CHAPTER 1

INTRODUCTION

Chapter Summary

This chapter contains a brief introduction on porous materials, hysteresis loop, types of isotherm etc. based on current literature review. This chapter initiates with an extensive discussion of zeolites, mainly their general synthesis, nomenclature, structure, properties, modifications, characterization and applications. This chapter also contains the advantages of using fluoride gel as mineralizer.

1. Porous Materials

Based on their pore size, porous materials can be classified into three classes:

Microporous (pore size < 2 nm), mesoporous (pore size 2-50 nm) and macroporous (pore size >50 nm) materials, according to International Union for Pure and Applied Chemistry (IUPAC) [1]. Again, porous solids with pores of the size of molecular dimensions 0.2-0.3 nm in diameter, which can separate components of a mixture on the basis of molecular size and shape like sieves are called molecular sieves. Thus microporous materials are a sub-category of molecular sieves. Mesoporous materials can be considered as mesoporous molecular sieves although its pore diameter falls outside the molecular sieve range since molecular sieves concern initially materials with microporosity and a crystalline structure, while mesoporous framework is often an amorphous solid. A schematic representation of classification of porous materials is given in Scheme 1.1.
1.1 History of molecular sieve materials

The porous materials have received utmost importance because of their molecular sieve properties among other properties. The theme of research on molecular sieve materials over the past nearly 60 years has been a quest for new structures and compositions. The major discoveries and advances in molecular sieve materials during that period are summarized in Table 1.1.
Table 1.1 Evolution of molecular sieve materials.

<table>
<thead>
<tr>
<th>Time of initial discovery</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Late 1940s to early 1950s</td>
<td>Low Si/Al ratio zeolites</td>
</tr>
<tr>
<td>Mid - 1950s to late 1960s</td>
<td>High Si/Al ratio zeolites</td>
</tr>
<tr>
<td>Early 1970s</td>
<td>SiO$_2$ molecular sieves</td>
</tr>
<tr>
<td>Late 1970s</td>
<td>AlPO$_4$ molecular sieves</td>
</tr>
<tr>
<td>Late 1970s to early 1980s</td>
<td>SAPO and MeAPO molecular sieves</td>
</tr>
<tr>
<td>Late 1970s</td>
<td>Metallo - silicates, aluminosilicates</td>
</tr>
<tr>
<td>Early to mid - 1980s</td>
<td>AlPO$_4$ - based molecular sieves</td>
</tr>
<tr>
<td>Early to mid - 1990s</td>
<td>Metallo-phosphates, Mesoporous molecular sieves, Octahedral – tetrahedral frameworks</td>
</tr>
<tr>
<td>Late 1990s</td>
<td>Metal organic frameworks</td>
</tr>
<tr>
<td>2000s</td>
<td>UZM aluminosilicate zeolites, Si/Al = 2 – 30</td>
</tr>
<tr>
<td></td>
<td>Germanosilicate zeolites SiO$_2$ molecular sieves in fluoride media</td>
</tr>
</tbody>
</table>

1.2 Types of isotherms of porous materials

There are six generic types of adsorption isotherms that have been observed in gas adsorption in porous materials, despite the multitude of different adsorbent/adsorbate combinations that have been employed. The
IUPAC classification scheme [2], based on the system devised by Brunauer, Deming, Deming, and Teller (the “BDDT” scheme), [3] is shown in Figure 1.1. These isotherm types are characteristic of (I) microporous materials or materials with strong adsorption in the first layer but negligible adsorption after that; (II) non-porous materials with relatively strong adsorbate-adsorbent interactions; (III) non-porous materials with weak adsorbate-adsorbent interactions; (IV) mesoporous materials with strong adsorbate-adsorbent interactions; (V) mesoporous materials with weak adsorbate-adsorbent interactions.

![Fig.1.1 Different types of isotherms of porous materials](image.png)

Types III and V are extremely rare, except in the case of water adsorbed on charcoal, graphite, or other hydrophobic surfaces. In these cases, however, it is nearly all that is ever seen. The Type VI isotherm was not part of the original BDDT scheme [3] and is very rare. It represents stepwise multilayer adsorption on a uniform, non-porous surface. Examples are argon or krypton on graphitized carbon at 77 K [2].
1.3 Hysteresis loop

A great deal of information can be learned about the magnetic properties of a material by studying its hysteresis loop. A hysteresis loop shows the relationship between the induced magnetic flux density \( (B) \) and the magnetizing force \( (H) \). It is often referred to as the B-H loop. The IUPAC classifies four different types of hysteresis loops, which are shown in Figure 1.2. Type H1 hysteresis are characteristic of well-defined mesopores with a narrow range of diameters somewhere between 4 nm and 50 nm. In such cases, it is typically assumed that the desorption branch of the isotherm yields a better reflection of the true pore size, since desorption is not hindered by nucleation. Types H3 and H4 hysteresis indicate broad distributions of pores, and are typically difficult isotherms from which to extract size distributions. Type H2 hysteresis, with asymmetric loops, indicate large pore volumes and typically a wide distribution of pores. Isotherms with Type H2, H3, or H4 hysteresis typically have their lower closure points dictated by the tensile strength effect.

Fig. 1.2 Different types of hysteresis loops
1.4 Zeolite: A brief idea

Zeolites are natural or synthetic crystalline microporous aluminosilicates consisting of tetrahedral units producing open framework structures. They can be represented by the general formula:

$$M_{2n}O\cdot Al_2O_3\cdot xSiO_2\cdot yH_2O$$

where M is an exchangeable metal cation of valency n for balancing the framework charge, x can assume a value equal to or greater than 2 following Lowenstein’s rule (Al-O-Al linkages in zeolite frameworks are forbidden), and y represents the number of water molecules present in the voids of the three dimensional network[4]. Zeolites have an open framework structure of three dimensional SiO₄ and AlO₄ tetrahedral units which generates a network of pores and cavities having molecular dimensions. The presence of one Al³⁺ ion in the tetrahedral position brings one unit negative charge in the framework. Loosely held inorganic cations (alkali or alkaline earth metal) or organic cations are trapped inside the tetrahedral network cavities preserving the electroneutrality of the zeolite. Some of these extra framework cations are amenable to cation exchange. The aluminosilicate framework of the zeolite is rigid enough to avoid collapsing and the micropore volume previously occupied by water is made available to reversibly adsorb other polar molecules [5-8].

1.5 History of zeolites

Swedish mineralogist Axel F. Cronstedt discovered natural zeolite, stilbite in 1756 [9], which was the beginning of the zeolite history. He named those hydrated aluminosilicate minerals as “zeolites” [originating from Greek words zein and lithos meaning to boil and rock respectively], because such minerals fused readily with intumescence (the phenomenon of melting and
boiling at the same time) when heated in a blowpipe flame [4]. Due to limited availability of the material, much improvement in the research field was not observed for the next 200 years [10]. Extensive research work on zeolites began in the 1930’s, when Richard M. Barrer started systematic studies on zeolite synthesis under high pressure and temperature and on the characterization of zeolite structure and chemistry [10, 11]. Mobil (USA) developed the research activities on zeolites by introducing organic cations into zeolite synthesis in the 1960’s and started to discover the catalytic importance of their MFI type zeolites in the 1970’s[10,12]. Till now several zeolite materials have been successfully prepared through continued synthetic efforts with new framework topologies, compositions and properties which correspond to 174 structure types of zeolites.

1.6 Nomenclature of zeolite

“The Structure Commission of the International Zeolite Association” and IUPAC have assigned each zeolite structure with official three-letter codes [13, 14]. The codes are derived from the name of the zeolite or the type of material, e.g. FAU from faujasite, LTA from Linde Type A, MFI from ZSM-5 (Zeolite Socony Mobil Five)[14]. The IUPAC designation and year of innovation of some zeolites are given in Table 1.2.

Table 1.2 IUPAC designation of some zeolites and year of innovation

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>IUPAC Nomenclature</th>
<th>Year</th>
<th>Zeolite</th>
<th>IUPAC Nomenclature</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analchime</td>
<td>ANA</td>
<td>1978</td>
<td>Linde Type A</td>
<td>LTA</td>
<td>1978</td>
</tr>
<tr>
<td>ALPO-11</td>
<td>AEL</td>
<td>1987</td>
<td>ZSM-5</td>
<td>MFI</td>
<td>1978</td>
</tr>
<tr>
<td>Beta</td>
<td>BEA</td>
<td>1992</td>
<td>Mordenite</td>
<td>MOR</td>
<td>1978</td>
</tr>
<tr>
<td>Erionite</td>
<td>ERI</td>
<td>1978</td>
<td>MCM-22</td>
<td>MWW</td>
<td>1997</td>
</tr>
<tr>
<td>Faujasite</td>
<td>FAU</td>
<td>1978</td>
<td>SSZ-23</td>
<td>STT-23</td>
<td>1998</td>
</tr>
</tbody>
</table>
1.7 Classification of zeolites

Compositional variation of zeolites (silicon to aluminium ratio) can be used to classify zeolites into low silica and high silica zeolites. Typical examples of low silica zeolites are A, X and Y. These zeolites cannot be synthesized over a wide range of silicon to aluminium ratio. On the contrary, high silica zeolites can be synthesized over a wide range of silica to alumina ratio, a classical example being ZSM-5, whose acidity can be tuned to desired level. Zeolites can also be classified on the basis of the SBU, as small pore zeolites with 8 membered rings like MTN, NU-1; medium pore zeolites, MFI, MEL; large pore zeolites FAU, MTW and extra large pore zeolites-UDT (Meir et al., 1992).

There are many naturally occurring zeolites but the mordenite and faujasite classes are of the greatest interest as catalysts. The name of some natural and synthetic zeolites is listed in Table 1.3 [15].

Table 1.3 Some natural and synthetic zeolites

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Ring size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Faujasite²</td>
<td>Na_{58}Al_{58}Si_{134}O_{384}.24H_{2}O</td>
<td>4,6,12</td>
</tr>
<tr>
<td>Natrolite²</td>
<td>Na_{16}Al_{16}Si_{24}O_{80}.16H_{2}O</td>
<td>4,8</td>
</tr>
<tr>
<td>Stilbite²</td>
<td>Na₆Ca₆Al₂₀Si₂₂O₁₄₄.5₆H₂O</td>
<td>4,5,6,8,10</td>
</tr>
<tr>
<td>Linde A²</td>
<td>Na₆Al₁₂Si₁₂O₄₈.2₇H₂O</td>
<td>4,6,8</td>
</tr>
<tr>
<td>ZSM-5³</td>
<td>Na₃Al₃Si₉O₁₉₂.₁₆H₂O</td>
<td>4,5,6,7,8,10</td>
</tr>
<tr>
<td>Boggsite²</td>
<td>Na₂₉Ca₇₈Al₁₈₅Si₇₇₅O₁₉₂.₇₀H₂O</td>
<td>4,5,6,10,12</td>
</tr>
<tr>
<td>Sodalite²</td>
<td>Na₆Al₆Si₆O₂₄.2H₂O</td>
<td>4,6</td>
</tr>
<tr>
<td>Mordenite²</td>
<td>Na₈₈Al₄₀Si₄₀O₉₆.2₄H₂O</td>
<td>4,5,6,8,12</td>
</tr>
</tbody>
</table>

n-natural    s-synthetic
1.8 Structure of zeolites

Like most silicates - the zeolites are based on TO$_4$ tetrahedra (the primary building units), where T is an aluminium or silicon atom (phosphorus in aluminophosphates). The T atom of the TO$_4$ tetrahedron is located at each of the corners, and the oxygens are located towards the mid-points of the lines joining each T atom. The vast 3-dimensional networks are a result of all four corners for the tetrahedra being shared, producing low density microporous materials. The chemical composition of the framework, the nature of the extra framework species and the type of post-synthesis modification play a very important role in determining the specific properties of a particular zeolitic material. Consequently, structural analysis is a fundamental aspect of zeolite chemistry [16].

Zeolite structures can be thought to exist of finite or infinite (chains, layers etc.) component units. The three different structural variations of zeolite 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 dimension, e.g. chabazite.
Zeolite framework can be classified on the basis of various schemes like by pore opening, structural subunit, channel system, framework density, loop configurations and/or by coordination sequences [17]. The zeolite framework consists of cross-linked $\text{TO}_4$ tetrahedra where T is Al or Si. Each T atom occupy four connected vertices of a three dimensional network and the oxygen occupy two connected positions between the four connected vertices [17]. Having been derived from silicate type network structures, the O/T ratio in a zeolite structure is always equal to 2 [17]. The O-T-O bond angle ($\alpha$ in Figure 1.3) is close to the ideal tetrahedra bond angle of 109.5°. The T-O-T bond angle ($\beta$ in Figure 1.3) is much more flexible than the O-T-O bond angle and is usually around 140° to 165°[17].

The $\text{TO}_4$ tetrahedra are often referred to as the primary building units of zeolite structures. Primary building units are linked together to form secondary building units. The notation $n^i m^i$ is often used to describe the number and type of rings that make up a cage within a structure. An example of the notation is shown in Figure 1.4 with the cancrinite cage structure. The cancrinite cage structure is described with the notation $4^6 6^5$ which means that it is composed of six 4-rings and five 6-rings.
At present, it is possible to visualize all possible existing structures of zeolites with nine such building units; these units are called secondary building units (SBU’s). These secondary building units can contain up to 16 T atoms. The SBU’s are formed by condensation of the primary building units. Such building units basically consist of n-ring structures which contain as many as 20 tetrahedra and as little as 4 [18]. These are shown in the Figure 1.5. These 9 units can be linked with different combinations forming cages or channels within the structure to form all the known zeolite structures. Connecting different ring sizes leads to different cage structures. Each corner in the secondary building units represents the center of a tetrahedra.

Fig.1.4 Cancrinite cage structure built from six 4-ring and five 6-ring secondary building units
The framework topology of zeolites consists of primary (the basic building unit) and secondary (the composite building units) building units [19].

**Structural Defects:** Zeolite framework structures that are closely related often form under very similar conditions leads to the formation of stacking faults or intergrowth structures. The first zeolite intergrowths examined was that of the members of ABC-6 family of structures, zeolite offretite (OFF) and erionite (ERI) with AABAAB and AABAAC 6 ring stacking sequences respectively [20] in which case as the number of C layers increases, the end number of OFF becomes the end number of ERI.
If a stacking fault occurs regularly, a new framework type with a new repeat period is formed. High-resolution electron micrographs of a faulted material will show the local stacking sequences and domain sizes quite clearly [21].

1.9 Properties of zeolites

Zeolites have found wide range of applications due to some of their important properties, which are discussed below:

1.9.1 Acidity of zeolites

The catalytic activity of zeolites is associated with the two types of acid sites:

**Brønsted acid sites:** When Al$^{3+}$ substitutes Si$^{4+}$ in the framework of zeolite one excess negative charge per aluminium atom is introduced. This negative charge can be compensated either by a proton or extra framework
cation, which is exchangeable that makes zeolites as ion exchangers. If the charge compensation occurs through proton, Bronsted acidity results that make zeolites suitable for acid catalyzed reactions. This types of acid sites also arises from the bridging hydroxyl group in SiO(H)Al which is associated with tetrahedrally coordinated or framework Al atoms. Each tetrahedrally coordinated Al atom contributes to one potential Brönsted Acid Site [22].

**Lewis acid sites:** This types of acid sites are capable of accepting electron pairs from adsorbed species like tri-coordinated Al$^{+3}$ [23]. The Lewis acidity is due to the presence of extra framework aluminum species.

There are different ways of generating acid sites in zeolite structure. Two most easy ways are

1. Treating zeolite with ammonium nitrate then calcining it at 480$^0$ C (Scheme 1.2) (Figure 1.6).

2. Directly treating with hydrochloric acid (Scheme-3) (Figure 1.7).

**Scheme 1.2**

![Scheme 1.2](image)

Fig.1.6 Generation of acid sites in MFI by treating with NH$_4$NO$_3$
1.9.2 Molecular sieving property

The three-dimensional framework of zeolites contains a series of channels and voids. These volumes contain cations and water molecules. When water is removed the voids created can take in other molecules. The geometry is the source of the ability of zeolites to separate mixtures of molecules (gases and liquids) on the basis of their effective sizes. Zeolites are therefore described as ‘molecular sieves’. There are three types of shape selectivity found in zeolite:

Reactant shape selectivity

It takes place when zeolite catalyst acts as a molecular sieve and excludes certain molecular sizes and structures from the intracrystalline voids (Figure 1.8), while other less bulky molecules are able to enter; a whole
variety of zeolite types with different sizes (and shapes) of the pore orifices are available so that this critical exclusion limit can be varied over a wide range of molecular sizes.

![Fig.1.8 Reactant shape selectivity of MFI](image)

**Transition state shape selectivity**

It occurs when the spatial configuration around a transition state or a reaction intermediate located in the intracrystalline volume is such that only certain configurations are possible (Figure 1.9). Transalkylation reactions of alkylaromatics are textbook examples of this kind of selectivity. In other cases, it is not always easy to distinguish between product and transition state shape selectivity. If the catalyst can be synthesized with crystal sizes which are significantly different, the distinction is easily made as only the former selectivity is dependent on crystal size. Transition state shape-selectivity is traditionally linked to the suppression of undesired side reactions such as coke formation.

![Fig.1.9 Transition state shape selectivity of MFI](image)
Product shape selectivity

It is the result of discrete diffusivities of the different reaction products in the pores of the zeolite crystals (Figure 1.10); typical examples are the isomerization reactions of alkylaromatics. This selectivity is not only dependent on the pore size but also on the crystal size of the catalyst particles.

Fig.1.10 Product shape selectivity of MFI

1.9.3 Ion exchange property

Zeolite cages are occupied by ions such as sodium or potassium, these ions are readily exchanged in external solutions (Figure 1.11). These cations are primarily present in the structure of the zeolite to counter balance the negative charge generated during isomorphous substitution of silicon atoms by other trivalent metal atoms in the tetrahedral sites [24]. As a result the zeolites have high cation exchange capacity (CEC) and it increases with the increase in aluminium content [25]. The cation exchange process is fully reversible. There are two alternative and equally valid ways of expressing a binary exchange reaction (and consequently the thermodynamic equilibrium constant).
The first of these (most commonly employed) was used by Vanselow [26]:

\[
Z_B^A A^{Z_A^+} (\text{solution}) + Z_A^B B L_{Z_B} \rightleftharpoons Z_A^B B^{Z_B^+} (\text{solution}) + Z_B^A A L_{Z_A}
\]

Where \(Z_A\) and \(Z_B\) are respectively the valencies of the exchanging cations A and B. There are also co-anions Y present in the external solution, which maintain electroneutrality in that phase, and these co-anions may be regarded as providing the "exchange capacity" of the electrolyte solution external to the zeolite. L is defined as a portion of zeolite framework holding unit negative charge. Note that the above equation excludes consideration of salt inclusion [27, 28] within the exchanger, since this would involve a net transfer of some co-anions Y from one phase to the other, resulting in an increase in the exchange capacity of the zeolite at the expense of the solution. However, adequate allowance for the possibility of salt inclusion may be made if required [29].

A second way of expressing the reaction may be traced to Gapon [30]:

\[
Z_B^A A^{Z_A^+} (\text{solution}) + Z_A^B B (1/Z_B) L \rightleftharpoons Z_A^B B^{Z_B^+} (\text{solution}) + Z_A^B A (1/Z_A) L
\]

The stoichiometric quantities of A, B, L (and consequently Y) involved in the second eq a are seen to be the same as in the first eq a, making the second eq a an alternative (if less familiar) way of expressing the exchange reaction.
1.9.4 Adsorption in zeolites

Due to high porosity zeolites provide a high capacity to absorb guest molecules into the voids of the zeolite structure. Adsorption properties of zeolites are used in different industrial processes, such as drying, separation of mixtures etc. CO₂ removal from nitrogen rejection plants using zeolite 4A is an important industrial process. Zeolites are also used in drying alcohols, benzene, natural gas, ethylene, methanol etc. Zeolites are also used for abatement of pollution due to this property.

1.9.5 Stability of zeolites

Zeolites have high thermal and hydrothermal stability. This property of zeolites makes them very important for catalysis with high reaction temperature. The enhanced stability of the zeolites depends on three main factors: aluminium content, crystal size and sodium level. Larger the crystal size and lower the aluminium and sodium content, more will be stability of the zeolite. There is a variation in thermal stability for different zeolites over a large temperature range. The amount of water loss from the zeolitic pores and
the fundamental solid state transformation are the main factors for structural changes governing their stability [31, 32]. The structural transformation might lead to structural collapse and formation of amorphous phases. Moreover, some other important properties of zeolites are:

- 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 (acid sites), whose number and strength can be modified in a wide range.

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

- Possibility of doping other metals in zeolite framework for use in oxidation chemistry [33].

### 1.10 Synthesis of zeolite

In general, for synthesis of zeolite an alkaline solution or fluoride solution is taken to this solution desired amount of template is added slowly with constant stirring, by an electrical stirrer. To the resulting solution required amount of silicon source is added slowly with constant stirring. The mixture is thoroughly stirred for half an hour to make a homogeneous gel (A).

In another beaker desired amount of H₂O is taken and to this required amount of aluminium source and salt (for *insitu* modification of the zeolite) is
added slowly with constant stirring. The mixture is thoroughly stirred for half an hour to make a homogeneous gel (B).

Now the gel (A) is added to the gel (B) and the resulting mixture is stirred thoroughly for about 3 hours. The gel is then transferred to a teflon based stainless steel autoclave and is heated in an oven at around 473 K. It is then filtered, washed with de-ionized water and dried at room temperature overnight. It is then calcined in a furnace at about ~ 753 K for about 6 hours. The sample thus prepared is Na form of the zeolite.

For preparation of the acid catalyst the synthesized sample is refluxed with 15% NH₄NO₃ at around 353 K for three times. Finally, it is washed, dried at room temperature and calcined in a furnace at about ~ 753 K for about 6 hours to get the H- form of the catalyst. The raw materials required for the synthesis of zeolites, the source of raw materials and their functions are given in Table 1.4.

The flow diagramme of the synthesis system of MFI is
Preparation of Catalyst

Na-MFI sample → NH₄NO₃ solution → 6 hr, stirring, reflux 3 times → NH₄⁺ MFI sample → Calcined at 480 °C → H⁻ MFI sample

Gel A → Gel B → Stirred for 1 h → Homogeneous mixture → Autoclave → Oven → Na-MFI samples → Template Na-MFI samples → Solid product filtered, washed, dried at RT
Table 1.4 The raw materials, the source of raw materials and their function in the zeolite synthesis

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Source</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>Soluble silicates and their hydrates, silica sols, fumed silica, silica gels, glasses, silicon esters, clays, volcanic tuffs, sand and quartz etc.</td>
<td>Primary building units of the framework.</td>
</tr>
<tr>
<td>Alumina</td>
<td>Metal aluminates like sodium aluninate, aluminium sulphates, aluminium alkoxides, freshly prepared aluminium hydroxides, alumina, aluminium phosphates, natural aluminium sources obtained from glasses, sediments, feldspars and aluminium rich industrial wastes etc.</td>
<td>Primary building units of the framework, origin of framework charge.</td>
</tr>
<tr>
<td>Metal hydroxides, metal fluorides</td>
<td>Alkali and alkaline earth metal hydroxides, alkali metal fluorides, ammonium fluorides etc.</td>
<td>Hydroxide and fluoride ions act as mineralizer and guest molecules, alkali metal cations act as counter ion of AlO₂.</td>
</tr>
<tr>
<td>Organic quaternary ammonium salt</td>
<td>Tetrapropyl ammonium ions, tetrabutylammonium ions tec.</td>
<td>Structure directing agent, guest molecule</td>
</tr>
<tr>
<td>Water</td>
<td>De-ionized water</td>
<td>Solvent, guest molecule</td>
</tr>
</tbody>
</table>
1.10.1 Role of template in zeolite synthesis

The frequent association of certain alkali cations with the presence of smaller cage structures led to the concept of a mechanistic role that was designated "templating." Templates are cationic species added to synthesis media to aid/guide in the polymerization/organization of the anionic building blocks that form the framework. In one of the first broad studies of zeolite crystallization in the presence of mixed alkali-organic bases, Aiello and Barrer [34] explained the observed structure specificity of the mixed cations by introducing the concept of templating of the different cage structures by the larger organic and smaller alkali cations. In particular, the quaternary organic tetramethylammonium (TMA) appeared to play an important role in the formation of the OFF and MAZ structures, since these structures were not observed in its absence. The authors suggested that the TMA helped form the aluminosiicate precursor of the gmelinite cage building unit that was common to both structures through a templating action. In a subsequent study of the role of multiple cations, H. Khatami [35] postulated that in the synthesis of zeolites from systems containing ternary, quarternary, or higher numbers of cations, "the zeolite framework structure is determined by one or at most two cations depending on their type and size. Additional cations, should they be included in the lattice, affect the zeolite properties but have minimal or no influence on the structure topology". In 1973 Flanigen reviewed the concepts governing zeolite crystallization and observed that cations play "a prominent structure-directing role in zeolite crystallization. The unique structural characteristics of zeolite frameworks containing polyhedral cages have led to the postulation that the cation stabilizes the formation of structural subunits which are the precursors or nucleating species in crystallization." [36-38]. The many zeolite compositions and complex cation base systems were compelling examples of the structure-directing role of the cation and the cation "templating" concept. In this early context "templating" and "structure-directing" were synonymous. While talking to the role of template, we may conclude that the template helps in the formation of highly ordered uniform
channels (Figure 1.12). The Small individual quaternary alkyl chain length acts as an agent to generate the formation of micropores in the solids.

Fig.1.12. Role of TPA-Br in micropore formation in MFI

1.10.2 Factors effecting the formation of zeolite

Synthesis of the zeolites depends mainly on the following factors:

(i) **Temperature:** For many zeolites the raising synthesis temperatures within a certain zeolite synthesis field increases the crystal growth rate [39-41]. As shown in Figures [1.13 a] and [1.13 b] for zeolite A and zeolite ZSM-5 (MFI), increasing temperature influences the crystal growth rate. In the case of zeolite A the crystal size does not change significantly compared to substantial variation in the ZSM-5 product.
Fig. 1.13 Influence of temperature on the crystallization of [a] Zeolite A and [b] Zeolite ZSM-5.

(ii) **Initial mole ratio**: The framework structure and composition of the crystallized product is greatly influenced by the SiO$_2$/Al$_2$O$_3$ ratio in the reaction system. Low Si/Al ratio (Si/Al ≤ 5) and strong alkalinity is the suitable condition for the preparation of zeolites A (LTA), X (FAU) and hydroxysodalite (SOD), whereas high Si/Al ratio and weak alkalinity is suitable condition for the preparation of zeolites like zeolite beta (BEA), ZSM-11 (MEL) and ZSM-5 (MFI). In general an increase in the SiO$_2$/Al$_2$O$_3$ molar gel ratio increases the thermal stability, acid resistance and hydrophobicity and decreases the ion-exchange capacity [42].

(iii) **Crystallization time**: The crystallization time plays an important role in zeolite synthesis. Increase in crystalline time favours the formation of more crystalline product. However, it is reported that zeolites are thermodynamically metastable phases. In general, Ostwald’s law of successive transformation is followed in zeolite synthesis, i.e. from amorphous to metastable to more stable phase. Hence monitoring the reaction time, any particular phase can be identified [43, 44]. However, thermodynamics alone
cannot rationalize the formation of zeolites, kinetics must also be considered [45].

(iv) **pH of the gel:** Raising pH of the synthesis mixtures using $\text{OH}^-$, mainly influences the crystallization of a certain zeolite in a positive way within the synthesis field. For zeolite A and zeolite ZSM-5 respectively, increasing the pH shows an increase in the crystallization rate. The OH$^-$ is a strong mineralizing agent for bringing reactants into solution. The higher the pH and thus the concentration of dissolved reactants the more the rate of crystal growth of zeolites is enhanced [39, 46].

(v) **Seeding:** In the seeding method, a small amount (2-5 wt %) of the pre-synthesized zeolite material is introduced in the synthetic gel system, in order to have faster crystallization towards a given zeolite and control the size of final crystals [47].

(vi) **Stirring time:** The crystallization kinetics is greatly influenced by the stirring time. The production of small crystals and selectivity for the formation of different zeolite phases can effectively be modified by stirring time. Smaller crystals are obtained by stirring since super saturation can be rapidly achieved due to the accelerated mass transfer [47].

(vii) **Aging period:** The period from homogeneous mixing of the reagents to the onset of heating to the crystallization temperature is referred to as aging. The aging process influences the nucleation crystallization of zeolites by increasing the nucleation rate, reducing the induction period and duration of crystallization period, reducing the crystal size and by increasing the crystal population [48]. It also acts as a good factor for the uniformity of the pores.

### 1.11 Zeolites as catalysts

Depending on the applications, molecular sieves are suitably modified structurally or chemically or in both ways. Chemical treatment, hydrothermal treatment, chemical vapour deposition and selective coking are the well
known methods for the modification of the zeolites. Molecular sieves can also be modified by varying the composition. In zeolites the compositional variation can be achieved by varying the Si/Al ratio or the extent of exchange of cations. Another method, that is of enormous importance, is the variation by isomorphous substitution. The replacement of Si in a purely siliceous molecular sieve by statistically compatible element is termed as isomorphous substitution. Isomorphous substitution of various hetero elements like Al, B, Ga, Ti and Fe have been carried out on various molecular sieves and the resulting systems are promising catalysts for various selective reactions (Perego et al., 1986; Szostak, 1989; Corma, 1997; Arneds et al., 1997). Isomorphous substitution in general can be carried out either to generate acidic or redox properties within the catalytic system. Zeolites have been explored as industrial catalysts in petrochemical and fine chemical industries. In most of these cases, the catalytic activity is due to their acidic nature. This has been in general achieved by isomorphous substitution where tetrahedral silicon will be replaced by a heteroatom. In the case of zeolites this heteroatom will be in general aluminium (Holderich et al., 1991). With the substitution of one aluminium in silicon network, a unit negative charge will be generated. In general this negative charge will be compensated by sodium ions, which are present in the synthetic gel. However, the exchanging these sodium ions with ammonium ions followed by high temperature calcination, one can generate acidic properties in the catalyst. Zeolites are used in a host of acid catalyzed reactions such as alkylation and acylation. The active sites in zeolites are mainly Brönsted acid sites and to some extent the Lewis acid sites. Lewis acidity is formed as a result of trigonally co-ordinated aluminium ions in tetrahedral lattice. Among various zeolites, faujasite, mordenite and ZSM-5 type zeolites are widely used as catalysts. The faujasite type zeolite, namely zeolite-Y has been mainly used for the fluid catalytic cracking and hydrocracking reactions. Mordenite is used in isomerization of light alkenes for octane enhancement of gasoline. ZSM-5 is used widely for the production of fine chemicals. A large array of organic reactions such as isomerization,
rearrangement, alkylation, hydroxylation and acylation has been studied and in all these cases, ZSM-5 has been exploited as a potential catalyst.

1.12 Modification of zeolites

Due to enhanced structural diversity as well as possibility of insertion of the transition metals into the framework structures by isomorphous substitution of silicon or/and aluminium, Zeolite provides considerable research interest in the catalysis field. Some of the important properties of zeolites like their structural features, surface area, crystallinity, pore size etc as well as their inherent properties like acidity, shape selectivity, catalytic properties etc can be modified by appropriate design. It is found that the modified zeolites are finding more applications as heterogeneous catalysts as compared to that the zeolites obtained by direct hydrothermal process [48].

Zeolites can be modified mainly by the following two methods:
(i) By \textit{insitu} modification
(ii) By post synthesis method

The different approaches for the modification of zeolite is shown in \textbf{Scheme 1.4}. 
Scheme 1.4 Different approaches to modify zeolites for improving their structural features and inherent properties.

(i) **Insitu** modification

(a) **Carbon templating**: This method is applied in order to obtain a crystalline, highly acidic material with appreciable amount of mesoporosity. This type of modification is carried out by hydrothermal synthesis of mesoporous zeolite in presence of a template with mesoscopic dimensions like carbon black, carbon rods, carbon spheres or carbon nanofibres [49-51]. Zeolite crystal consisting of extra voids in mesoporous range is obtained by removing the carbon template by calcination.

(b) **Isomorphous substitution**: The molecular sieves when synthesized are obtained in neutral form, so, some suitable method should be adopted to
generate catalytic properties within these materials. This, in general, has been achieved by isomorphous substitution. The isomorphous replacement of Al or Si in the zeolite framework by other heteroatoms to prepare metallosilicates having new physicochemical and catalytic properties is also an important research subject in the field of zeolite chemistry [52]. Isomorphous substitution in zeolite is achieved by incorporation of the desired metal during crystallization under hydrothermal conditions. This results into materials that do not occur naturally. Introduction of transition-metal ions into the zeolite lattice is very interesting because these ions are known to exhibit catalytic activity in homogeneous as well as heterogeneous catalysis. Incorporation of trivalent and tetravalent metal ions into zeolite framework can modify the physicochemical properties such as acidity strength [53], while incorporation of transition metal ions such as Zr, Ru etc. makes zeolites oxidation catalysts, which have been shown to be active in liquid-phase reactions with hydrogen peroxide as an oxidant [54,55]. Chu et al. [53] reported the substitution of Fe into the framework of MFI type silicalite (ferrisilicate), which has a weaker acid strength than its Al or Ga analogues and used it as an oxidation catalyst.

However, the following points have to be considered for an effective substitution (Szostak, 1989).

[i] Substitution of A by B is governed by their radius ratio. Closer the difference between their radius values, greater is the extent of isomorphous substitution.

[ii] The ability of the ion to form tetrahedral oxide ion coordination decides the possibility of isomorphous substitution in molecular sieves.

[iii] The ratios of electronegativities and ionization potentials of the ions A and B also limit isomorphous substitution.

However, it is important to note that ionic charge is not a deciding factor for the feasibility of isomorphous substitution. It only decides the overall framework charge of the molecular sieve. The ionic radii of some of the elements reported to have isomorphously substituted in the zeolite framework are given in Table 1.5.
Table 1.5. Metal ions exhibiting tetrahedral coordination and their ionic radii (Szostak, 1989).

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B⁺³</td>
<td>0.25</td>
</tr>
<tr>
<td>Fe⁺²</td>
<td>0.77</td>
</tr>
<tr>
<td>Fe⁺³</td>
<td>0.63</td>
</tr>
<tr>
<td>Ga⁺³</td>
<td>0.61</td>
</tr>
<tr>
<td>P⁺⁵</td>
<td>0.31</td>
</tr>
<tr>
<td>Ti⁺⁴</td>
<td>0.56</td>
</tr>
<tr>
<td>V⁺⁵</td>
<td>0.49</td>
</tr>
<tr>
<td>Cr⁺³</td>
<td>0.63</td>
</tr>
</tbody>
</table>

(c) **Zeolite-mesopore composite:** Several approaches have been made to synthesize a new type of nano composite materials both micro- and mesopores to provide some interesting features. The stability and acidity of mesoporous materials can be improved by preparing composite materials consisting of microporous domains (zeolites) inside mesoporous supports. For example, preparation of composite materials like beta/MCM-48 [58], beta/TUD-1[57] and MOR/MCM-41[58].

(ii) **Post synthesis modification**

(a) **Desilication:** The desilicated forms of the zeolites X, Y and ZSM-5 are prepared by the selective removal of silicon atoms from the parent zeolites in an aqueous solution of base [59]. Desilication of conventional zeolites in
alkaline medium generates variable intracrystalline mesoporosity, but inevitably changes other properties such as the Si/Al ratio and aluminium distribution. Assessing the individual effects of porosity and composition on the catalytic performance of desilicated zeolites is relevant for their optimal design. This treatment, which decreases the Si/Al ratio while keeping the zeolite framework almost unmodified, enhances the ion exchange capacities of all the zeolites, a property which can be exploited industrially for the X and Y zeolites since the desilicated forms had higher total ion removal rates of calcium and magnesium ions from hard water. Similarly, desilication results in a higher density of acid sites. In catalytic testing studies, the desilicated ZSM-5 zeolite was found to display a higher total conversion in the dehydration of absolute ethanol into ethylene, however the selectivity for ethylene was higher for the parent zeolite at lower reaction temperatures.

(b) Impregnation: Impregnation of zeolites does not change the basic structure of zeolites but is employed for modifying the surface behavior, acidity, basicity, reforming capability etc. This modification process is quite simple and can be tried in different concentration of the impregnating species to attain the desired property. A few examples of impregnations are – modification of FAU zeolite by CsOH to induce basic properties [59], modification of β zeolite by Pt impregnation shows high reforming capability to naphthenic feeds [60], E. David [61] prepared Mg clusters in zeolite 4A for use in catalytic processes. Zeolites play an excellent role as supporting material for metals [62]. Chemical nature and high surface area makes zeolites highly versatile for impregnation of metals.

(c) Ion exchange: Zeolites have a network of pores and cavities having molecular dimensions. The network of pores can accommodate a wide variety of cations, such as Na\(^{+}\), K\(^{+}\), Ca\(^{2+}\), Mg\(^{2+}\) and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. Barrer [52], first reported that by ion exchange modification of zeolites, their molecular sieving properties can be intensely changed. In order
to meet the best requirements of some applications like water softening and purification, for octane enhancement and good gasoline selectivity, in pollution abatement and toxic waste management etc. Zeolites had been modified both by cation exchange method as well as by rare earth exchange method for tailoring the molecular sieves. In order to enhance the sorption capacities of zeolites, the exchangeable $K^+$ and $Na^+$ cations in zeolite framework can be stoichiometrically exchanged by other mono-, di- or trivalent cations. Ion exchange process can simply be carried out by stirring a zeolite with the salt solution containing the cation to be exchanged with the cation of the zeolite at a particular temperature. Ion exchange can also be carried out via solid-solid reaction between the zeolite and the salt or oxide in hydrothermal conditions [63, 64].

(d) Delamination: The delamination of the layered precursor of the zeolite results in the formation of individual layers of variable thickness. The resultant material presents the strong acidity and stability, characteristic of the zeolite, but at the same time, offers the high accessibility to large molecules characteristic of the amorphous aluminosilicates. Much improvement in diffusion of initial products in catalytic applications, reducing consecutive reactions [65] is found in delaminated materials.

(e) Dealumination: Dealumination process is employed for the selective extraction of Al from the zeolite framework leading to the formation of more stable high silica zeolites with large pores/mesopores [66, 67]. The created mesopores are isolated and do not constitute an interconnected network of pores. The dealumination of zeolite can be carried by steaming, treatment with ammonium hexafluorosilicate, and with silicon tetrachloride. The zeolite framework can be dealuminated most effectively through ion exchange into the sodium form followed by treatment with silicon tetrachloride. The crystalline structure remains essentially intact.
(f) **Hydrothermal modification:** This modification is carried out for expulsion of tetrahedral Al from the framework into non-framework position. This modification is performed heating ammonium exchanged zeolites in presence of steam. On modification the framework Si/Al ratio increases while unit cell size decreases [1]. Thus ultrastable zeolites having fewer ion exchange as well as Brönsted acid sites are obtained.

1.13 Removal of template

Removal of the template plays an important role in the preparation of final microporous solid. In order to preserve the final micro-structure, in general, removal of the template can be achieved by calcination process, where the as synthesized material will be subjected to a controlled heat treatment. Calcination has to be done in a flow of inert gases at the initial stages followed by the flow of air. This is to maintain the crystallinity of the material.

1.14 Choice of fluoride medium

A significant breakthrough in the field of zeolite synthesis occurred when hydroxyl anions were replaced by fluorides, making the synthesis possible in neutral and even in acidic media (pH =5) [68]. Synthesis using a fluoride containing medium obtained by replacing the hydroxyl ion (OH\(^-\)) with fluoride ion (F\(^-\)) as a mineralizing agent, produces zeolites at lower pH values, but with the same morphology as the alkaline route [69].

Later on, Guth and Kessler developed the synthesis of several microporous materials: aluminosilicates, aluminophosphates and gallophosphates via this alternative non-alkaline route [70-74]. The use of the fluoride ion as mineralizer (by using NH\(_4\)F source) instead of the conventionally used hydroxide ion presents several advantages:
Fewer metastable phases are formed which implies a certain ease of preparation of any desired zeolite [73,75,76]

- Synthesis of materials not obtainable in alkaline media like the 20-T-ring gallophosphate cloverite [77]

- Formation of large crystals with few defects which are of interest as model host materials (for adsorption or diffusion studies) [78]

- Neutral (or acidic) medium enables the incorporation of elements sparingly soluble in alkaline media: Co$^{2+}$, Fe$^{3+}$, Ti$^{4+}$ [72,73]

- Direct formation of the quarternary ammonium form ZSM-5, instead of Na-ZSM-5 avoiding repeated ion-exchange; so only a calcination step is needed to burn off the template and to obtain the acidic H-ZSM-5.

Recent studies have shown that even after calcination fluorine remains occluded inside the small cages found in the MFI structure [75,78,79]. Inspite of the numerous advantages of the synthesis in fluoride media, the presence of such highly electronegative element modifies the electron density around the neighbouring Si by the formation of [Si$_{4/2}$F]$^-$ entities [78-80]. Thus, this may also influence the catalytic properties of the zeolite.

The introduction of transition metal cations inside zeolite micropores and/or framework, led to the development of many redox catalysts or even bifunctional catalysts [81,82]. Along with the design of novel “tailor-made catalysts” came the necessity to develop new characterization methods giving informations about the metal introduced in the framework (quantity, location, geometry), which are of primary importance to understand the catalytic activity.

### 1.15 Characterization of microporous materials

Characterization is one of the most important aspects in any type of synthesis. Without proper characterization we cannot definitely say that the
desired material is formed. For catalytic characterization of Zeolites, the important methods used are X-ray Diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), UV-Visible diffused reflectance spectroscopy (DRS), Scanning Electron Microscopy (SEM), Thermogravimetric analysis (TGA), \( \text{N}_2 \) Adsorption-desorption isotherm etc. These techniques have been employed in order to understand the physico-chemical properties like formation of the microphase, incorporation of the heteroatom in the framework, thermal stability, pore size, morphology and active surface area.

1.15.1 X-ray diffraction (XRD)

XRD is one of the most important techniques in catalytic characterization. The principle of XRD, suggested by Bragg [83] is that reflection of X-ray can take place only at certain angles which are determined by the wavelength of the X-ray and the distance between the planes in the crystal. The fundamental equation which gives a simple relation between the wave length of the X-ray (\( \lambda \)) the interplaner distance (d) in the crystal and the angle of reflection (\( \Theta \)) is known as Bragg equation which is

\[
n\lambda = 2dsin\Theta
\]

XRD study helps mainly in identification of the phase, crystallization and dimension of crystals. Microporous molecular sieves show characteristic peaks in the \( 2\theta \) range of 5-50°, whereas the mesoporous materials exhibit characteristic peaks in the low angle region between 1.5-10° (2\( \theta \)). Crystallinity of the MFI samples is calculated using the following relation:

\[
%C = 100 \times \frac{I_{hkl}}{I_b + I_{hkl}}
\]

For a particular crystallographic plane (\( hkl \)) where, \( I_{hkl} \) is the corrected integral XRD peak intensity and \( I_b \) is the integral background intensity for the same plane. Scherrer formula \( D_{hkl} = \frac{K\lambda}{\beta \times \cos \theta} \) was used to determine the crystallite dimension (\( D_{hkl} \)) of the identified crystalline phase [84]. Here, \( \beta \) is the full width at half maximum; \( K \) is the shape factor; \( \theta_{hkl} \) is the Bragg angle.
and $\lambda$ is the wavelength of Cu K$\alpha_1$ radiation. The information obtained from XRD patterns are given in Table 1.6.

Table 1.6 Information obtained from XRD patterns [85].

<table>
<thead>
<tr>
<th>Feature</th>
<th>Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak positions (2$\theta$ values)</td>
<td>Unit cell dimensions</td>
</tr>
<tr>
<td>Non-indexable lines</td>
<td>Presence of a crystalline impurity (or incorrect indexing)</td>
</tr>
<tr>
<td>Systematically absent reflections</td>
<td>Symmetry</td>
</tr>
<tr>
<td>Background</td>
<td>Presence (or absence) of amorphous material</td>
</tr>
</tbody>
</table>
| Width of peaks                       | Crystallite (domain) size  
Stress / strain                      |
| Peak intensities                     | Stacking faults  
Crystal structure                           |

1.15.2 Fourier transform infrared spectroscopy (FT-IR)

When infrared light is passed through a sample, some of the frequencies are absorbed while other frequencies are transmitted through the sample without being adsorbed. If we plot absorbance or transmittance against frequency the result is an IR spectrum. A particular molecule only absorb IR light of particular frequency if there is an energy transition within the molecule such that $\Delta E = h\nu$. The transition involved in IR absorption is associated with vibrational change within the molecule. From the characteristic band appeared, we can identify the sample [86]. The KBr pellet technique is frequently used for investigations of vibrations of the framework [87-89]. IR spectrums are shown by molecules when vibrational motion is accompanied by a change in the dipole moment of the molecule [90].
Vibrations of the frameworks of zeolites give rise to typical bands in the mid and far infrared. A distinction is made between external and internal vibrations of the TO$_4$ tetrahedra (with, for example, T = Si or Al). The positions of bands due to vibrations of external linkages are often very sensitive to structure. The assignments of main IR bands are given in Table 1.7.

Table 1.7 The assignments of the main IR bands [87].

<table>
<thead>
<tr>
<th>Structure</th>
<th>Vibrational Mode</th>
<th>Absorbance Band</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal tetrahedra</td>
<td>Asymmetric stretching</td>
<td>920-1250 cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Symmetric stretching</td>
<td>650-720 cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>T-O bending</td>
<td>420-500 cm$^{-1}$</td>
</tr>
<tr>
<td>External linkages</td>
<td>Double ring vibrations</td>
<td>500 - 650 cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Pore opening vibrations</td>
<td>300 - 420 cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Symmetrical stretch</td>
<td>750 - 820 cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Asymmetrical stretch</td>
<td>1050 - 1150 cm$^{-1}$</td>
</tr>
</tbody>
</table>

1.15.3 Thermal gravimetric analysis (TGA)

This method is used to determine the thermal stability, acidity as well as the isomorphous substitution in the zeolite. In the pure silica sample the differential gravimetry (DTG) shows an asymmetric, well defined single reaction interval commencing at 388$^0$C and ending at 626$^0$C. There is very little water loss and no drift in the DTG base line is observed, indicating the presence of hydrophobic material. Mass losses upto ~ 475$^0$C can be attributed to the degradation of three types of TPA$^+$ cations occluded in the framework as identified by El Hage-Al Asswad [91] and co-workers. Losses above
~ 475°C, causing the asymmetrical reaction interval is due to those TPA⁺ cations which are ion-paired to occluded mineralizer anions. In case of the DTG traces of the metal substituted gel compositions the reaction intervals increase with the increasing mole fractions and there are extended intermediate plateaus, which are due to the overlap of occluded and ion-paired losses, producing a DTG trace displaying two stages of weight loss. There is also broadening of the second mass loss interval with increasing levels of substitution. These changes are due to the increasing negative charges introduced into the previously uncharged pure silica framework being counterbalanced by the cationic species. TGA can be used to accurately detect the desorption of basic molecules from a zeolite as a function of temperature and the resulting data can be used to calculate the acid site strength and distribution of various zeolites. The acidity of a zeolite is calculated by the following formula and reported in units of millimoles of acid sites per gram of zeolite.

\[
\text{Acidity} = \left( \frac{\% \text{ Mass Loss}}{100} \right) \left( \frac{1}{\text{MW of Base}} \right) \left( \frac{1000 \text{ mg}}{1 \text{ g}} \right)
\]

Where MW stands for molecular weight of the base.

**1.15.4 Diffuse reflectance UV-Vis spectroscopy**

This is an important technique in characterizing sample where the absorption of UV-VIS radiation by a molecule leads to transition among the electronic energy level of the molecule [92]. The UV–Vis diffuse reflectance spectroscopy is a suitable technique to study solids, particularly dispersed oxides [93] and metal ions in constrained environment such as MCM, zeolites and clay materials [94–96] to obtain information on the coordination environment, oxidation state of the embedded transition and rare earth metal ions. The absorption in the UV-Vis range arises because of “ligand to metal charge transfer” (L→M). The position of the L→M band depends on the ligand field symmetry surrounding the metal centre. Hexa-coordinated L→M electronic transitions require less energy than for a tetra-coordinated metal ion.
Transitions in the UV region 200-400 nm are of great interest for most of the isomorphously substituted microporous and mesoporous metallo-silicate materials.

1.15.5 \( \text{N}_2 \) adsorption-desorption isotherm

Most methods used to measure surface area of solid catalysts are based on the isothermal adsorption of nitrogen. Either a single point or multipoint method is used to calculate the surface area. At Engelhard, the multipoint Brunauer, Emmett and Teller (BET) method is used to measure total surface area of fresh and equilibrium moving bed and fluid catalytic cracking (FCC) catalysts. It is also used as a quality control tool during catalyst manufacture. The textural properties of the metal substituted calcined zeolites are also evaluated from the nitrogen adsorption-desorption isotherm. As per IUPAC classification of adsorption in microporous material [97], \( \text{N}_2 \) adsorption-desorption isotherms of the calcined zeolites exhibit high nitrogen uptakes at low relative pressures. The closure of the hysteresis loop around 0.4 \( \frac{P}{P_0} \) relative pressures is due to the well-known tensile strength effect of the adsorptive, and does not represent any physical porosity at this particular relative pressure [98]. The sub step observed between 0.1 and 0.3 relative pressures in the isotherm is a characteristic of MFI-type zeolites [98] and is associated with a fluid-to- solid-like phase transition of the adsorbed nitrogen in the microporous network. These isotherms also reflect nitrogen uptake in the MFI type micropores at low \( \frac{P}{P_0} \) followed by capillary condensation in the void spaces created by the packing of nanoparticles. Micropore volume, micropore area and external surface area were calculated using t-plot method. \( \text{N}_2 \) adsorption is also observed at high relative pressures, which is explained to originate from the \( \text{N}_2 \) adsorption in the interparticle voids. At intermediate relative pressure, a significant adsorption takes place due to the \( \text{N}_2 \) adsorption on the external zeolite surface.
1.15.6 Scanning electron microscopy (SEM)

SEM is used to observe the surface topography that is terraces, steps, kinks and dislocations on a surface of solid samples. In this technique a focused beam of electrons with a well defined de-Broglie wave length replaces the lamp found in traditional light microscope. Instead of glass or quartz lenses, magnetic fields are used to focus the beam. Electrons scattered from the small irradiated area are detected and the electrical signal is sent to a video screen. An image of the surface is then obtained by scanning the electron beam and the detector across the sample. SEM imaging is often preferred in place of optical imaging because of the enhanced depth of field. The information that can be drawn from SEM pictures of zeolites is given in Table 1.8.

Table 1.8 Informations drawn from SEM pictures of zeolites [99].

<table>
<thead>
<tr>
<th>Subjects</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal form</td>
<td>Type of zeolite</td>
</tr>
<tr>
<td></td>
<td>Aspect ratio</td>
</tr>
<tr>
<td></td>
<td>Influence on crystal growth, eg. inhibition of crystal faces that indicate the presence of an unknown factor</td>
</tr>
<tr>
<td></td>
<td>Crystal size distribution phenomena, eg. Aggregation / twinning / intergrowth</td>
</tr>
<tr>
<td></td>
<td>Indication of single crystals</td>
</tr>
<tr>
<td>External surface</td>
<td>Relative roughness</td>
</tr>
<tr>
<td></td>
<td>Secondary nucleation effects</td>
</tr>
<tr>
<td>Purity of the phase</td>
<td>Other zeolite types</td>
</tr>
<tr>
<td></td>
<td>Amorphous material</td>
</tr>
<tr>
<td>Unknown species</td>
<td>New material?</td>
</tr>
</tbody>
</table>
1.16 Description of MFI zeolite used in the present investigation

ZSM-5 (MFI) catalyst was first synthesized by Argauer and Landolt in 1972 [100]. MFI is a synthetic zeolite, closely related to ZSM-11(MEL). There are many ways to synthesize MFI, a common method is as follows [101]:

\[
\text{SiO}_2 + \text{NaAlO}_2 + \text{NaOH} + \text{N(CH}_2\text{CH}_2\text{CH}_3)_4\text{Br} + \text{H}_2\text{O} \rightarrow \text{MFI}
\]

MFI is typically prepared at high temperature and high pressure in a Teflon-coated autoclave and can be prepared using varying ratios of SiO\textsubscript{2} and Al containing compounds. MFI Zeolite is composed of several pentasil units linked together by oxygen bridges to form pentasil chains. A pentasil unit consists of eight five-membered rings. In these rings, the vertices are Al or Si and an O is assumed to be bonded between the vertices. The pentasil chains are interconnected by oxygen bridges to form corrugated sheets with 10-ring holes. Like the pentasil units, each 10-ring hole has Al or Si as vertices with an O assumed to be bonded between each vertex. Each corrugated sheet is connected by oxygen bridges to form a structure with “straight 10-ring channels running parallel to the corrugations and sinusoidal 10-ring channels perpendicular to the sheets” [102]. Adjacent layers of the sheets are related by an inversion point. The estimated pore size of the channel running parallel with the corrugations is 5.4–5.6 Å [103]. The crystallographic unit cell of MFI has 96 T sites (Si or Al), 192 O sites, and a number of compensating cations depending on the Si/Al ratio, which ranges from 12 to infinity. The structure is orthorhombic at high temperatures, but a phase transition to the monoclinic occurs on cooling below a transition temperature, located between 300 and 350 K [104,105].
1.17 Objectives of the present research work

The advent of supra-molecular chemistry has given a new thrust to this field of porous solids. Even though various oxide materials have been prepared in mesoporous and microporous form, lack of proper crystallinity of the resulting solids made them not suitable for industrial applications. However, constructing solids with expected porous texture and architecture is one of the dreams of scientists. There are a number of possibilities and combinations for building up supra-molecular structures over which the porous solids can be constructed. It is therefore necessary to examine and probe scientifically the suitability of these materials especially with respect to their surface properties for the possible technical applications envisaged. The motivation of the present study is therefore to synthesize microporous solids at lower pH range and to examine their catalytic activity for some typical organic transformations.

The catalytic activity of molecular sieves can be improved by the incorporation of heteroatoms into the framework structure. The introduction of metals like Zr, Ru and In inside zeolite micropores and/or framework leads to the development of many redox catalysts or even bifunctional catalysts [106,107].

Zirconia-based materials have wide applications in the field of catalysis in dehydration, hydrogenation, hydroxylation, oxidation and epoxidation reactions owing to the moderate acidity and oxidizing capabilities.

In-MFI samples have found wide range of applications for selective catalytic reduction [108].

The Ru$^{3+}$ ion has a larger ionic radius (0.69 Å) than Al$^{3+}$ (0.57 Å) and like iron (preceding member of Group 8), it has a tendency to form insoluble hydroxides in a basic environment and an ability to change oxidation state that is why it can be used as redox catalyst in many organic reactions.

The Zr-HMFI catalyst was prepared by ion-exchange using a commercial H-MFI zeolite as the starting material. However, the catalysts prepared in this method have low surface areas which restrict their industrial applications. There are early claims of synthesis of crystalline zirconium
silicas with zeolitic properties, details of which are not available in the literature. Dongare et al. reported the synthesis and characterization Zr-MFI [109]. However synthesis was carried out in presence of solvent and crystallization was completed in 48 h.

Methods that have been tried so far for the preparation of In-MFI are the ion-exchange, precipitation, mechanical mixing and dry techniques based on the use of InCl₃: solid-state ion exchange, sublimation, and transport reaction processes mainly, but the *in situ* modification of the MFI zeolites with indium have not yet been reported.

The incorporation of ruthenium into zeolites has been recently reviewed [110]. This has been achieved using potassium ruthenate (VI), K₂RuO₄, and tetra-n-propylammonium perruthenate (VII), (Pr₄N)RuO₄. The method is somewhat cumbersome and quite a lengthy process. In the present study ruthenium salts are used as a source of Ru and the process takes comparatively shorter time for completion.

The specific aims of the present study are

• Synthesis of MFI zeolite in a broad range of silicon to aluminium ratios using fluoride gel as mineralizer.

• *in-situ* modification of the MFI samples (SAR= 200 and 100) by introduction of Zr, Ru & In metal.

• Characterization of the synthesized and modified samples by XRD, FT-IR, TGA, UV-Vis (DRS), N₂ adsorption and SEM techniques.

• Study of the catalytic activity of the synthesized and modified MFI zeolite with respect to organic reactions like hydroxylation of phenol.
1.18 Reference


