# ISOPROPYLATION OF C-8 AROMATIC COMPOUNDS (XYLENES, ETHYLBENZENE) OVER LARGE PORE HIGH SILICA ZEOLITES

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**BY**

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*Dedicated*
*To*
*My Beloved*
*MAA (PADMAVATI),*
*BABA (PANCHUGOPAL)*
*AND*
*TEACHERS*

# CERTIFICATE

Certified that the work incorporated in the thesis, **“Isopropylation of C-8 aromatic compounds (xylenes, ethylbenzene) over large pore high silica zeolites”** submitted by **Mr. Chitta Ranjan Patra,** for the Degree of **Doctor of Philosophy,** was carried out by the candidate under my supervision in the Catalysis Division, National Chemical Laboratory, Pune - 411008, India. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

**Dr. Rajiv Kumar**

**(Research Supervisor)**

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# ABBREVIATIONS

| | |
|---|---|
| AAS | Atomic absorption spectroscopy |
| BET | Brunauer, Emmett and Teller isotherm |
| BEA | Zeolite Beta |
| 2-BP | 2-bromopropane |
| Conv. | Conversion |
| Conv. (theo. Max.) | Conversion of theoretical maximum |
| 2-CP | 2-chloropropane |
| CP MAS NMR | Cross polarization Magic angle spinning nuclear magnetic resonance |
| CTABr | Cetyltrimethylammoniumbromide |
| DAP | Dialkylated product |
| DEB | Diethylbenzene |
| DIPEB | Diisopropylethylbenzene |
| DIPT | Diisopropyltoluene |
| DIPX | Diisopropylxylene |
| DISP | Disproportionation |
| 2,5-DMC | 2,5-dimethylcumene |
| DMC | Dimethylcumene |
| DTA | Differential thermal analysis |
| EB | Ethylbenzene |
| 2-EC | 2-ethylcumene |
| EC | Ethylcumene |
| EDX | Energy dispersive X-ray |
| EP | Ethylphenol |

| | |
|---|---|
| FAU | Faujasite |
| FID | Flame ionization detector |
| FT-IR | Fourier-transform infrared |
| GC | Gas chromatography |
| GCIR | Gas chromatography infrared spectroscopy |
| GCMS | Gas chromatography mass spectrometry |
| GGA | Generalized gradient approximation |
| IPA | Isopropyl alcohol |
| ISO | Isomerization |
| MAP | Monoalkylated product |
| MAS NMR | Magic angle spinning nuclear magnetic resonance |
| MCM-41 | Mobil Corporation Materials-41 |
| MFI [ZSM-5 (five)] | Zeolite Secondary Mobil -five |
| MOR | Mordenite |
| MTW [ZSM-12 (twelve)] | Zeolite Secondary Mobil -twelve |
| M-X | meta-xylene |
| NMR | Nuclear magnetic resonance |
| O-X | ortho-xylene |
| P-X | para-xylene |
| P-XRD | Powder X-ray diffraction |
| RPBE | Revised Perdew-Burke-Ernzerhof |
| SAL | Silica-alumina |
| SAR | Silica alumina ratio |
| Sel. | Selectivity |
| SEM | Scanning electron microscopy |

| | |
|---|---|
| SZ | Sulfated-zirconia |
| TEAOH | Tetraethylammoniumhydroxide |
| TGA | Thermogravimetric analysis |
| TMAOH | Tetramethylammoniumhydroxide |
| TMB | Trimethylbenzene |
| TOF | Turn over frequency |
| TPAOH | Tetrapropylammonium hydroxide |
| TOS | Time-on-stream |
| USY | Ultra stable-Y |
| WHSV | Weight hourly space velocity |
| XRD | X-ray diffraction |
| ZSM-5 | Zeolite Secondary Mobil -five |
| ZSM-12 | Zeolite Secondary Mobil -twelve |

## 1.1. GENERAL BACKGROUND AND INTRODUCTION

The introduction of an alkyl, aryl or acyl group into an aromatic nucleus in the presence of a Lewis or Brønsted acid catalyst is commonly known as the Friedel-Crafts reaction. Friedel-Crafts reaction can be classified into two groups namely (i) Friedel-Crafts alkylation and (ii) Friedel-Crafts acylation. The most important alkylating agents are alkyl halides, olefins and alcohols [1]. While aluminum chloride ($AlCl_3$) [2-6] is the most common classical acid catalyst for Friedel-Crafts reaction, other Lewis acids like $BF_3$-$Et_2O$ [3], $BF_3$-HF [5], $BF_3$– $P_2O_5$ – Kiselguhr [5], $BF_3$-$H_3PO_4$, $AlX_3 + I_2$ [6,7], $AlCl_3$ -$CH_3NO_2$ [8], $AlBr_3$, $GaCl_3$, $FeCl_3$, $TiCl_4$ [9], $SbCl_5$ [10], $ZrCl_4$, $SnCl_4$, $BCl_3$ [11], $BF_3$, $SbCl_3$ [12], $BF_3$-$H_3PO_4$ [13] aluminum phosphates [14] etc. have also been used. Similarly, quite often some Brønsted acids such as HF and $H_2SO_4$ [15,16], super acids [17], phase transfer catalysts [18], phosphoric acid [19] and chlorosulfonic acids [20-21] have also been used as catalyst.

## 1.2. DRAWBACKS OF HOMOGENEOUS CATALYSTS

The major disadvantage of the above-mentioned homogeneous Friedel-Crafts catalysts is their environmentally hazardous nature, giving rise to various problems concerning handling, storage, safety, corrosion, toxicity, separation, waste disposal, no reusability and troublesome work-up. Another difficulty with these catalysts is the low selectivity due to the polyalkylation reaction. In addition, when Lewis acids are employed, the products could be complexed with the Lewis acid catalyst themselves, thus leading to the separation problems as well as loss of catalytic species, thus necessitating the use of stoichiometric or even higher amounts of the catalysts.

## 1.3. HETEROGENEOUS CATALYSIS

In order to avoid the disadvantages and the environmental limitations of conventional homogeneous Friedel–Crafts catalysts, solid acid catalysts including zeolites were used in the alkylation reaction due to their numerous advantages such as easy handling, easy recovery, reusability, less or no corrosion, no disposal problem, high thermal stability and shape selectivity especially in aromatic electrophilic substitution reactions [22,23]. Venuto [24] has emphasized the utility of zeolites and related molecular sieves in (i) Catalytic Versatility, (ii) Process Engineering Flexibility and (iii) Environmental Advantages. Development of reusable solid acid catalysts like zeolites having high catalytic activity and selectivity for the alkylation reaction is, therefore, of great practical importance. This transition fits in well with the concept of environmentally benign systems for developing ecofriendly industrial processes.

## 1.4. ISOPROPYLATION OF AROMATIC

Alkylation of aromatic substrates, one of the examples of carbon-carbon (C-C) bond formation, catalyzed by solid acids including zeolites, constitute an important class of reactions of both the academic as well as the industrial importance. Among alkylation reactions, isopropylation of aromatic compounds has attracted considerable attention. For isopropylation of aromatic compounds several solid catalysts such as clays [25], heteropolyacids [26], metal and mixed metal oxides [27], Mg-Al hydrotalcites [28], zinc aluminate spinel [29], sulfate ion doped metal oxides [30], phosphates [31], mesoporous materials [26,32,33] and zeolites [34-68] have been used extensively.

The isopropylation of benzene [34-38], toluene [39-41], naphthalene [42-43], biphenyl [44], phenol [45], quinoline [46], furan [47] catalyzed by zeolites has been studied extensively, as these isopropylated aromatics are converted to corresponding phenolic compounds. Although, there are reports on the methylation of xylenes [48-49] and ethylbenzene [50], ethylation of xylenes [51] and ethylbenzene [52,53], and tertiary butylation of xylenes [54] and ethylbenzene [55,56] over solid catalysts, it is not the case with the isopropylation of C-8 aromatics (xylenes and ethylbenzene), particularly over solid acid catalysts like zeolites.

### 1.4.1. ISOPROPYLATION OF C-8 AROMATICS

Isopropylation of xylene isomer(s) leads to produce corresponding dimethyl (1-methylethyl) benzene or simply denoted as dimethylcumene(s) (DMCs), which could be used as raw material for the production of xylenols [57]. It is needless to mention that xylenols are an important source for the production of pesticides, perfumery, pharmaceuticals, heat-transfer media, polymers and special solvents, phenolic resins and electronic equipments, automobiles (polyethers etc.) and polycarbonates [58,59]. On the other hand, isopropylation of ethylbenzene produce ethylcumenes (ECs) or ethyl (1-methylethyl) benzenes, the precursors of ethylphenols (EPs), which exhibit antiseptics, antimicrobial, and preservative activities along with being used in production of resins, polymers and Mannich bases [58,59]. In fact, there are only few reports available in the literature on the isopropylation of C-8 aromatics using ã-radiolysis technique [60] and over solid acid catalysts including zeolites [61-68].

Table 1.1 summarizes the literature search on the isopropylation of C-8 aromatics (xylenes and ethylbenzene) using propylene, isopropanol and propyl halides as alkylating agents and different Lewis and Brønsted acids as homogeneous and heterogeneous catalysts.

**Table 1.1: Literature search on the Isopropylation of C-8 aromatics using various acid catalysts**

| Substrate | **Homogeneous Catalyst** | Ref. | Substrate | **Heterogeneous Catalyst** | Ref. |
|---|---|---|---|---|---|
| Ethylbenzene[a] | $AlCl_3$ | 2 | *o*-, *m*- & *p*-xylene[a] | ã-radiolysis technique | 60 |
| Ethylbenzene[a] | $BF_3$-$Et_2O$ | 3 | *m*-xylene[a] | $Al_2O_3$ promoted by $BF_3$ | 61 |
| xylenes[a] | $AlCl_3$ | 4 | Ethylbenzene[a] | Modified Mordenite | 62 |
| *m*-xylene[a] | $AlCl_3$ | 5 | *o*-, *m*- & *p*-xylene [b] | $TiO_2$-$SiO_2$-$Al_2O_3$ (Tisial) | 63 |
| *p*-xylene[a] | $AlCl_3$ | 5 | *o*- & *p*-xylene[b] | 0.91 NdNaY | 64 |
| *m*-xylene[a] | $BF_3$ (4.36)-HF | 5 | *p*-xylene[a] | Dodecasilicotungstic acid supported on silica gel | 65 |
| *m*-xylene[a] | $BF_3$–$P_2O_5$–Kiselguhr | 5 | *o*-xylene[b] | Dealuminated Y catalyst | 66 |
| *o*-xylene[a] | $BF_3$-$H_3PO_4$,<br>$AlCl_3$-$CH_3NO_2$ | 7 | *o*-, *m*- & *p*-xylene[b] | (Beta) Present work | 67 |
| *o*-, *m*- & *p*-xylene[a] | $BF_3$-$H_3PO_4$ | 14 | *o*-, *m*- & *p*-xylene[b] | (USY and other catalysts) Present work | 68 |
| *m*-xylene [b] | $H_2SO_4$ | 17 | | | |
| *p*-xylene[c] | $AlCl_3$ /$AlBr_3$ | 20 | | | |
| Ethylbenzene[a] | Chlorosulfonic acid | 21 | | | |

[a]Propylene, [b]isopropanol and [c]isopropylhalides have been used as alkylating agents respectively.

## 1.5. ZEOLITES (DEFINITION, PROPERTIES AND CLASSIFICATION)

Zeolites are hydrated, crystalline, microporous aluminosilicate molecular sieves [69-73] with a framework based on an extensive three-dimensional network of oxygen ions where corner-sharing tetrahedral sites can be occupied by $Si^{4+}$ and $Al^{3+}$ ions.

The crystallographic unit cell of the zeolites may be represented by the general formula

$M_{x/n}[(AlO_2)_x\,(SiO_2)_y].\,zH_2O$ ………………[69]

where M is a charge compensating cation from group I or group II with valency ‘n’. M can also be organic cations. The ratio ‘y/x’ may have any value ranging from one to infinity and (x+y) represents the total number of tetrahedra in the unit cell of zeolite. The number of water molecules, which can be reversibly adsorbed and desorbed in the zeolite pores, is represented by ‘z’. The presence of one Al atom in the lattice develops one unit negative charge in the framework. The negative charge, imposed by the presence of aluminum atom, is either compensated by group I or group II metals cations or by organic cation molecule in the case of as -synthesized zeolite material. The trivalent Al ion in the zeolite can either partly or completely be substituted by other trivalent ions like $Ga^{3+}$, $B^{3+}$, $Fe^{3+}$, $As^{3+}$ etc. or by tetravalent ions such as $Ti^{4+}$, $Zr^{4+}$, $Sn^{4+}$, $Ge^{4+}$ etc. These metallosilicate analogs of the zeolite are commonly referred to as molecular sieves.

The porous materials may be divided into three types based on their pore dimensions, namely, microporous (< 2 nm), mesoporous (2-50 nm) and macroporous (> 50 nm). The pores of the zeolites are of molecular dimensions ranging between 0.5 and 1.0 nm in diameter. Hence, zeolites are also known as molecular sieves because of their ability to discriminate the molecules of different size and shape. The characteristics, which make molecular sieves useful as catalysts are:

- Generation of highly acidic sites when exchanged with protons.
- Shape selective catalytic properties.
- High surface area and thermal stability.
- Ease of regeneration of the initial activity.

These crystalline, microporous molecular sieves/zeolites exhibit shape selective catalytic, adsorption and ion-exchange (viz. as water softener, detergent builders etc.) properties along with the raggedness in high temperature and pressure environments. They are also compared with catalytic antibodies [74] and metallo-enzymes [75].

### 1.5.1. CLASSIFICATION

Several attempts have been made to classify the families of zeolites on the basis of their morphological characteristics [69,70,76,77], crystal structure [69,70,78], chemical composition [69,70,79], effective pore diameter [69,70,80] and natural occurrence [69,70].

#### 1.5.1.1 Chemical Composition

According to chemical composition zeolites can be classified on the basis of their silica to alumina ratio [79] as low silica zeolites, medium silica zeolites, high silica zeolites and silicalites (Table 1.2).

#### 1.5.1.2. Pore Opening Size

All zeolites have been classified by the number of T atoms, where T = Si or Al, that define the pore opening. Zeolites containing these pore openings are also referred to as: small pore (6 or 8 member ring), medium pore (10-member ring), large pore (12-member ring) and ultra-large pore (14-or more member ring). Some examples on the basis of pore size classification are given below in Table 1.3.

**Table 1.2: Classification of zeolites on the basis of their Si/Al molar ratio**

| Type | Si/Al | Example |
|---|---|---|
| Low silica | 1.0 to 1.5 | Sodalite, A, X |
| Intermediate silica | 2 to 5 | L, Mordenite, Omega |
| High silica | 5 to several thousands | ZSM-5, EU-1 |
| Silicate (all silica) | | Silicate-1, Silicate-2, Si-NCL-1 |

**Table 1.3: Classification of zeolites based on pore size (pore diameter <2 nm)**

| Pore size | No. of Tetrahedra in pore opening/ Ring Size | Pore diameter (nm) | Example | Ref |
|---|---|---|---|---|
| Small | 6 and 8 | 0.36 X 0.51 | Erionite | 81 |
| | 8 | 0.42 | CaA | 76 |
| Medium | 10 | 0.53 X 0.56 | ZSM-48 | 82 |
| | 10 | 0.53 X 0.56<br>0.51 X 0.55 | ZSM-5 | 83 |
| Large | 12 | 0.74 | Faujasite | 84 |
| | 12 | 0.74 | USY | |
| | 12 | 0.55 X 0.59 | ZSM-12 | 85 |
| | 12 | 0.57 X 0.71 | Mordenite | 76,86 |
| | 12 | 0.75 X 0.57<br>0.65 X 0.56 | Beta | 87 |
| Extra large | 14 | 0.75 X 1.0 | Si-UTD-1 | 88 |

On the basis of their morphology, zeolites are classified as fibrous, lamellar etc. Structural classification of zeolites has been proposed depending on differences in secondary building units. With the addition of new synthetic and natural zeolites, they are grouped into ten classes: Analcime, Natrolite, Chabazite, Philipsite, Heulandite, Mordenite, Faujasite, Laumonite, Pentasil and Clatharate.

In Fig. 1.1, a broad classification of molecular sieves and porous materials has been shown schematically.

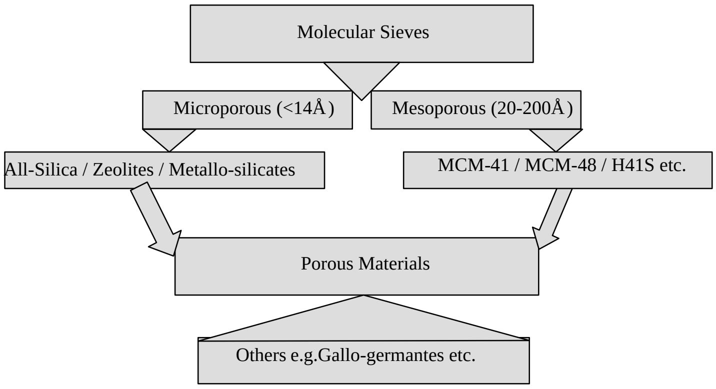


**Fig. 1.1:** Classification of molecular sieves: An over view

## 1.5.2. ZEOLITE SYNTHESIS

There are several basic steps in the synthesis of zeolites and related molecular sieves. The basic raw materials generally used are a silica source, an aluminum source, an organic quaternary ammonium salts (template) either in the form of hydroxide or halide and some inorganic bases like sodium hydroxide/potassium hydroxide, depending on the choice of the molecular sieve to be synthesized. Normally, zeolites are synthesized hydrothermally in an autoclave under autogeneous pressure. However, certain zeolitic materials like mesoporous materials, can also be synthesized in reflux conditions under atmospheric pressure. The basic steps which normally take place during the synthesis of a zeolite/molecular sieve are [69,70,89] given below:

- Hydrolysis of the silica/aluminum/metal source to form a initial gel phase.
- Dissolution/mineralization of the gel phase.
- A series of events that lead to nucleation of zeolite structure. This could be from the gel or solution phase.
- Continued crystallization and crystal growth of the structure from either the gel or from the solution.
- Dissolution of any initial but meta-stable phases.
- Continued crystallization and crystal growth of new, more stable crystalline phases while the initial meta-stable crystals are dissolving.
- Dissolution of further meta-stable phases.
- Nucleation of the equilibrium phases.
- Crystallization and final growth of the final crystalline condensed phases.

Hence, it is clear that hydrothermal synthesis of a zeolite consists of the series of complex physico-chemical processes.

### 1.5.2.1. Factors Influencing Zeolite Synthesis

There are several factors which influence some or all of the above mentioned processes, as summarized below:

**Chemical Parameters:** (a) Si/Al molar ratio, (b) alkalinity, i.e. $OH^-$ concentration, (c) organic template cation, (d) inorganic cation, (e) anions other than $OH^-$ and (f) amount of $H_2O$.

**Physical Parameters:** (a) aging, (b) stirring, (c) nature of mixing, (d) time and (e) temperature.

## Chemical Parameters

### (a) Si/Al Molar Ratio

The molar chemical composition of a synthesis hydrogel is expressed in terms of oxide formula of the following form:

$aSiO_2 : Al_2O_3 : bM_xO : cR : dH_2O$

in which M and R stand for alkali metal ion(s) and organic template, respectively. The a, b, c and d values (i.e. $SiO_2/Al_2O_3$, $SiO_2/MxO$, $SiO_2/R$, $SiO_2/H_2O$) can influence the nucleation and crystallization kinetics affecting the nature of the crystalline material, the lattice Al content, crystal size and morphology [90,91]. Zeolites normally incorporate all of the aluminum present in the reaction mixture into their framework structure, leaving various amounts of silica or silicate in solution. Ideally the desired Si/Al ratio of a zeolite chosen for a specific application should be obtainable through adjusting that ratio in the synthesis mixture. Generally, an increase in the Si/Al molar ratio in the framework leads to: (i) increased thermal stability, acid resistance, hydrophobicity and (ii) decreased ion-exchange capacity.

### (b) Hydroxide Ion ($OH^-$) Concentration

The main role of hydroxide ions in the synthesis of zeolite and related molecular sieves is to act as a mineralizer (by dissolving polymeric silicate anions into suitable monomeric / oligomeric anions e.g. $Q^0$, $Q^1$, $Q^2$, $Q^3$ and $Q^4$). Hence, hydroxide ion ($OH^-$) concentration helps in transport of the various silicate / aluminate ions from solid to liquid phase. The free $OH^-$ concentration influences the zeolite synthesis in the following manner.

- As structure directing agent through the control of the degree of polymerization of silicates in solution.

- By modifying nucleation time through transport of silicates from the solid phase to the solution.
- By enhancing crystal growth through transport between the solution phase and growing crystal.
- By influencing the phase purity.

The hydroxide ion is a moderately good complexing agent for silicon and aluminum. The interaction between these two species, silicon (or aluminum) ion and hydroxide ion is strong enough to dissolve these metal ions in the aqueous alkaline solutions. But the hydroxide complex of these ions are still weak enough that does not prevent the silicon (or aluminum) from further reacting to produce the desired zeolite. The hydroxide ion concentration accelerates crystal growth and shortens the induction period preceding crystal formation from the reaction mixture.

The solubility of the silicon species is greater than that of the aluminum containing species. Thus when hydroxide ion content is increased, the formation of lower silica/alumina ratio is encouraged. However, the amount of solid is decreased at high pH, because at very high caustic levels, the solution will remain unreacted but dissolved silicate species. Hence, optimum level of pH of the reaction mixture is a very important factor for the synthesis of molecular sieves. It is not directly related with the concentration of $OH^-$ used in the synthesis, but related with the presence of free $OH^-$ in the solution.

### (c) Role of the Template

In early sixties it was found that certain organic quaternary ammonium cations and amines can act as structure directing agent, void filler and/or gel modifie/mineraliser. These amines/

organic cations are trapped inside the pores of the molecular sieve during crystallization. The role of the organic cation in the synthesis mixture can be visualized as follows:

- Structure directing or templating role.
- Gel modifier, which would result in the formation of structures with higher Si/Al than could be obtained in the absence of it.
- Interact chemically with other components of the gel, altering the character of the gel. This is true particularly of weak organic bases, which could alter or buffer the pH of the crystallizing gel.
- Interact physically with other components of the gel so as to alter the gelling process, solubility of various species, aging characteristics, transport and thermal properties.

Interestingly, a particular organic molecule can lead to different molecular sieve framework and different organic molecules can be used for the synthesis of a particular molecular structure.

#### (d) Role of Inorganic Cation

Inorganic cation plays a complex role in the synthesis of molecular sieves. The role of inorganic cation can be categorized as: structure direction; balancing framework charge; morphology; crystal purity and yield.

The morphology of the zeolite crystals produced can be altered by the presence of various inorganic cations in the synthesis gel. For example, in the case of ZSM-5 these inorganic cations have pronounced effect both on the nucleation time and crystal size.

The crystallinity/purity of a zeolite phase can also be significantly influenced by the proper choice and amount of one or more inorganic cation used.

### (e) Role of Water

Water plays an important role in molecular sieve synthesis. In the presence of water it is not only the organic cation but also the precursors (mainly, $Q^0$, $Q^1$, $Q2$, $Q3$ and $Q^4$) remain hydrated. As a result, water along with the organic cation plays important role in the structure direction. However, the higher dilution level slows down the overall crystallization process.

### (f) Oxyanions as Promoters

The presence of certain oxyanions of V-VII group (perchlorate, phosphate, arsenate, chlorate, etc.) significantly enhances the nucleation and crystallization of zeolites [92]. There is almost a direct correlation between the crystallization time taken by a zeolite using a promoter oxyanion and the polarizing ability [as determined by Z/r (charge/radius ratio)] of the central cation of that promoter oxyanion. Based on detailed NMR studies (both liquid and MAS solid state), it is proposed that the promoter oxyanions reorient the water structure around silicate and template hydration spheres facilitating the overlap and thereby reducing the induction period leading to the faster synthesis of zeolitic matrials [92-94].

### (g) Effect of Temperature

Temperature influences several factors in zeolite synthesis. It can alter the zeolite phase obtained as well as the change the induction period before the start of the crystallization period. In general, the induction period decreases with increase in temperature. Domine and Quobex reported that at a fixed pH of 12.6 the induction period in the formation of Mordenite varied from 1 h at 623 K to 4 weeks at 373 K and 2 days at 473 K [95]. As the temperature is increased it may favour the formation of the other more meta-stable and more condense phases. In the synthesis of zeolite Mordenite, the sequence of formation of products with an increase in temperature was in the order: amorphous to Mordenite to analcime.

### (h) Time

Time plays an important role on the formation of a particular structure. At constant mixture composition, the transformation proceeds from amorphous to meta-stable to more stable phase. Therefore, monitoring the time any particular phase can be identified. The crystallization is found to increase with time. The thermodynamically least stable phase will crystallize fast, and will be successively replaced by more stable phases with time [96]. A typical example is the crystallization sequence:

Amorphous → Faujasite → NaP.

### (i) Aging, Seeding and Stirring

When the initial reaction mixture or gel is cured/aged at a certain temperature (commonly room temperature, as in the case of zeolite Y synthesis) it is called aging. This process helps in distribution of particular type of precursor units required for desired zeolites. Seeding means the addition of ca. 2-5 wt% of pre-synthesized material in the gel aimed to get the same material. It is believed that seeding helps in providing desired nuclei at the initial stage of the synthesis. Sometimes agitation or stirring either during aging or crystallization helps in obtaining a desired zeolite structure.

## 1.5.3. METALLOSILICATE MOLECULAR SIEVES

Various metal ions have been successfully incorporated in framework structures of different morphologies and the resultant molecular sieves are commonly termed as metallosilicate analogous of zeolites or simply metallosilicate molecular sieves. The difficulty in the synthesis of some metallosilicate arises because certain metal ions (like Fe, Ti, Zr etc.) form insoluble metal oxide/hydroxide during preparation of gel itself [97]. Therefore, the main emphasis is to avoid the formation of insoluble metal hydroxide/oxide and thereby facilitating the formation of more stable metallosilicate species and their further incorporation in the crystalline framework.

It is well known that transition metal ions form complexes with suitable complexing agents. These metal complexes are relatively stable towards hydrolysis and dissociate in stepwise manner at high pH. However, in the presence of silica, a stable metallosilicate complex may be formed. Using this concept, preparation of metallosilicate analogs of zeolites involving such metal ions which usually form insoluble hydroxide/oxides in basic medium can be conveniently achieved [98]. The presence of suitable complexing agents (like acetylacetone or oxalic acid) prevent the formation of insoluble hydroxides/oxides. Various metal ions with varying charges have been used for the synthesis of metallosilicates. They are briefly summarized in the following Table 1.4.

**Table 1.4: Classification of metallosilicate molecular sieves**

| Oxidation state of metal ions | Metal ions | Reference |
|---|---|---|
| $M^{3+}$ | $B^{3+}$, $Al^{3+}$, $Ga^{3+}$, $Fe^{3+}$, $As^{3+}$, $Cr^{3+}$, $V^{3+}$etc. | 99-101 |
| $M^{4+}$ | $Sn^{4+}$, $Zr^{4+}$, $Ti^{4+}$, $Ge^{4+}$, $V^{4+}$etc. | 102,103 |
| $M^{5+}$ | $As^{5+}$ | 104 |

## 1.5.4. MECHANISM FOR SYNTHESIS OF ZEOLITES

Zeolites are generally synthesized hydrothermally by the combination of cations (both organic and inorganic), i.e. template, a source of silicon, a source of aluminum and water. The importance of the interaction of hydrophobic organo-cation with the silicates in solution as a prenucleation step was recently demonstrated by Davis and Burkett [105]. Studying deuterated systems, they were able to cross-polarize from a TPA cation to $^{29}Si$ nuclei. A critical distance of proximity is needed for cross-polarization. They showed that key organizational events could be detected before any crystallization. The Fig. 1.2. gives a schematic of how these events are related to zeolite growth [105].

The presence of certain oxyanions of V-VII group (perchlorate, phosphate, arsenate, chlorate, etc.) significantly enhances the nucleation and crystallization of zeolites, as reported by Kumar *et al.* [92]. The mechanism of zeolite synthesis at molecular level is not fully and unambiguously understood. However, the experimental findings of various groups indicate that the silicate and template molecules are surrounded by hydration spheres and once these hydrophobic hydration spheres overlap, the condensation of the silicate structure building units (SBUs) start leading to crystal growth. Promoter anions (shown as $PO_4^{3-}$ in Fig. 1.2) polarize the hydration spheres towards itself, thereby accelerating the overlap of silicate and template (or to some extent aluminate) moieties. This is the main role of the promoter anions in enhancing nucleation and crystallization processes.

## 1.5.5. PROPERTIES OF ZEOLITES

### 1.5.5.1 Ion Exchange

Most zeolites are synthesized in the alkali cation form (mostly $Na^+$) in which the positively charged cations balance the negatively charged framework system. In aluminosilicates, these cations are readily exchanged by other mono-, di- and trivalent cations including $NH_4^+$. According to Ward (1984) the rate and degree of cation exchange in zeolites depends on:

- The type of cation being exchanged, its diameter and charge.
- The nature, size and strength of cation coordination complex.
- Ion exchange temperature.

- Thermal treatment of the zeolite, before or after exchange.
- The structural properties of the zeolite and its Si:Al ratio.
- The location of cations in the zeolite.
- The concentration of cation exchange solution.
- And previous treatment of the zeolite.

H-sieves (hydrogen ion-exchange sieves) are made first by ammonium ion exchange, followed by thermal decomposition.

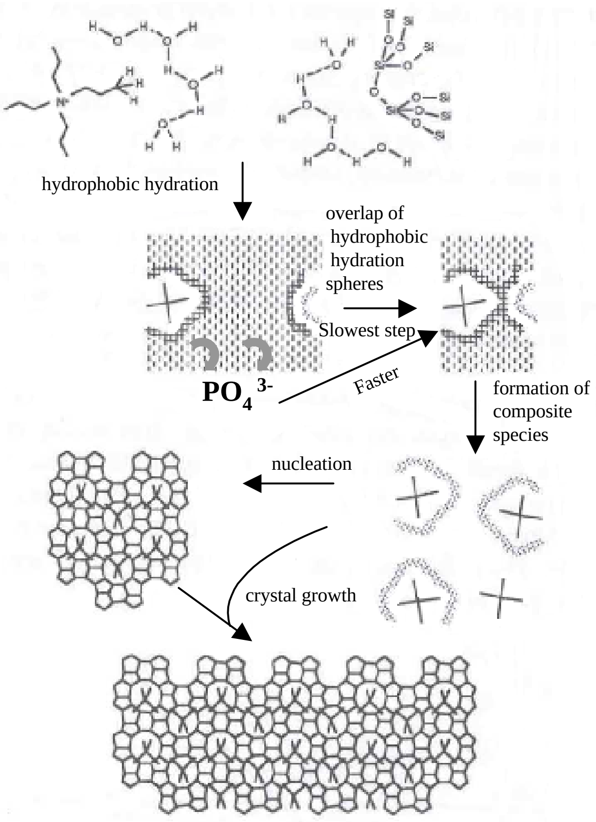


**Fig. 1.2:** Schematic representation of promoter assisted enhancement in the rate of zeolite nucleation and crystallization (Reproduced from Ref. 105).

### 1.5.5.2. Acidity

The Brønsted and Lewis acidities of zeolites play important roles in their abilities to catalyze various hydrocarbon reactions, e.g., cracking, isomerization, polymerization, alkylation etc. The Brønsted acid sites in zeolites can also generate Lewis acid sites on dehydroxylation under thermal treatments at temperatures usually above 773 K as described below (Fig. 1.3)[71,72].

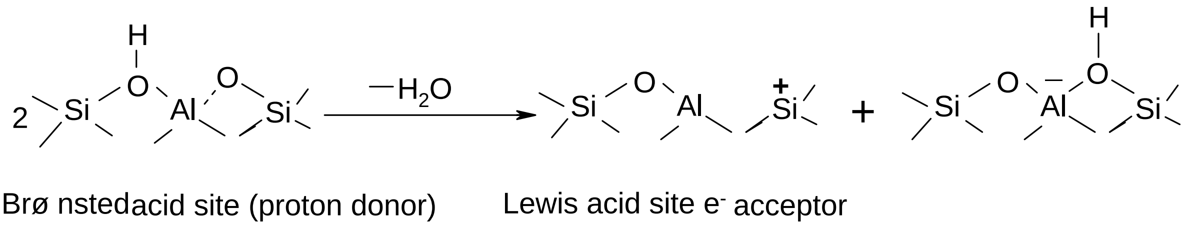


**Fig. 1.3:** Schematic showing Lewis and Brønsted acid sites on an aluminosilicate surface.

### 1.5.5.3. Shape Selectivity

The term ‘shape–selective catalysis’ was coined by Weisz and Frillette [106] more than four decades ago. Shape selectivity is a consequence of geometric restrictions on (i) access of reactants to the zeolite framework, (ii) diffusion of reactants in or products out and/or (iii) formation of transition states. These geometric restrictions result in following main shape selectivities as proposed by Sigmund M. Csicsery [107-110].

#### (a) Reactant Shape Selectivity (RSS)

RSS takes place only when a fraction of the reactants are small enough to diffuse through the catalyst pores. For example, preferential cracking of n-heptane (relative rate of 1.00) over dimethylhexane (relative rate of 0.09) is the best illustration of reactant selectivity for cracking of a straight chain versus branched $C_7$ (shown in Fig. 1.4 R) [109].

### (b) Product shape Selectivity (PSS)

PSS occurs when zeolite pores show ‘molecular sieving effect’ where some of the products formed within the pores are too bulky to diffuse out as observed products. They are either converted to less bulky molecules (e.g. by equilibriation) or eventually deactivate the catalyst by blocking the pores (Fig. 1.4 P). For example, the preferential production in modified pentasil zeolites of *p*-xylene over the ortho and meta forms due to pore diameter restrictions (Fig. 1.4 P)[109,110].

### (c) Restricted transition state shape selectivity (RTSSS)

RTSSS occurs when the space available in the pores of the zeolite strongly inhibits or prevents the formation of the reaction intermediate or unstable transition species that precedes that of a product (Fig. 1.4 T).

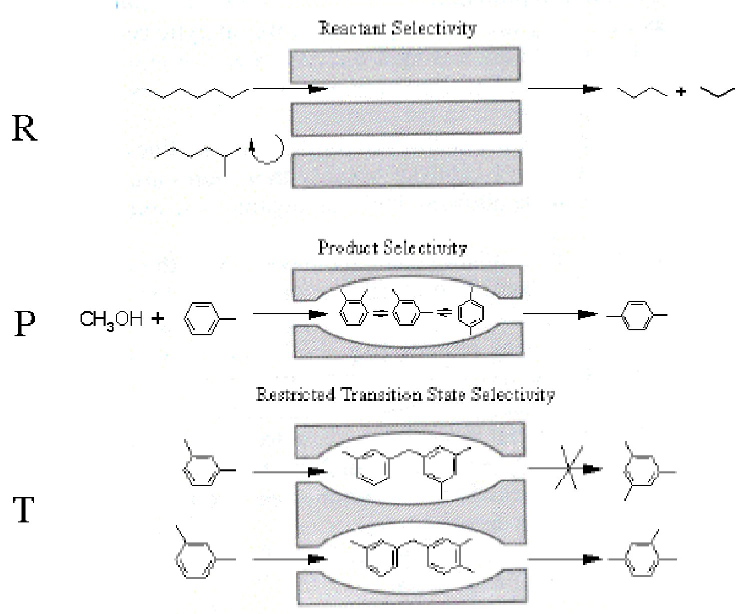


**Fig. 1.4:** Mechanisms of shape–selective catalysis.

For example, in the trans alkylation of *m*-xylene in Mordenite the 1,3,4 isomer can form, whereas the 1,3,5 isomer cannot because in the latter case the transition state is too bulky (Fig. 1.4 T) [107].

## 1.6. PHYSICO-CHEMICAL CHARACTERIZATION OF ZEOLITES

Several techniques are available for the characterization of various types of zeolites. Each technique is unique by itself and provides important information about the structure of a particular zeolite. The most commonly employed characterization techniques are powder X-ray diffraction (P-XRD), infrared spectroscopy (IR), adsorption and surface area analysis (BET), thermo gravimetric–differential thermal analysis (TG-DTA), scanning electron microscopy (SEM), chemical analysis by energy dispersive X-ray (EDX) and atomic absorption spectroscopy (AAS), and magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy.

### 1.6.1. Powder X-ray Diffraction (PXRD)

Among the different techniques available for the characterization of zeolites, X-ray diffraction is one of the most important, significant and versatile techniques [70,76,88,111]. The first step in characterization of the solid isolated from the synthesis mixture is X-ray powder diffraction. The most important outcome of PXRD of solid material includes the following.

- Uniqueness of structure.
- Level of crystallinity.
- Presence of single phase or mixture of phases.
- Incorporation of other elements into structural frame work sites.

- Determination of unit cell parameters.

The most intense characteristic peaks for zeolite occur in the range between the values of 5° (2è) and 40° (2è). The peaks at values higher than 40° (2è) are of significantly low intensity and depending on the level of crystallinity, may not be observable. Therefore, for most routine identification of zeolite phases by X-ray, the range between 5 and 40° (2è) is examined. When isomorphous substitution in zeolite occurs, the extent of incorporation of the isomorphous element can be correlated with the unit cell expansion or contraction [112,113].

### 1.6.2. Infrared Spectroscopy (IR)

IR spectroscopy is one of the classical techniques used routinely to derive information regarding the nature of phases, types of metal-ligand bonding and the presence of different functional groups. IR spectroscopy is a supplementary technique to X-ray diffraction since it is sensitive to zeolite framework vibrations. In the IR spectrum of zeolites in the range of 300-1300 $cm^{-1}$, the lattice vibrations can be divided 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. Flanigen *et al.* [114] assigned the following bands positions (shown in Table 1.5).

IR spectroscopy of OH groups [115] and adsorbed bases such as ammonia, pyridine and benzene [116] in zeolites can be used to confirm the acid characteristics of zeolites and it is also used to confirm the isomorphous substitution. Incorporation of Fe or Ga in place of Al shifts certain OH vibrations to lower wave numbers [101,117]. IR spectroscopy is also useful for the quick identification of materials of the pentasil family [118]. The absorption bands near 550 $cm^{-1}$ have been assigned to the presence of 5-membered rings in the structure [119]. The IR bands around 3600-3700 cm$^{-1}$ confirm the presence of the silanol groups [120] or bridged hydroxyl groups in the molecular sieves and their Brønsted acidities can be compared.

**Table 1.5: Zeolite infrared assignments (cm$^{-1}$)**

| **Internal tetrahedral** (structure insensitive vibration) | |
|---|---|
| Asymmetric stretch | 950-1250 |
| Symmetric stretch | 650-720 |
| T-O bend | 420-500 |
| **External linkages:** (structure sensitive vibration) | |
| Double ring | 500-650 |
| Pore opening | 420-300 |
| Symmetric stretch | 750-820 |
| Asymmetric stretch | 1050-1150 (sh) |

### 1.6.3. Thermal Analysis

Thermal analysis is used to study the structural stability of as–synthesized forms of zeolites, which makes zeolites applicable as selective sorbents and potential catalysts. It gives information about the temperature required for the removal of adsorbed water, decomposition of the occluded organic cations in the pores and channels of molecular sieves and dehydroxylation at higher temperatures to produce Lewis acid sites [121]. Thermal properties of zeolites can be evaluated from the data of TGA-DTA analysis [122].

### 1.6.4. Scanning Electron Microscopy (SEM)

This is another important tool for morphological characterization of microporous and mesoporous molecular sieve materials. Different type of morphology (e.g. cubic, circular etc.) of the synthesized materials as well as the presence of any amorphous phase in the samples can be characterized using this technique [123]. The major advantage of SEM is that bulk samples can also be studied directly by this technique.

### 1.6.5. Chemical Analysis

EDX, Atomic absorption spectroscopy etc. are useful techniques for elemental analysis of zeolites. The major advantages of these techniques are that bulk samples can also be studied directly.

### 1.6.6. Nuclear Magnetic Resonance (NMR) Spectroscopy

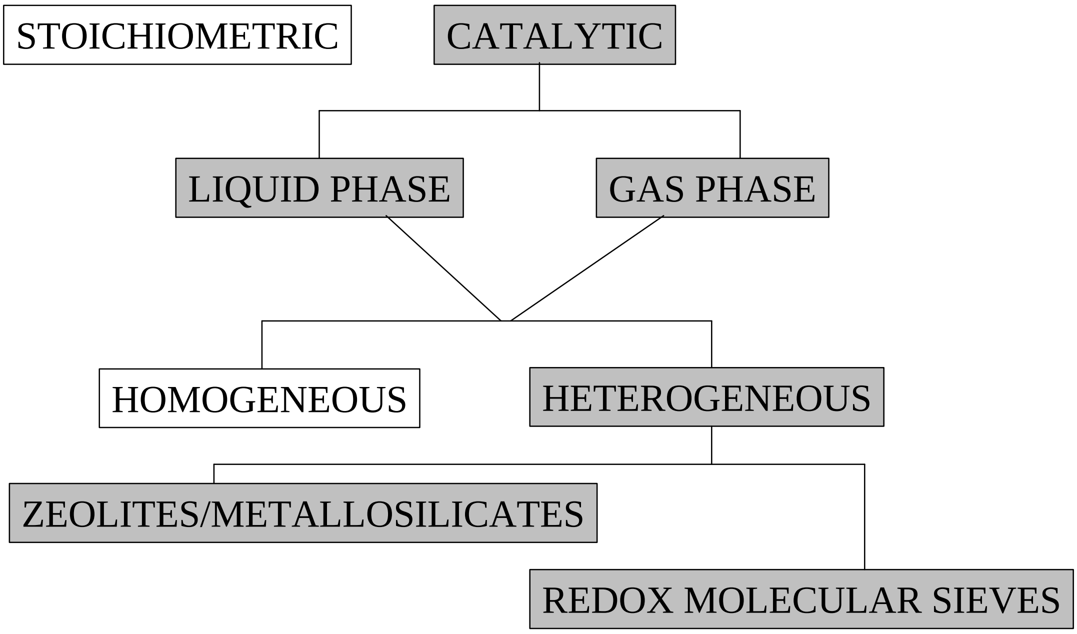
High Resolution magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy is a very important powerful technique to characterize the framework/non-framework elements in zeolites [124,125]. Lippama *et al.* [126] showed that $^{29}$Si MAS NMR spectra are very sensitive to the nature and chemical environment of the atoms. MAS NMR of $^{27}$Al, $^{51}$V etc. has also been extensively studied to characterize the incorporation of heteroatom in the framework by determining the local environment of Al, Ga, B, V etc. in corresponding metallosilicate molecular sieves [127,128]. Through magic angle spinning NMR spectra of $^{27}$Al, octahedral and tetrahedral [129,130] coordination can be distinguished.

## 1.7. SCOPE / OBJECTIVE OF THE THESIS

The present work deals with the detailed and systematic studies on the isopropylation of C-8 aromatics (xylenes and ethylbenzene) over zeolites such as Mordenite, Beta and USY. The effect of isomorphous substitution of other trivalent metal ions like $Ga^{3+}$, $B^{3+}$ and $Fe^{3+}$ in zeolite Beta was also studied in the isopropylation of C-8 aromatics. The effect of alkylating agents like isopropanol as well as isopropyl chloride and bromide were also studied at relatively low temperature range (313-353 K using alkyl halides in liquid phase and 393 to 453 K for isopropanol in vapour phase fixed bed down flow glass reactor). Interestingly, isopropylation of C-8 aromatic over iron exchanged zeolites using alkyl halides as alkylating agent at low temperature (313 to 353 K) with very short reaction time (20-60 min) was studied for the first time and results are given in the present dissertation. Moreover, to the best our knowledge the systematic and detailed studies on the isopropylation of all xylenes and ethylbenzene over zeolites, especially over zeolite Mordenite, Beta and USY are not reported earlier.

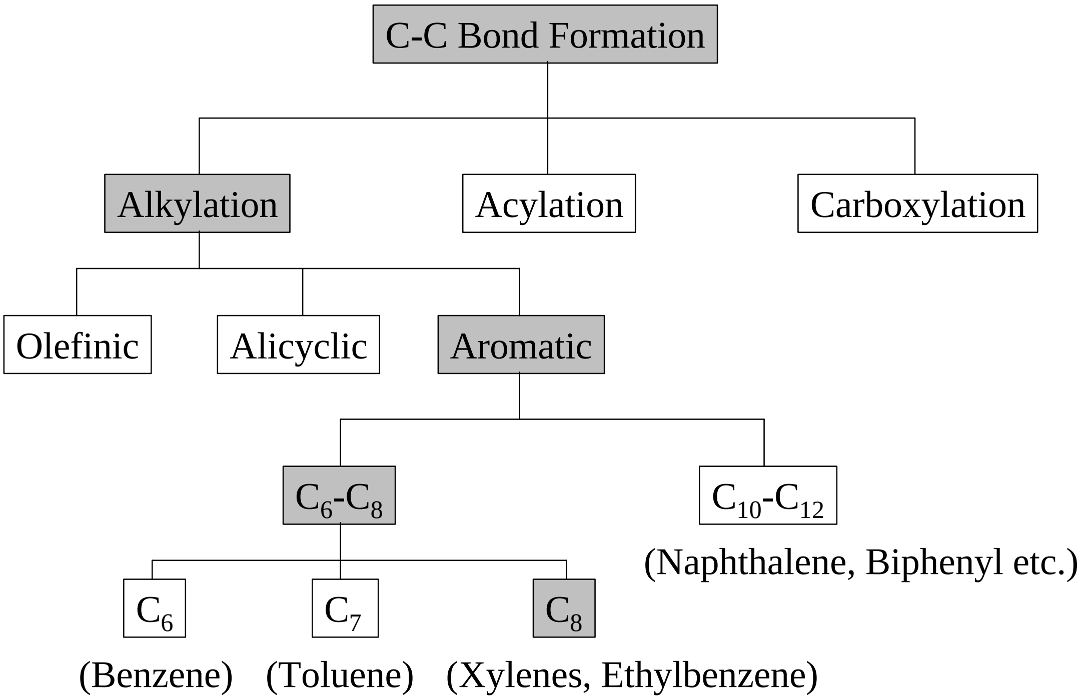
The purpose of this work is to study and understand the activity and selectivity patterns as a function of systematic variation of reaction conditions in the isopropylation of all the three xylenes and ethylbenzene over solid catalysts.

The focus of this work is vapour-phase isopropylation reactions under heterogeneous conditions as highlighted in Scheme 1.1. The Liquid phase solvent free, isopropylation of aromatic compounds, using isopropyl halides (2-bromopropane and 2-chloropropane) has also studied for the first using iron doped zeolites.



**Scheme 1.1:** Catalytic process options for the fine chemicals production.

The broad classification of carbon-carbon (C-C) bond formation reaction and the focus of the work (as highlighted) is schematically represented in Scheme1 2.



**Scheme 1.2:** Schematic representation of C-C bond formation in alkylation reaction.

## 1.8. OUTLINE OF THE THESIS

The thesis has been divided into six chapters.

### Chapter I: Introduction

Chapter I represents a general introduction to heterogeneous acid catalysis and earlier literature on the isopropylation of C-8 aromatic compounds. It also briefly describes the synthesis, modification and characterization techniques of different solid acid catalysts including zeolites and their catalytic application in the isopropylation of C-8 aromatic compounds using alcohols and alkyl halides as alkylating agents.

### Chapter II: Experimental

This chapter is divided into two parts.

The first part describes the synthesis & modification of various zeolites like Beta with different silica/alumina molar ratio and isomorphously substituted B-Beta, Ga-Beta and Fe-Beta. Synthesis of other solid acid catalysts like ZSM-12, Mordenite, sulfated-zirconia and MCM-41 were also incorporated for comparative purpose. Zeolite Mordenite, Beta and USY were modified with ferric nitrate solution by conventional ion exchange method and used for comparison of their catalytic activity.

The second part describes the characterization of the zeolite materials by XRD, surface area measurement, IR spectroscopy, TGA-DTA, SEM, EDX, AAS and NMR.

### Chapter III: Vapour Phase Isopropylation of Xylenes

This chapter describes the detailed study of vapor phase isopropylation reaction of all xylene isomers (*o*-, *m*- and *p*-xylene) with isopropanol as alkylating agent over zeolite H-Beta and USY. Other zeolites like H-Mordenite, H-ZSM-5, ZSM-12 and H-Y, and amorphous silica-alumina, sulfated zirconia and Al-MCM were also used for comparison of catalytic activity. Isomorphously substituted zeolites like B-Beta, Ga-Beta and Fe-Beta were also included for the vapor phase isopropylation of *m*-xylene with isopropanol. The influences of various reaction parameters such as temperature, time on stream (TOS), contact time (WHSV) and mole ratios of the substrate to alkylating agent were also investigated.

### Chapter IV: Vapour Phase Isopropylation of Ethylbenzene

This chapter describes the detailed study of vapour phase isopropylation reaction of ethylbenzene with isopropanol as alkylating agent over zeolite H-Mordenite, H-Beta and USY. Other zeolites like H-Y, H-ZSM-5, H-ZSM-12, H-Mordenite and isomorphously substituted zeolite Beta like B-Beta, Ga-Beta and Fe-Beta were also used for comparison of catalytic activity.

### Chapter V: Liquid Phase Isopropylation of C-8 Aromatics

Chapter V describes the detailed study of isopropylation reaction of C-8 aromatics (xylenes and ethylbenzene) with isopropyl halides over iron-exchanged zeolite Beta (Fe/Beta) in the liquid phase in relatively low temperature range (313 to 353 K) at atmospheric pressure with very short reaction time (20-60 min). The influences of various parameters such as reaction time, temperature and dilution of the substrates w. r. t. alkylating agents were investigated.

### Chapter VI: Summary and Conclusions

A summary of the results obtained and the conclusions drawn are presented in this chapter.

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## 2.1 SYNTHESIS AND MODIFICATION

The present chapter deals with the hydrothermal synthesis of zeolites like Beta with different silica to alumina molar ratio, Mordenite and ZSM-12 based on the procedures as described in the literature [1-6]. The metallosilicate analogs of the zeolite Beta like B-Beta, Ga-Beta and Fe-Beta have also been synthesized according to available literature [1-3]. It also includes a brief description for the synthesis of other solid acid catalysts like sulfated-zirconia [7], mesoporous molecular sieves (Al-MCM-41) [8] incorporated in the present thesis mainly for comparative purpose. The ultra-stable zeolite Y (USY) and silica-alumina (SAL) were obtained from Union Carbide and M/S Joseph Cross-field, respectively. Zeolites ZSM-5 and Na-Y were procured from Catalysis pilot plant of our laboratory.

Zeolite Beta, Y, USY and Mordenite were also modified by ion exchange method with aqueous ferric nitrate solution. All the synthesized and modified zeolites are characterized by various physico-chemical techniques.

## 2.2. EXPERIMENTAL

### 2.2.1. Materials Used For Synthesis and Modification of Catalysts

Chemicals for the synthesis of different microporous zeolites, metallosilicates, MCM-41, other solid acid catalysts and for the modification of Beta, USY, Y and Mordenite were used as received without any further purification if not mentioned specifically.

**Silica Source:** Fumed silica [99.8 %, Aldrich], Silica sol (30% $SiO_2$)

**Template:** Tetraethylammoniumhydroxide (TEAOH) [35 % aqueous soln., Aldrich]
Cetyltrimethylammoniumbromide(CTABr) [98 %, s.d. fine-CHEM LTd., India]
Tetrapropylammoniumhydroxide (TPAOH) [20 wt.%, aqueous soln., Aldrich]
Tetraethylammoniumbromide (TEABr) [98%, Aldrich]

**Boron source:** Borax, disodiumtetraborate [99.5 %, s.d. fine-CHEM LTd., India]

**Aluminium source:** Aluminium(III)sulphatehydrate [$Al_2 (SO_4)_3. 16H_2O$ (98%), s.d. fine-CHEM LTd., India ]

**Sodium aluminate: (**$NaAlO_2$) [39% $Na_2O$, 43.6% $Al_2O_3$, Catalysis pilot plant, NCL]

**Zirconium oxychloride: (**$ZrOCl_2$)[98.0%, LOBA Chemical, India]

**Aqueous ammonia: (**$NH_4OH$) [25% aqueous soln., s.d. fine-CHEM LTd., India]

**Silver nitrate: (**$AgNO_3$) [98.0%, LOBA Chemical, India]

**Sulfuric acid (GR.): (**$H_2SO_4$) [98.0%, LOBA Chemical, India]

**Gallium source:** Gallium (III) nitrate hydrate [99.9%, Aldrich]

**Iron source:** Ferric nitrate [$Fe (NO_3)_{3..} 9H_2O$, 98%, LOBA Chemical, India]

**Oxalic acid:** [$(COOH)_2. 2H_2O$, 99.5 %, s.d. fine-CHEM LTd., India]

### 2.2.2. Al-Beta

Three Al-Beta samples with different Si/Al molar ratios (Si/Al = 20, 30 and 40) were synthesized hydrothermally at 413 K [5]. In a typical synthesis of Beta zeolite (Si/Al = 20), solution A, containing 0.52 g NaOH in 10 g $H_2O$ was added to a slurry of 12 g fumed silica in 40 g $H_2O$. To this mixture 0.38 g KOH in 10 g $H_2O$ was added. The mixture was stirred for 1 h. To this mixture, a solution of 36.8 g TEA-OH (40% aqueous soln.) was added under vigorous stirring. The resultant slurry was stirred for another 1 h followed by the addition of an aqueous solution of 3.15 g aluminum sulfate hexahydrate (2.1g and 1.6 g for Si/Al = 30 and Si/Al = 40 respectively) in rest of water (14 g) and the stirring was continued for another 1 hour. Then the final gel (pH = 12.5 ± 2) was transferred into 300ml stainless steel autoclave, kept at oven of 413 ± 1K for 48 h at 120 r.p.m. and after cooling the autoclave, the synthesized solid product was filtered, washed thoroughly with deionized water till pH 8 and dried at 373 K for 2 h followed by calcination at 813 K for 12 h in a flow of air.

### 2.2.3. B- and Ga-Beta

The zeolite B- and Ga-Beta were synthesized hydrothermally at 413 K according to following molar gel composition [1]:

$20SiO_2$: 5 $(TEA)_2O$: 0.5 $M_2O_3$: 1.2 $Na_2O$ :0.6 $K_2O$ :300 $H_2O$ (Where M = B and Ga).

For the synthesis of B- and Ga-Beta zeolite (Si/M = 20), solution A, containing 0.96 g NaOH, 0.67 g KOH and required amount of metal source [1.28 g of $Ga(NO_3)_3$ or 3.82 g of borax ($Na_2B_4O_7.10H_2O$)] in 20 g $H_2O$ were added dropwise under vigorous stirring in solution B, which was prepared by slow addition of 12 g fumed silica in rest of water ( 6.7 g $H_2O$) over a 42 g of TEA-OH (40% aq. Aldrich) solution. The resultant slurry was stirred for another 1 h. Then the final gel was transferred into 300ml stainless steel autoclave, kept at an oven of 413 ± 1 K for 72 h at 120 r.p.m. After cooling the autoclave, the synthesized solid product was filtered, washed thoroughly with deionized water till pH 8 and dried at 373 K for 2 h followed by calcination at 813 K for 12 h in a flow of air.

### 2.2.4. Fe-Beta

The Fe-Beta sample was prepared hydrothermally at 413 K, according to a general and convenient method by using a complexing agent [2,3]. In a typical synthesis of Beta zeolite (Si/Fe = 40), using the following molar gel composition.

$20SiO_2$: 5 $(TEA)_2O$: 0.25 $Fe_2O_3$: 0.75 OX: 1.2 $Na_2O$ :0.6 $K_2O$ :300$H_2O$

Solution A containing 0.96 g NaOH and 0.67 g KOH in 10 g $H_2O$ was added dropwise under vigorous stirring over solution B, prepared by slow addition 12 g of fumed silica (99.8%, Aldrich) in 800 g $H_2O$ over a 42 g of TEA-OH (35 % aq. Aldrich) solution. The resultant slurry was stirred for another 1 h. Solution C containing 2.02 g ferric nitrate [$Fe(NO_3)_{3.}$ $9H_2O$] and 1.89 g oxalic acid (99.5%, s. d. fine-CHEM LTd. India) in 18 g $H_2O$ was added to the resulting mixture dropwise under vigorous stirring. Now the resultant slurry was stirred for another 1 h. Then the final gel was transferred into 300ml stainless steel autoclave, kept at an oven of 413 ± 1K for 72 h at 120 r.p.m. After cooling the autoclave, the synthesized solid product was filtered, washed thoroughly with deionized water till pH 8 and dried at 373 K for 2 h followed by calcination at 813 K for 12 h in a flow of air.

## 2.2.5. Mordenite

Zeolite Mordenite was synthesized hydrothermally at 443 K according to the available method [4] using following molar gel composition:

$30SiO_2 : 2.5\ Al_2O_3 : 6Na_2O : 780H_2O$

In a typical synthesis of Mordenite (Si/Al = 6), solution A, containing 1.23 g NaOH and 3.89 g $NaAlO_2$ [39% $Na_2O$, 43.68% $Al_2O_3$] in 33.6 g $H_2O$ was stirred for 15 minutes to make homogeneous solution. 12 g of fumed silica in 40 g water was slowly added to solution A, under vigorous stirring for 1 h. At last 0.3 g Mordenite (2.5 wt.% w. r. t silica) as mother seeds to improve the crystallization time, followed by rest of water (20 g) was added to final solution. The resultant slurry was stirred for another ½ h. Then the final gel was transferred into 150 ml stainless steel autoclave, kept at an oven of 443 ± 1K for 36 h. After cooling the autoclave, the synthesized solid product was filtered, washed thoroughly with deionized water till pH 8 and dried at 373 K for 2 h followed by calcination at 813 K for 12 h in a flow of air.

### 2.2.6. ZSM-12

The synthesis of ZSM-12 (Si/Al = 80) was carried out hydrothermally at 413 K [6]. The synthesis gel was prepared by mixing appropriate amount of silica-sol (30% $SiO_2$), sodium hydroxide, sodium aluminate (39% $Na_2O$, 43.68% $Al_2O_3$), ammonium hydroxide (25% aqueous soln.) and tetraethylammoniumbromide (98%) (TEABr). In a typical procedure, 26.25 g of TEABr was mixed with 20 g of water in a polypropylene beaker. While stirring this mixture, a solution of 0.39 g $NaAlO_2$ in 20 g of distilled water was added dropwise, followed by the addition of 0.88 g NaOH in 20 g water. The mixture was stirred for another 1/2 h. Then required amount of aqueous ammonia solution (25%) was added dropwise to maintain the pH around 13.1 Finally, 53.78 g of silica sol (30% $SiO_2$) was added to the solution. The final gel mixture was stirred for another 1 h and transferred into 200ml stainless steel autoclave, kept at oven of 413 ± 1K for 10 days. After cooling the autoclave, the synthesized solid product was filtered, washed thoroughly with deionized water till pH   8 and dried at 373 K for 2 h followed by calcination at 813 K for 12 h in a flow of air.

### 2.2.7. Sulfated-zirconia

$ZrOCl_2.8H_2O$ was hydrolyzed to zirconium hydroxide with aqueous ammonia (28%) in the pH range of 8-9 at temperature range of 333-343 K [7]; aqueous ammonia solution was added drop wise with stirring into 50 g of $ZrOCl_2.8H_2O$ dissolved in 11ml of distilled hot water. The precipitate was washed several times with hot water until the filtrate was chloride free checked by silver nitrate solution and finally dried at 383 K. The dried sample was then stirred with 1(N) sulfuric acid for 2h and filtered. After drying, the sample was calcined at 823 K in presence of air for 4 h.

### 2.2.8. Al-MCM-41

The syntheses of Al-MCM-41 samples were carried out using $NaAlO_2$ as the aluminum source [8]. For the synthesis of Al-MCM-41 sample, an aqueous solution of $NaAlO_2$ was added to the mixture of $Na_2SiO_3$, $SiO_2$ ($Na_2SiO_3/SiO_2$ (mol/mol) = 0.124:1) and aqueous TMAOH under stirring. Then, aqueous solution of CTABr was added to the synthesis mixture and stirred for 15 minutes after addition. The final molar gel composition of Al-MCM-41 sample was 1 $SiO_2$ : 0.05 $Al_2O_3$ : 0.12 $Na_2O$ : 0.08 TMAOH : 0.21 CTABr : 0.1 NaCl : 125 $H_2O$. At last an aqueous solution of NaCl was added to the synthesis mixture to maintain the $Na^+/SiO_2$ molar ratio. The final gel mixtures were refluxed under stirring for a period of 24h as shown in Table 2.1. The solid products were collected by filtration, washed thoroughly with deionized water and acetone, dried at 353 K and calcined in flowing air at 813 K for 8 h.

### 2.2.9. H-Form of Zeolites

The protonic forms of all the zeolites were prepared by repeated (3 times) ammonium exchange with (1M) $NH_4NO_3$ solution for 8h at 353 K. For MCM-41, the exchange procedure was carried out at room temperature for 24 h. Then the samples were filtered, washed thoroughly and dried at 393 K overnight and further calcined at 813 K for 12 hours in flowing air to obtain H-form of zeolites.

### 2.2.10. Preparation of Cation-Exchanged Zeolites

The metal ion ($Fe^{3+}$) loaded zeolite catalysts were prepared by stirring the mixture of (10 g) H-form of the zeolites with an 100ml of 0.1 (M) aqueous solution of ferric nitrate, at 353 K for 8 hours, where these experiments were repeated thrice, followed by filtration, washing with copious amount of water, dried overnight at 393K and further calcined at 673K for 4 hours in flowing air.

## 2.3. STRUCTURES OF SOME ZEOLITES

Framework structures of zeolites, available in the book of “Atlas of Zeolite Framework Types”[9], used in this study are presented in Fig. 2.1 and 2.2. The Fig. 2.1 (A-C) depicts representation of framework structures of (A) Mordenite, (B) Beta and (C) Faujasite, respectively. Zeolite Mordenite is having non-intersecting channels with 0.57 nm x 0.71 nm pore opening. Zeolite Beta consists of three dimensional interlinking channels with pore openings 0.57 nm x 0.75 nm for linear and 0.65 nm x 0.56 nm for tortuous channels. Zeolite Y consists of linked truncated octahedral called sodalite units, which have a cage of diameter 0.65 nm (â cage) and accessible through six membered rings of oxygen atoms. These units are connected along two six membered rings, giving rise to hexagonal prism. The polyhedra formed in this way encloses a supercage (á cage) with an internal diameter of 1.25 nm and accessible through four 12-membered rings of oxygen atoms with a free aperture of 0.74 nm. The framework structure of zeolite Y is depicted in Fig. 2.1 C.

The framework structures of ZSM-5 and ZSM-12 are given in Fig. 2.2. ZSM-5 consists of intersecting 10 membered ring channels and its pore opening are: 0.51 nm x 0.56 nm for straight and 0.54 nm x 0.56 nm for sinusoidal channels as shown in Fig. 2.2 (A). The pore structure of ZSM-12 consists of linear, non-interpenetrating, channels having 12 membered openings of aperture of 0.57 nm x 0.61 nm. (Fig. 2.2 B).

## 2.4. PHYSICO-CHEMICAL CHARACTERIZATION

Application of different type of physico-chemical techniques e.g. XRD, IR, TGA-DTA, SEM, EDX, NMR etc. and their principles to zeolites have been already described in section 1.5 of Chapter I. All the synthesized and modified zeolites were characterized by various physico-chemical techniques and summarized in Table 2.1 to Table 2.3.

**Table 2.1: Physical parameters for the synthesis of B-, Al-, Ga- and Fe-Beta samples**

| Sample | Si/M ratio | | Synthesis | | pH | |
|---|---|---|---|---|---|---|
| | $(Si/M)_{gel}$ | $(Si/M)_{solid}$ | Temperature, K | Time, h | Initial | Final |
| **Al-Beta (20)** | 20.0 | 20.0 | 413 | 48 | 12.7 | 12.9 |
| **Al-Beta (30)** | 30.0 | 30.8 | 413 | 48 | 12.5 | 12.6 |
| **Al-Beta (40)** | 40.0 | 40.5 | 413 | 48 | 12.8 | 12.9 |
| **B-Beta (20)** | 20.0 | 21.5 | 413 | 72 | 12.7 | 12.9 |
| **Ga-Beta (20)** | 20.0 | 22.0 | 413 | 72 | 13.2 | 12.5 |
| **Fe-Beta (40)** | 40.0 | 44.0 | 413 | 72 | 12.6 | 12.8 |
| **Mordenite(6)** | 6.0 | 5.9 | 443 | 36 | 12.4 | 12.1 |
| **ZSM-12 (80)** | 80 | 80.0 | 413 | 240 | 13.1 | 12.6 |
| **Al-MCM-41 (20)** | 20.0 | 20.5 | 373 | 24 | 11.1 | 11.2 |

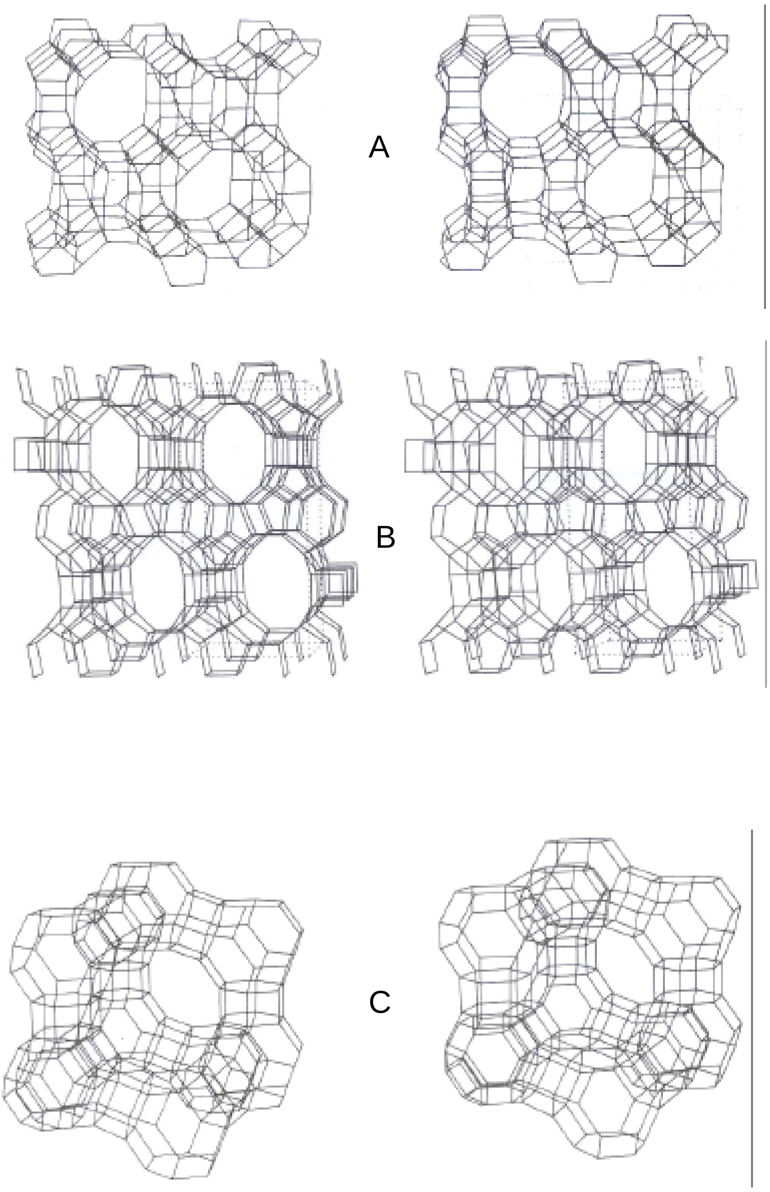


**Fig. 2.1:** Schematic diagram of zeolite (A) Mordenite, (B) Beta and (C) Faujasite.

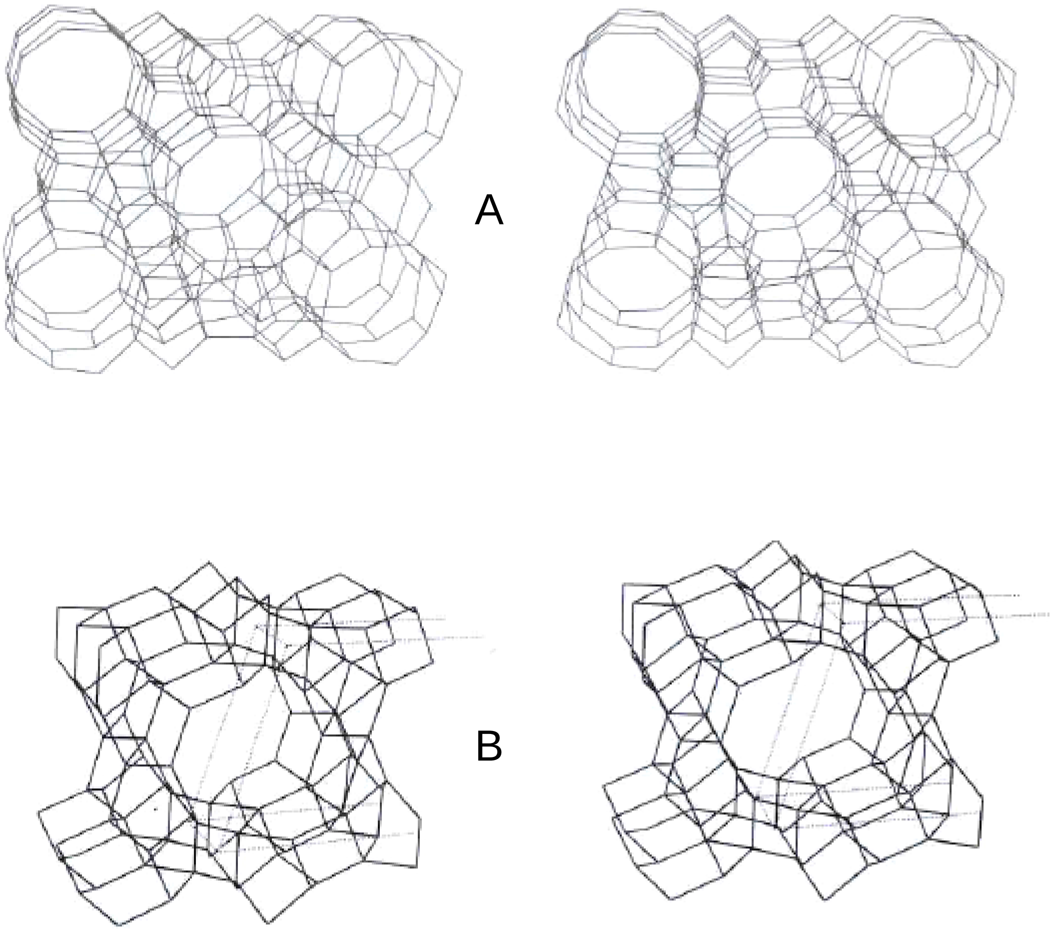


**Fig. 2.2:** Schematic diagram of zeolite (A) ZSM-5 and (B) ZSM-12.

### 2.4.1. Powder X-ray Diffraction (XRD)

To determine the crystallinity and phase purity, all synthesized and modified zeolite samples were examined by X-ray (powder) diffraction. The XRD patterns of the samples were recorded using an automated diffractometer (Model D-MAX – III VC, Rigaku, Japan or Rigaku Miniflex diffractometer) with a Ni filtered CuKα radiation ($\lambda$=1.5404 Å). Data were collected at a scan rate of 8°/min in the 2è range of 5° to 50° with silicon as an internal standard for zeolite samples. For sulfated-zirconia and Al-MCM-41 samples, X-ray data were collected in the 2è range of 20° to 80°, 8°/min, and 1.5° to 10°, 1°/min respectively.

The x-ray powder diffractograms of as-synthesized and various calcined Beta are shown in Fig.2.3 (curve a-g). In Fig. 2.3. curve a, a’, b, c, d, e, f and g indicate the XRD pattern of as-synthesyzed Al-Beta, calcined Al-Beta, B-Beta, Fe-Beta, Fe loaded Beta and Ga-Beta. The XRD of other solid acid catalysts including zeolites and MCM-41 are depicted in Fig. 2.4 and 2.5. No extra impurity peaks were obtained. The high intensity and narrow peak shape in the XRD patterns clearly indicate that the samples are highly crystalline.

### 2.4.2. Surface Area Measurement

Omnisorb 100 CX unit (supplied by COULTER Corporation, USA) was used for the measurement of surface area of all calcined samples from $N_2$ adsorption using BET method. The sample (~ 0.2 g) was activated at 673 K for 2h in high vacuum ($10^{-6}$ mm) and then it was allowed to cool at room temperature under vacuum and the anhydrous weight of the sample was taken. Adsorption of $N_2$ was carried out at liquid nitrogen temperature (77K) and finally the surface area of the sample was calculated by the BET method [10,11]. The specific BET surface area of all samples are presented in Table 2.2 and 2.3.

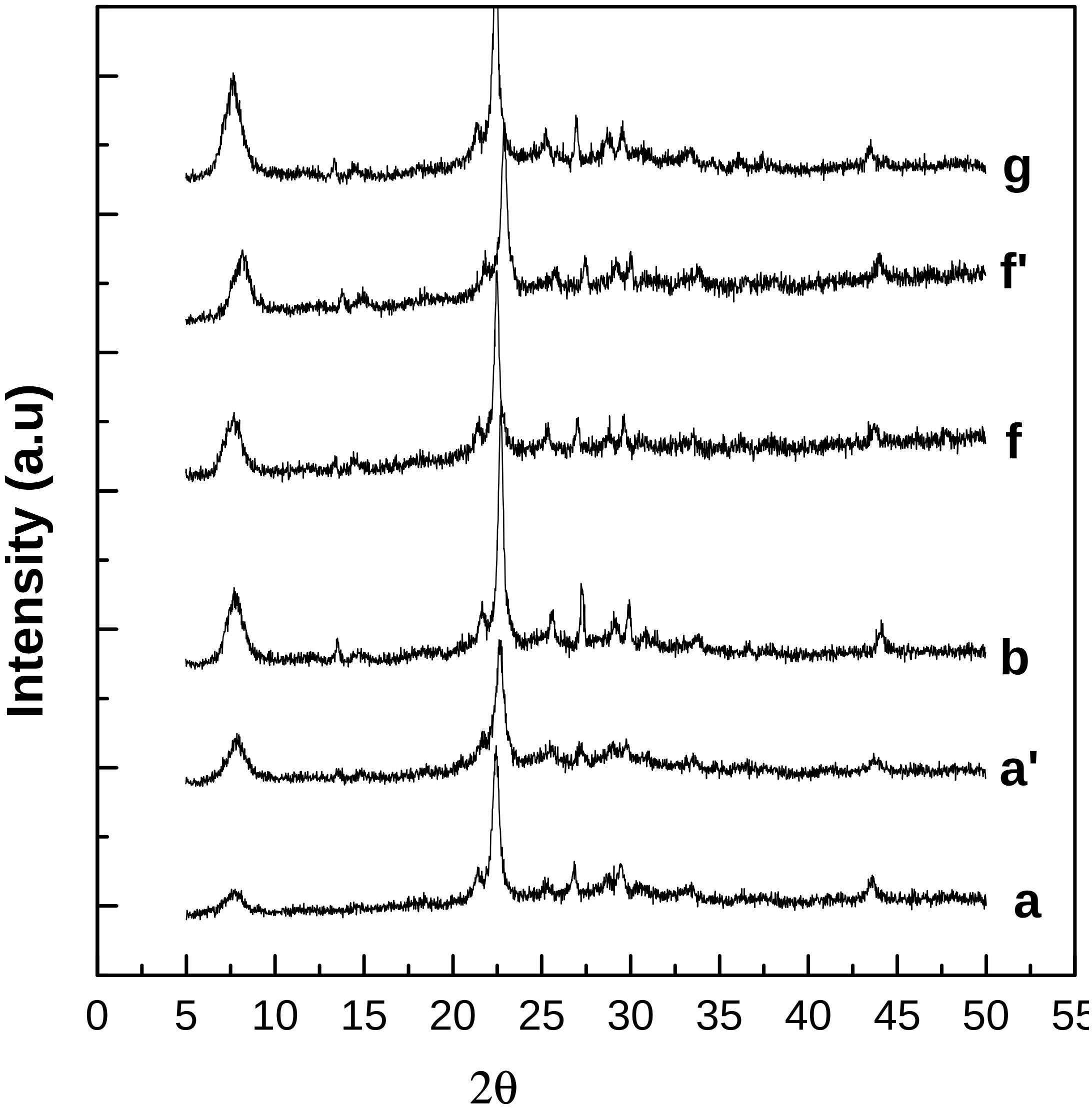


**Fig. 2.3:** X-ray diffraction pattern of as synthesized Al-Beta (curve a) and calcined Al-Beta (curve a'), B-Beta (curve b), Fe-Beta (curve f), Fe-loaded Beta (curve f') and Ga-Beta (curve g).

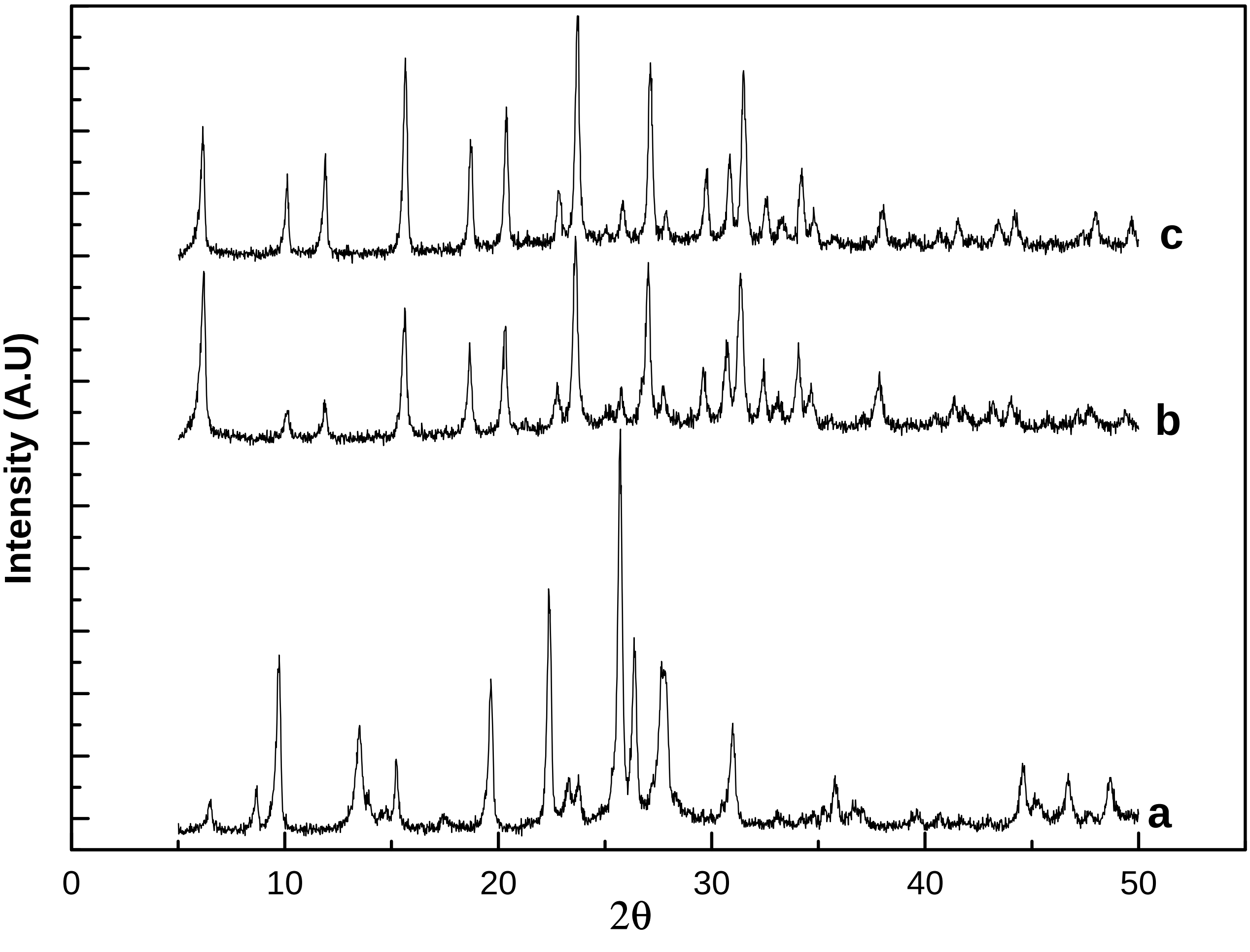


**Fig. 2.4:** X-ray diffraction patterns of calcined Mordenite (curve a), H-Y (curve b) and USY (curve c).

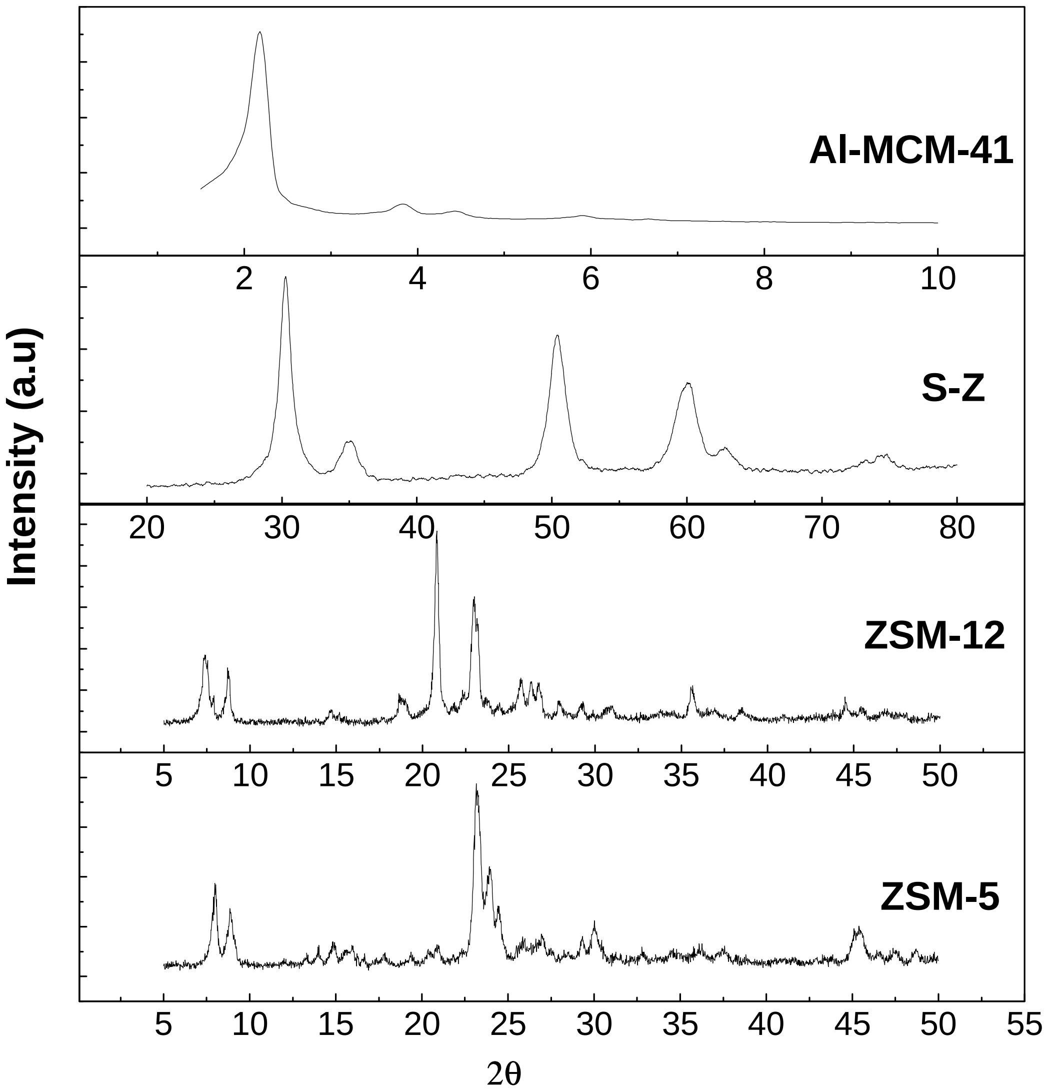


**Fig. 2.5:** X-ray diffraction patterns of calcined (i) ZSM-5, (ii) ZSM-12, (iii) Sulfated-zirconia (S-Z) and (iv) Al-MCM-41.

**Table 2.2: Si/Al molar ratio, crystallite size and BET surface area of different catalysts**

| Sample Name | (Si /M) | Crystal size,µm | Surface area ($m^2g^{-1}$) |
|---|---|---|---|
| Al-Beta (20) | 20.0 | 0.5 – 1.0 | 609.0 |
| Al-Beta (30) | 30.5 | 0.5 – 1.0 | 618.0 |
| Al-Beta (40) | 40.8 | 0.5 – 1.0 | 635.0 |
| B-Beta (20) | 21.5 | 0.5 – 1.0 | 640.0 |
| Ga-Beta (20) | 22.0 | 0.5 – 1.0 | 615.0 |
| Fe-Beta (40) | 44.0 | 0.5-0.6 | 630.0 |
| Al-Mordenite (6) | 5.9 | 0.6-0.9 | 519.0 |
| H-Y | 2.9 | 0.4-0.8 | 700.0 |
| Ultra stable-Y (USY) | 5.6 | 0.4-0.8 | 650.0 |
| Al-ZSM-5 | 21.0 | 0.3 – 1.0 | 460.0 |
| Al-ZSM-12 | 80.0 | 0.4 – 0.6 | 482.5 |
| Silica-alumina | 2.6 | - | 105.2 |
| Sulfated-zirconia | 3 wt% sulfur | 0.2 | 100.0 |
| MCM-41 | 20.5 | 0.2 | 948.0 |

**Table 2.3: Si/Al molar ratio, wt.% of Fe, crystallite size and BET surface area of different iron exchanged zeolites.**

| Sample Name | (Si /Al) | Wt.% of Fe | Crystal size,µm | Surface area ($m^2g^{-1}$) |
|---|---|---|---|---|
| Fe/Beta | 20.0 | 3.5 | 0.5 – 1.0 | 570.0 |
| Fe/Mordenite | 5.9 | 4.8 | 0.6-0.9 | 485.0 |
| Fe/Y | 2.9 | 4.0 | 0.4-0.8 | 630.0 |
| Fe/USY | 5.6 | 5.8 | 0.4-0.8 | 645.0 |

### 2.4.3. Infrared Spectroscopy (IR)

IR spectra of all samples were recorded in the range of 400–1300 $cm^{-1}$ using Shimadzu FTIR-8201 PC in Nujol mull on KBr plate.

The framework FTIR spectra (in the region 200-1300 $cm^{-1}$) of calcined zeolite Beta containing B-, Al-, Ga- and Fe are shown in Fig. 2.6. On introduction of B-, Ga- and Fe- instead of Al- in the zeolite Beta, most of the IR bands are shifted to lower (for Fe- and Ga-) or higher (for B-) wave numbers, which is in agreement with the expectations on basis of the nature of the metals. The bands at 1218, 1082 and 790 $cm^{-1}$ correspond to internal asymmetric stretching, external asymmetric stretching and external symmetric stretching respectively.

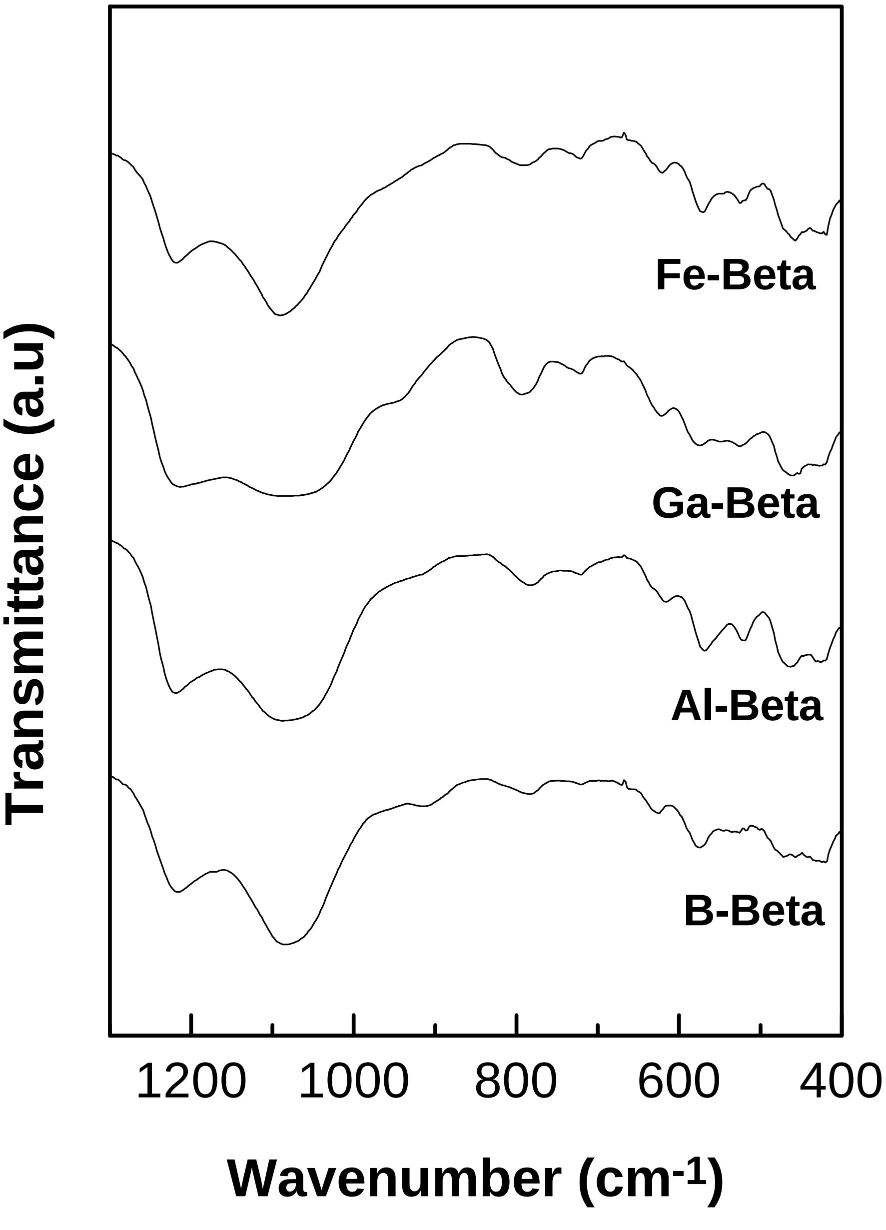


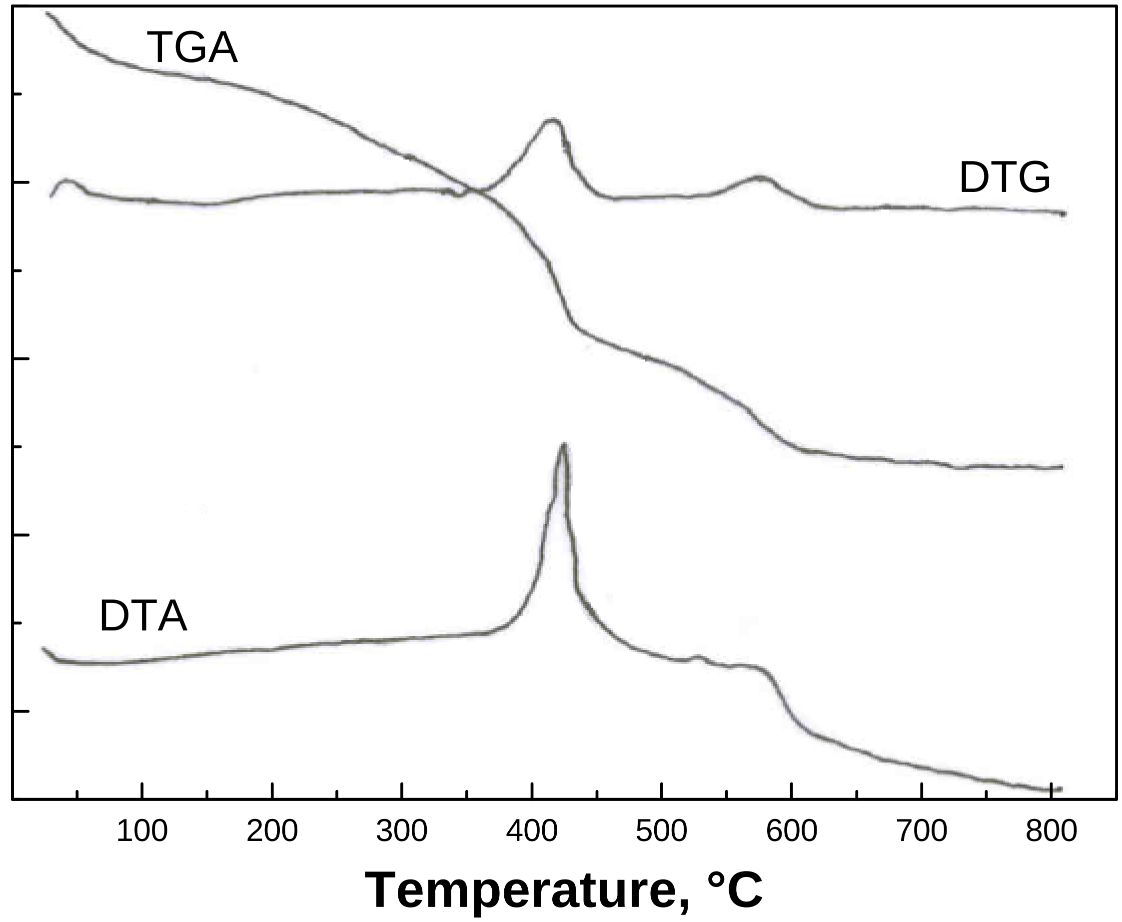
**Fig. 2.6:** IR framework vibration spectra of calcined B-, Al-, Ga- and Fe-Beta.

### 2.4.4. Thermal Analysis

The thermal analysis of the as-synthesized samples was carried out on a thermogravimetric–differential thermal analysis (TG-DTA) instrument (SEIKO Model No. TG/DTA, D.S.C. Model No. 220C) under a flow of air. The following analysis conditions are employed to find out the temperature of decomposition of the organic additive and weight loss.

| | |
|---|---|
| Heating rate: | 10K/min |
| Temperature range: | 298 K to 1073 K |
| Purge gas: | Air (2.5 lit/h) |
| Weight of the sample: | 4 to 6 mg |
| Reference material: | á –alumina (inert). |

The TGA-DTA-DTG pattern of as-synthesized Al-Beta sample (as representation) is shown in Fig. 2.7. The DTA pattern of Fig. 2.7 shows four stages, which corresponds to the temperature zones of approximately 25-350 °C, 350-450°C, 500-550°C and 550-800°C.The first step is slightly endothermic and assigned to the desorption of water. The other three steps are exothermic and are associated with the oxidation of organic materials. The first two exothermic steps are ascribed to the decomposition of TEAOH occluded in the zeolite and pyrolysis of $TEA^+$ cations, respectively. The final exothermic step at 550-800°C is ascribed to the oxidative decomposition of residual coke formed by the decomposed template materials occluded in the zeolite channels. These steps in DTA pattern are complementary to the steps in TGA and DTG patterns.



**Fug. 2.7:** Thermograms of as-synthesized zeolite Al-Beta.

### 2.4.5. Scanning Electron Microscopy (SEM)

The morphology of the samples was investigated by using a scanning electron microscopy (Model JSM 5200, JEOL, Japan). The sample was suspended in acetone (A.R grade) and made a very thin film on a brass sample holder. The sample was then coated with a thin film of gold to prevent surface charging and to protect the zeolite material from thermal damage by the electron beam. For all the samples a uniform thickness of about 0.1 mm was maintained.

The scanning electron micrographs (SEM) of metallosilicates analogues of zeolite Beta are shown in Fig. 2.8. Micrographs (‘A’ to ‘D’ in Fig. 2.8 refer to B-, Al- Ga- and Fe-Beta samples respectively), showed the absence of any amorphous matter external to zeolite or other crystalline phase impurities. All the metallosilicate samples consisted of crystals of about 0.5 – 1.0 μm in dimension. The SEM of calcined zeolite Mordenite, ZSM-12, H-Y and USY are shown as A, B, C and D in Fig. 2.9, respectively. The crystals of zeolite Mordenite are elongated in shape with average size of 0.6 to 0.9 µm. The crystal size along with other physico-chemical characteristics of zeolites and other solid acid catalysts studied in this work are summarized in Table 2.2 and 2.3.

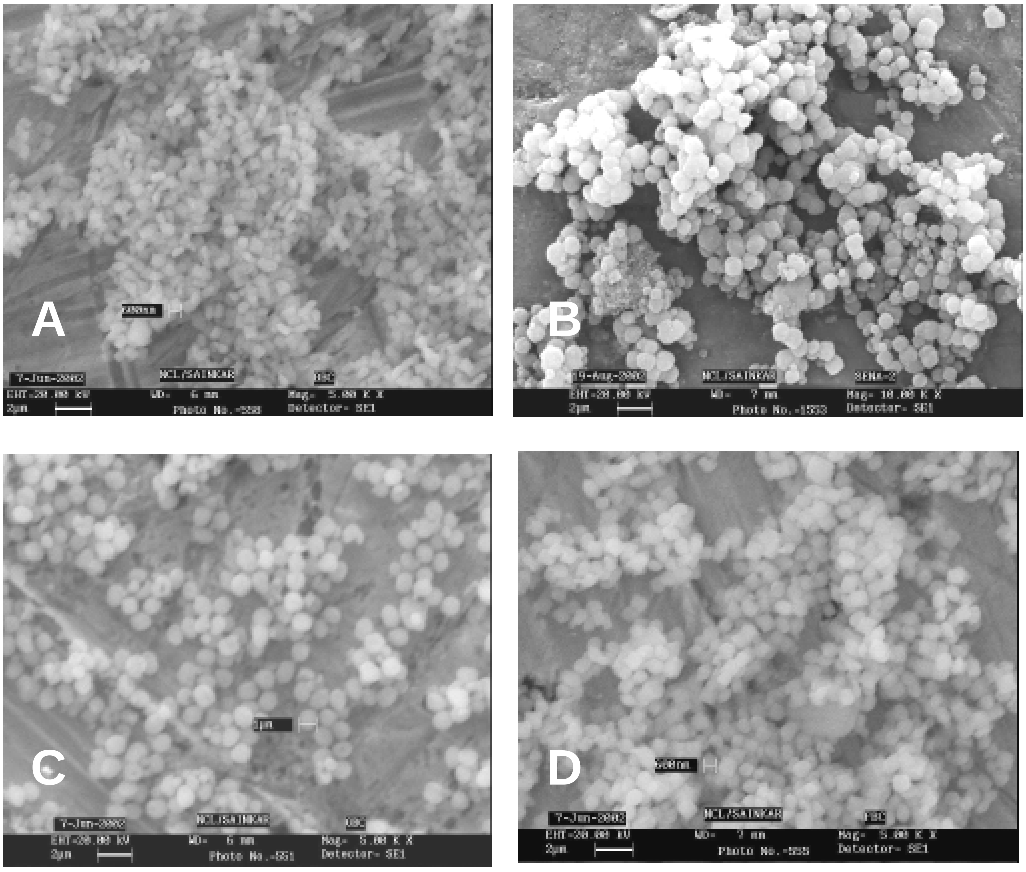


**Fig. 2.8:** Scanning electron micrographs of calcined (A) B-Beta (B) Al-Beta(C) Ga-Beta and (D) Fe-Beta.

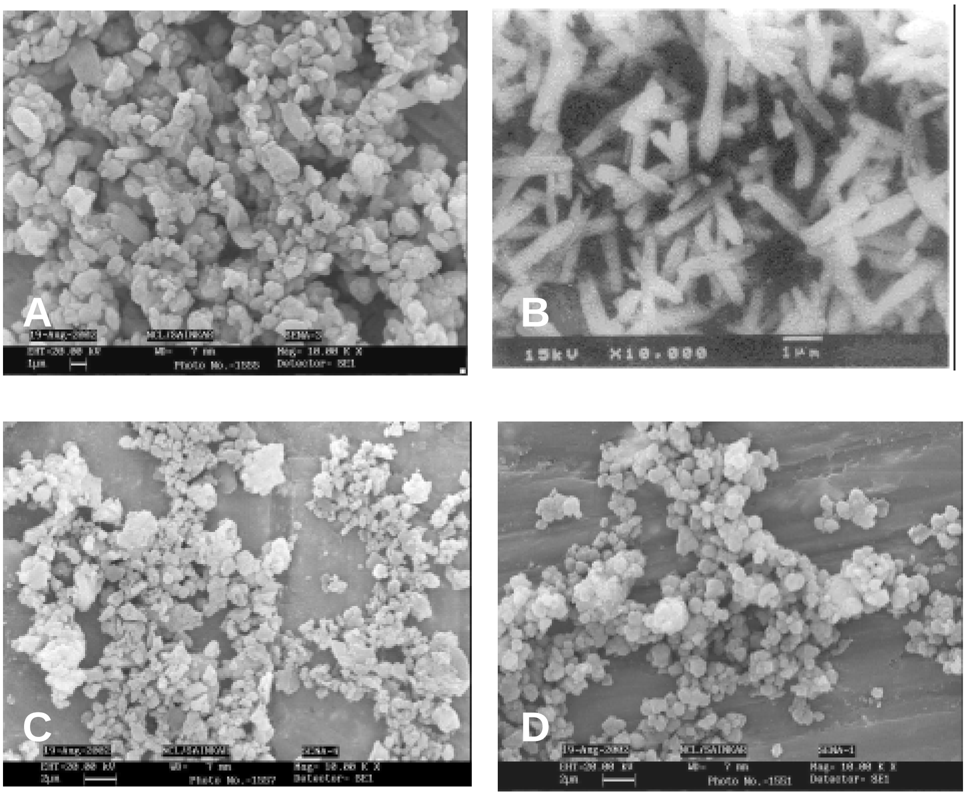


**Fig. 2.9:** Scanning electron micrographs of calcined (A) Mordenite (B) ZSM-12 (C) H-Y and (D) USY.

### 2.4.6. Chemical Analysis

The EDX analyses of calcined samples recorded on a Kevex equipment attached with the Jeol JSM-5200 scanning microscope. Silica to alumina molar ratios of samples were also verified by atomic absorption spectroscopy (AAS). The silica to alumina molar ratio of zeolites and other solid acid catalysts have been summarized in Table 2.2 and 2.3.

### 2.4.7. Solid State Nuclear Magnetic Resonance (NMR) spectroscopy

The solid state MAS and CP MAS NMR (magic angle spinning) spectra for $^{29}$Si, $^{27}$Al and $^{71}$Ga were obtained at room temperature on a Bruker MSL-300 spectrometers. The chemical shifts (in ppm unit) were measured with respect to aqueous $[Al(H_2O)6]^{3+}$ , tetraethylorthosilicate and gallium nitrate as external standard for $^{29}$Si , $^{27}$Al and $^{71}$Ga, respectively.

The solid state MAS NMR spectra of $^{29}$Si and $^{27}$Al of zeolite Beta and USY and $^{29}$Si and $^{71}$Ga of Ga-Beta are depicted in Fig. 2.10. The calcined Al-Beta, Ga-Beta and USY respectively, exhibited only one signal at –110 ppm (w. r. t. TMS) attributable to Si(0Al). The sample containing aluminium exhibited only one signal at 52 ppm in the $^{27}$Al spectrum characteristic of tetrahedral aluminium. No signal (at ca. 0 ppm) due to octahedral $Al^{3+}$ was observed. Fig. 2.10 also exhibits the solid state MAS NMR of Ga-Beta. The $^{71}$Ga MAS NMR spectrographs exhibiting single peak at ä = 148 ppm, confirms the presence of Ga(III) in framework sites.

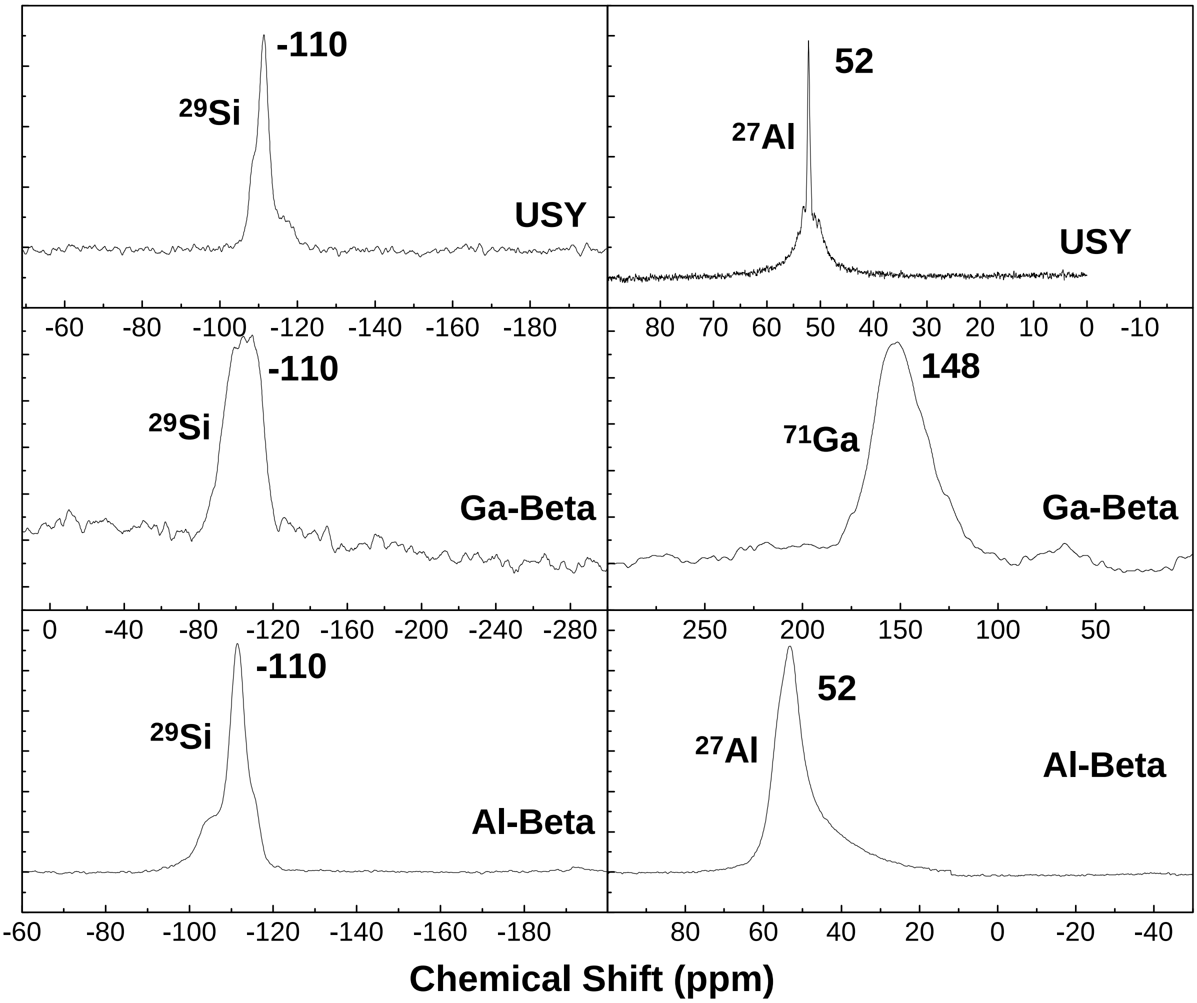


**Fig. 2.10:** MAS NMR spectra of calcined zeolite Al-Beta ($^{29}$Si and $^{27}$Al), Ga-Beta ($^{29}$Si and $^{71}$Ga) and USY ($^{29}$Si and $^{27}$Al) samples.

## 2.5. CONCLUSIONS

- In the present study, zeolites like Beta with different silica alumina ratios, metallosilicates analogs of zeolite Beta (B-, Ga- and Fe- Beta), ZSM-12, Mordenite and other solid acid catalysts like sulfated-zirconia, MCM-41 were synthesized successfully. Zeolite ZSM-5 and NaY were obtained from catalysis pilot plant of NCL. Silica-alumina and USY were commercially obtained. All samples were converted to H-form through $NH_4^+$ exchange.

- All the samples were characterized by various physico-chemical techniques.

- XRD patterns of the solid acid catalysts confirmed their crystallinity and phase purity.

- Scanning electron micrographs of the zeolites revealed their crystal size and morphology and confirmed their phase purity.

- TGA-DTA analysis showed that zeolite Beta is thermally stable and also provided other information such as the energies and weight loss due to desorption of water and organic template material.

- MAS NMR spectra of Al sample exhibited peak around 52 ppm suggesting the presence of aluminium in the tetrahedral environment. Similarly, for Ga-Beta, the peak corresponds to 148 ppm clearly suggests that all the gallium is successfully incorporated in the tetrahedral framework.

- Zeolite Mordenite, Beta, H-Y and USY were exchanged with $Fe^{3+}$ ions, which were used as redox catalysts for the alkylation of aromatics.

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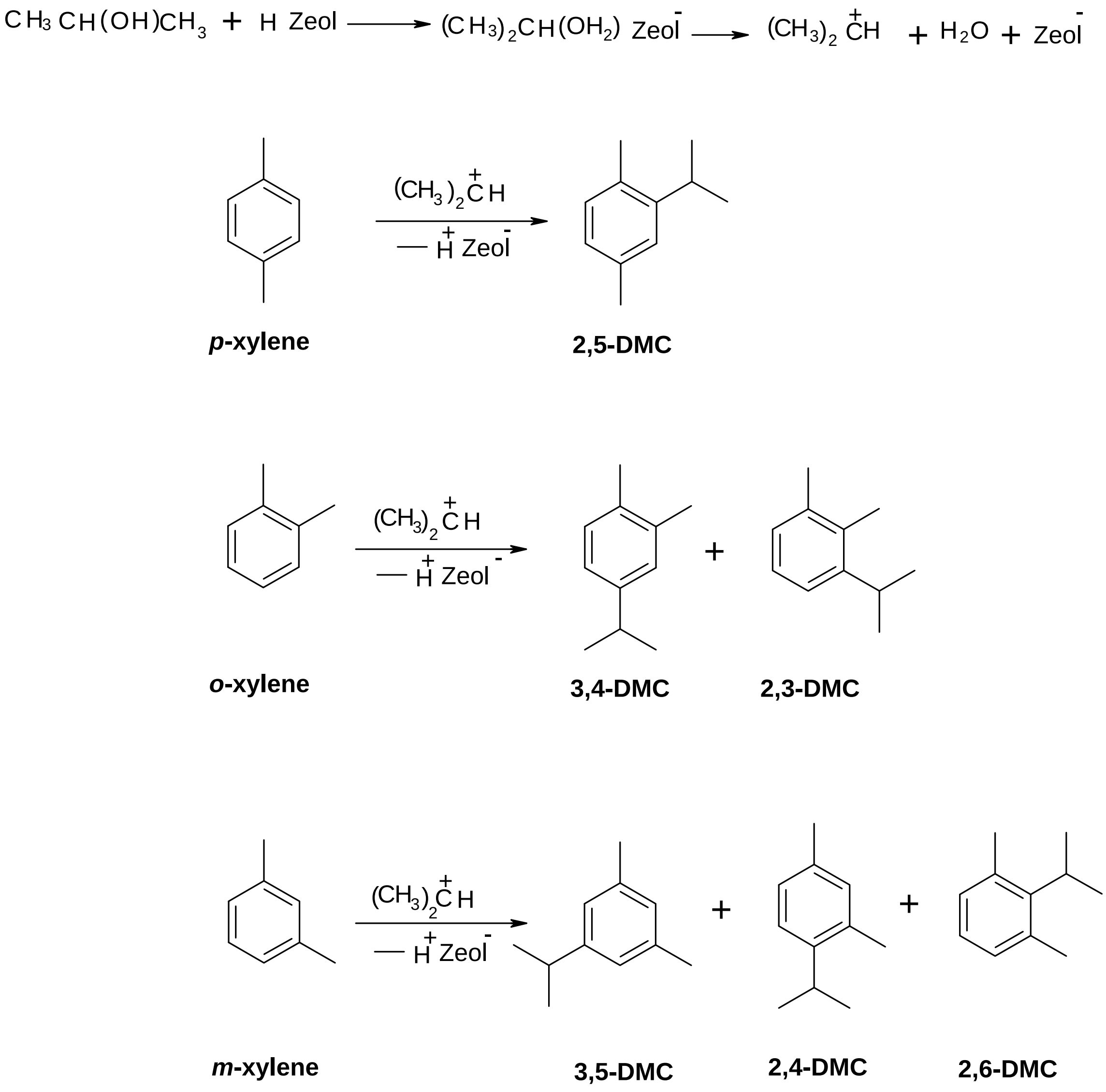
## 3.1. INTRODUCTION

It may be recalled that while, methylation [1,2], ethylation [3,4] and tertiary butylation [5] of xylenes over solid catalysts are relatively better-studied reactions, same is not the case with the isopropylation of xylenes, particularly over solid or zeolite catalysts. There is no report detailed and systematic studies in the isopropylation of xylenes catalyzed by zeolites, except this present work [6,7].

Isopropylation of xylenes produces corresponding dimethyl (1-methylethyl) benzene or simply denoted herein after as dimethylcumene(s) (DMCs). There are a total of six DMC isomers, which can be formed during isopropylation of xylene isomers (Scheme 3.1). While *p*-xylene will yield 2,5-DMC (all regio positions are same), *m*-xylene can give 2,4- and 2,6-DMC as primary product (alkylation being ortho-para directing electrophilic reaction) and 3,5-DMC as secondary product, and *o*-xylene can give 2,3- and 3,4-DMC as primary products.

The main aim of this chapter is to carry out detailed studies on the effects of various reaction parameters, such as reaction temperature, space velocity, xylene to isopropanol (isopropyl alcohol, IPA) molar ratio and time on stream (TOS), on xylene conversion and product distribution, particularly dimethylcumene(s) (DMCs) selectivity, in the isopropylation of xylene isomers catalyzed by ultra-stable zeolite Y (H-USY) and H-Beta, using isopropanol as alkylating agent. Some other solid acid catalysts such as zeolites B-, Ga- and Fe-Beta (in protonic form), H-ZSM-5, H-Y, and H-Mordenite, silica-alumina, sulfated-zirconia and H-MCM-41 were also included for comparative studies in the isopropylation of *m*-xylene.



**Scheme 3.1:** Isopropylation of xylenes over zeolites using isopropanol as alkylating agent.

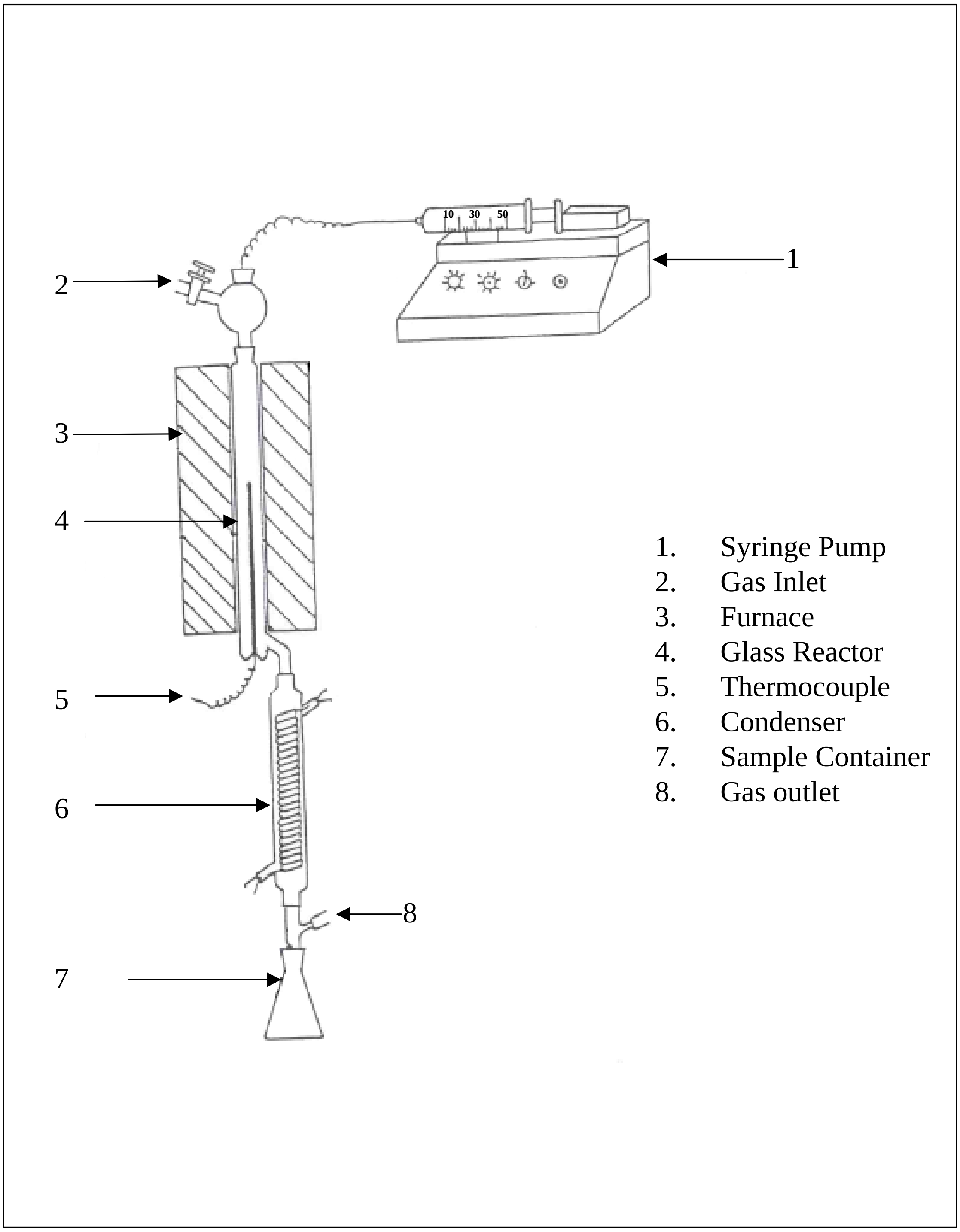
## 3.2. EXPERIMENTAL

All the synthesis, modification and characterization procedures along with their physico-chemical characteristics have been already described in detail in Chapter 2. The vapor phase catalytic isopropylation of xylene isomers (ACROS, USA, 99+%) with isopropanol (S. d. fine-chem. Ltd. Bombay, 99+%) was carried out at moderate temperature (393-453 K) and at atmospheric pressure using a fixed bed vertical down-flow glass reactor with 15 mm internal diameter (shown in Fig.3.1). The required amount of catalyst powder was pressed (under10 tons of pressure), palletized, crushed and sieved to obtain 30-40 mesh (ASTM, USA) size particles. The catalyst (0.5 g) diluted with four times of porcelain beads (wt. basis) of equal size was loaded at the center of the reactor in such a way that catalyst bed was sandwiched between inert porcelain beads. The reactor was placed in a double-zone furnace. It was equipped with a thermocouple in a thermo well for sensing the reaction temperature. The catalyst was activated at 673 K for 8 h in a flow of dry air followed by dry nitrogen before conducting the reactions. A mixture of xylene and isopropanol (isopropyl alcohol, IPA) with desired xylene to IPA molar ratio was introduced into the reactor by a syringe pump (Sage instruments, Model 352, USA) at a particular feed rate and at particular temperature. Nitrogen was used as a carrier gas with a flow-rate of 35 ml/min. Although fresh catalyst was used every time for different measurements, the reusability of the catalyst was also studied by regenerating the catalyst by thermal treatment in the presence of air at 773 K and reused.

The products were chilled, collected and analyzed by gas chromatograph (Agilent 6890 series, GC system) using flame ionization detector and SUPELCO BETA-DEX 110 high resolution (10% permethylated â-cyclodextrin) capillary column (30 m x 0.320 mm x 0.25 μm). Nitrogen was used as carrier gas (2ml/min) in the following GC temperature programme: 333 K(5min), 4 K/min to 423 K (5 min), 10 K/min to 493 K (10 min). The six

DMC isomers, on the isopropylation of equilibrium mixture of xylenes, can be identified in this temperature programme. The order of elution of six isomers matched with the published literature [8,9]. Here, on careful measurements of retention times of all dimethyl cumene (DMC) isomers (as shown in Fig. 3.2), in the above GC column show the following order of elution: 3,5-DMC (21.24 min) < 2,5-DMC (22.11 min) < 2,4-DMC (22.46 min) < 3,4-DMC (22.87 min) < 2,6-DMC (23.76 min) < 2,3-DMC (24.28 min) where the retention times are given in parentheses.

These retention times, with one exception, also follow the order of boiling points: 3,5-DMC (468.5 K) < 2,5-DMC (469.2 K) < 2,4-DMC (472.0 K) < 3,4-DMC (474.8 K) > 2,6-DMC (473.0 K) < 2,3-DMC (475.6 K). The products were also identified by using gas chromatography-mass spectrometry (Shimadzu, GCMS-QP 2000A) and gas chromatography-infrared spectrometry (Perkin Elmer, GC-IR 2000).



1. Syringe Pump
2. Gas Inlet
3. Furnace
4. Glass Reactor
5. Thermocouple
6. Condenser
7. Sample Container
8. Gas outlet

**Fig. 3.1:** Fixed bed down-flow glass reactor set-up for the isopropylation reaction of C-8 aromatics carried out at atmospheric pressure.

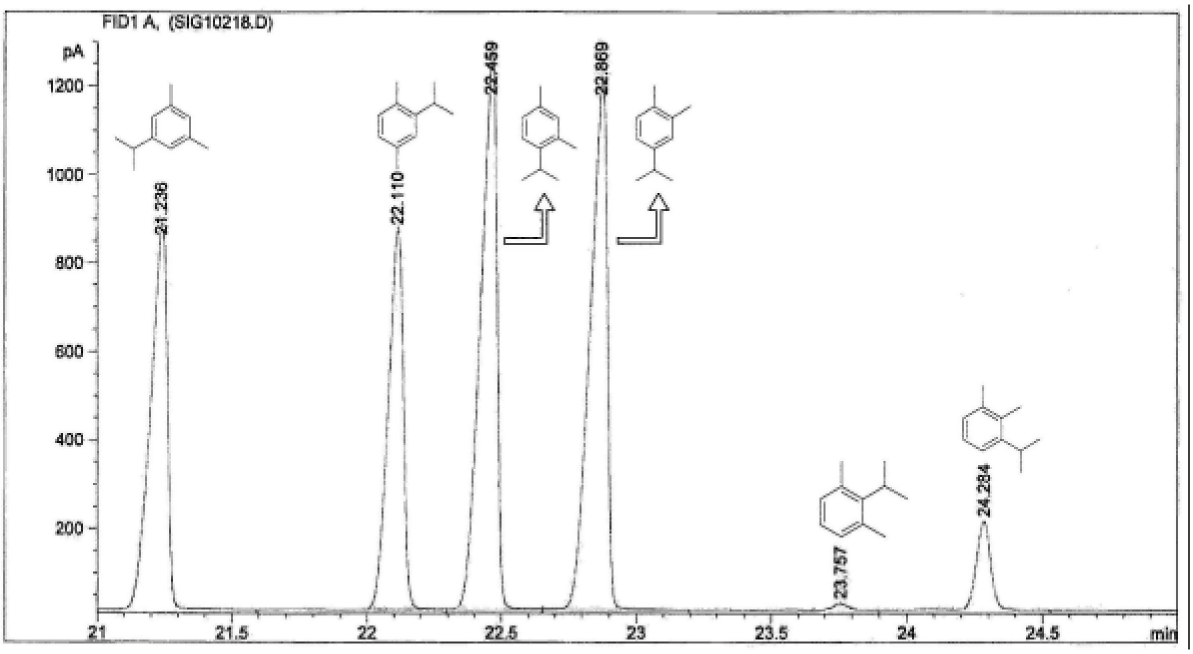


**Fig. 3.2:** Chromatogram for the six DMC isomers with retention times (min) where only that expanded portion of the chromatogram is displayed in which the all DMC isomers are separated.

## 3.3. RESULTS AND DISCUSSION

Although, the thermodynamic equilibrium values for all the DMC isomers (six isomers) are not readily available in the literature, we tried to calculate the thermodynamic equilibrium constants ($K_e$) from Gibbs free energy (ÄG°) of formation for 2,3-, 2,4-, 2,5- and 2,6-DMC isomers (Table 3.1) at different temperatures available in literature [10]. Similar values for other two isomers namely 3,5-DMC and 3,4-DMC were not available [10] and therefore Ke values for all six isomers could not be calculated. $K_e$ were calculated using the Eq.: ÄG° = –RT ln $K_{e.}$ (Where ÄG° in Joules per mol, gas constant R = 8.314 and temperature T is in K). Similar data for remaining 3,4- and 3,5-DMC isomers could not be obtained and hence the percent equilibrium distribution of all the isomers is not given. The Ä G° KJ/mol values were taken from Ref. [10]. The relative stability of these four isomers follows the order: 2,5-DMC ≈ 2,4-DMC >> 2,3-DMC >> 2,6-DMC.

However, in order to get the complete picture of the relative stability of all the DMC isomers, we contacted Rutkowska-Zbik and Witko [11], who kindly provided us the relative energies of all the DMC isomers (Table 3.2) by using generalized gradient approximation (GGA) based on the non-local revised Perdew-Burke-Ernzerhof Potential (RPBE) [12,13] functional for optimized geometries. The stability of all the six DMC isomers follows the order: 3,5-DMC > 3,4-DMC > 2,5-DMC ≥ 2,4-DMC >> 2,3-DMC >2,6-DMC.

The conversion of isopropanol (IPA) was complete in most of the experiments. However, no aromatic compound was obtained when pure IPA was fed as reactant (in the absence of xylene) under otherwise same reaction conditions. Only propylene was formed. Similarly blank experiments where pure xylene isomers were fed as reactant (in the absence of IPA) under the same reaction conditions were also carried out. Although, no or little isomerization and disproportionation products were formed at lower temperature (393-423 K), small amount of isomerized and disproportionated products were obtained only at higher temperature (433 K and above)

The mass balance, carried out for various experiments, ranged between 96 ± 2%. At lower xylene conversions the unreacted propylene was observed in the products (mainly gaseous stream) and is not given in the product distribution. However, it was included in computing mass balances.

**Table 3.1: Equilibrium constants ($K_e$) and standard Gibbs free energy of formation for DMC (s) isomers in KJ/mol. at different temperatures (K)**

| | 300 K | | 400 K | | 500 K | |
|---|---|---|---|---|---|---|
| Isomers | Ä G° KJ/mol | $K_e$ $(10^{-24})$ | Ä G° KJ/mol | $K_e$ $(10^{-27})$ | Ä G° KJ/mol | $K_e$ $(10^{-28})$ |
| 2,3-DMC | 136.2 | 1.945 | 203.1 | 3.032 | 272.5 | 0.344 |
| 2,4-DMC | 131.8 | 11.347 | 198.1 | 13.631 | 267.1 | 1.26 |
| 2,5-DMC | 131.8 | 11.347 | 198.1 | 13.631 | 267.1 | 1.26 |
| 2,6-DMC | 137.9 | 0.984 | 205.4 | 1.518 | 275.4 | 0.171 |

**Table 3.2: RPBE energy (Kcal/mol) of all DMC isomers**

| DMC Isomer | Relative RPBE Energy [kcal/mol] |
|---|---|
| 3,5-DMC | 1.00 |
| 3,4-DMC | 1.88 |
| 2,5-DMC | 2.70 |
| 2,4-DMC | 2.82 |
| 2,3-DMC | 5.27 |
| 2,6-DMC | 9.16 |

## 3.3.1. ISOPROPYLATION OF XYLENES OVER VARIOUS SOLID ACID CATALYSTS

### 3.3.1.1. Conversion and Intrinsic Activity

To find out suitable catalyst (s), the isopropylation of xylene isomers (*o*-, *m*- and *p-)* was investigated over different solid acids such as zeolites with different topologies like MOR (Mordenite), BEA (Beta), FAU (USY and zeolite Y) and MFI (ZSM-5), and other solid acid catalysts like MCM-41, amorphous silica-alumina (SAL) and sulfated-zirconia (SZ) under same reaction conditions. The catalytic activities and product selectivities over various acid catalysts are shown in Table 3.3, 3.4 and 3.5, for the isopropylation of *p*-, *m*- and *o*-xylene respectively. While, the overall activity (conversion) was quite high over H-USY and H-Beta (20) zeolites, amorphous silica-alumina (2.6) and sulfated-zirconia (3 wt.% sulfur) in all xylene isomers, the intrinsic activity (TOF $s^{-1}$) for *m*-xylene isopropylation followed the order: H-Beta (40) > H-Beta (30) > H-Beta (20) > H-MCM-41 (20) > H-USY (5.6) > H-Mordenite (5.9) > Silica-alumina (2.6) > H-Y (2.9) > Sulfated-zirconia (3 wt.% sulfur) > H-ZSM-5 (20), where the values in parentheses represent the Si/Al molar ratio of the corresponding catalyst.

It is clear that both, the acidic properties (density and strength of acid sites) and the void space of the zeolites/catalysts influence its overall activity. Zeolite H-ZSM-5 with three-dimensional intersecting 10-membered rings (0.54 nm X 0.56 nm for straight and 0.51 nm X 0.55 nm for sinusodial) channels exhibits no catalytic activity even though H-ZSM-5 possesses a high strength of acid sites [14]. This is attributed to the fact that strong acid sites are located within the 10-membered ring channels, where the ingress of reactants and egress of products, are severely constrained. In all the cases the activity trend can be easily interpreted in terms of the increasing dimensions of the void space of the catalysts coupled with their acidity. Mesoporous H-MCM-41 (Entry no 2, 4, 2 in Table 3.3, 3.4 and 3.5 respectively) exhibited comparatively low activity, reflecting the presence of weaker acid sites in this mesoporous aluminosilicates [15,16].

### Product Selectivity:

While, SAL, SZ, H-USY, H-Beta and H-Mordenite gave high conversion, the DMC selectivity (Sel.$_{\mathrm{DMC}}$ ) was quite high over H-Beta and H-Mordenite. The order of Sel.$_{\mathrm{DMC}}$ over these catalysts follows as: SZ < SAL < H-USY < H-Beta  H-Mordenite. Consequently, the selectivity towards diisopropylated product follows the reverse order (Table 3.3-3.5). Sulfated-zirconia and silica-alumina also give very high dialkylated fraction, Sel.$_{\mathrm{DIPT+DIPX}}$ (diisopropyl toluene, DIPT + diisopropylxylene, DIPX) (ca. 15 to 20%) probably due to the further isopropylation of cymene and dimethylcumene on the non-shape selective surface of the catalyst. H-USY also gives comparatively high selectivity to dialkylated fraction due to relatively the large void space. In the case of H-Mordenite, the Sel.$_{\mathrm{DIPT+DIPX}}$ is extremly low due to narrower uni-dimensional channels of H-Mordenite. Zeolite H-Beta follows the middle path.

### DMC Isomer Distribution:

Table 3.3, 3.4 and 3.5 also show the DMC isomer distribution obtained during the isopropylation of xylene isomers over various solid acid catalysts. In the case of *p*-xylene isopropylation, only 2,5-DMC isomer is formed as a primarily product and selectivity for 2,5-DMC (Sel.$_{\mathrm{2,5\text{-}DMC}}$) over various solid catalysts ranged between 94.4 and 99% (Table 3.3.). From Table 3.4, it is clear that all the catalysts, except H-USY, gave 2,4-DMC as predominant isomer (ranging between ca. 60-85%) where the Sel.$_{\mathrm{3,5\text{-}DMC}}$ ranged between ca.10-40%. By contrast, the corresponding isomer distribution over USY was just opposite where Sel. $_{\mathrm{2,4\text{-}DMC}}$ is 22% to be compared to Sel.$_{\mathrm{3,5\text{-}DMC}}$ of ca.75%. This may also be due to the reason of the isomerization of mainly 2,4-DMC to 3,5-DMC, quite prominent in H-USY. This isomerization may also be occurring, at least partly, through a bimolecular mechanism, on the similar lines as shown by Corma and Sastre [47] for xylene isomerization. It may be noted that even over SAL and SZ, with quite high and comparable conversion level, the 3,5-DMC was 22.3% and 26.8% respectively. This indicates that higher acid strength of H-USY compared to SAL and also to SZ, may be responsible for high 3,5-DMC selectivity. Further, the isomerization of 2,4-DMC to 3,5-DMC in H-USY with larger cavities compared to other zeolites (H-Beta, H-Mordenite), as the intermediate of this bimolecular reaction may be too bulky to be accommodated within void space of the BEA or MOR structures. During the isopropylation of *o*-xylene (Table 3.5), the selectivity of 3,4-DMC was significantly high vis-à-vis 2,3-DMC over all the catalysts particularly over H-USY, H-Beta, H-Mordenite and SZ.

### 3.3.1.2. Effect of Si/Al Molar Ratio in Zeolite H-Beta

Entries 1-3 in Table 3.4 show the influence of Si/Al molar ratio of zeolite H-Beta on the conversion and product distribution in the isopropylation of *m*-xylene. While there was an increase in the overall conversion with decreasing Si/Al ratio, as expected, the intrinsic activity of the catalyst (TOF) increased with increasing Si/Al ratio**.** It is quite likely that with increasing Al content (decreasing Si/Al ratio), increasing part of Al may occupy the Td sites within the walls, which are not available for this reaction. There was no significant change observed in conversion of *m*-xylene. While the selectivity for dialkylated fraction (Sel.$_{\text{DIPT}}$ + Sel.$_{\text{DIPX}}$) increases in the order: 0.8% H-Beta (20) < 3.5% H-Beta (30) < and 5% H-Beta (40), the selectivity for disproportionation follows the reverse order due to decreased disproportionation of dialkylated fraction on H-Beta (30) and H-Beta (40).

However, no significant difference was observed in the case of Sel.$_{\text{DMC,}}$ but the distribution of DMC isomer (3,5-DMC versus 2,4-DMC) was changed significantly with changing Si/Al ratio in zeolite H-Beta. There was an increase in the Sel.$_{\text{3,5-DMC}}$ and consequently decrease in the Sel.$_{\text{2,4-DMC}}$ with decreasing Si/Al ratio, as expected, the acidic density of the catalyst increased with decreasing Si/Al ratio and hence isomerization of 2,4-DMC to 3,5-DMC is increased.

Comparing the data tabulated in Table 3.3–3.5, it is clear that H-USY, H-Beta and H-Mordenite are highly active catalysts. But here all further studies were carried out over H-Beta (20) and H-USY catalysts with varying reaction parameters such as temperature, weight hourly space velocity (WHSV), xylene to alkylating agent molar ratio and time-on-stream (TOS).

### 3.3.1.3. Effect of TOS: Different Catalysts in *m*-Xylene Isopropylation

From the above studies it is clear that while in the isopropylation of *p*- and *o*-xylene, the product distribution, particularly DMC isomer distribution did not change significantly with various reaction parameters, the DMC isomer distribution in the case of *m*-xylene (2,4-DMC versus 3,5-DMC) was significantly influenced by different reaction parameters. Hence, it was thought worthwhile to investigate the influence of difference pore geometries using different solid acid catalysts. Therefore, the isopropylation of *m*-xylene was studied as a function of time-on-stream using different catalysts such as large pore zeolites (H-Mordenite, H-Beta and H-Y), amorphous silica-alumina and sulfated-zirconia (Fig. 3.3 A-F). Quite interestingly, all the catalysts, except H-USY, gave 2,4-DMC as predominant isomer (ranging between 60-85%) where the $\mathrm{Sel.}_{3,5\text{-DMC}}$ ranged between 10-35%. By contrast, the corresponding isomer distribution over H-USY was just opposite where $\mathrm{Sel.}_{2,4\text{-DMC}}$ ranged between 20-30% to be compared to $\mathrm{Sel.}_{3,5\text{-DMC}}$ of ca. 65-75%.

As mentioned earlier, this may also be due to the reason that isomerization of 2,4-DMC to 3,5-DMC may be occurring, at least partly, through a bimolecular mechanism in H-USY with larger cavities compared to other zeolites (H-Beta, H-Mordenite), as the intermediate of this bimolecular reaction may be too bulky to be accommodated within void space of the BEA or MOR structures.

Even at comparable conversion levels, for example, the DMC isomer distribution over silica-alumina (Fig. 3.3-C) and sulfated zirconia (Fig. 3.3-F) is completely different with that obtained over H-USY (Fig. 3.3-A). These results clearly indicate that the isomer distribution, particularly that of 2,4-DMC and 3,5-DMC in *m*-xylene isopropylation could be controlled by various factors such as (i) the ability of the catalysts towards the isomerization vis-à-vis alkylation of 2,4-DMC, (ii) selective poisoning of the stronger acid sites (responsible for isomerization) in certain zeolites and other catalysts, (iii) partial contribution of bimolecular isomerization in the case of H-USY, as well as (iv) partial blockage of channels due to coking.

While amorphous silica-alumina and sulfated zirconia exhibited very good alkylation activity in *m*-xylene isopropylation, the isomerization of 2,4-DMC to 3,5-DMC was rather suppressed. In the case of H-Mordenite and H-Beta (Fig. 3.3-B and E), the formation of 3,5-DMC might have even suppressed due to geometric constraints also. However, in H-Y zeolite, which also exhibited only ca. 10-12% 3,5-DMC, such constraints may be less pronounced. Hence, it is clear that both the acidity (mainly the strength of Brönsted acid sites) and geometric constraints of the catalysts significantly influence the product distribution. These results provide leads for further studies particularly on the isopropylation of *m*-xylene using different catalysts with same structure and varying acidity.

Fig. 3.3 also shows deactivation nature of different catalysts with time. While all the catalysts were deactivated with time, H-Mordenite was deactivated rather fast probably due to rapid formation of coke. It seems that both, the acid characteristics and the pore structure of the zeolites play a significant role during coking which is responsible for catalyst deactivation.

**Table 3.3: Catalytic activities and product selectivities over various solid acid catalysts in the isopropylation of *p*-xylene[a]**

| Entry No. | Catalysts | Conv. of Xyln[b]. | TOF[c] ($s^{-1}$x$10^{-3}$) | **$Sel._{DMC}$ [d]** | $Sel._{(DIPT+DIPX)}$ [e] | $Sel._{Others}$ [f] | Product Distribution (%) | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | $Sel._{2,5-DMC}$ | $Sel._{Others}$ |
| 1 | H-Beta (20) | 87.6 | **8.7** | **97.7** | 1.0 | 1.3 | 94.4 | 5.6 |
| 2 | H-MCM-41 (20) | 44.8 | 4.2 | 95.4 | 4.1 | 0.5 | 99.0 | 10.0 |
| 3 | H-USY (5.6) | 97.2 | 2.9 | **90.5** | 4.5 | 4.0 | 98.0 | 2.0 |
| 4 | H-M (5.9) | 74.0 | **2.3** | **96.0** | 0.5 | 3.5 | 95.8 | 4.2 |
| 5 | Silica-alumina | 92.8 | **1.5** | **84.2** | 14.7 | 1.1 | 99.0 | 1.0 |
| 6 | H-Y (2.9) | 41.2 | 0.7 | 93.0 | 3.9 | 3.1 | 99.0 | 1.0 |
| 7 | Sulfatedzirconia | 96.0 | **0.08** | **76.9** | 21.0 | 2.1 | 97.1 | 2.9 |
| 8 | H-ZSM-5 (20) | 0.0 | **-** | **-** | - | - | - | - |

[a]Reaction Conditions: Temperature = 413 K, WHSV = 3.25 $h^{-1}$, *p*-xylene:isopropanol = 4:1(molar), TOS = 1h, isopropanol conversion =100%, at low xylene conversion propylene was present in gaseous stream, observed mass balance = 96 ± 2% in all cases.

[b]Theoretical maximum conversion of xylene, [c]Turn over frequency i.e.the no of molecules converted per mole of Al (catalytic site) per second, [d]Total dimethylcumene selectivity in total products, [e]Selectivity of di-alkylated fraction (DIPT+DIPX) in the total products, [f]Selectivity of other products including isomerized and disproportionated products.

**Table 3.4: Catalytic activities and product selectivities over various solid acid catalysts in the isopropylation of *m*-xylene** [a].

| Entry No. | Catalysts | Conv. of Xyln [b] | TOF[c] ($s^{-1}x10^{-3}$) | **Sel.$_{DMC}$** [d] | Sel.$_{(DIPT+DIPX)}$ [e] | Sel.$_{Others}$ [f] | Product Distribution (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | 3,5-DMC | 2,4-DMC | Other |
| 1 | H-Beta (40) | 60.4 | **11.1** | **94.5** | 5.0 | 0.5 | 22.5 | 77.5 | 0.0 |
| 2 | H-Beta (30) | 62.0 | **8.6** | **96.0** | 3.5 | 0.5 | 26.0 | 74.0 | 0.0 |
| 3 | H-Beta (20) | 66.0 | **6.2** | **97.5** | 0.8 | 1.7 | 44.1 | 55.1 | 0.8 |
| 4 | H-MCM-41 (20) | 44.8 | 4.2 | 95.0 | 4.2 | 0.8 | 13.3 | 86.7 | 0.0 |
| 5 | H-USY (5.6) | 82.4 | 2.4 | **90.7** | 3.2 | 6.1 | 74.8 | 21.9 | 3.3 |
| 6 | H-M (5.9) | 64.4 | **2.0** | **95.1** | 0.5 | 4.4 | 12.8 | 77.2 | 0.0 |
| 7 | Silica-alumina | 96.4 | **1.6** | **80.4** | 18.6 | 1.0 | 22.3 | 76.2 | 1.5 |
| 8 | H-Y (2.9) | 37.2 | 0.7 | 90.0 | 5.5 | 4.5 | 20.4 | 75.5 | 4.1 |
| 9 | Sulfatedzirconia | 99.2 | **0.08** | **79.0** | 21.0 | 2.0 | 26.8 | 70.0 | 3.2 |
| 10 | H-ZSM-5 (20) | 0.0 | **-** | **-** | - | - | - | - | - |

[a] Reaction Conditions: Temperature = 413 K, WHSV = 3.25 $h^{-1}$, *m*-xylene:isopropanol = 4:1(molar), TOS = 1h, isopropanol conversion =100%, at low xylene conversion propylene was present in gaseous stream, observed mass balance = 96 ± 2% in all cases, [b-f] as in Table 3.3.

**Table 3.5: Catalytic activities and product selectivities over various solid acid catalysts in the isopropylation of *o*-xylene**[a]

| Entry No. | Catalysts | Conv. of Xyln.[b] | TOF[c] ($s^{-1}$x$10^{-3}$) | **Sel.$_{DMC}$**[d] | Sel.$_{(DIPT+DIPX)}$[e] | Sel.$_{Others}$[f] | Product Distribution (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | 3,4-DMC | 2,3-DMC | Other |
| 1 | H-Beta (20) | 62.0 | **5.8** | **95.9** | 1.0 | 3.1 | 88.5 | 9.7 | 1.8 |
| 2 | H-MCM-41 (20) | 48.4 | 4.6 | 93.0 | 6.0 | 1.0 | 65.0 | 35.0 | 0.0 |
| 3 | H-USY (5.6) | 97.2 | 2.9 | **80.0** | 7.0 | 13.0 | 94.6 | 4.2 | 1.2 |
| 4 | H-M (5.9) | 71.2 | **2.2** | **94.7** | 0.5 | 4.8 | 94.9 | 2.8 | 2.3 |
| 5 | Silica-alumina | 88.4 | **1.4** | **80.0** | 19.0 | 1.0 | 77.1 | 21.9 | 1.0 |
| 6 | H-Y (2.9) | 34.8 | 0.6 | 88.9 | 7.5 | 3.6 | 74.1 | 22.9 | 3.0 |
| 7 | Sulfatedzirconia | 96.4 | **0.08** | **87.6** | 10.4 | 2.0 | 97.4 | 1.6 | 1.0 |
| 8 | H-ZSM-5 (20) | 0.0 | **-** | **-** | - | - | - | - | - |

[a] Reaction Conditions: Temperature = 413 K, WHSV = 3.25 $h^{-1}$, *o*-xylene:isopropanol = 4:1(molar), TOS = 1h, isopropanol conversion =100%, at low xylene conversion propylene was present in gaseous stream, observed mass balance = 96 ± 2% in all cases, [b-f] as in Table 3.3.

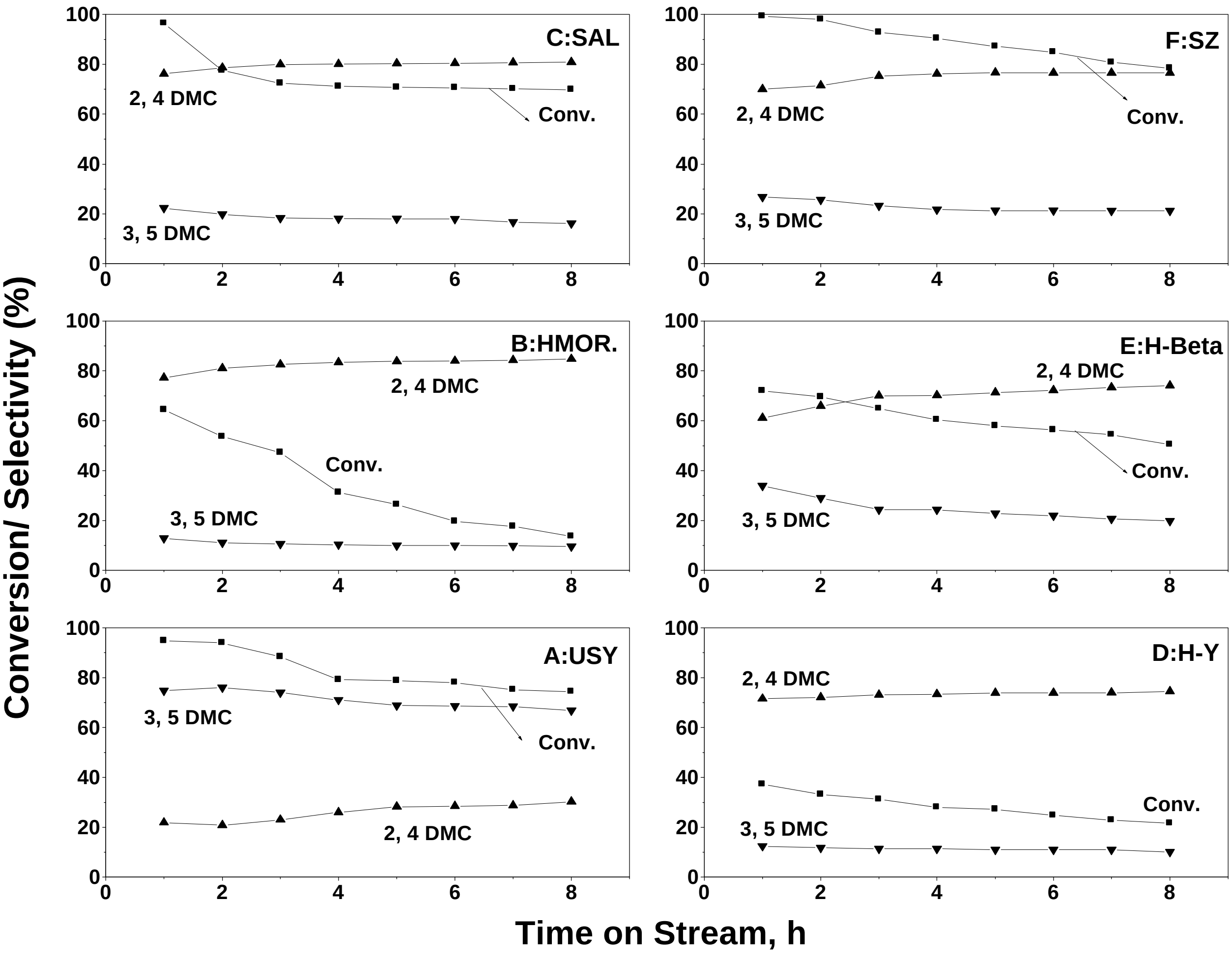


**Fig. 3.3:** Conversion versus time on stream (TOS, h), Sel.$_{3,5\text{-DMC}}$ and Sel.$_{2,4\text{-DMC}}$ versus TOS on the isopropylation *m*-xylenes over different catalysts ( A = H-USY, B = H-Mordenite, C = silica-alumina, D = H-Y, E = H-Beta and F = sulfated-zirconia).

Reaction conditions: Temperature = 413 K, *m*-xylene:isopropanol = 4: 1 (molar), WHSV = 3.25 h$^{-1}$.

## 3.3.2. ISOPROPYLATION OF XYLENES OVER H-USY

### 3.3.2.1. Influence of Reaction Temperature

As expected, the catalytic activity and selectivity for dimethyl cumene isomers in isopropylation of all the three xylene isomers over H-USY is highly influenced by temperature (Table 3.6 & Fig. 3.4 A-C). With increasing temperature, the conversion of xylenes increases reaching almost to the theoretical maximum value (according to xylene / isopropanol mole ratio taken). However, with increasing the reaction temperature there was an increase in the side reactions like disproportionation (forming toluene and trimethylbenzenes) and isomerization (forming xylenes other than the substrate one) of substrate xylene isomer. There is a marginal increase in the dialkylated fraction with increasing the temperature, as expected.

In the case of *p*-xylene isopropylation, the selectivity towards 2,5-DMC among DMCs (Sel.$_{2,5\text{-DMC}}$) also decreases slightly with increasing temperature (from ca. 100% at 393 K to 93.6% at 443 K) (Fig. 3.4-A). This could be possible due to (i) isomerization of 2,5-DMC to 3,5-DMC and 2,4-DMC via 1,2 methyl shift and (ii) by the isopropylation of other xylene isomers (*m*- and *o*-xylene) formed via isomerization of *p*-xylene.

In the case of *m*-xylene isopropylation, by increasing the temperature the selectivity for 2,4-DMC in total DMCs (Sel.$_{2,4\text{-DMC}}$) decreases with increasing the energetically most stable 3,5-DMC (Sel.$_{3,5\text{-DMC}}$) in total DMCs (Table 3.6 & Fig. 3.4-B). The 2,6-DMC was formed only in small quantities (< 2%), the 2,4-DMC and 3,5-DMC isomers being predominant. Hence, energetically most favored 3,5-DMC can easily be formed through isomerization of 2,4-DMC via 1,2 propyl shift, as evidenced by the fact that the Sel.$_{2,4\text{-DMC}}$ is decreased with a consequent increase in Sel.$_{3,5\text{-DMC}}$ with increasing temperature whereas Sel.$_{2,6\text{-DMC}}$ remained almost unchanged. However, the formation of 3,5-DMC can also be partly due to bimolecular isomerization of 2,4-DMC to 3,5-DMC in the case of H-USY, where there may be enough space to accommodate the bulky bimolecular intermediate, on the similar lines as shown by Corma and Sastre [17] for xylene isomerization.

In the case of *o*-xylene isopropylation, the selectivity of 2,3-DMC in total DMCs ($Sel._{2,3\text{-}DMC}$) decreases from ca. 26% at 393 K to ca. 3% at 443 K with consequent increase (from ca. 72% at 393 K to ca. 95% at 443 K) in the selectivity for 3,4-DMC ($Sel._{3,4\text{-}DMC}$), indicating that the energetically less favored 2,3-DMC decreases with increasing reaction temperature, as expected (Table 3.6 & Fig. 3.4-C). Here it may be pertinent to mention that Isakov et al. [18,19] have also reported the formation of mixture of DMCs with 70-97% selectivity for 3,4-DMC during isopropylation of *o*-xylene over NdNa-Y type zeolite, the remaining isomer being 2,3-DMC. It may be recalled that only *o*-xylene could be alkylated while no alkylation could be obtained when *p*-xylene was used as substrate [18,19]. These results are in contrast to the present data where significant conversion of all the xylene isomers was obtained during isopropylation over H-USY catalyst. Although, an unambiguous explanation for such difference in the reported and present results need further focused studies, it may be likely that stronger acidity of zeolite H-USY compared to that of zeolite Y in general and NdNa-Y in particular may be one of the main reasons.

### 3.3.2.2. Influence of Feed rate

The space velocity of the feed i.e. WHSV (weight hourly space velocity) is another parameter which influences the conversion and product selectivity (Table 3.7 & Fig. 3.5A-C). As expected, the conversion of xylene isomers decreases sharply with increasing WHSV from 3.25 $h^{-1}$ through 13 $h^{-1}$ (i.e. decrease in contact time of reactants with catalyst) and the $Sel._{DMCs}$ increases during isopropylation of all xylene isomers. The enhancement of $Sel._{DMCs}$ among products with increasing WHSV is due to consequent decrease in side reaction of xylene disproportionation.

The selectivity for primarily formed DMC isomer(s) among total DMCs also increased with increasing feed rate (decreasing residence time) (Table 3.7). In the case of *p*-xylene isopropylation $\text{Sel.}_{\text{2,5-DMC}}$ increased marginally from 98% to 100% (Fig. 3.5-A). For *m*-xylene isopropylation $\text{Sel.}_{\text{3,5-DMC}}$ is decreased from ca. 75 to 53% while $\text{Sel.}_{\text{2,4-DMC}}$ is increased correspondingly and $\text{Sel.}_{\text{2,6-DMC}}$ did not change significantly with increasing WHSV (Fig. 3.5-B). This may be due to the fact that at high feed rate (low contact times), alkylation reactions are favored over the isomerization of primarily formed 2,4-DMC into 3,5-DMC. Similarly in the case of *o*-xylene isopropylation also, with increasing WHSV and consequent decrease in conversion the $\text{Sel.}_{\text{3,4-DMC}}$ is decreased from ca. 95 to 81% with a consequent increase in the $\text{Sel.}_{\text{2,3-DMC}}$, corroborating the results obtained by varying reaction temperature as mentioned above (Fig. 3.5-C). In both the cases, viz. *m*-xylene and *o*-xylene, the selectivity for thermodynamically more stable product like 3,5-DMC (from *m*-xylene) and 3,4-DMC (from *o*-xylene) increases with increasing conversion. Consequently at lower reaction temperature and shorter contact time, the selectivity for 2,4-DMC and 2,3-DMC (from *o*-xylene) is higher, as expected, because as the severity of the reaction increases the isomer distribution tends to shift towards thermodynamic equilibrium values of DMC isomers.

**Table 3.6: Effect of temperature on conversion (Conv.) and product selectivity (Sel.) in the isopropylation of xylene isomers over zeolite H-USY[r]**

| Xyl. | Conv. or Sel. (mole %) | Reaction Temperature, K | | | | | |
|---|---|---|---|---|---|---|---|
| | | 393 | 403 | 413 | 423 | 433 | 443 |
| *p*-Xyl. | Conv. | 6.9 | 9.0 | 18.2 | 19.0 | 22.6 | 24.2 |
| | Conv. (theo. max.)[a] | 27.6 | 36.0 | 72.8 | 76.0 | 90.4 | 96.8 |
| | Sel.$_{\text{DMCs}}$ | 93.4 | 92.8 | 92 | 85.3 | 78.6 | 66.7 |
| | DMC Yield[b] | 25.8 | 33.4 | 67.0 | 64.8 | 71.1 | 64.6 |
| | Sel.$_{\text{ISO}}$ (*m*- + *o*-xylene) | 0.0 | 0.0 | 0.0 | 1.5 | 2.3 | 4.4 |
| | Sel.$_{\text{DISP}}$[c] | 0.0 | 0.9 | 2.0 | 5.2 | 10.9 | 21.1 |
| | Sel.$_{\text{DI PT}}$[d] + Sel.$_{\text{DIPX}}$[e] | 6.6 | 6.3 | 6.0 | 8.0 | 8.2 | 7.8 |
| | Sel. $_{\text{2,5-DMC}}$ | 100.0 | 100.0 | 100.0 | 97.3 | 95.0 | 93.6 |
| | Sel. $_{\text{Other (2,4-DMC )}}$ | 0.0 | 0.0 | 0.0 | 2.7 | 5.0 | 6.4 |
| *m*-Xyl. | Conv. | 9.3 | 12.3 | 17.5 | 21.8 | 23.8 | 24.9 |
| | Conv. (theo. max.)[a] | 37.2 | 49.2 | 70.0 | 87.2 | 95.2 | 99.6 |
| | Sel.$_{\text{DMCs}}$ | 95.3 | 94.8 | 91.6 | 90.2 | 88.5 | 73.8 |
| | DMC Yield[b] | 34.7 | 45.7 | 64.1 | 78.7 | 84.3 | 73.5 |
| | Sel.$_{\text{ISO}}$ (*p*- + *o*-xylene) | 0.0 | 0.9 | 1.4 | 1.9 | 2.2 | 5.7 |
| | Sel.$_{\text{DISP}}$[c] | 0.0 | 0.3 | 3.1 | 4.0 | 5.4 | 15.6 |
| | Sel.$_{\text{DI PT}}$[d] + Sel.$_{\text{DIPX}}$[e] | 4.7 | 4.0 | 3.9 | 3.9 | 3.9 | 4.9 |
| | Sel.$_{\text{3,5-DMC}}$ | 58.8 | 59.5 | 68.0 | 69.3 | 74.3 | 77.0 |
| | Sel.$_{\text{2,4-DMC}}$ | 40.7 | 39.5 | 29.6 | 28.0 | 22.8 | 19.5 |
| | Sel.$_{\text{2,6-DMC}}$ | 0.5 | 1.0 | 1.5 | 1.6 | 1.8 | 2.1 |
| | Sel. $_{\text{Other (2,5-DMC).}}$ | 0.0 | 0.0 | 0.9 | 1.1 | 1.1 | 1.4 |
| *o*- Xyl. | Conv. | 6.3 | 12.9 | 17.0 | 19.9 | 20.7 | 21.4 |
| | Conv. (theo. max.)[a] | 25.2 | 51.6 | 68.0 | 79.6 | 82.8 | 85.6 |
| | Sel.$_{\text{DMCs.}}$ | 92.7 | 90.7 | 85.3 | 84.2 | 82.1 | 79.1 |
| | DMC Yield[b] | 23.4 | 46.8 | 58.0 | 67.0 | 68.0 | 67.7 |
| | Sel. $_{\text{ISO}}$ (*m*- + *p*-xylene) | 0.0 | 0.9 | 1.1 | 1.2 | 1.5 | 1.9 |
| | Sel.$_{\text{DISP}}$[c] | 0.0 | 0.8 | 4.2 | 6.3 | 9.2 | 11.5 |
| | Sel.$_{\text{DI PT}}$[d] + Sel.$_{\text{DIPX}}$[e] | 7.3 | 7.6 | 9.4 | 8.3 | 7.2 | 7.5 |
| | Sel.$_{\text{3,4-DMC}}$ | 72.3 | 82.4 | 92.6 | 94.6 | 95.0 | 95.1 |
| | Sel.$_{\text{2,3-DMC}}$ | 26.5 | 16.1 | 6.4 | 3.1 | 2.9 | 2.7 |
| | Sel.$_{\text{Other(2,4- DMC)}}$ | 1.2 | 1.5 | 1.0 | 2.3 | 2.1 | 2.2 |

[r] Reaction Conditions: Xylene:isopropanol = 4:1 (molar), WHSV = 6.5 h$^{-1}$, TOS = 1h.

[a] Conv. of theoretical maximum, [b] DMC yield = (% Conv. (theo. max.) X% Sel. / 100), Sel.$_{\text{DMC}}$ = DMCs in total products, isopropanol conv.=100%, at low xylene conversion propylene was present in gaseous stream, observed mass balance = 95 ± 3% in all cases, [c]: disproportionation products (toluene + trimethyl benzenes), [d]: di-iso-propyl-toluenes, [e]: diisopropyl xylenes

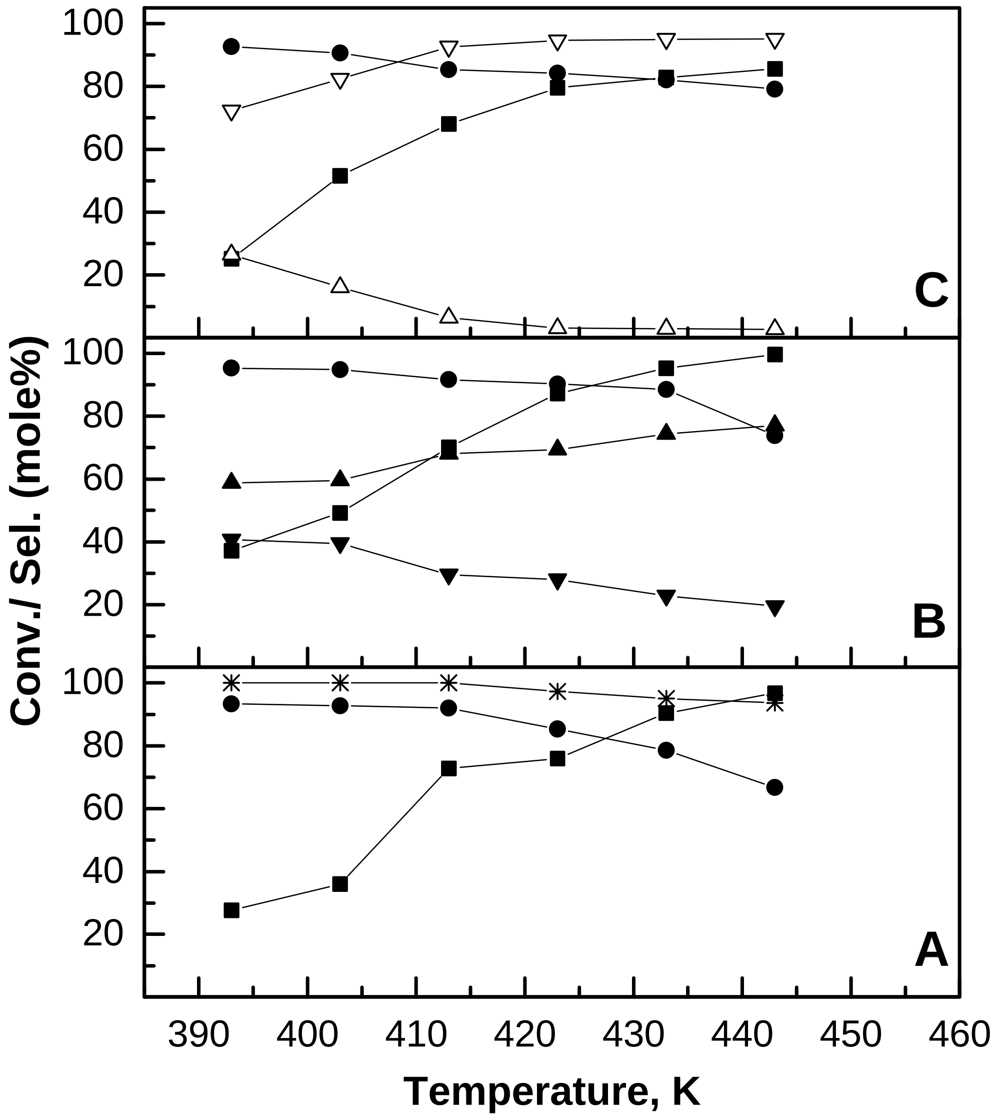


**Fig. 3.4:** Effect of temperature on the conversion and product selectivity and its distribution over zeolite H-USY catalyst in the isopropylation of *p*-xylene (A), *m*-xylene (B) and *o*-xylene (C). Conversion of xylene ( ), Sel.$_{\text{DMC}}$ ( ), Sel. $_{\text{2,5-DMC}}$ (□), Sel.$_{\text{2,4-DMC}}$ ( ), Sel.$_{\text{3,5-DMC}}$ (□), Sel.$_{\text{3,4-DMC}}$ (□), Sel.$_{\text{2,3-DMC}}$ (□), Reaction Conditions: xylene:isopropanol = 4:1 (molar), WHSV = 6.5 h$^{-1}$, TOS = 1h.

**Table 3.7: Effect of space velocity on conversion and product selectivity in the isopropylation of xylene isomers over zeolite H-USY[r]**

| Xylene isomer | Conv. or Sel. (mole%) | WHSV, $h^{-1}$ | | |
|---|---|---|---|---|
| | | 3.25 | 6.50 | 13.00 |
| *p*-Xyl. | Conv. | 24.3 | 18.2 | 11.8 |
| | Conv. (theo. max.)[a] | 97.2 | 72.8 | 47.2 |
| | Sel.$_{\text{DMCs}}$ | 90.5 | 92 | 93.3 |
| | DMC Yield[b] | 88.0 | 67.0 | 44.0 |
| | Sel. $_{\text{ISO}}$ (*m*- + *o*-xylene) | 1.3 | 0.0 | 0.0 |
| | Sel.$_{\text{DISP}}$[c] | 3.7 | 2.0 | 0.0 |
| | Sel.$_{\text{DI PT}}$[d] + Sel.$_{\text{DIPX}}$[e] | 4.5 | 6.0 | 6.7 |
| | Sel.$_{\text{2,5-DMC}}$ | 98.0 | 100 | 100 |
| | Sel.$_{\text{0ther(2,4-DMC)}}$ | 2.0 | 0.0 | 0.0 |
| m-Xyl. | Conv. | 20.6 | 17.5 | 10.7 |
| | Conv. (theo. max.)[a] | 82.4 | 70.0 | 42.8 |
| | Sel.$_{\text{DMCs}}$ | 90.7 | 91.6 | 93.1 |
| | DMC Yield[b] | 74.7 | 64.1 | 39.8 |
| | Sel. $_{\text{ISO}}$ (*m*- + *p*-xylene) | 1.8 | 1.4 | 0.5 |
| | Sel.$_{\text{DISP}}$[c] | 4.3 | 3.1 | 1.9 |
| | Sel.$_{\text{DI PT}}$[d] + Sel.$_{\text{DIPX}}$[e] | 3.2 | 3.9 | 4.5 |
| | Sel.$_{\text{3,5-DMC}}$ | 74.8 | 68.0 | 52.8 |
| | Sel.$_{\text{2,4-DMC}}$ | 21.9 | 29.6 | 45.0 |
| | Sel.$_{\text{2,6-DMC}}$ | 2.3 | 1.5 | 1.5 |
| | Sel. $_{\text{Other (2,5-DMC)}}$. | 1.0 | 0.9 | 0.7 |
| *o*-Xyl. | Conv. | 24.3 | 17.0 | 9.4 |
| | Conv. (theo. max.)[a] | 97.2 | 68.0 | 37.6 |
| | Sel.$_{\text{DMCs}}$ | 80.0 | 85.3 | 86.4 |
| | DMC Yield[b] | 77.8 | 58.0 | 32.5 |
| | Sel. $_{\text{ISO}}$ (*m*- + *p*-xylene) | 1.7 | 1.1 | 0.0 |
| | Sel.$_{\text{DISP}}$[c] | 11.3 | 4.2 | 2.9 |
| | Sel.$_{\text{DI PT}}$[d] + Sel.$_{\text{DIPX}}$[e] | 7.0 | 9.4 | 10.7 |
| | Sel.$_{\text{3,4-DMC}}$ | 94.6 | 92.6 | 81.3 |
| | Sel.$_{\text{2,3-DMC}}$ | 4.2 | 6.4 | 18.0 |
| | Sel.$_{\text{Other (2,4-DMC)}}$ | 1.2 | 1.0 | 0.7 |

[r] Reaction Conditions: Xylene:isopropanol = 4:1(molar), Temperature = 413 K, TOS = 1h, isopropanol conv.=100%, at low xylene conversion (WHSV = 13 $h^{-1}$) remaining unreacted propylene was present in gaseous stream, [a-e]: as in Table 3.6.

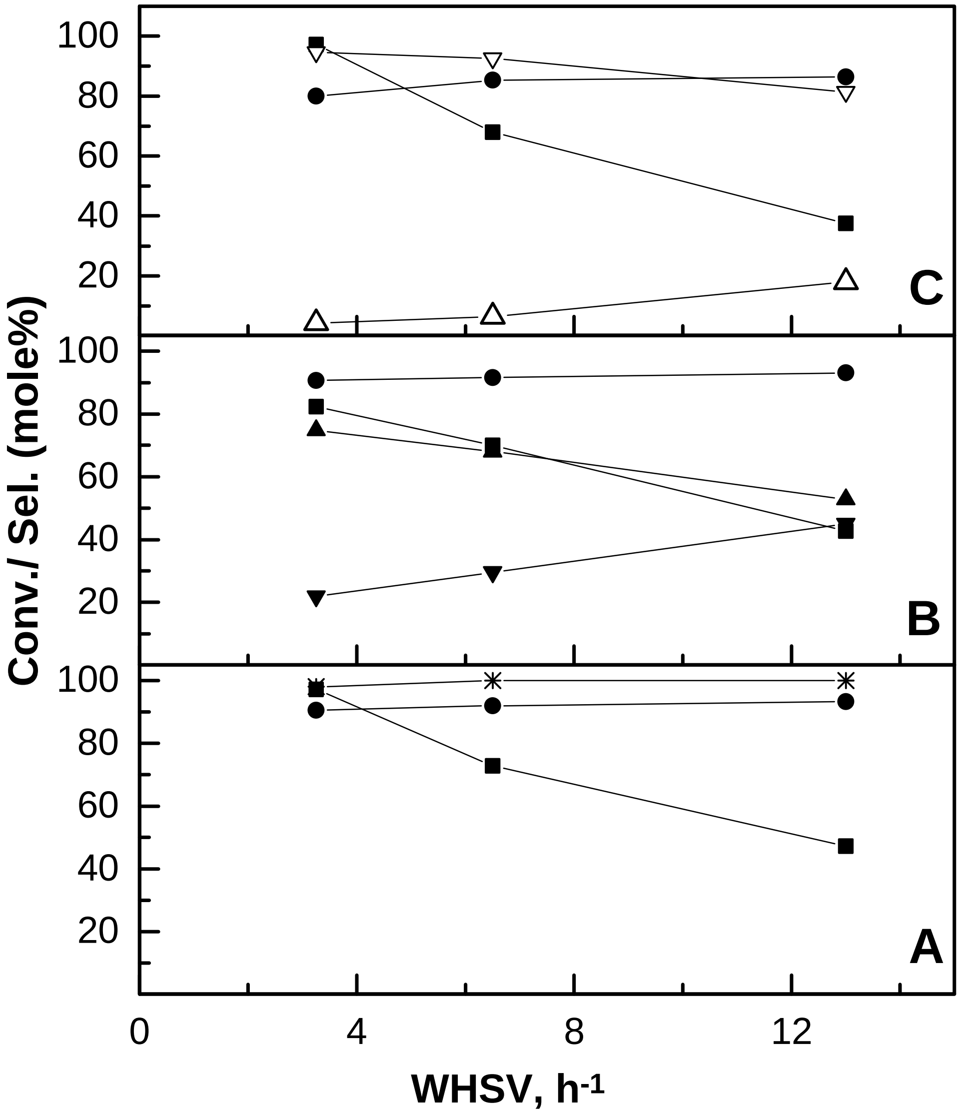


**Fig. 3.5:** Effect of WHSV on the conversion and product selectivity and its distribution over zeolite H-USY catalyst in the isopropylation of *p*-xylene (A), *m*-xylene (B) and *o*-xylene (C). Conversion of xylene ( ), Sel.$_{\text{DMC}}$ ( ), Sel. $_{\text{2,5-DMC}}$ (□), Sel.$_{\text{2,4-DMC}}$ ( ), Sel.$_{\text{3,5-DMC}}$ (□), Sel.$_{\text{3,4-DMC}}$ (□), Sel.$_{\text{2,3-DMC}}$ (□).

Reaction Conditions: Xylene:isopropanol = 4:1(molar), Temperature = 413 K, TOS = 1h.

### 3.3.2.3. Influence of xylene/isopropanol molar ratio

The results of the influence of the xylene to isopropanol (isopropyl alcohol, IPA) molar ratio on the catalytic activity and product distribution are presented in Table 3.8 & Fig. 3.6 (A-C). With increasing xylene/isopropanol molar ratio the efficiency for the utilization of the limiting reagent isopropanol for isopropylation reaction increased significantly in the cases of all the three xylene isomers used as feed. Although, absolute xylene conversion decreased with increasing xylene to isopropanol ratio expectedly, but the conversion based on theoretical maximum value increased in all the cases. At lower xylene to isopropanol molar ratio of 2, the selectivity of dialkylated fraction (DIPT+DIPX) is significantly high (22% for *p*- and *m*-xylene and ca.16% for *o*-xylene), mainly at the cost of DMC clearly indicating enhanced further isopropylation of DMC to dialkylated fraction. However, with increasing xylene to isopropanol mole ratio, the $\text{Sel.}_{\text{DMCs}}$ increased significantly because the limited isopropanol is totally reacted with xylene to produce DMCs and there is less chance for the formation of dialkylated fraction at higher xylene to isopropanol molar ratio i.e. at lower concentration of isopropanol.

With increasing xylene/isopropanol molar ratio, $\text{Sel.}_{\text{2,5-DMC}}$ in the case of *p*-xylene isopropylation did not change significantly (Fig. 3.6-A). In the case of *m*-xylene, $\text{Sel.}_{\text{3,5-DMC}}$ increased from ca. 53 to 72.0% and consequently the $\text{Sel.}_{\text{2,4-DMC}}$ is decreased from ca. 44 to 27% and $\text{Sel.}_{\text{2,6-DMC}}$ is almost unchanged (ca. 1.5%) with increasing xylene/isopropanol molar ratio from 2:1 through 10:1 (Table 3.8 & Fig. 3.6-B). These results indicate that with increasing xylene to isopropanol molar ratio, the isomerization of 2,4-DMC in to 3,5-DMC (via 1,2 propyl shift) is favored, once again corroborating the selectivity trend influenced by temperature and WHSV. It may be recalled here that the formation of 3,5-DMC can also be, at least partly, due to bimolecular isomerization of 2,4-DMC to 3,5-DMC in the case of H-USY with large void space where bulky bimolecular intermediate can be accommodated.

However, in the case of other zeolites (H-Mordenite and H-Beta) such bimolecular isomerization does not seem to occur. In the case of *o*-xylene isopropylation (Table 3.8 & Fig. 3.6-C), where the Sel.$_{2,3\text{-DMC}}$ decreased from ca. 12% (at xylene/isopropanol molar ratio = 2:1) to ca. 4% (at xylene/isopropanol molar ratio = 10:1) while the corresponding increase in Sel$_{3,4\text{-DMC}}$ was from ca. 87% to 96% due to isomerization of less stable 2,3-DMC to more stable 3,4-DMC.

### 3.3.2.4. Influence of time on stream (TOS)

Fig. 3.7(A-F) exhibits the effect of TOS on conversion and selectivity in the isopropylation of all the three xylenes. With increasing TOS the conversion of all xylenes (Fig. 3.7 A-C, shown as curve a, column A, B and C for *p*-, *m*- and *o*-xylene respectively), remained almost same for first two hours and then started decreasing rather sharply in the beginning from ca. 95% to 75% xylene conversion (of the theoretically maximum value of 25 mole%) before stabilizing to some extent.

The product distribution is plotted in Fig. 3.7 A-F. With TOS, the overall selectivity for alkylated products (S$_{\text{ALK}}$), (shown as curve b, in Fig. 3.7 A-C), containing both mono- (DMCs) and di-isopropylated products (DIPT+DIPX), remained constant or increased marginally. The selectivities for isomerized (Sel.$_{\text{ISO}}$, curve c) and disproportionated products (Sel.$_{\text{DISP}}$, curve d) also did not vary significantly and ranged between 0 and 5% in the case of *p*-, *m*- and *o*-xylene. The selectivity of dimethylcumenes (Sel.$_{\text{DMCs}}$) (curve e, Fig. 3.7 D-F) also remained constant over time at ca. 90% for *p*- and *m*-xylenes and ca. 80 to 85% for *o*-xylene.

**Table 3.8: Effect of xylene to isopropanol molar ratio on conversion and product selectivity in the isopropylation of xylene isomers over zeolite H-USY[r]**

| Xylene isomer | Conv./ Sel. (mole%) | Xylene to isopropanol (molar ratio) | | | |
|---|---|---|---|---|---|
| | | 2:1 | 4:1 | 8:1 | 10:1 |
| | Theoretical maximum conversion | 50.0 | 25.0 | 12.5 | 10.0 |
| *p*-Xyl. | Conv. | 34.4 | 18.2 | 9.7 | 8.9 |
| | Conv. (theo. max)[a] | 68.8 | 72.8 | 77.6 | 89.0 |
| | Sel.$_{DMCs}$ | 76.8 | 92.0 | 97.6 | 100.0 |
| | DMC Yield[b] | 52.8 | 67.0 | 75.7 | 89.0 |
| | Sel. $_{ISO}$ (*m*- + *o*-xylene) | 0.0 | 0.0 | 0.0 | 0.0 |
| | Sel.$_{DISP}$[c] | 1.6 | 2.0 | 0.4 | 0.0 |
| | Sel.$_{DI\ PT}$[d] + Sel.$_{DIPX}$[e] | 21.6 | 6.0 | 2.0 | 0.0 |
| | Sel.$_{2,5\text{-}DMC}$ | 97.3 | 100.0 | 100.0 | 100.0 |
| | Sel.$_{Other\ (2,4\text{-}DMC)}$ | 2.7 | 0.0 | 0.0 | 0.0 |
| *m*-Xyl. | Conv. | 22.2 | 17.5 | 10.3 | 8.8 |
| | Conv. (theo.max.)[a] | 44.4 | 70.0 | 82.4 | 88.0 |
| | Sel.$_{DMCs}$ | 74.6 | 91.6 | 98.0 | 99.0 |
| | DMC Yield[b] | 33.1 | 64.1 | 80.8 | 87.1 |
| | Sel.$_{ISO}$ (*o*- + *p*-xylene) | 1.0 | 1.4 | 0.0 | 0.0 |
| | Sel.$_{DISP}$[c] | 1.8 | 3.1 | 0.6 | 0.2 |
| | Sel.$_{DI\ PT}$[d] + Sel.$_{DIPX}$[e] | 22.6 | 3.9 | 1.4 | 0.8 |
| | Sel.$_{3,5\text{-}DMC}$ | 53.1 | 68.0 | 70.6 | 71.5 |
| | Sel.$_{2,4\text{-}DMC}$ | 44.1 | 29.6 | 27.8 | 27.1 |
| | Sel.$_{2,6\text{-}DMC}$ | 1.7 | 1.5 | 1.1 | 0.9 |
| | Sel.$_{Other\ (2,5\text{-}DMC)}$ | 1.1 | 0.9 | 0.5 | 0.5 |
| *o*-Xyl. | Conv. | 21.4 | 17.0 | 10.7 | 9.4 |
| | Conv. (theo. max.)[a] | 42.8 | 68.0 | 85.6 | 94.0 |
| | Sel.$_{DMCs}$ | 80.4 | 85.3 | 85.9 | 88.0 |
| | DMC Yield[b] | 34.4 | 58.0 | 73.5 | 82.7 |
| | Sel. $_{ISO}$ (*m*- + *p*-xylene) | 0.3 | 1.1 | 1.2 | 1.3 |
| | Sel.$_{DISP}$[c] | 3.1 | 4.2 | 5.5 | 5.4 |
| | Sel.$_{DI\ PT}$[d] + Sel.$_{DIPX}$[e] | 16.2 | 9.4 | 7.4 | 5.3 |
| | Sel.$_{3,4\text{-}DMC}$ | 86.5 | 92.6 | 94.4 | 95.6 |
| | Sel.$_{2,3\text{-}DMC}$ | 12.1 | 6.4 | 4.8 | 3.7 |
| | Sel.$_{Other\ (2,4\text{-}DMC)}$ | 1.4 | 1.0 | 0.8 | 0.7 |

[r] Reaction Conditions: WHSV = 6.5 $h^{-1}$, Temperature = 413 K, TOS = 1h, isopropanol conv.= 100%, at xylene:isopropanol = 2:1 (molar), remaining unreacted propylene was present in gaseous stream, [a-e]: as in Table 3.6.

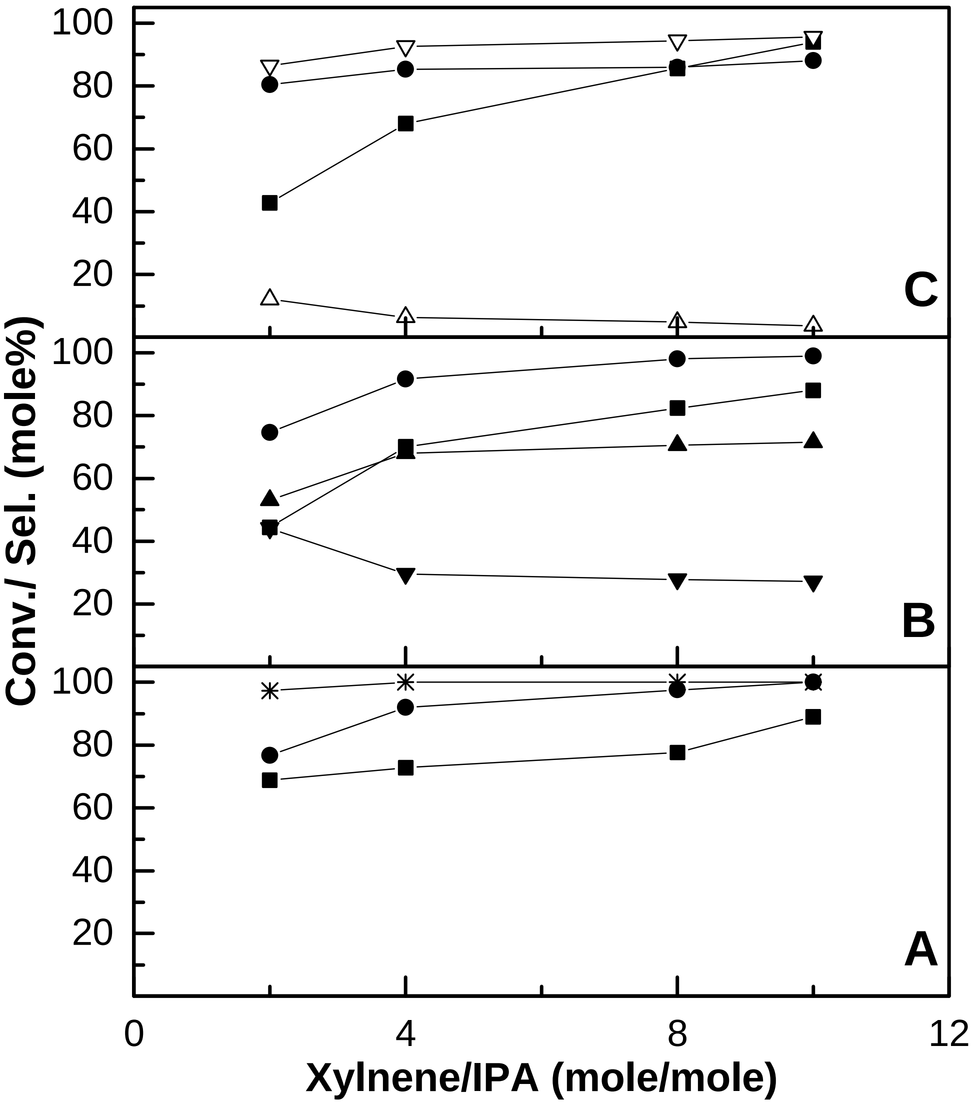


**Fig. 3.6:** Effect of xylene to isopropyl alcohol (IPA) mole ratio on the conversion and product selectivity and its distribution over zeolite H-USY catalyst in the isopropylation of *p*-xylene (A), *m*-xylene (B) and *o*-xylene (C). Conversion of xylene ( ), Sel.$_{\text{DMC}}$ ( ), Sel. $_{\text{2,5-DMC}}$ (□), Sel.$_{\text{2,4-DMC}}$ ( ), Sel.$_{\text{3,5-DMC}}$ (□), Sel.$_{\text{3,4-DMC}}$ (□), Sel.$_{\text{2,3-DMC}}$ (□).

Reaction Conditions: WHSV = 6.5 $h^{-1}$, Temperature = 413 K, TOS = 1h.

Regarding DMC isomer distribution, there was no significant change over TOS in the case of 2,5-DMC (Sel.$_{2,5\text{-DMC}}$) formed from *p*-xylene isopropylation (curve f, Fig. 3.7-D) with ca. 100% selectivity among DMCs. In the case of *m*-xylene, the distribution of DMC isomers was rather influenced significantly. While the selectivity for energetically less favored 2,4-DMC (curve h, Fig. 3.7-E) increased from ca. 22 to 30% at the cost of energetically more favored 3,5-DMC (curve g, Fig. 3.7-E). Selectivity of 2,6-DMC (Sel.$_{2,6\text{-DMC},}$ curve i, Fig. 3.7-E) remained almost unchanged (ca. 2%) with increasing TOS.

A decrease in selectivity for 3,5-DMC (Sel.$_{3,5\text{-DMC}}$) along with a decrease in conversion with TOS may be ascribed to (i) selective poisoning of stronger acid sites which are responsible for isomerization of 2,4-DMC to 3,5-DMC [(while isopropylation (primary reaction) reaction leading to 2,4-DMC may take place on the less strong acid sites)], and (ii) narrowing of the void space due to coking. In another way, where the diffusion of 3,5-DMC (as its more dimension compare to other isomers) becomes slower than that of the 2,4-DMC and hence selectivity of 2,4-DMC is increased at the cost of 3,5-DMC with increasing TOS. This observed selectivity trend of 3,5- and 2,4-DMC isomers also corroborates the results reported in Tables 3.6-3.8 and discussed accordingly in text above. However, the isomer distribution in the case of *o*-xylene isopropylation (Fig. 3.7-F) did not change with time where the selectivity of 2,3-DMC (Sel.$_{2,3\text{-DMC}}$) (curve k, Fig. 3.7-F) and selectivity of 3,4-DMC (Sel.$_{3,4\text{-DMC}}$) (curve j, Fig. 3.7-F) remained almost same at ca. 4 and 94%, respectively, the remaining 2% being 2,4-DMC.

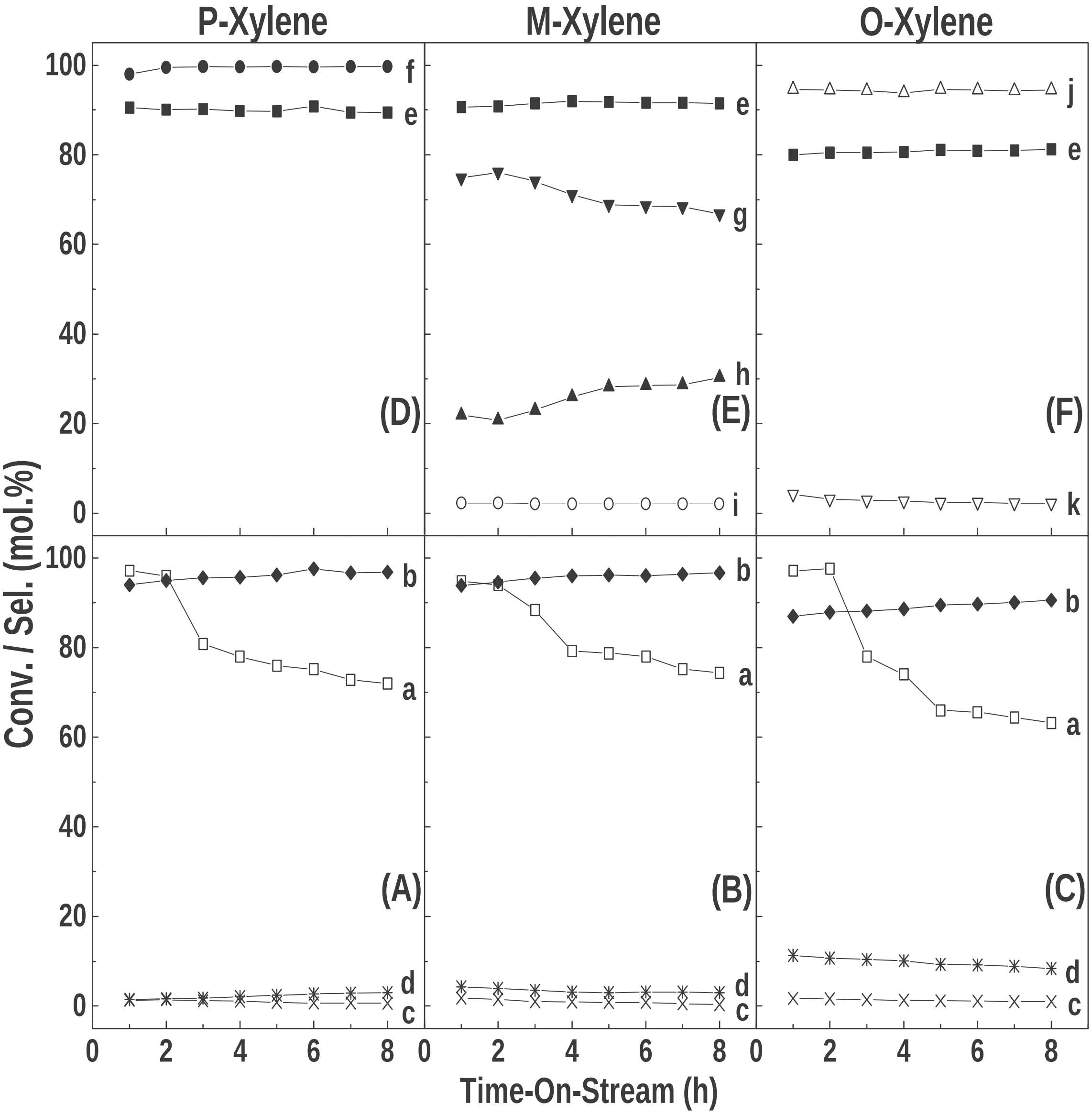


**Fig. 3.7:** A-C: Conversion versus time on stream (TOS, h) over H-USY (curve a), Sel.$_{ALK}$ (b), Sel.$_{ISO}$ (c) and Sel.$_{DISP}$ (d), D-F: Sel.$_{DMC}$ (e), Sel.$_{2,5\text{-}DMC}$ (f), Sel.$_{3,5\text{-}DMC}$ (g), Sel.$_{2,4\text{-}DMC}$ (h), Sel.$_{2,6\text{-}DMC}$ (i). Sel.$_{3,4\text{-}DMC}$ (j) and Sel.$_{2,3\text{-}DMC}$ (k). The alphabet in the parenthesis indicates the curve number. **S$_{ALK}$** = Selectivity of total alkylated product (DMC+DIPT+DIPX), **Sel.$_{ISO}$** = Selectivity of xylene isomerized products other than the substrate one, **Sel.$_{DISP}$** = Selectivity of diproportionated products, **Sel.$_{DMC}$** = Selectivity of dimethylcumenes among the total products, For Sel.$_{2,5\text{-}DMC}$, Sel.$_{3,5\text{-}DMC}$, Sel.$_{2,4\text{-}DMC}$, Sel.$_{2,6\text{-}DMC}$, Sel.$_{2,3\text{-}DMC}$ and Sel.$_{3,4\text{-}DMC}$ isomers, the number in the subscript indicate the corresponding dimethylcumene.

Reaction conditions: Temperature = 413 K, Xylene:isopropanol = 4: 1(molar), WHSV = 3.25 $h^{-1}$.

### 3.3.2.5. Isopropylation of Equilibrium Mixture of Xylenes Over Zeolite H-USY

In order to study the over all selectivity pattern of all DMC isomers, an equilibrium mixture of xylenes (24% *p*-xylene, 54% *m*-xylene and 22% *o*-xylene) was isopropylated over the H-USY catalyst as a function of TOS between 1 and 5 hours (Table 3.9). The over all xylene conversion ranged between 23.7 and 21.1 mole% (94.8 to 84.4% of theoretical maximum of 25 mole%, based on 4:1 xylene: isopropanol molar ratio). The relative distribution of the six isomers (Table 3.9) in their order of elution from GC (Fig. 3.2) was: 3,5-DMC (41.1 to 36.7%), 2,5-DMC (16.1 to 19.9%), 2,4-DMC (10.5 to 13.4%), 3, 4-DMC (30.6 to 28.8%), 2,6-DMC (0.5 to 0.4%) and 2,3-DMC (1.2 to 0.8%). The experimentally obtained selectivity order of all the DMC isomers follows the order: 3,5-DMC > 3,4-DMC > 2,5-DMC > 2,4-DMC > 2,3-DMC > 2,6-DMC. It may be recalled that the thermodynamic stability of the DMC isomers, also follows the same order. Formation of 3,5-DMC can be accounted for by the isomerization of mainly 2,4-DMC (as mentioned above) to energetically most stable 3,5-DMC. The total DMC selectivity ranged between 95.8 and 97.0 mole%, remaining 3.0 – 4.2 mole% being the disproportionated and dialkylated products.

**Table 3.9: Effect of TOS on conversion and product selectivity in the isopropylation of equilibriuam mixture of xylenes over zeolite USY[r]**

| Conv. or Sel. (mole %) | Time on stream, h | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 |
| Over all conversion xylene | 23.7 | 23.6 | 22.1 | 21.7 | 21.1 |
| Over all Conv. (theo. max.)[a] | 94.8 | 94.4 | 88.4 | 86.8 | 84.4 |
| Sel.$_{DMCs}$ in total products. | 95.8 | 96.2 | 96.4 | 96.8 | 97.0 |
| Sel.$_{DISP}$ in total products.[c] | 3.3 | 2.8 | 2.0 | 1.6 | 1.0 |
| Sel.$_{(DIPT^{d}+DIPX^{e})}$ in total products. | 0.9 | 1.0 | 1.6 | 1.6 | 2.0 |
| **DMC isomer distribution:** | | | | | |
| Sel.$_{3,5\text{-}DMC}$ | 41.1 | 39.6 | 39.6 | 37.6 | 36.7 |
| Sel.$_{3,4\text{-}DMC}$ | 30.6 | 30.4 | 29.1 | 28.8 | 28.8 |
| Sel.$_{2,5\text{-}DMC}$ | 16.1 | 17.3 | 18.2 | 19.4 | 19.9 |
| Sel.$_{2,4\text{-}DMC}$ | 10.5 | 11.0 | 11.8 | 13.0 | 13.4 |
| Sel.$_{2,3\text{-}DMC}$ | 1.2 | 1.2 | 0.9 | 0.8 | 0.8 |
| Sel.$_{2,6\text{-}DMC}$ | 0.5 | 0.5 | 0.4 | 0.4 | 0.4 |

[r] Reaction Conditions: Temperature = 413 K, Xylene mixture (24% *p*-xylene, 54% *m*-xylene and 22% *o*-xylene):isopropanol = 4:1(molar), WHSV = 3.25 h$^{-1}$, [a, c]: as in Table 3.6.

### 3.3.3. ISOPROPYLATION OF XYLENES OVER H-BETA

Isopropylation of all xylenes was carried out over zeolite H-Beta under the similar reaction conditions. A comparison of isopropylation of all xylene isomers over zeolite Beta is shown in Fig. 3.8. The activity towards isopropylation (denoted as conversion) and Sel.$_{DMC}$ follows the order: *p*-xylene > *m*-xylene  *o*-xylene.

There are total six DMC isomers, which can be formed during isopropylation of xylene isomers (Scheme 3.1). The distribution of five DMCs isomers out of six isomers (2,6-DMC was not formed at all) was depicted in the Fig. 3.8. While *p*-xylene gave 94.4% 2,5-DMC (all regio positions are same), *m*-xylene gave 55% of 2,4-DMC and 0.0% of 2,6-DMC as primary product (alkylation being ortho-para directing electrophilic reaction) and 44% of 3,5-DMC as secondary product, and *o*-xylene gave ca.11% of 2,3-DMC and 89% of 3,4-DMC as primary products.

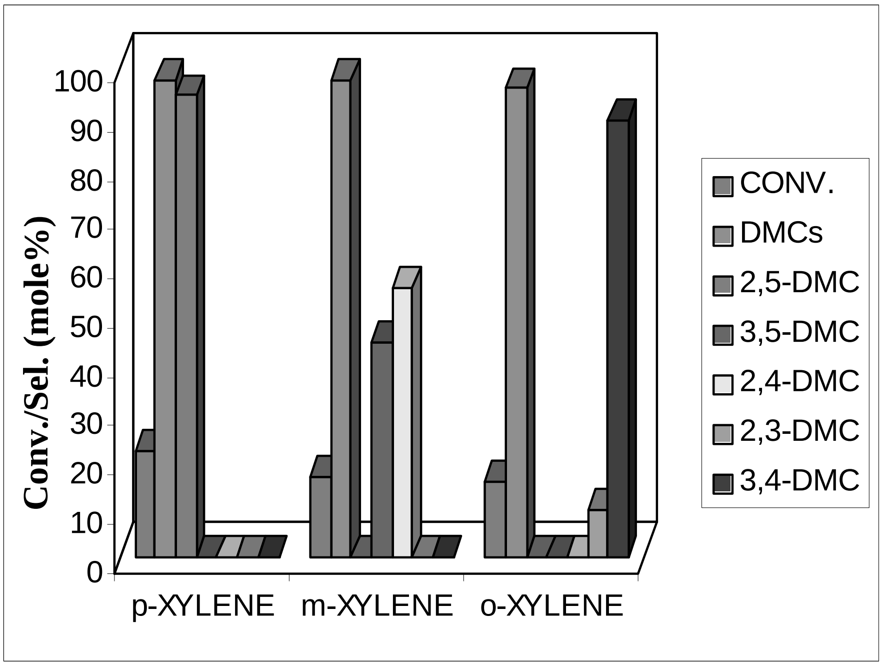


**Fig. 3.8:** A comparision of isopropylation of all xylene isomers over zeolite H-Beta.

Reaction conditions: Temperature = 413 K, Xylene:isopropanol = 4:1 (molar), WHSV = 3.25 h$^{-1}$, TOS = 1h.

### 3.3.3.1. Influence of Temperature

The influence of temperature on conversion of xylene isomers and dimethylcumene (DMC) selectivity are presented in Table 3.10 & Fig. 3.9 (A-C). As expected, the temperature has marked effect on the conversion of xylene isomers and DMC selectivity. With an increase in temperature, the conversion increases and reaches almost the theoretical maximum value. However, the selectivity for DMC among total products decreases slowly in the temperature range of 403 K to 433 K and then sharply thereafter (Fig. 3.9 A-C). At higher temperature (443-453 K) the isomerization of the xylene feed isomer as well as little disproportionation/transalkylation of xylene into toluene and trimethyl benzene also occurs, particularly after 443 K. Consequently, due to isomerization of xylene feed isomer, the isopropylation of isomerized xylene isomers leads to the lowering of the primarily formed DMC isomer, as can be seen from Table 3.10 below. Hence the present studies suggest that in order to maximize the yield of desired DMC isomer the isopropylation of xylene over zeolite H-Beta should preferably be carried out at lower temperature range of 423-433 K. At higher temperature, the isomerization of the xylene followed by alkylation takes place, thereby decreasing the selectivity for DMC in general and the primarily formed DMC isomer(s) in particular.

In the case of *m*-xylene isopropylation, it is clear that compared to 3,5-DMC, the 2,4-DMC is favored at low temperature (Fig. 3.9-B). However, with increasing temperature the selectivity for 3,5-DMC increases sharply at the cost of that of 2,4-DMC in the direction of attaining their respective thermodynamic equilibrium values (Fig. 3.9-B). In the case of *o*-xylene isopropylation, compared to the selectivity for 2,3-DMC, the 3,4-DMC is favored at all the temperatures (Fig. 3.9-C). However, the selectivity for 2,3-DMC decreases from ca. 14% at 403 K to ca. 3% at 453 K indicating that at lower temperature the formation of thermodynamically least favored isomer (2,3-DMC) is relatively favored at lower temperature and tends to attain thermodynamic value at higher temperatures.

**Table 3.10: Effect of reaction temperature on the conversion and product selectivity in the isopropylation of xylenes[r]**

| Xylenes | Conv. or Sel. (mole%) | Reaction Temperature, K | | | | | |
|---|---|---|---|---|---|---|---|
| | | 403 | 413 | 423 | 433 | 443 | 453 |
| *p*-Xyl. | Conv. of IPA | 99.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| | Conv. of *p*-xylene | 16.9 | 21.9 | 22.6 | 23.0 | 25.0 | 25.0 |
| | Conv. (theo.max.) | 67.6 | 87.6 | 90.4 | 92.0 | 100 | 100 |
| | Sel. $_{\text{DMCs}}$ | 95.4 | 95.0 | 92.0 | 89.0 | 77.0 | 66.6 |
| | Sel.$_{\text{Other products}}$[f] | 4.6 | 5.0 | 8.0 | 11.0 | 23.0 | 33.4 |
| | Sel. $_{\text{2,5-DMC}}$ | 99.8 | 94.4 | 87.9 | 87.0 | 86.0 | 83.3 |
| | Sel. $_{\text{Other (2,4-DMC)}}$ | 0.2 | 5.6 | 12.1 | 13.0 | 14.0 | 16.7 |
| *m*-Xyl. | Conv. of IPA | 88.0 | 99.5 | 99.8 | 100.0 | 100.0 | 100.0 |
| | Conv. of *m*-xylene | 7.1 | 16.5 | 21.5 | 23.6 | 24.1 | 24.9 |
| | Conv. (theo.max.) | 28.4 | 66.0 | 86.0 | 94.4 | 96.4 | 99.6 |
| | Sel. $_{\text{DMCs}}$ | 97.7 | 97.5 | 93.9 | 91.6 | 86.2 | 78.9 |
| | Sel.$_{\text{Other products}}$[f] | 2.3 | 2.5 | 6.1 | 8.4 | 13.8 | 21.1 |
| | Sel. $_{\text{3,5-DMC}}$ | 33.0 | 44.1 | 59.9 | 70.5 | 75.0 | 75.7 |
| | Sel. $_{\text{2,4-DMC}}$ | 66.5 | 55.1 | 37.9 | 27.0 | 22.3 | 21.0 |
| | Sel. $_{\text{2,6-DMC}}$ | - | - | - | - | - | - |
| | Sel. $_{\text{Other (2,5-DMC)}}$ | 0.5 | 0.8 | 2.2 | 2.5 | 2.7 | 3.3 |
| *o*-Xyl. | Conv. of IPA | 93.7 | 99.0 | 99.1 | 99.5 | 99.9 | 100.0 |
| | Conv. of *o*-xylene | 7.3 | 15.5 | 19.1 | 19.9 | 22.3 | 24.8 |
| | Conv. (theo.max.) | 29.2 | 62.0 | 76.4 | 79.6 | 89.2 | 99.2 |
| | Sel. $_{\text{DMCs}}$ | 97.3 | 95.9 | 95.1 | 93.8 | 92.4 | 87.6 |
| | Sel.$_{\text{Other products}}$[f] | 2.7 | 4.1 | 4.9 | 6.2 | 7.6 | 12.4 |
| | Sel. $_{\text{2,3-DMC}}$ | 14.3 | 9.7 | 8.0 | 6.2 | 4.6 | 3.2 |
| | Sel. $_{\text{3,4-DMC}}$ | 84.7 | 88.5 | 89.5 | 90.2 | 90.6 | 88.2 |
| | Sel. $_{\text{Other (2,4-DMC)}}$ | 1.0 | 1.8 | 2.5 | 3.6 | 4.8 | 8.6 |

[r] Reaction conditions: WHSV = 3.25 h$^{-1}$, Xylene:isopropanol = 4:1 (molar), TOS = 1h, Catalyst = H-Beta, at low xylene conversion propylene was present in gaseous stream, observed mass balance = 95 ± 3% in all cases, [f]The products were mainly other isomerized and disproportionated products of xylene along with less amount of DPX and DIPT.

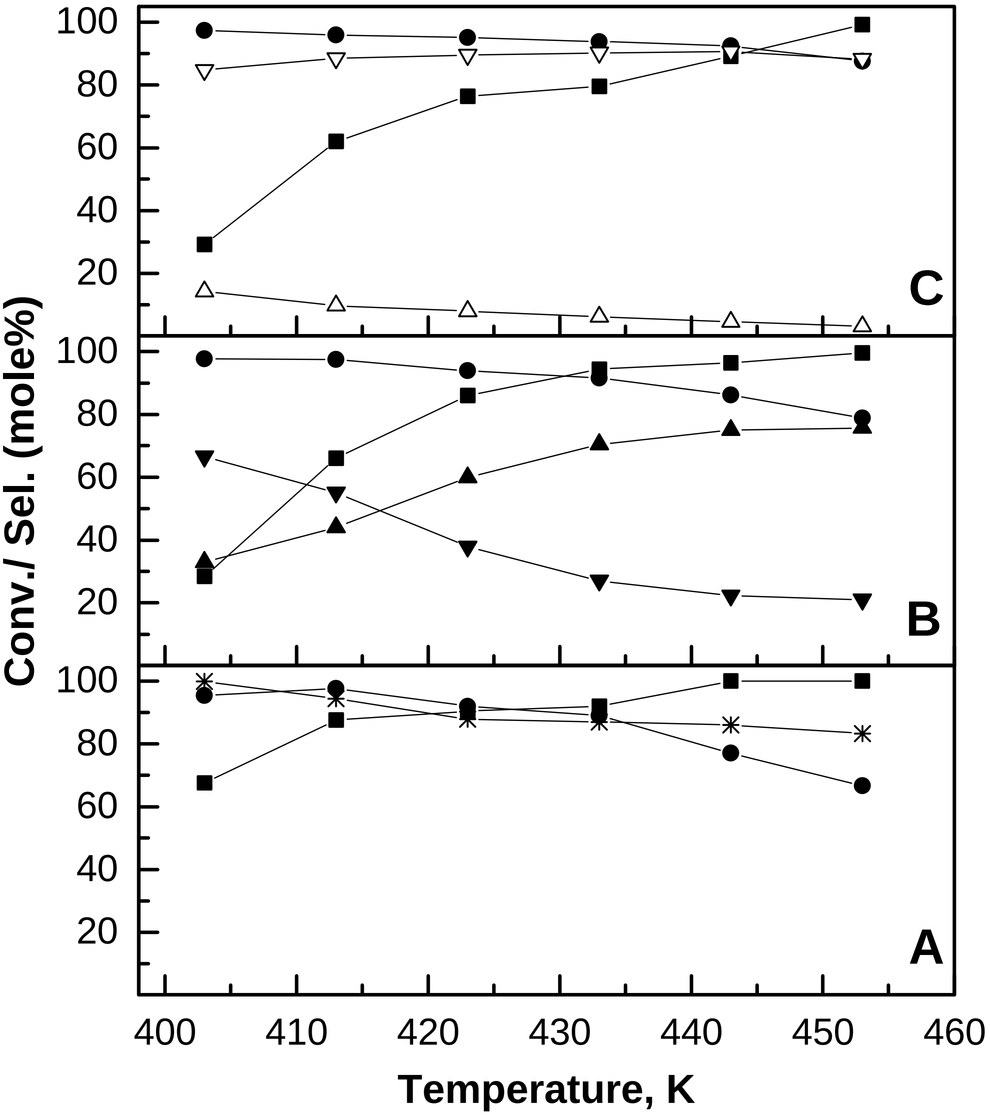


**Fig. 3.9:** Effect of temperature on the conversion and product selectivity and its distribution over zeolite H-Beta catalyst in the isopropylation of *p*-xylene (A), *m*-xylene (B) and *o*-xylene (C). Conversion of xylene (  ), Sel.$_{DMC}$ ( ), Sel. $_{2,5\text{-}DMC}$ (□), Sel.$_{2,4\text{-}DMC}$ (  ), Sel.$_{3,5\text{-}DMC}$ (□), Sel.$_{3,4\text{-}DMC}$ (□), Sel.$_{2,3\text{-}DMC}$ (□), Reaction conditions: Xylene:isopropanol = 4:1(molar) (molar), WHSV = 3.25 h$^{-1}$, TOS = 1h.

### 3.3.3.2. Influence of feed rate

The influence of weight hourly space velocity (WHSV) on activity and product distribution is given in Table 3.11 & Fig. 3.10 (A-C). As expected, with increasing feed rate, the xylene conversion decreased while the selectivity towards DMC increased. Similarly, the selectivity for primarily formed DMC isomer(s) among total DMCs also increased with increasing feed rate.

Here again, one can see from Table 3.11 that with increasing residence time (decreasing feed rate), the selectivity for 2,4-DMC decreases from ca. 80% (at WHSV = 12.65 $h^{-1}$) to ca. 20% (at WHSV = 1.62 $h^{-1}$) with a consequent increase in the selectivity of 3,5-DMC (Fig. 3.10-B). In the case of *o*-xylene isopropylation also, the selectivity for 2,3-DMC, vis-à-vis 3,4-DMC, increases with increasing WHSV (decreasing residence time) from 6.4% (at WHSV = 1.62 $h^{-1}$) to 25.8 (at WHSV = 12.65 $h^{-1}$) (Fig. 3.10-C). In both cases, viz. *m*-xylene and *o*-xylene (Table 3.11 & Fig. 3.10), the thermodynamically more stable product like 3,5-DMC (m-xylene) and 3,4-DMC (o-xylene), respectively increase with increasing conversion. Consequently at lower reaction temperature and shorter contact time, the selectivity for primary product 2,4-DMC (m-xylene) and 2,3-DMC (o-xylene) is higher, as expected, because as the severity of the reaction increases the isomer distribution tends to move towards thermodynamic equilibrium. In the case of *p*-xylene only 2,5-DMC is primarily formed isome.

### 3.3.3.3. Influence of xylene/isopropanol mole ratio

The effect of xylene/isopropanol (isopropyl alcohol, IPA) on the conversion and product selectivity over H-Beta catalysts is shown in table 3.12 and Fig. 3.11(A-C). The efficiency for the utilization of the limiting reagent isopropanol for isopropylation reaction increased significantly in the case of all three xylene isomers used as feed.

Although, the overall xylene conversion decreased with increasing xylene to isopropanol ratio, the conversion based on the theoretical maximum value increased in all the cases.

**Table 3.11: Effect of feed rate on the conversion and product selectivity in the isopropylation of xylene isomers over zeolite H-Beta**[r]

| Xylenes | Conv. or Sel. (mole%) | WHSV, $h^{-1}$ | | | |
|---|---|---|---|---|---|
| | | 1.62 | 3.25 | 6.67 | 12.65 |
| *p*-Xyl. | Conv. of IPA | 100.0 | 100.0 | 98.0 | 85.0 |
| | Conv. of *p*-xylene | 25.0 | 21.9 | 20.7 | 14.1 |
| | Conv. (theo.max.) | 100.0 | 87.6 | 82.8 | 56.4 |
| | Sel. $_{\text{DMCs}}$ | 91.0 | 97.7 | 98.0 | 98.4 |
| | Sel.$_{\text{Other products}}^{f}$ | 9.0 | 2.3 | 2.0 | 1.6 |
| | Sel. $_{\text{2,5-DMC}}$ | 88.0 | 94.4 | 95.2 | 99.7 |
| | Sel. $_{\text{Other (2,4-DMC)}}$ | 12.0 | 5.6 | 4.8 | 0.3 |
| *m*-Xyl. | Conv. of IPA | 100.0 | 99.5 | 99.8 | 62.8 |
| | Conv. of *m*-xylene | 20.1 | 16.5 | 12.3 | 8.6 |
| | Conv. (theo.max.) | 80.4 | 66.0 | 49.2 | 34.4 |
| | Sel. $_{\text{DMCs}}$ | 88.3 | 97.5 | 98.0 | 98.2 |
| | Sel.$_{\text{Other products}}^{f}$ | 11.7 | 2.5 | 2.0 | 1.8 |
| | Sel. $_{\text{3,5-DMC}}$ | 76.6 | 44.1 | 29.7 | 20.7 |
| | Sel. $_{\text{2,4-DMC}}$ | 20.1 | 55.1 | 69.7 | 79.3 |
| | Sel. $_{\text{2,6-DMC}}$ | - | - | - | - |
| | Sel. $_{\text{Other (2,5-DMC)}}$ | 3.3 | 0.8 | 0.6 | 0.0 |
| *o*-Xyl. | Conv. of IPA | 100.0 | 99.0 | 95.3 | 58.0 |
| | Conv. of *o*-xylene | 19.8 | 15.5 | 12.5 | 8.2 |
| | Conv. (theo.max.) | 79.2 | 62.0 | 50.0 | 32.8 |
| | Sel. $_{\text{DMCs}}$ | 89.0 | 95.9 | 96.5 | 97.9 |
| | Sel.$_{\text{Other products}}^{f}$ | 11.0 | 4.1 | 3.5 | 2.1 |
| | Sel. $_{\text{2,3-DMC}}$ | 6.4 | 9.7 | 19.4 | 25.8 |
| | Sel. $_{\text{3,4-DMC}}$ | 90.1 | 88.5 | 80.6 | 74.2 |
| | Sel. $_{\text{Other (2,4-DMC)}}$ | 3.5 | 1.8 | 0.0 | 0.0 |

[r] Reaction Conditions: Xylene:isopropanol = 4:1(molar), Temperature = 413 K, TOS = 1h, at low xylene conversion propylene was present in gaseous stream, observed mass balance = 95 ± 3% in all cases, [f] as in Table 3.10.

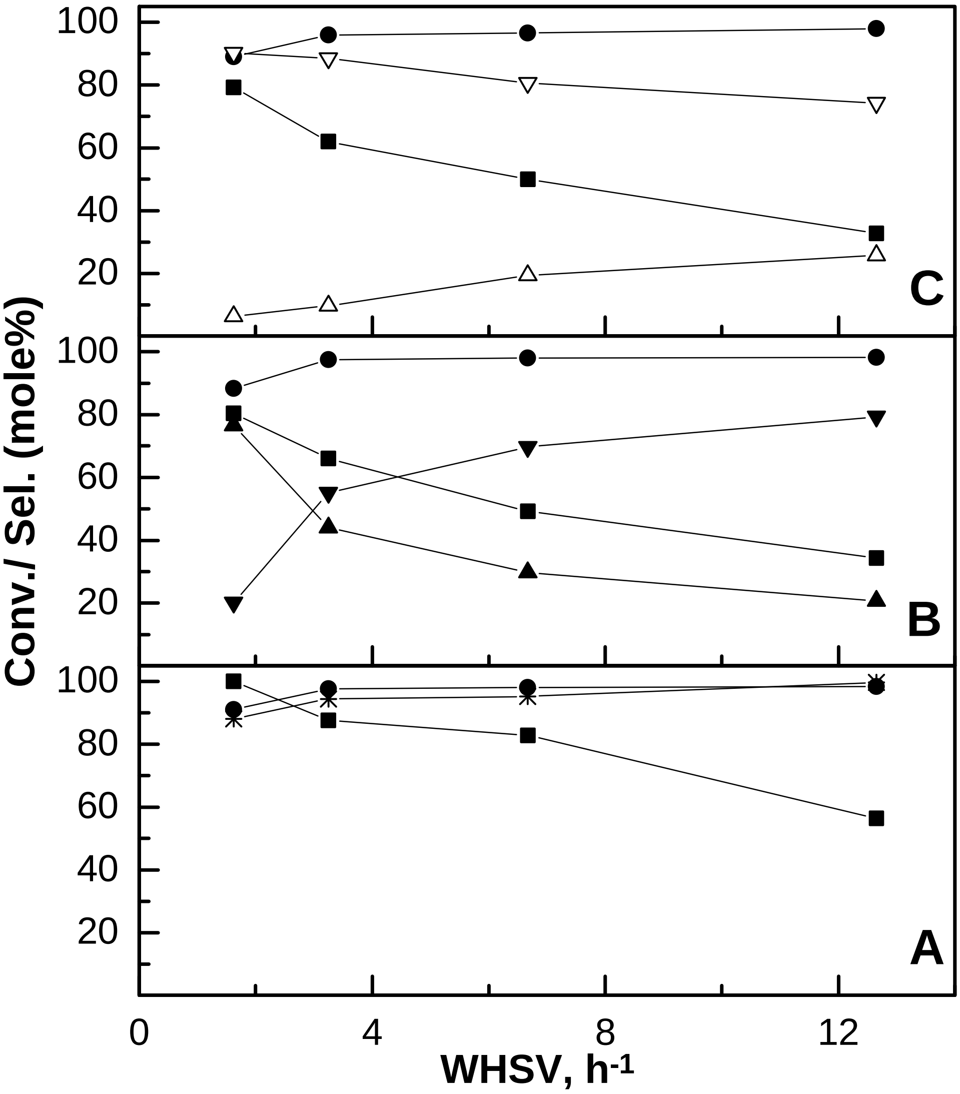


**Fig. 3.10:** Effect of WHSV on the conversion and product selectivity and its distribution over zeolite H-Beta catalyst in the isopropylation of *p*-xylene (A), *m*-xylene (B) and *o*-xylene (C). Conversion of xylene (  ), Sel.$_{\text{DMC}}$ ( ), Sel.$_{2,5\text{-DMC}}$ (□), Sel.$_{2,4\text{-DMC}}$ (  ), Sel.$_{3,5\text{-DMC}}$ (□), Sel.$_{3,4\text{-DMC}}$ (□), Sel.$_{2,3\text{-DMC}}$ (□). Reaction Conditions: Xylene:isopropanol = 4:1(molar), Temperature = 413 K, TOS = 1h.

However, with increasing xylene to isopropanol mole ratio selectivity of total DMCs among all the products increased marginally, if at all. The selectivity for 2,5-DMC among DMCs in the case of *p*-xylene isomerization did not vary to any significant extent (Fig. 3.11-A). In the case of *m*-xylene, the selectivity for 3,5-DMC increased slightly from 42.4% (at xylene/IPA molar ratio = 2) to 53.3% (at xylene/IPA molar ratio = 8, through 4) with xylene/isopropanol molar ratio and consequently, the 2,4-DMC isomer decreased (Table 3.12 & Fig. 3.11-B).

In the case of *o*-xylene isopropylation, the selectivity for 2,3-DMC decreased from 12.3% (at xylene/IPA molar ratio = 2) to 2.7% (at xylene/IPA molar ratio = 8 through 4) with increasing xylene to isopropanol molar ratio (Fig. 3.11-C).

### 3.3.3.4. Effect of Time-On-Stream (TOS)

The effect of time on stream on the conversion and selectivity in the isopropylation of xylene isomers is plotted in Fig. 3.12 (A-D). Although, there was no appreciable decrease in the conversion of *p*-xylene, other two xylene isomers namely *m*-xylene and *o*-xylene exhibited a slight decrease in the conversion, particularly after 2 h on stream. Further, the selectivity for DMCs in total products increased slightly with TOS, as expected. The selectivity for 2,5-DMC increased slightly. However, in the case of *m*-xylene and *o*-xylene, the isomer distribution changed significantly (Fig. 3.12). While 3,5-DMC steadily decreased from 44.1% (at TOS = 1 h) to 21.8% (at TOS = 8 h) with increasing 2,4-DMC during *m*-xylene isopropylation (reason is already discussed in case of USY catalyst). Similarly, in the case of *o*-xylene isopropylation the selectivity for 3,4-DMC decreased from ca. 90% (at TOS = 1h) to ca. 78% (at TOS = 8 h) whereas selectivity of 2,3-DMC increases.

**Table 3.12: Effect of xylene/isopropanol molar ratio on the conversion and product selectivity in the isopropylation of xylene isomers over zeolite H-Beta**$^{r}$

| Xylenes | Conv. or Sel. (mole%) | Xylene to isopropanol (molar ratio) | | |
|---|---|---|---|---|
| | | 2:1 | 4:1 | 8:1 |
| | Theoretical maximum conversion | 50.0 | 25.0 | 12.5 |
| *p*-Xyl. | Conv. of IPA | 99.4 | 100.0 | 100.0 |
| | Conv. of *p*-xylene | 38.8 | 21.9 | 12.2 |
| | Conv. (theo.max.) | 77.6 | 87.6 | 97.6 |
| | Sel.$_{\text{DMCs}}$ | 96.5 | 97.7 | 97.8 |
| | Sel.$_{\text{Other products}}{}^{f}$ | 3.5 | 2.3 | 2.2 |
| | Sel.$_{\text{2,5-DMC}}$ | 94.0 | 94.4 | 94.6 |
| | Sel.$_{\text{Other (2,4-DMC)}}$ | 6.0 | 5.6 | 5.4 |
| *m*-Xyl. | Conv. of IPA | 97.8 | 99.5 | 99.6 |
| | Conv. of *m*-xylene | 26.8 | 16.5 | 10.4 |
| | Conv. (theo.max.) | 53.6 | 66.0 | 83.2 |
| | Sel.$_{\text{DMCs}}$ | 95.0 | 97.5 | 98.0 |
| | Sel.$_{\text{Other products}}{}^{f}$ | 5.0 | 2.5 | 2.0 |
| | Sel.$_{\text{3,5--DMC}}$ | 42.4 | 44.1 | 53.3 |
| | Sel.$_{\text{2,4-DMC}}$ | 53.7 | 55.1 | 46.7 |
| | Sel.$_{\text{Other (2,5-DMC)}}$ | 3.9 | 0.8 | 0.0 |
| *o*-Xyl. | Conv. of IPA | 98.5 | 99.0 | 99.6 |
| | Conv. of *o*-xylene | 25.2 | 15.5 | 11.2 |
| | Conv. (theo.max.) | 50.4 | 62.0 | 89.6 |
| | Sel.$_{\text{DMCs}}$ | 95.5 | 95.9 | 96.3 |
| | Sel.$_{\text{Other products}}{}^{f}$ | 4.5 | 4.1 | 3.7 |
| | Sel.$_{\text{2,3-DMC}}$ | 12.3 | 9.7 | 7.9 |
| | Sel.$_{\text{3,4-DMC}}$ | 85.7 | 88.5 | 91.5 |
| | Sel.$_{\text{Other (2,4-DMC)}}$ | 2.0 | 1.8 | 0.6 |

$^{r}$Reaction conditions: Temperature = 413 K, WHSV = 3.25 $h^{-1}$, TOS = 1 h, at low xylene conversion propylene was present in gaseous stream, observed mass balance = 95 ± 3% in all cases, $^{f}$ as in Table 3.10.

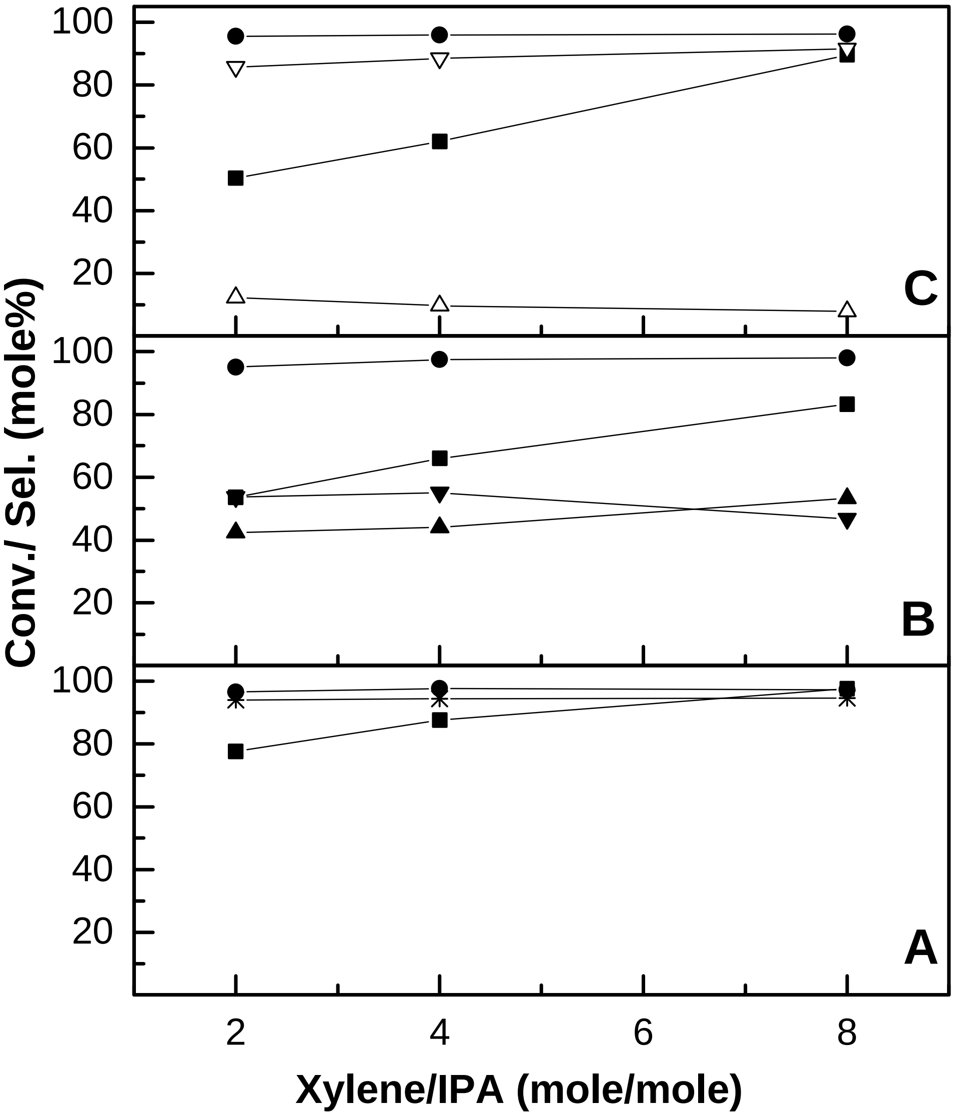


**Fig. 3.11:** Effect of xylene to IPA molar ratio on the conversion and product selectivity and its distribution over zeolite H-Beta catalyst in the isopropylation of *p*-xylene (A), *m*-xylene (B) and *o*-xylene (C). Conversion of xylene (  ), Sel.$_{\text{DMC}}$ ( ), Sel. $_{\text{2,5-DMC}}$ (□), Sel.$_{\text{2,4-DMC}}$ (  ), Sel.$_{\text{3,5-DMC}}$ (□), Sel.$_{\text{3,4-DMC}}$ (□), Sel.$_{\text{2,3-DMC}}$ (□).

Reaction conditions: Temperature = 413 K, WHSV = 3.25 h$^{-1}$, TOS = 1 h.

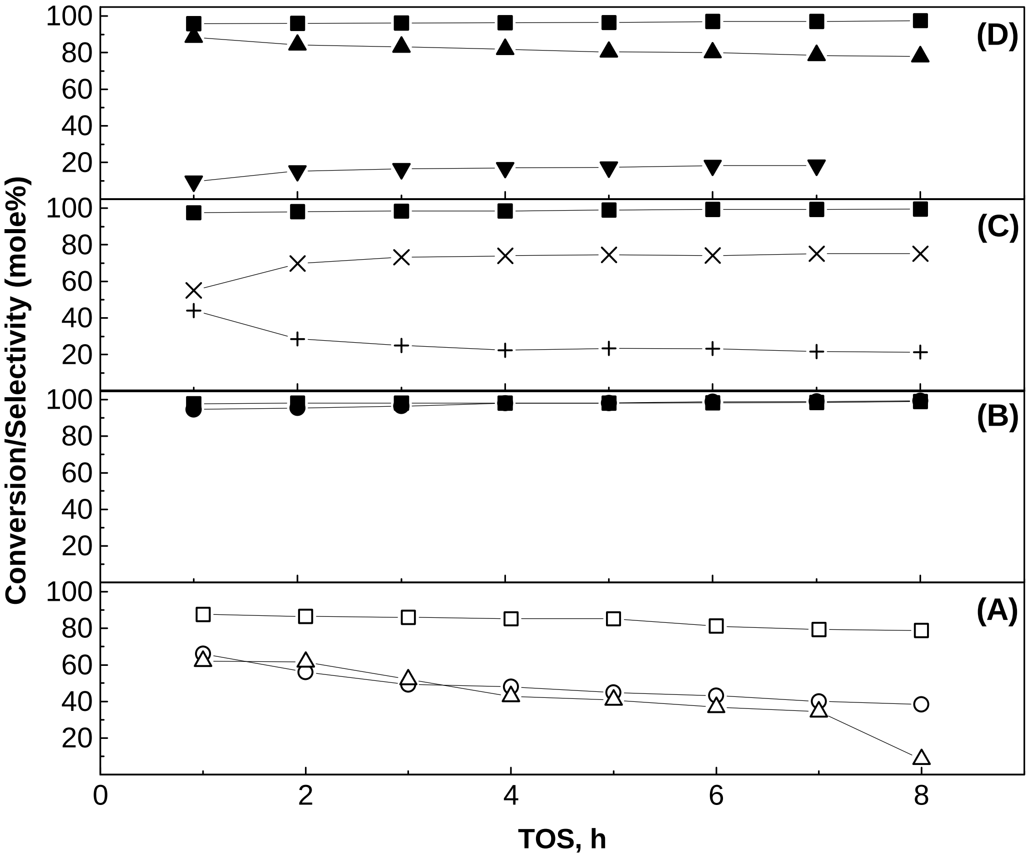


**Fig.3.12:** Xylene conversion and selectivity for DMC as a function of time-on-stream (TOS) over zeolite H-Beta. (A): Conversion of *p*-xylene (- -), *m*-xylene (- -) and *o*-xylene (- -); (B): Sel. total DMC (- -) and 2,5-DMC (- -) in *p*-xylene isopropylation; (C): Sel. total DMC (- -), 3,5-DMC (-+-), and 2,4- (-x-) in *m*-xylene isopropylation; and (D): Sel. total DMC (- -), 3,4-DMC (- -) and 2,3-DMC (- -) in *o*-xyelene isopropylation. Reaction conditios: Temperature = 413 K, WHSV = 3.25 $h^{-1}$, Xylene: isopropanol = 4: 1(molar).

### 3.3.3.5. Effect of nature of isomorphously incorporated trivalent metal ion ($B^{3+}$, $Ga^{3+}$ and $Fe^{3+}$) in Zeolite Beta

The isopropylation of *m*-xylene with isopropanol was carried out over B-, Al-, Ga- and Fe-silicate analogs of zeolite H-Beta to study the influence of acid strength of these metallosilicates on the activity and product selectivity. The strength of metallosilicates sieves varies in the order: Al- > Ga- > Fe- > B- [20,24]. The Table 3.13 compares the catalytic data for the H-B-Beta, H-Al-Beta, H-Ga-Beta and H-Fe-Beta zeolite catalysts at different temperatures. The conversion of isopropanol is less than 65% in case of H-B-Beta only. The selectivity towards dimethylcumene at a particular temperature follows the sequence: H-Al-Beta < H-Ga-Beta < H-Fe-Beta < H-B-Beta but the conversion of *m*-xylene and formation of disproportionated- products (toluene & trimethylbenzene) was found to be in the reverse order. This indirectly suggests that the acidity of metallosilicates sieves follows the order: H-Al-Beta > H-Ga-Beta > H-Fe-Beta > H-B-Beta. Again, these results confirm the observation made by Cynthia et al. [20]. According to that report [20] the relative Brönsted acidity was found to increase in the order: Si(OH) < B(OH) << Fe(OH)Si < Ga(OH)Si < Al(OH)Si based on the FTIR technique.

**Table 3.13: Isopropylation of *m*- xylene using isopropanol as alkylating agent. Influence of temperature and nature of trivalent element in zeolite Beta**[r]

| Conv./ Sel. (mole%) | Catalysts | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | H-B-Beta | | H-Fe-Beta | | H-Ga-Beta | | H-Al-Beta | |
| Tepmperature, K | 413 | 453 | 413 | 453 | 413 | 453 | 413 | 453 |
| Conv. of IPA | 30.0 | 65.0 | 73.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Conv. of *m*-xylene | 1.8 | 3.0 | 2.3 | 9.9 | 6.0 | 11.1 | 16.5 | 24.9 |
| Conv. (theo.max.) | 7.2 | 12.0 | 9.2 | 39.6 | 24.0 | 44.4 | 66.0 | 99.6 |
| Sel. $_{\text{DMCs}}$ [f] | 100.0 | 98.3 | 99.0 | 97.3 | 98.2 | 94.5 | 97.5 | 78.9 |
| Sel.$_{\text{ISO}}$ (*p*- + *o*-xyln.) | 0.0 | 0.0 | 0.0 | 0.0 | 0.2 | 0.4 | 0.5 | 1.4 |
| Sel.$_{\text{DISP}}$ | 0.0 | 0.6 | 0.0 | 1.0 | 0.0 | 2.6 | 0.3 | 16.8 |
| Sel. $_{\text{(DIPT+DIPX)}}$ | 0.0 | 1.1 | 1.0 | 1.7 | 1.6 | 2.5 | 1.7 | 2.9 |
| Sel. $_{\text{3,5--DMC}}$ | 25.4 | 27.0 | 26.5 | 28.7 | 36.1 | 65.6 | 44.1 | 75.7 |
| Sel. $_{\text{2,4-DMC}}$ | 74.6 | 72.0 | 73.0 | 70.6 | 63.4 | 31.9 | 55.1 | 21.0 |
| Sel. $_{\text{Other (2,5-DMC)}}$ | 0.0 | 1.0 | 0.5 | 1.7 | 0.5 | 2.5 | 0.8 | 3.3 |

[r] Reaction conditions: Xylene:isopropanol = 4:1(molar), WHSV = 3.25 $h^{-1}$, TOS = 1 h, at low xylene conversion propylene was present in gaseous stream, observed mass balance = 95 ± 3% in all cases, [f] as in Table 3.10.

## 3.4. CONCLUSIONS

- The isopropylation of all the three xylene isomers is readily catalyzed by zeolite H-USY & H-Beta. Detailed studies on the influence of different parameters (such as temperature, space velocity, xylene/isopropanol molar ratio and time-on-stream) governing the conversion and selectivity demonstrated that zeolite USY & H-Beta are quite active catalysts for the isopropylation of all the three xylene isomers.
- Quite moderate reaction temperature range (413-423 K) is suitable for high activity and DMC selectivity.
- The isopropylation of all xylenes was also carried out over other solid acid catalysts such as zeolites (HY, H-ZSM-5 and H-Mordenite), and silica-alumina and sulfated-zirconia and H-MCM-41 for comparative studies. Interestingly, while over H-USY, the $\mathrm{Sel.}_{3,5\text{-DMC}}$ was quite high (70-80%), all other solid acid catalysts including zeolites exhibited high selectivity for 2,4-DMC. Among all the catalysts studied, while H-USY was the most resistant towards deactivation, H-Mordenite deactivated much faster compared to all other catalysts studied.
- H-ZSM-5 with 0.54 nm channels exhibit no catalytic activity even though it possesses a high strength of acid sites due to medium sized 10-membered ring channels.

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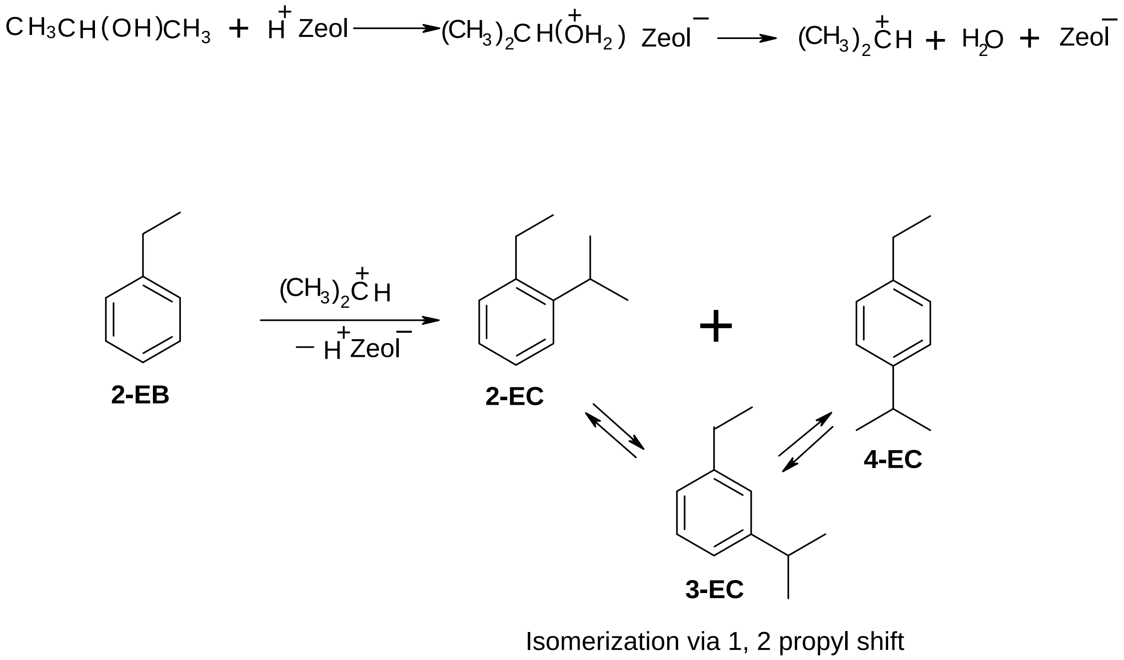
## 4.1. INTRODUCTION

Although, the methylation [1], ethylation [2-6] and tertiarybutylation [7] of ethylbenzene over solid catalysts have been rather well studied, the same is not true for ethylbenzene isopropylation. Isopropylation of ethylbenzene produces corresponding ethyl (1-methylethyl) benzene or simply denoted herein after as ethylcumene(s) (EC), which could be precursors of ethylphenol(s) (EPs) having antiseptics, antimicrobial, and preservative activities [8-10].

It may be recalled that the alkylation of ethylbenzene in the presence of chlorosulfonic acid [11-12], $AlCl_3$ [13,14], $BF_3$-$Et_2O$ [14], HF [15], $BF_3$-$H_3PO_4$ [16] has been reported long back. However, these catalytic systems were used under homogeneous conditions, having many environmental and economic disadvantages. More recently, in an European patent [17] brief information on the preparation of ethylcumenes (ECs) using propylene as alkylating agent and dealuminated Mordenite as catalyst in pressure autoclave (batch reactor) is reported.

Alkylation reaction using solid heterogeneous catalyst in fixed bed reactors offer many advantages such as easy handling, easy recovery, reusability, less or no corrosion, no disposal problem, easy to work up product (s) and specially continuity of the operation. To the best of our knowledge, reports on vapor phase isopropylation of ethylbenzene over solid acid catalysts like zeolites in the fixed–bed reactor are not available.

The isopropylation of aromatic compounds over acid catalysts is an electrophilic (and hence ortho-para directing) reaction, ortho-ethylcumene (2-EC) and para-ethylcumene (4-EC) can be formed as primary products and meta-ethylcumene (3-EC) is expected to be formed as a secondary product through isomerization of the 2-EC and 4-EC isomers via 1,2 alkyl shift (Scheme 4.1).



$$CH_3CH(OH)CH_3 + \overset{+}{H}\,Zeol \longrightarrow (CH_3)_2CH(\overset{+}{O}H_2)\,Zeol^{-} \longrightarrow (CH_3)_2\overset{+}{C}H + H_2O + Zeol^{-}$$

**Scheme 4.1:** Isopropylation of ethylbenezene over zeolites.

In the present chapter, systematic detailed studies on the vapor phase isopropylation of ethylbenzene over large pore high silica zeolites like H-Beta, H-Mordenite and H-USY in fixed bed down flow reactor at atmospheric pressure and moderate temperature (393-453 K) are discussed. The results obtained over these zeolites were also compared with that obtained using other zeolites like H-ZSM-5, H-ZSM-12 and H-Y and solid acid catalysts like H-MCM-41, amorphous silica-alumina and sulfated-zirconia. The isopropylation of ethylbenzene with isopropanol was also carried out over B-, Al-, Ga- and Fe-silicate analogs of zeolite Beta to compare the effect of isomorphously incorporated trivalent metal ion ($B^{3+}$, $Fe^{3+}$ and $Ga^{3+}$).

## 4.2. EXPERIMENTAL

### 4.2.1. Catalyst Preparation and Characterization

Zeolites Al-Beta with different silica alumina ratios, B-, Ga-, Fe-Beta, Mordenite, ZSM-12 and MCM-41, sulfated-zirconia were synthesized hydrothermally as per the details given in Chapter 2. The silica-alumina (SAL) and the ultra-stable zeolite Y (USY) were obtained from M/S Joseph Crossfield and Union Carbide respectively. ZSM-5 and Na-Y were procured from the Catalysis Pilot Plant of our laboratory. All the synthesis, modification and characterization procedures along with their physico-chemical characteristics have been already described in detail in Chapter 2.

### 4.2.2. Catalytic Measurement

The vapor phase catalytic isopropylation of ethylbenzene (Lancaster, USA, 99+%) with 2-propanol (S. d. fine -chem. Ltd. Bombay, 99+%) was carried at moderate temperature (393–453 K) and at atmospheric pressure using a fixed bed vertical down-flow glass reactor of 15mm internal diameter. The reactor set up is same as already described in Fig.3.1 in Chapter 3.

The products were chilled (ice cold), collected and analyzed by gas chromatograph (Agilent 6890series, GC system) using flame ionization detector and HP high-resolution (20% permethylated â-cyclodextrin) capillary column (30 m x 0.32 mm x 0.25 μm). Nitrogen was used as carrier gas (2ml/min) in the GC. The products were also identified by using gas chromatography-mass spectrometry (Shimadzu, GCMS-QP 2000A) and gas chromatography-infrared spectrometry (Perkin Elmer, GC-IR 2000).

## 4.3. RESULTS AND DISCUSSION

Alkylation of aromatics like ethylbenzene with isopropanol (isopropyl alcohol, IPA) over zeolite catalyst, an electrophilic substitution reaction, leads to the formation of mainly corresponding isopropyl aromatics compounds as primary product with no or little formation of n-propyl-isomer due to the reason that $CH_3$-$CH^+$-$CH_3$ ion (stable secondary carbocation) formed through acid catalyzed dehydration of isopropanol is not isomerized to $CH_3$-$CH_2$ -$CH_2^+$ (less stable primary carbocation). Isopropylation of ethylbenzene gives three isomers of ethylcumene (EC) (Scheme 4.1) namely, 2-EC and 4-EC as primary products and 3-EC as a secondary product. The active species can further react with primary product to produce diisopropyl ethylbenzenes due to increased tendency for electrophilic attack in ethylcumene. A small amount of benzene, diethylbenzenes (due to disproportionation of ethylbenzene) and diisopropylethylbenzene (due to further isopropylation of isopropyl ethylbenzene) can also be produced during the isopropylation of ethylbenzene reaction particularly at more severe reaction conditions.

The conversion of IPA was complete in most of the experiments. However, no aromatic compound was obtained when pure IPA was fed as reactant (in the absence of ethylbenzene) under same reaction conditions. Only propylene was formed. Similarly blank experiments where pure ethylbenzene was fed as reactant (in the absence of IPA) under same reaction conditions were also carried out where a small amount of disproportionated products (benzene and diethylbenzenes) was obtained only at higher temperature (423 K and above). The mass balance, carried out for various experiments, ranged between 96 ± 2%. At lower ethylbenzene conversions the unreacted propylene was observed in the products (mainly gaseous stream) and is not given in the product distribution. However, it was included in computing mass balances.

## 4.3.1. ISOPROPYLATION OF ETHYLBENZENE OVER VARIOUS SOLID ACID CATALYSTS

### Conversion and Intrinsic Activity

To find out suitable catalyst(s), the isopropylation of ethylbenzene was investigated over different solid acids such as zeolites with different topologies like BEA (Beta), MOR (Mordenite), FAU (USY and zeolite Y), MTW (ZSM-12) and MFI (ZSM-5) along with some other solid acid catalysts like MCM-41, amorphous silica-alumina (SAL) and sulfated-zirconia (SZ) under same reaction conditions. The catalytic activities and product selectivities over various acid catalysts are shown in Table 4.1. While, the overall activity (conversion) was quite high over H-USY and H-Beta (20) zeolites, the intrinsic activity (TOF $s^{-1}$) followed the order: H-Beta (40) > H-Beta (30) > H-Beta (20) ≈ H-ZSM-12 (80) > H-USY (5.6) > H-Mordenite (5.9) > H-MCM-41 (20) > H-Y (2.9) ≈ Silica-alumina (2.6) > Sulfated-zirconia (3% sulfur) > H-ZSM-5 (20), where the values in parentheses represent the Si/Al molar ratio of the corresponding catalyst.

It is clear that both, the acidic properties (density and strength of acid sites) and void space of zeolites/catalysts play significant role in determining the overall activity of the catalysts.

From Table 4.1 it is seen that H-USY, H-Beta and H-Mordenite are highly active catalysts due to higher acid strength and large pores compared to other solid acid catalysts to the isopropylation of ethylbenzene.

The activity trend can be interpreted in terms of the increasing dimensions of the void space of the catalysts coupled with their acidity. Mesoporous H-MCM-41 (Entry no 7, in Table 4.1) exhibits low activity, reflecting the presence of weaker acid sites in this mesoporous aluminosilicate [18,19]. On the other hand, H-ZSM-5 with three-dimensional intersecting 10-membered ring (0.54 nm x 0.56 nm for straight and 0.51nm x 0.55 nm for sinusoidal) channels exhibits no catalytic activity even though H-ZSM-5 possesses a high strength of acid sites [20]. This is attributed to the fact that strong acid sites are located within the 10-membered ring channels, where the ingress of reactants and egress of products, is severely constrained.

### Product Selectivity

H-MCM-41, H-Mordenite and H-ZSM-12 exhibited quite high selectivity for EC in the products, followed by SAL, H-Y, H-Beta, H-USY and SZ. EC selectivity was found to be dependent on overall activity as well as pore architecture of the catalysts (Table 4.1). While H-Mordenite and H-ZSM-12 with different pore dimension as well as different conversion level gave comparable EC selectivity, H-ZSM-12 and H-MCM-41 with very different pore dimensions and at comparable conversion gave similar $Sel._{EC}$. The main reason for decreased EC selectivity exhibited by H-USY was the significant formation of disproportionated ($Sel._{DISP}$) as well as dialkylated ($Sel._{DIPEB}$) product. Over SZ the $Sel._{EC}$ decreased only due to dialkylated products as no disproportionations of EB was found. Regarding the $Sel._{DIPEB}$, it may be mentioned that SZ gave very high selectivity for diisopropylated products, followed by H-USY and H-Beta, mainly at the cost of primary product EC.

## Distribution of Ethylcumene(s)(EC) Isomers

Table 4.1 also shows that the distribution of EC isomers over various solid catalysts. 3-EC is a secondary product which is produced due to the isomerization of 2-EC and 4-EC via 1,2 alkyl shift. Due to strong acidity and large pore channels of H-Beta and H-USY [20], Sel.$_{3\text{-EC}}$ is high. In other solid acid catalysts like amorphous silica-alumina, sulfated-zirconia and H-MCM-41, distribution of 2-, 3- and 4-ethylcumene are almost same. H-Mordenite and H-ZSM-12, however, exhibit quite high selectivity for 4-EC due to their more shape selective channel structure.

The relative selectivity of 4-ethylcumene (sel.$_{4\text{-EC}}$) over the active catalysts increases in the following order:

H-ZSM-12 > H-Mordenite > H-Beta     H-USY

This is inversely proportional to the void space of the zeolites.

## Effect of Si/Al Molar Ratio in Zeolite H-Beta

Entries 1-3 in Table 4.1 show the influence of Si/Al molar ratio of zeolite H-Beta on the conversion and product distribution in the isopropylation of ethylbenzene. While there was an increase in the overall conversion with decreasing Si/Al ratio, as expected, the intrinsic activity of the catalyst (TOF) increased with increasing Si/Al ratio**.** It is quite likely that with increasing Al content (decreasing Si/Al ratio), increasing part of Al may occupy the Td sites within the walls, which are not available for this reaction. While the selectivity for di-isopropylethylbenzene (Sel.$_{\text{DIPEB}}$) increases in the order: 9.8% H-Beta (20) < 13.2% H-Beta (30) < 14.6% H-Beta (40), the selectivity for disproportionation follows the reverse order due to decreased disproportionation of DIPEB on H-Beta (30) and H-Beta (40).

No significant difference was observed in the case of Sel.$_{EC}$ and distribution of EC isomers over different H-Beta samples.

### Influence of Time-On-Stream (TOS) Over Various Solid Acid Catalysts

A comparison of catalytic activity and stability of catalysts used for isopropylation of EB is presented in Fig. 4.1 as a function of reaction time. Activity of each catalyst was tested up to 8 hours. From this figure it is obvious that H-USY is most active catalyst whereas H-Mordenite and H-Beta have comparable catalytic activity and other catalysts are very less active. However, H-Beta and H-USY have slower deactivation but a faster deactivation is noticed in H-Mordenite with time on stream (TOS), probably related to its uni-dimensional pore structure. All further studies were carried out over H-Mordenite, H-Beta (20) and H-USY catalysts with varying reaction parameters such as temperature, weight hourly space velocity (WHSV), ethylbenzene to alkylating agent molar ratio and time-on-stream (TOS).

Fig. 4.2 (A-H) depicts the product distribution as a function of reaction time (TOS), while H-Mordenite (Fig. 4.2-F) exhibited high EC selectivity without any decrease with TOS, H-USY (Fig. 4.2-A) showed slight decrease in EC selectivity with TOS. Further, H-Mordenite and H-ZSM-12 (Fig. 4.2-G) due to their relatively constrained pore dimension also gave very high selectivity for 4-EC, compared to that obtained over H-Beta (Fig. 4.2-B) and H-USY. H-MCM-41 (Fig. 4.2-C), H-Y (Fig. 4.2-E) and SAL (Fig. 4.2-D) gave comparable EC isomer distribution.

**Table 4.1: Catalytic activities and product selectivities over various solid acid catalysts in the isopropylation of ethylbenzene[a]**

| Entry No. | Catalyst | Conv. EB[b] | TOF[c] ($s^{-1}x10^{-3}$) | Sel.$_{EC}$[d] | Sel.$_{DISP}$[e] | Sel. $_{DIPEB}$[f] | Product Distribution (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Sel.$_{2-EC}$ | Sel.$_{3-EC}$ | Sel.$_{4-EC}$ |
| 1 | H-Beta (40) | 66.0 | 12.1 | 82.1 | 3.3 | 14.6 | 11.2 | 47.5 | 41.3 |
| 2 | H-Beta (30) | 72.0 | 10.0 | 83.0 | 3.8 | 13.2 | 13.1 | 49.6 | 37.3 |
| 3 | H-Beta (20) | 80.4 | 7.6 | 83.6 | 6.6 | 9.8 | 13.4 | 49.5 | 37.1 |
| 4 | H-ZSM-12(80) | 20.8 | 7.5 | 92.8 | 2.9 | 4.3 | 4.2 | 31.1 | 64.7 |
| 5 | H-USY (5.6) | 96.0 | 2.8 | 72.0 | 17.5 | 10.5 | 6.8 | 56.1 | 37.1 |
| 6 | H-M (5.9) | 68.0 | 2.1 | 97.0 | 2.0 | 1.0 | 3.5 | 40.7 | 55.8 |
| 7 | H-MCM-41(20) | 18.4 | 1.7 | 95.0 | 2.1 | 2.9 | 30.0 | 27.7 | 42.3 |
| 8 | H-Y (2.9) | 18.4 | 0.3 | 85.8 | 1.8 | 12.4 | 31.7 | 27.0 | 41.3 |
| *9* | Silica-alumina | 21.6 | 0.3 | 89.8 | 1.5 | 8.7 | 27.5 | 27.2 | 45.3 |
| 10 | Sulfatedzirconia | 33.6 | 0.03 | 69.4 | 0.0 | 30.6 | 20.3 | 29.4 | 50.3 |
| 11 | H-ZSM-5 (20) | 0.0 | - | - | - | - | - | - | - |

[a] Reaction Conditions: Temperature = 413 K, WHSV = 3.25 h$^{-1}$, Ethylbenzene:isopropanol = 4:1 (molar),TOS = 1h, isopropanol conversion = 100%, at low ethylbenzene conversion propylene was present in gaseous stream, observed mass balance = 96 ± 2% in all cases. [b] Conversion of ethylbenzene based on theoretical maximum conversion of ethylbenzene, [c] Turn over frequency i.e.the no of molecules converted per mole of Al (catalytic site) per second, [d] Total ethylcumene selectivity in total products, [e] Disproportionation products (benzene +diethylbenzenes), [f] Selectivity of di-isopropylethylbenzene in the total products.

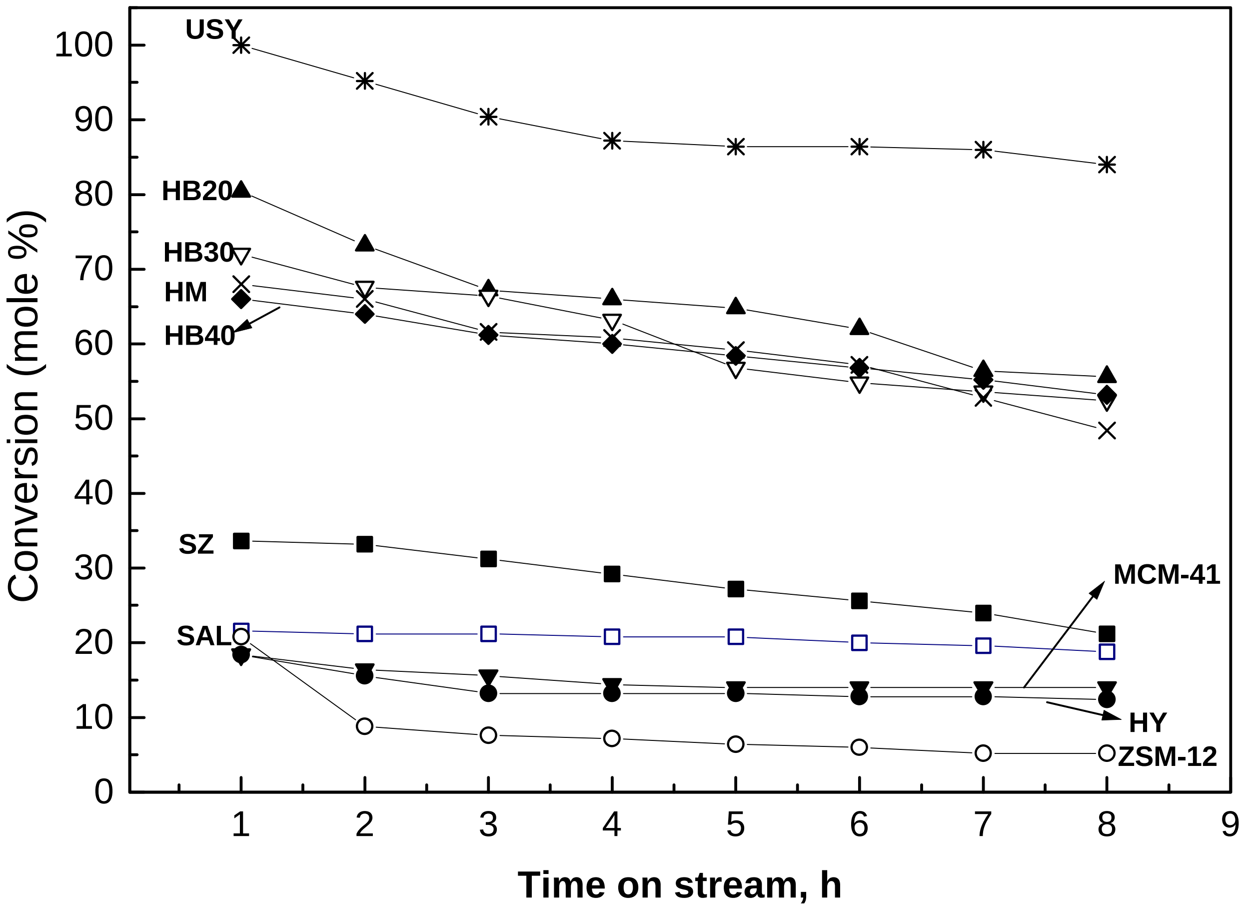


**Fig. 4.1:** Effect of time on stream (TOS, h) on the conversion of ethylbenzene over various solid catalysts. Reaction Conditions: Temperature = 413 K, WHSV = 3.25 $h^{-1}$, ethylbenzene:isopropanol = 4:1 (molar).

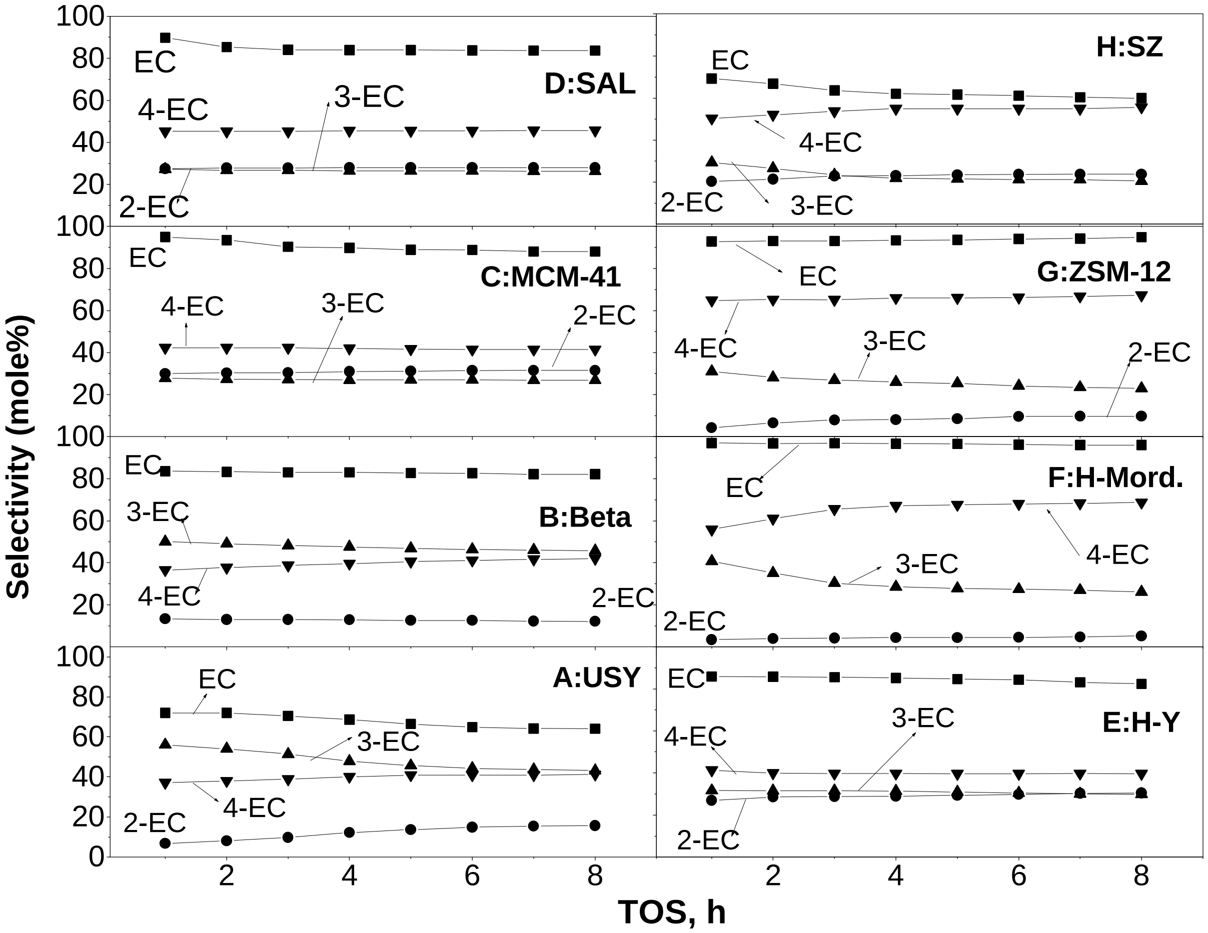


**Fig. 4.2:** Effect of time on stream (TOS, h) on the total ethylcumene selectivity and distribution of ethylcumene in the isopropylation of ethylbenzene over various solid acid catalysts Reaction Conditions: Temperature = 413 K, WHSV = 3.25 $h^{-1}$, ethylbenzene:isopropanol = 4:1 (molar).

## 4.3.2. DETAILED STUDY ON THE ISOPROPYLATION OF ETHYLBENZENE OVER H-MORDENITE, H-BETA AND H-USY

### 4.3.2.1. Effect of Reaction Temperature

In Table 4.2, the results obtained in the isopropylation of ethylbenzene over H-Mordenite, H-Beta and H-USY at various temperatures ranging 393 K to 453 K are presented. As expected, with increasing the reaction temperature, the conversion increased in the case of all the three zeolites (Fig. 4.3 A-C). At higher temperature (433 to 453 K) dealkylation and disproportionation reactions are enhanced leading to the formation of undesired products. Consequently, $Sel._{ECs}$ decreases with increase in temperature. It is found that over H-Mordenite (Fig. 4.3-A) and H-Beta (Fig. 4.3-B) in relatively high temperature range (423 to 453 K) the amount of disproportionated products (benzene and diethylbenzene) were significant i.e. 5 to 9% for H-Mordenite, 12 to 26% for H-Beta. However, in the case of H-USY (Fig. 4.3-C) even in low temperature range (393 to 423 K) the amount of disproportionated products was ca. 7 to 26%. The selectivity towards disproportionation ($Sel._{DISP}$) follows the order: H-USY > H-Beta > H-Mordenite. Fig. 4.3 (A-C) shows that with increasing temperature, the selectivity of 2- and 4-EC in total products is slightly decreased and that of 3-EC is increased due to isomerization of 2-EC and 4-EC to 3-EC, which is energetically most stable product. Quite interestingly, the selectivity of DIPEB decreased over all these catalysts with increasing temperature, probably due to transalkylation reaction of DIPEB with EB to EC, as in the case of isopropylation of toluene [21]. The $Sel_{EC}$ and para-selectvity exhibited by these catalysts follow the order: H-Mordenite > H-Beta > H-USY, as expected from their void structure. It may be recalled that the channel dimensions of these zeolites follows the order: H-Mordenite < H-Beta < H-USY.

**Table. 4.2: Effect of temperature on the conversion of ethylbenzene and product distribution in the isopropylation of ethylbenzene over various zeolites[a]**

| Catalysts | Conversion or Selectivity | Temperature, K | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 393 | 403 | 413 | 423 | 433 | 443 | 453 |
| **H-Mord.** | Conv. of EB | 1.7 | 8.5 | 17.0 | 20.4 | 23.4 | 23.5 | 24.8 |
| | Theo. Max.Conv[b] | 6.8 | 34.0 | 68.0 | 81.6 | 93.6 | 94.0 | 99.2 |
| | TOF ($s^{-1}$ x $10^{-3}$)[c] | 0.2 | 1.0 | 2.1 | 2.5 | 2.9 | 2.9 | 3.1 |
| | Sel.Total-EC[d] | 97.7 | 97.3 | 97.0 | 94.1 | 92.9 | 91.3 | 90.0 |
| | Sel.$_{\text{DISPR}}$(Bz +DEBs)[e] | 0.0 | 1.1 | 2.0 | 4.9 | 6.0 | 7.8 | 9.1 |
| | Sel.DIPEB[f] | 2.3 | 1.6 | 1.0 | 1.0 | 0.9 | 0.9 | 0.9 |
| | Sel.$_{\text{2-EC}}$ | 4.1 | 3.5 | 3.5 | 3.4 | 3.2 | 2.9 | 2.0 |
| | Sel.$_{\text{3-EC}}$ | 28.8 | 35.0 | 40.7 | 41.0 | 41.9 | 42.7 | 44.0 |
| | Sel.$_{\text{4-EC}}$ | 67.1 | 61.5 | 55.8 | 55.6 | 55.1 | 54.4 | 54.0 |
| **H-Beta** | Conv. of EB | 1.8 | 14.8 | 20.1 | 21.3 | 24.9 | 25.0 | 25.0 |
| | Theo. Max.Conv[b] | 7.2 | 59.2 | 80.4 | 87.2 | 99.0 | 100.0 | 100.0 |
| | TOF ($s^{-1}$ x $10^{-3}$)[c] | 0.7 | 5.6 | 7.6 | 8.2 | 9.3 | 9.4 | 9.4 |
| | Sel.Total-EC[d] | 89.8 | 84.5 | 83.6 | 79.0 | 70.9 | 68.4 | 68.0 |
| | Sel.$_{\text{DISPR}}$(Bz +DEBs)[e] | 0.0 | 5.0 | 6.6 | 12.0 | 22.5 | 25.4 | 25.9 |
| | Sel.DIPEB[f] | 10.2 | 10.5 | 9.8 | 9.0 | 6.6 | 6.2 | 6.1 |
| | Sel.$_{\text{2-EC}}$ | 17.3 | 16.9 | 13.4 | 10.2 | 7.2 | 6.2 | 4.8 |
| | Sel.$_{\text{3-EC}}$ | 45.2 | 46.0 | 50.0 | 54.3 | 59.5 | 60.5 | 61.9 |
| | Sel.$_{\text{4-EC}}$ | 37.5 | 37.1 | 36.6 | 35.5 | 33.3 | 33.3 | 33.3 |
| H-**USY** | Conv. of EB | 15.1 | 18.8 | 24.0 | 25.0 | 25.0 | 25.0 | - |
| | Theo. Max.Conv[b] | 60.4 | 75.2 | 96.0 | 100.0 | 100.0 | 100.0 | - |
| | TOF ($s^{-1}$ x $10^{-3}$)[c] | 1.8 | 2.2 | 2.8 | 3.0 | 3.0 | 3.0 | - |
| | Sel.Total-EC[d] | 74.0 | 72.5 | 72.0 | 67.3 | 6.2 | 50.0 | - |
| | Sel.$_{\text{DISPR}}$(Bz +DEBs)[e] | 6.6 | 11.2 | 17.5 | 26.3 | 31.8 | 44.0 | - |
| | Sel.DIPEB[f] | 19.4 | 16.3 | 10.5 | 6.4 | 6.2 | 6.0 | - |
| | Sel.$_{\text{2-EC}}$ | 25.3 | 13.3 | 6.8 | 4.8 | 4.0 | 3.7 | - |
| | Sel.$_{\text{3-EC}}$ | 32.1 | 47.2 | 56.1 | 60.7 | 63.0 | 64.0 | - |
| | Sel.$_{\text{4-EC}}$ | 42.6 | 39.5 | 37.1 | 34.5 | 33.0 | 32.4 | - |

[a] Reaction Conditions: TOS = 1h, WHSV = 3.25 $h^{-1}$, Ethylbenzene:isopropanol = 4:1 (molar), at low ethylbenzene conversion remaining unreacted propylene was present in gaseous stream, [b-f]as in Table 4.1.

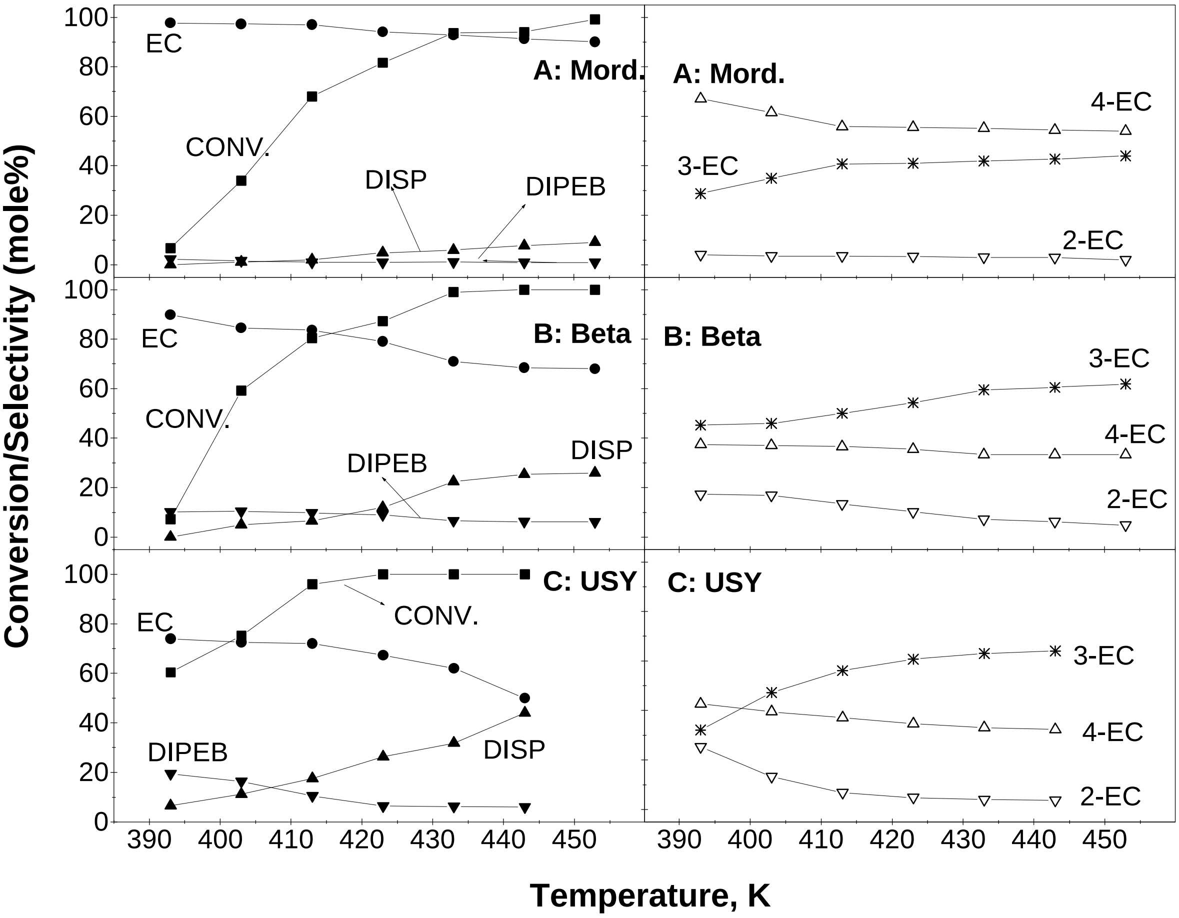


**Fig. 4. 3:** Effect of temperature on the conversion of ethylbenzene and product selectivity over various zeolite catalysts. Isopropylation of ethylbenzene over H-Mordenite (A), H-Beta (B) and H-USY (C). Conversion of ethylbenzene ( ) , Total ethylcumene selectivity ($Sel._{EC}$) ( ), $Sel._{2-EC}$ (□), $Sel._{3-EC}$ (□), $Sel._{4-EC}$ ( ) , $Sel._{DISP}$ ( ) and $Sel._{DIPEB}$ ( ).

Reaction Conditions: TOS = 1h, WHSV = 3.25 $h^{-1}$, Ethylbenzene:isopropanol = 4:1 (molar).

### 4.3.2.2. Effect of Feed Rate

Generally, longer contact time (lower space velocity) favours the secondary and successive reactions whereas shorter contact time (higher space velocity) increases the selectivity of the primary products. Here, in the case of EB isopropylation over H-Mordenite, H-Beta and H-USY, conversion is highly influenced by WHSV (Table 4.3 & Fig. 4.4 A-C). For example, the ethylbenzene conversion was decreased from 68% (at WHSV = 3.25 $h^{-1}$) to 8% (at WHSV = 24.4 $h^{-1}$) for H-Mordenite, from 80.4 % (at WHSV = 3.25 $h^{-1}$) to 8% at (at WHSV = 24.4 $h^{-1}$) for H-Beta and from 96% (at WHSV = 3.25 $h^{-1}$) to 26% (atWHSV = 24.4 $h^{-1}$) for USY with increasing WHSV. At higher WHSV (shorter contact times), disproportionation, dealkylation reactions are suppressed resulting in the decreased formation of other aromatics such as benzene and diethylbenzenes. Hence, the disproportionated products (benzene+DEBs) are decreased with increasing WHSV for all the catalysts studied. However, quite interestingly, the $Sel._{ECs}$ is not influenced significantly with WHSV over all these catalystsv following the order: H-Mordenite >> H-Beta > H-USY. The selectivity towards diisopropyl ethylbenzene ($Sel._{DIPEBs}$) is increased significantly with increasing WHSV in the case of H-USY (Fig. 4.4-C) and to a lesser extent over H-Beta (Fig. 4.4-B) and remained almost unchanged at 1.0 ± 0.1 over H-Modernite (Fig. 4.4-A). These results clearly indicate the influence of pore geometry on product selectvities, where bulky diisopropylethylbenzenes (DIPEBs) are easily formed in more open structures like H-USY and H-Beta vis-a-vis H-Mordenite. Regarding the distribution of EC isomers it was observed that while 3-EC selectivity ($Sel._{3\text{-}EC}$) decreases with the increasing WHSV, the selectivity of 2-EC ($Sel._{2\text{-}EC}$) and 4-EC ($Sel._{4\text{-}EC}$) (both being the primary products) increases, as expected, because of the formation of secondary product 3-EC formed by the isomerization of 2-EC and 4-EC is decreased at shorter contact time. Here again it can be seen that H-Mordenite is highly para selective compared to H-Beta and H-USY, due to slightly narrower pores of H-Mordenite vis-à-vis H-Beta and H-USY.

**Table 4.3: Effect of WHSV on the conversion of and product selectivity in the isopropylation of ethylbenzene over various zeolites[a]**

| Catalysts | Conversion or Selectivity (mole%) | Weight hourly space velocity (WHSV), $h^{-1}$ | | | | | |
|---|---|---|---|---|---|---|---|
| | | 3.25 | 6.50 | 9.75 | 13.00 | 16.25 | 24.40 |
| **H-Mord.** | Conv. of IPA | 100 | 92.0 | 91.6 | 84.0 | 79.5 | 70.0 |
| | Conv. of EB | 17.0 | 8.1 | 7.7 | 5.4 | 3.6 | 2.0 |
| | Theo. Max.Conv[b] | 68.0 | 32.4 | 30.8 | 21.6 | 14.4 | 8.0 |
| | TOF ($s^{-1}$ x $10^{-3}$)[c] | 2.1 | 2.0 | 2.9 | 2.7 | 2.2 | 1.9 |
| | Sel.Total-EC[d] | 97.0 | 96.6 | 97.5 | 99.0 | 99.1 | 98.8 |
| | Sel.$_{DISPR}$(Bz +DEBs)[e] | 2.0 | 2.5 | 1.5 | 0.0 | 0.0 | 0.0 |
| | Sel.DIPEB[f] | 1.0 | 0.9 | 1.0 | 1.0 | 0.9 | 1.2 |
| | Sel.$_{2-EC}$ | 3.5 | 4.1 | 4.3 | 4.4 | 4.7 | 5.2 |
| | Sel.$_{3-EC}$ | 40.7 | 27.9 | 24.5 | 23.6 | 22.7 | 21.8 |
| | Sel.$_{4-EC}$ | 55.8 | 68.0 | 71.2 | 72.0 | 72.6 | 73.0 |
| **H-Beta** | Conv. of IPA | 100.0 | 99.1 | 97.5 | 83.6 | 75.5 | 68.4 |
| | Conv. of EB | 20.1 | 12.1 | 9.2 | 5.2 | 4.7 | 2.0 |
| | Theo. Max.Conv[b] | 80.4 | 48.4 | 36.8 | 22.8 | 18.8 | 8.0 |
| | TOF ($s^{-1}$ x $10^{-3}$)[c] | 7.6 | 9.1 | 10.4 | 8.6 | 8.9 | 5.6 |
| | Sel.Total-EC[d] | 83.6 | 83.4 | 83.2 | 83.0 | 82.7 | 82.3 |
| | Sel.$_{DISPR}$(Bz +DEBs)[e] | 6.6 | 3.9 | 2.5 | 2.2 | 1.7 | 1.4 |
| | Sel.DIPEB[f] | 9.8 | 12.7 | 14.3 | 14.8 | 15.6 | 16.3 |
| | Sel.$_{2-EC}$ | 13.4 | 15.0 | 15.6 | 16.2 | 16.6 | 16.8 |
| | Sel.$_{3-EC}$ | 50.0 | 47.8 | 46.9 | 44.8 | 44.2 | 41.2 |
| | Sel.$_{4-EC}$ | 36.6 | 37.2 | 37.5 | 39.0 | 39.2 | 42.0 |
| H-**USY** | Conv. of IPA | 100 | 100 | 98.0 | 96.0 | 90.0 | 89.2 |
| | Conv. of EB | 24.0 | 18.0 | 16.5 | 14.0 | 10.6 | 6.5 |
| | Theo. Max.Conv[b] | 96.0 | 72.0 | 66.0 | 56.0 | 42.4 | 26.0 |
| | TOF ($s^{-1}$ x $10^{-3}$)[c] | 2.8 | 4.3 | 5.9 | 6.6 | 6.3 | 5.8 |
| | Sel.Total-EC[d] | 72.0 | 70.8 | 70.2 | 69.9 | 69.1 | 68.9 |
| | Sel.$_{DISPR}$(Bz +DEBs)[e] | 17.5 | 8.8 | 7.5 | 6.8 | 6.3 | 5.0 |
| | Sel.DIPEB[f] | 10.5 | 20.4 | 22.3 | 23.3 | 24.6 | 26.1 |
| | Sel.$_{2-EC}$ | 6.8 | 13.6 | 15.1 | 17.9 | 18.4 | 21.3 |
| | Sel.$_{3-EC}$ | 56.1 | 47.6 | 43.9 | 39.6 | 36.7 | 33.1 |
| | Sel.$_{4-EC}$ | 37.1 | 38.8 | 41.0 | 42.5 | 44.9 | 45.6 |

[a]Reaction Conditions: Temperature = 413 K, TOS =1h, Ethylbenzene:isopropanol = 4:1 (molar), at low ethylbenzene conversion remaining unreacted propylene was present in gaseous stream, [b-f]as in Table 4.1.

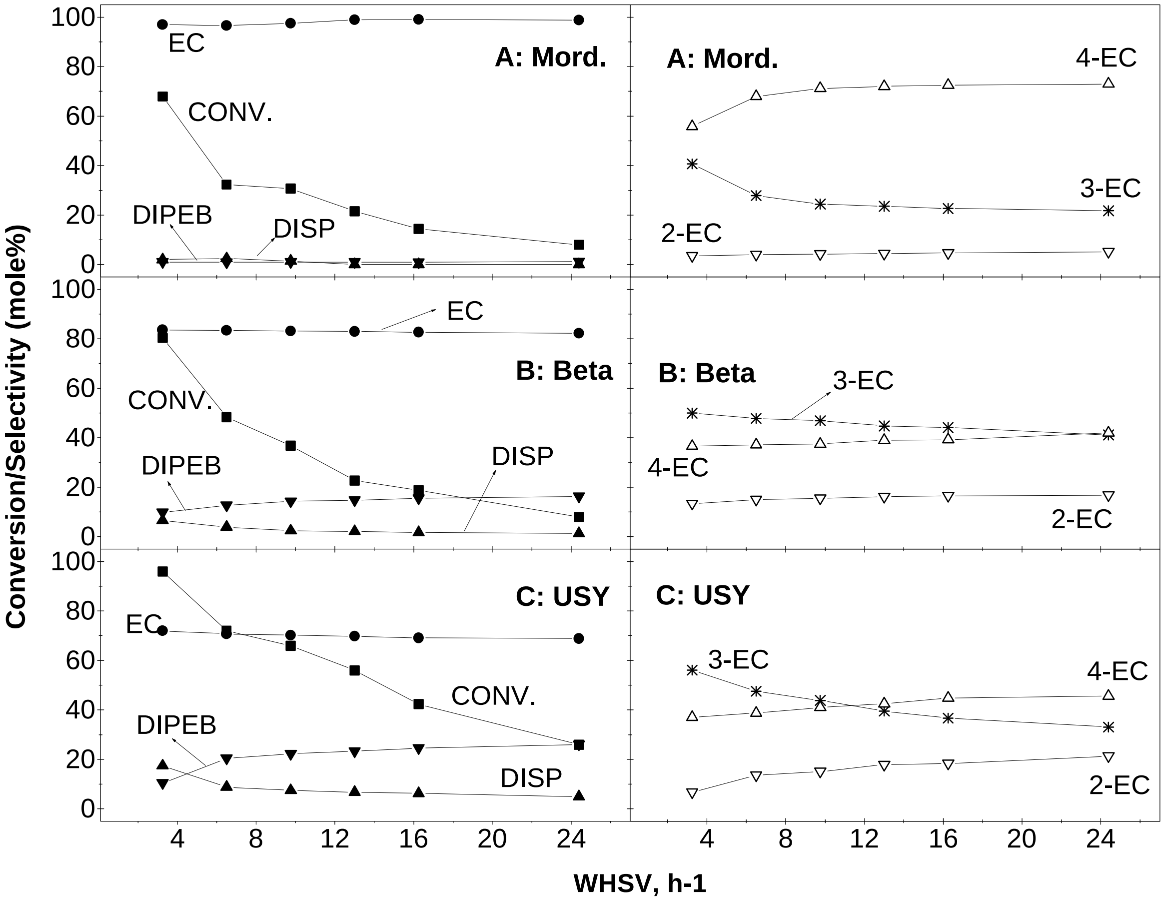


**Fig. 4.4:** Effect of WHSV on the conversion of ethylbenzene and product selectivity over various zeolite catalysts. Isopropylation of ethylbenzene over H-Mordenite (A), H-Beta (B) and H-USY (C). Conversion of ethylbenzene ( ), Total ethylcumene selectivity (Sel. $_{\text{EC}}$) ( ), Sel. $_{\text{2-EC}}$ (□), Sel.$_{\text{3-EC}}$ (□), Sel.$_{\text{4-EC}}$ ( ), Sel. $_{\text{DISP}}$ ( ) and Sel.$_{\text{DIPEB}}$ ( ).

Reaction Conditions: Temperature = 413 K, TOS = 1h, Ethylbenzene:isopropanol = 4:1 (molar).

### 4.3.2.3. Influence of Ethylbenzene to Isopropanol Molar Ratio

The influence of ethylbenzene (EB) to isopropanol (isopropyl alcohol, IPA) molar ratio on the isopropylation of EB over H-Mordenite, H-Beta and H-USY is depicted in Table 4.4 & Fig. 4.5 (A-C). Both, the conversion and total ECs selectivity are increased significantly with increasing EB to IPA molar ratio, because the limited isopropanol is totally reacted with ethylbenzene to produce Ecs. The formation of DIPEB is significantly reduced. At lower EB to IPA molar ratio (2:1), $\mathrm{Sel.}_{\mathrm{DIPEB}}$ is significantly high in the case of H-USY (Fig. 4.5-C) and H-Beta (Fig. 4.5-B). In the case of H-Mordernite (Fig. 4.5-A) the $\mathrm{Sel.}_{\mathrm{DIPEB}}$ decreaed from 3.5 % to 0.0 % with increasing EB/IPA ratio, again due to relatively less void space in H-Mordernite. It is also observed from Fig. 4.5 (A-C) that with the increase of EB/IPA ratio the slight decrease in $\mathrm{Sel.}_{\mathrm{DIPEB}}$ was accompanied with corresponding increase in $\mathrm{Sel.}_{\mathrm{EC},}$ clearly suggesting that the formation of DIPEB is mainly due to further isopropylation of EC. However, with increasing EB/IPA ratio, the formation of 3-EC increased slightly at the cost of 2-EC and 4-EC (Table 4.4). At higher EB to IPA molar ratio, isomerization of 2-EC and 4-EC to 3-EC is increased due to limiting concentration of isopropanol.

**Table 4.4: Influence of substrate to alkylating agent molar ratio on the conversion and product selectivity in the isopropylation of ethylbenzene over Various zeolites[a]**

| Catalysts | Conversion or Selectivity (mole%) | Ethylbenzene to isopropanol (molar ratio) | | | |
|---|---|---|---|---|---|
| | | 2:1 | 4:1 | 6:1 | 8:1 |
| **H-Mord.** | Conv. of IPA | 97.0 | 100.0 | 100.0 | 100.0 |
| | Conv. of EB | 22.0 | 17.0 | 14.6 | 12.1 |
| | Theo. Max.Conv[b] | 44.0 | 68.0 | 87.6 | 96.8 |
| | TOF (s$^{-1}$ x 10$^{-3}$)[c] | 1.2 | 2.1 | 2.8 | 3.2 |
| | Sel.Total-EC[d] | 94.6 | 97.0 | 97.3 | 97.5 |
| | Sel.$_{DISPR}$(Bz +DEBs)[e] | 1.9 | 2.0 | 2.2 | 2.5 |
| | Sel.DIPEB[f] | 3.5 | 1.0 | 0.5 | 0 |
| | Sel.$_{2-EC}$ | 4.0 | 3.5 | 1.2 | 1.3 |
| | Sel.$_{3-EC}$ | 34.5 | 40.7 | 43.4 | 44.3 |
| | Sel.$_{4-EC}$ | 61.5 | 55.8 | 55.4 | 54.4 |
| **H-Beta** | Conv. of IPA | 99.5 | 100.0 | 100.0 | 100.0 |
| | Conv. of EB | 26.8 | 20.1 | 14.7 | 11.2 |
| | Theo. Max.Conv[b] | 53.6 | 80.4 | 88.2 | 89.6 |
| | TOF (s$^{-1}$ x 10$^{-3}$)[c] | 4.5 | 7.6 | 8.6 | 9.0 |
| | Sel.Total-EC[d] | 78.2 | 83.6 | 87.1 | 87.9 |
| | Sel.$_{DISPR}$(Bz +DEBs)[e] | 1.2 | 6.6 | 6.7 | 6.8 |
| | Sel.DIPEB[f] | 20.6 | 9.8 | 6.2 | 5.3 |
| | Sel.$_{2-EC}$ | 14.4 | 13.4 | 12.5 | 12.2 |
| | Sel.$_{3-EC}$ | 49.5 | 50.0 | 50.7 | 50.8 |
| | Sel.$_{4-EC}$ | 36.1 | 36.6 | 36.8 | 37.0 |
| **H-USY** | Conv. of IPA | 95.0 | 100.0 | 100.0 | 100.0 |
| | Conv. of EB | 32.4 | 24.0 | 16.1 | 12.4 |
| | Theo. Max.Conv[b] | 64.8 | 96.0 | 96.6 | 99.2 |
| | TOF (s$^{-1}$ x 10$^{-3}$)[c] | 1.7 | 2.8 | 3.0 | 3.1 |
| | Sel.Total-EC[d] | 62.8 | 72.0 | 69.1 | 64.0 |
| | Sel.$_{DISPR}$(Bz +DEBs)[e] | 8.9 | 17.5 | 26.0 | 33.6 |
| | Sel.DIPEB[f] | 28.3 | 10.5 | 4.9 | 2.4 |
| | Sel.$_{2-EC}$ | 8.7 | 6.8 | 5.2 | 4.9 |
| | Sel.$_{3-EC}$ | 51.8 | 56.1 | 56.9 | 58.8 |
| | Sel.$_{4-EC}$ | 39.5 | 37.1 | 37.9 | 36.3 |

[a] Reaction Conditions: Temperature = 413 K, WHSV = 3.25 h-1, TOS = 1h, at low ethylbenzene conversion remaining unreacted propylene was present in gaseous stream, [b-f] as in Table 4.1.

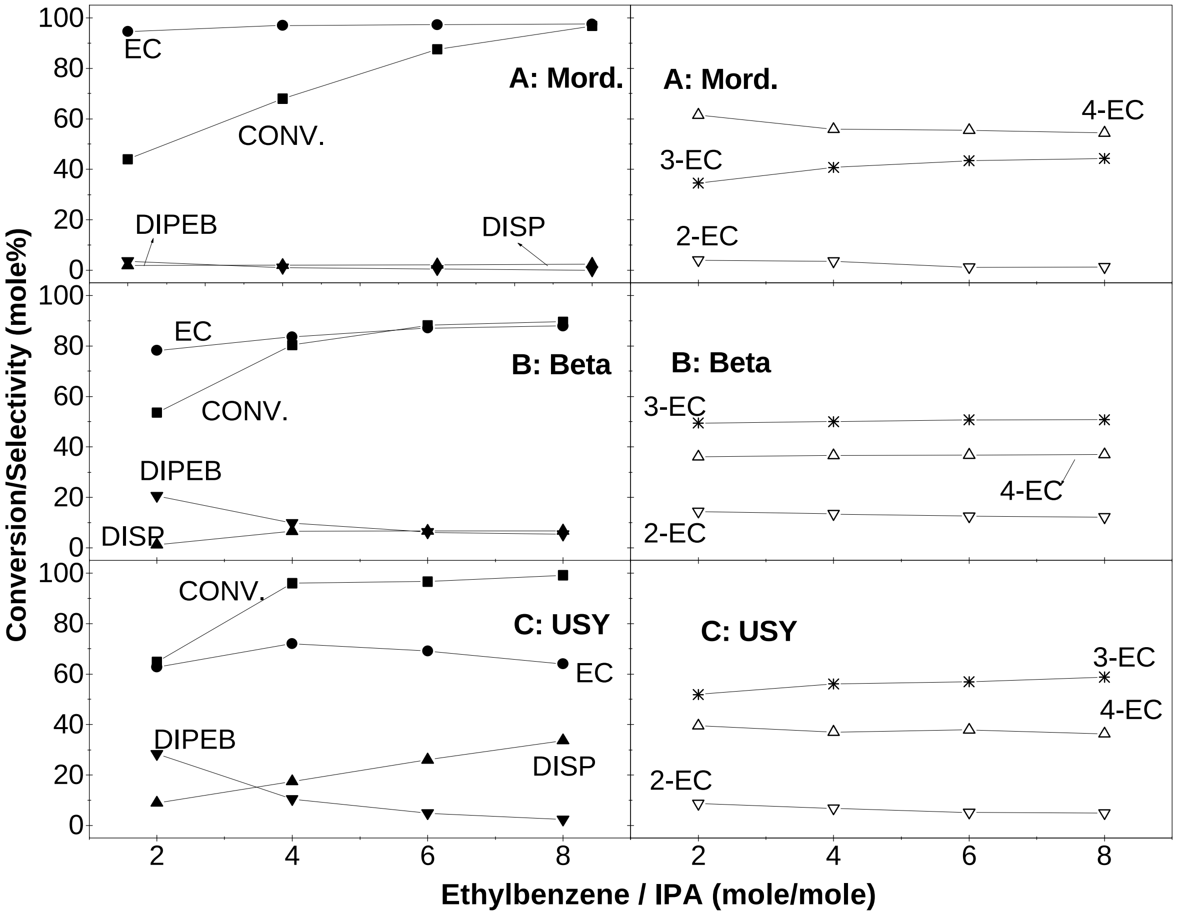


**Fig. 4.5:** Effect of ethylbenzene to isopropyl alcohol (IPA) molar ratio on the conversion of ethylbenzene and product selectivity over various zeolite catalysts. Isopropylation of ethylbenzene over H-Mordenite (A), H-Beta (B) and H-USY (C). Conversion of ethylbenzene ( ), Total ethylcumene selectivity (Sel. $_{\text{EC}}$) ( ), Sel.$_{\text{2-EC}}$ (□), Sel.$_{\text{3-EC}}$ (□), Sel.$_{\text{4-EC}}$ ( ), Sel. $_{\text{DISP}}$ ( ) and Sel.$_{\text{DIPEB}}$ ( ).

Reaction Conditions: Temperature = 413 K, WHSV = 3.25 h$^{-1}$, TOS = 1h.

### 4.3.2.4. Effect of Nature of Isomorphously Incorporated Metal Ion ($Fe^{3+}$and $Ga^{3+}$) in Zeolite Beta

The isopropylation of ethylbenzene was carried out over Al-, Ga- and Fe-silicate analogs of zeolite Beta to study the influence of acid strength of these metallosilicates on the activity and product selectivity. The Table 4.5 compares the catalytic activity data for the H-Al-Beta, H-Ga-Beta and H-Fe-Beta zeolite catalysts at the same reaction conditions. The conversion of isopropanol was 40%, 80% and 100% over H-Fe-Beta, H-Ga-Beta and H-Al-Beta respectively. The conversion at the temperature of 413 K follows the sequence: H-Al-Beta > H-Ga-Beta > H-Fe-Beta Sel.$_{EC,}$ the selectivity was found to be in the reverse order, according to the strength of their acid sites (H-Al-Beta > H-Ga-Beta > H-Fe-Beta). It is well known that, the relative strength of Brönsted acid sites increases in the order: Si(OH) < B(OH) << Fe(OH)Si < Ga(OH)Si < Al(OH)Si [22-26].

**Table 4.5: Isopropylation of ethylbenzene using isopropanol as alkylating agent and effect of nature of isomorphously incorporated trivalent metal ion in zeolite Beta[a]**

| Conversion / Selectivity (mole%) | Catalysts | | |
|---|---|---|---|
| | H-Fe-Beta | H-Ga-Beta | H-Al-Beta |
| Conv of IPA | 40.0 | 80.0 | 100.0 |
| Theo. Max.Conv[b] | 7.2 | 41.6 | 80.4 |
| Sel.$_{EC}$[d] | 95.7 | 87.4 | 83.6 |
| Sel.$_{DISP}$[e] | 0.0 | 1.3 | 6.6 |
| Sel.$_{DIPEB}$[f] | 4.3 | 11.3 | 9.8 |
| Sel.2-EC | 16.6 | 17.0 | 13.4 |
| Sel.3-EC | 38.5 | 48.1 | 50.0 |
| Sel.4-EC | 44.9 | 34.9 | 36.6 |

[a] Reaction Conditions: Temperature =413 K, WHSV = 3.25 $h^{-1}$, Ethylbenzene:isopropanol = 4:1 (molar), TOS = 1h, [b-f] as in Table 4.1.

### 4.3.2.5. Recycling of the Catalyst H-Beta (20)

The regenerability of H-Beta (SAR = 20) sample used for the isopropylation of ethylbenzene was also tested. Three cycles were carried out on the same catalyst sample in the following way. After reaction, sample was calcined at 773 K for 12 hours in the presence of air, followed by flushing with dry nitrogen and cooled to reaction temperature. The results (Fig. 4.6) show that, there was no change in the catalytic behavior after regenaration. There is almost no decrease in the conversion of ethylbenzene and no change in the selectivity of ethylcumene after each cycle. X-ray diffraction patterns, recorded after each cycle, indicate that the catalyst retains the H-Beta structure with any loss of crystallinity.

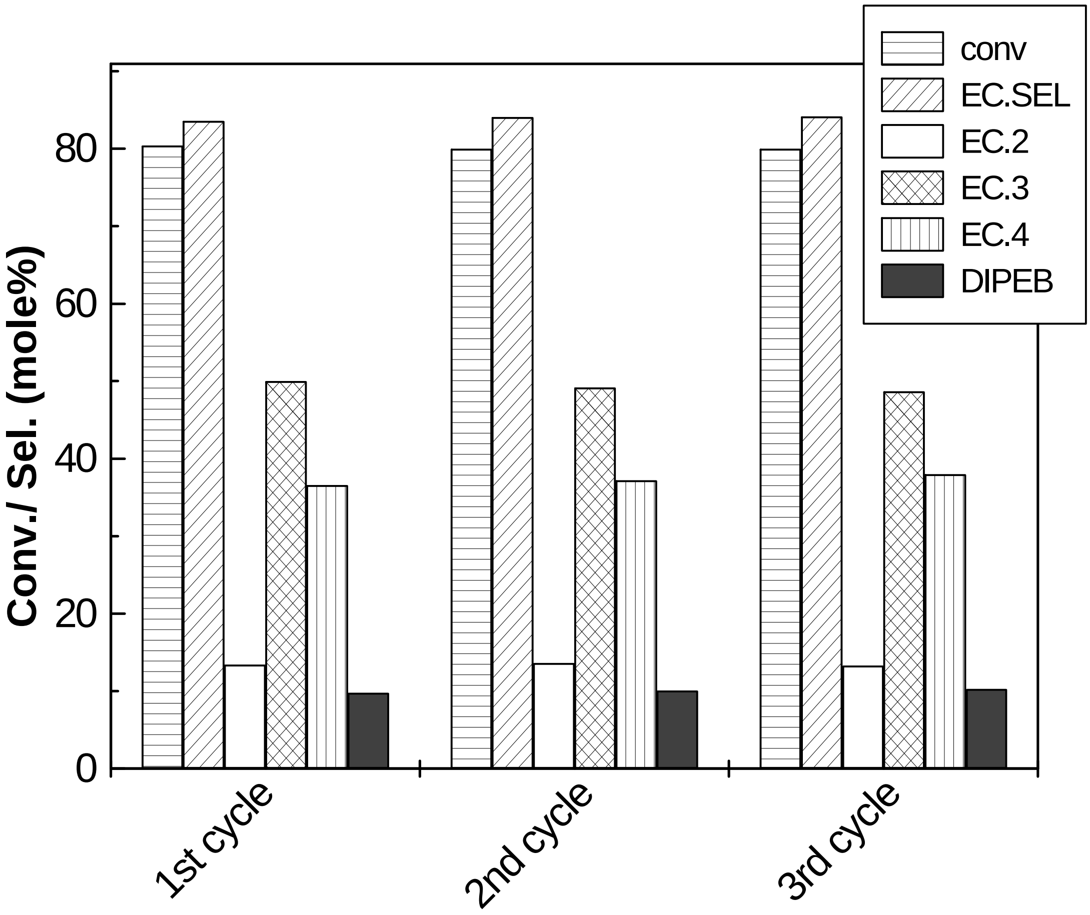


**Fig. 4.6:** Effect of regeneration of catalysts H-Beta (20) in the isopropylation of ethylbenzene. Reaction Conditions: Temperature = 413 K, WHSV = 3.25 $h^{-1}$, ethylbenzene:isopropanol =4:1 (molar), TOS = 1h.

## 4.4. **CONCLUSIONS**

The alkylation of ethylbenzene with isopropanol was carried out over various catalysts like H-Beta, H-USY, H-Y, H–Mordenite, H-ZSM-5, H-ZSM-12, amorphous silica-alumina, sulfated-zirconia and H-MCM-41 under identical reaction conditions. Among these catalysts zeolite H-Beta, H-USY and H-Mordenite were found to be quite active catalysts. H-ZSM-5 with three-dimensional intersecting 10-membered rings (0.54 nm x 0.56 nm for straight and 0.51nm x 0.55 nm for sinusoidal) channels did not show any catalytic activity even though H-ZSM-5 possesses a high strength of acid sites [20], due to its 10-membered ring medium sized pores.

Among the three active catalysts (H-Modernite, H-Beta and H-USY), the H-Mordenite exhibited very high selectivity towards EC and 4-EC, on the other hand H-USY was less selective for EC. Zeolite H-Beta follows the middle path. Detailed studies on the influence of different parameters like temperature, space velocity, ethylbenezene to isopropanol molar ratio and time on stream governing the conversion and selectivity over H-USY, H-Beta and H-Mordenite demonstrated that these zeolites are the quite suitable catalyst (considering both activity and selectivity to EC into account) among the active catalysts used in this study.

The distribution of EC isomers was significantly influenced by pore architecture of the zeolites. H-Mordenite with relatively narrow pores was highly para-selective, while H-Beta and H-USY exhibited less para-selectivity, due to their larger pores, vis-à-vis H-Mordenite. The reaction takes place at relatively lower temperature (413-433 K) exhibiting quite high selectivity for mono isopropylated products.

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## 5.1. LIQUID PHASE ISOPROPYLATION

In chapters 3 and 4, the details of isopropylation of C-8 aromatics (xylenes and ethylbenzene) using isopropanol as alkylating agent over acid catalysts have been presented. It may be recalled that the selectivity towards DMC (from xylenes isopropylation) or EC (from ethylbenzene isopropylation) was found to be dependent on both the pore architecture of the zeolite catalyst and their acidity (both strength and density). Side reactions like isomerization and disproportionation reactions were also found to occur to a significant extent. The main reason for these side reactions and formation of thermodynamically more stable isomers could be somewhat higher reaction temperature, needed for vapour phase conditions. Recently, it is reported that Fe-loaded zeolite Y (Fe/Y) effectively catalyzes t-butylation of aromatics under liquid phase low temperature (313-353 K) reaction conditions using alkyl halides as alkylating agents [1]. There are few reports on benzylation of benzene with benzylclhoride over Fe containing zeolites [2] and mesoporous molecular sieves [3,4]. However, these methods have not been explored systematically and have not been extended to the isopropylation of aromatics.

In this present chapter, the details of liquid phase low temperature (313-353 K) isopropylation of C-8 aromatics using 2-chloropropane and 2-bromopropane catalyzed by Fe-loaded zeolites like Fe/Beta, Fe/Mordenite, Fe/Y and Fe/USY are given. The reactions were carried out in batch reactor at atmospheric pressure.

## 5.2. EXPERIMENTAL

The iron ($Fe^{3+}$) loaded zeolite catalysts (preparation procedure has been already described in section 2.2.10), were characterized by various physico-chemical techniques (Table 2.2 and Table 2.3, in Chapter 2). The weight percent of iron (as Fe) in zeolite Beta (Si/Al = 20), Mordenite (Si/Al = 5.9), Y (Si/Al = 2.9) and USY (Si/Al =5.6) was 3.5%, 4.8%, 4% and 5.8% respectively.

### 5.2.1. Catalytic Reaction

Benzene, toluene, xylenes (ACROSS, India) and ethylbenzene (EB) (Lancaster, USA, 99+%), isopropyl alcohol (IPA), 2-chloropropane (2-CP) and 2-bromopropane (2-BP) (EMERCK) were used without further distillation and purification. The activity of the catalyst was investigated over Fe/Beta in a magnetically stirred batch reactor (capacity: 25ml) without using any organic co-solvent. In a typical reaction, a required amount of isopropyl halide (3.1 g of 2-bromopropane; 0.025 mol) was added to a reaction vessel containing 0.2 g of catalyst and 10.6 g *m*-xylene (0.1mol)(under neat conditions without using any co-solvent where substrate, taken in excess, itself functions as solvent), used as solvent too, at 353 K under a flow of moisture-free nitrogen (30 $cm^3$, $min^{-1}$) through the liquid reaction mixture. The catalyst was pre-activated at 473 K for 2h before doing reaction. Samples were withdrawn at regular intervals through a syringe, then centrifuged and analyzed by gas chromatograph and identified by GC-MS and GC-IR (as described in chapter 3 and 4).

The course of the reaction was followed by measuring quantitatively the HCl/HBr evolved in the reaction by acid-base titration (by absorbing the HCl/HBr carried by nitrogen in a 0.1 M NaOH solution containing phenolphthalein indicator) as a function of time and also by analyzing the reaction mixture for unconverted isopropyl halide and isopropylated products at different interval of the experiment by gas chromatography. There was a good agreement between the isopropyl halide conversion obtained from the acid-base titration and the GC analysis.

A blank experiment containing 2-bromopropane, iron loaded zeolite Beta and acetonitrile as solvent was carried out under the similar reaction conditions. There was no change of colour in the acid-base titration, which indicates no conversion of 2-bromopropane. Similarly, another experiment containing only *m*-xylene and catalyst was also carried out. No isomerized and isopropylated products were obtained.

## 5.3. RESULTS AND DISCUSSION

The schematic representation of the reaction is depicted in Scheme 5.1.

For benzene R = $R_1$ = H,$_{,}$ for toluene R = $CH_3$ and $R_1$ = H, for xylenes R = $R_1$ = $CH_3$ and for ethylbenzene R = $C_2H_5$ and $R_1$ = H.

**Scheme 5.1:** Isopropylation of aromatic compounds over iron loaded zeolites using isopropyl halides as alkylating agent.

### 5.3.1. Catalyst comparison

In order to investigate the suitable iron loaded acid catalyst(s), the isopropylation of C-8 aromatics using 2-bromopropane (2-BP) as alkylating agent was studied with different topologies like MOR (Mordenite), BEA (Beta) and FAU (USY and Y). The product selectivity and time for complete conversion of 2-bromopropane are shown in Table 5.1. It is clear that over all the four catalysts tested, the reaction was complete in 15-20 min (*p*-xylene), 30-40 min (*m*- and *o*-xylene) and 45-60 min (ethylbenzene). The reactivity of the substrates follow the order: *p*-xylene > *m*-xylene   *o*-xylene > ethylbenzene. The activity of these catalysts for the isopropylation reaction follows the order: Fe/USY   Fe/Beta   Fe/Y   Fe/Mordenite. The relative selectivity towards monoalkylated product over these catalysts decreases in the following order: Fe/Mordenite > Fe/Beta > Fe/Y > Fe/USY, which is inversely proportional to the void space. Even though the catalytic activities (in terms of time) of Fe/Beta and Fe/USY were almost same, Fe/Beta was more selective towards monoalkylated product (91- 94.7%) compared to Fe/USY (85 – 89% only).

The isomer distribution of monoalkylated products was not significantly changed by the pore architecture of different zeolites. This is contrary to the results obtained under fixed bed vapour phase conditions (Chapter 3 and 4). This is an important point. It may be recalled that in the case of *m*-xylene isopropylation, using isopropanol under vapour phase (Chapter 3), USY gave very high selectivity towards 3,5-DMC. However, in the present conditions where 2-bromopropane is used as alkylating agent, the 3,5-DMC is not preferred isomer. This observation indicates that under liquid phase, the kinetic aspect is more favoured compared to thermodynamic aspect as expected at lower temperature. For further studies, Fe/Beta was used as catalyst.

**Table 5.1: Effect of various catalysts in the isopropylation of C-8 aromatics using 2-bromopropane as alkylating agent[a]**

| Substrates | Selectivity (mole%) | Catalysts | | | |
|---|---|---|---|---|---|
| | | Fe/Mordenite | Fe/Beta | Fe/Y | Fe/USY |
| *p*-Xyl. | Time[b](min) | 20.0 | 20.0 | 20.0 | 15.0 |
| | Sel.$_{\text{DMCs}}$ | 95.0 | 93.0 | 88.0 | 85.0 |
| | Sel.$_{\text{DIPX}}$ | 5.0 | 7.0 | 12.0 | 15.0 |
| | Sel. $_{\text{2,5-DMC}}$ | 100.0 | 100.0 | 100.0 | 100.0 |
| *m*-Xyl. | Time[b] (min) | 40.0 | 30.0 | 40.0 | 30.0 |
| | Sel.$_{\text{DMCs}}$ | 95.2 | 94.7 | 91.7 | 89.0 |
| | Sel.$_{\text{DIPX}}$ | 4.8 | 5.3 | 8.3 | 11.0 |
| | Sel. $_{\text{3,5-DMC}}$ | 10.8 | 10.2 | 14.6 | 12.8 |
| | Sel. $_{\text{2,4-DMC}}$ | 89.2 | 89.8 | 85.4 | 87.2 |
| *o*-Xyl. | Time[b] (min) | 40.0 | 35.0 | 40.0 | 30.0 |
| | Sel.$_{\text{DMCs}}$ | 94.7 | 93.2 | 91.4 | 88.0 |
| | Sel.$_{\text{DIPX}}$ | 5.3 | 6.7 | 8.6 | 12.0 |
| | Sel. $_{\text{3,4-DMC}}$ | 58.2 | 60.7 | 57.1 | 62.2 |
| | Sel. $_{\text{2,3-DMC}}$ | 41.8 | 39.3 | 42.9 | 37.8 |
| EB | Time[b] (min) | 60.0 | 50.0 | 50.0 | 45.0 |
| | Sel.$_{\text{ECs}}$ | 94.5 | 91.5 | 90.0 | 89.0 |
| | Sel.$_{\text{DIPEB}}$ | 5.5 | 8.5 | 10.0 | 11.0 |
| | Sel. $_{\text{2-EC}}$ | 28.2 | 30.0 | 29.8 | 31.0 |
| | Sel. $_{\text{3-EC}}$ | 30.8 | 27.3 | 29.4 | 32.8 |
| | Sel. $_{\text{4-EC}}$ | 41.0 | 42.7 | 40.8 | 37.2 |

[a] Reaction conditions: Temperature = 353 K, Substrate = 10.6 g, 2-bromopropane =3.1 g, catalyst = 0.2 g, [b] Time required for complete conversion of 2-bromopropane.

## 5.3.2. Effect of Alkyl Halides

When 2-chloropropane (2-CP) and 2-bromopropane (2-BP) were used as alkylating agent over Fe/Beta with various C-8 aromatic compounds (as shown in Table 5.2), it was observed that the reaction takes more time for the complete conversion of 2-CP compared to that of 2-BP probably due to the higher bond energy of C-Cl bond compared to C-Br bond. However, the product distribution was comparable in both the cases.

The *p*-xylene isopropylation gave 100% selectivity of 2,5-dimethylcumene ($\text{Sel.}_{2,5\text{-DMC}}$) in the case of both 2-CP and 2-BP. In the case of *m*-xylene isopropylation, the selectivity for 2,4-DMC in total DMCs ($\text{Sel.}_{2,4\text{-DMC}}$) increases slightly from 89.8% to 92.4% when the alkylating agent is changed from 2-bromopropane to 2-chloropropane. In the case of *o*-xylene isopropylation, the selectivity for 3,4-DMC in total DMCs ($\text{Sel.}_{3,4\text{-DMC}}$) decreases from 60.7% to 54% and the selectivity of 2,3-DMC increases from 39.3 to 46.0% when the alkylating agent is changed from 2-bromopropane to 2-chloropropane. However, the difference in isomer distribution was very significantly. In the case of ethylbenzene isopropylation, there is no significant change in the distribution of ethylcumene isomers. For all further work 2-BP was used as alkylating agent.

**Table 5.2: Isopropylation of C-8 aromatics over Fe/Beta using 2-bromopropane and 2-chloropropane as alkylating agent[a]**

| Substrates | Selectivity (mole%) | Alkylating agents | |
|---|---|---|---|
| | | 2-bromopropane (2-BP) | 2-Chloropropane (2-CP) |
| *p*-Xyl. | Time[b] (min) | 20.0 | 50.0 |
| | Sel.$_{DMCs}$ | 93.0 | 94.0 |
| | Sel.$_{DIPX}$ | 7.0 | 6.0 |
| | Sel. $_{2,5\text{-}DMC}$ | 100.0 | 100.0 |
| *m*-Xyl. | Time[b] (min) | 30.0 | 60.0 |
| | Sel.$_{DMCs}$ | 94.7 | 97.4 |
| | Sel.$_{DIPX}$ | 5.3 | 2.6 |
| | Sel. $_{3,5\text{-}DMC}$ | 10.2 | 7.6 |
| | Sel. $_{2,4\text{-}DMC}$ | 89.8 | 92.4 |
| *o*-Xyl. | Time[b] (min) | 35.0 | 90.0 |
| | Sel.$_{DMCs}$ | 94.8 | 97.0 |
| | Sel.$_{DIPX}$ | 5.2 | 3.0 |
| | Sel. $_{3,4\text{-}DMC}$ | 60.7 | 54.0 |
| | Sel. $_{2,3\text{-}DMC}$ | 39.3 | 46.0 |
| EB | Time[b] (min) | 50.0 | 100.0 |
| | Sel.$_{ECs}$ | 91.0 | 95.0 |
| | Sel.$_{DIPEB}$ | 9.0 | 5.0 |
| | Sel. $_{2\text{-}EC}$ | 30.0 | 32.0 |
| | Sel. $_{3\text{-}EC}$ | 27.3 | 28.3 |
| | Sel. $_{4\text{-}EC}$ | 42.7 | 39.7 |

[a] Reaction conditions: Temperature = 353 K, Substrate = 10.6 g and 3.1 g of 2-BP or 1.96 g of 2-CP, Catalyst (Fe/Beta) = 0.2 g, [b] Time required for complete conversion of alkylating agent.

### 5.3.3. Effect of Different (C6 to C8) Substrates

Isopropylation of different aromatic substrates over Fe/Beta catalyst using 2-bromopropane as isopropylating agent is illustrated in Table 5.3 along with conversion of 2-bromopropane, selectivity for monoalkylated and dialkylated products, and isomeric distribution of monoalkylated products. From Table 5.3, it is clearly observed that *p*-xylene and toluene take only 20 minutes to complete the reaction whereas benzene takes ca. 50 min, probably due to the presence of methyl group (s), which activates the benzene ring in toluene. The complete conversion of 2-bromopropane with different aromatic substrates, the Fe/Beta catalyst follows the order: *p*-xylene (20) ≡ toluene (20) > *m*-xylene (30) > *o*-xylene (35) > Ethylbenzene (50) ≡Benzene (50). In the case of benzene (C-6) and toluene (C-7) isopropylation compared to C-8 aromatics (xylenes and ethylbenzene), the slightly higher amount of dialkylated product was formed, due to further isopropylation of cumene and cymenes respectively.

**Table 5.3: Isopropylation of C-6 to C-8 aromatic compounds over Fe/Beta catalyst using 2-bromopropane as alkylating[a]**

| Substrates | Time[b], min | Sel.$_{MAP}$[c] (mole%) | Sel.$_{DAP}$[d] (mole%) | Attacking position of isopropyl group[e] | | |
|---|---|---|---|---|---|---|
| | | | | **2-** | **3-** | **4-** |
| Benzene | 50.0 | 84.5 | 15.5 | - | - | - |
| Toluene | 20.0 | 87.0 | 13.0 | 21.6 | 34.1 | 44.3 |
| Ethylbenzene | 50.0 | 91.0 | 9.0 | 30.0 | 27.3 | 42.7 |
| *p*-xylene | 20.0 | 93.0 | 7.0 | 100.0 | - | - |
| *m*-xylene | 30.0 | 94.7 | 5.3 | - | 10.2 | 89.8 |
| *o*-xylene | 35.0 | 94.8 | 5.2 | - | 39.3 | 60.7 |

[a] Reaction Conditions: Temperature = 353 K, Substrate = 10.0 g, 2-bromopropane = 2.9 g, 3.3 g and 3.9 g for C-8, C-7 and C-6 aromatic respectively, amount of catalyst (Fe/Beta) = 0.2 g,

[b] Time = Time required for complete conversion of limiting agent, [c] Sel. $_{MAP}$ = selectivity of mono alkylated product, [d] Sel.$_{DAP}$ = selectivity of dialkylated product and [e] 2, 3 and 4 indicate the position of incoming isopropyl group at 2, 3 and 4 position with respect to alkyl group already present in the benezene. For *p*-xylene isopropylation, 2 ≡ 2, 5 dimethyl cumene (2,5-DMC), for *m*-xylene isopropylation, 2 ≡ 2,6-DMC, 3 ≡ 3,5-DMC and 4 ≡ 2,4-DMC, for *o*-xylene isopropylation 3 ≡ 2,3-DMC and 4 ≡ 3,4-DMC.

### 5.3.4. Effect of Temperature

In Table 5.4, the results obtained in the isopropylation of C-8 aromatics using 2-BP as alkylating agent with Fe/Beta catalyst at three different temperatures are recorded. The increase in the temperature significantly decreases in the time for complete conversion of 2-BP, as expected. For example, in the case of *p*-xylene isopropylation, it takes 20 min, 90 min and 200 min for complete conversion of 2-BP at the temperature of 313 K, 333K and 353 K respectively. Similarly, it is true for the *m*-xylene, *o*-xylene and ethylbenzene isopropylation. In the case of ethylbenzene isopropylation, there was no conversion of 2-BP after 300 min and 180 min at the temperature of 313 K and 333 K respectively. However, with increasing temperature there was a little difference in the product selectivity. As the temperature is increased, the selectivity for monoalkylated product is decreased slightly from 97 to 93% for *p*-xylene, from 100 to 94.7% for *m*-xylene, from 100 to 93.2% for *o*-xylene isopropylation, respectively with a consequent increase in dialkylated product. No isomerized or disproportionated products were observed in the temperature range of 313 to 353 K.

In case of *p*-xylene isopropylation, only 100% of 2,5-dimethylcumene ($Sel._{2,5\text{-}DMC}$) was observed. In the case of *m*-xylene isopropylation, by increasing the temperature the selectivity for 2,4-DMC in total DMCs ($Sel._{2,4\text{-}DMC}$) decreases slightly from 92.5 to 89.8% and the energetically most stable 3,5-DMC ($Sel._{3,5\text{-}DMC}$) in total DMCs increases (Table 5.4) from 7.5 to 10.2%. The 2,6-DMC was not observed at all, probably due to sterically hindered isomer. In case of *o*-xylene isopropylation, the selectivity of 2,3-DMC in total DMCs ($Sel._{2,3\text{-}DMC}$) decreases from 47.5% at 313 K to 39.3% at 353 K with consequent increase in the selectivity for 3,4-DMC ($Sel._{3,4\text{-}DMC}$) from ca. 52.5% at 313 K to ca. 60.7% at 353 K, indicating that the energetically less favored 2,3-DMC decreases with increasing reaction temperature, as expected (Table 5.4). In case of ethylbenzene isopropylation, the distribution of the three EC isomers among total ethylcumenes at the temperature of 353 K is: 30% for 2-EC, 27.3% for 3-EC and 42.7% for 4-EC. These results of EC and DMC isomers distribution are quite different from those obtained in the vapour phase isopropylation of xylenes (Chapter 3) and ethylbenzene (Chapter 4).

**Table 5.4: Effect of Temperature on the conversion and product selectivity in the isopropylation of C-8 aromatics over Fe/Beta using 2-bromopropane as alkylating agent[a]**

| Substrates | Conversion or Selectivity (mole%) | Temperature, K | | |
|---|---|---|---|---|
| | | 313.0 | 333.0 | 353.0 |
| *p*-Xyl. | Time[b] (min) | 200.0 | 90.0 | 20.0 |
| | Sel.$_{DMCs}$ | 97.0 | 94.2 | 93.0 |
| | Sel.$_{DIPX}$ | 3.0 | 5.8 | 7.0 |
| | Sel. $_{2,5\text{-}DMC}$ | 100.0 | 100 | 100.0 |
| *m*-Xyl. | Time[b] (min) | 180.0 | 130.0 | 30.0 |
| | Sel.$_{DMCs}$ | 100.0 | 97.5 | 94.7 |
| | Sel.$_{DIPX}$ | 0.0 | 2.5 | 5.3 |
| | Sel. $_{3,5\text{-}DMC}$ | 7.5 | 8.5 | 10.2 |
| | Sel. $_{2,4\text{-}DMC}$ | 92.5 | 91.5 | 89.8 |
| *o*-Xyl. | Time[b] (min) | 300.0 | 140.0 | 35.0 |
| | Sel.$_{DMCs}$ | 100.0 | 97.1 | 93.2 |
| | Sel.$_{DIPX}$ | 0.0 | 2.9 | 6.7 |
| | Sel. $_{3,4\text{-}DMC}$ | 52.5 | 54.5 | 60.7 |
| | Sel. $_{2,3\text{-}DMC}$ | 47.5 | 45.5 | 39.3 |
| EB | Time[b] (min) | 300.0[T] | 180.0 [T] | 50.0 |
| | Sel.$_{ECs}$ | - | - | 91.5 |
| | Sel.$_{DIPEB}$ | - | - | 8.5 |
| | Sel. $_{2\text{-}EC}$ | - | - | 30.0 |
| | Sel. $_{3\text{-}EC}$ | - | - | 27.3 |
| | Sel. $_{4\text{-}EC}$ | - | - | 42.7 |

[a]Reaction conditions: Substrate = 10.6 g, 2-bromopropane = 3.1 g, Catalyst = 0.2 g, [b]Time required for the complete conversion of 2-bromopropane, [T] No conversion of 2-bromopropane was not obtained after 300 min at 313 K and 180 min at 333 K.

## 5.3.5. Effect of Dilution of Substrates

The influence of the dilution of C-8 aromatics w. r. t. 2-BP (i.e. substrate to alkylating agent molar ratio) and product distribution is presented in Table 5.5. Selectivity of monoalkylated product in the isopropylation of C-8 aromatics is highly influenced by the dilution of aromatic substrates, which itself act as solvent also. With increasing molar ratio of C-8 aromatic compound to 2-BP, the time required for the complete conversion of the limiting reagent, 2-BP, decreased marginally for xylenes. In the case of ethylbenzene (EB), however, there was more pronounced effect as the time required for complete conversion of 2-BP was reduced form 20 min for 8:1 EB:2-BP molar ratio to 60 min, for 2:1 EB:2-BP molar ratio. This is in lime with earlier observation in temperature effect; where EB is less active correspond to xylenes.

In case of isopropylation of xylenes, at lower molar ratio of substrate to 2-bromopropane of 2:1, the selectivity of diisopropylated product is slightly high (8.6% for *p*- and 6.5% for *m*-xylene and 10.7% for *o*-xylene isopropylation) mainly at the cost of DMC, clearly indicating enhanced further isopropylation of DMCs to dialkylated product. However, with increasing xylene to 2-bromopropane molar ratio, the Sel.$_{\mathrm{DMCs}}$ increased because the limited 2-bromopropane selectively reacted with xylene to produce DMCs and there is less chance for the formation of dialkylated product at higher xylene to 2-bromopropane molar ratio i.e. at lower concentration of 2-bromopropane.

With increasing xylene/2-bromopropane molar ratio from 2:1 to 8:1, Sel.$_{\mathrm{2,5\text{-}DMC}}$ in the case of *p*-xylene isopropylation was constant (100%). In the case of *m*-xylene isopropylation, the distribution of 3,5-DMC and 2,4-DMC selectivity almost unchanged but in the case of *o*-xylene, Sel.$_{\mathrm{3,4\text{-}DMC}}$ decreased marginally from ca. 65.0 to 55.0% and consequently the Sel.$_{\mathrm{2,3\text{-}DMC}}$ is increased from ca. 35.0 to 45.0%. Similarly, the increase of EB/2-BP ratio leads to decrease Sel.$_{\text{DIPEB}}$ from 16.4 to1.0% with corresponding increase in Sel.$_{\text{EC,}}$ (from 83.6 to 99%) clearly suggesting that the formation of DIPEB is mainly due to further isopropylation of EC. However, with increasing EB/2-BP ratio, the distribution of three ethylcumene isomers were not changed significantly.

**Table 5.5: Effect of dilution of substrates w. r. t. alkylating agent in the isopropylation of C-8 aromatics over Fe/Beta using 2-bromopropane as alkylating agent**[a]

| Substrates | Selectivity (mole%) | Substrate to 2-bromopropane (molar ratio) | | | |
|---|---|---|---|---|---|
| | | **2:1** | **4:1** | **6:1** | **8:1** |
| *p*-Xyl. | Time[b] (min) | 25.0 | 20.0 | 16.0 | 15.0 |
| | Sel.$_{\text{DMCs}}$ | 91.4 | 93.0 | 94.2 | 95.5 |
| | Sel.$_{\text{DIPX}}$ | 8.6 | 7.0 | 5.8 | 4.5 |
| | Sel. $_{\text{2,5-DMC}}$ | 100.0 | 100.0 | 100.0 | 100.0 |
| *m*-Xyl. | Time[b] (min) | 35.0 | 30.0 | 25.0 | 25.0 |
| | Sel.$_{\text{DMCs}}$ | 93.5 | 94.7 | 98.0 | 99.0 |
| | Sel.$_{\text{DIPX}}$ | 6.5 | 5.3 | 2.0 | 1.0 |
| | Sel. $_{\text{3,5-DMC}}$ | 10.9 | 10.2 | 10.0 | 10.0 |
| | Sel. $_{\text{2,4-DMC}}$ | 89.1 | 89.2 | 90.0 | 90.0 |
| *o*-Xyl. | Time[b] (min) | 40 | 35 | 30 | 30 |
| | Sel.$_{\text{DMCs}}$ | 89.3 | 94.8 | 95.5 | 96.3 |
| | Sel.$_{\text{DIPX}}$ | 10.7 | 5.2 | 4.5 | 3.7 |
| | Sel. $_{\text{3,4-DMC}}$ | 64.7 | 60.7 | 56.2 | 54.9 |
| | Sel. $_{\text{2,3-DMC}}$ | 35.3 | 39.3 | 43.8 | 45.1 |
| EB | Time[b] (min) | 60.0 | 50.0 | 36.0 | 20.0 |
| | Sel.$_{\text{ECs}}$ | 83.6 | 91.0 | 97.0 | 99.0 |
| | Sel.$_{\text{DIPEB}}$ | 16.4 | 9.0 | 3.0 | 1.0 |
| | Sel. $_{\text{2-EC}}$ | 28.0 | 30.0 | 25.8 | 27.3 |
| | Sel. $_{\text{3-EC}}$ | 24.2 | 27.3 | 30.5 | 27.5 |
| | Sel. $_{\text{4-EC}}$ | 47.8 | 42.7 | 43.4 | 45.2 |

[a]Reaction conditions: Temperature = 353 K, Substrate = 10.6 g, 2-BP = 6.2 g, 3.1 g, 2.1 g and 1.54 g for 2:1, 4:1, 6:1 and 8:1 (molar ratio) respectively, Catalyst (Fe/Beta) = 0.2 g, [b]Time required for the complete conversion of 2-bromopropane.

### 5.3.6. Effect of Catalyst Concentration

In Table 5.6, the results obtained where different amount of catalyst (Fe/Beta) was used at otherwise same reaction conditions in the isopropylation of *p*-xylene. As the concentration of the catalyst was increased from 0.1 g to 0.4 g through 0.2 g, it takes less time for the complete conversion of 2-bromopropane in the isopropylation of *p*-xylene (Table 5.6). With increasing the catalyst concentration, the selectivity towards monoalkylated product decreases, consequently selectivity for dialkylated product increases.

### 5.3.7. Effect of Reaction Time

The effect of time on the conversion of alkylating agent and product selectivity in the isopropylation of C-8 aromatics (xylenes and ethylbenzene) is shown in Table 5.7. As expected, the conversion of alkylating agent increases with time in all cases, the selectivity for dialkylated product increases slightly with a consequent decrease in monoalkylated product gradually with increasing reaction time. This is because of further isopropylation of monoalkylated product to dialkylated product, with time and at higher temperature.

Quite interestingly, there was no significant variation in the isomer distribution in all the cases. This is probably due to fact that the reaction is carried out at lower temperature and the isomerization of primarily formed isomers, particularly in the case of *m*-xylene and ethylbenzene, is restricted. In the case of *m*-xylene, the reaction was continued for longer period (80 min) after completion of the reaction (30 min) to find out whether any increase in the selectivity of 3,5-DMC, energetically most favoured isomer, takes place. However, there was negligible change in the product-spread.

**Table 5.6: Effect of catalysts concentration in the isopropylation of *p*-xylene over Fe/Beta using 2-bromopropane as alkylating agent[a]**

| | Catalyst Concentration (wt.% w.r.t. total reaction mixture)(g) | | |
|---|---|---|---|
| | 0.73 | 1.44 | 2.84 |
| Amount of catalyst | 0.1 | 0.2 | 0.4 |
| Time[b] (min) | 35.0 | 20.0 | 14.0 |
| $Sel._{DMCs}$ | 94.0 | 93.0 | 89.6 |
| $Sel._{DIPX}$ | 6.0 | 7.0 | 10.4 |
| $Sel._{2,5\text{-}DMC}$ | 100.0 | 100.0 | 100.0 |

[a] Reaction conditions: Temperature = 353 k, *p*-xylene = 10.6 g, 2-bromopropane = 3.1 g, [b] Time required for complete conversion of 2-bromopropane.

**Table 5.7: Effect of reaction time on the conversion and product selectivity in the isopropylation of C-8 aromatics using 2-bromopropane as alkylating agent over Fe/Beta catalysts[a]**

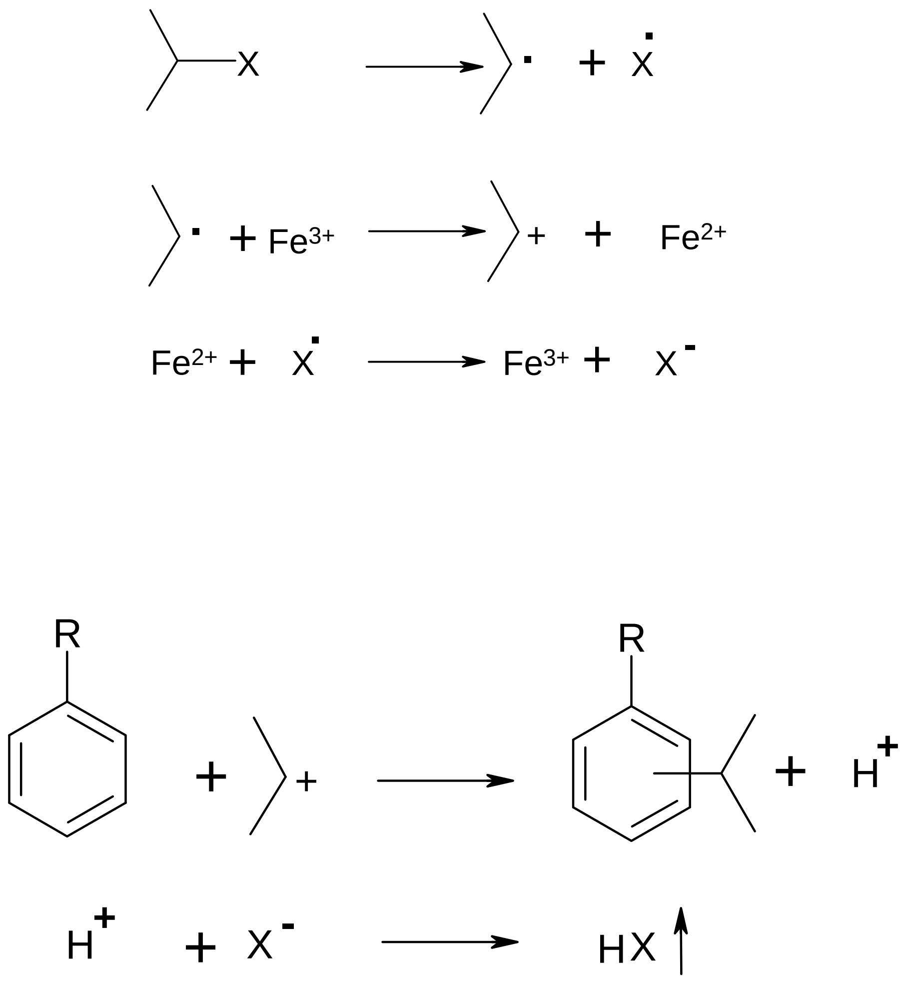
| Substrates | | Conversion or Selectivity (mole%) | | | |
|---|---|---|---|---|---|
| *p*-Xyl. | Time (min) | 5.0 | 10.0 | 15.0 | 20.0 |
| | Conv. of 2-BP | 51.4 | 61.0 | 91.4 | 100.0 |
| | Sel.$_{\text{DMCs}}$ | 97.0 | 95.3 | 94.7 | 93.0 |
| | Sel.$_{\text{DIPX}}$ | 3.0 | 4.7 | 5.3 | 7.0 |
| | Sel. $_{\text{2,5-DMC}}$ | 100.0 | 100.0 | 100.0 | 100.0 |
| *m*-Xyl. | Time (min) | 10.0 | 20.0 | 30.0 | 80.0 |
| | Conv. of 2-BP | 69.2 | 83.6 | 100.0 | 100.0 |
| | Sel.$_{\text{DMCs}}$ | 98.2 | 95.7 | 94.7 | 94.1 |
| | Sel.$_{\text{DIPX}}$ | 1.8 | 4.3 | 5.3 | 5.9 |
| | Sel. $_{\text{3,5-DMC}}$ | 8.2 | 8.6 | 10.2 | 10.3 |
| | Sel. $_{\text{2,4-DMC}}$ | 91.8 | 91.4 | 89.8 | 89.7 |
| *o*-Xyl. | Time (min) | 5.0 | 10.0 | 25.0 | 35.0 |
| | Conv. of 2-BP | 45.0 | 72.9 | 94.0 | 100.0 |
| | Sel.$_{\text{DMCs}}$ | 98.0 | 96.3 | 95.0 | 94.8 |
| | Sel.$_{\text{DIPX}}$ | 2.0 | 3.7 | 5.0 | 5.2 |
| | Sel. $_{\text{3,4-DMC}}$ | 56.5 | 57.5 | 57.5 | 57.0 |
| | Sel. $_{\text{2,3-DMC}}$ | 43.5 | 42.5 | 42.5 | 43.0 |
| EB | Time (min) | 10.0 | 20.0 | 40.0 | 50.0 |
| | Conv. of 2-BP | 57.4 | 69.3 | 92.0 | 100.0 |
| | Sel.$_{\text{ECs}}$ | 95.8 | 94.6 | 91.9 | 91.0 |
| | Sel.$_{\text{DIPEB}}$ | 4.2 | 5.4 | 8.1 | 9.0 |
| | Sel. $_{\text{2-EC}}$ | 31.4 | 31.0 | 30.1 | 30.0 |
| | Sel. $_{\text{3-EC}}$ | 26.8 | 27.0 | 27.4 | 27.3 |
| | Sel. $_{\text{4-EC}}$ | 41.8 | 42.0 | 42.5 | 42.7 |

[a] Reaction conditions: Temperature = 353 K, Substrate = 10.6 g, 2-bromopropane = 3.1 g, Catalyst = 0.2 g.

### 5.3.8. Reaction Pathway

Although, the detailed mechanistic studies are beyond the scope of the present work, it is reasonable to look into possible reaction pathway. The observed very high catalytic activity of Fe/loaded Beta and other Fe/zeolites in the isopropylation of C-8 aromatic using alkyl halides as alkylating agent is attributed to the presence of non-framework Fe-oxide species. The non-framework iron oxide species are known for their redox properties, which are expected to play a significant role in the activating both the reactants in the isopropylation reaction of aromatic compounds.

Radical pathway type mechanism has been proposed by different authors for the benzylation of aromatics over iron exchanged clays and zeolites [3,5-6]. It is well known that Friedel-Crafts reactions proceed through carbocations [7] and that radicals are powerful reductants, which should readily be oxidized to cations in presence of reducible metallic ions such as $Fe^{3+}$. The high activity observed with those reducible cations could then be ascribed to a different initiation of the reaction, for instance homolytic rupture of the carbon-halogen bond followed by the oxidation of the radical. The probable mechanism is shown in scheme 5.2.



**Scheme 5.2:** The probable mechanism for the formation of isopropylated aromatics over Fe-loaded zeolites using 2-bromopropane as alkylating agent.

## 5.4. CONCLUSIONS

The iron-loaded zeolites are highly active catalysts for the isopropylation of aromatic compounds with very high monoalkylated product selectivity. The high catalytic activity of these zeolite catalysts is attributed probably due to the presence of non-framework Fe-oxide species. The non-framework iron oxide species are known for their redox properties, The aromatic compounds can be effectively isopropylated in liquid phase using Fe/Beta with isopropyl halides at atmospheric pressure and moderate temperature (313 to 353 K) with high catalytic activity (+99%) and > 98% selectivity for monoalkylated products in short reaction times. In addition, the catalyst is solid heterogeneous, reusable and “environmentally friendly”.

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## 6.1. Summary and Conclusions

The objective of the thesis was to explore the systematic and detailed study of the isopropylation of C-8 aromatics (xylenes and ethylbenzene) over zeolites in a fixed bed vapour phase down flow as well as batch reactor and to optimize the reaction conditions for the highest selectivity of dimethylcumenes or ethylcumenes in the isopropylation of xylenes and ethylbenzene respectively.

The ***Chapter one*** presents a general introduction to the isopropylation of C-8 aromatic compounds (xylenes and ethylbenzene) using homogeneous (Friedel-Crafts acid catalysts) as well as heterogeneous acid catalysts. It also briefly describes the synthesis, modification and characterization techniques of different type of microporous metallosilicates and their catalytic application in the isopropylation reaction of C-8 aromatic compounds using alcohols and alkyl halides as alkylating agent.

The ***Chapter two*** describes the synthesis procedure of various large pore zeolites like Beta with different silica-alumina ratio and metallosilicate analogs of the zeolite Beta like B-Beta, Ga-Beta and Fe-Beta. A brief description for the synthesis of other solid acid catalysts like ZSM-5, ZSM-12, Mordenite, MCM-41 and sulfated-zirconia incorporated mainly for comparative purpose. Modification of zeolite Beta, Mordenite and Faujasite using ion exchange method with aqueous solution of ferric nitrate was also described. All the synthesized and modified samples were thoroughly characterized by modern analytical tools like XRD, IR, BET surface area, TG-DTA, SEM and NMR.

The ***Chapter three*** provides the detailed study of vapour phase isopropylation reaction of all xylene isomers (*o*-, *m*- and *p*-xylene) with isopropanol as alkylating agent over zeolite H-Beta and USY. Some other solid acid catalysts like zeolites H-Y, H-Mordenite, silica-alumina, sulfated-zirconia and MCM-41 were also included for comparative studies. B-, Ga- and Fe-Beta were also included for comparative studies in the isopropylation of *m*-xylene. The influences of various reaction parameters such temperature, contact time or WHSV, mole ratios of the substrate to alkylating agent and time on stream have been investigated.

The ***Chapter four*** gives some important informations of the detailed study of vapour phase isopropylation reaction of ethylbenzene with isopropanol as alkylating agent over zeolite Beta, Moredenite and USY. Some other solid acid catalysts like zeolites like H-Y, silica-alumina, sulfated-zirconia and MCM-41 were also used for comparison of catalytic activity. The effect of various reaction parameters such temperature, contact time, substrate to alkylating agent mole ratio and time on stream have been investigated.

The ***Chapter five*** describes the isopropylation reaction of C-8 aromatics (xylenes and ethylbenzene) with isopropyl halides as alkylating agent using iron-exchanged zeolite Beta (Fe/Beta) in the liquid phase batch reactor at relatively low temperature (353K) at atmospheric pressure with very short reaction time. Fe exchanged USY (Fe/USY) and Mordenite (Fe/Mord.) have been used for comparative catalytic activity and selectivity.

The major findings of the thesis include:

### Vapour phase Isopropylation of Xylenes

- The isopropylation of xylene isomers over Beta and USY takes place at relatively lower temperature (413-453 K) exhibiting quite high selectivity for total DMCs.
- The effect of various reaction parameters such as temperature, feed rate, xylene/isopropanol molar ratio and TOS were studied. The optimum conditions for high DMC selectivity are: temperature (423 ± 10 K), WHSV = 3.25 $h^{-1}$, xylene to isopropanol = 6 to 8 (molar) for 1h.

- The isopropylation of m-xylene was also carried out over other solid acid catalysts such as zeolites (HY, H-beta and H-mordenite), and silica-alumina and sulfated-zirconia for comparative studies. Interestingly, while over USY, the $\mathrm{Sel}_{3,5\text{-DMC}}$ was quite high (70-80%), all other solid acid catalysts including other zeolites exhibited high selectivity for 2,4-DMC. It may be recalled here that the formation of 3,5-DMC can also be, at least partly, due to bimolecular isomerization of 2,4-DMC to 3,5-DMC in the case of USY with large void space where bulky bimolecular intermediate can be accommodated. However, in the case of other zeolites (Mordenite and Beta) such bimolecular isomerization does not seem to occur.
- ZSM-5 with 10 membered ring (0.54 x 0.56 nm and 0.51 x 0.55 nm) channels exhibits no catalytic activity even though H-ZSM-5 possesses high strength of acid sites. This is due to the reason that medium sized 10-membered ring channels are too small to accommodate the reactants and products.
- Isopropylation of equilibrium mixture of xylenes (24% *p*-xylene, 54% *m*-xylene and 22% *o*-xylene) over the USY catalyst as a function of TOS, provides the selectivity of all the DMC isomers which follows the order: 3,5-DMC > 3,4-DMC > 2,5-DMC > 2,4-DMC > 2,3-DMC > 2,6-DMC. It may be recalled that the thermodynamic stability of the DMC isomers, also follows the same order.

### Vapour phase Isopropylation of Ethylbenzene

- The alkylation of ethylbenzene with isopropanol was carried out over various catalysts like H-Beta, USY, H-Y, H–Mordenite, ZSM-12, ZSM-5, amorphous silica-alumina, sulfated-zirconia and MCM-41 under identical reaction conditions. Among these catalysts zeolite Beta, USY and Mordenite are quite active catalysts.

- ZSM-5 with three-dimensional intersecting 10-membered rings (0.54 nm x 0.56 nm for straight and 0.51nm x 0.55 nm for sinusoidal) channels exhibits no catalytic activity even though H-ZSM-5 possesses a high strength of acid sites, due to its 10-membered ring medium sized pores.
- Among these three active catalysts (USY, Beta and Modernite), the Mordenite was highly selective towards EC and *p*-EC but less active, on the other hand USY is highly active and less selective for EC. Zeolite Beta follows the middle path.
- The distribution of EC isomers was significantly influenced by pore architecture of the zeolites. Mordenite with relatively narrow pores was highly para-selective, while Beta and USY exhibited less para-selectivity, due to their larger pores, vis-à-vis Mordenite.
- The reaction takes place at relatively lower temperature (413-433 K) exhibiting quite high selectivity for mono isopropylated products.

## LIQUID PHASE ISOPROPYLATION

- The iron-exchanged zeolites are highly active catalysts for the isopropylation of aromatic compounds with very high monoalkylated product selectivity.
- The high catalytic activity of these zeolite catalysts is attributed due to the presence of non-framework $Fe^{3+}$ species. The non-framework iron species are known for their redox properties.
- The aromatic compounds can be effectively isopropylated in liquid phase using Fe-Beta with 2-bromopropane at atmospheric pressure and moderate temperature (313-353 K) with high catalytic activity and selectivity for monoalkylated products in short reaction times (20–60 min).

- The catalyst is solid heterogeneous, reusable and “environmentally friendly”.

## 6.2. FUTURE OUTLOOK

The present thesis describes the detailed and systematic study of isopropylation of C-8 aromatic compounds over zeolites and other solid acid catalysts. As these isopropylated aromatics are converted to corresponding phenolic compounds which are very important sources for the production of pesticides, perfumery, pharmaceuticals, heat-transfer media, polymers, phenolic resins etc., using this procedure the obtained dimethylcumenes (from xylene isopropylation) and ethylcumenes (from ethylbenzene isopropylation) can be used in industrial xylenol/ethylphenol-production process which, involves the following three steps:

1. Isopropylation of C-8 aromatics to DMCs/ECs
2. Oxidation of DMCs/ECs to corresponding dimethylcumene hydroperoxide (DMCHP)/ethylcumene hydroperoxide (ECHP).
3. Acid cleavage of DMCHP/ECHP to corresponding xylenols/ethylphenols and acetone.

Conventionally, xylenols are produced by dimethylation/methylation of phenol / cresols. The main drawback of this route is rather low yield and selectivity for desired product. Further, this route for producing xylenol is a multi-step one and gives a mixture of almost all the xylenol isomers. Therefore, in order to enhance the efficiency of xylenols/ethylphenols production our process could be used effectively.

The iron-loaded zeolites are highly active catalysts for the isopropylation of aromatic compounds with very high monoalkylated product selectivity. The high catalytic activity of these zeolite catalysts is attributed probably due to the presence of non-framework $Fe^{3+}$ species. To find out the exact mechanism more work is needed in this relating new area.

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- Formation of gold nanoparticles by spontaneous reduction of aqueous chloroaurate ions with amorphous silica: A novel approach to nanoparticles synthesis.
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