined above, gives the number of aluminium atoms per unit cell, $N_{Al}$, from the relation $N_{Al}=96/(1+R)$ where R is the ratio of the number of Si atoms to the number of Al atoms per unit cell.
1.4 Characterization of Zeolites

Zeolites are characterized by using techniques like X-ray diffraction [28], infrared spectroscopy [29,30], Nuclear magnetic resonance spectroscopy [31,32], scanning electron microscopy, thermogravimetry, differential thermal analysis [33], etc. A brief outline of these techniques, as applied to zeolites, is given below:

1.4.1 X-Ray Diffraction (XRD)

This is the most widely used technique to identify the zeolite species and also to understand the kinetics and mechanism of zeolite crystallization [21,34]. Variation in the lattice parameters and framework symmetry [28], collapse of crystal structure and presence of alien phases are also detected by X-ray diffraction measurements. X-ray measurements have been used to quantitatively estimate alumina content of ZSM-5 zeolite [35]. The spacings between \( \theta = 45 \) to \( 45.5^\circ \) are shown to vary with Si/Al ratio in the zeolites. This can be made use of to determine silicon and alumina content in an unknown zeolite after due calibration using standard samples. The presence of \( \alpha \)-quartz in zeolites [35] can be identified and estimated using the characteristic peaks at 2\( \theta = 26.7 \) and 20.9° in the XRD. Quartz is formed during the synthesis under unfavourable conditions. The intensities of the lines around 7-10° and 23-25° indicates
the crystal symmetry.

1.4.2 Infrared spectroscopy (IR)

It is a technique complementary to XRD. The zeolites have characteristic framework vibrations. The fundamental vibrations of Al, SiO$_4$ tetrahedra are in the mid infrared region (200-1300 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 [30]. The crystallization of the zeolite during synthesis can be studied by monitoring the changes in important IR vibrational frequencies [e.g. Si-O stretching, Si-O-Si, Al stretching, Al-O stretching, O-Si-O, O-Al-O, Si-O-Si, Si-O-Al deformation frequencies] and comparing these with those of the reactants [37]. Also progressive incorporation of the organic cation into the zeolite lattice can also be studied by measuring the intensity of the peaks characteristic of the organic cation. Jacob et al. [38] has studied IR spectra of a series of five membered ring containing zeolites in the region 400-1500 cm$^{-1}$. The presence of the near 1200 and 550 cm$^{-1}$ IR bands is related to the five membered ring chains and block respectively. The most important impurity in the pentasil zeolites is the amorphous silica which has an absorption band at 450 cm$^{-1}$ but does not show a band at 550 cm$^{-1}$. The optical density ratio of the 550 and 450 cm$^{-1}$ bands could therefore indicate if pure and crystallized samples are formed in a synthesis.
The framework vibration frequencies for ZSM-5[32] are given below:

<table>
<thead>
<tr>
<th>Wave Number (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>450 (s)</td>
<td>T - O bend</td>
</tr>
<tr>
<td>550 (m)</td>
<td>Double ring</td>
</tr>
<tr>
<td>790 (w)</td>
<td>Sym. stretching (external)</td>
</tr>
<tr>
<td>1093 (s)</td>
<td>Asym. stretching (internal)</td>
</tr>
<tr>
<td>1225 (sh)</td>
<td>Asym. stretching (external)</td>
</tr>
</tbody>
</table>

The IR technique has been extensively used to distinguish between types of structural and other hydroxyl groups. Atleast two bands, around 3740 and 3610cm\(^{-1}\), representing the OH stretching region in zeolites, have been reported. The wave numbers given by various investigators range from 3600 to 3610 and from 3720 to 3740cm\(^{-1}\). The band around 3740cm\(^{-1}\) is associated with the terminal OH groups bound to framework Si atoms, while the band around 3610cm\(^{-1}\) is due to vibration of bridge OH groups linking framework Al and Si atoms [40,41]. In the case of a non-dehydroxylated zeolite, the intensity of 3610cm\(^{-1}\) band is proportional to the framework Al content [42]. Recently, IR study has been used to investigate formation of coke on zeolites [43].

1.4.3 Nuclear Magnetic Resonance (NMR)

The strong acidity of zeolites is generated by bridging hydroxyl groups. Their acid strength depends on the
electronic charge of the hydrogen atom which can be measured by means of nuclear magnetic resonance (NMR). O’Reilly et al. [44] had earlier attempted to obtain information about OH groups on surface from HNMR line shapes and chemical shift. With the advent of superconducting magnets and the development of magic-angle spinning (MAS), it becomes possible to measure highly resolved solid state spectra of zeolites.

$^{29}$Si and $^{27}$Al NMR/MAS have revealed a wealth of information on the local environment of these elements in zeolite. Nagi et al. [45] have demonstrated the use of $^{29}$SiNMR spectra to obtain structural information for ZSM-5 zeolite. $^{29}$Si NMR has been used to provide information as to the number, concentration and structure of constituent species [31,46,47]. $^{27}$Al NMR has been used to investigate mechanism of zeolite precipitation. Barrer and Ibbiston [45] have used $^{13}$C NMR technique to study adsorbate-adsorbent interaction. $^{27}$Al NMR has been used to investigate mechanism of zeolite precipitation. Derouane et al. [49] have used NMR to study the effect of pH and replacement of Na$^+$ by Cs$^+$ on the formation of precursors in synthesis of ZSM-5. NMR studies have been used recently to characterize the acidic sites on a new zeolite MCM-22 [50].

1.4.4 Scanning Electron Microscopy (SEM)

High resolution electron microscopy provides valuable information on zeolite characterization. X-ray diffraction
and other techniques provide only spatially averaged information, while electron microscopy can provide finer, more detailed information on subtle aspects of the framework structure[2]. In zeolite synthesis, scanning electron micrographs have been used to examine the presence of residual amorphous material and the size and habit of crystalline phases. Several workers [51-55] have studied the synthesis and crystal growth of zeolite ZSM-5 using scanning electron microscopy. Hay et al.[56] have examined the systematic intergrowth of ZSM-5 crystals with scanning electron microscopy.

1.4.5 Thermogravimetry :Differential Thermal Analysis

(TG - DTA)

This technique has been used to provide information on the synthesis, mechanism as well as thermal behaviour of the synthesized zeolites. Derouane et al[52] used this technique to identify the role of TPA ions in the synthesis of ZSM-5. It was shown that TPA is progressively incorporated in to zeolite framework during crystallization and that one TPA entity is introduced per channel intersection during the process. Various physico-chemical changes, occurring during the thermal treatment are reflected in the DTA/TG curves. Dehydration of adsorbed water, decomposition of occluded organic cations, dehydroxylation at higher temperature to produce Lewis sites are accompanied by changes in these
curves. In certain cases, it has been possible to identify the location of water molecules in hydrated zeolites from the splitting of the endothermal peak due to dehydration. The measurement shows that thermal stability of zeolites increases with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio [3] and that the crystal structure of ZSM-5 changes from orthorhombic to monoclinic by calcination[57].

1.4.6 Sorption

Sorption measurements can be used in approximately estimating the size and shape of the pores in zeolites and compare them with those determined from X-ray crystallographic measurements[58]. They help in determining specific interactions between sorbate molecules and framework structure in the intercrystalline channels. A large number of different molecules have been in use as sorption-probes. For example Anderson et al.[58] used n-hexane, 3-methyl-pentane, 2,2-dimethyl butane, ammonia, n-butyl-amine, t-butyl and 4-methylquinoline as the probes. Sorption and Diffusion properties of ZSM-5 have been evaluated systematically by many workers[59-64]. Derouane et al.[65] have evaluated the channel length per unit cell of ZSM-5 from a knowledge of the sorbate molecules adsorbed per unit cell and their dimensions. From such a study it has been possible to show the ease of accessibility of different hydrocarbon molecules to different channels during adsorption and diffusion. Choudhary and Mayadevi[66] have recently reported the
detailed sorption properties of NaX, NaY and Na-mordenite zeolites by working out the isotherms with respect to methane, ethane, ethene and carbon dioxide as the probe molecules.

Other techniques such as x-ray photo electron spectroscopy (XPES) and ESR have also been used for characterization of zeolites. X-ray fluorescence (XRF) has been used to characterize the chemical state of alumina in zeolites. Borade et al.[42] have used x-ray photo electron spectroscopic method for the identification and quantitative estimation of Bronsted and Lewis acid sites in ZSM-5 zeolites.

1.5 Acid Sites on zeolites

The acid sites on zeolites have been studied extensively with both physical and catalytic characterization techniques. These include infrared spectroscopy, measurements of adsorption/desorption properties of probe molecules such as ammonia and pyridine, and isomerisation of organic molecules. Ward [67] has reviewed the creation of acid sites on zeolites. Zeolites possess both Bronsted and Lewis types of acid sites[3,68]. Both types of acid sites play an important role in various catalytic reactions like alkylation, hydrogenation and dehydrogenation. Bronsted acidity is usually related to hydroxyls and the Lewis acidity
to cations (alkaline, alkaline earth) and/or to Al extra framework Species[69].

1.5.1 IR Study

Infrared spectroscopy has been used for detection and estimation of acid sites. The most commonly employed technique is to look at the infrared spectra of adsorbed pyridine. Several investigators have studied the adsorption of pyridine on ZSM-5 by IR technique[42,70]. Pyridine forms pyridinium ion at the Bronsted acid sites and is co-ordinated to the Lewis acid sites. Both have a number of bands due to the ring vibration of the pyridine molecule. Borade et al. [42] assigned the band at 1545cm\(^{-1}\) exclusively to the pyridinium ions (bound to Bronsted acid sites) and the band at 1455cm\(^{-1}\) to coordinately bound pyridine (bound to Lewis acid sites). Besides, there is a band at 1490cm\(^{-1}\) to which both forms of pyridine contribute. From the relative absorbances of 1545 and 1455cm\(^{-1}\) bands, the relative bulk concentration of Bronsted and Lewis acid sites could also be calculated[42].

IR bands of the hydroxyl region (3745, 3670 and 3600cm\(^{-1}\)) almost disappear after the adsorption of pyridine at 423K. The band at 3745cm\(^{-1}\) appears on heating at 523K and then intensifies at 623K indicating that pyridine is released from the zeolite. From the hydroxyl spectra it is clear that the strongest acid sites are the ones showing hydroxyl frequency at 3600cm\(^{-1}\) and those giving rise to 3745cm\(^{-1}\) are the Weakest
Bronsted acid sites. Some authors have used ammonia as a probe molecule for surface acidity of zeolite ZSM-5 [70-73]. Organic molecules such as propene have also been used as probes for zeolite acidity[74]. Some investigators have used the FT-IR technique to study the zeolite acidity[72,75-77].

1.5.2 Temperature Programmed Desorption (TPD)

TPD is another important technique to characterize and estimate acid sites in zeolites. Temperature programmed desorption (TPD) of ammonia is commonly used to measure both acid sites concentration and strength. There are two methods of preparing the samples for examination by TPD:

(a) ion exchange to obtain the NH$_4^+$ form and
(b) adsorption of ammonia gas on the acid form of the zeolites.

TPD involves monitoring the loss of ammonia with increasing temperature. The temperature at which most of the ammonia (in the form of NH$_4^+$) is no longer retained within the material has been related to the acid strength of that material. The desorption peak maximum however, is related to the rate at which the sample is heated.

Lok et al.[72] have used NH$_3$-TPD techniques to study acidity of zeolites. The results indicate that, in general three desorption peaks are observed. The three peaks fall in the temperature range of: less than 473K, 473-673K and higher than 673K. Investigators [58,78,81], studying ZSM-5 type zeolites by NH$_3$-TPD method, also reported three peaks.
The peak at 353K was attributed to weakly adsorbed molecules on the external surface or to the interaction of NH$_3$ molecules with surface oxides or hydroxyl groups by non-specific hydrogen bond or to extraneous material. The 448K peak was attributed to the chemisorbed molecules. These two peaks correspond to the 3720 - 3740 cm$^{-1}$IR bands of lower acidity hydroxyl groups. The peak at 733K was attributed to strongly chemisorbed molecules and is partially responsible for the 3600 cm$^{-1}$ IR band which characterizes strong Lewis acid sites. Anderson et al.[58] reported results on TPD of ammonia on ZSM-5, HZSM-5 and silicalite. It was suggested that the TPD maximum observed at 780K corresponded to the probable sites used for hydrocarbon conversion process.

A typical NH$_3$–TPD profile obtained by Santra et al.[82] is shown in Fig. 1.2 which shows three distinct regions of ammonia desorption. More rigorous identification of acid sites in the zeolites generally involves two more techniques. A common set of techniques includes TPD and infrared spectroscopy. A combination of TPD and NMR also has been used[83]. Microcalorimetric techniques are also used to characterize the strength and distribution of acid sites in zeolites. The C-13 chemical shift of acetone adsorbed on zeolites has also been shown as a possible probe of Bronsted acidity on zeolites [84].
FIG. 1.2 TEMPERATURE PROGRAMMED DESORPTION OF AMMONIA FROM Al-ZSM-5 (ref. 82)
1.6 Catalysis by Zeolites

1.6.1 General Considerations

During the past decade, synthetic zeolites have been extensively used in Petrochemical processes and they share the following six properties that make them attractive for heterogeneous catalysis [85].

1. Well defined crystalline structure.
2. High internal surface area ( > 600 m²/g ).
3. Uniform pores with one or more discrete sizes.
4. Good thermal stability.
5. Ability to sorb and concentrate hydrocarbons.
6. Highly acidic sites, obtained by exchange with protons.

The most important advances in zeolite catalysis have been made through the ability to synthesize a large variety of crystal structures. Zeolites, ion-exchanged with multivalent cations, are extensively used in Petroleum and Petrochemical processes for cracking, isomerization, alkylation, dealkylation, hydrogenation, hydrocracking and related processes. Transition metal zeolites are active in polymerisation of olefins[86] and isomerization and disproportionation of toluene [87].

1.6.2 Shape Selective Catalysis

Shape selectivity is one of the unique properties possessed by zeolites which have pores of dimensions similar
to the kinematic diameters of simple organic molecules. The principles of shape selective catalysis on zeolites have been discussed in a number of comprehensive reviews[88-96]. Chen and Garwood[91,95] have summarized the impact of shape selective catalysis on the Petroleum and the Petrochemical industries, with special emphasis on medium pore zeolites. Recently Choplin[97] has shown that the shape selective properties of a zeolite can be modified by changing the surface functional groups by reacting with hydrides, alkyl or alkoxy complexes of main group elements. It is also shown that finely tuned size and shape selective catalysts can be designed from zeolites to mimic natural enzymes as well as for selective hydrogenation and amination reactions[98].

Molecular shape selectivities are distinguished or classified into four main types—reactant selectivity, product selectivity, restricted transition state selectivity and molecular traffic control[94]. The different types of shape selectivities are depicted in Fig. 1.3 (a to c) and are discussed below:

(a) Reactant Shape Selectivity

This is expected to occur when only part of the reactant molecules are small enough to penetrate the zeolite pores and also when the reactant molecules differ widely in their Configurational diffusion in the zeolites [Fig.1.3 (a)]. The reactants which cannot enter the zeolite channels and also those which possess lower diffusivity have a zero or small
local concentration inside the zeolite channels and therefore, will not be converted to any reasonable extent in comparison to the others.

In catalytic reactions over ZSM-5, only those of the reactant molecules having dimensions appropriate to the channel openings of ZSM-5 can diffuse through the intracrystalline channels to undergo reaction. Such molecules include among the aliphatic hydrocarbons, in decreasing order of ease of entry, linear paraffins, isoparaffins and methyl substituted paraffins. Dimethyl paraffins and ethyl paraffins are least favoured. Among the aromatic hydrocarbons, benzene, toluene and P-Xylene are most favoured. Polyaromatics are strictly avoided. Some applications of the effects due to "Reactant Selectivity" are in the cracking and hydrocracking reactions of hydrocarbons over ZSM-5 [99,100]. n-paraffins are selectively cracked in these processes.

(b) Product Selectivity

In catalysis over zeolites, product selectivity is observed when some of the products formed in the zeolite channels are too bulky to diffuse out and also when the products differ widely in their configurational diffusivity in zeolite channels [Fig.1.3 (b)]. Examples of product selectivity effects are found in the selective formation of P-Xylene[101], conversion of methanol to hydrocarbons[102] etc. The longer life of ZSM-5 type zeolites has been partly due to product selectivity effects. Such effects reduce the
formation of bulkier molecules and thus limit the possibility of coking in ZSM-5 [103] and "reverse molecular size selectivity" which is one of the reasons for deactivation of other zeolite system[104].

(C) Restricted Transition State Selectivity

Restricted transition state selectivity [Fig.1.3 (C)] is observed in zeolites containing low volume cavities in which the active centres are located. Because of the local configurational constraints imposed on the molecular dimensions of the transition state complex by the size of the zeolite cavities, certain reactions requiring formation of larger transition state complexes, which is not favoured in the zeolite, are inhibited or the probability of their occurrence is greatly reduced. The reactions requiring smaller transition states proceed unhindered, by contrast. Example of transition state selectivity is in the isomerization of isobutane over HZSM-5 zeolite[105]. This reaction has been shown to take place by a bimolecular transition state mechanism over a variety of acidic catalysts to give propane and pentanes. Inspite of the presence of stronger acid sites in HZSM-5, the reaction does not take place by a bimolecular mechanism on this catalyst. The lower rate and absence of pentane among the products indicate that the bimolecular transition state cannot be formed over HZSM-5.
(a) REACTANT SELECTIVITY

(b) PRODUCT SELECTIVITY

(c) RESTRICTED TRANSITION STATE SELECTIVITY

FIG. 1.3 SHAPE SELECTIVITY IN ZEOLITES
(d) Molecular Traffic Control

A new type of shape selectivity in zeolites, containing intersecting channels of different diameters has been proposed and termed as molecular traffic control effect by Derouane and Gabelica[65].

According to this concept, in the case of zeolites with more than one type of intersecting channels, the reactants enter preferentially through one type of channels, whereas products diffuse out by the other, thus minimizing counter diffusion. Derouane and Gabelica proposed that the traffic control in the conversion of methanol over ZSM-5 occurs as follows: The smaller reactant molecules enter the sinusoidal circular channels, whereas, the larger product molecules exit from the straight elliptical channels [Fig.1.1 (e)]. However, the existence of the molecular traffic control is not yet supported by experimental findings.

Recently, Beschmann and Riekert[106] have also discussed the dependence of shape selectivity on size of ZSM-5.

1.6.3 Deactivation of ZSM-5 Zeolites

ZSM-5 zeolites show high resistance to coking and ageing compared to large pore zeolites. Its unique structural features are responsible for this. Product selectivity, transition state selectivity and molecular traffic control effects minimise or prevent formation of bulky molecules in the channel intersections via steric and spatial restr-
ictions. If there is any deactivation of the catalyst, it is possible to study it by surface-sensitive techniques[107].

There have been several studies on coking and ageing of the zeolite catalysts. Venuto [104] showed that in zeolites having cavities or cages larger than the opening to the crystal exterior (e.g. erionite), coke may be trapped in these cages. As the trapped coke cannot escape, it may cause deactivation and site blockage. It was described as deactivation by "reverse molecular selectivity".

From a study of various reactions over zeolites of different pore structure, Rollmann[103] concluded that intracrystalline coking is a shape selective reaction directly related to zeolites pore structure. It was also demonstrated[108] that the differences in the coke yield for some reactions between 10-membered (ZSM-5) and 12-membered (Y type zeolite) zeolites are not the result of differing basic origins for coke. These differences must arise from structural constraints on the reactions of the same intermediate (transition state selectivity) in the formation of the coke in the two cases. Dejaifve et al.[109] have provided experimental evidence to show that coking and deactivation are determined by structural properties. According to them, coking in HZSM-5 is only over the external surface. The coke precursors synthesised in the channel intersections diffuse out and these polymerise on the external surface to form coke. This coke on the external
surface may deactivate the catalyst and modify selectivity of the products by partial blockage of the poor openings.

The high silica/alumina ratio of HZSM-5 is also partly responsible for its resistance to coking and ageing. Sometimes coking can also induce certain amount of stabilizing influence on catalytic activity [e.g.110].

1.6.4 Catalytic Reactions over ZSM-5 Zeolites

With the discovery of ZSM-5 and the realization of its superior shape-selective properties, its performance as a catalyst for several reactions has been studied. Some of these reactions are the following :-

(i) Conversion of methanol, ethanol and other oxygenated Compounds to hydrocarbons.

(ii) Aromatic reactions like

(a) Isomerization of Xylene.

(b) Alkylation of aromatics and

(c) disproportionation of toluene.

(iii) Other hydrocarbon reactions like cracking, hydrocracking, dewaxing, hydrogenation, dehydration etc.

Some of the industrially important reactions based on shape selective zeolite are given in Table 1.4[88]. Ono [111] has recently reviewed the transformation of lower alkanes into aromatic hydrocarbons over ZSM-5 while Hutchings et al.[112] have compared the activities of zeolite B, ZSM-5 and Y for zeolite conversion of alcohols, ethers and carbonyl compounds.
Table 1.4 Industrial processes based on shape selective zeolites

<table>
<thead>
<tr>
<th>PROCESS</th>
<th>OBJECTIVE</th>
<th>MAJOR CHEMICAL/PROCESS CHARACTERISTICS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selecto-forming</td>
<td>Octane number increase in gasoline; LPG production.</td>
<td>Selective n-paraffin cracking.</td>
</tr>
<tr>
<td>M-Forming</td>
<td>High yield; octane number increase in gasoline.</td>
<td>Cracking depending on degree of branching; aromatics alkylation by cracked fragments.</td>
</tr>
<tr>
<td>Dewaxing</td>
<td>Light fuel from heavy fuel oil; lube oil with low temperature pour point.</td>
<td>Cracking of high molecular weight n- and mono-methyl paraffins.</td>
</tr>
<tr>
<td>Xylene isomerisation</td>
<td>High yield para-xylene production.</td>
<td></td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>High yield ethyl benzene production; eliminate AlCl$_3$ handling</td>
<td>High throughput, long cycle life; suppression of side reactions.</td>
</tr>
<tr>
<td>Toluene disproportionation</td>
<td>Benzene and xylenes from toluene</td>
<td></td>
</tr>
<tr>
<td>Menthanol to gasoline</td>
<td>Methanol (from coal or natural gas range to high grade gasoline)</td>
<td>Synthesis of hydro carbons only, restricted to gas (C$<em>4$ to C$</em>{10}$) including aromatics.</td>
</tr>
</tbody>
</table>

1.6.5 Catalytic Dewaxing

Catalytic dewaxing is probably the first industrial application of shape selective zeolite catalysis. This process is based on the same principles as gasoline selectoforming, where by n-paraffin (wax) molecules are...
selectivity hydrocracked to lighter components, thereby improving the cold flow properties (e.g. Pour Point) of the lubricating oil. The traditional method for the removal of these hydrocarbons (wax) is solvent dewaxing. In solvent dewaxing process, waxy Oil was dissolved in a solvent that would keep the oil in solution: the wax separated as crystals when the temperature was lowered. Commercially used solvents were propane, sulfur dioxide, acetone-benzene, tri-chloroethylene, ethylene dichloride benzene, methyl ethyl ketone-benzene (benzol), methyl-n butyl ketone and methyl n-propyl ketone. Then most of the modern dewaxing processes, a mixture of methyl ethyl ketone and benzene has been used[113]. The operating costs of the solvent dewaxing are very high and the desired pour point of the dewaxed oil has to be compromised with the enormous cost of refrigeration to very low temperature. The present trend is therefore the substitution of solvent dewaxing with catalytic dewaxing. The catalyst used is a bifunctional one containing both hydrogenation and acidic components. Several companies, Mobil[114], British Petroleum [115,116] and Chevron[117] have developed dewaxing processes. Mobil’s dewaxing catalysts are based on ZSM-5 [118,119] while that of British Petroleum are based on erionite and mordenite[120,121]. The critical zeolite properties that are important for dewaxing are reactant and transition state selectivity. Reactant selectivity is essential to convert selectively the high pour
point normal alkane component of the oil, while the latter selectivity is necessary to prevent the deposition of coke within the Pores. By restricting the size of transition state complexes that can be formed within the pores of the zeolite, bulky coke precursors like fused ring aromatics can be prevented from forming. This reduces the coking tendency of the zeolite improving its life. The size of some typical hydrocarbons relative to the pore aperture of erionite, ZSM-5 and mordenite are depicted in Fig.1.4.

Erionite (small pore zeolite, 4x4Å² pore size) permits the entry of only straight chain compounds, excluding even slightly branched molecules. Due to the small pore dimensions of erionite, the cracking of alkanes larger than C\textsubscript{12} is diffusion limited. Therefore, erionite cannot be used to dewax oils heavier than atmospheric fractions.

On the other hand, the larger pore opening of ZSM-5 (medium pore zeolite, 5.4 x 5.6 Å², Pore size) permits its use as a dewaxing catalyst for heavier fractions, like lubricating oils (lubes). It allows the entry of both normal and slightly branched alkanes but still excludes other larger molecular weight lube range molecules. In the case of mordenite (large pore zeolite, 6.7 x 7 Å², pore size), it is less shape selective than ZSM-5. ZSM-5 will tend to dewax by preferentially converting the higher pour point normal and slightly methyl branched carbon chains, while
ERIONITE  
(4x4Å°)  
MORDENITE  
(6.7x7Å°)

* ALKANE/ALKYL-GROUP  
-Straight -Chain  
C-C(C)n-C-C

- SINGLE BRANCH  
\[ \begin{array}{l}
C \\
\uparrow
\end{array}
C-(C)_n-C
\]

- DOUBLE BRANCH  
\[ \begin{array}{l}
C \\
\uparrow\downarrow
\end{array}
C-(C)_n-C
\]

* AROMATIC RING  
BENZENE

* MULTIRING COMPOUND  
5,6 BENZOQUINOLINE

FIG. 1.4 MOLECULAR SIZE AND SHAPE MATCHING OF HYDROCARBONS WITH THE PORE DIMENSIONS OF SOME ZEOLITES.
mordenite will be less selective, and crack away the more desirable lube components. Bendaraitis et al. [121] have reported larger lube oil yields from ZSM-5 than from mordenite. The viscosity index of the ZSM-5 product is also significantly higher than for mordenite. A further advantage of ZSM-5 over mordenite for dewaxing heavy petroleum fractions which have high coking tendencies is the operation of restricted transition state selectivity [123] in ZSM-5. ZSM-5 has a coking tendency at least one order of magnitude less than mordenite [124].

Heavy petroleum oils contain considerable amounts of nitrogen compounds which are catalytic poisons. These are usually large aromatics. These compounds will be excluded by ZSM-5 and not by mordenite. Hence ZSM-5 will be less susceptible to nitrogen poisoning than mordenite. Fig. 1.4 depicts a similar situation. ZSM-5 does not permit the entry of 5,6 benzoquinoline into its pores, but mordenite does.

In the Mobil Lube Oil dewaxing (MLDW) technology, two catalysts are used, one for pour point reduction and other for imparting oxidation stability to the MLDW product. The zeolite catalysts (ZSM-5) selectively cracks waxy molecules such as normal and slightly branched alkanes to lower boiling ranges, but does not convert any significant number of the lube oil molecules. As a result of the cracking reactions, some olefins are formed in the lube boiling range. The non zeolite catalysts (generally Group VI or Group VIII metal)
is an amorphous type which is used to saturate small amount of alkenes that are created in the lube by the dewaxing catalyst. Thus it improves the stability, colour and demulsibility of the base oil. Along with dewaxing i.e. removal of long chain paraffins from crude oil, it is also important to reduce the high aromatic content to limit emission of undesirable products to the atmosphere during utilization of various fuels. For this purpose, the aromatics are often hydrogenated using catalysts such as sulfides Ni-Mo, Ni-W, Co-Mo etc. supported on alumina or a zeolite. The various studies in this regard have been reviewed recently by Stanislaus and Coper[125].

1.7 Aims of the present work

Synthesis of a large variety of zeolites and their expanding sphere of uses as catalysts and catalytic supports have been receiving wide attention during the last two decades. The catalysts based on high silica zeolites of type ZSM-5 have many advantages over other zeolites due to their high activities, resistance to coking and nitrogen poisoning, and shape selectivity. In fact, entirely new processes for petroleum refining and petrochemicals production have become possible due to the above properties. These processes have been the outcome of a large amount of research carried out on the physico-chemical and catalytic properties of pentasil
zeolites.

ZSM-5 exhibits unique behaviour in the cracking of hydrocarbons. By virtue of the large field gradients existing inside the pores of the zeolite, the cracking activities and product selectivities differ very considerably from those of the commercially important large pore faujasites. ZSM-5 was introduced by Mobil in 1986 as an octane-enhancing additive to Fluid Catalytic Cracking (FCC) because ZSM-5 cracked less gasoline and produces less liquid petroleum gas (LPG).

At present, catalytic dewaxing processes are available commercially for dewaxing lube oils and middle distillates of crude oil. The principle behind dewaxing is shape selective cracking. Although the application of catalytic dewaxing processes to control cold flow properties of middle distillates has already been in practice in several developed countries, most of the oil refineries in our country do not use the catalytic dewaxing technology. The present work has been carried out to gather some information on catalytic dewaxing by high silica zeolite ZSM-5.

The aims and objectives of the present work are:

(i) Synthesis of high silica zeolites of ZSM-5 type with different SiO₂/Al₂O₃ ratios by hydrothermal process,

(ii) Characterization of these zeolites with X-ray diffraction, infrared spectroscopy, scanning electron microscopy and chemical analysis,
(iii) Investigation of Bronsted and Lewis acid sites of the synthesized zeolites by ammonia and pyridine adsorption studies using FT-IR and temperature programmed desorption studies, and also to investigate the active sites for catalytic cracking reaction by stepwise thermal desorption of ammonia and pyridine, and

(iv) Preparation of a suitable catalyst based on ZSM-5 for carrying out dewaxing of a crude petroleum sample in order to selectively crack straight chain and slightly branched higher hydrocarbons to improve the fluidity-characteristics.

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