

**CATALYTIC REACTIONS OVER ZSM-5
ZEOLITES**

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COMPUTERISED



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Certified that the work incorporated in the thesis 'CATALYTIC REACTIONS OVER ZSM-5 ZEOLITES', submitted by Shri I. Balakrishnan was carried out under my supervision. Such material as has been obtained from other sources has been acknowledged in the thesis.

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A C K N O W L E D G E M E N T

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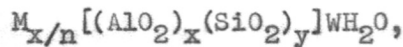
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CHAPTER I : GENERAL INTRODUCTION

1.1 INTRODUCTION

Zeolites are hydrated crystalline aluminosilicates having the unit cell formula



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

Although natural zeolites and their properties were known more than 200 years ago, their unique properties came to receive increasing attention only in 1940s. With the advent of x-ray crystallography, it soon became possible to synthesise several of these for use in commercial applications. Some of those synthesised were analogs of zeolite minerals and others not found in nature. In this way, zeolites type A, X, Y, mordenite, etc. were synthesised and characterised¹⁻³. The earliest uses of these zeolites were for adsorption and drying of gases, separation of gases and ion exchange. Soon their importance as catalysts for reactions was realized. They were thus first employed as cracking catalysts in 1964^{4,5}. The beginning and development of zeolites in the early period have been reviewed⁶. Some recent reviews illustrate the various applications of zeolites⁷⁻¹¹.

The subsequent success of zeolites as catalysts has been primarily due to the discovery of new zeolites - those containing high silica in late 1960s and early 1970s. The most important of these, ZSM-5, was discovered by Argauer and Landolt in 1972¹².

The generic name 'Pentasil Zeolites' has been used to refer to ZSM-5 type zeolites. The other members of the pentasil family are ZSM-8, ZSM-11 and Silicalite. Silicalite contains essentially no aluminium¹³.

1.2. GENERAL METHOD OF SYNTHESIS OF ZEOLITES

The reactants essentially consist of sources of oxides to provide a four component system $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$. Hydrothermal action on this system, which is thermodynamically unstable, provides several metastable phases. Each of these phases may be considered to represent a zeolite phase. It is therefore possible to have several zeolite phases depending upon the composition of the reactant mixture, the nature and period of hydrothermal treatment. Some general conditions for the synthesis of zeolites are the following¹⁴ :

- (1) Reactive starting materials such as freshly prepared coprecipitated gels or amorphous solids.
- (2) Relatively high pH introduced in the form of an alkali metal hydroxide or other strong base.

(3) Low temperature hydrothermal conditions with concurrent low autogeneous pressure at saturated water vapour pressure.

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

In nearly all the syntheses of zeolites prior to 1960, inorganic bases were used to supply the necessary alkalinity to the system. The introduction of organic bases in the synthesis systems, first by Barrer and Denny¹⁵, Barrer et al¹⁶ and later by Kerr¹⁷⁻²⁰ was one of the major events in zeolite chemistry and catalysis. This enabled synthesis of more siliceous materials culminating in the discovery of ZSM-5.

A : Synthesis of ZSM-5 zeolite

The synthesis system for ZSM-5 is $(\text{TPA})_2\text{O}-\text{M}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, where TPA stands for tetrapropyl ammonium and M for an alkali metal cation.

The synthesis is carried out by mixing aqueous solutions containing the organic cation and oxides of sodium, aluminium and silicon. These oxides are supplied by choosing appropriate reagents from among sodium silicate, sodium aluminate, aluminium salts, alumina, silica hydrosol, silicic acid, sodium hydroxide and tetrapropyl ammonium hydroxide or bromide.

A range of composition of reaction mixtures in terms of mole ratios of oxides described in a patent is given below²¹

<u>Ratio</u>	<u>Broad range</u>	<u>Preferred</u>
OH^-/SiO_2	10^{-8} -1.0	0.01-0.2
Na^+/SiO_2	0.1-1.5	0.1-0.6
$\text{Pr}_4\text{N}/\text{SiO}_2$	0.01-0.6	0.02-0.2
$\text{H}_2\text{O}/\text{SiO}_2$	5-200	15-50
Si/Al	6.2- ∞	10-1000
Al/Na	1.6-0	1.0-0.003
$\text{Na}_2\text{O}/(\text{TPA})_2\text{O}$	0.17-150	5-30

A typical temperature range for hydrothermal treatment is given as 373-473 K with a period lasting upto 6 hrs or 60 days¹³.

Crystallisation of ZSM-5 occurs in two stages - nucleation and crystal growth - and period and mechanism of these stages are strongly influenced by the synthesis variables and conditions used. Several experimental techniques are used to monitor the various events during nucleation and crystallisation. X-ray diffraction, infrared spectroscopy, thermogravimetry and differential thermal analysis, nuclear magnetic resonance and scanning electron micrograph are some of these.

B : Mechanism of formation of ZSM-5

Two mechanisms have been advanced for nucleation and subsequent crystallisation of ZSM-5. Zhdanov et al^{22,23} and Sand et al²⁴ have advanced a liquid phase ion transportation mechanism. Breck and Flanigen²⁵ and McNicol et al²⁶ have proposed a solid hydrogel phase transformation mechanism. Derouane et al²⁷ presented evidence for both and showed that the relative importance of each depended on synthesis variables and conditions. Both the mechanisms, however, recognise the role of the 'Clathrating-templating' effect of the organic cations during nucleation and crystallisation of the zeolite^{28,29}.

In the liquid phase ion transportation mechanism preferably applicable to synthesis systems containing polymeric silica (e.g. colloidal silica) as the source of the silica and aluminium-rich ingredients and (NaOH + TPAOH), the depolymerisation of silica to monomeric silicate ions is the slowest and rate determining step. The monomeric silicate ions either condense with aluminate species to yield aluminosilicate species, which exist either as a sol or a gel. The formation of the latter is favoured by presence of alkali cations. Some of the monomeric silicate ions may also interact with TPA⁺ ions and become stable nuclei for crystal growth. It is known that TPA⁺ ions order around themselves silica rich tetrahedral units preferentially in the formation of stable nuclei. Further depolymerisation gives silicate ions which are incorporated into the gel or the sol and also utilized in crystal growth but not in nucleation which is

slower than crystal growth. When all the silicate species are exhausted, dissolution of the sol/gel takes place to reestablish equilibrium throughout the process. The aluminosilicate species produced in solution are incorporated into the outer layers of the growing crystallites. The resulting crystallites are thus expected to have an inhomogeneous aluminium distribution with an aluminium deficient core surrounded by an aluminium rich layer terminating in the outer shell of intermediate aluminium content. Experimental evidence for such a scheme for crystallisation has been obtained²⁷.

In the solid hydrogel transfer mechanism preferably applicable to systems containing higher Si/Al ratio and monomeric silicates (sodium silicate), a hydrous silica alumina gel is rapidly formed. This gel includes within itself the structure directing TPA⁺ ions which intimately interact with numerous aluminosilicate ions and accelerate nucleation. Rapid nucleation, formation of large number of crystallites and a homogeneous radial distribution of aluminium in the crystallites are features of this mechanism having experimental support.

It has been shown that both mechanisms occur simultaneously³⁰. The relative importance of each depends on the alkali cations used, their radius, hydration number, structure-forming role towards water and salting out power. Morphology, size, chemical composition and aluminium distribution

in the crystallites would naturally depend on the relative importance of the two mechanisms in the synthesis procedure used³⁰.

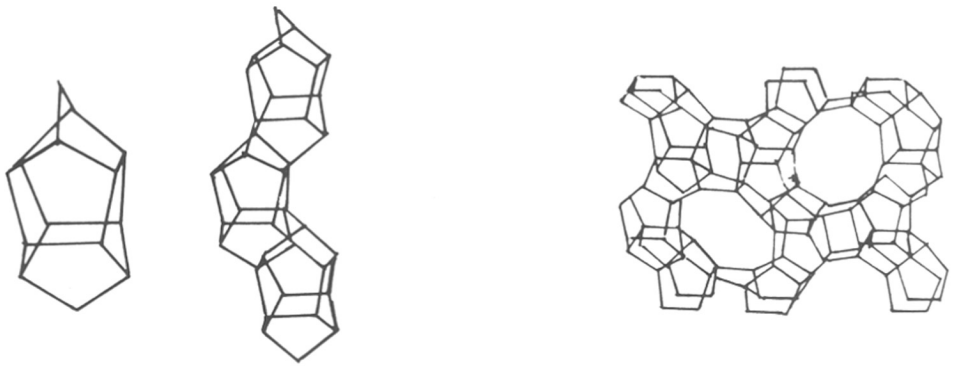
C : Kinetics of crystallisation

Several workers have studied the kinetics of crystallisation under different experimental conditions. Activation energy for nucleation and for crystallisation in certain synthesis systems has been determined³¹⁻³³. It has been shown that with other synthesis variables remaining constant, the rate of nucleation and crystallisation can be increased by increasing temperature³³, $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio^{34a}, or $(\text{TPA})_2\text{O}/\text{SiO}_2$ ratio³⁵.

1.3. STRUCTURE AND CHARACTERISATION OF ZSM-5 ZEOLITE

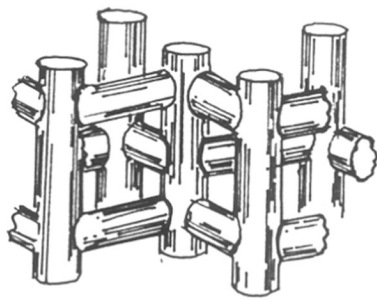
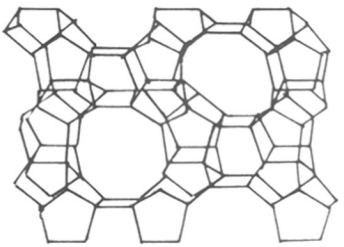
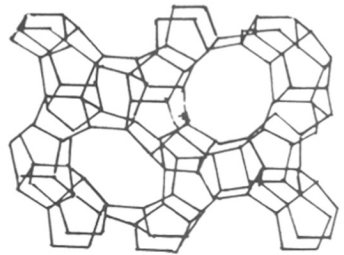
The structure of ZSM-5³⁶ zeolites consists of a novel configuration of linked tetrahedra which are bound together in groups consisting of 8 five-membered rings. The latter are then attached to each other through oxygen to form chains which are then connected to form planes (Fig. 1, a and b). These planes are then linked to give a 3 dimensional structure having the following features :

The structure contains two intersecting channel systems, defined by 10 membered ring openings. One of them is sinusoidal running parallel to the (001) plane and the other



a) CHARACTERISTIC CONFIGURATION OF ZSM-5
 b) LINKAGE OF ZSM-5

c) SKELETAL DIAGRAM OF 010 FACE
 d) SKELETAL DIAGRAM OF 100 FACE



e) CHANNEL STRUCTURE OF ZSM-5 ZEOLITE

FIG. 1 . STRUCTURE OF ZSM-5 ZEOLITE .

straight and parallel to (010) plane. The planes and the channel systems are shown in Fig. 1 c, d and e.

Sinusoidal channel has near circular opening having a diameter 5.4-5.6 Å and the straight channel has elliptical opening having diameter 5.2-5.8 Å. Silicalite which contains no aluminium has been shown to have a similar structure¹³.

It can thus be seen that the pore structure of ZSM-5 type zeolite has pore dimensions intermediate between those of the so-called 'large pore' zeolites (e.g. faujasite, dia. 7.4 Å) and small pore zeolite (e.g. zeolite type A) (erionite = 3.8 x 5.2 Å). This is an important feature of ZSM-5 structure having a bearing on its shape selective catalytic properties.

The crystallographic unit cell of ZSM-5 has the composition represented by the formula¹²



where n is generally less than 27. This value is less than that for X or Y type zeolites (Si/Al = 2.4) and gives the zeolite better thermal, hydrothermal and acid stability.

The crystallographic formula, as defined above, gives the number of aluminium atoms per unit cell, N_{Al} , from the relation, $N_{\text{Al}} = 96/(1 + R)$ where R is the ratio of the number of Si atoms to the number of Al atoms per unit cell.

The zeolite as-synthesised exhibits orthorhombic symmetry with lattice constants $a = 20.1 \text{ \AA}$, $b = 19.9 \text{ \AA}$ and $c = 13.4 \text{ \AA}$. However, transformation to monoclinic symmetry has been observed upon high temperature calcination and ion exchange³⁷.

A : Some structure related properties³⁸

(i) Sorption : In view of the intermediate size of the pore openings of the ZSM-5 zeolite, it can adsorb only small and medium size molecules. Larger molecules like o-xylene, m-xylene and 1,2,4,trimethyl benzene are adsorbed slowly indicating steric hindrance. Pentamethyl benzene and 1,3,5,trimethylbenzene (7.8 \AA) are essentially excluded.

(ii) Influence of channel dimensions on diffusivity and catalytic properties

Molecules like benzene and p-xylene whose kinetic dimensions are comparable to the channel dimensions, show high diffusivity and mobility in the zeolite. The diffusivity of p-xylene is 3 orders of magnitude greater than that of o- or m-xylene. It is therefore expected that the similarity of size of benzene and other aromatic molecules and the channel size of ZSM-5 type zeolite would have significant influence on the performance of this zeolite as catalyst for aromatic reactions. This is discussed separately in a subsequent section.

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

B : X-Ray Diffraction (XRD)

This is the most widely used technique to identify the zeolite species and also understand the kinetics and mechanism of zeolite crystallisation^{33,39}. Variations in the lattice parameters and framework symmetry^{40,41}, collapse of crystal structure and presence of alien phases are also detected by x-ray diffraction measurements.

XRD measurements have also been used to quantitatively estimate alumina content of ZSM-5 zeolites⁴². The spacings between $2\theta = 45^\circ$ and 45.5° are shown to vary with Si/Al ratio in the zeolites. This can be made use of to determine silica and alumina content in an unknown zeolite after due calibration using standard samples.

Presence of α -quartz in zeolites⁴³ can be identified and estimated using the characteristic peaks at $2\theta = 26.7$ and 20.9° in the XRD. Quartz is formed during the synthesis under unfavourable conditions.

C : Infrared Spectroscopy (IR)

It is a technique complementary to XRD. The zeolites have characteristic framework vibrations. The fundamental

vibrations of Al/SiO_4 tetrahedra are in the mid-infrared region ($200\text{-}1300\text{ cm}^{-1}$) and these have been used in conjunction with XRD to identify the zeolite structure. It is found that the main Si, Al-O band occurs at about 1100 cm^{-1} and is related to the Si/Al ratio in the zeolite framework⁴⁴. Crystallisation of the zeolite during synthesis can be studied by monitoring the changes in important IR vibrational frequencies and comparing these with those of the reactants⁴⁵. Also progressive incorporation of the organic cation into the zeolite lattice can also be studied by measuring the intensity of the peaks characteristic of the organic cation.

The IR technique has been extensively used to distinguish between different types of structural hydroxyl groups and those from other types of OH groups, for instance, an OH group attached to a cation in cation exchanged zeolite formed by hydrolysis. It has been shown⁴⁶ that OH groups characterised by absorption band at 3600 cm^{-1} and 3700 cm^{-1} correspond to strong and weak Brönsted acid sites respectively in zeolites.

Further use of IR is for detection and estimation of acid sites by pyridine adsorption and study of transformation of Brönsted to Lewis sites occurring at high temperatures or specified conditions. Ward⁴⁷ has reviewed its applications for study of zeolite surfaces and surface reactions.

D : Nuclear Magnetic Resonance (NMR)

Nagi et al⁴⁸ have demonstrated the use of ^{29}Si NMR spectra to obtain structural information for ZSM-5 zeolite. ^{29}Si NMR has been used to provide information as to the number, concentration and structure of the constituent species⁴⁹⁻⁵². It has also been used to study differences in the number, nature and distribution of ^{29}Si NMR detectable species in solution⁵³. A small intensity and broad resonance is sometimes observed at c.a. 103 ppm in the high resolution spectra of ZSM-zeolites⁴⁸. This has been shown to be due to the silanol groups associated with the presence of defects in the zeolite lattice. It has been shown⁵⁴ that the position of the ^{29}Si NMR resonance is not only dependent on the number of tetrahedral (T) atoms in the first cationic sphere of Si but also on the actual geometry of the T-O-T linkages. Barrer and Ibbitson⁵⁵ have used ^{13}C NMR technique to study adsorbate-adsorbent interaction.

^{27}Al NMR has been used to investigate mechanism of zeolite precipitation⁵⁶. Derouane et al⁵⁷ have used NMR to study the effect of pH and replacement of Na^+ by Cs^+ on the formation of precursors in synthesis of ZSM-5. It was concluded that the cations interact with aluminate species in the absence of silicate species and that this interaction is reduced by the presence of large amount of alkali cations.

E : Temperature Programmed Desorption (TPD)

TPD is another important technique to characterise and estimate acid sites in zeolites. The various techniques used for acidity measurements have been reviewed by Tanabe⁵⁸ and Jacobs⁵⁹.

Vedrine et al⁶⁰ and Auroux et al⁶¹ have reported acidity of ZSM-5 type zeolites. Anderson et al⁶² reported results on TPD of ammonia on NaZSM-5, HZSM-5 and silicalite and suggested that TPD maximum observed at 780 K are the probable sites used for hydrocarbon conversion processes.

The above study and a subsequent one by Borade et al⁶³ showed three desorption maxima in the TPD spectrum of ammonia on HZSM-5. Kerr and Mikovsky as quoted by Weisz et al⁶⁴, on the other hand, found only one TPD maximum occurring at 400°C. The molar amount of NH₃ eliminated due to this peak has been shown to be equal to the molar concentration of aluminium for a series of HZSM-5 samples.

Acidity measurements on ultrastable Y and ZSM-5 zeolites have been carried out by Jacobs et al⁶⁵ who characterised acid sites as weak, medium and strong according to the release of ammonia over a large temperature range. The amount of ammonia released above 753 K was considered to represent the very strong sites on HZSM-5.

Acidic properties of fresh and partially deactivated catalysts have been studied by Topsøe et al.⁴⁶. Three different states, α , β and γ corresponding to ranges of temperature of desorption of ammonia, 330-370 K, 423-473 K and 693-773 K were distinguishable for fresh catalyst. In the case of partially deactivated catalyst (the reaction of methanol to hydrocarbons at 645 K), the β state was absent and α state was strongly reduced. The activation energies for desorption of ammonia from α , β and γ states were found to be 84.6, 96.7 and 162.3 kJ mole⁻¹ respectively.

F : Microcalorimetry

Microcalorimetric techniques are also used to characterise the strength and distribution of acid sites in zeolites^{60,61,66-68,75,103}. Differential heats of sorption of ammonia at 416 K showed a more heterogeneous distribution of the strong sites in HZSM-5. The initial chemisorption energy showed strong dependence on the outgassing temperature. It has been shown that a higher activation temperature reduces the total number of acid sites and increases the strength of the strong acid sites. This has been attributed to dehydroxylation. Differential heats of adsorption for HZSM-5 with varying SiO₂/Al₂O₃ ratios indicated that the strength of strongest acid sites increases with SiO₂/Al₂O₃ ratio upto 17.5 and then falls on further increase. The total acidity falls continuously.

G : Thermogravimetry -
Differential Thermal Analysis (TG-DTA)

This technique has been used to provide information on the synthesis, mechanism²⁷ as well as thermal behaviour of the synthesised zeolites⁶⁹. Derouane et al²⁷ used this technique to identify the role of TPA ions in the syntheses of ZSM-5. It was shown that TPA is progressively incorporated into the zeolite framework during crystallisation and that one TPA entity is introduced per channel intersection during the process.

Various physico-chemical changes, occurring during the thermal treatment are reflected in the DTA/TG curves. Dehydration of adsorbed water, decomposition of occluded organic cations, dehydroxylation at higher temperatures to produce Lewis sites are accompanied by changes in these curves. In certain cases, it has been possible to identify the location of water molecules in hydrated zeolites from the splitting of the endothermal peak due to dehydration⁷⁰.

The measurements show that the thermal stability of zeolites increases with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio⁷¹ and that the crystal structure of ZSM-5 changes from orthorhombic to monoclinic by calcination⁷². Silicalite, the end member of the ZSM-5 type zeolites, is stable in air upto 1373 K and is converted to amorphous silica at 1573 K¹³.

Other techniques such as x-ray photoelectron spectroscopy and ESR have also been used for characterisation of zeolites. Vedrine et al⁷⁴ have used these techniques to show electron transfer between the metal and the support being responsible for enhanced catalytic activity of type Y zeolite supported Pt and Pd catalysts.

H : Sorption

Sorption measurements can be used in approximately estimating the size and shape of the pores in zeolites and compare them with those determined from x-ray crystallographic measurements⁶². They help in determining specific interactions between sorbate molecules and framework structure in the intracrystalline channels⁷⁶. Isosteric heats of adsorption reflect the nature and strength of such interactions^{38,76} between the sorbate molecules and the channel force field of the intercrystalline structure. Void volume in the zeolites can be measured by adsorption of molecules which have free access into the voids⁷⁷. In the case of ZSM-5, volume of hexane, heptane or p-xylene gives an estimate of the void volume of the zeolite³⁸. Derouane and Gabelica⁷⁸ and Valyon et al⁷⁹ have evaluated the channel length per unit cell of ZSM-5 from a knowledge of the sorbate molecules adsorbed per unit cell and their dimensions. From such a study it has been possible to show the ease of accessibility of different hydrocarbon molecules to different

channels during adsorption and diffusion. Gabelica et al⁸⁰ have studied adsorption of hexane to investigate influence of zeolite modification on sorption properties.

Barrer and coworkers^{81,82} have made numerous studies on sorption of various gases and vapours on synthetic zeolites and evaluated various thermodynamic properties such as entropy, heat and free energy of sorption. Sorption of various hydrocarbons on ZSM-5 type zeolites has been reported^{79,83}.

1.4. MOLECULAR SHAPE-SELECTIVE CATALYSIS

The concept of 'Molecular Shape-Selective Catalysis' was first used by Weisz and Frilette⁸⁴ to explain the difference in catalytic properties shown by conventional silica-alumina catalyst and zeolite type A and X. It is now used to signify various types of selectivities observed in zeolite based reactions^{73,100,159,160}. It can be developed in the light of the following considerations all of which emanate from the special structural characteristics of zeolites, ZSM-5, in the present study.

The framework structure of ZSM-5 consists of two types of intersecting channels. These have ring openings intermediate between those of faujasite and erionite as described earlier. The sinusoidal channel system has near circular pore openings ($5.4 \text{ \AA} \times 5.6 \text{ \AA}$) and the linear, elliptical pore openings ($5.2 \times 5.8 \text{ \AA}$). The total length of the pore system has been

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calculated to be 8.8 \AA as per unit cell, to which the elliptical channel system contributes 5.9 \AA ⁷⁸. Access to the channel intersections where the active sites are probably located⁷⁹ is controlled by these two pore systems.

A : Reactant Selectivity (RS)

Only those of the reactant molecules having dimensions appropriate to the channel openings of ZSM-5 can diffuse through the intracrystalline channels to undergo reaction. Such molecules include among the aliphatic hydrocarbons, in decreasing order of ease of entry, linear paraffins, isoparaffins and methyl substituted paraffins. Dimethyl paraffins and ethyl paraffins are least favoured and these pass over. Among the aromatic hydrocarbons, benzene, toluene and p-xylene are most favoured. Polyaromatics are strictly avoided. Some applications of the effects due to 'Reactant Selectivity' are in the cracking and hydrocracking reactions of hydrocarbons over ZSM-5^{85,86}, n-Paraffins are selectively cracked in these processes.

B : Product Selectivity (PS)

This manifests itself in the selective formation of products which can diffuse out faster from the intracrystalline channels. Other products, when formed, are converted to smaller molecules by subsequent reaction (e.g. equilibration) and these diffuse out. In certain cases they deactivate the catalysts by pore blocking.

Examples of product selectivity effects are found in the selective formation of p-xylene⁸⁷, conversion of methanol to hydrocarbons, etc.⁸⁸

The longer life of ZSM-5 type zeolites has been partly due to product selectivity effects. Such effects reduce the formation of bulkier molecules and thus limit the possibility of coking in ZSM-5⁸⁹ and 'reverse molecular size selectivity' which is one of the reasons for deactivation of other zeolite systems⁹⁰.

C : Transient State Selectivity (TSS)

Occurrence of certain reactions is prevented because the transient state complexes involved cannot be accommodated in the intracrystalline channels due to steric and spatial restrictions. The diffusion of reactants and products is not however affected. Complete absence of 1,2,3 and 1,3,5 trimethyl benzenes in a side reaction (transalkylation) in the isomerisation of xylenes over HZSM-5 is due to transient state selectivity effects⁸⁷. Another example is in the isomerisation of isobutane over HZSM-5 zeolite⁹¹. This reaction has been shown to take place by a bimolecular transition state mechanism over a variety of acidic catalysts to give propane and pentanes. In spite of the presence of stronger acid sites in HZSM-5, the reaction does not take place by a bimolecular mechanism on this catalyst. The lower rate and absence of pentane among the products indicates that the bimolecular transition state cannot be formed over HZSM-5.

TSS effects also limit coke formation and therefore deactivation of ZSM-5 catalyst.

D : Molecular Traffic Control (MTC)

Derouane and Gabelica⁷⁸ have proposed a novel effect of shape selectivity in ZSM-5 zeolite initially to account for absence of 'counter diffusion' effects in the conversion of methanol to hydrocarbons. The existence of two types of intersecting channels is supposed to favour the entry of the reactant molecules preferentially through one of the pore systems (sinusoidal, circular) and exit of the bulkier product molecules by the other (straight, elliptical). Evidence for this appears to come from hydrocarbon adsorption measurements⁹² which show that

- (1) The linear aliphatic hydrocarbons are adsorbed in both channel systems.
- (2) The isoaliphatics, due to steric hindrance, are adsorbed nearly completely only in the linear and elliptical channels, and
- (3) Aromatic compounds and methyl substituted aliphatics have a strong preference for adsorption and diffusion in the linear and elliptical channels.

Molecular traffic effects seem to show up in other reactions also (alkylation of benzene with ethylene, and toluene with methanol, over HZSM-11 catalyst). The presence of

MTC effect is reflected in the remarkable activity of ZSM-5 for alkylation of benzene with ethylene. Its absence is probably responsible for the greater activity of HZSM-11⁹³ for alkylation of toluene with methanol. This catalyst has only one kind of intersecting channel so that counter-diffusion of methanol against the aromatic product molecules diffusing outwards causes further ring alkylation to yield larger amounts of polyalkylbenzenes.

Sequential adsorption measurements carried out by Pope⁹⁴ do not provide support for the MTC concept, although the validity of such experimental data itself has been questioned⁹⁵

Other shape selectivity effects such as 'concentration effect' and 'molecular circulation effect' have been proposed to explain certain selectivity behaviour of type Y, erionite and offretite zeolites^{96,97}.

E : Diffusion

Diffusion of molecules in shape selective catalysts is an important aspect that determines the activity of the catalysts for reaction and selectivity of the products. A certain type of molecule having a high diffusivity in the catalyst may react faster than another. Similarly, the faster rate of diffusion of a product may increase its selectivity among the products by shifting the equilibrium towards its formation within the intracrystalline space. Those with lower diffusivities may

undergo further reaction. The size and shape of diffusing molecules strongly influence their diffusivity in the 'configuration regime' where these properties (the size and shape of the molecules) have to be continuously matched with those of the pores for diffusion to take place⁹². Influence of diffusivity on product selectivity has been dramatically brought out in a study of n-C₂₂H₄₆ cracking over erionite catalyst⁹⁸.

F : Deactivation of ZSM-5 zeolites

ZSM-5 zeolites show high resistance to coking and aging compared to large pore zeolites. Its unique structural features are responsible for this. Product selectivity, transient state selectivity and molecular traffic control effects minimise or prevent formation of bulky molecules in the channel intersections via steric and spatial restrictions.

There have been several studies on coking and aging of the zeolite catalysts. Venuto⁹⁰ showed that in zeolites having cavities or cages larger than the opening to the crystal exterior (e.g. erionite), coke may be trapped in these cages. As the trapped coke cannot escape, it may cause deactivation and site blockage. It was described as deactivation by 'reverse molecular selectivity'.

From a study of various reactions over zeolites of different pore structures, Rollmann⁸⁹ concluded that intracrystalline coking is a shape selective reaction directly

related to zeolite pore structure. It was also demonstrated⁹⁹ that the differences in the coke yield for same reactions between 10-membered (ZSM-5) and 12-membered (Y type zeolite) zeolites are not the result of differing basic origins for coke. These differences must arise from structural constraints on the reactions of the same intermediates (TSS) in the formation of the coke in the two cases. Dejaifve et al⁶⁷ have provided experimental evidence to show that coking and deactivation are determined by structural properties. According to them, coking in HZSM-5 is only over the external surface. The coke precursors synthesised in the channel intersections diffuse out and these polymerise on the external surface to form coke. This coke on the external surface may deactivate the catalyst and modify selectivity of the products by partial blockage of the pore openings.

The high silica/alumina ratio of HZSM-5 is also partly responsible for its resistance to coking and aging.

1.5. CATALYTIC REACTIONS OVER ZSM-5 ZEOLITES

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

- (i) Conversion of methanol and other oxygenated compounds to hydrocarbons.
- (ii) Aromatic reactions like (a) isomerisation of xylene, (b) alkylation of aromatics, and (c) disproportionation of toluene.
- (iii) Other hydrocarbon reactions like cracking, hydrocracking, dewaxing, etc.

Table 1.1⁷³ lists some of the industrially important reactions based on shape selective zeolites.

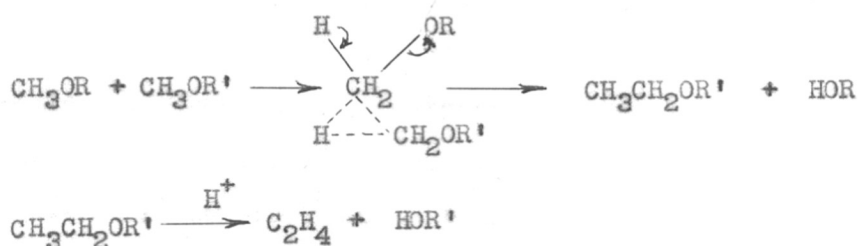
A : Conversion of methanol over HZSM-5

One of the earliest reactions to be studied was the conversion of methanol to hydrocarbons. This provides an alternate route for the conversion of coal and other non-petroleum carbon materials to useful hydrocarbons. It has also generated great academic interest for providing a satisfactory reaction mechanism to account for the various products and the formation of the first C-C bond during the reaction.

Chang and Silvestry¹⁰² in the first study of this reaction, proposed a carbene mechanism for the formation of light olefins believed to be intermediates in the reaction. A concerted bimolecular reaction between a methylene donor (stabilised by the zeolite crystal field) and an acceptor (methanol or DME) and subsequent protolysis yields C_2H_4 :

TABLE - 1.1INDUSTRIAL PROCESSES BASED ON SHAPE SELECTIVE ZEOLITES⁷³

Process	Objective	Major chemical/process characteristics
Selectoforming	Octane number increase in gasoline; LPG production.	Selective n-paraffin cracking.
M-Forming	High yield; octane number increase in gasoline.	Cracking depending on degree of branching; aromatics alkylation by cracked fragments.
Dewaxing	Light fuel from heavy fuel oil; lube oils with low temperature pour point.	Cracking of high molecular weight n- and mono-methyl paraffins.
Xylene isomerisation	High yield para-xylene production.	High throughput, long cycle life; suppression of side reactions.
Ethyl benzene	High yield ethyl benzene production eliminate $AlCl_3$ handling	
Toluene disproportionation	Benzene and xylenes from toluene	
Methanol-to-gasoline	Methanol (from coal or natural gas) conversion to high grade gasoline	Synthesis of hydrocarbons only, restricted to gasoline range (C_4 to C_{10}) including aromatics.



In the above equation $\text{R}, \text{R}' = \text{alkyl or H.}$

The possibility of carbene addition to the double bond of the initially formed olefin (C_2H_4) was suggested¹⁰². Such an addition and subsequent rapid isomerisation of the labile cyclopropane intermediate would give propene. Butenes could be formed from propylene in the same manner.

Derouane et al^{88,104} preferred a carbenium ion mechanism according to which methanol is first dehydrated into DME (dimethyl ether) and then the latter converted into a carbenium ion like C_2 -surface species. This species can either desorb C_2H_4 or react with methanol (or DME) to yield C_3 and C_4 olefins. This mechanism was able to explain⁸⁸ (a) the formation of traces of methyl ethyl ether observed in the earlier study¹⁰², (b) the higher yield of branched hydrocarbons on the basis of stability differences of the carbenium ions and (c) similarity of product distribution for conversion of methanol and ethanol. C_2 and C_3 olefins were thus considered to be the primary intermediates according to this mechanism as well.

According to Anderson et al⁶² the primary intermediates in the conversion of methanol are C₃ and C₄ olefin residues. They provided evidence to show this by noting the poor activity for the conversion of C₂H₄ and C₂H₅-OH over the catalyst in contrast to the high activity of C₃H₆.

Additional evidence for the observation came from studies on alkylation of benzene with methanol and deuterated methanol¹³⁷.

Chen and Reagan¹⁰⁶ studied the conversion of methanol and observed that it is autocatalytic. The rate of higher olefin formation was higher than the rate of initial formation of ethylene. This was attributed to alkylation of olefins with methanol/DME to produce higher olefins, ethylene producing propylene, propylene producing butenes and so on. The autocatalytic nature of the reaction has been confirmed¹¹⁹.

There were several studies aimed at identifying the primary olefins produced in the reaction. Sorption and conversion reactions¹⁰⁷⁻¹⁰⁹ of light olefins were studied at different temperatures using several techniques such as IR, ¹³CNMR, TPD and Mass Spectrometry. These have shown that both ethylene and propylene could act as intermediates in the conversion of methanol over ZSM-5.

Some recent studies¹¹⁰⁻¹¹² have confirmed the formation of C₂H₄ as the initial olefin. The reaction was carried out at

very low conversions and nearly 100% selectivity for ethylene was obtained in accordance with the calculated values for the thermodynamic equilibrium distribution at low conversions. The earlier confusion regarding the primary olefins was attributed to "the neglect of thermodynamic and autocatalytic contribution, i.e. non-recognition of the location of the reaction path, where experimental observations are made¹¹¹."

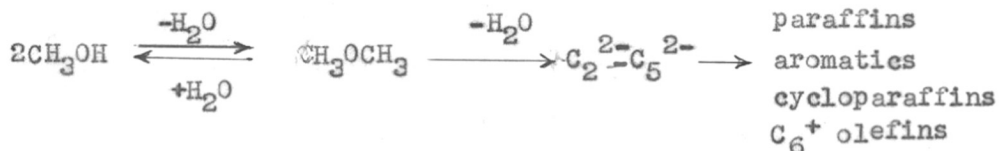
(1) Formation of the C-C bond

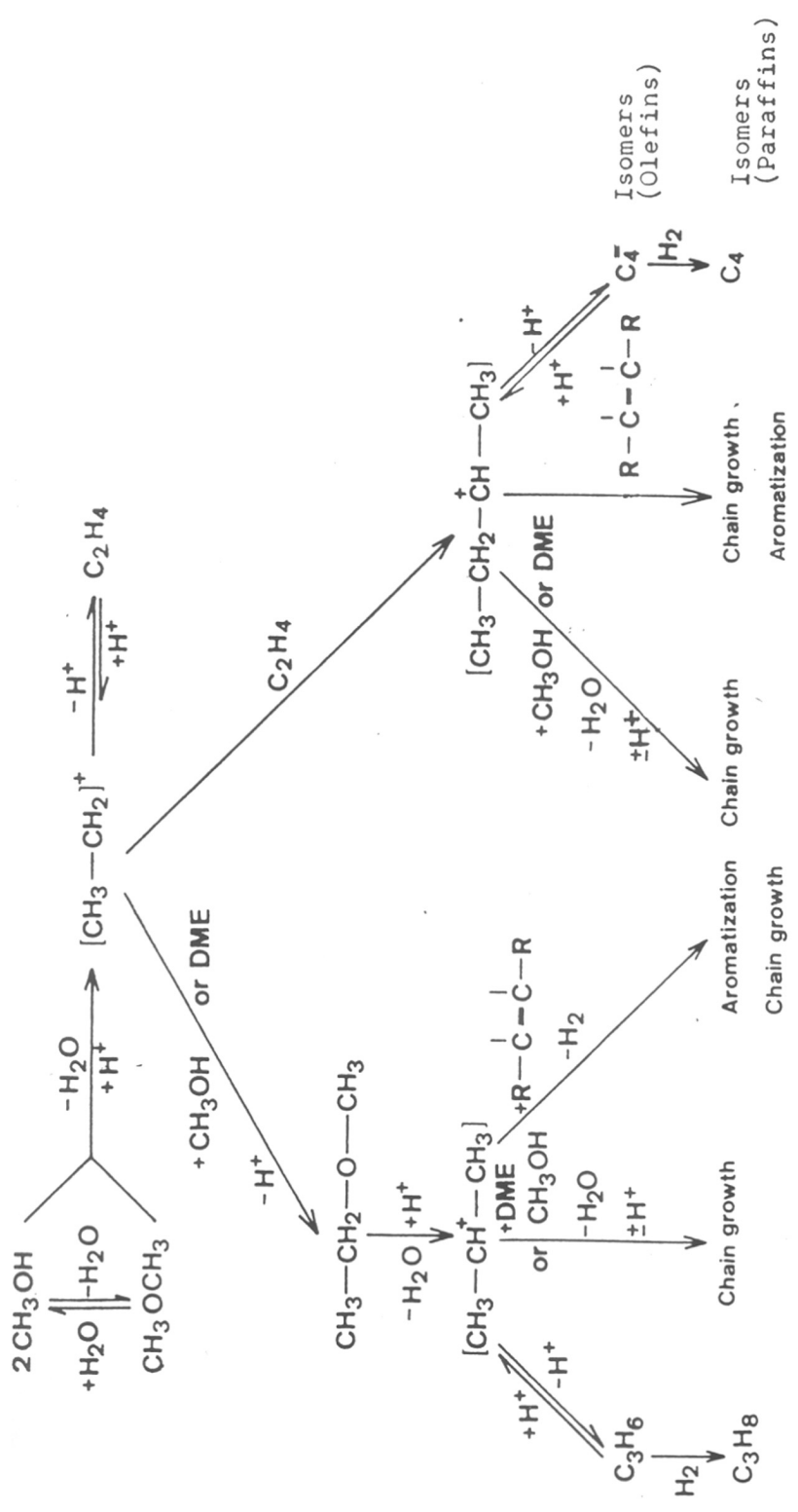
Several mechanisms have been proposed to explain the formation of the first C-C bond. The first proposed by Chang and Silvestry¹⁰² involves the concerted insertion of 'carbene' or carbenoid species from one methanol or DME into the C-H bond of another¹¹¹. The second due to Derouane et al^{88,104} involves formation of a carbenium ion (or a C₂ adsorbed species) which gives ethylene or reacts with methanol/DME to yield higher olefins. VanderBerg et al¹¹³ and Kaeding and Butter¹¹⁴ proposed a mechanism involving oxonium ions, which has probably wider acceptance^{115,117}. In this mechanism, an intermediate methyl ethyl oxonium ion formed through a sequence of steps eliminates methanol in presence of water to give C₂H₄ or react with methanol/DME eventually yielding propylene¹¹³. Another mechanism involves formation of highly reactive CH₃⁺ (or a strongly polarised

methoxy group) from surface methoxy groups originating in Si-OH sites¹¹⁸. It attacks methanol/DME to give C₂H₄. Subsequent attack on C₂H₄ yields C₃H₆ and on C₃H₆ yields C₄H₈ etc. The different mechanisms are shown schematically in the following pages.

(ii) Formation of higher hydrocarbons

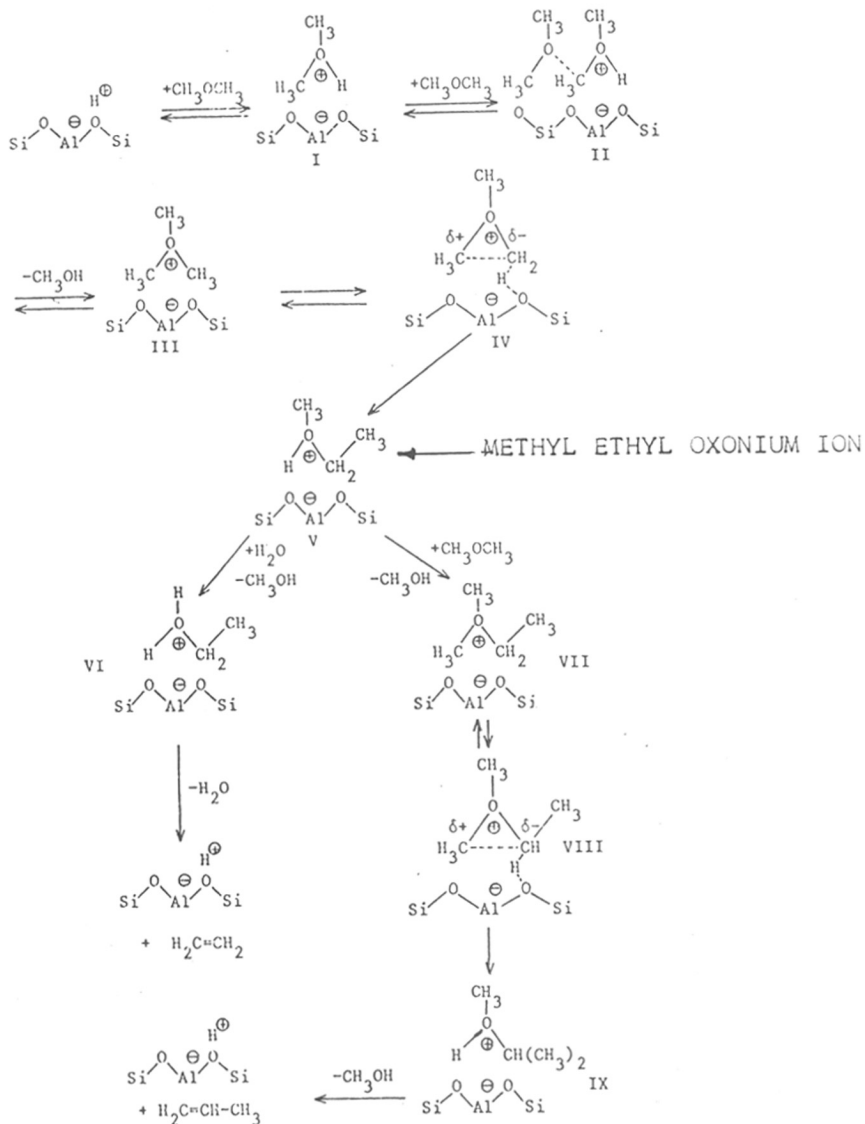
The primary olefins produced in the reaction are believed to be ethylene and propylene. The higher olefins are formed from these by alkylation with methanol/DME and oligomerisation catalysed by the Brönsted acid sites. The olefins undergo various acid catalysed reactions like isomerisation, cyclisation (to cycloparaffins) dehydrogenation (to aromatics) and hydrogenation (to paraffins)^{120,121}. The aromatics produced also undergo reactions¹²¹ such as isomerisation, alkylation, disproportionation, transalkylation, etc. to give rise to the final product distribution. The following general reaction path can be used to represent the conversion of methanol to hydrocarbons¹²².



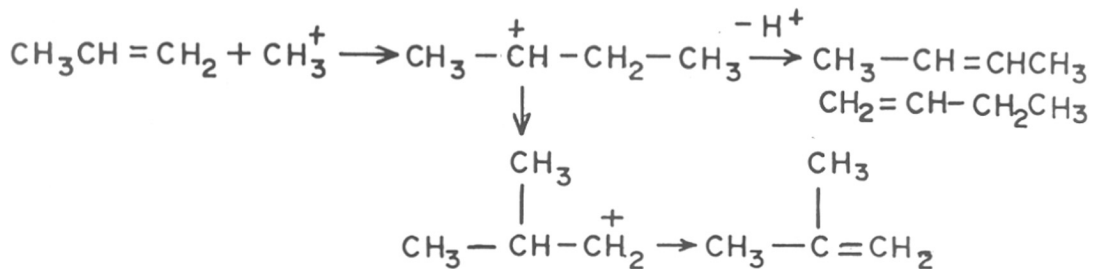
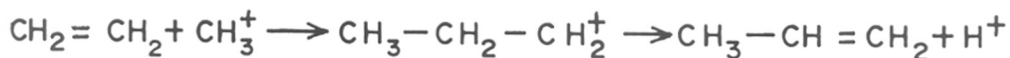
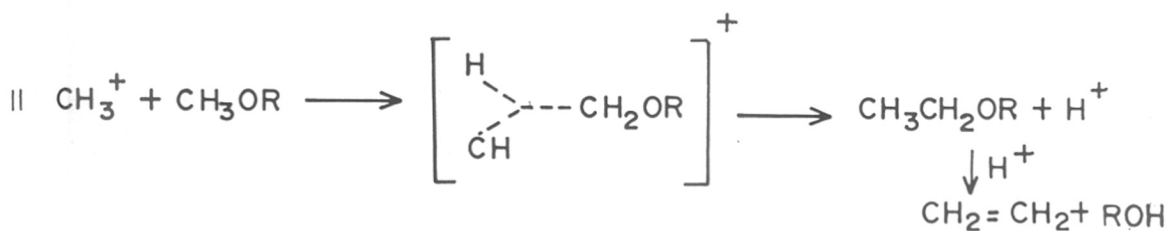
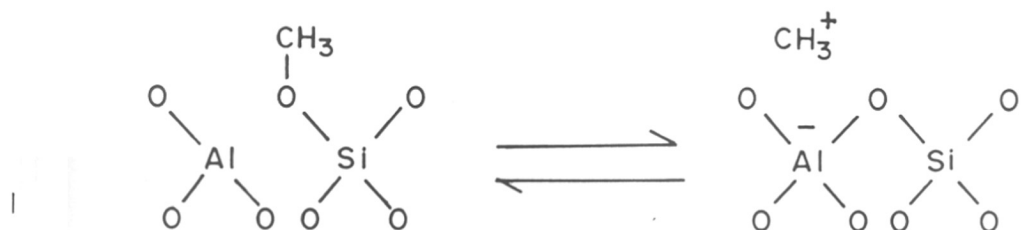


SCHEME (Ref. 104)

Mechanism of formation of primary olefins



Mechanism of formation of the first C - C bond and primary olefins. (Ref. 113).



SCHEME (Ref 118)

MECHANISM OF FORMATION OF THE FIRST C-C BOND AND PRIMARY OLEFINS.

As discussed in Section 1.4, shape selectivity characteristics and diffusion influence the type of products formed during the reaction. In the case of methanol, for instance, molecules containing upto 10-11 carbon atoms are only formed. Other features and product distribution for this reaction have been accounted for and summarised by Derouane⁹².

The methanol reaction has been studied with different objectives. Some of the studies for elucidation of reaction mechanism have been already reviewed. Others deal with evolving a kinetic model for the reaction^{124,125}, product distribution under different catalyst/process parameters^{123,126-128}, comparison of activity and product distribution with different catalysts^{129,130} and process applications of the reaction¹³¹⁻¹³⁴.

In view of the importance of the light olefins, especially ethylene and propylene, several researchers have tried to curtail/terminate their subsequent reaction by varying the reaction or catalyst parameters or both. These works would be reviewed briefly in appropriate places in the context of the present work.

B : Mechanism of conversion of ethanol and ethylene

Conversion of ethanol⁸⁸ and ethylene¹⁰⁵ have been studied in some cases for a comparison with the methanol

reaction. Derouane et al¹⁰⁴ have postulated that the initial step in the formation of aromatics is a 'concerted' cycloaddition of an olefin and a carbenium ion. The growth of the hydrocarbon chain has been shown to occur by a C_1 step addition showing the existence of cracking during the enlargement of the hydrocarbon^{104,105}.

Similarity of products in methanol and ethanol conversions at high temperatures has been reported^{88,134}. The minor differences could be attributed to reactions involving aromatics. For instance, the alkylation of aromatics with methanol is an important reaction while similar reactions with C_2H_4 or C_2H_5OH are less important¹³⁴. Also polyethyl substituted aromatics are negligible in reaction with C_2H_4 or C_2H_5OH .

C : Some aromatic reactions

Some industrially important aromatic processes are alkylation of benzene with ethylene to produce ethyl benzene, (Mobil Badger Process¹³⁵), disproportionation and alkylation of toluene to produce xylenes^{136, 37}, and isomerisation of xylenes²⁷. ZSM-5 based catalysts have been found to be superior to conventional silica-alumina catalysts and other zeolite based catalysts for these reactions.

Xylenes are produced by catalytic reforming. The C_8 aromatic cuts from the distillate of reformates contain xylenes in their equilibrium mixture and ethyl benzene in larger amounts.

The most important of these aromatics, para-xylene is the key component used for the production of DMT for the synthetic fibre industry. It is usually separated by the crystallisation process with about 60-70% efficiency. The residual cut is further isomerised to enrich p-xylene content. A bifunctional noble metal acid catalyst is used for this reaction. The noble metal has a hydrogenating function to bring about hydrocracking of EB and the acid support providing the active sites required for the reaction. ZSM-5 based supports have replaced the conventional or zeolite-based supports used for this purpose.

Xylenes can also be produced by alkylation of toluene with methanol or by disproportionation of toluene to benzene and xylenes. The product of interest in these reactions is p-xylene. The superior performance of the ZSM-5 compared to other catalysts stands out. As discussed in Section 1.4 this is due to its shape-selective properties which reduce or prevent side reactions like transalkylation (via TSS) and favour high selectivity to p-xylene (via PS). P-xylene produced diffuses out of the pores rapidly (its diffusion coefficient is about 1000 times greater than that of m- or o-xylene³⁸). M or o-xylene produced is further isomerised to p-xylene towards the thermodynamic equilibrium distribution which is not obtained inside the pores. Product selectivity and transient state selectivity also ensure stable activity

of the zeolite by preventing formation of polyalkyl aromatics which may block pores or cause coke formation.

Chen et al⁸⁷ and Kaeding et al¹³⁸⁻¹⁴⁰ have studied the above reactions. Several patents¹³⁶ claim para-selectivity as high as 98% in the alkylation of toluene with methanol. Such high selectivity has been made possible by increasing the diffusional constraints within the channels geometrically or chemically or both. Diffusional constraints, for example, are brought about by using larger crystals⁸⁷ which provide longer diffusion path for m- and o-xylene. This leads to further isomerisation of these. Chemical modifications enhance selectivity in two ways. They eliminate external surface reactions by poisoning the active sites for side reactions^{138,141,142}. They may reduce the size of pore apertures and channels^{75,155} which would further hinder the diffusion of m- and o-xylenes via steric effects and also poison the undesirable active sites within channels responsible for side reactions^{138,141,153}.

Three mechanisms have been proposed to account for aromatic hydrocarbon isomerisation¹²⁰, an intramolecular mechanism, an intermolecular mechanism via transalkylation products and a dealkylation-alkylation mechanism. The intramolecular mechanism has been favoured^{140,143-146} on account of the severe restrictions on the formation of a bimolecular transition state within the ZSM-5 pores.

Xylene isomerisation has been shown to be a unimolecular process¹⁴³ catalysed by Brönsted acid sites^{147a} rather than Lewis acid sites.

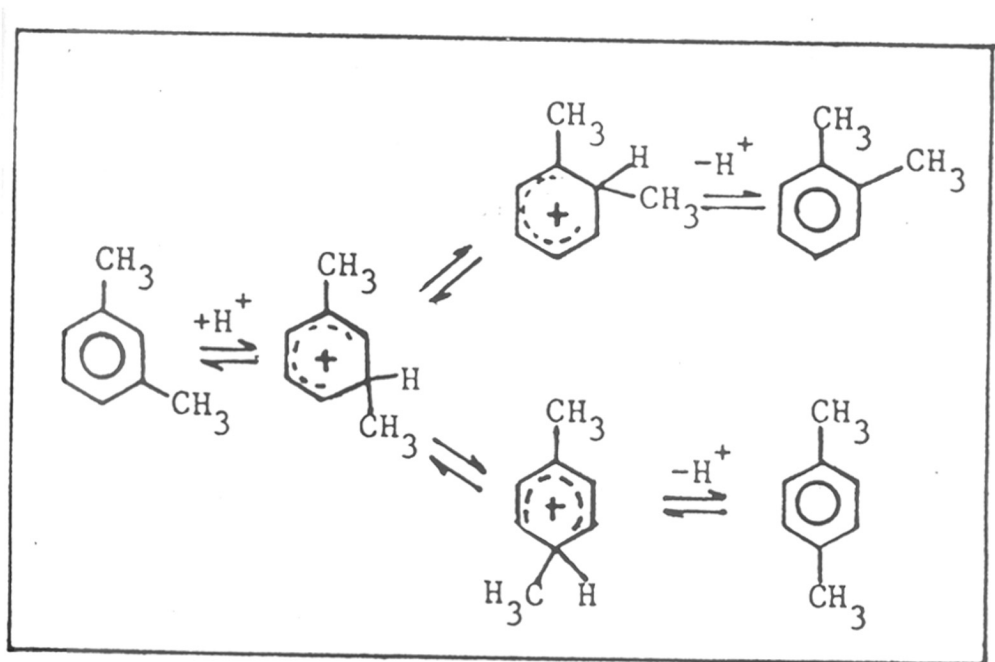
The mechanism is shown in the following page. Meisel et al^{147b} has measured the ratio of the rate constants for isomerisation and disproportionation on different zeolite catalysts. This is shown in Table 1.2.

TABLE 1.2

ISOMERISATION VS DISPROPORTIONATION^{147b}

<u>Catalyst</u>	<u>k_i/k_d</u>
Faujasite, Y	10-20
Mordenite	70
ZSM-5	1000

Wie^{148a} has formulated a mathematical theory for p-xylene selectivity in zeolite catalysts which shows a decline of such selectivity with increase in conversion. Molecular orbital studies on the mechanism of catalytic isomerisation of xylene have been reported¹⁴⁹. The active sites for xylene isomerisation have been reported as strongest sites in HZSM-5 zeolite¹⁵⁰. An attempt to correlate sorption and catalytic properties has been reported¹⁵¹. It is further reported that by proper selection of synthesis conditions and variables, catalysts which show

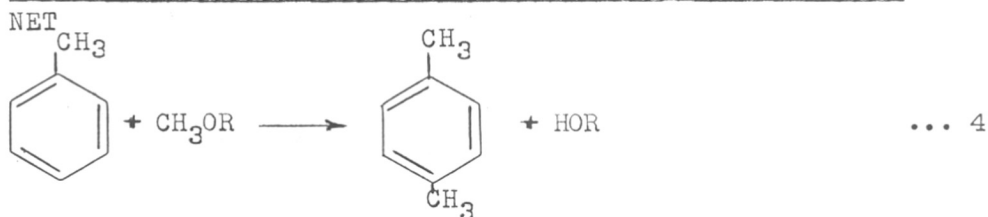
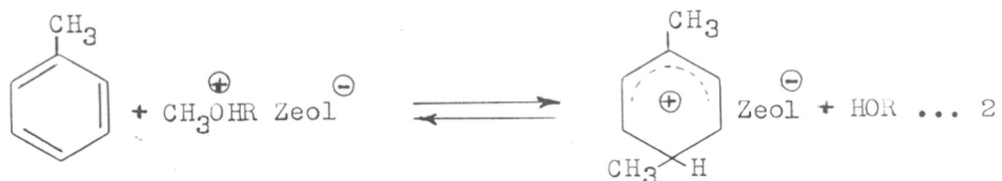
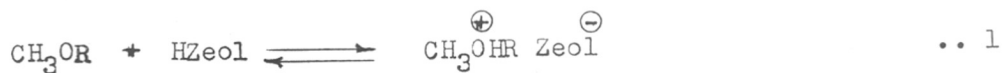


Intramolecular mechanism of xylene isomerization

high selectivity to p-xylene can be synthesised¹⁵¹. The effect of Si/Al ratio, degree of cation exchange, and poisoning of strong acid sites has been reported¹⁵². The poisoning effect shows that the comparative strength of acid sites required for the different reactions are in increasing orders of strength as follows : Iso < Dealkyl < Disp. Namba et al¹⁵³ report results on the use of quino- line and its derivatives of different sizes to poison HZSM-5 catalyst and compare the effects of such poisoning on p-xylene isomerisation. HZSM-5 and ferrisilicates have been compared for activity and selectivity for xylene isomerisation¹⁵⁴.

Comparatively few studies have been reported on the alkylation and disproportionation reactions of toluene over HZSM-5 zeolites. Kaeding et al¹³⁸ have briefly reviewed the importance of zeolites as alkylation catalysts and used shape-selective properties of modified ZSM-5 zeolites to increase para-xylene selectivity^{139,140}. The mechanism of alkylation of toluene is via electrophilic substitution. Besides, the xylene isomers, other polyalkylated products are also produced. The mechanism is shown in the following page. Isomerisation and transalkylation also take place in addition to the above reactions. Conversion of methanol itself has also to be considered when it is in large excess among the reactants.

Haag et al¹⁵⁹ have recently drawn attention to the importance of shape-selective catalysts in aromatic processing.



R = H or CH₃

Scheme for alkylation of toluene. (Ref. 138).

Csicsery¹⁶⁰ has stressed its application in relation to synthesis of p-xylene by alkylation and disproportionation of toluene as well as by isomerisation of xylene.

1.6. SCOPE OF THE PRESENT WORK

The present work was undertaken with the following objectives :

1. To synthesise and characterise ZSM-5 type zeolites and study their activity and selectivity to hydrocarbons, especially aromatics in the conversion of methanol, ethanol and ethylene.
2. To study influence of temperature, WHSV, $\text{SiO}_2/\text{Al}_2\text{O}_3$ and dilution on product distribution in the conversion of methanol.
3. To prepare modified ZSM-5 type zeolites (by impregnation with phosphorous and boron) for conversion of methanol to olefins and correlate their activity with their acidity and sorption properties, and
4. To prepare and characterise catalysts of the ZSM-5 type by substitution of tetrahedral aluminium with iron, boron and lanthanum and study their catalytic properties in regard to conversion of methanol to olefins (MTO) and some aromatic reactions - isomerisation of xylene and alkylation and disproportionation of toluene - for a comparison with those of HZSM-5. The effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio on the above aromatic reactions has also been investigated.

CHAPTER II : SYNTHESIS AND CHARACTERIZATION OF ZSM-5
TYPE ZEOLITES FOR ALCOHOL REACTIONS

2.1. SYNTHESIS OF ZSM-5

The synthesis of high silica ZSM-5 type zeolite was carried out according to directions reported in patent¹².

The following raw materials were used for synthesis :

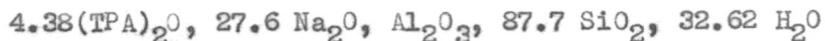
Sodium silicate : Composition (wt.%) $\text{SiO}_2 = 27.2$;
 $\text{Na}_2\text{O} = 8.4$; and water = 64.4.

Aluminium sulphate : $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ (E. Merck).

Sulphuric acid : (wt.%) 98 (BDH Analytical grade).

Tetrapropyl ammonium bromide or triethyl n-propyl ammonium bromide (TPA Fluka or TEPA synthesised for the present study).

Appropriate amounts of aluminium sulphate and sulphuric acid were dissolved in distilled water to yield solution A. A calculated quantity of TPABr (or TEPABr) was added to a solution of sodium silicate of required strength to yield solution B. The two solutions A and B were then mixed in a stainless steel reactor vessel (cap. 250 ml) with continuous stirring to form a free flowing gel which had the molar composition



The reactor was then closed and heated to the desired temperature ($180 \pm 5^\circ\text{C}$). It was held at this temperature under the auto-genous pressure for about 24 hours depending upon the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the gel mix. The reactor was cooled after completion of crystallisation and contents were filtered and washed with water till the filtrate was free of the anion.

The residue was dried in a static air oven at 120°C overnight and cooled to room temperature. A part of the sample was used to determine crystallinity by XRD and thermochemical properties. The remaining sample was slowly heated to 550°C and held at this temperature for 8 hours to decompose the intracrystalline organic (TPA or TEPA) base. The sample (NaZSM-5) was then cooled and kept over saturated ammonium chloride solution.

XRD and IR spectroscopic measurements confirmed the identity of the sample as NaZSM-5 as would be shown shortly (Section 2.3).

By repeated exchange with 5 M ammonium chloride solution under reflux at 95°C on waterbath, sodium ions in NaZSM-5 were exchanged with NH_4^+ ions. The sample was then dried at 120°C and calcined at 550°C to convert NH_4 ZSM-5 to the H^+ form (HZSM-5). It was then cooled and kept over saturated NH_4Cl solution.

Three samples containing different $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios were prepared in the above manner. They were analysed by conventional wet chemical methods for estimation of Al and Si. Residual sodium was determined by flamephotometry.

2.2. MODIFIED ZSM-5 ZEOLITES

A : Boron impregnated HZSM-5 (BHZSM-5)

This sample was prepared by impregnating NH_4 ZSM-5 sample with appropriate quantity of boric acid in aqueous

solution. The well homogenised slurry was slowly evaporated at 90°C with stirring, dried at 120°C and calcined at 550°C for several hours. The sample was kept over saturated NH_4Cl solution after cooling.

B : Phosphorous impregnated HZSM-5 (PHZSM-5)

The same procedure for preparation of BHZSM-5 was followed except that boric acid was replaced with appropriate quantities of phosphoric acid in aqueous solution.

2.3. C H A R A C T E R I S A T I O N

A : X-ray Diffraction (XRD)

The x-ray diffractograms were recorded using Philips 1700 X-Ray diffractometer with Ni filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) in the range $2\theta = 6$ to 40° .

Results and Discussion :

The interplanar spacings 'd' in \AA obtained from values of 2θ are shown in Table 2.1 and Fig. 2.1. The intense peaks occurring at $2\theta = 7.9 \pm 0.1$ and 23 ± 0.22 are characteristic of ZSM-5 type zeolite. The values of d and the relative intensities of peaks with respect to the most intense peaks at $2\theta = 23^{\circ}$ are in agreement with those reported in the literature¹².

An increase in the intensity of the characteristic peaks and appearance of a doublet at $2\theta = 24.2^{\circ}$ and 24.32°

TABLE - 2.1

LATTICE SPACING, (d), AND RELATIVE INTENSITY
 (I/I₀) VALUES FOR NaZSM-5

2θ	Interplanar spacing 'd' Å (obs.)	Interplanar spacing 'd' Å * ₁₂	Relative intensity (obs) I/I ₀	Relative intensity * ₁₂ I/I ₀
7.90	11.15	11.10 ± 0.2	62.3	S
8.80	10.04	10.0 ± 0.2	45.4	S
11.90	6.70	-	7.0	-
13.90	6.36	6.3 ± 0.1	13.8	W
14.80	5.99	6.04 ± 0.1	15.4	W
15.55	5.71		10.8	-
15.90	5.57	5.56 ± 0.1	13.8	W
19.20	4.62	4.60 ± 0.08	7.7	W
20.80	4.27	4.25 ± 0.08	13.8	W
22.12	4.02	-	6.2	-
23.00	3.86	3.85 ± 0.07	100.0	VS
23.9	3.72	3.71 ± 0.05	52.3	S
24.41	3.64	-	30.8	-
29.30	3.04	3.04 ± 0.03	12.3	W
29.90	2.99	2.99 ± 0.02	16.9	W
30.39	2.94	2.94 ± 0.02	7.7	W

* Ref. 12

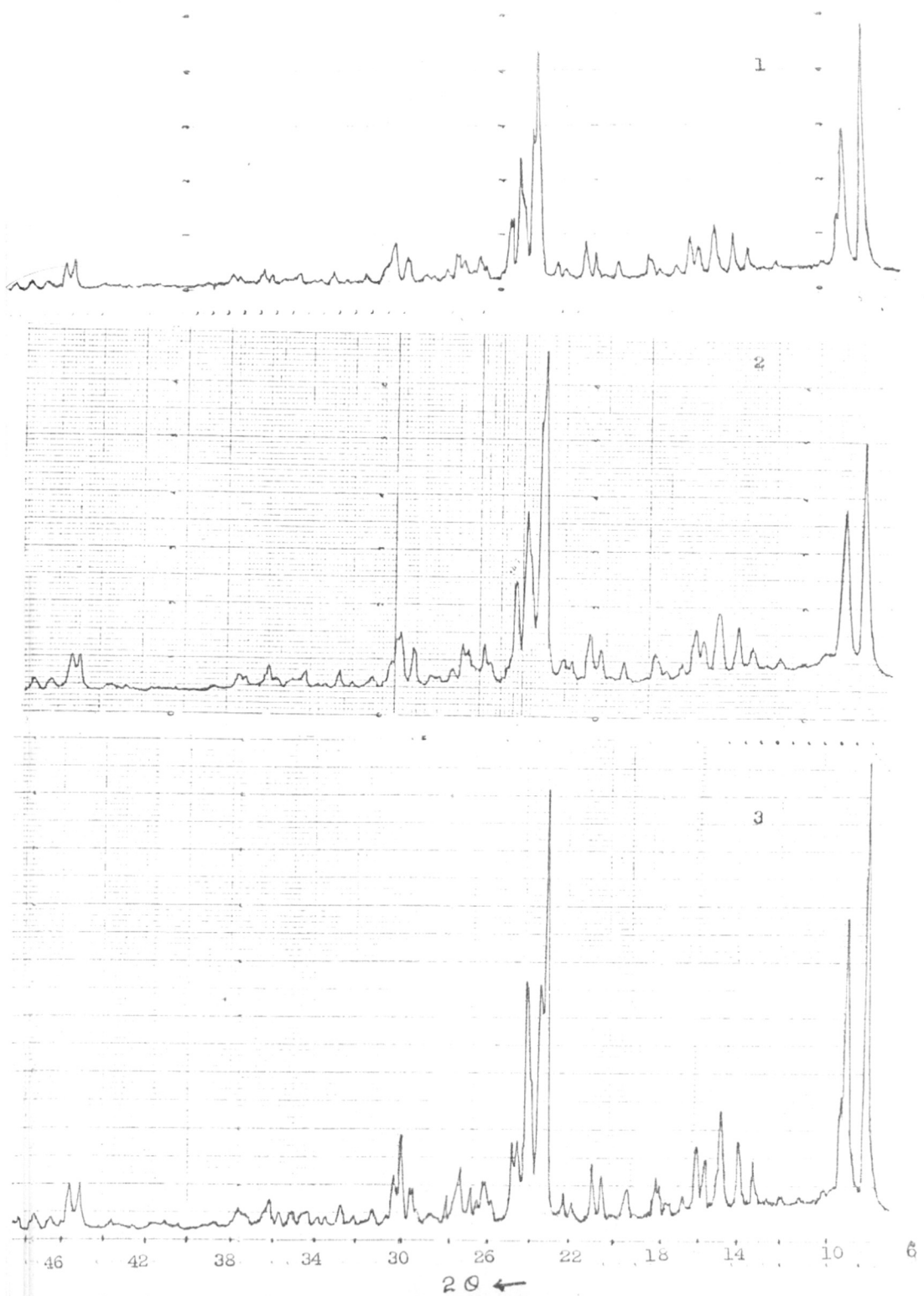


Fig. 2.1 : XRD of HZSM-5 Zeolites. $\text{SiO}_2/\text{Al}_2\text{O}_3$ for (1) 82, (2) 174 and (3) 318.

(in place of a singlet at 24.25°) with increase in $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio are observed. These are respectively associated with increase in crystallite size and a change in crystal symmetry³⁷ (orthorhombic to monoclinic).

B : Infrared Spectroscopy (IR)

IR spectra were recorded on a Perkin-Elmer 221 Spectrophotometer using nujol mull technique with KCN as the internal standard. The spectra for samples of 3 different molar ratios ($\text{SiO}_2/\text{Al}_2\text{O}_3$) are shown in Fig. 2.2 and the characteristic stretching frequencies in Table 2.2.

Absorption band at 540 cm^{-1} is assigned to highly distorted double five membered ring which is characteristic of ZSM-5¹⁶¹. The frequencies for samples 1-3 are in agreement with the reported values.

XRD and IR spectroscopic data therefore show that the zeolites prepared belong to the ZSM-5 type.

The unit cell compositions of the samples were calculated from the chemical data assuming the number of Si+Al tetrahedra per unit cell to be equal to 96^{36} . The number of protons was calculated as the difference between the number of Al and Na atoms per unit cell.

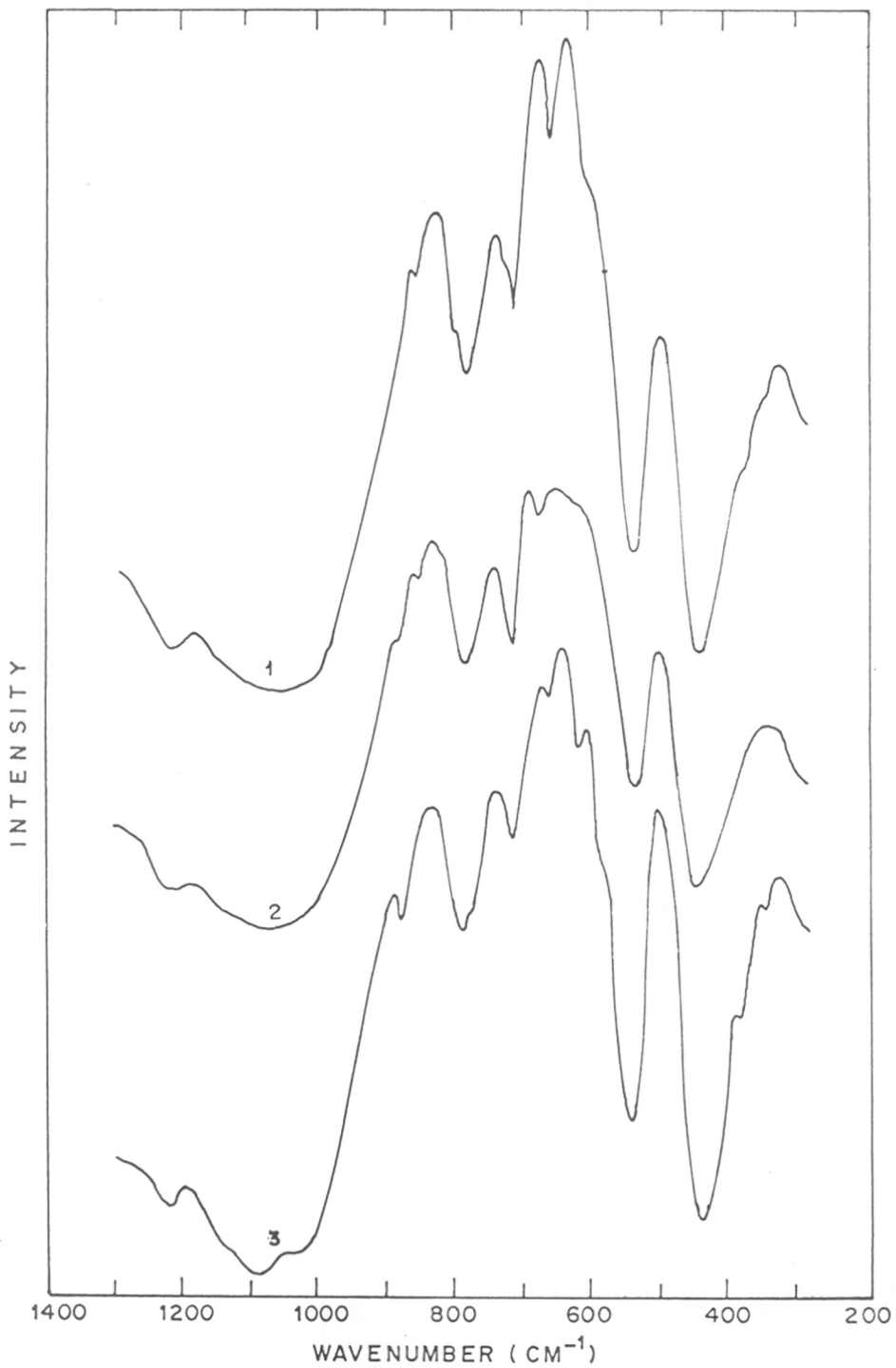


FIG.2 2 IR SPECTRA OF HZSM-5 ZEOLITES.
NUMBERS 1-3 REFER TO SiO₂ / Al₂O₃
RATIOS, 82, 174 AND 318 RESPECTIVELY

TABLE - 2.2FRAMEWORK VIBRATION FREQUENCIES FOR NaZSM-5¹⁶¹

Wave Number (cm^{-1})	Assignment*
450	Si-O bending
540	Distorted double 5 rings.
590	ELC5
620	ELC5
720	ITSS
790	ELSS
840	ELSS
1075	ITAS
1020	Si-O asymmetric stretch

* ELC5 = External link complex 5 membered ring.

ITSS = Internal tetrahedral symmetric stretch.

ELSS = External link symmetric stretch.

ITAS = Internal tetrahedral asymmetric stretch.

<u>Sample*</u>	<u>Unit cell composition</u>
HZSM-5(82)	$\text{Na}_{0.03}\text{H}_{2.25}(\text{AlO}_2)_{2.28}\text{SiO}_2_{93.72} \cdot 21\text{H}_2\text{O}$
HZSM-5(174)	$\text{Na}_{0.07}\text{H}_{1.02}(\text{AlO}_2)_{1.09}\text{SiO}_2_{94.91} \cdot 18\text{H}_2\text{O}$
HZSM-5(318)	$\text{Na}_{0.07}\text{H}_{0.53}(\text{AlO}_2)_{0.60}\text{SiO}_2_{95.40} \cdot 10\text{H}_2\text{O}$

*The figures in the bracket indicate $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the zeolite.

The modified catalysts contained different amounts (wt.%) of phosphorous or boron and have been designated as shown below. In all cases HZSM-5 (82) was used to study the effect of modification :

Sample containing 1% phosphorous	- HZSM-5 (82-P-1)
" 3% "	- HZSM-5 (82-P-3)
" 5% "	- HZSM-5 (82-P-5)
" 1% boron	- HZSM-5 (82-B-1)
" 3% "	- HZSM-5 (82-B-3)

C : Scanning Electron Microscopy (SEM)

The morphology of the zeolite crystals was studied by SEM (Sterioscan Model 150, Cambridge, UK). The sample was dusted on aluminium pegs and coated with an Au-Pd evaporated film. The SEM photographs of crystalline samples of different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios are shown in Fig. 2.3. The crystals show morphology similar to those reported³¹. The crystallite size of the samples increases with the ratio^{34a,b} and is in the range of 0.5-6 nm.



FIG. 2.3 : SEM PHOTOGRAPHS OF ZSM-5 ZEOLITES OF DIFFERENT $\text{SiO}_2/\text{Al}_2\text{O}_3$ RATIOS. (1) 82, (2) 174, (3) 318.

D : Thermal Analysis

The thermal analysis was carried out using a Hungarian Derivatograph (MOM 102 Budapest). The thermograms were recorded under the following conditions :

Sample weight	:	70 mg
Heating rate	:	10° C/min.
Sensitivity (a)	:	DTA 1/5
	(b)	: DTG 1/5
	(c)	: TGA 70 mg
Atmosphere	:	Air suction.

Preheated and finely powdered α -alumina was used as inert standard.

Results and discussion

A typical thermogram of the as-synthesised ZSM-5 is shown in Fig. 2.4. Two successive weight losses are seen in the TG curve. The first stage for 25-200°C is due to loss of zeolitic water and the second is associated with the decomposition of the organic cations (TEPA).

While pure TEPA decomposes in the temperature range 80-200°C, the decomposition of the TEPA occluded in the channels of ZSM-5 (TEPA-ZSM-5) takes place between 320° and 600°C. Hence there must exist a strong bonding between the organic molecules and the framework atoms of the zeolite. The two exotherms observed at about 397° and 482°C may be attributed to the

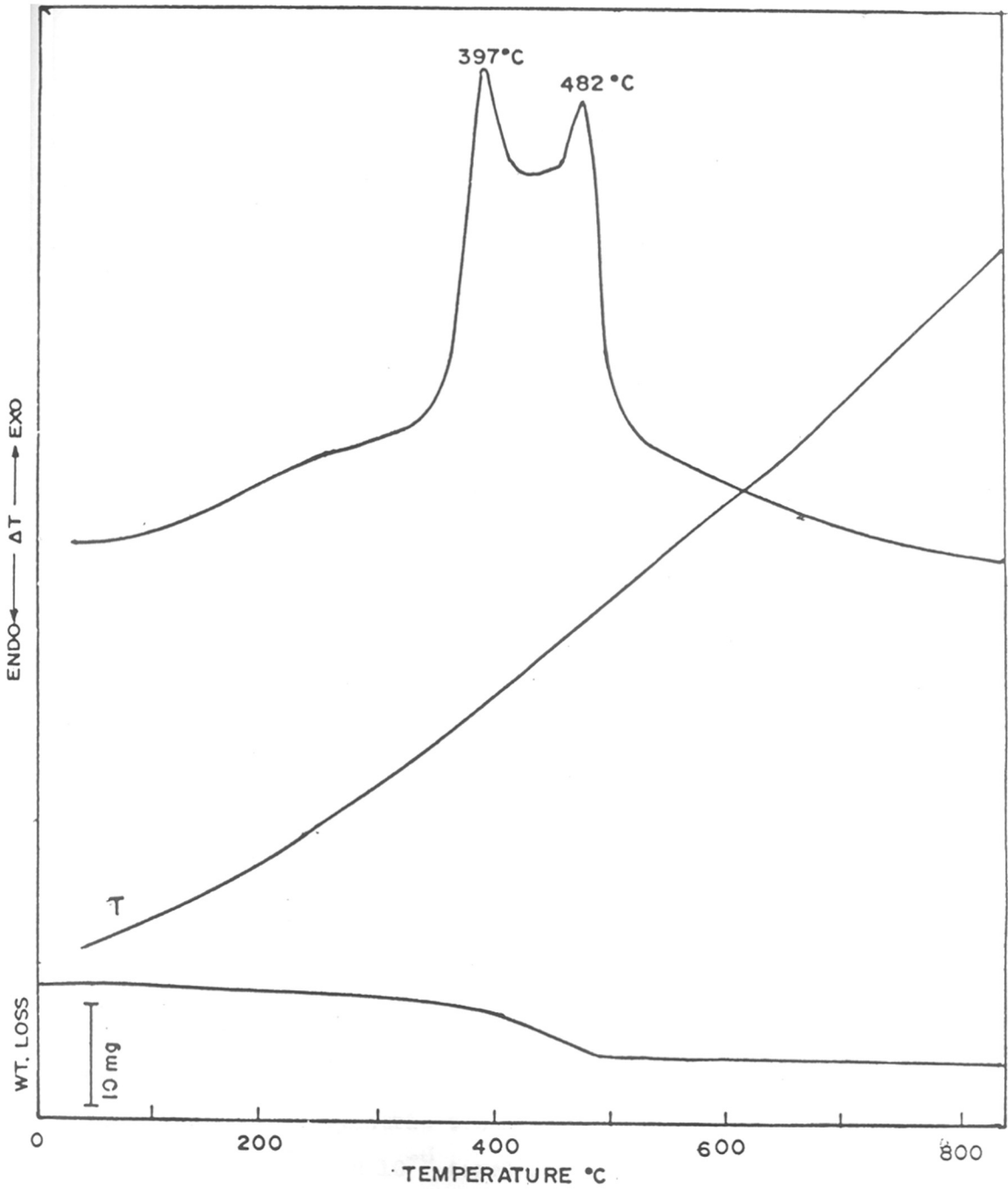


FIG 2.4 DTA AND TG THERMOGRAMS OF TEPA ZSM-5 ZEOLITE, $\text{SiO}_2/\text{Al}_2\text{O}_3:82$

presence of two different sites where TEPA molecules are bound in the intracrystalline channels. The weight loss observed in the temperature range 320-600°C is equivalent to the loss of about 3.5 TEPA cations per unit cell in fair agreement with the occlusion of 3.64 TPA cations reported by Gabelica et al¹⁶². The weight loss observed in the temperature range 477-600°C is equivalent to 1.8 TEPA cations/unit cell which is roughly equal to the number of aluminium cations per unit cell for HZSM-5 (82). The high temperature required to decompose these organic species shows that they are interacting strongly with the aluminium in the channel intersection. Parker et al¹⁶³ have reported that the tetraalkyl ammonium ions are occluded at two different sites namely where they are associated with acid sites and act as counter ion, and where they are not associated with acid sites as in aluminium free silicalite. In the latter case, they decompose upon calcination to give rise to olefins and trialkyl amines.

The TG curves for decomposition of HZSM-5 samples are shown in Fig. 2.5. The weight loss between 25 and 400°C is attributed to loss of zeolitic water. The quantity of water determined from the TG curve is compared with that determined by gravimetric technique (using McBain spring balance at 400°C and 10^{-6} torr) for the 3 samples

The number of OH groups per unit cell in the zeolite can be calculated from the weight loss in the temperature range 400-1000°C assuming it to be entirely due to dehydroxylation.

Last column in Table 2.3 shows the number of OH groups per unit cell calculated in this manner. The results are in line with the increasing hydrophobicity and decreasing acidity of the zeolites as the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio is increased.

E : Sorption Measurements

These were carried out on a calibrated McBain silica spring balance. The experimental set up is shown in Fig. 2.6. The zeolite sample, about 100 mg was pressed into a pellet and weighed into an aluminium bucket which was then suspended from the silica spring. The assembly was evacuated by means of a two stage rotary pump and mercury diffusion pump to a vacuum of 10^{-6} torr. The sample was heated slowly to 400°C by continuous pumping till a constant weight was obtained. The temperature of the sample was then lowered to 25°C and the sorbate vapor admitted to the sample at constant temperature and pressure. The amount sorbed was measured from the extension of the spring which was recorded using a cathetometer.

The quantity adsorbed during 30 minutes was taken as the equilibrium adsorption. All sorption measurements were carried out at 25°C and relative pressure $p/p_0 = 0.5$.

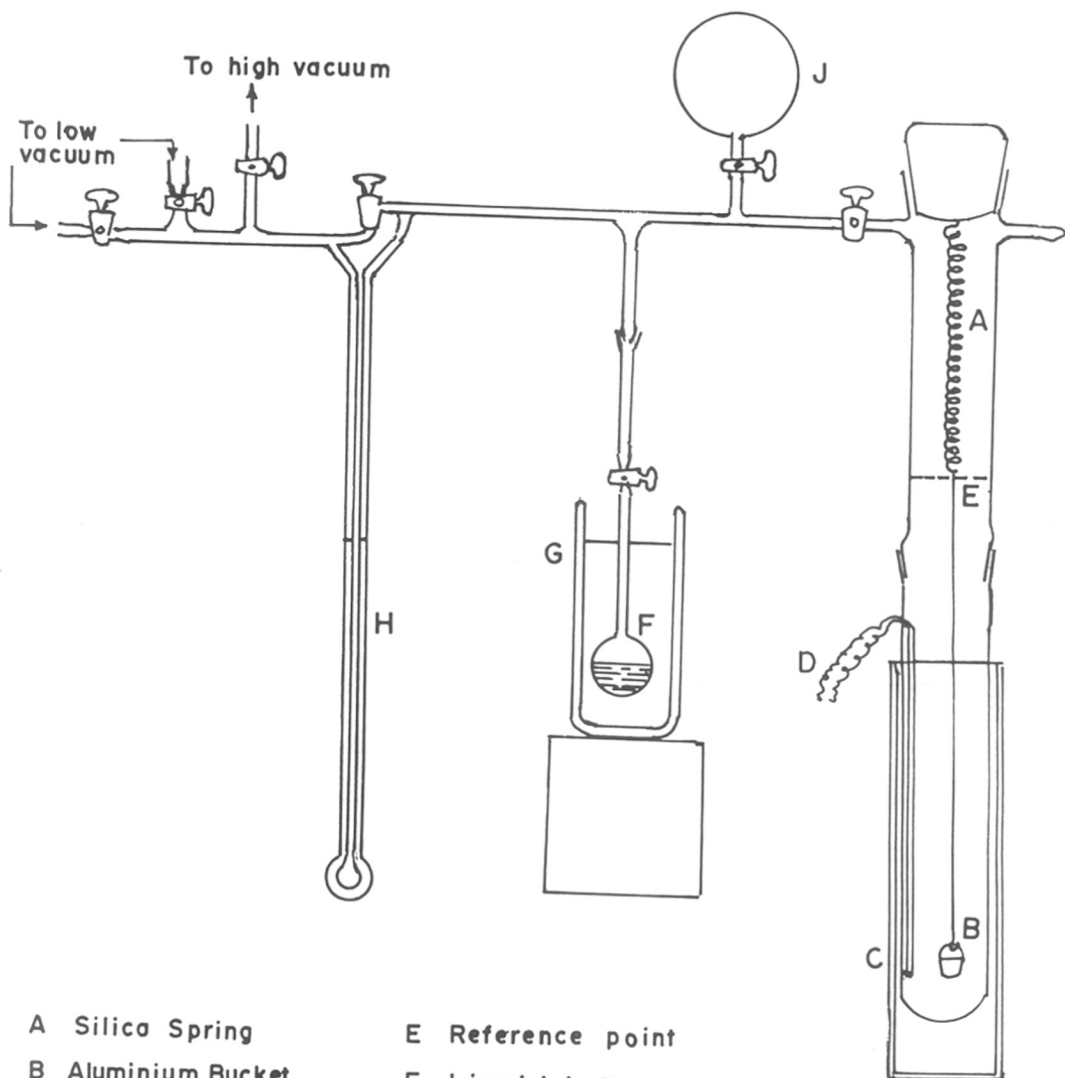
TABLE - 2.3THERMAL ANALYSIS OF HZSM-5 ZEOLITES

Sample	Al atoms/ unit cell	% wt. loss (a)	% wt. loss (b)	No. of OH groups/ unit cell (c)
HZSM-5 (82)	2.3	7.2	7.6	8.9
HZSM-5 (174)	1.1	4.5	5.3	6.2
HZSM-5 (318)	0.64	3.0	3.1	3.5

(a) - % wt. loss in the temperature range 25-400°C

(b) - % wt. loss due to dehydration upto 400°C under vacuum 10^{-6} torr.

(c) - Number of OH groups per unit cell estimated from the wt. loss in the temperature range 400-1000°C from the TG curves.



- | | |
|-------------------------|-------------------|
| A Silica Spring | E Reference point |
| B Aluminium Bucket | F Liquid bulb |
| C Furnace or Thermostat | G Thermostat |
| D Thermocouple | H Manometer |
| | J Gas Reservoir |

FIG. 2-6. GRAVIMETRIC ADSORPTION UNIT

Results and discussion

Equilibrium adsorption was obtained for water, n-hexane, n-heptane, benzene and p-xylene in about 10-15 minutes. For others like o-xylene, m-xylene and 1,2,4-trimethylbenzene which have larger kinetic diameter, it was not reached even after thirty minutes. Table 2.4 compares the critical and kinetic diameters of some molecules used in the present study. Anderson et al⁶² have shown that the effective molecular size separating fast and slow sorption in HZSM-5 and silicalite is > 0.58 nm and < 0.61 nm. Sorption data for some hydrocarbons and water are shown in Tables 2.5 and 2.6.

RAI, Relative Affinity Index, defined as the ratio of volume of n-hexane adsorbed to the volume of water adsorbed has been used to distinguish between conventional zeolites and high silica zeolites of the ZSM-type¹⁶⁴. RAI is < 1 for the former zeolites. It can be seen from Table 2.5 that with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio, RAI increases indicating increasing hydrophobicity of the zeolite samples. The adsorption data presented are in fair agreement with those reported for ZSM-5 zeolites⁶². For instance, the greater adsorption of n-aliphatics compared to methyl substituted aliphatics is as expected. Similarly, the dimethyl substituted aliphatics have lower sorption compared to monosubstituted aliphatics. These observations have been summarised and accounted for by Derouane⁹².

TABLE - 2.4

CRITICAL AND KINETIC DIAMETERS OF SOME
SORBATE MOLECULES

Sorbate	Critical ^a diameter nm	Kinetic ^b diameter nm
n-Hexane	0.49	0.43
2-Methyl pentane	0.59	0.53
3-Methyl pentane	-	0.55
2,3-Dimethyl butane	-	0.61
Cyclohexane	0.61	0.60
Benzene	0.67	0.58
n-Heptane	0.45	0.43
Toluene	0.67	0.58
p-Xylene	0.67	0.58
o-Xylene	0.74	0.68
m-Xylene	0.71	0.70
1,3,5-Trimethyl benzene	0.78	0.75
Ammonia, methanol	0.35-0.37 ^c	0.38 ^d
Water	0.32	0.27 ^d

a - Ref. 164

b - Ref. 166

c - Ref. 55

d - Ref. 13

TABLE - 2.5
SORPTION (MOLECULES U.C.⁻¹) OF WATER AND HYDRO-
CARBONS ON HZSM-5 ZEOLITES AND MODIFIED ZEOLITES

Sorbate	HZSM-5			HZSM-5 (modified)				
	(82)	(174)	(318)	P-1	P-3	P-5	B-1	B-3
Water	33.2	21.2	10.2	-	21.2	-	-	32.2
n-Hexane	7.9	7.9	7.9	-	-	-	-	-
2-Methyl pentane	5.6	-	-	-	-	-	-	-
2-3Dimethyl butane	3.5	-	-	-	-	-	-	-
Cyclohexane	3.6	2.0	1.6	2.2	0.8	0.2	1.3	0.1
n-Heptane	7.8	-	-	7.4	5.1	4.2	7.0	3.8
Benzene	9.0	-	-	7.9	5.1	1.8	6.2	1.3
Methanol	16.5	-	20.2	-	15.8	-	-	18.1
RAI ²	1.7	2.7	5.6	-	-	-	-	-
Pore Vol. (ml/g.)	0.16	-	-	0.15	-	0.09	0.15	0.11
BET surface area(m ² /g)	393	-	-	370	-	326	355	327

Note : (1) Figures in bracket indicate SiO₂/Al₂O₃ ratio.

(2) RAI = Relative Affinity Index.

TABLE - 2.6

SORPTION OF SOME AROMATIC HYDROCARBONS
ON HZSM-5 ZEOLITES*

Sample	Benzene	p-Xylene	o-Xylene	1,2,4 TMB	Sorption ratio P-Xyl/O-Xyl
HZSM-5 (82)	9.0	8.3	2.0	0.8	4.2
HZSM-5 (174)	-	7.2	1.3	0.7	5.5
HZSM-5 (318)	8.4	7.3	0.9	0.5	8.1

* Molecules per unit cell.

Adsorption of p-xylene is higher than what has been reported^{62,78}. However, it agrees with the value reported by Olson et al³⁸. As reported by the latter workers, adsorption of benzene is lower than that of p-xylene. This has been attributed to special packing arrangements for p-xylene within the zeolite pores due to extra hydrogen from the CH₃ groups being available for interaction with the framework structure. The absence of such interactions and its being a weaker base is responsible for the lower uptake of cyclohexane, though both cyclohexane and p-xylene have comparable molecular size¹⁵⁵. The decrease in adsorption of aromatics with increasing SiO₂/Al₂O₃ mole ratio can be attributed to a decrease in such interactions between the aromatics and protonic sites in the zeolites. Such decrease in adsorption with increasing SiO₂/Al₂O₃ ratio was also found with cyclohexane, o-xylene and 1,2,4-trimethyl benzene (1,2,4-TMB). Another possible explanation for this is that with increase in SiO₂/Al₂O₃ ratio, the crystallite size increases^{34a,b} and this slows down the pore filling process. Equilibrium adsorption is thus not reached during the time given, namely, thirty minutes for the process. The decrease in adsorption of ortho xylene with increase in mole ratio is also reflected in decrease in its conversion in the isomerisation reaction (Chapter 4). SEM photographs of samples show that crystallite size increases with increase in SiO₂/Al₂O₃ ratio (Fig. 2.3).

F : Adsorption on Modified Zeolites

Modification of the catalyst with P and B leads to a decrease in adsorption of the hydrocarbon compounds. This is illustrated in Table 2.5. This may be partly due to a lowering of the effective pore diameter of the zeolite by the modifier species sitting near the pore mouths. They may also be plugging the channels thus reducing the available volume for the sorbate molecules¹⁵⁵. Consistent with this explanation, the pore volume as studied by argon adsorption and BET surface area are also found to decrease (Table 2.5). The effect of modification is not as pronounced on n-heptane as on the large molecules. This indicates that the effect of modification on adsorption is more due to pore mouth blocking than due to reduction in void volume caused by reduction in effective dimensions of the channels.

G : Characterisation of acid sites

The acidity in zeolites is believed to be the result of isomorphous substitution of trivalent aluminium for tetravalent silicon in the framework. Such substitution creates a negative charge on the aluminium atom which is neutralised by the presence of a cation or a proton. In the latter case, a Brønsted acid site is created. Lewis sites which can be the charge compensating cations or trigonal aluminium atoms at oxygen deficient sites or at cation positions are also present in zeolites⁵⁹.

The active centres for most of the zeolite based organic reactions are Brönsted acid sites and their number and strength depend upon several factors like the type of zeolite and its Si/Al ratio, nature of aluminium distribution in the zeolite and their location^{59,168}.

TPD of NH_3 has been used in the present study to characterise and evaluate the acid sites in HZSM-5 zeolites. The experimental set up is shown in Fig. 2.7. 0.4 gm of the zeolite sample (HZSM-5, 10-20 mesh) was taken in a microreactor. It was initially heated to 400°C at a rate of $10^\circ\text{C min}^{-1}$ in a flow of pure and dry nitrogen and then coupled to sorptiometer for evacuation. It was activated at 400°C for 2 hours and cooled to 150°C . A calibrated volume of NH_3 (RCF, 99.5%) was admitted to the sample which was further allowed to cool to 25°C . The equilibrium adsorption of NH_3 was determined at 25°C and 200 mm pressure. The loosely bound ammonia was evacuated at the same temperature. Equilibrium adsorption was once again determined at the same temperature and pressure. The difference between the amounts adsorbed during the first and second determinations was taken as the chemisorbed ammonia.

The microreactor was then coupled to the on-line GC after allowing sufficient time to stabilise the GC. The sample was heated at a linear rate of $10^\circ\text{C min}^{-1}$ with carrier gas flow rate of 60 ml. min^{-1} and the TPD spectrum was obtained with percentage area of the peaks. The total volume chemisorbed at

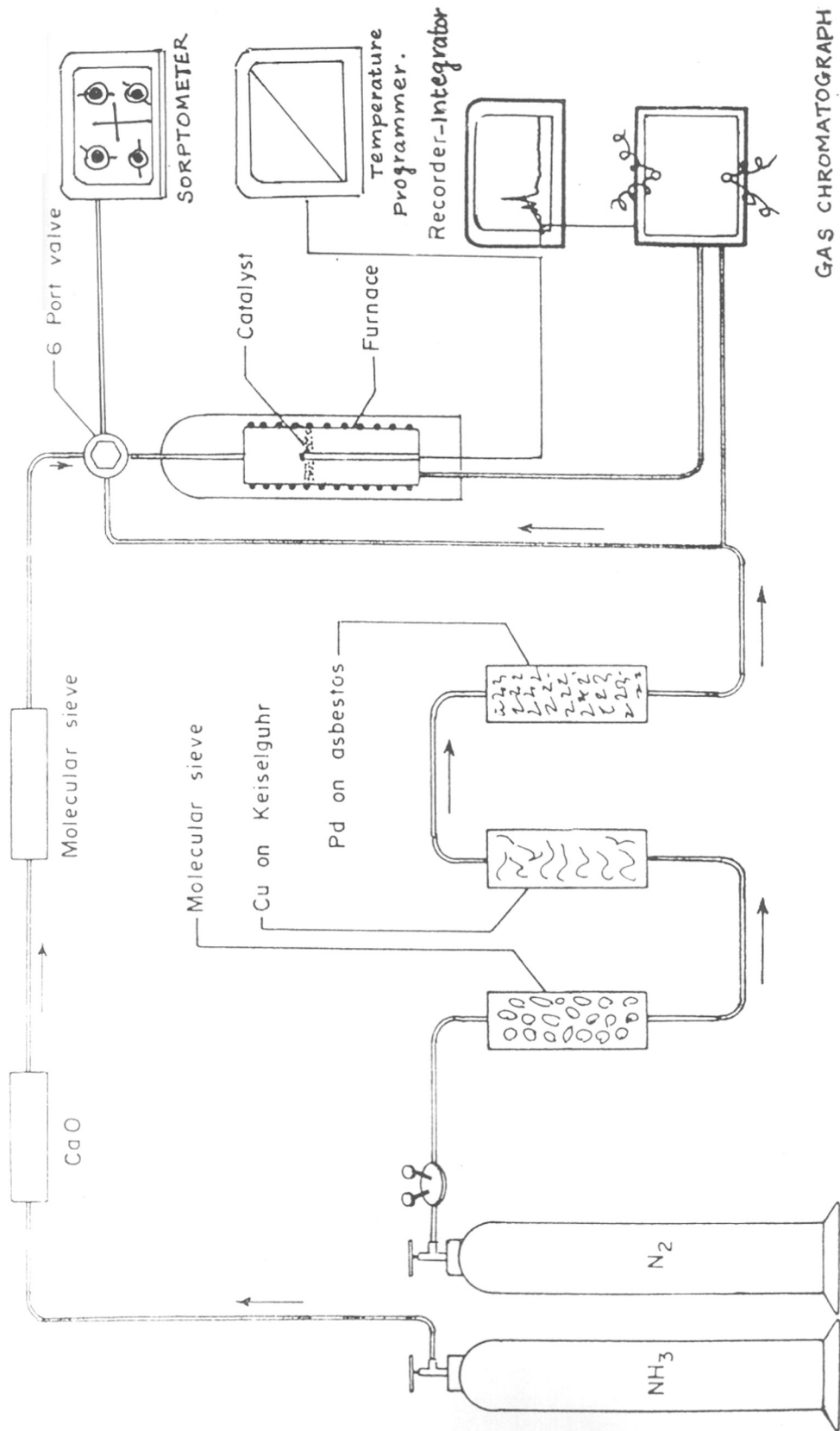


FIG. 2-7 . SCHEMATIC DIAGRAM OF TPD UNIT

25°C obtained by volumetric measurements and the area % of the desorption peaks are then used to calculate the acid strength distribution in the sample.

Results and discussion

The temperature programmed desorption spectra of ammonia on HZSM-5 exhibit two or more maxima which have been shown to arise from different adsorption sites in zeolites. Those obtained in the present study are shown in Fig. 2.8. Some of the results reported earlier on the TPD study are presented in Table 2.7 which also show the assignments of the TPD maxima to different adsorption sites for ammonia in the zeolite. It can be seen that the number of TPD maxima and the temperature range in which they appear are in broad agreement with those reported^{46,62,168,171}.

Table 2.8 shows the number of acid sites calculated corresponding to the individual peak areas (designated as weak, medium and strong acid sites).

Topsøe et al⁴⁶ have measured the desorption activation energies of the chemisorbed ammonia and obtained values 20.2, 23.1 and 38.8 K. Cal. mole⁻¹, respectively, for the three peaks (α , β and γ) (Table 2.7). According to Post and Van Hoof¹⁷¹ the ammonia adsorbed on weak sites such as silanol or on OH attached to extra framework aluminium may have desorption heats \sim 16.3 K. Cal. mole⁻¹ and ammonia adsorbed on strong sites \sim 32.8 K. Cal. mole⁻¹.

TABLE - 2.7 - TPD OF CHEMISORBED AMMONIA ON HZSM-5 ZEOLITE

Sample ($\text{SiO}_2/\text{Al}_2\text{O}_3$, protonation method*)	Temperature range for desorption maxima ($^{\circ}\text{C}$) (Assignments for desorption sites)	Ref.
HZSM-5(64, a*)	130-160 (Hydrogen bonding interaction of NH_3 with surface oxides; hydroxyls)	105
HZSM-5(65, a)	117-167 (Weakly acidic OH groups responsible for 3700 cm^{-1} band in infrared spectrum; silanol groups or OH groups attached to non-framework aluminum.)	168, 169
HZSM-5(24, b)	59-97 (Surface oxide, hydroxyls or surface impurities; OH groups responsible for 3700 cm^{-1} band, silanol groups, or cation sites.)	46
HZSM-5(50, a)	230 (Silanol or protonic group located in channel structure.)	170a
HZSM-5(41, NH_4OH)	180-250 (Silanol, OH attached to extra framework Al.)	171
HZSM-5(82, a)	100-120 150-200 380-450	Present work

* Protonation method a - exchange with NH_4Cl and calcination, b - HCl treatment.

TABLE - 2.8 - THE CONCENTRATION OF SURFACE ACID SITES

Sample	SiO ₂ /Al ₂ O ₃	Al/U.C.	T _{max} (strong sites)	Weak + Medium	Acid sites/ U.C.		No. of OH groups/ U.C.	R
					Strong	Total		
HZSM-5 (82)	82	2.3	425	6.7	1.6	8.3	8.9	0.7
HZSM-5 (174)	174	1.1	387	4.8	0.9	5.7	6.2	0.82
HZSM-5 (318)	318	0.6	362	1.8	0.5	2.3	3.5	0.83
HZSM-5 (82-P-3)	82	-	315	5.9	0.2	6.1	-	-
HZSM-5 (82-B-3)	82	-	325	6.5	0.5	7.0	-	-

* Number of OH groups on the surface calculated assuming weight loss above 400°C to be due to dehydroxylation.

R - Number of strong acid sites/number of Al atoms.

Microcalorimetric measurements⁶¹ yielded comparable values for heats of adsorption of ammonia > 28.7 K. Cal. mole⁻¹ for strongest sites although there was a broad range of distribution of acid sites in the range 21.5 to 35.9 K. Cal. mole⁻¹. The weak sites corresponded to adsorption heat < 19.1 K. Cal. mole⁻¹. The number of such sites was found to be greater in NaZSM-5 in which the strong sites were absent or negligible. These data and findings help in assigning the three desorption maxima observed in the present study. Accordingly, the high temperature desorption peak may be assigned to ammonia adsorbed on strong acid sites (3600 cm⁻¹ in the infrared spectrum). The β and α peaks may be assigned to desorption of ammonia from Brönsted sites attached to extra framework aluminium atoms (3650 cm⁻¹) or ammonia adsorbed on traces of cations and silanol groups (OH band at 3700 cm⁻¹), respectively. These bands observed in the infrared spectrum of sample HZSM-5 (82) are shown in Fig. 2.9.

Jacobs and Ballmoos¹⁶⁹ have shown that under controlled conditions it is possible to prepare pure HZSM-5 which shows only one band in the infrared spectrum. Derouane et al¹⁷² have shown that the molar amount of ammonia eliminated is equal to that of the chemically determined total aluminium concentration for a series of HZSM-5 samples contradicting the results of an earlier study⁴⁶.

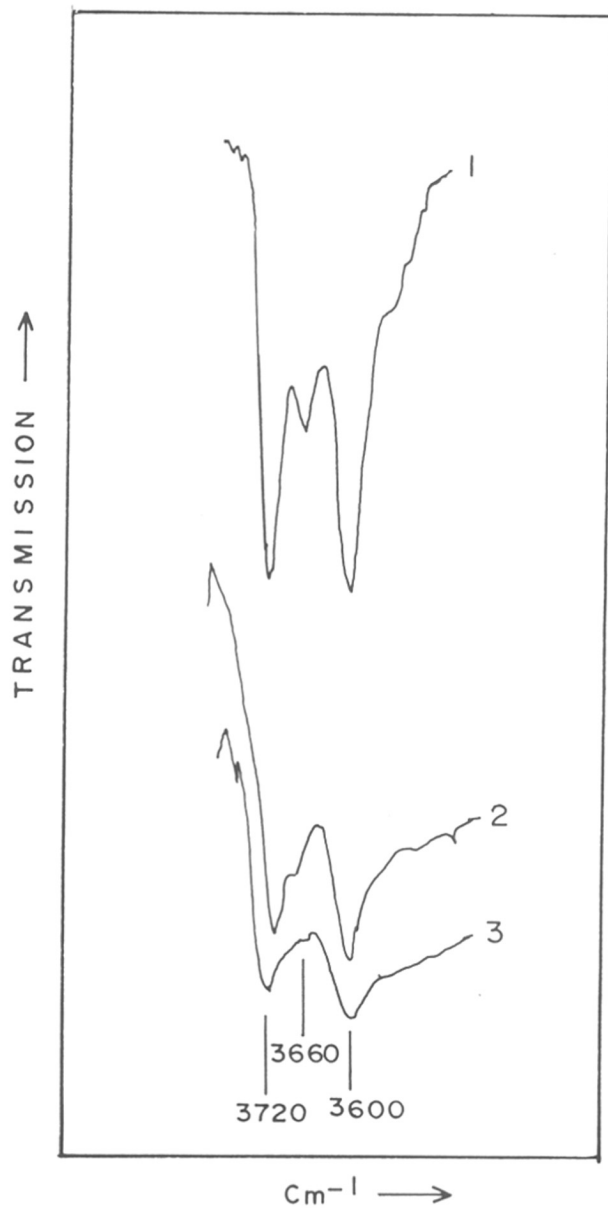


FIG. 2·9 IR SPECTRA OF HZSM-5 ZEOLITES. $\text{SiO}_2/\text{Al}_2\text{O}_3$ RATIOS 82(1), 174 (2) AND 318(3)

H : Effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio on acidity

The TPD profiles, for samples containing different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios have been shown in Fig. 2.8. It can be seen that the intensity of the three peaks decreases with an increase in the ratio from 82-318 as expected. A small but gradual shift in the temperature maximum for the high temperature peak is also observed.

An increase in heat of desorption (ΔH desorption) with increase in $\text{SiO}_2/\text{Al}_2\text{O}_3$ upto ~ 50 followed by a possible decrease in ΔH for further increase in the ratio has been reported by Post and Van Hoof¹⁷¹ from a TPD study. Auroux et al⁶⁸ from their calorimetric studies of heats of adsorption observed a similarity of acid strength distribution when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios were in the range 30-70 and a substantial shift in distribution to lower strength upon increasing the ratio to 120. They further observed a decrease in strength of sites when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was about 28. These two separate results^{171,103} may be explained on the basis of the interplay of two effects - one the probability of formation of superacid sites which should increase with decrease in $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio^{170b} and the other due to proton mobility^{103,217} restriction which should also increase with decrease in $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. These two effects would influence the strength of acid sites in opposite direction and may even result in a maximum strength (desorption energy is maximum) at

a particular ratio. Probably in agreement with this, Post and Van Hoof¹⁷¹ observed in their TPD studies a maximum desorption energy of 32.8 K.Cal./mole (for the desorption peak corresponding to strong sites) at $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio ~ 49 and Auroux et al⁶⁸ observed a maximum in the range 30-70. The ratio 49 (or the range 30-70) is significant in that it represents four aluminium atom/u.c. representing maximum number of strong Brönsted acid sites possible per u.c.⁷⁹. At increased $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, the effect of superacid sites would be predominant and would probably decide the strength of acid sites and this being less, the strength would be reduced. The observed shift in T_{max} for the high temperature peak may therefore be attributed to a lowering of acid strength as the ratio is increased in the range used in the present study. The number of sites would of course decrease as it is related to Al content.

The explanation given for the $\text{SiO}_2/\text{Al}_2\text{O}_3$ effect is admittedly an over simplified picture as Derouane et al have discussed the importance of synthesis conditions in aluminium distribution and hence acid strength distribution in ZSM-5 zeolites. Besides the desorption energy reported by Topsøe et al⁴⁶ for TPD of ammonia on HZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 24$) is 38.8 K.Cal./mole⁻¹ which is higher than that reported by Auroux et al⁶⁸ and Post and Van Hoof¹⁷¹ for similar ratios.

Comparing the number of aluminium atoms per unit cell of the samples (Section 2.3B) and the number of strong acid sites (Table 2.8) the ratio of the number of strong acid sites to the number of aluminium atoms (R) is found to be less than unity. R varies from 0.69 to 0.80. From the results of the microcalorimetric measurements of the Auroux et al⁶⁸, for $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the range used in the present study, a value of $R = 0.7$ to 0.9 in agreement with the present work can be calculated. The departure of R from unity may be due to the fact that part of aluminium atoms is not located in the interchannel cross-sections and hence does not contribute to strong sites. It may be present in the extra framework (Table 2.7)^{168,169,171}.

I : Acidity of modified zeolites

TPD spectra of zeolites impregnated with phosphorous and boron are shown in Fig. 2.10 and results presented in Table 2.8.

Two changes are noticeable upon modification of the HZSM-5.

1. A redistribution of the strong acid sites represented by the γ peak whose maximum is now shifted to lower temperatures. This indicates that the number and strength of the strong sites originally present is now substantially reduced, and
2. A decrease in the total number of acid sites.

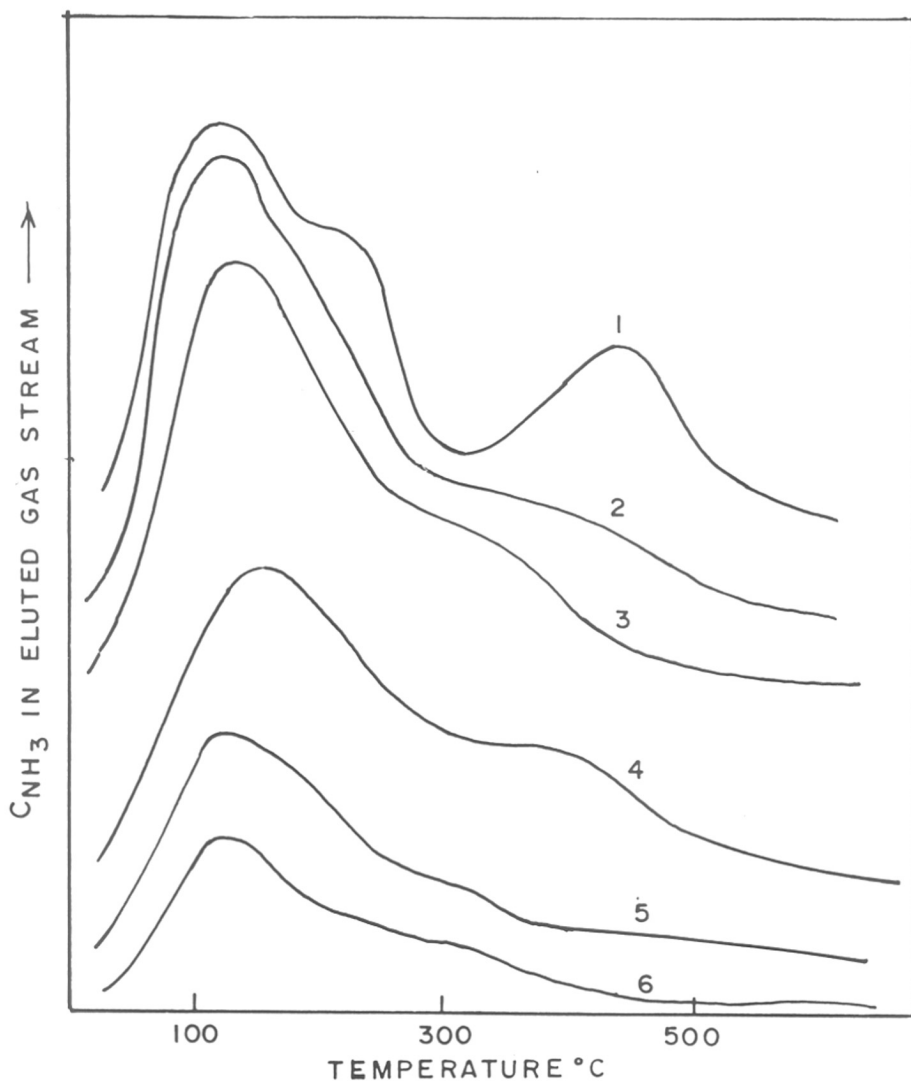
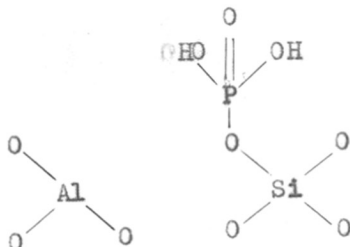


FIG 2:10 TPD OF HZSM-5 AND MODIFIED HZSM-5 ZEOLITES:
 1) HZSM-5(82), 2) HZSM-5(82-B-1), 3) HZSM-5(82-B-3),
 4) HZSM-5(82-P-1), 5) HZSM-5(82-P-3) AND 6) HZSM-5
 (82-P-5)

Kaeding and Butter¹¹³ had visualized a permanent attachment of the phosphorous to the zeolite framework through oxygen to give the species



in the formation of which the original strong protonic site has been replaced. An increase in the total acidity and a decrease in the strength of the sites was observed in the modified zeolite consistent with the above picture.

Microcalorimetric studies of acid sites on phosphorous modified zeolites⁷⁵ have, however, shown that the range of acid strength in the modified zeolites is the same as in the parent zeolite. The total number of acid sites corresponding to all type of sites detected by the technique was also found to decrease. These findings are in agreement with the results of the present study (Table 2.8).

2.4. CATALYTIC REACTIONS

A : Conversion of methanol to hydrocarbons over HZSM-5 type zeolites

There have been a large number of studies on the conversion of methanol to hydrocarbons. Several of these have been directed towards establishing the reaction mechanism to

explain the formation of the first C-C bond and the autocatalytic nature of the reaction^{102-104,111-118}. Such mechanistic studies had to be undertaken at very low conversion levels¹¹¹, thus requiring comparatively low temperatures and high space velocities. The primary intermediates could then be identified and theory concerning their formation developed. Further reactions of these intermediates and the secondary intermediates that they produce are oligomerisation, isomerisation, cyclisation, dehydrogenation and hydrogenation. These reactions which lead to the observed product distribution could then be explained by the well known carbenium ion chemistry^{120,175}.

Other studies have been directed to the production of a high octane number gasoline^{134,176,177} (C_5^+ fraction in the reaction) and yet others to the production of light olefins useful to the petrochemical industry^{114,126,178}. The present work was undertaken to study the influence of temperature, SiO_2/Al_2O_3 mole ratio and catalyst modification on hydrocarbon distribution. The effects of the above parameters on the yields of C_5^+ fraction, especially, aromatics in C_5^+ , and the yield of light olefins (C_2-C_4) are particularly studied in view of their commercial importance. The temperature was kept high enough to ensure complete conversion of methanol in almost all the studies. There have been only a few studies of this reaction above $400^\circ C$ ^{102,127} and the present study extends it to $500^\circ C$.

B : Experimental

(a) Materials : Methanol, ethanol and diethyl ether used were high purity reagents (not less than 99.5%), Ethylene used was 99 + % pure.

(b) Catalyst : The zeolites used as catalysts for the reactions were binder-free, pelleted and crushed to proper size (10-20 mesh). Their unit cell compositions have been shown in Section 2.3.B. About one gram of the catalyst was used for the reaction.

(c) Experimental set up and procedure : All reactions were carried out at atmospheric pressure in fixed bed downflow integral reactor (Fig. 2.11). The catalyst was positioned in a cylindrical, silica reactor (1.5 x 40 cm) provided with a thermowell at the centre. The thermowell top and the catalyst upper surface in the reactor were kept at the same level. The reactor was placed in the constant temperature zone of an electrically heated furnace. The thermocouple attached to the reactor could be used to measure the temperature inside the different layers of the catalyst bed during the reaction.

The catalyst was first activated in air at 500-550°C for 2 hours and then flushed with N₂ to remove air. It was then brought to a temperature close to but lower than reaction temperature. The reactant (methanol, diethyl ether, ethanol or aqueous methanol) was fed into the vaporiser filled

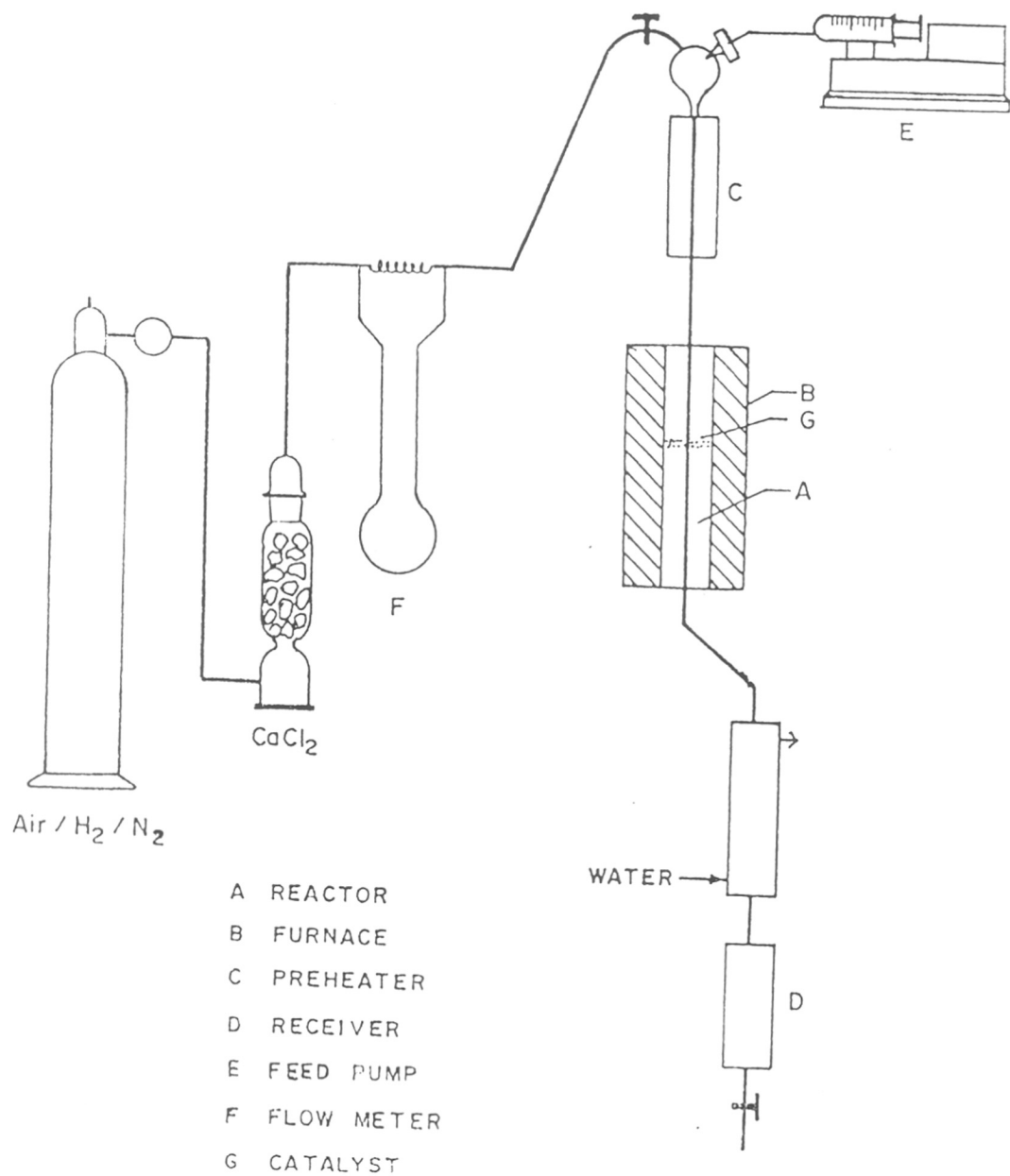


FIG 2·II. SILICA REACTOR USED FOR CATALYTIC REACTIONS

with porcelain beads at the desired rate using a feed pump supplied by Sage Instruments. The vapours pass over the catalyst at the desired temperature. Since the reaction was highly exothermic, the desired temperature had to be obtained by adjusting the furnace temperature initially and subsequently when the reaction was started.

Ethylene, after passing through an activated 3A molecular sieve column was fed at the desired rate using a calibrated manometer arrangement.

The products passing through the condenser were cooled with ice cold water. The condensible liquids (C_5 + and aqueous layer) and the effluent gas mixture were analysed by gas chromatography using HP 5840A GC. The gas chromatographic columns and GC conditions used for analysis of products are shown in the following page.

The advantage of n-octane porasil C column for hydrocarbon gas analysis in the alcohol reaction has been reported elsewhere^{173,174}.

It was initially established that the loss of carbon through coke formation was negligible as mass balance upto 98% was obtained by monitoring gas and liquid yields.

Total product distribution was calculated from the corresponding area % in the individual analysis, applying response factor corrections wherever necessary. The calculations were on CH_2 basis ($CH_3OH \rightarrow CH_2 + H_2O$) and the product

GAS CHROMATOGRAPHIC ANALYSIS
OF REACTION PRODUCTS

Instrument : 5840A H.P. G. C .
 Detector (FID) Temp. : 100°C (for gaseous products)
 : 200°C (for condensible liquids)
 Carrier (N₂) flow rate : 25 ml/min.

	<u>Column</u>	<u>Conditions</u>	<u>Product analysed</u>
1.	n-Octane Porasil-C 1/8" x 5', 80-100 mesh	40°C, 10 mins., programmed at 10°C min ⁻¹ to 150°C held for 5 min.	Gaseous products.
2.	Porapak Q, 1/8" x 6'.	100°C, 10 mins., programmed at 10°C min. ⁻¹ to 150°C held for 25 mins.	Gaseous products and aqueous layer.
3.	SE-30 (20%) on chromosorb A.W. 1/8" x 6'.	150°C iso- thermal.	C ₅ + hydrocarbons.
4.	Bentone 34 (5%) + diisodecyl phthalate (5%) on chromosorb A.W. 1/8" x 6'.	120°C iso- thermal	C ₅ + "

distribution was expressed as wt. %. DME (dimethyl ether) has not been treated as a product. It has been shown separately. In most of the reactions the reaction temperature was kept high enough to ensure complete conversion.

C : Results and Discussion

Table 2.9 presents data for the temperature effect on product distribution in the conversion of methanol. Included in the table is the product distribution reported by Derouane et al⁸⁸ at 400°C under fairly identical conditions. It can be seen that the differences in distribution are minor thus ensuring validity of the method of experimentation. Some pattern in product distribution can be noted as the effect of increasing the temperature. (i) Increasing amount of methane is produced as the temperature is raised¹²⁹. This is an undesirable reaction in the production of higher hydrocarbons and related to coke formation. The optimum reaction temperature for the higher hydrocarbons is in the range 350-400°C^{102,123}. At much lower temperatures, conversion of methanol is not complete and lower amounts of aromatics are produced^{88,102}. About 58% C₅⁺ (gasoline) fraction with 34% selectivity to BTX aromatics (in C₅⁺) is produced at 350°C. (ii) C₁-C₄ hydrocarbons increase with temperature. The decrease in higher aromatics (C₉⁺) is small and that in higher aliphatics large. These effects can be attributed to dealkylation of aromatics and cracking of higher aliphatics both of which are favoured thermodynamically by increase in reaction temperature. The

TABLE - 2.9

EFFECT OF TEMPERATURE ON HYDROCARBON DISTRIBUTION
IN METHANOL CONVERSION OVER HZSM-5(82), WHSV (HR-1)= 2.2

	Temperature °C				
	350	400	450	500	400*
α^*	99.4	100	100	100	100
DME	0.2	-	-	-	-
<u>Hydrocarbon distribution(wt.%)</u>					
C ₁	0.6	0.7	1.2	4.2	-
C ₂	1.4	1.8	3.9	10.1	3.8
C ₃	12.9	19.0	23.7	27.5	21.4
C ₄	26.9	31.6	25.6	20.7	25.8
C ₁ -C ₄ aliphatics	41.8	53.0	54.4	62.5	51.1
C ₅ + aliphatics + cyclic	26.0	19.4	15.0	11.0	17.0
<u>Aromatics</u>					
Benzene (B)	2.3	0.9	1.7	1.4	1.6
Toluene (T)	4.3	7.1	10.3	8.1	8.8
Ethyl benzene(EB)	-	0.8	-	-	-
Xylenes	13.9	13.1	13.7	12.1	15.3
BTX + EB	20.5	21.9	25.7	21.7	25.7
1,2,4-Trimethylbenzene	-	2.3	-	-	2.6
C ₉ + C ₁₀	11.7	1.5	4.9	4.9	-
(P + M) Ethyl toluene	-	1.9	-	-	3.6
O. Ethyl toluene	-	0.1	-	-	-
Selectivity to BTX in total aromatics	64	79	84	82	80

* Data from Ref. 88; recalculated as wt. %

α -Methanol conversion (wt. %)

DME = Dimethyl Ether (wt. %)

former reaction is responsible for the increase in selectivity to BTX in total aromatics (Table 2.9). (iii) The yield of aromatics is increased with temperature because its formation is favoured at higher temperatures.

Distribution of aromatics in the aromatic fraction is shown in Table 2.10. Isomer distribution for xylenes is close to the equilibrium distribution. Among the trimethyl benzenes, 1,2,4-trimethyl benzene, is, however, more than at its equilibrium concentration. Its other isomers have lower diffusivities due to steric constraints and hence their formation is less favoured¹⁰².

Table 2.11 and Fig. 2.12 present data for the influence of $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio on product distribution at 400°C . It is seen that there is an increase in $\text{C}_2\text{-C}_4$ olefins accompanying a decrease in $\text{C}_1\text{-C}_4$ paraffins as the ratio is increased. Decrease in the total aromatics is marginal. An increase in higher aliphatics is also observed resulting in decreased selectivity to aromatics in the $\text{C}_5 +$ fraction (Table 2.12). These results may be attributed to the decrease in acidity-number and strength of acid sites - with increase in $\text{SiO}_2/\text{Al}_2\text{O}_3$ as discussed in Section 2.3.F. According to Dejaive et al¹⁰⁴ and Vedrine et al¹⁰⁵ strong acid sites are responsible for dehydrocyclisation of the low molecular weight olefins into aromatics. Fig. 2.12 also shows that the ratio $\text{C}_2\text{-C}_4$ olefins/ $\text{C}_2\text{-C}_4$ paraffins increases with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. The small paraffins are the direct consequence of the reactions of the small olefins, via hydrogen transfer and these reactions are

TABLE - 2.10

DISTRIBUTION OF AROMATICS IN THE CONVERSION
 OF METHANOL TO HYDROCARBONS, WHSV(HR⁻¹) = 2.2

Temperature 400°C

	Normalised distribution (wt. %)	Normalised isomer dis- tribution	Equilibrium* distribution at 400°C
Benzene	3.3		
Toluene	25.1		
Ethyl benzene	2.7		
<u>Xylenes</u>			
o-Xylene	11.2	23.6	23.6
m-Xylene	26.1	55.2	52.4
p-Xylene	10.0	21.2	24.1
<u>Ethyl toluene</u>			
p-ethyl tol.	2.0		
m-ethyl tol.	4.9		
o-ethyl tol.	0.3		
<u>Trimethyl benzenes</u>			
135 TMB	0.8	8.2	26.2*
124 TMB	8.4	85.7	66.0
123 TMB	0.6	6.1	7.8
Other C ₉ +C ₁₀	4.6		

* from ref. 102

TABLE - 2.11

HYDROCARBON DISTRIBUTION IN THE CONVERSION
OF METHANOL :

EFFECT OF SiO₂/Al₂O₃ MOLE RATIO

REACTION TEMPERATURE 400°C, WHSV (HR⁻¹) = 2.2

SiO ₂ /Al ₂ O ₃	82	174	318
α	100	100	>99
DME			0.3
<u>Hydrocarbon distribution (wt.%)</u>			
C ₂ -C ₄ olefins	4.6	10.2	21.5
C ₁ -C ₄ paraffins	48.4	40.1	30.3
C ₅ Aliphatics	19.4	22.7	23.5
<u>Aromatics</u>			
C ₆	0.9	0.9	1.1
C ₇	7.1	6.6	6.3
C ₈	13.8	13.0	13.3
C ₆ -C ₈	21.8	20.5	20.7
C ₉ + C ₁₀	5.8	6.5	4.2

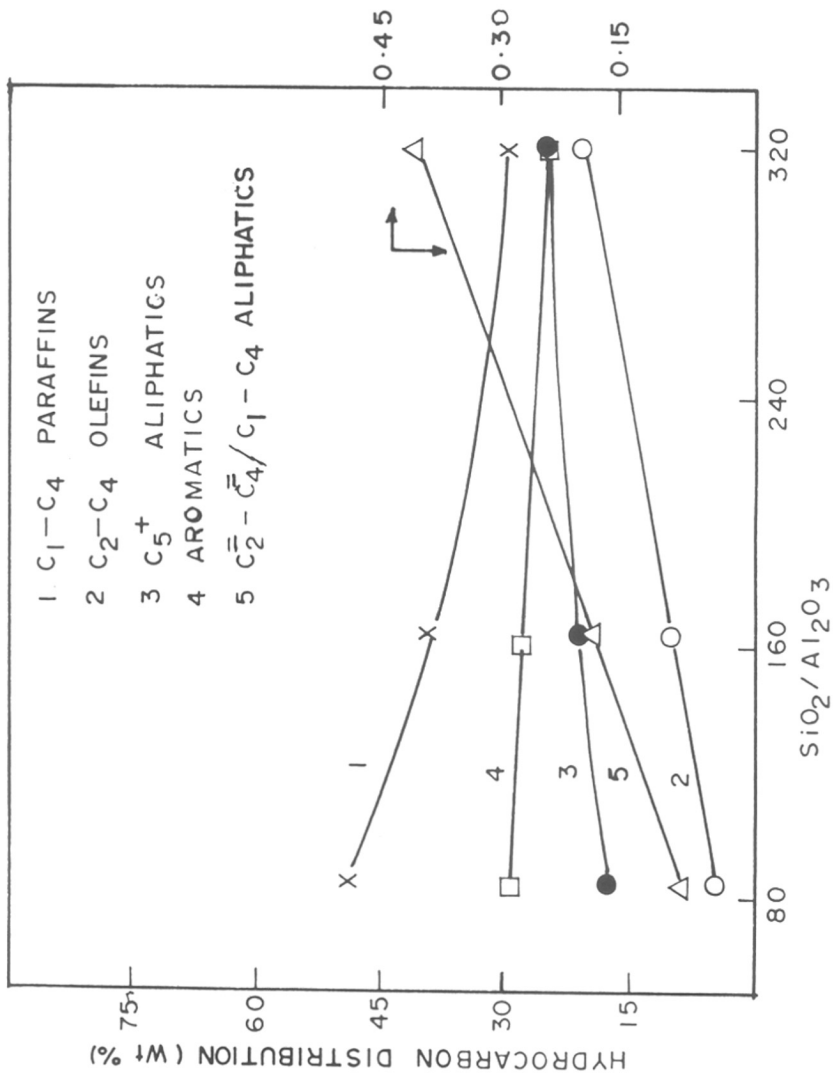


FIG 2·12 METHANOL CONVERSION TO HYDROCARBONS, EFFECT OF SiO₂/Al₂O₃
 MOLE RATIO OF HZSM-5 ON PRODUCT DISTRIBUTION. TEMP. 400°C
 WHSV = 2.2 hr⁻¹

less favoured at lower acidities of the samples^{129,184}. The higher aliphatics are also slightly increased with the increase in ratio as reported in patent literature¹⁷⁶.

Tables 2.12 and 2.13 show selectivity to aromatics in $C_5 +$ and selectivity to $C_9 + C_{10}$ aromatics in total aromatics respectively at different temperatures and SiO_2/Al_2O_3 ratios. The observed effects may be explained, as above. On the basis of (i) high temperature favouring aromatics and (ii) lower acidity reducing aromatics formation. Selectivity to $C_9 + C_{10}$ aromatics is reduced due to dealkylation as stated earlier. Comparing the catalysts with SiO_2/Al_2O_3 ratio 82 and 318, it can be seen that the selectivity to $C_9 + C_{10}$ at $500^\circ C$ (Table 2.13) is reduced to about 25% of that at $350^\circ C$. This is probably because of a more extensive dealkylation of the polyalkyl aromatics on this catalyst with a larger crystallite size. The larger crystallite size further retards the diffusion of the polyalkyl aromatics which are now more amenable to this reaction. For the same reason (i.e. differences in crystallite size) the ratio of (p + m) xylenes to ortho-xylene is increased with increase in SiO_2/Al_2O_3 molar ratio (Table 2.13, last column).

Increase in WHSV reduces further reactions of the olefin intermediates and is one way of decoupling the aromatic formation from the olefin forming reaction^{123,127} (Table 2.14).

TABLE - 2.12

SELECTIVITY TO AROMATICS IN C₅ + FRACTION AS
 A FUNCTION OF SiO₂/Al₂O₃ AT DIFFERENT TEMPERATURES

WHSV (HR⁻¹) = 2.2, CATALYST : HZSM-5

SiO ₂ /Al ₂ O ₃	Temperature °C			
	350	400	450	500
82	55.3	58.8	68.1	70.1
174	-	54.4	65.6	65.3
318	37	51.4	55.7	56.8

TABLE - 2.13

SELECTIVITY TO (C₉ + C₁₀) AROMATICS IN TOTAL
 AROMATICS AS A FUNCTION OF SiO₂/Al₂O₃ AT
 DIFFERENT TEMPERATURES WHSV = 2.2 HR⁻¹

SiO ₂ /Al ₂ O ₃	Temperature °C				(P+M) xyl*
	350	400	450	500	$\frac{\text{o-Xyl}}{400^\circ\text{C}}$
82	36.4	21.0	15.8	18.3	3.7
174	-	23.9	17.5	15.6	4.2
318	35.3	16.8	10.6	8.7	6.8

* Thermodynamic equilibrium ratio for (P + M)
 xylenes/o-xylenes = 3.1

TABLE - 2.14

INFLUENCE OF WHSV ON PRODUCT DISTRIBUTION IN
THE CONVERSION OF METHANOL TO HYDROCARBONS

CATALYST: HZSM-5(82)

	Temperature °C			
	400		500	
WHSV (hr ⁻¹)	2.2	3.73	2.2	3.73
α (wt. %)	100	100	100	100
DME (wt. %)	-	-	-	-
<u>Aliphatics (wt. %)</u>				
C ₂ -C ₄ olefins	4.6	34.2	21.6	46.1
C ₁ -C ₄ paraffins	48.4	24.2	40.8	17.0
C ₅ + aliphatics	19.4	27.1	11.0	24.6
<u>Aromatics (wt. %)</u>				
Benzene	0.9	1.2	1.4	0.9
Toluene	7.1	1.7	8.1	2.4
C ₈ aromatics	13.8	6.2	12.1	5.7
C ₉ + C ₁₀ aromatics	5.8	5.3	4.9	3.5
Selectivity to aromatics in C ₅ +	58.8	34.7	70.7	33.6

However, at large WHSV conversion of methanol goes down and products containing increasing amounts of dimethyl ether (DME) are formed. Table 2.14 shows that the selectivity to aromatics is lower, the higher the WHSV. This is also part of the general pattern of the reaction at higher WHSVs. The increased amounts of water available (at high WHSVs) to poison the strong sites may also be responsible for the lowering of selectivity to aromatics¹⁰⁴. The somewhat lower yield of C₅⁺ aliphatics observed at 500°C for WHSV = 2.2 may be due to cracking of these at this temperature. Such cracking reactions are important for C₅ + aliphatics and they yield C₂, C₃, C₄ hydrocarbons⁸⁵.

D : Conversion of ethanol, diethyl ether
and ethylene to hydrocarbons

Hydrocarbon product distribution in the conversion of ethanol over HZSM-5 (82) is shown in Table 2.15a along with data obtained for the same reaction under fairly identical conditions by Derouane et al⁸⁸. The differences are probably due to difference in molar ratio of the catalyst. A comparison with the data presented in Col. 2, Table 2.9, for methanol conversion shows that there is similarity of products formed, as pointed out by several others^{88,134,179}. The following marginal differences may be noted :

(1) There is smaller amount of CH₄ formed in the ethanol reaction.

TABLE - 2.15 a

CONVERSION OF ETHANOL (EtOH) TO HYDROCARBONS
OVER HZSM-5 ZEOLITE AT 400°C, WHSV (HR⁻¹) = 2.2

SiO ₂ /Al ₂ O ₃	82	44*
<u>Hydrocarbons (wt. %)</u>		
C ₁	Trace	-
C ₂	1.9	3.3
C ₃	17.3	20.4
C ₄	36.7	28.4
C ₅ + aliphatics	17.3	13.5
Benzene	2.3	3.1
Toluene	8.9	11.5
Ethyl benzene	2.1	1.8
Xylenes	9.0	13.8
Ethyl toluenes	3.2	3.2
124 TMB	1.0	0.6
C ₉ + C ₁₀ aromatics	0.5	-
Selectivity to aromatics in C ₅ ⁺	61	72

* Derouane et al. Ref. 88, the data were obtained after conversion to wt. %.

(11) The amount of methylated aromatic products is comparatively less and of ethylated products more because of differences in the alkylating agents. The amount of polyalkylated products seem to be less for the ethanol reaction as these are too big to be formed due to product selectivity effect of the zeolite.

In a preliminary study of the ethanol reaction, it was found that ethanol is nearly quantitatively converted to ethylene at about 300°C. At 350°C and above only 2-5% of the products were olefins. Maximum yield of C₅⁺ was observed at ~ 350°C. Its composition changed with temperature in the same manner as observed in the methanol reaction (Table 2.15b). For instance, the increase in BTX and the decrease in C₅⁺ aliphatics and C₉-C₁₀ aromatics (Tables 2.12 and 2.13). These trends in product distribution are common to both systems and suggest a common reaction pathway involving light olefins¹⁷⁹.

Diethyl ether also reacts over HZSM-5. A single run carried out at 400°C (stabilised temperature) gave hydrocarbon distribution shown in Table 2.15b. The catalyst was found to be extensively coked at the end of 30 minutes reaction. Also the rise in temperature observed due to reaction (approximately 25°C) was maintained only during 20 minutes which is probably another indication of deactivation in a short time. However, it can be seen that C₅⁺ composition is essentially similar to that for ethanol.

TABLE - 2.15 b

EFFECT OF TEMPERATURE ON THE YIELD AND COMPOSITION
OF C₅ + IN THE CONVERSION OF ETHANOL TO HYDROCARBONS
ON HZSM-5 (82), WHSV (hr⁻¹) = 2.9

Hydrocarbon composition (wt. %)	Temperature °C				
	300	350	400	450	500
Aliphatics	99.5*	52	59 (65)**	63	73
C ₅ +	0.5	48	41 (35)	37	27
<u>Composition of C₅ +</u>					
C ₅ + aliphatics	Trace	14	16 (16)	6	5
C ₆ -C ₈ aromatics	Trace	59	69 (61)	88	89
C ₉ + C ₁₀ "	Major	27	15 (23)	6	6
Selectivity to C ₉ + C ₁₀ in total aromatics	-	31.4	17.9	6.4	6.3

* Consists essentially ethylene

** The bracket figures are for diethyl ether over the same catalyst at 400°C and WHSV (hr⁻¹) = 1.33.

The low reactivity of C_2H_4 observed by Anderson et al.⁶² and confirmed by Derouane et al.¹⁰⁴ was later disproved by Van Hooff et al.¹¹³ who observed nearly complete conversion of ethylene at $310^\circ C$. In the present study, it is found that C_2H_4 is equally reactive and yield hydrocarbon distribution similar to those of ethanol and methanol (Table 2.16).

Bragino et al.¹⁸⁰ had found that C_2H_4 and methanol gave almost identical product distribution at a conversion of about 90%. Their data for C_2H_4 conversion at $400^\circ C$ are also shown in Table 2.16 for comparison. The differences in catalyst composition are too large for valid comparison to be made in the product distribution. But the point is sustained as shown by several others^{113,179,180} that C_2H_4 is equally reactive and that earlier results might have been due to low temperature and high space velocities being used for the reaction. The high reactivity and similarity in product distribution are further confirmed by the data to be presented in a later part of the Section where these are compared for different reactions at same temperature.

The effect of time on stream on the yield and composition of C_5^+ is shown in Table 2.17 and Fig. 2.13A. It is found that the yield of C_5^+ reaches a value of 40-45% of the weight of C_2H_4 passed and this yield remains constant during 60 hours of time on stream. A change in composition in C_5^+ was, however, found with increasing amounts of aliphatics with time on stream (TOS). This may be because some of the strong sites required for aromatics formation are deactivated or made inaccessible by pore mouth blocking due to formation of coke. $C_9 + C_{10}$

TABLE - 2.16

CONVERSION OF ETHYLENE OVER HZSM-5(82)
TO HYDROCARBONS AT 400°C, WHSV = 0.90,
% CONVERSION = 95
OF ETHYLENE

<u>Hydrocarbons wt. %</u>		
C ₁	Trace	0.6*
C ₂	8.3	4.3
C ₃	17.4	18.5
C ₄	25.2	38.6
C ₁ -C ₄	50.9	62
/ C ₅ + aliphatics	13.4	3
<u>Aromatics</u>		
Benzene	1.7	3.8
Toluene	9.2	10.6
Ethyl benzene	3.0	-
Xylenes	11.9	7.6
C ₉ + C ₁₀ aromatics	8.4	12.9
DEB (1,4)	1.5	-
Selectivity to aromatics	73.0	92.0

* From Ref. 180

TABLE - 2.17

EFFECT OF TIME ON STREAM IN CONVERSION
OF ETHYLENE TO C₅ + HYDROCARBONS AT 415°C
ON HZSM-5(82), WHSV = 0.9 hr⁻¹

	Time on stream, hrs.					
	5	15	19	38	48	60
C ₅ + yield (wt.%) [*]	38	47	46	43	43	45
<u>C₅ + composition</u> <u>(wt. %)</u>						
C ₅ + aliphatics	13	17	21	44	49	52
BTX	64	62	53	34	32	30
C ₉ + C ₁₀ aromatics	23	21	26	22	19	18
Selectivity to aromatics in C ₅ +	87	83	79	56	41	48

* Based on C₂H₄ passed.

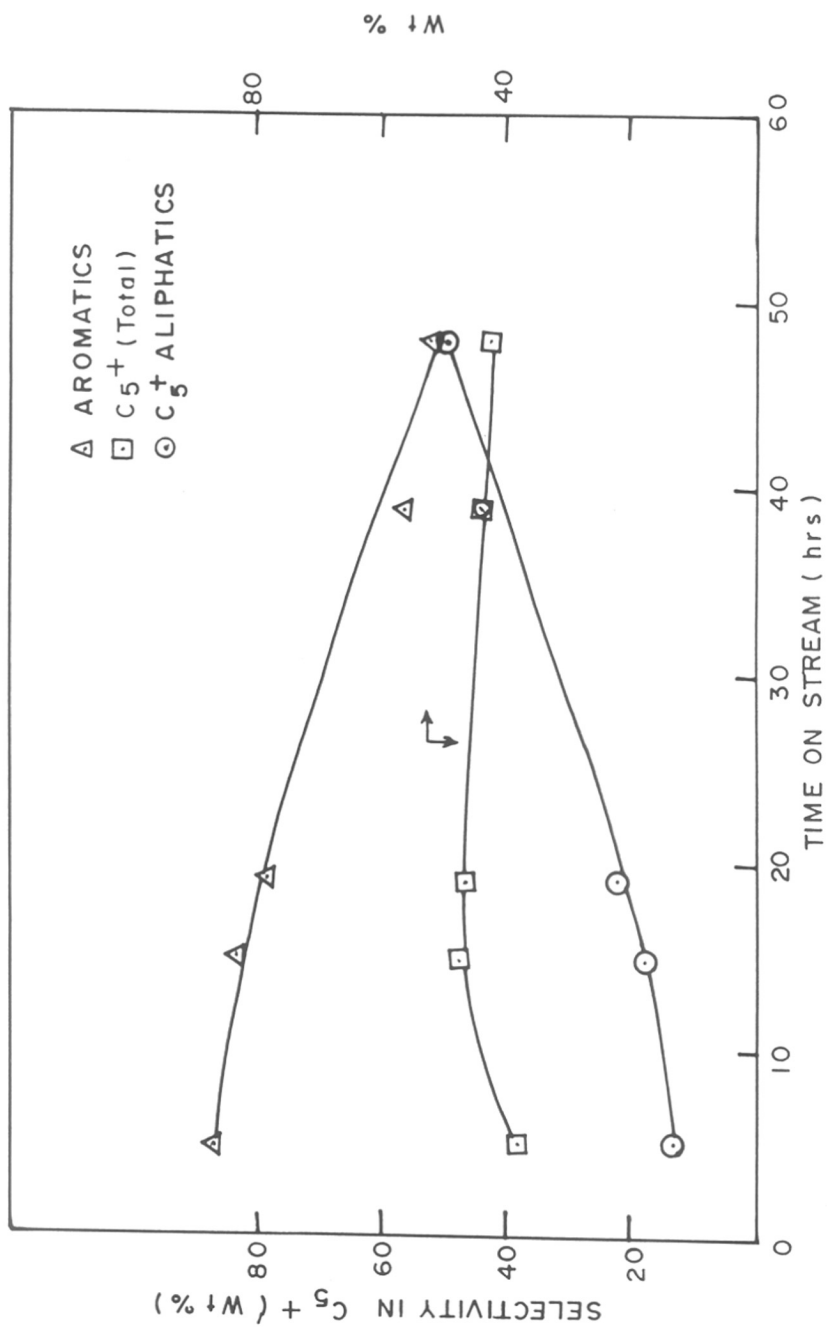


FIG 2.13A EFFECT OF TIME ON STREAM ON C₅⁺ COMPOSITION IN THE CONVERSION OF ETHYLENE TO HYDROCARBONS OVER HZSM-5 (82).
TEMP. = 400°C WHSV = 0.9 hr⁻¹

aromatics are less affected by this, probably because they are also formed on the active sites on the external surface of the zeolite whose contribution to catalytic activity is not negligible¹⁸¹. It is also probable that the effective residence time of BTX within the pores is somehow increased, probably by 'bulk restriction'¹⁸² so that the incidence of further alkylation of toluene and xylenes is increased. This of course presupposes that 'bulk restriction' is sufficiently small so as not to affect the diffusion of the higher aromatics to any significant extent. Increase in residence time does increase the yield of ($C_9 + C_{10}$) aromatics slightly in the methanol reaction (Table 2.14). Rajadhyaksha and Anderson have reported a very large increase in $C_9 + C_{10}$ aromatics for large values of TOS with the corresponding decrease in toluene and xylenes¹⁸³.

Effect of temperature on aromatics distribution in the $C_5 +$ fraction in the conversion of C_2H_4 is shown in Table 2.18 and Fig. 2.13B. It can be seen that as in the case of methanol, with increase in temperature, C_6-C_8 aromatics are increased and higher aliphatics and higher aromatics are decreased (Tables 2.12 and 2.13).

Approximate yields of the $C_5 +$ fraction for methanol (Me), ethanol (E), diethyl ether (DEE) and ethylene are shown in Table 2.19 for reaction at different temperatures. The maximum yield in all cases is at about $350^\circ C$ as against $340-380^\circ C$ reported in an earlier study¹⁷⁹.

TABLE - 2.18

EFFECT OF TEMPERATURE ON AROMATICS DISTRIBUTION
(WT. %) IN THE C₅ + FRACTION IN THE CONVERSION OF
ETHYLENE OVER HZSM-5(82)** , WHSV (HR⁻¹) = 0.9

Temperature °C	C ₅ ⁺ ali- phatics	B	T	C ₈ aro- matics	C ₆ -C ₈ aromatics	C ₉ +C ₁₀
250	35	*	*	*	36	29
300	45	*	*	*	30	25
350	46	5	9	18	32	22
400	27	4	19	30	53	20
450	7	10	36	39	85	8
500	5	12	39	38	89	5

* Only total BTX are estimated.

** The values given are initial values. There was a large effect of TOS on product distribution.

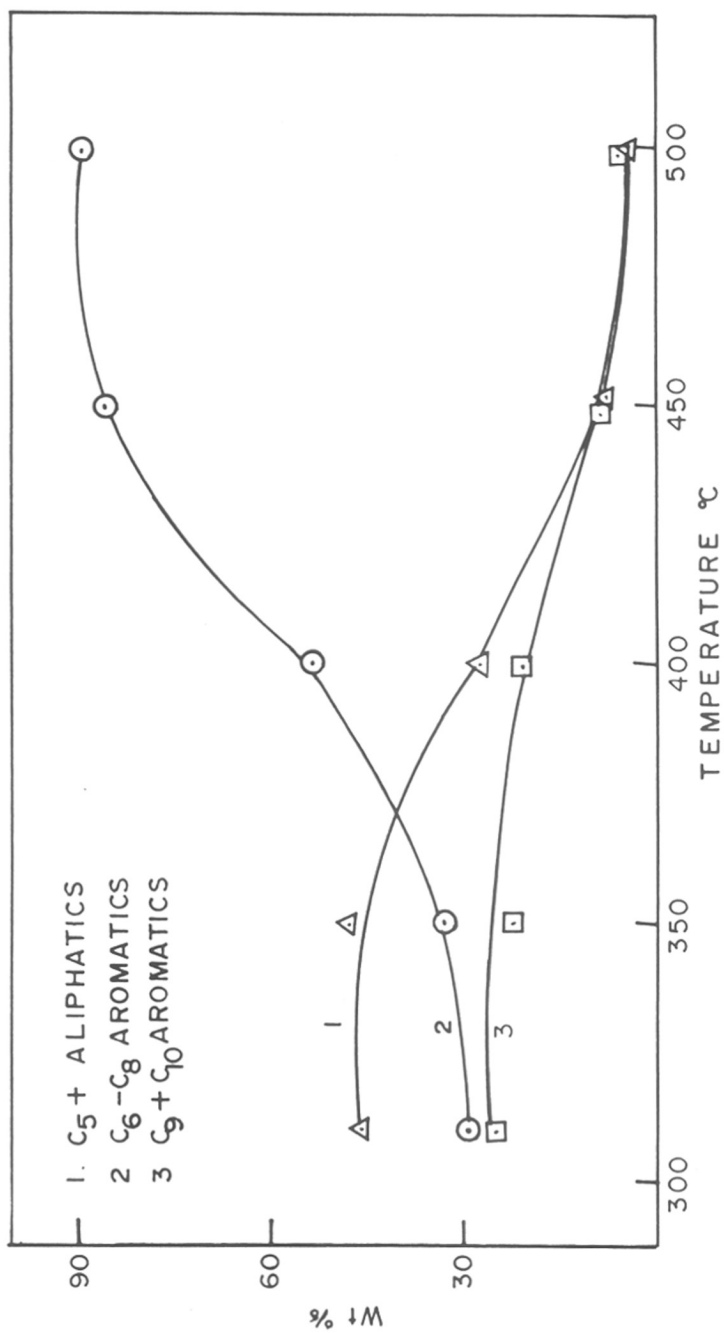


FIG 2-13 B CONVERSION OF C₂H₄ TO HYDROCARBONS OVER HZSM-5 (8.2)
EFFECT OF TEMPERATURE ON C₅ + COMPOSITION

TABLE - 2.19

YIELD* OF C₅ + HYDROCARBONS (WT. %) ON HZSM-5 (82)
FOR DIFFERENT REACTANTS AT VARIOUS TEMPERATURES (°C)

WHSV (hr⁻¹) 2.2 (MeOH), 2.9 (EtOH), 1.33 (DEE), 0.9 (C₂H₄)

Reactant	250	300	350	400	450	500
Methanol	-	< 20 ^a	58	47	46	37
Ethanol ^c	-	Trace	48	44	37	27
				39 ^c		
Diethyl ether ^b	-	-	-	35	-	-
Ethylene	4	35	66 ^{**}	49	37	37
				58 ^d		

* Calculated on CH₂ basis.

** Average of many runs.

a - Precise value was difficult due to unsteady temperature conditions.

b - Available for only one temperature. c - for WHSV 1.46 hr⁻¹.

d - For WHSV (hr⁻¹) = 1.8

The composition of aromatics in $C_5 +$ fraction for all reactions at $400^\circ C$ is shown in Table 2.20. The product distribution is qualitatively and quantitatively similar. The TOS effect for C_2H_4 reaction shows high selectivity to aromatics only in the initial stage of the reaction (Table 2.17).

Table 2.21 shows the BTX aromatics yield for the different reactions at various temperatures. Again, there is a fair agreement for the yields observed.

The data presented for various systems indicate similarity of reaction intermediates and their subsequent reactions^{128,179,181,185}. According to Derouane et al¹⁸⁵ similarities in product distribution are imposed by the shape selectivity of the zeolite and no proofs for identity of the of the active intermediates in different systems whereas according to Minachev et al^{179,180} they do indicate the presence of common intermediates i.e. light olefins. According to Itoh et al¹¹⁶ shape selective properties of the zeolite play only a secondary role in the conversions and that the products obtained from different zeolites and feeds show essentially the same product distribution. The acid properties of the zeolites are proposed to be the dominant factor in directing product distribution. The present results are in agreement with the proposal for a common reaction pathway with light olefins as intermediates^{113,179,180}. The acidity of the catalysts plays its role in the selectivity effects observed and this is further shown in the study of reactions over modified zeolites discussed in a subsequent section.

TABLE - 2.20

DISTRIBUTION OF AROMATICS IN C₅ + FRACTION OBTAINED
 BY REACTION OF DIFFERENT FEEDS ON HZSM-5(82) AT
 400°C, WHSV = 2.2(MeOH), 1.46(EtOH), 1.3(DEE) AND
0.88(C₂H₄)

Feed	% C ₅ + in total hydro- carbon	Hydrocarbon distribution in C ₅ +					Selectivity to aromatics in C ₅ +
		C ₅ + aliph.	B	T	C ₈ * arom.	C ₉ +C ₁₀	
Methanol	47	41	2	15	30	12	59
Ethanol	39	28	5	25	29	13	72
Diethyl ether	35	16	3	23	35	23	84
Ethylene	49	27	4	19	30	20	73

* C₈ aromatics = Xyl + EB.

TABLE - 2.21

NORMALISED YIELD OF BTX AND
C₅ + (GASOLINE FRACTION) PER MOLE OF
CH₂ FROM DIFFERENT FEEDS

Feed	Temperature °C							
	350		400		450		500	
	BTX	C ₅ +	BTX	C ₅ +	BTX	C ₅ +	BTX	C ₅ +
Methanol	5.9	17	6.5	13.8	7.6	13.5	6.2	10.9
Ethyl alcohol	-	-	7.2	12.3	-	-	-	-
Diethyl ether	-	-	5.8	9.7	-	-	-	-
Ethylene	6.8	21.2	8.4	15.8	10.0	11.9	10.6	11.9

E : Conversion of methanol to light olefins

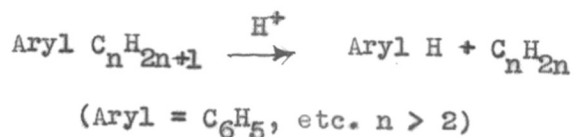
In view of the importance of light olefins to petrochemical industry, several efforts have been made to convert methanol to these materials by minimising drastically the occurrence of their subsequent reactions in the methanol conversion. This can be achieved by altering the acidity of the zeolite and/or its shape selective characteristics. In many cases this is done by incorporating various inorganic compounds such as oxides of phosphorous^{75,114,192,167} magnesium^{187,192}, molybdenum¹⁸⁸, boron¹⁸⁹, etc. either singly or in mixed forms¹⁸⁷ into the zeolite. The use of dilute aqueous solutions of methanol as feed is known to increase selectivity to olefin in the conversion of methanol^{167,190,192}. The use of high space velocities, high temperature and high $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio has also been reported¹²⁷. Zeolites prepared by isomorphous substitution of aluminium with boron or transition metal elements are reported to be good catalysts for methanol to olefin (MTO) reaction in patent literature¹⁹³⁻¹⁹⁶.

In this section, the effects of $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio and temperature on selectivity to various products especially light olefins are reported. Effects of progressive dilution of methanol and modification of catalyst on selectivity are also shown. All reactions were carried out at 400°C and above as high temperatures enhance the yield of olefins at complete conversion of methanol.

F : Results and Discussion

(1) Effect of SiO₂/Al₂O₃ ratio

The effect of temperature on HZSM-5(82) and HZSM-5(318) for conversion of methanol to olefins was studied. Results are presented in Tables 2.22, 2.23 and Fig. 2.14. The yield of olefins is found to drop to a minimum for both catalysts and increase at temperature above 400°C. The trend is reversed for C₂-C₄ paraffins. C₅ + also shows a drop with increase in temperature in both cases. The observed effects of temperature can be attributed to secondary reactions like cracking of higher aliphatics and dealkylation of aromatics. It has been shown that dealkylation of aromatics provide an alternate route for formation of olefins and can be represented as shown below¹⁹⁷ :



Increase in SiO₂/Al₂O₃ ratio increases the olefin yield by reducing the acidity (strength and number of acid sites) of the sample. Conversion of olefins to paraffins and dehydrocyclisation leading to aromatics requiring strong acid sites are reduced which result in increased olefin yield. The relative increase in olefins is found to be largest for butenes (Tables 2.22 and 2.23). This is in keeping with their largest contribution to the formation of aromatics¹⁰⁴.

TABLE - 2.22

EFFECT OF SiO₂/Al₂O₃ RATIO ON HYDROCARBON
DISTRIBUTION IN THE CONVERSION OF METHANOL
TO OLEFINS

CATALYST : HZSM-5, TEMP. 400°C, WHSV = 2.2 hr⁻¹

	<u>SiO₂/Al₂O₃ ratio</u>		
	82	174	318
α (wt. %)	100	100	>99
DME (wt. %)	-	-	0.3
<u>Hydrocarbon distribution(wt.%)</u>			
C ₂ =	1.30	2.3	4.8
C ₃ =	2.3	3.8	8.6
C ₄ =	1.1	4.1	8.2
C ₂ — C ₄ olefins	4.6	10.2	21.5
C ₁ - C ₄ saturates	48.4	40.2	30.0
C ₅ +	47.0	49.7	48.4

TABLE - 2.23

EFFECT OF SiO₂/Al₂O₃ MOLE RATIO ON HYDRO-
CARBON DISTRIBUTION IN THE CONVERSION OF
METHANOL TO OLEFINS

TEMP. 500°C, WHSV 2.2 hr⁻¹, CATALYST : HZSM-5

	<u>SiO₂/Al₂O₃ ratio</u>		
	82	174	318
α (wt. %)	100	100	>99
DME (wt. %)	-	-	0.3
<u>Hydrocarbon distribution (wt. %)</u>			
C ₂ =	8.3	8.70	13.2
C ₃ =	10.4	11.8	20.5
C ₄ =	3.0	5.8	9.1
C ₂ — C ₄ olefins	21.6	26.2	42.8
C ₁ - C ₄ saturates	40.8	37.8	23.3
C ₅ +	37.5	35.9	33.9

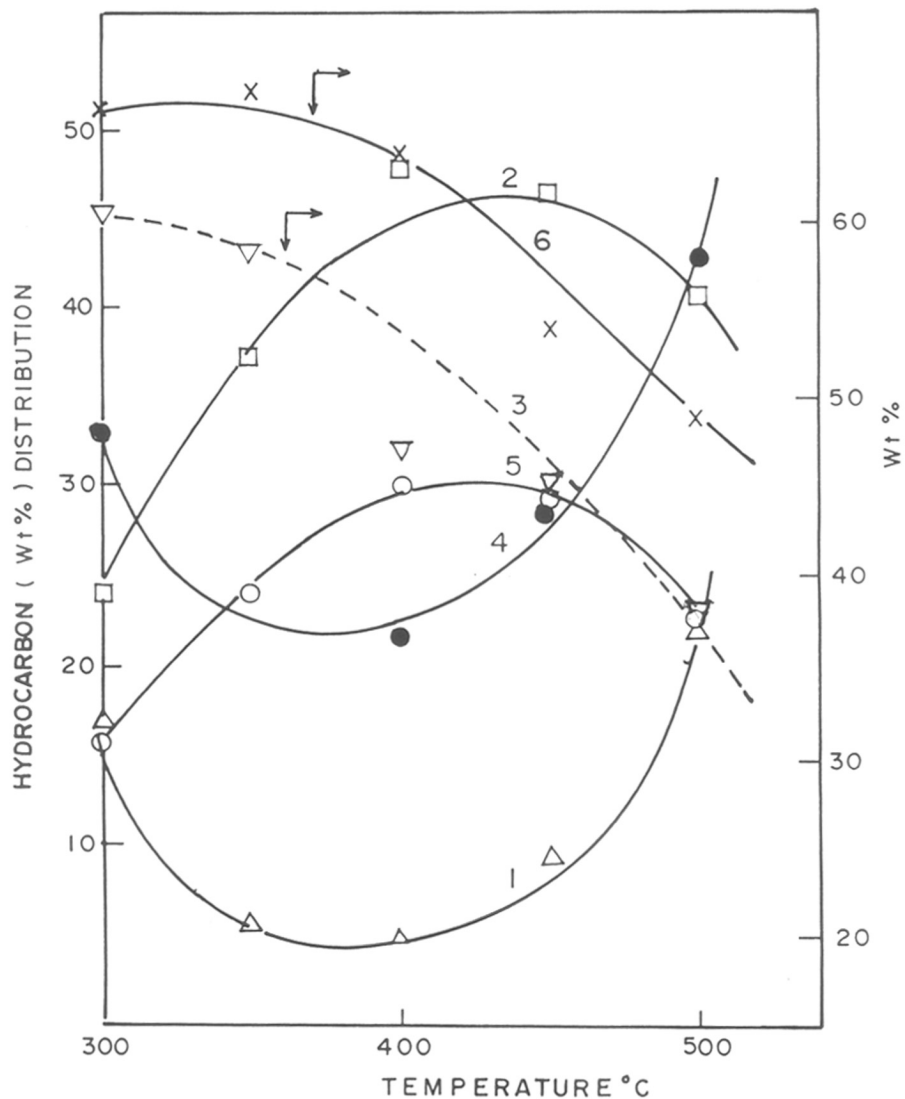


FIG 2-14 HYDROCARBON DISTRIBUTION IN THE CONVERSION OF METHANOL OVER HZSM-5. CURVE NOS 1, 2 & 3 ARE FOR C_2-C_4 OLEFINS, C_1-C_4 PARAFFINS AND C_5^+ RESPECTIVELY $SiO_2/Al_2O_3 = 82$, 4, 5 & 6 ARE THE SAME FOR $SiO_2/Al_2O_3 = 318$

(ii) Effect of dilution of methanol with water

Figs. 2.15 and 2.16 show that dilute solutions of methanol yield higher amounts of olefins at the expense of $C_5 +$ as reported by several others^{167,193-196} and patent literature^{198,199}. The increase in olefins reaches a maximum (about 62%) at 500°C at about 45-50% (w/w) water in the feed. The effect of dilution on C_2-C_4 paraffins is negligible (Fig. 2.15). Table 2.24 shows that the effect is essentially due to a decrease in $C_5 +$ aliphatics. The aromatics are almost unaffected at all temperatures although the feed contained about 70% (w/w) water. The observed increase in light olefins in presence of water may be due to increased rate of alkylation of $C_2 =$ and $C_3 =$ with CH_3OH to produce C_3-C_4 olefins compared to the chain growth reactions of these olefins¹¹². Easier desorption of olefins into the gaseous phase due to presence of large amounts of water vapour may also be responsible for the increase in olefin yield^{108,192}. The amount of CH_4 is found to increase with water content above 60% in the feed (Fig. 2.16).

(iii) Effect of modification of zeolite

Table 2.25 shows data for conversion of methanol to olefins over phosphorous and boron modified zeolites. It can be noted that both catalysts show high selectivity to olefins, but at lower conversions.

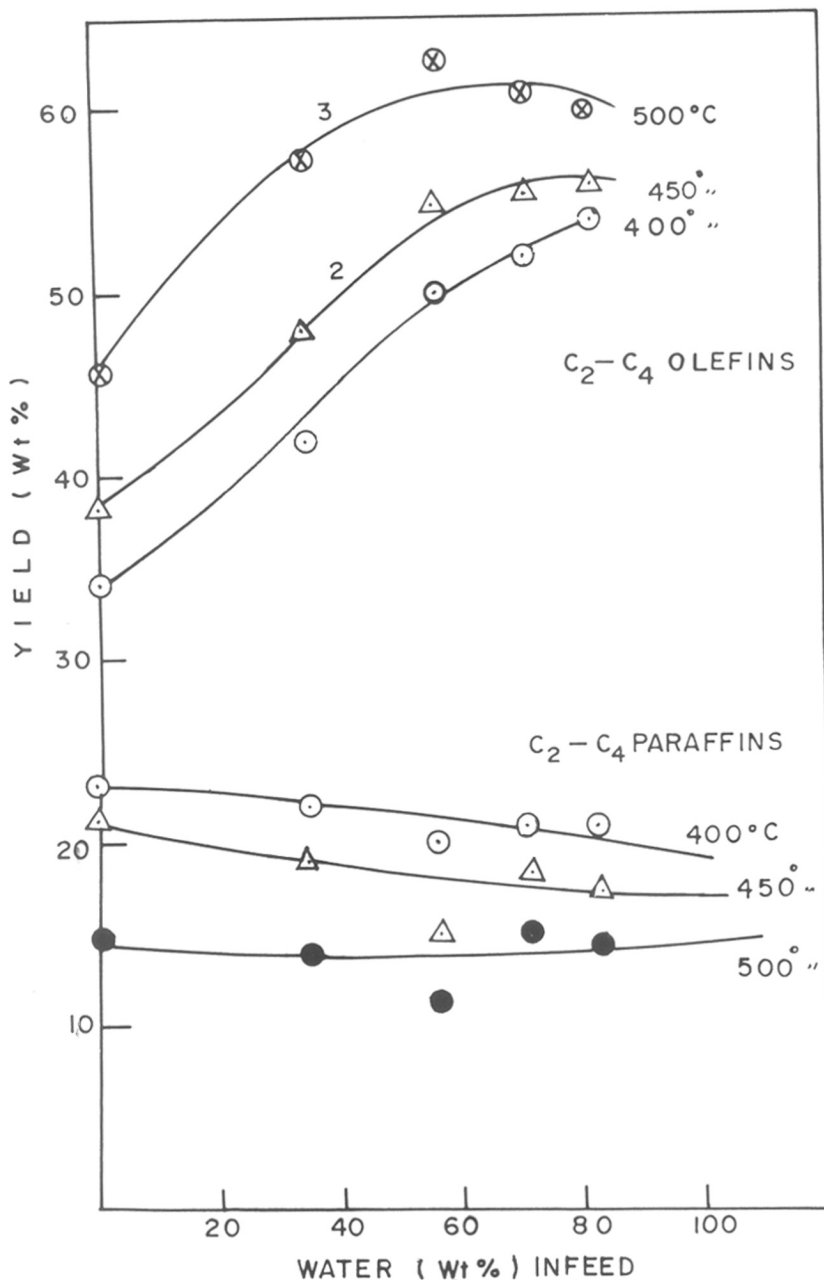


FIG. 2.15 CONVERSION OF METHANOL OVER HZSM-5 (82). EFFECT OF DILUTION ON THE YIELD OF LIGHT OLEFINS AND C₂-C₄ PARAFFINS AT DIFFERENT TEMPERATURES. LINEAR CONTACT TIME 0.3 Sec.

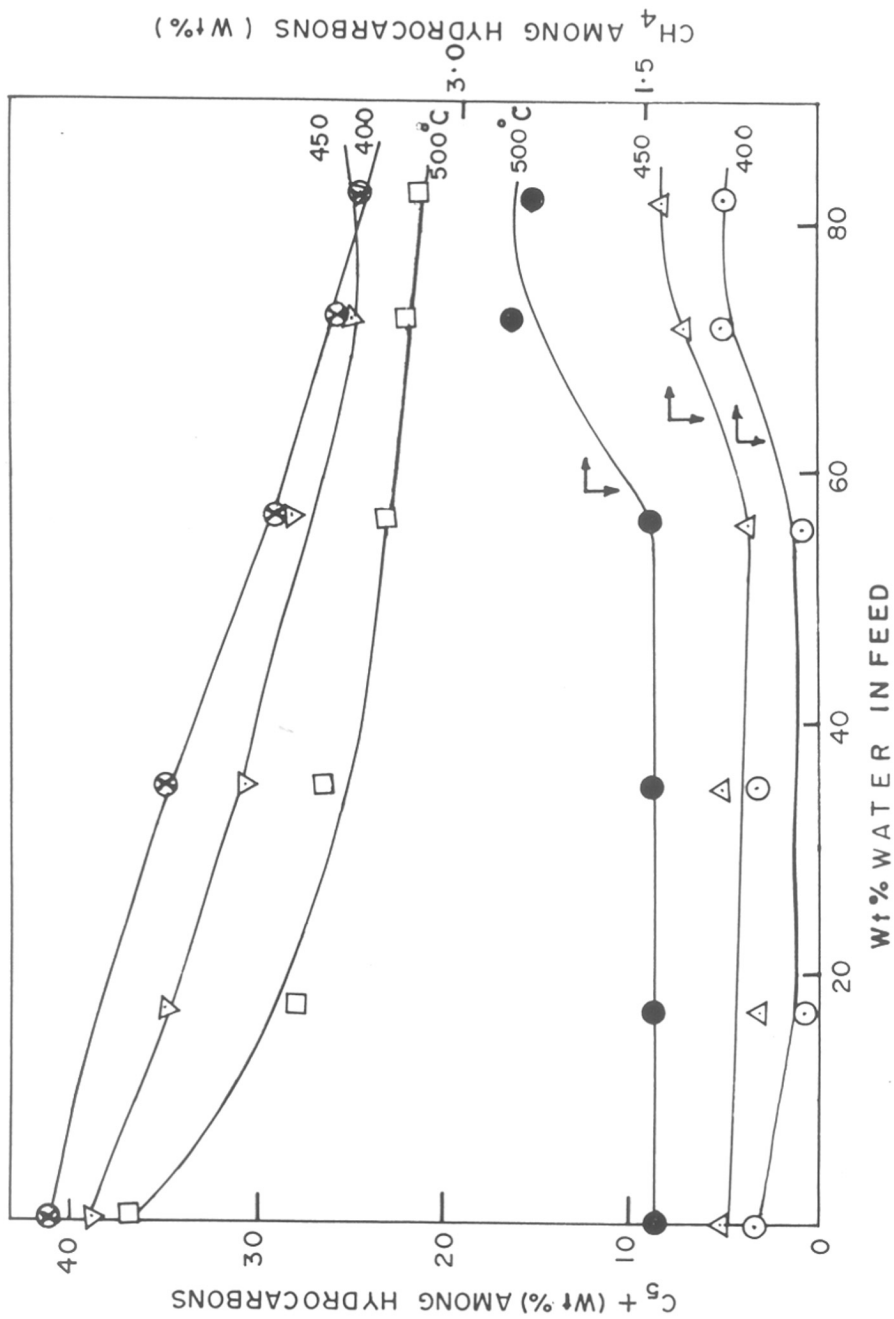


FIG 2.16 CONVERSION OF METHANOL OVER HZSM - 5 (82)
EFFECT OF DILUTION ON CH₄ AND C₅+ YIELD AT DIFFERENT TEMP.

TABLE - 2.24

COMPARISON OF PRODUCT COMPOSITION IN THE
 CONVERSION OF METHANOL AND AQUEOUS METHANOL
 (28 % W/W) OVER HZSM-5 (82)

LINEAR CONTACT TIME = 0.3 SEC.,
 METHANOL = I, AQUEOUS METHANOL - II,

Hydrocarbon* Composition Wt. %	Temperature °C					
	400		450		500	
	I	II	I	II	I	II
Ethylene	10.5	19.3	8.5	19.9	9.7	19.9
Propene	9.9	20.1	14.0	24.1	20.8	30.7
Butenes	13.8	12.3	16.0	11.5	15.5	10.2
C ₂ -C ₄ olefins	34.2	51.7	38.5	55.4	46.1	60.7
C ₁ -C ₄ paraffins	24.2	22.1	21.9	19.5	17	17
C ₅ + aliphatics	27.2	11.8	25.7	12.3	24.6	10.4
BTX aromatics	9.1	9.9	9.4	8.7	9.0	8.1
C ₉ + C ₁₀ aromatics	5.3	4.5	4.4	4.0	3.5	3.5
Selectivity to aromatics	34.6	55.0	34.9	50.8	42.4	52.7

* Conversion of methanol, wt.% = 100, DME, wt.% = 0.

TABLE - 2.25

EFFECT OF IMPREGNATION OF HZSM-5(82) WITH
PHOSPHOROUS AND BORON ON HYDROCARBON DIS-
TRIBUTION IN THE CONVERSION OF METHANOL TO

OLEFINS

TEMP. 400°C; WHSV = 2-2.2 hr⁻¹;

CATALYST : AS INDICATED

	HZSM-5(82)	HZSM-5(82)	
		(-P-3)	(-B-3)
α (wt. %)	100	64.3	87.7
DME (wt. %)	-	49.1	2.8
<u>Hydrocarbon distribution(wt.%)</u>			
C ₂ =	1.3	14.3	27.1
C ₃ =	2.3	41.1	19.6
C ₄ =	1.1	17.8	10.1
C ₂ -C ₄ olefins	4.7	73.2	56.8
C ₁ -C ₄ saturates	48.4	4.1	11.9
C ₅ +	47.0	22.6	31.4
C ₂ = C ₂ -C ₄ (%)* (olefins)	28.0	19.5	47.7

* Selectivity to ethylene in C₂-C₄ olefins.

The observed effects, high selectivity to olefins and low conversions, may be attributed to adsorption and acidic properties of the modified zeolites. A reduction in effective dimensions of the channels, reflected in reduced pore volume and surface area (Table 2.5) is observed upon modification¹⁵⁵. The sorption uptake and rate was greatly reduced indicating channel plugging and partial pore mouth blocking by the phosphorous species. Such reduction in effective channel size (and pore mouth blockage) can enhance selectivity (via product selectivity) to olefins. Thus products rich in light olefins, as observed in the case of small pore zeolite catalysts^{186,200} are formed. The lower acidity of the modified zeolites as illustrated in the TPD spectra (Fig. 2.10) and Table 2.8 must be reducing the incidence of hydrogen transfer^{129,184} and dehydrocyclisation¹⁰³ reactions thus lowering selectivity to saturated hydrocarbons and aromatics respectively observed in the study at 500°C (Table 2.26). This table also shows the effect of space velocity on hydrocarbon distribution. It is found that selectivity to ethylene in C₂-C₄ olefins is higher for the boron modified catalyst. The greater hydrophilicity of this zeolite (Table 2.5) compared to the phosphorous modified zeolite may be responsible for this. The methyl ethyl oxonium ion which has been proposed as an intermediate in the formation of the first C-C bond¹¹³ has two parallel reactions, one leading

TABLE - 2.26

EFFECT OF WHSV ON CONVERSION AND SELECTIVITY
IN THE CONVERSION OF METHANOL TO OLEFIN ON A
PHOSPHOROUS MODIFIED HZSM-5

CATALYST : HZSM-5(82-P-3)

TEMP . : 500°C

	WHSV (hr ⁻¹)		
	0.55	1.1	2.2
α (wt. %)	89.6	81.0	77.9
DME (wt. %)	Trace	3.3	9.2
<u>Hydrocarbon distribution (wt. %)</u>			
C ₂ =	12.7	9.8	7.8
C ₃ =	43.4	42.1	40.6
C ₄ =	19.0	18.9	21.0
C ₂ -C ₄ olefins	75.1	65.6	69.4
C ₁	1.6	1.6	4.0
C ₂	Trace	Trace	0.2
C ₃	2	1	0.3
C ₄	2.3	1.7	0.4
C ₁ -C ₄ paraffins	5.8	4.3	4.9
C ₅ +	19.1	24.8	27.1
C ₅ + aliphatics	15.6	20.5	-
Selectivity to aromatics in C ₅ +	18.4	17.5	-

to C_2H_4 formation by reaction with water and the other leading to propene by reaction with methanol/DME. A larger concentration of water in the pores may therefore be favouring preferentially formation of C_2H_4 in the case of HZSM-5 (82-B-3) catalyst.

Vedrine et al⁷⁵ who have studied acidity of HZSM-5 and modified HZSM-5 by IR and microcalorimetric measurements have reported that the changes on selectivity brought about by modification are more likely to be due to reduction in channel size and increased tortuosity due to the phosphorous compounds binding to the zeolite framework, rather than to changes in acid strength. They observed neutralisation of a part of the acid sites by phosphorous rather than a decrease in the strength of the acid sites responsible for catalytic reaction. Earlier an increase in number and decrease in strength were proposed by Kaeding and Butter¹¹⁴ to be responsible for the increased selectivity to olefins by the modification.

The results of the present study are in agreement with those of Vedrine et al^{75,192} because adsorption, TPD and activity measurements for methanol conversion have indicated the following :

1. There is a reduction in pore volume and surface area caused by plugging of the channel interior by phosphorous species penetrating into the channel which is further confirmed by the lower uptake of heptane (Table 2.5).

2. There is a reduction in the uptake of benzene and cyclohexane (Table 2.5).
3. There is only a reduction in the number of strong acid sites as indicated by the TPD spectra (Fig. 2.10). The strong sites represented by γ peaks in the original HZSM-5 sample are still present though their number is considerably less). This is reflected in a reduction in the yield of aromatics and C_1-C_4 paraffins whose formation requires strong sites (Table 2.26).
4. There is also a reduction in the total number of acid sites (Table 2.25) which results in lower conversion of methanol. Also larger amounts of $C_9 + C_{10}$ aromatics in total aromatics are found because their dealkylation which requires strong sites is less.
5. There is diffusional restriction introduced by the presence of the phosphorous compounds which results in higher selectivity to p-xylene^{87,138} (Table 2.27).

The higher selectivity to olefins for HZSM-5 (32-B-3) may also be explained in a similar manner. The acidity and hence the activity of this catalyst is found to be higher than that of HZSM-5(32-P-3) (Fig. 2.10 and Table 2.25).

TABLE - 2.27

EFFECT OF IMPREGNATION OF PHOSPHORUS
ON DISTRIBUTION OF AROMATICS (WT. %)
IN THE CONVERSION OF METHANOL

TEMPERATURE °C - 400.

WHSV (hr^{-1}) = 2.2 [for HZSM-5(82)] (I);
 1.1 [HZSM-5(82-P-3)] (II)

	CATALYST	
	I	II
Benzene	3.3	6.5
Toluene	25.7	7.6
Ethyl benzene	2.7	2.6
P-Xylene	11.2	41.9
m-Xylene	26.1	9.9
o-Xylene	10.0	4.9
C ₉ + C ₁₀ aromatics	21.0	26.6

2.5. C O N C L U S I O N S

1. ZSM-5 type zeolites having different $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratios (R) have been prepared and characterised. Adsorption and acidic properties of these and their variation with R are in essential agreement with those reported in literature. The decrease in sorption of ortho-xylene, 1,2,4-trimethyl benzene and cyclohexane with increase in R is only apparent and may be due to an increase in crystallite size.
2. Methanol, ethanol, diethyl ether and ethylene react over HZSM-5 zeolite yielding nearly the same hydrocarbon product distribution. $\text{C}_5 +$ yield is maximum in the temperature range $350\text{--}400^\circ\text{C}$ in the conversion of these reactants. Above 400°C , the yield of light olefins ($\text{C}_2\text{--C}_4$) increases. Cracking of higher aliphatics and dealkylation of higher aromatics are suggested to be responsible for this.
3. Yields of $\text{C}_5 +$ and BTX aromatics, the composition of $\text{C}_5 +$ and the influence of temperature on these are similar in the conversion of the above reactants. These suggest a common reaction scheme involving light olefins for their conversions.
4. Methanol can be converted to light olefins in large yields by different methods such as using dilute aqueous solutions at high temperatures, a high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the catalysts and catalysts modified by incorporation of

phosphorous or boron. The use of dilute aqueous solutions results in increase in the yield of C_2-C_4 olefins as high as 62% among the hydrocarbon products. This is explained as being due to easier desorption of olefins from the pores in presence of large amounts of water vapour. Decrease in the yield of $C_5 +$ observed is essentially due to decrease in $C_5 +$ aliphatics.

5. Increase in SiO_2/Al_2O_3 molar ratio in the catalyst increases the yield of olefins by virtue of the catalyst's lower acidity. Subsequent reactions of the light olefin intermediates such as hydrogen transfer (mainly) and dehydrocyclisations are reduced and this results in the increase observed.

6. Sorption properties of the modified zeolites suggest pore mouth blocking and channel plugging by modifier species. A reduction in the acidity of the modified zeolites, especially in the number of strong acid sites is also found. Thus enhanced product selectivity effects and suppression of olefin-disappearing reactions are registered in high yields of light olefins among the products.

CHAPTER III : MODIFICATION BY HETEROATOM SUBSTITUTION -
EFFECT ON CONVERSION OF METHANOL TO LIGHT
OLEFINS.

I N T R O D U C T I O N

There are reports mostly in patent literature^{193,195} that aluminium in the zeolite can be replaced with trivalent metal ions like boron, iron, chromium, etc. Since the zeolites so prepared are reportedly good catalysts^{198,220} for conversion of methanol to light olefins, it was part of the present investigation to prepare some of these, namely, ferric, boro and lanthanum silicates and study their adsorption, acidic and catalytic properties with reference to this reaction. Subsequently, their catalytic properties with respect to some wellknown aromatic reactions were compared and these would be discussed in Chapter 4. These zeolites have been designated as Fe/HZSM-5(86), B/HZSM-5(72) and La/HZSM-5(90), the figures in brackets representing $\text{SiO}_2/\text{M}_2\text{O}_3$ ratio, M being the substituent metal. They have been further abbreviated as Fe(86), B(72) and La(90) for convenience. The aluminosilicate zeolites have been accordingly abbreviated as Al(82), Al(174) and Al(318).

3.1. Preparation of Fe/ZSM-5^{35,154}

This was prepared as follows:

Solution A was made by mixing aqueous solution of ferric sulphate hexahydrate [$\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$, Loba G.R.] and sulphuric acid (98% W/W BDH A.R.) of appropriate strengths in required proportions. Solution B was prepared by mixing aqueous solutions of sodium silicate and tetra propylammonium bromide (TPA-Br) of appropriate strengths in the required proportions.

Solutions A and B were mixed to obtain a gel (pH 10.2) following patent procedure¹² for the preparation of ZSM-5 zeolite. The gel was stirred well for 10 minutes before transferring to an autoclave. The autoclave was closed and heated under autogeneous pressure in an air oven to a temperature of about 180°C. It was held at this temperature for about 24 hours and then quenched to stop the crystallisation process. The solid product was separated by filtration, washed with distilled water and dried in an air oven at 120°C for about 24 hours.

A : Preparation of protonated
ferrisilicate (Fe/HZSM-5)

The ferrisilicate sample synthesised as above was calcined in a current of dry air in a muffle furnace to decompose completely the organic cation. The temperature of the furnace was slowly increased (2.5°C/min.) to 550°C and the sample held at this temperature for about 10 hours. It was cooled and kept over saturated ammonium chloride solution for 24 hours. To obtain Fe/NH₄ZSM-5, Na⁺ ions in the sample were exchanged with NH₄⁺ at 90-95°C at a liquid to solid ratio of 15. The sample was filtered and washed with hot water till Cl⁻ free and dried at 120°C overnight. The procedure was repeated twice to obtain maximum exchange. The H form of the sample was then obtained by air calcination of the NH₄ZSM-5 at 550°C for 10 hours. It was cooled and stored over saturated NH₄Cl solution.

Two samples of Fe/HZSM-5 were prepared. These had $\text{SiO}_2/\text{Fe}_2\text{O}_3$ mole ratio 86 and 220.

3.2. Preparation of borosilicate(B/HZSM-5(72)¹⁹⁴,
lanthanum silicate (La/HZSM-5(90) and silicalite

B/HZSM-5(72) and La/HZSM-5(90) were prepared by substituting boric acid (A.R. grade, E. Merck) and lanthanum chloride (99.9%, Indian Rare Earths Ltd.) respectively in place of ferric sulphate hexahydrate in the procedure for Fe/HZSM-5(86). Silicalite was prepared by omitting the source of aluminium in the preparation. The samples were converted to sodium form and then to H form following exactly the procedure described for preparation of Fe/HZSM-5 samples.

3.3. C H A R A C T E R I S A T I O N

A : X-ray Diffraction (XRD)

The x-ray diffraction patterns of the crystalline product obtained are shown in Fig. 3.1. The interplanar spacings, 'd' values and the corresponding relative intensities of the peaks are shown in Table 3.1. In each case it is noticed that the 'd' values for Fe/HZSM-5(86) and the relative intensities of the peaks match with those corresponding to Al/HZSM-5. XRD of B/HZSM-5 and La/HZSM-5 also matched closely with that of Al/HZSM-5 (Fig. 3.1).

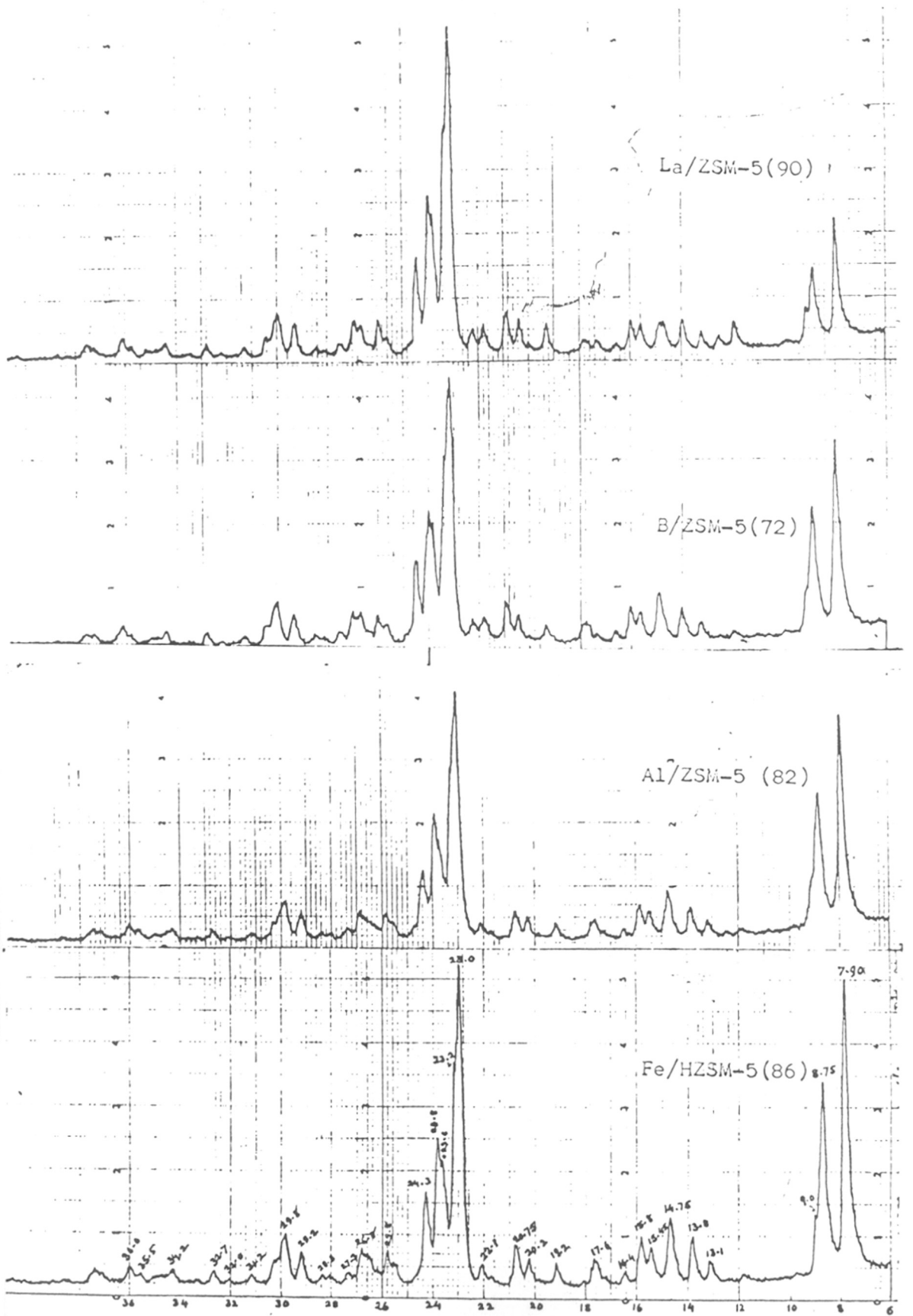


Fig: 3.1 X-ray diffractograms of ZSM-5 type zeolites.

TABLE - 3.1

LATTICE SPACING, (D), AND RELATIVE INTENSITY (I/I₀) VALUES FOR Fe/ZSM-5

<u>Interplanar spacing 'd' Å</u>	<u>Relative Intensity I/I₀</u>
11.04	41.9
9.93	28.5
6.32	11.5
6.01	11.6
5.68	11.5
5.54	12.3
4.6	11.4
4.25	15.2
4.0	10.0
3.85	100.0
3.72	49.5
3.65	31.4
3.04	11.4
2.98	15.2
2.92	5.7

B : Infrared Spectroscopy (IR)

IR spectral bands of ZSM-5 zeolite have been already listed (Table 2.2). The bands observed in the IR spectra of the ferrisilicate and aluminosilicate are shown in Fig. 3.2.

The strongest absorption band at about 1100 cm^{-1} is related to the asymmetric stretching vibrations of the T-O band and the shift in position of this band may be taken as evidence of framework substitution by other tetrahedral cations as shown by Flanigen²⁰².

It can be seen that the band at 1100 cm^{-1} mentioned above is shifted to lower frequency in the case of the ferrisilicate. This shift to lower frequency may be attributed to the Fe-O bond being longer (1.97 Å) compared to the Al-O bond (1.75 Å) in Al/HZSM-5³⁵.

B/HZSM-5 and La/HZSM-5 showed IR spectral bands characteristic of the ZSM-5 type zeolite.

In the case of Fe/HZSM-5, experimental evidence using other techniques is presented to show that Fe^{3+} has replaced silicon.

C : Other Techniques

XPS measurements can be used to determine the binding energy of atoms and ions and hence their valence state and chemical environments^{203,204}, XPS and EPR

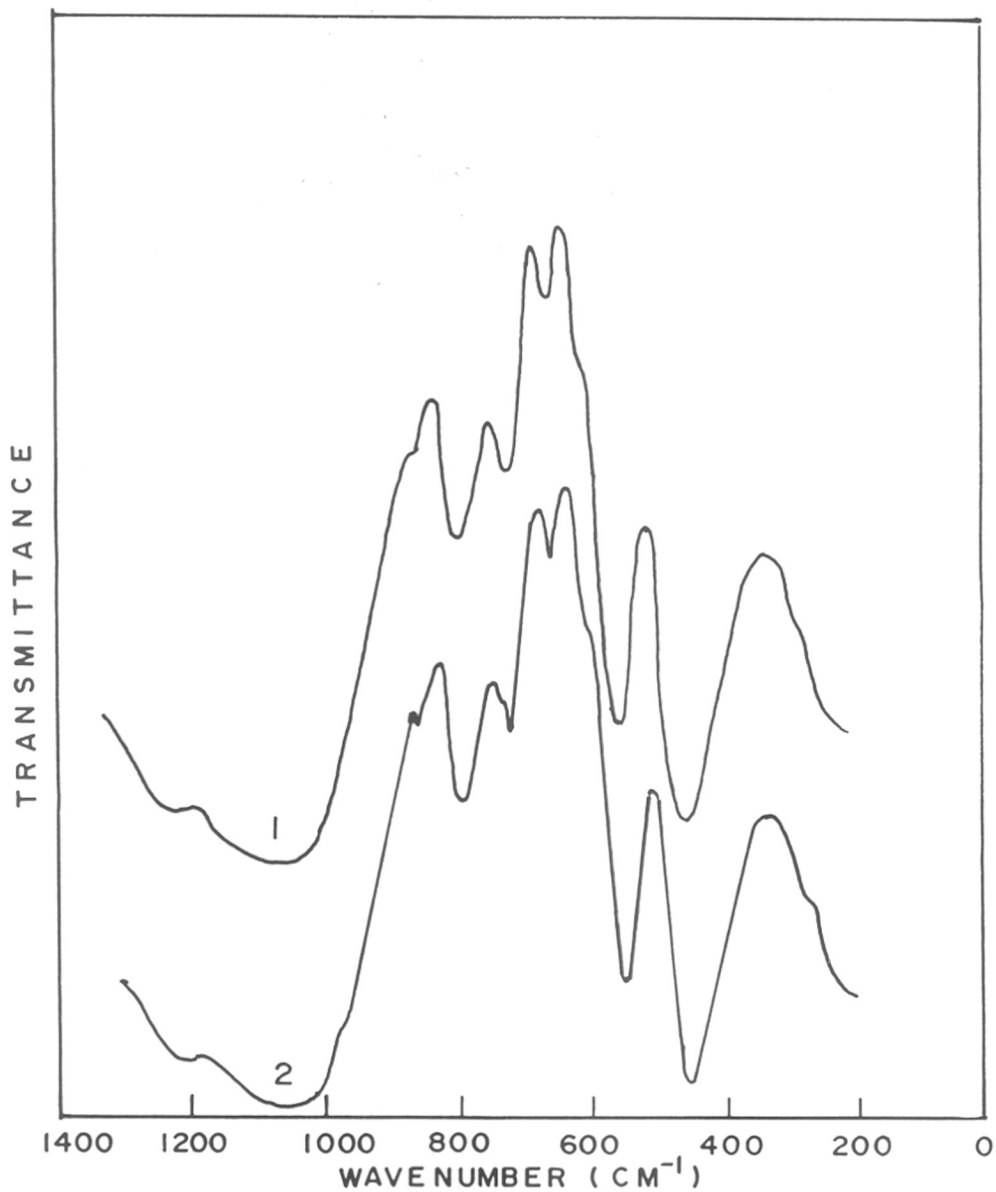


FIG.3.2 IR SPECTRA OF Al/HZSM-5(1)AND Fe/HZSM - 5(2)

studies of the ferrisilicates carried out in the present work show the following :

(i) The XPS spectrum of the sample (value of 103.3 eV for Si_{2p} level as the internal standard) shows 3 peaks (Fig. 3.3). Two of these are characteristic of iron in the trivalent state and associated with the splitting $2P_{3/2} - 2P_{1/2}$ (binding energy 711 eV and 725 eV). These two are found in the XPS spectrum of silicalite impregnated with Fe₂O₃. A third peak found in the same position for spectra of Fe/HZSM-5 and silicalite impregnated with Fe₂O₃ (at 532 eV) is attributable to the lattice oxygen (O1S). The latter sample also shows a fourth peak (529 eV) due to oxygen associated with occluded Fe₂O₃ phase. This peak is absent in Fe/HZSM-5 and therefore it may be concluded that the Fe³⁺ in Fe/HZSM-5 has most probably replaced silicon. Stencil et al.²⁰⁵ have also observed two peaks for oxygen for a sample of ZSM-5 containing occluded Fe₂O₃ at 532 and 529 eV, respectively.

(ii) The ESR study³⁵ shows peaks at $g = 2.0, 4.3$ and 5.3 (Fig. 3.4). While the peak at $g = 2$ ^{206,207} can be ascribed to the Fe³⁺ hexacoordinated complex located at cationic sites of the hydrated zeolite. The peak at $g = 4.3$ is normally ascribed to tetrahedrally coordinated Fe³⁺ in the framework²⁰⁶⁻²⁰⁹. The intensity of this peak (at $g = 4.3$) increases with vacuum treatment at temperatures increasing upto 300°C and then decreases. The peak at $g = 5.3$ ^{209,210} or greater can be attributed to the presence of Fe³⁺ in

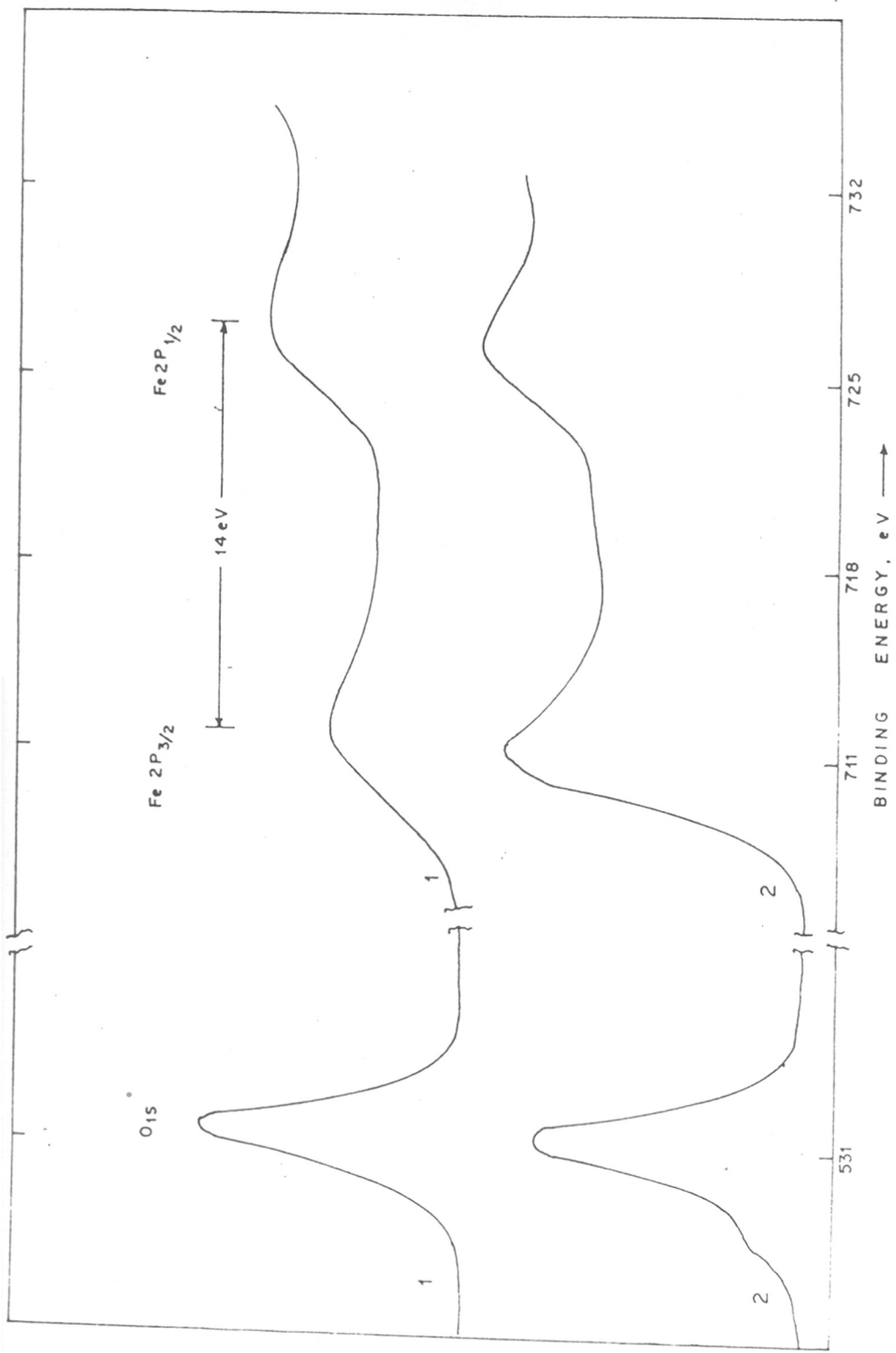


FIG 3.3 XPS SPECTRA OF 1) Fe/ZSM-5 2) Fe₂O₃ + SILICALITE

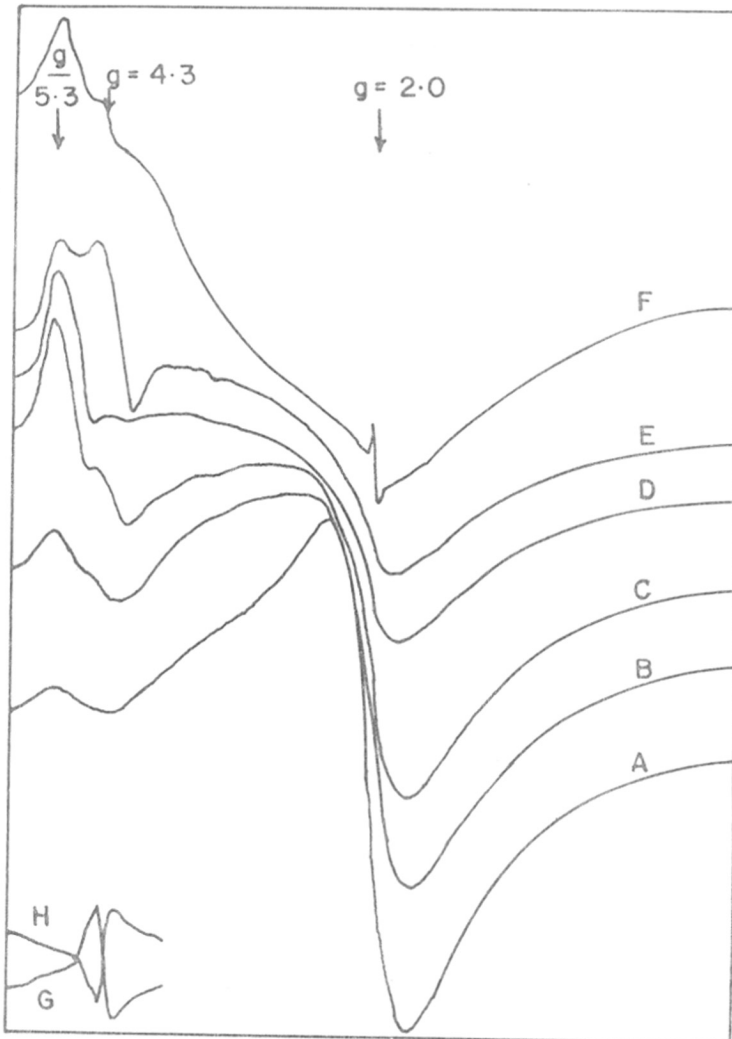


Fig. 3.4. E.p.r. spectra of Fe^{3+} in Fe/ZSM-5. A) Fe/HZSM-5, and samples treated in vacuum at B) 22°C , C) 100°C , D) 200°C , E) 300°C , and F) 500°C (G and H) Al_2O_3 containing Fe^{3+} in lattice position.

other environments.

There is literature evidence to show that it is possible to replace silicon with boron in the framework of the zeolite. Gabellica et al^{211,212} have presented evidence for boron incorporation in tetrahedral sites of zeolites by high resolution solid state MAS ¹¹B-NMR study of the borosilicate during and after synthesis of the material. Taramasso et al²¹³ have presented evidence for isomorphous substitution of silicon with boron on the basis of XRD data. A decrease in unit cell constant was found as expected on the basis of theoretical calculations in view of the smaller size of boron. The sample prepared did not show the splitting characteristic of silicalite at $2\theta = 45^\circ$ in the XRD nor did it show any splitting at $2\theta = 24.2^\circ$ associated with symmetry change. Scholle et al^{214A} have also shown substitution of boron into the framework from a study of the 'H/Boralite' by NMR and TPD measurements of the acidity of the sample. The acidity and adsorption properties of the sample B/HZSM-5 prepared in the present work show that the sample is different from silicalite. Its catalytic properties are also different from those of silicalite. Therefore, at least part of the boron in the sample synthesised may be expected to be in the framework. Recently, Ione et al^{214B} have also presented evidence on the basis of ¹¹B-NMR spectral data for isomorphous substitution of boron

for silicon in the zeolite.

In the case of lanthanum zeolite [La/HZSM-5(90)], part of the La^{3+} may be present in occluded form, part may be present in the tetrahedral position in the framework and the remaining in exchangeable cation position. It is not established that La^{3+} is incorporated into the framework but it has unique catalytic and adsorption properties and these are different from those of silicalite as would be seen shortly.

D : Adsorption Properties

These were measured using experimental set up and procedure described in Chapter 2.3 E.

Results and Discussion : The adsorption data are presented in Tables 3.2 and 3.3. It can be seen that the degree of hydrophobicity is in the following order

$$\text{Al}(82) < \text{B}(72) < \text{Fe}(86) < \text{La}(90)/\text{HZSM-5}$$

Adsorption of methanol shows the trend (Table 3.2)

$$\text{La, Fe}/\text{HZSM-5} > \text{B}/\text{HZSM-5} > \text{silicalite} > \text{Al}/\text{HZSM-5}.$$

The value of 9-10.7 % for adsorption of methanol in the case of Al/HZSM-5 calculated from data presented in Tables 3.2 and 2.5 agrees with that reported for HZSM-5¹⁴⁶. The reason for the differences in adsorption of methanol is

TABLE - 3.2

SORPTION OF WATER, METHANOL, n-HEXANE
AND CYCLOHEXANE ON ZSM-5 TYPE ZEOLITES

Sample	Amount sorbed (molecules/u.c.)			
	n-Hexane	Water	Cyclohexane	Methanol
HZSM-5 (82)	9.2	34	5.7	16.5
Silicalite	8.2	11.4	3.0	24.4
Fe/HZSM (86)	9.8	20.6	6.4	28.7
Fe/HZSM (220)	-	8.4	4.5	-
B/HZSM (72)	10.1	24.1	5.3	26.2
La/HZSM (90)	8.7	6.1	1.9	28.4

TABLE - 3.3SORPTION OF AROMATIC HYDROCARBONS

Sample	Amount sorbed (molecules/u.c.)				Sorption ratio p-Xyl/ o-Xyl.
	Benzene	p-Xyl.	o-Xyl.	1,2,4 TMB	
HZSM-5 (82)	9.0	8.3	2.0	0.8	4.2
Silicalite	8.3	8.2	0.6	0.4	13.7
Fe/HZSM-5(86)	10.2	9.0	3.7	1.9	2.4
B/HZSM-5(72)	8.9	6.5	1.6	1.4	4.1
La/HZSM-5(90)	8.8	8.2	0.85	0.7	9.6

not evident. It has been reported that there is a large increase in temperature of the system as the heat of adsorption is released¹⁴⁶. This might reduce the amount of MeOH sorbed so that what is measured is not the true amount that would have been adsorbed at 25°C. For the less active adsorbents, however, the amount sorbed is more accurate as the temperature rise is small. This explanation is less likely to be true as the time given for saturation adsorption may be long enough to restore the initial temperature. The observed difference in adsorption is more likely to be due to difference in adsorption properties of the zeolites.

The ratio of quantity of p-xylene to o-xylene adsorbed is in the order

$$\text{La}(90) > \text{Al}(82) \geq \text{B}(72) > \text{Fe}(86)/\text{HZSM-5} \quad (\text{Table 3.3})$$

and this is the order in which selectivity to p-xylene in xylenes (or its equivalent) varies in the xylene-forming reactions discussed in Chapter 4. There is a decrease in adsorption of 1,2,4 trimethyl benzene as one goes in the order Fe, B and La/HZSM-5. The value is particularly low for La/HZSM-5 and may be due to partial blocking of channel openings so that equilibrium adsorption is not attained for the larger molecules during thirty minutes. This is further proved from the sorption data for cyclohexane which is sorbed very little. The low uptake may not be due to channel plugging

by occlusion of the molecules because adsorption of n-hexane, benzene or p-xylene does not show any significant decrease (Table 3.3). Tables 3.2 and 3.3 also show the differences in sorption uptake between La/HZSM-5 and silicalite.

E : Acidic properties of Fe, B, La/HZSM-5 and silicalite

Temperature programmed desorption of NH_3 was used to estimate the strength and number of acid sites in the zeolites Fe, B, La/HZSM-5 and silicalite. The experimental set up and procedure have been described in Chapter 2.3 G. The peak maxima temperatures were used to classify the strengths of the acid sites as weak, medium and strong, represented by α , β and γ peaks in the TPD spectra⁴⁶.

While TPD spectra of borosilicates have been reported²¹⁴, TPD spectral data for Fe/HZSM-5 and La/HZSM-5 have not been reported before. In the present work the acidic properties of the above zeolites are compared with those of Al/HZSM-5 and silicalite, the measurements being carried out under identical conditions.

Results and Discussion : The TPD spectra of the samples are shown in Fig. 3.5A. The number and strengths of the acid sites (represented by T_{max}) are shown in Table 3.4.

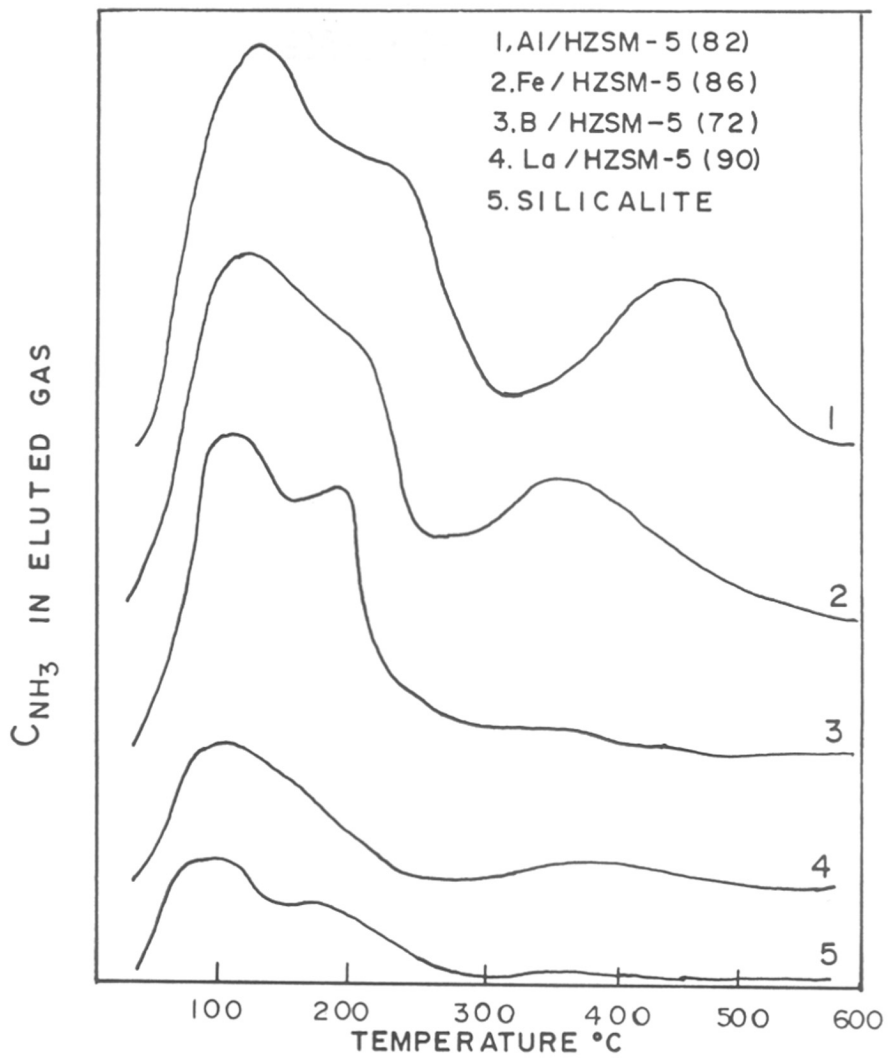


FIG 3.5A TPD SPECTRA OF DIFFERENT ZEOLITES

TABLE - 3.4

ACID STRENGTH DISTRIBUTION IN ZEOLITES
(NUMBER OF SITES/U.C)

Sample	Weak + medium	Strong	T_{\max} °C*
Al/HZSM-5	6.6	1.6	420
Silicalite	1.1	0.3	320
Fe/HZSM-5	4.6	2.0	350
Fe/HZSM-5(220)	3.1	1.2	340
B/HZSM-5	4.2	0.4	345
La/HZSM-5	1.0	0.3	400

* Temperature for peak maximum corresponding to strong acid sites (Y peak)

Earlier studies by Gabellica et al^{211,212} and Scholle et al²¹⁴ have shown that silicon in tetrahedral (framework) position can be isomorphously substituted by boron. The latter on the basis of NMR and TPD measurements showed that the sample termed 'H-Boralite' which has the same symmetry as for ZSM-5 with small differences in unit cell dimensions, has acidity lower than that of HZSM-5 but greater than that of silicalite. An explanation for the low acidity of H-boralite was given on the basis of the qualitative electrostatic valence model of Pauling²¹⁵. According to this model, the bond strength between the cation and each of the anions surrounding it^{is} related to number of charges on the cation (Z_c) and coordination number of the cation (V) expressed as²¹⁴

$$S = Z_c/V \quad \dots 1$$

In the case of Si^{4+} surrounded by 4 oxygen anions (Fig. 3.5B)

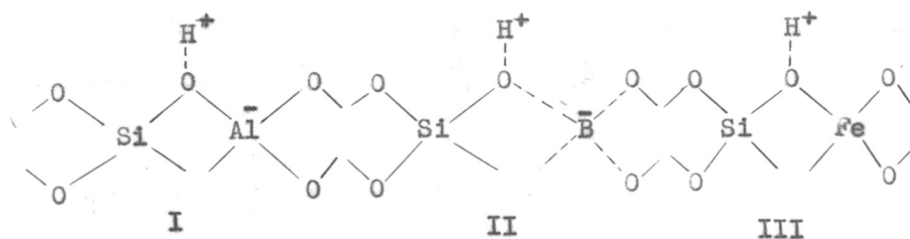


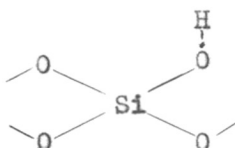
Fig. 3.5B

Brønsted acid sites in I - Al/HZSM-5, II B/HZSM-5 and III - Fe/HZSM-5.

the strength of Si-O bond thus is equal to 1 (4/4) and that of Al-O bond, when Al^{3+} is attached to 4 oxygen anions, is 3/4. Further the charge on the anion is equal to the sum of the bond strengths of all bonds of the anion. Thus the charge on oxygen in the Brönsted acid site of HZSM-5 is equal to the sum of the bond strength of all its bonds, i.e.

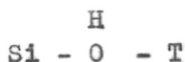
$$2 = S_{\text{Si-O}} + S_{\text{Al-O}} + S_{\text{O-H}} \quad \dots 2$$

Therefore, the strength of the $S_{\text{O-H}}$ bond, responsible for Brönsted acidity is $(2-1-3/4)$ equal to 1/4. In a similar manner the strength of the O-H bond in silanol group,



$(2 = S_{\text{Si-O}} + S_{\text{O-H}})$ is equal to 1 and hence silanol OH group (in silicalite) is not as acidic as the Brönsted site on HZSM-5.

If the aluminium ion in HZSM-5 is replaced with another trivalent ion $\text{T}^{(3+)}$ whose electronegativity is greater than that of aluminium, the $S_{\text{T-O}}$ bond would be weaker than that of Al-O bond. Then, by equation (2), the bond O-H in



would be stronger i.e. a lower acid strength for the new zeolite as a consequence. Boron, iron and lanthanum have

electronegativity values 2.0, 1.9 and 1.1 respectively in place of 1.5 for Al. Thus the strength of the acid site on the basis of the model may be expected to follow the order



It is not possible to estimate the order of strength of acid sites in these zeolites on the basis of TPD spectra shown in Fig. 3.5 and Table 3.4, but it appears that it is in the order (considering T_{max} of the γ peak), $\text{Al} > \text{Fe} > \text{B} > \text{La/HZSM-5} > \text{silicalite}$, treating the peak responsible for the strong sites in La/HZSM-5 to be due to impurity. Thus most of the La^{3+} in the zeolite may be in extra lattice position so as to give a catalyst with very low acidity.

3.4. CONVERSION OF METHANOL TO OLEFINS OVER Fe, B, La/HZSM-5 ZEOLITES

Reaction of methanol over Fe, B, La/HZSM-5 has been carried out in order to compare the activity and selectivity of these catalysts with respect to formation of light olefins. Published literature^{213,220} on this reaction over such zeolites is scanty and mostly in patents^{193,195,198}.

Experimental set up and procedure have been described in Chapter 2.

A : Results and Discussion

Table 3.5 presents data for the influence of temperature in the conversion of methanol to olefins. It can be seen that unlike Al/HZSM-5 the conversion is not complete even at 365°C. This is due to the weaker acid sites in Fe/HZSM-5. By carrying out reaction at higher temperature complete conversion of methanol to hydrocarbons is achieved. Strong acid sites required for the formation of the first C-C bond in the reaction¹⁶⁷ are probably generated only at high temperatures. The possibility of increasing strength of acid sites by increasing temperature has been shown by IR²¹⁶ and NMR^{217,218} studies of proton mobility in zeolites. In keeping with its lower acidity, it shows lower selectivity to aromatics (Table 3.5) as compared to Al/HZSM-5 (Table 2.8). Also C₁-C₄ paraffins are lower. A temperature of 450°C is found to be optimum for high olefin yield since at high temperatures especially above 500°C small quantities of H₂, CO and CO₂ are formed.

Table 3.6 compares product distribution for the reaction over Fe/HZSM-5 with SiO₂/Fe₂O₃ molar ratios of 86 and 220. The catalyst (R = 220) yields higher amounts of C₃ = and C₄ = because of its greater hydrophobicity (Table 3.2) and lower acidity. But its activity for conversion to hydrocarbons is low.

TABLE - 3.5

CONVERSION OF METHANOL TO OLEFINS OVER

Fe/HZSM-5(86)

EFFECT OF TEMPERATURE. WHSV = 2 hr⁻¹

	Temperature °C					
	300	365	405	450	500	555
α	54	83.6	99	100		
DME	92.5	7.4	1.2	-	-	-
Hydrocarbon distribution (wt.%)						
C ₂ =	26.7	8.5	5.2	10.3	11.1	15.5
C ₃ =	27.9	8.4	10.7	21.6	19.2	25.4
C ₄ =	18.7	10.8	12.1	15.5	15.1	12.3
C ₂ -C ₄ olefins	73.3	27.7	28.0	47.4	45.4	53.2
C ₁ -C ₄ paraffins	5.6	15.7	18.7	15.5	12.3	8.7
C ₅ + aliphatics	21.1	36.1	36.9	20.7	22.3	13.9
C ₆ -C ₈ aromatics	Trace	11.2	9.7	11.3	13.7	16.6
C ₉ + C ₁₀ "	"	9.4	6.7	5.0	6.4	7.6
% Selectivity to aromatics in C ₅ +	-	36.3	30.8	44.1	47.5	63.5

TABLE - 3.6

CONVERSION OF METHANOL TO OLEFINS OVER
 Fe/HZSM-5. EFFECT OF $\text{SiO}_2/\text{Fe}_2\text{O}_3$ MOLE
 RATIO. TEMP. 450°C , WHSV = 2 HR^{-1}

	$\text{SiO}_2/\text{Fe}_2\text{O}_3$	
	86	220
α	100	87.8
DME	-	2.5
<u>Hydrocarbon distribution (wt.%)</u>		
$\text{C}_2 =$	10.3	5.2
$\text{C}_3 =$	21.6	37.9
$\text{C}_4 =$	15.5	22.9
$\text{C}_2\text{-C}_4$ olefins	47.4	66.0
$\text{C}_1\text{-C}_4$ paraffins	15.5	6.5
$\text{C}_5 +$ aliphatics	20.7	18.9
$\text{C}_6 - \text{C}_8$ aromatics	11.3	4.4
$\text{C}_9 + \text{C}_{10}$ aromatics	5.0	4.3
selectivity to aromatics in $\text{C}_5 +$	44.1	31.8

It is advantageous to use aqueous solutions of methanol to obtain higher yields of olefins as seen in Chapter 2 and reported by several others^{192,198}. Table 3.7 shows that 70-75% yield of olefins among the hydrocarbons can be obtained in this way. Column 3 in Table 3.7 shows corresponding hydrocarbon product distribution for AlHZSM-5(82). The stabilising role of water for product distribution with respect to C₅ + and aromatics in C₅ + is evident from the distribution shown in Table 3.8.

Table 3.9 shows the effect of time on stream in the conversion of an aqueous solution of methanol on product distribution. The catalyst gives stable performance during the period of testing.

Temperature screening of the reaction using B/HZSM-5 indicated that at temperatures < 400°C although conversion was nearly complete, C₅ + and C₁-C₄ paraffins were higher. The highest selectivity to olefins was observed at about 550°C. The ratio of SiO₂/B₂O₃ of the catalyst showed little effect on product distribution (Table 3.19). The samples showed about the same selectivity to olefins. The results are in agreement with those reported in the literature²¹⁹ and confirm that borosilicates are good catalysts for production of light olefins from methanol. An important

TABLE - 3.7

CONVERSION OF METHANOL TO OLEFINS.
EFFECT OF DILUTION OF METHANOL WITH
WATER. TEMP. 450°C

Water (wt. %) in feed	55	70	70
Catalyst	Fe/HZSM-5 (86)	Al/HZSM-5 (82)	
WHSV (hr ⁻¹)	4.0	4.0	5.5
α	100	100	100
DME	-	-	-
Hydrocarbon distribution (wt. %).			
C ₂ =	9.4	9.4	16.7
C ₃ =	37.6	43.7	24.4
C ₄ =	23.7	20.5	9.7
C ₂ -C ₄ olefins	70.8	73.6	50.8
C ₁ -C ₄ paraffins	6.0	4.6	18.9
C ₅ ⁺	23.3	21.8	30.3

TABLE - 3.8

AROMATICS DISTRIBUTION IN THE C₅ + FRACTION
IN THE CONVERSION OF AQUEOUS METHANOL. TEMP. 450°C

	Catalyst		
	Fe/HZSM-5(86)	70	Al/HZSM-5(82)
Water(wt.%) in feed:	55	70	70
C ₅ + total (wt.%)	23.3	21.8	30.3
Benzene	0.3	0.1	0.4
Toluene	1.1	0.9	1.8
C ₈ aromatics	3.4	3.3	7.7
(C ₉ +C ₁₀) aromatics	3.6	3.6	4.4
Selectivity to aromatics in C ₅ +	36.1	36.2	47.1

TABLE - 3.9

CONVERSION OF AQUEOUS (70 WT.% WATER)
METHANOL TO OLEFINS OVER Fe/HZSM-5(86)
EFFECT OF TIME ON STREAM. TEMP. 450°C
WHSV, 4.4 HR⁻¹

TOS (hrs.)	8	22	26	45
α	-----	100	-----	-----
DME	-	-	-	-
<u>Hydrocarbon distribution (wt. %)</u>				
C ₂ =	9.4	9.7	9.4	9.7
C ₃ =	43.7	45.6	43.5	45.3
C ₄ =	20.5	20.0	21.0	17.0
C ₂ -C ₄ olefins	73.6	75.3	73.9	72.0
C ₁ -C ₄ paraffins	4.6	4.4	4.2	6.6
C ₅ +	21.8	20.4	21.9	21.2

TABLE - 3.10

CONVERSION OF METHANOL TO OLEFIN OVER
B/HZSM-5 ZEOLITE, EFFECT OF SiO₂/B₂O₃
MOLE RATIO; TEMP. 550°C, WHSV = 2 HR⁻¹

<u>SiO₂/B₂O₃</u>	<u>35</u>	<u>72</u>	<u>200</u>
α	>99	98.8	98
DME	-	Trace	0.8
<u>Hydrocarbon distribution(wt.%)</u>			
C ₂ =	24.2	23.8	23.1
C ₃ =	35.6	35.4	36.3
C ₄ =	14.9	14.7	13.1
C ₂ -C ₄ olefins	74.7	73.9	72.5
C ₁ -C ₄ paraffins	9.9	11.0	10.4
C ₅ + aliphatics	5.9	6.0	7.7
C ₆ -C ₉ aromatics	7.1	6.9	8.1
C ₉ +C ₁₀ aromatics	2.4	2.4	1.1
Selectivity to aromatics in C ₅ +	61.7	61.2	54.1

observation is that borosilicate yields comparatively large amount of ethylene. This may be because the greater hydrophilicity of this zeolite favours reaction of the methyl ethyl oxonium ion with water in preference to reaction with methanol (Chapter 2.4 D(iii)]. Selectivity to aromatics is lower (Table 3.10) on account of its lower acidity. Table 3.11 shows that increase in space velocity increases olefin selectivity only marginally. Trends in selectivity to C_1 - C_4 paraffins and C_5 + aliphatics and aromatics follow the general pattern for Al/HZSM-5 (Table 2.14).

Unlike Fe/HZSM-5(86), B/HZSM-5(72) cannot accept feeds containing large amounts of water. Fig. 3.6 shows effect of dilution of methanol on conversion and product distribution. Data obtained by Marosi²¹⁹ for the reaction over a borosilicate zeolite (ZSM-5 type) at 600°C are also shown in the figure. Introduction of water seems to lower the yield of ethylene, probably by poisoning the strong sites required for its formation¹⁶⁷. $C_2 H_4$ yield has been shown to be proportional to the number of strong acid sites¹¹⁶. Table 3.12 shows the effect of cumulative feed (CFD—ml/gm) on product distribution. The yield of $C_2 H_4$ and selectivity to aromatics in C_5 + decreases with increase in CFD. These effects may be attributed to aging of the catalyst. The life

TABLE - 3.11

CONVERSION OF METHANOL TO OLEFINS OVER
B/HZSM-5(72). EFFECT OF WHSV, TEMP. 550°C

WHSV (hr^{-1})	2.4	4.8	8	12
α	99.5	97.5	93.6	94.3
DME	-	0.31	0.66	1.9
Hydrocarbons distribution (wt.%)				
$\text{C}_2=$	23.8	19.5	16.1	13.4
$\text{C}_3=$	35.4	39.1	41.5	38.1
$\text{C}_4=$	13.8	17.5	18.6	20.7
$\text{C}_2\text{-C}_4$ olefins	73.0	76.1	76.2	72.1
$\text{C}_1\text{-C}_4$ paraffins	11.9	5.4	5.0	4.2
$\text{C}_5 +$ aliphatics	6.0	11.2	13.0	19.9
Benzene	0.2	0.2	0.1	0.1
Toluene	1.9	1.4	1.1	0.6
C_8 aromatics	4.8	3.9	3.0	1.7
$\text{C}_9 + \text{C}_{10}$ aromatics	2.4	1.9	1.5	1.1
Selectivity to aromatics in $\text{C}_5 +$	61.2	39.4	30.1	14.7

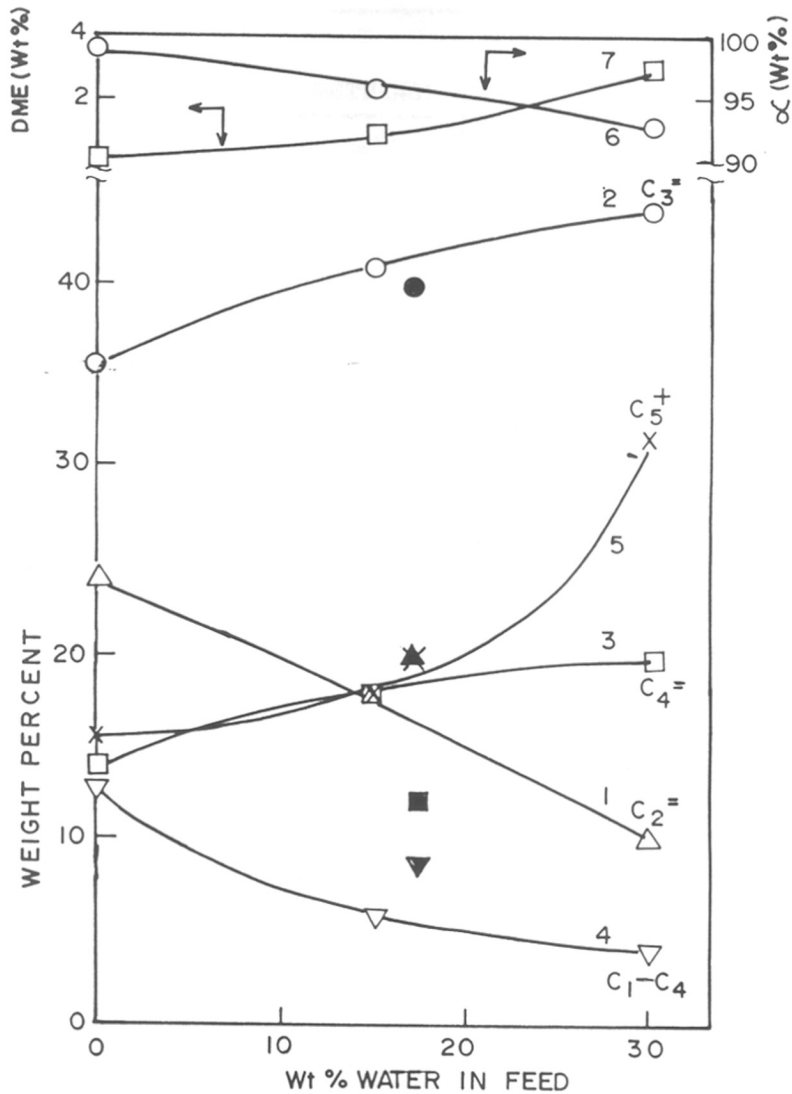


FIG 3.6 EFFECT OF DILUTION ON HYDROCARBON DISTRIBUTION IN METHANOL CONVERSION OVER B/HZSM-5. REACTION TEMP. 550°C, WHSV(hr⁻¹): 3.2 SOLID SYMBOLS REPRESENT VALUES FROM REF. 219.

TABLE - 3.12

CONVERSION OF METHANOL TO OLEFINS OVER
B/HZSM-5(72) ZEOLITE. EFFECT OF
CUMULATIVE FEED (ml/g), TEMP. 550°C
WHSV = 2.4 hr⁻¹

CFD (ml/g)	18	54	126	198	270	342
α	>99	>99	>99	97.4	94.8	86.7
DME	-	-	Trace	0.7	1.0	2.8
Hydrocarbon distribution (wt. %)						
C ₂ =	24.2	21.3	18.6	16.6	14.5	9
C ₃ =	35.6	35.9	37.7	40.8	39.6	33.8
C ₄ =	14.9	17.0	17.7	18.4	18.0	17.7
Total olefins	74.7	74.2	73.9	75.8	72.1	60.5
C ₁ -C ₄ paraffins	9.9	7.5	6.3	5.7	5.5	5.5
C ₅ +	15.4	18.4	19.5	18.6	22.3	33.7
C ₆ -C ₈ aromatics	7.1		6.7		6.2	
C ₉ -C ₁₀ aromatics	2.4		2.5		2.4	
Selectivity to aromatics in C ₅ +	61.7		47.2		38.5	

of the acid leached catalyst is longer (Fig. 3.7). The reason for the longer life of the acid leached catalyst is not clear but it may be due to removal of occluded material (B_2O_3)²²⁰. But the acid leached sample showed essentially same adsorption and acidic properties.

La/HZSM-5 also yields about 70% C_2-H_4 olefins at 450°C (Table 3.13). Removal of occluded lanthanum species by acid leaching improves olefin yield slightly. Such acid leaching did not affect the XRD, adsorption and acidic properties in any significant manner. Table 3.13 (col. 3) also shows the product distribution for the reaction over silicalite under identical conditions. Conversion to hydrocarbons is very small. Yield of CH_4 was almost 65% among the hydrocarbons which indicates fast coking of the catalyst.

Table 3.14 shows effect of dilution of methanol on product distribution. A small increase in the total yield of olefins (C_2-C_4) is found with increase in extent of dilution. A corresponding decrease in C_2-C_4 and $C_5 +$ is also observed which may be due to poisoning of acid sites responsible for hydrogen transfer reactions. A further increase in olefin yield can be obtained by using a double reactor system in which methanol is first converted to DME over alumina and then the DME to olefins over La/HZSM-5 (Table 3.15).

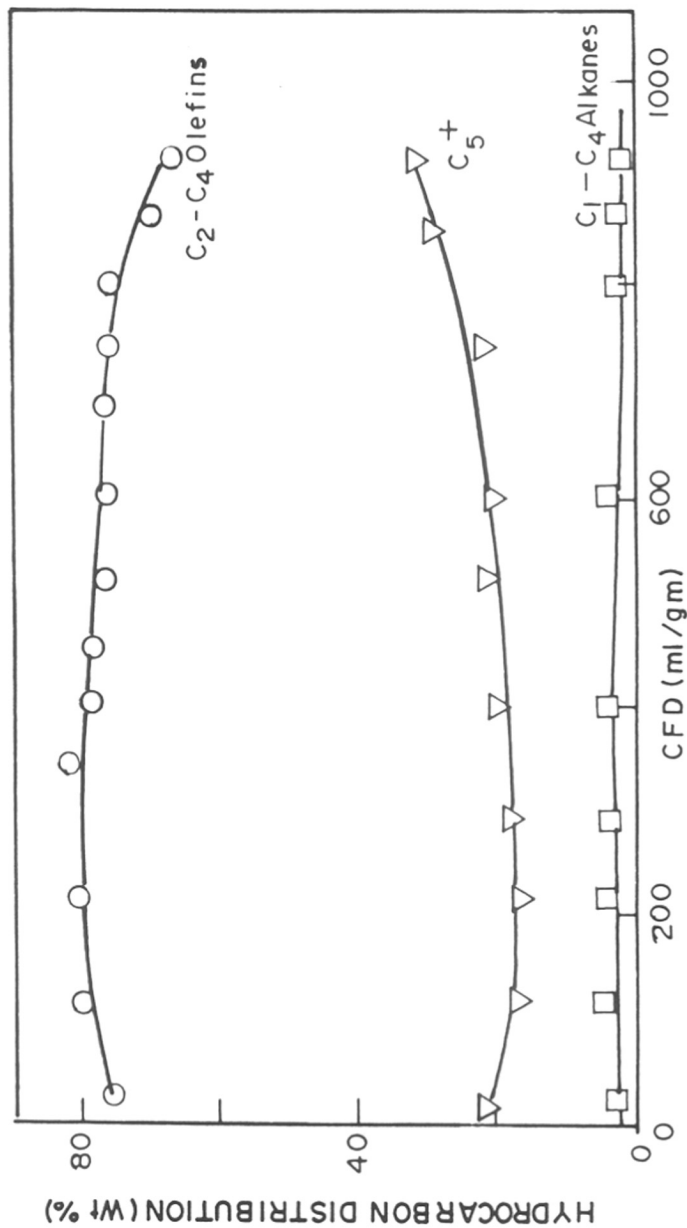


FIG 3.7 EFFECT OF CFD ON HYDROCARBON DISTRIBUTION IN METHANOL CONVERSION OVER B/HZSM-5 (ACID LEACHED). FEED 80(Wt %) MeOH ; WHSV = 2.6 hr⁻¹, TEMP. = 550°C

TABLE - 313

CONVERSION OF METHANOL TO OLEFINS OVER
La/HZSM-5(90) AND SILICALITE. TEMP 450°C
WHSV = 2 HR⁻¹

		*	**
α	99	100	55
DME	0.5	-	90
<u>Hydrocarbon distribution (wt.%)</u>			
C ₂ =	11.14	12.3	16.3
C ₃ =	37.60	41.4	1.9
C ₄ =	20.5	19.3	0.5
C ₂ -C ₄ olefins	69.2	73.0	18.7
C ₁ -C ₄ paraffins	9.0	6.6	69.7 ^a
C ₅ +	21.8	20.4	11.6

* Catalyst after treatment with acid to remove extra framework La³⁺ species.

** Silicalite.

a-Contains 65% methane.

TABLE - 3.14

CONVERSION OF AQUEOUS METHANOL TO OLEFINS
OVER La/HZSM(90); TEMP. 485°C; WHSV = 5 HR⁻¹

Water (wt. %)	0	20	40	60
α	99.2	99	99	89.3
DME	< 1	Trace	Trace	3.3
<u>Hydrocarbon distribution (wt.%)</u>				
C ₂ =	12.3	12.8	13	12.4
C ₃ =	41.4	42.4	45.3	46.5
C ₄ =	19.3	20.0	18.5	18.0
C ₂ -C ₄ olefins	73.0	75.2	76.7	77
C ₁ -C ₄ paraffins	6.6	4.6	3.4	2.8
C ₅ + aliphatics	13.5	11.0	11.8	12.5
C ₆ -C ₈ aromatics	5.7	7.4	6.5	6.0
C ₉ +C ₁₀ aromatics	1.3	1.9	1.7	1.7
Selectivity to aromatics in C ₅ +	34.1	45.8	40.9	38.2

TABLE - 3.15

CONVERSION OF AQUEOUS METHANOL TO
OLEFINS OVER La/HZSM-5(90) IN A
DOUBLE REACTOR SYSTEM.

TEMP. 350°C (REACTOR I), 510°C (REACTOR II)
 WHSV = 2.5 hr⁻¹

CFD (ml/gm)	20	110	250	430
α	>99	>99	>99	76.6
DME	-	-	-	10.4
<u>Hydrocarbons</u> <u>distribution(wt.%)</u>				
C ₂ =	15.2	13.5	11.9	8.0
C ₃ =	47.4	49.8	50.9	46.3
C ₄ =	18.3	20.2	20.4	19.7
C ₂ -C ₄ olefins	80.9	83.5	83.1	74.0
C ₁ -C ₄ paraffins	4.9	4.7	4.6	4.6
C ₅ +	14.2	11.7	12.4	21.4

A comparison of the hydrocarbon product distribution for methanol conversion to hydrocarbons over different catalysts is shown in Table 3.16 and schematically in Fig. 3.8. La/HZSM-5 is found to be superior for production of olefins which agrees with its lowest acidity (Table 3.4, Fig. 3.5). The lowest yield of aromatics in product distribution for this catalyst suggested that the strong sites represented by γ peak are responsible for their formation^{88,116}. The high selectivity for p-xylene (among xylenes) observed in the case of La/HZSM-5 may be due to occluded lanthanum species reducing the effective size of the channel in this zeolite. The formation of $C_9 + C_{10}$ aromatics is less favoured for the same reason.

3.5. C O N C L U S I O N S

1. Fe/HZSM-5 and B/HZSM-5 have been synthesised. From the evidence presented it is concluded that Fe^{3+} has been substituted for silicon in the framework of the ZSM-5 type zeolite. In the case of B/HZSM-5 some evidence is presented on the basis of XRD, TPD and adsorption properties indicating possible formation of borosilicate zeolite of the ZSM-5 type. In the case of La/HZSM-5, La^{3+} may exist in any or all of the three possible sites.

TABLE - 3.16

COMPARISON OF CATALYTIC ACTIVITY AND PRODUCT
DISTRIBUTION IN THE CONVERSION OF METHANOL TO
HYDROCARBONS OVER DIFFERENT ZSM-5 TYPE ZEOLITES
 TEMP. 450°C, WHSV = 2.0 hr⁻¹

	H-ZSM-5			
	Al	Fe	B*	La
α	100	100	99 +	99
DME	-	-	-	0.5
<u>Hydrocarbons</u> <u>distribution (wt. %)</u>				
Ethylene	3.1	10.3	8.3	11.1
Propylene	4.6	21.6	15.8	37.6
Butenes	1.0	15.5	12.9	20.5
C ₂ -C ₄ olefins	8.7	47.4	37.0	69.2
Methane	1.2	2.7	1.6	1.4
Ethane	0.9	Trace	Trace	0.2
Propane	19.1	5.1	7.2	3.0
Butanes	24.6	7.7	14.1	4.4
C ₁ -C ₄ paraffins	45.8	15.5	22.9	9.0
C ₅ + aliphatics	14.5	20.7	25.0	16.7
BTX aromatics	26.1	11.3	9.7	3.9**
C ₉ + C ₁₀ aromatics	4.9	5.0	5.6	1.2
Total aromatics	31.0	16.3	15.3	5.1

* Ratio SiO₂/B₂O₃ = 35.

** Selectivity to p-xylene in xylenes = 67.9%.

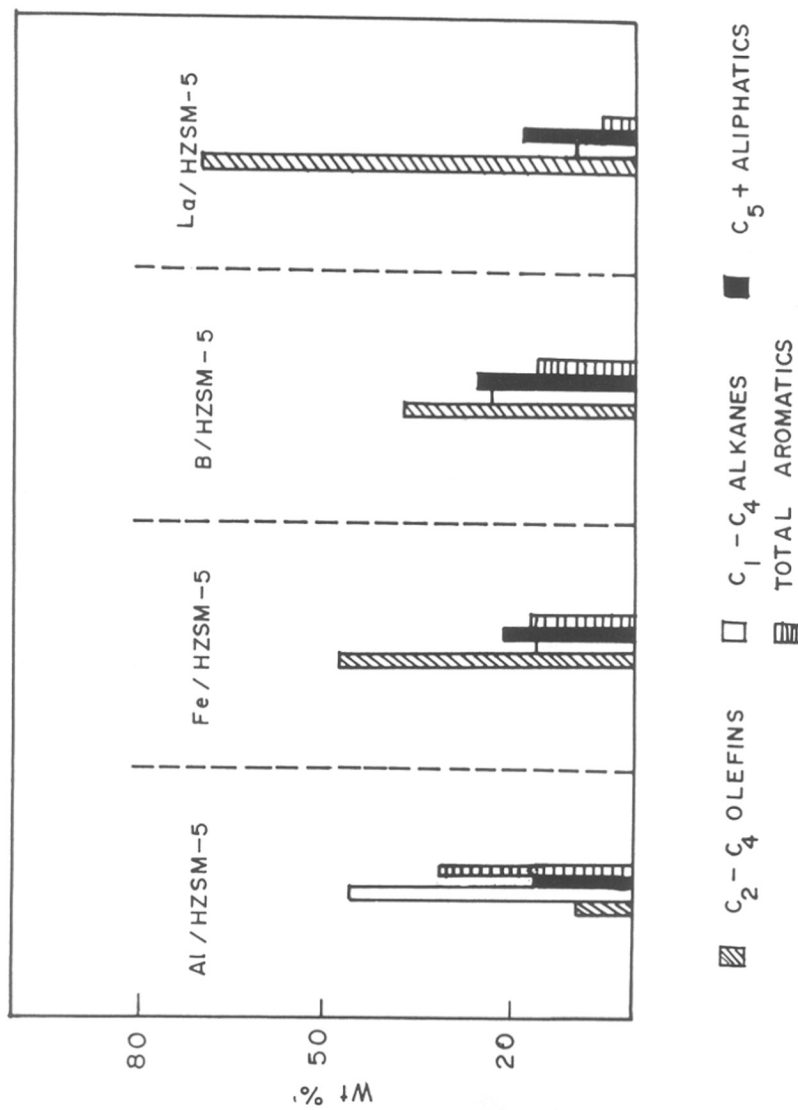


FIG 3-8. COMPARISON OF HYDROCARBON DISTRIBUTION IN
CONVERSION OF METHANOL OVER DIFFERENT ZEOLITES

2. Adsorption measurements do not indicate appreciable reduction in pore volume (n-hexane, cyclohexane and p-xylene adsorption).
3. TPD measurements show that the acidity of the catalysts is in the order Al/HZSM-5 > Fe/HZSM-5 > B/HZSM-5 > La/HZSM-5.
4. Activity studies show that all the three zeolites are good catalysts for conversion of methanol to olefins and that Fe/HZSM-5 is particularly useful for conversion of very dilute aqueous solutions (30% w/w MeOH) to olefins. Yield of olefins as high as 70-75 % (among hydrocarbons) can be obtained. With pure methanol, the same yield can be obtained using B/HZSM-5 at a reaction temperature 550°C. Use of a double reactor system consisting of alumina to produce dimethyl ether and La/HZSM-5 for conversion of DME gives yield of C₂-C₄ olefin > 80% among the hydrocarbons.

CHAPTER IV : SOME AROMATIC REACTIONS OVER ZSM-5
TYPE ZEOLITES.

4.1. INTRODUCTION

Aromatic reactions such as isomerisation of xylenes, disproportionation of toluene and alkylation of toluene with methanol are industrially important reactions. The most useful product of these reactions is p-xylene which is the raw material for production of DMT required for the synthetic fibre industry. The advantage of using ZSM-5 type zeolites as catalysts for these reactions has been brought out in a number of publications^{140,159,160}. This can be attributed to the shape-selective properties of these zeolites and the scope of further modifying these to obtain what are often referred to as 'tailor-made' catalysts.

Isomerisation of xylenes (or C₈ aromatics to include ethyl benzene) over HZSM-5 zeolites yields xylenes at their equilibrium concentrations. But modified ZSM-5 zeolites are known to yield selectivity to p-xylene as high as 95 %¹⁴⁰. One of the effects of such modification has been on the strength¹¹⁴ and number of acid sites¹⁷⁵ i.e. to reduce the acidity. It is also known that isomerisation needs comparatively weak acid sites^{152,201}. It was therefore of interest to study the activity and selectivity of the less acidic Fe, B and La/HZSM-5 zeolites in comparison with those of HZSM-5 zeolites for ortho-xylene isomerisation as a model reaction. The reaction over HZSM-5 was studied in some

detail with reference to reaction temperature and $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio. It was carried out at comparatively low temperatures to minimise side reactions. There seems to be no published data on the effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio on aromatic reactions mentioned above.

Disproportionation of toluene and alkylation of toluene with methanol were also carried out over Fe, B and La/HZSM-5 for a comparison of their activity and selectivity to p-xylene with those of HZSM-5.

4.2. EXPERIMENTAL SET-UP AND PROCEDURE

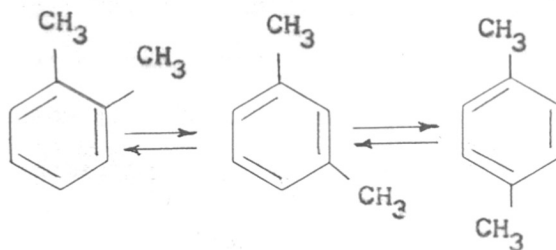
All reactions were carried out in a fixed bed down flow integral reactor. Reactor set up and procedure have been described earlier (Chapter 2.4.B). The catalysts were activated in a flow of dry air at $540-550^\circ\text{C}$ (4 hours) followed by nitrogen (30 minutes) and then brought to reaction temperature in an atmosphere of nitrogen.

Materials : These were ortho-xylene (99 + %) for isomerisation, toluene (99.5 %) for disproportionation and methanol (99 + %) and toluene for alkylation reactions.

Analysis : All analyses were carried out using H.P. 5840A gas chromatograph, A 5 % Bentone + 5 % diisodecyl phthalate on chromosorb AW (80-100 mesh) column (6 x 1/8") was used for analysis of the condensable products. n-Octane-porasil C column was used for analysis of gas products.

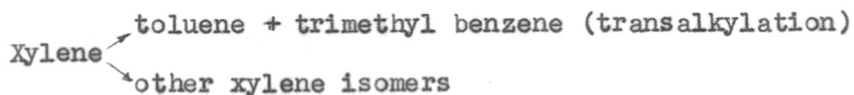
4.3. RESULTS AND DISCUSSIONA : Isomerisation of ortho-xylene

Isomerisation of xylenes can occur by two different reaction mechanisms. According to several authors^{143,147,149b}, it occurs by intramolecular re-arrangement (1,2 methyl shift) thus requiring only one Brönsted acid site. An intermolecular reaction involving a Lewis site, or a Brönsted-Lewis pair has also been proposed. In ZSM-5 zeolites, the intramolecular mechanism has been favoured on account of the spatial restriction on the formation of the bimolecular transient state complex involved in the latter reaction. The reaction scheme can be represented as a series^{one} in which meta-xylene is the intermediate :



A direct ortho to para-xylene conversion has been included for reaction in the pores of zeolites with large crystallite size^{148a}.

According to Collins et al^{143b}, the reactions of xylene can be represented as shown below :



On a conventional zeolite (LaY zeolite), they observed ortho-xylene to give 1,2,3 and 1,2,4-trimethyl benzenes (TMBs) and para-xylene to give 1,2,4 TMB as expected from the directing effect of CH_3 groups. In contrast, C_9 aromatics from ZSM-5 zeolite catalysed isomerisation contain predominantly 1,2,4-trimethyl benzene. Transalkylation on the external surface gives rise to other isomers also.

Dealkylation of xylene also takes place as a side reaction. For very active catalysts the ratio of toluene to C_9 aromatics (mole ratio) is greater than one. Dealkylation of toluene also takes place. Thus the side products observed are toluene, trimethyl benzene (1,2,4) and benzene.

Fig. 4.1 illustrates the effect of temperature on ortho-xylene conversion. All catalysts show increase in conversion with temperature. The trend in the case of Fe/HZSM-5 is different. At lower temperatures conversion is initially less and then increases rapidly with temperature.

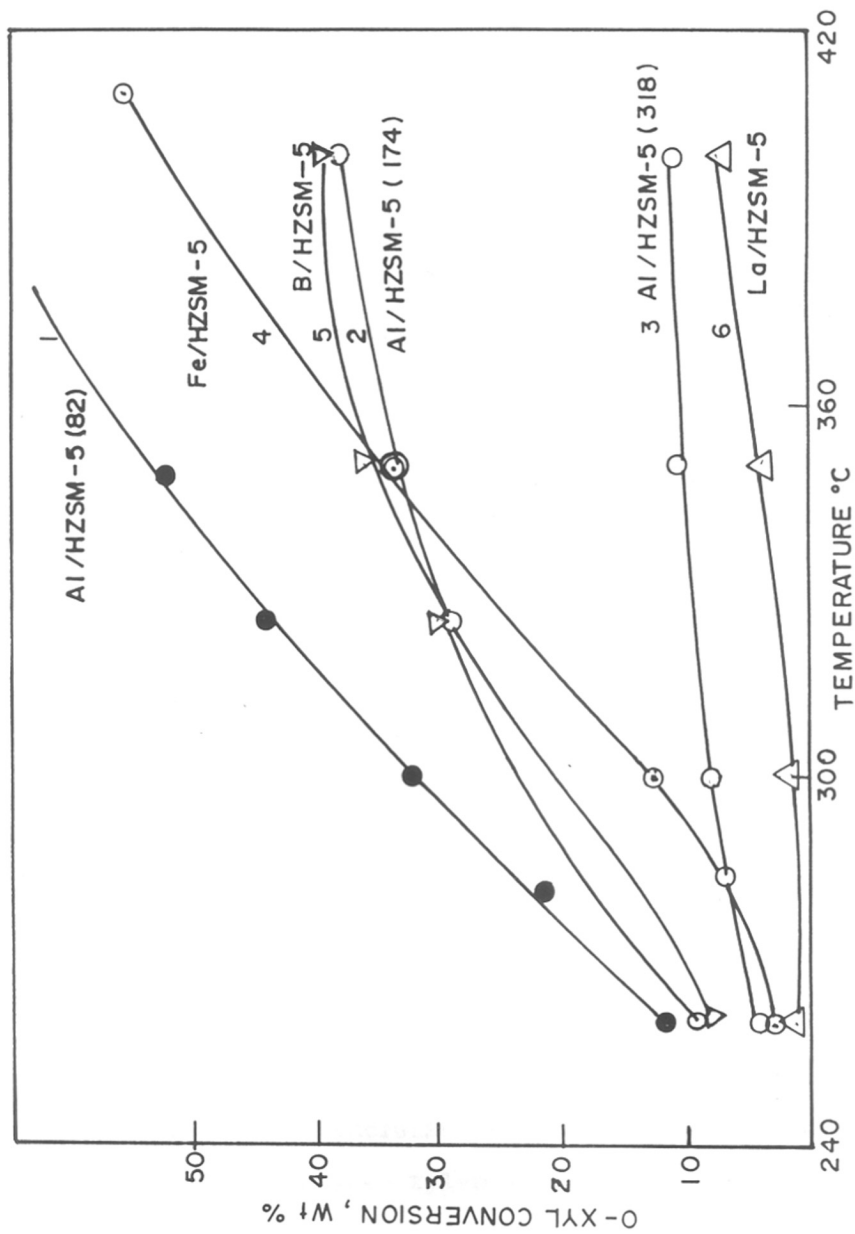


FIG 4-1 EFFECT OF TEMP. ON O-XYLENE CONVERSION

It is generally accepted that isomerisation needs acid sites of weaker strength compared to the sites required for disproportionation and cracking^{152,201}. In agreement with this observation, B/HZSM-5 zeolite which possesses few strong acid sites shows good activity for isomerisation. Low conversion observed on Fe/HZSM-5 which has both medium and strong acid sites (Table 3.4) is thus surprising. La/ZSM-5, which is the least acidic, is the least active for this reaction.

The effect of temperature on para-xylene selectivity (para-xylene in m + p xylenes) and disproportionation + dealkylation products is shown in Figs. 4.2 and 4.3. There is a slight fall in selectivity with increase in temperature. This may be because of the increase in the rate of diffusion of sterically hindered meta-xylene with temperature as observed by Chen and Garwood⁸⁵, in the case of 2,3 dimethyl butane. The effect of this change in para-selectivity with temperature is highest in the case of HZSM-5 (318) which shows maximum selectivity to para-xylene. Para-selectivity of the different zeolites would be considered shortly.

Figs. 4.2 and 4.3 show that disproportionation plus dealkylation products increase with increase in temperature. Disproportionation between xylenes is not favoured due to

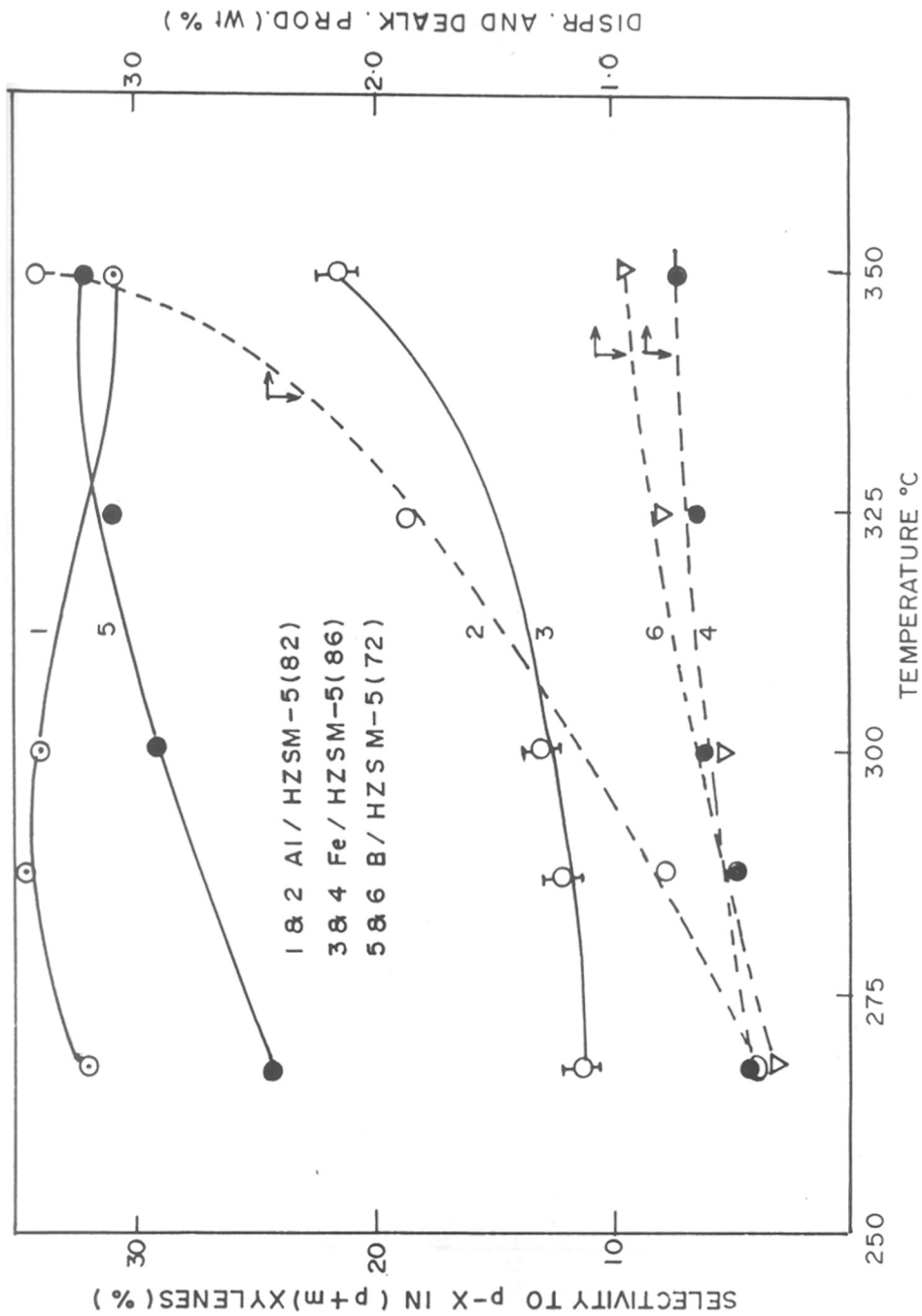


FIG 4-2 o-XYLENE REACTIONS, EFFECT OF TEMPERATURE (WHSV = 8.8 hr⁻¹) ON
 1) SELECTIVITY TO p-XYLENE (CURVES 1,3,5)
 2) DISP. + DEALK. PRODUCTS (" 2,4,6)

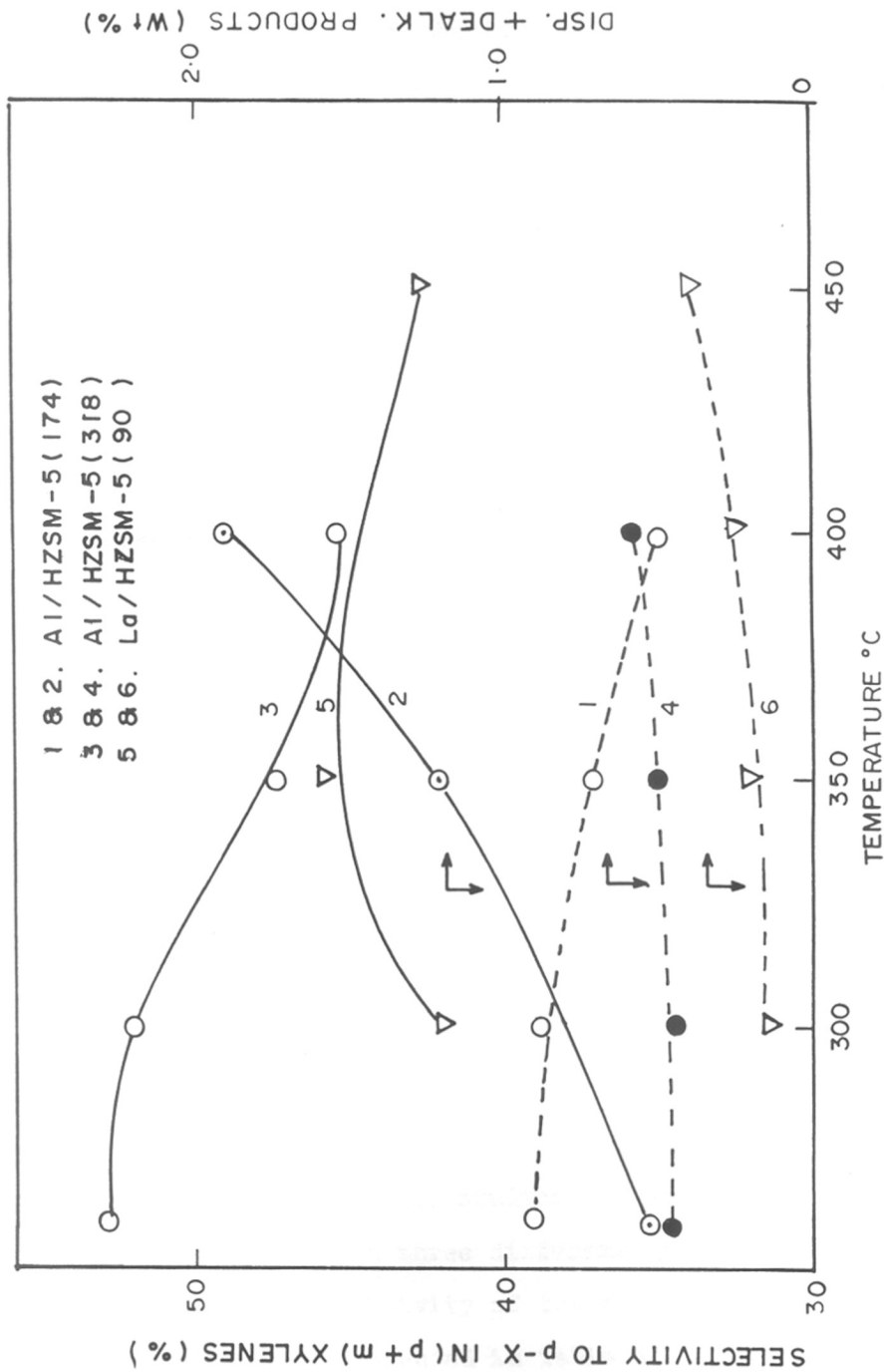


FIG 4-3 o-XYLENE REACTIONS; EFFECT OF TEMPERATURE; WHSV: 8.8 hr⁻¹

CURVE NOS. 1,3,5 FOR p-XYL SELECTIVITY

" 2,4,6 FOR DISP.+DEALK. PRODUCTS

spatial restriction on the formation of transition state complex involving the transalkylation of xylenes (T.S.S. effect)^{73,92}. Since toluene can also be formed via dealkylation of xylenes, the ratio T/C₉ is greater than 1. Disproportionation and dealkylation which is more favoured thermodynamically at higher temperature^{148b} increase with increase in reaction temperature.

Only dealkylation products were observed with B, Fe, La/HZSM-5. This is probably due to enhanced shape selectivity effects of these zeolites, caused by presence of occluded material in intracrystalline channels.

It seems that ~~some~~ aspects of shape selectivity effects, especially transient state selectivity effect, have been not considered in arriving at the order of acid strength required for reaction, namely isomerisation > dealkylation > disproportionation in a recent work¹⁵² as against the generally accepted scale, isomerisation > disproportionation > dealkylation²⁰¹.

The activity of the various catalysts shows the trend at 300°C, Al/HZSM > B > Fe > La.

In separate studies the effect of calcination of NH₄ZSM-5 (82) at three different temperatures (350, 400, 500°C) on the catalytic activity of the resultant HZSM-5 was determined. The results are presented in Table 4.1. It can be seen that

TABLE - 4.1

ISOMERISATION OF ORTHO-XYLENE
EFFECT OF CALCINATION TEMPERATURE ON PRODUCT
DISTRIBUTION

CATALYST. Al/NH₄ZSM-5(82); REACTION TEMP. 300°C
 WHSV = 8.8 hr⁻¹

Products wt. %	Calcination Temperature °C		
	350	400	500
Aliphatics	Trace	0.1	Trace
Benzene	0.1	0.1	Trace
Toluene	0.3	0.5	0.6
p-Xylene	10.4	10.6	10.8
m-Xylene	23.6	23.1	23.3
o-Xylene	65.1	64.9	64.6
Ethyl toluene	-	-	-
1,2,4-Trimethyl benzene	0.3	0.3	0.5
Other aromatics	0.2	0.4	0.1

there is no perceptible difference in the product distribution. This indicates that strong acid sites are not required for the isomerisation reaction as it is known that the most strongly bound NH_3 molecules (representing the strong sites) are not released until activation temperature is well above 400°C ⁴⁶.

Effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio (R)

With increase in R, conversion of ortho-xylene decreases (Figs. 4.1 and 4.2). This is in part due to the decrease in acidity of the samples with increase in R. Also, increase in crystallite size (with increase in R) may slow down the diffusion of ortho-xylene molecules into the channels which may also contribute to the decrease in activity observed^{150b}. Silicalite does not show any activity in the temperature range $250\text{--}450^\circ\text{C}$, thus showing that Brönsted acid sites are required for the reaction.

The ratio T/C_9 first increases and then decreases with increase in temperature (Fig. 4.4 and Table 4.2A). Dealkylation and to a lesser extent disproportionation increase with increase in temperature as both are endothermic reactions. The fall in T/C_9 at higher temperature may be attributed to increase in diffusivity of the sterically hindered trimethyl benzene molecule. Increasing amount of C_9 diffuse out of the pores escaping further reactions. Yield of benzene formed by dealkylation of toluene increases slightly with temperature

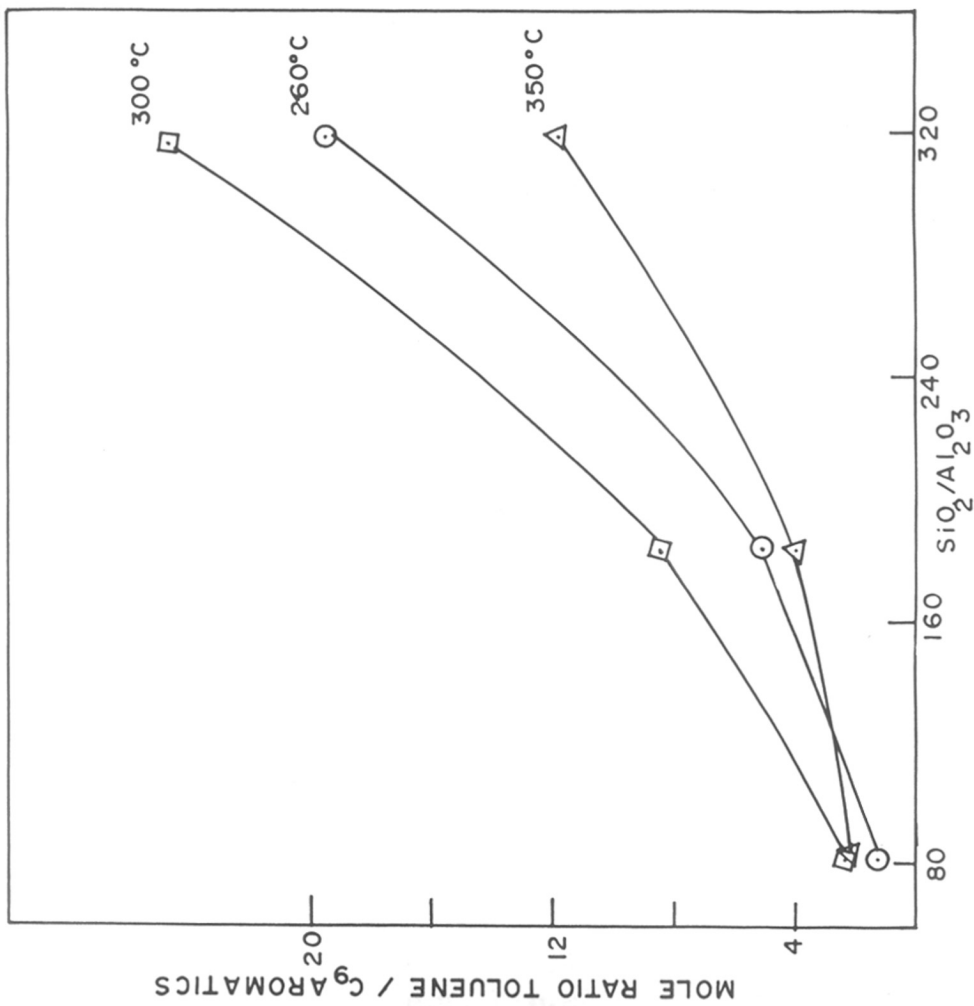


FIG 4.4 ISOMERISATION OF o-XYLENE. EFFECT OF SiO₂/Al₂O₃ ON TOLUENE / C₉ AROMATICS WHSV = 8.8 hr⁻¹

TABLE - 4.2 AISOMERISATION OF ORTHO-XYLENE

EFFECT OF $\text{SiO}_2/\text{Al}_2\text{O}_3$ RATIO (R) ON MOLE RATIO
TOLUENE/ C_9 AROMATICS AT DIFFERENT TEMPERATURES

WHSV = 8.8 hr⁻¹

$\text{SiO}_2/\text{Al}_2\text{O}_3$	TEMPERATURE °C				
	260	300	325	350	400
82	1.3	2.2	2	1.9	-
174	5.2	8.4	-	4.0	3.3
318	19.5	24.7	-	11.7	8.8

TABLE - 4.2 B

EFFECT OF R ON YIELD OF BENZENE AT DIFFERENT TEMPS.

	BENZENE (wt. %)				
	260	300	325	350	400
82	0.3	0.4	0.5	0.5	-
174	0.2	0.3	-	0.3	0.3
318	0.2	0.2	-	0.2	0.2

and decreases with increase in R (Table 4.2.B). In the latter case, the decrease in acidity of the sample is responsible for the observed effect.

It is found that increase in silica-alumina ratio increases para-xylene selectivity. The increase is observed at all temperatures (Fig. 3.4⁴⁻⁵). A similar effect (an increase in the ratio of (p + m xylenes) to ortho-xylenes) is also observed in the methanol reaction in which xylenes are among the major aromatics (Table 2.13). Adsorption measurements showed that the quantity of cyclohexane and ortho-xylene adsorbed apparently decreases with increase in silica-alumina ratio, sorption time being kept constant (Table 2.5 and 2.6). This apparent decrease in adsorption was attributed to slower diffusion of these molecules into the pores caused by increase in the diffusional path for the sorbate molecules (crystallite size effect). For the same reason, meta-xylene produced during the isomerisation reaction (and meta and ortho xylene produced in the methanol reactions) would be further isomerised to para-xylene (which would diffuse out faster), the extent of this isomerisation being larger, the larger the crystallite size⁸⁷. This might explain the enhanced selectivity to para-xylene (expressed as p + m/o or p/p + m) observed in the two reactions as well as in the other aromatic reactions described later.

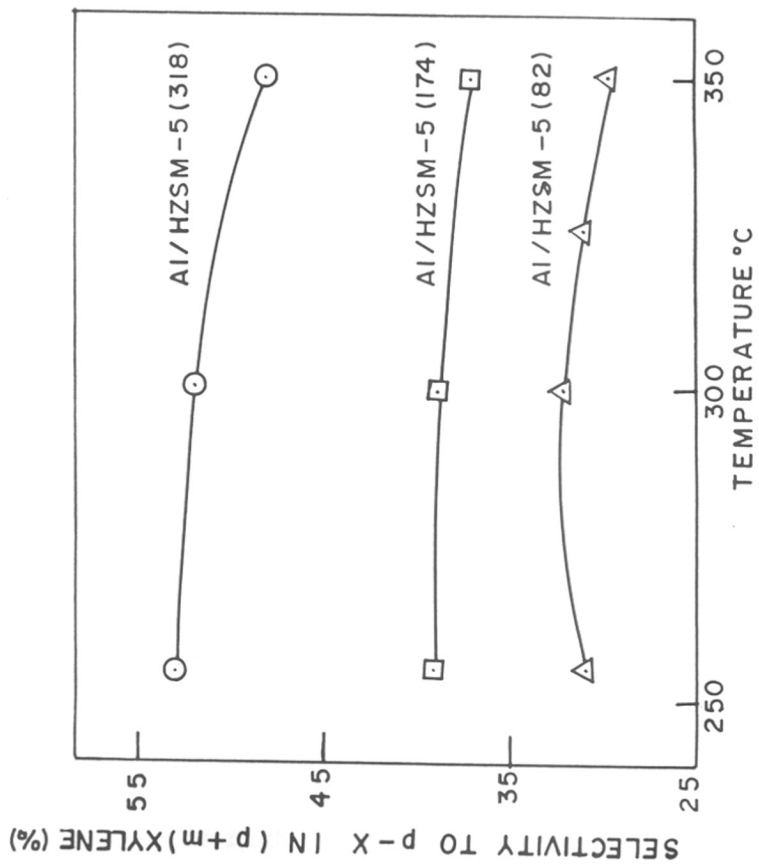


FIG 4.5 o-XYLENE ISOMERISATION. EFFECT OF TEMP. ON P-XYLENE SELECTIVITY WHSV = 8.8 hr⁻¹

A comparison of the catalytic properties of the different zeolites with respect to isomerisation of ortho-xylene shows that while the activity is in the order : HZSM-5(82) > B > Fe > La/HZSM-5 the selectivity to para-xylene (in p + m xylenes) follows the order : La(90) > Al(82) > B(72) > Fe(86).

Assuming the rate of adsorption of m and ortho-xylenes and hence quantity of each adsorbed during equal sorption time to be nearly identical, the latter order approximately holds good for the ratio of para-xylene to ortho-xylene adsorbed in the case of these zeolites (Table 3.3).

B : Toluene Disproportionation

Disproportionation of toluene over zeolites provides another route for production of xylenes^{139,140,156,157}. Comparatively high temperatures are required for this reaction. With unmodified zeolites (HZSM-5), xylenes in their equilibrium concentrations are produced and therefore the reaction is of less industrial importance. By proper selection of catalysts e.g. by modification of ZSM-5, the xylene formation can be directed to give high selectivity to para-xylene; but again this is achieved only at high temperatures and also at lower activity of the catalyst¹³⁹. Increase in crystallite size also leads to increase in selectivity to para-xylene. Thus, modification and use of large crystals may be expected to give high selectivity to para-xylene in the disproportionation

reaction⁸⁷. There are few published data on the toluene disproportionation reaction.

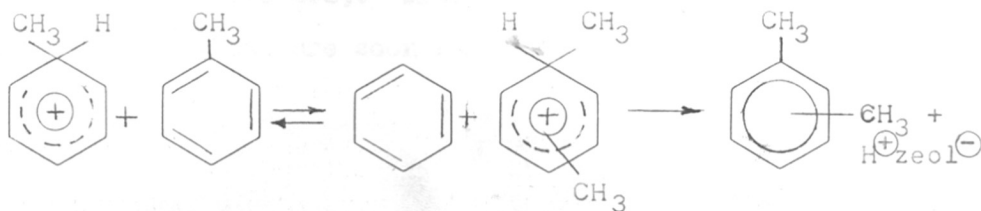
The present study is concerned with comparing the catalytic properties of the different zeolites (Fe, B and La/HZSM-5).

Mechanism of toluene disproportionation

Three mechanisms have been suggested for disproportionation of toluene; one involving a dealkylation and alkylation step which requires the formation of the very unstable CH_3^+ and is considered unlikely. A second one based on the diphenyl methane-type intermediate is not favoured because of spatial restrictions on the formation of this intermediate. The third mechanism visualises formation of benzenium ion by the adsorption of a toluene molecule on the Brönsted site of the zeolite^{139,196}.



A nucleophilic attack by a second toluene molecule on the above species results in transfer of a methyl group and the release of the original Brönsted site.



Dealkylation of toluene also takes place to some extent as a side reaction especially on unmodified HZSM-5 zeolites. Thus, on such catalysts, the ratio of benzene to xylenes is greater than one.

Results of the toluene disproportionation reaction over different catalysts have been presented in Figs. 4.6 to 4.9. Increase in reaction temperature increases conversion (Figs. 4.6 to 4.8), but it also increases dealkylation of toluene¹⁵⁷, thus raising the value of B/X above unity. The activity and B/X is lower (~ 1) for catalysts with higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio as their acidity is lower (Fig. 4.6). There is no reaction with silicalite catalyst which indicates Brönsted sites are required for the reaction.

By contrast, the zeolites, Fe, B and La/HZSM-5 show lower activity for toluene disproportionation in agreement with their lower acidity (Figs. 4.7 and 4.8). Also dealkylation of toluene does not take place to any significant extent as shown by the ratio of B/X staying at unity even at higher temperature (B and Fe/HZSM5). Para selectivity of the catalysts follows the trend (at 450°C) : $\text{La} > \text{B} > \text{Al} > \text{Fe/HZSM-5}$. HZSM-5(318) and La/HZSM-5 show low conversion (Figs. 4.6 and 4.8). They also show higher selectivity to ortho-xylene at 450°C than at thermodynamic equilibrium distribution at this temperature (Table 4.3). With increase in temperature the equilibrium values are soon reached in the case of HZSM-5(318).

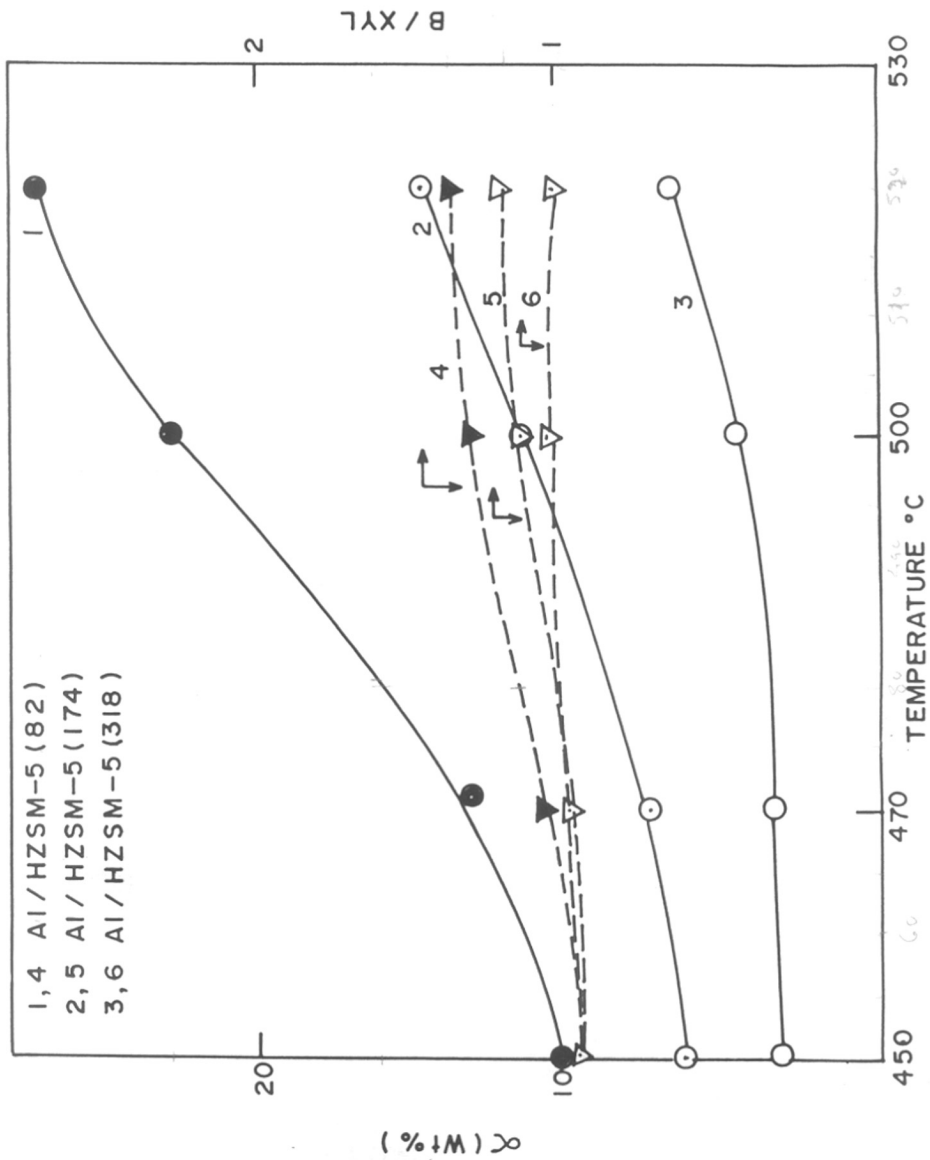


FIG. 4-6 DISPROPORTIONATION OF TOLUENE OVER HZSM-5 ZEOLITES. EFFECT OF TEMPERATURE ON 1. CONVERSION (1, 2, 3). 2.B/X RATIO (4, 5, 6)

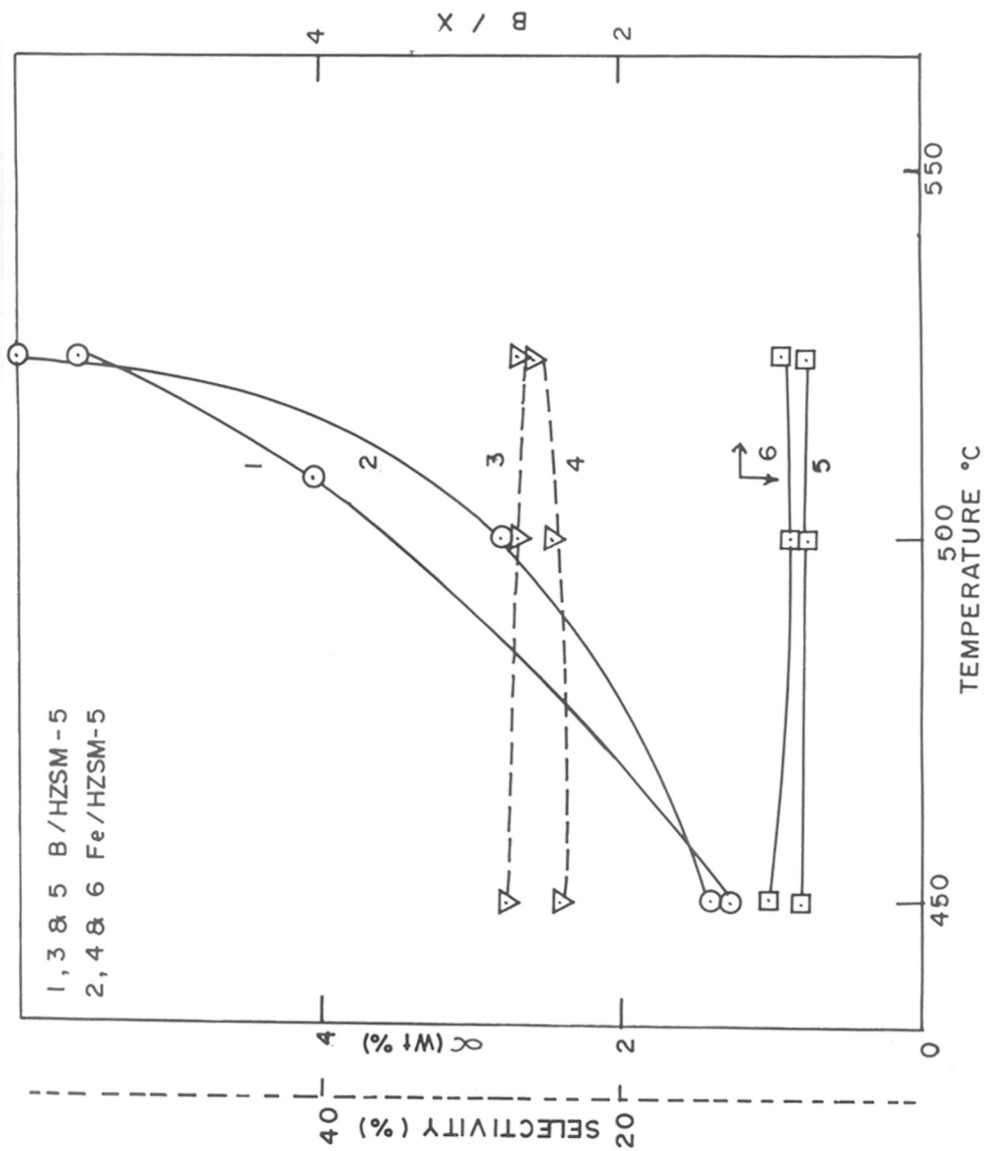


FIG 4-7 DISP. OF TOLUENE OVER ZSM - 5 ZEOLITES . EFFECT OF TEMP. 1 & 2 CONVERSION OF TOLUENE, α (WT %) . 3 & 4 SELECTIVITY TO P - XYLENE IN XYLENES . 5 & 6 B / X MOLE RATIO

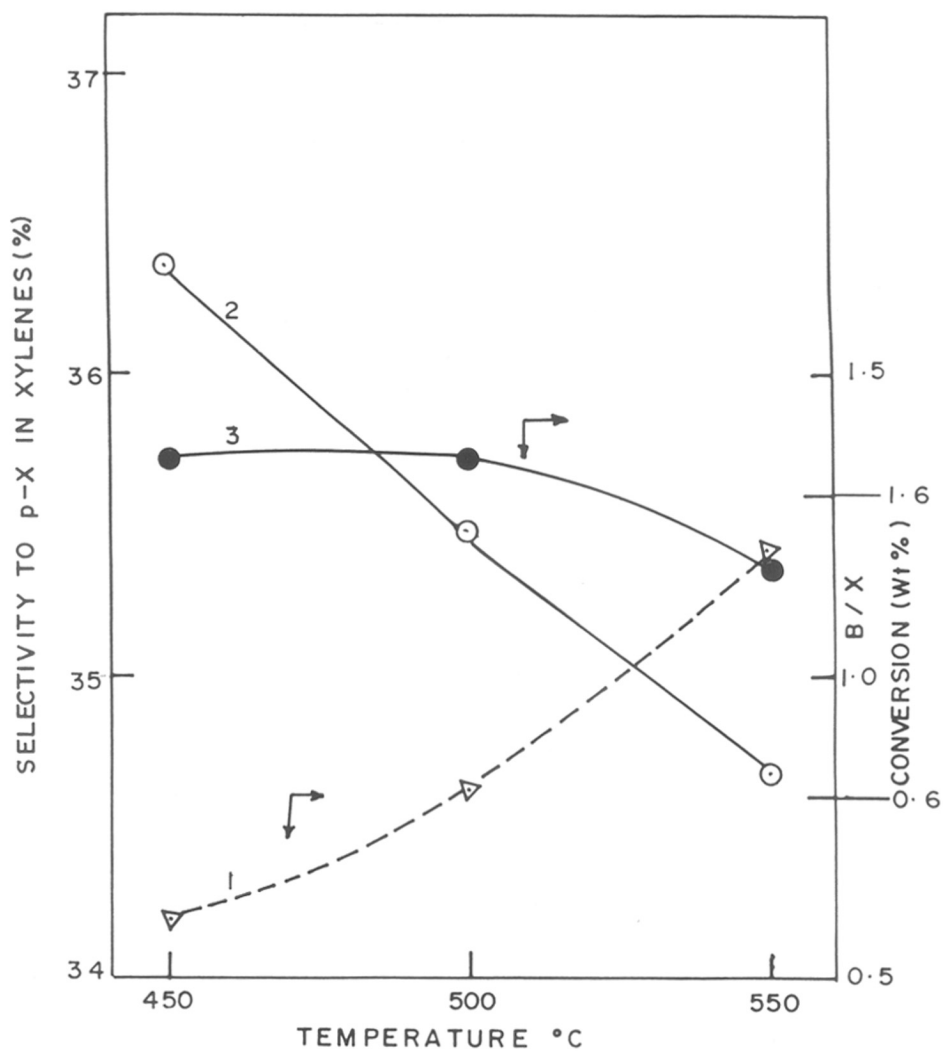


FIG 4-8 TOLUENE DISPROPORTIONATION OVER $La/HZSM-5$
 EFFECT OF TEMP. ON CONVERSION (1), p-XYLENE
 SELECTIVITY (2) AND B/X MOLE RATIO (3)
 $WHSV = 3.5 \text{ hr}^{-1}$

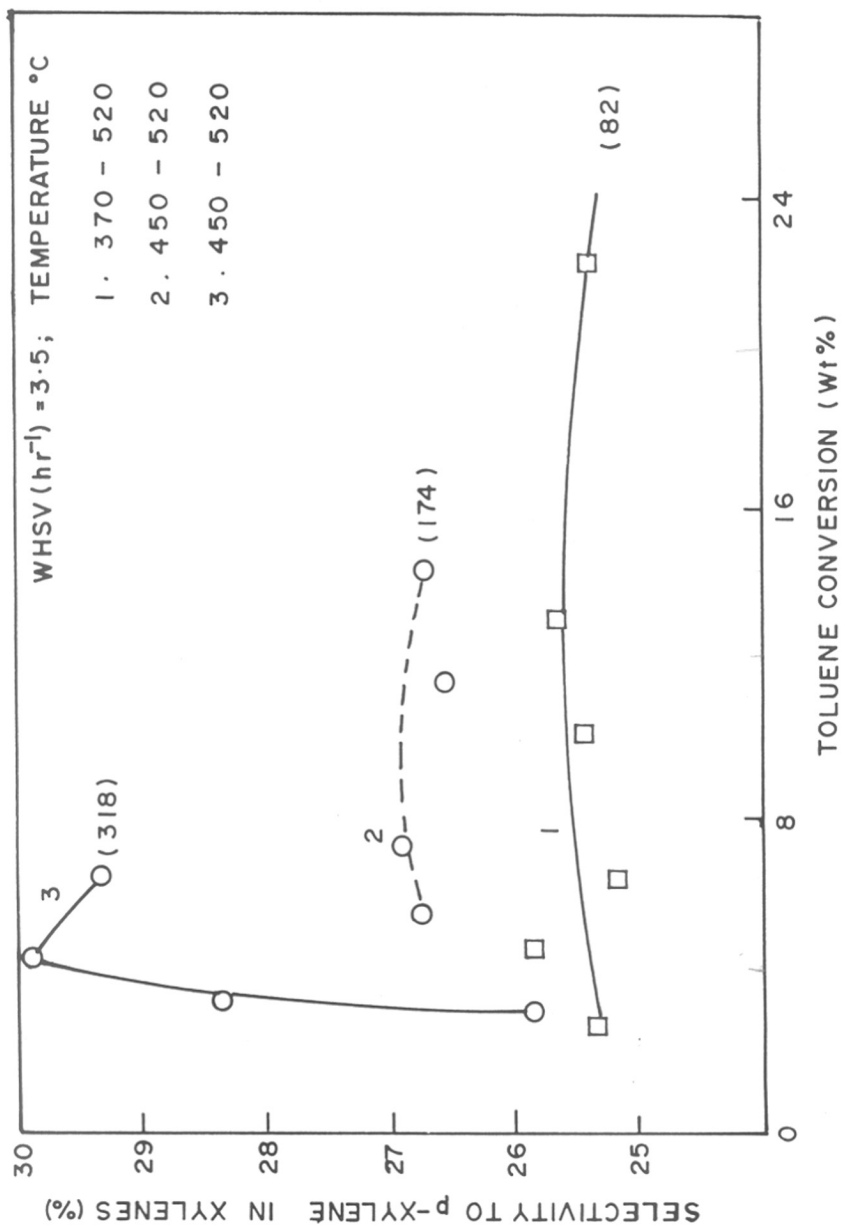


FIG 4.9 TOLUENE DISPROPORTIONATION OVER Al / HZSM-5. FIGURES IN BRACKETS REFER TO SiO₂/Al₂O₃ MOLE RATIO

TABLE - 4.3

TOLUENE DISPROPORTIONATION OVER HZSM-5(318)(A)
AND La/HZSM-5(B) EFFECT OF TEMPERATURE ON CON-
VERSION AND SELECTIVITY TO P-XYLENE

$$\text{WHSV} = 3.5 \text{ hr}^{-1}$$

T°C	Conversion wt%		ortho-Xylene		meta-Xylene		para-Xylene	
	A	B	A	B	A	B	A	B
450	3.1	0.5	34.8	26.9	39.3	38.5	25.8	34.6
500	4.5	1.4	25.1	20.3	45.0	43.2	29.9	36.5
550	6.6*	3.8	24.4	20.6	46.3	45.9	29.3	33.5

* at 520°C

Isomerisation rate (ortho-xylene - m-xylene) is increased as the temperature is increased and this accelerates the approach to equilibrium. The selectivity with respect to p-xylene does not change very much. In the case of La/HZSM-5 enhanced diffusional effects due to occluded lanthanum species may also be important in influencing the final distribution of the isomers.

C : Alkylation of toluene with methanol

This reaction provides yet another route for production of para-xylene. Easy availability of the comparatively cheap methanol and toluene has been responsible for the commercial interest in the process. Several patents¹⁸⁹ and few published data^{138,140,155} claim high selectivity to para-xylene using this relatively simple and practical process. Both modified and unmodified catalysts, have been used for the reaction. Since alkylation of aromatics needs only less strong acid sites on the scale of acidity required for various reactions²⁰¹, Fe, B and La/HZSM-5 catalysts were tested for activity and selectivity to p-xylene with respect to this reaction. Initially a study of the reaction over HZSM-5 at comparatively low temperatures was carried out. The effect of temperature, $\text{SiO}_2/\text{Al}_2\text{O}_3$ and WHSV on product distribution and para-selectivity was studied. Most of the earlier studies have been at high temperatures where side reactions of toluene, such as disproportionation and dealkylation become important.

A mole ratio of 5:1 (toluene:methanol) was chosen for the reactant mixture in order to minimise contribution from methanol reaction towards products. Also, it was expected that larger amount of toluene would prolong stable activity of the catalyst so that the observed changes in product distribution could be attributed to changes in experimental parameters such as feed rate and temperature. The amount of gaseous products formed during reaction has been small.

Mechanism

Mechanism of formation of xylenes by alkylation of toluene has been already described in Chapter 1. While the formation of the three isomers is possible in the inter-channel cross sections, formation of para-xylene is probably favoured on modified HZSM-5. According to Yashima et al^{141a} the primary product in alkylation over HZSM-5 is para-xylene which later isomerises on strong acid sites to yield the other isomers.

Results and discussion

Table 4.4 presents data for the product distribution at different temperatures. Toluene conversion increases with temperature. Methanol conversion is complete except at very high space velocities. Selectivity to para-xylene is slightly above thermodynamic equilibrium concentration

TABLE - 4.4

ALKYLATION OF TOLUENE WITH METHANOL OVER
HZSM-5(82) : TOLUENE/METHANOL (MOLE RATIO) 5/1

	T E M P E R A T U R E °C					
	350	400	450	450	450	450
WHSV (hr ⁻¹) ^a	3.4	3.4	3.4	5.2	8.6	25.8
Conversion (wt. %)						
Toluene	10.0	15.2	16.8	16.8	14.9	12.7
(theoretical maximum)			20			
Methanol			100			
Product distribution ^b (wt. %)						
(organic liquid)						
Aliphatics	0.1	0.2	0.1	0.1	0.1	0.2
Benzene	1.4	2.2	3.5	2.5	2.2	0.8
Toluene	88.6	82.7	80.8	81.7	82.9	85.7
Ethyl benzene	Trace	Trace	-	-	-	-
p-Xylene	2.0	3.0	3.3	3.3	3.1	2.9
m-Xylene	4.1	6.2	7.0	6.6	6.5	5.3
o-Xylene	1.7	2.7	3.1	3.0	2.8	2.3
Ethyl toluenes	0.9	1.2	0.6	0.9	1.0	1.3
<i>m</i> -Xylene	Trace	Trace	-	-	-	-
1,2,4-Trimethyl benzene	0.6	1.0	0.9	1.2	0.9	0.8
Other aromatics	0.7	0.8	0.7	0.8	0.6	0.5
<u>Xylene Comp. (%)</u>						
Para	25.6	25.2	24.6	25.6	25.0	27.6
Meta	52.6	52.1	52.2	51.2	52.4	50.5
Ortho	21.8	22.7	23.2	23.2	22.6	21.9

a : weight of (toluene + methanol) per hour per gm of catalyst

b : Traces of gas were formed.

due to product selectivity effect. Selectivity to para-xylene decreases slightly at higher temperature probably because of diffusional effects, higher temperatures favouring faster diffusion of the other isomers. Kaeding et al¹³⁸ have reported near equilibrium distribution for the xylenes at 400°C in this reaction. The amount of benzene increases slightly with temperature due to disproportionation, probably also by dealkylation of toluene. Among the trimethyl benzenes, 1,2,4-trimethyl benzene predominates as observed in the case of xylene isomerisation and toluene disproportionation.

Table 4.4 also shows the effect of WHSV on product distribution. Conversion decreases and para selectivity increases slightly. These are on the same pattern as observed for xylene-forming reactions^{138,141}. Other effects observed are decrease in benzene, 1,2,4-trimethyl benzene and higher aromatics and increase in ethyl toluenes. At the lower residence times the loss of the ethyl toluenes by dealkylation is less. According to Mole et al¹⁹⁷ such dealkylation reactions are important in the reaction of methanol to hydrocarbons. Presence of ethyl toluene (which is formed by alkylation with ethylene) in the alkylation reaction further proves that ethylene is one of the primary intermediates in the conversion of methanol¹¹⁴.

The effect of cumulative feed on product distribution is shown in Table 4.5, in which column 4 of Table 4.4 is reproduced for comparison of experimental data. Conversion decreases and para-selectivity increases slightly due to coking effect. This has been attributed to reduction in effective channel size (due to internal coking¹³⁸ or partial blocking of the channel opening by external coke deposit¹⁰⁰). This reduces the outward diffusion rate of the o- and m-xylene which would further isomerise and thus increase selectivity to p-xylene. Coking effect is also reflected in a small reduction in the yield of ethyl toluenes and higher aromatics. Product selectivity effect is thus enhanced by coking.

Increasing WHSV over a coked catalyst has profound effect on para selectivity. Thus para selectivity is increased about 1.3 times as against 1.1 times on an uncoked catalyst (Table 4.4, Cols. 4, 5 and 6 and Table 4.5 Col. 4 and 5).

The amount of gaseous products collected under the experimental condition has been very small. The composition of the gaseous products in early and final period of the run is shown in Table 4.6. The gas composition in the early period of the run resembles that obtained in the

TABLE - 4.5

ALKYLATION OF TOLUENE WITH METHANOLEFFECT OF TIME ON STREAMREACTION TEMP. °C 450; TOLUENE/METHANOL : 5/1

WHSV (hr ⁻¹)		5.2			25.8
Time on stream(hr.)	5	20	30	40	41
Conversion (wt.%)					
Toluene	16	14.1	13.2	10.3	9.3
Methanol		100			92
Product distribution (wt.%)					
(organic liquid)					
Aliphatics	0.2	0.1	0.2	0.2	0.2
Benzene	2.5	1.7	1.5	1.4	0.3
Toluene	81.7	83.8	84.8	88.1	89.5
p-Xylene	3.3	3.0	2.9	2.4	2.9
m-Xylene	6.6	5.9	5.4	4.1	3.6
o-Xylene	3.0	2.6	2.5	1.9	1.6
Ethyl toluenes	0.9	1.0	1.0	0.7	0.9
1,2,4 Trimethyl benzene	1.2	1.1	1.1	0.7	0.6
Other aromatics	0.8	0.7	0.6	0.6	0.1
<u>Xylene composition %</u>					
para	25.5	26.2	26.8	28.6	36.3
meta	51.5	51.3	50.3	49.3	44.0
ortho	23.0	22.5	22.9	22.1	19.7

TABLE - 4.6

COMPOSITION OF GASEOUS HYDROCARBON
PRODUCTS IN THE ALKYLATION OF
TOLUENE OVER HZSM-5(82)

REACTION TEMP. = 450°C; WHSV = 5.2 hr⁻¹

<u>Weight %</u>	<u>A</u>	<u>B</u>	<u>C</u>
Methane	6.7	34.5	42.2
Ethylene	2.7	17.6	23.6
Ethane	Trace	Trace	< 1
Propane	78.3	37.4	22.4*
Propylene	2.3	5.3	-
Butanes (iso)	6.2	2.9	11.3**
Butane (n)	2.6	1.0	-
Butenes	Trace	Trace	-
C ₅ ⁺	1.2	1.3	-

A Fresh catalyst HZSM-5(82); conversion of toluene α (wt. %) = 14.5

B Same, after coking α = 9.2.

C Fe/HZSM-5(86); WHSV = 3.5; " = 9.9.

* Includes propylene.

** Includes all C₄

methanol reaction and consists of C_1 - C_4 paraffins as the largest fraction. The gas mixture is rich in CH_4 towards the final period of the run indicative of coking. A partially deactivated catalyst in the methanol reaction also gives more CH_4 and larger amounts of olefins¹²⁹ as seen here.

Effect of SiO_2/Al_2O_3 mole ratio

As observed in the case of the other aromatic reactions, conversion decreases with increase in SiO_2/Al_2O_3 ratio, but selectivity to para-xylene in xylenes (and para-ethyl toluene in ethyl toluenes) increases. Amounts of benzene and other aromatics (C_{10} +) are also found to decrease. These effects are shown in Fig. 4.10 and may be attributed to decrease in acidity and increase in crystallite size of the samples. Also less external surface is available for reactions leading to higher aromatics when the crystallite size is large.⁹² A comparison of activity and product distribution for the catalysts with mole ratios 82, 174 and 318 for the alkylation reaction at $400^\circ C$ is shown in Table 4.7.

Yashima et al^{141a} proposed that para-xylene is the primary product in the alkylation reaction which subsequently isomerises on strong acid sites to give m and o xylenes. By physical treatments such as steaming the catalyst at $950^\circ C$, incorporation of MgO etc., which destroyed strong sites (as shown by TPD data) a high selectivity to para-xylene could be

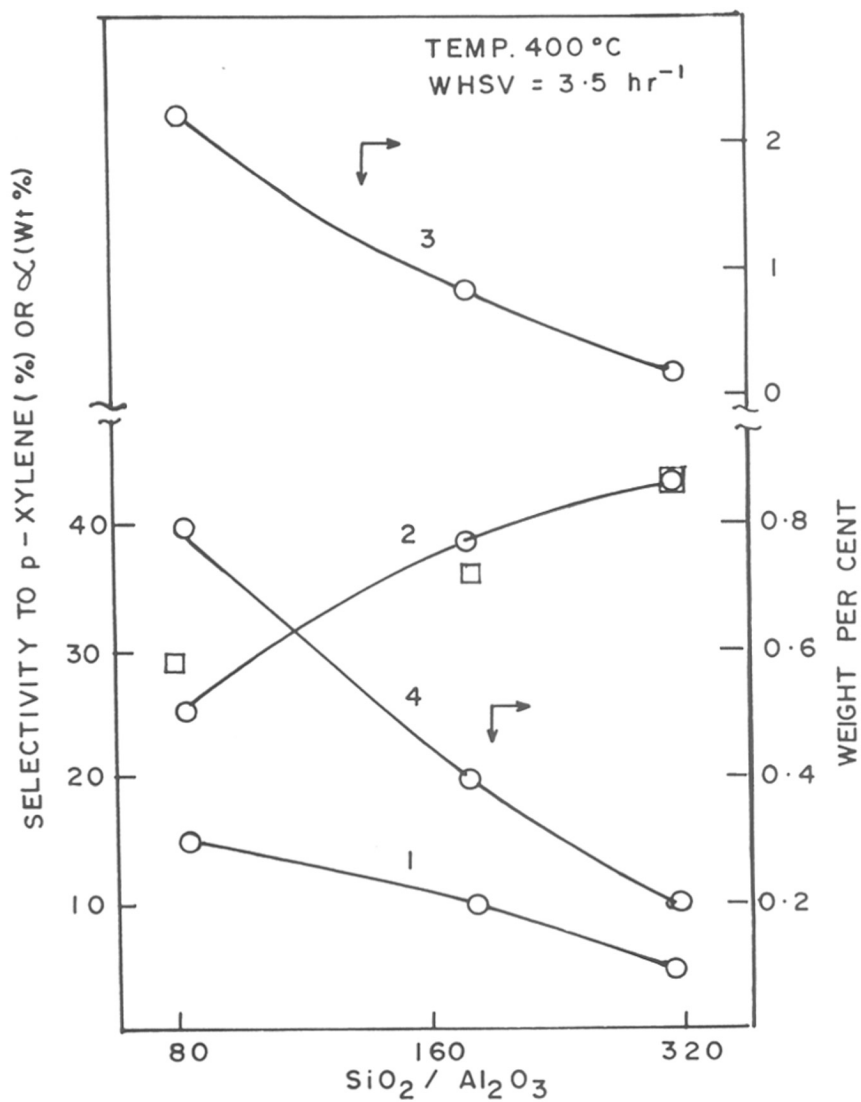


FIG 4.10 ALKYLATION OF TOLUENE WITH METHANOL.
EFFECT OF SiO₂/Al₂O₃ ON 1. CONVERSION(∞)
OF TOL.(1), 2. SELECTIVITY TO p-X,
3. BENZENE YIELD (Wt %) (3) AND C₁₀+
AROMATICS YIELD (4). □ SHOWS SELECTI-
VITY TO p-ETHYL TOL. IN ETHYL TOLS..

TABLE - 4.7

ALKYLATION OF TOLUENE WITH METHANOL
 EFFECT OF $\text{SiO}_2/\text{Al}_2\text{O}_3$ MOLE RATIO
 REACTION TEMP. 400°C ; WHSV = 3.4 hr^{-1}

	$\text{SiO}_2/\text{Al}_2\text{O}_3$		
	72	174	318
<u>Conversion (wt. %)</u>			
Toluene	15.2	10.9	8.8
Theoretical maximum		20	
Methanol	100	100	100
<u>Product distribution (wt. %)</u> (organic liquid)			
Aliphatics	0.2	0.2	0.1
Benzene	2.2	0.8	0.3
Toluene	82.7	87.5	90.0
Ethyl benzene	Trace	-	-
p-Xylene	3.0	3.6	3.5
m-Xylene	6.2	3.9	3.1
o-Xylene	2.7	1.8	1.4
Ethyl toluenes	1.2	1.2	0.9
Mesitylene	Trace	-	-
1,2,4 Trimethyl benzene	1.0	0.7	0.5
Other aromatics	0.8	0.4	0.2
<u>Xylene composition (%)</u>			
para	25.2	38.8	43.5
meta	52.1	42.4	39.0
ortho	22.7	18.8	17.5

obtained. According to Haag^(141a, discussion), however, the effects observed in that study could be explained on the basis of diffusional effects alone. In a study of the isomerisation of ortho-xylene^{150b} disproportionation and alkylation of toluene⁸⁷ it was reported that the use of large crystals could bring about high para selectivity. Activity was reduced^{150b} because less ortho-xylene could enter the pores for reaction. Since the Si/Al ratio used in the study was same for all the samples the increase in para-xylene selectivity could be clearly attributed to the role of crystallite size.

Though the role of crystallite size in influencing para selectivity has been recognised earlier^{87,144} little published data seem to be available on the effect of Si/Al on crystallite size^{34a,b} of samples prepared under identical conditions and hence on selectivity. Acidity differences may be influencing selectivity but the observed effect (increase in para-xylene selectivity) in the present study is most likely to be due to differences in crystallite size and fit well with the sorption properties of the samples. A similar effect, i.e. increase in para-ethyl toluene selectivity, has been reported in the ethylation of toluene using ethanol^{141b}, with increase in $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

Product distribution data for alkylation over Al, Fe, B and La/HZSM-5 catalysts are shown in Tables 4.8. It can be seen that the activity for alkylation follows the same trend as for acidity (Section 3.2 E). The yield of 1,2,4-trimethyl benzene is substantially higher in the case of Fe/HZSM-5. The relative amount of 1,2,4-trimethyl benzene produced follows the trend of sorption of this compound by the zeolites (Table 3.3) i.e. $Fe > B > Al > La$ showing thereby that Fe/HZSM-5 probably allows diffusion of the large molecules (1,2,4 trimethyl benzene and ortho-xylene). In La/HZSM-5, the diffusion is hindered to a greater extent probably because of occluded La^{3+} species increasing channel tortuosity to diffusing molecules.

The relation between 1,2,4 TMB produced versus uptake in sorption experiments is further illustrated in Fig. 4.11A. The linear curve passing through the origin brings out the importance of diffusion controlled product selectivity effects in HZSM-5 zeolites.

Other differences in the product distribution are the following :

Fe/HZSM-5 gives much less ethyl toluene. It may not be a good catalyst for ethylation as shown by the inefficient use of ethylene generated in the reaction. The effluent stream contains large fraction of ethylene (Table 4.6, Col. 3). The higher aromatics decrease when going from

TABLE - 4.8

COMPARISON OF CATALYSTS FOR ALKYLATION OF TOLUENE.
TEMPERATURE - 450°C; WHSV = 3.4 hr⁻¹

	HZSM-5			
	Al	Fe	B	La
<u>Conversion (wt. %)</u>				
Toluene	16.8	12.8	11.8	9.8
Methanol	100			
<u>Organic product (wt.%)</u>				
Aliphatics	0.1	-	-	0.2
Benzene	3.5	0.4	0.5	0.2
Toluene	80.8	85.3	86.4	88.8
p-Xylene	3.3	3.1	3.7	4.5
m-Xylene	7.0	5.6	5.0	3.3
o-Xylene	3.1	2.9	2.3	1.5
Ethyl toluene	0.6	0.1	0.7	0.8
1,2,4 TMB	0.9	2.0	1.2	0.6
Other aromatics	0.7	0.6	0.3	0.1
<u>Xylene composition (%)</u>				
p-Xylene	24.6	26.7	33.2	48.3
m-Xylene	52.2	48.3	45.6	35.6
o-Xylene	23.2	25.0	21.2	16.1

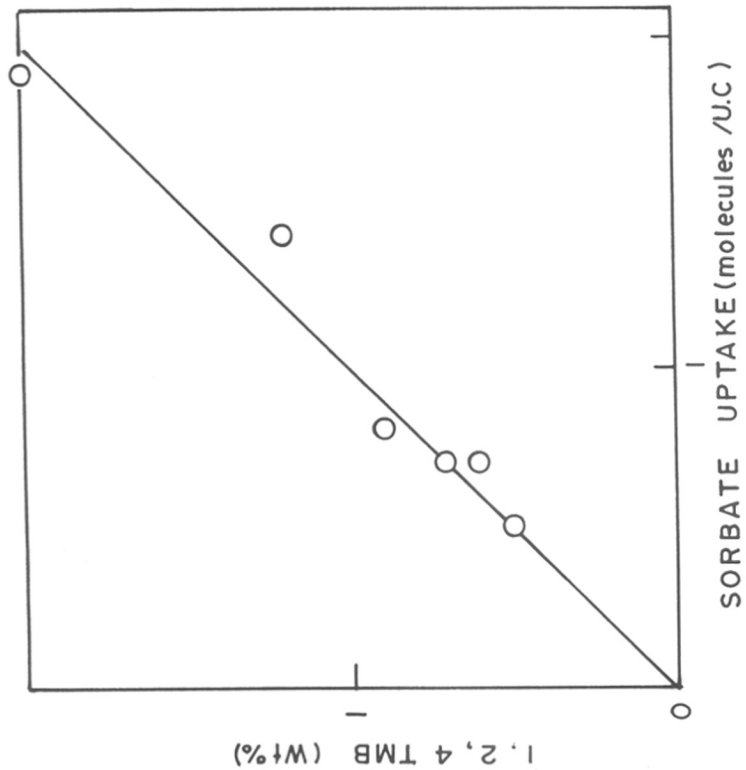


FIG 4-II A

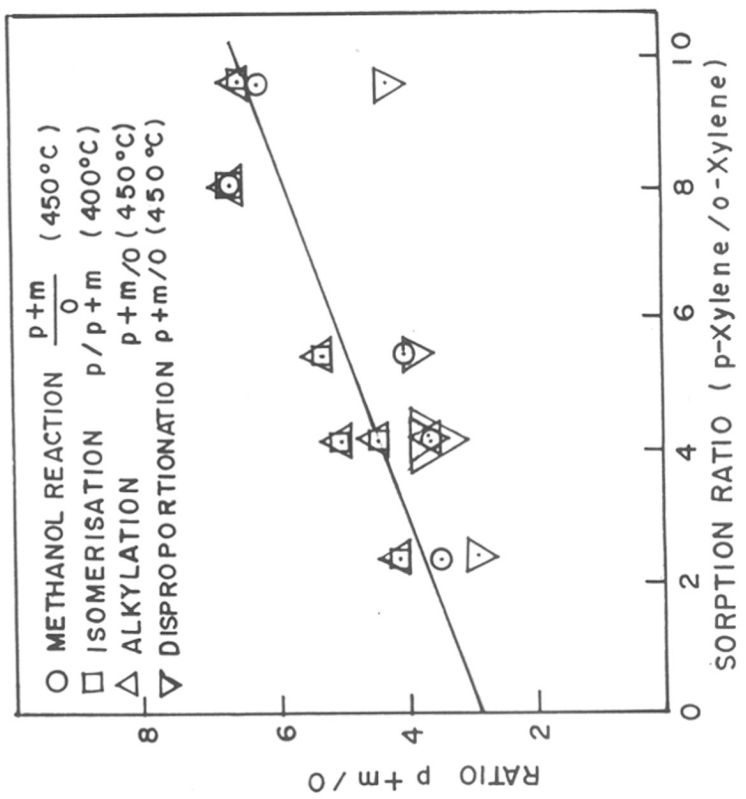


FIG 4-II B

Al to La/HZSM-5. The decrease in the yield of benzene formed mainly from dealkylation and disproportionation reactions also follows the trend in acidity (Table 4.8).

Irrespective of the reaction being studied for formation of para-xylene, selectivity to para-xylene seems to depend on some common factor not controlled by details of the mechanism of its formation. This can only be due to the relative diffusion rates of the xylene isomers and any subsequent isomerisation that occurs on the external surface as recently demonstrated by Nunan et al²²² and several others in the past^{73,221}. Assuming that the contribution due to isomerisation on the external surface is negligible, the higher the ratio of the rates of diffusion of para-xylene to that of the other isomers, the higher the selectivity to para-xylene. That is, as an approximation the ratio of the quantity of para-xylene sorbed to the quantity of other isomer sorbed in equal sorption time (30 minutes in the present case) could show the trend of selectivity to para-xylene. A superior method is to plot the time required by the sample for sorption of equal fraction of the equilibrium sorption of ortho-xylene against the selectivity factor^{73,221}.

Fig. 4.11B, shows the plot of the sorption ratio of para-xylene/ortho-xylene measured at 25°C versus selectivity to para-xylene (or its equivalent) in different reactions over ZSM-5 type zeolites studied in the present work. Since

separation of the isomers has not been carried out in all cases, only the available analytical data have been used to illustrate the point. Also it is assumed that the meta- and ortho-xylene are sorbed to the same extent (the ratio of sorption of these are similar at 120°C¹⁴⁰) and that the ratio of the quantity of the two isomers (para and ortho-xylenes) adsorbed at the reaction temperature is of similar magnitude as at room temperature. With these approximations the plot illustrated in Fig. 4.11B shows the importance of relative rates of diffusion of isomers on para-selectivity.

The experimental data presented on different aromatic reactions show that La/HZSM-5, though least active gives highest selectivity to para-xylene. The selectivity in alkylation reaction can be further enhanced by operating at high temperature and space velocity (Table 4.9). Such selectivity enhancement with temperature for para-selective (modified) zeolites has been reported by Kaeding et al¹⁴⁰.

4.4. C O N C L U S I O N S

1. Isomerisation of xylene, disproportionation of toluene and alkylation of toluene with methanol are industrially important reactions for production of para-xylenes. Data are presented to show that among the zeolite catalysts (Al, Fe, B and La/HZSM-5), Al/HZSM-5 gives highest activity for the reactions but low para-xylene selectivity and

TABLE - 4.9

ALKYLATION OF TOLUENE OVER La/HZSM-5
MOLE RATIO, TOL/METHANOL 5/1;
WHSV = 8.8 hr⁻¹; TEMP. 650°C

<u>Conversion (wt.%)</u>	
Toluene	5.6
Methanol	100
<u>Organic products (wt.%)</u>	
Aliphatics	0.4
Benzene	1.6
Toluene	93.5
p-Xylene	4.1
m-Xylene	0.1
o-Xylene	0.1
C ₉ aromatics	0.2
<u>Xylene composition (%)</u>	
para	95.4
meta	2.3
ortho	2.3

La/HZSM-5, the least active among them, gives the highest para selectivity.

2. Study of the influence of silica-alumina ratio(R) on activity and selectivity for the reactions shows that with increasing R, activity decreases but para-xylene selectivity increases. Increase in selectivity has been attributed to the observed increase in crystallite size with R. The effect of temperature on product distribution can be explained on the basis of side reactions such as dealkylation and disproportionation both of which are favoured at high temperatures. The effect of increasing WHSV and coking in the alkylation reaction is to increase selectivity to para-xylene. Increasing WHSV on a coked catalyst seems to increase selectivity to a greater extent.

3. The differences in product distribution observed for reactions over different catalysts can be correlated with differences in acidic and adsorption properties. For instance the increased amounts of dealkylation and disproportionation products for reaction over Al/HZSM-5 may be attributed to its greater acidity. The increased amounts of 1,2,4 TMB observed with Fe/HZSM-5 in alkylation reaction indicates that this hydrocarbon has greater diffusivity within the intracrystalline space as shown by its greater uptake during sorption.

4. From a comparison of the xylene distribution in products from different reactions and hydrocarbon synthesis from methanol over ZSM-5 type zeolites, it is found that the distribution is almost independent of the reaction. The distribution (expressed differently in the plot) follows the same trend as the sorption ratio of para to ortho-xylene. The importance of the relative diffusion rates of the isomers with respect to para selectivity demonstrated by other workers is once again brought out.

5. La/HZSM-5 appears to be a good catalyst for selective production of para-xylene using alkylation reaction at high temperature and space velocity. The 'high temperature - high selectivity' effect observed is characteristic of modified ZSM-5 zeolites.

S U M M A R Y

Zeolites of the ZSM-5 type have found applications as catalysts in a variety of chemical transformations such as methanol to gasoline (MTG) or olefins (MTO), ethyl benzene synthesis and xylene isomerization. The reason for this superior performance lies in their better shape selective properties and high thermal, hydrothermal and acid stability, all of which arise from their special structural features.

The present work briefly describes in Chapter I the general methods of synthesis of zeolites in general and ZSM-5 in particular. Different mechanisms suggested for crystallisation of ZSM-5 have also been described. The important structural features have been reviewed. Several of the experimental techniques used for monitoring various chemical events during synthesis and physicochemical characterisation of the final product have also been described. Factors responsible for the superior catalytic properties of ZSM-5 type zeolites have been described under molecular shape-selective catalysis. Work done in respect of reactions carried out in the present work has been briefly reviewed and scope of the present work presented.

Synthesis and characterisation of the ZSM-5 type zeolites used in the present study have been described in Chapter II. These are HZSM-5 zeolites having different

$\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratios ($R = 82, 174$ and 318) which are indicated in brackets. HZSM-5(82) is also represented as Al/HZSM-5(82) or simply Al(82) for purposes of comparison of catalytic properties with those of other zeolites.

The identity of the zeolites as belonging to the ZSM-5 type has been established. SEM photographs of the zeolites show increase in crystallite size with increase in $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio (R). This is in accordance with the literature. Differences in adsorption and acidic properties of the zeolites with increase in R are noted. Uptake of most of the aromatic compounds and cyclohexane and water is reduced by increase in R . This may be due to decrease in interaction between sorbate molecules (para-xylene, 1,2,4-trimethyl benzene, ortho-xylene, water) and the framework structure or increase in crystallite size with increase in R which slows down diffusion of sorbate molecules (cyclohexane, ortho-xylene and 1,2,4 TMB) into the pores or due to both. In the second case, the observed effect may be more apparent than real. Zeolites modified by impregnation with phosphorous or boron also show low uptake of sorbate because the modifier species may be plugging the channels and blocking the pore openings. Both the number and strength of acid sites are found to decrease with increase in R as seen in

the TPD (temperature programmed desorption) spectra of NH_3 . For a comparison of the strength of the acid sites, the temperatures at the maximum of the peak (T_{max}) representing the strongest sites in the TPD spectra have been compared.

According to the concept of super acid sites in zeolites, these acid sites are created as a result of dealumination from the framework structure (during calcination) or introduction of aluminium in octahedral coordination sphere in extra lattice position during synthesis. Whatever be the source of this extra lattice aluminium, the possibility of its being available for generation of super acid sites and hence the number of super acid sites may be expected to decrease with increase in $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio. Thus, there may be a redistribution of the strong acid sites and an associated shift in T_{max} of the high temperature peak in the TPD spectra of ammonia. The number of acid sites which is directly related to the Al-content also decreases. Zeolites modified by impregnation with phosphorous or boron show TPD spectra of ammonia which indicate reduction in number and strength of the acid sites. An increase in the number of weak acid sites reported in the literature is not observed.

Conversion of methanol, ethanol, diethyl ether and ethylene has been studied under different experimental

conditions and at complete conversion levels. The results presented in Chapter II show close similarity of product distribution. The products of interest in these reactions have been the $C_5 +$ hydrocarbons (gasoline fraction) or in other places, the light olefins (C_2-C_4 olefins). The influence of temperature on the distribution of products has been studied and explained on the basis of temperature effect on secondary reactions such as dealkylation of aromatics and cracking of higher aliphatics. The yield of olefins and BTX aromatics increase with reaction temperature. Maximum yield of $C_5 +$ is between 350 and 400°C irrespective of the reactant. The temperature dependence of the $C_5 +$ composition is similar and the yield of $C_5 +$ (or BTX aromatics) per mole of CH_2 for the different feeds is of the same order. It is therefore reasonable to conclude that the different reactions have identical reactive intermediates (light olefins) and these undergo same acid catalysed reactions to yield nearly the same hydrocarbon distribution at complete conversion levels. The shape selective properties play, probably a limited role in these reactions, for instance, eliminating reactions responsible for coke formation and limiting products to hydrocarbons with $C < 11$ as have been demonstrated in a recent work.

In the conversion of methanol to olefins over HZSM-5 it is found that high yields of olefins can be obtained

by combining the effects of high temperature and high $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio. High temperature favours cracking of higher aliphatics and dealkylation reactions. Dealkylation has been shown to be an alternate route to the production of olefins in the methanol reaction. Increasing R has the effect of reducing acidity and hence hydrogen transfer (formation of $\text{C}_2\text{-C}_4$ paraffins) and dehydrocyclisation (formation of aromatics) are less favoured. All these lead to increase in olefin yield. The higher aliphatics are however, found to increase slightly with increase in $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. Increase in WHSV which reduces subsequent reaction of the primary olefins also gives higher yields of olefins. Use of dilute aqueous solution of methanol as feed gives rise to olefin yields as high as 62 % (wt. %) when the water content in the feed is about 50 %. The aromatic yield does not seem to be affected by introduction of water. It is the $\text{C}_5 +$ aliphatics whose yield is found to be drastically reduced. Faster desorption of light olefins and increase in the rate of alkylation of the $\text{C}_2\text{-C}_3$ olefins with methanol (compared to their oligomerisation and subsequent reactions) may be responsible for the observed increase in olefin yield. Modified zeolites are also found to give large amounts of olefins. The modifier species neutralise the strong sites responsible for hydrogen transfer (yield of paraffins is drastically reduced) and dehydrocyclisation (yield of aromatic is reduced). Also increased tortuosity in the

zeolite channels restricts formation of large molecules via diffusion controlled product selectivity effects and thus contributes to increased selectivity to olefins. The increased para selectivity observed in phosphorous modified zeolites in the methanol reaction also illustrates this effect. Boron modified zeolites yield large amounts of olefins for the same reason, but the yield of ethylene is high probably because it ensures larger amounts of water in the pores for reaction with the ethyl methyl oxonium ion which is an intermediate proposed in one of the reaction mechanisms for the first C-C bond formation.

Isomorphous substitution of Al^{3+} in HZSM-5 with Fe^{3+} , B^{3+} and La^{3+} has been attempted (Chapter III). XRD and IR spectra of samples (designated as Fe/HZSM-5, B/HZSM-5 and La/HZSM-5) show that the zeolites prepared belong to the pentasil family (ZSM-5 type). Evidence on the basis of XPS and EPR have been presented to show that such a replacement has taken place in the case of iron. XPS data show that there is only one peak characteristic of framework oxygen (O_{1s} observed at 531.5 eV) against the two peaks expected from a silicalite impregnated with Fe_2O_3 (at 531.5 and 529.1 eV). EPR data show a peak at $g = 4.3$ characteristic of tetrahedrally coordinated Fe^{3+} whose intensity increases with degassing temperature. Boron substitution may be

inferred on the basis of its adsorption, catalytic and acidic properties which are different from those of HZSM-5 or silicalite. Besides, there is enough literature evidence about the feasibility of boron substitution into the tetrahedral position. In La/HZSM-5, La^{3+} may be present in any or all of the possible positions, cation exchange position, as occluded La^{3+} species or tetrahedral position. Amounts of various sorbates adsorbed on these zeolites measured for a fixed sorption period of 30 minutes differ. Measurements indicate that hydrophobicity of these zeolites varies as follows : $\text{Al} < \text{B} < \text{Fe} < \text{La/HZSM-5}$. Pore volume indicated by adsorption of n-hexane is highest for Fe/HZSM-5 and B/HZSM-5. Sorption of cyclohexane and ortho-xylene is lowest for La/HZSM-5 which shows hindered diffusion into the pores due to occluded La^{3+} species. Since para-xylene sorption is slightly different for the individual zeolites, the ratio of para-xylene to ortho-xylene adsorbed during a fixed period (30 minutes) has been used to approximately estimate the relative diffusion rates of these isomers. Adsorption of 1,2,4 TMB is highest for Fe/HZSM-5 which shows the highest diffusivity of this hydrocarbon in pores of Fe/HZSM-5.

Application of the Pauling's electrostatic model for the strength of Brönsted acid centers in these zeolites shows that the strength should follow the trend : $\text{La} > \text{Al} > \text{Fe} > \text{B/HZSM-5}$ while the observed trend in strength is $\text{Al} > \text{Fe} > \text{B} > \text{La/HZSM-5}$ (in this analysis the small high

temperature peak found in the TPD of NH_3 on La/HZSM-5 has been attributed to impurity, probably aluminium introduced as impurity into the tetrahedral framework). This means that nearly all the La^{3+} ions may be present in the occluded form. The low uptake of cyclohexane and ortho-xylene also support presence of La^{3+} in the occluded form. The low catalytic activity for aromatic reactions and high selectivity to para-xylene in such reactions to be described later also support this assumption. The number of acid sites is also found to be lowest in the case of La/HZSM-5. Thus the acidity trend may be represented as follows : $\text{Al} > \text{Fe} > \text{B} > \text{La/HZSM-5}$.

All these zeolites (Fe, B and La/HZSM-5) are good catalysts for conversion of methanol to olefins. Fe/HZSM-5 is particularly useful for converting dilute aqueous solution of methanol to olefins. Acid leached B/HZSM-5 has long life and shows high selectivity to olefins. In a double reactor system comprising of alumina in the first reactor to convert MeOH to dimethyl ether and La/HZSM-5 in the second to convert DME to olefins, the reaction of methanol gives product distribution containing 80-85% $\text{C}_2\text{-C}_4$ olefins. La/HZSM-5 is found to be superior for conversion of methanol to olefins.

Chapter IV presents and discusses results on some aromatic reactions - isomerisation of ortho-xylene, disproportionation of toluene and alkylation of toluene over Fe, B and La/HZSM-5 zeolites. In these reactions para-xylene, an industrially important chemical, is the product of interest. Of the above reactions, isomerisation and alkylation are believed to require only weak acid sites. For these and toluene disproportionation, most active catalyst is Al/HZSM-5 (82) and the least active La/HZSM-5. The influence of temperature, WHSV and coking of the catalyst on product distribution and para-xylene selectivity have been studied. It is found that the most active Al/HZSM-5 gives the lowest selectivity to para-xylene and the least active La/HZSM-5 shows the highest selectivity to para-xylene.

Influence of $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio on activity and selectivity in the above reactions has also been studied. Catalyst with highest $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio gives the highest selectivity to para-xylene in all the reactions.

An analysis of the data shows that para-selectivity is dependent primarily on the relative diffusion rates of para-xylene to that of the other isomers. Assuming this ratio to be approximately equal to the sorption ratio of para to ortho-xylene measured in a fixed sorption time, the trend in this ratio follows the trend in para-selectivity in different

reactions over different catalysts. This confirms as has been shown earlier and also more recently, that the predominant factor determining para-selectivity in all xylene-forming reactions is diffusion controlled product selectivity effect.

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