CHAPTER III

THEORY

3.1 The structure of the zeolite

Zeolite are highly crystalline, hydrated aluminosilicates that upon dehydration develop in the ideal crystal a uniform pore structure having minimum channel diameters(aperture) of from about 0.3 to 1.0 nm. The size depends primarily on the type of zeolites and secondarily on the cations present and the nature of treatments such as calcination, leaching, and various chemical treatments. Zeolites have been of intense interest as catalysts for some three decades because of the high activity and unusual selectivity they provide, mostly in a variety of acid–catalyzed reaction. In many cases, but not all, the unusual selectivity is associated with the extremely fine pore structure, which permits only certain molecules to penetrate into the interior of the catalyst particles, or only certain products to escape from the interior. In some cases unusual selectivity seems to stem instead from constrains that the pore structure sets on allowable transition states, sometimes termed spacio – selectivity.

The structure of the zeolite consists of a three–dimensional framework of the SiO_4 and AlO_4 tetrahedra as presented in Figure 3.1 [19], each of which contains a silicon or aluminum atom in the center. In 1982, Barrer defined zeolites as the porous tectosilicates[20], that is, three-dimensional networks built up of TO^{4-} tetrahedra where T is silicon or aluminum. The oxygen atoms are sheared between adjoining tetrahedral, which can be present in various ratios and arrange in a variety of ways. The framework thus obtained pores, channels, and cages, or interconnected voids.

A secondary building unit (SBU) consists of selected geometric groupings of those tetrahedral. There are sixteen such building units, which can be used to describe all of known zeolite structures; for example, 4 (S4R), 6 (S6R), and 8 (S8R) – member single ring, 4-4 (D6R), 8-8 (D8R)-member double rings. The topologies of these units are shown in Figure 3.2 [22]. Also listed are the symbols used to describe them. Most zeolite framework can be generated from several different SBU's. Descriptions of known zeolite structures based on their SBU's[21]. Both ZSM-5 zeolite and Ferrierite are described by their 5-1 building units. Offertile, Zeolite L, Cancrinite, and Erionite are generated using only single 6- member rings. Some zeolite structures can be described by several buildings. The sodalite framework can be built from either the single 6-member ring or the single 4- member ring. Faujasite (type X or type Y) and zeolite be constructed using 4 ring or 6 ring building units. Zeolite a can also be formed using double 4 ring building units, whereas Faujasite cannot.

Zolites may be represented by the empirical formula:

$$M_{2/n} Al_2O_3 x SiO_2 y H_2O$$
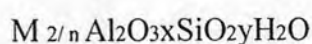
or by a structural formula:

$$M_{x/n} [(Al_2O_3)_x (SiO_2)_y] w H_2O$$
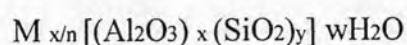
Where the bracketed term is the crystallographic unit cell. The metal cation (of valencen) is present it produces electrical neutrality science for each aluminum tetrahedron in the lattice there is an overall charge of − 1. Access to the channels is limited by aperture consisting of a ring of oxygen atoms of connected tetrahedra. There may be 4, 5, 6, 8, 10, or 12 oxygen atoms in the ring. In some cases an interior cavity exists of larger diameter in the aperture; in others, the channel is of uniform diameter like a tube [22].
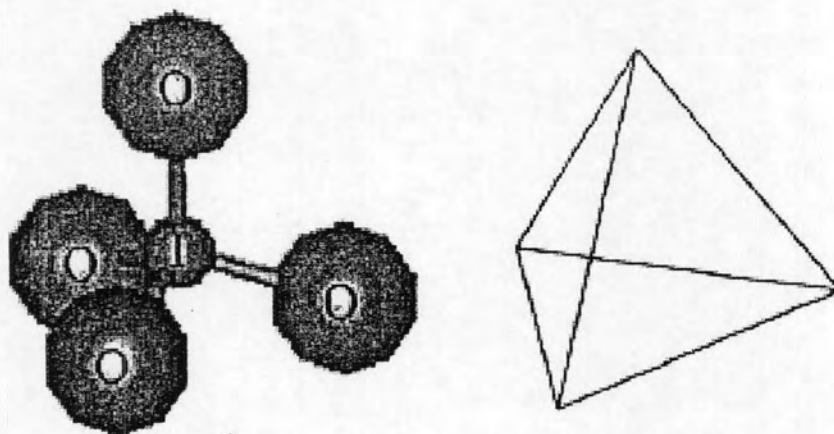
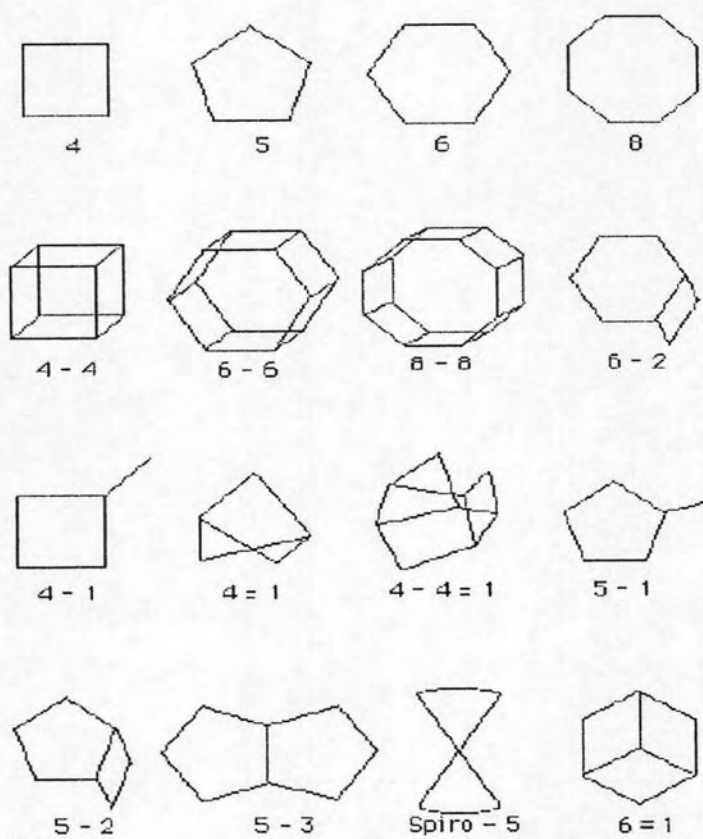**Figure 3.1** TO4 tetrahedral (T= Si or Al) [19]

Figure 3.2 Secondary building units (SBU's) found in zeolite structures[22]

3.2 Category of Zeolite

There are over 40 known natural zeolites and more than 150 synthetic zeolites have been reported [23]. The number of synthetic zeolites with new structure morphologies grows rapidly with time. Based on size of their pore opening, zeolites can be roughly divided into five major categories, namely 8 -, 10 -, and 12- member oxygen ring systems, dual pore systems and mesoporous systems. Their pore structures can be characterized by crystallography, adsorption, measurements and/or through diagnostic reactions. One such diagnostic characterization test is the "constraint index" test. The concept of constraint index was defined as the ratio of the cracking rate constant of n-hexane to 3-methylpenthane. The constraint index of a typical medium-pore zeolite usually ranges from 3 to 12 and those of the large-pore zeolites are the range 1-3. For materials with an open porous structure, such as amorphous silica alumina, their constraint indices are normally less than 1. On the index for erionite is 38.

A comprehensive bibliography of zeolite structures has been published by the International Zeolite Association [23]. The structural characteristics of assorted zeolites are summarized in Table 3.1

Zeolite with 10-membered oxygen rings normally possesses a high siliceous framework structure. They are of special interest in industrial applications. In fact, they were the first family of zeolite that was synthesized with organic ammonium salts. With pore openings close to the dimensions of many organic molecules, they are particularly useful in shape selective catalysis. 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 MTT – type(ZSM-23) zeolite is high-silica zeolite as presented in Figure 3.3 containing 5-, 6-, and 10-ring subunits that generate undimensional 10-member-ring channels which are parallel to the short 5 A axis.

Crystallization of this structure also occurs under more acidic conditions in the presence of fluoride ion, with an F/SiO_2 ratio between 0.1 and 6 (EP 347,273(1989))

Table 3.1 Structural characteristics of selected zeolites [23] Although the 10-membered oxygen ring zeolite was found to possess remarkable shape selectivity, catalysis of large molecules may require a zeolite catalyst with a large-pored opening. Typical 12-membered oxygen ring zeolites, such as faujasite-type zeolites, normally have pore opening greater than 5.5 Å and hence are more useful in catalytic applications with large molecules, for example in trimethylbenzene (TMB) conversions. Faujasite (X or Y; Figure 3.4 [23]) zeolites can be synthesized using inorganic salts and have been widely used in catalytic cracking since 1960s. The framework structures of beta zeolite and ZSM-12 are shown in Figure 3.5 and 3.6 , respectively.

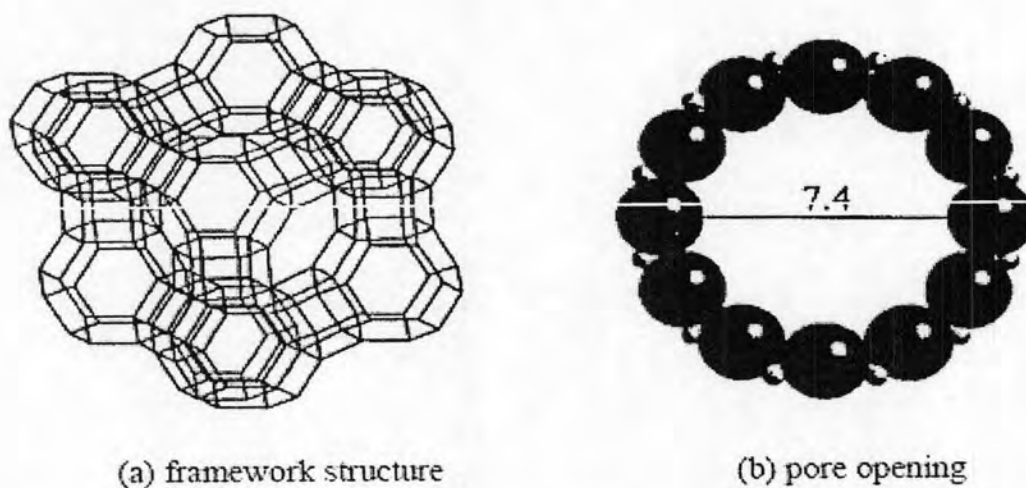**Table 3.1** Structural characteristics of selected zeolites [23].

Zeolite	Number of rings	Pore opening Å	Pore/Channel structure	Void volume (ml/g)	D_{Frame}[a] (g/ml)	CI[b]
8-membered oxygen ring						
Erionite	8	3.6x5.1	Intersecting	0.35	1.51	38
10-membered oxygen ring						
ZSM-5	10	5.3x5.6 5.1x5.5	Intersecting	0.29	1.79	8.3
ZSM-11	10	5.3x5.4	Intersecting	0.29	1.79	8.7
ZSM-23	10	4.5x5.2	One-dimensional	-	-	9.1
Dual pore system						
Ferrierite (ZSM-35, FU-9)	10,8	4.2x5.4 3.5x4.8	One-dimensional 10:8 intersecting	0.28	1.76	4.5
MCM-22	12 10	7.1 Elliptical	Capped by 6 rings	-	-	1-3
Mordenite	12 8	6.5x7.0 2.6x5.7	One-dimensional 12:8 intersecting	0.28	1.70	0.5
Omega (ZSM-4)	12 8	7.4 3.4x5.6	One-dimensional One-dimensional	- -	- -	2.3 0.6
12membered oxygen ring						
ZSM-12	12	5.5x5.9	One-dimensional	-	-	2.3
Beta	12	7.6x6.4 5.5x5.5	Intersecting	-	-	0.6
Faujasite (X,Y)	12 12	7.4 7.4x6.5	Intersecting 12:12 intersecting	0.48	1.27	0.4
Mesoporous system						
VPI-5	18	12.1	One-dimensional	-	-	-
MCM41-S	-	16-100	One-dimensional	-	-	-

[a]Framework density

[b]Constraint index
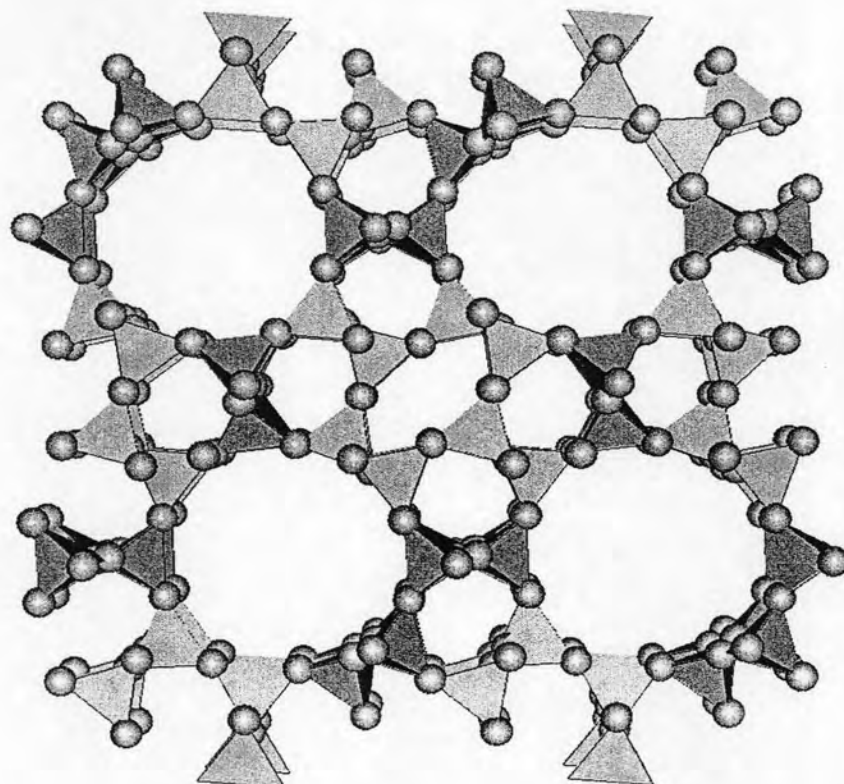
Figure 3.3 Structure of ZSM-23 (http://www.personal.utulsa.edu/~geoffrey-price/zeolite/mtt.jpg).

(a) framework structure   (b) pore opening

Figure 3.4 Structure of Faujasite [23].
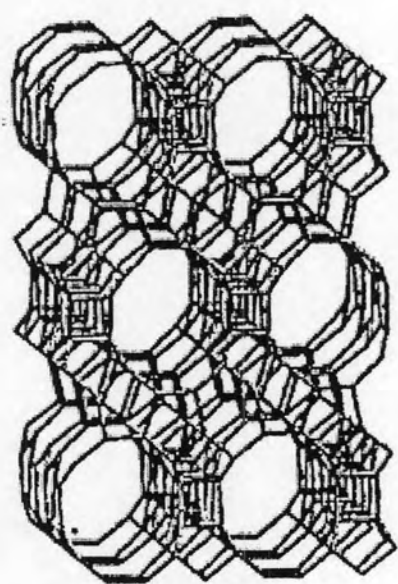
(a) framework structure
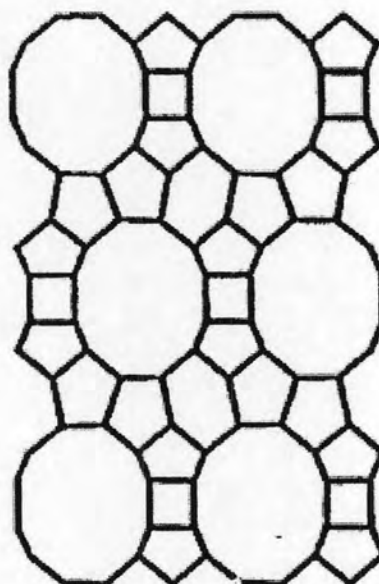
(b) framework projection
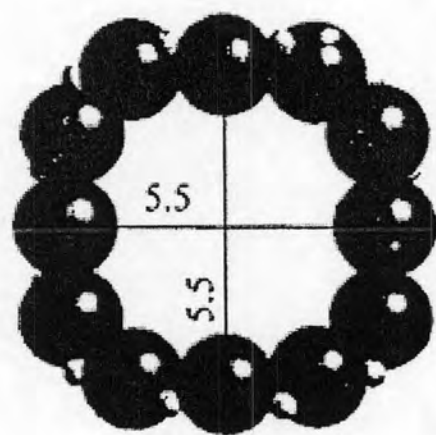
(c) tortous channel
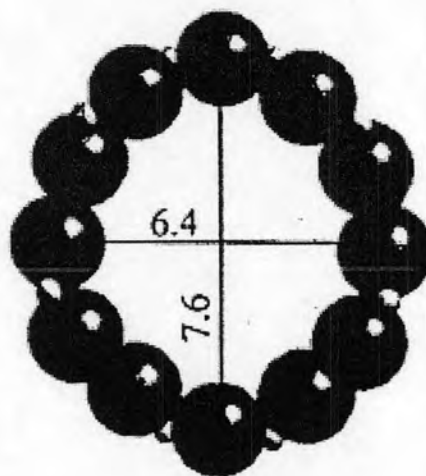
(d) straight channel

Figure 3.5 Structure of beta zeolite [23].

(a) framework projection   (b) pore opening
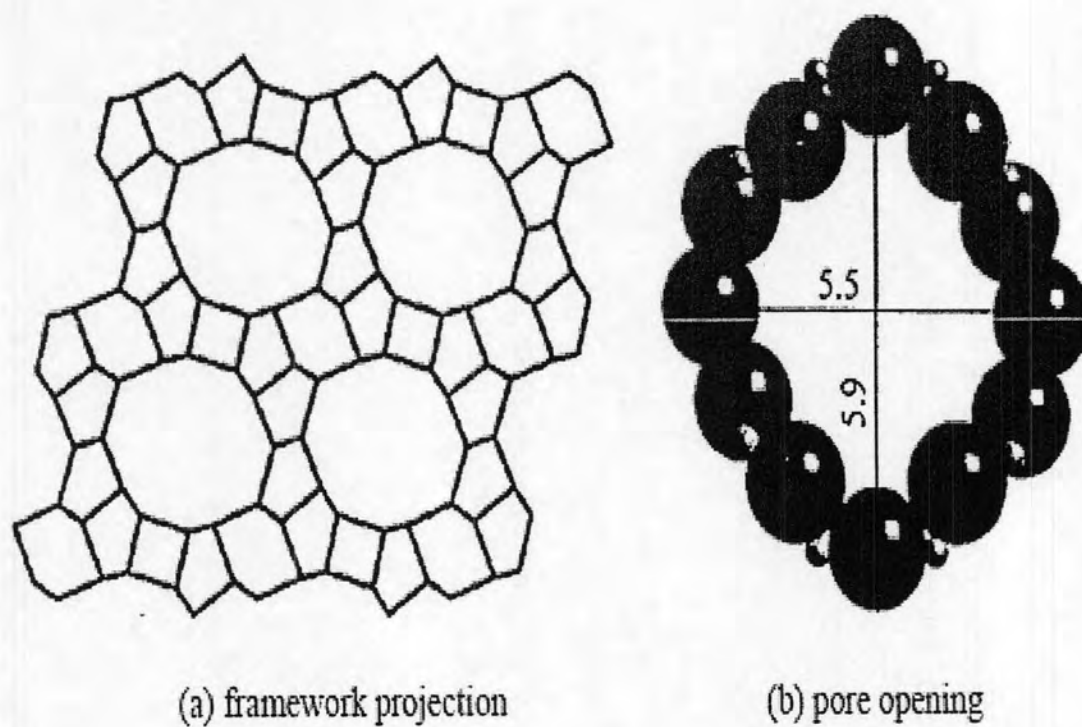
Figure 3.6 Structure of zeolite ZSM-12 [23].

(a) framework projection   (b) pore opening
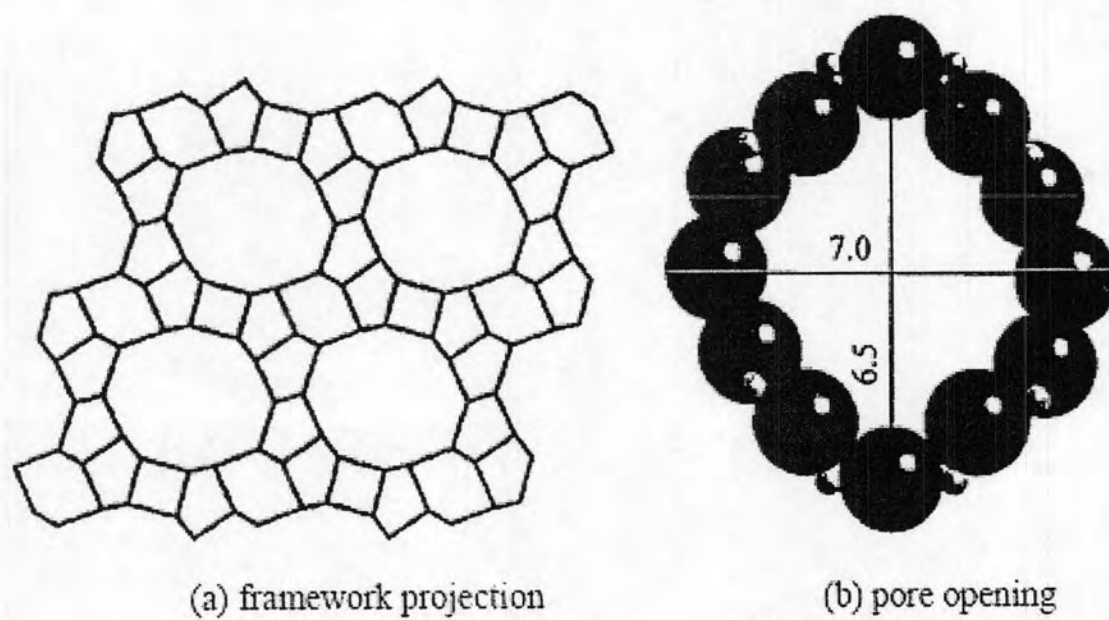
Figure 3.7 Structure of Mordenite [23].

Zeolites with a dual pore system normally possess interconnecting porechannels with two different pore opening sizes. Mordenite is a well-known dual pore zeolite having a 12-membered oxygen ring channel with pore opening 6.5x6.7 Å which id interconnected to 8-membered oxygen ring channel with opening 2.6x5.7 Å (Figure 3.7 [18]. MCM -22, which was found more than 10 years, also possess a dual pore system. Unlike Mordenite, MCM-22 consists of 10- and 12- membered oxygen rings (Figure 3.8 [23]) and thus shows prominent potential in future applications.

In the past decade, many research efforts in synthetic chemistry have been invested in the discovery of large-pored zeolite with pore diameter greater than 12-membered oxygen rings. The recent discovery of mesoporous materials with controllable pore opening (from 12 to more than 100 Å) such as VPI-5, MCM-41S undoubted will shed new light on future catalyst applications.
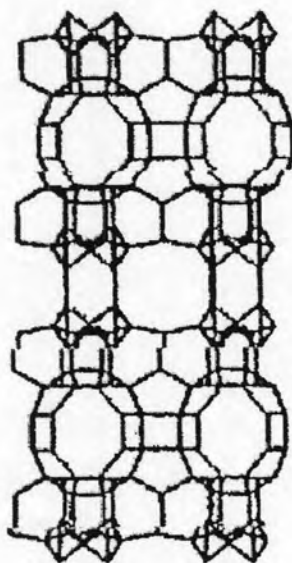
Figure 3.8 Framework structure of MCM-22 [23].

3.3 Zeolite Active sites

3.3.1 Acid sites

Classical Brønsted and Lewis acid models of acidity have used to classify the active sites on zeolites. Brønsted acidity is proton donor acidity; a tridiagonally coordinated alumina atom is an electron deficient and can accept an electron pair, therefore behaves as a Lewis acid [24, 25].

In general, the increase in Si/Al ratio will increase acidic strength and thermal stability of zeolite [26]. Since the numbers of acidic OH groups depend on the number of aluminium in zeolites framework, decrease in Al content is expected to reduce catalytic activity of zeolite. If the effect of in crease in the acidic centers, increase in Al content, shall result in enhancement of catalytic activity

Based on electrostatic consideration, the charge density at a cation site increase with increase Si/Al ratio. It was conceived that these phenomena are related to reduction of electrostatic interaction between framework sites, and possibly to
difference in the order of aluminum in zeolite crystal-the location of Al in crystal structure [25].

An improvement in thermal or hydrothermal stability has been ascribed to the lower density of hydroxyl groups, which id parallel to that of Al content [24]. A longer distance between hydroxyl groups decrease the probability of dehydroxylation that generates defects on structure of zeolites.

3.3.2 Generation of Acid Centers

Protonic acid centers of zeolite are generated in various was. Figure 3.9 depicts the thermal decomposition of ammonium-exchanged zeolite yielding the hydrogen form [27].

The Brønsted acidity due to water ionization on polyvalent cations, described below, is depicted in Figure 3.10 (Tanake et al., 1989).

$$M^{n+} + xH_2O \text{ ----------------> } M(OH)x^{(n-x)} + xH^+ \qquad (3.1)$$
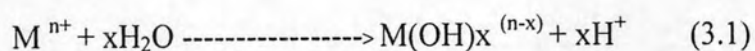
The exchange of monovalent ions by polyvalent cations could improve the catalytic property. Those highly charged cations create very centers by hydrolysis phenomena. Brønsted acid sites are also generated by the reduction of transition metal cations. The concentration of OH groups of zeolite containing transition metals was note to increase by hydrogen at $275.5 - 723$ K to increase with the rise of the reduction temperature [19].

$$Cu^{2+} + H_2 \text{ ---------------> } Co^o + 2H^+ \qquad (3.2)$$

$$Ag^+ + 1/2H_2 \text{ -------------> } Ag^o + H \qquad (3.3)$$
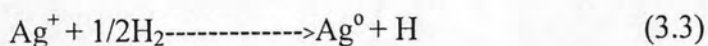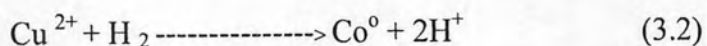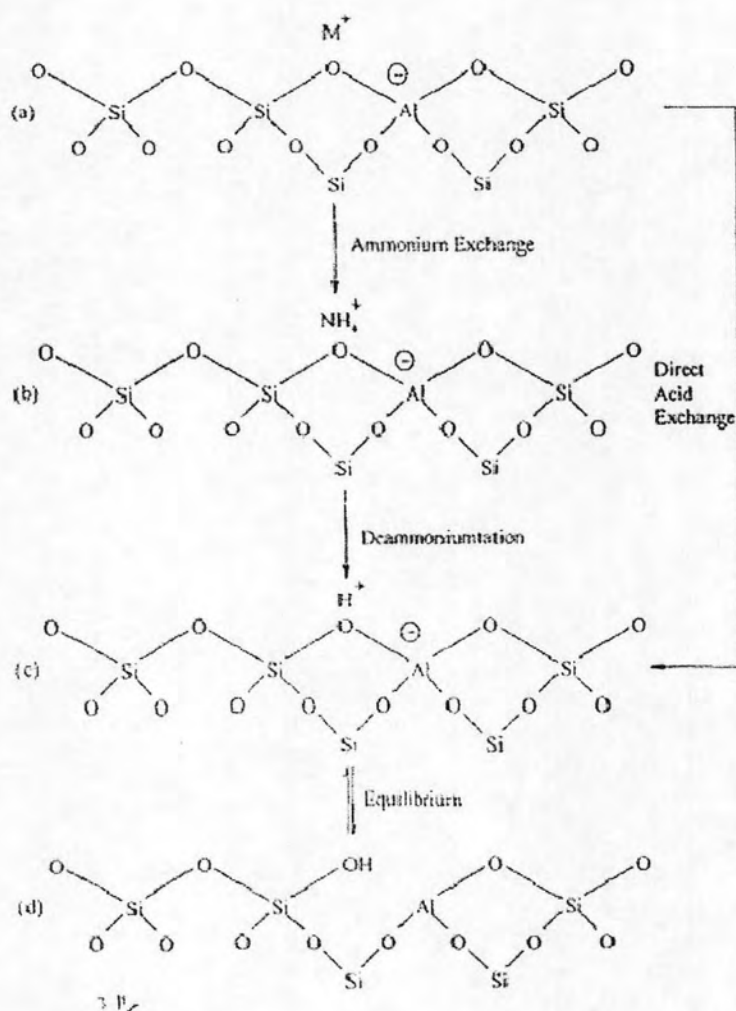
Figure 3.9 Diagram of the surface of a zeolite framework [21].

a) In the as-synthesis form M+ either an organic cation or an alkali metal cation.

b) Ammonium in exchange produces the NH+ exchanged form.

c) Thermal treatment is used to remove ammonia, producing the H+, acid form.

d) The acid form in (c) is in equilibrium with the shown in (d), where is a silanol group adjacent to tricoordinate aluminium.

The formation of Lewis acidity from Brønsted acid sites is depicted in Figure 3.11 [28]. The dehydration reaction decrease the number of protons and increases that of Lewis sites. Brønsted (OH) and Lewis (-Al-) sites can be present simultaneously in the structure of zeolite at high temperature. Dehydroxylation is thought to occur in ZSM-5 zeolite above at 773 K and calcination at 1073 to 1173 K produces irreversible dehydroxylation, which causes defection in crystal structure of zeolite.
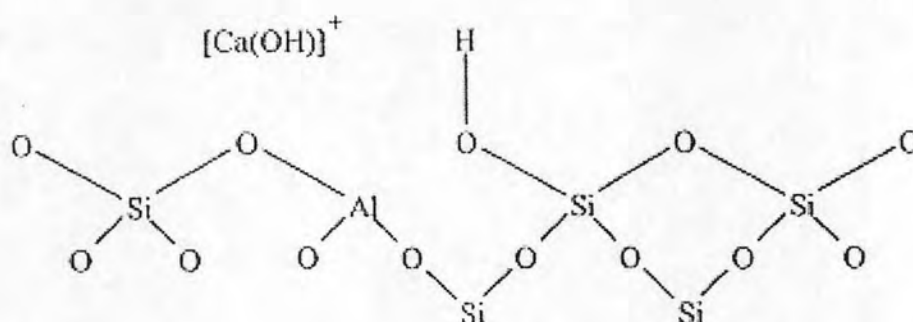
Figure 3.10 Water molecules co-ordinated to polyvalent cation are dissociated by heat treatment yielding Brønsted acidity [28].
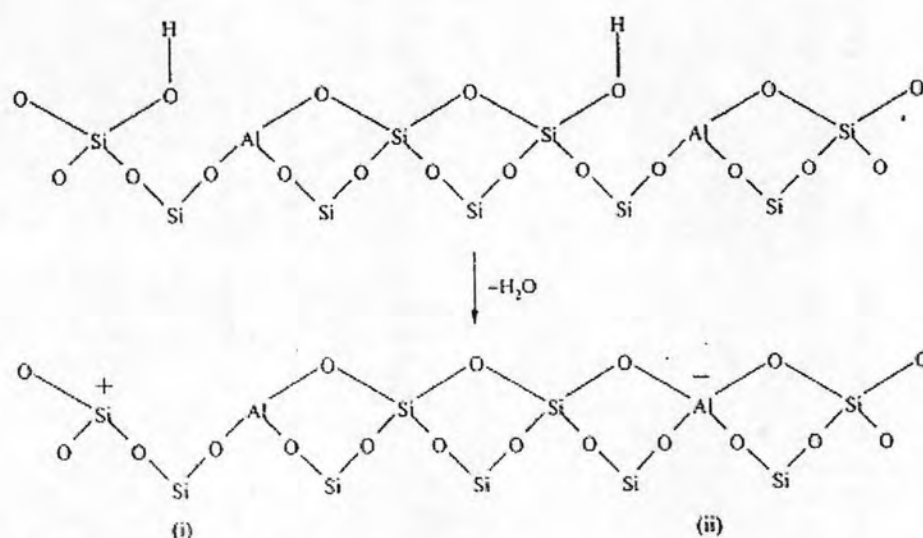
Figure 3.11 Lewis acid site developed by dehydroxylation of Brønsted acid site [28].

Dealumination is believed to occur during dehydroxylation, which may result from the steam generation within the sample. The dealumination is indicated by an increase in the surface concentration of aluminum on the crystal. The dealumination process is expressed in Figure 3.12 [28].The extent of dealumination monotonously increases with the partial pressure of steam.
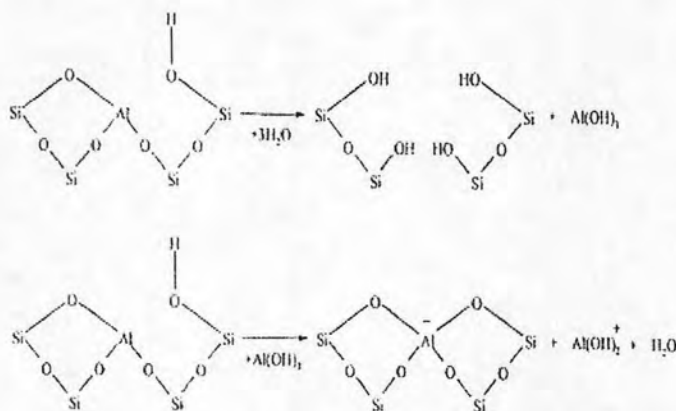
Figure 3.12 Steam dealumination process in zeolite [28]

The enhancement if the acid strength of OH groups is recently proposed to be pertinent to their interaction with those aluminum species sites tentatively expressed in Figure 3.13 [28]. Partial dealumination might therefore yield a catalyst of higher activity while severe steaming reduces the catalytic activity.
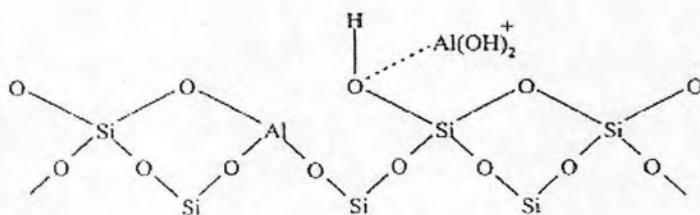
Figure 3.13 The enhancement of the acid strength of OH groups by their interaction with dislodged aluminum species [28].

3.3.3 Basic Sites

In certain instances reactions have been shown to be catalyzed at basic (cation) site in zeolite without any influences from acid sites. The best-characterized example of this is that K −Y which splits n-hexane isomers at 773 K. The potassium cation has been shown to control the unimolecular cracking (β-scission). Free radial mechanisms also contribute to surface catalytic reactions in these studies.

3.4 Shape Selective

Many reactions involving carbonium intermediates are catalyzed by acidic zeolite. With respects to a chemical standpoint the reaction mechanisms are nor fundamentally different with zeolites or with any the acidic oxides. What zeolite add is shape selectivity effect. The shape selective characteristics of zeolites influence their catalytic phenomena by three modes: shape selectivity, reactants shape selectivity, products shape selectivity and transition states shape selectivity. These types of selectivity are illustrated in Figure 3.14.

Reactants of charge selectivity results from the limited diffusibility of some of the reactants, which cannot effectively enter and diffuse inside crystal pore structures of the zeolites. Product shape selectivity occurs as slowly diffusing product molecules cannot escape from the crystal and undergo secondary reaction. This reaction path is established by monitoring changes in product distribution as a function of varying contact time.

Restricted transition state shape selectivity is a kinetic effect from local environment around the active site, the rate constant for a certain reaction mechanism is reduced of the space required for formation of necessary transition state is restricted.
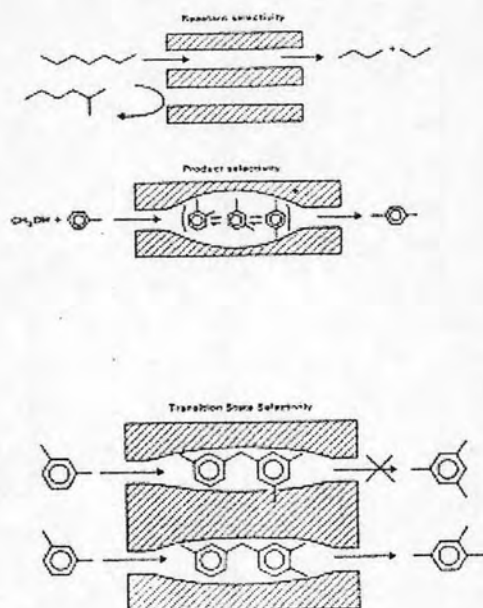
Figure 3.14 Diagram depicting the three type of selectivity [21].

The critical diameter (as opposed to the length) of the molecules and the pore channel diameter of zeolites are important in predicting shape selective effects. However, molecules are deformable and can pass through opening, which are smaller than their critical diameters. Hence, not only size but also the dynamics and structure of the molecules must be taken into account.

3.5 Zeolite Synthesis

Zeolites are generally synthesized by a hydrothermal process from a source of alumina (e.g., sodium aluminate or aluminium sulfate) and of silica (e.g., a silica sol, fumed silica, or sodium water glass) 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 temperature that may range up to 473 K 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 SiO_2/Al_2O_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.

Bauer and coworkers in the early 1960s developed the use of reaction mixtures containing quaternary ammonium ions or other or other cations to direct the crystallization process. In their work and succeeding studies, a primary motivation was to attempt to synthesize zeolites with large apertures than X and Y. This did not occur, but instead organic species were found to modify the synthesis process in a variety of ways that led to the discovery of many new zeolites, and new methods of synthesizing zeolite with structures similar to previously know zeolite.

The mechanism of action of the organic species is still controversial. It was originally thought to be primarily a templating effect, but later it was found that at least some of zeolites could be synthesized without an organic template. Further, organic species other than quaternary ammonium compounds had directing effects not readily ascribed to their size or shape. However, an important result was the zeolites of higher SiO_2/Al_2O_3 ratio than before could be synthesized. Previously, only structures with SiO_2/Al_2O_3 ratios of about 10 or less could be directly forms, but with organic additives, zeolites with ratio of 20 to 100 or more can be directly prepared.

After synthesis the zeolite are washed, dried, heated to remove water of crystallization, and calcined in air, e.g., at about 813 K. Organic species are also thus

removed. For most catalytic purpose, the zeolite is converted into acidic form. For some zeolites this can be achieved by treatment with aqueous HCl without significantly altering the framework structure. For other zeolites Na^+ is replaced with NH_4^+ via an ammonium compound such as NH_4OH, NH_4Cl or NH_4NO_3. Upon heating NH_3 is driven off, leaving the zeolite in the acid form. For some reaction a hydrogenation component such as platinum or nickel is introduced by impregnation or ion exchange [29].

3.6 ZSM-5 Zeolite

ZSM-5 zeolite has two types of channel systems of similar size, one with a straight channel of pore opening 5.3 x 5.6 $A^0$and the other with tortuous channel of pore opening 5.5 x 5.5 A^0. Those intersecting chanels aer perpendicular to each other, generating a three-dimension framework. ZSM-5 zeolite with a wide rang of SiO_2/Al_2O_3 ratio can easily be synthesized. High siliceous ZSM-5 zeolite are more hydrophobic and hydrothermally stable compared to many other zeolite. Althougn the first synthetic ZSM-5 zeolite was discovered more than three decades ago (1972) new interesting application are still emerging to this day. For example, its recent application in NOx reduction, especially in the exhaust to lean-burn engine, has drawn much attention. Among various zeolite catalyst, ZSM-5 zeolite has greatest number of industrial application, covering from petrochemical production and refiner processing to environmental treatment.

3.7 Light Olefins

The olefin or ethylene series (type formula C_nH_{2n}) is composed of unsaturated hydrocarbon ;i.e., the members of this series are capable of uniting directly with other material such as chlorine, bromine, hydrochloric acid, and sulfuric acid, without displacing a hydrogen atom. The name of these hydrocarbons end in –ene, as ethane(ethylene) , propene (propylene) and butene(butylenes). Unsaturated compounds react with and dissolve in sulfuric acid and may thus be remove from petroleum oils. The low boiling olefin are probably not present in crude petroleum, but they are round in
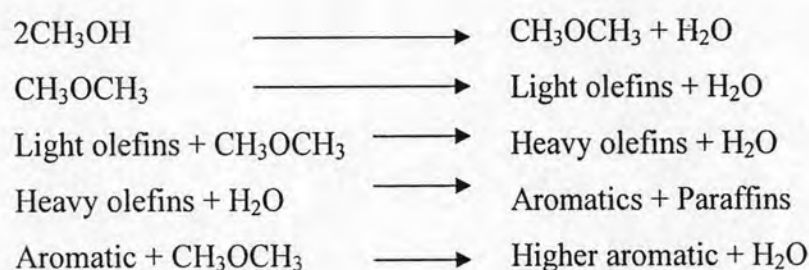
cracked products. Egloff, Schaad, and Lowry have made an excellent study of the literature of the olefin hydrocarbons.

Ethylene is used primarily as an intermediate in the manufacture of other chemicals, especially plastics. Ethylene may be polymerized directly to produce polyethylene (also called polyethylene or polythene), the world's most widely-used plastic. Ethylene can be chlorinated to produce ethylene dichloride (1,2-Dichloroethane), a precursor to the plastic polyvinyl chloride, or combined with benzene to produce ethylbenzene, which is used in the manufacture of polystyrene, another important plastic. Smaller amounts of ethylene are oxidized to produce chemicals including ethylene oxide, ethanol, and polyvinyl acetate. Global demand for ethylene exceeded 100 million tones per year in 2005. Ethylene was once used as an inhaled anesthetic, but it has long since been replaced in this role by nonflammable gases. It has also been hypothesized that ethylene was the catalyst for utterances of the oracle at Delphi in ancient Greece. Ethylene is used in greenhouses and is sprayed on crops to speed ripening. It is also found in many lip gloss products.

Propylene, also known by its IUPAC name propylene, is an organic compound having the chemical formula C_3H_6. It is the second simplest member of the alkene class of hydrocarbons, ethylene (ethylene) being the simplest. At room temperature and pressure, propylene is a gas. It is colorless, highly flammable, and has an odor similar to garlic.(this smell is added to make it easily detectable, pure propylene, like most simple hydrocarbons, has no natural scent.) It is found in coal gas and can be synthesized by cracking petroleum. Propylene is a major commodity in the petrochemicals industry. The main use of propylene is as a monomer, mostly for the production of polypropylene. Propylene is also used as a fuel gas for various industrial processes. It has a similar calorific value to propane but a lower mass of combustion products so a higher flame temperature. Propylene also has approximately twice the vapor pressure of propane at room temperature and pressure.

3.8 Reaction mechanism of methanol to hydrocarbons

The reaction of methanol to hydrocarbon products is vigorously exothermic, with a theoretical adiabatic temperature rise of about $600°C$. The reaction path is believed to pass through a number of series and parallel steps. The mechanism is complex and is discussed elsewhere. A simplified path is given below

$$2CH_3OH \longrightarrow CH_3OCH_3 + H_2O$$
$$CH_3OCH_3 \longrightarrow \text{Light olefins} + H_2O$$
$$\text{Light olefins} + CH_3OCH_3 \longrightarrow \text{Heavy olefins} + H_2O$$
$$\text{Heavy olefins} + H_2O \longrightarrow \text{Aromatics} + \text{Paraffins}$$
$$\text{Aromatic} + CH_3OCH_3 \longrightarrow \text{Higher aromatic} + H_2O$$

Methanol is made from synthesis gas (a mixture of carbon monoxide and hydrogen) which is formed by stream reforming of natural gas or gasification of coal. The first step in the reaction sequence is the dehydration of methanol to an equilibrium mixture of dimethylether (DME), methanol and water is then converted to light olefins. In the last step of this scheme, the light olefins react to from paraffins, aromatic, naphthenes and higher olefins by hydrogen transfer, alkylation, polycondensation, which proceeds via classical carbenium ion mechanisms with concurrent hydrogen transfer, is well known from hydrocarbon chemistry in acid media . However, the second step, which represents the initial C–C bond formation from the C_1 reactants[2, 29]. The key step is the formation of the first carbon-carbon bond, for which more than 20 distinct mechanistic proposals have been suggested .Of all the direct mechanisms, the oxonium yield proposal has received the strongest experimental attention.

G.B. Marin et al [30] postulated that dimethyl ether interacts with a Brønsted acid site of the solid catalyst to form a dimethyl oxonium ion, which reacts further with another dimethyl ether to form a trimethyl oxonium ion. This trimethyl oxonium ion is

subsequently deprotonated by a basic site to form a surface associated dimethyl oxonium methyl yield species. The next step is either an intramolecular Stevens rearrangement , leading to the formation of methylethyl ether, or an intermolecular methylation , leading to the formation of the ethyldimethyl oxonium ion. In both cases ethylene is formed via β-elimination.A bifunctional acid–base catalyzed condensation was suggested by Olah. Methanol and dimethyl ether form a trimethyl oxonium ion (using for example WO_3 on alumina), which is deprotonated to dimethyl oxonium methyl yield. However, Olah concluded (based on labelling experiments) that the yield undergoes bimolecular methylation to form the ethyldimethyl oxonium ion, rather than an intramolecular Stevens rearrangement.
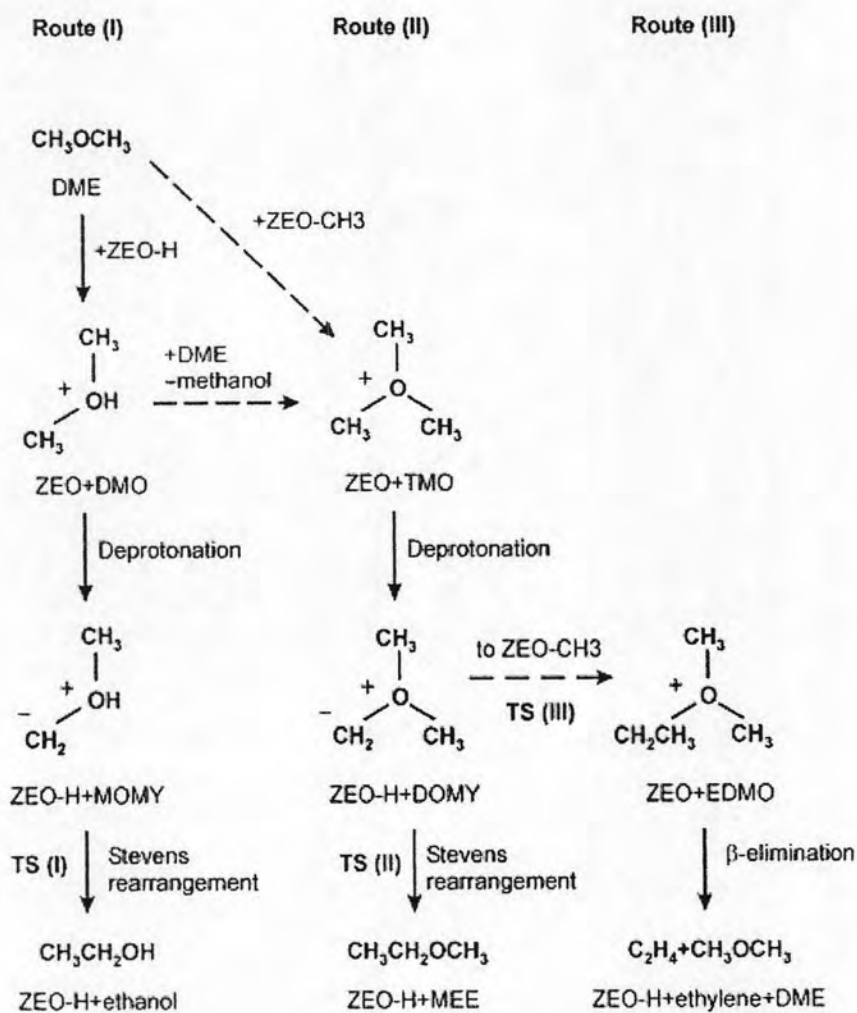
Figure 3.15 Reaction scheme including oxonium ions and oxonium ylides.

In the last step of this scheme, the light olefins react to from paraffins, aromatic, naphthenes and higher olefins by hydrogen transfer, alkylation, polycondensation. These 12 major steps are:
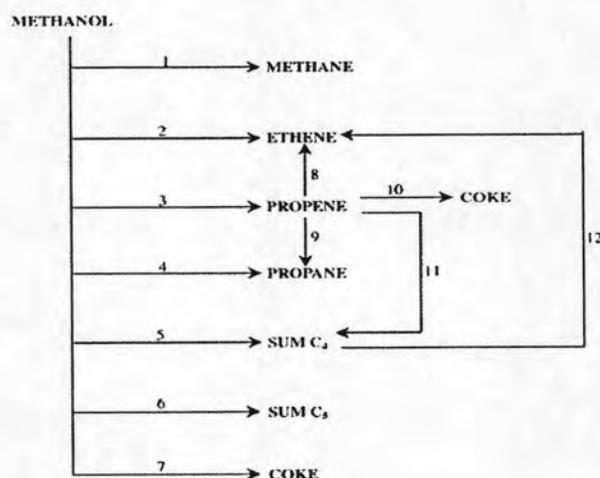
Figure 3.16 Final reaction scheme from model discrimination Bos et al

1. The etherification reaction takes place concurrently with the thermal decomposition of the methanol in to hydrogen and carbon monoxide. The ether generates the carbene.

2. The carbene attacks the ether and the alcohol, forming light olefins.

3. The carbene attacks the olefin, forming higher olefin.

4. The carbene attacks the hydrogen, forming methane.

5. The light olefin generate carbeniums ions.

6. The carbeniums on attacks the light olefins forming higher olefin.

7. The carbeniums on attacks the higher olefins forming paraffin and cyclodiene.

8. The carbeniums on attacks the diene forming higher olefin.

9. The carbeniums on attacks the cyclodienes forming paraffins and aromatics.

10. The aromatic undergo condensation.

11. The aromatic undergo alkylation with methanol.

12. The paraffins undergo demethanization forming olefin and methane.