

CHAPTER III

THEORY

3.1 Molecular Sieves for Use in Catalysis

With the recent discoveries of molecular sieves materials containing other elements in addition to, or in lieu of, silicon and aluminum, the casual interchange of the terms "molecular sieve" and "zeolite" must be reconsidered. In 1932 McBain proposed the term "molecular sieve" to describe a class of materials that exhibited selective adsorption properties. He proposed that for a material to be a molecular sieve, it must separate components of a mixture on the basis of molecular size and shape differences. Two classes of molecular sieves were known when McBain put forth his definition: the zeolites and certain microporous charcoals. The list now includes the silicates, the metallosilicates, metalloaluminates, the AlPO_4 's and silico- and metalloaluminophosphates, as well as the zeolites. The different classes of molecular sieve materials are listed in **Figure 3.1**. All are molecular sieves, as their regular framework structures will separate components of a mixture on the basis of size and shape. The difference lies not within the structure of these materials, as many are structurally analogous, but in their elemental composition.

A molecular sieve framework is based on an extensive three-dimensional network of oxygen ions containing generally tetrahedral type sites. In addition to the Si^{+4} and Al^{+3} that compositionally define the zeolite molecular sieves, other

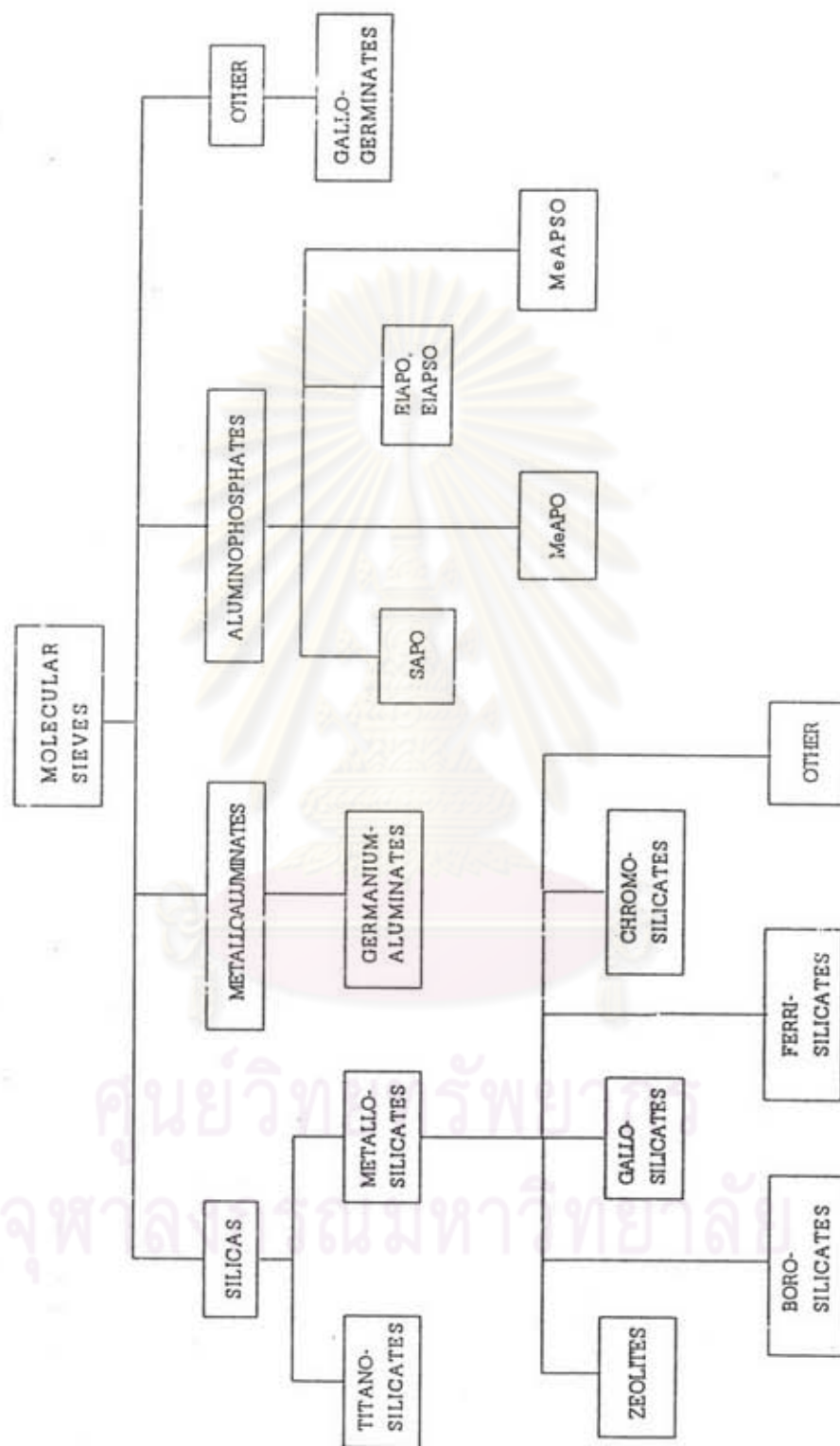


Figure 3.1 Classification of molecular sieve materials [31].

cations also can occupy these sites. These cations need not be isoelectronic with Si^{+4} or Al^{+3} , but must have the ability to occupy framework sites. The zeolite molecular sieves display a net negative framework charge; however, a molecular sieve framework need not display any charge. Molecular sieves containing only Si^{+4} in the tetrahedral sites will have a neutral framework and exhibit a high degree hydrophobicity and no ion exchange capacity. The net charge on the AlPO_4 molecular sieves is also zero, arising from framework AlO_2^- and PO_2^+ units existence in equal amounts in these structures [31].

3.2 Zeolites

The history of zeolites began in 1756 when the Swedish mineralogist Cronstedt discovered the first zeolite mineral, stilbite [32]. He recognized zeolites as a new class of minerals consisting of hydrated aluminosilicates of the alkali and alkaline earths. Because the crystals exhibited intumescence when heated in a blowpipe flame, Cronstedt called the mineral a "zeolite" derived from two Greek words, "zeo" and "lihtos" meaning "to boil" and "a stone".

Zeolites are crystalline aluminosilicate that are constructed from TO_4 tetrahedral (T= Tetrahedral atom, e.g., Si, Al); each apical oxygen atom is shared with an adjacent tetrahedron [33]. Thus, the ratio of O/T is always equal to 2. A SiO_4 unit in framework (structure) is neutral since an oxygen bridges two T atoms and shares electron density with each other (**Figure 3.2**). However, since Al is +3, for every aluminum containing tetrahedron there is a net -1 charge which must be balanced by a cation. The tetrahedra are coordinated such that the zeolites have open framework structure with high

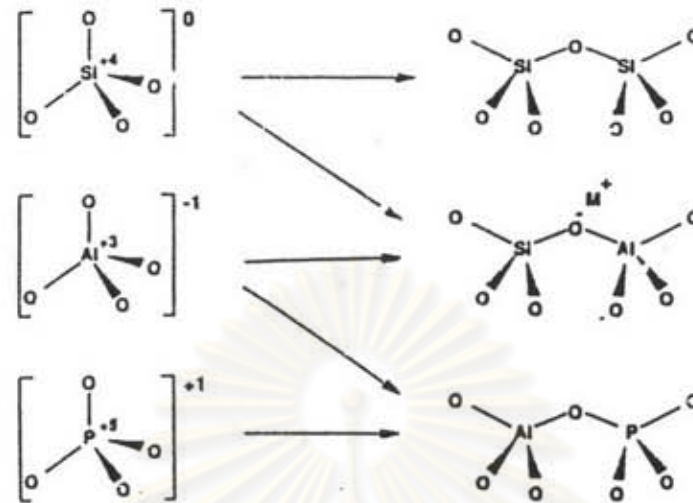
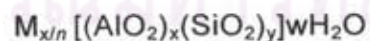


Figure 3.2 Basic building blocks of zeolite-molecular sieves [33]

surface areas. The framework thus obtained contains pores, channels, and cages, or interconnected voids. Access to the cavity is possible through voids of various sizes which are of the size of small molecules. Because of these unique properties, zeolites are able to be shape and size selective in catalytic molecular rearrangements.

Zeolites may be represented by the general formula,



where the term in brackets is the crystallographic unit cell. The metal cation of valence n is present to produce electrical neutrality since for each aluminum tetrahedron in the lattice there is an overall charge of -1 [34]. M is a proton, the

zeolite becomes a strong Brønsted acid, w is the number of water molecules per unit cell, and x, y are the total number of tetrahedra per unitcell [35].

Approximately 70 distinct structures of zeolites and molecular sieves are known [36]. There are natural zeolites, synthetic analogues of natural zeolites, and synthetic zeolite with no natural counterparts. Their pore sizes range from 4 \AA to 13 \AA . Zeolites with pores that are comprised of eight T-atoms (and eight oxygen atoms) are considered small pore zeolites. They have free diameters of $3.0\text{-}4.5 \text{ \AA}$, e.g., zeolite A. Medium pore zeolites have pores formed by ten T-atom rings with $4.5\text{-}6.0 \text{ \AA}$ free diameter, e.g., ZSM-5. Zeolites with twelve or more T-atoms in rings that make up the pores are considered large pores zeolites. They have free diameters of 8.0 \AA or more, e.g., zeolites X and Y[37]. To date, no zeolite (aluminosilicate) exists with pores larger than $\sim 8 \text{ \AA}$ [33].

In type A zeolite, large cavities are connected through apertures of 0.5 nm , determined by eight-membered rings (**Figure 3.3a**). The mordenite pore structure consists of elliptical and noninterconnected channels parallel to the c -axis of the orthorhombic structure. Their openings are limited by twelve-membered rings ($0.6\text{-}0.7 \text{ nm}$) (**Figure 3.3c**) [34].

In silicalite and ZSM-5, the tetrahedra are linked to form the chain-type building block [31]. The chains can be connected to form a layer, as shown in **Figure 3.4** [38]. Rings consisting of five O atoms are evident in this structure; the name pentasil is therefore used to describe it. Also evident in **Figure 3.4** are rings consisting of 10 oxygen atoms; these are important because they provide openings in the structure large enough for passage of

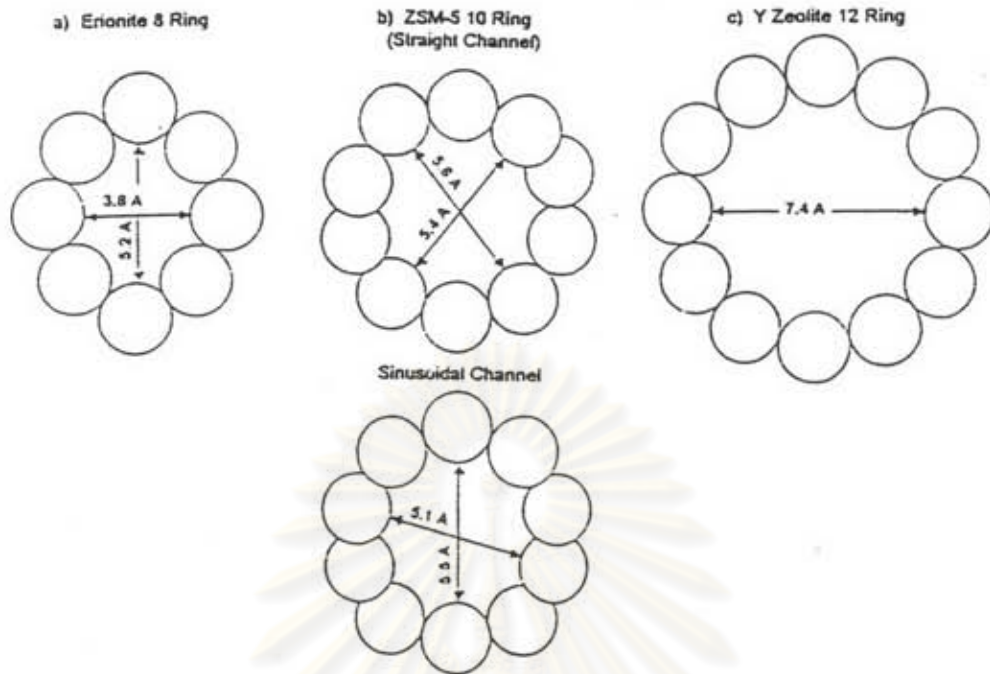


Figure 3.3 Typical zeolite pore geometries [31].

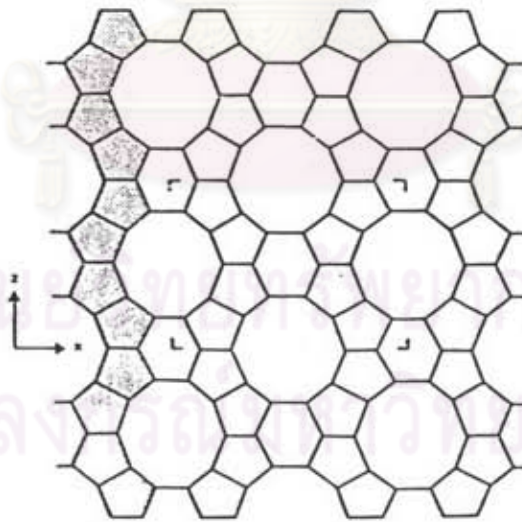


Figure 3.4 Schematic diagram of silicalite layers, formed by linking of the chains through sharing of oxygen in linked SiO_4 tetrahedral [38].

even rather large molecules. The layers can be linked in two ways; the neighboring layers being related either by the operation of a mirror or an inversion. The former pertains to the zeolite ZSM-11, the latter to silicalite or ZSM-5; the intermediate structures constitute the pentasil series.

The three-dimensional structure of silicalite (MFI type catalysts) is represented in **Figure 3.5a** [38]. The ten-membered rings (ca. 0.55 nm in diameter) (**Figure 3.3b**) provide access to a network of intersecting pores within the crystal. The pore structure consists of two intersecting channel systems as shown in **Figure 3.5b**: one straight and the other sinusoidal and perpendicular to the former [34]. Many molecules are small enough to penetrate into this intracrystalline pore structure, where they may be catalytically converted.

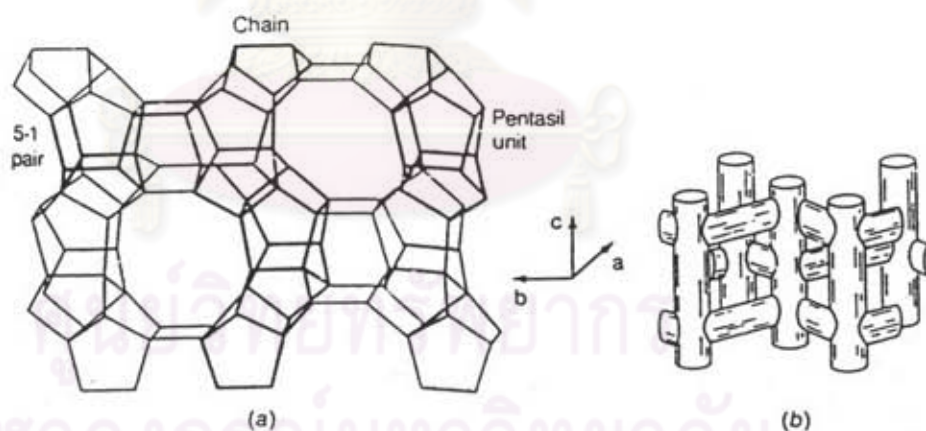


Figure 3.5 Three-dimensional structure of silicate (MFI type) [38].

- (a) Structure formed by stacking of sequence of layers.
- (b) Channel network.

The properties of a zeolite depend on the structure of zeolite, the size of the free channels, the location, charge and size of the cation within the framework, the presence of faults and occluded material, and the ordering of T atoms (framework metal atoms). Therefore, structural information is important in understanding the adsorptive and catalytic properties of zeolites [39].

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 trigonally co-ordinated alumina atom is an electron deficient and can accept an electron pair, therefore behaves as a Lewis acid [40,41].

In general, the increase in Si/Al ratio will increase acidic strength and thermal stability of zeolite [42]. Since the number of acidic OH groups depend on the number of aluminum in zeolite's framework, decrease in Al content is expected to reduce catalytic activity of zeolite.

Based on electrostatic consideration, the charge density at a cation site increases with increasing Si/Al ratio. It was conceived that this phenomenon is related to the reduction of electrostatic interaction between framework sites, and possibly to the difference in the order of aluminum in zeolite crystal [41].

Recently it has been reported that the mean charge on the proton was shifted regularly towards higher values as the Al content decreased [40]. Simultaneously the total number of acidic hydroxyls, governed by the Al atoms,

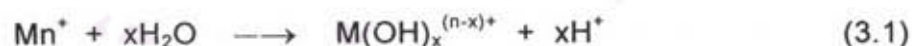
were decreased. This evidence emphasized that the entire acid strength distribution (weak, medium, strong) was shifted towards stronger values. That is, weaker acid sites become stronger with the decrease in Al content.

An improvement in thermal or hydrothermal stability has been ascribed to the lower density of hydroxyls groups which parallel to that of Al content [40]. A longer distance between hydroxyl groups decreases 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 3.6** depicts the thermal decomposition of ammonium exchanged zeolites yielding the hydrogen form [31].

The Brønsted acidity due to water ionization on polyvalent cations, described below, is depicted in **Figure 3.7** [34].



The exchange of monovalent ions by polyvalent cations could improve the catalytic property. Those highly charged cations create very acidic centers by hydrolysis phenomenon.

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 reduction with hydrogen at 250-450 °C and to increase with the rise of the reduction temperature [34].

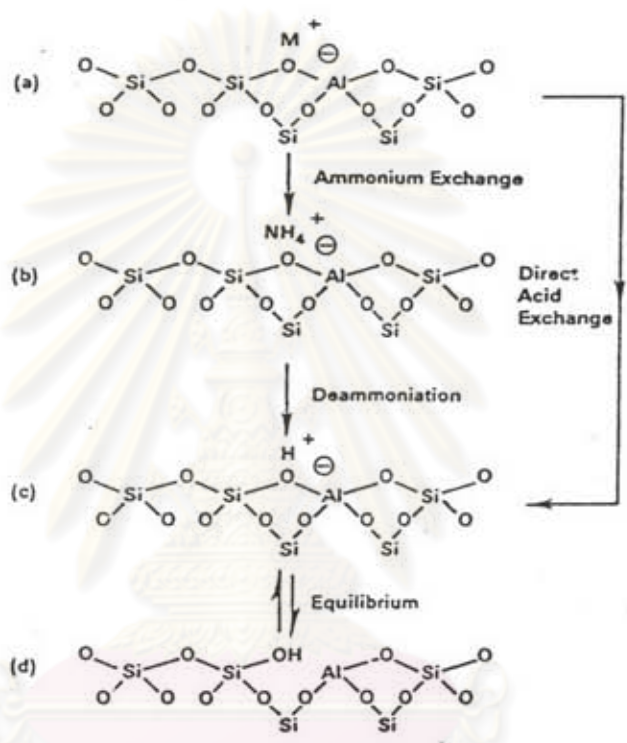
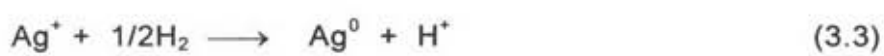
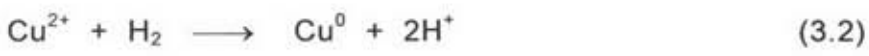


Figure 3.6 Diagram of the surface of a zeolite framework [31].

- a) In the as-synthesized from M⁺ is either an organic cation or an alkalimetal cation.
- b) Ammonium in exchange produces the NH₄⁺ 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 a tricoordinate aluminum.

The formation of Lewis acidity from Brønsted sites is depicted in **Figure 3.8** [34]. 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 calcination at 800 to 900 °C produces irreversible dehydroxylation which causes deflection in crystal structure of zeolite.

Dealumination is believed to occur during dehydroxylation which may result from the steam generation within the sample [34]. The dealumination is indicated by an increase in the surface concentration of aluminum on the crystal. The dealumination process is expressed in **Figure 3.9** [34]. The extent of dealumination monotonously increases with the partial pressure of steam.

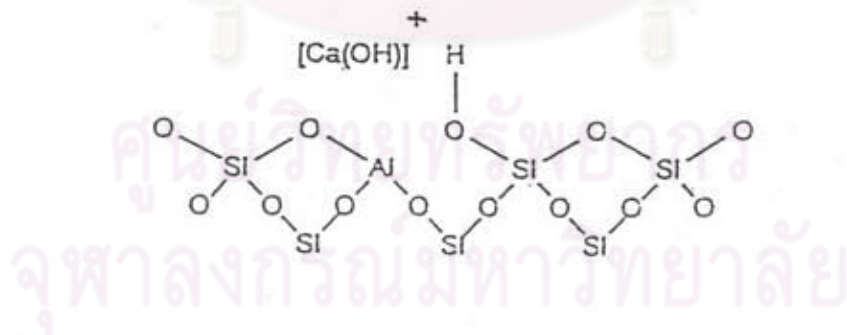


Figure 3.7 Water molecules coordinated to polyvalent cation are dissociated by heat treatment yielding Brønsted acidity [34].

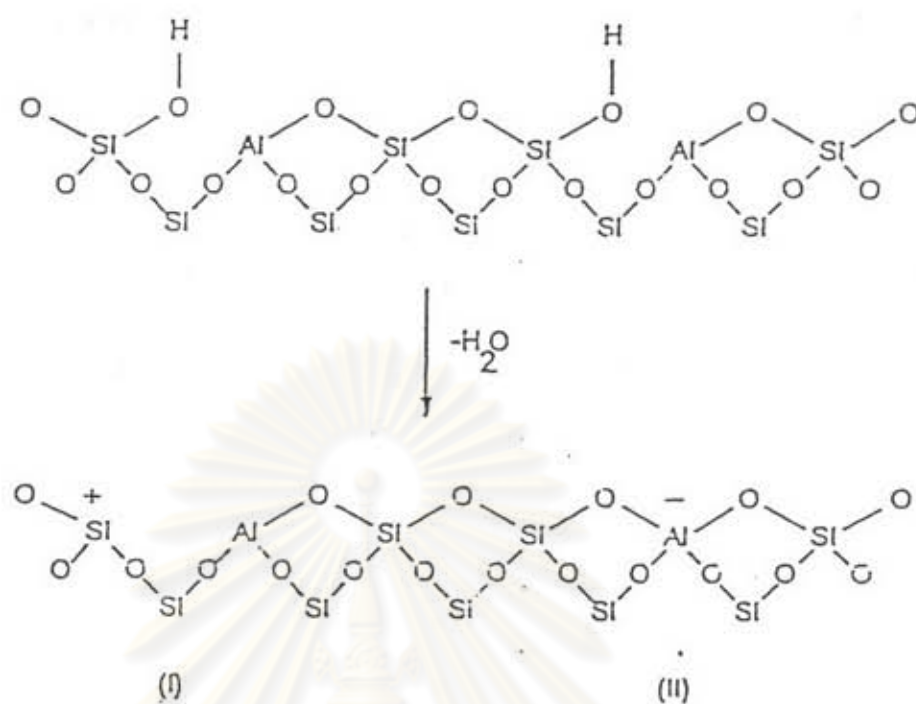


Figure 3.8 Lewis acid site developed by dehydroxylation of Brønsted acid site [34].

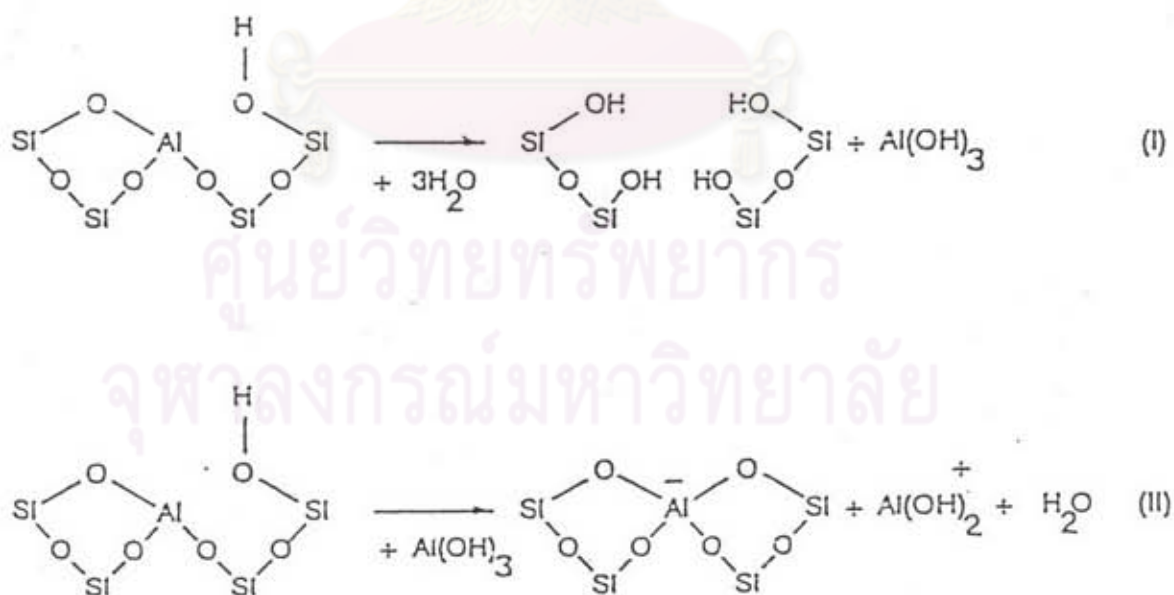


Figure 3.9 Steam dealumination process in zeolite [34].

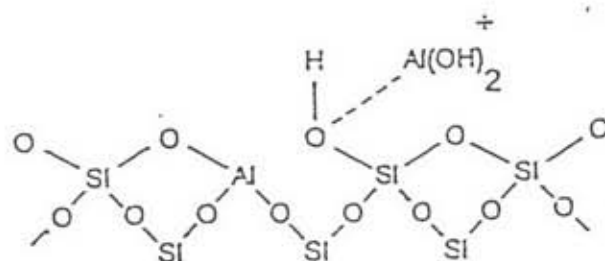


Figure 3.10 The enhancement of the acid strength of OH groups by their interaction with dislodged aluminum species [34].

The enhancement of the acid strength of OH groups is recently proposed to be pertinent to their interaction with those aluminum species sites and are tentatively expressed in **Figure 3.10** [34]. 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) sites in zeolites without any influence from acid sites. The best characterized example of this is that of K-Y which splits n-hexane isomers at 500 °C. The potassium cations have been shown to control the unimolecular cracking (β -scission). Free radical mechanisms also contribute to surface catalytic reactions in these studies.

3.4 Shape Selectivity

There are several types of shape and size selectivity in zeolites. Firstly, reactant or charge selectivity results from the limited diffusibility of some of reactants, which cannot effectively enter and diffuse inside crystal pore structures of the zeolites. A particularly good illustration of this behavior is given by Weisz and co-workers [43]. Zeolites A and X were ion exchanged with calcium salts to create acid sites within the zeolite. These acid sites are formed as the water of hydration around the calcium ions hydrolyzes. When these zeolites are contacted with primary and secondary alcohols in the vapor phase, both alcohols dehydrate on CaX but only the primary one reacts on CaA. Since the secondary alcohol is too large to diffuse through the pores of CaA, it cannot reach the active sites within the CaA crystals. This kind of selectivity is called reactant shape selectivity and is illustrated in **Figure 3.11(a)**.

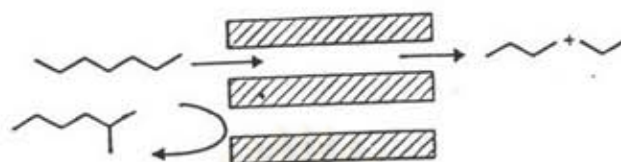
Product shape selectivity occurs when reaction products of different sizes are formed within the interior of the zeolite crystals and some of the products formed are too bulky to diffuse out [44]. The products which cannot escape from the cavities may undergo secondary reactions to smaller molecules or may deactivate the catalyst by blocking pores. A classic example of this type of selectivity is the monomolecular isomerization reactions of alkylaromatics as depicted in **Figure 3.11(b)**. The diffusion coefficient for para-xylene in ZSM-5 is approximately a thousand times that of either ortho or meta-xylene. Hence, essentially pure para-xylene is observed leaving the zeolite. Direct evidence for this type of shape selectivity has been reported by

Anderson and Klinowski [45] for the catalytic conversion of methanol to hydrocarbons in ZSM-5. During the reaction, methanol is dehydrated to dimethyl ether (DME). The equilibrium mixture between methanol and DME reacts to form olefins, aliphatics and aromatics. By using in situ magic angle spinning NMR, 29 different organic species were identified in the adsorbed phase; however not all of these were observed with gas chromatography. For example, the tetramethylbenzenes that are formed in the pores of ZSM-5 do not diffuse out from the zeolites to be observed with gas chromatography.

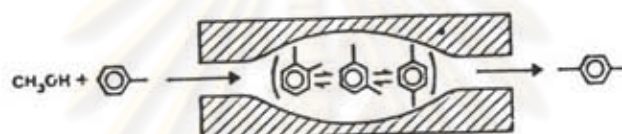
Another type of shape selectivity is transition-state shape selectivity. For this type of selectivity, certain types of transition-state intermediates are too large to be accommodated within the pores/cavities of the zeolites. However, neither the reactants or the products are restricted from diffusing through the pores of zeolites. A good example of this type of selectivity is the transalkylation of dialkylbenzenes. In this reaction, an alkyl group is transferred from one molecule to another through a diphenylmethane transition state. For meta-xylene, this reaction will produce 1,3,5- as well as 1,2,4-trialkylbenzene. However, the transition state for the reaction that yields 1,3,5-trialkylbenzene is too large to be accommodated within the pores of mordenite. Consequently, only 1,2,4-trialkylbenzene is selectively formed inside the zeolite as illustrated in **Figure 3.11(c)**.

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

a) Reactant selectivity



b) Product selectivity



c) Transient state selectivity

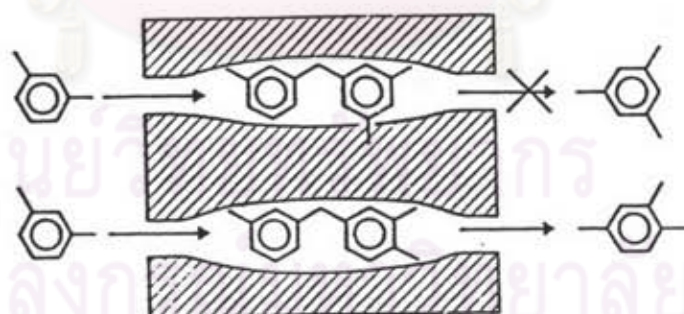


Figure 3.11 Schematic representation of the types of shape selectivity exhibited by zeolites [39].

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. Correlation between pore size of zeolites and kinetic diameter of some molecules are depicted in **Figure 3.12** [47].

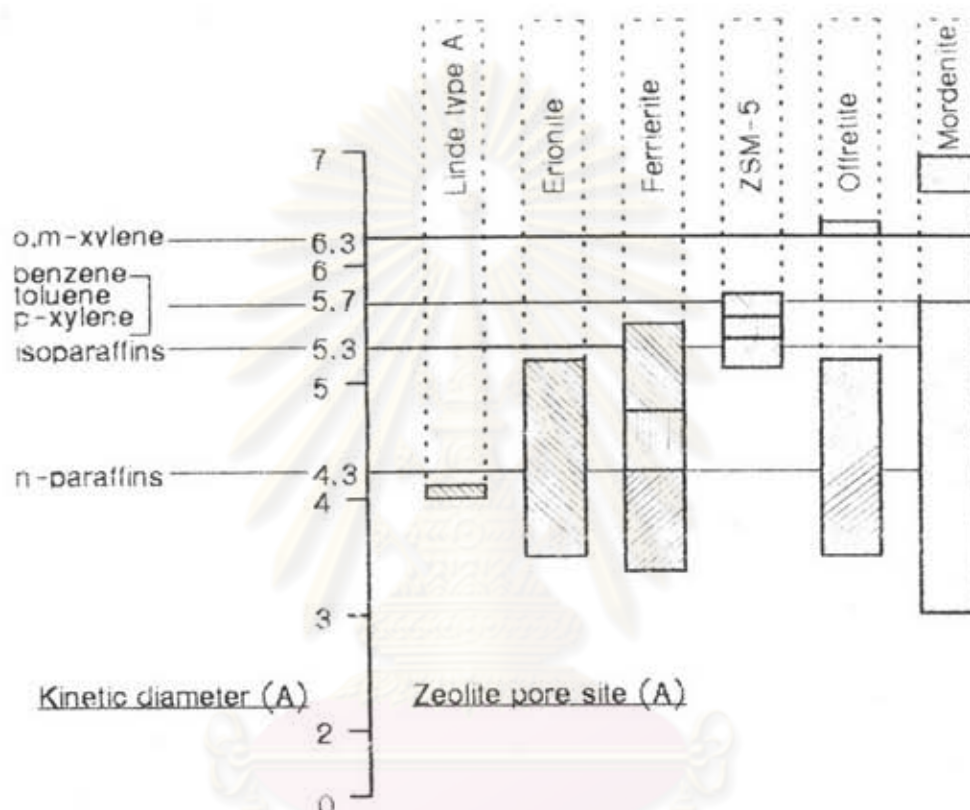


Figure 3.12 Correlation between pore size(s) of various zeolites and kinetic diameter of some molecules [47].

Table 3.1 [36] presents values of selected critical molecular diameters and **Table 3.2** [31] presents value of the effective pore size of various zeolites correlation between pore size of zeolites and kinetic diameter of some molecules are depicted in **Figure 3.12** [47]

Table 3.1 Kinetic diameters of various molecules based on the Lenard-Jones relationship [46].

	KINETIC DIAMETER (ANGSTROMS)
He	2.6
H ₂	2.89
O ₂	3.46
N ₂	3.64
NO	3.17
CO	3.76
CO ₂	3.3
H ₂ O	2.65
NH ₃	2.6
CH ₄	3.8
C ₂ H ₂	3.3
C ₂ H ₄	3.9
C ₃ H ₈	4.3
n-C ₄ H ₁₀	4.3
Cyclopropane	4.23
i-C ₄ H ₁₀	5.0
SF ₆	5.5
Neopentane	6.2
(C ₄ F ₉) ₃ N	10.2
Benzene	5.85
Cyclohexane	6.0

Table 3.2 Shape of the pore mouth opening of known zeolite structures. The dimension are based on two parameters, the T atom forming the channel opening (8, 10, 12 rings) and the crystallographic free diameters of the channels. The channels are parallel to the crystallographic axis shown in brackets (e.g. $\langle 100 \rangle$) [31].

STRUCTURE	8-MEMBER RING	10-MEMBER RING	12-MEMBER RING
Bikitaite	$3.2 \times 4.9[001]$		
Brewsterite	$2.3 \times 5.0[100]$ $2.7 \times 4.1[001]$		
Cancrinite			$6.2[001]$
Chabazite	$3.6 \times 3.7[001]$		
Dachiardite	$3.6 \times 4.8[001]$	$3.7 \times 6.7[010]$	
TMA-E	$3.7 \times 4.8[001]$		
Edingtonite	$3.5 \times 3.9[110]$		
Epistilbite	$3.7 \times 4.4[001]$	$3.2 \times 5.3[100]$	
Erionite	$3.6 \times 5.2[001]$		
Faujasite			$7.4 \langle 111 \rangle$
Ferrierite	$3.4 \times 4.8[010]$	$4.3 \times 5.5[001]$	
Gismondine	$3.1 \times 4.4[100]$ $2.8 \times 4.9[010]$		
Gmelinite	$3.6 \times 3.9[001]$		$7.0[001]$
Heulandite	$4.0 \times 5.5[100]$ $4.1 \times 4.7[001]$	$4.4 \times 7.2[001]$	
ZK-5	$3.9 \langle 100 \rangle$		
Laumontite		$4.0 \times 5.6[100]$	
Levyne	$3.3 \times 5.3[001]$		
Type A	$4.1 \langle 100 \rangle$		
Type L			$7.1[001]$
Mazzite			$7.4[001]$
ZSM-11		$5.1 \times 5.5[100]$	
Merlinoite	$3.1 \times 3.5[100]$ $3.5 \times 3.5[010]$ $3.4 \times 5.1[001]$ $3.3 \times 3.3[001]$		
ZSM-5		$5.4 \times 5.6[010]$ $5.1 \times 5.5[100]$	
Mordenite	$2.9 \times 5.7[010]$		$6.7 \times 7.0[001]$
Natrolite	$2.6 \times 3.9 \langle 101 \rangle$		
Offretite	$3.6 \times 5.2[001]$		$6.4[001]$
Paulingite	$3.9 \langle 100 \rangle$		
Phillipsite	$4.2 \times 4.4[100]$ $2.8 \times 4.8[010]$ $3.3[001]$		

3.5 Acidity of Metallosilicate

The synthesis of zeolites containing various elements such as B, P, or Ge has been carried out for a long time. Since the discovery of ZSM-5 (aluminosilicate) and silicalite, many attempts have been made to synthesize the metallosilicate with the ZSM-5 structure. The isomorphous substitution of aluminum with other elements greatly modifies the acidic properties of the silicate. The elements introduced include, Be, B, Ti, Cr, Fe, Zn, Ga, and V. These elements were usually introduced by adding metal salts as one of the starting materials for the synthesis of the metallosilicate. It is also known that boron can be directly introduced by reacting ZSM-5 with boron trichloride. Metallosilicate with a ZSM-5 structure having metal M as a component will be denoted [M]-ZSM-5, hereafter. Silicate II (the framework topology of which is structurally identical to that of ZSM-11) can be transformed into gallosilicate with its reaction with NaGaO_2 in an aqueous solution.

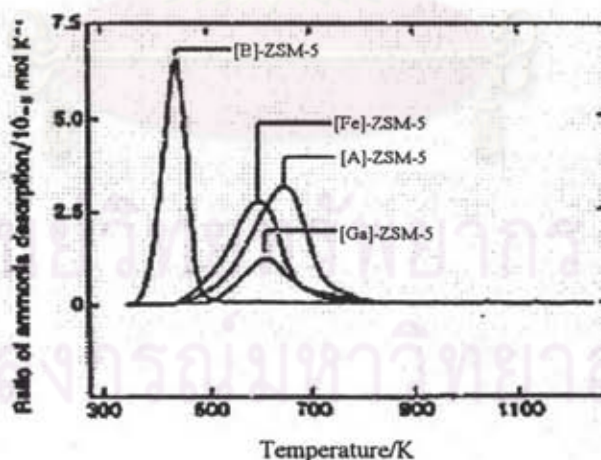
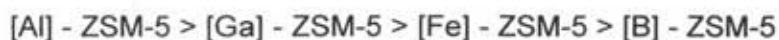


Figure 3.13 Temperature programmed desorption of ammonia from metallosilicate (Reported with permission by C.T - W. Chu, C.D. Chang, *J. Phys. Chem.*, 1571 (1985)) [34].

Figure 3.13 [34] shows the TPD spectrum of ammonia adsorbed on various metallosilicate. The acid strength of metallosilicate changes in decreasing order as follows:



The fact that the acid strength of [B]-ZSM-5 is much weaker than that of [Al]-ZSM-5 has been reported by several authors.

Table 3.3 Product distribution of the conversion of 1-butene over over H-ZSM-5, H-[B]-ZSM-5 and Zn-[B]-5 [34].

Catalyst	H-[Al]-ZSM-5	H-[B]-ZSM-5	Zn-[B]-ZSM-5
conversion/%	77.3	71.7	81.2
Products/% ¹¹			
C ₁ -C ₄ alkanes	41.3	5.1	6.3
C ₂ H ₄ +C ₃ H ₆	14.6	38.3	21.1
C ₄ H ₈ ¹²	6.2	28.3	27.7
C ₅ ⁺	2.4	25.3	7.0
aromatics	37.0	3.0	38.0

Reaction conditions, 773 K, W/F=5.3 g h mol⁻¹

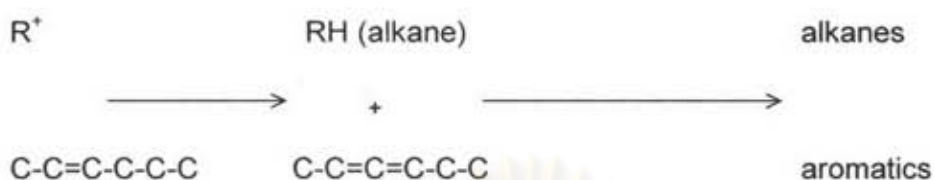
1-butene=23.0 kPa

¹¹ carbon-number basis, ¹² including 1-butene

Weaker acid strength of [B]-ZSM-5 is confirmed also by catalytic reactions.

Table 3.3 [34] shows the product distribution of 1-butene reaction over [B]-ZSM-5 and [Al]-ZSM-5 at 773 K. It is clear that there is a great difference in the product distribution of aromatic hydrocarbons, while over [B]-ZSM-5, lower alkenes are the main products.

This indicates that the hydride transfer reactions from alkenes to carbonium ion does not proceed over [B]-ZSM-5.



For the same reasons, alkenes are the main products in the conversion of methanol over [B]-ZSM-5, while [Al]-ZSM-5 is a unique catalyst for gasoline production.

The yield of aromatic hydrocarbons greatly increases by introducing zinc cations into [B]-ZSM-5 (Table 3.3). In this case, however, the yield of alkanes remains low. This is because the aromatics are formed by the direct dehydrogenation of olefins by the action of zinc species. As exemplified by this case, it is possible to achieve catalysis by metal cations at the same time suppressing catalysis by acid.

The acid strength of [Fe]-ZSM-5 can be inferred to be weak from the very low yield of alkanes and aromatics in the conversion of methanol to olefins. Holderich reported that ketone can be isomerized to aldehyde in a high selectivity over [B]-ZSM-5. ZSM-5 gave only low selectivity.



Since the acidic strength of [B]-ZSM-5 is weak, the role of the trace amount of aluminum impurity may not be negligible in their catalysts. Chu *et al.* examined the catalytic activities of [B]-ZSM-5 containing varying amounts of framework B for a number of acid-catalyzed reactions and concluded that the catalytic activity was due, if not entirely, to trace amounts (80-580 ppm) of framework aluminium [34].

3.6 C₁-C₄ Gases Conversion on Zeolites.

The seek for cheaper feedstocks has made the researchers and industrialists to look the possibilities of C₁-C₄ alkanes. Much work is being done on the conversion of methane to methanol, ethane and ethylene; of ethane to vinyl chloride, and propane to acrylonitrile. Butane has been already successfully oxidized to maleic anhydride. Zeolites can also contribute to upgrade C₁-C₄ paraffins through the reactions presented in **Figure 3.14** [10].

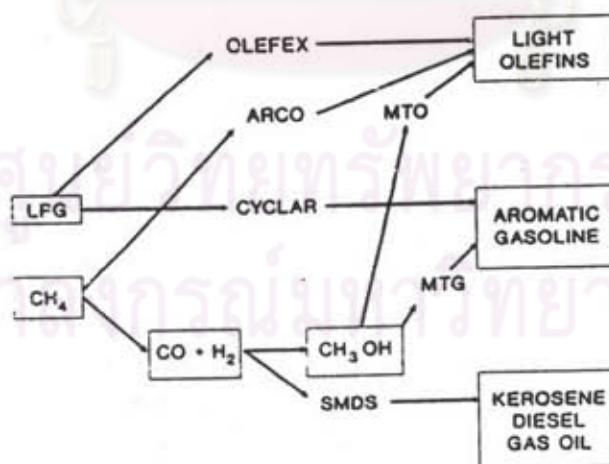


Figure 3.14 Upgrading C₁ - C₄ paraffins.

Propane and butane are transformed on the corresponding olefin using a catalyst comprising alumina-chromia on supported and promoted platinum or tin. C_1 - C_4 olefins can also be obtained from methanol on ZSM-5 zeolites. Methanol in turn could be obtained from synthesis gas produced from methane, or in the future may be produced directly from methane. When olefins are produced they can easily be used for petrochemicals or reacted on zeolites to produce aromatics, fuels, or fine chemicals and commodity products.

When methane or coal is used to produce synthesis gas, zeolites offer an alternative to classical Fisher-Tropsch catalysts. Indeed, when ZSM-5 or SAPO-11 is mixed with methanol synthesis catalysts, hydrocarbons are produced in a single step directly from the synthesis gas. The boiling range of the hydrocarbons produced can be narrowed and gasoline high in aromatics is produced. The final product distribution depends on zeolite Si/Al ratio, the incorporation of the reducing catalyst component on the zeolite, and the reaction temperature. Without the zeolite component catalyst, the liquid products are composed mainly by waxy normal olefins and paraffins.

One of the limitations using this multifunctional catalysts arises when the process is directed to the obtention of C_5^+ . **Figure 3.15**, taken from Huang and Haag shows the uncoupling between the temperature needed for reduction of CO, and the temperature at which the zeolite becomes effective. It is clear that a Fisher-Tropsch catalyst active at temperatures above 260 °C and producing low C_4 - gases at this reaction temperature, is needed to adequately combine with medium pore zeotypes to convert, in a single stage, synthesis gas into gasoline. The temperature limitation can be overcome by using a two stage slurry Fisher-Tropsch-ZSM-5 process.

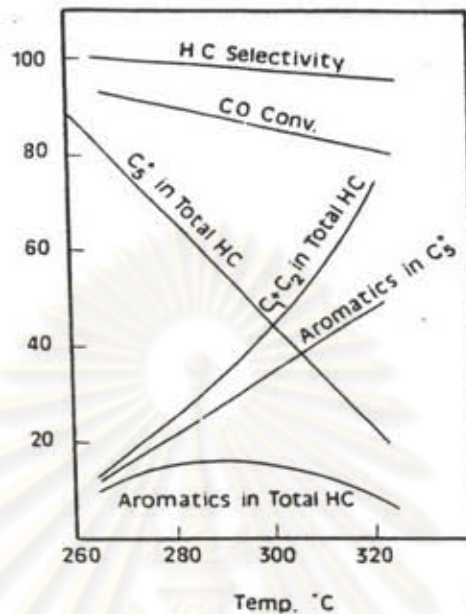


Figure 3.15 Effect of temperature on synthesis gas conversion on RuO₂/ZSM-5 [10].

LPG can be directly converted to aromatics by means of the cyclar process which uses a catalyst composed by Gallium on a ZSM-5 zeolite. Conversions higher than becomes deactivated after a relatively short time on stream, and the process is carried out in a moving bed type reactor with continuous regeneration.

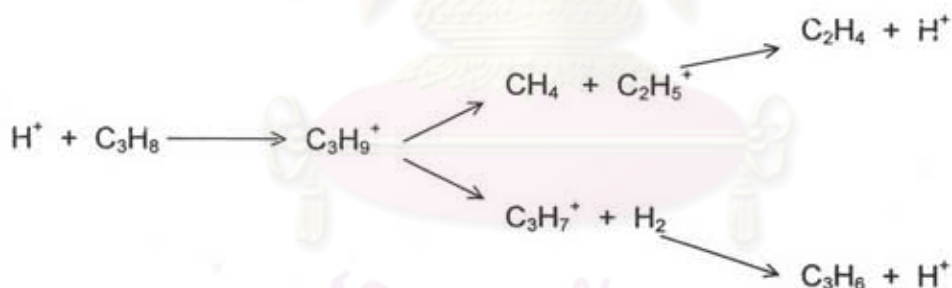
It is believed that the reaction occurs in four steps :

- Dehydrogenation on the metal component.
- Oligomerization and Cyclization of the formed olefins on the acid component of the zeolite.
- Aromatization (dehydrogenation) : Mainly on the metal component.

- Dealkylation, transalkylation and isomerization of the alkylaromatics, occurring on the zeolite component.

The ZSM-5 zeolite gives the acidity while it is stable to deactivation by coke. This is due to its channel dimensions which do not allow the formation of aromatic compounds with more than eleven carbon atoms, nor the formation of poliaromatics which can lead to coke deposits. Moreover, the tridirectional channel structure of ZSM-5 makes less critical the diffusional limitations created by coke deposits, than on other unidirectional zeolites such as mordenite, omega, ZSM-12, offretite, ferrierite, etc..

The HZSM-5, is also able to crack and dehydrogenate propane and butane through the attack of a Bronsted acid site to a carbon-carbon or a carbon-hydrogen bond. The cracking will produce the undesired methane and ethylene, while the dehydrogenation will produce propylene [10,4] :



3.7 Dehydrogenation of propane to propylene

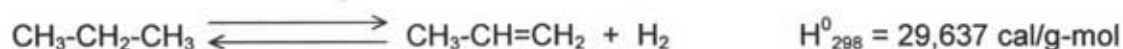
Dehydrogenation is a class of chemical reactions by means of which less saturated and more reactive compounds can be produced. There are many important conversion processes in which hydrogen is directly or indirectly removed. In principle, any compound containing hydrogen atoms can be dehydrogenated [48].

Dehydrogenation of less specific character occur frequently in the refining and petrochemical industries, where many of the processes have names of their own. Some in which dehydrogenation plays a large part are pyrolysis, cracking, gasification by partial combustion, carbonization, and reforming. In general, dehydrogenation reactions are difficult reactions. They require high temperatures for favorable equilibria as well as for adequate reaction velocities. Pure dehydrogenations are endothermic by 15 to 35 kcal/g-mol, and hence have large heat requirements. Active catalysts are usually necessary.

Table 3.4 Enthalpies of Reaction for Vapors at 800 K [48].

Reaction	ΔH_{800} (cal/g-mol)
Ethane \rightarrow ethylene + H ₂	34,300
Propane \rightarrow propylene + H ₂	30,900
Butane \rightarrow 1-butene + H ₂	31,300
Butane \rightarrow <i>t</i> -2-butene + H ₂	28,500
<i>n</i> -Dodecane \rightarrow 1-dodecene + H ₂	31,200
1-Butene \rightarrow 1,3-butadiene + H ₂	28,400
<i>t</i> -2-Butene \rightarrow 1,3-butadiene + H ₂	31,100
1-Butene + $\frac{1}{2}$ O ₂ \rightarrow 1,3-butadiene + H ₂ O	-30,500
Methylcyclohexane \rightarrow toluene + 3H ₂	51,500
Methanol \rightarrow formaldehyde + H ₂	21,700
Methanol + $\frac{1}{2}$ O ₂ \rightarrow formaldehyde + H ₂ O	-37,200
Methanol + H ₂ O \rightarrow 3H ₂ + CO ₂	15,900
Isopropyl alcohol \rightarrow acetone + H ₂	14,200
Isopropyl alcohol + $\frac{1}{2}$ O ₂ \rightarrow acetone + H ₂ O	-44,700
Ethylbenzene \rightarrow styrene + H ₂	29,700

The dehydrogenation of propane to propylene reaction is involved[5] :



The reaction is highly endothermic and exentropic, and is favored at high temperature ($>700^{\circ}\text{C}$) and low pressure ($<100\text{ kPa}$ absolute). A number of cracking, hydrocracking and dehydrogenation side reactions occur, especially with rising temperature, and lead to the formation of methane, ethylene, ethane, coke, mehtylacetylene, allene, etc. To operate at a more accessible thermal level (550 to 650°C), while maintaining an acceptable conversion rate, catalysts must be employed.



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