

CHAPTER III

THEORY

3.1 Structure of Zeolite

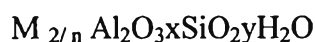
Zeolites are highly crystalline, hydrated aluminosilicates that upon dehydration develop in the ideal crystal a uniform pore structure having minimum channel diameters (aperture) of from about 0.3 to 1.0 nm. The size depends primarily on the type of zeolites and secondarily on the cations present and 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 reactions. 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 constraints 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 [49], each of which contains a silicon or aluminum atom in the center. In 1982, Barrer defined zeolites as the porous tectosilicates [50], that is, three-dimensional networks built up of TO_4 tetrahedra where T is silicon or aluminum. The oxygen atoms are sheared between adjoining tetrahedra, 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.

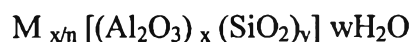
A secondary building unit (SBU) consists of selected geometric groupings of those tetrahedra. There are sixteen such building units, which can be used to describe all of known zeolite structures; for example, 4 (S4R), 6 (S6R), and 8 (S8R) – member single ring, 4-4 (D6R), 8-8 (D8R)-member double rings. The topologies of these units are shown in Figure 3.2 [51]. Also listed are the symbols used to describe them. Most zeolite frameworks can be generated from several different SBU's. Descriptions

of known zeolite structures based on their SBU's are list in Table 3.1 [52]. 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:



or by a structural formula:



Where the bracketed term is the crystallographic unit cell. The metal cation (of valence n) 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 [53].

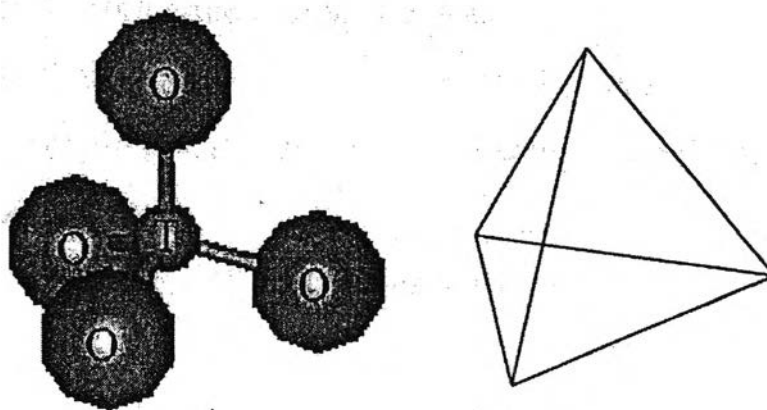


Figure 3.1 TO_4 tetrahedra (T=Si or Al) [49]

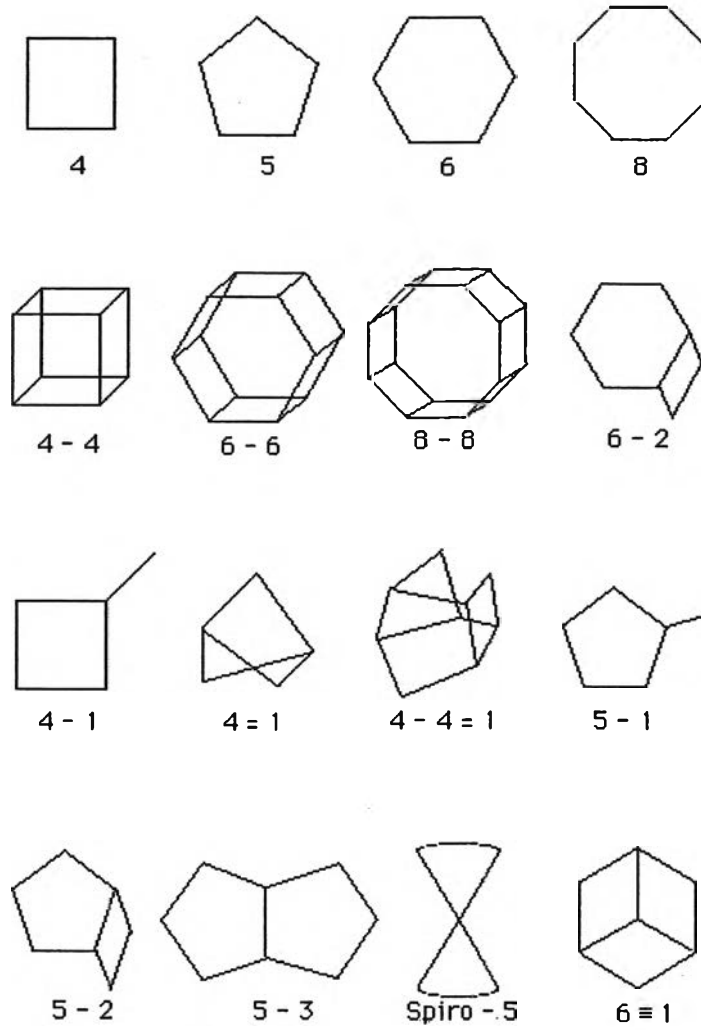


Figure 3.2 Secondary building units (SBU's) found in zeolite structures [51]

Table 3.1 Zeolites and their secondary building units. The nomenclature used is consistent with that presented in Figure 3.4 [52]

ZEOLITE	SECONDARY BUILDING UNITS							
	6	4	4-4	6-6	8-8	4-1	5-1	4-4=1
Bikilaite							X	
Li-A (BW)	X	X	X					
Analcime	X	X						
Yagawaralite	X		X					
Episibite							X	
ZSM-5							X	
ZSM-11							X	
Ferrierite							X	
Cachiardite							X	
Brewsterite	X							
Laumonite		X						
Modenite							X	
Sodalite	X	X						
Henulandite								X
Stibite								X
Natrolite						X		
Thomdonite						X		
Edingtonite						X		
Cancrinite		X						
Zeolite L		X						
Mazzite	X							
Merlinoite	X		X		X			
Phillipsite	X		X					
Zeolite Losod		X						
Erionite	X	X						
Paulingite	X							
Offeretite		X						
TMA-E(AB)	X	X						
Gismondine	X		X					
Levyne		X						
ZK-5	X	X	X		X			
Chabazite	X	X			X			
Gmelinite	X	X	X		X			
Rho	X	X	X			X		
Type A	X	X	X	X				
Faujasite	X	X			X			

3.2 Category of Zeolite

There are over 40 known natural zeolites and more than 150 synthetic zeolites have been reported [54]. 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 [2]. 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-methylpentane. 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 [54]. The structural characteristics of assorted zeolites are summarized in Table 3.2

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 MFI - type (ZSM-5) zeolite as presented in Figure 3.3 is probably the most useful one. ZSM-5 zeolite has two types of channel systems of similar sized, one with a straight channel of pore opening $5.3 \times 5.6 \text{ \AA}$ and the other with a tortuous channel of pore opening $5.1 \times 5.5 \text{ \AA}$. Those intersecting channels are perpendicular to each other, generating a three dimensional framework. ZSM-5 zeolites with a wide range of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio can easily be synthesized. High siliceous ZSM-5 zeolites are more hydrophobic and hydro thermally stable compared

with many other zeolites. Although the first synthetic ZSM-5 zeolite was discovered more than two decades ago (1972) new interesting applications are still emerging to this day. For example, its recent application in NO_x reduction, especially in the exhaust of lean-burned engine, has drawn much attention. Among various zeolite catalysts, ZSM-5 zeolite has the greatest number of industrial applications, covering from petrochemical production and refinery processing to environmental treatment.

Table 3.2 Structural characteristics of selected zeolites [55]

Zeolite	Number of rings	Pore opening Å	Pore/Channel structure	Void volume (ml/g)	D _{Frame} ^a (g/ml)	CI ^b
<i>8-membered oxygen ring</i>						
Erionite	8	3.6x5.1	Intersecting	0.35	1.51	38
<i>10-membered oxygen ring</i>						
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
<i>Dual pore system</i>						
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	7.1	Capped by 6 rings	-	-	1-3
Mordenite	10	Elliptical				
	12	6.5x7.0	One-dimensional	0.28	1.70	0.5
	8	2.6x5.7	12:8 intersecting			
Omega (ZSM-4)	12	7.4	One-dimensional	-	-	2.3
	8	3.4x5.6	One-dimensional	-	-	0.6
<i>12membered oxygen ring</i>						
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	7.4	Intersecting	0.48	1.27	0.4
	12	7.4x6.5	12:12 intersecting			
<i>Mesoporous system</i>						
VPI-5	18	12.1	One-dimensional	-	-	-
MCM41-S	-	16-100	One-dimensional	-	-	-

^aFramework density

^bConstraint index

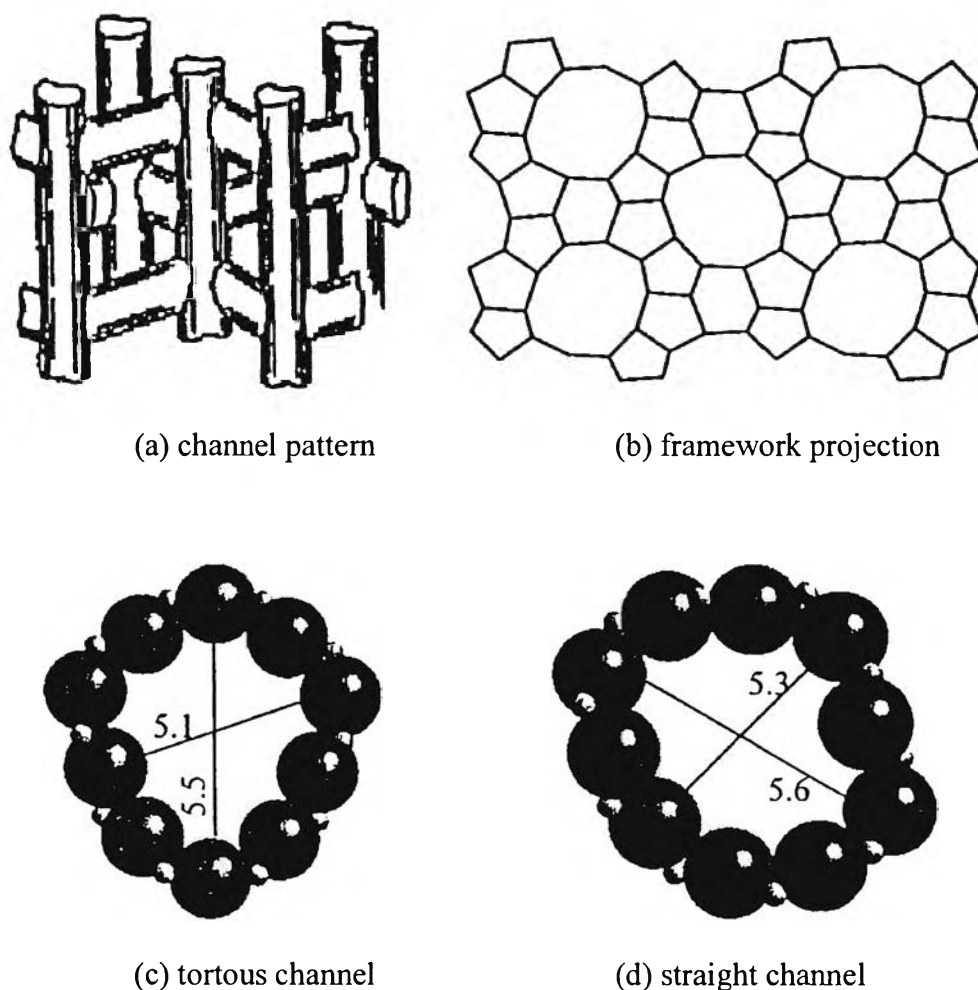
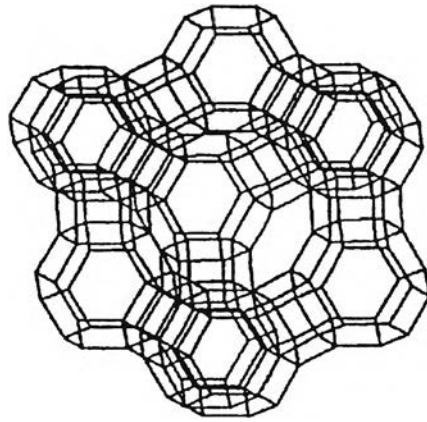
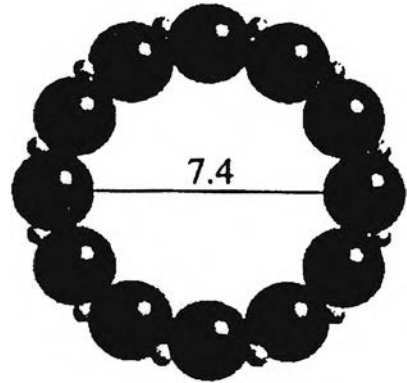


Figure 3.3 Structure of ZSM-5 [54]

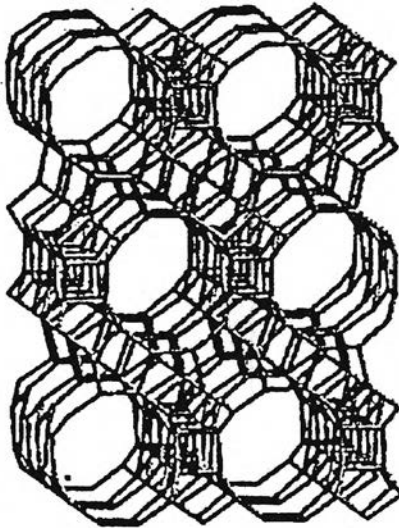
Although the 10-membered oxygen ring zeolite was found to possess remarkable shape selectivity, catalysis of large molecules may require a zeolite catalyst with a large-pored opening. Typical 12-membered oxygen ring zeolites, such as faujasite-type zeolites, normally have pore opening greater than 5.5 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 [54]) 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.



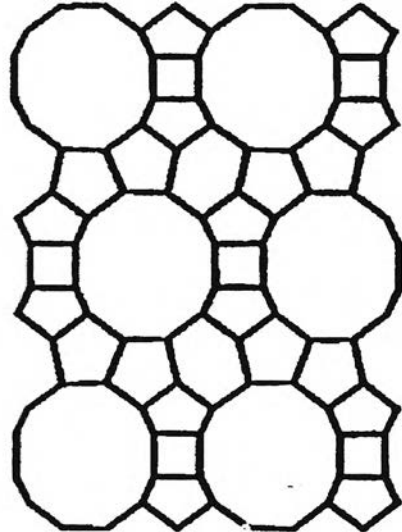
(a) framework structure



(b) pore opening

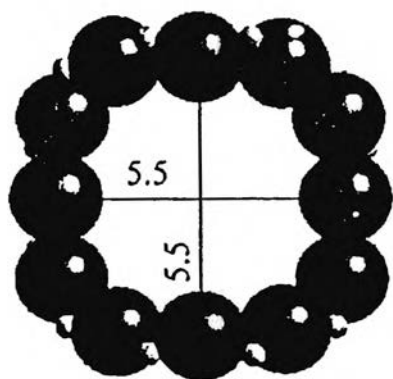
Figure 3.4 Structure of Faujasite [54]

(a) framework structure

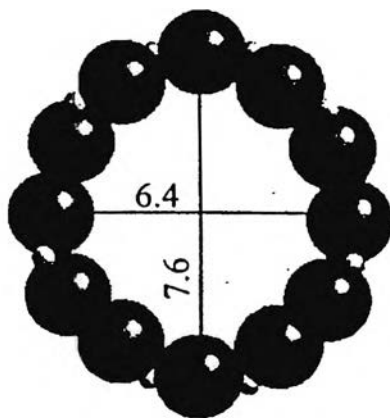


(b) framework projection

Figure 3.5 Structure of beta zeolite [54]

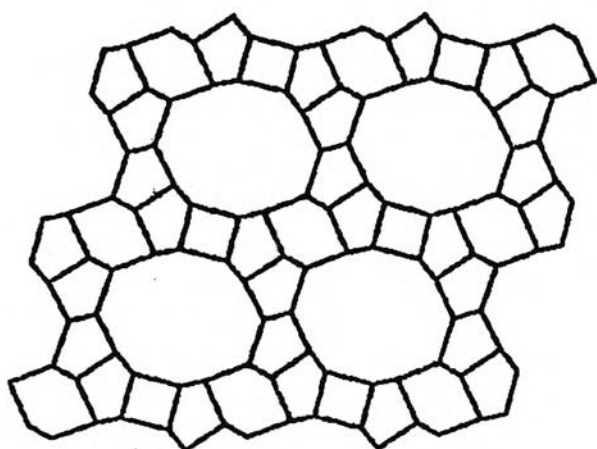


(c) tortuous channel

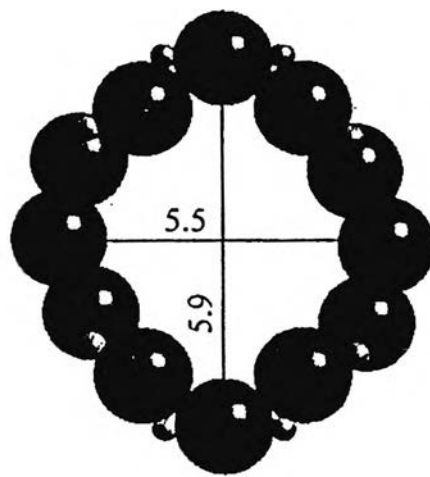


(d) straight channel

Figure 3.5 Structure of beta zeolite [54]



(a) framework projection



(b) pore opening

Figure 3.6 Structure of zeolite ZSM-12 [54]

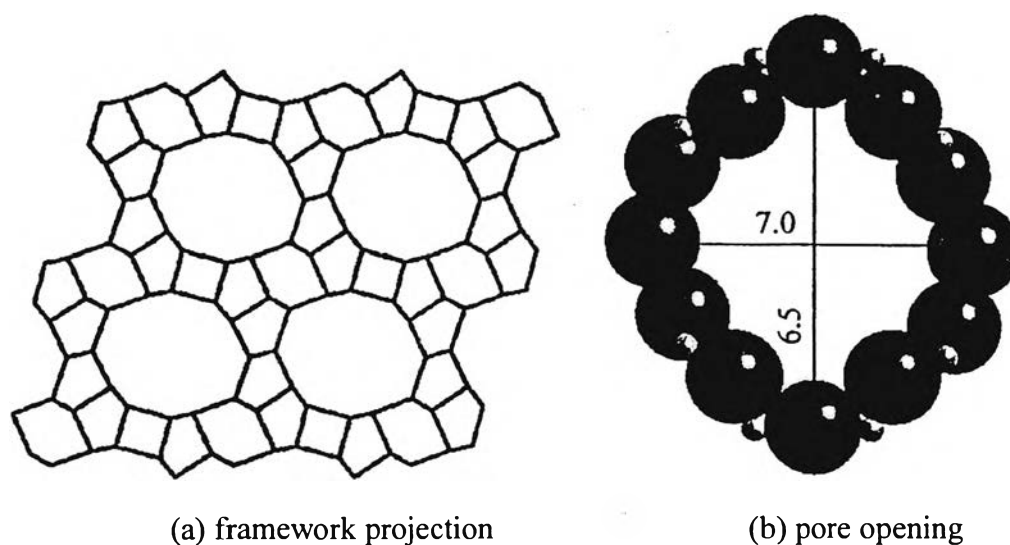


Figure 3.7 Structure of Mordenite [54]

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 with pore opening $6.5 \times 6.7 \text{ \AA}$ which is interconnected to 8-membered oxygen ring channel with opening $2.6 \times 5.7 \text{ \AA}$ (Figure 3.7 [44]). 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 [54]) 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 \AA) such as VPI-5, MCM-41S undoubtedly will shed new light on future catalyst applications.

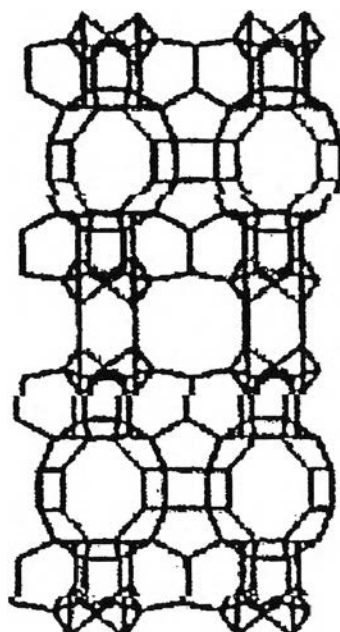


Figure 3.8 Framework structure of MCM-22 [54]

3.3 Zeolite Active sites

3.3.1 Acid sites

Classical Brønsted and Lewis acid models of acidity have been 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 [56, 57].

In general, the increase in Si/Al ratio will increase acidic strength and thermal stability of zeolite [58]. 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 increase 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 increased 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 [57].

An improvement in thermal or hydrothermal stability has been ascribed to the lower density of hydroxyl groups, which is parallel to that of Al content [56]. A longer distance between hydroxyl groups decreased the probability of dehydroxylation that generates defects on structure of zeolites.

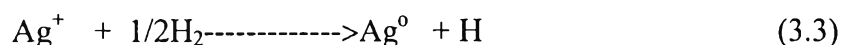
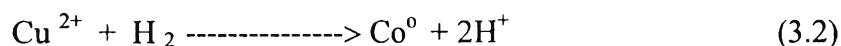
3.3.2 Generation of Acid Centers

Protonic acid centers of zeolite are generated in various ways. Figure 3.9 depicts the thermal decomposition of ammonium-exchanged zeolite yielding the hydrogen form [53].

The Brønsted acidity due to water ionization on polyvalent cations, described below, is depicted in Figure 3.10 [59].



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 noted to increase by hydrogen at 2.5 – 450 °C to increase with the rise of the reduction temperature [49].



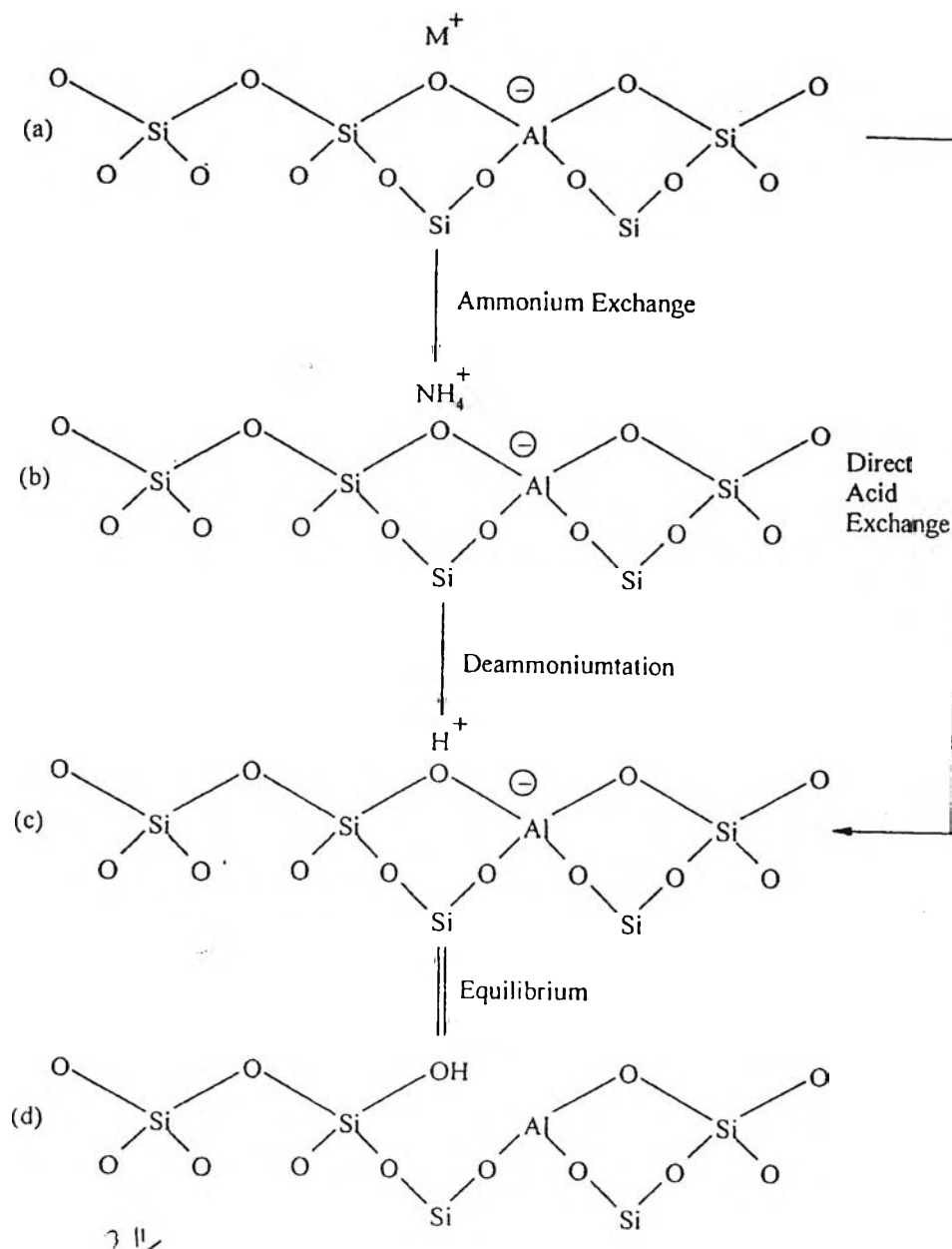


Figure 3.9 Diagram of the surface of a zeolite framework [52].

- In the as-synthesis form M^+ either an organic cation or an alkali metal cation.
- Ammonium in exchange produces the NH_4^+ exchanged form.
- Thermal treatment is used to remove ammonia, producing the H^+ , acid form.
- 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 [59]. The dehydration reactions decrease the number of protons and increase 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 500 °C and calcination at 800 to 900 °C produces irreversible dehydroxylation, which causes deflection in crystal structure of zeolite.

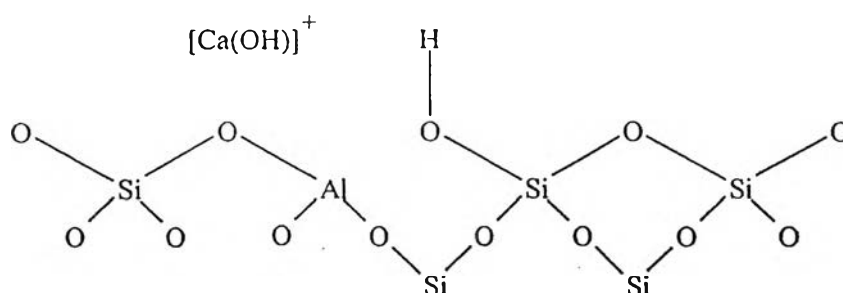


Figure 3.10 Water molecules co-ordinated to polyvalent cation are dissociated by heat treatment yielding Brønsted acidity [59].

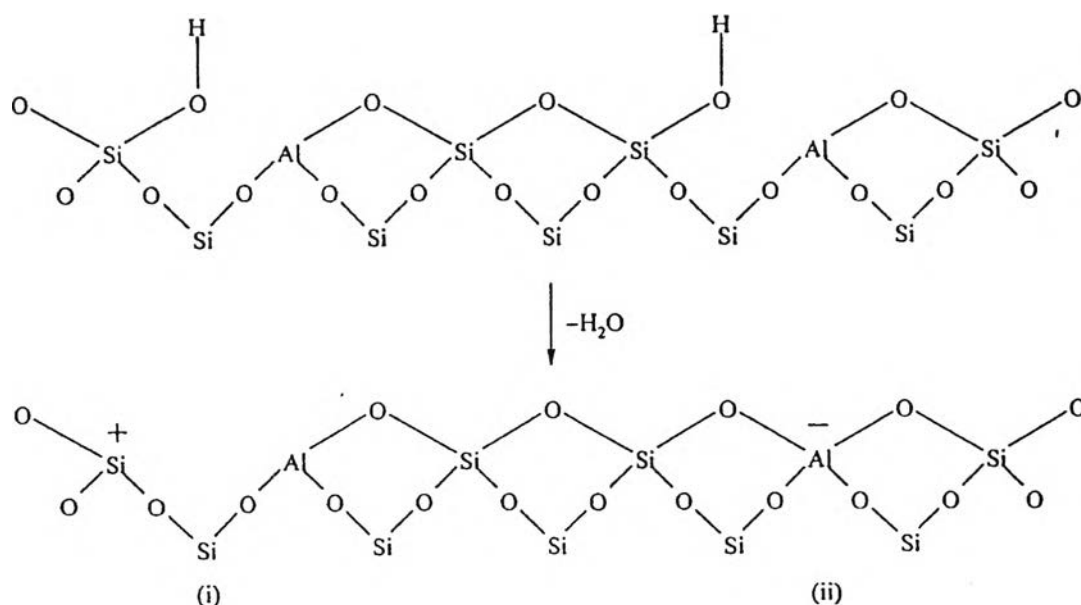


Figure 3.11 Lewis acid site developed by dehydroxylation of Brønsted acid site [59].

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 [59]. The extent of dealumination monotonously increases with the partial pressure of steam.

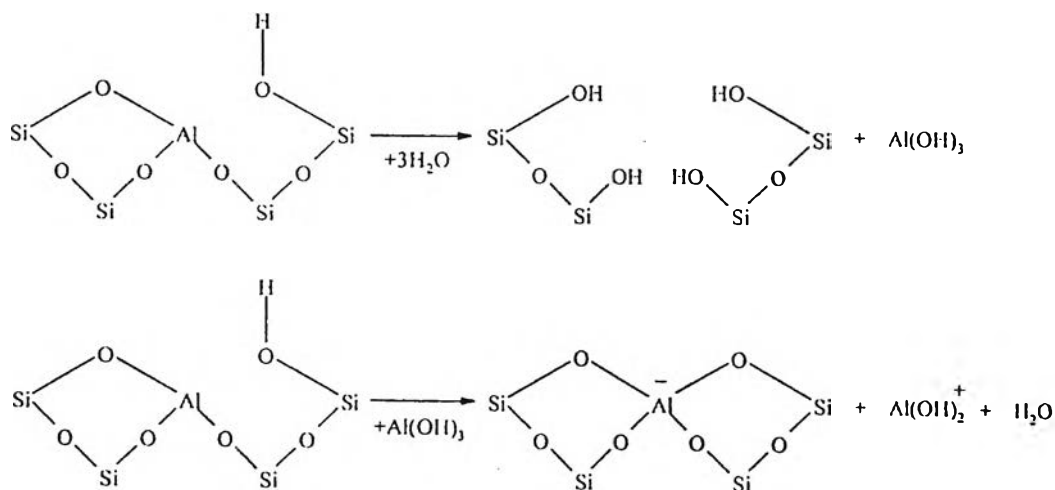


Figure 3.12 Steam dealumination process in zeolite [59]

The enhancement of 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 [59]. Partial dealumination might therefore yield a catalyst of higher activity while severe steaming reduces the catalytic activity.

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 500°C . The potassium cation has been shown to control the unimolecular cracking (β -scission). Free radical mechanisms also contribute to surface catalytic reactions in these studies.

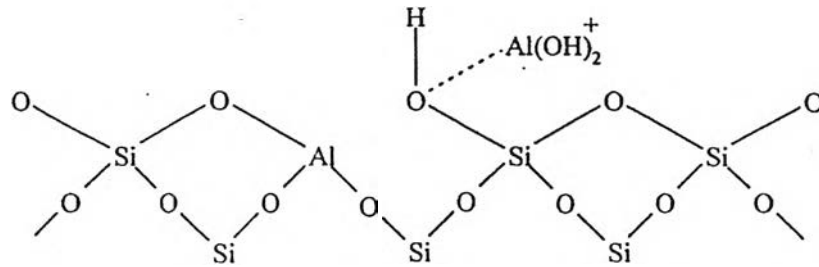


Figure 3.13 The enhancement of the acid strength of OH groups by their interaction with dislodged aluminum species [59].

3.4 Shape Selective

Many reactions involving carbonium intermediates are catalyzed by acidic zeolite. With respects to a chemical standpoint the reaction mechanisms are not fundamentally different with zeolites or with any the acidic oxides. What zeolite adds 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.

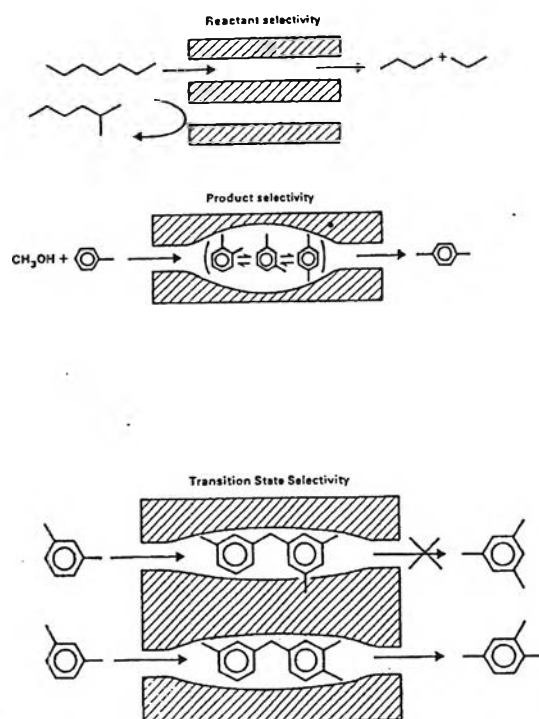


Figure 3.14 Diagram depicting the three type of selectivity [52]

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 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.

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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio than before could be synthesized. Previously, only structures with $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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.

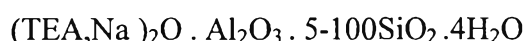
After synthesis the zeolite are washed, dried, heated to remove water of crystallization, and calcined in air, e.g., at about $550\text{ }^\circ\text{C}$. Organic species are also thus removed. For most catalytic purpose, the zeolite is converted into acidic form. For some zeolites this can be achieved 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 [53].

3.6 Beta zeolite

Beta Zeolite is an old zeolite discovered before Mobil began the “ZSM” naming sequence. Beta Zeolite was initially synthesized by Wadlinger et al. [1] using tetraethylammonium hydroxide as the organic template. The structure of beta zeolite was recently determined because the structure is very complex and interest was not high until it becomes important for some dewaxing process.

The tetrahedral framework structure of beta zeolite is disordered along the [001]. The disordered structure and the three simple ordered polytypes are related through layer displacements on 001 planes. These polytypes have mutually perpendicular 12-ring channel systems, and beta zeolite exhibits characteristic properties of the presence of 12-member-ring channels and the intersecting 6.5 x 5.6 and 7.5x5.7Å. The smaller building units are double six-ring units connected by two four-rings and four five-rings unit. These are connected to form chains along the [001] direction. Polytypes A and B contain 9 unique T sites, whereas polytype C contain 32 [56].

The chemical composition of beta zeolite is:



The zeolite may offer interesting opportunities as a catalyst, since it combines three important characteristics: large pore (12 membered oxygen ring), high silica to alumina synthesis ratio, three dimension network or pores. In addition, the dimensions of on type of pores (5.5Å) can give a certain level of shape selectivity. This has been suitable for isomerization of C₄-C₇ hydrocarbons to gasoline fraction with increasing octane number [28,49], to transalkylation of xylenes [61], and to condensation of benzene and formaldehyde [62].

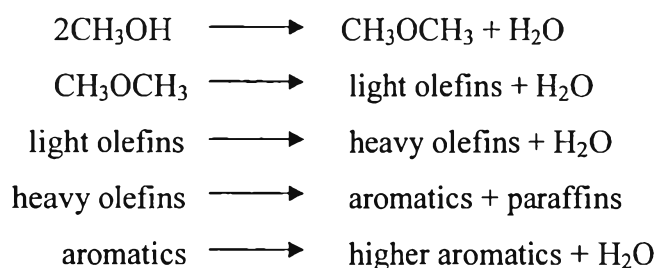
Recently, beta zeolite has been studied in a large range of reaction, and it is a potential catalyst in several processes [23] because it has a unique structure, acidity, and activity as a solid acid catalyst, hydrothermal and acid treatment stability in reaction such as cracking, isomerization, alkylation, disproportionation of

hydrocarbon compounds [63-65] and conversion of methanol to hydrocarbon over beta zeolite has been investigated earlier [37].

3.7 Methanol Conversion

The conversion of methanol into hydrocarbons using zeolite catalysts has attracted significant research attention since the publication of the landmark paper by Chang and Silvestri in 1977 [38]. They have been reported this reaction using H-ZSM-5 as catalyst. Subsequently, it was shown that WO_3 supported on $\gamma\text{-Al}_2\text{O}_3$ could also catalyze this reaction [66]; however, the hydrocarbon yield was far superior with zeolite catalysts. The extensive literature concerning the conversion of methanol to hydrocarbons over zeolite catalysts has recently been reviewed by Vora et al. [67] for the formation of light alkenes, and earlier reviews have discussed the conversion of methanol to gasoline [68-70]. The reaction has been observed with a range of zeolites and microporous materials, e.g., Y zeolite [71], beta zeolite [38], mordenite [72], $\text{AlPO}_4\text{-5}$, SAPO-5 and MeAPO-5 [73], EU-2 [74], clinoptilolite [75] and SAPO-34 [67], as well as nonzeolite catalysts, e.g., 12-tungstophosphoric acid [77].

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.



The first step in the reaction sequence is the dehydration of methanol to equilibrium mixture of dimethylether (DME), methanol and water. The DME then reacts further to form a mixture of light olefins. As the concentration of DME is depleted and further dehydration of methanol takes place. The DME alkylates the

light olefins (mostly propylene and butanes) to higher olefins. If any residual DME remains at the point where aromatics form, those aromatics are readily alkylates to higher carbon number of C_{10} . The heaviest component is durene (1,2,4,5-tetramethylbenzene), which lies near the high end the gasoline boiling range. No components with normal boiling points above the gasoline boiling range are produced.

The early work of Chang and Silvestri [38] showed that, high temperature favors selectivity to light olefins. Mobil found that by combining the factors of reduced catalyst activity with high operation temperature, it was possible to switch the methanol to gasoline (MTG) selectivity towards an olefin rich spectrum. This route was named the methanol to olefins (MTO) process, and gives a product that is rich in propylene and butenes.

The MTO process had an incipient development on H-ZSM-5 zeolites, in order to increase the yield of olefins and to fill (by means of the process of oligomerization of olefins to diesel oil) the gap in the MTG process commercialized by Mobil, which does not allow for obtaining gas-oil for automotion. The MTO process may be considered the first step in the MTG process, which may be described by means of the two steps in series shown in Fig. 3.15 [39,70].

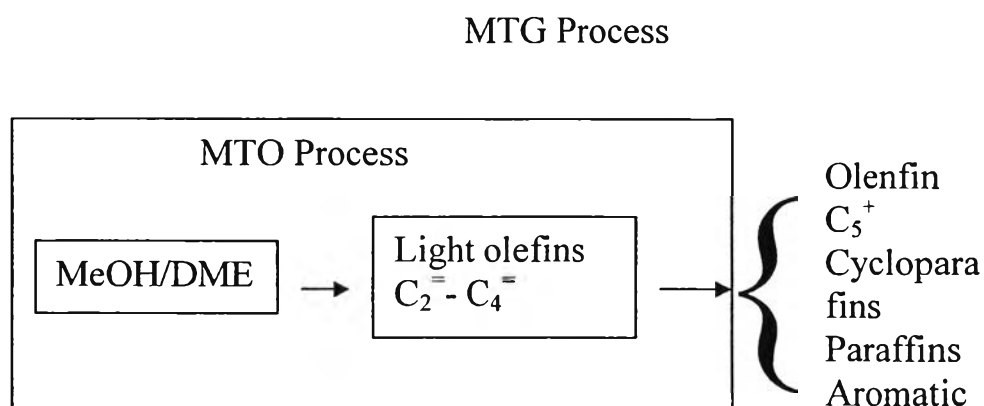


Figure 3.15 Scheme of MTG process

The primary products formed from oxygenates (methanol and dimethyl ether, in equilibrium) are light olefins (ethene, propene and, to a lesser extent, butenes) and the secondary products are heavier hydrocarbons, corresponding to the gasoline

fraction (C₅–C₁₀). Selective obtaining of light olefins (MTO process) is attained by stopping the reaction mechanism subsequent to the first step and, in order to make the process profitable, total conversion of methanol must be achieved.