CHAPTER II

THEORY

2.1   Zeolites

Zeolites[34] are crystalline, hydrated aluminosilicates of group I and group II elements, in particular, sodium, potassium, magnesium, calcium, strontium and barium. Structurally the zeolites are "framework" aluminosilicates, which are based on an infinitely extending three-dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all of the oxygens.
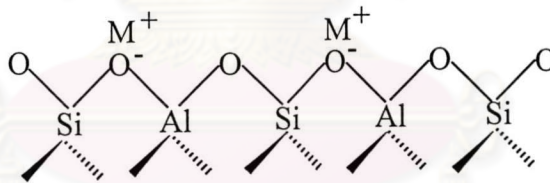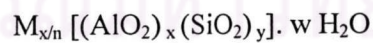

Figure 2.1   The structure of zeolites.

Zeolites may be represented by the formula

$$M_{x/n} [(AlO_2)_x (SiO_2)_y]. \ w \ H_2O$$

Where M is the cation of valence n, w is the number of water molecules.

2.2 Zeolite Structures

Zeolites[34,35] have a common subunit of structure so called primary building units of $(Al,Si)O_4$ tetrahedra, therein the Si or Al distribution is neglected. A secondary building unit (SBU) consists of selected geometric groupings of those tetrahedra. There are nine such building units, which can be used to describe all of the known zeolite structures. The secondary building units (SBU's) consist of 4, 6 and 8-member single rings, 4-4, 6-6 and 8-8-member double rings, and 4-1, 5-1 and 4-4-1 branched rings as illustrated in Figure 2.2. In some cases, the zeolite framework can be considered in terms of polyhedral units, such as the truncated octahedron (sodalite cage or β cage). Only the Si and Al positions are shown at the corners of each building unit shown in Figure 2.3. The oxygen atoms lie near the lines connecting the metal atoms. The connection of these building units in various ways results in different structures, i.e. different types of zeolites; for example, zeolite A and faujasite-type zeolites (including zeolite X and zeolite Y). Connecting the sodalite units with double 4 rings or double 6 rings forms the structures. A new larger cage is formed at the center which is called supercage (α cage) for both types of structure. The supercage type I belongs to zeolite A structure and supercage type II for faujasite and both are shown in Figure 2.3.
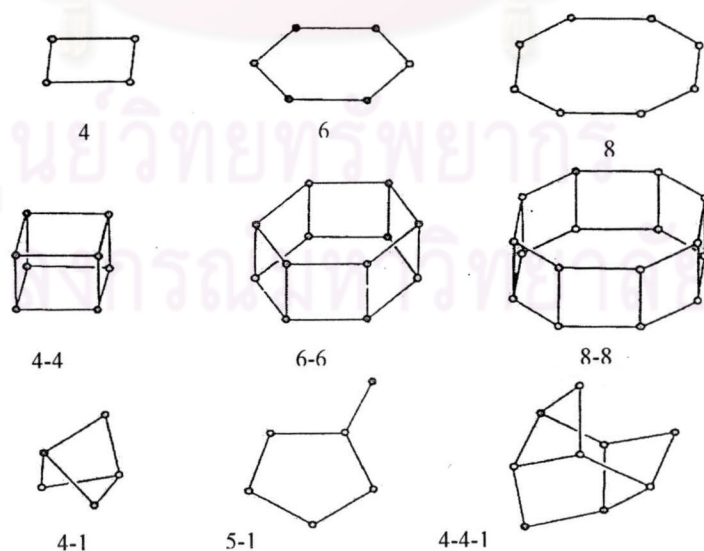

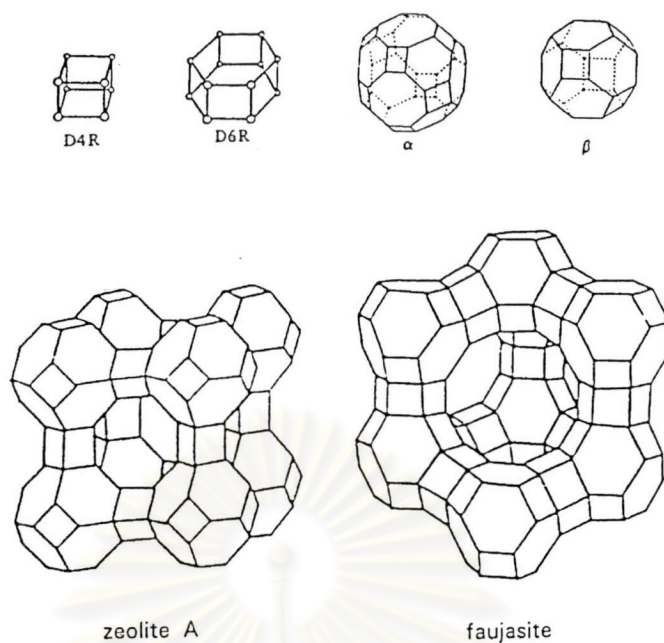**Figure 2.2** Secondary building units found in zeolite structures.

Figure 2.3 Topologies of the building units and the structures of zeolite A and faujasite-type zeolites.

2.3 Acid Form of Zeolites

Only the silica-riched sodium-form zeolite can be readily exchanged for protons by direct reaction with a mineral acid, giving surface hydroxyl groups the Brønsted acid sites. The usual method for preparing hydrogen form zeolites is the thermal treatment of ammonium exchanged zeolites leaving hydrogen (or proton) on the zeolite framework. The hydrogen form (acid form) can be generated indirectly by replacing the sodium ions of the zeolite by ammonium ions from an aqueous solution of ammonium chloride or ammonium nitrate and heating above 300°C under vacuum. The bridged OH group across a pair of Si and Al atoms behaves as a classical Brønsted acid. Further thermal treatment at higher temperature results in a loss of water from two nearby hydroxyl groups. This process is called dehydroxylation. The dehydroxylation causes the loss of one oxygen from zeolite framework per water molecule removed, exposing a tricoordinated Al ion, which is an

electron-pair acceptor, i.e. a Lewis acid site. The formation of these sites is shown in Figure 2.4.
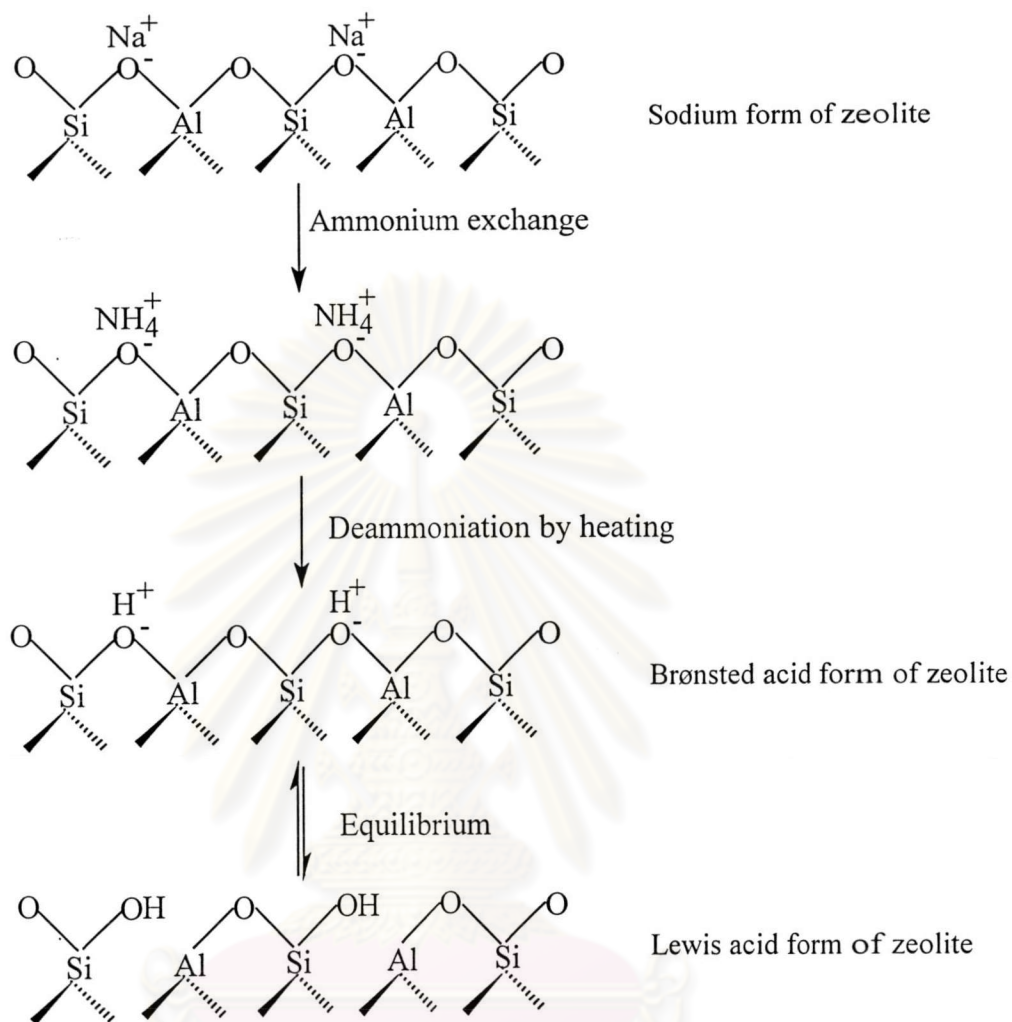

Figure 2.4 Generation of acid sites in zeolite.

Dealumination, the removal of the aluminum from the lattice is believed to occur during dehydroxylation due to the steam generation within the zeolite pores. Dealumination was claimed to produce a "nest" of four Si-O-H silanols. The mechanism of the framework dealumination[35] is illustrated by Figure 2.5. The framework tetrahedral sites of aluminum are hydrolyzed by steam at elevated temperatures giving aluminum hydroxide phase on the zeolite surface. The hydroxyl groups produced on the tetrahedra, are subsequently removed during the final calcination procedure and new Si-O-Si linkages are

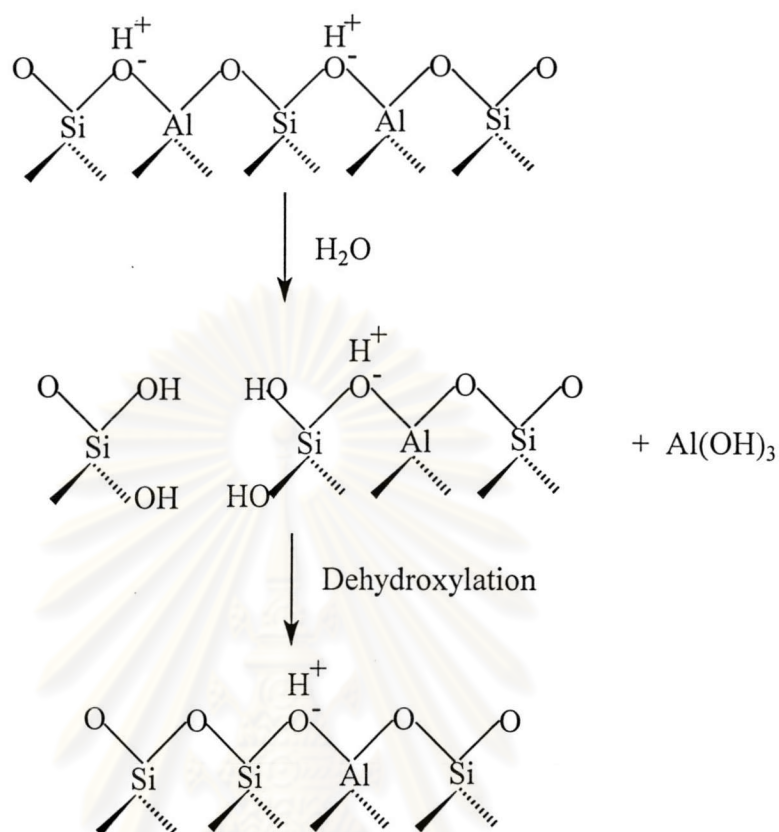formed. The loss of aluminum from the tetrahedral positions results in the contraction of the unit cell.

Figure 2.5 The mechanism of framework dealumination.

Dealumination is a major result of hydrothermal treatment of zeolites. Steaming of the zeolites has been found to produce a variety of cations and neutral species that occupy the pores and active sites of the molecular sieve catalyst. It has been proposed[35] that some of these cations interact with neighboring Brønsted sites to induce the catalytic superacid sites. The new cations have been suggested to function as Lewis acids, which have been considered to induce activity on nearby Brønsted sites as shown in Figure 2.6. In general, the steaming process causes the decrease of the number of strong acid sites. If a steam treatment is used for dealumination, the extraframework Al generated stays in the channels. This causes blocking of the channels and increasing the diffusional problems. Meanwhile, the steam treatment produces mesopores, which somehow allows connection between channels, forming, limitedly a pseudo tridirectional network.
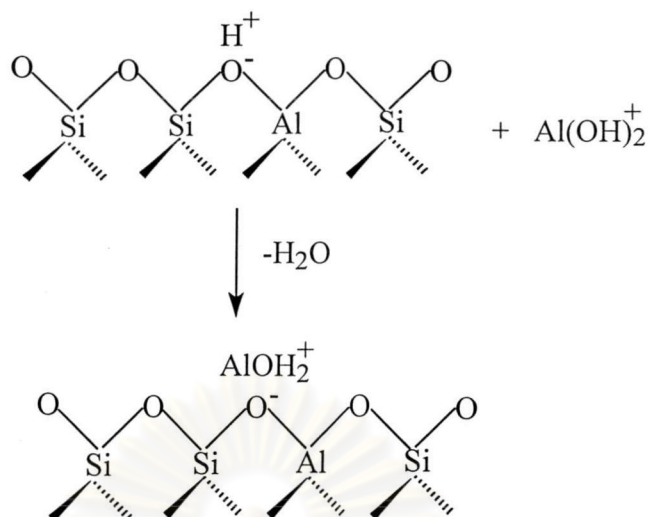
Figure 2.6   Formation of the catalytic superacid site ($AlOH_2^+$).

Direct acid treatment is not only dealumination but also removes the extraframework Al. Dealumination by acid treatment of some zeolite like ZSM-5 results in a material that shares some properties with dealuminated zeolites resulting from dehydroxylation. In general, chemical treatments, including acid extraction of aluminum from the framework, usually affect the external surfaces of the crystal. Hydrochloric acid treatment; for example, removes aluminum to yield a silica-rich external surface.

2.4   Shape Selectivity

Shape selectivity[35] plays a very important role in zeolite catalysis. Highly crystalline and regular channel structures are among the principal features that zeolite used as catalysts offer over other materials. Shape selectivity are divided into 3 types: reactant shape selectivity, product shape selectivity or transition-state shape selectivity. These types of selectivities are depicted in Figure 2.7. Reactant shape selectivity results from the limited diffusivity of some of the reactant, which cannot effectively enter and diffuse inside the crystal. Product shape selectivity occurs when slowly diffusing product molecules cannot

rapidly escape from the crystal, and undergo secondary reactions. Restricted transition-state shape selectivity is kinetic effect arising from the local environment around the active site. The rate constant for a certain reaction mechanism is reduced if the necessary transition-state is too bulky to form readily.
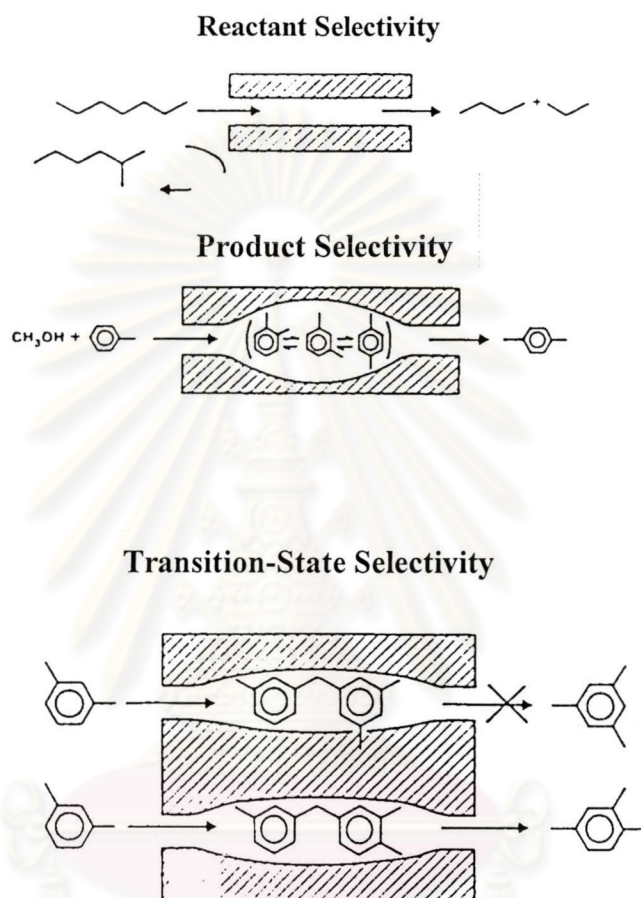
Figure 2.7 Three types of selectivity in zeolites: reactant, product and transition-state shape selectivity.

Transition-state shape selectivity has been termed spatioselectivity. Spatioselectivity implies that monomolecular rather than bimolecular transition states are favored in small pore: thus, this steric effect and/or diffusional effects may operate to produce shape selectivity. The methanol to gasoline (MTG) conversion process is a good example of transition-state shape selectivity, where the available space in the cavities of zeolite ZSM-5 determines the largest bimolecular reaction complexes that can form. Hence, all products have fewer than 11 carbon atoms, with xylenes predominating.

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

2.5 Structure and Chemical Composition of Zeolite Mordenite

Mordenite,[34-36] with a nearly constant Si/Al ratio of 5, is the most siliceous zeolite mineral. This constant ratio indicates an ordered distribution of Si and Al in the tetrahedral framework sites, there is a small Al-enrichment in the four-member rings which connect hexagonal sheets. Mordenite is a large-pore zeolite having an orthorhombic crystalline structure. The structure consists of chains that are crosslinked by the sharing of neighboring oxygens. The building units of this structure consist of four- and five-member rings. Each tetrahedron belongs to one or more five-member rings in the framework. The high degree of thermal stability of mordenite is probably due to the large number of 5-member rings, which are energetically favored in terms of stability. For the diffusion of small molecules, the mordenite zeolite is considered to contain a two-dimensional channel system. For practical applications to larger molecules it is considered to be a unidimensional, large-pore molecular sieve with side pockets because of the constraint on the eight-member ring openings for diffusion. The main cage has two exits, through two eight-member rings. The main channels parallel c axis with dimensions of 6.7 × 7.0 Å (12-member ring) and are linked by small channels parallel to b axis with 2.9 × 5.7 Å (8-member ring) as shown in Figure 2.8.

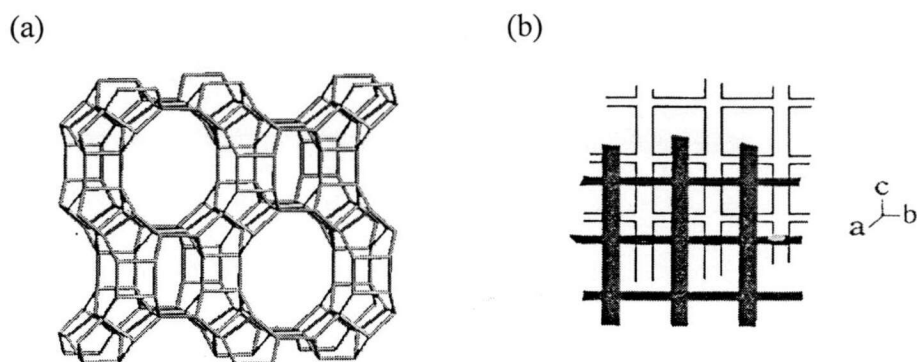(a)   (b)

Figure 2.8 (a) Framework structure of mordenite.

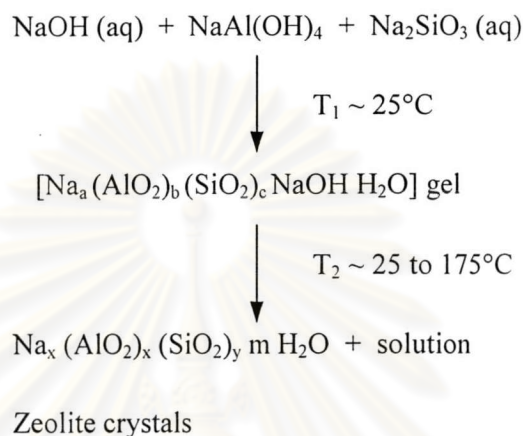(b) Schematic illustration of the two-dimensional channels in mordenite.

The chemical formula of a typical unit cell of hydrated Na-mordenite (Si/Al = 5) is $Na_8[(AlO_2)_8(SiO_2)_{40}].24H_2O$. In the hydrated crystal, the positions of 4 of the 8 sodium ions have been located in the constrictions with a minimum diameter of 2.8 Å. Locations of the remaining 4 sodium ions and water molecules are not known. Large cations such as cesium cannot occupy the positions determined for sodium. Natural mordenite contains crystal stacking faults in the *c* direction or amorphous material or cations in the channels that severely restrict diffusion into the large channel system. Many of the synthetic mordenite do not exhibit such pore restriction.

2.6 Zeolite Synthesis

Zeolites are generally synthesized by the hydrothermal method in a closed cyclindrical vessel, so called an autoclave. Mixing sources of aluminum, sodium, silicon in water results in a gel, four-component system $Na_2O-Al_2O_3-SiO_2-H_2O$.[34,37] The gel is crystallized in an autogenic pressure autoclave at temperatures varying, generally, from room temperature to about 200°C. The pressure is generally the autogenous pressure approximately equivalent to the saturated vapor pressure of water at temperature crystallized. The time required for crystallization varies from a few hours to several days. The alkali metals form soluble

hydroxides, aluminates, and silicates. These materials are well suited for the preparation of homogeneous mixtures. The aluminosilicate gel is formed by a process of copolymerization of the silicate and aluminate species that takes place via a condensation mechanism. The gel composition and structure appear to be controlled by size and structure of the polymerizing species.

$$NaOH\ (aq)\ +\ NaAl(OH)_4\ +\ Na_2SiO_3\ (aq)$$

$$\downarrow\quad T_1 \sim 25°C$$

$$[Na_a\,(AlO_2)_b\,(SiO_2)_c\,NaOH\ H_2O]\ gel$$

$$\downarrow\quad T_2 \sim 25\ to\ 175°C$$

$$Na_x\,(AlO_2)_x\,(SiO_2)_y\ m\ H_2O\ +\ solution$$

Zeolite crystals

A schematic representation of the crystallization of an amorphous aluminosilicate gel to a zeolite[35] is depicted in Figure 2.9. The gel structure, represented in two diamensions, is depolymerized by the hydroxyl ions, which produce soluble aluminosilicate species that may regroup to form the nuclei of the ordered zeolite structure. In this case the hydrated cation acts as a template.
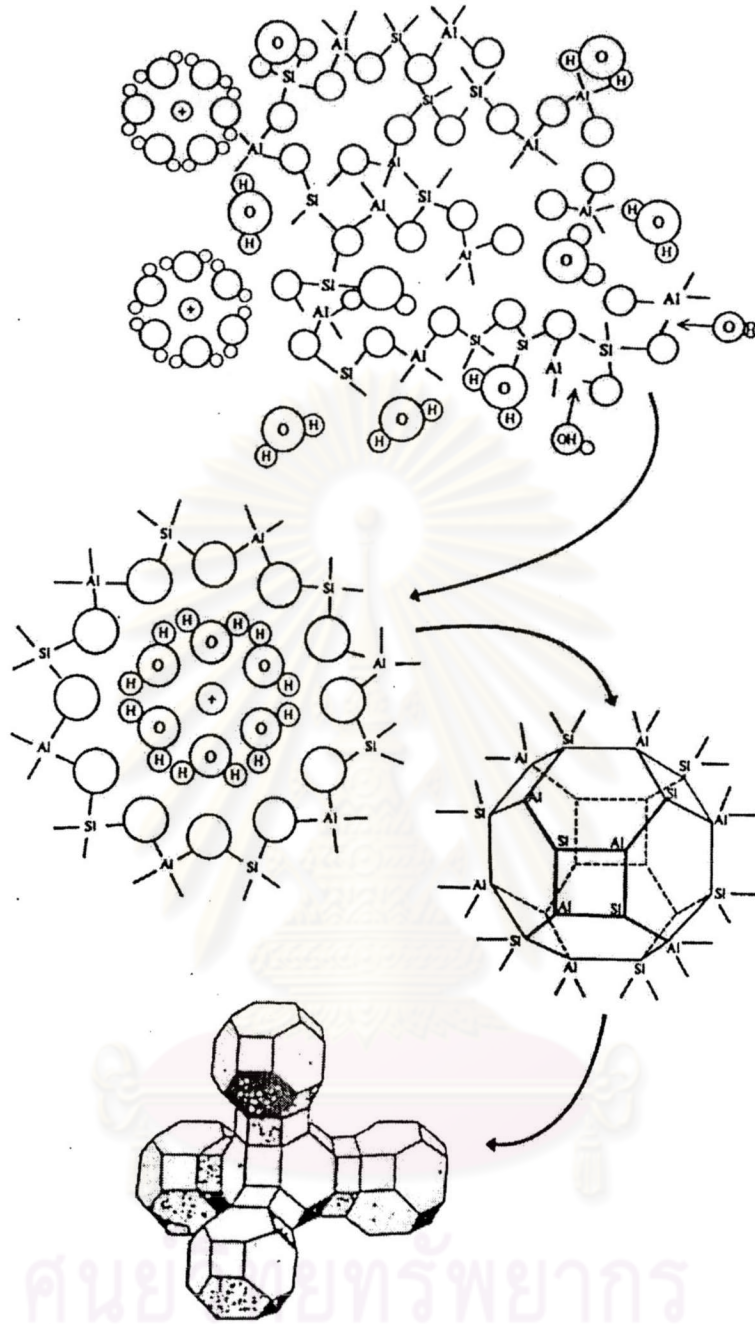
Figure 2.9 Schematic representation of the formation of zeolite crystal nuclei in a hydrous

gel.

2.7 Factors Influencing Zeolite Formation

Three variables have a major influence on the zeolite structure crystallized: the gross composition of the reaction mixture, time, and temperature. There are also history-dependent factors such as digestion or aging period, stirring, nature (either physical or chemical) of the reaction mixture, and order of mixing.

Table 2.1 Factors influencing zeolite crystallization

- Gross composition
    1. SiO_2/Al_2O_3
    2. $[OH^-]$
    3. Cations
        a. Inorganic
        b. Organic
    4. Anions (other than $[OH^-]$)
    5. $[H_2O]$
- Time
- Temperature
    1. Ambient - ca. 25 to 60°C (natural zeolite formation)
    2. Low - ca. 90 to 120°C
    3. Moderate - ca. 120 to 200°C
    4. High - ca 250°C or higher
- History-dependent factors
    1. Aging
    2. Stirring
    3. Nature of mixture
    4. Order of mixing

2.7.1 Reaction Mixture Components

Each component in the reactant mixture contributes to specific characteristic of the gel and to the final material obtained. Table 2.2 provides a broad listing of individual components of the mixture and the primary influence each component has within that reactant mixture.

Table 2.2 The effects of selected variables on the final crystalline product in zeolite synthesis

Variables	Primary influence
SiO_2/Al_2O_3	Framework composition
H_2O/SiO_2	Rate, crystallization mechanism
OH^-/SiO_2	Silicate molecular weight, OH^- concentration
Inorganic cation(s)/SiO_2	Structure, cation distribution
Organic additives/SiO_2	Structure, framework aluminum content

The SiO_2/Al_2O_3 mole ratio, the hydroxide content of the gel, and the presence of inorganic cations also contribute to determining which structure(s) would finally crystallize. For example, at the ratio below 20 the mordenite phase is to appear, no matter with or without the presence of the organic quaternary amine. The crystallization of a particular zeolite structure from the gel system containing these four components strongly depends on the SiO_2/Al_2O_3 ratio of the starting gel mixture. The inorganic or organic actions not only influence the structure crystallized but also other features of the final crystalline products produced, such as morphology and crystal size.

2.7.2 Time

Time, as a parameter, can be optimized in the synthesis of many zeolites. In systems which produce only one zeolite phase, optimizing maximum crystallization over a short span of time is important. Crystallization parameters must be adjusted to minimize the

production of the other phase while also minimizing the time needed to obtain the desired crystalline phase.
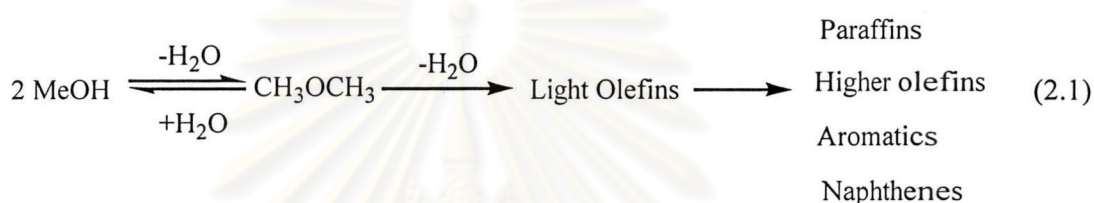
2.7.3 Temperature

Temperature influences several factors in zeolite synthesis; it can alter the zeolite phase obtained as well as change the induction period before the start of crystallization. This induction period decreases with increasing temperature. Also, for any mixture as the temperature increases, the rate of crystallization increases. As the temperature is changed, conditions may favor formation of other phases. As the temperature increases, the solubilities of aluminate and silicate species increase, causing a shift in the concentration of the liquid phase. Loosen zeolites prefer crystallization at lower temperature while denser zeolites do at high temperature.

2.8   Methanol to Olefins (MTO) Process

The methanol is initially converted to an equilibrium mixture of methanol, dimethyl ether and water, which can be processed catalytically to either gasoline (methanol-to-gasoline, MTG) or olefins (methanol-to-olefin, MTO), depending on the catalyst and/or the process operation conditions. Although methanol itself is a potential motor fuel or can be blended with gasoline, it would require large investments to overcome the technical problems connected with the direct use of methanol as a motor fuel. There was a report of a commercial MTG reaction using ZSM-5 as the catalyst operated at temperature around 400°C and at a methanol partial pressure of several bars. Under such a condition, the intermediate olefins that form within the catalyst channels can convert to paraffins and aromatics. However, at one point in the MTG reaction, the product mixture consist of about 40% light olefins. The importance of light olefins as intermediates in the conversion of methanol to gasoline was recognized early. Consequently, a number of attempts were made to selective preparation of light olefins from methanol, not only on medium-pore zeolites but

also on small-pore zeolites, SAPO type molecular sieves and large-pore zeolites (to a much less extent). If one interrupted the reaction at the point of about 40% light olefin formation, one could harvest these C_2-C_4 olefins. By adjusting the reaction conditions (such as, for example, raising the temperature to 500°C) as well as the catalyst applied, one could increase drastically the olefin yield.

The main reaction steps of methanol conversion to olefins can be summarized as follows:

$$2 \text{ MeOH} \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} CH_3OCH_3 \xrightarrow{-H_2O} \text{Light Olefins} \longrightarrow \begin{matrix} \text{Paraffins} \\ \text{Higher olefins} \\ \text{Aromatics} \\ \text{Naphthenes} \end{matrix} \qquad (2.1)$$

There is general consensus that the intermediate in the dehydration of methanol to dimethyl ether (DME) [step 1 in Eq.(2.1)] over solid acid catalysts is a protonated surface methoxyl, which is subject to a nucleophilic attack by methanol. The subsequent conversion of light olefins to paraffins, aromatics, naphthens and higher olefins [step 3 in Eq.(2.1)] proceeds via classical carbenium ion mechanisms with concurrent hydrogen transfer, which is well known in hydrocarbon chemistry.

2.8.1 Reaction Mechanisms for MTO Process

The MTO process consists of three steps of reactions: (1) the formation of dimethyl ether, (2) the initial C-C bond formation resulting in light olefins, and (3) the subsequent conversion of the primary products (light olefins) into higher olefins. Brønsted acidity is known to be the main source of catalyst activity for the MTO products, while the conjugate Lewis basic site would be responsible for the initial C-C bond formation.

2.8.1.1 Formation of Dimethyl Ether

Park *et al.*[38] studied a reaction for the formation of dimethyl ether which is shown in Scheme 2.1. The magic-angle-spinning (MAS) NMR data showed that the methanol was reversibly adsorbed through hydrogen to the bridged hydroxyl on Brønsted acid sites. The protonation took place very fast on strong acidic sites and reached equilibrium finally. The protonated methanol transformed via dehydration to a surface methoxy species, which was covalently bonded to the lattice oxygen of ZSM-5 and reacted in turn with methanol to form a dimethyloxonium ion (DMO$^+$). Deprotonation of the latter yielded dimethyl ether and H$^+$.
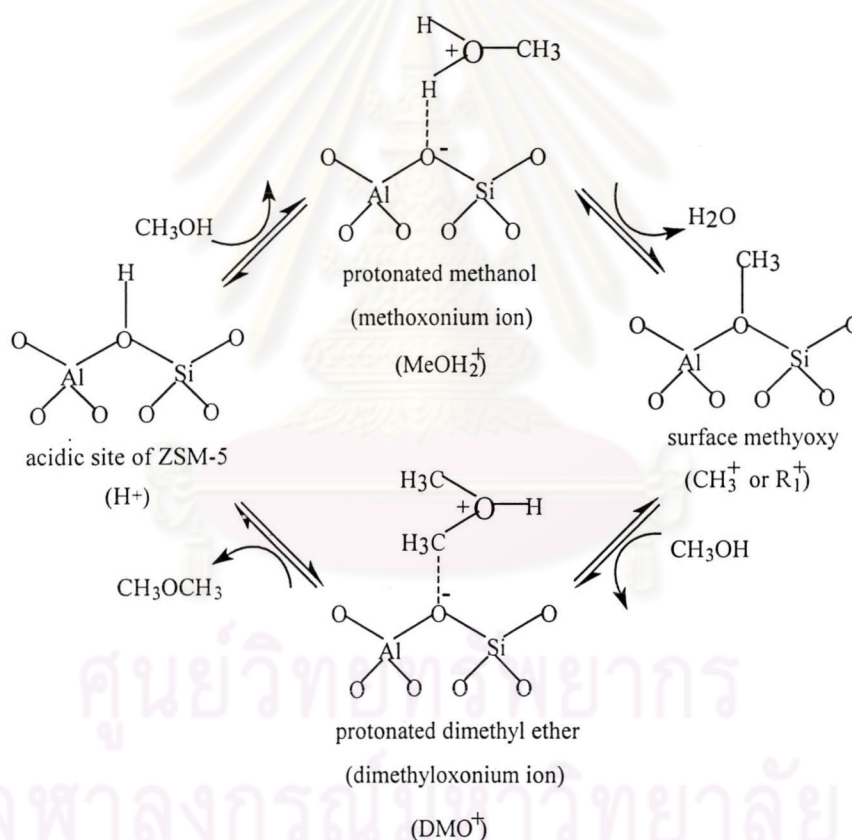

Scheme 2.1 Formation of dimethyl ether during the course of MTO process.

2.8.1.2 Formation of Primary Hydrocarbon Products

The mechanism of initial C-C bond formation has been proposed to account for the conversion of methanol to olefins. There are several patterns of this kind of mechanism. Although, there is little experimental evidence, the C-C formation is presently the most promising mechanism to express the formation of light olefins from the equilibrium system of methanol, dimethyl ether and water.

a. Oxonium ylide mechanism

Van den Berg et al.[2] postulated that dimethyl ether interacted with a Brønsted acid site on the solid catalyst to form a dimethyl oxonium ion, which reacted further with another dimethyl ether to form a trimethyl oxonium ion. This trimethyl oxonium ion was subsequently deprotonated by a basic site to form a surface associated dimethyl oxonium methyl ylide species. The next step was 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 was formed via β-elimination as shown in Scheme 2.2. Bimolecular methylation of the dimethyl oxonium ylide resulted in the ethyldimethyl oxonium ion, rather than an intramolecular Stevens rearrangement. In addition, a number of other investigators favor this mechanism as a result of the linear dependence of hydrocarbon formation and zeolite Brønsted acidity.

$$CH_3OCH_3 \xrightarrow{CH_3O\overset{+}{H}_2} \underset{\underset{CH_3}{|}}{\overset{CH_3 \quad CH_3}{\underset{\overset{+}{O}}{\diagdown\diagup}}}$$
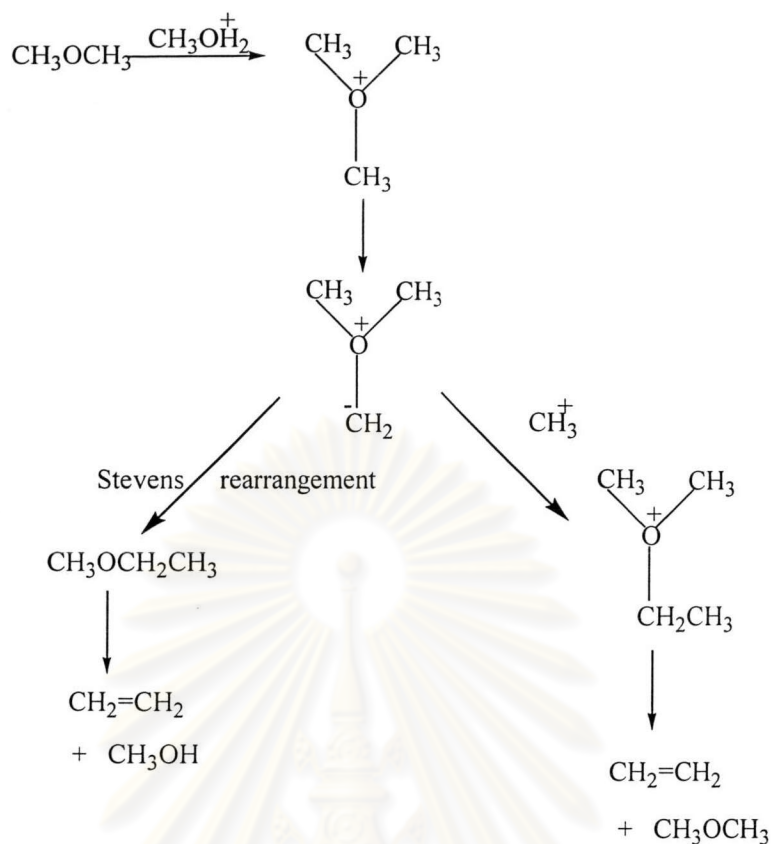
Scheme 2.2 A proposed oxonium ylide mechanism in the MTO process.

In summary, the oxonium ylide mechanism involves the formation of a surface-bound intermediate as the initial reaction step. The zeolite surface OH-group is methylated to form the methyloxonium intermediate, which gives rise to a surface-bound methylene-oxonium ylide due to deprotonation. The surface-bound methylene oxonium ylide is isoelectronic with a surface-associated carbene, as outlined in Scheme 2.3.

$$Z\text{-OH} + CH_3OH \longrightarrow Z\text{-O-CH}_3 + H_2O$$

$$Z\text{-O-CH}_3 \longrightarrow Z\text{-O-CH}_2 \qquad \text{surface-incorporated ylide}$$

$$Z\text{-O:} \quad :CH_2 \qquad \text{surface-associated carbene}$$
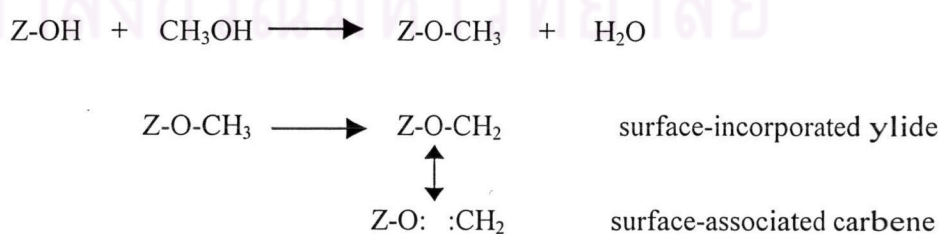
Scheme 2.3 A proposed oxonium ylide mechanism applied to the zeolite surface.

Hutchings *et al.*[39] proposed a mechanism for the formation of the nucleophilic carbon atom in the form of a surface ylide species. An adsorbed methanol molecule was dehydrated to form a surface-bound methoxy species of which a proton was then transferred to a neighboring bridged oxygen to form a charged surface ylide nearby a BrØnsted acide site. The formation of the surface methoxy in which the surface oxygen, methyl carbon and the leaving OH group were roughly colinear follows a classic S_N2 mechanism (Eq. 2.2 in Scheme 2.4). The initial C-C bond should then be formed in a more facile reaction between a methanol (or dimethyl ether) and the surface ylide (Eq. 2.3 in Scheme 2.4) which would lead to the formation of a surface ethoxy group. Ethylene was able to be formed by β-elimination along with reforming the Brønsted acid site. Alternatively, the surface ethoxy species could react with further methanol molecules to form a surface iso-propoxy group and subsequently a tertiary butoxy group. These surface species undergoing β-elimination would lead to the formation of propylene and *iso*-butylene, respectively.
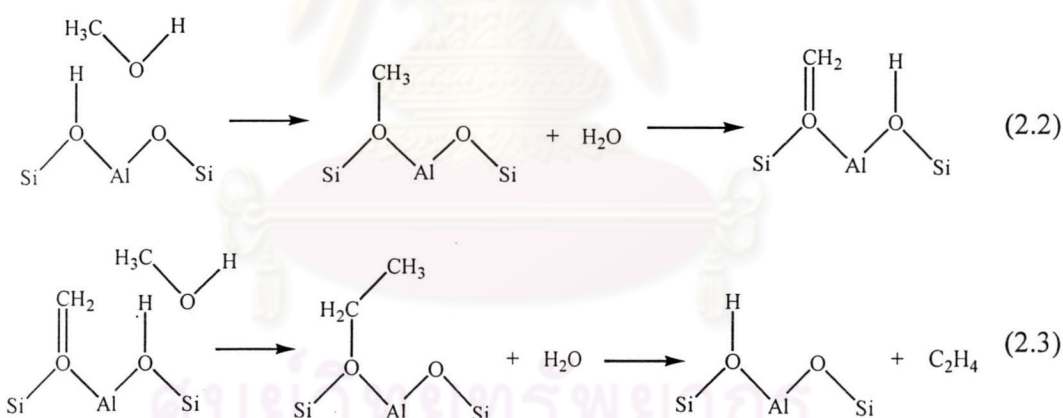
Scheme 2.4 A proposed mechanism for the formation of surface ylide species.

Sánchez del Campo *et al.*[40] supported the oxonium ylide mechanism for methanol transformation into olefins on SAPO-34. The oxonium ions were successively methylized by propagation reaction in solid phase resulting in the formation of ethyloxonium and propyloxonium. The oxonium ions formed were decomposed to give ethylene and propylene, as shown in Scheme 2.5.
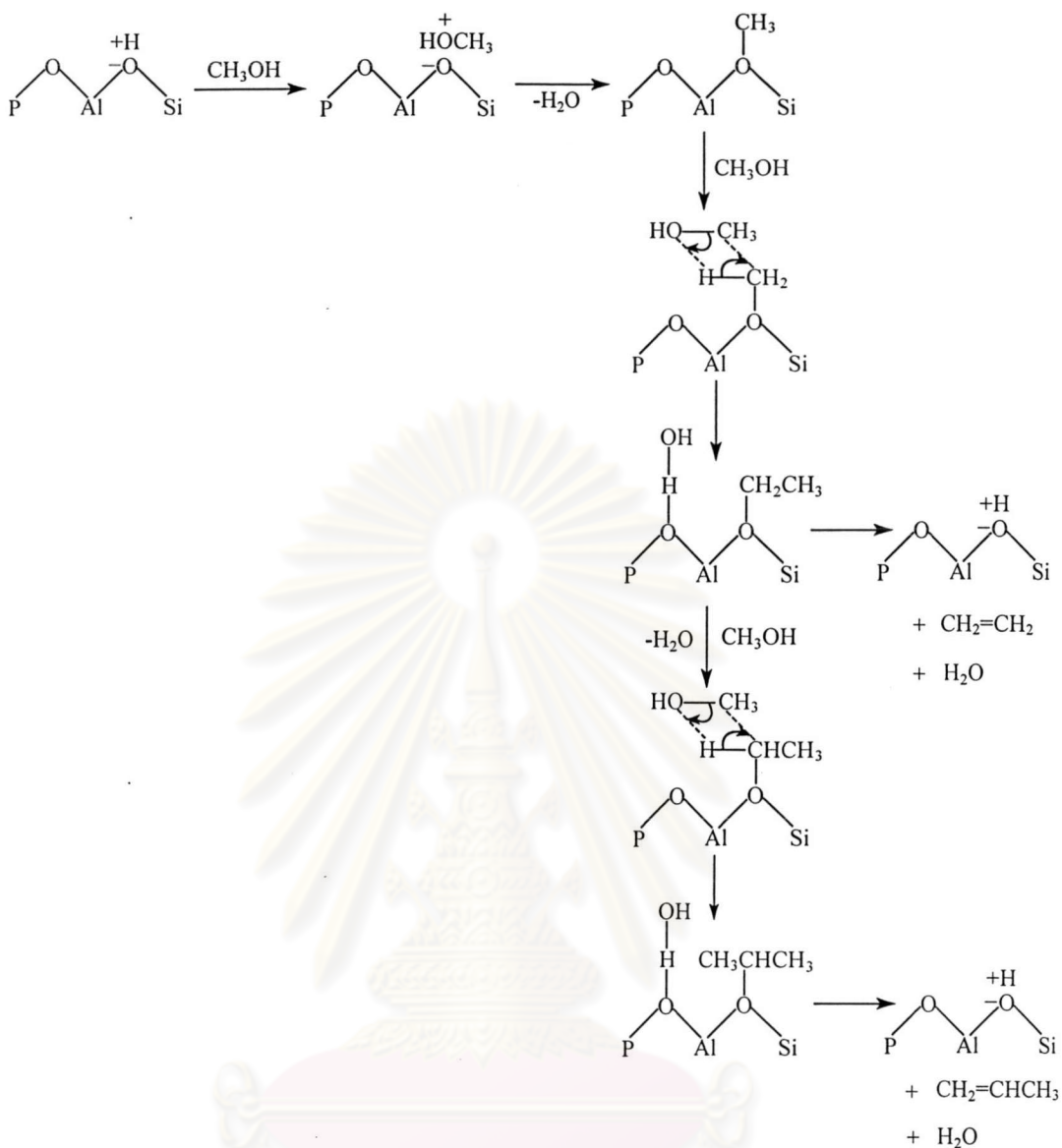
Scheme 2.5 Another proposed mechanism of surface oxonium ions.

b. Carbene mechanism

The carbene mechanism[2] involved the α-elimination of water from methanol followed by either polymerization of the resultant cerbene to olefins or by concurrent sp^3 insertion of carbene into methanol or dimethyl ether. The formation of the carbene by the cooperative action of acid and basic sites in mordenite was suggested by Swabb and Gates and can be summarized in Scheme 2.6.

$$:CH_2 + HO—ZeO + H_2O$$

$$n \ :CH_2 \longrightarrow (CH_2)_n \quad , \quad n = 2, 3, 4,...$$

Scheme 2.6 The carbene formation from methanol adsorbed on the zeolite surface.

Whereas the oxonium ylide mechanism essentially involves the formation of a surface-bound intermediate as the initial reaction step, the carbene mechanism involves only surface associated intermediates. As previous mentioned the surfaced-associated carbene is isoelectronic with the surface-bound methylene oxonium ylide species.

c. Carbenium ion intermediates

While C_3-C_7 olefins apparently result from the direct transformation of dimethyl ether (or methanol), this is not the case for ethylene, even during the initial stages. At high temperatures (400-450°C) and low methanol pressure (10^{-2} bar) the reaction does not favor the secondary transformation of olefin (repeated methylation, oligomerization and cracking of higher olefins) and the size of molecules seems to be over the average pore-size of the zeolite.

Fougerit *et al.*[41] investigated at a contact time which allows a quasicomplete conversion (90%) of the dimethyl ether-water mixture into hydrocarbons. It should be emphasized that C_6-C_7 olefin are mainly transformed by cracking with the formation of the products expected from an acid mechanism (with carbenium ion intermediates), i.e. propylene from hexenes and, to a smaller extent, butylenes/ethylene mixture, and essentially propylene and butylenes from n-heptenes. Propylene, butylenes and

pentenes are mainly transformed through successive oligomerization and cracking steps as shown in Scheme 2.7.

$$2\ C_3^= \rightleftharpoons C_6^= \underset{-\ C_3^=}{\overset{+\ C_3^=}{\rightleftharpoons}} C_9^=$$
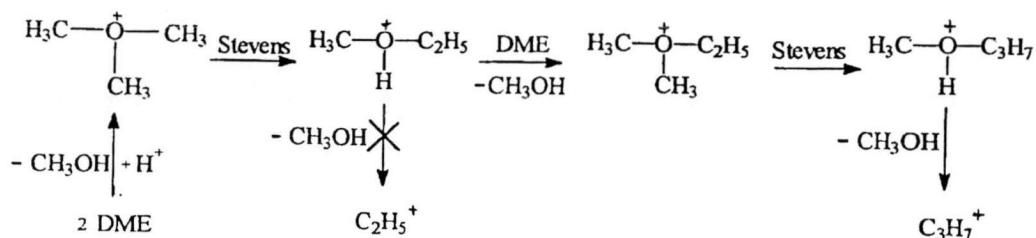
$$C_2^= + C_4^= \qquad C_4^= + C_5^=$$
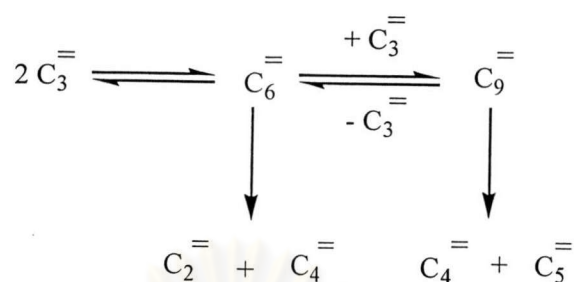
Scheme 2.7 Possible products from the transformation of C_6 olefin.

All the reactions allowing the formation of ethylene require very unstable carbenium ions as intermediates, e.g. the cracking of iso-hexenes resulting from 1-hexene isomerization as shown in Scheme 2.8. This is why the formation of other products that involve more stable intermediates is much more favored.
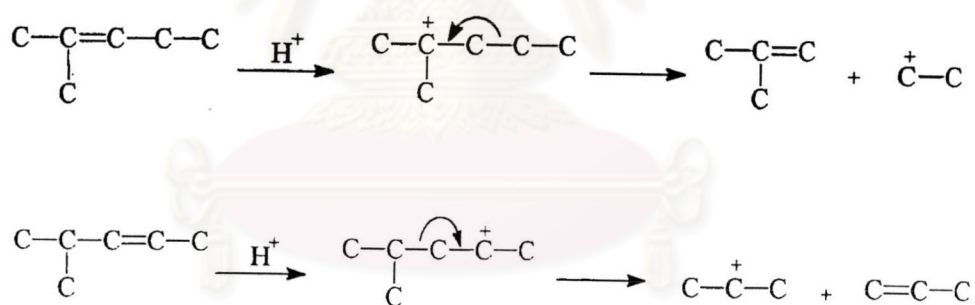
Scheme 2.8 Cracking of *iso*-hexenes to ethylene and other products via carbenium ion intermediates.

It was proposed that the formation of the ethyldimethyloxonium ion, the Stevens rearrangement and the formation of an isopropyl carbenium ion were much faster than the formation of the very unstable ethyl carbenium ion (see Scheme 2.9).

$$H_3C-\overset{+}{\underset{CH_3}{O}}-CH_3 \xrightarrow{\text{Stevens}} H_3C-\overset{+}{\underset{H}{O}}-C_2H_5 \xrightarrow[-CH_3OH]{\text{DME}} H_3C-\overset{+}{\underset{CH_3}{O}}-C_2H_5 \xrightarrow{\text{Stevens}} H_3C-\overset{+}{\underset{H}{O}}-C_3H_7$$

$- CH_3OH \big| + H^+$ $- CH_3OH \big/\!\!\!\!\times$ $- CH_3OH \big|$

2 DME $C_2H_5^+$ $C_3H_7^+$

Scheme 2.9   The formation of the isopropyl carbenium ion via carbenium ion and

Stevens rearrangement.

It should, however, be emphasized that the Stevens rearrangement occurs through ylide intermediates. In the rearrangement of the ethyldimethyloxonium ion, the ylide intermediate $(\overset{-}{C}H_2)\overset{+}{O}(CH_3)CH_2CH_3$ which leads to an unstable propyl carbenium ion, should be favored in comparison to $(CH_3)\overset{+}{O}(CH_3)\overset{-}{C}HCH_3$.

$$H_3C-\underset{+}{O}-\underset{-}{\overset{CH_3}{|}}CH-CH_3$$
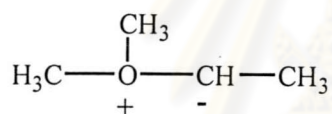
which leads to the isopropyl-carbenium ion, because of the higher acidity of the hydrogens of the methyl group.
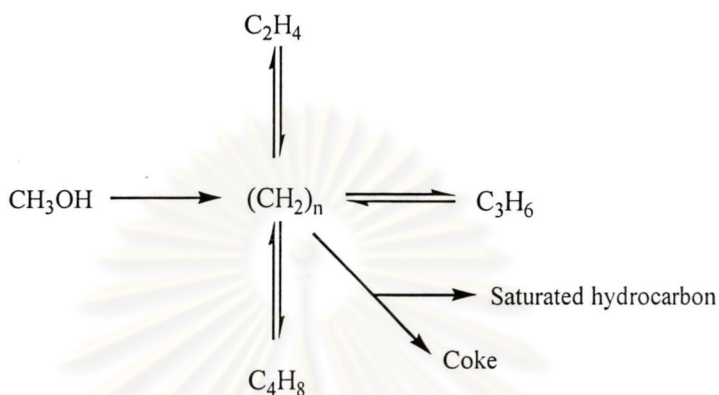
d. Hydrocarbon Chain

The consecutive type mechanism with one carbon from methanol adding during each step, addition of methanol and cracking of olefin intermediates may take place as illustrated in Scheme 2.10.

$$2C_1 \longrightarrow C_2H_4 + H_2O$$

$$C_2H_4 + C_1 \longrightarrow C_3H_6$$

$$C_3H_6 + C_1 \longrightarrow C_4H_8 \ldots$$

Scheme 2.10   The consecutive-type mechanism of the hydrocarbon chain reactions.

A parallel type mechanism, known as "hydrocarbon pool mechanism" was suggested by Dahl et al.,[42-44] who studied the methanol conversion to hydrocarbon using SAPO-34 as catalyst, ^{13}C-labeled methanol as feed and ^{12}C-ethylene made in situ from ethanol (Scheme 2.11).

Scheme 2.11 The parallel-type mechanism of hydrocarbon chain reaction.

The 'hydrocarbon-pool' = $(CH_2)_n$ represents an adsorbate which may have characteristic in common with ordinary coke, and which might easily contain less hydrogen than indicated. It would perhaps be better represented by $(CH_x)_n$ with $0 < x < 2$. Using SAPO-34 in the methanol conversion reaction, the product pattern is thus simpler than the case using ZSM-5, where a much wider range of products was found. Therefore, it might be easier to obtain a picture of the reaction pathway using SAPO-34, and the authors showed that the consecutive mechanism, as far as propylene formation was concerned, did not turn out to be valid. Only a minor part of the propylene molecules might have been formed by addition of methanol to ethylene since this would imply a $^{12}C/^{13}C$ ratio larger than one. In fact, the ratio seemed to be lower, thus the majority of the propylene molecules should be formed directly from methanol.