Worldwide merchant catalyst market is worth nearly $6 billions and it supports chemical processing and manufacturing industries that produce goods worth more than a hundred times that amount. The worldwide market for catalysts is expected to grow about 4% per year during coming few years (1). Almost 60% of all commercial chemicals are obtained in processes using heterogeneous catalysis and that 90% of all new large scale plants involve heterogeneous catalysis. Hence there is no need to overemphasize the practical importance of catalysis in chemical and petroleum processes. Of the chemical conversions being carried out on commercial scale, petroleum and petrochemical industries form a significant fraction. Among various reactions involved in petroleum and petrochemical industries, many reactions, such as catalytic cracking, catalytic reforming, distillate dewaxing, alcohols to hydrocarbons, alkalyation of paraffins and aromatics, isomerization, acylation, toluene disproportionation, hydrolysis etc. are acid catalyzed. All of these reactions yield value-added products.

1.1 ALKYLATION OF AROMATICS

Among above mentioned reactions, alkylation of aromatics has always been the subject of lively concern because of numerous applications of the products. Bulk chemicals e.g., ethyl benzene, cumene, linear alkylbenzenes, alkyl phenols as well as fine chemicals e.g., cymones, diisopropyl benzenes etc. are produced through alkylation reactions (2-4).
1.1.1 Early reports

Various facets of alkylation reactions have been dealt with in detail in many reviews (e.g., 5). Electrophilic alkylation reactions producing afore listed chemicals require acid catalysts. Different types of acid catalysts have been reported (2) for the alkylation reactions. They include Lewis acids (metal halides), Bronsted (protonic) acids, acidic oxides or phosphides, supported acids, acidic resins, etc. Lewis acids or Friedel-Crafts catalysts e.g., AlCl₃, BF₃, BCl₃, BBr₃, BeCl₂, CdCl₂, ZnCl₂, GaCl₃, GaBr₃, FeCl₃, SbCl₃, BiCl₃, TiCl₄, ZrCl₄, SnCl₄ and UCl₅, SbCl₅ are capable of attracting electrons from basic reagent making it active species to alkylate the aromatic hydrocarbons (8-10, 14). Of metal halides referred to above AlCl₃ (2,6,7) and BF₃ (11,12) are widely used due to their low cost and abundant availability. Metal alkyls and alkoxides possess less acidity as compared to that of metal halide. However, they have been reported (2) to catalyze Friedel-Crafts reactions. Similarly use of protonic acids e.g., H₂SO₄, HF, HCl and H₃PO₄ either alone (2,13,16) or in combination with Lewis acids forming conjugate supere acids (15,17) has been documented. Synthesis of ethylbenzene using a mixture of AlCl₃ and HCl in a commercial process is an example of application of combination of Bronsted and Lewis acids (14).

Acids supported on substrate have been employed for alkylation reactions (18-20). BF₃ and Al₂O₃, and SbF₅, TaF₅ or NbF₅ on flourinated Al₂O₃ or graphite are the examples of
supported acid catalysts. (2). BF supported on Al₂O₃ in Alkar process for benzene ethylation (21) and H₃PO₄ on kieselguhr for benzene isopropylation to cumene in the UOP process (22) are the illustrations of commercial applications of supported acid catalysts. For vapour-phase alkylation reactions acidic oxides or phufides are generally used. Most widely encountered systems are based on SiO₂, Al₂O₃, alumino silicates containing oxides of Cr, Mg, Mo, Ti, Th, W, Zr, B, Sn, Pd etc. (2,23-25).

Alkylation can be accomplished using olefin producing species as an alkylating agent (26). However, for practical reasons olefins are preferred for this purpose. Besides, alkyl halides were also widely studied as alkylating reagents (27). Some of the conclusions reported for alkyl halide - metal halide - aromatic systems are discussed here. The activity of alkylhalides had been shown to decrease in the order R - F > R - Cl > R - Br > R - I, (R = alkyl) (28). Product obtained in alkylation reaction using alkyl halide would depend on the type of catalyst and conditions employed as shown below (29).

\[
\text{H}_2\text{C} = \text{CH} \quad \text{CH}_2\text{Cl} \quad \text{H}_3\text{C} - \text{C} - \text{CH}_2\text{Cl}
\]

\[
\text{H}_2\text{C} = \text{CH} \quad \text{CH}_2\text{Cl} \quad \text{FeCl}_3 \quad -15^\circ\text{C}
\]
Severe operating conditions and strong acidity of the catalyst result in predominance of m-isomer in the product (30-32). When alcohols are used as alkylating agents, the ease of the reaction decreases in the sequence tertiary > secondary > primary > methyl. Due to this reason benzene could not be methylated with methanol at lower temperatures (33). Lewis acids SbF₅ and AlCl₃ have been judged to be the strong acids whereas other metal halides like BF₃, FeCl₃, etc., Bronsted acids, inorganic oxides and zeolites are milder acids (34). Thus different product distributions are expected on the catalysts depending on their acid strengths.

1.1.2 Drawbacks of the conventional systems

Hitherto encountered catalyst systems though active enough, are inherently accompanied by several practical problems which necessitate to look for other catalyst systems. Following are the unfavourable factors which render the liquid and supported acids less suitable.

- No product selectivity can be expected on high strength acid catalysts due to uncontrolled isomerization of products. Acidity of the catalysts cannot be minutely tuned in accordance with the requirements.

- Large amounts of catalyst are consumed. In case of ethylbenzene synthesis 10-30 kg of AlCl₃ + HCl is consumed per ton of ethylbenzene produced and in case of cumene 150-180 kg H₂SO₄ is consumed per ton of cumene produced (36).
Even when catalyst consumption is less e.g., for cumene synthesis only 1 kg of H_3PO_4 is consumed per ton of cumene formed, the problem of severe corrosion of the equipment is encountered. This also requires special resistant material for construction of product handling equipment.

- Difficult separation of the catalyst from the product for re-use and contaminated products are obtained.
- Spent catalyst requires special and environmentally-acceptable disposal.
- Process water pollution abatement measures are required.

1.2 USE OF ZEOLITES

There is thus a need to develop a catalyst which can overcome aforementioned drawbacks. From this point, zeolites are strong candidates. Zeolites as solid acids offer certain advantages over liquid acid catalysts (38,39). Some of them are listed below.

- Well defined crystal structure
- High surface area (\( > 600 \text{ m}^2/\text{g} \))
- Uniform pores with one or more discrete sizes
- Good thermal stability
- Ability to sorb and concentrate hydrocarbons
- Highly acidic sites
- Regenerability of the catalysts
- Easy separation of product, reduced cost of production
- Increasing the supply of products from unconventional feed stocks
- Fine control of acidity and pore size resulting in enhanced product selectivity

Zeolites are crystalline aluminosilicate and possess well defined active sites predominantly > 97% inside the crystals. Building-in catalytically active sites within the intracrystalline cavities and pores of zeolites is the basis for molecular shape selectivity (40), a unique feature of zeolites which discriminates the molecules involved in the reactions based on their size and shape. The shape selectivity is achieved by virtue of geometric factors, coulombic field interactions and diffusional effects (41).

1.2.1 Initial attempts

Taking advantage of these particular properties of zeolites, many alkylation reactions have been attempted and few of them have successfully been transformed into commercial processes. Earliest reference to the use of zeolites as catalysts for alkylation reaction dates back to 1966 (42,43). Venuto et al. (42,43) employed rare earth exchanged high aluminium zeolites X and Y for alkylation of benzene and toluene with olefins and alcohols. Higher para selectivity (45-50%) in the reaction of toluene methylation over modified zeolite Y was attributed to the suppression of isomerization of the primary, para product (44,45). For the
reaction of benzene ethylation faujasite as well as mordenite has been reported \(42,43,46,47\). Though these zeolites were active, they suffered from rapid aging due to coking. Since their Al content is high they are susceptible to structure collapse in the hydrothermal conditions prevailing during the reaction.

With the advent \(48\) of high silica zeolite, ZSM-5, a new era started in the field of zeolite catalysis. This zeolite presented certain advantages over previously known zeolites in terms of better hydrothermal stability and negligible aging with time. Efforts were made by many workers to attenuate the channel cross section and acidity of the zeolite ZSM-5 so as to give maximum yields of the desired product in the reactions of alkylation of aromatics. Synthesis of variety of bulk as well as specialty aromatics have been attempted over different zeolites. Pertinent results of the studies on varied alkylation reactions are summarized below.

1.2.1.1 Bulk aromatics

1.2.1.1.1 Mono alkylated aromatics

1.2.1.1.1.1 Benzene ethylation

Monoalkylated benzene, ethylbenzene, is a key intermediated in the manufacture of styrene, one of the most important polymers. Approximately 90% of all ethylbenzene is produced via acid catalyzed alkylation of benzene with
ethylene. Remaining 10% is obtained directly from petroleum (39). Modification of zeolite ZSM-5 by steaming and impregnation of P and La resulted in improved ethylbenzene selectivity (49). Chandavar et al. (50) studied the mechanistic aspect of benzene ethylation. They concluded that ethylation with ethanol does not proceed through dehydration of ethanol but direct alkylation with ethanol takes place. Kinetic study by Tao (51) indicates that benzene is less strongly adsorbed than ethylene and surface reaction is the rate controlling step. The Mobil-Badger process, announced in 1976 (52), for ethylbenzene synthesis employs ZSM-5 based catalyst. Using ethylene feed stocks as low as 10 mol % purity (such as FCC off-gas) (53), this process gives 99.6% ethylbenzene reaction selectivity (54). Operating parameters for prior processes and Mobil-Badger process have been compared (55) and shown that the latter is highly energy efficient. The advantages offered by this process resulted in installation of ethylbenzene manufacturing capacity exceeding 6 million MTPY since the commercialization of this process in 1980 (53). Recently Levesque (56) has reported of a process being developed at Union Carbide in which ethylbenzene selectivity as low as 68% was observed using steamed ZSM-5. However, the positive point of the process is that, it can tolerate dilution typically up to 10% ethanol concentration dispensing with requirement of concentrating ethanol, an energy consuming step.
1.2.1.1.2 Benzene isopropylation

The other mono-alkylated benzene, being produced in the bulk quantity is cumene. Recent statistics (57) show a significant increase in cumene production capacity worldover. UOP process (22) employing HPO on kieselguhr ($62 - 65\%$ PO$_4^{3-} + 25\%$ SiO$_2$) is still widely used.

Kaeding and Holland (58) and Balakrishnan et al. (59) used ZSM-5 for benzene isopropylation. The former have shown cumene selectivity to decrease with reaction temperature. Zeolites modified with Zn and Cu (60), Fe (61) and P and B (62) were studied for the title reaction. Chandavar et al. (62) observed improved cumene selectivity upon poisoning acid sites with pyridine and held higher acid strength of the sites responsible for cumene isomerization to n propylbenzene. Of the B and Fe substituted ZSM-5, the latter was found (63) to be more effective and successive regenerations did not affect its activity. Pradhan et al. (64) showed zeolite Eu-1 to be more selective to cumene than ZSM-5 with very less formation of n propyl benzene. In addition to above mentioned medium pore zeolites, large pore zeolites e.g., Y (65), M (66), omega (67), beta (68), ZSM-12 (59,69) have been studied for benzene isopropylation reaction. General conclusion of the study on these zeolites was that over large pore zeolites n propylbenzene did not form at all. Steaming decreases the number of strong acid sites of ZSM-12 increased as reported by Weiyi et al. (69) from TPD, IR and pyridine pulse measurements. Moderately
strong acid sites were shown to be useful in the main alkylation reaction. Reddy et al. (68) modified zeolite beta with La, Ca and Mg and studied influence of operating parameters.

1.2.1.1.2 Dialkylated benzenes

The dialkylated benzenes also form a very important base for variety of commercial petrochemicals. In the ensuing discussion, the prominent results of studies on the production of dialkyl benzenes employing zeolite catalysts are reviewed.

1.2.1.1.2.1 Toluene methylation

The commercial importance of the primary product of the title reaction, p-xylene, need not be overemphasized. It is known (70) that unmodified ZSM-5 gives the isomer distribution near thermodynamic equilibrium composition, in which the proportion of the valued p-isomer is only ca. 25%. Hence the zeolite requires modification to obtain higher p-xylene selectivity. With P, B and Mg modified HZSM-5, 90% of p-isomer in xylenes was obtained in the reaction of toluene methylation as against 24% on unmodified HZSM-5 (71). In studying impregnation of ZSM-5 with Ni, Mg and P, Derewnski et al. (74) showed that P preferentially neutralized the strongest acid sites whereas Ni and Mg did not exhibit such selectivity and they reduced only weak acid sites to the extent proportional to their loadings. P-HZSM-5 showed p-
xylene selectivity in the range of 95 - 100%. Based on these results they concluded that metal impregnation involved chemical phenomenon of altering the concentration and strength of acid sites in addition to causing diffusional hindrance to the molecules of xylenes formed inside the channels. Chen (75) attributed higher p-selectivity to the diffusional effects based on his study with ZSM-5 zeolite having different crystal sizes. Similar conclusion was reached by Unneberg and Kolboe (76) and Ducarme and Vedrine (77). Higher p-selectivity in xylenes over highly siliceous ZSM-5 (Si/Al = 100 - 1000) was ascribed (78) to lower concentration of Bronsted acid sites resulting in suppression of isomerization of p-xylene. Giordano et al. (79) studied Fe, B and P modified ZSM - 5. They showed preferential adsorption of m - and o-isomers as compared to that of less polar p-xylene resulting in the rapid desorption for higher para selectivity. Bhat (80) and Cavallaro et al. (81) had also advanced such an opinion. Huang et al. (82) obtained 95% para selectivity by double impregnation of P and Mg on ZSM-5. In addition to elements mentioned above, use of Ba and Co also was reported (83) to impregnate ZSM-5. Ca impregnated, F-containing zeolite gave 94% p-xylene selectivity at enhanced toluene conversion (84). Isomerization of p-xylene was suppressed by modifying ZSM-5 with MgO and thereby poisoning strong acid sites in the reaction of toluene methylation (86). Contribution of diffusional effects was rated more than that of weakening of strong Bronsted, acid sites upon modifications (85). Though all these modifications
enhanced para selectivity, activity of modified zeolite was less than that of parent zeolite and also aging was faster.

Borade et al. (87) modified Cr-ZSM-5 with B, Mg and P and achieved p-xylene selectivity of 75%. The enhancement of p-xylene selectivity was ascribed to moderate acid sites of isomorphous zeolites. Among zeolites containing B, Fe, Cr or Al in the tetrahedral position, the one with B was found to give highest p-xylene selectivity, which was related with zeolites weak acidity (88) of the zeolite.

Weisz (73) reported that all the three isomers of xylene form inside the channels of ZSM-5. Contrary to this, Paparatto et al. (89) proposed that p-isomer selectivity forms inside the channels, which by secondary isomerization on the external surface converts to other two isomers. Acid sites on external surface can be selectivity neutralized by chemical vapor deposition of Si. This technique was shown (90) to narrow the pores and passivate the external surface acid sites resulting in enhanced para selectivity.

In addition to zeolite ZSM-5, other zeolites varying in their channel dimensions and structure also have been reported. These include ZSM-8 (91), ZSM-22 (92,93), ZSM-35 (94), ZSM-48 (95) and ZSM-57 (96). Kumar and Ratnasmay (97) established the sequence in decreasing p-selectivity for the reaction of toluene methylation as, ZSM-22 \( \sim \) ZSM-23 \( > \) ZSM-48 \( > \) ZSM-5.
1.2.1.1.2.2 Toluene ethylation

The desired product of this reaction is p-ethyltoluene. Dehydrogenation of p-ethyltoluene gives p-methylstyrene, an important monomer for the production of poly para methylstyrene. Cheaper raw material toluene instead of benzene-and better physical and processing properties of poly paramethylstyrene than those of conventional polystyrene have contributed for the development of this process. In fact, based on modified ZSM-5 zeolite catalyst, one unit with production capacity of 35 million lbs of p-ethyltoluene is in operation (53).

As for the reaction of toluene methylation for this reaction too, several studies dealt with the para selectivity enhancement. Fraenkel and Levy (98) observed similar effect of large crystals of ZSM-5 on its catalytic performance in the reaction of toluene ethylation as was reported by Unneberg and Kolboe (76). Workers at Mobil R & D (70) assigned the enhanced p-selectivity with modified zeolite to the diffusional hindrance caused to the movement of molecules involved in the reactions. However, others like Lonyi et al. (99), Chandavar et al. (100) and Paparatto et al. (89) correlated p-ethyltoluene selectivity with weakened acidity upon modification of the zeolite. Lee and Wang (101) studied the kinetics of the title reaction over HZSM-5 and concluded that adsorption of ethylene controlled the reaction.
1.2.1.2 Specialty chemicals

Many alkylated benzenes find applications in drugs, perfumery, agro chemicals, dyes and polymer industries. Some of them are reviewed here.

1.2.1.2.1 Dialkylated benzenes

1.2.1.2.1.1 Toluene isopropylation

Desired product of the title reaction, p-cymene, forms an important intermediate for perfumery, agrochemical and dye industries. In addition to this, it can also be used as a heat transfer medium. Zeolites with variety of channel dimensions and structures have been attempted for cymene synthesis. Young et al. (102) and Flockhart et al. (109) alkylated toluene with propylene over HZSM-5 on which p- and o-cymenes were selectively cracked. The enriched m-isomer was intended for the production of m-cresol. Zn substituted ZSM-5 gave 98% of p-cymene selectivity at 573K as reported by Desimone and Haddad (103). Fraenkel and Levy (98) observed p-selectivity even on small crystals of ZSM-5 ascribing to larger molecular size of cymenes. They did not observe formation of o-cymene at lower toluene conversions. The other medium pore zeolite reported for the title reaction was ZSM-48 (95).

In addition to medium pore zeolites, the ones with 12-oxygen membered rings e.g., HZSM-12 (102), steamed AlPO4 – 5 (107) and Ni/Sn modified zeolite Y (108) were reported to
catalyze this reaction. Large port zeolites, in general, gave thermodynamic equilibrium composition of cymenes.

1.2.1.2.1.2 Cumene isopropylation

An important intermediate for the production of numerous polymers (110, 111), diisopropylbenzenes (DIPBs) can be synthesized by cumene isopropylation. Resorcinol and hydroquinone are commercially manufactured following new synthetic route using DIPBs. Due to molecular size of DIPBs only large pore zeolites were the choice for the title reaction.

Use of zeolites Y (112), steamed and unsteamed ZSM-12 (113, 114), steamed AlPO4 - 5 (107), alkali or alkaline earth metal modified zeolite L (116) was reported for cumene isopropylation. Because of the channel size and dimensionalities of the above mentioned zeolites, their life cannot be expected to be longer. For this reason the zeolite with 12 oxygen membered rings and channels running in three dimensions can be the most suitable catalyst.

1.2.1.2.1.3 Ethylbenzene ethylation

Para-diethylbenzene, the desired product of the reaction finds commercial application as a desorbent in the selective separation of p-xylene from its isomers. Dehydrogenation of diethylbenzene gives divinylbenzenes, which is used as a cross linking agent for styrene. As in the case of toluene methylation, in this reaction also high
concentration of m-isomer is obtained with unmodified zeolite ZSM-5 whereas upon modification, p-diethylbenzene concentration as high as 99+% could be obtained (54). High (96%) p-selectivity obtained over La and Mg modified ZSM-5 has been ascribed not only to reduction in pore dimensions but also to the modification of acidity (118). Similar attribute was made by Kim et al. (119) after studying the reaction over Mg, P and B oxide modified ZSM-5 zeolites. Halgeri et al. (120) observed an increase in p-selectivity from 68% to 99.7% following modification of external surface sites of Ga-ZSM-5 with Si and established a relationship between extent of silylation and catalytic performance of the zeolite. On tetraethyl orthosilicate treated B-, Cr- and Al-ZSM-5 92% diethylbenzene selectivity and 99+% p-selectivity were observed (121).

1.2.1.2.2 Multialkylations

Multialkylated benzenes e.g., trimethylbenzenes, tetramethylbenzenes, dimethylethylbenzenes etc. form starting materials for manufacturing dyes, pharmaceuticals, heat resistant polymers, antioxidants, plasticizers for polymers, fragrances etc. (122). Yashima (86) alkylated individual xylene isomers with methanol on unmodified ZSM-5 and observed a selective (99%) formation of 1,2,4 trimethylbenzene. Ease of alkylation of xylene followed the trend, p->m->o-xylene. Performance of the catalyst was explained on the basis of close matching of dimensions of the channels and those of 1,2,4 trimethylbenzene molecules.
Similar selectivity for dimethylethylbenzene has been reported by Kaeding et al. (54). Yashima (86) compared the performance of various zeolites namely, ZSM-5, Y and M for alkylation of 1,2,4 trimethylbenzene with methanol and observed the selectivity of 98%, 44% and 42% for 1,2,4,5 tetramethylbenzene on these zeolites, respectively. Distribution of tetramethylbenzenes could be easily correlated to the channel dimensions of the zeolites. By poisoning the external surface acid sites with 2,4 dimethylquinoline Yashima et al. (124) observed suppression of the production of aromatics larger than 1,2,4,5 tetramethylbenzene.

1.2.1.2.3 Alkylation of multiring aromatics

In the foregoing discussions alkylation of aromatics with single ring has been dealt with. Of late alkylation of naphthalene has drawn attention of many workers. 2-isopropyl naphthalene, product of selective isopropylation of naphthalene, is a raw material for manufacture of 2-naphthol, which in turn is useful for the production of medicinal organics, dyes, perfumes, antioxidants etc. So far use of zeolite for naphthalene isopropylation has not been reported.

Extension of the product of the former reaction of 2,6 diisopropynaphthalene and 4,4' diisopropylbiphenyl is of interest since these two products form potential raw materials for monomers used for polymers having high tensile strength. An equilibrium distribution of products is obtained
Katayama et al., using either AlCl or SiO$_2$-Al$_2$O$_3$ (125). Katayama et al. (126) have shown mordenite to be an effective catalyst for this synthesis. Fellmann et al. (127) stressed on proper Si:Al ratio and certain Al NMR features to be possessed by mordenite catalyst to have good life and high selectivity for 2,6 diisopropynaphthaene synthesis.

1.3 CURRENT TRENDS

Thus one can have idea as to the importance of alkylation reactions carried out on commercial scale. Also a trend towards the use of more and more environment friendly and energy efficient catalysts is evident. Replacement of liquid acids with zeolites is an illustration of this trend. Hence it is appropriate to have a look at the peculiarities of zeolites as catalysts. Ensuing discussion relates to the zeolite structures, acidity and shape selectivity, acidity modifications by various treatments, kinetics of zeolite catalyzed reactions etc.

1.3.1 Zeolite structure

Zeolites are crystalline, hydrated alumino-silicates of Group I and II elements. Their structures comprise of a framework based on an infinitely extending, three dimensional network of SiO$_4$ and AlO$_4$ tetrahedra linked together through 4 common oxygen atoms. Presence of Al gives rise to a net negative charge compensated by the cations. Their unit cell
composition can be presented as,

\[ M \left[ \left( \frac{Al}{x} \right) \left( \frac{Si}{2} \right) \right]_x \left( \frac{H}{2} \right)_0 \]

where \( n \) is valency of cation \( M \).

Of naturally occurring 34 zeolites very few found commercial applications. Synthetic zeolites offer a channel size ranging from ca. 3Å to ca. 12Å. Diameters of the channels depend on number of tetrahedral units or, alternately, oxygen atoms and the nature of cations that are present in the pores. Zeolites are generally lumped into three classes according their channel dimensions (39). They are shown in Table 1.1.

### Table 1.1 Classification of the zeolites

<table>
<thead>
<tr>
<th>Pore size</th>
<th>Number of terahedra</th>
<th>Maximum free diameter, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small</td>
<td>6, 8</td>
<td>3.0-4.3</td>
</tr>
<tr>
<td>Medium</td>
<td>10</td>
<td>6.3</td>
</tr>
<tr>
<td>Large</td>
<td>12</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Table 1.2 gives an idea on channel systems of commercially important zeolites (35).

Shape of 8-membered oxygen ring varies from circular to puckered to elliptical and accordingly dimension of pore opening varies. These zeolites can sorb straight chain molecules such as n-paraffins, olefins and primary alcohols. Channel systems of these zeolites also contain interconnecting supercages of sizes larger than those of the
Table 1.2 Crystallographic information on the zeolites

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Channel size and dimensionality</th>
<th>Cavity</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Small pore</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linde type A</td>
<td>(8) 4.1, 3D</td>
<td>6.6, 11.4</td>
</tr>
<tr>
<td>Erionite</td>
<td>(8) 3.6 x 5.2, 3D</td>
<td>6.3 x 13</td>
</tr>
<tr>
<td>Ferrierite</td>
<td>(8) 3.4 x 4.8, 1D (10) 4.3 x 5.5, 1D</td>
<td>interconnected channels</td>
</tr>
<tr>
<td><strong>Medium pore</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZSM-5</td>
<td>(10) 5.4 x 5.6, 1D (10) 5.1 x 5.5, 1D</td>
<td>9, interconnected channels</td>
</tr>
<tr>
<td>ZSM-11</td>
<td>(10) 5.1 x 5.5, 3D</td>
<td>interconnected channels</td>
</tr>
<tr>
<td><strong>Large pore</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Offretite</td>
<td>(8) 3.6 x 5.2, 2D (12) 6.4, 1D</td>
<td>6.0 x 7.4, interconnected channels</td>
</tr>
<tr>
<td>Faujasite</td>
<td>(12) 7.4, 3D</td>
<td>13, 6.6, 11.8</td>
</tr>
<tr>
<td>Mordenite</td>
<td>(8) 2.8 x 5.7, 1D (12) 6.7 x 7.0, 1D</td>
<td>interconnected channels</td>
</tr>
</tbody>
</table>

(a) number of oxygen atoms forming rings determining their size (in parantheses), pore dimensions in Å, and channel dimensionality
(b) cavity free dimensions in Å

Connecting windows. Bulky molecules such as polycyclic aromatics form inside the supercages and due to narrowness of the windows trap inside resulting in coking (104). Erionite, a small pore zeolite is an example of an industrial application in the Selectoforming process (105).
Zeolites with 10-membered oxygen ring opening are also known as medium pore Zeolites. Among varieties of unique crystal structure types in this group are ZSM-5 and ZSM-11 which are known as pentasils, theta-1 which is isostructural with ZSM-22, ZSM-23, ZSM-48 etc. The shape and size of 10-membered oxygen rings varies from one structure to another. They range from near circular to elliptical to teardrops. Among the zeolites mentioned above only ZSM-5 and ZSM-11 possess bidirectional intersecting channels. Remaining zeolites possess unidirectional nonintersecting channels. Hence the deactivation due to pore blockage in case of the latter zeolites is faster. ZSM-5 and HZSM-11 are remarkably stable as acid catalysts. Unlike other zeolites, they have pores of uniform dimension without any supercages. In addition to this, higher Si/Al ratios and geometrical constraints imposed by 10-membered rings have been found to be the attributes for less propensity of the zeolites to coking. Fig.1.1 depicts schematically the channel system of zeolite ZSM-5 (128). Two channels differ in their pore size (129). Sinusoidal channels have a near circular opening of 5.4x5.6Å whereas straight running channels are with elliptical cross section of 5.1x5.5Å. The free diameter at channel intersections is about 9Å. ZSM-11, another medium pore zeolite possesses two straight, elliptical (5.1x5.5Å) channels intersecting at right angles (130).
1.3.2 Rise of acidity and shape selectivity in zeolites

Fig. 1.2 shows how Bronsted and Lewis acidity form in the zeolites.

When zeolite is calcined at temperature above 773K, the number of Bronsted acid sites gradually decreases with temperature accompanied by an increase in number of Lewis
acid sites. Pyridine adsorption on Bronsted and Lewis acid sites gives IR frequency stretching at 1540 and 1450/cm, respectively. This helps know proportion of Bronsted and Lewis acid sites. Number of acid sites equals the number of Al present in tetrahedral position in the zeolite. However, the activity of zeolite or total acidity does not depend solely on number of acid sites but density of acid sites, their location, strength and efficiency coefficient would also play role in determination of the total acidity of the zeolite. Though both, Bronsted and Lewis types of acid sites, prevail in the zeolite, the former predominates if the zeolite had not undergone severe heat treatments. The frequency of stretching of hydroxyl groups decreases as the framework Si to Al ratio increases reflecting weakening of hydroxyl bond which is commonly associated with increased acidity (131). From IR and H-NMR studies it could be concluded that upto a Si/Al ratio of 5-6 for faujasite and 9-10 for MFI structure, acid strength increases and this was confirmed with catalytic reaction (132-134). Olson et al. (135) and Derouane et al. (136) showed catalytic activity per site to be independent of Si/Al ratio of HZSM-5. This is not unexpected since the ratio of Si to Al employed by them far exceeded 10. Acidity of the sites depends also on the topology of zeolite in addition to its chemical composition. Strong protons are generated by AlO tetrahedra with no other Al atoms in its next nearest neighborhood (NNN) positions. The NNN tetrahedra irrespective of Al or Si, depends on
structural topology of the zeolite (137). Hence strength of a site is a function of zeolite structure also. Presence of cations (e.g., extraframework Al) in the zeolite gives rise to the presence of protons. However, a recent theoretical study confirmed that the more acidic protons were those attached to AlO tetrahedra (138). Hence, all the protonic sites are not similar and they chemically differ in nature of their closest neighbors. Thus it is evident that location of Al atoms induce specific properties to the protons attached to them and each zeolite structure generates typical site environment (131). Using Sanderson electronegativity model, charges on O and H have been calculated. The value for the latter had been worked out to be in the range of 0.09 to 0.15, the higher the charge, the higher the acidity (139). Local environment has the other influence of weakening or strengthening Al-O bonds. Weak Al-O bonds would leave the oxygen orbitals available to form a strong O-H bond, i.e., to give rise to weak acidity (137).

1.3.3 Shape selectivity

As seen earlier, zeolites have almost no pore size distribution. Adsorption and diffusion of molecules with dimensions larger than those of pore openings are ruled out. Also, uniform dimensions of channels in zeolite require the molecules involved in the reactions to be smaller than channel cross section. Thus zeolites neither allow larger sized reactants to penetrate inside the channels nor products with large size to form and diffuse freely inside the
crystals. Based on the restrictions imposed at different stages during the occurrence of the reactions, various types of selectivities have been proposed. They are,
- reactant selectivity,
- transition state selectivity, and
- product selectivity.
- other selectivities

Each of these is discussed below in brief.

Reactant selectivity is observed when only a fraction of reactants find access to the internal active sites because of molecular sieving effects. Excluded reactants would have zero or small local concentration inside the zeolite and will not be converted to any reasonable extent in comparison to molecules allowed to diffuse inside the channels. More of n-butanol was dehydrated than i-butanol over small pore zeolite CaA. Such a discrimination based on size of alcohol molecules was not observed over large pore zeolite CaX (140). Similar other examples of preference for linear aliphatics to the branched ones and linear diolefins and piperylene to isoprene (141) and n-hexane to 3-methyl pentane (142) were reported.

Product selectivity is observed when some of the product molecules are too bulky to diffuse out or when they possess a low diffusivity relative to others. They convert either to less bulky products by subsequent reactions (e.g., cracking) or to bulkier products which eventually deactivates
the catalyst (e.g., coking). In the reaction of toluene methylation, though all the three isomers of xylene form inside the channels of ZSM-5, para-xylene predominates as the observed product. This is due to its higher diffusivity by 3 to 4 order of magnitude than the remaining two isomers (72,73).

Transition state shape selectivity is observed when reactant and product molecules are small enough to diffuse through the channels, but the reaction intermediates are larger and spatially constrained. Reaction leading to larger transition molecules does not proceed inside the channels. Csicsery (143) observed the absence of symmetrical trialkybenzenes in the products from the disproportionation of dialkylbenzene over HM. Since the reaction is bimolecular, the diphenylalkane type intermediates must require more space than available in mordenite channels. Independent experiments ruled out the roles of size exclusion or configuration diffusion of 1,3,5 trialkylbenzene. Hence the selectivity observed derives its name. In the reaction of xylene isomerization, desired monomolecular isomerization proceeds far ahead of the undesired bimolecular disproportionation on HZSM-5 as observed by Haag and Dwyer (144). When same reaction was carried out over large pore zeolite, HY, disproportionation reaction predominates over isomerization reaction. The question of transport mechanism does not apply for the spatial inhibition mechanism operating on the intermediate complex (145). This selectivity is
independent of crystal size and activity, but depends on pore diameter (105). Amelse (146), in studying the mechanism of transethylation of ethylbenzene over medium and large pore zeolites, concluded that on the former, reaction proceeds via dealkylation-alkylation mechanism whereas on the latter, reaction goes through the formation of biphenylethane. This difference in mechanism was ascribed to the transition-state selectivity.

Other somewhat less important expressions of molecular shape selectivity e.g., concentration effects (147), molecular traffic control (148), molecular circulation (149) etc. were advanced. However, their existence and actual operative mechanisms are still polemic.

Above discussed selectivities are schematized in Fig.1.3

1.3.4 Need for modifications

As seen above, diffusivity of molecules in the channels of zeolite plays a paramount role in the determination of selectivities. Hence, to enhance the specificity to the desired product, different post-synthesis modifications have been attempted. These modifications resulted in reduced channel cross sectional area(70). Also, strong acid sites have been held responsible for undesired subsequent reactions. Due to the absence of spatial constraints, the sites residing on the external surface can catalyze nonshape selective reactions.
Consequently it is necessary
- to reduce the strength of acid sites inside the channels,
- to deliberately cause diffusional hindrance inside the channels,
- to poison or weaken acid sites on the external surface,
- to finely reduce pore opening on the surface,
- to reduce Al content of the zeolite, or
- to substitute Al with other trivalent elements e.g., B, Fe, Ga, Cr etc. in the framework of the zeolite
to manipulate the acidity of zeolite to achieve an enhanced selectivity to the desired product, though at slightly reduced activity. Afore-mentioned modifications except isomorphous substitutions are accomplished after the synthesis of zeolite. However, other modifications are also known which can be carried out during synthesis of the zeolite. These include growing larger crystals and zeolites with different Si to Al ratios. Ensuing discussion relates to the pertinent influences of various modifications and their operative mechanisms.

1.3.4.1 Impregnation

Kaeding and his co-workers impregnated zeolite ZSM-5 with oxides of variety of metals e.g., Mg, P, Ca, Mn, B, Si etc. for toluene methylation (71), toluene ethylation (70) and ethylbenzene ethylation (151) and observed enhanced selectivity to p-isomers of the primary products. They held increased difference between diffusivities of para isomer and other two isomers responsible for this enhancement. Kim et al. (119), Chandavar et al. (100) and Syed et al. (153) also modified zeolite with Mg, P and B. From ammonia TPD and pyridine adsorption studies they concluded that reduced acidity rather than increased diffusivity difference was responsible for enhanced para selectivity. Lercher et al. (154) proposed a model shown in Fig.1.4 depicting the formation of two weak acidic OH upon modification of strong Bronsted acid sites with HPO$_3^{4-}$. 

\[ \text{HPO}_3^{4-} \]
Lonyi et al. (99) adsorbed pyridine and lutidine on HZSM-5 zeolite. Of these two bases, former is smaller in size and stronger in basicity and its adsorption resulted in higher p-selectivity than that yielded by the adsorption of lutidine. This supported the proposition that acidity is a predominating factor in determination of p-selectivity. Hence the existence of diffusional constraints specifically adjusted to allow para selectivity seems to become more and more questionable. Although partial filling of the pore volume by P containing phases can be affected, kinetic and catalytic data including poisoning experiments seem to support intrinsic kinetic effect rather than a diffusional one (156).

1.3.4.2 External surface site passivation

Paparatto et al. (89) opined that para isomer formed inside the channels of ZSM-5 zeolite and its subsequent isomerization towards thermodynamic equilibrium proceeded on the external surface. Various workers neutralized sites on external surface by adsorbing either large molecule organic bases or Si compounds. Attempts also have been reported where surface Al was selectively leached out and substituted.
by Si. Yashima (86) observed 100% selectivity to 1,2,4,5-isomer in tetramethylbenzenes produced in the reaction of 1,2,4-trimethyl benzene methylation over ZSM-5 previously poisoned with 2,4 dimethylquinoline. He showed a selective dealumination of external surface upon contacting ZSM-5 with SiCl at higher temperature for short time. This reduces the number of nonshape selective acid sites.

Of late, vapor phase deposition of Si compounds has drawn much attention. This treatment leaves the zeolite with countermanded surface sites and narrower channel openings. Wang and Ay (157) deposited Si on ZSM-5 using various alkoxides and found ethoxide to be most suitable. Large molecules (~8-9Å) of alkoxides are prevented from entering the channels of ZSM-5 zeolite and hence internal pore structure and acid strength distribution remain unaffected as confirmed from ammonia TPD and IR spectroscopy (158). Results of XPS studies also confirmed the Si deposition on the external surface only (159). Loading to the extent of 10 wt% SiO reduces external surface area by half (160). Niwa and Murakami (161) proposed a mechanism shown in Fig. 1.5 to explain the propagation of SiO layer on the surface of zeolite. Recently Halgeri et al. (120) studied various alkylation reactions on silylated gallosilicate of MFI structure. They observed an increase in para selectivity in the order, xylene < ethyl toluene < diethylbenzene.
Fig. 1.5 Passivation of acid sites by silylation.

1.3.4.3 Isomorphous substitution of Al

Foregoing discussion establishes that weakening of strong acid sites results in suppression of subsequent reactions. The other way of modifying the acid sites is to substitute Al with other trivalent metals. Recently metallosilicates have drawn a lot of attention as new
catalytic materials (162). Though substitution by number of elements is possible relatively few and that too only in pentasil zeolites have found wide considerations. These substitutions were reported to alter the acidic and catalytic properties of the zeolites (163). Among isomorphously substituted ZSM-5 zeolites, B-ZSM-5 has been studied in much detail as to physico-chemical characterization as well as catalytic aspects. In fact, B-ZSM-5 is used as a xylene isomerization catalyst on commercial scale in Amoco process (164). Halgeri and co-workers (e.g., 165) have studied variety of reactions over B, Fe, Cr, Ga etc. substituted ZSM-5 zeolites and found paradialkyl benzene selectivity to decrease with acidity of the zeolite. Kim et al.(166) found para selectivity to decrease on various ZSM-5 zeolites in the order of Sb > B > Fe > Ga > Al for the reaction of ethylbenzene ethylation.

1.3.4.4 Dealumination and alumination

As shown earlier, acidity and hence catalytic activity of the zeolite is a function of its tetrahedral Al content. Also, hydrothermal stability of the zeolite rich in Al is less. Many catalytic reactions e.g., catalytic cracking warrant removal of Al from the zeolite. Variety of techniques have been reported for extracting Al. They are listed below(167).
Dealumination of High Silica zeolites

A. Chemical treatments

1. Acids (HCl, HF)
2. SiCl vapor
3. \((\text{NH}_4)_2\text{SiF}_6\)
4. F gas
5. Chelating agents

B. Hydrothermal treatment followed by chemical treatments

1. Steaming and leaching

Dealumination by hydrothermal treatment process can be expressed as shown in Fig. 1.6 (168). The Al defect in the above scheme created by dealumination may be eliminated by Si species from the zeolite structure or amorphous silica contained in the material. When dealumination is carried out using SiCl no such vacancy forms since Al is directly substituted by Si.

Removal of tetrahedral Al is expected to reduce the catalytic activity. However, the reverse behaviour also has been observed (e.g., 169). Also, total acidity of zeolite decreases with increase in Si to Al ratios. Thus if the
effect of increase in acid strength per site surpasses the
effect of decrease in number sites, dealumination results in
enhanced catalytic activity. This enhancement is caused by
interaction of OH groups with dislodged Al left in the
channels. Miradatos and Barthomeuf (170) confirmed this
enhancement from ammonia TPD. Ashton et al. (171) inferred a
mechanism for this increase in acidity was similar to one
proposed earlier (170). Strong acid site can be expressed
as, show in Fig. 1.7. Lago et al. (172) studied the influence

![Fig. 1.7 Strong acid sites stemming due to dealumination.](image_url)

of steaming on catalytic activity of HZSM-5 for hexane
cracking and deduced that paired Al atoms in the framework
are required for enhanced acidic centres, which have 45-75
times higher specific activity than normal acid sites. Mild
steaming increases activity of the zeolite whereas severe
hydrothermal treatment ( > 300 torr water vapor pressure for
ZSM-5) (172) reduces the acidity which is proportional to
Al content of the zeolite.

Analogous to dealumination, demetallation of
metallosilicates of ZSM-5 structure has also drawn attention.
In case of Fe- and Ga-ZSM-5, physical characterization has shown a decline in acidity and ion exchange capacity with time of steam treatment (173).

Generating acid sites in the zeolite by insertion of Al in the framework by treating zeolite with aluminium halide has attracted attention of many researchers. (e.g., 174). By this technique Al can be left in extralattice position also in addition to the framework (175). Ammonia TPD, Si NMR and IR results substantiate Al substitution. Chang et al. (176) treated silicalite with different Al sources e.g., AlCl₃, AlBr in gas phase and (NH₄)₂SiF₆ in aqueous solution and concluded from Al MAS-NMR results that only last technique could leave Al in tetrahedral coordination. Generation of strong acidity was confirmed from IR and catalytic results.

So far discussed aspects enable one to make choice of the right zeolite catalysts. However, a successful reactor design to carry out the reaction on commercial scale requires to be preceded by the kinetic study leading to the rate expressions valid in the certain range of the operating parameters.

1.3.5 Kinetics of zeolite catalyzed reactions

Since the channel dimensions of zeolites and molecules involved in the common reactions are comparable, larger diffusional hindrances can be expected. Fig. 1.8 shows the relationship between diffusivity and pore size of the
catalyst (177). It also depicts the activation energies involved in different types of diffusions. Due to this peculiarity it is not possible to overcome intracrystalline diffusional resistances in the case of zeolite catalysts. Hence it can be inferred that the result obtained from the kinetic study is not truly chemical or intrinsic in nature but is diffusion disguised.

Palekar and Rajadhkysha (178) proposed that free gas phase would terminate at the external surface of the zeolite crystallites which contains the sorbed phase inside the channels. This leads one to envisage the adsorption taking

![Graph showing the influence of pore dimensions on diffusivity and activation energy for diffusion.](image)

Fig. 1.8 Influence of pore dimensions on diffusivity and activation energy for diffusion.
place on the crystal surface from the bulk phase. Sorbed reactant molecules surface-diffuse inside the channels and react in sorbed phase. Such a visualization of physical and chemical steps during catalysis has an important implications as to validity of Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic models for zeolites. In the LHHW models adsorption, surface reaction, and desorption is envisaged at each reaction site which is not the case with zeolites. As shown by Palekar and Rajadhyaksha (179), though rate expression is similar to the LHHW models, the significance of the constants involved is not still well understood.

Intrinsic picture free of diffusional effects, can be obtained using effectiveness factors. However, poor precision of diffusivity values imposes restriction on this aspect. In addition to this, diffusion in the zeolite is concentration dependent (180). Various correlations have been reported for this purpose (181). Estimation of intrinsic rate constants for zeolite catalyzed reaction is another difficulty. As shown by Dadyburjor (181) if kinetic study is carried out in a wide temperature range, the value of intrinsic rate constants can be calculated. However, lower temperature of the reaction is limited by the boiling points of the reactants. The corrections for intrinsic activation energies determination have been advanced by Rajadhyaksha and Palekar (37) and employed by Dadyburjor and Bellare (115) for the reaction of cumene cracking on REY.
It also has been proposed (106) that in zeolites active sites are not located so near that conventional dual site mechanism can stand valid. Following the diffusional phenomena in zeolite Eley-Riedal models have been found (152) to represent kinetic data reasonably well. Despite this controversy many workers showed LHHW rate expressions fitting the kinetic data for zeolite catalyzed reactions. Bhat et al. (91) and Mantha et al. (150) studied toluene methylation over HZSM-8, and Hy and HZSM-5, respectively and concluded that for the proposed reaction net work dual site mechanism is operative. However, they did not correct the observed activation energies to the intrinsic ones. Dooley et al. (155) showed that no diffusional hindrance prevails with zeolite Y and NiY for toluene disproportionation at 748K. They (155) showed from the results of Kaeding et al. (123) that upon modification of ZSM-5 with B and Mg, effectiveness factor significantly deviates from 1 for the same reaction. Many other examples have been reported by them (155) where intracrystalline mass transport affected the rates of reactions over variety of zeolites including large port zeolite, mordenite. However, it is not possible to conclude as to the influence of temperature on effectiveness factor since crystal size of zeolites employed by various workers has not been included in the report by Dooley et al. (155). Lee and Wang (101) studied toluene ethylation on HZSM-5 and showed adsorption of ethylene to be the rate controlling step. However, Hsu et al. (117) eliminated external film resistance to mass transfer by fast flow of the feed in the
reaction of ethylbenzene and m-xylene isomerization over Pt-ZSM-5. After elaborate model selection and comparison, the model obtained following law of mass-action (reaction stoichiometry) was found to result in the smallest error. Influence of intracrystalline diffusivity was lumped in the reaction rate constants. Thus there is no conclusive theory as far as kinetics at zeolite catalyzed reactions are concerned.

1.4 OBJECTS OF THE PRESENT STUDY

The literature survey presented on applications of zeolite catalysts for alkylation reactions indicates the detailed work to be done on certain aspects. They are, for example,

- application of isomorphously substituted ZSM-5 zeolites and novel, large port zeolites like beta and SAPO-5.
- modification of the zeolites by various techniques like silylation, steaming, (NH₄)SiF₆ treatment etc.
- mechanistic reaction network and explanation for the formation of certain isomers.
- kinetic studies in detail in the light of the recent advancements.

The industrial importance of the alkylation reactions has already been emphasized. Ethylbenzene, cumene, p-diethylbenzene, p-ethyltoluene etc. are the examples of
chemicals of commercial interest produced following the alkylation reactions. A look at the literature survey showed the following reactions requiring detailed investigations which were covered in this work.

- Benzene isopropylation to cumene
- Toluene ethylation to p-ethyltoluene
- Toluene isopropylation to p-cymene
- Cumene isopropylation to diisopropyl benzenes

Development of the bench scale process know-how for the above mentioned reactions was the basic aim behind this work. Thus, the main object of this study is to cover those areas which lacked detailed investigation earlier. With these objectives in view it is proposed to study in this investigation the following aspects with special reference to the fourth reactions mentioned:

- To synthesize zeolites varying in their channel system, acid properties and crystal size. They include M-ZSM-5 (M = Al, Ga, Fe or B), Y, mordenite, beta and SAPO-5.

- Characterization of the synthesised zeolites by techniques such as X-ray diffraction, scanning electron microscopy, magic angle spinning nuclear magnetic resonance spectroscopy, infrared spectroscopy, wet chemical analysis, atomic absorption spectroscopy, temperature programmed desorption of ammonia etc.
To study the effects of various physico-chemical properties of the zeolites e.g., crystal size, zeolite structure, channel cross sections, acid properties etc. on their catalytic performance.

To study the effects of modification of the zeolites by various methods including impregnation of inorganic oxides, silylation, organic base adsorption, steaming, \((\text{NH}_4\text{)}_2\text{SiF}_6\) treatment etc. on the selectivity to the desired products.

The cost factor involved in the process has also a bearing on down stream separation and recycling of the raw materials. For this reason effects of operating parameters (reaction temperature, space velocity and aromatic to alcohol ratio in the feed) on the yields of the desired products need be studied.

Successful reactor design and operation warrant the study on transport phenomena during the reactions. Aspects of the reactions with respect to diffusional resistances and related parameters are also proposed to be studied in this investigation.
1.5 REFERENCES

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