CHAPTER 1

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Chapter Summary

This chapter mainly deals with current literature review on zeolites in general and zeolites Y, mordenite, beta and MCM-22 in particular. The chapter starts with a broad outline of zeolites mainly their general synthesis, structure, properties, characterization and applications. The structural characteristics, synthesis and industrial applications of mordenite, Y, beta and MCM-22 have been highlighted.

1.1 Zeolites: A Brief Idea

According to the IUPAC recommendations, micro porous materials are defined as porous solids with pore size below 2 nm. Porous solids with pore size between 2 nm and 50 nm are called mesoporous materials and those with pore size larger than 50 nm are called macroporous materials [1-4].

Zeolites describe a broad class of microporous materials [1] with crystalline walls and unique internal pore systems. They can be defined more precisely as the crystalline microporous aluminosilicates possessing an anionic framework; the electro neutrality of the crystals requires the presence of cations in extra framework positions such as Na⁺, K⁺, H⁺, 1/2Ca²⁺, 1/2Mg²⁺, 1/3La³⁺, 1/3Ce³⁺ etc [5-8]. During the 1930's, R. Barrer and J. Sameshima did extensive work in zeolite synthesis. In 1948, Richard Barrer first produced a synthetic zeolite that did not have a natural counterpart. At approximately the same time, Milton made the first materials that had no natural counterpart such as zeolite- A.
An empirical formula of $M_{2n}O\cdot Al_2O_3\cdot XSiO_2\cdot YH_2O$ is used to represent the different zeolites, where $M$ represents the exchangeable cations of valency $n$ and is used to balance the framework charge, $X$ can assume a value equal to or greater than 2 ($2 - \infty$) as no two $Al^{3+}$ can occupy the adjacent tetrahedral positions (Lowenstein's rule), and $Y$ is the number of water molecules present in the channel or cavities of the 3 dimensional network [9-11].

The word “zeolite” is Greek in origin, coming from the words ‘zein’ and ‘lithos’ meaning “to boil” and “rock” respectively. The name ‘Zeolite’ was first christened by the Swedish mineralogist ‘Cronstedt’ who found that upon heating, the zeolite sample evolved steam and appeared boiling [12]. In fact the history of Zeolites began with his discovery of stilbite in the year 1756. There was little interest in zeolites until the late 1930’s when the modern founder of zeolite chemistry, Barrer began extensive work on the characterization of zeolite structure and chemistry [13]. There are 40 naturally occurring zeolites whereas more than 150 other zeolites have been synthesized.

1.2 Structure of Zeolites

Zeolites are complex crystalline aluminosilicates that are made of oxygen tetrahedrons, each generally encasing either a Si or Al atom ($[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ polyhedra) [14, 15]. As oxygen atoms can be shared by only two tetrahedrons and no two aluminium atoms can share the same oxygen atom; the $Al/O$ ratio is always equal to or less than unity [16]. The crystal structure that results is complex 3-D frameworks of aluminosilicates with precisely dimensioned cavities and channels (typically 0.25-0.8 nm units) running through them.
Naturally all zeolites contain molecular water as an intracrystalline fluid which can be removed by heat and evacuation. Water can be re-sorbed by exposing the crystals to water vapour. And this accounts for the well-known desiccant properties of zeolites [14].

The channels and cavities of zeolites may also contain different cations. The size and shape of the channel system and the nature and location of cations determine the absorption and rate of diffusion into the zeolite. The stability and catalytic property are also functions of the structural characteristics [17] of zeolites.

Zeolites have basically three different structural variations. These are:

(a) Chain-like structures which generally form needle-like prismatic crystals, e.g. natrolite.

(b) Sheet-like structures where the crystals are flattened platy or tubular with usually good basal cleavages, e.g. heulandites.

(c) Framework structures where the crystals are more equant in dimensions, e.g. chabazite.

The framework topology of zeolites consists of primary (the Basic Building Unit) and secondary (or the Composite Building units) building units [18]. The primary building units of a zeolite or a porous material are the individual tetrahedral TO₄ unit, where T is Si or Al or other metals like Ti, Fe, and V etc. These tetrahedra (TO₄) units can be monomeric, dimeric, trimeric or tetrameric etc.

These Primary Building Units (PBUs) often consists of 4 or 6 T- atoms (known as 4 and 6 membered ring or 4 membered ring or 6 membered ring) in a closed ring configuration.
Since molecules such as nitrogen and water cannot diffuse through 6 membered ring, only apertures of 8 membered ring and larger are considered for micro porosity. The PBUs condense and form various polymeric units known as Secondary Building Units (SBUs). In other words, a secondary building unit is nothing but the selected grouping of the above mentioned tetrahedra. There are 9 such building units. The different combinations of these 9 secondary building units can form all the known zeolite structures. The secondary building units consist of 4-4, 6-6 and 8-8 double rings and 4-1, 5-1 & 4-4-1 branched rings. With the development of zeolite science, various other possibilities of formulating zeolite framework topologies have been developed.

Zeolites with identical framework structure often appear in the literature under different names. According to the *Atlas of Zeolite Framework Types* [19] there are over 133 different structures of both classical- zeolites and zeolite-like molecular sieves. The different zeolite structures are designated by a three letter code to identify the structure of the zeolite. A few examples are provided in Table 1.1.

New zeolite structures are being continuously reported. The framework topology of zeolites plays an extremely important role in their successful application as industrial catalysts.

Much of the interest in zeolites as catalysts and selective sorbents depends upon the arrangement and free dimensions of the intracrystalline channel structures. The use of zeolites as catalysts are basically dependent upon the accessibility of intracrystalline catalytically active centres to reactants, and so upon the shape and size of penetrant molecules [20-24].
Fig. 1.1. Primary, Secondary and Tertiary building units (PBU, SBU and TBU) leading to three dimensional zeolite framework.
Table 1.1. IUPAC designation of a few zeolites

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Designated Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5</td>
<td>MFI</td>
</tr>
<tr>
<td>MCM-22</td>
<td>MWW</td>
</tr>
<tr>
<td>Y</td>
<td>FAU</td>
</tr>
<tr>
<td>Beta</td>
<td>BEA</td>
</tr>
<tr>
<td>Mordenite</td>
<td>MOR</td>
</tr>
</tbody>
</table>

1.3 Properties of Zeolites:

The superior catalytic performance of zeolites is related to some important properties [25-35].

- The solid zeolite catalysts can be recovered and regenerated easily after the desired reaction, which eliminates the catalyst disposal problems. As a result they have no negative impact on the environment. Zeolites can be regenerated using relatively easy methods such as heating to remove adsorbed materials, ion exchanging with sodium to remove cations, or pressure swing to remove adsorbed gases.

- Separation of reactants and products from the catalysts is easy and inexpensive, thus simplifying their repeated use.
• The very large surface area of zeolites has also increased their application manifold.

• High concentration of active sites, whose number and strength can be modified in a wide range.

• Possibility of modulating the electronic properties of the active sites.

• Possibility for pre activating the molecules when in the pores by strong electric fields and molecular confinement.

• High thermal and hydrothermal stability, which is important in processes occurring at high reaction temperature and when high temperature regeneration is required.

• High cation-exchange capacity (CEC).

• Possibility of doping other metals in zeolite framework for use in oxidation chemistry.

• Shape selectivity, which allows for directing the reaction pathway towards the formation of desired products by means of reactant/product size exclusion or transition state selectivity [36].

The well-defined micro porosity of zeolites allow space for large cations such as sodium, potassium, barium, calcium etc and even relatively larger molecules and some other molecules such as water, ammonia, carbonate ions, nitrate ions etc. In both natural and synthetic zeolites, these spaces are generally interconnected and form long wide channels of varying sizes (from simple uni- directional to complex 3-dimensional) depending on the minerals. These channels allow the easy movement of sorbed ions and molecules into and out of the structure and enable the zeolite crystals to be selectively permeable to various gases or liquids. Thus the geometry of
their framework pertains them the capability to separate mixtures of molecules on the basis of their effective sizes. This property is termed as "Molecular Sieving" [14]. Zeolites act as the shape selective catalyst either by reactant or product or transition state selectivity. This property will be discussed in details in section 1.3.4. The spaces between the tetrahedra in zeolitic structures are normally occupied by H₂O molecules. The zeolites are characterized by their ability to lose and absorb water without damage to their crystal structure. These large channels in zeolite framework topology account for their consistent low specific gravity.

Zeolites have a high internal surface area available for adsorption due to the channels or pores which uniformly penetrate the entire volume of the solid and thus making them very effective solid catalysts. The external surface of the adsorbent particles contributes only a small amount of the total available surface area. Importantly their very open structure can not make them thermally unstable. Thermal stability depends on the structure and Al content of the zeolite. For example, low silica NaX (SiO₂/Al₂O₃ = 2.5) collapses at 660°C, whereas structurally equivalent NaY (SiO₂/Al₂O₃ = 5.0) is stable up to 700°C. Highly dealuminated zeolite Y is stable at temperatures > 1000°C [37].

Increasing attention has been focused on fine-tuning the topology and the properties of zeolite catalysts in order to carry out various specific syntheses of high value chemicals, e.g., pharmaceuticals and cosmetics.
1.3.1. Physical Properties

Morphology.

In nature zeolites occur in igneous rocks as well-developed, single crystals which may be as large as several millimeters. Natural zeolite crystals may be found as dense polycrystalline aggregates such as mordenite amygdales in typical basalt. Zeolites have been found in sedimentary deposits as well.

Synthetic zeolites are crystalline powders, which is an aggregation of either well developed or irregular faces. Zeolites with alkali and alkaline earth metal cations are normally colorless crystalline powders. Colors may occur in zeolites if they contain transition metal impurities or if they have been modified by ion exchange with these elements [38].

Particle size of synthetic zeolites

The average particle size of synthetic zeolite crystals is small (1-5 microns), the external surface of the crystals is small relative to the internal adsorption void space that becomes available after dehydration of the zeolite.

Density

The density of zeolite is low, ranging from 1.9 to 2.3 g/cc. The density depends on the openess of the zeolite structure and the cation. Cation exchange with heavy ions increases the density; some barium exchanged zeolites have densities as high as 2.8.

The hardness of zeolite crystals ranges from 4-5 on the Mohs scale.

1.3.2. Chemical Properties

Brønsted and Lewis acid sites

The catalytic activity of zeolites is associated with the presence of Brønsted and Lewis acid sites on their surface. The catalytic sites in aluminosilicate zeolites are
associated with tetrahedral aluminium atoms in substitution positions in the framework of silica. Incompletely coordinated aluminium atoms are considered to be the source of Lewis acidity in dehydrated alumina which may be formed as follows [39]-

$$\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{O} & \quad \text{Al} \\ \\
\text{O} & \quad \text{O} \\
\text{Al} & \quad \text{Al} \\
\end{align*}$$

In case of hydrogen zeolites, protons associated with the negatively charged framework aluminium is the source of Brønsted acid activity. The proton attached to the oxygen atom connected to neighbouring silicon and aluminium atoms, results in the so-called bridged hydroxyl group which is the site responsible for the Brønsted acidity of zeolites [40, 41]. So, it can be inferred that Lewis acid sites...
get converted to Brönsted acid sites by adsorption of moisture. Zeolite acidity is very important for hydrocarbon transformation reactions.

Both Brönsted and Lewis acid sites are found and several methods have been developed to determine acidity. Chemical method includes temperature-programmed desorption (TPD), which exploits the fact that more thermal energy is required to detach a base from stronger acid sites than weaker acidic sites. Typical bases used are NH₃ or pyridine. This method cannot distinguish between Brönsted or Lewis sites. In order to do so, infrared spectroscopy is the method of choice. For example, pyridine can be adsorbed as pyridinium ion on a Brönsted site whereas it is coordinatively bonded to a Lewis acid site.

**Basic sites**

The basicity in zeolites may also exist in two forms, Brönsted and Lewis. The Brönsted basicity arises due to framework OH⁻ groups linked to extra framework species and the Lewis basic sites are the framework oxygen atoms. The basic strength of zeolites depends on the extent of charge on the oxygen atom. This basic property of zeolites has been used in many fields starting from adsorption to catalysis [42-46].

1.3.3 *Stability of Zeolites*:

Three key parameters influence the stability of zeolites.

- **The Aluminium content:** Lower the aluminium content, more stable is the zeolite.
- **Crystal size:** Larger the crystal size, more stable is the zeolite.
- **Sodium level:** Lower the sodium level, more stable is the zeolite.
Thermal stability of zeolites varies over a large temperature range and type of zeolite. Some zeolites show structural change at ambient temperature while some others undergo structural change at very high temperatures. Decomposition temperature for low silica zeolites is low and for highly siliceous zeolites, decomposition temperature is high. The structural changes occur either due to fundamental solid state transformation or promoted by water loss. The amount of water in zeolitic pores is one of the main factors which govern their stability [47]. The structural transformation might lead to structural collapse and formation of amorphous phases or it could result in recrystallization to non-zeolitic materials like silica phases, feldspars, high sanidine, feldspathoids or to clay minerals. Due to their high thermal stability sometimes it becomes very difficult to remove the templates from zeolite structures and that might lead to disorganization of the framework. The organic template can be decomposed at a low temperature and the decomposition products can be expelled by high-temperature hydrothermal treatment. Cation exchangers may be added to the water. The zeolite is then calcined at a high temperature, preferably 500°C, to burn off any residue that has not been previously expelled. Thus the organic material is removed without disrupting the framework with a corresponding improvement in the adsorptive and thermal properties. Sometimes, some zeolites (Ex. Stilbite) contract in presence of some exchangeable cations on heating and the framework is destroyed. These contraction and destruction are related to the attractive force of the extra framework cations.
Stability to acids and bases

Generally zeolites show low resistance to mineral acids. Treatment with mineral acids results in leaching of aluminium from zeolite framework. The leached aluminium then gets hydrolyzed to form some hexacoordinated species. Some other leaching agents include ethylenediamine tetraacetic acid, silicon tetrachloride, fluorosilicates, organic acids, acetyl acetone etc. Some zeolites like clinoptilolite, mordenite and ZSM-5 can be exposed to prolong acid leaching that lead to complete removal of all aluminium from their framework structure.

The treatment of zeolite with mineral acids results in replacement of framework cations with the hydronium ion. On heating, water is lost and a ‘hydrogen zeolite’ is formed:

\[ \text{H}_3\text{O}^+\text{Z}^- \rightarrow \text{H}^+\text{Z}^- + \text{H}_2\text{O} \]

For high silica zeolites these ‘hydrogen zeolite’ species are stable and show high efficiency in catalysis.

1.3.4 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 [48] 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 other authors [49] have described this concept in the light of different types of selectivities observed in zeolite based reactions. Shape selectivity operates by either reactant
shape selectivity, product shape selectivity or transition state selectivity. These type of selectivities are depicted in Fig.1.3.

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 [50,51]. Product selectivity effects are found in selective formation of p-xylene [52] and in conversion of methanol to hydrocarbons [53], while effect of transition state selectivity is manifested in the isomerization of isobutane over HZSM-5 zeolite [54]. 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 in spite of the presence of stronger acid sites in this zeolite.

Molecular traffic Control (MTC) which was initially proposed by Derouane and Gabelica [55] to explain the absence of 'counter diffusion' effects in the conversion of methanol to hydrocarbons. Hydrocarbon adsorption measurement of derouane [56] also explains this effect clearly and diffusion of molecules.

1.3.5 Deactivation of Zeolite

Deactivation of catalyst [57-63] happens due to the following reasons-

i) Thermal Effect

ii) Poisoning of the catalyst.
iii) Fouling, coking or carbon deposition etc

iv) Loss of catalytic phases

v) Attrition.

Poisoning of catalytic sites occur due to chemisorption of impurities, reactants, products or by-products. The larger the strength of chemisorption, the stronger the poisoning effect. Poisoning might block the active centres or could electronically modify the adjacent active centres. Fouling of a catalyst takes place when carbonaceous materials or extraneous metal oxides are deposited on the catalyst. Coking can block the pores and thereby decrease the pore volume of the catalyst. In petroleum refining, metal deposition is a major problem. Thermal effect also pose a great threat to catalyst deactivation especially in supported metal catalysts (Pt-Al₂O₃, Ni-Al₂O₃ etc) and oxide catalysts (zeolites, Fe-Molybdate etc). Thermal damage may cause loss of metal surface area due to crystallite growth, loss of support surface area due to pore collapse or transformation of the catalytic phase into a non-catalytic phase.

1.4. Application of Zeolites

Use of catalysts in each and every sphere, starting from fine chemical synthesis to other organic reaction pathways; is one of the 12 essences of green chemistry [64]. Zeolites are environmentally benign catalysts and are used in heterogeneous systems. More and more complicated organic reactions have been investigated with the help of this material [65-67]. So, fundamental zeolite research has become an area of great interest [68].
The remarkable applicability of zeolites ranges from uses in biochemistry, the agro industry, detergents, soil improvements, the nuclear industry, energy storage, the textile industry and the medicine industry etc[69]. Zeolites contribute to a cleaner and safer environment in a great number of ways. In fact, nearly every application of zeolites is driven by environmental concerns [70].
There are three main fields of application of zeolites in industry:

- Catalysis
- Adsorption
- Ion-Exchange

1.4.1 Catalysis

Zeolites are extremely useful as catalysts for several industrially important organic reactions. The most important ones are cracking, isomerization, acylation, alkylation and hydrocarbon synthesis. Zeolites can promote a diverse range of catalytic reactions including acid-base and metal induced reactions. Zeolites are also finding increasing use in synthesis of organic intermediates and fine chemicals. As already discussed above, zeolites can be shape selective catalysts either by ‘Transition State Selectivity’ or ‘by exclusion of competing reactants or products on the basis of molecular diameter’. The reactions can take place within the pores of the zeolites, which allow a greater degree of product control.

Because of their shape selectivity and of their remarkable acid properties, zeolites are being extensively used in refining and petrochemical industries. Another essential property of zeolites is their adaptability. The size of the pores and their tortuosity can be changed in order to allow the desired sieving of the molecules of reactants and products. Similarly the strength and density of the acid sites of zeolites can be adjusted. Basic and redox sites can be treated with various catalytic applications in organic synthesis and in depollution. Zeolites are also model catalysts well adapted for understanding the effect of the site characteristics on the rate and selectivity of reactions.
1.4.2 Adsorption

Zeolites are very efficient adsorbents used for drying and for separation of mixtures by molecular sieving (e.g. n/iso alkanes) or by preferential adsorption (e.g. paraxylene from the C8 aromatic cut) [14]. The simplest use of zeolites is found in gas drying columns as adsorber. Zeolites beads or pellets are used for drying different important feedstocks like hydrogen or oxygen, to dry liquid hydrocarbons (like LPG), halocarbons and natural gas. Zeolite 4A is used very often to remove CO₂ in nitrogen rejection plants. It is also used in drying alcohols, benzene, natural gas, cracked gas, ethylene, propylene, methanol etc. The adsorption and gas separation capability of zeolites has led to their ever growing use in pollution abatement. Zeolites are effectively used to trap hazardous pollutants (both gas and liquid) like mercury vapour, sulphur dioxide and nitrogen oxides (NOx). Zeolites like mordenite can be used to remove pollutants like SO₂, NO₂, NO and acidic contents like HCl from chlorine, chlorinated hydrocarbons and reformer catalyst gas streams[71,72].

1.4.3 Ion-exchange

Zeolites are among the most important inorganic cation exchangers. The aluminosilicate structure is negatively charged and so attracts cations that come to reside inside the pores and channels. Zeolites have large empty spaces or cages within their structures that can accommodate large cations such as Na⁺, K⁺, Br⁺ & Ca²⁺, and even relatively large molecules and cationic groups such as water, ammonia, carbonate ions and nitrate ions etc. The presence of cation in the framework results in a neutral zeolite framework.
The ion exchange process is reversible, allowing for adsorption of ions and molecules making zeolites useful as filters for dust, toxin removal and as chemical sieves. This process has been exploited and applied in medicine, farm animal feed and other types of research. Nowadays, zeolites compete with cation exchange resins in water processing and in purification of waste and sewage. The major use of zeolites as ion exchange agents includes water softening, where hard ‘calcium’ and ‘magnesium’ ions present in water are being replaced by alkali metal ions such as ‘sodium’ or ‘potassium’ present in Zeolite [6,14].

Zeolites are extensively used as ion exchangers for pollution abatement and toxic waste management. Zeolites like clinoptilolite, mordenite, phillipsite and chabazite etc are used most often to remove effluents like ammonia and ammonium ions. The idea of using zeolite to replace environmentally hazardous polyphosphates as builders was first suggested in 1970s and since then all readily available zeolites have been tested as “builders” [14]. Accordingly zeolite A has been chosen as the most effective “builder” in detergent industry [6,14].

Cation -containing zeolites are extensively used as dessicants due to their high affinity for water and also find application in gas separation, where molecules are differentiated on the basis of their electrostatic interactions with the metal ions. Conversely, hydrophobic silica zeolites preferentially absorb organic solvents. Zeolites can thus separate molecules based on differences of size, shape and polarity. Using zeolites, the rate of product diffusion can also be varied and the selectivity of desired products can be enhanced. For example, in the acylation of 2-methoxynaphthalene with acetic anhydride to produce 2-acylmethoxynaphthalene, an intermediate for the synthesis of an anti-inflammatory Naproxen, product
selectivity was markedly increased by the application of silylated zeolite Beta catalyst [73].

1.4.4 Other Applications

Zeolitic membranes offer the possibility of organic transformations and separations coupled into one [74]. Zeolitic membranes are generally used as a catalyst by both processes when one of the reaction products has a higher permeability than the reactants. For example, when used in the dealkylation of ethylbenzene, the high permeable ethylene leads to a higher degree of dealkylation in greater selectivity[75].

Redox molecular sieves are expected to find use in synthesis of fine chemicals, exploiting both the considerable flexibility in designing the framework topology and insertion of reactive elements and compounds into the framework [76-79].

Bulk applications for zeolite powders have emerged for odor removal and as plastic additives.

Due to their high absorption capacity, capability of undergoing reversible adsorption/desorption accompanied by their structural stability, enable them to be used in solar-powered refrigerators and to store energy during off-peak periods and release it during peak periods. They can also be used in refrigeration and air cooling systems to reduce water in the air to very low concentrations, allowing very effective evaporative cooling to occur. Other niche applications include sensors, photochemical organic transformations, radioactive waste decontamination, controlling soil pH, moisture content, manure malodour and polymer waste recovery etc [14]. The microporous zeolite can be effectively used to improve nitrogen retention in soil. In fact, the main use of zeolite, in agriculture,
is nitrogen capture, storage and slow release. Zeolites, with their specific selectivity for ammonium (NH$_4^+$) ions, can take up this specific cation from farmyard manure, composts or ammonium bearing fertilizers, thereby reducing the loss of nitrogen to the environment.

Ammonium charged zeolites have also been tested successfully for their ability to increase the solubilization of phosphate minerals, leading to improved phosphorous uptake. Urea-impregnated zeolite chips were developed in 1992, which can be used as slow release nitrogen fertilizers. Zeolites have also been reported to find application in potting media in horticulture (‘zeoponics’), where nutrient-charged zeolites together with other mineral phases provide the plants with substrate and nutrients for growth.

It has been proved by several workers that zeolite can abate all four main types of wastes viz, agricultural, industrial, municipal and nuclear [80,81]. Soil contaminated by heavy metals may pose a threat to human health if the heavy metals enter the food chain.

Remediation should be carried out to ensure that agricultural produce from such areas can safely be eaten. The remediation of soil contaminated by lead and cadmium can be overcome by application of zeolite and thus reducing the level of heavy metals in the soil.

Zeolites (like ZSM-5 used by Fuji Tech and Mobil) used in polymer waste recovery facilitates thermal depolymerization of polymer wastes. Zeolites are also used as animal feed supplements and in several health related areas [82].
1.5 Classification of Zeolites

Zeolites can be classified into different sub-categories depending upon the following factors [83]:

1.5.1 Classification based on Chemical Composition

Zeolites are classified on the basis of chemical composition [6,8,84] as low silica (Si/Al ratio = 1.5: SiO₂/Al₂O₃ < 4), intermediate silica (4 < SiO₂/Al₂O₃ < 20), high silica (Si/Al ratio =5-500: 20 < SiO₂/Al₂O₃ < 200) and all silica (Si/Al= infinity).

1.5.2 Classification based on Pore Opening Size.

All zeolites are classified by the number of T atoms, where T=Si or Al that define the pore opening. Based on their pore/channel systems, Zeolites are classified as Small pore (8MR), Medium pore (10MR), Dual pore have interconnecting channels, Large pore (12MR) & Ultra Large pore (14 or more MR). Small pore zeolites are having free diameters of 0.30 – 0.45nm. Medium pore zeolite are having free diameters of 0.45 – 0.60 nm. Large pore zeolites are having diameters of 0.60 – 0.80 nm [6, 8, 85-87].

1.5.3 Other Classifications

Classification based on their morphology

Zeolites are classified as fibrous, lamellar and those having framework structures [6, 8, 88, 89].

Classification based on their occurrence

Both natural and synthetic zeolites are classified into ten classes: Analcime, Natrolite, Chabazite, Philipsite, Heulandite, Mordenite, Faujasite, Laumonite, Pentasil and Clantharate [6, 8].
1.6 Synthesis of Zeolites

Zeolites are synthesized typically by hydrothermal processes. The reagents employed in this process are a silica source, an alumina source and a mineralizing agent such as OH$^-$ or F$^-$ in high pH conditions at temperatures ranging from 100°C - 200°C [90, 91]. At present synthetic zeolites are used commercially more often than natural zeolites due to the purity of crystalline products and the uniformity of particle sizes (Breck, 1974). The first zeolite was synthesized and characterized successfully by R.M. Barrer and coworkers around 1940. Later in 1956 zeolite A was synthesized and characterized completely by scientists in Union Carbide Laboratories and this is regarded as the first synthesis of a completely characterized new zeolitic structure unknown in nature.

Generally metal aluminates like sodium aluminate are used as the aluminium source. Some other aluminium sources include freshly prepared Al(OH)$_3$, Al$_2$O$_3$, aluminum alkoxides, aluminium phosphates or other aluminium salts etc. Natural aluminium sources obtained from glasses, sediments, feldspars, felspathoids and aluminum-rich industrial wastes are also being used as the aluminum source.

The most common silicon sources [92] include soluble silicates and their hydrates, silica sols etc. Some other less common sources include silica gels, glasses, silicon esters, clays, volcanic tuffs, sand and quartz etc.

The cation sources used in industrial zeolite synthesis include alkali metals and alkaline earth hydroxides etc. Other cation sources include some oxides and salts. The soluble silicates and aluminates used as aluminium and silicon sources may also behave as cation sources.
The organic reagents like quaternary alkyl ammonium ions (e.g. Tetrapropyl ammonium ions) which are called as ‘Templates or Structure Directing Agents’ are also used as the cation sources to produce zeolites with higher Si/Al ratio. Barrer and Denny first used tetramethyl ammonium (TMA) as cation source in their earlier work in 1961. Templates play an important role in the crystallization process of zeolites, silicalite and some zeotypes like AlPO₄ materials.

The zeolite crystallization is a process with multiple pathways. It is commonly observed that mixing up of all these precursors lead to the formation of unstable germ nuclei; some of these embryos become large enough to form stable nuclei, which then get accumulated to form the larger crystallites. The conversion of these unstable nuclei to crystals is quite rapid once the crystallization process gets started [14]. This suggests that the nucleation is the rate-limiting step and is consistent with studies that report addition of seed crystals decrease the induction time. Tezak [93] suggested that rather than viewing the synthesis process as nucleation and crystallization at least 4 subsystems can be considered (a) formation of simple and polymeric aluminosilicates, (b) aggregation of these complexes to form embryo, (c) nucleation as aggregate formation with a well ordered core and micelle formation (primary particles) and (d) aggregation of primary particles via oriented aggregation. The synthesis pathways are specific for all zeolites and hence a slight variation in the reaction parameters might lead to a completely different topology. In fact the different synthetic zeolites had been invented by applying trial and error technique to already known methods of zeolite synthesis. The quaternary alkyl ammonium ions are observed to form water “icebergs” around themselves. Earlier reports [94-97] showed the presence of these template cations inside the sodalite cages which is
against the fact, that these sodalite cages are too restricted to permit the entry of large molecules/ions like template cations. So, it corroborates the fact that the water icebergs surrounding the template cation in solution had been replaced by aluminosilicate sheaths, partially and then fully enclosing template in sodalite cages. The role of inorganic metal cations, such as Na$^+$ or K$^+$, is also quite profound. These small inorganic cations are energetically hydrated and so hold water molecules in charged clusters. It is now obvious that the cations play an important role in determining the reaction pathways and products. [98-103]. L.D. Rollemann et al started the use of linear polyelectrolytes [97, 104] as the template in zeolite synthesis. These polyelectrolytes are made by reaction between 1, 4-diazobicyclo[2.2.2]octane (Dabco) and Br(CH$_2$)$_n$Br, where $n= 3, 4, 5, 6$ and 10.

The synthesis processes of zeolites are highly influenced by some chemical and physical parameters. These are described below.

1.6.1 Alkalinity of the Gel

The optimal pH range for zeolite synthesis is normally 11-13. Within the stability field of a given zeolite, increasing alkalinity at constant temperature influences the kinetics. So the induction time for a zeolite decrease effectively with increase in alkalinity of synthesis gel. But this increase is observed up to a certain limit; specific for different zeolites, beyond this, the excess alkalinity might lead to disproportionation of the desired structure[105]. The strong dependence of the incubation time on OH- concentration was reported earlier in literature [106]. R.M.Barrer and S.P. Zdhanov et al had shown that the desired SiO$_2$/Al$_2$O$_3$ ratio from a silica rich solution can be obtained at a faster rate [107,108], when the solution is
having greater OH\(^-\) ion concentration, (i.e. high pH). Thus, by increasing the OH\(^-\) concentration the tendency of Al and Si to be ordered on the tetrahedral sites is increased wherever the avoidance rule is valid [109].

1.6.2. SiO\(_2\)/Al\(_2\)O\(_3\) Molar Ratio

The SiO\(_2\)/Al\(_2\)O\(_3\) molar ratio of the gel imposes constraints on the framework composition of the zeolite produced. Generally, an increase in the SiO\(_2\)/Al\(_2\)O\(_3\) gel molar ratio leads to increase in thermal stability, acid resistance and hydrophobicity and decrease in ion-exchange capacity [110].

1.6.3 Presence of Organic Template:

The presence of organic templates is essential for crystallization of many known zeolite structures. The use of organic species in synthesis gels was initiated by Barrer in the early sixties. The amines or organic cations get trapped inside the pores of the zeolites during crystallization and act as structure directing templates. Sometimes they might act as gel modifier and help in formation of zeolites with higher Silica content [94,111,112]. They could also interact chemically with other components of the gel and could alter or buffer the pH of the gel [113]. Templates can also interact physically with other components of the gel leading to alteration in gelling process, solubility of various species, ageing characteristics and thermal properties.

1.6.4 Presence of Inorganic Cation.

Inorganic cations can also act as the structure directing agent [114] in zeolite synthesis and hence play an important role in the synthesis of zeolites. It also influences crystallinity, morphology as well as final yield of the product [6].
Adjustment of the cation content of the gel can be used to eliminate the intergrowth of one zeolite with another [115]. The SiO\textsuperscript{-}M\textsuperscript{+} interaction is also known to have a structure stabilizing effect [94].

1.6.5 Effect of Water Content

The water content influences the transport properties within the gel and the viscosity of the gel. The water content of the gel may also sometimes be responsible for directing certain zeolite structures, in conjunction with the cations present in the gel [115,116]. Generally an increase in water contents in gel leads to an increase in overall synthesis time and larger crystallites.

1.6.6 Effect of Promoters

Certain oxyanions (perchlorate, phosphate, arsenate, chlorate etc) can enhance the nucleation and crystallization of a zeolite and thereby reduce the overall time of synthesis [117].

1.6.7 Effect of Source of Raw Materials:

The source of raw materials and their formulation treatment is often found to influence the product obtained [118]. This factor may also affect the induction period and the crystallization rate as well as the crystal size and/or morphology of the synthesized zeolite.

The physical parameters which influence the synthesis process are:

1.6.8 Temperature

Reaction Temperature also plays an important role in the growth of zeolite crystals. The induction times in zeolite formation decrease rapidly with increasing
temperature [105, 119, 120]. To obtain larger crystals by using higher temperature, these temperatures must be within the crystallization field of the zeolite. Those zeolites that can be synthesized at higher temperatures tend to be less porous and to have lower water content, rather than heavily hydrated structures. At elevated temperatures aluminosilicate precursor species may be increasingly replaced by monomeric Al (OH)₄⁻ and Si (OH)₄ and anions derived from Si (OH)₄. These factors should in turn favour the appearance of less open tectosilicates.

1.6.9 Synthesis Time.

Reaction time also plays a distinguished role in zeolite synthesis. It has been proved by earlier studies that the presence of induction period prior to crystallization results in higher zeolite yield. In addition to above parameters few historical Parameters are also important. For example, ageing prior to crystallization is required for synthesis of some Zeolites. The use of seed crystals can be employed to increase the crystal size. Kacirek and Lechert had showed that a little additional nucleation occurred when Na-X seed were used in growth of Na-Y crystals[121,122].

Sometimes liquor from previous successful syntheses can be used as the source of seeds.

1.7 Modification of Zeolites:

One of the greatest advantages of zeolites molecular sieves is the ease with which their properties can be tuned using different techniques, leading to the formation of modified zeolites which can be used more advantageously than the parent zeolite material. Modification implies that a given material is tailored by appropriate treatments in order to change its physical properties such as its structural features,
surface area, crystallinity and pore size, as well as its inherent properties like acidity, shape selectivity, catalytic properties etc. Quite often, a zeolite obtained by direct hydrothermal synthesis is not useful for catalytic applications unless either or some of its above mentioned properties are modified suitably.

Modified zeolites are finding new applications as heterogeneous catalysts in many organic reactions in the liquid phase and at moderate temperatures [123].

Modifications in zeolites can be brought about mainly by two methods-

- By direct synthesis
- By post-synthesis modification.

1.7.1 Modifications by Direct Synthesis:

This is the most common method used for zeolite modification. Generally modification is achieved by changing the molar ratio of the reagents. Besides changing the Si/Al ratio, the crystalline product obtained can be altered to some extent by factors like the type of raw materials used, ratio between reaction components, ageing conditions, crystallization temperature [118,119,120] and the use of seed crystals [121,122].

Providing a fluoride medium to the reaction mixture substitutes F⁻ for OH⁻ resulting in a decrease in acidity [124,125]. However, the most significant modification by direct synthesis is isomorphous substitution. Isomorphous substitution has attracted a lot of attention during the last few years. Modification of zeolites by isomorphous substitution gives rise to materials with new properties, which may have potential for novel catalytic applications. The most important isomorphous substitution is the replacement of the framework T-atom of the zeolite molecular sieve by other bi-, tri-
and tetravalent metal ions like B/Be/Ga/Fe/Ti/V etc. In principle, the following replacements can be brought about in zeolites by isomorphous substitution [126].

i) One element by one of its isotopes; this type of substitution is important in characterization of zeolites materials.

ii) One guest molecule by another; this type of substitution has no significance as far as catalytic applications are concerned.

iii) One cation by another; this type of replacement is useful in making bifunctional catalysts.

iv) Replacement of one element in tetrahedral position by another; this last type of replacement is very important in substituting different elements into zeolite frameworks.

Goldsmith [127] was the first to report the isomorphous substitution of Si$^{4+}$ by Ge$^{4+}$ in the lattice. The possibility of isomorphous substitution and the stability of that particular metal ion in the zeolite tetrahedral framework was originally predicted by Pauling’s theory [128]. Literature showed the subsequent development reviewed in many articles [129-133]. According to Pauling criterion, the metal ion is stable in the tetrahedral framework when $S$ is in the range $0.414>S>0.225$, where $S = rc/ro$, ($ro$ is the radius of the oxygen ion and $rc$ is the cation radius). However, some metal ions like Fe$^{3+}$, Ti$^{4+}$, Ga$^{3+}$ and V$^{4+}$, for which the value of the Pauling criterion falls out of this range have been successfully substituted into the zeolite tetrahedral framework due to their stability in tetrahedral environments.

In the recent years, with the use of organic templating agents, a large number of elements like B/Fe/Ga/Ti [127,134] have been incorporated into the zeolite framework by direct hydrothermal synthesis and shown to result in materials with
novel catalytic properties. A recent review of isomorphous substitution in zeolites by primary (or direct) synthesis methods speculates on the potential impact of such substances on catalysis [127].

Isomorphous substitution modifies the strength of the Brønsted acid sites. The relative Brønsted acidity of the zeolite molecular sieves is found to increase in the order [135]:

\[ \text{SiOH} < \text{B(OH)}\text{Si} < \text{Fe(OH)}\text{Si} < \text{Ga(OH)}\text{Si} < \text{Al(OH)}\text{Si} \]

Besides alumino and the other metallic silicates, AlPO\(_4\)s, SAPOs and MeAlPOs form another important class of isomorphous substituted molecular sieves. The aluminophosphates i.e., AlPO\(_4\)s are molecular sieves wherein Si\(^{4+}\) from the framework is replaced by P\(^{5+}\). They were first reported by Wilson et al. [136] in 1982. Recent additions to the AlPO\(_4\) family which include extra large-pore molecular sieves like VPI-5 [137] MCM-9 [138] and JDF-20 [139]. Metallo aluminophosphates (MeAlPOs), where a metal ion like Co/Fe/Mg/Mo etc. replaces Al partially or completely in the AlPO\(_4\) framework, have also been synthesized [140]. Recently, a new gallophosphate christened Cloverite [141] has been reported. Silicoaluminophosphates (SAPOs) are molecular sieves where Si\(^{4+}\) replaces P\(^{5+}\) and Al\(^{3+}\) + P\(^{5+}\) in the AIPO framework [142]. SAPOs exhibit cation exchange and mild-to-weak acidic properties. As in the case of AlPO\(_4\)s, SAPOs too exhibit excellent thermal and hydrothermal stabilities [143,144].

1.7.2 Post Synthesis Modifications:

Post synthesis modifications in zeolites become important when a zeolite with the desired physico-chemical properties cannot be obtained by direct hydrothermal
synthesis. In such cases, the hydrothermally synthesized parent zeolite molecular sieves can be modified further to varying degrees in a number of ways.

1.7.2.1 Ion-exchange

Barrer [6], first proved that the molecular sieving properties of a zeolite can be profoundly changed if the zeolite is modified by ion exchange. Since then ion exchange has been established as a standard method of tailoring zeolite molecular sieves so as to meet the best requirements of a particular separation. The exchangeable K⁺ or Na⁺ cations in the zeolite framework can be stoichiometrically replaced with other mono, di or trivalent cations (e.g. La/Ca/Ba and Li) giving rise to varying sorption capacities. Ion exchange may also be brought about via solid-solid reaction between the zeolite and the given salt or oxide in dry or hydrothermal conditions [145,146].

Besides cation exchange, rare earth exchange is another modification brought about mainly in fluid. All these modified zeolites are used in cracking, for octane enhancement and good gasoline selectivity.

1.7.2.2 Metal Loading

Zeolite containing catalysts can be loaded with metals in several ways like ion-exchange of the zeolite from solution, impregnation from solution, sorption from gas phase and comulling during catalyst formulation with a solid metal component or its solution. Metal loading, leading to catalytically active components in zeolites is particularly necessary for many industrial reactions like hydrogenation or oxidations. Metals generally desirable for introduction in the zeolite containing catalysts include Ni/Co/Pt/Pd/Ag/Mo/Cr/W.
1.7.2.3 Modification into High-silica Zeolites

High silica zeolites with large pores and cavities are attractive materials for catalytic applications in a variety of industrial processes, because of their high hydrothermal stability, hydrophobicity, strong acidity and particularly good resistance to deactivation [147].

Unfortunately, not all types of known zeolite structures can be obtained as high silica zeolites by direct hydrothermal synthesis. Hence it often becomes necessary to modify them into high silica zeolites by post synthesis methods. Therefore thermal, hydrothermal and chemical methods or a combination of some/all of these have been used to increase the Si/M ratios in previously synthesized zeolites by subsequent modifications. All these techniques essentially involve the dealumination process. The term dealumination is used in zeolite chemistry to describe the extraction of framework aluminium.

(A) Hydrothermal Modifications:

Hydrothermal modification is brought about by subjecting an ammonium exchanged zeolites to thermal treatment in the presence of steam, resulting in the expulsion of tetrahedral aluminium from the framework into non-framework positions. This results in the high-temperature hydrolysis of Si-O-Al bonds, leading to the formation of non-framework aluminium species while increasing the framework Si/Al ratio and decreasing the unit cell size [148-151]. Thus the ultrastable zeolites having fewer ion exchange as well as Brønsted acid sites are obtained. Such differences in acidity have a noticeable impact on the catalytic activity and selectivity of the modified zeolites.
(B) Chemical Modifications

Dealumination to varying degrees can be brought about by various chemical reagents, depending upon the treatment used. It may be carried out by treating the zeolite with a suitable reagent in solution phase or by passing the reagent in the gas phase at high temperature. Another type of chemical modification consists of grafting a given compound on the outer surface of the zeolite crystallites or the inner pores by chemical reaction with external or internal –OH groups, respectively. Depending upon the reagent used, dealumination may be accomplished both with or without silicon enrichment.

Dealumination without silicon enrichment may be brought about by hydrothermal treatment [147] followed by acid leaching with mineral acids or chelating agents like EDTA, acetyl acetone, amino acid derivatives, etc. This results in extraction of framework Al\(^{3+}\) which is accompanied by the formation of framework defects arising out of the vacancies left by the extracted Al\(^{3+}\). It also often gives rise to extra-framework aluminium species (EXFAI) in non-framework positions, which too contribute to modified catalytic activity.
A. DEALUMINATION

\[
\begin{align*}
&\text{Al}^3+ + 3\text{HOH} \rightarrow \text{Al}^3\text{OH}_2^+ + 3\text{H}^+ \\
&\text{Al}^3\text{OH}_2^+ + 3\text{H}^+ \rightarrow \text{Al}^3\text{OH}_2^+ [Z] + 3\text{H}^+
\end{align*}
\]

B. STABILIZATION

\[
\begin{align*}
&\text{Al}^3\text{OH}_2^+ [Z] + \text{SiO}_2 \rightarrow \text{Al}^3\text{OH}_2^+ [Z] + 2\text{OH}^-
\end{align*}
\]

Fig. 1.4 Dealumination and stabilization scheme of zeolites

The process of dealumination with silicon enrichment minimizes these limitations to a great extent. There are many techniques available for Al-replacement by Si. Two of these are: Chemical Vapour Deposition (CVD) using SiCl₄; and the use of salts like ammonium hexafluorosilicate \((\text{NH}_4)_2\text{SiF}_6\).
The treatment of zeolites, with ammonium hexafluorosilicate (AFS) solution, under controlled conditions of pH and temperature brings about dealumination effectively with simultaneous insertion of silicon to a certain extent [152,153]. All these dealumination procedures have certain advantages and disadvantages, the method adopted depends upon the requirements.

1.8 Characterization of Zeolites.

Different physical techniques are used to characterize zeolites.

1.8.1 XRD

X-ray powder diffraction is the single most important technique used to characterize zeolites. A wealth of structural information may be derived from careful analysis of X-ray powder data. X-ray diffraction data provides all information about the degree of crystallinity, phase purity, uniqueness of the structure, isomorphic substitution, and also makes possible the estimation of unit cell parameters [154,155]. The position of the diffraction peaks are determined by the geometry of the crystal lattice i.e. the size and the shape of the unit cell. The intensities of the peaks in a profile are related to the specific atoms in a crystal and their arrangement in the unit cell of the crystal [156]. When isomorphic substitution occurs, the extent of incorporation of the isomorphic element is correlated with the unit cell expansion or contraction. Modern methods have used ab initio calculations and ReitVeld analyses to solve zeolite structure using powder X-ray patterns [157-161].
1.8.2. Ion-exchange

The ion exchange property of metallosilicate zeolites originates from framework $\text{MO}_2^+$ groups bonded with $\text{SiO}_2$ groups. Hence the ion exchange capacity of a zeolite can be taken as a direct quantitative evidence for the presence of $M^{3+}$ ions in tetrahedral positions [162] in the zeolite lattice. Therefore, ion exchange capacity exhibited by zeolites becomes a simple and handy tool for characterization by providing evidence for the incorporation of the metal ion in a zeolite framework.

1.8.3. Infra-red Spectroscopy

Infrared spectroscopy plays an important role in characterization of aluminosilicates and is considered to be complementary to XRD. Infrared spectroscopy is one of the most sensitive tools for the investigation of the structural features of zeolites, the isomorphous substitution in them, their acidity and the nature of zeolite-adsorbate interactions [163-165].

Zeolites have characteristic framework vibrations. The fundamental vibrations of (Al, Si) $\text{O}_4$ 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 [166].

Progress in the crystallization during synthesis [167] 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. Topse et al. [168] has shown that OH groups characterized by adsorption band at 3600 cm$^{-1}$ and 3700 cm$^{-1}$ correspond to strong and weak Br"{o}nsted acid sites respectively in
zeolites. Ward [169], Datka et al. [170] and Kiricsi and Forster [171] have discussed
the application of infra red spectroscopy for zeolite characterization.

Isomorphous substitution of various elements into the zeolite framework shifts the
OH- vibrations as well as the asymmetric and symmetric framework vibrations, to
higher or lower wave numbers in case of lighter and heavier elements respectively.
In most of the metal substituted alumino silicates, a characteristic band due to Si-O-
T (or >Si-O-T = 0) asymmetric vibrations is seen around 960 cm⁻¹. The intensity of
this band is correlated with the amount of T-atom of the isomorphous element
incorporated into the zeolite lattice. IR spectroscopy can also distinguish large pore
zeolites from small & medium pore ones on the basis of OH stretching vibrations.
This technique is also used to estimate the acid sites by the adsorption of various
basic probe molecules like ammonia, pyridine and benzene & to measure the acidity
qualitatively as well as quantitatively.

1.8.4. Scanning Electron Microscopy

Microscopic examination is of great help to distinguish different phases. It is
possible to distinguish the zeolite crystals from other compounds. Particle size
distribution is another property which can be observed from SEM.

1.8.5. Nitrogen Adsorption Measurement

The ability of the zeolites to adsorb only selected molecules inside the channels and
cavities enable adsorption measurements to be a useful tool in providing information
about their void volume, crystal size, degree of crystallinity, acidity, diffusion
limitations and pore blockages, if any. Besides, sorption studies also help in
determining specific interactions between the sorbate and sorbents as well as the
strength of such interactions [172]. Various thermodynamic parameters such as entropy, heat & free energy of sorption can also be estimated with the help of sorption measurements.

1.8.6: Acidity Measurement.

Infrared spectroscopy is one of the most valuable techniques for the characterization of an acidic surface [174]. Pyridine (pKₐ 8.75) and NH₃ (pKₐ 4.75) have been used frequently as bases to determine the nature (Bronsted or Lewis), number and strength of acid sites. n-butylamine (pKₐ 3.23), which is a relatively strong base, is commonly used in the titration methods using Hammett indicators and thermometry, and it will react with weaker acid sites than either pyridine or ammonia. The use of n-butylamine in infrared spectroscopy for the characterization of solid surfaces like silica, alumina, silica-alumina and montmorillonite has been reported. Various amines were adsorbed on a number of cation exchanged X and Y zeolites and the adsorption studied by infrared spectroscopy.

1.8.7: Thermal Analysis.

This technique provides information regarding the thermal behaviour of zeolites. It is used extensively in the study of kinetics and dehydration of zeolites and also for studying the oxidative combustion of occluded organics in zeolites [173]. Besides this, other physico-chemical changes like the desorption of adsorbed water, dehydroxylation leading to the formation of Lewis sites during thermal treatment, phase transformation or structure collapse occurring during thermal treatment (if any), are all indicated in the thermoanalytical curves [174,175]. DTA curves provide
qualitative and quantitative information about the energy of activation and enthalpy of the zeolites systems.

1.8.8 Nuclear Magnetic Resonance Spectroscopy

High resolution solid state NMR spectroscopy using Magic Angle Spinning (MAS) has become a powerful method to characterize zeolite materials [176-182]. NMR is used to characterize the chemical and structural environment of atoms in the catalysts or in species adsorbed at the surface. NMR can provide information about the structure of the catalyst and its thermal stability or chemical transformation, sorbent-sorbate interactions, nature of chemically deposited species and catalytically active species and chemical reactions at the catalyst [183].

Till now about twenty different NMR active nuclei have been studied. Much attention has been focused towards $^{29}$Si and $^{27}$Al MAS NMR in order to investigate the nature of Si and Al ordering in the zeolites framework [184] as well as the crystallographically equivalent and nonequivalent Si$^{24}$ and Al$^{125}$ ions in various sites. Further information such as framework Si/Al ratios [185], coordination number of Si [127] and Al [128] and spectral correlations with Si-O-T bond angles and Si-O bond lengths [186] can also be obtained.

Newly developed techniques like 2D NMR can be used to establish connectivities in the solid state [187], 1H-29Si cross-polarization technique [188] provides semiquantitative information regarding silanol groups. High-resolution liquid NMR ($^{29}$Si and $^{27}$Al) helps to detect the various silicate and aluminosilicate species leading to the identification of SBUs. 13CP/MAS NMR helps to locate and determine the configuration of organic Templates [189-194], types of intermediates formed during
catalytic reactions and the nature of the adsorbed species present on the zeolites surface [195]. $^1$H MAS NMR has been used to study zeolites acidity [196,197], arising out of the various types of protons.

1.9 Description of Zeolites used in the Present Investigation

1.9.1 Zeolite Mordenite.

Mordenite is another important industrial solid acid catalyst, having a composition of Na$_8$Al$_8$Si$_{40}$O$_{96}$·nH$_2$O [198,199]. Mordenite is a large pore zeolite, having a one-dimensional channel structure. Mordenite belongs to the orthorhombic crystal system (Cmcm, a=18.1, b = 20.5, and c=7.5 Å). Structure of mordenite composed of main channels with side pockets [200]. It has 12-membered ring pores of about 6.5×7.0Å running along the [001] direction [201]. These are connected by small 8-membered ring pores of about 3 × 5.7 Å running perpendicularly along the [010] direction. In practice these latter pores are too narrow for the transport of most molecules and responsible for the mono dimensional nature of mordenite. Since mordenite is, in practice, a one-dimensional large pore zeolite, transport of molecules within the zeolite occurs only along the c axis. This is a crucial characteristic with several important implications. First, diffusion in one dimension is inherently a slower process than diffusion in 2 or 3 dimensions. This is even more so when molecules are of about the same size as the pore diameter, a case that forces molecules to move in “single file” because of steric constraints. Single file diffusion is a very slow process [202]. It implies that under typical reaction conditions, only a small fraction of the pore volume is actually accessible to the reacting molecules, i.e., the fraction of the pores that is very close to the pore mouths. Second, one-
dimensional pore zeolites are also highly prone to fouling (pore blockage) because it is easy to completely block access to one micro pore by blocking the pores near their entrances. It is not possible to do so in multidimensional pore zeolites.

![Fig.1.5 Structure of mordenite](image)

**Application of mordenite**

Mordenite is used extensively in various industrially important reactions like hydrocracking, hydroisomerization, alkylation, reforming, and cracking[203-205]. They are also used in adsorptive separation of gas or liquid mixtures involving acidic components [198,206]. Another important application of mordenite involves upgrading the octane number of gasoline[207].

### 1.9.2. Zeolite Y

**Structure of zeolite Y**

Zeolite Y, has a three dimensional pore structure (NaY: Na$_x$Si$_{192-x}$O$_{384}$Al$_x$) and a void volume fraction of 0.48. There are 3 composite building units and these are the double 6-ring, the sodalite cage and a very large cavity with four 12-ring windows along the [111] direction (i.e. 4, 6 and 6-6 units).
This cavity is of tetrahedral point symmetry and it is known as the supercage. The windows in this cage allow much larger molecules to diffuse in three dimensions in the crystal interior. The Y zeolites belong to the space group Fd3m and having a unit cell parameter, \( a = \text{approx} \ 24.7 \ \text{Å} \). A unit cell contains 8 large cavities (super cages, also known as the alpha cages), 8 sodalite cages and 16 double 6-ring units. Sodalite cages are linked through double 6-rings (pseudo hexagonal prisms) to form the alpha cages, which have an inside diameter of about 12. Again, each alpha cage is tetrahadrally linked to four others via 12-ring windows. The 12-ring windows, with a free diameter approximately 7.4 Å are perpendicular to the [111] directions but because of the tetrahedral symmetry of the cavity there are no straight channels along this direction. Channels can be thought to run along the [110] directions. Molecules larger than water or ammonia can access only the super cages and cannot pass into the empty space inside sodalite cages. Thus, all reactions and the adsorption of most sorbates are confined to the supercages structure and characterization.

Fig.1.6 Structure of Faujasite-Y
Applications of zeolite Y

The most important use of zeolite Y is as a cracking catalyst. It is used in acidic form in petroleum refinery catalytic cracking units to increase the yield of gasoline and diesel fuel from crude oil feedstock by cracking heavy paraffins into gasoline grade napthas. Zeolite Y has superseded zeolite X in this use because it is both more active and more stable at high temperatures due to the higher Si/Al ratio. It is also used in the hydrocracking units as a platinum/palladium support to increase aromatic content of reformulated refinery products [208,209].

1.9.3. Zeolite Beta

Structure of zeolite beta

Beta, a large pore zeolite with a three dimensional pore system, was first synthesized by the Mobil Oil Corporation in the year 1967 [210]. Zeolite beta is having a unit cell composition of: $[x \text{ Na}_{(1-x)} \text{ TEA}][\text{AlO}_2\text{(SiO}_2\text{)y}]w\text{H}_2\text{O}$, Where $x$ is less than or equal to 1. It is an important zeolite used in different industrial processes [211].

Zeolite beta is a three dimensional high silica zeolite with a 12-membered ring pore systems (7.6 x 6.4 Å) that has always been observed as the intergrowth of two polytypes (A and B). These two polytypes or polymorphs are very closely related [212-214]. The polytype A has been assigned the three-letter code *BEA (the asterisk indicates that the pure polytype has not been observed experimentally). The structure of this zeolite consists of “layer” or “periodic building units”.

The stacking layers are related not only by translations but also by rotation. If the layers are stacked in a pure right or left handed fashion, the structure polytype A is formed (enantiomeric pair) and if the layers are stacked in a sequential left and right handed fashion, the achiral structure polytype B is formed. The unique feature of
this zeolite structure is that regardless of the form of stacking, a three dimensional 12-membered ring channel system is always formed. This characteristic makes zeolite Beta very useful in catalysis.

Application of zeolite beta:

Zeolite beta is an effective solid acid catalyst due to its unique pore structure and high acidity. These properties have led to its increasing use in several industrial processes like catalytic cracking, disproportionation of hydrocarbons, isomerization, aromatic/isobutane alkylation with alkenes and n-butene respectively [215-220].
1.9.4 Zeolite MCM-22

Structure of MCM-22

Structure of MCM-22 consists of two sets of independent pore systems [221]. One of these pore systems is made up from sinusoidal 10-membered ring channels which extend into two dimensions. The second pore system consists of very large cages 1.82 nm in height and 0.71 nm in diameter which can be reached through 10-membered ring windows only. It was revealed by different workers [222-224] that the pore width of zeolite MCM-22 is in between those of medium pore and the very large pore materials.

Fig. 1.8 Structure of MCM-22
Application of MCM-22

MCM-22 is an active catalyst used in a variety of fields like catalytic cracking, olefin isomerization, conversion of paraffins to olefins and aromatics, alkylation of paraffins with light olefins [225].

1.10. Scope of this Thesis

Over the last few decades, use of zeolites in different fields, particularly in organic transformation, synthesis, ion-exchange and adsorption has increased overwhelmingly largely due to 'green nature' of the catalyst. That is zeolites are environmentally benign and used in heterogeneous systems advantageously. Their remarkable shape selectivity, ease of handling, non corrosiveness, low cost and reusability have made this brand of catalysts almost indispensable in chemical processes.

Zeolites Y, mordenite and beta are three large pore zeolites useful as solid acid catalysts because of their peculiar porosity and high surface area. Unfortunately it is difficult to prepare these material with desired SiO$_2$/Al$_2$O$_3$ through primary synthesis alone [226]. Post synthesis dealumination can be used not only to produce the desired SiO$_2$/Al$_2$O$_3$ but also in the process to improve activity, stability and porosity of the zeolites.

MCM-22 discovered in 1990, is a microporous high silica zeolite with potential applicability. But difficulties in synthesis of MCM-22 limits its extensive studies.

With the above background, the aims of the present study were formulated as-

2. Synthesis of zeolite MCM-22 with different silicon to aluminium ratios.
3. Conversion of these samples to hydrogen forms.

4. Dealumination of Zeolites HY, Hmordenite and Hbeta by acid treatment for different periods.


6. Investigation of catalytic activity of parent and dealuminated HY, Hmordenite and Hbeta zeolites in acylation of anisole reaction. Comparison of activity among the parent and among the dealuminated samples. Study of product distribution pattern with variation of different reaction conditions such as reaction temperature, reaction time, catalyst amount etc.

7. Investigation of the catalytic activity of HMCM-22 in acylation of phenol with varying experimental conditions such as reaction time, temperature, silicon to aluminium ratio of HMCM-22, acylating agent etc.
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