CHAPTER III
THEORY

3.1 Zeolite

The name "zeolite" comes from the Greek words zeo (to boil) and lithos (stone). The classical definition of a zeolite is a crystalline, porous aluminosilicate. However, some relatively recent discoveries of materials virtually identical to the classical zeolite, but consisting of oxide structures with elements other than silicon and aluminum have stretched the definition. Most researchers now include virtually all types of porous oxide structures that have well-defined pore structures due to a high degree of crystallinity in their definition of a zeolite.

In these crystalline materials we call zeolites, the metal atoms (classically, silicon or aluminum) are surrounded by four oxygen anions to form an approximate tetrahedron consisting of a metal cation at the center and oxygen anions at the four apexes. The tetrahedra metals are called T-atoms for short, and these tetrahedra then stack in beautiful, regular arrays such that channels form. The possible ways for the stacking to occur is virtually limitless, and hundreds of unique structures are known. Graphical depictions of several representative types are given under "Representative Structures".

The zeolitic channels (or pores) are microscopically small, and in fact, have molecular size dimensions such that they are often termed "molecular sieves". The size and shape of the channels have extraordinary effects on the properties of these materials for adsorption processes, and this property leads to their use in separation processes. Molecules can be separated via shape and size effects related to their possible orientation in the pore, or by differences in strength of adsorption.

Since silicon typically exits in a 4+ oxidation state, the silicon-oxygen tetrahedra are electrically neutral. However, in zeolites, aluminum typically exists in

the 3+ oxidation state so that aluminum-oxygen tetrahedra form centers that are electrically deficient one electron. Thus, zeolite frameworks are typically anionic, and charge-compensating cations populate the pores to maintain electrical neutrality. These cations can participate in ion-exchange processes, and this yields some important properties for zeolites. When charge-compensating cations are "soft" cations such as sodium, zeolites are excellent water softeners because they can pick up the "hard" magnesium and calcium cations in water leaving behind the soft cations. When the zeolitic cations are protons, the zeolite becomes a strong solid acid. Such solid acids form the foundations of zeolite catalysis applications including the important fluidized bed cat-cracking refinery process. Other types of reactive metal cations can also populate the pores to form catalytic materials with unique properties. Thus, zeolites are also commonly used in catalytic operations and catalysis which zeolites is often called "shape-selective catalysis".

3.2 Structure of Zeolite
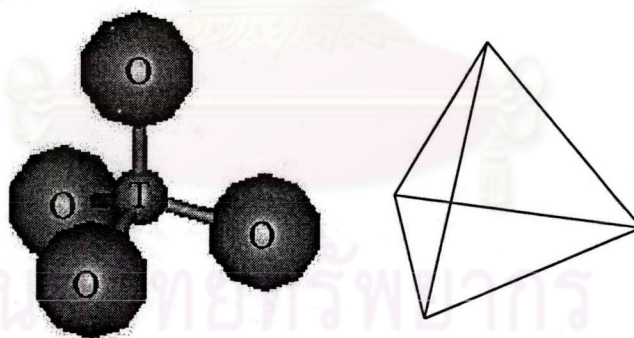
Figure 3.1 TO_4 tetrahedra (T = Si or Al) [Halgeri and Das (1999)].

Zeolites are porous, crystalline aluminosilicate that develop uniform pore structure having minimum channel diameter of 0.3-0.1 nm. This size depends primarily upon the type of zeolite. Zeolites provide high activity and unusual selectivity in a variety of acid-catalyzed reactions. Most of the reactions are caused by the acidic nature of zeolites.

The structure of zeolite consists of a three-dimensional framework of SiO_4 or AlO_4 tetrahedra, each of which contains a silicon or aluminum atom in the center (Figure 3.1) [Halgeri and Das (1999)]. The oxygen atoms are shared between adjoining tetrahedra, which can be present in various ratios and arranged in a variety of way. The framework thus obtained contains 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 [Bekkum et al. (1991)]. 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 are listed in Table 3.1 [Szoztak (1989)]. Both zeolite ZSM-5 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 building units. 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 A can 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.

Zeolite may be represented by the general formula,

$$M_{x/n}[(AlO_2)_x(SiO_2)_y]wH_2O$$
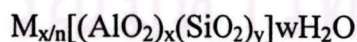
Where the term in brackets is the crystallographic unit cell. The metal cation of valence n is present to produce electrical neutrality since for wash aluminum tetrahedron in the lattice there is an overall charge of -1 [Tanake et al. (1989)]. M is a proton, the zeolites becomes a strong Brønsted acid. As catalyst, zeolite becomes a strong Brønsted acid. As catalysts, zeolite are unique in their ability to discriminate between reactant molecular size and shape [Barthoment (1984)].

Table 3.1 Zeolites and their secondary building units. The nomenclature used is consistent with that presented in Figure 3.2 [Szoztak (1989)]

ZEOLITE	SECONDARY BUILDING UNITS								
	4	6	8	4-4	6-6	8-8	4-1	5-1	4-4=1
Bikitaite								X	
Li-A (BW)	X	X	X						
Analcime	X	X							
Yagawaralite	X		X						
Episitbite								X	
ZSM-5								X	
ZSM-11								X	
Ferrierite								X	
Dachiardite								X	
Brewsterite	X								
Laumonite		X							
Mordenite								X	
Sodalite	X	X							
Henulandite									X
Stibite									X
Natrolite							X		
Thomsonite							X		
Edingtonite							X		
Cancrinite		X							
Zeolite Liquid		X							
Mazzite	X								
Merlinoite	X		X			X			
Philipsite	X		X						
Zeolite Losod		X							
Erionite	X	X							
Paulingite	X								
Offretite		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				
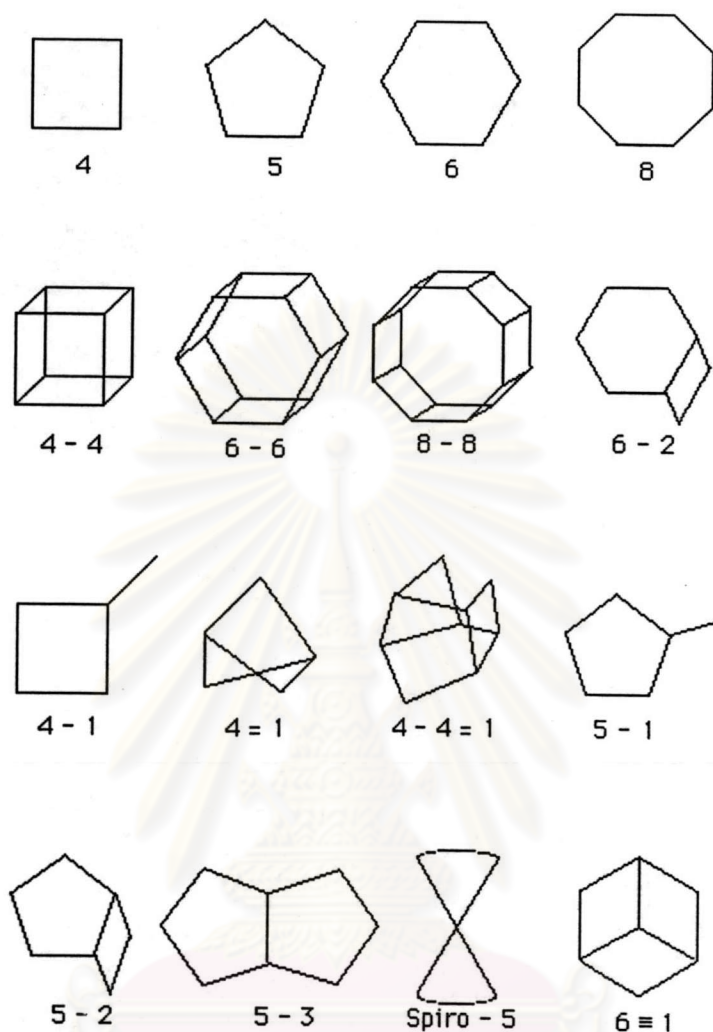
Figure 3.2 Secondary building units (SBU's) found in zeolite structures [Bekkum *et al.* (1991)]

3.3 Category of Zeolite

There are over 40 known natural zeolites and more than 150 synthetic zeolites have been reported [Meier and Olson (1992)]. The number of synthetic zeolites with new structure morphologies grows rapidly with time. Based on the size of their pore opening, zeolites can be roughly divided into five major categories, namely 8-, 10- and 12-member oxygen ring systems, dual pore systems and mesoporous systems [Chen *et al.* (1996)]. 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 in the range 1-3. For materials with an open porous structure, such as amorphorous silica alumina, their constraint indices are normally less than 1. On the contrary, small-pore zeolites normally have a large constraint index; for example, the index for erionite is 38.

A comprehensive bibliography of zeolite structures has been published by the International Zeolite Association [Meier and Olson (1992)]. The structural characteristics of assorted zeolites are summarized in Table 3.2.

Zeolites with 10-membered oxygen rings normally possess a high siliceous framework structure. They are of special interest in industrial applications. In fact, they were the first family of zeolites that were synthesized with organic ammonium salts. With pore openings close to the dimensions of many organic molecules, they are particularly useful in shape selective catalysis. 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 (Figure 3.3) is probably the most useful one.

Although the 10-membered oxygen ring zeolites were found to possess remarkable shape selectivity, catalysis of large molecules may require a zeolite catalyst with a large-pore 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) zeolites can be synthesized using inorganic salts and have been widely used in catalytic cracking since the 1960s. The framework structures of zeolite Beta and ZSM-12 are shown in Figure 3.5 and Figure 3.6, respectively.

Table 3.2 Structural characteristics of selected zeolites [Tsai *et al.* (1991)].

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	3.6×5.1	Intersecting	0.35	1.51	38
10-membered oxygen ring						
ZSM-5	10	5.3×5.6 5.1×5.5	Intersecting	0.29	1.79	8.3
ZSM-11	10	5.3×5.4	Intersecting	0.29	1.79	8.7
ZSM-23	10	4.5×5.2	One-dimensional	-	-	9.1
Dual pore system						
Ferrierite (ZSM-35, FU-9)	10,8	4.2×5.4 3.5×4.8	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	6.5×7.0 2.6×5.7	One-dimensional 12:8 intersecting	0.28	1.70	0.5
Omega (ZSM-4)	12 8	7.4 3.4×5.6	One-dimensional One-dimensional	- -	- -	2.3 0.6
12-membered oxygen ring						
ZSM-12	12	5.5×5.9	One-dimensional	-	-	2.3
Beta	12	7.6×6.4 5.5×5.5	Intersecting	-	-	0.6
Faujasite (X,Y)	12 12	7.4 7.4×6.5	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

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 6.5×7.0 Å which is interconnected to 8-membered oxygen ring channel with opening 2.6×5.7 Å (Figure 3.7). MCM-22, which was found more than 10 years, also possesses a dual

pore system. Unlike Mordenite, MCM-22 consists of 10- and 12-membered oxygen rings (Figure 3.8) and thus shows prominent potential in future applications.

(a) channel pattern   (b) framework projection

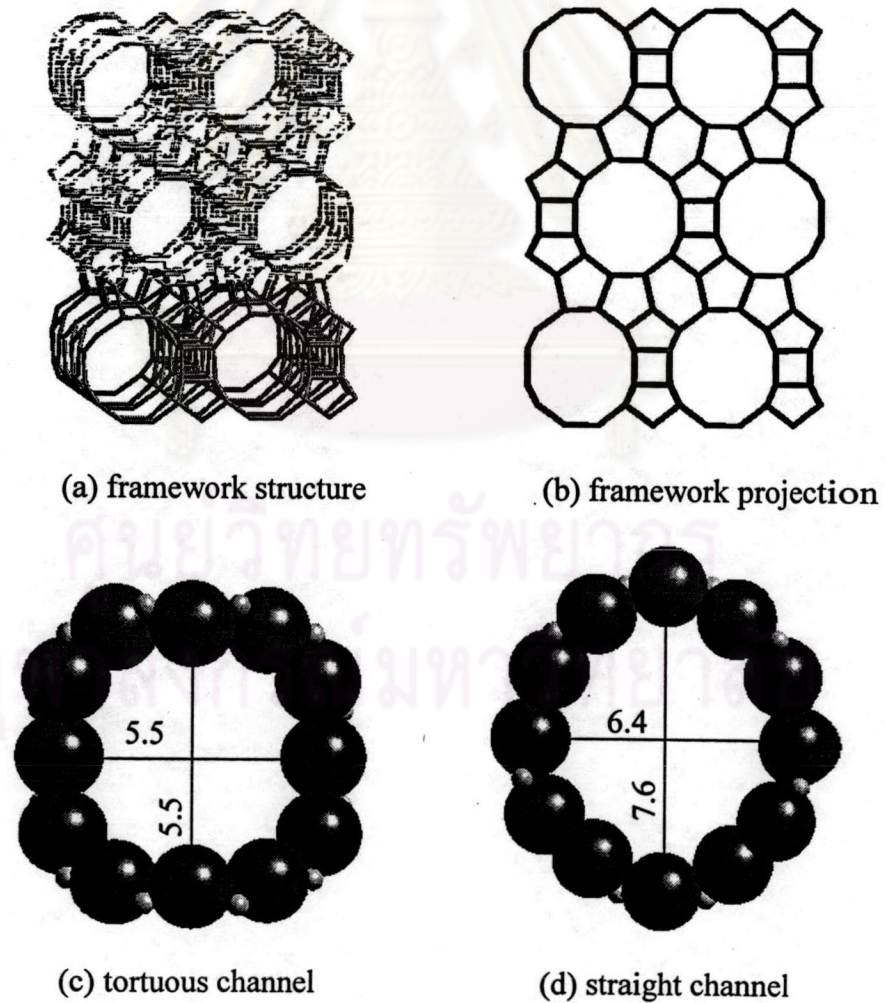(c) tortuous channel   (d) straight channel
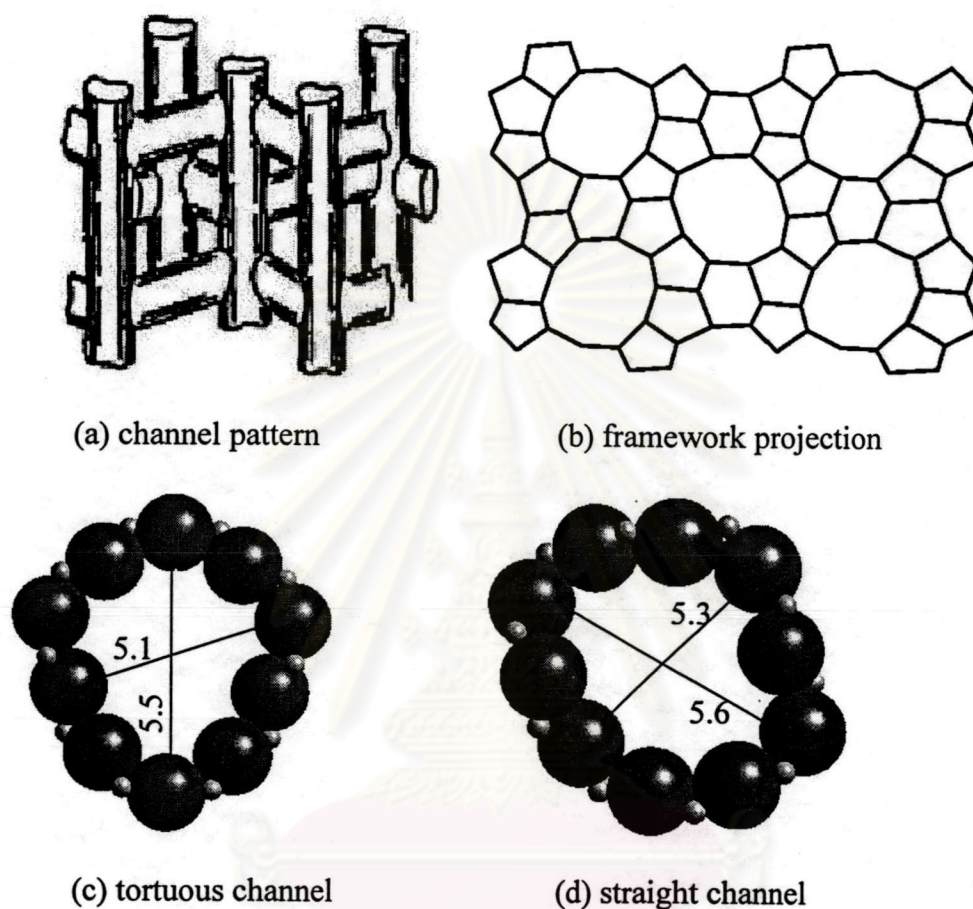
Figure 3.3 Structure of ZSM-5 [Meier and Olson (1992)]

In the past decade, many research efforts in synthetic chemistry have been invested in the discovery of large-pore zeolite with pore diameter greater than 12-membered oxygen rings. The 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 catalysis applications.
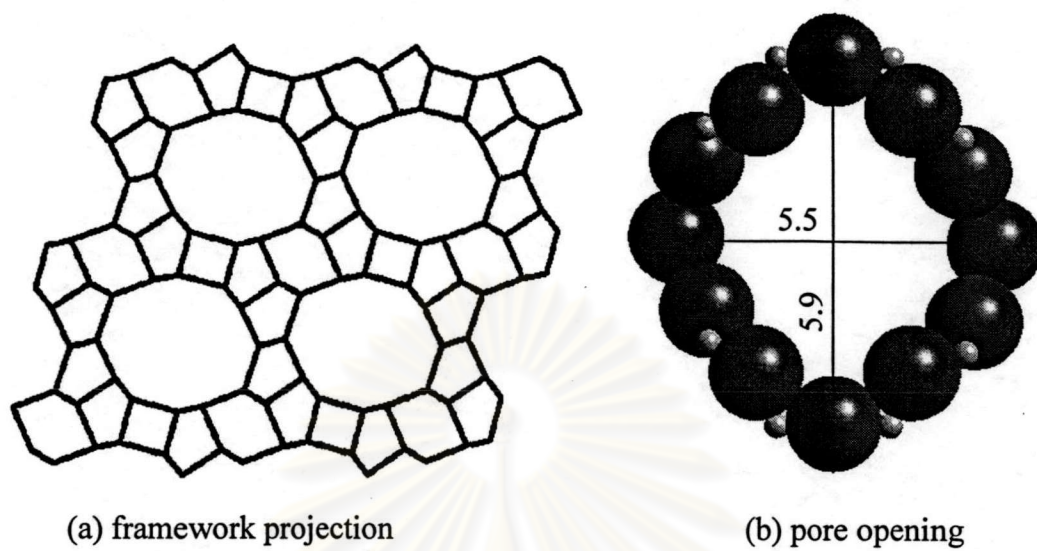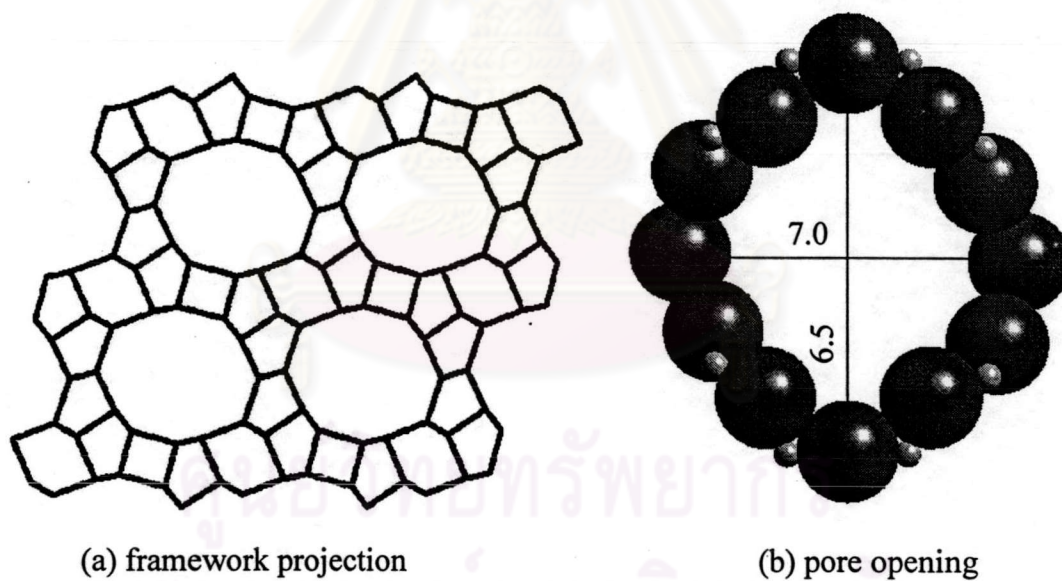
(a) framwork structure

(b) pore opening
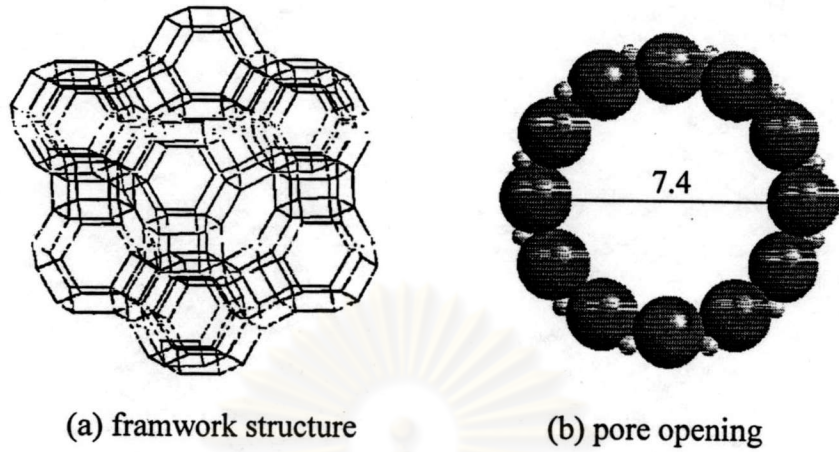
Figure 3.4 Structure of Faujasite [Meier and Olson (1992)]

(a) framework structure

(b) framework projection

(c) tortuous channel

(d) straight channel

Figure 3.5 Structure of Beta zeolite [Meier and Olson (1992)]

(a) framework projection   (b) pore opening

Figure 3.6 Structure of ZSM-12 [Meier and Olson (1992)]

(a) framework projection   (b) pore opening

Figure 3.7 Structure of Mordenite [Meier and Olson (1992)]
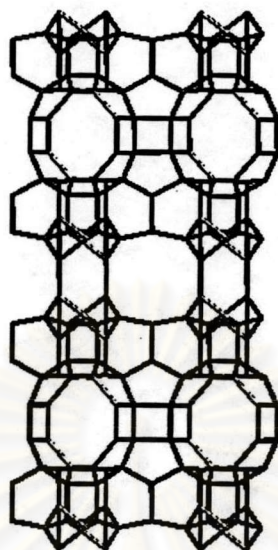
Figure 3.8 Framework structure of MCM-22 [Meier and Olson (1992)]

3.4 Zeolite Active Sites

3.4.1 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 [Barthoment (1984), Ashton *et al.* (1985)].

In general, the increase in Si/Al ratio will increase acidic strength and thermal stability of zeolites [Sano *et al.* (1987)]. Since the numbers of acidic OH groups depend on the number of aluminum 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 increases with increasing 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 [Ashton *et al.* (1985)].

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 [Barthoment (1984)]. A longer distance between hydroxyl groups decreases the probability of dehydroxylation that generates defects on structure of zeolites.

### 3.4.2 Generation of Acid Centers

Protonic acid centers of zeolite are generated in various ways. Figure 3.9 depicts the thermal decomposition of ammonium-exchanged zeolites yielding the hydrogen form [Szoztak (1989)].

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

$$M^{n+} + xH_2O \longrightarrow M(OH)_x^{(n-x)} + xH^+ \qquad (3.1)$$

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 250-450°C to increase with the rise of the reduction temperature [Tanake *et al.* (1989)].

$$Cu^{2+} + H_2 \longrightarrow Cu^0 + 2H^+ \qquad (3.2)$$
$$Ag^+ + \tfrac{1}{2}H_2 \longrightarrow Ag^0 + H^+ \qquad (3.3)$$
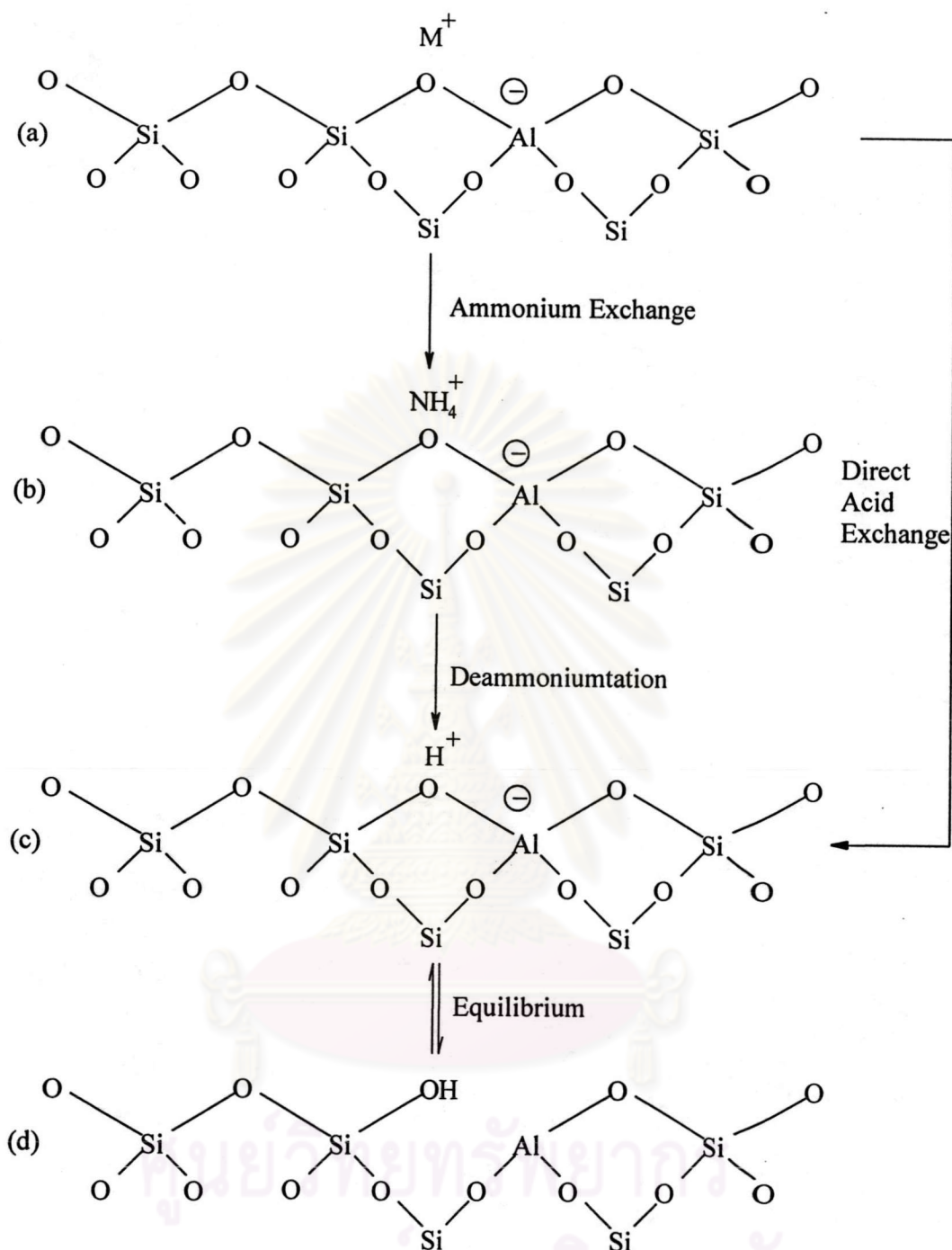
Figure 3.9 Diagram of the surface of a zeolite framework [Szoztak (1989)].

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

    b) Ammonium in exchange produces the NH_4^+ 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 form shown in (d), where there is a silanol group adjacent to tricoodinate aluminum.

The formation of Lewis acidity from Brønsted acid sites is depicted in Figure 3.11 [Tanake *et al.* (1989)]. The dehydration reaction decreases 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 500°C and calcinations at 800 to 900°C produces irreversible dehydroxylation, which causes defection in crystal structure of zeolite.
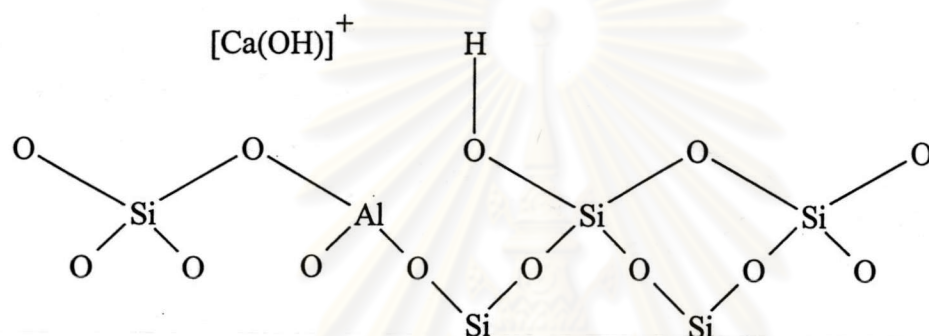

Figure 3.10 Water molecules co-ordinated to polyvalent cation are dissociated by heat treatment yielding Brønsted acidity [Tanake *et al.* (1989)]
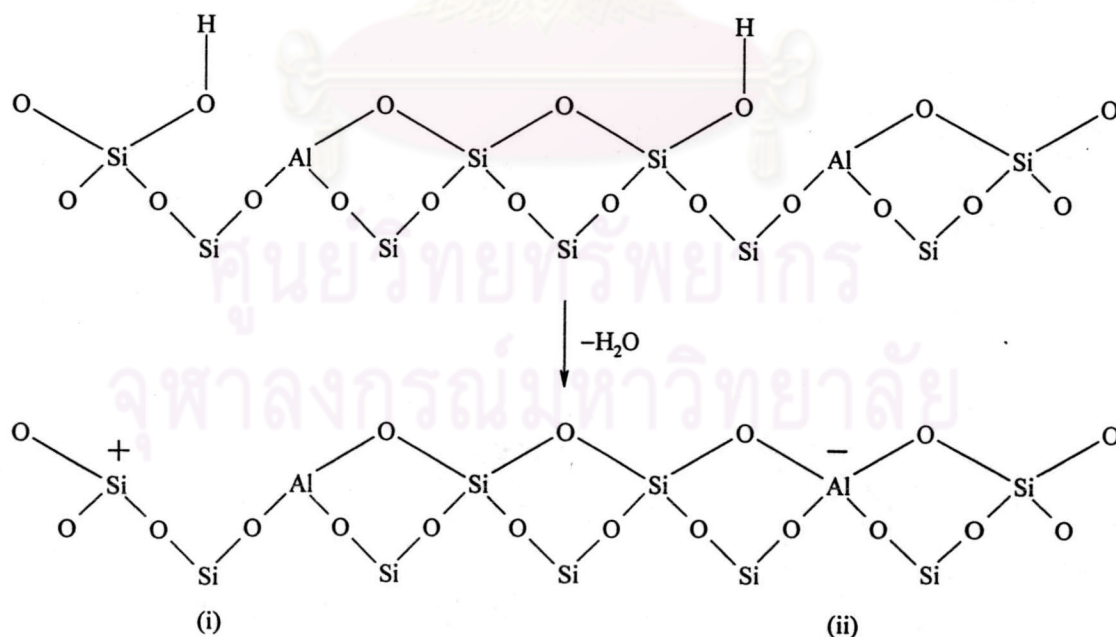

Figure 3.11 Lewis acid site developed by dehydroxylation of Brønsted acid site [Tanake *et al.* (1989)]

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. The extent of dealumination monotonously increases with the partial pressure of steam.
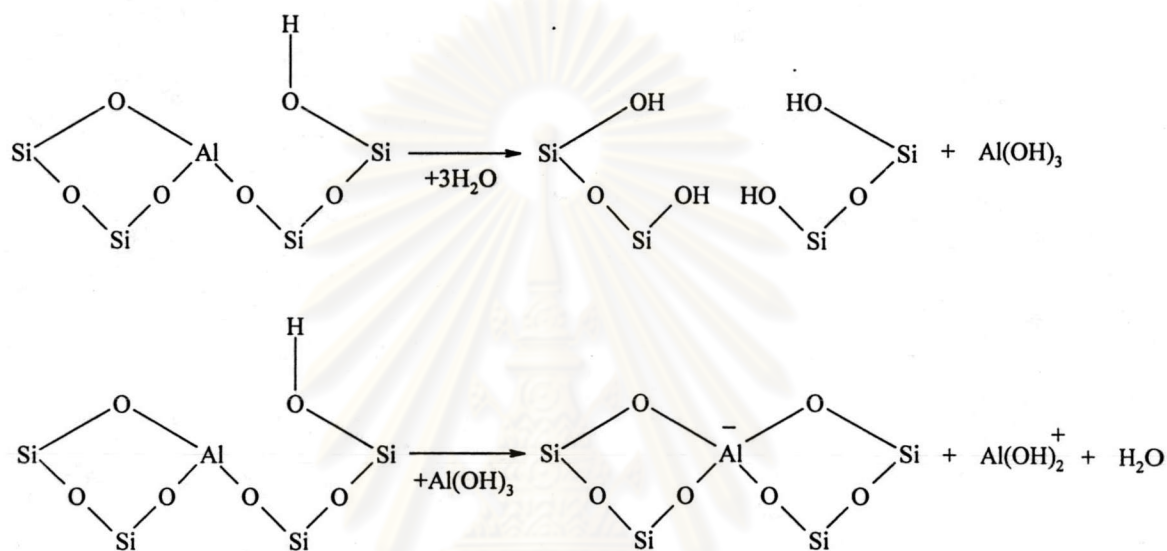
Figure 3.12 Steam dealumination process in zeolite [Tanake *et al.* (1989)]
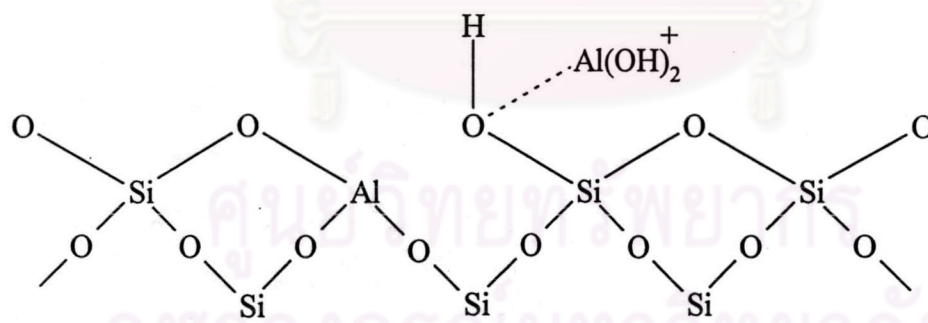
Figure 3.13 The enhancement of the acid strength of OH groups by their interaction with dislodged aluminum species [Tanake *et al.* (1989)]

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 [Tanake *et al.* (1989)]. Partial dealumination might therefore yield a catalyst of higher activity while severe steaming reduces the catalytic activity.

3.4.3 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.

3.5 Shape Selective

Many reactions involving carbonium intermediates are catalyzed by acidic zeolites. With respect to a chemical standpoint the reaction mechanisms are not fundamentally different with zeolites or with any other acidic oxides. What zeolite add is shape selectivity effect. The shape selective characteristics of zeolites influence their catalytic phenomena by three modes; reactants shape selectivity, products shape selectivity and transition states shape selectivity. These types of selectivity are illustrated in Figure 3.14 [Szoztak (1989)].

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 reactions. 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 arising 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.
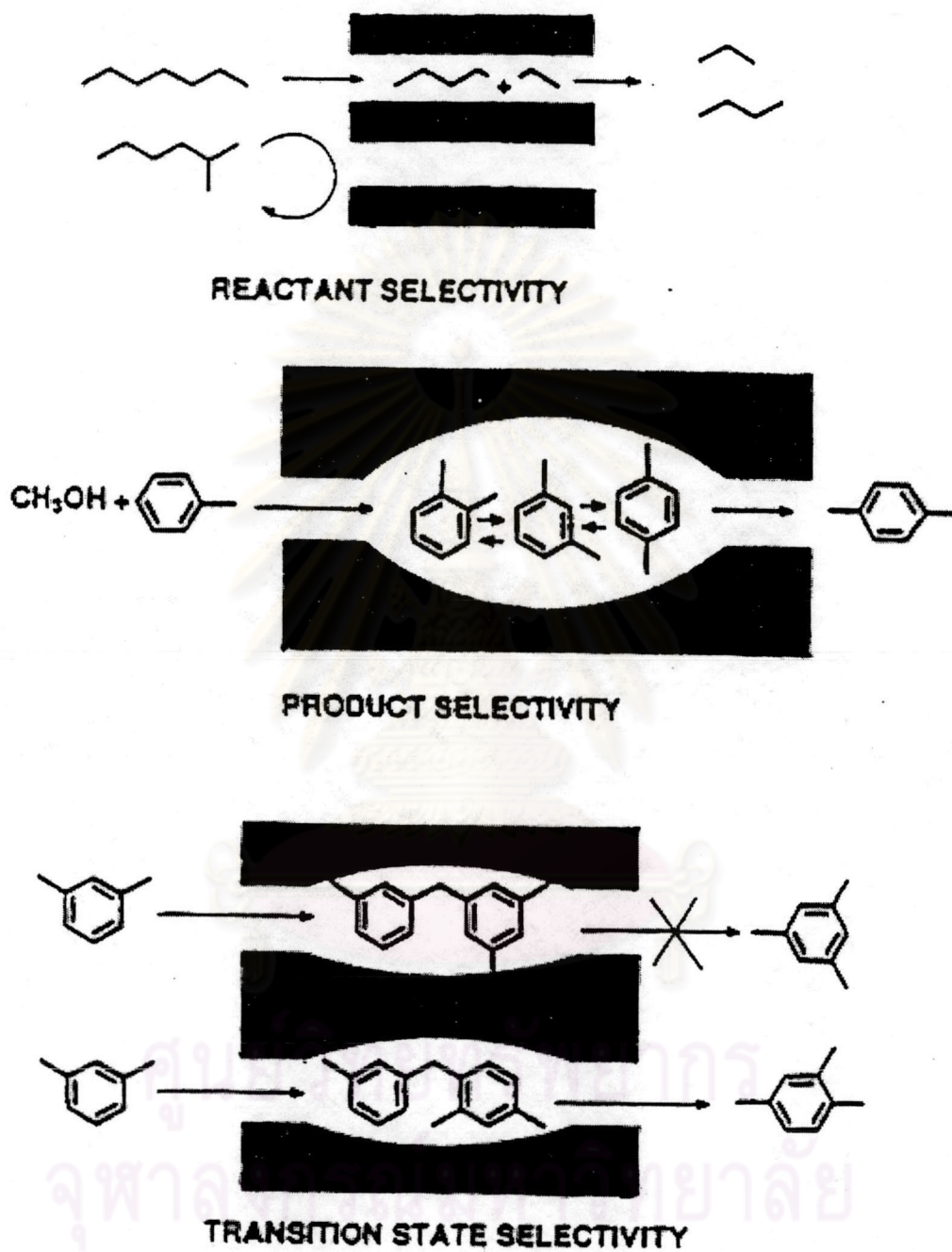
Figure 3.14 Diagram depicting the three type of selectivity [Szoztak (1989)]

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 openings, 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.

3.6 ZSM-5 Zeolite

ZSM-5 zeolite has two types of channel systems of similar size, one with a straight channel of pore opening 5.3×5.6 Å and the other with a tortuous channel of pore opening 5.1×5.5 Å. Those intersecting channels are perpendicular to each other, generating a three-dimensional framework. ZSM-5 zeolites with a wide range of SiO_2/Al_2O_3 ratio can easily be synthesized. High siliceous ZSM-5 zeolites are more hydrophobic and hydrothermally stable compared to 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-burn 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.

3.7 Y Zeolite

The zeolites finding the largest-scale application in catalysis belong to the family of faujasites, including zeolite X and Y [Gates (1992)]. The framework structure of the zeolite Y contains a three-dimensional pore system consisting of supercages of about 13 Å in diameter. These supercages are interlinked through cage windows of about 7.4 Å in diameter. Zeolite Y was discovered by R.M. Milton and coworker between 1949 and 1954. Also in 1959 a zeolite Y-based catalyst was marketed by Union Carbide as an isomerization catalyst. Subsequently, it found applications in many areas of catalysis and molecular sieve, generating interest in an industrial and academic laboratories. As catalyst, zeolite Y exhibits appreciable acid activity with sharp selectivity features not available in the compositional equivalent

amorphous catalysts. In addition, these material can act as supports for numerous catalytically active metals. The porous frameworks of the zeolites enable them to act as molecular sieves i.e., they are used to separate molecular mixtures on the basis of size and shape molecule compounds or for the selective adsorption of gases. These unique properties are utilized in diverse industrial processes such as the purification of water as well as other liquids and gases, chemical separations, catalysis, and decontamination of radioactive wastes [Jiratthitikan (1997)].
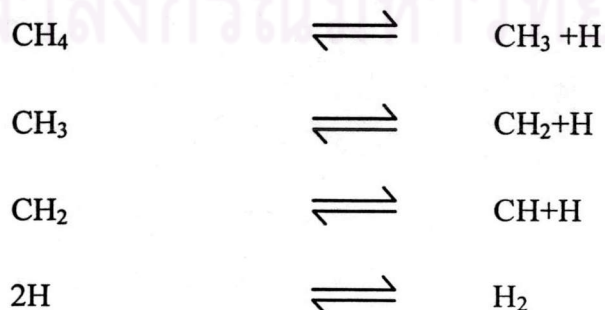
3.8 The dehydrogenation of methane

The dehydrogenation of methane on MoO_3/SiO_2 requires a high temperature. In the first stage of the reaction of MoO_3 proceeds to give CO (CO_2) and H_2O which can be described by the following over all equations:

$$3MoO_3 + CH_4 \rightleftharpoons CO + 2H_2O + 3MoO_2$$

$$4MoO_3 + CH_4 \rightleftharpoons CO_2 + 2H_2O + 4MoO_2$$
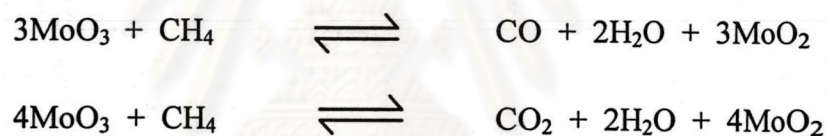
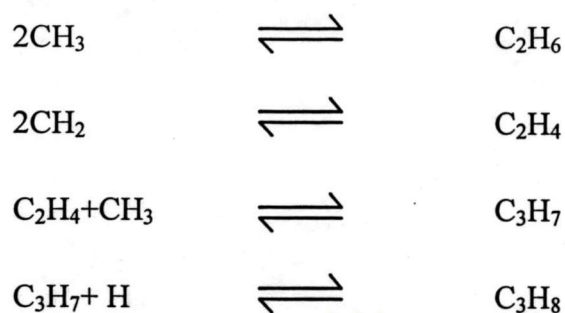This reaction is followed by the dehydrogenation of CH_4 on practically reduced catalyst which could be an oxidative dehydrogenation process,

$$CH_4 + O_{(s)} \rightleftharpoons CH_3 + OH_{(s)}$$

$$2OH_{(s)} \rightleftharpoons H_2O + O_{(s)}$$

or a gradual decomposition of CH_4

$$CH_4 \rightleftharpoons CH_3 + H$$

$$CH_3 \rightleftharpoons CH_2 + H$$

$$CH_2 \rightleftharpoons CH + H$$

$$2H \rightleftharpoons H_2$$

Besides H_2, saturated and unsaturated hydrocarbons are also formed, indicates the couplings of CH_x compounds,

$$2CH_3 \quad \rightleftharpoons \quad C_2H_6$$

$$2CH_2 \quad \rightleftharpoons \quad C_2H_4$$

$$C_2H_4+CH_3 \quad \rightleftharpoons \quad C_3H_7$$

$$C_3H_7+ H \quad \rightleftharpoons \quad C_3H_8$$

These elementary steps have been observed on metal single crystal surfaces. The dehydro-aromatization of methane, thermodynamically, is a more favorable reaction than dehydro-dimerization. The key compound in the formation of benzene is the ethane (formed in the coupling of two CH_3 radicals), which dehydrogenated to ethylene on the catalyst surface. This step is followed by dehydrogenative cyclization and aromatization of ethylene [Solimosi et al. (1995)].