

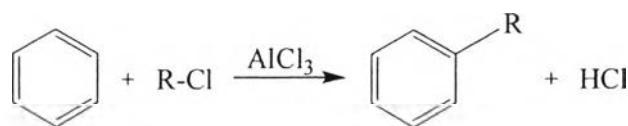
## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Alkylation Reaction

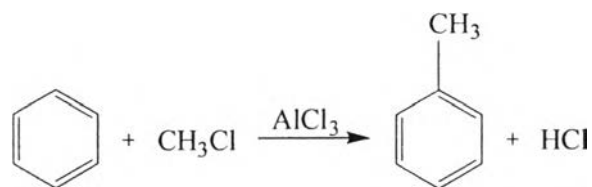
Alkylation reaction is a substitution reaction that removes an alkyl group from one molecule to another. There are many different types of alkylation. These types are classified on the character of the alkylating agent. There are nucleophilic alkylating agent and electrophilic alkylating agent (Mcketta, 1993).

Nucleophilic alkylating agents transport a negatively charged alkyl group to the hydrocarbon, while electrophilic alkylating agents transport a positively charged alkyl group to the hydrocarbon. The catalyst used in this reaction depended on the mechanism. Nucleophilic alkylating agents are the use of organometallic compounds such as Grignard (organomagnesium), organolithium, organocopper, and organosodium reagents. Electrophilic alkylating agents are the use of alkyl halides with a Lewis acid catalyst to alkylate aromatic substrates in Friedel-Crafts reactions. Figure 2.1 shows the example of alkylation reaction.



**Figure 2.1** Alkylation reaction.

Methylation reaction is the substitution of an atom or group is replaced by a methyl group or the addition of a methyl group to a substrate. Methylation is a form of alkylation with specifically a methyl group, rather than a larger carbon chain, replacing a hydrogen atom. The example of methylation reaction is shown in Figure 2.2.



**Figure 2.2** Methylation reaction.

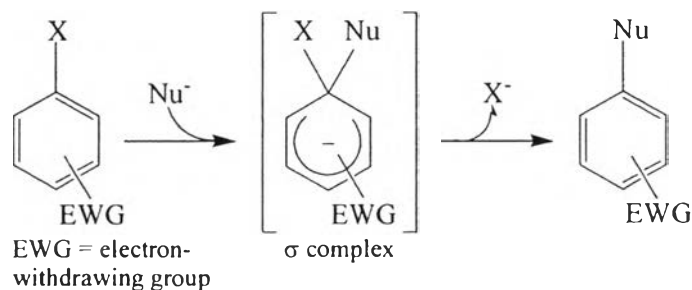
### 2.1.1 Nucleophilic Substitution

Nucleophilic substitution occurs when the reagent is a nucleophile, which means, an atom or molecule with free electrons.

Nucleophilic aliphatic substitution reactions are the reactions between a nucleophile with aliphatic substrate that have the ability to rotate plane-polarized light (optical activity) present those two mechanisms for these types of reactions:  $S_N1$  (unimolecular nucleophilic substitution) and  $S_N2$  (bimolecular nucleophilic substitution). The  $S_N1$  mechanism follows first-order kinetics (the reaction rate depends on the concentration of one reactant), and its intermediate contains only the substrate molecule and is therefore unimolecular. This mechanism has two steps. In the first step, the leaving group departs, forming a carbocation. In the second step, the nucleophilic reagent attacks the carbocation and forms a sigma bond. The  $S_N2$  mechanism follows second-order kinetics (the reaction rate depends on the concentrations of two reactants), and its intermediate contains both the substrate and the nucleophile and is therefore bimolecular. This mechanism has only one step. The attack of the reagent and the expulsion of the leaving group happen simultaneously.

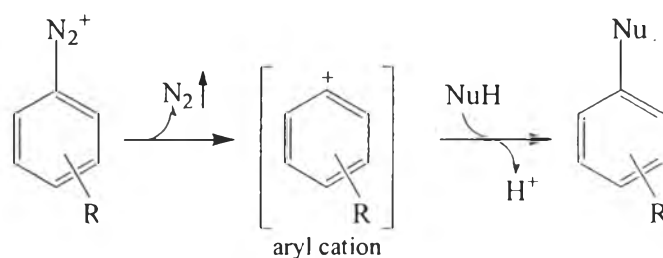
Nucleophilic aromatic substitution reactions are the reaction in which the nucleophile with an aromatic substrate. There are 6 nucleophilic substitution mechanisms came upon with aromatic systems.

- the free radical  $S_{RN}1$  mechanism
- the ANRORC mechanism
- Vicarious nucleophilic substitution
- the  $S_{NAr}$  (addition-elimination) mechanism, as shown in Figure 2.3



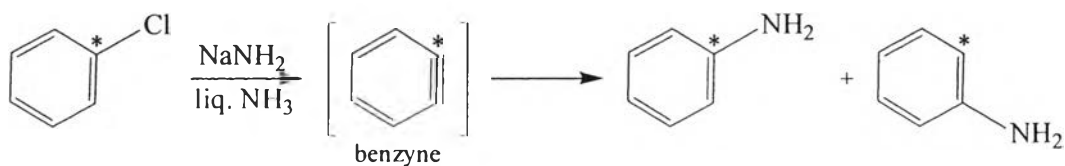
**Figure 2.3**  $S_NAr$  mechanism.

- the aromatic  $S_N1$  mechanism encountered with diazonium salts, as shown in Figure 2.4.



**Figure 2.4** Aromatic  $S_N1$  mechanism encountered with diazonium salts.

- the benzyne mechanism, as shown in Figure 2.5.



**Figure 2.5** Benzyne mechanism.

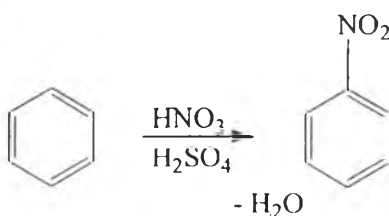
### 2.1.2 Electrophilic Substitution

Commonly lead to electrophilic addition reaction instead of electrophilic substitution reaction when electrophilic reactions to other unsaturated compounds than arenes. A difference between these two reaction types is that in the

former the  $\pi$  bond is lost and replaced by two sigma bonds, and in the latter there is no net loss of  $\pi$  electrons.

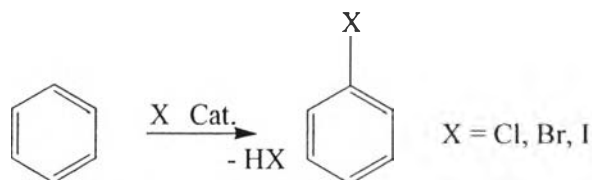
Electrophilic aromatic substitution is one of the primary methods for functionalizing aromatic rings. It is an organic reaction wherein an atom, usually hydrogen, appended to an aromatic system is replaced by an electrophile. The mechanism has two steps. The first step is the attack on the electrophile. In the second step, a pair of electrons from the  $\pi$  cloud attacks the electrophile breaking the aromaticity of the ring and generating a carbocation intermediate. In the final step of the reaction a strong base abstracts a proton from the carbon atom that received the electrophile to regenerate the aromatic ring. The most important reactions of this type that take place are (see Figure 2.6 - Figure 2.10):

- the nitration



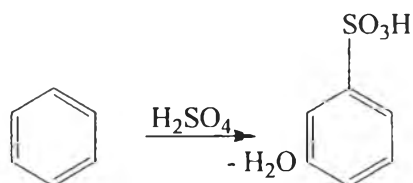
**Figure 2.6** Nitration of benzene.

- the halogenation



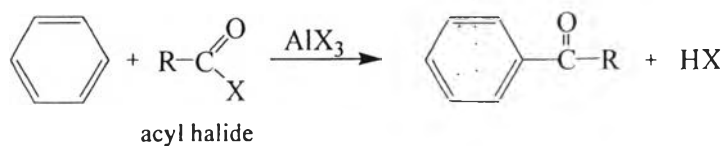
**Figure 2.7** Halogenation of benzene.

- the sulfonation



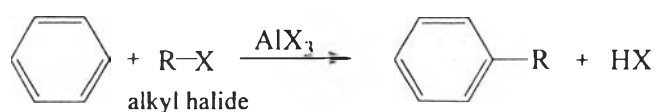
**Figure 2.8** Sulfonation of benzene.

- the Friedel-Crafts acylation



**Figure 2.9** Friedel-Crafts acylation of benzene.

- the Friedel-Crafts alkylation

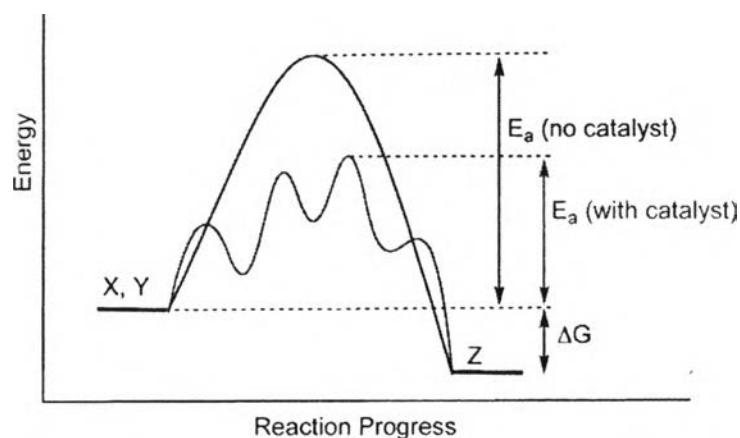


**Figure 2.10** Friedel-Crafts alkylation of benzene.

## 2.2 Alkylation Catalysts

A catalyst is any substance which modifies the rate of a chemical reaction but is not changed chemically at the end of the reaction. Catalysts can be organic, synthetic or metal. The process by which the catalyst speeds up or slows a reaction is identified catalysis.

Catalysts lower the activation energy and lower free energy of the transition state, by providing an alternative pathway. Catalyst does not affect overall free energy change of reaction (see Figure 2.11).



**Figure 2.11** Generic potential energy diagrams.

Catalysts can be homogeneous or heterogeneous, dependent on whether a catalyst exists in the same or difference phase as the reactant.

### 2.2.1 Homogeneous Catalysts

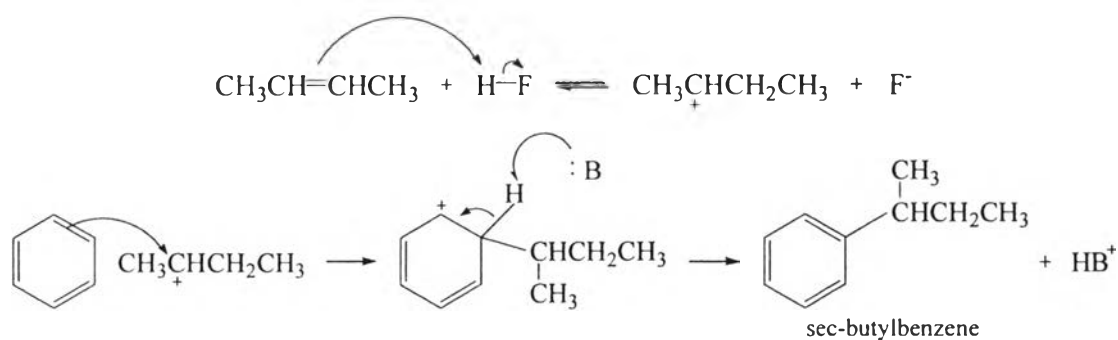
Homogeneous catalyst is in the same phase as the reactants. Typically everything will be present as a gas or contained in a single liquid phase.

A widely used homogeneous alkylation catalyst may be Lewis acid catalysts such as  $\text{AlCl}_3$  (aluminium chloride),  $\text{FeCl}_3$  (ferric chloride), and  $\text{BF}_3$  (boron trifluoride) or Brønsted acid catalysts such as HF (hydrogen fluoride) and  $\text{H}_2\text{SO}_4$  (sulfuric acid).

Note that, HF is advantageous in that its chemical stability makes it suitable for use over a wide range of conditions. However, HF is disadvantageous in that it is a volatile substance.

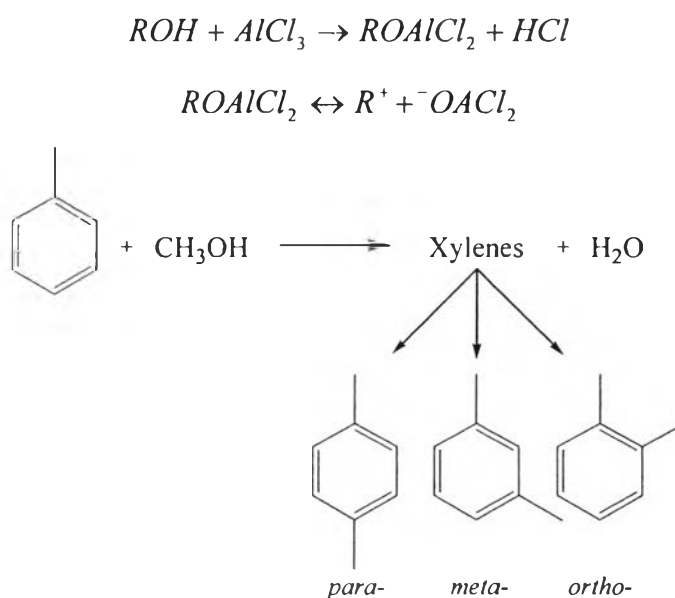
When using alkenes as alkylating agents, alkenes are treated with a Lewis acid catalyst, a small amount of a proton acid is typically added as a co-catalyst to promote the formation of carbocation.

In the presence of Brönsted acid catalyst, a proton is donated by the acid to substrate. Figure 2.12 shows formation of carbocation by using alkenes in Brönsted acid catalyst.



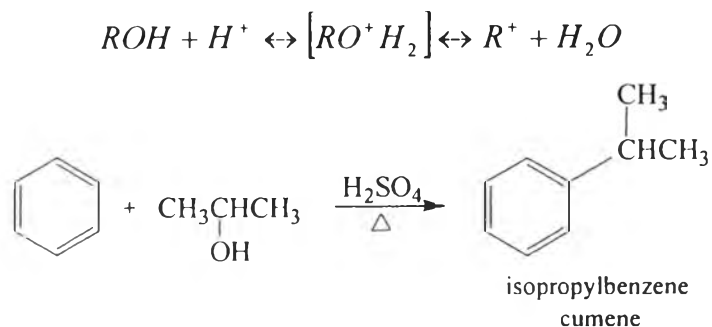
**Figure 2.12** Formation of carbocation by using alkenes in Brönsted acid catalyst.

If the alkylating agents are alcohols, in presence of Lewis acids, a complex is first formed with the alcohol and HCl is released. The complex then donates the carbocations. Formation of carbocation by using alcohol in Lewis acid catalyst is shown in Figure 2.13.



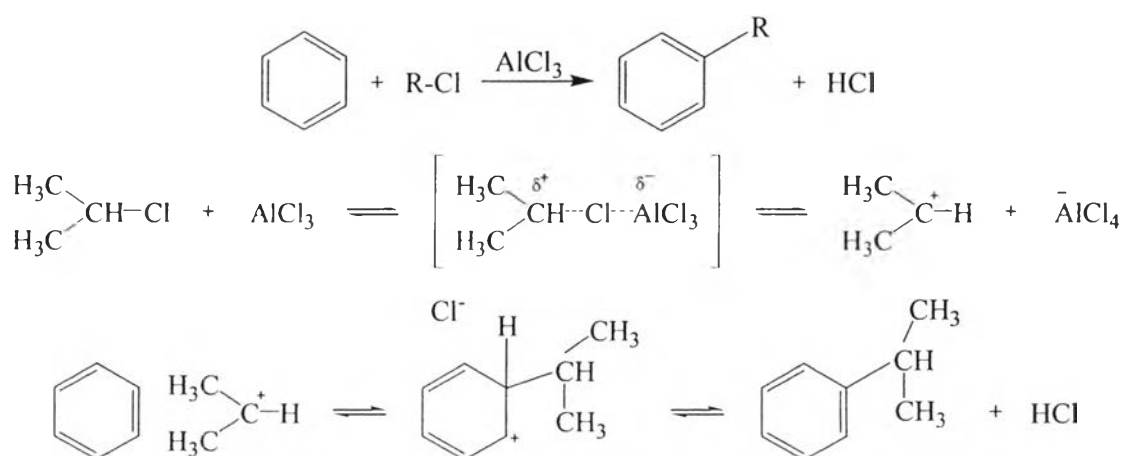
**Figure 2.13** Formation of carbocation by using alcohol in Lewis acid catalyst (Breen *et al.*, 2007).

In the presence of Brönsted acids, they are protonated and carbocations may be formed. Figure 2.14 show formation of carbocation by using alcohol in Brönsted acid catalyst.



**Figure 2.14** Formation of carbocation by using alcohol in Brönsted acid catalyst.

In the Friedel-Crafts alkylation reaction (see Figure 2.15) as aluminum chloride ( $AlCl_3$ ) is used as the catalyst, Alkyl halide has been generally used to alkylating agent. In this mechanism an alkyl halide with  $AlCl_3$  formed the carbocation, an activated electrophile, which subsequently attacked the aromatic ring.



**Figure 2.15** Friedel-Crafts alkylation reaction.



There are many other sources of carbocations such as alcohols, esters, ethers and olefins (Mcketta, 1993).

However, the Friedel-Crafts alkylation reaction has some limitations. Polyalkylation can occur when the product of this alkylation is more reactive than benzene. Furthermore, carbocation rearrangement can occur. Accordingly primary alkyl chlorides typically give secondary alkylbenzenes as the major product. The Friedel-Crafts alkylation reaction is not an appropriate reaction to make the primary alkyl-substituted benzene derivatives.

Sridevi *et al.* (2001) studied the alkylation of benzene with ethanol on  $\text{AlCl}_3$  impregnated 13X zeolite to determine the kinetics of benzene alkylation, to develop a kinetic model, and to estimate the unknown parameters of the kinetic model so as to obtain an intrinsic rate expression. The experiments carried out with different amounts of  $\text{AlCl}_3$  gave the maximum benzene conversion with catalyst containing 15%  $\text{AlCl}_3$ . Moreover, the results indicated no deactivation of  $\text{AlCl}_3$  by hydrolysis with water generated by the reaction.

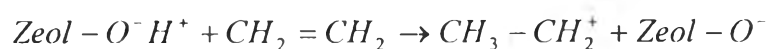
### 2.2.2 Heterogeneous Catalysts

Heterogeneous catalyst is present in a different phase (i.e. solid, liquid and gas, but also oil and water) to the reactants. Most heterogeneous catalysts are solids that operate on substrates in a liquid or gaseous reaction mixture. Diverse mechanisms for reactions on surfaces are known, depending on how the adsorption takes place (Langmuir-Hinshelwood, Eley-Rideal, and Mars-van Krevelen) (Knözinger *et al.*, 2003). The total surface area of solid has an important effect on the reaction rate. One will get the larger surface area for a given mass of particles when one uses the smaller catalyst particle size.

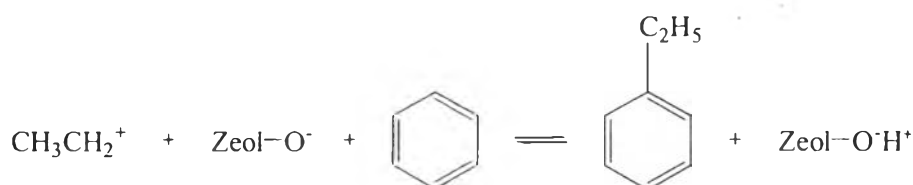
Heterogeneous catalysts are typically “supported,” which means that the catalyst is dispersed on a second material that improves the effectiveness or minimizes their cost. Sometimes the support is only a surface on which the catalyst is spread to increase the surface area. More often, the support and the catalyst interact, affecting the catalytic reaction.

Heterogeneous catalysts in alkylation reaction have been carried out using a variety of acidic oxides such as  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3/\text{SiO}_2$ . These catalysts also

promote carbonium ion typed reactions. By varying the method of preparation, silica/alumina catalysts may be amorphous or crystalline. These compounds have both Brönsted and Lewis acid sites. For example, when alkylating benzene with ethylene on a zeolite catalyst, adsorbed ethylene is protonated at a Brönsted acid site on the catalyst surface forming an ethylcarbonium ion (Matar *et al.*, 1989).

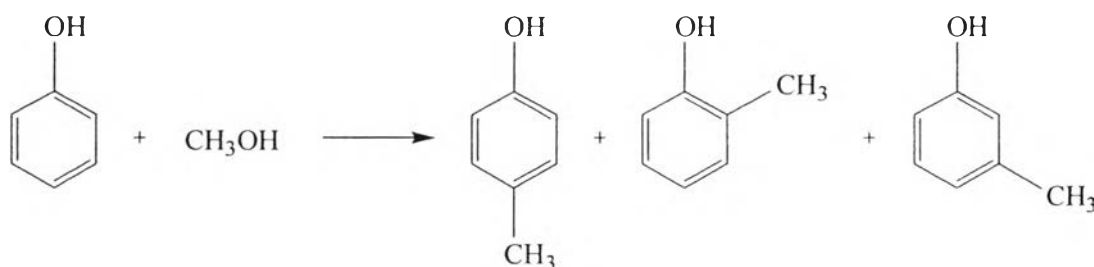


The carbocation then attacks the benzene ring (see Figure 2.16) giving ethylbenzene and the proton is regained by zeolite.



**Figure 2.16** Carbocation attacks the benzene ring (Matar *et al.*, 1989).

Zeolites were found to be more suitable alkylation catalysts than the amorphous types because of their activities and selectivity toward certain reactions. For example, when phenol was alkylated with methanol in the presence of zeolite type catalyst, as shown in Figure 2.17, a higher percentage of *p*-cresol was obtained than homogeneous or amorphous silica/alumina catalysts were used (Matar *et al.*, 1989).



**Figure 2.17** The alkylation of phenol with methanol using zeolite as catalyst (Matar *et al.*, 1989).

The solid alkylation catalysts are advantageous in that they may be removed from an alkylated product by simple filtration or decantation. Alkylations using the solid catalysts also may be amenable to a flow system in which the liquid feed materials to be alkylated are allowed to flow down a column containing the catalyst. Table 1 shows solid alkylation catalyst types and uses.

**Table 2.1** Solid alkylation catalyst types and uses (Rase, 2000)

Catalyst	Description	Suppliers	Licensors	Use
Boron trifluoride on $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Small amount of BF <sub>3</sub> on alumina	UOP LLC	UOP LLC (Alkar process)	Alkylation of benzene with ethylene (vapor-phase) to produce ethylbenzene
Zeolite, Y-type (faujasite)	USY-type (ultra stable) pore site: 7.4 Å SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> >3	UOP LLC	(original catalyst developed by Unocal)	Alkylation of benzene with ethylene (liquid-phase) to produce ethylbenzene
Zeolite, ZSM-5 (pentasil)	Specially modified medium pore zeolite high silica/alumina ratio (>20) pore size 5.5 Å extrudates	Mobil	Mobil-Badger, (now Mobil-Raytheon Engineers & Constructors) (Third generation EP process)	Alkylation of benzene with ethylene (vapor-phase) to produce ethylbenzene
EBMAX or EBEMAX catalyst	MCM-22 pentasil zeolite extrudates	Mobil United Catalysts	Mobil-Raytheon Engineers & Constructors (EBMAX)	Alkylation of benzene with ethylene (liquid-phase) to produce ethylbenzene
Packaged zeolite	Pentasil zeolite packaged	CDTECH	ABB Lummus Global	Catalytic distillation simultaneous alkylation of benzene with (ethylene or propylene) to produce ethylbenzene or cumene

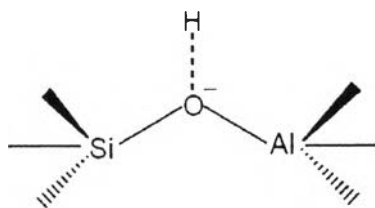
**Table 2.1** Solid alkylation catalyst types and uses (Cont.)

<b>Catalyst</b>	<b>Description</b>	<b>Suppliers</b>	<b>Licensor</b>	<b>Uses</b>
Phosphoric acid on Kieselguhr (SPA process, i.e. solid H <sub>3</sub> PO <sub>4</sub> process)	65-70% H <sub>3</sub> PO <sub>4</sub> -n-silica Extrudates: 1/4 and 3/16 in, sphere: 1/4 × 5/16 in, 3/16 × 1/4 in	United Catalysts UOP LLC	UOP LLC (SPA process, i.e. solid phosphoric acid process)	Alkylation of benzene with propylene (vapor-phase) to produce cumene
Q-Max catalyst	Beta zeolite extrudates	UOP LLC	UOP LLC	Alkylation of benzene with propylene (liquid-phase) to produce cumene
MCM-22 catalyst	Pentacil zeolite extrudates	Mobil	Mobil-Raytheon Engineers & Constructors	Alkylation of benzene with propylene (liquid-phase) to produce cumene
3-DDM	Dealuminated mordenite to create controlled 3-dimensional structure	Dow	Dow/Kellogg	Alkylation of benzene with propylene (liquid-phase) to produce cumene
Solid-acid catalyst (not revealed)	Heterogeneous acid catalyst	UOP LLC	UOP (Detal process)	Alkylation of higher molecular weight olefins w/ benzene to produce LAB for detergent

### 2.2.3 Zeolites

Zeolites are crystalline microporous minerals which are widely distributed in nature, which have been known for almost 250 years. It was the Swedish mineralogist Axel Fredrick Cronsted who in 1756 had the honour to discover the so called stilbite. He observed that a large amount of steam was obtained upon heating. Therefore, this material was named “zeolite”, which stems from classical Greek, where ζεω (zeo) means “to boil” and λιθος (lithos) means “stone”.

Zeolite structures consist of silicon ( $\text{Si}^{+4}$ ) and aluminium ( $\text{Al}^{+3}$ ) cations, which are tetrahedrally coordinated by four oxygen anions ( $\text{O}^{-2}$ ), thus forming a macromolecular three-dimensional framework in such a way that uniform voids and channels are created in the crystals, with pore sizes ranging between 4-12 Å (Ward, 1967). The aluminium in this polymeric structure generates a negative charge, which will be located on one of the oxygen anions connected to each aluminium cation, according to Figure 2.18 (Lobo *et al.*, 2005).



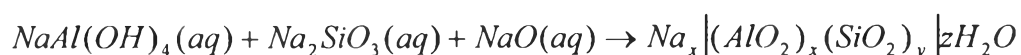
**Figure 2.18** Basic chemical structure of a zeolite (Lobo *et al.*, 2005).

Zeolites have a porous structure that can accommodate a wide variety of cations, such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution.

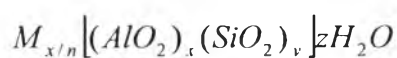
Natural zeolites form where volcanic rocks and ash layers react with alkaline groundwater. Zeolites also crystallize in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins. Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz, or other zeolites. For this reason, naturally

occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential.

Synthetic zeolites are crystalline compounds which have similar structure to natural faujasite and modernite. Zeolites can be synthesized by reacting sodium aluminate and sodium silicate in presence of sodium hydroxide under proper reaction conditions.



A general formula for zeolite could be represented as:



where M represents the metal cation and n is the oxidation number of the cation, and a general structure of tetrahedral building units form ring structures and polyhedral. Zeolite catalysts are strongly desired because of their high density of active acid sites, hydrothermal stability, and high size selectivity (Matar *et al.*, 1989).

Zeolites are the aluminosilicate members of the family of microporous solids known as molecular sieves. The term molecular sieve refers to a particular property of these materials, i.e., the ability to selectively sort molecules based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the dimensions of the channels. These are conventionally defined by the ring size of the aperture, where, for example, the term "8-ring" refers to a closed loop that is built from 8 tetrahedrally coordinated silicon (or aluminum) atoms and 8 oxygen atoms. These rings are not always perfectly symmetrical due to a variety of effects, including strain induced by the bonding between units that are needed to produce the overall structure, or coordination of some of the oxygen atoms of the rings to cations within the structure. Therefore, the pores in many zeolites are not cylindrical.

Furthermore acid sites result from the imbalance of the metal and the oxygen formal charge in the primary building unit. This can easily be recognized in the case of zeolites, which consist of a three-dimensional network of Si–O tetrahedral. A lattice comprising of only Si–O tetrahedral is neutral (the  $4^+$  charge at the silicon is balanced by four oxygen atoms with each  $2^-$  charge, however, belonging to two tetrahedral). Replacing one  $\text{Si}^{4+}$  atom by  $\text{Al}^{3+}$  causes a formal charge on the tetrahedron of  $1^-$ . This negative charge is then balanced by a proton or metal cation forming an acid site. The bare, negatively charged tetrahedron is then the corresponding base (Stocker, 2005).

In  $\text{AlPO}_4$  type microporous materials the framework structure consists of a strictly alternating Al–O–P sequence ( $\text{Al}^{3+}$  and  $\text{P}^{5+}$ , balanced by four oxygen atoms with each  $2^-$  charge, however, belonging to two tetrahedral), resulting in a completely neutral lattice as well, like in the case of pure silica zeolites. Depending on the combinations of the metal cation in the lattice, frameworks with positive or negative charges are in principle possible; however, so far only cation exchanged microporous materials are known. Vijayaraghavan *et al.* (2004) studied the activity of large pore  $\text{AlPO}_4$ -5 molecular sieves substituted with Mg, Mn and Zn in the vapor-phase ethylation of benzene with ethanol. They found that MAPO-5, ZAPO-5 and MnAPO-5 give higher conversion than  $\text{AlPO}_4$ -5 due to isomorphous substitution of metal in the framework of the catalyst. Among the catalyst, MnAPO-5 is more active than others because of the presence of unpaired electrons in the d-subshell.

Table 2.2 summarizes the application of zeolites sequentially. The first relevant application was for the physical separations of liquid or gas mixtures; therefore, they were included in the family of molecular sieves, where their well-defined pores system has been recognized to allow separations at molecular levels with high selectivities (Meier *et al.*, 1968 and Barrer *et al.*, 1982). It motivated the first investigations about the structural characterization of zeolites, mainly by X-ray diffraction (XRD) (Meier *et al.*, 1979 and Barrer *et al.*, 1979). At the beginning, zeolites were applied as adsorbents in the purification of gas flows to remove water and volatile organic species, and in the separation of different isomers and gas-mixtures (Dessau *et al.*, 1984).



**Table 2.2** Historical events and future application for the zeolites (Lobo *et al.*, 2005)

Year	Event
1756	Cronsted discovered intumescence of stilbite in blowpipe flame: zeolite
1862	Claire Deville synthesized levynite
1896	Friedel developed open-framework idea: occlusion various liquids
1925	Weigel and Steinhoff discovered the molecular sieve effect (they observed that dehydrated chabazite adsorbed water, methanol, ethanol, but excluded acetone, ether and benzene)
1927	Leonard used XRD for structural identification
1930	Taylor and Pauling determined the first structures
1932	McBain introduced the concept of “Molecular Sieves”
1945	Barrer presented the first classification based on molecular size considerations
1948	Barrer synthesized synthetic analogue of mineral mordenite
1949-1954	Milton and Breck discovered zeolites A, X, and Y
1954	Union Carbide commercialized zeolites as separation and/or purification materials
1955	Breck and Reed reported on the structure of zeolite A
1959	Union Carbide developed <i>n</i> /iso-paraffin separation and isomerization catalyst based on zeolite Y
1962	Mobil Oil used zeolite X as cracking catalyst
1969	Grace described first modification: steaming of zeolite Y to ultra-stable zeolite Y (US-Y)
1974	Henkel used zeolite A in detergents
1982	Union Carbide described aluminophosphates (AlPO <sub>4</sub> )
In our days	Zeolitic materials are mainly being explored as support materials for highly active homogeneous catalysts

However, the major use of zeolites is as ion exchange, due to its interchanging cation (see Figure 2.18). For example, they remove calcium and magnesium dissolved in water in laundry detergents.

Furthermore, the enormous interest in these materials is due to their wide catalytic applications within industrial areas such as oil refining, petrochemistry, and the synthesis of special chemicals. Nowadays, zeolites are broadly available on a large scale and used in a variety of applications (Hölderich *et al.*, 1986).

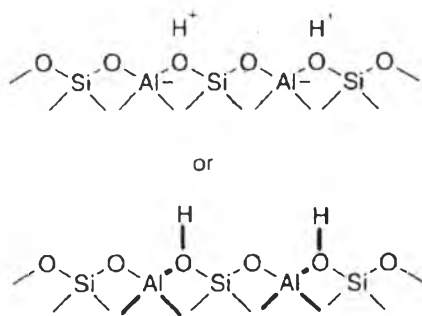
In general the major benefit of the zeolites as catalysts is that they contain a unique microporous structure (Hölderich *et al.*, 1989). The shape and size of the particular pore system exerts a steric influence on the reaction, controlling the adsorption of reactants and desorption of products. It is for that reason that zeolite's micropores can induce various kind of shape selectivity (reactant, transition state, and product shape selectivity). Besides the highly favourable role in providing shape selectivity, the presence of micropores in some cases limits the catalytic performance of the zeolites. For example, titanium silicalate (TS-1) can bring about selective heterogeneous epoxidation with aqueous hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), but its catalytic activity is limited by the small pore diameter (c.a. 5.5 Å); therefore, the oxidation of olefins with molecular sizes larger than 5.5 Å has been ineffective.

Zeolites are commonly obtained by hydrothermal synthesis, which consist of water as the solvent, a silicon source, an aluminium source, a mineralizing agent and a structure-directing agent (Barrer *et al.*, 1961). The latter component plays a very important role in the control of the resulting structures, and in the prediction of a specific structure (Venuto *et al.*, 1968). With regards to this have stated some general rules between the structure-directing agent and the structure of zeolites with high silica content:

- In the absence of structure-directing agent dense crystalline and layered materials are obtained.
- One-dimensional structures with 10 or 12-ring channels are obtained from linear structure-directing agents, for example in the case of mordenite (MOR).

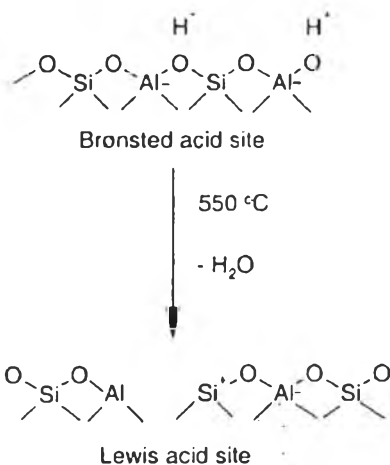
- Multi-dimensional zeolites with pore diameters of 4-7 Å are formed when branched structure-directing agents are used. Two typical examples are ferrierite (FER) and zeolites X and Y (FAU). Ferrierite is a two-dimensional zeolite with 10-ring main channels, which are interconnected via smaller 8-ring side channels. Zeolites X and Y are three-dimensional structures with large cavities that are interconnected by 12-ring channels, which means that there are 12 cations ( $\text{Si}^{+4}$  and  $\text{Al}^{+3}$ ) and 12  $\text{O}^{-2}$  anions present in the ring (Lobo *et al.*, 2005).

An important property relating to the activity of zeolites is their acidity. The activity requested is based on the formation of Brønsted acid sites arising from the creation of “bridging hydroxyl groups” within the pore structure of the zeolites. These “bridging hydroxyl groups” are usually formed either by ammonium or polyvalent cation exchange followed by a calcinations step. The “bridging hydroxyl groups”, which are protons associated with negatively charged framework oxygen linked into alumina tetrahedra, are the Brønsted acid sites, as shown in Figure 2.19.



**Figure 2.19** Brønsted acid sites (“bridging hydroxyl groups”) in zeolites (Stocker, 2005).

The protons are quite mobile at higher temperatures, and at 550 °C they are lost as water molecules followed by the formation of Lewis acid sites, as shown in Figure 2.20. For zeolites, it can be stated that the concentration of aluminum in the lattice is directly proportional to the concentration of acid sites (Stocker, 2005).



**Figure 2.20** Formation of Lewis acid sites in zeolites (Stocker, 2005).

#### 2.2.4 ZSM-5 Zeolites

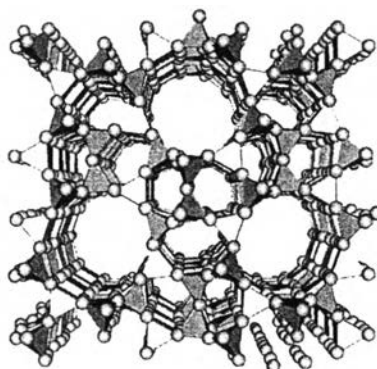
Zeolite Sieve of Molecular porosity (or Zeolite Socony Mobil) – 5, (the structure type MFI-Mordenite Framework Inverted) is an aluminosilicate zeolite mineral belonging to the pentasil family of zeolites. It contains a two dimensional 10-ring pore structure, with one set of pores in zig-zag, or sinusoidally shaped.

In ZSM-5 (or to be precise  $H^+$ -ZSM-5), there are very few replacements of Si by Al, so that the concentration of  $H^+$  ions in the solid is relative small. In absolute terms, however, it is considerable, and the ease with which the  $H^+$  ions (protons) are detached from the “active site”, at which they are initially anchored, lies at the root of the remarkable catalyst performances of ZSM-5.

Zeolite ZSM-5 (MFI) is perhaps the most versatile solid-acid catalyst known. There are more than 50 processes that use zeolite ZSM-5 as one of the main components of the catalysts. It is the second most used zeolite catalyst after zeolite Y. The zeolite is form largely of 5-rings that are organized as columns and connected to each other as in Figure 2.21. This zeolite belongs to the orthorhombic crystal system, but this framework is quite flexible and the exact crystallographic symmetry depends on composition, temperature and the presence of adsorbed molecules. There are two distinct 10-ring channels of nominally about 5.6 Å apertures. A straight channel runs along the  $[0\ 1\ 0]$  direction and a sinusoidal channel runs along the  $(100)$  direction.

The geometry of the channel intersection (slightly larger than the free diameter of the channels) is also illustrated (Scott *et al.*, 1996).

One of the reasons for the catalytic versatility of this zeolite is the broad range of compositions in which we can prepare it. It is possible to prepare ZSM-5 with Si/Al ratios from about 8 to infinity. In addition, it is possible to prepare material with the MFI framework with B, Ga, Ti, Co, and many others in the framework. This flexibility allows the industrial chemist and engineer to tune their catalytic properties to the desired optimum.



**Figure 2.21** Framework structure of zeolite ZSM-5 (MFI).

### 2.2.5 Zeolite Synthesis

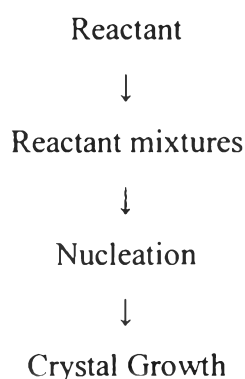
Zeolites are generally synthesized by a hydrothermal process from a source of alumina, source of silica and an alkali such as NaOH, and/or a quaternary ammonium compound. An inhomogeneous gel is produced which gradually crystallizes, in some cases forming more than one type of zeolite in succession. Nucleation effects can be important, and an initial induction period at near ambient temperature may be followed by crystallization temperatures that may range up to 200 °C or higher. The pressure is equal to the saturated vapor pressure of the water present.

The final product depends on a complex interplay between many variables including  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in the starting medium, nucleating agents, temperature, pH, water content, aging, stirring, and the presence of various inorganic and organic cations. Much remains to be learned about how the initial reaction

mixture forms the precursor species and how these arrange into the final crystalline products. A key concept is that the cations present give rise to a templating action, but clearly the process is more complex than this.

Synthetic zeolites are generally made by mixing solutions of aluminates and silicates, often with the formation of a gel, and by maintaining the mixture at temperatures of 100 °C or more for selected periods.

The synthesis of zeolites involves several steps, as shown below:



The mechanisms of zeolite formation are very complex due to the plethora of chemical reactions, equilibrium, and solubility variations that occur through the heterogeneous synthesis mixture during the crystallization process. The process of zeolitization is thermally activated and usually takes place at elevated temperatures in order to achieve a high yield of crystals in an acceptable period of time. The variables in the synthesis of zeolites are temperature, alkalinity (pH), and chemical composition, of the reactant mixtures. These variables do not necessarily determine the products obtained in hydrothermal reactions, because nucleation appears to be kinetically rather than thermodynamically determined and controlled. The kinetic variables include the treatment of reactants prior to crystallization, their chemical and physical nature.

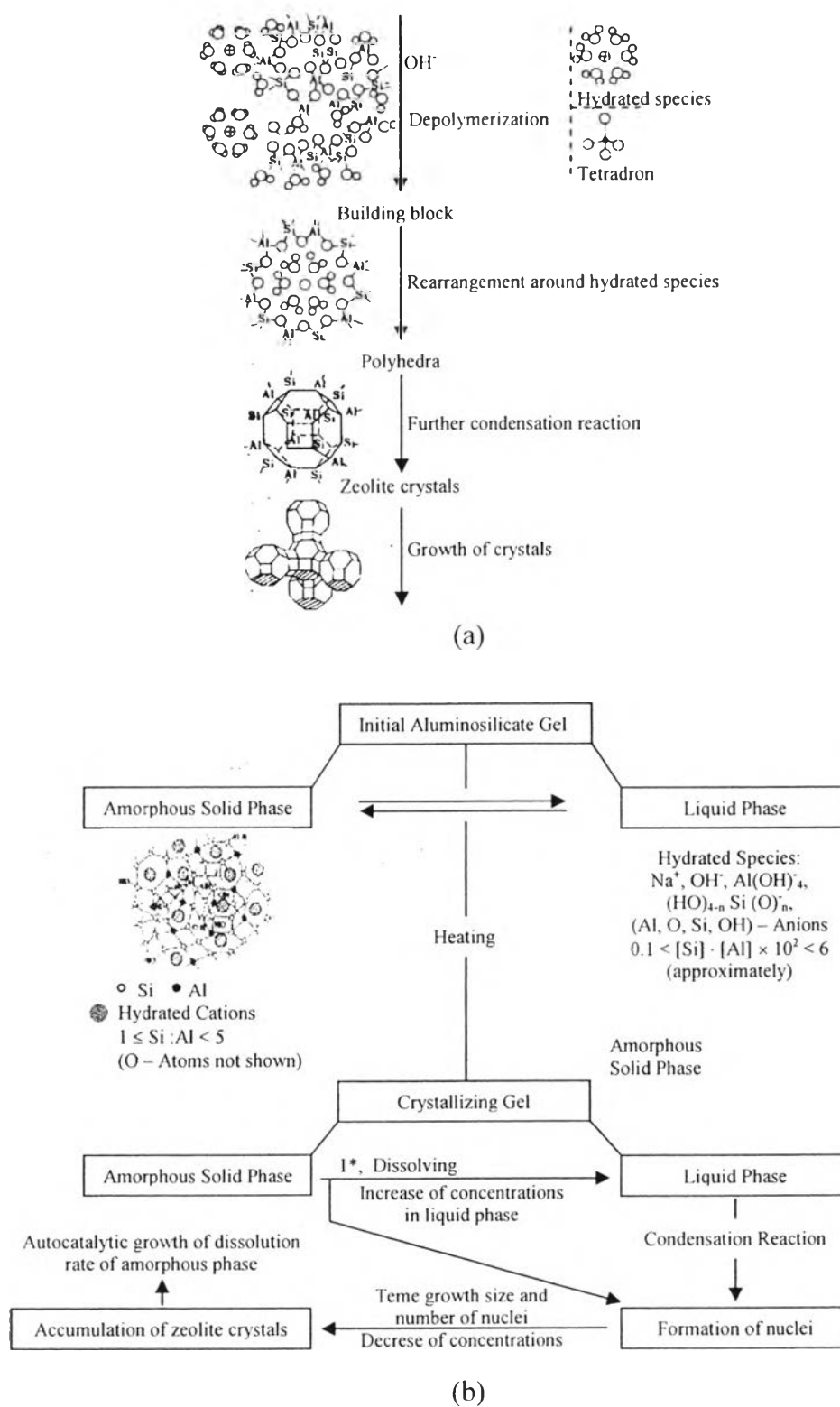
With reference to the source materials, one would hope that a mole of  $\text{SiO}_2$  would be equivalent to another  $\text{SiO}_2$ , from whatever source, when compounded into a gel. Experience teaches us that this is not the case;  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  are to some degree polymeric before gelation. Any reagent contains some unsuspected impurities, which can be active on the synthesis. To duplicate the work, one has to

repeat with the same source material. The starting material cannot be just silica, but precipitated silica, fumed silica, or silica sol, from a designated supplier. For very high silica phases, the alumina content of the silica source may be very important. Besides, one has to carefully prepare the gel and the step-by-step procedure has to be followed as noted. These steps include the order of mixing, the device used to mix, the aging time and temperature, nucleation, and batch composition. For example, the ingredients are not added sequentially, but combined into two (or three) subgroups that are blended to make the final gel. After a careful preparation of the precursor, a suitable reaction vessel has to be selected to provide the desired temperature, pressure, agitation, and the facility to withdraw an occasional sample. Several companies from the USA, Japan, and Germany, manufacture autoclaves with all such facilities for the synthesis of zeolites.

For the commercial production of zeolites, large size autoclaves or batch reactors are usually employed. The rate of heating is very important. If possible, a periodic/continuous monitoring facility is necessary to obtain the values of pH, percent of crystallinity, and the rate of crystallization. After carrying out the experimental runs, the filtration, washing, drying, and yield estimation are to be done carefully. For a better reproducibility of the results, the above aspects are to be kept in mind.

Several techniques are used to characterize the zeolite phases obtained. The most commonly used techniques are x-ray powder diffraction, Rietveld technique of structure refinement, neutron scattering, NMR, IR, Thermal, SEM, Laser Raman, measurement of sorptive capacity, particle size and pore size distribution, and so on (Byrappa *et al.*, 2001).

Davis and Lobo (1992) proposed two extremes of the mechanisms of zeolite synthesis, (i) the solution-mediated transport mechanism, and (ii) the solid-phase transformation mechanism. Figure 2.22 shows the schematic illustrations of (a) the solution-mediated transport, and (b) solid hydrogen transformation crystallization mechanisms. The first one involves the diffusion of aluminate, silicate, and/or aluminosilicate species from the liquid phase to the nucleation site for crystal growth. There are many examples of solution-mediated transport in the crystallization of aluminumrich zeolites.



**Figure 2.22** (a) Schematic illustrations of the solution-mediated transport. (b) Solid-hydrogen transformation crystallization mechanism (Byrappa *et al.*, 2001).



Ueda *et al.* (1984) prepared zeolites Y, S (GME), and P (GIS), which were synthesized from clear solutions, i.e., without the presence of hydrogel (solid phase). The solid-phase transformation mechanism suggests that the solid hydrogel reorganizes in forming the zeolite structure.

Xu *et al.* (1989) well illustrated phase diagram by the synthesis of ZSM-35 (FER) and ZSM-5 from non-aqueous reaction mixtures. There are several such reports on the synthesis of various zeolites using both of the proposed mechanisms of zeolite crystallization. In some cases, zeolites like Z.Y were found to crystallize by a combination of the two mechanisms. As a particular structure can be formed via different crystallization processes, extreme caution is necessary when attempting to generalize conclusions from one zeolite to a class of zeolites or molecular sieves.

## 2.3 Production of Xylenes

### 2.3.1 Alkylation of Toluene with Methanol

Xylenes are mainly produced by a distillation-extraction scheme from reformed gasolines. Xylenes are important precursors for many chemicals. The ratio of isomers, *para:ortho:meta* is approximately 1:1:2, which is very close to the thermodynamic equilibrium values for the three isomers at the reforming temperature as shown in Table 2.3.

**Table 2.3** Thermodynamic equilibrium values for xylene isomers at three temperatures (Matar *et al.*, 1989)

Aromatics (wt%)	Comparison		
	200 °C	300 °C	400 °C
<i>p</i> -Xylene	21.8	21.1	18.9
<i>o</i> -Xylene	20.6	21.6	23.0
<i>m</i> -Xylene	53.5	51.1	47.1
Ethylbenzene	4.1	6.2	11.0

*p*-Xylene is the most important of the three isomers since it is utilized for the synthesis of terephthalic acid for polyester production. A process that selectively produces *p*-xylene may be economically competitive to the currently used scheme.

Recent work for alkylation of toluene with methanol using HY-zeolite and ZSM-5 at a temperature range of 300 °C to 700 °C has shown that over 90% selectivity for *p*-xylene could be reached. If this process proves feasible, the alkylation of toluene over shape-selective zeolites may be utilized in the future (Matar *et al.*, 1989).

### 2.3.2 Process Chemistry: Feeds, Products and Reactions

No commercial processes are in operation currently for production of *p*-xylene by the methylation of toluene with methanol. As methanol becomes more favorable feedstock over time, toluene methylation might become competitive for *p*-xylene production. This process has the potential advantages of increasing *p*-xylene production throughput and lowering the operating and capital cost via the adoption of single-stage crystallization for *p*-xylene purification. However, there are still several technical hurdles that need to be resolved before commercial viability is realized. The reaction typically requires operating at toluene to methanol molar ratios greater than unity and at a high degree of dilution, the process typically operates at temperature greater than 400 °C to avoid methanol conversion to hydrocarbons via MTO/MTG pathways instead of toluene alkylation (Kulprathipanja, 2010).

### 2.3.3 Catalysts

The catalysts are predominantly modified ZSM-5 zeolite. In general, the modifications are intended to restrict pore mouth size to promote the shape selective production of *p*-xylene within the microporous structure. The same modifications also serve to remove external acid sites and eliminate the consecutive isomerization of *p*-xylene. Methods used to modify the zeolite pore openings have included silylation, incorporation of metal oxides such as MgO, ZnO and P<sub>2</sub>O<sub>5</sub>,

steaming and the combination of steaming and chemical modification (Kulprathipanja, 2010).

Zhu *et al.* (2004) studied the catalytic performance of MCM-22 zeolite for alkylation of toluene with methanol. Toluene methylation was carried out in a fixed bed reactor at 420 °C, 2.0 h<sup>-1</sup> WHSV and toluene/methanol molar ratio of 2:1 using the continuous nitrogen flow at atmospheric pressure. The result obtained a high catalytic activity and selectivity for alkylation of toluene with methanol because catalyst with mid-strong acidity and openings of 10-membered ring channels is suitable for this reaction. The research was investigated a comparison between MCM-22 and modification of MCM-22 by using silicon as a modifier. Modification of MCM-22 with La(NO<sub>3</sub>)<sub>3</sub> was a promising way to improve the catalytic selectivity of *p*-xylene and in 2006, they investigated the roles of acidity and structure of zeolite for catalyzing toluene alkylation with methanol to *p*-xylene. By comparison, the catalytic selectivity and activity for the methylation of toluene mainly depended on zeolites with 10-membered ring channels and the acidity of zeolite. The reactivity for the toluene alkylation was approximately linear with the number of mid-strength acidic sites. On the other hand, zeolites with 8-membered ring channels restricted toluene alkylation, only favorable for forming non-aromatic hydrocarbons. Zeolites with 12-membered ring channels may lead to the further alkylation of xylenes and the rapid deactivation by coking.

Ghiaci *et al.* (2007) investigated the internal and external surface active sites in ZSM-5 zeolite in toluene alkylation with methanol using the modified and unmodified H<sub>3</sub>PO<sub>4</sub>/ZSM-5. The reaction was studied in a down flow reactor under atmospheric conditions using N<sub>2</sub> gas carrier over a series of surface modified and unmodified ZSM-5 (Si/Al = 60 – 170) loaded with H<sub>3</sub>PO<sub>4</sub>, differing in the external surface treatment of the zeolites. The result showed that the process used modification of ZSM-5 zeolite, which can enhance the selectivity of *p*-xylene, possibly by deposition of phosphoric acid on the entrances and inside of the pores of the zeolite. The 2.1 wt% P-ZSM-5-surf-170 was a suitable catalyst for alkylation of toluene with methanol. The appropriate acidic sites, needed for catalyzing alkylation of toluene with methanol was supplied by loading 2.1 wt% P on ZSM-5 with optimum Si/Al ratio of 170. The optimum feed ratio of toluene/methanol was less

than 0.5. Space velocity used in toluene methylation reported as WHSV (toluene) =  $1.2 \text{ h}^{-1}$ . The methylation reaction was carried out in the temperature range of 350 °C to 500 °C.

Breen *et al.* (2007) observed the improved selectivity in the toluene alkylation with methanol and optimized the condition of process. Experiments were carried out at a reaction temperature of 400 °C. The effects of boron content of catalyst; methanol feed concentration, weight hourly space velocity (WHSV) and water concentration in the feed were studied. The results were found that with content of  $\geq 6.5 \text{ wt\% B}$ , when increasing concentration of methanol and decreasing WHSV of the liquid feeds, toluene conversion was increased but no effect on selectivity to *p*-xylene which remains constant at  $> 99.9\%$ , and a ratio of water/methanol of 9:1 are the optimized condition of the toluene alkylation reaction over a B/ZSM-5 catalyst to produce *p*-xylene with  $> 99.9\%$  selectivity.

Joshi *et al.* (2007) investigated toluene alkylation to selective formation of *p*-xylene over co-crystalline ZSM-12/ZSM-5 catalyst. The activity of toluene alkylation with methanol was observed over the ZSM-12, ZSM-12/ZSM-5 co-crystalline, ZSM-5, and physical mixture of ZSM-12/ZSM-5 catalysts synthesized by hydrothermal methods, by varying synthesis temperature and periods. The ZSM-12/ZSM-5 co-crystalline sample was observed to be a better combination as far as *p*-xylene selectivity was 89.34% and total xylene yield was 36.77%, at a favorable toluene conversion of 44.03%.

Bokade *et al.* (2007) studied toluene alkylation with methanol to *p*-xylene over heteropoly acids supported by clay. The reaction was studied at 250 °C, the molar ratio of the toluene:methanol of 1:1.5 and weight hourly velocity (WHSV) of  $2.5 \text{ h}^{-1}$  at atmospheric pressure for a period of 6 h. The research coped with the use of different heteropoly acids (HPAs). The HPA-loaded samples were observed to be better compared with plain clay as far as activity, selectivity, and yields were concerned. The 20% PMA/Clay sample was observed to be the best among the samples studied. The toluene conversion, *p*-xylene yield were 62%, and *p*-xylene selectivity was 100%. The increases in activity, selectivity, and yield of *p*-xylene with 20%PMA/Clay catalyst may be caused by an increase in acidity up to 28.4%, as compared with plain clay.

Aboul-Gheit *et al.* (2010) investigated the promotion of HZSM-5 zeolite by Pt and HF doping for use as catalysts in toluene alkylation with methanol. The research studied the activity of alkylation of toluene with methanol in a flow type reactor at temperatures between 300 °C and 500 °C using HZSM-5 zeolite, 0.2% Pt/HZSM-5 and hydrofluorinated 0.2% Pt/HZSM-5 with HF concentrations of 1.0%, 2.0%, 3.0%, or 4.0%. The result showed that Pt primarily enhances toluene conversion, total xylenes production, and *p*-xylene relative to its thermodynamic equilibrium. As the concentration of HF increases from 1.0% to 3.0%, the catalyst activity increases because of the increase in the number of acid sites and their strength. Additionally, the surface area and Pt dispersion also increases. An advantage of increased HF doping is that the formation of voluminous trimethylbenzene (TMB) by-products is inhibited.