A COMPARATIVE STUDY OF MEDIUM AND LARGE PORE ZEOLITES IN ALKYLATION REACTIONS

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by

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.....to my Appachan n' Ammachi

CERTIFICATE

This is to certify that the thesis herewith is an authentic record of research work carried out by the author under my supervision, in partial fulfilment of the requirements for the degree of Doctor of philosophy of Cochin University of Science and Technology, and further that no part thereof has been presented before for any other degree.

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DECLARATION

I hereby declare that the work presented in this thesis entitled, “A comparative study of medium and large pore zeolites in alkylation reactions” is entirely original and was carried out by me independently under the supervision of Dr.S.Sugunan, Professor in Physical Chemistry, Department of Applied Chemistry, Cochin University of Science and Technology, Kochi-22, India, and has not been included in any other thesis submitted previously for the award of any degree.

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PREFACE

Zeolites have established themselves as industrial catalysts for over two decades for a variety of hydrocarbon processing reactions where acidity and shape selectivity are important factors. As solid catalysts, zeolites may be advantageous and superior compared to their homogenous counterparts due to their characteristic properties. It is only in recent years that the utility of zeolites for organic synthesis is recognized for producing specific organic intermediates and fine chemicals in high selectivity.

In this thesis an attempt has been made to compare the catalytic activity of some medium and large pore zeolites in a few alkylation and acylation reactions. The work reported in the present study is basically centered around the following zeolites namely, ZSM-5, mordenite, zeolite Y and beta. The major reactions carried out were benzoylation of o-xylene, propionylation of toluene and anisole and benzylation of o-xylene.

The programme involves the synthesis, modifications and characterization of the zeolite catalysts by various methods. The influence of various parameters such as non-framework cations, Si/Al ratio of zeolites, temperature of the reaction, catalyst concentration, molar ratio of the reactants and recycling of the catalysts were also examined upon the conversion of reactants and the formation of the desired products in the alkylation / acylation reactions.

The general conclusions drawn by us from the results obtained are summarized in the last chapter of the thesis. Zeolite beta offers interesting opportunities as a potential catalyst in alkylation reactions and the area of catalysis by medium and large pore zeolites is very fascinating and there is plenty of scope for further research in this field. Moreover, zeolite based catalysts are effective in meeting current industrial processing and more stringent environment pollution limits.

CHAPTER I

GENERAL INTRODUCTION

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1.0 INTRODUCTION

Catalysis and catalysts play a very vital role not only in various industrial processes but also in the existence and efficient functioning of all biological systems. Tremendous advances have been made during the last few decades towards understanding of fundamental process in catalysis at a microscopic level. Zeolites have been widely used as heterogeneous, shape selective catalysts for a great variety of processes in the refining and petroleum industry. The use of zeolites have now been extended to other exciting areas such as supramolecular catalysis, photochemistry, nanochemistry and electrochemistry. The applications of zeolites as industrial catalysts and the recognition of the *'shape selective'* properties of these materials has stimulated an immense amount of synthetic work aimed at preparing new microporous materials with vastly different pore sizes and void structures that are capable of catalysing new processes.

1.1 ZEOLITES

Zeolites form an extraordinary diverse and exciting class of advanced inorganic materials which are attracting increasing attention owing to their ion-exchange, molecular sieving but above all their wide ranging shape selective catalytic properties. These in turn arise from their acidity, from their ability to accommodate a wide range of metallic species and from their microporous crystal structure.

From a chemical point of view, zeolites [1, 2] are crystalline microporous aluminosilicates made up of a three dimensional network of [SiO_4] and [AlO_4] tetrahedra linked by corner sharing of oxygen ions. The negative charge on alumina tetrahedra is compensated by cations resulting in an electrically neutral framework. If H^+ ions are the charge balancing species, Bronsted acid sites are generated. The Al^{3+} ion itself has a tendency to acquire a pair of electrons to fill its vacant p orbitals resulting in the formation of a Lewis acid site. The structural formula of the crystallographic unit cell of a zeolite is expressed as,

$$\mathbf{M_{2/n}O.\ Al_2O_3.\ xSiO_2.\ yH_2O.}$$

'M' represents the exchangeable cations, generally from the group I or II ions and 'n' represents the cation valence. These cations are present either during synthesis or through post synthesis ion exchange. The value of 'x' is always equal to or greater than 2, since two Al^{3+} cannot occupy adjacent tetrahedral sites [3].

1.1.1 Structural overview

The primary building unit of zeolite structure is the individual tetrahedral TO_4 unit, where T is either Si or Al. Lowenstein has formulated that whenever two tetrahedra are linked by an oxygen bridge, the centre of only one of them can be occupied by Al; the other centre must be occupied by Si or other small ions of electrovalence four or more [4].

The secondary building unit (SBU) consists of selected geometric groupings of primary tetrahedra. There are nine such building units, which can be used to describe all of the known zeolite structures. These secondary building units consist of 4, 6 and 8-membered single rings, 4-4, 6-6 and 8-8 member double rings, and 4-1, 5-1 and 4-4-1 branched rings [3]. The topologies of these units are shown in Fig. 1.1.

There are two types of structures: one provides internal pore system comprised of interconnected cage like voids; the second provides a system of uniform channels which, in some instances, are one dimensional channel systems. Since 1950, approximately 150 synthetic zeolites [5], have been made though only about 37 natural zeolites are known. It is estimated by the crystallographers that [6] the zeolite structures known till today represents less than 10% of all possible zeolite structure types that could be theoretically formed. The structure of a zeolite usually depends on the crystallization conditions, on the gel composition and particularly, on the nature of the templating agent, which can be specific to a given structure.

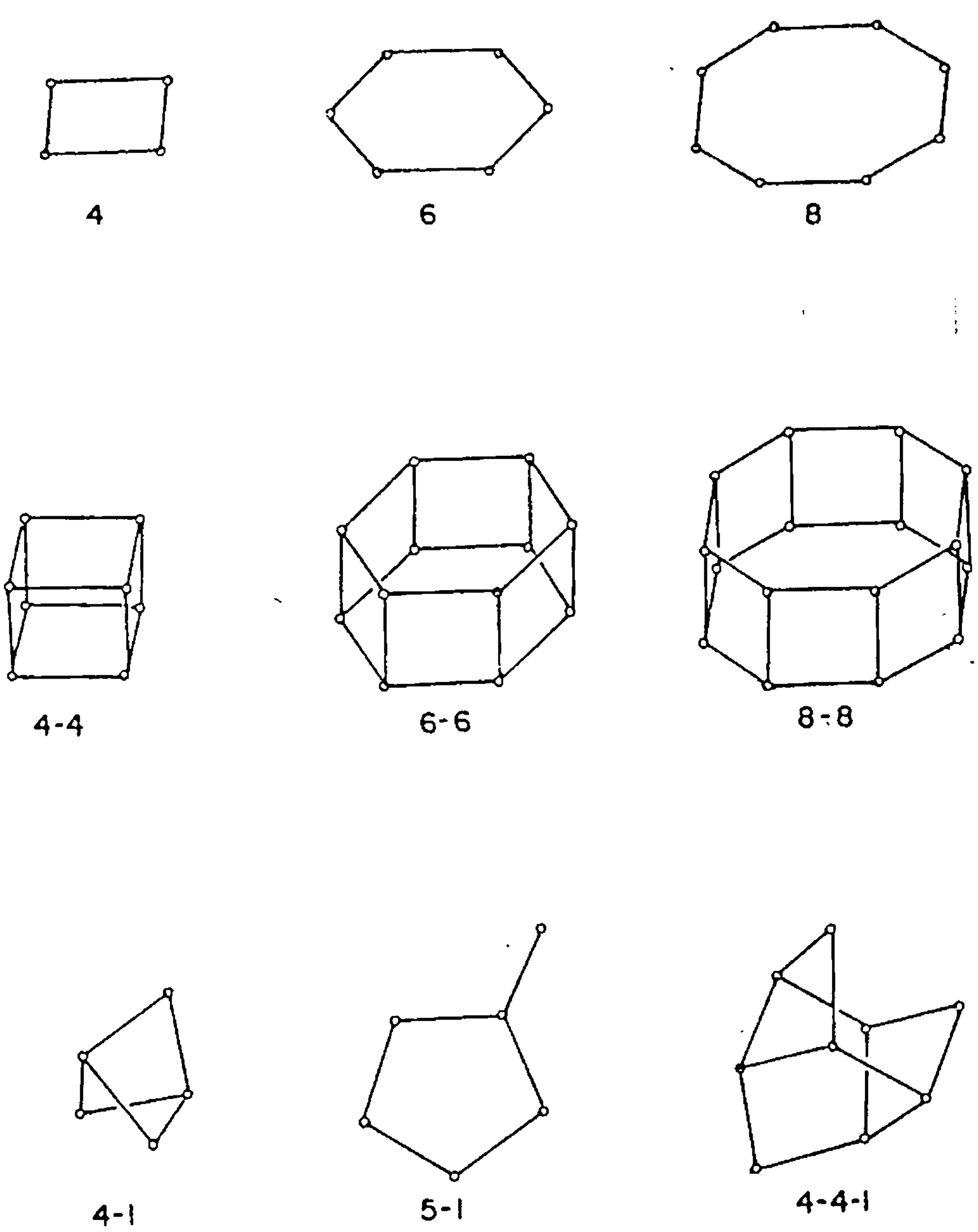


Fig. 1.1 Secondary building units (SBUs) found in zeolite structures

1.1.2 Synthesis of zeolites

Natural zeolites are formed by the reaction of mineralizing aqueous solutions with solid aluminosilicates. The formation of such zeolites with volcanic glass and saline water as reactant must have occurred in the temperature from 298K - 348 K and $[H^+] < 10^{-13}$, requiring several hundred years for crystallization [7-9].

Hydrothermal synthesis of aluminosilicate zeolites involves a few elementary steps by which a mixture of Si and Al species, metal cations, organic molecules and water is converted via. an alkaline supersaturated solution into a microporous crystalline aluminosilicate. The complex chemical processes involved in this transformation can be denoted as ***Zeolitization.*** The method developed by Milton in the late 1940's involves the hydrothermal crystallization of reactive alkali metal aluminosilicate gels at low temperatures and pressures. During the synthesis of the low silica zeolites with alkali aluminosilicates, it has been proposed that the hydrated alkali cation 'templates' or stabilizes the formation of zeolite structural subunits. The process of zeolitization is thermally activated and usually takes place at elevated temperatures inorder to achieve high yield of crystals in an acceptable period of time. On the basis of the chemical phenomena occurring during zeolite genesis, the process can be divided in to three basic steps: *achievement of supersaturation, nucleation and crystal growth.* The type of zeolite depends mainly on the nature and concentration of the bases (organic and inorganic), composition of reactants, reaction temperature, sequence of mixing the constituents and reaction time.

Table 1.1 Organic template- Zeolite structure relationship

Organic template	Structure
Tetraethylammonium (TEA)	Beta, ZSM-48, ZSM-12, ZSM-20, ZSM-25, mordenite
Tetrapropylammonium (TPA)	ZSM-5
n-propylamine	ZSM-5
Tetrabutylammonium (TBA)	ZSM-11
Choline	ZSM-38, ZSM-43, ZSM-34, CZH-5
Tetramethylammonium (TMA)	ZSM-39
Pyrrolidine	ZSM-5, ZSM-21, ZSM-29, ZSM-35, ZSM-48, ZSM-50
1,2-diaminoethane	ZSM-5, ZSM-21, ZSM-35
1,8-diaminooctane	ZSM-11, ZSM-48
Hexamethonium bromide (HMBr)	EU-1, EU-2
Neopentylamine	mordenite

In 1960's the organic quarternary cations (templates) were introduced in the zeolite synthesis [10] Table 1.1. The use of organic cations [11] is an important step in the hydrothermal synthesis of high silica zeolites, whose characteristic features are high acidity, high resistance to water and acids and high thermal stability. The manner in which such templates affect the zeolite crystallization is not straight forward. The template sensitivity has been described by many authors [12-14]. In selecting possible templates, however, one has to bear in mind some general criteria regarding templating potential in zeolitization, such as solubility in the solution, stability under synthesis conditions, steric compatibility and possible framework stabilization [15]. Computer modelling methods can play a substantial role in understanding how to stabilize particular frame work structures by specific templating agents.

Organic cation has the primary structure directing role, but secondary effects are due to the presence of inorganic cation [16]. During the crystallization, both aluminium and silicon will dissolve to form aluminate and silicate anions. These anions are brought together (by template and / or metal ion) to form a gel by condensation or polymerization. The stabilization of the zeolite product is brought about by the guest species that fills the channels and cavities of the aluminosilicate framework [17].

Zeolite crystallization is a poorly understood but reproducible phenomenon, involving a plethora of chemical reactions and complicated equilibria. Empirical procedures are well established for altering the internal pore and channel size and connectivity of zeolites, by the addition of structure directing agents to the synthesis mixture.

1.1.3 Classification of zeolites

Classification of zeolites has been made on the basis of their morphological characteristics [18], crystal structure [19-22], chemical composition [23], effective pore diameter [28, 29] and natural occurrence.

The classification based on morphology was made by Bragg [18]. According to this, zeolites are classified as fibrous, lamellar and those having framework structures. This was further modified by Meier and Barrer according to the secondary building units present in them.

Classification of zeolites according to their chemical composition has been made on the basis of their silica to alumina [23] ratio (Table 1.2). The thermal stability increases from about 700^0 C in the low silica zeolites to 1300^0 C in the high silica molecular sieves.

Table 1.2 Classification of zeolites according to chemical composition

Sl.No	Class	Si/Al ratio	Examples
1	Low silica zeolites	1-1.5	A, X
2	Intermediate silica zeolites	2-5.0	(a) Natural zeolites: erionite, chabazite, clinoptilolite, mordenite (b) Synthetic zeolites: L, Y, omega, large port mordenite
3	High silica zeolites	10- several thousands	(a) By direct synthesis: ZSM-5, ZSM-11, EU-1, EU-2, Beta (b) By thermochemical framework modification: mordenite, erionite, highly silicious variant of Y
4	Silica molecular sieves	several thousands to ∞	Silicate

Table 1.3 Classification of zeolites according to the pore openings

8-membered ring (small pore)	**10-membered ring** (medium pore)	**12-membered ring** (large pore)
Linde A	dachiardite	cancrinite
bikitaite	epistilbite	Linde X, Y, L, EMT
brewsterite	ferrierite	gmelinite
chabazite	heulandite	mazzite
TMA-E	laumonitite	mordenite
edingtonite	ZSM-5	ZSM-12
erionite	ZSM-11	omega
gismondine	EU-1	Beta
ZK-5	EU-2	
Levynite	stilbite	
merlinoite	ZSM-22	
paulingtite	ZSM-23	
natrolite	ZSM-25	
phillipsite	ZSM-39	
Rho	ZSM-57	

The zeolites are classified according to their pore openings. Small, medium and large pore zeolites contain 8, 10 and 12 membered ring pore openings, respectively. Some of the common zeolites which include both natural and synthetic zeolites are listed in Table 1.3 according to their pore opening. Zeolites with pores that are comprised of eight T-atoms and eight oxygen atoms are considered as small pore zeolites. They have free diameters of 3.0 - 4.5 Å. Medium pore zeolites have pore formed by ten T-atom rings with 4.5 - 6.0 Å free diameter. Zeolites with twelve or more T-atoms in rings that make up the pores are considered as large pore zeolites. They have free diameter of 8.0 Å or more [24].

1.2 PHYSICO-CHEMICAL CHARACTERIZATION OF ZEOLITES

Catalyst characterization is essential if reaction chemistry and catalyst performance are to be adequately understood. For characterization of zeolites and related molecular sieves, several instrumental and chemical techniques are required [22]. Some of these techniques along with the relevant information provided by them are discussed below.

1.2.1 Powder X-ray Diffraction (XRD)

Powder X-ray diffraction is the single most important technique used in the study of zeolites. It is used in (i) the identification of the crystalline phases (ii) calculation of the unit cell parameters and (iii) to find out the degree of crystallinity. A substance is assumed to be pure when the X-ray signature matches exactly in the number and relative intensities with the reported one [25, 26]. For phase identification, by X-ray diffraction generally the 2θ range in between 4^0 and 40^0 is preferred, since within this range most intense peaks characteristics of zeolite structure occur.

1.2.2 Infra-red spectroscopy

Infra-red spectroscopy is a sensitive tool complementary to XRD, as it is a sensitive analytical technique for the investigation of structural details of the zeolite framework vibrations. The lattice vibrations of the zeolites in the IR spectrum are observed in the range of 300-1300 cm^{-1}. These vibrations can be classified into two groups, (i) internal vibrations of the TO_4 units or structure insensitive vibrations and (ii) vibrations due to external linkages of the TO_4 units or structure sensitive vibrations [27, 28].

Infra-red spectroscopy can be used to confirm acidic characteristic and isomorphous substitution. Different types of hydroxyl groups are characterized by the presence of absorption bands with 366 - 3720 cm^{-1} depending upon stronger or weaker Bronsted acid sites [29, 30]. The substitution of lighter elements such as B shifts the framework vibrations to higher wave numbers [31], while the incorporation of heavier metal ions such as Fe, Ga and Ti shift to lower wave numbers [32].

1.2.3 Nuclear Magnetic Resonance Spectroscopy

NMR spectroscopy is an important tool to rationalize the knowledge of the structure of zeolites and to predict their catalytic properties. Eversince Lippamaa *et al.* [33] showed that Si MAS (Magic Angle Spinning) [34] NMR spectra are sensitive to the nature and chemical environment of the atoms, considerable knowledge has been gained during last five years about the structure of zeolites from the study of their Si and Al MAS NMR spectra [35, 36].

1.2.4 Thermal analysis

Thermo-analytical technique has been used [37, 38] to get the information on the synthesis, mechanism as well as thermal behaviour of the synthesised zeolites. The shape and temperature of the high temperature DTA exotherm is often used in characterizing the thermal stability of the zeolites [39]. Similarly, the shape and splitting of low temperature endotherm [40] helps to identify the location of the water molecules and also helps in studying kinetics of desorption of water molecules [41]. It is well known that the thermal stability of zeolitic framework structure increases with the increase in silica to alumina ratio [42] and the method of thermal / acid treatment [43] or ion-exchange.

1.2.5 Sorption and Diffusion properties

Zeolites are microporous crystalline materials with ability to sorb selected molecules inside the channels and cavities. In zeolites, usually intracrystalline surface area constitutes about 97% of total surface area. The reports [44, 45] on the sorption of gases and vapours by dehydrated zeolites started appearing since 1896. Study of the sorption characteristics of zeolites can provide information about their void volume, the size of the pore opening, the level of crystallinity, the acidity and diffusion properties and pore breakages, if any.

In heterogeneous catalysis, adsorption and diffusion properties play an important role in the rate of chemical reaction at the catalytic active site. The diffusion in zeolites may be divided into three types: configurational diffusion, Knudsen diffusion and bulk diffusion. A detailed review on diffusion in zeolites is given by Barrer [46].

1.3 MODIFICATION OF ZEOLITES

The zeolites in the as-synthesized form typically contain quarternary amine cations along with residual inorganic cations such as the alkali cations, most typically sodium. The reactivity and the selectivity of molecular sieve zeolites as catalysts are determined by active sites provided by an imbalance in charge between the silicon and aluminium ions in the framework. To produce the zeolite acid catalyst, it is necessary to replace the cations present in the freshly synthesized material with protons.

The zeolites can be modified suitably by one or more of the following ways.

1.3.1 Isomorphous substitution

Isomorphous substitution of lattice silicon and or aluminium atoms by other elements can be performed either during hydrothermal synthesis (primary synthesis) [47-60] or by post synthesis (secondary synthesis) methods [61-63]. In recent years, isomorphous substitution of Si by foreign elements [64, 65] such as B [66-68], Fe [67], Ga, Ti [69], V [70], etc. has been largely studied and has been shown to result in different catalytic properties. Isomorphous substitution modifies the strength of the Bronsted acid sites.

The substitution of other ions for Al^{+3} and Si^{+4} in the zeolite frameworks may change the zeolite properties (although they still have the same topology and channel system). The discovery of titanium substituted ZSM-5 has lead to remarkable progress in new technology for the production of chemicals which are obtained through selective oxidation reactions especially with aqueous H_2O_2 as the oxidant. Rossin *et al.* [71] showed that Co^{2+} can be incorporated into tetrahedral atom positions in the framework of ZSM-5. The studies illustrated the possibility of using framework atoms as isolated redox centers within microporous environments.

Barrer classified four types of isomorphous replacements in zeolites.

1. one guest molecule by another (i.e. substitution of NaCl by sodium sulphate transforms sodalite into Nosean.)
2. one cation by another (i.e. treatment of a zeolite with an aqueous solution of the salt containing the different cation ; it is the base of water sweetening.)

3. one element by one of its isotopes (i.e. mainly H_2, O_2 and Si)
4. one element in the tetrahedral position by another (i.e. substitution of Si or Al with sterically compatible elements.)

The first one is not important in catalytic applications. The second is useful in making bifunctional catalysts. The third one is useful in characterizing the zeolite materials. The last one is very important in substituting different elements into the zeolite framework.

The modification of zeolites by isomorphous substitution may give new properties, which may lead to interesting catalytic applications. T-elements can occupy one or more of the following positions in zeolites.

* framework sites

* inside the pores or on the external sites as metal oxide.

* exchange positions

* defect sites

1.3.2 Cation exchange

Most of the zeolites are synthesised in a cationic form in which the positively charged cations balance the negatively charged framework system. These extra-framework cations can be replaced by other cations [72]. The possibility of metal substitution into the zeolite framework has been reviewed in many articles [73-77].

The rate and degree of cation exchange depends on the following factors:

1. The type of cation being exchanged, the size and charge.
2. The nature, size and strength of any cation co-ordination complex.
3. The temperature of the ion-exchange treatment.
4. The thermal treatment of the zeolite, before or after exchange.
5. The structural properties of the zeolite and its silica / alumina ratio.
6. The locations of the cations in the zeolite structure.
7. The concentration of the cation exchange solution.
8. The previous treatment of the zeolite.

The unique structure and the ability of zeolites to be ion-exchanged with metal ions show promise for the development of inorganic mimics of various enzymes. Herron [78] prepared a mimic of cyochrome-P-450 by exchanging Pd^{II} and Fe^{II} ions into different zeolite structures.

1.3.3 Metal loading

For many industrial reactions, e.g. those involving hydrogenation or oxidation, it is necessary to have additional components in the catalyst to perform the total or partial catalytic function. Such components are frequently metals, their oxides, or sulphides similar to those used in nonzeolite or amorphous catalyst systems.

Metals which are desirable for the introduction into the zeolite and / or catalysts include the common hydrogenation and oxidation components such as Ni, Co, Pt, Ag, Pd, Mo, W, Cr and the like. The metal loading can be done by several ways. These include ion-exchange of the zeolite from solution, adsorption from the gas phase and co-mulling during the catalyst formation of the solid metal component or its solution.

1.4 NATURE OF ACTIVE SITES

1.4.1 Acidity

The activity of zeolites in acid catalyzed reactions originates from the tetrahedral framework aluminium atoms. There are two types of acid catalytic activity associated with zeolites namely, Bronsted acidity (H^+) and Lewis acidity. These acid centres are created by the imbalance in the charge between silicon and aluminium ions in the framework of zeolites. Each aluminium atom of the framework induces a potentially active acid site. Silicates do not have acidity. Bronsted acid site in catalyst arises when cations (often Na, K or Cs) are replaced by proton (H^+, from ammonium ion exchange, followed by the thermal decomposition of the ammonium form to H^+ form of the zeolites). The strength of these acid sites is found to vary with (i) zeolite structure (ii) Si/Al ratio and (iii) isomorphously substituted metal ions in the zeolite framework [79-81]. Bronsted acidity is normally associated with trivalent metal ions (e.g. Al^{3+}, B^{3+} or Ga^{3+}). However, when Al is replaced by a tetravalent ion (like Ti^{4+}, Sn^{4+} etc.), the resultant molecular sieves do not show strong acidity [82].

Lewis acid sites arise at the defect sites where triagonal Al is present either in the framework or at charge compensating ions [80]. The Lewis acidity can also be formed by high temperature ($>500^0$ C) dehydroxylation of the Si (OH) Al (i.e. Bronsted) sites. Several methods have been developed to determine the number and strength of both types of acid sites [83-85] :

(a) IR spectroscopy of -OH groups.

(b) Desorption of bases: Temperature Programmed Desorption (TPD)

(c) ^{1}H MAS NMR of -OH group and ^{13}C,^{15}N or ^{31}P NMR respective probes

(d) IR spectroscopy of adsorbed bases

(e) UV-visible spectroscopy

(f) ESR spectroscopy

(g) Titration methods and

(i) Catalytic probe reactions (test reactions)

1.4.2 Basicity

The basic properties of zeolites in catalysis and adsorption also have been reported [86-89]. Like acid sites, basic sites may be of Bronsted (basic -OH groups) or Lewis (framework oxygen atoms) type. The number of potential basic sites are proportional to the number of oxygen atoms in the framework. Barthomeuf *et al.*[90], have extensively studied the basicity of zeolites. They have shown that the actual basic strength of a zeolite depends not only on the chemical composition but also on the structural environment of the framework oxygen. Bronsted basic sites in zeolites are not well known. But alkali and alkaline earth metal ion- exchanged zeolites show Lewis basicity [91].

1.5 CATALYSIS BY ZEOLITES

Zeolites have advantages over conventional heterogeneous catalysts in many applications, involving acid, acid-base, base, oxidation, reduction and polyfunctional catalysis. The important properties that make them attractive as heterogeneous catalysts are [92]:

* well defined crystalline structure
* high internal surface areas (> 600 m^2/g)
* uniform pores with one or more discrete sizes
* good thermal stability
* ability to sorb and concentrate hydrocarbons
* highly acidic sites when ion -exchanged with protons
* ease of regeneration to initial activity
* non- corrosive nature
* easy preparation of bi- functional catalysts

Catalytic properties of zeolites are very much depending on both their chemical and physical features. The former aspect corresponds to acidic, metallic, basic or redox type reactions. Since it involves active sites whose nature, chemical strength, density and distribution in strength have to be determined. The physical aspect is known to greatly influence shape selectivity, confinement and diffusion properties [93, 94].

1.5.1 Shape selectivity in zeolites

Shape selectivity is a unique property of zeolites and related molecular sieves. The intracrystalline surface area of zeolites is an inherent part of the crystal structure and hence they are topologically well defined. As a consequence, zeolites are able to restrict or prevent the passage of organic molecules based on size and steric effects. The effect is commonly referred to as **shape selectivity**. The basic concept of shape selectivity has been discussed in detail by many authors [95-97]. The shape selective properties of zeolite catalysts are due to the confinement of acid sites within the zeolite pore architecture. The actual pore size within a given ring structure can be varied within limits by the cation present in the system. Based on the geometric constraints, four types of shape selectivities are attributed to zeolites [98].

1.5.1.1 Reactant shape selectivity

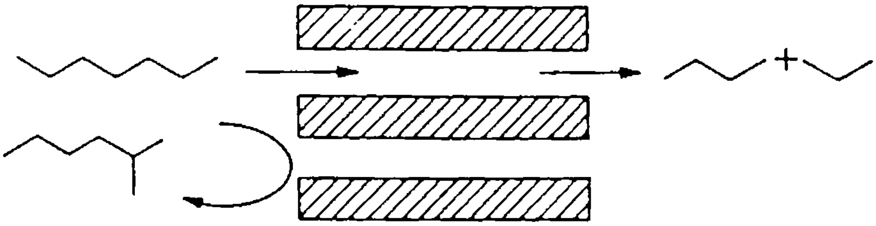
When in a mixture of two or more organic molecules with different size and shape come in contact with zeolite, smaller molecules are allowed to diffuse in the channels while the other larger molecules are hindered (or sieved out), this phenomenon is called reactant shape selectivity (Fig. 1.2). Chen *et al.* [95] have explained reactant shape selectivity on the basis of coulombic interaction between the reactant and the zeolite. An important application of reactant shape selectivity is in the cracking of linear alkanes by protecting the branched chain ones particularly in petrochemical industry.

1.5.1.2 Product shape selectivity

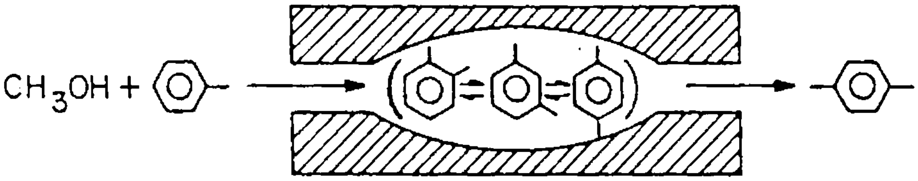
Product shape selectivity occurs when one or more of the products formed within the pores or cavities of the zeolite diffuse out faster than the other products, leaving behind the bulkier molecules which are either converted into less bulky molecules that can diffuse out easily or subsequently deactivate the catalyst. For e.g. p-xylene is produced preferentially in modified zeolites over the more bulky o- and m-isomers due to the pore diameter restrictions (Fig. 1.2). Direct evidence for this type of shape selectivity has been reported by Anderson and Klinowski [99] for the catalytic conversion of methanol to hydrocarbons in ZSM-5.

1.5.1.3 Restricted transition state shape selectivity

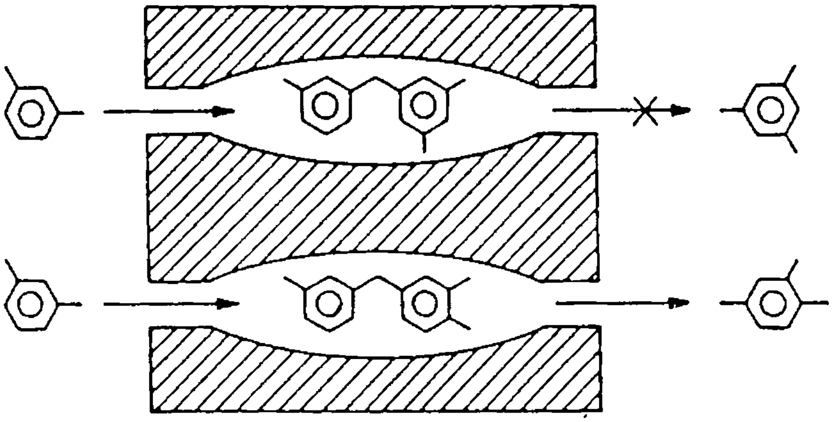
Restricted transition state shape selectivity (Fig. 1.2) occurs when shape selective restrictions act on the intrinsic kinetics rather than via. diffusion limitations. This mainly depends upon the size and shape of the transition state complex formed during catalytic transformations inside the cavities of the zeolite. The products which result from less bulky transition states are preferentially



a) REACTANT SELECTIVITY



b) PRODUCT SELECTIVITY



c) RESTRICTED TRANSITION STATE SELECTIVITY

Fig. 1.2 Shape selectivity in zeolites

formed. This type of shape selectivity was first proposed by Csissery in order to explain the absence of symmetrical trialkylbenzenes in the product from the dispropotionation of dialkylbenzenes over mordenite. It has been found that the restricted transition state selectivity does not always guide the reaction path in zeolites, but electronic as well as thermodynamic effects predominate over steric effects [100]. Direct observation of transition state shape selectivity has been observed from the low temperature cyclization of dienes inside H- mordenite and H-ZSM-5 [101].

1.5.1.4 Molecular traffic control

This type of shape selectivity has been proposed by Derouane and Gabelica [102]. According to this concept, in the case of zeolites with more than one type of intersecting channels, the reactant molecules preferentially enter through one type of channel, while the products diffuse out through the other one, minimizing counter diffusion. However the existence of the molecular traffic control is not yet supported by experimental finding.

Recently the role of chemical nature in directing the selectivities in zeolites has been interpreted by Corma on the basis of Pearson's concept of hard and soft acids and bases and the perturbation theory [103].

1.5.2 Zeolite catalysts in petrochemical processes

Many of the zeolite based catalysts are used today in the petroleum and petrochemical industries. A number of shape selective zeolite based processes are commercially available to improve the octane quality of the reformate and gasoline streams. These are developed and commercialized by Mobil Oil Co. and by British Petroleum Co. Some of such important processes are the following: (i) selectoforming (ii) M-forming (iii) M-2 forming (iv) cyclar process and (v) Aromaxs M [104-105].

1.5.3 Zeolite catalysts for synthesis of Organic compounds

Heterogeneous catalysis is gaining importance in the synthesis of chemical intermediates and fine chemicals. In the shift away from homogeneous catalysis, zeolites play a major role. The zeolite based catalysts are effective in meeting current industrial processing and more stringent environment pollution limits. Zeolites as solid catalysts may be advantageous and superior compared to their homogenous counterparts due to their characteristic properties. Zeolites and zeolite-like molecular sieves are able to recognize, descriminate and organize molecules with precisions that can be less than 1Å [105b]. The experience gained thereby with zeolitic catalysts in the petrochemical industry has in recent years, been increasingly applied to the selective synthesis of organic compounds.

At the beginning of the 1970's, P.B.Venuto and P.S.Landis indicated how zeolites - at that time principally X- and Y- zeolites and mordenite - could be used for the synthesis of organic compounds [106-108]. The discovery of ZSM-5 [109], the first member of pentasil zeolite family and its employment as a highly acidic, exceptionally shape selective and thermally stable catalyst in new technical petrochemical processes have continued to influence and stimulate zeolite chemistry right up to the present day. An increasing number of studies on the synthesis of organic fine chemicals [110-113] were also evident.

The many reasons for the speed with which this field has expanded include the easily reproducible preparation of well defined catalyst surfaces as well as the remarkable progress made in the synthesis not only of new zeolitic and non-zeolitic molecular sieves but also of isomorphously substituted materials [114, 115]. Further contributory factors are the high catalytic activity and the possibility of varying and adjusting the properties of zeolite catalysts to encompass the broad spectrum ranging from strongly acid via neutral to strongly basic. The application of zeolites in organic reactions has been comprehensively reviewed by many authors [116-122].

1.6 MEDIUM AND LARGE PORE ZEOLITES

The crystal structure of a zeolite is defined by the specific order in which a network of tetrahedral units are linked together. The size of the zeolite pore openings is determined by (1) the number of tetrahedral units, or alternatively oxygen atoms required to form the pore and, (2) the nature of the cations that are present in or at the mouth of the pore. Because the pores of the zeolites are similar in size to many organic molecules of practical interest, it became possible to design novel catalysts on a molecular level by controlling the ingress and egress of reactants and products.

Recent efforts in the synthesis of new molecular sieves and their modification have resulted in a very large number of molecular sieve materials with vastly different pore sizes and void structures. There are many reasons for desiring uniformly sized, large pore molecular sieves. The most obvious reason is to perform shape-selective catalysis on reactants too large to enter the pores of small and medium pore zeolites. Beginning with the original discovery of selective conversion of straight chain molecules using small pore zeolites, the realm of the industrial application of shape selective catalysts has been extended by the discovery of ZSM-5 and other medium pore zeolites [123]. Thus medium pore zeolites can selectively convert both linear and selected branched molecules and single ring aromatics, naphthenes and non hydrocarbons with critical molecular dimensions less than about 6Å [124]. In the last two decades, the medium pore zeolites have been extensively used as shape selective catalysts in the petroleum and petrochemical industry. Large pore zeolites are widely used in the transformation of large organic substrates in the synthesis of organic fine chemicals. It is clear that, the trend towards the catalytic application of large pore zeolites is occuring and will continue to occur in the future.

ZSM-5 is a medium pore zeolite and belongs to the pentasil family and zeolite beta, zeolite-Y and mordenite are examples of large pore zeolites with 12-membered ring openings. A comparison of the above four zeolites has been made (see below) on the basis of SBU, framework density, symmetry of point group, unit cell volume and channel characteristics.

1.6.1 Zeolite beta

Zeolite beta is a high silica, large pore crystalline material first synthesized by Wadlinger, Kerr and Rosinski [125]. It possess a 12-MR ring pore system. The silica to alumina ratio of the as-synthesized zeolite beta is in the range of 10-200. Zeolite beta belongs to a family of zeolites, the two end members of which have tetragonal (polymorph A) and monoclinic (polymorph B) [126, 127] (Fig. 1.3). Both isomorphs results from the same centrosymmetrical tertiary building units arranged in layers. The dimensions of the pores are 7.5 x 5.7 Å along the linear channels and 6.5 x 5.6 Å along the tortuous channels [128] (Fig. 1.4). It has a total pore volume around 0.2ml / g.

Chemical composition	$Na_n\,[\,Al_n\,Si_{64-n}\,O_{128}]$ with n< 7
Symmetry	Tetragonal
Frame work density	15.0 T/1000 A^3
Unit cell constants	a = 12.7 Å
	b = 12.469 Å
	c = 26.4 Å
Pore structure	12- member rings; intersecting 6.5 x 5.6 and 7.5 x 5.7 Å

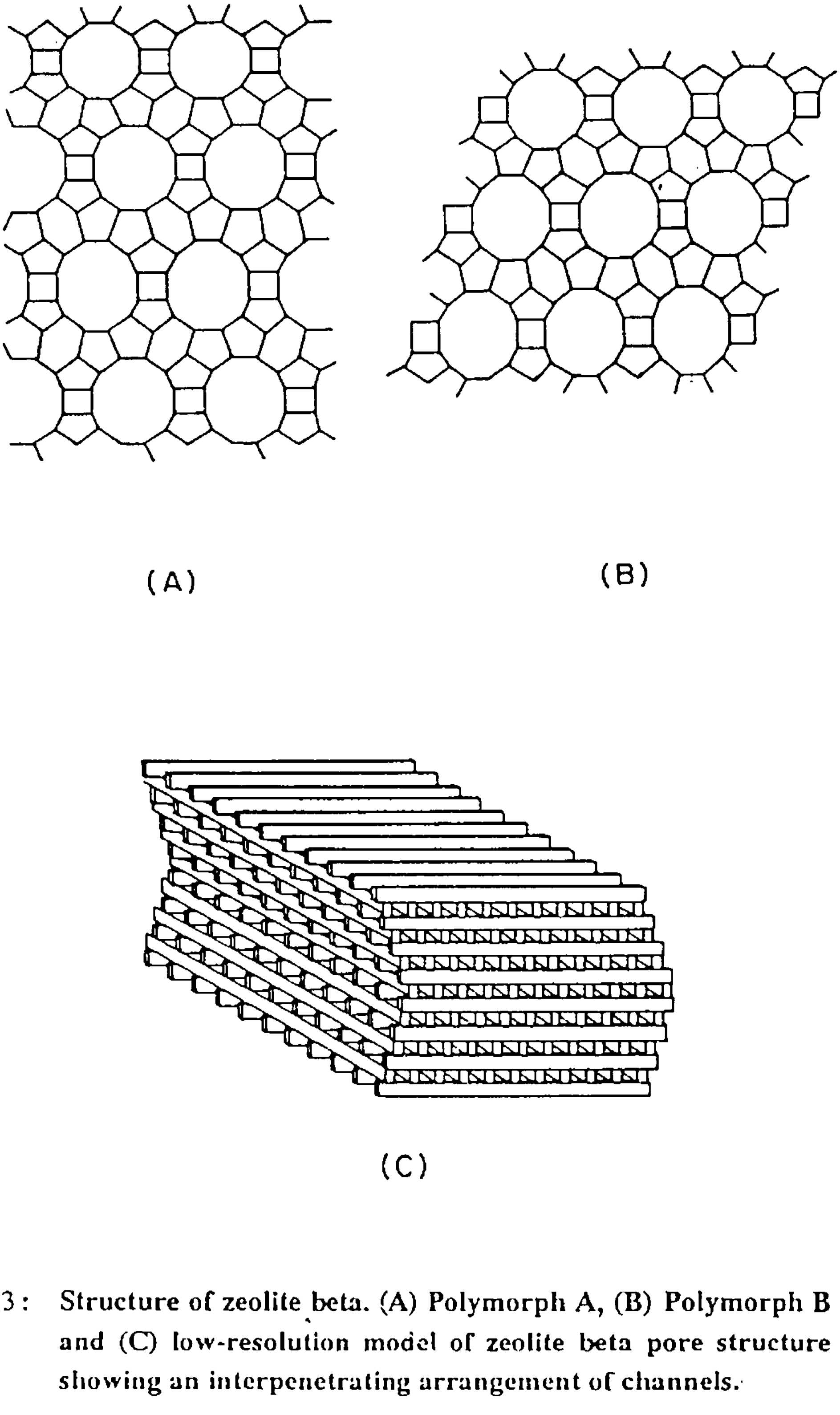


Fig.1.3 : Structure of zeolite beta. (A) Polymorph A, (B) Polymorph B and (C) low-resolution model of zeolite beta pore structure showing an interpenetrating arrangement of channels.

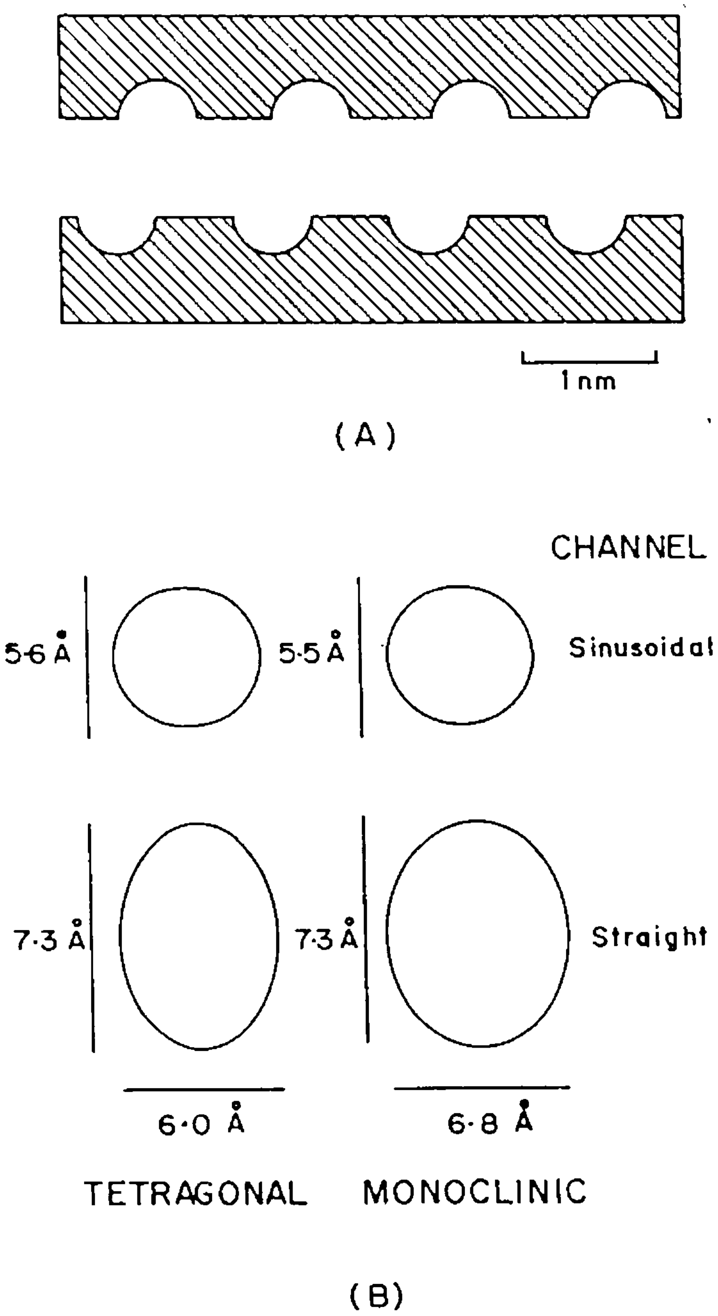


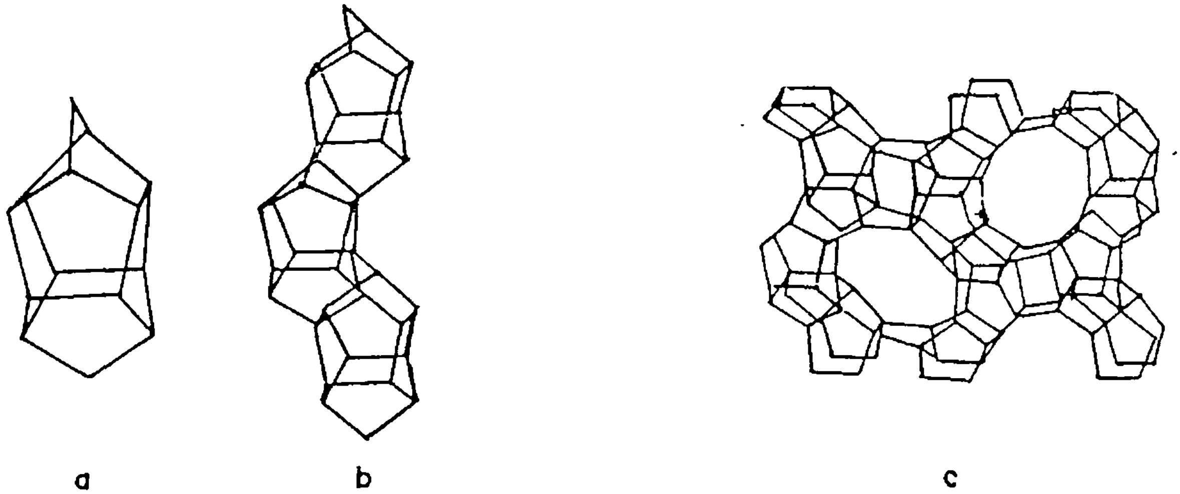
Fig. 1.4 (A) cross section of the linear channel of zeolite beta (B) pore openings of zeolite beta.

Zeolite beta have several unique and interesting features. It is the only high silica zeolite to have fully three dimensional 12-membered ring pore system and also the only large pore zeolite to posses chiral pore intersections. It has high catalytic potential compared to the faujasite type zeolite by virtue of its high silica content, acid site distribution and stacking faults [129]. In addition, the comparatively smaller dimension of one of the two types of pores (5.5 Å) offers a certain level of the shape selectivity similar to that observed in medium pore zeolites.

The above characteristics made zeolite beta a potential candidate for a variety of hydrocarbon conversion reactions. Cracking of paraffins and methylation of toluene reactions over zeolite beta are reported [130, 131]. Das *et al.* [132] studied the alkylation activity of zeolite beta for cumene isopropylation and reported that zeolite beta is potential candidate for commercial processes like cumene synthesis and transalkylation and dispropotionation of C_7 and C_9 aromatic streams.

1.6.2 ZSM-5

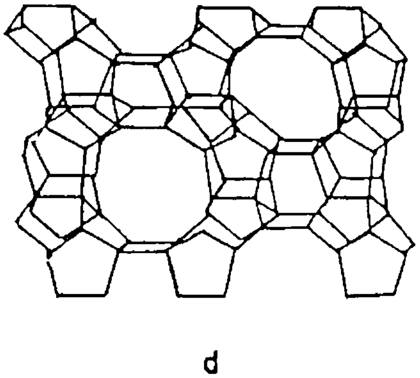
ZSM-5 is a member of the pentasil family and its structure has been determined by Kokotailo *et al.* [133]. It consists of a novel configuration of linked tetrahedra which are bound together in groups consisting of 8 five - membered rings (Fig. 1.5). These units link together to form chains and the interconnection of these chains leads to the formation of the channel system in the structure. The combination of these building units results in a framework containing two intersecting channel systems, one sinusoidal and the other straight. Sinusoidal

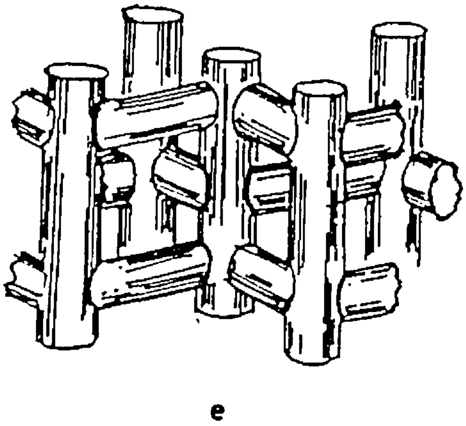


a) CHARACTERISTIC CONFIGURATION OF ZSM-5
b) LINKAGE OF ZSM-5

c) SKELETAL DIAGRAM OF 010 FACE

d) SKELETAL DIAGRAM OF 100 FACE





e) CHANNEL STRUCTURE OF ZSM-5 ZEOLITE

Fig. 1.5 Structure of zeolite ZSM-5

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 [134].

Chemical composition	Na_n [Al_n Si_{96-n}. O_{196}] ~ 16 H_2O
Symmetry	Orthorhombic
Frame work density	17.9 T/ 1000 A^3
Unit cell constants	a = 20.1 Å
	b = 19.9 Å
	c = 13.4 Å
Unit cell volume	5345.6 A^3
Pore structure	[010] **10** MR ; 5.3 x 5.6Å, [100] 5.1 x 5.5, Å(two channels are interconnecting and three dimensional)

It has been seen that the pore structure of ZSM-5 zeolite has pore dimensions intermediate between those of the so called 'large' and 'small' pore zeolites. This is an important feature of ZSM-5 structure having a bearing on its shape selective catalytic properties. When converted into the H^+ cationic form, ZSM-5 can function as a solid catalyst and a shape selective matrix in hydrocarbon transformation reactions [135]. The realization of the superior shape selective properties of ZSM-5 lead to the development of industrially important processes. One such process is the alkylation of aromatics, in particular benzene alkylation using dilute ethanol [136].

1.6.3 Mordenite

Zeolite mordenite is considered to be the most siliceous, unidimensional, large pore molecular sieve with a nearly constant silica to alumina ratio of 10. The structure, (Fig. 1.6) consists of chains that are cross linked by the sharing of neighbouring oxygens. The SBU of this structure consists of four and five membered rings. Recently, zeolite mordenite has gained much attention because of its unique catalytic properties.

Chemical composition	$Na_8 [Al_8 Si_{40} O_{96}] 24 H_2O$
Symmetry	Orthorhombic
Frame work density	17.2 T / 1000 Å^3
Unit cell constants	a = 18.1 Å
	b = 20.5 Å
	c = 7.5 Å
Pore structure	[001] **12** 6.5 x 7.0 ; [010] **8** 2.6 x 5.7
	(one dimensional)

1.6.4 Zeolite-Y

Zeolite Y consists of linked truncated octahedra called 'sodalite units', which have a cage of diameter 6.5 Å (β cage) and accessible through six membered rings of oxygen atoms [137]. These units are connected along two six membered rings, giving rise to hexagonal prism. The polyhedra formed in this way encloses a supercage (α-cage) with an internal diameter of 12.5 Å and accessible through four 12-membered rings of oxygen atoms with a free aperture of 7.4 Å. The frame work structure of zeolite-Y is depicted in (Fig. 1.7). An analogue of zeolite-Y, sometimes called hexagonal Y, has also been synthesized [138].

Chemical composition	$(Na_2, Ca, Mg)_{29} [Al_{58} Si_{134} O_{384}]. 240 H_2O$
Frame work density	12.7 T / 1000 Å^3
Unit cell constants	a = 24.7 Å
Pore structure	[111] **12** 7.4 ; three dimensional

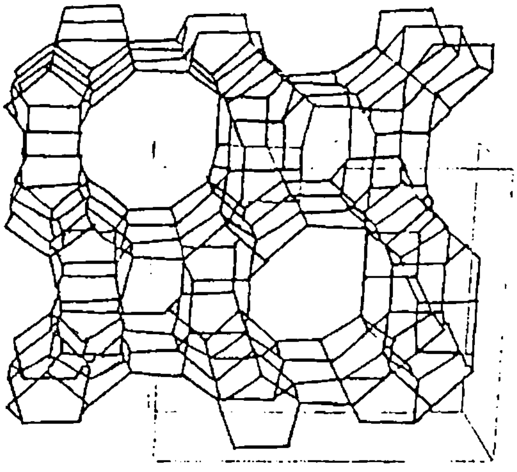


Fig. 1.6 Structure of mordenite

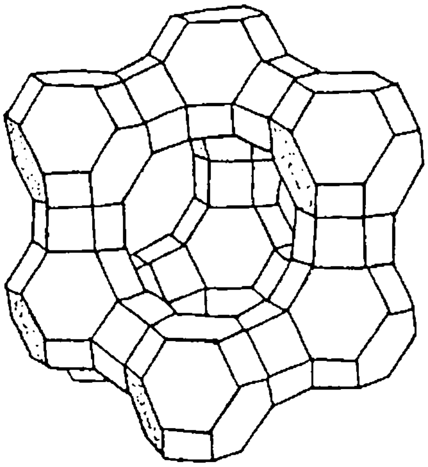


Fig. 1.7 Structure of zeolite Y

1.7 ALKYLATION AND ACYLATION REACTIONS OF AROMATIC HYDROCARBONS

Alkylation and acylation reactions similar in character to the Friedel-Crafts synthesis were reported in the chemical literature prior to the first publication on the subject by Charles Friedel and James Mason Crafts [139] on the amylation of benzene using anhydrous aluminium chloride catalyst, in 1877. The ever increasing number of investigators following the work of Friedel and Crafts found a large number of other Lewis acid type halides [140] like $SbCl_5$, $FeCl_3$, $TiCl_2$, $SnCl_4$, $TiCl_4$, $TeCl_4$ and $ZnCl_2$ to be active catalysts for the reactions. In further development of the work, proton acids such as sulphuric, hydrofluoric, phosphoric acids etc. were found to catalyse similar reactions.

The use of these homogeneous catalysts may give rise side reactions such as intra or intermolecular migration of alkyl groups, removal of alkyl groups preceding or accompanying acylation. Later, acidic oxide catalysts of silica alumina type and cation exchange resins are becoming increasingly useful as catalysts.

Microporous materials, notably zeolites, are presently widely applied as suitable catalysts in fine organic synthesis and particularly in the alkylation and acylation reactions. Because of their high and tailorable acidity and their specific pore structures with channels and cavities of molecular dimensions which allow shape-selective conversions of organic molecules, zeolites occupy a prominent place as catalysts in the above reactions.

The choice of a catalyst for a particular alkylation depends upon the activities of both the substrate to be alkylated, the alkylating agent, solvent, reaction temperature and several other conditions. Although the alkylating agent involved in the Friedel-Crafts reaction was an alkyl halide, many other alkylating agents such as olefines, alcohols, esters, ethers, sulphides and thiocyanates are widely used [141, 142]. But owing to their availability and low cost, alkyl chlorides and bromides are most frequently used as alkylating agents.

It is possible to carryout not only alkylations, but also Friedel-Crafts acylations on zeolitic catalysts. Aromatics such as toluene [143, 144], phenol [145-147] and also heteroaromatics [148] can be acylated using carboxylic acids, acid anhydrides or acid chlorides.

The work by Katayama *et al.* [149] illustrates the use of H-mordenite as a shape selective catalyst for the liquid phase alkylation of naphthalene with propene to produce 2,6-dialkyl naphthalene (2,6-DIPN) which also is a monomeric starting material for the preparation of polymers. The activities and selectivities for this alkylation of various zeolites were tested, and the activities of the zeolites decrease in the order HY > HL > H-mordenite > H-ZSM-5.

H.Yashima *et al.* [150] have studied the alkylation of toluene by methanol to xylenes over La, Ce, Co, Ni and Sr exchanged zeolite Y. In this case, the amount of para- isomers in reaction products is higher than the predicted one. This is attributed to the sieve effect and peculiarities of adsorption interactions between reagent and catalyst.

Man-Hoe Kim *et al.* [151] studied the alkylation of meta-diisopropyl benzene with propylene over the acid form of molecular sieves is suggested as a new test reaction to characterize the effective pore size of larger (12T- atom rings or above) molecular sieves. In the alkylation of benzene and toluene with a bifunctional alkylating agent (cinnamyl alcohol) over a series of HY- type catalysts, Armengol *et al.* [152] found high regioselectivity with respect to the allylic system in the primary alkylation.

In a study of m-xylene acylation with benzoyl chloride over a series of modified Y catalysts with different degrees of dealumination, Fang *et al.* [153] found that the most highly active catalyst was a crystalline, deep bed-calcined, highly dealuminated Y that had considerable mesoporosity.

A novel and convenient procedure for the catalytic acylation of a series of aromatic compounds such as benzene, toluene and xylenes to the corresponding ketones using medium and large pore zeolites as catalyst and acetyl chloride as acetylating agent is demonstrated by Singh *et al.* [154].

Recent studies have shown that H-beta is also a promising catalyst for the acylation of aromatic hydrocarbons [154-156], it produces selectively β-benzoyl-naphthalene during the benzoylation of naphthalene.

For the side chain alkylation, the co-operative action of both acidic and basic sites are needed. Kumari *et al.* [157] studied the side chain alkylation of toluene over alkali exchanged beta, Y and ZSM-5 zeolites and found that the activity of zeolite beta is comparable with that of zeolite Y, which is higher than the activity of ZSM-5.

In a study of medium and large pore zeolites as catalysts for alkylation of substituted furans with 3-substituted allylic alcohols, Algarra *et al.* [158] found regioselective attack at the 5-position of the furan ring. In this reaction H-ZSM-5 showed the highest turn over number, although H-mordenite, H-beta and H-Y were also effective.

Y-faujasite type zeolite exchanged with Ce^{3+} cation have shown remarkable reactivity in the acylation of aromatic hydrocarbons such as toluene, especially when used in conjugation with straight chain carboxylic acids (C_{12} - C_{20}) as acylating agents [159].

In a study of toluene alkylation with isopropanol over Y, mordenite, and MFI-type zeolites, Cejka *et al.* [160] concluded that the desorption / transport of bulky propyltoluene products was the reaction rate-controlling step. Also, changes in kinetics and selectivities with coke build up with time on stream have been observed in toluene alkylation with methanol over Mg-ZSM-5 [161].

Very interesting Friedel-Crafts acylation reactions using zeolites can also be found in the work of Bayer's team [162] as well as Prins [163]. In both cases, work was realized on activated aromatics such as anisole. In the latter, zeolite H-beta was found to exhibit particularly high activity and selectivity independently of the Si-to-Al ratio of the zeolite.

The Friedel-Crafts benzoylation (using benzoyl chloride- aluminium chloride) of the isomeric dichlorobenzenes has been studied by Goodman *et al.* [164]. Recently, Lee *et al.* utilised a novel de-aluminated H-mordenite catalyst (DHM) for the liquid phase alkylation of biphenyl with propene to produce 4,4'-diisopropyl biphenyl (DIPBP) in high yields. This reaction illustrates the potential of zeolite to perform alkylation of polynuclear aromatic hydrocarbons, which are important intermediates in the preparation of monomers for thermotropic liquid crystal polymers.

1.8 OBJECTIVES OF THE THESIS

The chemical industry is facing increasing pressure to reduce its impact on environment. This is particularly true in the area of electrophilic aromatic substitution reactions (acylation and alkylation), which are the mainstay of much of the aromatic chemistry practiced in industry. Such reactions often require large quantities of mineral or Lewis acid catalysts that are destroyed or diluted during aqueous work-up procedures, leading to problems with equipment corrosion and to effluent streams that are difficult and expensive to treat. Furthermore, the reactions frequently use excess of reagents and are notoriously unselective resulting in the need for costly separation processes and wastage of valuable resources. The overall result is excessive energy consumption, wastage of large quantities of materials and extensive impact on the environment.

The problems created by the homogeneous non shape-selective Lewis acid catalysts could be easily overcome using zeolite catalysts. Zeolites due to their shape-selectivity, thermostability, ease of separation from the products and the regeneration of the deactivated catalysts, have been widely used in the field of petrochemistry. However, the use of zeolite catalysts in fine organic synthesis and particularly in the acylation and alkylation reactions of aromatics is limited.

The propionylation of toluene and anisole and benzoylation and benzylation of *o*-xylene have considerable significance from the point of industrial use. Aromatic ketones such as 4-methylpropiophenone, 4-methoxypropiophenone, 2-methoxypropiophenone, 3,4-dimethylbenzophenone and 3,4-dimethyldiphenylmethane (synthesized during the present study) are used for the production of pharmaceutical, perfumery, pesticide, paints and dyes. The large volume of application of these materials has prompted us to develop highly efficient shape-selective zeolite catalysts for making these compounds.

In the present work, the synthesis, modification and characterization of some medium and large pore zeolite catalysts (synthesized or commercially available) are reported. The catalytic activity of these zeolite catalysts in the selective propionylation, benzoylation and benzylation reactions of aromatics is investigated.

The following objectives are to be achieved from the present work:

(1) The primary objective of the thesis is to compare the surface properties and catalytic activity of some medium and large pore zeolites (i.e. ZSM-5, H-mordenite, H-Y and H-beta) and their modified forms in some alkylation and acylation reactions.

(2) Another main objective of this work is to replace the presently used hazardous conventional homogeneous catalysts such as $AlCl_3$, $FeCl_3$ and H_2SO_4 etc. by non-polluting, environmentally clean, heterogeneous shape selective solid zeolite catalysts in some alkylation and acylation reactions.

(3) The next objective is to define a selective solid catalyst for the production of the following industrially useful chemicals, i.e. 4-methyl propiophenone, 4-methoxy propiophenone, 3,4-dimethyl benzophenone, and 3,4-dimethyl diphenylmethane.

(4) One of the main goal is to improve the selectivity for the desired product in the benzylation, benzoylation and propionylation reactions by the use of zeolites, which are solid aluminosilicates well known for their shape selective and acidic properties and to

investigate the effect of pore structure of different zeolites on the selectivity in the above reactions.

(5) One more objective regarding the development of solid zeolite catalysts for the propionylation, benzoylation and benzylation reactions is to study the influence of the following variables in the conversion of aromatics and selectivity for the para- and desired products in the alkylation and acylation reactions:

(I) The type of zeolite used

(II) The influence of non-framework cations

(III) The influence of SiO_2/ Al_2O_3 ratio of zeolites

(IV) The temperature of the reaction

(V) Catalyst concentration

(VI) Molar ratio of the reactants

(VII) Alkylating or acylating agents

(VIII) Recycling of the catalyst

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CHAPTER II

EXPERIMENTAL - SYNTHESIS AND CHARACTERIZATION OF VARIOUS ZEOLITES

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2.1 MATERIALS

The materials used in the synthesis of zeolites are summarized in Table 2.1. The purity of these materials is also mentioned in the same table.

2.2 PROCEDURES

2.2.1 Synthesis of zeolites

Hydrothermal synthesis of zeolites were carried out under autogeneous pressure in stainless- steel PTFE- lined autoclaves (Fig. 2.1). Before use, the autoclaves were thoroughly cleaned with 35% HF to minimize the seeding effect of residual crystalline products.

2.2.1.1 Zeolite beta

In a typical synthesis [1], 0.5g NaOH, 0.3g KOH and 18.4g tetraethylammonium hydroxide were taken in a 250 ml polypropylene beaker to which 6.0 g fumed silica and 10 ml deionized water were gradually added and the gel was stirred for one hour. 2.1 g aluminium sulphate in 15 ml deionized water

Table: 2.1 Specification of the materials used in the synthesis

Reagent and source	**Chemical formula**	**Purity (%)**
Aluminium sulphate (s.d. fine chemicals; India)	$Al_2(SO_4)_3.16H_2O$	98
Fumed silica (Sigma chemical Co. USA)	SiO_2	99.8
Potassium hydroxide (s.d. fine chemicals; India)	KOH	98
Sodium hydroxide (Loba chemicals; India)	$NaOH$	98
Sodium silicate (Loba chemicals; India)	Na_2SiO_3	28.9
Tetraethylammonium hydroxide (Aldrich chemical company, Inc., USA.)	$(C_2H_5)_4NOH$	40 (aqueous)
Tetrapropylammonium bromide	$(CH_3CH_2CH_2)_4NBr$	98
Sulphuric acid	H_2SO_4	98

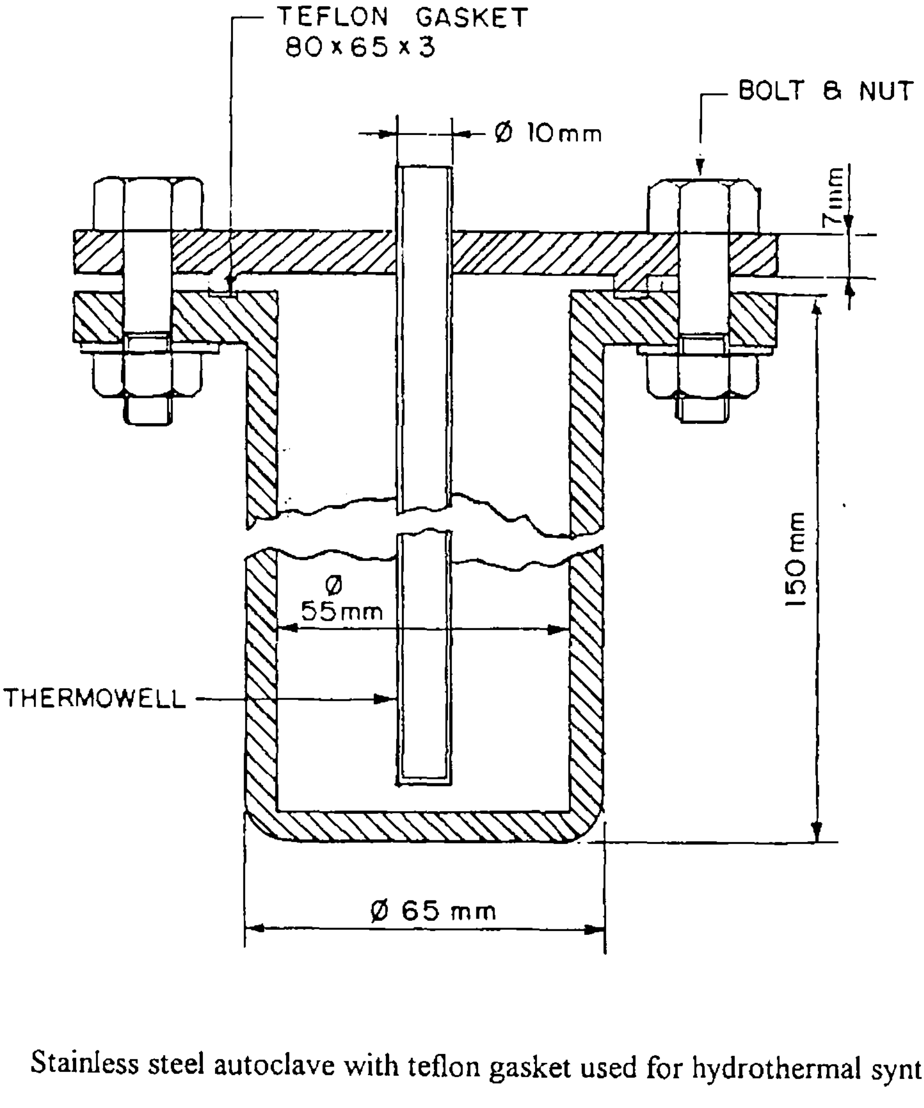


Fig. 2.1 Stainless steel autoclave with teflon gasket used for hydrothermal synthesis

was added to the gel over a period of half an hour after which stirring was continued for one more hour. 11 ml of deionized water was then added to the resulting gel. The final gel with pH 12.5 was transferred to a stainless steel autoclave and allowed to crystallize at 413 K for 168 h. On the termination of the reaction, the autoclaves were quenched under the cold water to stop the crystallization process. The solid materials thus obtained were filtered, washed with deionized water and dried at 373 K for 2 h.

2.2.1.2 ZSM-5

The synthesis of high silica ZSM-5 type zeolite was carried out according to the reported procedure [2]. In a typical preparation, appropriate amounts of aluminium sulphate and sulphuric acid were dissolved in distilled water to yield solution A. A calculated quantity of tetrapropylammonium bromide (TPABr) 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 autoclave with continuous stirring to form a free flowing gel which had the molar composition:

$$4.38\ (TPA)_2O,\ 27.6\ Na_2O,\ Al_2O_3,\ 44.3\ SiO_2,\ 32.62\ H_2O$$

The reactor was then closed and heated to the desired temperature (180 ± 5^0C). It was held at this temperature under the autogeneous pressure for about 24h depending upon the SiO_2 / Al_2O_3 ratio of the gel mix. The reactor was cooled after completion of crystallization and contents were filtered and washed with water till the filtrate was free of the anion. The residue was dried at 120^0 C overnight. H-mordenite and H-Y were obtained from Laporte Inorganics, Chechire, UK.

2.2.1.3 Pretreatment procedures

The as-synthesised zeolites containing organic templates were carefully calcined to remove the organic molecules occluded during the zeolite growth, inorder to restore the porosity of the material. The calcination was carried out at 773 K. The temperature of the furnace was raised at a rate of 2.5 K/min. The sample after calcination contained the alkali cations used in the synthesis at the exchangeable sites.

2.2.1.4 H-form

The template free (Na/K)-form samples were subjected to ammonium exchange treatment. 5 g of the sample was slurried in 50 ml of 1 M ammonium nitrate solution. The mixture was stirred at 353 K for 8 hours, and the procedure was repeated three times to ensure complete exchange. The ammonium form of zeolites (NH_4-form) were then calcined at 773 K to get the catalytically active proton form (H-form).

2.2.1.5 Na-form

The Na-form of the sample was prepared by three exchanges of the calcined sample with aqueous $NaNO_3$ solution [1 M: solid/soln (g/g) =1:10] for 8 h at 353 K.

2.2.1.6 RE-Y

RE-Y is prepared from the Na-Y by exchanges with NH_4NO_3 (three times) and 5% RE-chloride (one exchange) solutions, respectively, maintaining the following conditions: NH_4NO_3 (1M; 10 ml/g zeolite, 353 K; 6 h; pH=7-8; three exchanges) followed by calcination at 823 K for 8 h. The H-RE (42.2)-Y and H-RE (70.6)-Y were prepared by treating NH_4-Y with 5% rare earth chloride solution by following the above exchange conditions. The washed zeolites were dried at 383 K for 2 h and calcined at 823 K for 8h.

2.2.2 Catalyst Characterization

2.2.2.1 Chemical analysis

A known weight of the zeolite sample was taken in a platinum crucible with lid , and ignited for 1 hour. The sample was then cooled in a desiccator and weighed. The difference in weights gave the loss on ignition. The anhydrous residue was dissolved in 15 ml aqueous hydrofluoric acid (40%) after adding a few drops of con. sulphuric acid (96%) and evaporated on a hot plate to remove Si in the form of H_2SiF_6. The remaining sample was taken after cooling the desiccator. The loss in the weight of the sample was determined to get the content of silica in the sample. The residue was fused in potassium pyrosulphate and dissolved in hot water. This solution was analyzed by an atomic absorption spectrometer (Model Hitachi Z-8000) for Na and Al.

2.2.2.2 Powder X-ray diffraction (XRD)

The X-ray powder diffraction patterns of the samples were recorded to ascertain the phase purity and also to detect the change in crystallinity during the framework modification treatments, viz., ion exchange. The XRD patterns of the samples were recorded using a Rigaku (model, D/MAX-VC, Japan) X-ray diffractometer using Ni filtered CuKα radiation (λ=1.5404A^0). Silicon was used as an internal standard to calibrate X-ray line positions.

2.2.2.3 Infrared spectroscopy

The infrared spectra were recorded through a FTIR spectrometer (Perkin Elmer Series 1600) in the range of 400-1300 cm^{-1} wave numbers using nujol mull technique. 20 mg of the sample was taken and mulled with nujol to form a homogeneous mixture. This was applied on KBr plates before recording the spectrum. The prominent bands attributed to the different internal tetrahedral and external linkage vibrations are summarized below:

Structure insensitive vibrations	
Assymmetric stretching	1250 - 950 cm^{-1}
Symmetric stretching	720 - 650 cm^{-1}
T- O bond	420 - 500 cm^{-1}
Structure sensitive vibrations	
Assymmetric stretching	1050 - 1150 cm^{-1}
Symmetric stretching	750 - 820 cm^{-1}
Double ring	650 - 500 cm^{-1}
Pore opening	300 - 420 cm^{-1}

2.2.2.4 Thermal analysis

Simultaneous TG-DTA analysis of the crystalline phases were performed on an automatic derivatograph (SETARAM TG-DTA 92). The thermograms of the samples were recorded under the following conditions.

weight of the sample = 30mg
heating rate = 10Kmin^{-1}
atmosphere = flowing air

Preheated and finely powdered α-alumina was used as the reference material.

2.2.2.5 Scanning electron microscopy (SEM)

The morphology and crystal size of zeolites were investigated using scanning electron microscopy (Stereoscan 440: Cambridge, UK). The sample was dusted on alumina and coated with a thin film of gold to prevent surface charging and to protect the zeolite material from thermal damage by electron beam. In all the samples a uniform film thickness of about 0.1 mm was maintained.

2.2.2.6 Surface area measurements

Omnisorb 100 CX (supplied by COULTER Corporation, USA) unit was used for the measurment of nitrogen adsorption to determine surface areas. The samples were activated at 673 K for 2 hours in a high vacuum (10^{-6} Torr). After the treatment , the anhydrous weight of the sample was taken. The samples were then cooled to 94 K using liquid nitrogen. After this, the samples were allowed to adsorb nitrogen gas. Finally, the BET surface area was calculated. The general form of the BET equation may be written as follows:

$1/\ V_{ads}(p_0-p) = 1/V_mC+[C-1/V_mC]\ p/p_0$ [1]

Where,

V_{ads} = volume of the gas adsorbed at pressure p,

p_0 = saturated vapour pressure

V_m = volume of the gas adsorbed for monolayer coverage,

C = BET constant

By plotting left side of the Eq.[1] against p/p_0, a straight line is obtained with a slope of $(C-I)/V_mC$ and an intercept $1/V_mC$. The BET surface area is calculated using the formula,

$$S_{BET} = X_M.N.A_m.10^{-20}.$$

where N is the Avogadro's number, A_m is the cross-sectional area of the adsorbate molecule and X_m is the moles of N_2 adsorbed.

2.2.2.7 Temperature programmed desorption (TPD) of ammonia

Acidity measurement of the samples were carried out by temperature programmed desorption of ammonia [3-5]. The sample 20-30 mesh (~ 1g) was placed in a silica tube (1.5cm i.d. x 30cm long) and activated in a flow of dry N_2 at 773 K for 6 h. The sample was then cooled in flowing N_2 (flow rate : 100 ml/min) to room temperature. NH_3 gas (25 ml/min) was introduced into the sample holder and passed continuously for a period of 30 min. N_2 (25 ml/hr) was passed for a period of 15h at 300K to desorb the physically adsorbed NH_3. The sample was then heated stepwise at the rate of 10^0C/min in N_2 flow (25 ml/min) and held for 1/2 h at each step. The amount of NH_3 desorbed at each step was absorbed in 1N HCl and estimated titrimetrically.

2.2.3 Results and Discussion

2.2.3.1 Synthesis

The synthesis of zeolite beta and ZSM-5 was carried out in basic medium under hydrothermal conditions. The phase purity of zeolite beta was found to be influenced by the following factors: synthesis temperature, template concentration, gel alkalinity, Na^+ ion concentration, SiO_2/Al_2O_3 ratio and the nature of the Al source [6, 7].

In order to study the effect of SiO_2/Al_2O_3 ratio in the gel on the crystallization, mixtures with different SiO_2/Al_2O_3 ratio (i.e 30, 50 and 80) were synthesized in the case of zeolite beta. It has been reported that, as the concentration of Al_2O_3 was increased in the gel, the nucleation and crystallization time increased marginally. Ghamami and Sand [8] also observed the higher crystallization period for lower SiO_2 / Al_2O_3 ratios in the ZSM-5 system.

2.2.3.2 Characterization

The powder X-ray diffraction patterns of the different zeolites used in the present study are presented in Fig. 2.2 - 2.4. These are similar to those reported in the literature [9-11]. The XRD patterns of these molecular sieves did not show the presence of any other crystalline impurity phases. The decrease in intensity in the calcined sample of zeolite beta as compared to the as-synthesized form may be due to the loss of organic template during calcination. The XRD pattern of H-RE-Y did not suggest any damage to the zeolite structure due to metal loading. Also, no change in the XRD patterns was observed after the reaction indicating the absence of any structural damage during reaction or regeneration.

The IR data of all the samples are similar to those reported in the literature. Fig. 2.5 and 2.6 illustrates the framework infra red spectra of the various zeolites used in the present study. The prominent bands attributed to the different internal tetrahedral and external linkage vibrations are summarized in Table 2.2.

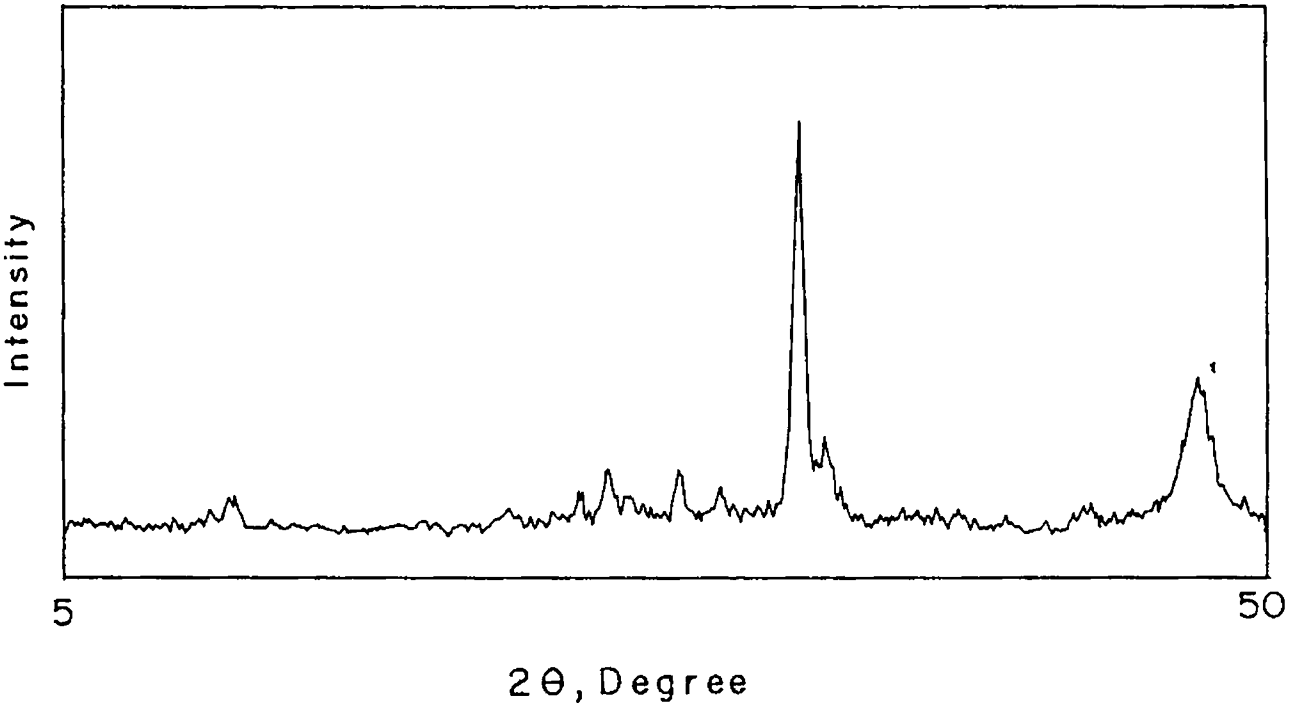


Fig. 2.2 X-ray diffraction pattern of zeolite beta (calcined)

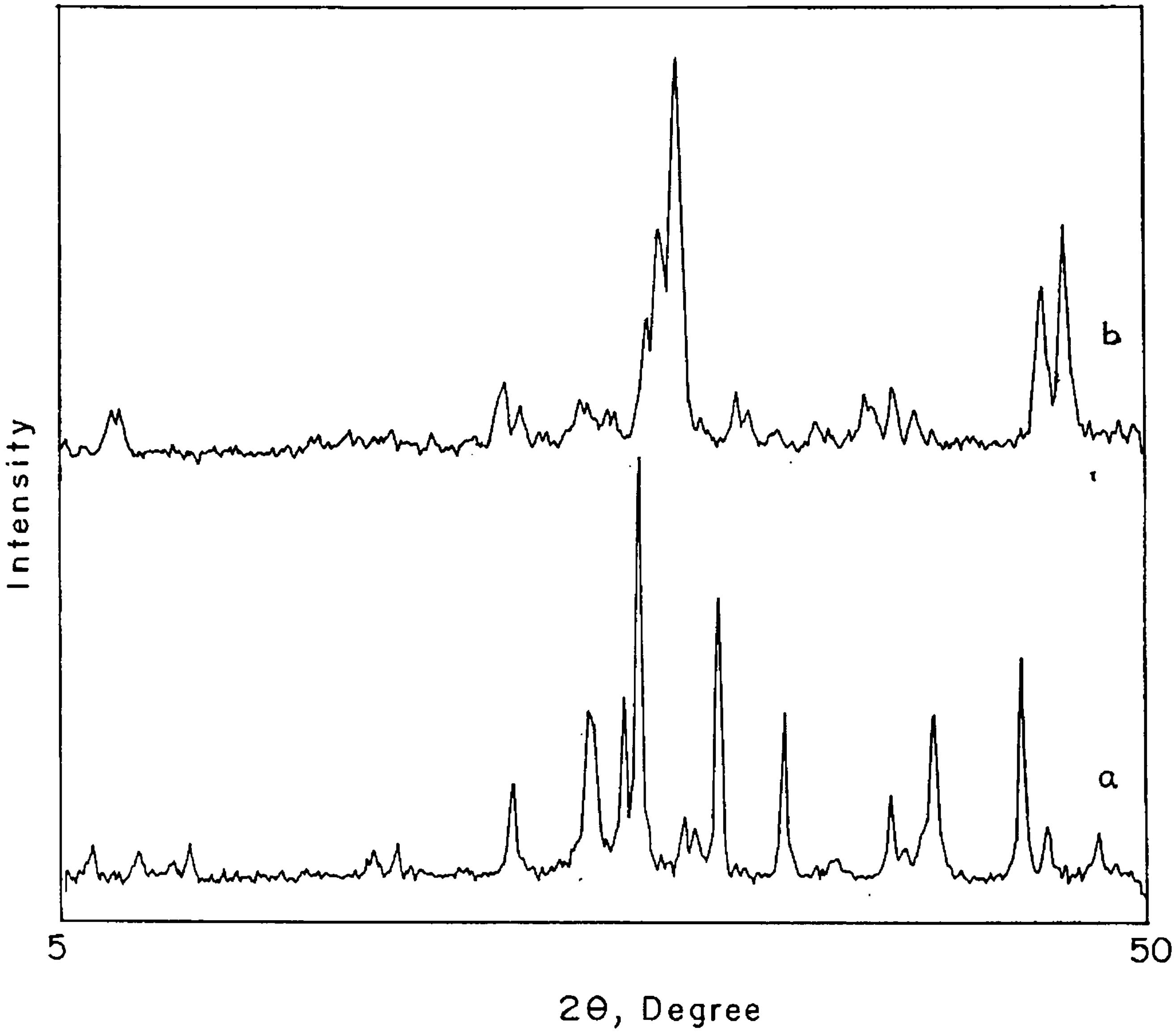


Fig. 2.3 X-ray diffraction patterns of (a) H-mordenite (b) H-ZSM-5

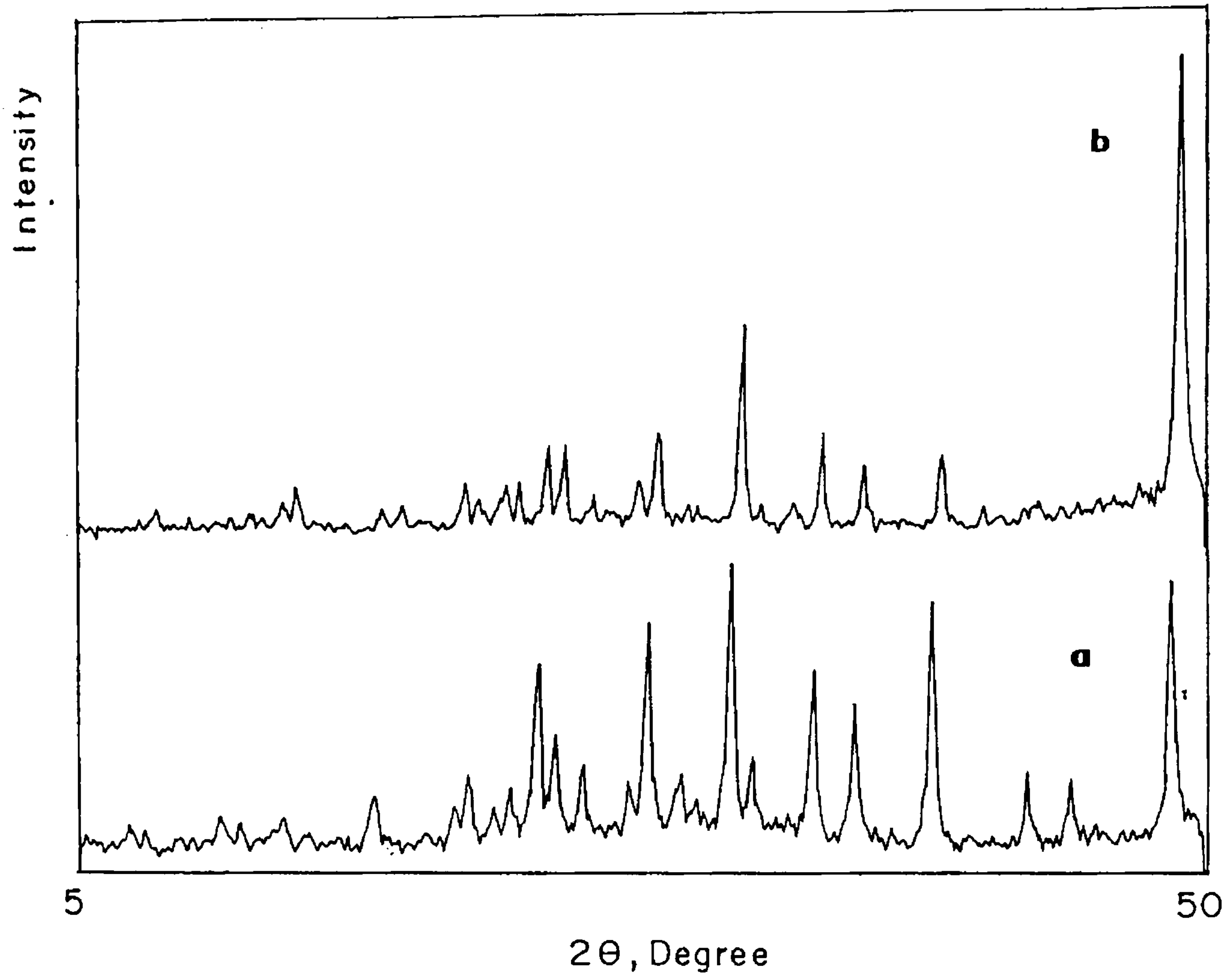


Fig. 2.4 X-ray diffraction patterns of (a) H-Y (b) H-RE-Y

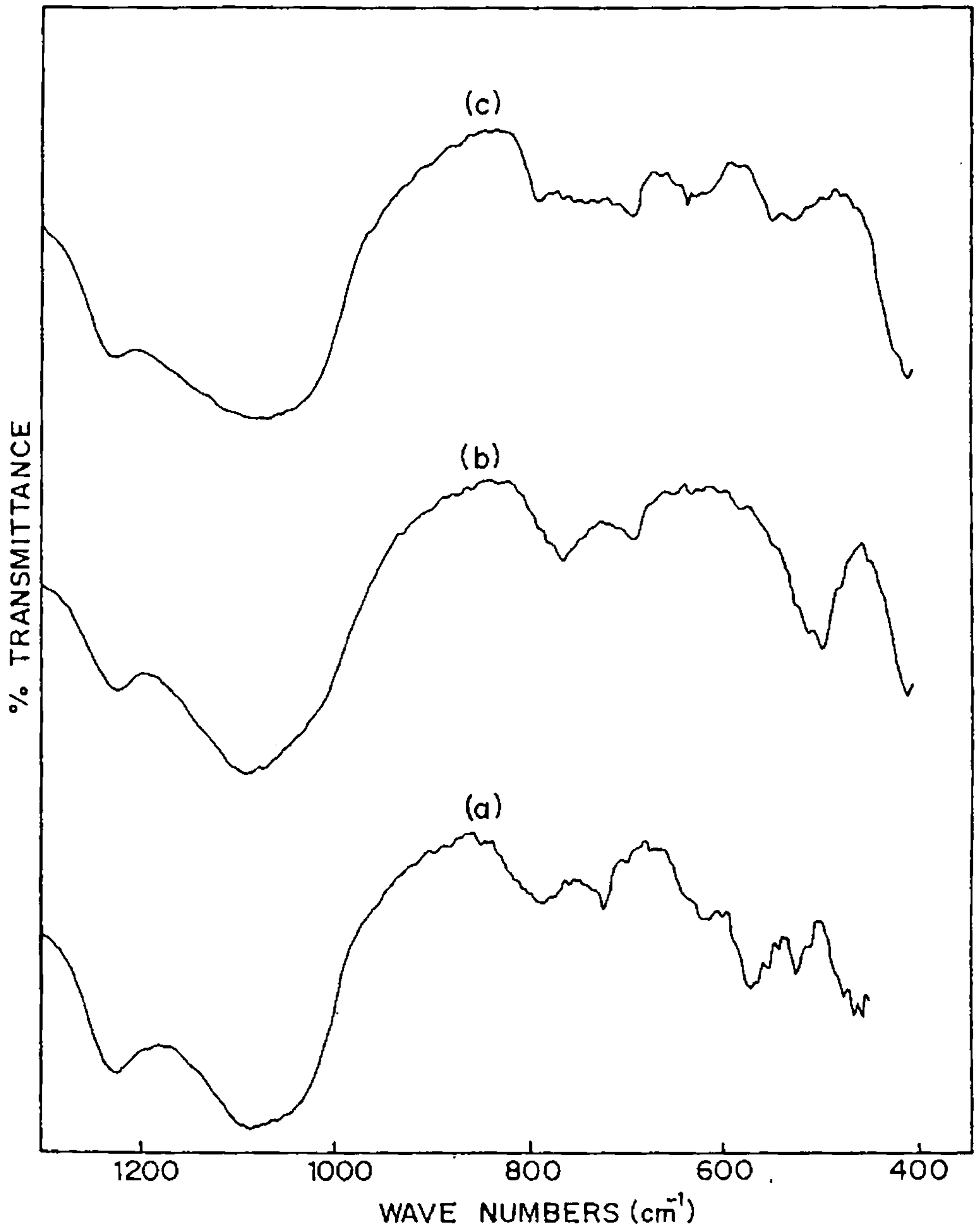


Fig. 2.5 Frame work IR spectra of zeolites (a) H-beta (b) H-ZSM-5 (c) H- mordenite

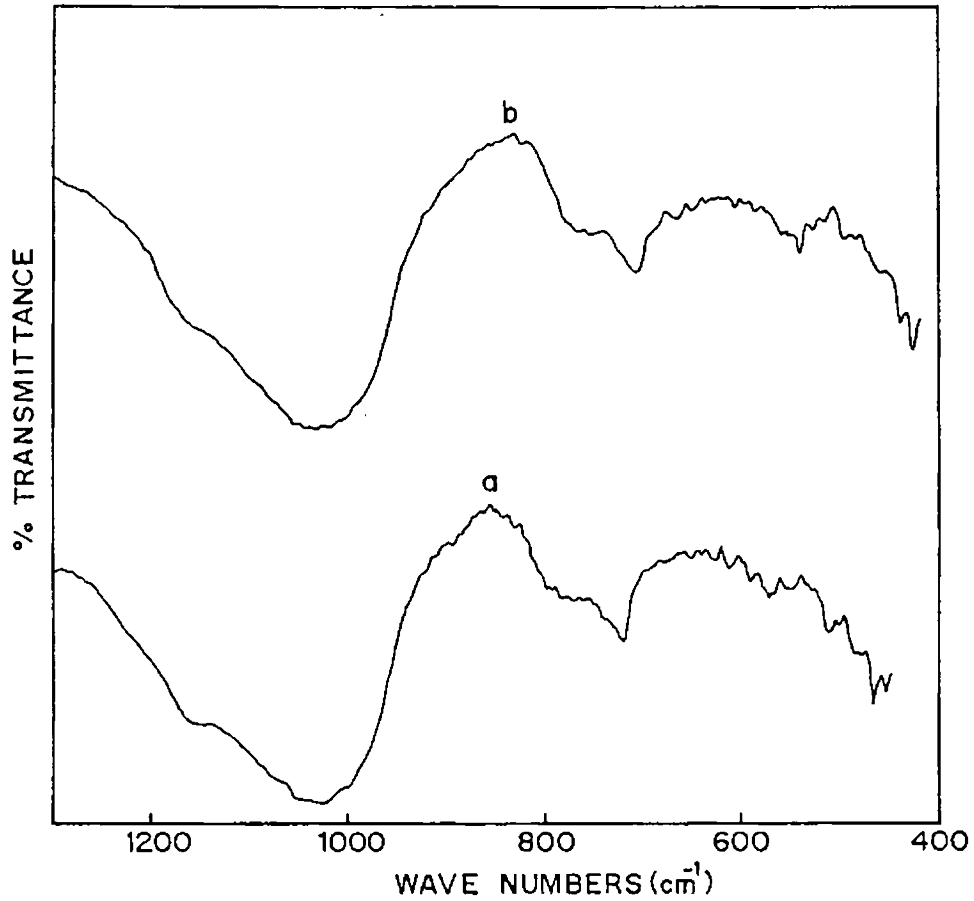


Fig. 2.6 Frame work IR spectra of zeolites (a) H-Y (b) H-RE-Y

Table 2.2 IR data for ZSM-5, H-Beta, H-Y and H-mordenite

Mode of vibration	**ZSM-5**	**H-beta**	**H-Y**	**mordenite**
(assymmetric stretching)				
External	1223	1224	1024	1089
Internal	1100	1088	721	812
(symmetric stretching)				
External	791	785	571	722
Internal	666	569	512	668
Double	539	524	467	587
(ring)				
T-O	455	458	455	456

Fig. 2.7 presents the DTA, DTG and TG profiles for zeolite beta. The weight and energy loss during the thermal decomposition of the as-synthesized fully crystalline sample is shown. An endothermic zone of weight loss at 368 K and three distinct zones of exothermic weight losses are seen in the DTA/TG curves with peak maxima at 674, 723 and 853 K respectively. Perez-Periente *et al.* reported three exothermic weight losses between 493 - 973 K during the decomposition of TEA-beta zeolites [12]. The endothermic peak at 363 K is due to the physisorbed water. The exothermic weight loss at 674 K is due to the decomposition of physically occluded TEA-OH. The other two exothermic weight losses at 723 and 853 K were ascribed by them to pyrolysis / oxidative decomposition of occluded TEA-OH and charge balancing TEA^+ cations respectively. The DTG experiment shows four separate weight losses related to the desorption of surface water (333 K), the decomposition of occluded TEA-OH (523-573 K), the decomposition of TEA^+ cations balancing the framework negative charge (623-693 K), and the burning of the coke residue (873-973 K) formed during the TEA^+ decomposition. The thermal analysis shows the absence of any structural damage.

The scanning electron micrograph (SEM) of zeolite beta samples showed in Fig. 2.8 indicates the absence of any amorphous material outside as well as inside the zeolite channels. The crystals of 0.5-1.2 μm had a uniform crystal size. The crystal size varies slightly with SiO_2/Al_2O_3 ratio.

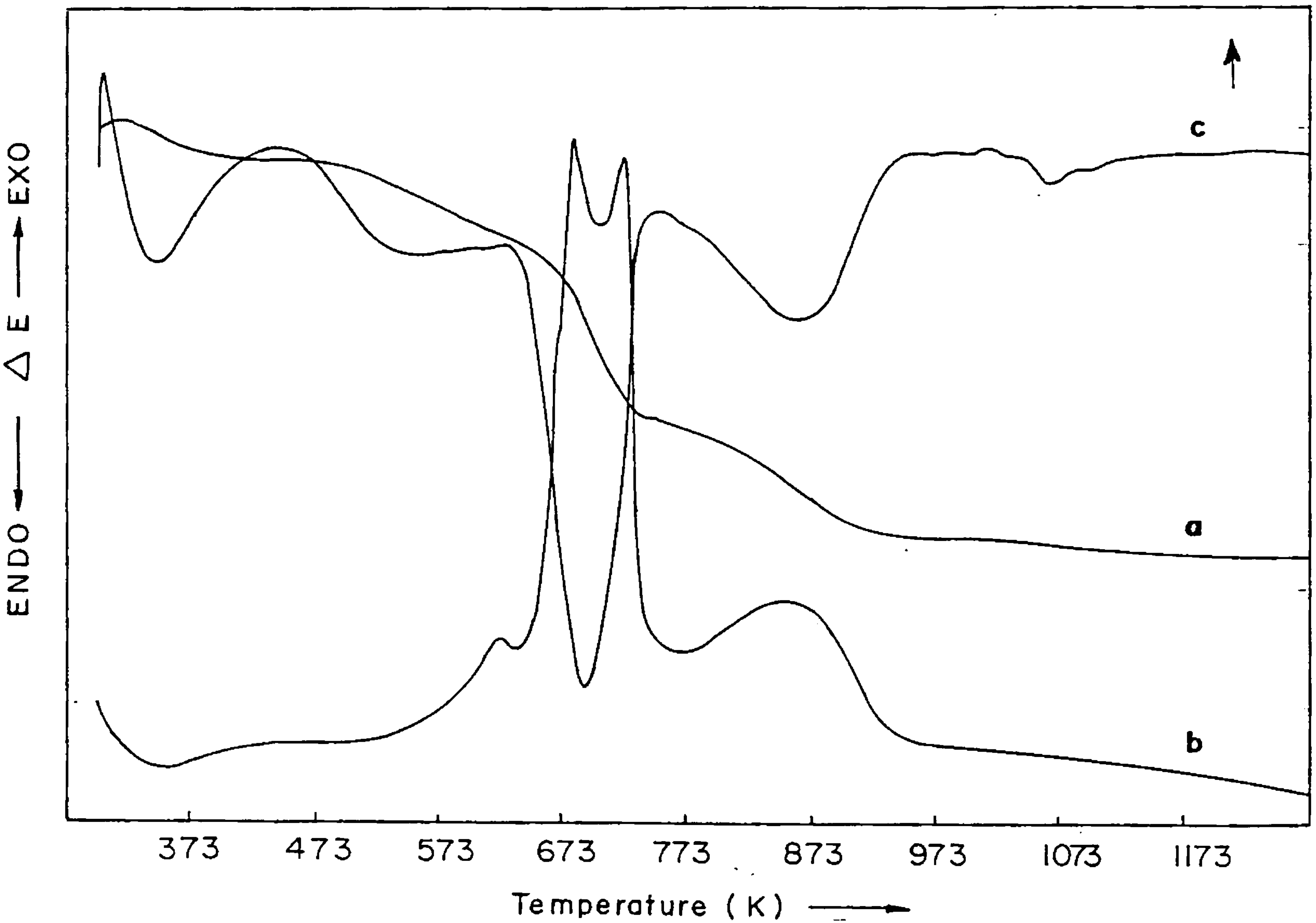
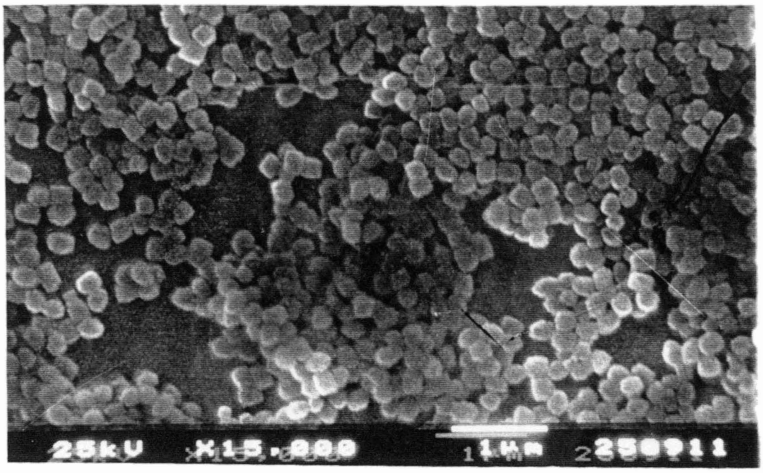
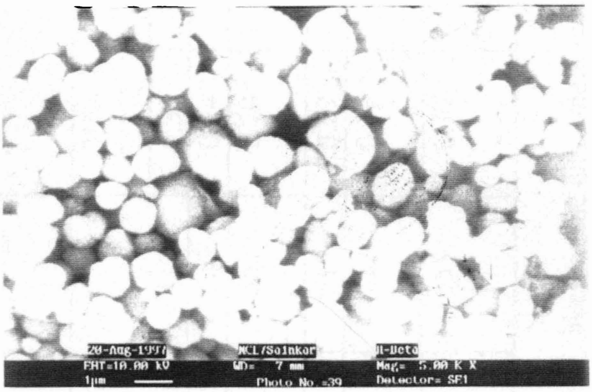


Fig. 2.7 Thermograms of zeolite beta (as-synthesized) (a) TG (b) DTG (c) DTA





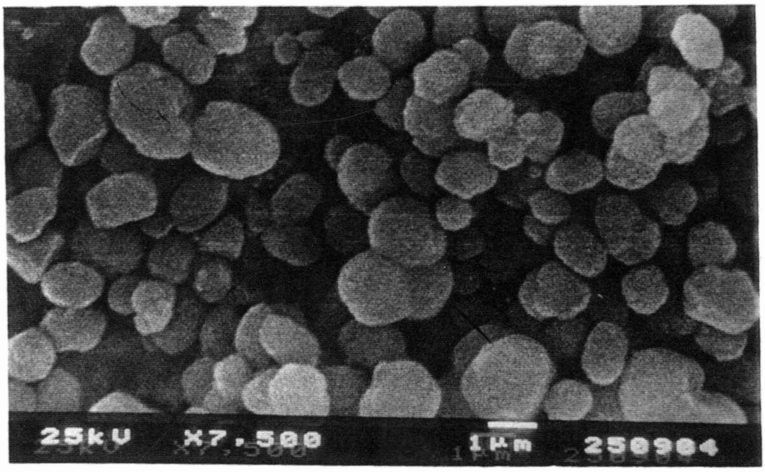


Table : 2.8: SEM of zeolite beta with 30. 50 and 80 SiO_2/Al_2O_3 ratios.

Table 2.3 Physico-chemical properties and acid strength distribution of zeolite catalysts

Catalyst	SiO_2/Al_2O_3 molar ratio	Degree of[a] H^+ or RE^{+3} exchange(%)	Crystal size(μm)	Surface[b] area (m^2/g)	NH_3 desorbed ($mmolg^{-1}$)[c]					NH_3 chemisorbed at 303K(m mol/g)
					303-353K	353-433K	433-513K	513-653K	653-773K	
H-ZSM-5	41.0	>98	0.4	413	0.55	0.16	0.05	0.26	0.21	1.23
H-beta	26.0	>98	0.5	745	0.14	0.24	0.05	0.16	0.16	0.75
H-mordenite	22.0	>98	1.0	552	0.20	0.17	0.15	0.12	0.07	0.71
H-Y	4.1	>98	1.0	615	0.29	0.55	0.49	0.11	0.01	1.45
H.RE(42.2) Y[d]	4.1	>42.2	1.0	712	0.19	0.45	0.12	0.10	0.04	0.90
H.RE(70.6) Y[d]	4.1	>70.6	1.0	659	0.17	0.10	0.26	0.11	0.10	0.74

[a] values are reported as percent of the total cation sites, taken as the aluminium content 100%.

[b] measured by N_2 adsorption

[c] measured by temperature programmed desorption(t.p.d) of ammonia

[d] values in paranthesis represent the amount of RE^{+3} -exchange in HY

The results of the stepwise thermal desorption of ammonia from the zeolites are presented in Table 2.3. The total amount of NH_3 desorbed at 303 K is also given in in the same table. The results reveal that the total acid sites and the site energy distribution are dependent on the type of the zeolite and are strongly influenced by the nature of the cation and degree of exchange in the zeolite. The number of sites of higher strength increase with the increase in the degree of RE^{+3}- exchange in H-Y.

Table 2.3 compares the crystal size, acidity, surface area, SiO_2/Al_2O_3 molar ratio and the degree of cation exchange of the various zeolites used in the present study.

2.2.4 Catalytic reactions

The liquid phase catalytic runs were carried out batchwise in a mechanically stirred, closed 50 ml glass reactor fitted with a reflux condenser, a thermometer and a septum for withdrawing the product samples. The temperature of the reaction vessel was maintained using an oil bath. In a typical run, appropriate amounts of corresponding aromatic and benzylating or acylating agent were charged in the reactor along with the known amount of activated catalyst. The reaction mixture was heated to the required temperature under stirring. The progress of the reaction was followed by gas-chromatograph (HP 6890) fitted with flame ionization detector and a capillary column (50m x 0.2mm) with methyl silicon gum. Some selected runs were analysed by

GC-MS (Shimadzu MS QP 2000A) for product identification. The composition of the reaction mixture was also determined by comparing their gas-chromatograph with those of authentic samples.

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CHAPTER III

PROPIONYLATION OF TOLUENE AND ANISOLE

PART - I

3.1 PROPIONYLATION OF TOLUENE

3.1.1 Introduction

Propionylation of toluene to 4-methyl propiophenone (4-MPP) is of considerable interest due to its commercial importance in various industries. Several homogeneous acidic catalysts ($AlCl_3$, $TiCl_4$, $FeCl_3$, $SnCl_4$ and H_2SO_4) have been widely used for the acylation reactions [1, 2]. The reaction of toluene with propionaldehyde in the presence of protonic and Lewis acid catalysts (like H_2SO_4 and $AlCl_3$) has been reported to take place in resemblance with aldol condensation type reactions [3, 4]. These catalysts tend to be less selective for the expected product 4-MPP. Zeolites are known for their shape selective properties and they have been used widely in a variety of acid and base catalysed shape selective reactions. However, not much attention has been paid to the use of zeolites in acylation reactions [5-10].

The objective of the present work is to study the selective propionylation of toluene to 4-methyl propiophenone over acidic medium and large pore zeolites. We report the effect of different zeolite catalysts, various level of RE^{3+}- and Na^{+}- exchange in Y-zeolite, acidity of the zeolite catalysts, duration of the run, SiO_2/Al_2O_3 ratio, catalyst concentration, reaction temperature, molar ratios of reactants and reuse of the zeolite catalyst (H-beta) on the conversion of propionyl chloride (PC) and the formation of 4-methyl propiophenone (4-MPP). The results obtained over various zeolite catalysts were compared with conventional catalysts like $AlCl_3$ and amorphous SiO_2/Al_2O_3.

3.1.2 Experimental

3.1.2.1 Catalyst preparation

Zeolites ZSM-5 and beta were synthesized following the procedures described in literature [11, 12]. They are calcined at 823 K and subjected to ammonium exchange under the following conditions: NH_4NO_3 = 1M, 10 ml. NH_4NO_3 /g zeolite, 353 K, 6 h exchange run, pH 7-8, and calcined at 823 K for 8 h to get the protonic form. The modified forms of H-beta such as H-Na(13.6)- beta and H-Na(37.3)- beta were obtained by exchange with 0.1M and 1M solutions of $NaNO_3$, respectively, at 353 K for 8h. Zeolites H-mordenite and Na-Y were obtained from Laporte Inorganics, Cheshire, U.K. The H-RE(42.2)-Y and H-RE(70.6)-Y were prepared by treating NH_4-Y with 5% rare earth chloride solution [13, 14].

Table 2.3 lists the chemical composition and the major characteristics of the samples. The detailed experimental procedure for the various characterization techniques are described in Section 2.2.2.

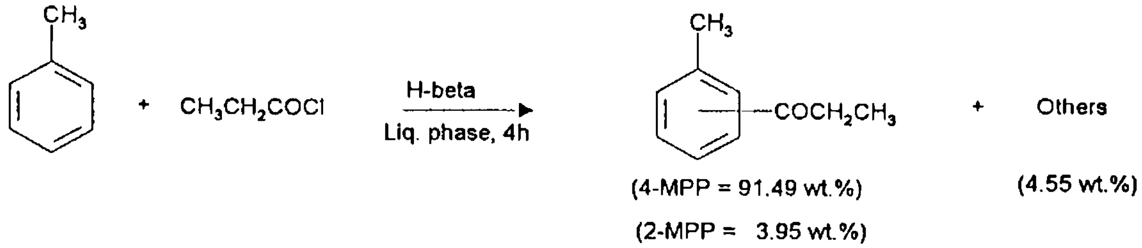
3.1.2.2 Catalytic testing

Anhydrous AR grade chemicals were used without further purification. The reaction between toluene and propionyl chloride was carried out in a 50 ml. two necked flask attached to a condenser, and a septum used to withdraw samples from the reaction mixture. The temperature of the reaction mixture was maintained using an oil bath. In a typical run, appropriate amounts of toluene and propionyl chloride (5:1molar ratio) was charged in the reactor along with 0.3g catalyst. The reaction mixture was heated to 383 K under stirring. Samples were withdrawn periodically and analysed with a gas chromatograph.

3.1.3 Results and discussion

3.1.3.1 Activity of various catalysts

Table 3.1 summarizes the catalytic activities of H-beta, H-Y, H-mordenite, H-ZSM-5, H-RE(70.6)-Y, H-RE(42.2)-Y, H-Na(13.6)-beta, H-Na(37.3)-beta, $AlCl_3$ and SiO_2-Al_2O_3(amorphous), in the propionylation of toluene at similar reaction conditions. The main products of the reaction are 4-methyl propiophenone (4-MPP) and 2-methyl propiophenone (2-MPP) (Scheme: 1).



(Scheme: 1)

There was no substantial change in the product distribution after 4h of run for these catalysts.

Among the zeolite catalysts, H-beta was found to be the most effective catalyst. At 1h of reaction time, the conventional Lewis acid catalyst $AlCl_3$ produces 26.12 wt.% 4-MPP, 52.30 wt. % 2-MPP and 16.57 wt.% consecutive products at 81.82 wt.% conversion level of PC, while H-beta gave 83.98 wt.% 4-MPP, 13.76 wt.% 2-MPP, along with 2.26 wt.% consecutive products at 31.86 wt.% PC conversion. The higher activity and selectivity of H-beta may be attributed to its stronger acid sites and mesoporous system (Table 2.3). $AlCl_3$ does not posses shape selectivity and it give rise to a large amount of consecutive products.

The activity of H-Y was found to enhance considerably with increase in the degree of RE^{3+}- ion exchange which may be due to the higher strength of acid sites generated by RE^{3+}- cations [13, 14]. The conversion of PC over H-ZSM-5 and H-mordenite were 13.27 wt.% and 1.13 wt.% respectively. The lower activity of H-

Table 3.1 Propionylation of toluene[a]

Catalyst	Reaction time (h)	Conversion [b] of PC (wt%)	Rate of[c] PC conversion (mmolg^{-1}h^{-1})	Product distribution (wt.%)[d]		
				4-MPP	2-MPP	Others
H-ZSM-5	1	2.65	1.61	100	-	-
	4	13.27	2.01	26.07	19.28	54.65
H-beta	1	31.86	4.84	83.98	13.76	2.26
	4	59.54	9.06	91.49	3.95	4.55
H-Na(13.6) beta[e]	1	7.87	4.79	94.45	-	5.54
	4	32.10	4.88	96.63	-	3.36
H-Na(37.3) beta[e]	1	2.57	1.56	94.88	-	5.12
	4	12.95	1.97	88.99	-	7.29
H-Y	1	7.31	4.45	96.31	-	3.68
	4	14.23	2.16	97.34	-	2.65
H-mordenite	1	1.05	0.63	100	-	-
	4	1.13	0.17	100	-	-
H-RE (42.2)Y[f]	1	9.56	5.80	94.63	-	5.37
	4	27.64	4.20	93.05	-	6.94
H-RE (70.6)Y[f]	1	16.61	10.11	92.39	7.5	0.1
	4	36.02	5.48	91.63	6.38	1.98
$AlCl_3$	1	81.82	49.81	26.12	52.30	16.57

[a] Reaction conditions: catalyst (g) = 0.3; catalyst / C_2H_5COCl (wt./wt.) = 0.17; Toluene/ C_6H_5COCl (molar ratio) = 5; reaction temperature(K) = 383

[b] PC = propionyl chloride (C_2H_5COCl)

[c] Rate of PC conversion(mmolg^{-1}h^{-1}) = (amount of PC reacted)/(weight of catalyst x reaction time)

[d] 4-MPP = 4-methyl propiophenone; 2-MPP = 2-methyl propiophenone; others = consecutive products

[e] Values in parenthesis represents the percentage of Na exchanged in the H-beta

[f] Values in parenthesis represents the percentage of RE^{+3}-exchanged in zeolite H-Y

ZSM-5 may be attributed to its small pore openings than the size of the products, and that of H-mordenite is due to its weaker acid sites (Table 2.3).

The conversion of PC wt.% decreases drastically from 59.54 wt.% to 32.10 wt.% when H-beta is exchanged with Na^+ ions. H-beta is much more active than H-Na(13.6)-beta and H-Na(37.3)-beta catalysts. From this data it is clear that the performance of the catalyst is governed by the number and nature of acid sites present in the structure of the zeolite. Amorphous SiO_2-Al_2O_3 was almost inactive under the reaction conditions and a blank run (no catalyst) also failed to give any product. The catalysts used in the study show the following decreasing order of activity:

$AlCl_3$ > H-beta > H-RE(70.6)-Y > H-Na(13.6)-beta > H-RE(42.2)-Y > H-Y > H-ZSM-5 > H-Na(37.3)-beta > H-mordenite > SiO_2-Al_2O_3 (amorphous)

The influence of various parameters on the PC conversion over H-beta is reported in the following section.

3.1.3.2 Effect of reaction temperature

The effect of reaction temperature on the rate of propionylation of toluene with propionyl chloride was studied over zeolite H-beta in the temperature range 353 K to 383 K. (Table 3.2). The rate of conversion of PC is found to increase from 4.83 mmol$g^{-1}h^{-1}$ to 9.06 mmol$g^{-1}h^{-1}$ with increase in temperature from 353 K to 383 K. In addition, an increase in temperature enhances the selectivity for the major product 4-MPP (Fig. 3.1).

Table 3.2 Effect of reaction temperature[a]

Reaction temp.(K)	Conversion of[b] PC (wt%)	Rate of PC[c] conversion(mmolg^{-1}h^{-1})	Product distribution (wt.%)[d]		
			4-MPP	2-MPP	Others
353	31.80	4.83	82.89	10.98	6.13
363	37.38	5.68	66.77	8.82	24.40
373	39.96	6.07	86.56	13.43	-
383	59.54	9.06	91.49	3.95	4.55

[a] Reaction conditions : catalyst (H-beta)/C_2H_5COCl(wt./wt.) = 0.17

Toluene/ C_2H_5COCl (molar ratio) = 5; toluene = 10; C_2H_5COCl = 1.69

Reaction time (h) = 4; b,c & d See footnotes to Table 3.1

Table 3.3 Influence of SiO_2/Al_2O_3 ratio of zeolite H-beta[a]

	SiO_2/Al_2O_3 (molar ratio)		
	26	**50**	**80**
Reaction time (h)	4	4	4
Conversion of PC (wt.%)[b]	59.54	19.84	9.32
Rate of PC conversion (mmolg^{-1}h^{-1})[c]	9.06	3.01	1.42
Product distribution[d] (wt.%)			
4-MPP	91.49	87.18	90.83
2-MPP	3.95	2.32	10.5
Others	4.55	10.5	3.36

a,b,c & d see foot notes to Table 3.1

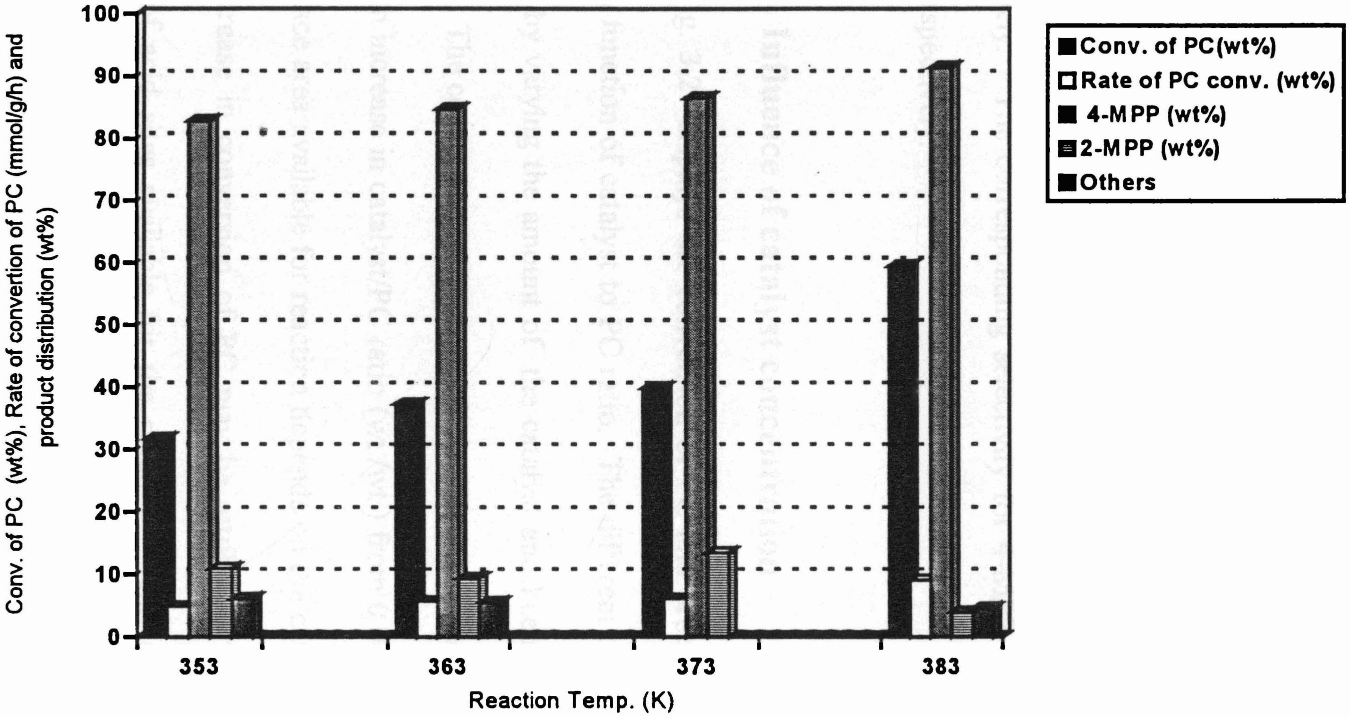


Fig. 3.1 Influence of reaction temperature on the conversion of PC (wt.%), rate of PC conversion (m mol $g^{-1}h^{-1}$) and product distribution.

3.1.3.3 Influence of SiO_2-Al_2O_3 molar ratio

The effect of the SiO_2-Al_2O_3 ratio of H-beta upon the PC conversion was investigated and the results are shown in Table 3.3. The conversion of PC decreases with increasing SiO_2-Al_2O_3 ratio. This is due to the decrease in the number of active sites with increase in SiO_2-Al_2O_3 ratio of the catalyst. The conversion of PC over 26, 50 and 80 SiO_2-Al_2O_3 ratio of H-beta is found to be 59.54, 19.84 and 9.32 wt.% respectively. The corresponding selectivity for 4-MPP is 91.49, 87.18 and 90.83 wt.%, respectively.

3.1.3.4 Influence of catalyst concentration

Fig. 3.2 displays the conversion of PC and product yields at 4h of reaction time as a function of catalyst to PC ratio. The different ratios of catalyst to PC were obtained by varying the amount of the catalyst and keeping the concentration of PC constant. The conversion of PC wt. % is found to increase from 43.07 wt. % to 89.92 wt.% with increase in catalyst/PC ratio (wt./wt.) from 0.05 to 0.41 (Table 3.4). The total surface area available for reaction depends on the catalyst loading [15]. So the linear increase in conversion of PC may be attributed to the increase in the total number of acid sites available for the reaction. But the selectivity of the major product i.e. 4-MPP is found to be almost independent upon catalyst/PC ratio.

Table 3.4 Effect of catalyst concentration[a]

Catalyst/PC (wt./wt.)	Convertion of [b]PC (wt%)	[c]Rate of PC conversion (mmolg^{-1}h^{-1})	Product distribution(wt%)[d]		
			4-MPP	2-MPP	others
0.05	43.07	19.66	87.72	3.91	22.43
0.17	59.54	9.06	91.49	3.95	23.16
0.29	67.95	6.19	87.03	6.65	6.32
0.41	89.92	5.86	88.59	8.53	10.38

[a]Reaction conditions as in Table 3.1; Reaction time (h) = 4
b,c & d see foot notes to Table 3.1

Table 3.5 Effect of toluene/PC molar ratio[a]

Toluene/PC (wt./wt.)	Convertion [b] of PC (wt%)	[c]Rate of PC conversion (mmolg^{-1}h^{-1})	Product distribution(wt%)[d]		
			4-MPP	2-MPP	others
1	6.64	5.98	90.33	8.67	1.0
3	46.31	13.76	86.25	5.3	8.44
5	59.54	9.06	91.49	3.95	4.55
7	48.09	6.06	82.46	6.83	10.7

a,b,c & d see foot notes to Table 3.1 ; reaction time (h) = 4

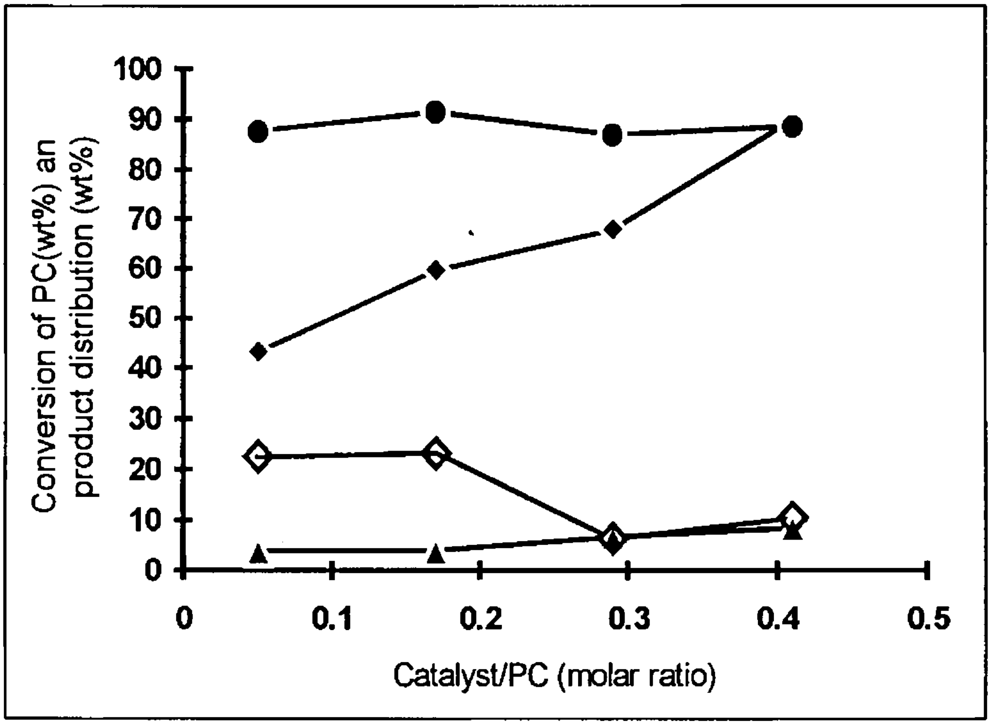


Fig. 3.2 Effect of catalyst/PC molar ratio on the conversion of PC (♦) and product distribution: 4-MPP (●), 2-MPP (▲) and others (◊); Reaction conditions: see footnotes to Table 3.1; reaction time (h) = 4.

3.1.3.5 Effect of toluene / PC molar ratio

Upon increasing the ratio of toluene to PC from 1 to 7 in the reaction mixture the conversion of PC is found to be increase from 6.64 wt. % to 48.09 wt.%. (Fig. 3.3). The selectivity for product was not influenced by toluene/PC molar ratio (Table 3.5).

3.1.3.6 Recycling of the catalyst

H-beta samples used in the propionylation of toluene was recycled three times inorder to check the activity, and stability of the catalyst. After the reaction, the catalyst was filtered, washed with acetone and calcined at 763 K in dry air for 16h. The results of these experiments is shown in Table 3.6. X-ray diffraction measurements indicated that zeolite beta did not suffer any reduction in the x-ray crystallinity (Fig. 3.4). However, the Al content of the zeolite decreases progressively with successive recycling in the propionylation reaction. The conversion of PC (wt. %) after second and third recycling is 22.49 wt.% and 14.20 wt.% respectively. The results indicate that the catalyst can be recycled a number of times without loosing its activity to a greater extent.

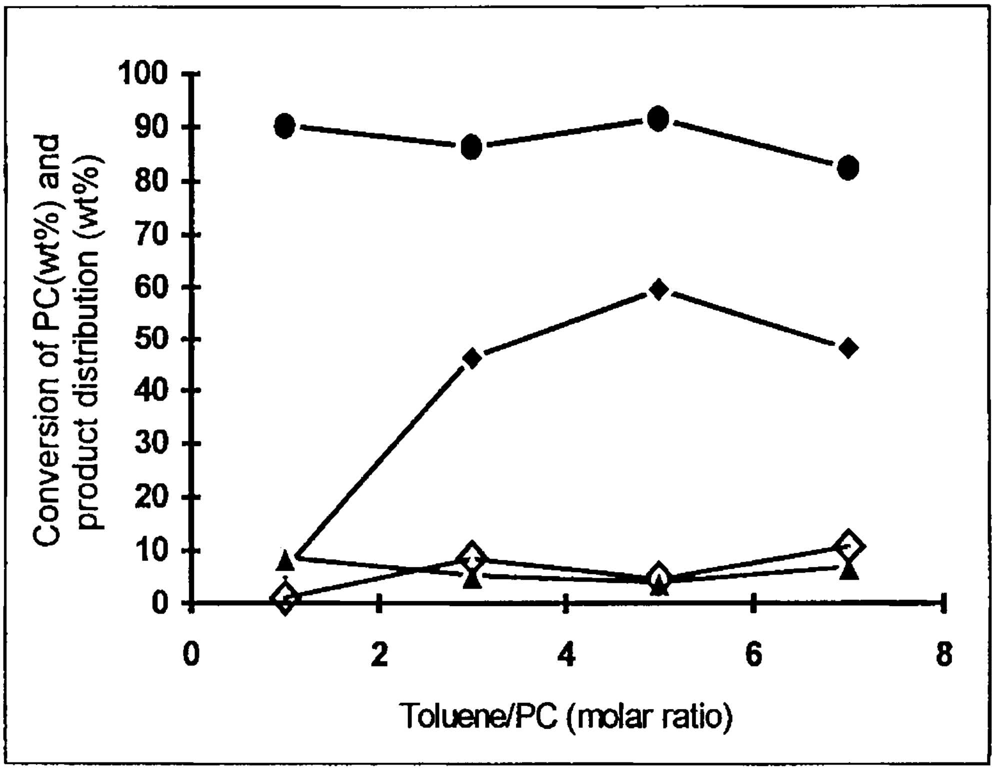


Fig. 3.3 Effect of Toluene/PC molar ratio on the conversion of PC (♦) and product distribution, 4-MPP (●), 2-MPP (▲) and others (◊); Reaction conditions: see footnotes to Table 3.1; reaction time (h) = 4.

Table 3.6 Recycling of H-beta[a]

Run	Change in SiO_2/Al_2O_3 (molar ratio)	Conv.of[b] PC (wt%)	Rate of[c] PC conversion ($mmolg^{-1}h^{-1}$)	Product distribution(wt%)			Crystallinity of H-beta (%)
				4-MPP	2-MPP	Others	
1(fresh catalyst)	26.0	57.95	6.95	87.03	6.65	6.32	100
2	27.43	22.49	2.46	78.76	5.85	15.39	81.3
3	29.1	14.20	2.12	80.39	4.92	14.68	77.4

[a] Reaction conditions, same as given in Table 3.1; reaction time (h) = 4

[b,c&d] see foot notes to Table 3.1

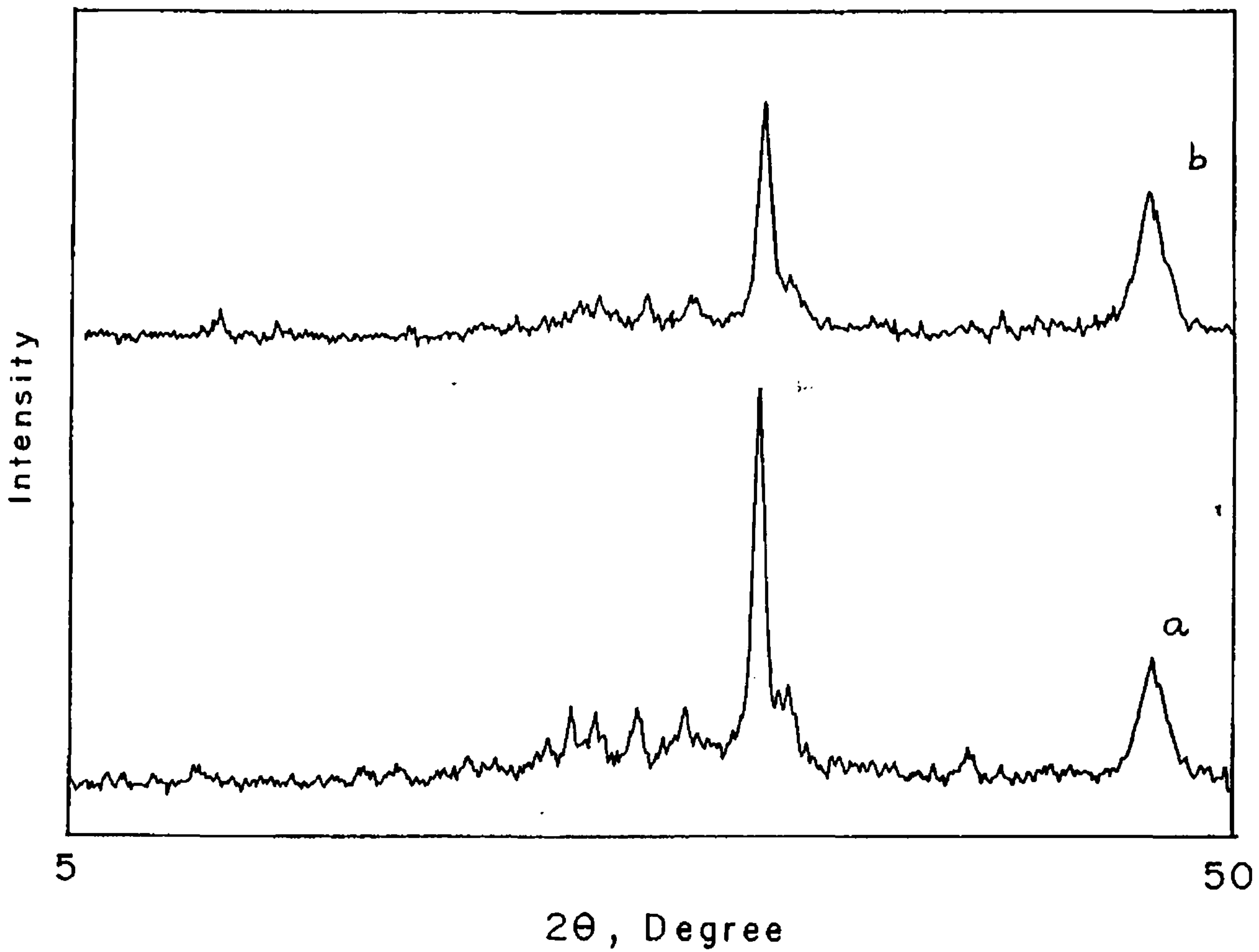


Fig. 3.4 X-ray diffraction patterns of (a) fresh H-beta and (b) H-beta after recyling

3.1.3.7 Mechanism

The classical Friedel-Crafts acylation is an electrophilic aromatic substitution in which an electrophile ($CH_3CH_2CO^+$) is generated by the activation of propionylchloride on the protonic sites of the zeolite which attacks the toluene ring resulting in the formation of 4-MPP. Such chemistry is well documented in zeolite catalyzed systems [16, 17]. The mechanism of acylation reaction is represented schematically in Chapter IV (Fig. 4.5).

3.1.4 Conclusions

In summary, the zeolite H-beta catalyse the propionylation of toluene to 4-methyl propiophenone selectively and efficiently using propionyl chloride as the propionylating agent. One of the reasons of higher catalytic activities of H-beta and H-RE-Y may be their strong acid sites. The medium pore zeolite H-ZSM-5 is found to be an unsuitable catalyst for the reaction due to its small pore openings. The conversion of propionyl chloride increases with increase in reaction temperature, catalyst/PC ratio, and toluene to PC molar ratio. Most probably, the acylation reaction takes place by an electrophile ($C_2H_5CO^+$) which is produced by an acidic catalyst from propionyl chloride. Thus the generated electrophile attacks the toluene ring and produce methyl propiophenones. An increase in the SiO_2/Al_2O_3 ratio and reuse of the H-beta decreases the formation of methyl propiophenones.

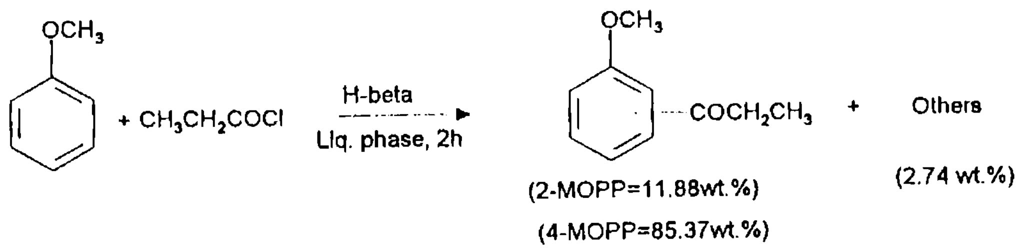
PART-II

3.2 PROPIONYLATION OF ANISOLE

3.2.1 Introduction

Methoxy propiophenones are found to have wide applications in the area of fine chemical synthesis. They are usually prepared by the Friedel-Crafts acylation of anisole with propionyl chloride/propionic anhydride using $AlCl_3$ catalyst [18]. The use of various types of catalysts like $ZnCl_2$, $FeCl_3$ [19, 20], H_3PO_4 [21], and cobalt (II) chloride [22] have been reported recently in the liquid phase propionylation of anisole.

In this section, we report the propionylation of anisole with propionyl chloride (PC) over various zeolites such as H-ZSM-5, H-beta, H-Na(13.6)-beta, H-Na(37.3)-beta, H-mordenite, H-Y, H-RE(42.2)-Y and H-RE (70.6)-Y. In addition, homogenous catalysts $AlCl_3$ and amorphous SiO_2-Al_2O_3 were also included for comparison. The catalyst and process parameters are optimised to enhance the conversion of PC and selectivity to 4-methoxy propiophenone (4-MOPP) (Scheme: 2).



(Scheme: 2)

3.2.2 Experimental

The synthesis, modification and characterization techniques of various zeolites used are same as reported in Part - I of this section.

The acylation of anisole was carried out in liquid phase at 343 K under atmospheric pressure. In a typical run, appropriate amounts of anisole and propionyl chloride (5:1) molar ratio was charged in the reactor along with 0.3 g catalyst. Samples were withdrawn periodically and analyzed with a gas chromatograph.

3.2.3 Results and discussion

3.2.3.1 Activity of various catalysts

The conversion of PC(wt.%), rate of PC conversion(mmolg-1h-1) and the product distribution(wt.%) of the products, 4-methoxy propiophenone (4-MOPP) and 2-methoxy propiophenone (2-MOPP) obtained over various zeolite catalysts are listed in Table 3.7. As in the case of toluene, among zeolite catalysts, H-beta

Table 3.7 Propionylation of anisole[a]

Catalyst	Reaction time (h)	Conversion[b] of PC (wt%)	Rate of[c] PC conversion (mmolg^{-1}h^{-1})	Product distribution (wt.%)[d]		
				4-MOPP	2-MOPP	Others
H-ZSM-5	2	62.02	19.10	83.45	15.55	0.99
H-beta	2	69.76	21.48	85.37	11.88	2.74
H-Na(13.6) beta[e]	2	63.64	19.60	75.07	17.27	7.65
H-Na (37.3) beta[e]	2	48.39	14.90	55.73	30.48	13.78
H-mordenite	2	57.15	17.60	78.20	20.02	1.78
H-Y	2	58.66	18.07	67.56	24.76	7.58
H-RE (42.2)Y[f]	2	59.81	18.42	68.21	26.62	5.27
H-RE (70.6)Y[f]	2	65.32	20.11	58.03	30.70	11.27
$AlCl_3$	2	82.93	25.54	59.7	22.07	18.23
SiO_2-Al_2O_3 (amorphous)	2	47.47	14.62	64.88	31.35	3.76

[a] Reaction conditions: catalyst (g) = 0.3; catalyst / C_2H_5COCl (wt./wt.) = 0.17 ; anisole / C_2H_5COCl (molar ratio) = 5; reaction temperature (K) = 343

[b] PC = propionyl chloride (C_2H_5COCl)

[c] Rate of PC conversion (mmolg^{-1}h^{-1}) = (amount of PC reacted)/(weight of catalyst x reaction time)

[d] 4-MOPP = 4-methoxt propiophenone; 2-MOPP = 2-methoxy propiophenone others = consecutive products

[e] Values in parenthesis represents the percentage of Na exchanged in the H-beta

[f] Values in parenthesis represents the percentage of RE^{+3}-exchanged in zeolite H-Y

catalyzes the reaction efficiently and selectively to 4-methoxypropiophenone and it is found to be superior to other zeolite catalysts and $AlCl_3$. The conversion of PC, rate of PC conversion and selectivity for the major product, 4-MOPP over zeolite H-beta after 2h of reaction time were found to be 69.76 wt.%, 21.48 mmol$g^{-1}h^{-1}$, 85.37 wt.% respectively. The highest activity of H-beta may be attributed to its stronger acid sites and the space available in the 12-membered three dimensional pore system (5.4 x 5.6 and 5.1 x 5.5 Å) (Table 2.3). $AlCl_3$ gave higher amounts of consecutive products due to its non-shape selective character.

The conversion of PC over H-Y, H-RE(42.2)-Y and H-RE(70.6)-Y are found to be 58.66 wt.%, 59.81 wt.% and 65.32 wt.% respectively. The enhancement in catalytic activity may be due to the increase in strength of acid sites due to RE-cation exchange [13, 14]. The activity of zeolite H-beta in the propionylation reaction decreases drastically with the increase in Na^+ content in H-beta (Table 3.7). This may be due to the removal of some amount of stronger Bronsted acid sites by Na^+ exchange in H-beta. A blank run carried out at the same reaction conditions in the absence of any catalyst gave a PC conversion of 19.65 wt.%.

3.2.3.2 Effect of reaction temperature

Table 3.8 shows the temperature dependency of this reaction. A significant increase in the rate of PC conversion is achieved with the increase in the reaction temperature from 343 K to 383 K. However, the product distribution is not

Table 3.8 Effect of reaction temperature[a]

Reaction temp.(K)	Conversion of[b] PC (wt%)	Rate of PC[c] conversion(mmolg^{-1}h^{-1})	Product distribution (wt.%)[d]		
			4-MOPP	2-MOPP	Others
343	69.76	21.48	85.37	11.88	2.74
353	73.18	22.54	82.76	15.72	1.51
363	84.94	26.16	77.84	11.58	10.18
373	97.34	29.98	78.27	19.13	2.6

[a] Reaction conditions : catalyst (H-beta)/C_2H_5COCl(wt./wt.) = 0.17
Anisole/ C_2H_5COCl (molar ratio) = 5; anisole = 10; C_2H_5COCl = 1.71
Reaction time (h) = 2; b,c & d See footnotes to Table 3.7

Table 3.9 Influence of SiO_2/Al_2O_3 ratio of zeolite H-beta[a]

	SiO_2/Al_2O_3 (molar ratio)		
	26	50	80
Reaction time (h)	2	2	2
Conversion of PC (wt.%)[b]	69.76	23.25	18.11
Rate of PC conversion (mmolg^{-1}h^{-1})[c]	21.48	7.16	5.57
Product distribution (wt.%)			
4-MOPP	85.37	82.07	84.93
2-MOPP	11.88	12.95	6.98
Others	2.74	4.98	8.09

a,b,c & d see footnotes to Table 3.7

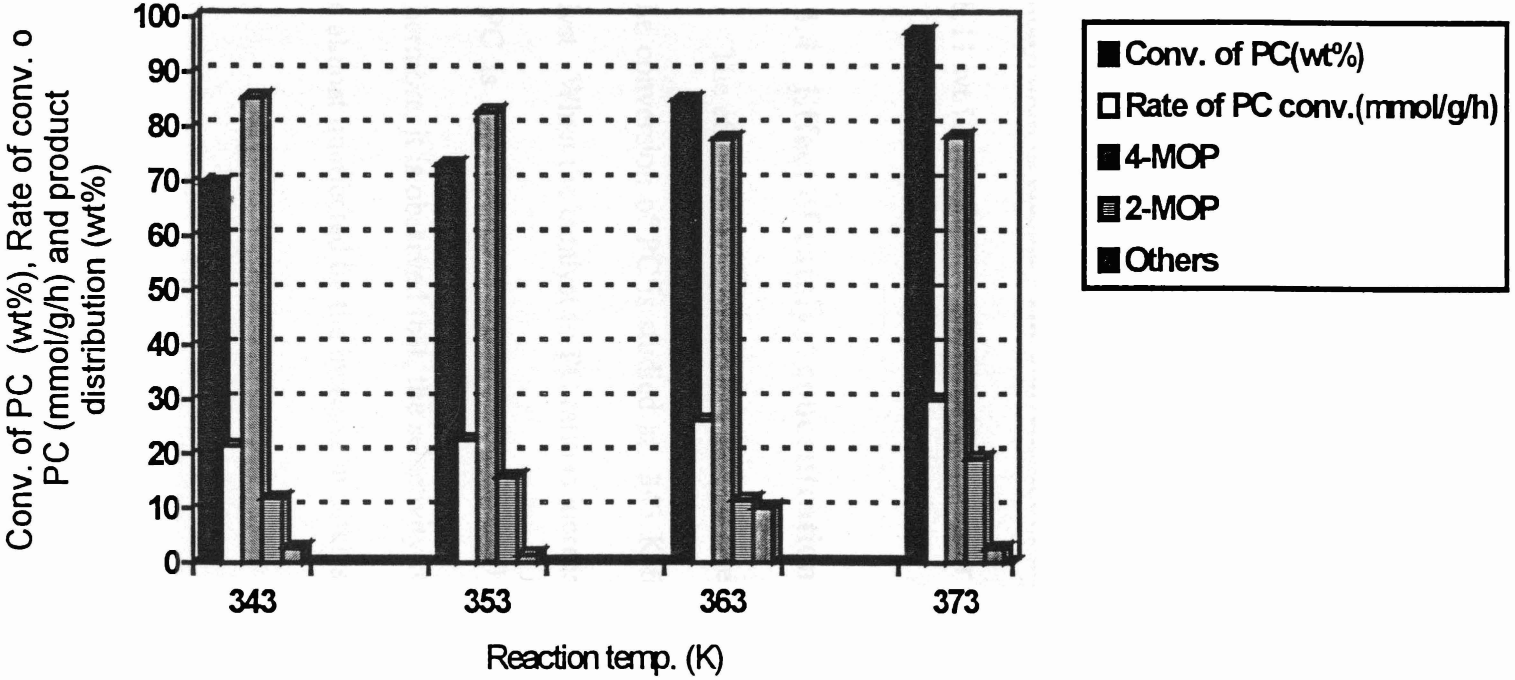


Fig. 3.5 Influence of reaction temperature on the conversion of PC (wt.%), rate of PC conversion (m mol $g^{-1}h^{-1}$) and product distribution.

significantly influenced. The selectivity towards 4-MOPP remains more or less constant in the range of temperature studied (Fig. 3.5).

3.2.3.3 Effect of SiO_2/Al_2O_3 ratio

Table 3.9 shows the effect of SiO_2/Al_2O_3 molar ratio of zeolite H-beta in the propionylation of anisole. The conversion of PC is found to decrease from 69.76 wt.% to 18.11 wt.% with increase in SiO_2/Al_2O_3 molar ratio from 26 to 80.

3.2.3.4 Effect of catalyst concentration

The effect of catalyst concentration in the range of 0.05 to 0.41 g/mole of PC on the conversion of PC is studied at 343 K for 2h of reaction over zeolite H-beta catalyst. When the catalyst to PC ratio is increased from 0.05 to 0.41, the conversion of PC is also found to increase from 50.20 wt.% to 64.15 wt.% (Table 3.10). Furthermore, it is observed that, the selectivity of the major product, 4-MOPP is found to be almost unaffected by the increase in catalyst concentration (Fig. 3.6).

3.2.3.5 Effect of anisole/PC molar ratio

Figure 3.7 shows the effect of varying the anisole /PC molar ratio in the reaction mixture on the activity of H-beta and product distribution at a fixed anisole concentration. An increase in both the conversion of PC selectivity of 4-MOPP is observed with increase in anisole /PC molar ratio. The conversion of PC at 1, 3, 5 and

Table 3.10 Effect of catalyst concentration[a]

Catalyst/PC (wt./wt.)	Convertion [b] of PC (wt%)	Rate of PC conversion(mmolg^{-1}h^{-1})	Product distribution(wt%)[d]		
			4-MOPP	2-MOPP	others
0.05	50.20	46.38	87.23	8.13	4.64
0.17	69.76	21.48	85.37	11.88	2.74
0.29	65.32	12.07	76.05	13.48	10.46
0.41	64.15	8.46	74.80	19.12	6.08

a,b,c & d see foot notes to Table 3.7 ; reaction time (h) = 2

Table 3.11 Effect of anisole/PC molar ratio[a]

Anisole/PC (wt./wt.)	Convertion [b] of PC (wt%)	[c]Rate of PC conversion (mmolg^{-1}h^{-1})	Product distribution(wt%)[d]		
			4-MOPP	2-MOPP	others
1	15.50	23.89	60.03	36.85	3.11
3	31.14	15.98	83.35	14.03	2.6
5	69.76	21.48	85.37	11.88	2.74
7	71.66	15.74	88.95	10.69	0.35

a,b,c & d see foot notes to Table 3.7 ; reaction time (h) = 2

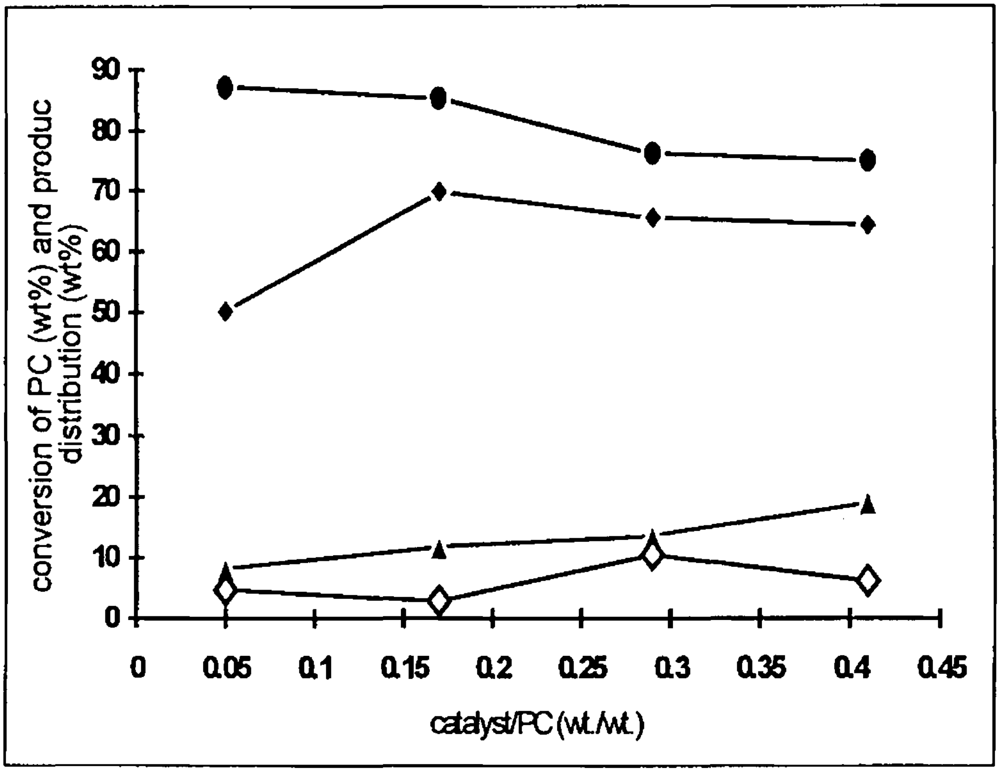


Fig. 3.6 Effect of catalyst/PC molar ratio on the conversion of PC (♦) and product distribution, 4-MOPP (●), 2-MOPP (▲) and others (◊); Reaction conditions: see footnotes to Table 3.7; reaction time (h)= 2

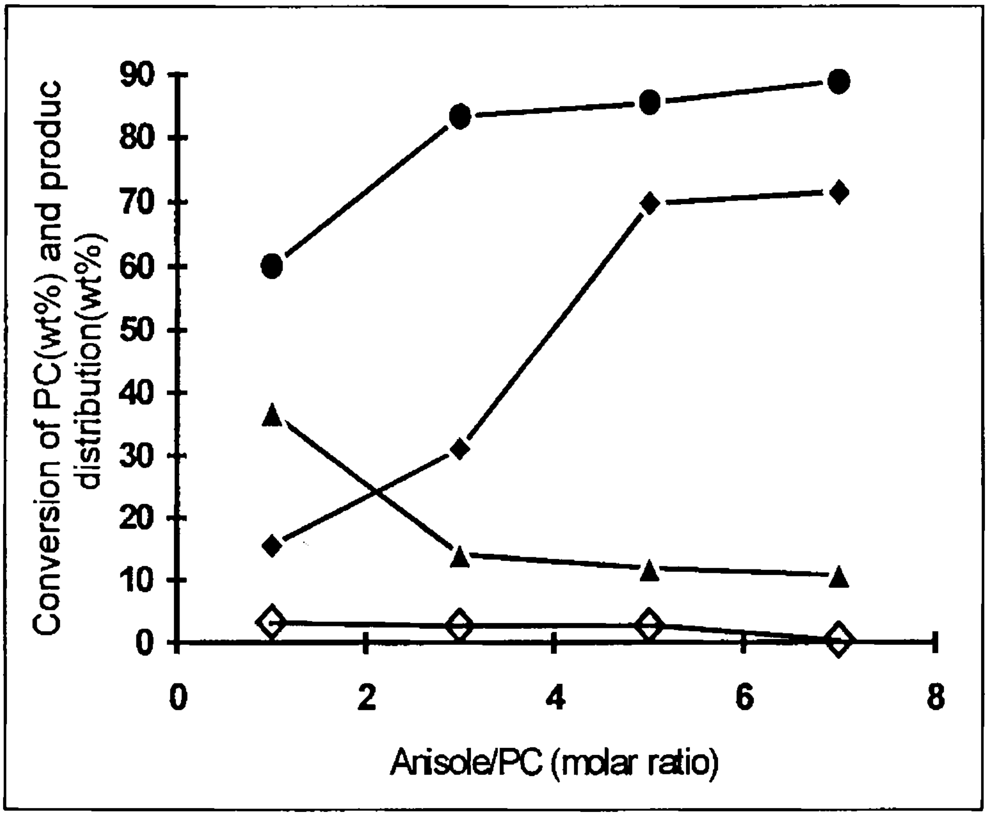


Fig. 3.7 Effect of anisole /PC molar ratio on the conversion of PC (♦) and product distribution, 4-MOPP (●), 2-MOPP (▲) and others (◊); Reaction conditions: see footnotes to Table 3.7; reaction time (h) = 2.

Table 3.12 Recycling of H-beta [a]

Run	Change in SiO_2/Al_2O_3 (molar ratio)	Conversion[b] of PC(wt.%)	Rate of PC[c] conv. (mmolg^{-1}h^{-1})	Product distribution (wt%)[d]			% crystallinity of H-beta
				4-MOPP	2-MOPP	Others	
1(parent catalyst)	26.0	68.73	21.16	68.85	23.58	7.57	100
2	29.56	41.32	12.72	61.03	29.51	9.46	79.1
3	31.38	29.89	9.2	58.72	31.43	9.85	75.3

a,b,c & d see foot notes to Table 3.7 ; reaction time (h) = 2

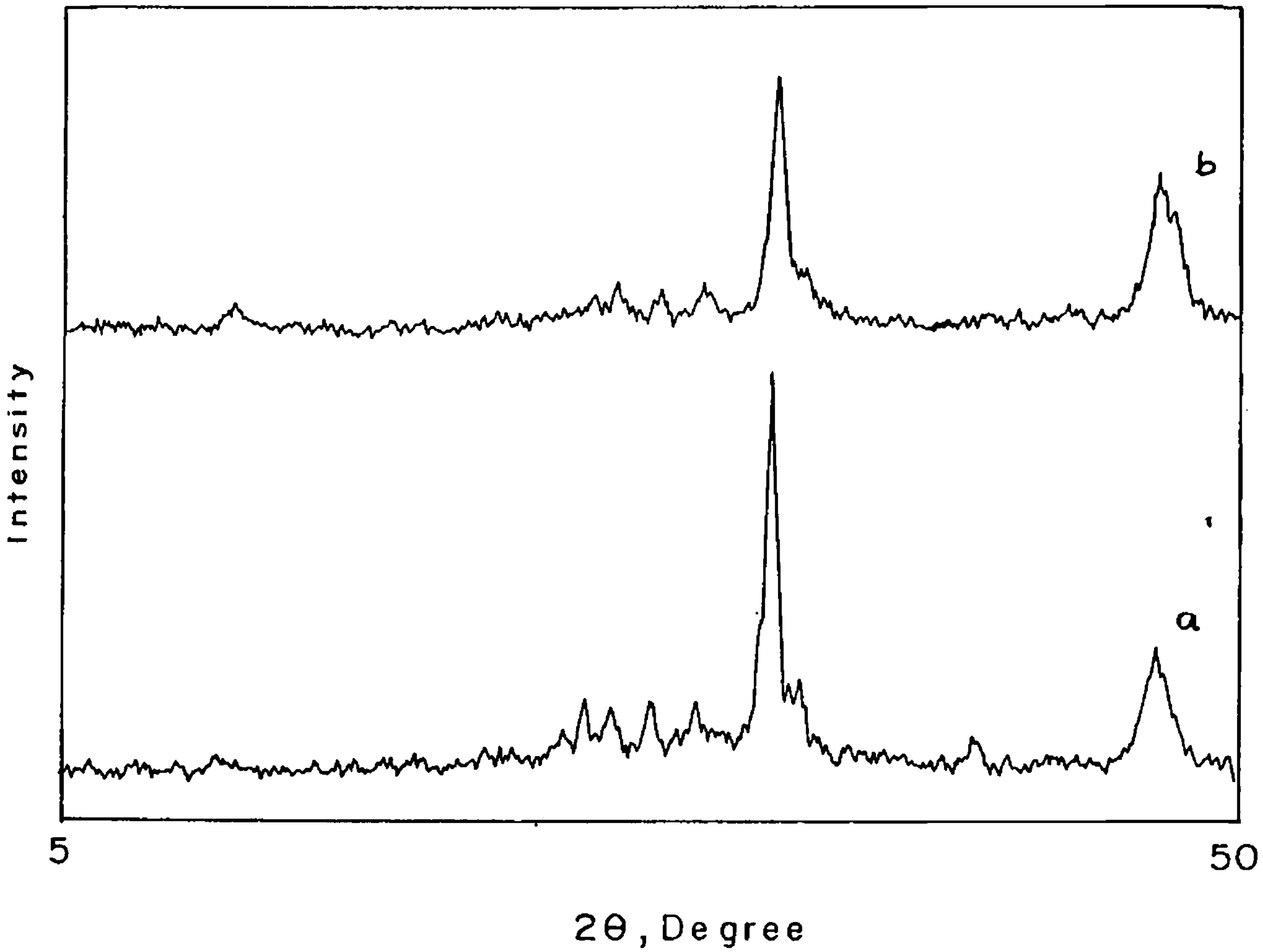


Fig. 3.8 X-ray diffraction patterns of (a) fresh H-beta and (b) H-beta after recyling

$AlCl_3$ > H-beta > H-RE(70.6)-Y > H-Na(13.6)-beta > H-ZSM-5 > H-RE(42.2)-Y > H-Y > H-mordenite > H-Na(37.3)-beta > SiO_2-Al_2O_3(amorphous)

The yield of the product decreases with an increase in SiO_2-Al_2O_3 ratio of H-beta. A higher yield of methoxypropiophenone is obtained by increasing the reaction temperature, catalyst concentration and molar ratios of anisole to propionyl chloride.

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CHAPTER IV

BENZOYLATION OF *O*-XYLENE

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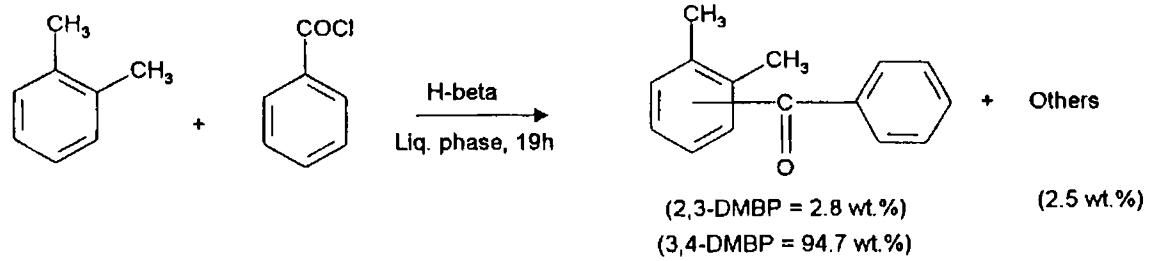
4.1 Introduction

3,4-Dimethyl benzophenone is used for the production of dyes and several organic intermediates for the production of fine chemicals. Traditionally, these reactions are carried out using homogeneous Lewis acid catalysts such as $AlCl_3$, $TiCl_4$, $FeCl_3$ and H_2SO_4 [1]. Homogeneous catalysts have several disadvantages: difficulty in catalyst recovery, separation of the final product from the catalyst and use of stoichiometric amounts of the catalyst with respect to the benzoylating agent. In addition, these halides of iron and aluminium, being strong Lewis acids, also catalyze other undesirable side reaction like production of a substantial amounts of consecutive products. In addition, the use of $Fe(CO)_5$ [2], Fe (II) phthalocyanine [3] and metal oxides like Fe_2O_3, ZnO, MoO_3 and Na_2WO_4 etc. [4] have been reported for the benzoylation of *o*-xylene with benzoyl chloride. This reaction is also known to proceed over $AgNO_3$ catalyst using acid chloride as the acylating agent [5]. These non-shape selective catalysts gave a lower selectivity for 3,4-DMBP.

Zeolite catalysts have been widely used in the field of petrochemistry [6, 7] due to their shape-selectivity, thermostability, the easy separation from the products and the possibility of regeneration of the deactivated catalysts. However, their use in fine organic synthesis has been limited [8-10]. Recently zeolite catalysts were found to be active in the acylation of aromatics [11-20]. However, there is no report to date on the benzoylation of *o*-xylene using zeolite H-beta as catalyst. The objective of the present work is to replace the homogeneous non shape-selective Lewis acid catalyst, $AlCl_3$, by the shape-selective and environmentally friendly zeolite catalyst. The another objective is to enhance the selectivity for 3,4-DMBP and consequently to minimize the formation of consecutive products using zeolite catalysts.

In this chapter, we disclose a new catalytic method for the selective benzoylation of *o*-xylene to 3,4-DMBP using zeolite H-beta as catalyst and benzoyl chloride as benzoylating agent (Scheme:1). The catalyst and process parameters are optimized to enhance the conversion of BOC and selectivity to 3,4-DMBP. The results obtained over zeolite catalysts are compared with the conventional catalyst $AlCl_3$ and amorphous SiO_2-Al_2O_3.



(Scheme: 1)

4.2 Experimental

4.2.1 Catalyst preparation

Zeolites ZSM-5 and beta were synthesized and modified following the procedures described in literature [21,22]. The detailed procedure is reported in section 2.2.1.

4.2.2 Catalyst characterization

Table 2.3 lists the chemical composition and the major characteristics of the various zeolite samples. The detailed experimental procedure for the various characterization techniques are described in Section 2.2.2.

4.2.3 Catalytic testing

The liquid phase catalytic runs were carried out batchwise in a mechanically stirred, closed 50 ml glass reactor fitted with a reflux condenser, a thermometer and a septum for withdrawing the product samples. The temperature of the reaction vessel was maintained using an oil bath. In a typical run, appropriate amounts of *o*-xylene and benzoyl chloride (5:1molar ratio) was charged in the reactor along with 0.75g catalyst. The reaction mixture was heated to 411 K under stirring. Samples were withdrawn periodically and analysed with a gas chromatograph.

Conversion of BOC is reported as the wt.% of the BOC is consumed. The rate of BOC conversion (mmolg^{-1}h^{-1}) indicates moles of BOC converted per g of catalyst in an hour. The product distribution (selectivity) wt.% for a product is expressed as the amount of the particular product divided by the amount of total products and multiplied by 100.

4.3 Results and discussion

4.3.1 Catalyst characterization

The zeolites used in this study and their physico-chemical properties are presented in Table 2.3. The crystallinity and phase purity of the zeolite samples as well as the absence of amorphous matter within their pore structure were first ensured. The x-ray diffraction of all zeolites matched with those in the literature. In addition, XRD examination gave no evidence of structure damage or change of the zeolites as a result of various treatments. The surface area and scanning electron micrographs showed the absence of amorphous matter inside the channel as well as on the external surface of the zeolites, respectively.

All the samples consisted of particles of about 0.4-1.0 μm. Table 2.3 also list the chemical composition and acidity data of zeolites used in the present study.

4.3.2 Activity of various catalysts

Table 4.1 shows the conversion of BOC (wt.%), rate of BOC conversion (mmol $g^{-1}h^{-1}$) and the product distribution (wt.%) obtained over various catalysts in the benzoylation of *o*-xylene. Under identical reaction conditions, 3,4-dimethybenzophenone (3,4-DMBP) and 2,3-dimethylbenzophenone (2,3-DMBP) are the main reaction products. In some cases, a significant amount of dibenzoylated products (others) is also formed (Scheme: 1).

Both 2,3-DMBP and 3,4-DMBP are formed by parallel reactions while dibenzoylated products arise from secondary consecutive reactions of mono-benzoylated products [20]. Among zeolite catalysts, H-beta catalyses the reaction efficiently and selectively to 3,4-DMBP and it is found to be superior to other zeolite catalysts and $AlCl_3$. The conversion of BOC, rate of BOC conversion and selectivity for 3,4-DMBP over zeolite H-beta after 19 h of reaction time are found to be 52.8 wt.%, 0.7 m mol $g^{-1}h^{-1}$ and 94.7 wt.%, respectively. Under similar reaction conditions, $AlCl_3$ gave 64.4 wt.% conversion of BOC with a selectivity of 76.5 wt.% for 3,4-DMBP. Presumably, the higher activity of H-beta may be attributed to its stronger acid sites (Table 2.3) [12, 17-19]. The higher selectivity of H-beta for 3,4-DMBP might be due to its

Table 4.1 Benzoylation of o-xylene [a]

Catalyst	Reaction time (h)	Conversion [b] of BOC (wt%)	Rate of[c] BOC conversion (mmolg^{-1}h^{-1})	Product distribution (wt.%)[d]		
				2,3-DMBP	3,4-DMBP	Others
H-ZSM-5	1	0.8	0.2	-	35.1	64.9
	19	4.4		-	47.3	52.7
H-beta	1	12.0	3.0	-	100.0	-
	19	52.8	0.7	2.8	94.7	2.5
H-Na(13.6) -beta[e]	1	4.7	1.2	-	100.0	-
	19	29.4		1.8	94.9	3.3
H-Na(37.3) -beta[e]	1	3.1	0.8	-	94.5	5.5
	19	6.3		-	92.3	7.7
H-mordenite	1	0.7	0.2	-	100.0	-
	19	7.7		1.1	75.0	23.9
H-Y	1	3.4	0.9	6.8	75.2	18.0
	19	12.6		7.5	79.1	13.4
H-RE (42.2)-Y[f]	1	7.1	1.8	6.1	64.9	29.0
	19	32.7		8.8	81.2	10.0
H-RE (70.6)-Y[f]	1	11.6	2.9	7.7	76.2	16.1
	19	49.6		8.8	87.7	3.5
$AlCl_3$	1	64.4	16.2	7.3	76.5	16.2
SiO_2-Al_2O_3 (amorphous)	1	1.9	0.5	67.8	24.4	7.8
	19	3.5		53.9	30.6	15.5

[a] Reaction conditions: catalyst (g) = 0.75; catalyst / C_6H_5COCl (wt./wt.) = 0.28; o-xylene / C_6H_5COCl (molar ratio) = 5; o-xylene (mol) = 0.09; reaction temperature(K)=411

[b] BOC = benzoyl chloride (C_6H_5COCl)

[c] Rate of BOC conversion(mmolg^{-1}h^{-1}) = (amount of BOC reacted)/(weight of catalyst x reaction time)

[d] 2,3-DMBP = 2,3-dimethylbenzophenone; 3,4-DMBP = 3,4-dimethylbenzophenone; others= secondary benzoylated products (consecutive products)

[e] Values in parenthesis represents the percentage of Na exchanged in the H-beta

[f] Values in parenthesis represents the percentage of RE^{+3}-exchanged in zeolite H-Y

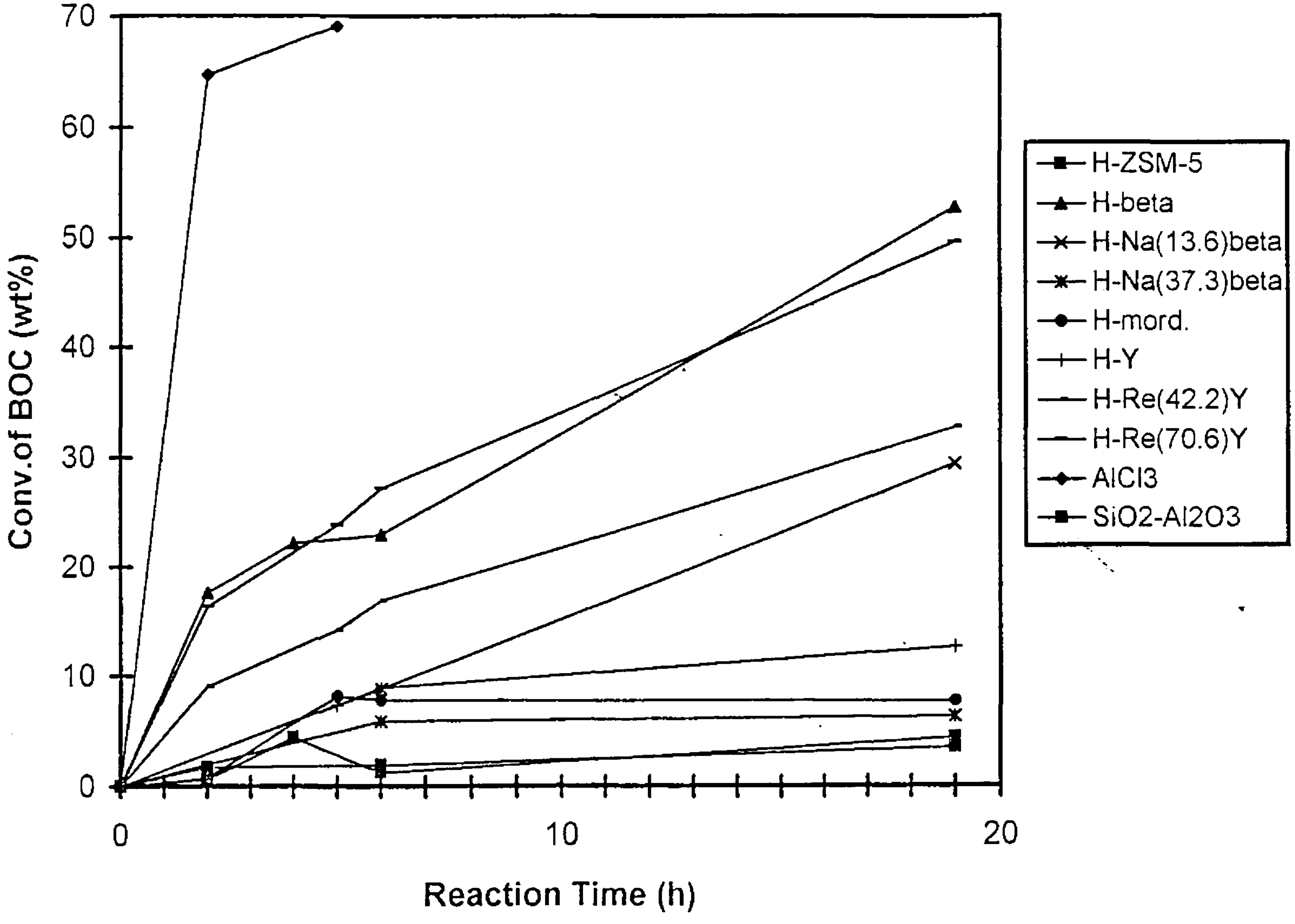


Fig. 4.1 Conversion of BOC versus reaction time over various zeolites; Reaction conditions: see footnotes to Table 4.1.

smaller pore openings (7.5 x 5.5Å) than H-Y (7.4 Å) zeolite catalysts. The small pores of zeolite H-beta prevent the secondary reactions in the zeolite channels and consequently the formation of dibenzoylated products of *o*-xylene. The lower activity of H-ZSM-5 may be attributed to its small pore openings (5.4 x 5.6 and 5.1 x 5.5 Å) than the size of the *o*-xylene and reaction products.

When H-Y is exchanged to H-RE(42.2)-Y and H-RE(70.6)-Y, the catalytic activities are enhanced considerably which may be due to the higher strength of acid sites generated by RE^{+3}-cations [18, 19]. The activity of H-beta decreases drastically with the increase in Na^+- content of H-beta. The conversion of BOC (wt.%) over H-beta, H-Na(13.6)- beta and H-Na(37.3)- beta catalysts after 19 h of reaction time is found to be 52.8, 29.4 and 6.3 wt.%, respectively. The lower activity of Na-exchanged beta may be attributed to the removal of some amount of stronger Bronsted acid sites by Na^+ ion exchange in H-beta.

4.3.3 Duration of the run

The relationship between conversion of BOC (wt.%) and reaction time for the benzoylation of *o*-xylene over various zeolite catalysts is illustrated in Fig. 4.1. Reaction conditions were those detailed in Table 4.1. $AlCl_3$ gave higher conversion of BOC compared to other catalysts but it is a poor catalyst in terms of selectivity. The conversion of BOC over zeolite H-beta is found to be increased with the increase in reaction time and reaches a maximum (52.8 wt%) in 19 h of the run. Zeolites H-ZSM-5, H-mordenite and amorphous SiO_2-Al_2O_3 exhibit comparatively lower activities in this reaction. Based on the conversion of BOC after 19 h of reaction time, the trend in activities for the catalysts studied is as follows:

$AlCl_3$ > H-beta > H-RE(70.6)-Y > H-RE(42.2)-Y > H-Na(13.6)-beta > H-Y > H-mordenite > H-Na (37.3)-beta > H-ZSM-5 > amorphous SiO_2-Al_2O_3.

The results of the preceding section have revealed that zeolite H-beta is the best catalyst for the benzoylation of *o*-xylene to 3,4-DMBP. The influence of various parameters on the conversion of BOC, rate of BOC conversion and product distribution over H-beta is reported in the following sections.

4.3.4 Effect of SiO_2/Al_2O_3 ratio

The results obtained for the benzoylation of *o*-xylene over different SiO_2/Al_2O_3 ratios of H-beta are presented in Table 4.2. It is shown that the conversion of BOC in the benzoylation of *o*-xylene is markedly affected by the SiO_2/Al_2O_3 molar ratio of H-beta. The higher the SiO_2/Al_2O_3 molar ratio of H-beta, the lower the BOC conversion. The conversion of BOC over 26, 50 and 80 SiO_2/Al_2O_3 molar ratios of H-beta is found to be 25.9, 7.6 and 3.9 wt.%, respectively. The corresponding selectivity for 3,4-DMBP is 96.7, 96.2 and 100 wt.%, respectively.

4.3.5 Effect of reaction temperature

The temperature dependency of this reaction is shown in Table 4.3. The rate of BOC conversion over zeolite H-beta increases steadily from 0.9 to 3.9 mmol$g^{-1}h^{-1}$ as the temperature is raised from 393 to 411 K. The selectivity for 3,4-DMBP remains nearly constant through out the range of temperature studied.

4.3.6 Effect of catalyst concentration

The effect of catalyst concentration in the range of 0.19 to 0.38 g/mol of BOC on the conversion of BOC is studied at 411 K for 6 h of reaction over zeolite H-beta as catalyst (Table 4.4). The catalyst to BOC ratios are changed by keeping the constant concentration of BOC in the reaction mixture. When the catalyst to BOC ratio is increased from 0.19 to 0.38, the conversion of BOC is also found to increase from 9.8 to 35.7 wt.%, respectively (Fig. 4.2). Furthermore, it is observed that the concentration of the unwanted products (others) decreases with the increase in catalyst/ BOC ratio. These results confirm that with an increase in catalyst loading the conversion of BOC increases linearly because of the increase in the total number of acid sites available for the reaction.

4.3.7 Effect of *o*-xylene / BOC molar ratio

Fig. 4.3 shows the effect of varying the *o*-xylene/BOC molar ratio in the reaction mixture on the activity of H-beta and product distribution at a fixed *o*-xylene concentration. Thus an increase in the conversion of BOC is observed with the increase in

Table 4.2 Effect of SiO_2 / Al_2O_3 ratio of zeolite H-beta[a]

	SiO_2/Al_2O_3 molar ratio		
	26	**50**	**80**
Reaction time (h)	6	6	6
Conversion of BOC (wt.%)[b]	25.9	7.6	3.9
Rate of BOC conversion ($mmolg^{-1}h^{-1}$)[c]	1.1	0.3	0.2
Product distribution (wt.%)[d]			
2,3-DMBP	1.2	-	-
3,4-DMBP	96.7	96.2	100
Others	2.1	3.8	-

a,b,c &d see footnotes to Table 4.1

Table 4.3 Effect of reaction temperature[a]

Reaction temp.(K)	Conversion of[b] BOC (wt%)	Rate of BOC[c] conversion($mmolg^{-1}h^{-1}$)	Product distribution (wt.%)[d]		
			2,3-DMBP	3,4-DMBP	Others
393	4.8	0.9	-	100	-
400	9.1	1.7	-	100	-
411	20.8	3.9	1.9	96.0	2.1

[a] Reactions conditions: catalyst (H-beta) =1g; catalyst / C_6H_5COCl (wt/wt) = 0.38; o-xylene /C_6H_5COCl (molar ratio) =5; o-xylene (mol) = 0.09; reaction time (h)= 1

[b,c& d] see footnotes to Table 4.1

Table 4.4 Effect of catalyst concentration[a]

Catalyst/BOC (wt./wt.)	Conv. [b] of BOC (wt%)	Rate of BOC conversion(mmolg^{-1}h^{-1})	Product distribution(wt%)[d]		
			2,3-DMBP	3,4-DMBP	others
0.19	9.8	0.6	-	94.4	5.6
0.28	25.9	1.1	1.5	94.8	3.7
0.38	35.7	1.1	1.7	96.3	2.0

a,b,c & d see foot notes to Table 4.1 ; reaction time (h) = 1

Table 4.5 Effect of o-xylene/BOC molar ratio[a]

o-xylene/BOC (wt./wt.)	Convertion [b] of BOC (wt%)	Rate of BOC conversion(mmolg^{-1}h^{-1})	Product distribution(wt%)[d]		
			2,3-DMBP	3,4-DMBP	others
1	3.2	1.0	-	87.9	12.1
3	15.1	1.6	1.8	93.6	4.6
5	22.1	1.4	2.4	95.5	2.1
7	28.7	1.8	2.3	96.2	1.5

a,b,c & d see foot notes to Table 4.1 ; reaction time (h) = 1

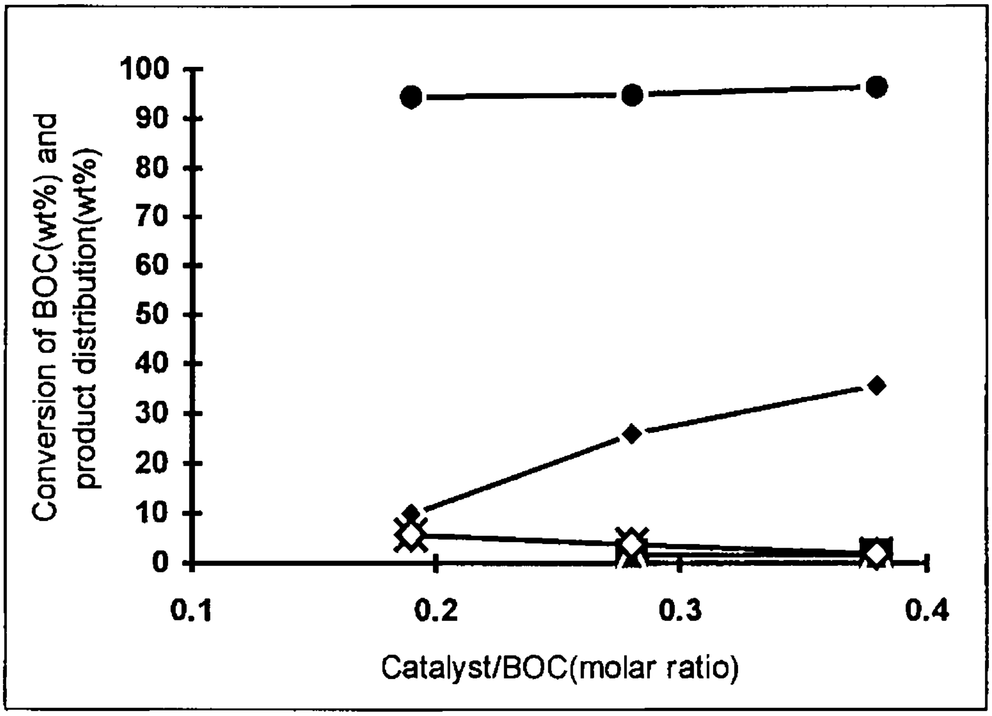


Fig. 4.2 Effect of catalyst/BOC molar ratio on the conversion of BOC (♦) and product distribution, 2,3-DMBP (▲), 3,4-DMBP (●) and others (◊); Reaction conditions: see footnotes to Table 4.1; reaction time (h)=6.

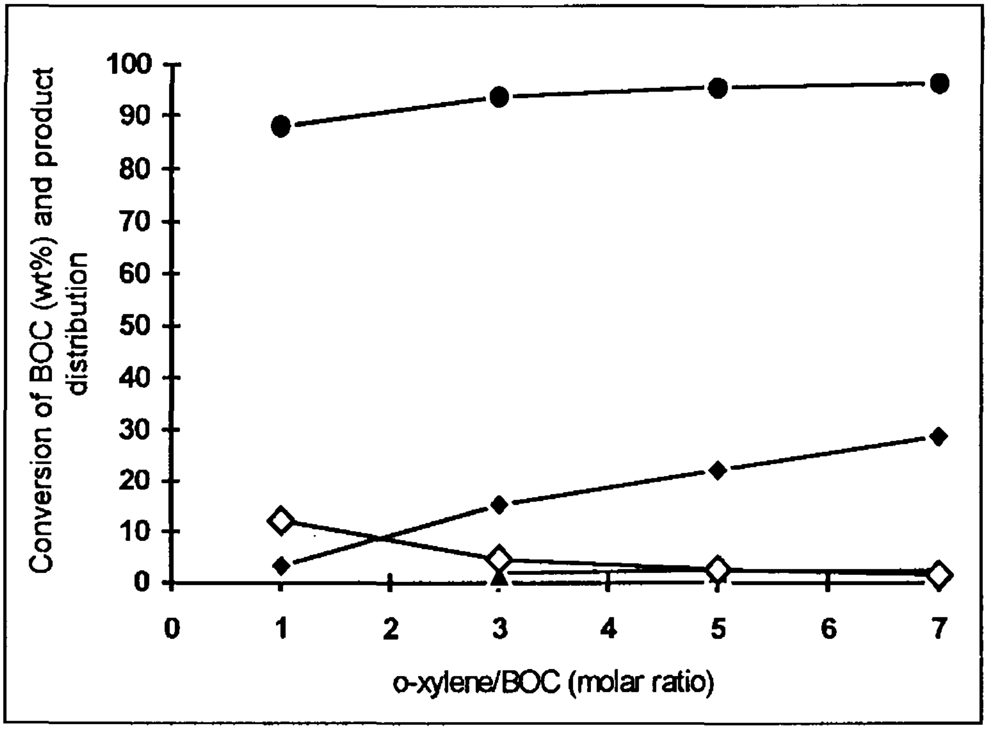


Fig. 4.3 Effect of o-xylene/BOC molar ratio on the conversion of BOC (♦) and product distribution: 2,3-DMBP (▲), 3,4-DMBP (●) and others (◊); Reaction conditions: see footnotes to Table 4.1; reaction time (h)= 4.

o-xylene/BOC molar ratio. The conversion of BOC at 1, 3, 5 and 7 molar ratios of *o*-xylene to BOC is found to be 3.2, 15.1, 22.1 and 28.7 wt.%, respectively (Table 4.5). The selectivity for 3,4-DMBP remains roughly constant beyond the molar ratio of 3 (*o*-xylene/BOC). The formation of dibenzoylated products (others) is minimized with the increase of *o*-xylene to BOC molar ratios in the benzoylation of *o*-xylene (Fig. 4.3).

4.3.8 Catalyst recycle

The results of the catalyst recycling experiments using zeolite H-beta in the benzoylation of *o*-xylene are shown in Table 4.4. After completion of the reaction of each recycle for 6 h, the catalyst was removed by filtration from the reaction solution, washed thoroughly with acetone, calcined at 773 K for 16 h in the presence of air and characterised for its chemical composition (SiO_2/AlO_3) and crystallinity. The activity of the catalyst decreases progressively on recycling, however, selectivity for 3,4-DMBP remains unaffected (Table 4.6). In order to check the structure and crystallinity of the catalyst after reaction, X-ray powder diffraction patterns were recorded. XRD measurement indicated that the catalyst retains the H-beta structure and the crystallinity was found to be 71.4 % (after third recycle) when compared to the parent catalyst (100 % crystallinity) (Table 4.6, Fig. 4.4). The HCl liberated during the reaction promotes the extraction of aluminum to some extent from the framework positions of the zeolite H-beta. Such types of extractions and a little decrease in crystallinity of H-beta may be responsible for the decrease in catalytic activity after each cycle. The results reported

Table 4.6 Recycling of H-beta in the benzoylation of o-xylene[a]

Run	Change in SiO_2/Al_2O_3 (molar ratio)	Conversion[b] of BOC (wt.%)	Rate of BOC[c] conv. ($mmol g^{-1} h^{-1}$)	Product distribution (wt%)[d]			% crystallinity of H-beta
				2,3-DMBP	3,4-DMBP	Others	
1(parent catalyst)	26.0	25.9	1.1	1.2	96.7	2.1	100
2	27.56	12.4	0.5	-	96.8	3.2	80.5
3	29.38	8.1	0.3	-	96.7	3.3	71.4

[a] Reaction conditions same as given in Table 4.1; reaction time(h) = 6

[b,c & d] see footnotes to Table 4.1

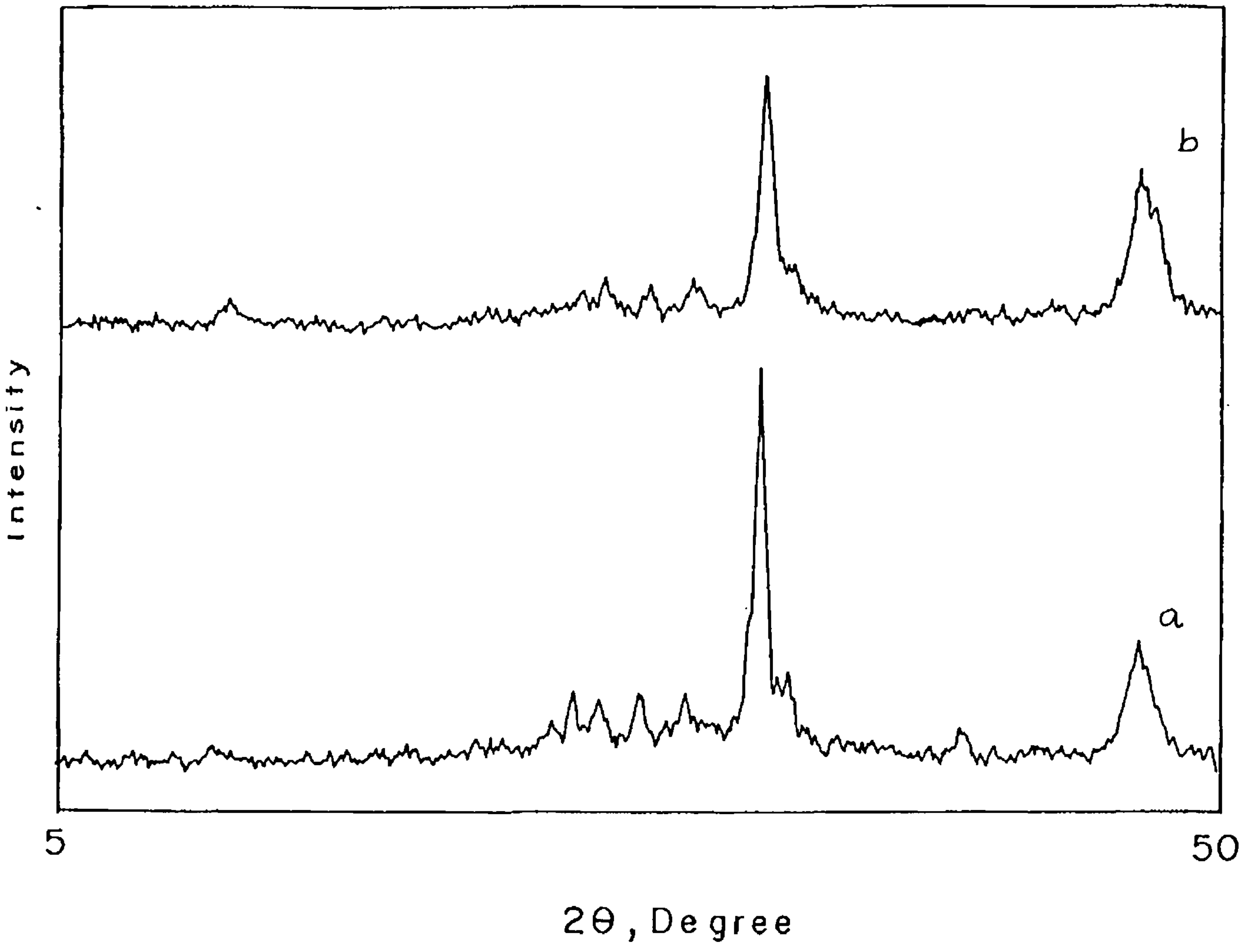


Fig. 4.4 X-ray diffraction patterns of (a) fresh H-beta and (b) H-beta recycled third time.

here are in good agreement with the earlier reported data for the acylation of aromatics using zeolite catalysts [18].

4.3.9 Benzoylation of isomeric xylenes (o-, m-, p-)

Ortho-, meta- and para- xylenes are separately acylated by benzoyl chloride over H-beta catalyst at 411 K under identical reaction conditions. The performance of zeolite H-beta is compared with that of conventional catalyst, $AlCl_3$, for each reaction. The results are shown in Table 4.7. The position of methyl groups on the benzene ring plays an important role in defining the type of products. The benzoylation of *o*-xylene leads to the formation of 3,4-DMBP in higher selectivity (94.7 wt.%). With $AlCl_3$, the benzoylation of *o*-xylene gave a conversion of BOC 64.4 wt% and a product selectivity (3,4-DMBP) of 76.5 wt%. With m-xylene, the reaction gives mainly 2,4-DMBP with a selectivity of 91 wt%. For the same reaction, $AlCl_3$ gave 91.3 wt.% selectivity and 78.2 wt.% conversion of BOC. Similarly, benzoylation of p-xylene gives almost single monoacylated product i.e. 2,5-DMBP with a BOC conversion of 22.1 wt.% and a selectivity of 96.7 wt.%. With $AlCl_3$, the BOC conversion and selectivity are 87.2 wt.% and 85.8 wt.% respectively. It can be concluded that xylenes may be benzoylated to the corresponding ketones [26, 27].

Table 4.7 Benzoylation of xylenes (o-,m-,p-)[a]

Xylenes	Catalyst	Reaction time(h)	Conversion[b] of BOC(wt%)	Rate of BOC[c] conversion(mmolg^{-1}h^{-1})	Product distribution (wt%)[d]					
					2,3-DMBP	3,4-DMBP	2,6-DMBP	2,4-DMBP	2,5-DMBP	Others
o-xylene	H-beta	1	12.0	3.0	-	100.0	-	-	-	-
		19	52.8	-	2.8	94.7	-	-	-	2.5
	AlCl$_3$	1	64.4	16.2	7.3	76.5	-	-	-	16.2
m-xylene	H-beta	1	4.3	1.1	-	-	12.3	85.7	-	2.0
		19	15.5	-	-	-	7.0	91.0	-	2.0
	AlCl$_3$	1	78.2	19.7	-	-	6.4	91.3	-	2.3
p-xylene	H-beta	1	6.2	1.6	-	-	-	-	93.3	6.7
		19	22.1	-	-	-	-	-	96.7	3.3
	AlCl$_3$	1	87.2	21.9	-	-	-	-	85.8	14.2

[a,b& c] see footnotes to Table: 2

[d] 2,3-DMBP = 2,3-dimethylbenzophenone; 3,4-DMBP = 3,4-dimethylbenzophenone; 2,6-DMBP = 2,6-dimethylbenzophenone; 2,4-DMBP = 2,4-dimethylbenzophenone; 2,5-DMBP= 2,5-dimethybenzophenone ; others = concecutive products

4.3.10 Mechanism

It seems reasonable from the results presented in this chapter and earlier reports [12, 18] that the benzoylation of *o*-xylene proceeds through electrophilic substitution.

Fig. 4.5 shows the schematic diagram of the catalytic cycle which is in agreement with the reported data [12, 18, 25-29]. The Figure suggests that acidic zeolite polarizes the benzoyl chloride molecule into an electrophile ($C_6H_5CO^+$) which then attacks the *o*-xylene ring resulting in the formation of dimethylbenzophenones.

4.4 Conclusions

In summary, *o*-xylene can be benzoylated selectively to 3,4-DMBP using zeolites as catalyst and benzoyl chloride as benzoylating agent. Zeolite H-beta exhibits higher activity and selectivity than that of the other zeolite catalysts. Conventional homogeneous non shape-selective Lewis acid catalyst $AlCl_3$ produces a higher amount of dibenzoylated products (consecutive products) and lower amount of 3,4-DMBP under identical reaction conditions. The higher activity of H-beta may be attributed to its stronger acid sites and mesoporous system.

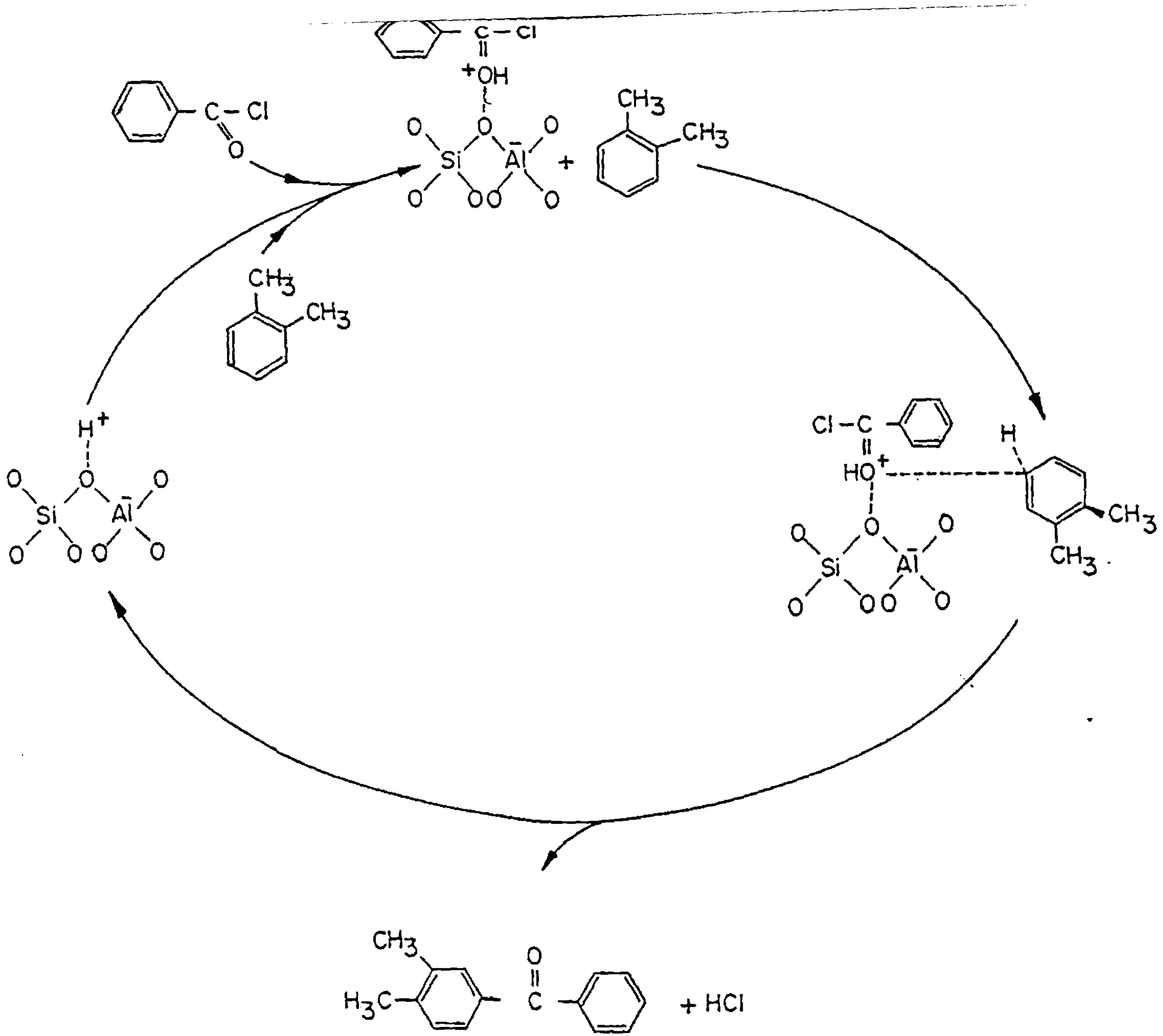


Fig. 4.5 · A plausibe mechanism for the benzoylation of o-xylene using zeolite catalyst and benzoyl chloride

The catalytic activity of H-Na(13.6)-beta and H-Y were found to be almost identical. However, the former was more selective due to the small pore openings than that of H-Y. RE^{+3}- exchanged zeolite Y enhanced the conversion of BOC considerably due to the higher strength of acid sites generated by RE^{+3}- cations. H-ZSM-5 and H-mordenite were found to be less active compared to other zeolite catalysts.

The higher yield of product can be achieved by increasing the values of the reaction parameters such as: reaction time, catalyst concentration and reaction temperature, while the conversion is found to decrease with SiO_2/Al_2O_3 molar ratio and Na^+ ion exchange of H-beta. The decrease in activity with recycling experiments may be attributed in part to the changes in chemical composition and crystallinity of zeolite H-beta by HCl, which is a by-product of the reaction. The formation of dimethyl benzophenone is explained by an electrophilic attack of the benzoyl cation ($C_6H_5CO^+$) on the *o*-xylene ring whose formation is facilitated by the stronger acid sites of catalyst.

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CHAPTER V

BENZYLATION OF *O*-XYLENE

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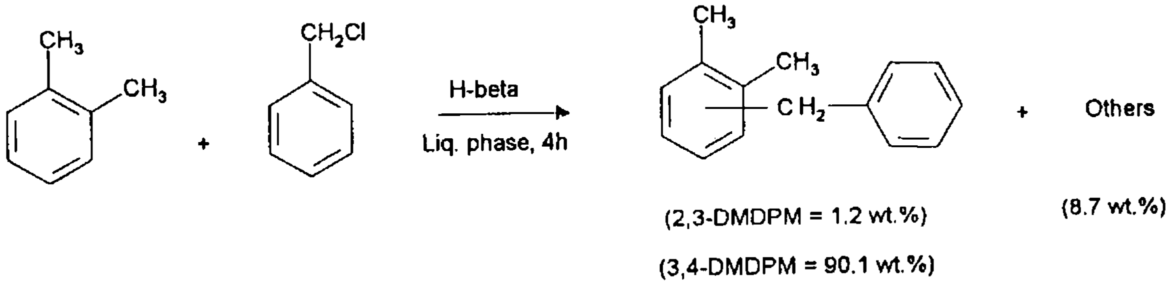
BENZYLATION OF *O*-XYLENE

5.1 Introduction

Dimethyldiphenylmethanes are used as synthetic intermediates for the production of dielectric fluids [1]. Benzylation of *o*-xylene with benzyl chloride, which is a typical example of Friedel-Crafts alkylation, is generally known to proceed over homogeneous Lewis acid catalyst, $AlCl_3$ [2]. Olah has surveyed the Lewis acids used as catalyst in the Friedel-Crafts reactions and has provided a scale of their efficiency [3]. However, use of standard Lewis acid catalysts is fraught with problems such as their handling, the necessity of using large amounts with substrates and removal from the products. In addition, halides of iron and aluminum, being strong Lewis acids also catalyze other undesirable reactions like alkyl isomerization and trans alkylation reactions [4]. For such reasons, and also because of a greater ease of set up and work up, several solid acid catalysts relevant to Friedel-Crafts reactions have recently been developed to replace conventional problematic homogeneous catalysts; those include heteropoly acid [5], montmorillonite supported transition metals [6], the graphite-aluminum-chloride intercalate [7], modified alumina [8], transition metal cations [9], sulfated zirconia [10], calcined nickel sulphate [11, 12] and clays [13-17]. These heterogeneous catalysts have shown drawbacks such as lower para-selectivity, formation of higher amount of polyalkylated products and drastic reaction conditions.

Zeolite catalysts due to their shape-selectivity, thermostability, the easy separation from the products and the possibility of regeneration of the deactivated catalysts are used extensively in the petroleum refining and petrochemical industries for various cracking, hydrocracking, isomerization, alkylation, dehydrogenation and rearrangement reactions of hydrocarbons and their derivatives. During the last decade, a beginning has also been made in their use as selective chlorination and oxidation catalysts [4, 18]. The use of zeolite catalysts in the synthesis of fine chemicals is an increasing area of application of growing importance in recent years [19]. By contrast, the utility of zeolite catalysts in the benzylation of aromatic compounds has not been explored in sufficient detail [20]. In this chapter, we report the benzylation of *o*-xylene with benzyl chloride over zeolite H-beta for the first time.

The objective of this study is to enhance the conversion of *o*-xylene and selectivity for 3,4-DMDPM and consequently to minimize the formation of polyalkylated products over zeolite catalysts in the benzylation of *o*-xylene (Scheme: 1). Here we report the results obtained in the benzylation of *o*-xylene under various reaction conditions and on the effects of some catalyst variables on catalyst performance. The results obtained over zeolite H-beta are also compared with the Lewis acid catalyst, $AlCl_3$.



(Scheme: 1)

5.2 Experimental

5.2.1 Materials

Zeolites Na-Y and H-mordenite were obtained from Laporte Inorganics, Cheshire, U.K. Zeolites ZSM-5 and beta were prepared using the methods described in the literature (21, 22). The detailed procedure is reported in section 2.2.1.

5.2.2 Characterization

The catalysts were characterised using various characterisation techniques. The detailed experimental procedure is reported in section 2.2.2.

5.2.3 Acidity of Zeolites

Temperature programmed desorption (TPD) measurements of ammonia were carried out to evaluate the acidic properties of the zeolites using NH_3 as an adsorbate (Table 2.3) [23, 24].

5.2.4 Catalytic reaction experiments

Anhydrous AR grade chemicals were used without further purification. The liquid phase benzylation of *o*-xylene with benzyl chloride was carried out in a 50 ml. two necked flask attached to a condenser and a septum (used to sample the reaction mixture). The temperature of the reaction vessel was maintained using an oil bath . In a typical run, *o*-xylene and benzyl chloride (5:1 molar ratio) were added to the activated zeolite catalyst (0.5g). The reaction mixture was magnetically stirred and heated to the required temperature at atmospheric pressure. The product samples were analyzed periodically by a gas-chromatograph equipped with a flame ionization detector.

5.3 Results and discussion

5.3.1 Catalyst characterization

Table 2.3 lists the SiO_2/Al_2O_3 ratios, H^+- or Na^+-exchange (%), crystal size and surface areas of zeolites used in this work. These data reveal that zeolite samples are highly crystalline. No reflections of a dense phase or any other zeolite phase are found. Table 2.3 also illustrates the amount of NH_3 desorbed from zeolites in different temperature steps.

5.3.2 Catalytic activity

The results of the catalytic activities in the benzylation of *o*-xylene with benzyl chloride using H-ZSM-5, H-beta, H-Na(13.6)-beta, H-Na(37.3)-beta, H-mordenite and H-Y are depicted in Table 2.3. The results with amorphous SiO_2-Al_2O_3 and Lewis acid catalyst, $AlCl_3$, are compared under identical reaction conditions. The main product of the reaction is 3,4-dimethyl diphenylmethane (3,4-DMDPM). Small amount of 2,3-dimethyldiphenylmethane (2,3-DMDPM) is also observed, however, the concentration of polyalkylated products (others) depends upon the reaction conditions and the type of catalyst used in the study. The formation of 3,4-DMDPM and 2,3-DMDPM results from the aromatic substitution of *o*-xylene by parallel reactions while polyalkylated products are obtained by the consecutive reactions of 3,4-DMDPM and 2,3-DMDPM. The activities of catalysts are compared using data after the initial 1h of the run .

As can be seen from the Table 5.1, zeolites H-beta (12.6 mmol $g^{-1}h^{-1}$) and H-Y (11.6 mmol $g^{-1}h^{-1}$) exhibit nearly comparable activity. However, in terms of selectivity H-beta is found to be more selective (92.2 wt.%) than H-Y (82.6 wt.%) in the benzylation of *o*-xylene. The higher selectivity of H-beta might be explained on the basis of its smaller pore opening (7.5 x 5.5Å) than H-Y (7.4 Å). The results from Table 5.1 show that geometrical constraints produced by H-beta did not allow the formation of bulkier polybenzylated products in the small channels of H-beta and hence a higher selectivity for 3,4-DMDPM is achieved over H-beta than H-Y zeolite. Partial

Table 5.1 Benzylation of o-xylene[a]

Catalyst	Reaction time(h)	Conv.of[b] BC (wt.%)	Rate of BC[c] conv. ($\text{mmolg}^{-1}\text{h}^{-1}$)	Product distribution (wt.%)[d]		
				2,3-DMDPM	3,4-DMDPM	Others
H-ZSM-5	1	0.3	0.1	-	80.1	19.3
	4	4.3		-	79.1	21.9
H-beta	1	33.5	12.6	0.9	92.2	6.9
	4	83.3		1.2	90.1	8.7
H-Na (13.6) - beta[e]	1	19.9	7.5	1.1	90.0	8.9
	4	77.6		1.2	86.4	12.4
H-Na (37.3) - beta[e]	1	17.6	6.6	1.2	91.4	7.4
	4	50.6		1.1	81.8	17.1
H-mordenite	1	1.0	0.4			
	4	3.4		-	88.9	11.1
H-Y	1	30.7	11.6	0.5	82.6	16.9
	4	77.5		0.8	81.4	17.8
$AlCl_3$	1	76.6	28.8	1.6	65.5	32.9
SiO_2/Al_2O_3 (amorphous)	1	0.8	0.3	-	100.0	-
	4	4.5		-	97.7	2.3

[a] Reaction conditions: catalyst (g) = 0.5; catalyst/$C_6H_5CH_2Cl$ (wt./wt.) =0.21, o-xylene/$C_6H_5CH_2Cl$ (molar ratio) =5; o-xylene (mol) = 0.09

[b] BC = benzyl chloride ($C_6H_5CH_2Cl$)

[c] Rate of BC conversion ($\text{mmolg}^{-1}\text{h}^{-1}$) is expressed as the amount of BC converted /wt. of the catalyst x reaction time (h)

[d] 2,4-DMDPM = 2,4-dimethyldiphenylmethane;

3,4-DMDPM = 3,4-dimethyldiphenylmethane; others = consecutive products

[e] Percentage of Na-exchange in H-beta is given in brackets

removal of H^+ by Na^+ -ions in the zeolite H-beta results in much lower activity than H-beta [25]. H-ZSM-5 and H-mordenite are not found to be active in the reaction. The inactivity of H-ZSM-5 may be attributed to its small pore openings than the size of the products. Amorphous SiO_2-Al_2O_3 is also failed to enhanced the conversion of BC. $AlCl_3$ catalyst is found to be more active (28.8 m $molg^{-1}h^{-1}$) compared to all zeolite catalysts, however, a higher amount of consecutive products (32.9 wt%) is obtained due to its non shape-selectivity character. The activity of various catalysts at 363 K after 1h of reaction time is found to be in the decreasing order:

$AlCl_3$ > H-beta > H-Y > H-Na (13.6) beta > H-Na (37.3) beta > H-mordenite > SiO_2-Al_2O_3 > H-ZSM-5

The various parameters on the above reaction are discussed using H-beta in the following section .

5.3.3 Influence of SiO_2/Al_2O_3 molar ratio

The influence of SiO_2-Al_2O_3 ratio of H-beta on its catalytic activity in the benzylation of *o*-xylene is investigated at 363 K (Table 5.2). It is shown that conversion of BC in the benzylation of *o*-xylene is markedly affected by the SiO_2-Al_2O_3 molar ratio of H-beta . The higher the SiO_2-Al_2O_3 molar ratio of H-beta, the lower the BC conversion. The results are in agreement with the earlier reports of Friedel-

Table 5.2 Influence of SiO_2/Al_2O_3 ratio of zeolite H-beta[a]

	SiO_2/Al_2O_3 (molar ratio)		
	26	**50**	**80**
Reaction time (h)	4	4	4
Conversion of BC (wt.%)[b]	83.3	49.1	21.4
Rate of BC conversion (mmolg^{-1}h^{-1})[c]	7.8	4.6	2.0
Product distribution (wt.%)			
2,3-DMDPM	1.2	1.2	0.9
3,4-DMDPM	90.1	89.5	92.8
Others	8.7	9.3	6.3

a,b,c & d see footnotes to Table 5.1

Table 5.3 Effect of catalyst concentration[a]

Catalyst/BC (wt./wt.)	Convertion [b] of BC (wt%)	Rate of BC[c] conversion(mmolg^{-1}h^{-1})	Product distribution(wt%)[d]		
			2,3-DMDPM	3,4-DMDPM	others
0.11	11.6	4.4	-	100	-
0.21	63.8	12.0	2.56	95.6	1.84
0.32	84.9	10.6	3.98	92.3	3.72
0.42	85.0	8.0	4.47	94.4	1.13

[a] Reaction conditions as in Table 5.1; reaction time (h) = 2

b,c & d see foot notes to Table 5.1

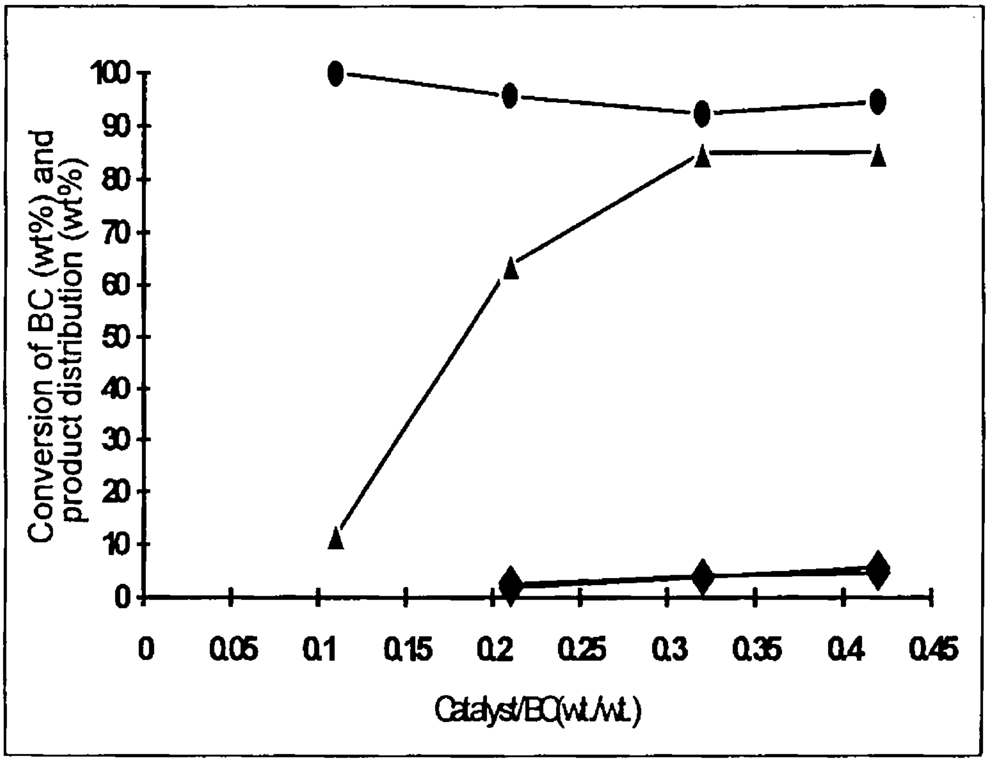


Fig. 5.1 Influence of catalyst/BC ratio (wt./wt.) on the conversion of BC (♦) and product distribution: 3,4-DMDPM (●), 2,3-DMDPM(▲), others (◊)

Crafts reactions [24, 26]. Furthermore, it is observed that the selectivity for 3,4-DMDPM is not affected significantly by the SiO_2-Al_2O_3 ratio of H-beta. The conversion of BC over 26, 50 and 80 SiO_2-Al_2O_3 ratio of H-beta is found to be 83.3, 49.1 and 21.4 wt.% respectively. The corresponding selectivity for 3,4-DMDPM is 90.1, 89.5 and 92.8 wt.%, respectively .

5.3.4 Influence of catalyst concentration

Fig. 5.1 displays the conversion of BC and product distribution at 2h of reaction time as a function of catalyst to BC (wt./wt.) ratio. The different ratios of catalyst to BC are obtained by varying the amount of the zeolite H-beta and keeping the constant concentration of BC. An initial steep increase in the conversion of BC is observed when catalyst to BC ratio is increased up to 0.32 (Table 5.3). Beyond this ratio, the conversion of BC and even the selectivity for 3,4-DMDPM leveled off in the reaction mixture. These results indicate that only a small amount of catalyst is active in the benzylation of *o*-xylene .

5.3.5 Influence of reaction temperature

The dependence of the rate of BC conversion (m mol $g^{-1}h^{-1}$), conversion of BC (wt.%) and product distribution (wt.%) on the reaction temperature is investigated in the temperature range 363 to 408 K using the H-beta catalyst (Fig. 5.2). The conversion of BC and rate of BC conversion are found to increase with increase in the reaction temperature. The conversion of BC and rate of BC conversion increase from 54.9 to 100 wt% and 10.3 to 18.8 mmol g^{-1} h^{-1}, respectively, when temperature is raised from 363 to 408 K (Table 5.4). However, the selectivity for 3,4 - DMDPM decreases with the increase in reaction temperature as shown in Fig. 5.2. A maximum in 3,4 - DMDPM selectivity (96.3 wt.%) over this catalyst is observed at 363 K. At higher temperature (408 K), selectivity for 3,4 -DMDPM decreases sharply which may be attributed to the formation of consecutive products at higher temperature.

The apparent activation energy of BC conversion over H-beta estimated in the temperature range of 363 - 408 K is found to be 16.6 kJ/mol (Fig. 5.3).

5.3.6 Influence of *o*-xylene to BC molar ratio

Fig. 5.4 exhibits the effect of the *o*-xylene/BC molar ratio on the catalytic activity of H-beta. The ratios are changed by keeping the amount of *o*-xylene constant. The data at 363 K show that as the *o*-xylene/BC molar ratio is increased up to 5, the conversion of BC increased linearly and above this ratio the conversion of BC roughly leveled off. The results are in agreement with the earlier reported data in the benzylation of toulene over zeolite H-Y [20]. In addition, the selectivity for 3,4-DMDPM is found to be unaffected over the wide range of *o*-xylene to BC ratio (1 to 7) (Table 5.5).

Table 5.4 Effect of reaction temperature[a]

Reaction temp.(K)	Conversion of[b] BC (wt%)	Rate of BC[c] conversion(mmolg^{-1}h^{-1})	Product distribution (wt.%)[d]		
			2,3-DMDPM	3,4-DMDPM	Others
363	54.9	10.3	1.36	97.5	1.14
373	68.3	12.8	1.32	97.2	1.44
383	78.1	14.7	1.65	96.7	1.65
408	100	18.8	6.58	88.2	5.22

[a] Reaction conditions: catalyst(g) = 1.0; catalyst (H-beta)/$C_6H_5CH_2Cl$ (wt./wt.) = 0.42 o-xylene/ $C_6H_5CH_2Cl$ (molar ratio) = 5; o-xylene(g) = 10; $C_6H_5CH_2Cl$ = 2.38; reaction time (h) = 1

Table 5.5 Effect of o-xylene/BC molar ratio[a]

o-xylene/BC (wt./wt.)	Convertion [b] of BC (wt%)	Rate of BC [c]conversion(mmolg^{-1}h^{-1})	Product distribution(wt%)[d]		
			2,3-DMDPM	3,4-DMDPM	others
1	25.4	23.9	-	97.1	2.9
3	43.0	12.3	-	97.0	3.0
5	63.8	12.0	-	95.6	4.4
7	68.6	9.2	-	96.4	3.7

a,b,c & d see foot notes to Table 5.1; reaction time (h) = 2

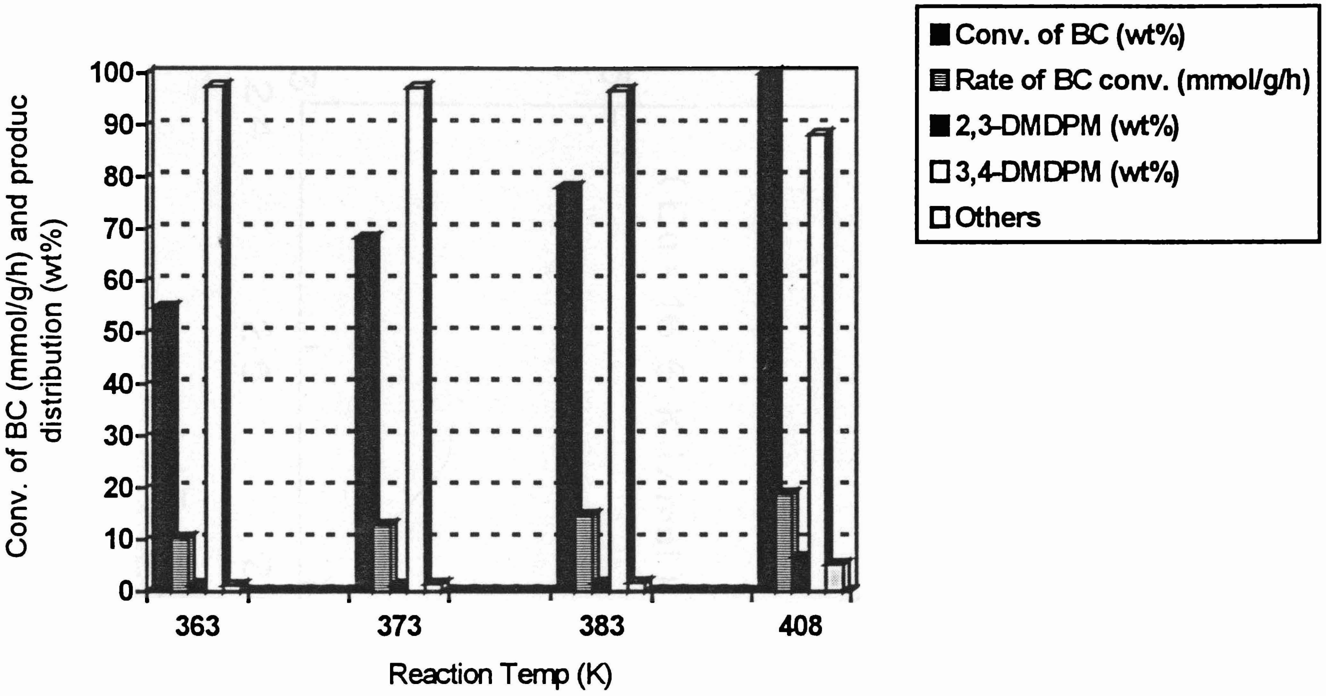


Fig. 5.2 Influence of reaction temperature on the conversion of BC (wt.%), rate of BC conversion (m mol $g^{-1}h^{-1}$) and product distribution.

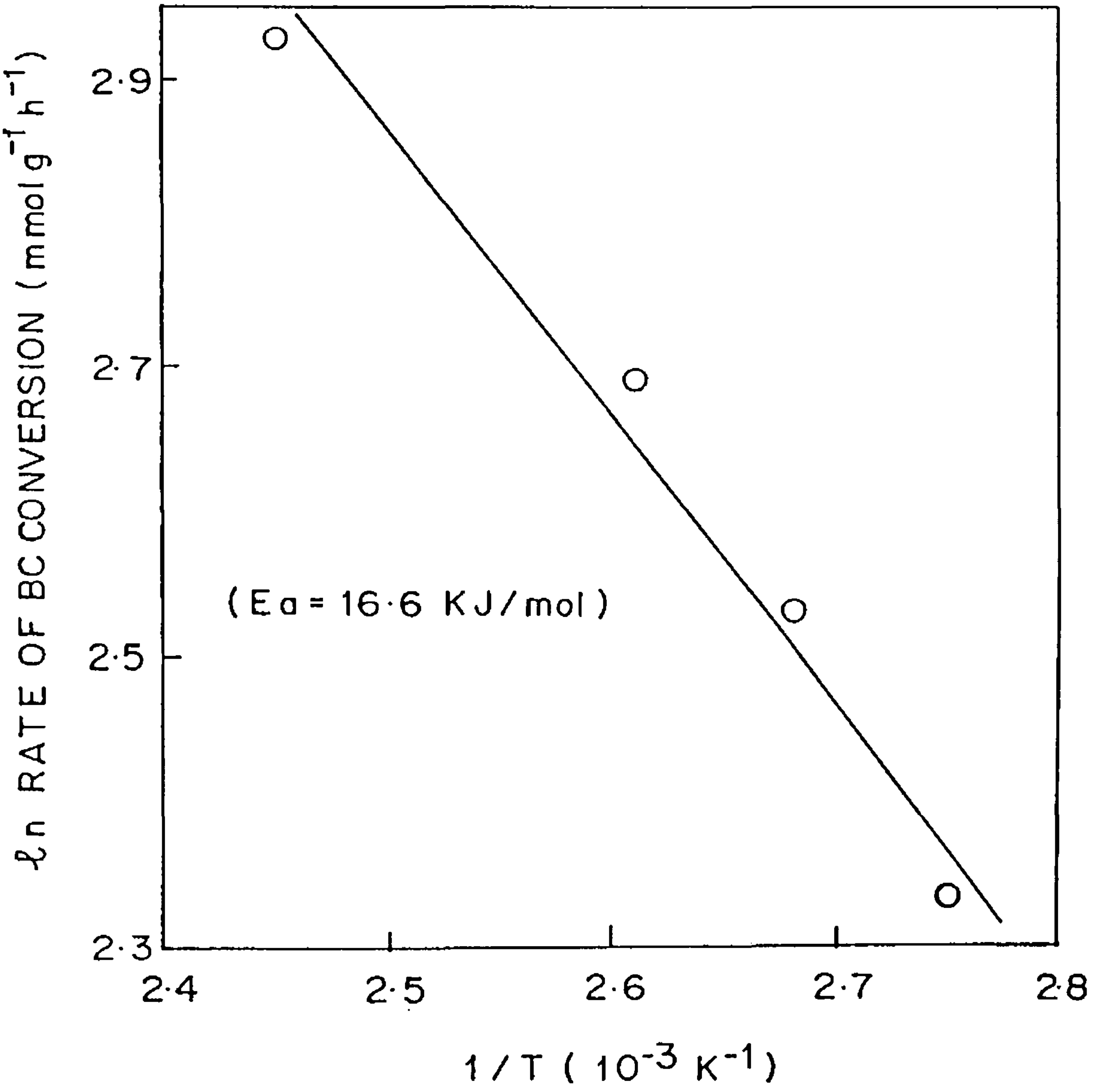


Fig. 5.3 Arrhenius plot for the benzylation of o-xylene by benzylchloride over zeolite H-beta.

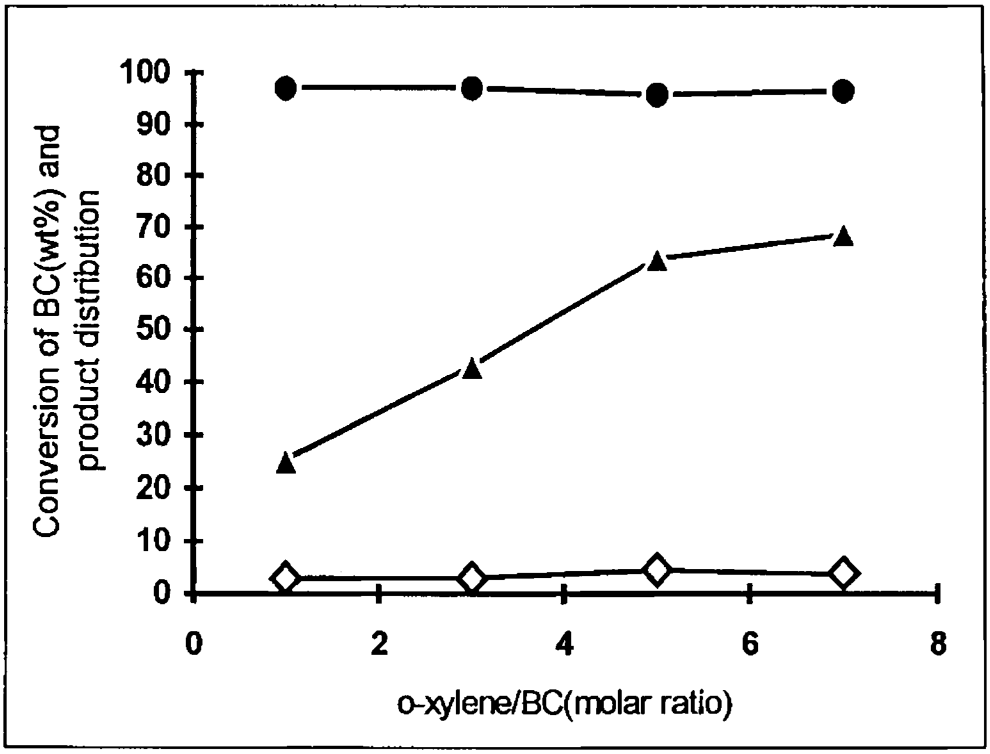


Fig. 5.4 Influence of o-xylene/BC molar ration on the conversion of BC (♦) and product distribution: 2,3-DMDPM (▲), 3,4-DMDPM (●), others (◊)

5.3.7 Recycling of the catalyst

H-beta sample used in the benzylation of *o*-xylene is recycled four times in order to check the activity and stability of the catalyst. After reaction of each cycle, the catalyst was filtered off, washed with acetone and calcined at 773 K for 16 h in the presence of air. Table 5.6 lists the results of these experiment. H-beta shows an immediate decrease in the conversion of BC (wt.%) as well as rate of BC conversion (m mol $g^{-1}h^{-1}$) after each recycle. However, the selectivity for 3,4-DMDPM is similar to that for the fresh catalyst. X-ray diffraction patterns are recorded after each cycle and it indicates that the catalyst retains the H-beta structure (Fig. 5.5). The results of the chemical composition and XRD of the catalysts show that the loss of the activity with the increase in the number of cycles may be correlated with the slight increase in SiO_2-Al_2O_3 ratio and reduction in relative crystallinity (Table 5.6). The hydrogen chloride produced in the electrophilic benzylation of *o*-xylene is responsible for the deactivation of the H-beta. These results are consistent with the earlier reports [24, 27].

5.3.8 Benzylation of xylenes (o-,m-,p-)

The generality of the benzylation of xylenes (*o*-xylene, *m*-xylene and *p*-xylene) is investigated over zeolite H-beta at 363 K. The results are listed in Table 5.7. The conversion of BC, rate of BC conversion and product distribution obtained after 1h of reaction time using conventional catalyst, $AlCl_3$, are also included for comparison.

Table 5.6 Recycling of H-beta [a]

Run	Change in SiO_2/Al_2O_3 (molar ratio)	Conv.of [b]BC (wt%)	Rate of [c] BC conversion (mmolg-1h-1)	Product distribution(wt%)			% crystallinity of H-beta
				2,3-DMDPM	3,4-DMDPM	Others	
1(fresh catalyst)	26.0	33.5	12.6	-	100.0	-	100.0
2	27.93	20.0	7.5	1.1	90.2	8.7	89.54
3	29.12	13.9	5.2	1.0	93.4	5.6	78.86
4	30.08	10.7	4.0	1.1	92.1	6.8	75.97

a Reaction conditions, same as given in Table 5.1; reaction time (h) = 1.0

b,c & d see foot notes to Table 5.1

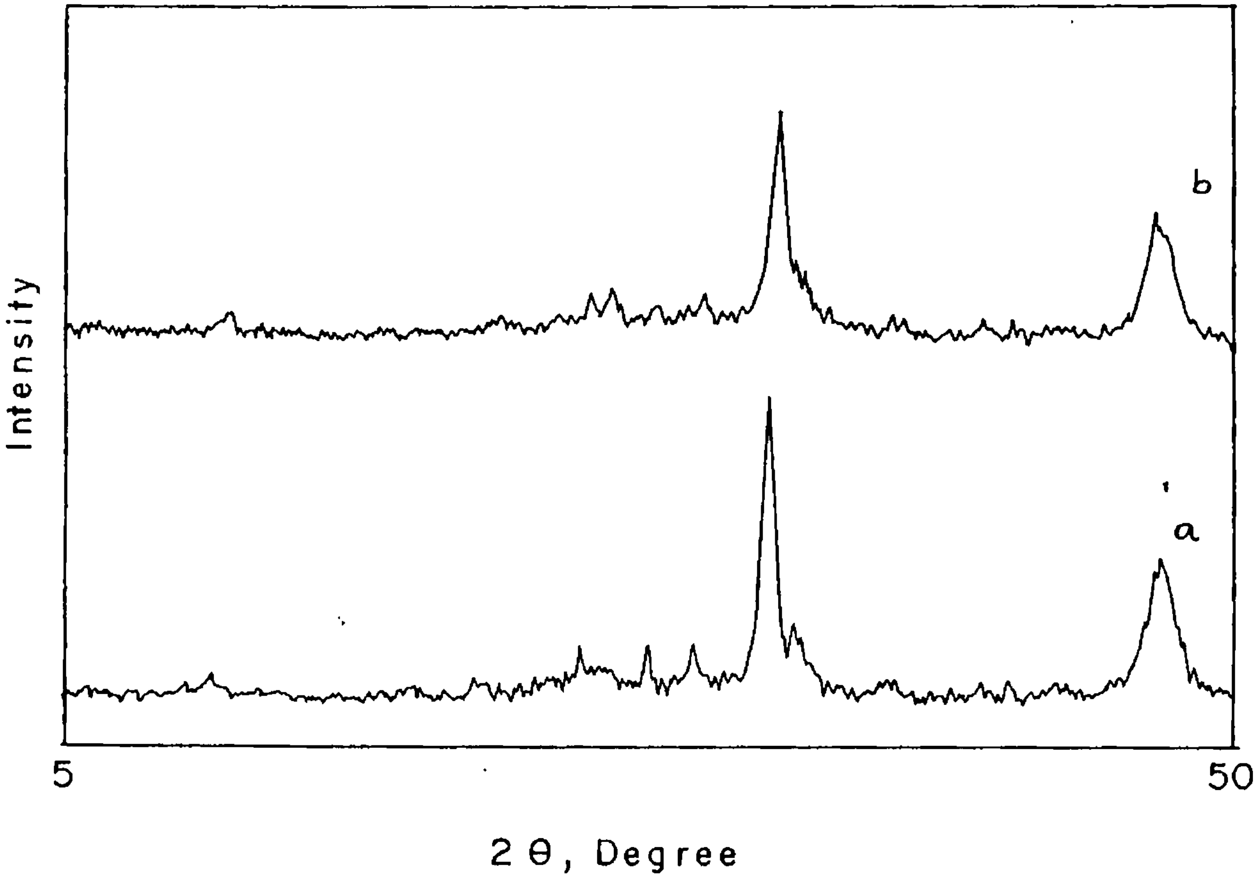


Fig. 5.5 X-ray diffraction patterns of (a) fresh H-beta and (b) H-beta after recyling

The benzylation of xylenes over H-beta leads to high yield of monobenzylated products whereas $AlCl_3$ gave a higher amounts of consecutive products of monobenzylated *o*-xylenes in all cases due to its non shape-selectivity character. The benzylation of *o*-xylene over zeolite H-beta leads to the formation of 2,3-DMDPM and 3,4-DMDPM. With m-xylene, the reaction gives 2,6-dimethyldiphenylmethane (2,6-DMDPM) and 2,4-dimethyldiphenylmethane (2,4-DMDPM). Similarly benzylation of p-xylene gave only a single monobenzylated product, 2,5-dimethyldiphenylmethane (2,5-DMDPM). Some amounts of others are also detected in all reactions over zeolite H-beta. The results show that zeolite H-beta enhances the formation of monobenzylated products and consequently decreases the concentration of consecutive products in the benzylation of xylenes.

5.3.9 Mechanism

The reaction appears to proceed by an electrophile which involves the reaction of benzyl choride with the acidic zeolite catalyst. The acidic zeolite polarizes the benzylating agent and in turn produces an electrophile ($C_6H_5CH_2^+$). Thus the generated electrophilic species attack the xylenes ring resulting in the formation of the corresponding dimethyldiphenylmethanes [20, 28].

Table 5.7 Benzylation of xylenes (o-, m-, p-)[a]

Xylenes	Catalyst	Reaction time (h)	Conv.of[b] BC (wt.%)	Rate of[c] BC conv. (mmolg^{-1}h^{-1})	Product distribution (wt%)[d]					
					2,3-DMDPM	3,4-DMDPM	2,6-DMDPM	2,4-DMDPM	2,5-DMDPM	others
o-xylene	H-beta	1	33.5	12.6	0.9	92.2	-	-	-	6.9
		4	83.3	-	1.2	90.1	-	-	-	8.7
	$AlCl_3$	1	76.6	28.8	1.6	65.5	-	-	-	32.9
m-xylene	H-beta	1	24.1	9.1	-	-	7.3	89.8	-	2.9
		4	72.8	-	-	-	7.2	92.2	-	0.6
	$AlCl_3$	1	80.4	30.3	-	-	-	30.6	-	69.4
p-xylene	H-beta	1	10.7	4.0	-	-	-	-	95.1	4.9
		4	42.2	-	-	-	-	-	95.6	4.4
	$AlCl_3$	1	53.4	20.2	-	-	-	-	31.5	68.5

[a,b&c] see footnotes to Table 5.1

[d] 2,3-DMDPM = 2,3-dimethyl diphenylmethane ; 3,4-DMDPM = 3,4-dimethyl diphenylmethane ;
2,6-DMDPM = 2,6-dimethyl diphenylmethane ; 2,4-DMDPM = 2,4-dimethyl diphenylmethane ;
2,5-DMDPM = 2,5-dimethyl diphenylmethane ; Others = secondary products.

5.4 Conclusions

It is demonstrated for the first time that the zeolite H-beta catalyses the benzylation of *o*-xylene with benzyl chloride efficiently, which leads to the formation of 3,4 - DMDPM in high selectivity compared to the other zeolite catalysts. Conventional homogeneous catalyst, $AlCl_3$, does not possess shape selectivity and favours the formation of large amounts of polybenzylated products (others). A selectivity of the order of 90.1 wt% to 3,4-DMDPM is achieved at 83.3 wt.% conversion of BC over H-beta where as $AlCl_3$ gave lower selectivity for 3,4-DMDPM (65.5 wt%) and higher selectivity for polybenzylated products (32.9 wt%) under certain reaction conditions. The conversion of BC, rate of BC conversion and product distribution largely depend on the experimental condition. The conversion of BC increases with increasing reaction time, catalyst concentration, reaction temperature and *o*-xylene to BC molar ratio. The yield of the products decreases with an increase in SiO_2 /Al_2O_3 and degree of Na^+ - exchange of H-beta. Recycling of the catalyst progressively decreases the BC conversion and crystallinity of zeolite H-beta. All xylenes (o-, m-, p-) can be benzylated selectively to the corresponding dimethyldiphenylmethanes. It is concluded that the presence of strong as well as weak acid sites in the zeolite catalysts appears to be very important for the polarization of benzyl chloride into an electrophile ($C_6H_5CH_2^+$) which then attacks the xylene ring resulting in the formation of dimethyldiphenylmethanes.

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CHAPTER VI

SUMMARY AND CONCLUSIONS

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6.1 SUMMARY

In the present work, the synthesis, modification and characterization of some (synthesised or commercially available) medium and large pore zeolites catalysts are reported. The catalytic activity of these zeolite catalysts in the selective propionylation, benzoylation and benzylation reactions of aromatics is investigated.

The work is presented in six chapters.

A review of the published and patented literature on the synthesis of zeolites and their characterisation by various physico-chemical techniques is included in **Chapter-I**. Literature on the use of zeolite catalysts in the synthesis of fine chemicals particularly in the acylation and alkylation reactions of aromatics with shape-selective characteristics is also reported in this chapter.

Chapter-II describes the experimental details for the synthesis of zeolite beta and ZSM-5. This chapter also contains the modification techniques of zeolites into protonic, Na- and RE^{+3}- forms. An experimental set up for the evaluation of catalytic activity, product analysis and physicochemical methods such as XRD, infrared spectroscopy, thermal analysis, scanning electron microscopy and surface area measurement are also included. Acidity measurement using temperature programmed desorption of ammonia is also discussed.

Chapter III focuses on the propionylation of toluene and anisole over various zeolites using propionyl chloride as propionylating agent. Zeolite H-beta is found to be superior compared to other zeolites and conventional catalyst, $AlCl_3$. In the presence of zeolite H-beta the conversion of propionyl chloride increases with increase in the reaction time, amount of catalyst, molar ratio of substrate to propionyl chloride and reaction temperature. The rate of propionyl chloride conversion decreases with the increase in SiO_2/Al_2O_3 ratio of zeolite H-beta.

Chapter IV deals with the liquid phase selective benzoylation of *o*-xylene to 3,4-dimethylbenzophenone (3,4-DMBP) using zeolites as catalyst and benzoyl chloride (BOC) as benzoylating agent. The results obtained over various zeolite catalysts are compared with the homogeneous Lewis acid catalysts, $AlCl_3$. The protonic form of zeolite beta is found to be an efficient catalyst compared to the other zeolites and $AlCl_3$ in the benzoylation of *o*-xylene. The conversion of BOC, rate of BOC conversion and selectivity for 3,4-DMBP over zeolite H-beta are found to be 52.8 wt.%, 0.7 mmol $g^{-1}h^{-1}$ and 94.7 wt.%, respectively. $AlCl_3$ catalyst produces lower amount of 3,4-DMBP (76.4 wt.%). The effect of various catalyst and reaction parameters such as reaction time, catalyst concentration, reaction temperature, *o*-xylene to BOC molar ratio, degree of Na-exchange in H-beta and SiO_2 / Al_2O_3 molar ratio of H-beta are investigated on the conversion of BOC and selectivity for 3,4-DMBP.

Chapter V presents the results of the liquid phase catalytic benzylation of *o*-xylene with benzyl chloride (BC) over various zeolite catalysts. Acidic zeolite beta is found to be an effective catalyst for the selective conversion of *o*-xylene to 3,4-dimethyldiphenylmethane (3,4-DMDPM). The performance of various zeolite catalysts is also compared with that of conventional catalyst $AlCl_3$. The conversion of BC and selectivity for 3,4-DMDPM over zeolite H-beta are found to be 83.3 wt.% and 90.1 wt.%, respectively, whereas $AlCl_3$ gave 67.1 wt.% selectivity for 3,4-DMDPM at 76.6 wt.% conversion of benzyl chloride. The conversion of *o*-xylene to 3,4-DMDPM increases with the increase in reaction time, catalyst concentration, reaction temperature and *o*-xylene to BC ratios, whereas it decreases with the increase in degree of Na-exchange and SiO_2 / Al_2O_3 molar ratio of H-beta.

Chapter VI contains the summary of the results which are obtained from the propionylation of toluene and anisole, benzoylation of *o*-xylene and benzylation of *o*-xylene using zeolites as catalyst and propionyl chloride or benzoyl chloride as acylating agents and benzyl chloride as alkylating agent.

6.2 CONCLUSIONS

The results suggest that H-beta catalyses the propionylation of toluene and anisole, benzoylation of *o*-xylene and benzylation of *o*-xylene efficiently and selectively. Conventional homogeneous Lewis acid catalyst, $AlCl_3$, does not posses shape-selectivity and favours the formation of consecutive products in larger amounts compared to the zeolite H-beta. The pore size of the zeolite was found to be a critical parameter in order to ensure a good reactivity. It is concluded that the presence of strong Bronsted acid sites in the zeolite catalyst appears to be very important which polarises the acylating or alkylating agent into an electrophile which then attacks the aromatic ring resulting in the formation of substituted products.

The higher yield of the products is achieved by increasing the values of the reaction parameters such as reaction time, catalyst amount, reaction temperature and substrate to acylating or alkylating agent. An increase in the SiO_2/Al_2O_3 ratio and reuse of the H-beta decrease the formation of products. In addition, these reactions turn out to be a very " environmentally friendly" process compared to the classical Friedel-Crafts reaction catalysed by $AlCl_3$, generating only by- products such as acidic acid which can easily be recovered and recycled.

6.3 SCOPE FOR FURTHER WORK

Catalysis is continuing to be one of the most important fields for investigation and application of zeolite materials. In recent years the catalytic chemistry of zeolite was enriched with the new application of crystalline aluminosilicates and various zeolite like porous solids for the production of fuel components, monomers, organic intermediates, bioactive compounds and others.

In view of the continuing interest in the use of zeolites as shape selective catalysts in fine chemical synthesis, a more detailed study on the medium and large pore zeolite catalyzed Friedel-Crafts alkylation and acylation reactions were undertaken. Our main interest is to elucidate the parameters which determine the selectivity when zeolites are used as catalysts in Friedel-Crafts reactions. Parameters of interest were the strength and concentration of acid sites and the nature of the pore system of the zeolite.

The present thesis describes the formation of 4-methyl propiophenone, 4-methoxy propiophenone, 3,4-dimethylbenzophenone and 3,4-dimethyl diphenylmethane over some medium and large pore zeolites by alkylation and acylation reactions. These investigations could be extended by choosing aromatic molecules with different substituents and examining their activity in other novel alkylation and acylation reactions.

The results presented in various chapters imply that the potentialities of using zeolite base systems in organic chemistry are far from being exhausted. New applications of these systems for catalytic transformations of various substances and for novel or untraditional synthesis of many practically important products can be envisaged.

LIST OF PUBLICATIONS

[1] Surface acidity / basicity and catalytic activity of ternary oxides of La, Ce and Al. (S.Sugunan, **Bindhu Jacob**, S.Ampily, Rani Varghese), *Indian Journal of Chemistry*, **35** A (1996) 160

[2] Surface acidity / basicity and catalytic activity of ternary oxides of La, Ce and Dy. (S.Sugunan and **Bindhu Jacob**), *Indian Journal of Engineering and Material Sciences* **4** (1997) 120-122.

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[4] Selective benzoylation of *o*-xylene to 3,4-dimethyl benzophenone using zeolite H-beta catalyst (**Bindhu Jacob**, S.Sugunan and Anand P. Singh) *Journal of Molecular catalysis* (accepted)

[5] Liquid phase selective benzylation of *o*-xylene using zeolite catalysts (A.P.Singh, **B. Jacob** and S.Sugunan) *Applied Catalysis* (communicated)

[6] Propionylation of Toluene to 4-methyl propiophenone over zeolite H-beta (**Bindhu Jacob**, S.Sugunan and Anand P. Singh) (under preparation)

[7] Propionylation of Anisole to 4-methoxy propiophenone over zeolite H-beta (**Bindhu Jacob**, S.Sugunan and Anand P. Singh) (under preparation)

[8] Catalytic activity studies of some rare-earth ions exchanged zeolite Y (S.Sugunan and **Bindhu Jacob**) (under preparation)

[9] Effect of transition metal ion exchange in the activity of zeolite H-Y (S.Sugunan and **Bindhu Jacob**) (under preparation)