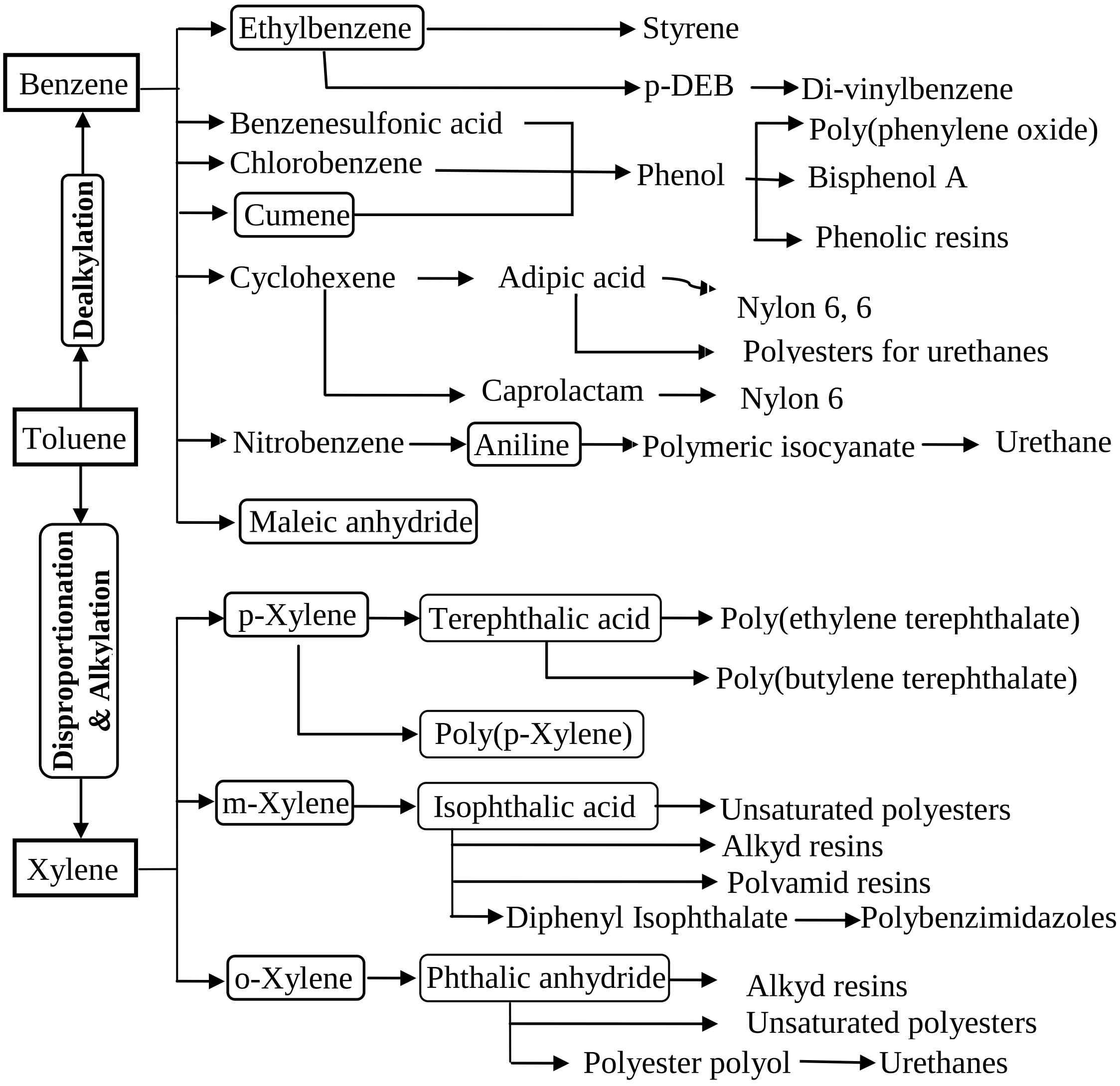
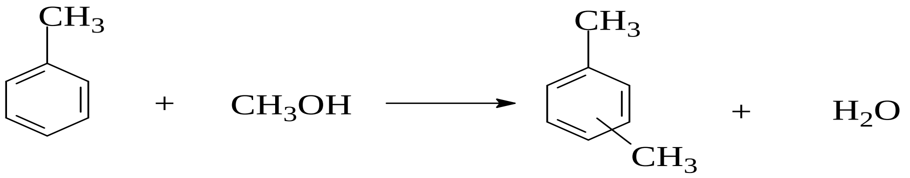
1. INTRODUCTION

Aromatics have a wide variety of application in the petrochemical and chemical industries. They are an important raw material for many intermediates of commodity petrochemicals and valuable fine chemicals such as monomer for polyesters, engineering plastics, intermediates for detergents, pharmaceuticals, agricultural-products and explosives **[1].** Among them, benzene, toluene and xylenes are the three basic materials for most intermediates of aromatic derivatives (scheme 1) **[2].**

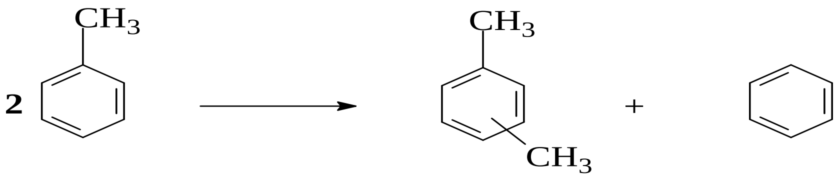


Scheme 1. Derivatives of benzene and xylene; from refs. **[1,2]**

Toluene, which has the lowest market demand, is always in surplus from the production of reformate and pyrolysis gasoline, whereas benzene and xylenes are in strong demand with the average annual growth rates of around 10% **[3-5]**. As a result of demand and supply, the price of toluene is always lower than the other aromatics. Aromatics interconversion is therefore an important research task with great industrial demands. The conversion of dispensable toluene into the more valuable aromatics therefore has an economic incentive beside its use as a high-octane component in gasoline; toluene can be used as a starting material to produce xylenes via either alkylation of toluene with methanol or toluene disproportionation.



(eq. 1)



(eq. 2)

Several workers on zeolites as catalysts have studied the alkylation of toluene with methanol and disproportionation of toluene before and after modification for production of xylenes **[6-18].** Among these xylene isomers, para-xylene is a valuable product in chemical industries because of large demand for oxidation to terephthalic acid, a major component in polyester fibers, and demand in the synthesis to vitamins and pharmaceuticals. Growth rate of polyethylene terephthalate resin demand is particularly high, up to around 17% **[5].** Pure H-ZSM-5 can be used as the catalyst in the alkylation reaction but the selectivity of para-xylene is poor. The xylene isomers isomerise simultaneously with the alkylation of toluene to reach equilibrium proportion of 22%, 54%, and 24% of ortho, meta, and para-xylenes, respectively **[19]**. However, the selectivity can be significantly enhanced by modification by several agents **[9,11].** Such a mixture of xylenes requires repeated separation and isomerization processes to obtain a certain degree of purity of para-xylene.

The work under study includes toluene methylation and disproportionation to produce xylenes over the following catalysts:

(1) Tow series of Pt/H-ZSM-5 and Pd/H-ZSM-5 catalysts containing 0.1, 0.2 and 0.3wt%Pt% Pt or Pd.
(2) Hydrofluorinated H-ZSM-5 catalysts doped with 1, 2, 3 and 4%HF.
(3) Hydrofluorinated 0.1%Pt/H-ZSM-5 and 0.3%Pt/H-ZSM-5 catalysts doped with 1, 2, 3 and 4%HF.
(4) Bimetallic catalysts containing Pt and Pd loaded untreated and hydrofluorinated H-ZSM-5 zeolite.
(5) Hydrochlorinated H-ZSM-5 catalyst doped with 3%HCl.
(6) Hydrofluorinated H-mordenite catalysts doped with 2 and 4%HF.

The catalytic alkylation and disproportionation runs are carried out in a fixed bed down flow reactor operating at atmospheric pressure using hydrogen as a carrier gas.

1.1. ALKYLATION OF TOLUENE WITH METHANOL

Xylene, especially para-xylene, is an important row material for producing chemical additives, agricultural chemicals and polymeric materials etc. One of the main sources of para-xylene production is the alkylation of toluene with alcohol. Several zeolites have been tried experimentally for this process. Much attention has been focused on H-ZSM-5 (MFI), due to its high activity and predominant shape selectivity **[11]**. This reaction of alkylation produces a primary distribution of xylene isomers at the catalytic site. This primary distribution is subsequently changed by the coupling of the physical transport process (pore diffusion) and the isomerization of xylene isomers. This results in the secondary distribution of these isomers at the surface of the catalyst pellet or in the bulk solution.

The privilege of using H-ZSM-5 zeolite over other acidic solids is its intermediate pore type, possessing three intersecting channels formed by 10 oxygen atoms. These channels are of slightly different size. One sinusoidal channel with an elliptical opening (5.1x5.5Å) running parallel to the a-axis of the unit cell, whereas the other channels are straight and have nearly circular openings (5.4x5.6Å). These two types of channels intersect to form a three dimensional network of pores. These channels dimensions can accommodate the formation of the smallest xylene (para-xylene) preferably in comparison with the other xylenes (meta and ortho-xylenes).

1.1.1. Previous Work on Toluene Alkylation with Methanol:

Methylation of toluene was carried out over several acidic zeolites in the previous studies, such as ZSM-5, mordenite, SAPO-11, and Y zeolites **[20-25]**. As a result, there were great difference in the catalytic activity and selectivity among these zeolites. Moreover, by means of modifying acidity and pore structure of ZSM-5, some co-reactions could be restricted effectively, and the selectivity of methylation of toluene to para-xylene is improved as well **[26,27]**.

Ding et al. [28] have studied the alkylation of toluene with methanol using nanoscale H-ZSM-5 zeolite catalysts. Hydrothermal treatment is carried out on the nanoscale H-ZSM-5 catalyst in a fixed bed reactor under different conditions with pure steam. They have concluded that the total amount of acid sites decreases significantly and strong acid sites almost totally disappear with the hydrothermal treatment temperature higher than 500^{o}C. High temperature hydrothermal dealuminated nanoscale ZSM-5 zeolite catalyst results in high catalytic activity for the alkylation of toluene with methanol and improves para-xylene selectivity (37.35%) especially when the catalyst is treated at 700^{o}C. the alkylation activity was very low when the hydrothermal treatment temperature was 800^{o}C.

Joshi et al. [29] have studied the alkylation of toluene with methanol to selective formation of p-xylene over ZSM-12, ZSM-5, ZSM-12/ZSM-5 co-crystalline, and physical mixture of ZSM-12 and ZSM-5. They have concluded that the ZSM-12, ZSM-12/ZSM-5 co-crystalline, ZSM-5, and physical mixture of ZSM-12/ZSM-5 samples are synthesized by hydrothermal methods, by varying synthesis temperature and periods. The ZSM-12/ZSM-5 co-crystalline sample is observed to be a better combination as far as p-xylene selectivity (89.34%) and total xylene yield (36.77%), at a favorable toluene conversion of 44.03%. The use of ZSM-12/ZSM-5 catalyst combination for the alkylation reactions, could be probably, reported for the first time.

Breen et al. [30] have shown that it is possible to produce para-xylene with near perfect selectivity by optimizing the process variables of the toluene alkylation reaction over a B/H-ZSM-5 catalyst. The following parameters are found to be important in producing such high selectivity:

(1) A catalyst boron content ≥ 6.5%.

(2) Addition of water vapour to the feed to increase the conversion of toluene and selectivity of para-xylene. A ratio of H_2O/MeOH of 9:1 has given the best results.

(3) A high gas hourly space velocity obtained by increasing the flow of diluent gas resulted in increasing selectivity to para-xylene, without necessarily losing conversion. This was particularly noticeable at low toluene : MeOH ratio (≤ 4 : 1).

(4) High toluene : methanol ratio (> 4 : 1). This has limited the degree of conversion of toluene simply because there is insufficient methanol to react with toluene. This is beneficial because para-xylene has inhibited the reaction, and at higher conversions of toluene (achieved by decreasing the toluene : methanol ratio) increasing proportions of methanol are converted to ethane (eq. 3) which is an undesirable side product of the reaction.

$$2CH_3OH \xrightleftharpoons[+\,H_2O]{-\,H_2O} CH_3OCH_3 \xrightarrow{-\,H_2O} C_2H_4 \xrightleftharpoons[-\,H_2]{+\,H_2} C_2H_6 \quad \text{(eq.3)}$$

Inagaki et al. [31] have investigated the toluene alkylation with methanol at 250^{o}C over MCM-22 and ITQ-2 zeolites pocessing an MWW structure. Whereas ITQ-2, produced by the dealumination of MCM-22 precursor, has shown a poor para-xylene selectivity of 23% at 1.7% of the level of toluene conversion, a high para-xylene selectivity of 80% at 0.6% of the level of toluene conversion is obtained by poisoning the external surface of ITQ-2 with collidine. Similarly, MCM-22 treated with collidine has shown a high para-xylene selectivity of 74% at 3.4% of the level of toluene conversion. It has been concluded that the high selectivity of para-xylene in MCM-22 zeolite is caused by shape selectivity originated from the interlayer 10-membered ring micropores with 12-membered ring supercages, as well as the intralayer sinusoidal 10-membered ring micropores in the MWW structure.

Ghiaci et al. [32] have studied the methylation of toluene with methanol using a series of surface modified and un-modified ZSM-5 (Si/Al = 60-170) loaded with H_3PO_4, differing in the external surface treatment of the zeolites. N-cetylpyridinium bromide, a cationic surfactant, is used for modifying the external surface of the zeolites. The toluene conversion on the unmodified H_3PO_4/ZSM-5 with Si/Al =170, is found to follow the order of: 2.1wt%H_3PO_4/ZSM-5 > 3.5wt%H_3PO_4/ZSM-5 > 4.9wt%H_3PO_4/ ZSM-5 > 0.7wt%H_3PO_4/ZSM-5 > ZSM-5. For the unmodified catalyst, the toluene conversion and para-xylene selectivity have increased by increasing the Si/Al ratio. The external modification of catalyst with surfactant before H_3PO_4 loading, led to passivation of the unselective Brönsted acid sites and to narrowing of the pores of the zeolite. Both effects resulted in enhanced shape selectivity of para-xylene in the toluene alkylation reaction.

Van vu et al. [33] have studied the alkylation of toluene with methanol using three different Si/Al ratios in H-ZSM-5 zeolite coated with polycrystalline silicalite-1. The silicalite/H-ZSM-5 catalysts have shown excellent para-xylene selectivity, >99.9% under all of the reaction conditions. The enhanced para-xylene selectivity may be originated from diffusion resistance through the inactive silicalite layer on the H-ZSM-5, resulting in increased diffusional length. The toluene conversion over the silicalite/H-ZSM-5 catalyst was almost constant, indicating that the silicalite coating inhibited coke formation on the external surface of H-ZSM-5.

Zhu et al. [34] have studied the catalytic alkylation of toluene with methanol over a variety of zeolite, including mordenite, MCM-22, SAPO-34, SAPO-11, SAPO-5 and ZSM-5 with different SiO_2/Al_2O_3 ratio. The total toluene conversion has decreased during toluene methylation, in the following order: mordenite > ZSM-5 (Si/Al = 25) > ZSM-5 (Si/Al = 48) > MCM-22 > ZSM-5 (Si/Al = 136) > SAPO-11 ∼ SAPO-5 > SAPO-34. This order for above catalytic activity is approximately in agreement with their acidity. The catalytic activity of zeolite for toluene alkylation is approximately proportional to the number of its mid-strength acidic sites, except SAPO-34 with small channels and mordenite with strong acidity. Moreover, the acidic sites for catalyzing toluene alkylation are weaker in strength than those for catalyzing toluene disproportionation, but slightly stronger than those for catalyzing the reaction of methanol to hydrocarbons. On the other hand, zeolites with 12 membered ring channels (mordenite and SAPO-5) may lead to the further alkylation of xylenes and the rabid deactivation by coking. Zeolites with 8- membered ring channels (SAPO-34) have restricted toluene alkylation, only favorable for forming non-aromatic hydrocarbons. Zeolites with mid-strength and 10-membered ring channels, such as, ZSM-5 (Si/Al = 136), SAPO-11, and MCM-22 have shown high catalytic selectivity and activity for toluene alkylation with methanol to xylenes. As a result, ZSM-5 (Si/Al = 136), SAPO-11 and MCM-22 have more than 70% selectivity of toluene alkylation to xylenes and more than 30% single-pass toluene conversion.

Raj et al. [35] have studied the alkylation of toluene with methanol reaction using MnAPO-11. Effect of time on stream on toluene conversion over MnAPO-11 has been studied at 400°C, a weight hourly space velocity of $2h^{-1}$ and feed ratio of 2:1 (toluene:methanol). It has been concluded that the toluene conversion decreases with increasing the reaction time; however, para-xylene selectivity increases with increasing the reaction time.

Ghosh et al. [23] have studied the alkylation of toluene with methanol using a reactor containing a non-steamed, phosphorus treated ZSM-5-type zeolite catalyst. The catalyst is contacted with a toluene/methanol feed and a cofeed of hydrogen under reactor conditions suitable for the methylation of toluene. Water is introduced into the reactor during the methylation reaction under conditions that provide substantially no structural aluminum loss of the catalyst from such introduction of water. It has been concluded that the use of steam in combination of H_2 is shown to be advantageous over the use of only H_2 as cofeed.

Ghosh et al. [36] have studied a method of modifying a ZSM-5-type zeolite catalyst to increase selectivity of the catalyst for para-isomers in aromatic alkylation reactions. The method includes containing a ZSM-5-type zeolite catalyst with a fluoride-containing compound. The fluoride-containing zeolite catalyst can be used in aromatic alkylation to provide di-alkyl aromatic products. A method of preparing a xylene product is also accomplished by providing a fluoride-treated ZSM-5-type zeolite catalyst within a reactor. The fluoride-treated ZSM-5 zeolite catalyst is contacted with a toluene/methanol feed under reaction conditions suitable for toluene methylation to form a xylene product containing at least 50% para-xylene by total mixed xylenes.

Zhu et al. [37] have used mordenite, ZSM-5, SAPO-11, MCM-22, Si-MCM-22, and La-MCM-22 catalysts to investigate the catalytic alkylation of toluene with methanol in a fixed bed reactor. MCM-22 zeolite with mid-stronger acidity and opening of 10-membered ring channels may obtain a high catalytic activity and selectivity for toluene alkylation with methanol. The acid sites for catalyzing alkylation of toluene with methanol are weaker than that for catalyzing toluene disproportionation. Toluene conversion has decreased with the following order: mordenite > ZSM-5 > MCM-22 > SAPO-11 > La-MCM-22 > Si-MCM-22. The selectivity of para xylene, especially for La-MCM-22 is obviously improved thanks to its smaller opening of channels resulting from surface modification of La-$(No_3)_3$ or silicone. Less trimethylbenzene or large size molecules are produced over two modified MCM-22 catalysts due to the partial coverage of super cages on surface. In addition, the experimental results also clearly indicate the characteristics of MCM-22 structure consisting of large intracrystalline cages, some of which may locate on surface of MCM-22.

Fechete et al. [38] have prepared (Al, Ga)EMT-type zeolites (Al:Ga =1:0, 0.75:0.25 and 0.5:0.5), which are used as catalysts to study the alkylation of toluene with methanol reaction. The ammonia temperature programmed desorption (TPD) measurement has indicated that the isomorphous substitution of aluminum by gallium leads to a decrease of both acidic strength and acid sites concentration. The catalytic performances of the EMT-type solids in the conversion of methyl aromatic hydrocarbons are correlated with their acid properties. Thus the less acidic (Al,Ga)EMT samples has exhibited a lower activity, but a higher selectivity towards the xylenes formation by comparison with (Al)EMT. In the case of most active (Al)EMT catalyst the distribution of xylene isomers is very close to those of thermodynamic equilibrium, but a certain selectivity for the para-xylene formation can be observed over the Ga-containing sample. For instance, at 300^oC, the selectivity for para-xylene was 27.1% with

Al(EMT), while with (Al,Ga)EMT50 the selectivity of para-xylene reached 45.1%.

Aboul-Gheit et al. [39] have studied the catalytic alkylation of toluene with methanol using catalysts containing different platinum contents (0.2, 0.4 and 0.6 wt%) supported on H-ZSM-5 or H-mordenite (H-MOR) zeolites in a fixed flow reactor operated atmospherically at temperatures of 300-500^{o}C. They have concluded that toluene methylation has increased with increasing the platinum content in H-ZSM-5 in Pt/H-ZSM-5, although the acid sites number and strength as well as Pt dispersion decrease. This is attributed to suppressing the demethylation (backward) reaction, compared to that occurring on the unloaded zeolite. Obviously, the action of platinum in the zeolite is to facilitate the carbocation formation on acid sites by virtue of its vacant d-orbital. Trimethylbenzenes formation has decreased with increasing the Pt content on H-ZSM-5 zeolite, whereas they have increased with increasing the Pt in H-MOR zeolite. The para-xylene selectivity is highest on the 0.6%Pt/H-ZSM-5 catalyst, but is lowest on the 0.6%Pt/H-MOR catalyst. The selectivities of para-, meta- and ortho-xylene production are found largely dependent on the platinum content in the catalysts, particularly when supported on H-ZSM-5 zeolite. However, using platinum / H-mordenite catalysts, these selectivities are not strictly controlled by platinum content in the catalysts.

Aboul-Gheit et al. [40] have used two series of catalysts A and B, each containing 0.2, 0.4 and 0.6 wt% Pt on H-ZSM-5 zeolite. These catalysts are prepared via two different procedures; catalysts of series A are prepared via impregnating H-ZSM-5 with the Pt precursor (H_2PtCl_6) solution, whereas those of series B are prepared via impregnating NH_4-ZSM-5 zeolite with the Pt precursor solution followed by deammoniation to the Pt / H-ZSM-5 forms. The prepared catalysts are examined for toluene alkylation with methanol in a flow reactor under atmospheric conditions using H_2 gas carrier. The catalysts are characterized for acidity magnitude and strength via temperature programmed desorption of ammonia (TPD) and for Pt dispersion in the zeolite via H_2 chemisorption. Correlation of the catalysts characteristics with their reactivities for toluene conversion, xylenes production, trimethylbenzenes formation and xylene isomers in product relative to their thermodynamic equilibrium values are carried out. The activities of series A catalysts for toluene conversion and xylenes production have been found to be in the order: 0.6% Pt / H-ZSM-5 > 0.4% Pt / H-ZSM-5 > 0.2% Pt / H-ZSM-5. Whereas those of series B catalysts are found to be in the following order: 0.2% Pt / H-ZSM-5 > 0.4% Pt / H-ZSM-5 > 0.6% Pt / H-ZSM-5. Trimethylbenzenes are much more pronounced on the catalysts of series B than on those of series A. On the other hand, the para-xylene selectivity (percentage of para xylene-xylene in the xylene mixture in the product) on the Pt-loaded zeolite of series A and B catalysts is found to follow the order: 0.6% Pt / H-ZSM-5 > 0.4% Pt / H-ZSM-5 > 0.2% Pt / H-ZSM-5.

Faramawy et al. [41] have obtained H-ZSM-5 zeolite modified with phosphorus. The obtained P/ZSM-5 catalyst is subjected to further treatments with chromium and nickel. The distribution and strength of different acid sites of zeolites are investigated by means of temperature-programmed desorption of ammonia. The active and strong acid sites are confirmed by measuring the rate constants for cracking of n-hexane, as a probe molecule. Reduction of pore opening size of the modified ZSM-5 is monitored by a standard test reaction of probe molecules of m-xylene and ethylbenzene. Selective alkylation of toluene with methanol to p-xylene is studied over ZSM-5 and modified zeolite catalysts. The P/ZSM-5 zeolite is the most selective catalyst to p-xylene but the toluene conversion decreases drastically. The addition of chromium to P/ZSM-5 zeolite increases the toluene conversion and the yield of p-xylene is very close to P/ZSM-5 catalyst. The addition of nickel does not exhibit a significant improvement of the catalyst performance. The deactivation of catalysts, due to coke deposition during run, is also considered. P/ZSM-5 zeolite shows the lowest stability with time on stream. The addition of chromium and nickel to P/ZSM-5 zeolite increases the stability of the catalyst

Kiricsi et al. [42] have synthesized ZSM-5 zeolite disc by a new method in which reactions occur in the solid state. The hydrogen form of the zeolite has been prepared by ion exchange of the sodium ion of the disc shape pellet for hydrogen ion hydrochloric acid solution. High para-xylene selectivity (76.3%), at 450^{o}C reaction temperature, has been observed for the new disc shape ZSM-5 zeolite catalyst in the alkylation of toluene with methanol. This feature is attributed to the inherent character of the catalyst, since its structure consists of intergrown individual H-ZSM-5 crystals forming secondary mesopores. This structural agreement led to a substantial decrease in the outer surface between the adjacent crystals, the probability of secondary reactions therefore being suppressed.

Faramawy [43] has studied the alkylation of toluene with methanol using H-ZSM-5 zeolite, which modified with phosphorus, chromium, zirconium, and titanium in order to control pore size. The effect of reaction parameters such as reaction temperature, weight hourly space velocity and methanol/toluene molar ratio has been investigated. The P/H-ZSM-5 has shown the highest para-xylene selectivity (70-80wt% at reaction temperatures between 300-500^{o}C). However, the stability of this catalyst with time on stream has seemed to be lower than that acceptable one. Modification with chromium and zirconium increases the abundance and strength of the stronger acid sites and reduces the pore opening dimensions of ZSM-5 zeolite. These changes have enhanced activity and selectivity of the obtained catalyst. Cr/H-ZSM-5 catalyst can be used advantageously for the alkylation reaction since it has exhibited much better stability against deactivation by coke deposition than phosphorus modified catalyst, and also has shown a good para-xylene selectivity (45 wt% at 450^oC).

Medium pore size H-ZSM-5 zeolite and large pore size dealuminated H-mordenite catalysts have been used by **faramawy et al. [44]** to study the alkylation of toluene with methanol. The SiO_2/Al_2O_3 molar ratios of the studied H-mordenite are 11, 14, 19.6 and 29.6. It has been concluded that the products of the alkylation are mainly xylene isomers and small amounts of ethyl benzene and benzene. Trimethylbenzenes are detected in significant concentrations (14.8-22.3wt %) due to a further alkylation of the produced xylenes on the external surface of these zeolites **[15]**. For the mordenite catalysts, concentration levels of benzene are higher as compared with the ZSM-5 catalyst. Furthermore, the concentration of produced benzene has increased by increasing the SiO_2/Al_2O_3 molar ratio. The production of benzene over mordenite catalysts is due to disproportionation of toluene. The activity of mordenite catalysts has increased by dealumination, reaching a maximum limit of SiO_2/Al_2O_3 ratio of 19.6. Large pore size permitted by dealumination has decreases the para-xylene selectivity due to re-entry of the primary product into the channel system of mordenite.

Prakash et al. [45] have used medium pore molecular sieves SAPO-11, SAPO-31, and SAPO-41 in catalytic alkylation of toluene with methanol. They have concluded that the activities of the SAPOs catalysts are found to be in the following order: SAPO-41 > SAPO-31 > SAPO-11. This is in accordance with the decreasing of acidity, as shown by the temperature programmed desorption of ammonia. All the three SAPOs showed some para-xylene selectivity among the various xylene isomers in the product but this followed the opposite order of their catalytic activity. Secondary alkylation of xylene isomers with methanol yields 1,2,4-trimethylbenzene (1,2,4-TMB) selectivity. SAPO-41 has given the highest amount of 1,2,4-TMB among the three SAPOs studied. It can be assumed that TMB is formed by alkylation of xylenes. Alkylation of para-xylene will lead to only 1,2,4-trimethylbenzene, whereas ortho-xylene would give both 1,2,4- as well as 1,2,3-trimethylbenzenes. Meta xylene would give all three trimethylbenzenes.

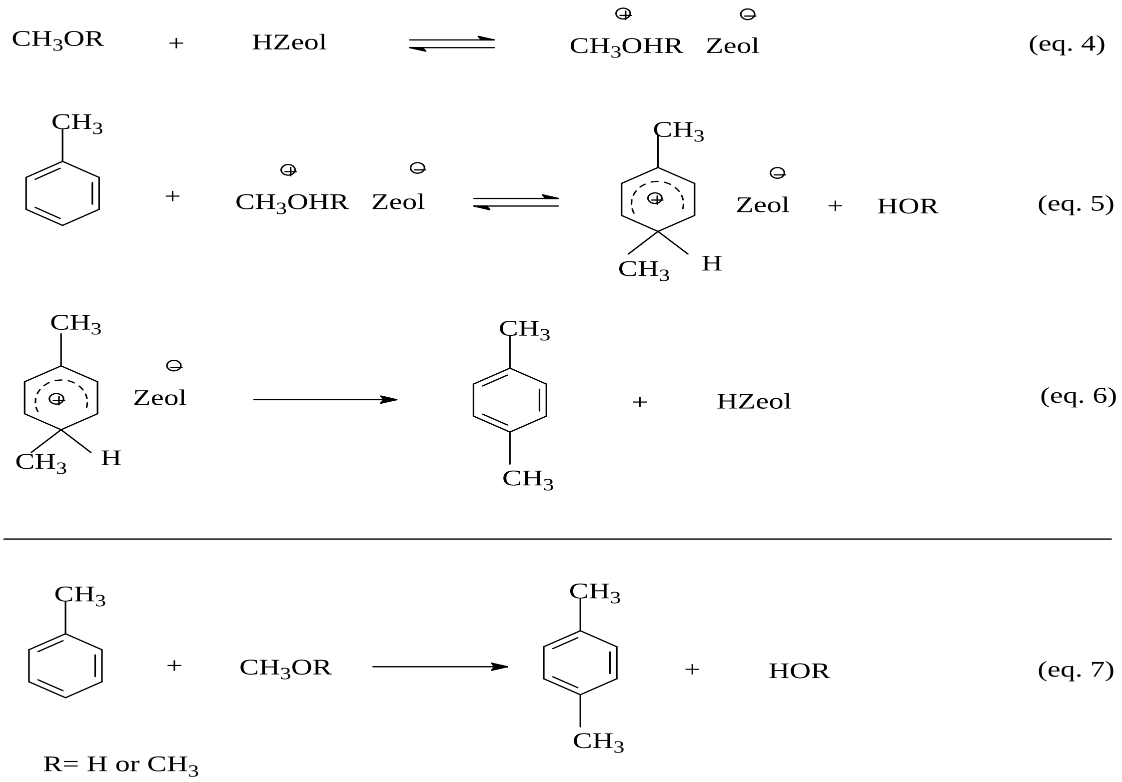
Kodama et al. [25] have used the chlorofluorocarbon (CFC) to fluorination of protonated mordenite (HM). The treatment is carried out in a flow reactor under ordinary pressure, at 600^oC for 10 mints. It has been found that the availability of HM as catalyst for alkylation of toluene with methanol is remarkably enhanced by the CFC treatment. In particular, the activity maintenance is remarkably improved. Thus, in the alkylation of toluene at 300^oC under the molar ratio of methanol/toluene = 1 and W/F_M (W: mass of catalyst, g; F_M: flow rate of feed, mol/h) = 81.2 g.h/mol, the conversion is increased from 27 to 65% by CFC treatment of the HM catalyst. There are two reasons for the enhancement of the availability. The first one is related to the modification of the surface properties, such as surface acidity and adsorptive activity of the zeolite, due to CFC treatment. Namely, the treatment is effective for the removal of the excessively strong acid sites on the surface, which may promote various side reactions, including low polymerization and carbonization taking place on the active sites. The treatment is consequently useful for the improvement of the selectivity for the alkylation and the catalytic activity maintenance. At the same time, the surface is changed to be hydro- and lipophobic by the treatment. Such a change may contribute to the promotion of the desorption or removal of the products such as H_2O and alkylated compounds, resulting in the enhancement of the frequency for the use of active sites on the zeolite. The second one is concerned with the enlargement of the channel-size resulting from the dealumination. Such an enlargement should be effective for the active migrations of reactants and products. As well as the enhancement of the desorptive activity due to the change of surface property described above, the enlargement should be effective for increasing the frequency of the use of active sites, resulting in the increase in the apparent catalytic activity shown by the increase in the conversion of the reactants.

Bezouhanova et al. [46] have concluded that the variation of the Brönsted acid site concentration in H-ZSM-5 zeolite with different Si/Al ratio (11, 50, 140, 250 and 500) has proved to be a good method for changing the selectivity for the formation of para-xylene from the methylation of toluene. The alkylation of toluene with methanol is investigated in the temperature range 320-470^{o}C. It is found that with similar values of toluene conversion (between 23-30%) the yield of para-xylene has increases with increasing Si:Al ratio in H-ZSM-5. para-Xylene selectivity has increased from 35% at Si:Al ratio=250 to 55.5% at Si:Al=500. A probable reason for the higher para-xylene selectivity of the samples with the lower Brönsted acid site concentrations is the preferred formation of this isomer in the narrow channels in the initial reaction and suppression of secondary isomerization.

1.1.2. Mechanism of Catalytic Alkylation of Toluene with Methanol:

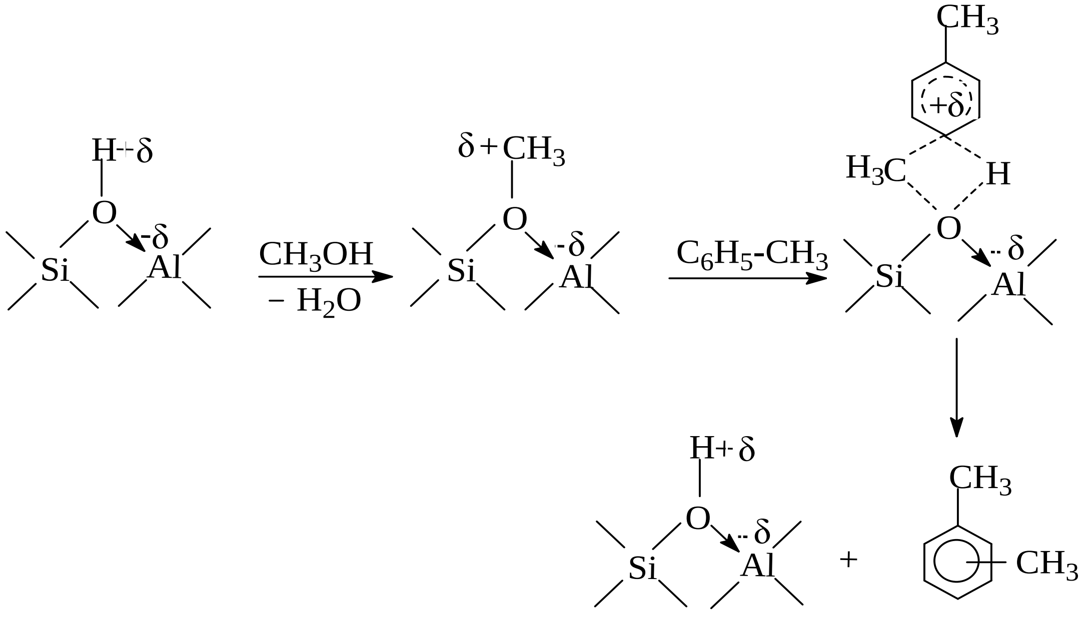
The mechanism of catalytic alkylation of toluene with methanol is generally considered by way of carbonium ion, which attacks the aromatic nucleus **[47-49].**

Kaeding et al. [11] have proposed that the two starting reagents, toluene and methanol, readily enter the pores of ZSM-5 class zeolites. Each by itself will undergo reaction under the conditions used. Methanol is relatively reactive by comparison with toluene, and is converted to methyl ether and water under mild conditions and to hydrocarbons and additional water at high temperatures over H-ZSM-5. Protonation of methanol or methyl ether to form the corresponding oxonium ion is proposed as the initial step (eq. 4). This is followed by transfer of the methyl group to the aromatic ring (eq. 5), and transfer of a proton pack to a catalyst site (eq. 6). Less steric hindrance for alkylation at the para-position within the confines of the catalyst pores is predicted by comparison with meta- and ortho-positions. These same acid sites, however, can also rapidly isomerize any xylene isomer formed initially as it diffuses out of the zeolite, especially in the larger spaces where channels intersect, to give the near-equilibrium mixtures. Isomerization may also occur by interaction with acid sites on the external surface.



The ring methylation with methanol over acid catalysts would proceed via the formation of methoxonium ion ($CH_3OH_2^+$), which requires Brönsted acid sites **[50,51].** Thus, the surface concentration of methoxonium ion, and therefore the catalytic activity for ring alkylation would depend on the density and strength of the Brönsted acid sites. Molecular modeling studies **[52]** on the methanol interaction with zeolites have shown that physically adsorbed methanol is the most stable binding geometry while a methoxonium cation represents a transition state and not a local minimum. It has also been suggested that zeolite methoxy groups can form another adsorption complex with toluene **[53]**. Although the nature of the alkylating species is not clear, but in this respect some researchers believe that methoxy species alkylate toluene [**53-56]**, while the others favor methoxonium species **[11,51,57,58]** and some authors reported dimethylether as the alkylating agent **[59,60].**

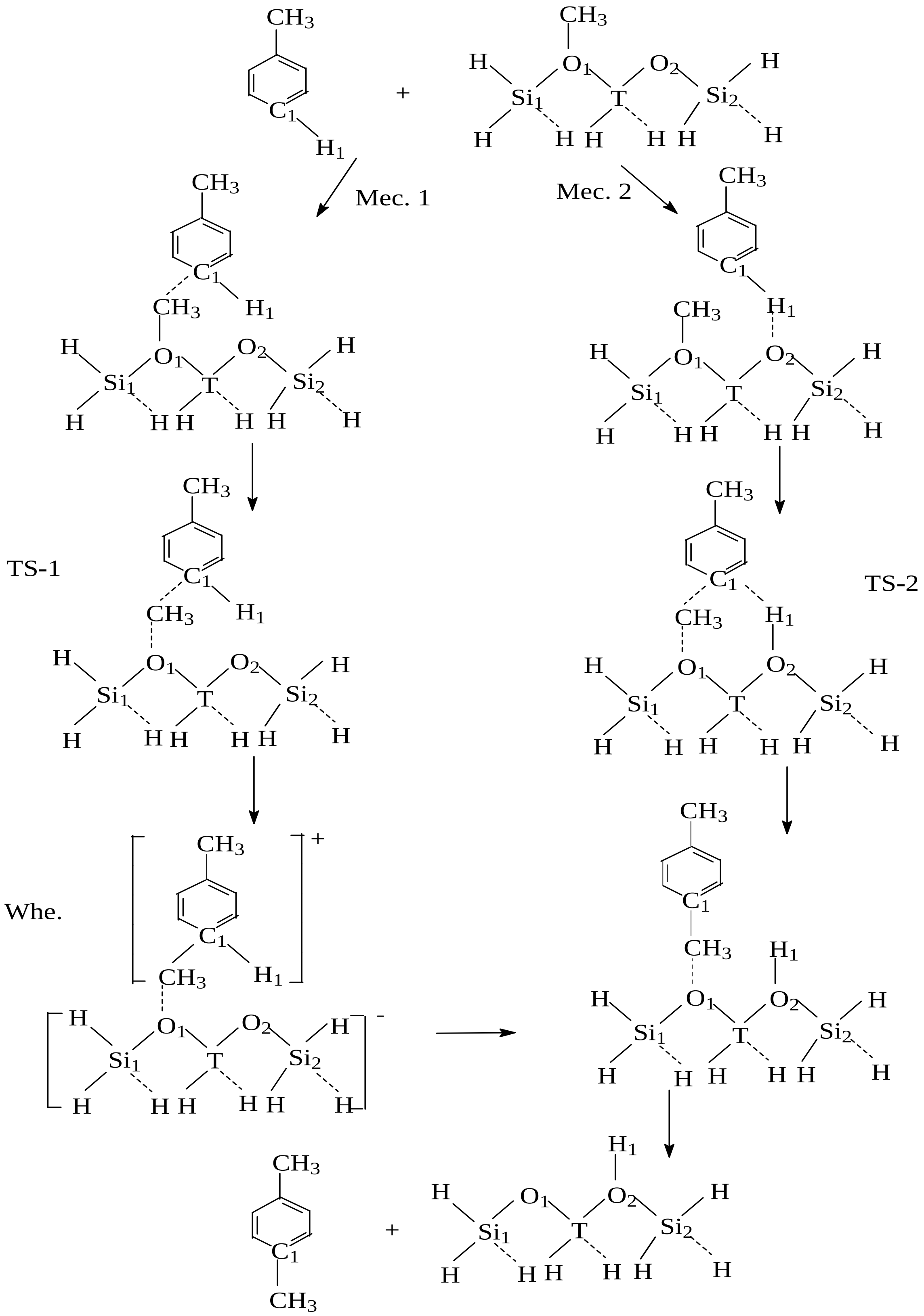
Rakoczy et al. [53] have concluded that the formation of stable methoxy groups on H-ZSM-5 or HY zeolite surface is the first step in the toluene alkylation with methanol. The proposed mechanism of toluene alkylation on zeolite catalysts could therefore be visualized as follow:



Corma et al. [61] have employed PM3 (modified neglect of differential overlap parametrization method 3) and MNDO (modified neglect of differential overlap) methods to study the mechanism of toluene alkylation by methanol on zeolites, by means of the cluster $(H)_3SiO(CH_3)T(H)_2OSi(H)_3$ in were T = Al, B, Ga. In the first step of the reaction, there is an attack of methanol to the acid center of the zeolite, and as a result, the alkylating agent is obtained **[62]**. Two possible reaction mechanisms have been found in the molecular orbital calculations of the alkylation reaction of toluene on zeolite clusters. In these mechanisms, they have localized the different intermediate species and transition states. The first mechanism is analogous to the classical two-step aromatic alkylation, passing through a Wheland intermediate. The second is a concerted one-step mechanism.

In the first mechanism, after de adsorption localized on the C-C_1 atoms, the transition state (TS-1) is characterized by the transference of the methyl group to the toluene. The geometry of this transition state shows distances and angles according to the precursor of the Wheland intermediate. After the transition state, the Wheland intermediate (Whe) is formed, with analogous geometry to the classical mechanism, and finally, the proton of the toluene is transferred to an oxygen atom of the zeolite cluster.

The second mechanism begins with a different adsorption mechanism in which not only the C-C_1 atoms participate, but also the H_1-O_2 atoms. The transition state is characterized by a strong H_1-O_2 interaction. The transference of the methyl group is simultaneous to the transference of the proton, in a one-step concerted mechanism. The possibility of this second mechanism suggests that the basic oxygen centers of zeolite could be important for its reactivity. This mechanism correspond to acid catalysis because need the Bronsted acid sites to form the alkylating agent. The role of hydrogen bonding interaction is remarked as a starting point of the reaction. The two mechanisms can be illustrated as follow:



1.2. DISPROPORTIONATION OF TOLUENE:

Toluene disproportionation is defined as the conversion of two molecules of toluene to one molecule of benzene and one molecule of xylene.

At first, toluene disproportionation has been carried out using aluminum chloride catalyst **[63]**. The reaction also proceeds in the vapor phase over solid acidic catalysts, such as silica-alumina and natural or synthetic zeolites. The selective catalysts, with channels reduced in size, may favor the transfer of the methyl group to the least hindered position of toluene and the resultant para-form diffuses along the pores to the outside at a relatively fast rate. In addition, ortho and meta-isomers within the pores would isomerize to para-xylene as the concentration of the latter is reduced by its rapid outward diffusion **[64].**

1.2.1. Previous Work on Disproportionation of Toluene:

Mihályi et al. [65] have prepared zeolite precursor MCM-22 samples by hydrothermal synthesis. The H-zeolites, obtained from the precursors, are characterized by scanning electron microscopy (SEM), Fourier-transform infrared (FT-IR) spectroscopy, and by their activity in the title reaction. Despite of the lower Brö◌nsted acid site concentration of the zeolite having smaller crystallites, shows higher activity, while the zeolite, having larger crystals are more selective for p-xylene formation.

Ren et al. [66] have prepared Catalysts by dealumination of H-MCM-22 zeolite with oxalic acid leaching, followed by shaping and liquid phase modification with siloxane. The catalytic performance was measured with selective disproportionation of toluene in a fixed-bed reactor. The unmodified H-MCM-22 has exhibited a much higher catalytic activity and para-selectivity in the disproportionation toluene than H-ZSM-5 at low reaction temperatures around 300◦C. However, it deactivated quickly due to coking. The oxalic acid treatment of H-MCM-22 has improved the selectivity for para-xylene by 10–18%. The modification by siloxane of the oxalic acid treated H-MCM-22 turned out to be highly selective for para-xylene (97%), however, with the expense of toluene conversion (2%). It is proposed that the high para-selectivity is closely associated with the contraction of micropore windows and the elimination of acid sites at the external surface by the deposited silica. Therefore, the modified H-MCM-22 is a potential catalyst for the selective disproportionation of toluene with a high para-selectivity.

Bhavani et el. [67] have prepared Ni–Pt/H–Y zeolite catalysts with different Ni contents and applied to the disproportionation of toluene and 1,2,4-trimethylbenzene in the temperature range 250–400^{o}C. A TEM study has shown the formation of bimetallic (Ni–Pt) particles of nanoscale size and the average particle size is found to increase with increasing Ni loading. The catalytic activity of Ni–Pt/H–Y zeolite and Pt/H–Y catalysts is compared; and it is found that addition of Ni up to 0.3 wt.% increases conversion of toluene (67.5%) and para-xylene selectivity (26.0%). Further addition of Ni leads to a decrease in conversion and para-xylene selectivity and increasing dealkylated products, which may be due to the presence of unreduced Ni species and pore blockage by large-sized bimetallic particles formed.

Wu et al. [68] have studied the disproportionation of toluene over dealuminated MCM-22 zeolites. The dealumination of MCM-22 is performed by acid reflux and combination of calcination or steaming with subsequent acid reflux. This treatment effectively has eliminated Al atoms from the framework site but left most of them in the crystallites as non-acidic extra-framework species. The activity of MCM-22 for toluene disproportionation, measured at relatively low temperatures (200-300°C) is comparable to that of mordenite and much higher than that of ZSM-5. Toluene disproportionation is found to occur mainly within the supercages of MCM-22 but not in 10-membered ring (10MR) channels of MCM-22 at these temperatures. The fraction of para-xylene in xylenes mixture formed on MCM-22 is higher than its equilibrium value, and increases further by the dealumination. The improvement in para-selectivity by dealumination results from the suppression of isomerization activity probably because the dealumination treatments have eliminated framework Al atoms predominantly on the external surface and inside the 10MR channels compared with those inside the supercages.

Mavrodinova et al. [69] have studied the conversion of toluene and the accompanying formation of coke on the H-forms of the zeolites offretite, omega, and ZSM-5. A qualitative correlation between the initial activity, the acidity and coke formation could be established. The para-xylene selectivity of the ZSM-5 sample has remained constant over a long time on stream. The selectivities of omega and especially that of offretite have increased with decreasing activity. As an explanation for these effects, an increase of the diffusion paths by a closure of the pore entrances for the ZSM-5 and the interior of the pores of the omega and the offretite is discussed together with transition state selectivity. The results are further compared with (a) the selectivities of a number of other zeolites and (b) the results of theoretical calculations by **Weis [70,71]**

Meshram et al. [72] have studied the acid strength distribution and catalytic behaviour in the disproportionation of toluene of HZSM-5 zeolites with varying $Si0_2/A1_20_3$ ratios and calcined at different temperatures. At high $SiO_2/A1_20_3$ values, the rates of both disproportionation and demethylation are decreased. Catalyst life is, however, prolonged considerably. The specific catalytic activity is proportional to the concentration of both strong and medium acid sites, implying that acid sites with a broad spectrum of acid strength are active centers for the disproportionation of toluene.

Young et al. [12] have studied the disproportionation of toluene using H-ZSM-5 zeolite class. They concluded that the transalkylation reaction to form benzene and xylenes within the pores is relatively slow. Possible mechanism leading to enhancement of para-xylene selectivity is discussed as benzene diffuses out of the pores rapidly. The xylenes isomerize rapidly within the pores, para-xylene diffuses out moderately fast, while the ortho- and meta- isomers have more time and further convert to the para isomer before escaping from the channel system (Figure i).

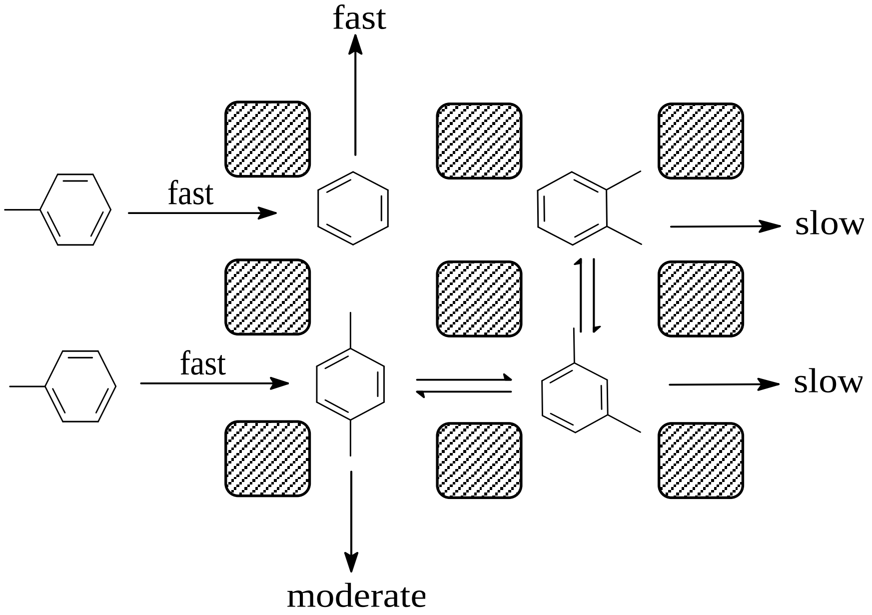
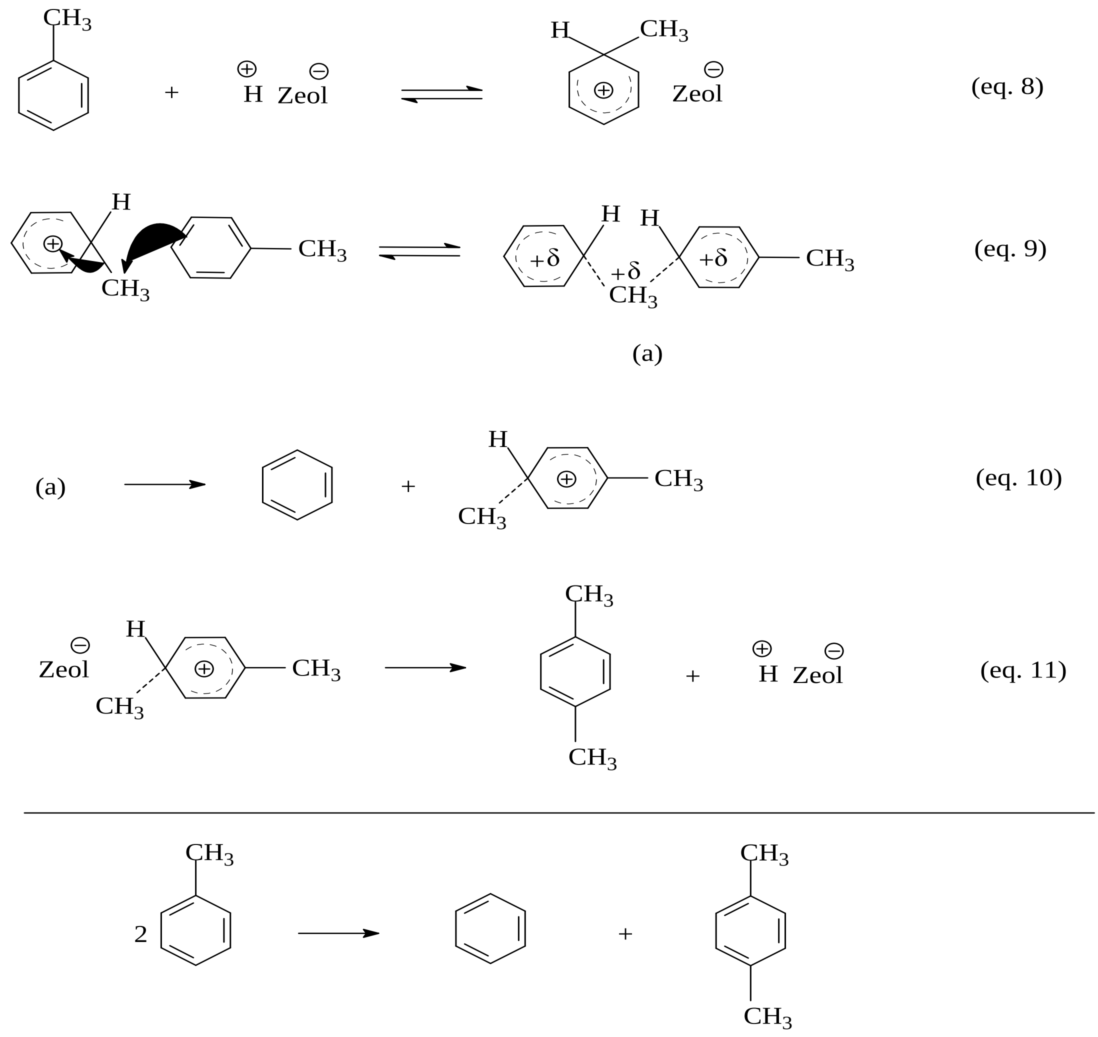


Fig. i. Selective toluene disproportionation

1.2.2. Mechanism of Disproportionation Reaction:

According to **Aneke et al [64]** and **Kaeding ea al. [73]**, the mechanism for toluene disproportionation reaction has been described as follow: the proton from the acid form of the zeolite, H^+ $Zeol^-$, attacks a toluene molecule, equation (8). This weakens the carbon methyl bond, equation (9), and initiates transfer to a second toluene molecule, equation (10). Since this reaction occurs within the zeolite pores, the para position is the least hindered one and consequently would be most available to attack. Transfer to proton back to an anionic site in the catalyst from the protonated xylene gives the xylene product and regenerates the acid sites in the catalyst, equation (11). Ortho and meta-xylenes also isomerize to the para-isomer within the zeolite pores.



1. 3. ZEOLITES:

Zeolite and zeolite-related materials assume a very important role in the heterogeneous catalysis field have seen a significant increase in the available range of catalysts in the last few years. The interest in zeolitic catalysts arises from their unique properties, namely:

- Their unique microporous structure, which allows them to have the well-known molecular sieving behaviour that justifies their use in a wider field than catalysis and that makes their activity related to both the composition and the geometry of the structure.
- The large number of available structures, ranging from the very narrow pore systems to those having pores large enough to process heavy molecules.
- The possibility to control, in a variety of ways, not only the geometry of the structure but also its composition in a relatively wide range. This feature assumes a particular importance in the area of analysis where zeolites have the largest impact–acid catalysts.
- The capability of zeolites to act as hosts for a variety of guests with catalytically attractive properties, such as transition metal ions, small metal clusters or transition metal complexes.

1.3.1. Zeolite Structures

Zeolites are crystalline aluminosilicates of group IA and group IIA elements such as sodium, potassium, magnesium, and calcium **[74]**. Chemically, they are represented by the empirical formula:

$$\mathbf{M_{2/n}\,O.Al_2O_3.xSiO_2.wH_2O}$$

where x is 2 to 10, n is the cation valence, and w represents the water contained in the void of the zeolite.

Zeolites are crystalline and microporous aluminosilicates materials with an open structure that consist of **AlO_4** and **SiO_4** tetrahedral units linked together at the centers by shared oxygen atoms **[75]**. Owing to their unique properties in ion exchange, adsorption capacity and catalytic activity, zeolites have been widely used as adsorbents, molecular sieving agents and catalysts for a variety of different chemical reactions. They have also been modified by isomorphous substitution of silicon and aluminium by incorporating other atoms such as titanium, iron, gallium, boron, phosphorus, etc. in the framework.

It is possible to say that zeolites are the most widely used catalysts in industry. They are extremely successful as catalysts for oil refining, petrochemistry, and organic synthesis in the production of fine and speciality chemicals, particularly when dealing with molecules having kinetic diameters below 10 Å. The reason for their success in catalysis is related to the following specific features of these materials:

- They have very high surface area and adsorption capacity.
- The adsorption properties of the zeolites can be controlled, and they can be varied from hydrophobic to hydrophilic type materials.
- Active sites, such as acid sites for instance, can be generated in the framework and their strength and concentration can be tailored for a particular application.
- The sizes of their channels and cavities are in the range typical for many molecules of interest (5-12 Å), and the strong electric fields existing in those microporous together with an electronic confinement of the guest molecules are responsible for a preactivation of the reactants **[76,77]**.
- Their intricate channel structure allows the zeolites to present different types of shape selectivity, i.e., product, reactant and transition state

selectivities, which can be used to direct a given catalytic reaction toward the desired product avoiding undesired side reactions.

- All of these properties of zeolites, which are of paramount importance in catalysis and make them attractive choices for the types and processes mentioned above, are ultimately dependent on the thermal and hydrothermal stability of these materials. Zeolites can be activated to produce very stable materials not just resistant to heat and steam but also to chemical attacks **[78]**.

There are over 40 known natural zeolites and more than 150 synthetic zeolites have been reported **[79,80]**. The number of synthetic zeolites with new structure morphologies grows rapidly with time. Based on the size of their pore opening, zeolites can be roughly divided into five major categories, namely 8-, 10- and 12-membered oxygen ring systems, dual pore systems and mesoporous systems **[81]**.

A comprehensive bibliography of zeolite structures has been published by the International Zeolite Association **[79]**. The structural characteristics of assorted zeolites are summarized in Table i.

Zeolites with 10-membered oxygen rings normally possess a high siliceous framework structure. They are of special interest in industrial applications. In fact, they were the first family of zeolites that were synthesized with organic ammonium salts. With pore openings close to the dimensions of many organic molecules, they are particularly useful in shape selective catalysis **[81].** The 10-membered oxygen ring zeolites also possess other important characteristic properties including high activity, high tolerance to coking and high hydrothermal stability. Among the family of 10-membered oxygen ring zeolites, the MFI-type (ZSM-5) zeolite (Fig. ii) is probably the most useful one. ZSM-5 zeolite has two types of channel systems of similar size, one with a straight channel of pore opening 5.3x5.6 Å and the other with a tortuous channel of pore opening 5.1x5.5 Å. Those intersecting channels are perpendicular to each other, generating a three-dimensional framework. ZSM-5 zeolites with a wide range of SiO_2/Al_2O_3 ratio can easily be synthesized. High siliceous ZSM-5 zeolites are more hydrophobic **[82]** and hydrothermally stable **[83]** compared to many other zeolites.

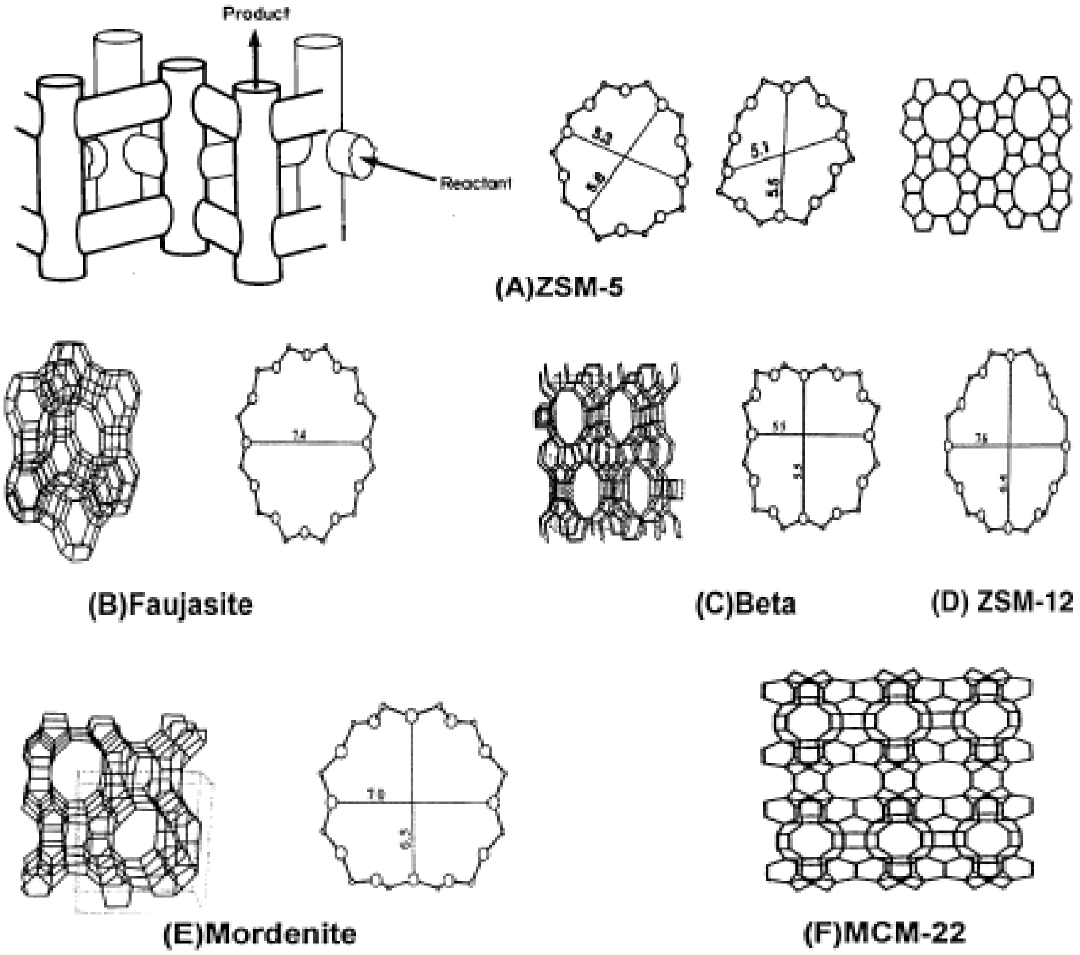


Fig. ii. Framework structure of zeolites: (A) ZSM-5 (B) Faujasite (C) Beta (D) ZSM-12 (E) Mordenite (F) MCM-22; **[79,84].**

Although the 10-membered oxygen ring zeolites were found to possess remarkable shape selectivity, catalysis of large molecules may require a zeolite catalyst with a larger-pore opening. Typical 12-membered oxygen ring zeolites, such as faujasite-type zeolites, normally have pore opening greater than ca. 5.5 Å and hence are more useful in catalytic applications with large molecules, for example in trimethylbenzene conversion. Faujasite (X or Y; Fig. ii) zeolites can be synthesized using inorganic salts and have been widely used in catalytic cracking since 1960s. The framework structures of zeolite Beta and ZSM-12 are shown in Fig. ii.

Zeolites with a dual pore system normally possess interconnecting pore channels with two different pore opening sizes. Mordenite is a well-known dual pore zeolite having a 12-membered oxygen ring channel (12-MR) with pore opening 6.5x7.0 Å, which is interconnected to 8-membered oxygen ring channel with opening 2.6x5.7 Å (Fig. ii). MCM-22, is a high silica zeolite first synthesized by Mobil in 1990 **[85]**. The framework topology is composed of two independent pore systems (Fig. ii). One of them is defined by two-dimensional sinusoidal channels **[84]**, which maintain an effective 10- membered oxygen ring diameter (0.41 × 0.51 nm) throughout the structure, and the other consists of supercages with 12-MR inner free diameter of 0.71 nm and inner height of 1.82 nm, and with 10-membered oxygen ring windows (0.40×0.55 nm). It is notable that the size of 10- membered oxygen ring windows of MCM-22 is very close to that of ZSM-5 and their acidities are very similar to each other **[86]**.

Many research efforts in synthetic chemistry have been invested in the discovery of large-pore zeolite with pore diameter greater than 12-membered oxygen rings. The discovery of mesoporous materials with controllable pore opening (from ca. 12 to more than 100 Å) such as VPI-5 **[87]**, MCM-41S **[88,89]** undoubtedly will shed new light on future catalysis applications.

Table i: structural characteristics of selected zeolites [79,81]:

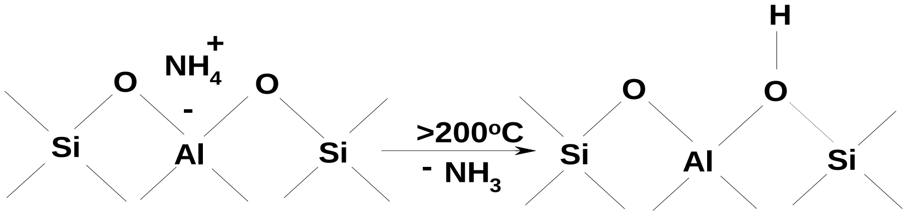
Zeolite	Number of rings	Pore opening (Å)	Pore/ channel structure
8-membered oxygen ring zeolites			
Erionite	8	3.6 X 5.1	Intersecting
10-membered oxygen ring zeolites			
ZSM-5	10	5.4 X 5.6 5.1 X 5.5	Intersecting
ZSM-11	10	5.3 X 5.4	Intersecting
ZSM-23	10	4.5 X 5.2	One-dimensional
Dual pore system			
Ferrierite (ZSM-35, FU-9)	10, 8	4.2 X 5.4	One-dimensional
		3.5 X 4.8	10:8 intersecting
MCM-22	12	7.1	Capped by six rings
	10	Elliptical	Two-dimensional
Mordenite	12	6.5 X 7.0	One-dimensional
	8	2.6 X 5.7	12:8 intersecting
Omega (ZSM-4)	12	7.4	One-dimensional
	8	3.4 X 5.6	One-dimensional
12-membered oxygen ring zeolites			
ZSM-12	12	5.5 X 5.9	One-dimensional
Beta	12	7.6 X 6.4	Intersecting
	12	5.5 X 5.5	
Faujasite (X, Y)	12	7.4	Intersecting
	12	7.4 X 6.5	12:12 intersecting
Mesoporous system			
VPI-5	18	12.1	One-dimensional
MCM41-S	–	16-100	One-dimensional

1.3.2. Acidic Properties of Zeolites

A solid acid is capable of converting an adsorbed basic molecule into its conjugate acid form. Therefore, the acid site is able to either transfer a proton from the solid to the adsorbed molecule (this type of acid center is called a Bronsted site) or transfer an electron pair from the adsorbed molecule to the solid surface (this type of acidity in called Lewis acidity). Generally, both types of acid sites are simultaneously present in zeolites.

In most catalytic applications, zeolites are used as solid acids **[90-95]** For the generation of Bronsted acid sites in zeolites, such OH groups should be formed on the surface, which are able to transfer protons to the adsorbed molecules. This requires OH groups with loosely bound protons. Every procedure is suitable to generate Bronsted acidity, which leads to the formation of surface OH groups of the previous mentioned nature.

Surface hydroxyl groups can be generated in zeolites by different methods: (i) Direct ion exchange of zeolites with acids such as diluted HCl, HNO_3, acetic acid etc. using this method only zeolites with a high Si/Al ratio may be transformed into their protonic form. (ii) Furthermore, Bronsted acidity is introduced by exchanging the nonframework cations (M^+) with ammonium or alkyl-ammonium ions followed by calcinations. iii) Dissociation of water molecules under the influence of the strong electrostatic field of multivalent cations, and (iv) Reduction of transition metal ion containing zeolites with hydrogen, resulting in Bronsted acid sites and metal particles in the zeolite hollow. Examples of these reactions are:



eq. 12

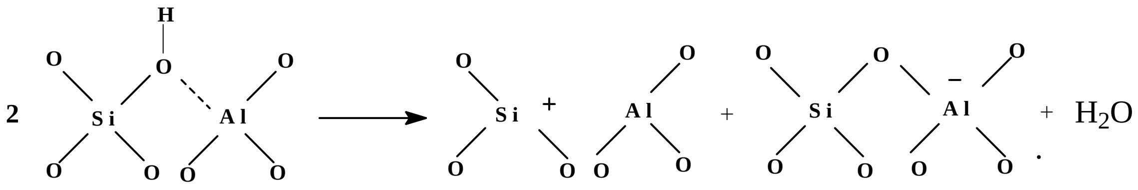
$$Mg^{2+}(H_2O) \longrightarrow Mg(OH)^{+} + H^{+} \qquad \text{eq. 13}$$

$$La^{3+}(H_2O) \longrightarrow La(OH)^{2+} + H^{+} \qquad \text{eq. 14}$$

$$La^{3+}(H_2O) \longrightarrow La(OH)_2^{+} + 2H^{+} \qquad \text{eq. 15}$$

$$Ni^{2+} + H_2 \longrightarrow Ni^{o} + 2H^{+} \qquad \text{eq. 16}$$

Lewis acid sites can be the charge-compensating cations or trigonal aluminum atoms at oxygen-deficient sites, which are unstable and undergo dealumination to form non-framework alumina with Lewis acidity. Protons within zeolites are generally associated with anionic framework sites, giving rise to readily ionizable hydroxyl groups with strong Brönsted acidity (proton donor). Calcination (at 773K) leads to formation of Lewis acid sites (electron acceptor) via dehydroxylation of two Brönsted acid sites. This theoretical model shows the presence of two Lewis acid sites (trigonal Al species and positive Si^+) and a Lewis basic site (tetrahedral negative Al species). Actually, the structure reorganizes and an aluminum ion leaves the framework, compensating for the negative charge of the adjacent aluminum as AlO^+. Jacobs and Beyer **[96]** suggested this extra-framework AlO^+ species to be the true Lewis acid site.



The acidic catalytic properties of zeolites have been extensively used in many commercial processes; X, Y, mordenite, L, pentasil high silica zeolites (ZSM-5, ZSM-8, ZSM-11), are commonly used. The hydroxyl groups with very acidic hydrogen have been recognized as the main source of these properties, especially of the efficient carboniogenic activity in zeolites **[97]**. Several parameters have to be taken into account to evaluate the acidity of zeolites in relation to a particular application. Besides the structure, other parameters such as the total number of Brönsted and Lewis sites, their strength distributions and their location, have a significant influence on the effective acidity of any particular site in relation to a particular reaction.

There is usually an increase in the number of strong Brönsted acid sites when the Si/Al ratio is increased, despite the reduction the total amount of acid sites **[98]**. The aluminium atoms induce a higher degree of electron donation than silicon, resulting in a higher oxygen charge and proton-oxygen interaction. Consequently, the acid site strength is reduced as the number of aluminium neighbors increases, and will be dependent on the Al ordering, for a given composition **[99,100]**. Many data for acid catalyzed process revealed a parallel trend with the aluminium framework content **[101]**, for limited Si/Al range. Generally, the catalytic activity goes through a maximum under further Si/Al increases **[102]**. This optimum value depends on the framework density of the zeolite.

Some dealumination processes, commonly used, can originate the formation and deposition on the porous structure of cationic aluminium species, which can act as Lewis sites of poison the strongest acid sites **[103]**. The presence of Lewis acid sites also has some influence on the Brönsted acidity strength. The inductive effect associated with the Lewis sites on the neighboring protonic sites increases the latter's, acid strength, resulting in an enhancement of some catalytic reactions **[104,105]**.

1.3.3. Shape Selectivity of Zeolite

The term ‘shape-selective catalysis’ refers to the fact that zeolites can be shape and size selective in catalytic molecular rearrangements. Shape selectivity depending on whether pore size limits the entrance of the reacting molecule, the departure of the product molecule or the formation of certain transition states.

Over the past years, many new zeolitic materials have been discovered. Of particular importance was the discovery of the synthetic medium pore zeolites with ‘port’ sizes of 5 to 6 Å, especially of ZSM-5 **[106]**. One of the unique shape-selective characteristics of ZSM-5 is its para-selectivity in electrophilic substitution reactions, such as alkylation and disproportionation of alkyl aromatics.

ZSM-5 is remarkably stable as an acid catalyst. This is probably due to its peculiar structure with l0-membered oxygen-ring-sized pores of uniform dimension and absence of large supercages with smaller size windows **[9]**. These geometrical factors impose geometrical constraints on the formation of large polynuclear hydrocarbons responsible for coking **[107]**. The combination of acidity, shape selectivity and low coke formation are responsible for the successful industrial applications of ZSM-5 based zeolites **[108]**, such as: manufacture of petrochemicals (ethylbenzene and p-xylene), octane improvement of reformate gasoline, dewaxing of middle distillates and lubricating oils and production of gasoline from methanol. HZSM-5 is also used as an additive in some FCC catalysts for octane enhancement of gasoline. Another commercial shape-selective process, Mobil’s Selectoforming, uses an erionite-based catalyst **[109]**.

H-ZSM-5 zeolite is para selective catalyst in toluene disproportionation, methylation of toluene and xylene isomerization **[110]**. Further enhancement of the shape selectivity can be achieved by post synthetic modification, which leads to removal of unselective acid sites located in the pore mouth region and/or to a narrowing of the pore openings. This modification of H-ZSM-5 effectively suppresses the secondary isomerization to undesired o- and m-xylenes and enlarges the differences in the diffusivity between o- or m-isomers and p-isomer **[111]**.

1.3.3.1. Generalities on shape-selective catalysis

A number of comprehensive reviews and critical discussions on the principles and applications of sh36-37ape-selective catalysis **[112-115]** have been published by several authors.

The concept of molecular shape-selective catalysis implies an intimate interaction between the shape, size, and configuration of reactants, transition states and products, and the dimensions, geometry and tortuosity of the channels and cages of the zeolite

Csicsery has categorised the following three shape selective effects:

1. **Reactant Selectivity**, which takes place when some molecules of the feed are too bulky to diffuse through the zeolite pores and are prevented to react. An example is Mobil's Selectoforming process where linear paraffins are selectively hydrocracked from a mixture of paraffinic and aromatic hydrocarbons over an erionite based catalyst **[109].** Branched, cycloparaffins and aromatic hydrocarbons are not affected (Fig. iii).

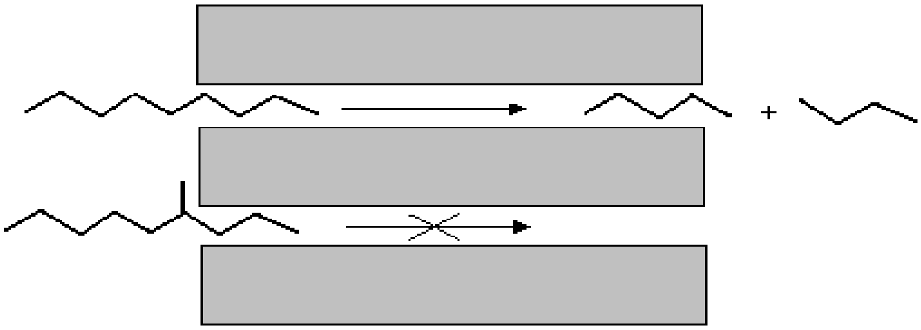


Fig. iii. Reactant Selectivity

2. Product Selectivity, which occurs when similar restrictions apply to the product molecule (Fig. iv). It plays an important role in the selective production of para-aromatic compounds on ZSM-5 based catalysts **[9]** and also affects the deactivation by coking of catalysts in general **[107].**

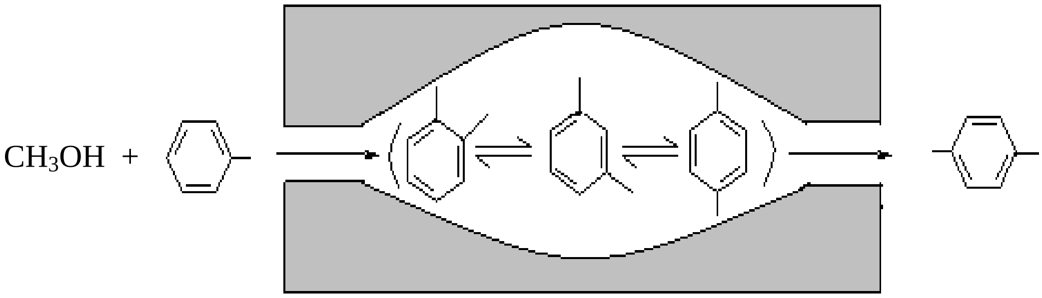


Fig. iv. Product Selectivity

3. Restricted transition state-type selectivity, in which, certain reactions are prevented because the corresponding transition state is too large and would require more space than available in the cavities. However, neither reactants nor potential products are prevented from diffusing through the pores; only the formation of the transition state is hindered. An interesting example is acid-catalyzed transalkylation of dialkylbenzenes (Fig. v). This and an isomerization are only two of the many possible reactions **[116-118]**.

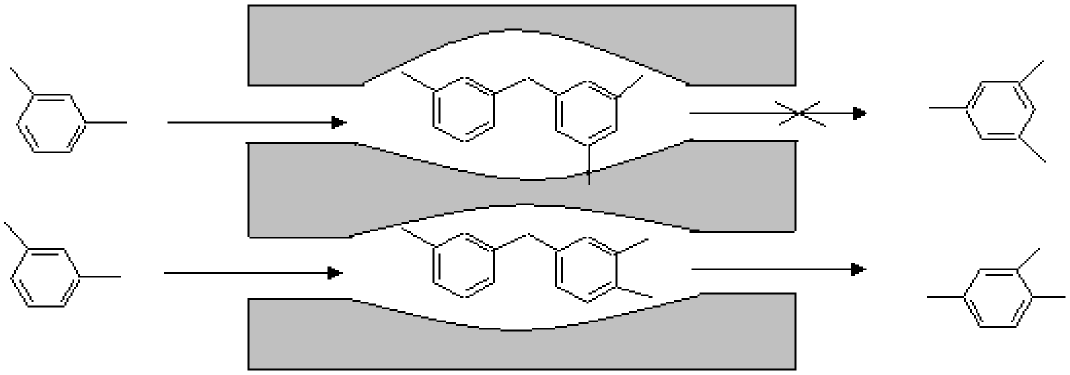


Fig. v. Restricted transition state selectivity

4. Molecular traffic control is a special type of shape selectivity. It could occur in zeolites with more than one type of intersecting pore system. Reactant molecules here may preferentially enter the catalyst through one of the pore system while the products diffuse out by the other. This may minimize counterdiffusion and this increase reaction rates.

Apparent lack of rate limitation by counterdiffusion in certain reactions in ZSM-5 suggested the concept of molecular traffic control **[119,120]**. ZSM-5 and silicalite have two types of channels, both of which have ten-membered ring openings. One channel system is sinusoidal and has a nearly circular (5.4 x 5.6 Å) cross-section. The other channel system has elliptical openings (5.2 × 5.8Å). These are straight and perpendicular to the first system **[121,122].**

1.3.3.2. Diffusion

The importance of diffusion in shape-selective catalysis cannot be overemphasized. In general, one type of molecule will react preferentially and selectively in a shape-selective catalyst if its diffusivity is at least one or two orders of magnitude higher than that of competing molecular types. Too large molecules will be absolutely unable to diffuse through the pores. Even those molecules which react preferentially have much smaller diffusivities in shape-selective catalysts than in large-pore catalysts. For example, normal paraffins have diffusivities at least five orders of magnitude lower in the zeolite KT than in the large-pore Y-type zeolite. Decreased diffusivities, of course, affect reaction rates. Alkylation of toluene with methanol provides an example for the decrease of reaction rate with increasing selectivity. An equilibrium distribution of all xylene isomers is obtained over small (diameter <0.5 µ) crystals of ZSM-5. Over larger crystals (~ 3 µ diameter) the mixture contains 46% p-xylene **[9].** If the ZSM-5 zeolite is impregnated with phosphoric acid or other phosphorus compounds, its channel size decreases, tortuosity increases **[123],** and diffusion becomes more hindered **[11,124]**. Although p-xylene selectivity can reach 97% here, the activity of the phosphorus treated catalyst is less at 600°C than that of the pure ZSM-5 at 500°C **[9]**.