CHAPTER 1

INTRODUCTION

1.1 Historical perspective

The history of zeolite began in 1756, when the Swedish mineralogist, A.F.Cronstedt (1) used the term to describe Stilbite which gave off copious amounts of steam upon heating. The word 'zeolite' literally means 'boiling stone' in Greek. Stilbite ranks among the first identified naturally occuring zeolite minerals; it consists of hydrated aluminosilicates of alkali and alkaline earth metals. The first synthesis of a synthetic zeolite is credited to Barrer (2) who characterised it using X-ray diffraction technique and also studied its chemical and physical properties. Milton (3) discovered a number of commercially significant synthetic zeolites designated as zeolites A, X and Y (*vide infra*). Both Barrer's and Milton's work showed that zeolites possess a large surface area and have well defined uniform pore structures that permit them to function usefully as molecular sieves. In 1959, Union Carbide marketed zeolite-Y as an isomerisation catalyst, followed in 1962 by Mobil who introduced the use of synthetic zeolite- X as a cracking catalyst. The 1980's saw a growth in new zeolite compositions as well as in our knowledge of the structures of zeolites. Extensive work was carried out on the synthesis and applications of ZSM-5 and other high silica zeolites. The new developments in the field of porous crystalline aluminophosphate- based molecular sieves were described by Wilson *et al* (4). Considerable effort has been expended in recent years in synthesising modified zeolites such as silicon-enriched zeolites and metal substituted zeolites (5,6). Presently over 600 zeolite materials are known and their number is growing continually .

1.2 Nomenclature

The zeolites posses a variety of names derived from sources which are sometimes descriptive, sometimes obscure. Many of the natural zeolites take their names from noted geologists, mineral collectors or other persons whom the zeolite discoverer wished to honour. Naming of the synthetic zeolites is slightly less random, and not nearly as creative. Each research group appears to have applied its own identification system. Usually the name can easily identify the laboratory of origin for that particular material, but rarely is the composition or structure of the phase obvious from the name. Linde Type A refers to the zeolite first synthesised in the laboratory of the Linde Division of Union Carbide. Barrer and his research group in England also used alphabet designation for his new phases. ZSM-5 is a well known material prepared in the laboratory of the Mobil Corporation. The ZSM- designation began in the 60's and was used for the silica and aluminosilicate phases. The name continued to be used through the 80's. Academic institutions have used their university names as a prefix to identify new phases that researchers there had prepared. Thus, UIO-6 is a microporous aluminophosphate prepared at the University of Oslo and UTD-1 a very large pore silicate prepared at the University of Texas at Dallas. The use of the prefix $AlPO_4^-$ by researchers at Union Carbide, has been the only nomenclature system that provides any consistent indication of the chemical composition of the phase. The substitution of other elements into the aluminophosphate topology is also indicated in the prefix. CoAPO- represents a cobalt aluminophosphate, and TAPO, the titanium aluminophosphate. The number after the prefix, such as $AlPO_4$-5 designates a structure, generally a unique framework topology. Thus the materials, $AlPO_4$-5, CAPO-5, and SAPO-5, all have the same fundamental structure but differ in their compositions, being respectively aluminophosphate, chromium aluminophosphate, and silicoaluminophosphate. These days synthetic zeolites are designated by a letter (or letters), for example, Zeolite-Y, Zeolite-X, and ZSM-5. Prefixes are used to indicate the nature of exchangeable cations within a zeolite - the hydrogen form by H, alkyl ammonium cations by N, and other cations by their elemental abbreviation, e.g. Ca-Y.

1.3 Structure of zeolites

Zeolites are three dimensional, microporous, crystalline solids with well defined structures. The fundamental building blocks of these structures are infinitely extended three dimensional networks of SiO_4 and AlO_4 tetrahedra linked to each other through oxygen atoms. The structural formula of a cation containing zeolite is based on the crystallographic unit cell (7).

$$M_{x/n}\,[(AlO_2)_x\,(SiO_2)_y]\,ZH_2O$$

where M is a cation whose valency is n, Z is the number of water molecules, x and y are the total number of tetrahedra per unit cell. Usually y/x has a value between 1 and 5, although it can be between 10 and 100 in high silica zeolites. The isomorphous substitution of trivalent aluminium by tetravalent silicon in the zeolite lattice creates a net negative charge on the framework. This charge is neutralised by the cations that are present during the synthesis. These cations are mobile and are usually exchangeable. Such an exchange has little effect on crystal structure, it does, however, affect other relevant properties of the zeolite such as acidity and internal electric fields.

1.3.1 Framework structure

The framework of a zeolite is based on a three-dimensional network in which the polyhedral sites, usually tetrahedral, are linked by oxygen atoms. The crystalline framework contains cages and channels of discrete size ranging from 3 to 30 A° in diameter. The primary building unit of a zeolite is the individual SiO_4 and AlO_4 tetrahedra (Fig. 1.1) . The topology of all molecular sieve types can be described in terms of a finite number of specific combination of tetrahedra called secondary building units (SBU's) (8,9).

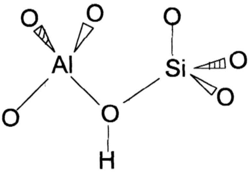


Fig.1.1 The primary building units found in zeolite frameworks

A total of 8 SBU have been found in zeolite structures shown in Fig (1.2). The T atom belonging to a TO_4 tetrahedron (T = Al or Si) is located at each corner; the oxygens located near the mid-points of the lines joining each pair of the T atoms are not shown. Description of the framework topology of a molecular sieve involves "tertiary" building units corresponding to different arrangements of the SBU's in space. The framework may be considered in terms of large polyhedral building blocks (rings) forming characteristic cages. For example, sodalite, zeolite-A and zeolite-Y can all be generated by truncated octahedron known as the beta- cage (10).

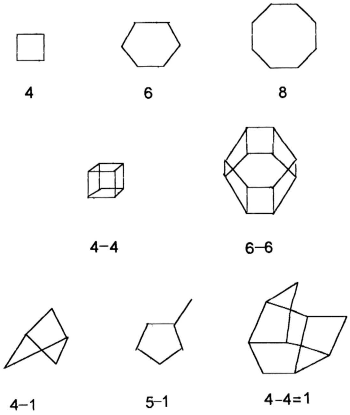


Fig. 1.2 *Secondary Building Units of zeolite framework (Ref. 8)*

An alternative method of describing extended structures uses the two-dimensional sheet building units. Sometimes various kinds of chains can be used as the basis for constructing a molecular sieve framework (10). According to the so-called Loewenstein rule (11), Al-O-Al linkages in zeolitic frameworks are forbidden. As a result, all aluminate tetrahedra must be linked to 4 silicate tetrahedra, but a silicate tetrahedron may have 5 different possible environments: Si (OAl,4Si),Si (1Al, 3Si), Si (2Al, 2Si), Si (3Al,1Si) and Si (4Al, 0Si).

A topological description and classification of zeolite framework types has been proposed by Meier and Moeek (12) who considered 'coordination sequences', representing the number of T atoms in the first, second, third etc. tetrahedral coordination sphere of each topologically non-equivalent T- site. The topology of the framework is then expressed by sequences of these numbers. The concept of a coordination sequence has proved to be very useful in evaluating the degree of similarity among different zeolite structure types.

In accordance with the IUPAC recommendations on the chemical nomenclature of zeolites and related materials (13), topologically distinct framework types are represented by a nemonic code consisting of 3 capital letters generally derived from the name of the 3 species, e.g. SOD for sodalite. These symbols describe all variants of a framework with a given topology irrespective of composition, Si/Al distribution, cell dimension and symmetry.

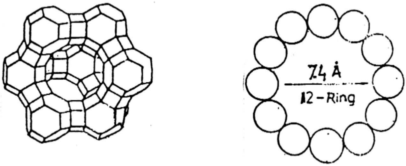
There are small, medium and large pore zeolites (Fig. 1.3). Small pore zeolites (chabazite) have a eight ring system of diameter 4.1 A°. In medium pore zeolites, ten tetrahedra form a ring of diameter 5.6 A°. The large pore Y-type zeolites have a 12 ring system with a pore diameter of 7.4 A°; they admit even hydrocarbon molecules larger than naphthalene. Their chief application is in catalytic cracking of petroleum molecules giving smaller gasoline range molecules (14). In ZSM-5 there are two types of channels, one being a straight channel, with an elliptical shape and the other a zigzag channel with near circular cross section shown in Fig (1.3).

The pore sizes of certain commercial zeolites are summarised in Table. 1 below.

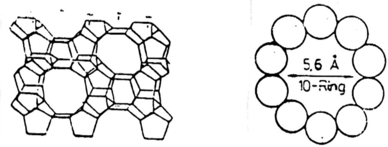
Table. 1 Pore diameter of zeolites and tetrahedra in ring

No of tetrahedra in a ring	Pore diameter (A^0)	Example
8	4.1	Erionite, Chabazite
10	5.6	HZSM-5
12	7.4	Zeolite-Y, Zeolite-X

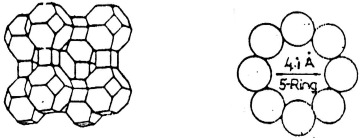
The discovery of ZSM-5, the first representative of the family of pentasil zeolites, was a milestone in zeolite chemistry during the 1970's.The structural assembly of uniform channels is an advantageous special feature of the pentasil zeolites. The use of silicon-rich pentasil zeolites as highly acidic, extremely shape-selective and heat-stable catalysts has led to their industrial application in processes such as isomerisation, cracking, alkylation, dehydration, etc.



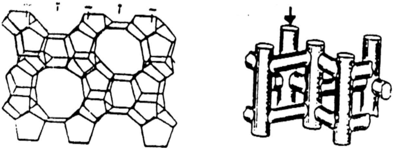
Y-zeolite



Pentasil zeolite



A-zeolite



Pentasil zeolites with channel system

Fig. 1.3 *Zeolite structures (Ref. 15)*

1.4 Synthesis of zeolites

Zeolites are normally synthesised hydrothermally from basic reaction gels at temperatures between 60^0 and 200^0C under autogenious pressure and in the presence of a large excess of water. Most of the highly siliceous zeolites are formed in the presence of organic bases known as templates introduced in the early 1960's (16).

The structure and properties of zeolites are highly dependent on the physical and chemical nature of the reactants used in their preparation, the overall chemical composition, the types of cations and organic template used, and the conditions (temperature, pressure, and duration) of the hydrothermal treatment.

Most of the synthetic molecular sieves are produced under non-equilibrium conditions and are considered, in a thermodynamic sense, as metastable phases. Upon the mixing of the reagents used in the synthesis, the system is in a disordered state with a higher entropy than the ordered crystalline state of the molecular sieve. For crystalline systems which can exist in several different polymorphic forms, the one with the highest entropy will develop from the highly disordered synthesis mixture. According to the Ostwald rule of successive transformations, long reaction times favour the recrystallization of metastable molecular -sieves to other more stable structures under certain conditions. Two theories have been proposed to account for the mechanism of zeolite synthesis. In the solid-solid transformation mechanism, crystallization of the zeolite occurs directly from the amorphous phase (17). In the solution crystallization mechanism, nuclei form and grow in the liquid phase (18). In the latter case, it is envisaged other equilibrium exist between the solid gel phase and the solution, and that nucleation occurs in the solution. The gel dissolves continuously and the dissolved species are transported to the nuclei crystals in the solution. In addition, zeolite formation can sometimes occur simultaneously. In some cases zeolites can also be crystallised from a single solution system containing no secondary solid gel phase (19). From the single phase solution studies, it appears that nucleation and subsequent crystallization can occur readily in the solution phase, leading to the possibility that the presence of a solid gel phase acts only to supply nutrients to the solution.

Fig. 1.4 shows the characteristic S-shaped crystallization curve of a molecular-sieve, divided into three periods a, b and c. Part a is the 'induction period' during which crystalline nuclei form but no crystalline product is observed. The length of the induction period is reduced by adding crystal seeds to the initial mixture. During the growth period b, crystal nuclei grow rapidly in size. Finally during the period c, the crystallisation is over and the products may transform into a more stable phase requiring a longer reaction time.

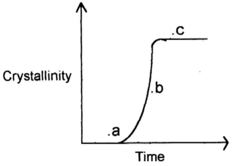


Fig. 1.4 *crystallisation curve of a zeolite*

1.4.1 Role of organic template

The incorporation of an organic template, typically a tetraalkylammonium salt, into the synthetic process can promote a desired zeolite product. The organic template acts as a base. The shape of the templating ion directs the crystallization of the aluminate and silicate tetrahedra and determines the structure of the zeolite product. The organic template directs the formation of the structure with the alkyl groups filling the channels. The templating molecule that is left behind in the zeolite cavities after synthesis can be larger than the entrance to cavities thereby forcing the zeolite to form around the templating molecule. Templating agents can be removed after synthesis by substitution or chemically breaking down the template.

1.5 Characterisation of zeolites

The zeolite once synthesised can be characterised using a variety of both simple and complex techniques. In the case of naturally occuring zeolites, simple analysis of the mineralogy of the sample can be used to identify the zeolite type, e.g. colour, shape of crystallite, hardness, etc. However, for synthetic zeolites which are white powders with small crystal sizes, characterisation is achieved using one or more of the following techniques.

- ***Microscopy***
  - Optical Microscopy
  - Scanning Electron Microscopy (SEM)
  - Transmission Electron Microscopy (TEM).
- ***Spectroscopy***
  - X-ray Diffraction (XRD)
  - Nuclear Magnetic Resonance (NMR)
  - Infrared and Raman spectroscopy
  - Atomic Absorption Spectroscopy (AAS)
  - Atomic Emission Spectroscopy (AES)
  - X-ray Photoelectron Spectroscopy (XPS) [also called Electron Spectroscopy for Chemical Analysis (ESCA)]
- ***Thermogravimetric techniques.***

1.5.1 Microscopy

Microscopic studies help in distinguishing different phases, especially as high resolution instrumentation is able to visualise the lattice planes and therefore to distinguish between zeolite crystals and other compounds. Micro- diffraction studies may be used in addition to identify any foreign compounds that may be present in the zeolite. The use of microprobe analysis may identify elements in the zeolite microcrystals and even monitor their distribution within a single zeolite crystallite.

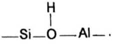
1.5.2 Spectroscopy

1.5.2.1 X-ray diffraction

X-ray diffraction can be used as a basic fingerprinting technique in the determination of the zeolite structure. Single crystal X-ray diffraction is the most powerful method for the determination of crystal structure because it gives very accurate access to the position and intensity of all reflections, and therefore gives the atomic positions, in contrast to X-ray powder diffraction where only a few peaks can be observed. It is often difficult to obtain sufficiently large single crystals of molecular sieves. It is therefore usual to use X-ray powder diffraction (hereinafter abbreviated as XRD) to obtain information about the structure. XRD provides information on long-range order and is a recognised method for identifying crystalline materials by comparing the d-spacing and intensity of diffraction peaks with those of standard samples. The crystallinity of a series of samples is measured by comparing the peak heights (areas) with those of a standard sample taken to be 100% crystalline.

1.5.2.2 *Infrared spectroscopy*

Infrared spectroscopy can be used to characterise various structural aspects of zeolites, including vibrations of the framework, the presence of adsorbed molecules, the nature of OH groups in the structure, and how the introduction of different cations can affect the strength of the acid- sites.

In the case of large pore zeolites Ward *et al* (20) observed the vibrations in the region 2600-3650cm-1 and assigned them to bridged  $-\mathrm{Si}-\overset{\mathrm{H}}{\underset{}{\mathrm{O}}}-\mathrm{Al}-$. The higher the acid strength, the weaker the OH bond and therefore the lower the IR frequency. For example, in ZSM-5 (Al form) the hydroxyl bands occur at 3740cm^{-1} and 3610cm^{-1} . In the boron form of ZSM-5 the bands occur at 3740cm^{-1} and 3710cm^{-1} i.e. the bridged hydroxyl band is at a higher frequency and the acid strength is lower (21) .

1.5.3 *Thermogravimetric analysis*

Thermogravimetric analysis (TGA) is used to determine the framework weight of the zeolite samples. Synthesised zeolite samples contain template and, of course, water. Hence adsorption/ diffusion studies are important to determine whether all volatile materials from the zeolite framework have been removed.

1.6 Properties of zeolites

Zeolites have many unique properties, namely :

(i) large surface area; (ii) well defined and uniform pore structure; (iii) well-defined crystal structure; (iv) high thermal stability; (v) shape selectivity; (vi) possibility of easy regeneration of spent catalyst; (vii) modified forms of zeolite can be prepared by ion-exchange method; (viii) possibility of controlling the strength and number of their acid sites.

The most notable among these are :

Ion-exchange property, *Acid-Base property*, *Thermal stability* and *Shape-selectivity*

1.6.1 Ion-exchange property

The cavity cations in zeolites interact only weakly with the framework and may therefore undergo ion-exchange reactions readily at room temperature. For example:

$$\text{Na-Zeolite A} + \tfrac{1}{2}\,Ca^{2+}_{(aq)} \longrightarrow Ca_{0\cdot5}\,\text{Zeolite A} + Na^{+}_{(aq)}$$

The particular ion-exchange characteristics of a zeolite are determined by the sizes of the cages/ pores and the co-ordination environments present within the zeolite. Acidic zeolites are obtained by direct ion-exchange with acids, typically HCl. Exchange with ammonium ions followed by heating to 500^0C also yields hydrogen zeolites.

$$\text{Na-Zeolite} \xrightarrow{NH_4^+} NH_4\text{- Zeolite} \xrightarrow{500^0C} \text{H- Zeolite}$$

1.6.2 Acid-Base property

Zeolites possess both Bronsted and Lewis acid sites. The framework aluminiums and silicons are bound to each other through shared oxygen atoms. In this situation the SiO_4 fragments are neutral, $Si^{4+}/4O^-$, but not the AlO_4 fragments which acquire a net negative charge. This charge can be neutralised by extra framework cations or protons. If the charge is neutralised by a proton, then a Bronsted acid site is generated. In the absence of a compensating cation, the aluminium atom tends to acquire a pair of electrons to fill its vacant 3p-orbital, and a Lewis acid site is generated. Under high temperature treatment the Bronsted acid sites get dehydrated and are converted to Lewis acid sites. Both types of acid sites play an important role in the various catalytic reactions such as cracking, isomerisation, alkylation, hydrogenation and dehydrogenation. The strength and number of the acid sites (both Bronsted and Lewis) can be adjusted in a controlled manner during synthesis/ or by subsequent ion-exchange.

1.6.3 Thermal stability

Zeolites have high operational stability which allows the chemist to conduct reactions at higher temperatures. Many zeolites are thermally stable to over 500^0C. Breck (22) has summarised the thermal properties of various zeolites and reported that the thermal stability of zeolite structures increases with the Si/Al ratio. Upon calcination the structural stability depends on the method of heat treatment and the Si/Al ratio. The thermal stability of zeolites permits them to be used above 150^0C.

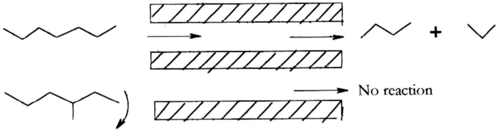
They can therefore be used for reactions in which the attainment of thermodynamic equilibrium requires high temperatures.

1.6.4 Shape selectivity in zeolites

Shape- selective catalysis can be used to increase yields of preferred products or to hinder undesirable reactions. Weisz and Frilette (23) were the first to describe the concept of shape selectivity . Csicsery (24) has reviewed the most important features of shape selectivity . In heterogeneous catalysis the reaction proceeds through several steps: diffusion and adsorption of the reactant, formation of the intermediate and, finally, desorption and diffusion of the product. The shape selectivity principle is based on these different steps and results in three major types of shape selectivity.

Reactant selectivity

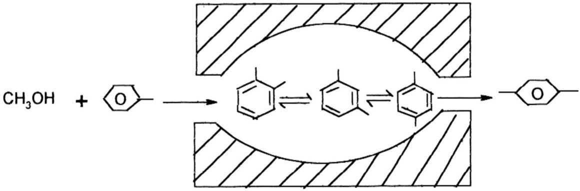
This occurs when some of the molecules in a reactant mixture are too large to diffuse through the zeolite pores. The shape of the reactant determines if it can pass into the zeolite pores. There are wide ranges of zeolite types available with different size and shape pore orifices. This is illustrated by the selective cracking of the linear alkanes in preference to branched alkanes on small and medium pore zeolites shown in Scheme 1.1 .



Scheme 1.1 *Reactant selectivity*

Product selectivity

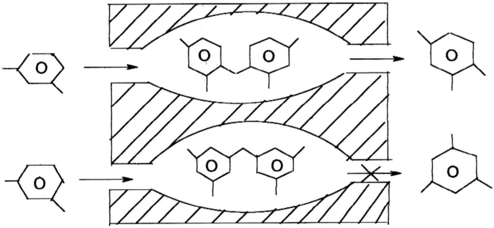
This takes place inside the inter-crystalline voids and is the result of discrete diffusivities of the reaction products in the pores of the zeolite crystals. Products of certain shapes are unable to diffuse out of the zeolite channels, and hence react further to form less bulky products that are able to diffuse out of the channels. A good example is the selective isomerisation of xylenes into a product mixture rich *p*-xylene, shown in Scheme 1.2.



Scheme 1.2 *Product selectivity*

Restricted transition state selectivity

In restricted transition state selectivity certain reactions are prevented because the transition state is too small for the space available inside the molecular sieve. An example is the selective isomerization of 2-phenylpropanal to phenylacetone rather than to propinophenone over an iron pentasil zeolite (25). Another example cited by Csiscery (24) concerns the selective formation of 1,2,5-trimethylbenzene in preference to the more stable 1,3,5-trimethylbenzene during the disproportionation of *m*-xylene, because the transition state leading to the latter is more space demanding than the one leading to the former as shown in Scheme -1.3.



Scheme 1.3 *Restricted transition state selectivity*

1.7 Applications of zeolites

The applications of zeolites in organic synthesis embraces both catalytic and non-catalytic uses.

1.7.1 Non-catalytic uses

Essentially, the applications here are based on the ion-exchange properties of the zeolites

1. **Detergents**

   Detergents are by far the largest application of zeolites. Zeolite A is the primary zeolite used, and acts as a sequestering agent to substitute phosphates.

2. **Wastewater treatment**

   Naturally available zeolites are used to remove ammonia and ammonium ions from waste water. Elintoptilolite is mainly used due to its availability and selectivity for ammonium ions over Na, Ca, Mg ions. Once used, the zeolites can be regenerated and cleaned for re-use.

3. **Separation of products**

The separation may be a result of differences in size and shape of the molecules to be separated or may due to different affinity of the zeolite towards the compounds to be separated. This includes applications such as drying agents in gas separation and in important processes like the formation of *p*-xylene and its isomers, and *n* - paraffins from branched paraffins .

4. **As reactant concentrator**

The porous zeolite material concentrates the reactants for the biomolecular reaction and the effect is comparable to the result obtained under high pressure conditions . An example is the cyclodimerisation of butadiene over large pore Cu-zeolites to yield vinylcyclohexene (26).

5. **Drying and purification of reactants**

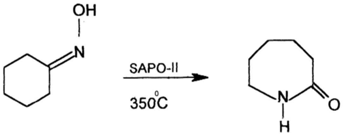
Zeolite A and Chabazite are used for drying liquids and gases. This contributes one of the early and well established applications of zeolites.

1.7.2 Catalytic uses

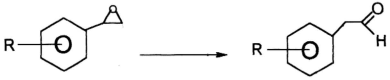
The following section gives a brief review of the use of zeolites as catalysts in organic synthesis.

1. Rearrangement reactions

i. ε- caprolactum, one of the most important fibre precursors is mainly prepared by a Beckmann rearrangement of cyclohexanone oxime. By using SAPO-11 at 350°C and atmospheric pressure, cyclohexanone oxime has been converted to ε- caprolactum with 95% selectivity and 98% conversion (27).



ii. The reaction of styrene oxide or alkyl-substituted or alkoxy substituted styrene-oxides using titanium zeolites in acetone or methanol at 30-100°C results in phenylacetaldehydes, with selectivities higher than 90% at conversions between 90 and 100% (28).



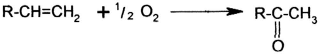
R= alkyl, aryl, arylalkyl, halogen, haloalkyl, alkoxy, alkylthio

2. Addition reactions to epoxides

Under mild conditions (25-100°C), the addition reaction between water and ethylene oxide or cyclohexene oxide on HZSM-5 gives the corresponding diols in yields of over 90% (29).

3. Oxidation reactions

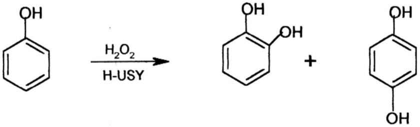
i. The oxidation of lower olefins to carbonyl compounds can be carried out in the gas phase on Pd/Cu-Y zeolites. It is essential to add water in order to ensure high selectivity and long catalyst service life. The rate of oxidation falls off as the olefin chain length increases (30,31).



$$R\text{-}CH{=}CH_2 + {}^1/_2\, O_2 \longrightarrow R\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3$$

ii. Oxidation reactions with hydrogen peroxide

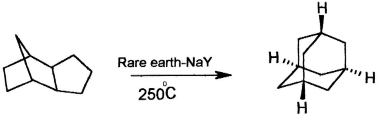
The hydroxylation of phenol can be carried out in the presence of aluminosilicates HZSM-5 or HZSM-11, doped with coinage metals or Fe, Co, and Ni or their homologs . The selectivity of hydroquinone was 99% (32).



4. Isomerization reactions

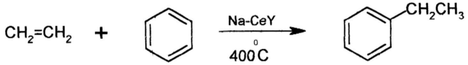
Skeletal isomerization reactions takes place under surprisingly mild conditions over strongly acidic zeolites. An interesting example is the skeletal rearrangement of tetrahedrodicyclopentadiene to adamantane, reported by

Honna *et al* (33) over rare earth exchanged Y zeolites at 250°C with 50% selectivity.



5. Substitution reactions with arenes

Alkylation

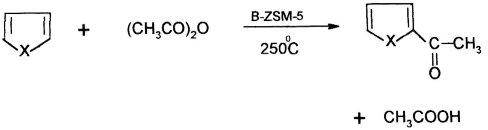


Ethylbenzene preparation by the Mobil-Badger process using Na-CeY at 400°C is an outstanding and technically proven example of the alkylation of aromatic compounds (34,35). Ethylbenzene is the source material for styrene which in turn is polymerised to polystyrene and/or copolymers.

Acylation

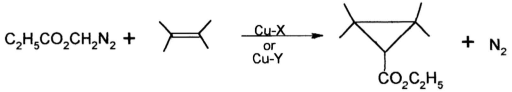
i. Acylation reactions of arenes using zeolites have gained industrial importance because of their high selectivity, especially for the production of anthraquinone from benzene and phthalic anhydride. At 350 to 550°C, Na-X zeolite loaded with 0.1% of Pt affords a product mixture containing 98% of anthraquinone and 2% of benzophenone (36).

ii. The reaction of thiophene with acetic anhydride at 250°C on a boron ZSM-5 zeolite leads to 2-acetyl thophene with 24% conversion and 99% selectivity (37).

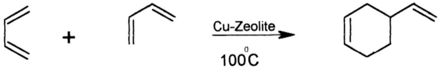


6. Cyclopropanation

Cyclopropanation of various olefins has been carried out by the application of NaCu-X zeolite as a catalyst for the decomposition of ethyldiazoacetate (38). Copper exchanged X and Y zeolites are active catalysts for the decomposition of diazocompounds leading to carbenoid intermediates.



7. Zeolite- catalysed cyclisations



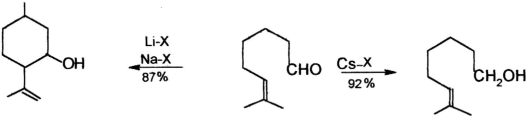
Maxwell *et al* (26) reported the highly selective cyclodimerisation of butadiene to vinylcyclohexene using a large pore Cu-zeolite at 100°C. In contrast, in homogeneous catalysis a mixture of cyclic dimers and trimers is normally obtained.

8. Condensation reactions

i. Aldol condensations - The preparation of unsaturated aldehydes from formaldehyde and aldehydes takes place with high selectivity using boron zeolite H-AMS-1B (39).

$$\text{R-CH}_2\text{CHO} + \text{HCHO} \longrightarrow \text{CH}_2\text{=CR-CHO} + \text{H}_2\text{O}$$

ii. Citronellal can react with isopropanol at 150°C on alkali-containing X-zeolites to give isopulegol or citronellol, depending on the metal used for doping (40).



1.8 Industrial applications based on shape- selective zeolite

Xylene isomerization

Xylene isomerization is an industrially important reaction, which converts the less useful *meta* isomer into *para-* and *ortho-*xylenes. The reaction has been investigated on various zeolites and is reported to occur in both liquid and vapour phase (41).

Dewaxing process

The use of zeolites here have made it possible to use a larger fraction of heavy portions of petroleum raw material as diesel and heating oils and to provide high grade lubricating oils with low energy expenditure. The zeolite removes selectively those paraffinic portions of heavy oil (42, 43).

Toluene disproportionation catalysis

Toluene disproportionation (i.e., transalkylation) is the conversion of two moles of toluene to one mole each of xylene and benzene. The ZSM-5 catalyst used here provides high product selectivity in the manufacture of xylene and benzene from toulene. Side product supression is achieved by the catalyst (44, 45).

Methanol to gasoline (MTG) process

ZSM-5 catalyst is capable of converting oxygen compounds such as alcohols, ketones, carboxylic acids, and esters to hydrocarbons as has been demonstrated by Chang *et al* (46). The reaction is carried out on ZSM-5 in the temperature range of 300 - 450^0C and a pressure of over 20 atmospheres.

1.9 Scope of the present study

In the present study cation-exchanged Y- and ZSM-5 zeolites were prepared and characterised. Their catalytic potential for alkylation of aniline and heterocycles such as pyridine, pyrrole and thiophene with *n*-propanol and/or isopropanol was investigated using a flow reactor. The effects of contact time (i.e. flow rate), temperature, and possible isomerisation of the alkylanilines and alkylheterocycles were investigated. The factors affecting zeolite deactivation were also studied along with the thermal stability of the heterocyclic substrates when contacted with the zeolites in the absence of the alcoholic reactant.

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