

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 metasilicates, metalloaluminates, the AlPO_4 's and silico and metalloaluminophosphates, as well as the zeolites. The different classes of molecular sieve materials are listed in Table 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 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 [46]

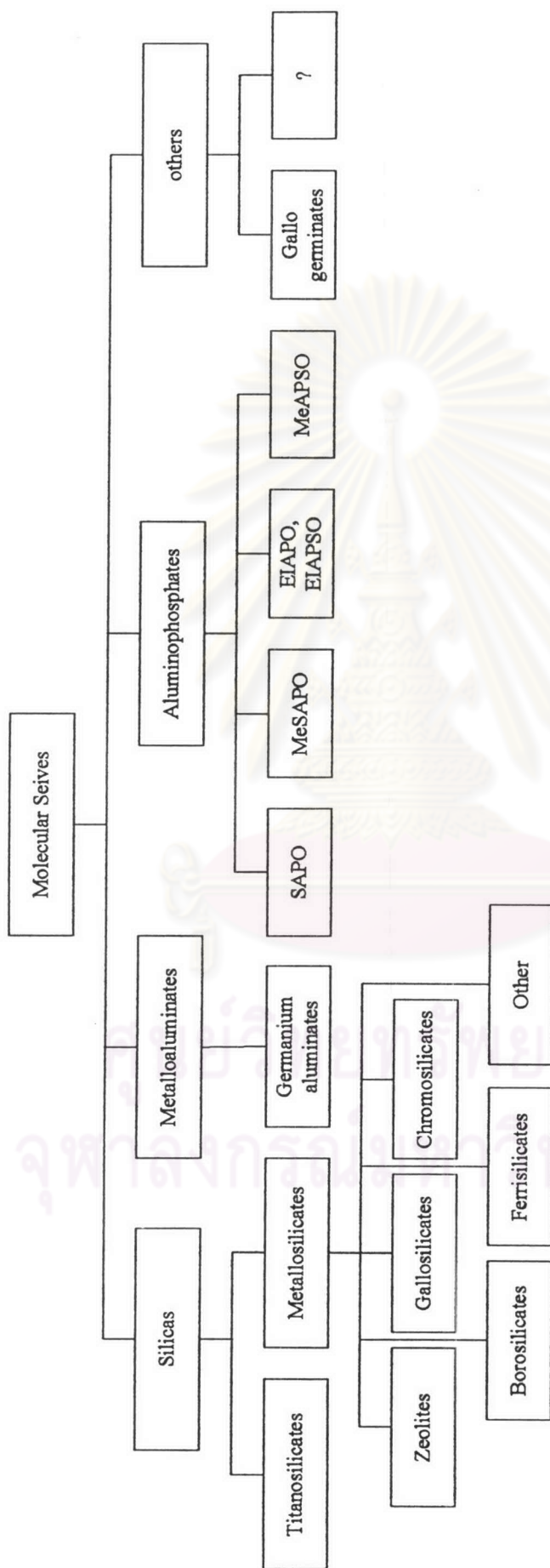


Table 3.1 Classification of molecular sieve materials indicating extensive variation in composition.

The zeolites occupy a subcategory of the metallosilicates (Flaginin 1991 [47]).

3.1.1 Molecular sieve

Zeolite, or crystalline aluminosilicates having pore of molecular dimension, occur naturally in the vugs and vesicles of basaltic lava, in volcanic deposits from saline, alkaline lake and nonmarine tuff beds. These naturally occurring zeolites, the first known examples of molecular sieves, were studied scientifically as early as 1760, whereas their selective adsorption and ion-exchanged properties have been known for decades. Today, zeolites and other molecular sieves, the crown jewels of catalysis, promise to revolutionize chemicals manufacture, petroleum refining and coal and/or natural gas conversion processes through the concept of catalysis by molecular design.

3.1.1.1 Composition of molecular sieves

Strictly speaking, the term molecular sieve refers to a class of crystalline materials having a range of compositions that exhibit shape-selective adsorption and reaction properties, whereas the term zeolite refers to the shape-selective materials composed only of aluminosilicates. The range of materials that make up molecular sieves includes carbon, silica, aluminosilicates, aluminophosphates, metasilicates (e.g. gallosilicates, chromosilicates, borosilicates, and ferrisilicates) and metalloaluminates (e.g. germanium aluminates). In fact, the list of cations that can be incorporated into molecular sieve frameworks has been expanded to include 16 or more elements (Si, Al, Ga, Ge, Be, Li, Mg, Ti, Cr, Mn, Fe, Co, Zn, B, C, P etc.)

3.1.1.2 Pore structure of molecular sieves.

The zeolites listed in Table 3.2 are just a few of the many possible molecular sieve structures. According to Vaughan [48]: 'few fields of chemistry offer such chemical diversity; although only about 60 structures are known, tens of thousands of theoretical structures are possible.

Probably the simplest level of classifying molecular sieve structure is in terms of pore diameter and ring size. By convention, ring size is specified by the number of T atoms or TO_4 units where $T = Si, Al, P$ or B . Pore diameters of aluminosilicate

molecular sieves (A, erionite, pentasil, mordenite and faujasite) range from 3 to 8 Å, whereas ring sizes from 8 Å for erionite to 12 Å for Y-Zeolite.

3.2 Zeolites

Zeolites were first identified by Constredt in 1756 [49]. The word 'Zeolite', from the Greek words meaning "boiling stones", alludes to the frothing and bubbling observed by Constredt when he heated several crystals.

Zeolites are finding applications in many areas of catalysis, generating interest in these materials in industrial and academic Laboratories. As catalyst, zeolites exhibit appreciable acid activity with shape-selectivity features not available in the compositional equivalent amorphous catalysts. In addition, these materials can act as supports for numerous catalytically active metals. Major advances have occurred in the synthesis of zeolites since the initial discovery of the synthetic zeolite's type A, X and Y, and a great number of techniques have evolved for identifying and characterizing these materials. Added to an extensive and ever growing list of aluminosilicate zeolites are molecular sieves containing other elemental compositions. These materials differ in their catalytic activity relative to the aluminosilicate zeolites and may have potential in customizing or tailoring the molecular sieves catalyst for specific applications. Elements isoelectronic with Al^{+3} or Si^{+4} have been proposed to substitute into the framework lattice during synthesis. These include B^{+3} , Ga^{+3} , Fe^{+3} , and Cr^{+3} substituting for Al^{+3} , and Ge^{+4} and Ti^{+4} for Si^{+4} . The incorporation of transition elements such as Fe^{+3} for framework Al^{+3} positions modifies the acid activity and, in addition, provides a novel means of obtaining high dispersions of these metals within the constrained pores of industrially interesting catalyst materials.

3.2.1 Structure of Zeolite

Zeolites are porous, crystalline aluminosilicates that develop uniform pore structure having minimum channel diameter of 0.3-0.1 nm. This size depends primarily upon the type of zeolites. 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). 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.

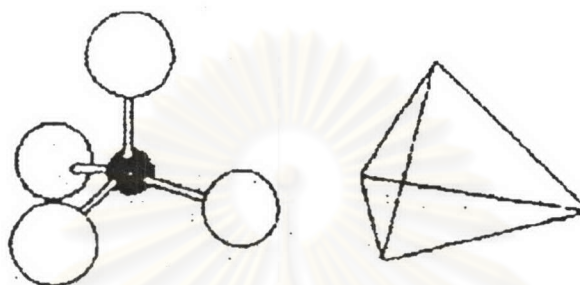


Figure 3.1 SiO_4 or AlO_4 tetrahedra [49]

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 known zeolite structures. These secondary building units consist of 4(S4R), 6(S6R), and 8(S8R)-member single ring, 4-4(D4R), 6-6(D6R), 8-8(D8R)-member double rings, and 4-1, 5-1, and 4-4-1 branched rings[50]. The topologies of these units are shown in figure 3.2. 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[50]. Both zeolite ZSM-5 and ferrierite are described by their 5-1 building units. Offretite, 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.

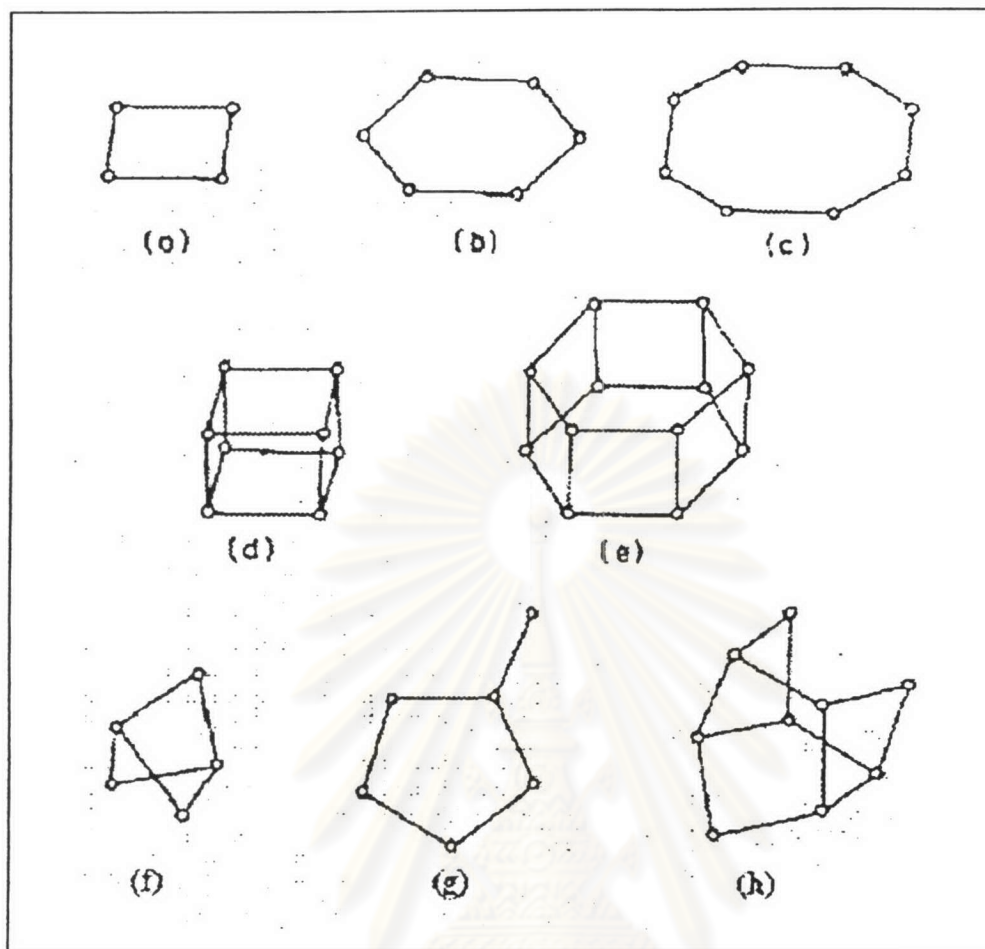
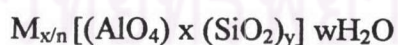


Figure 3.2 secondary building units (SBU's) found in zeolite structures [51]

Zeolites may be represented by the general formula,

The general formulation of zeolite structure is described as the follow below:



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 [52]. M is a proton, the zeolite becomes a strong Bronsted acid. As catalysts, zeolites are unique in their ability to discriminate between reactant molecular size and shape [53].

The catalytically most significant are those having pore openings characterized by 8-, 10-, and 12- rings of oxygen atoms. Some typical pore geometries are shown in figure 3.3 [54].

Table 3.2 Zeolites and their secondary building units. The nomenclature used is consistent with that presented in Figure 3.2 [50]. (continued)

ZEOLITE	SECONDARY BUILDING UNITS								
	4	6	8	4-4	6-6	8-8	4-1	5-1	4-4-1
Stibite									x
Natrolite							x		
Thomsonite							x		
Edingtonite							x		
Cancrinite		x							
Zeolite L		x							
Mazzite	x								
Merlinoite	x		x			x			
Phillipsite	x		x						
Zeolite Losod		x							
Erionite	x	x							
Paulingite	x								
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			

3.2.1.1 Small pore zeolites

Structures of some of small pore zeolite are illustrated in Figure 3.4. The erionite structure, Figure 3.4(a), is hexagonal containing “supercage” supported by columns of cancrinite units linked through double 6 rings. Access to, and between, the supercages is gained through 8 rings.

In the chabazite framework, Figure 3.4(b), the double 6 ring layer sequence is ABCABC, and the double 6 ring units are linked together through tilted 4 ring units. The framework contains large ellipsoidal cavities, Figure 3.3(c), each entered through six 8 ring units. These cavities are joined together via their 8 ring units, forming a 3 dimensional channel system.

3.2.1.2 Medium pore zeolites

The channel system of zeolite ZSM-5, represented in Figure 3.5, consists of straight channels running parallel to [010] and intersecting sinusoidal channels parallel to [100]. The channels are ellipsoidal with 10 oxygen ring opening, having the approximate free dimensions $5.4 \times 5.6 \text{ \AA}^0$ (straight channel) and $5.1 \times 5.4 \text{ \AA}^0$ (sinusoidal channel) based on oxygen radii 1.35 \AA^0 .

3.2.1.3 Large pore zeolites

The faujasite structure, Figure 3.6(a), is built up of truncated octahedral interconnected via double 6 ring units Faujasite contains extremely large supercages ($\sim 13 \text{ \AA}^0$ diameter) entered through 12 oxygen ring. Mordinite, Figure 3.6(b), is characterized by a one dimensional system of parallel elliptical channels, defined by 12 oxygen ring.

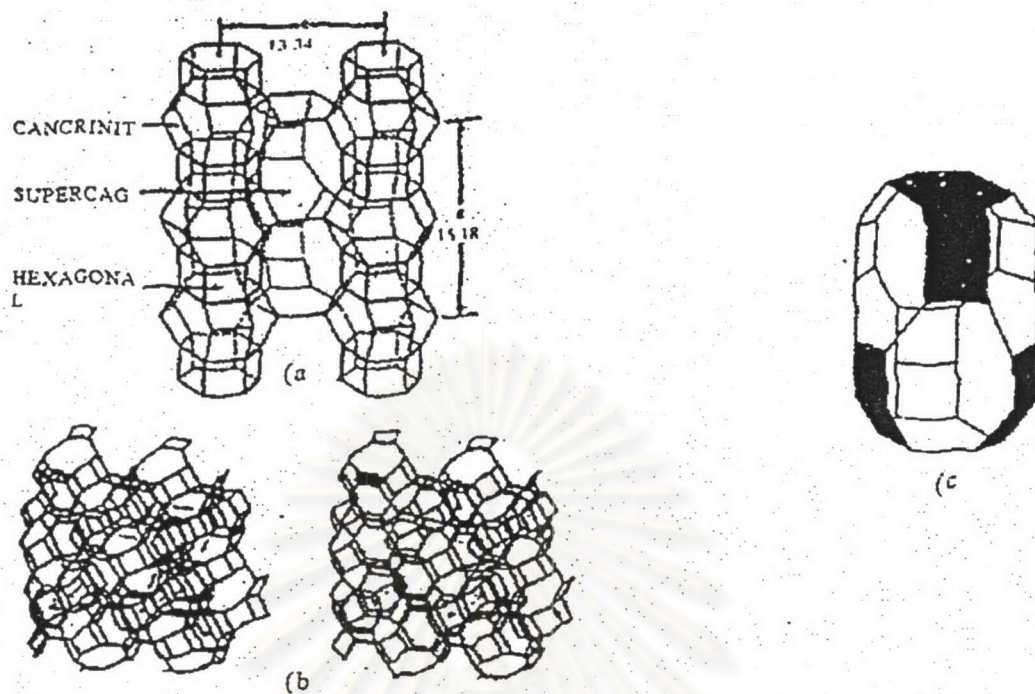


Figure 3.4 Small pore zeolites (a) Erionite framework (b) Chabazite Framework (c) Chabazite cavity [54].

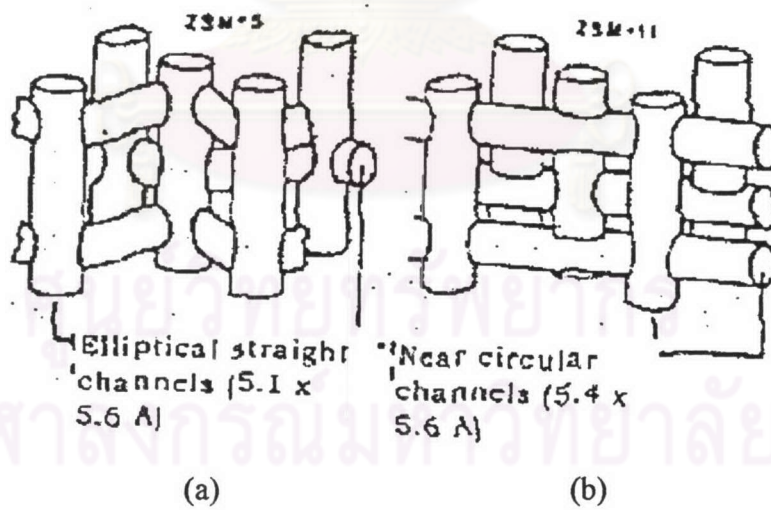


Figure 3.5 ZSM-5 and ZSM-11 channel system [54].

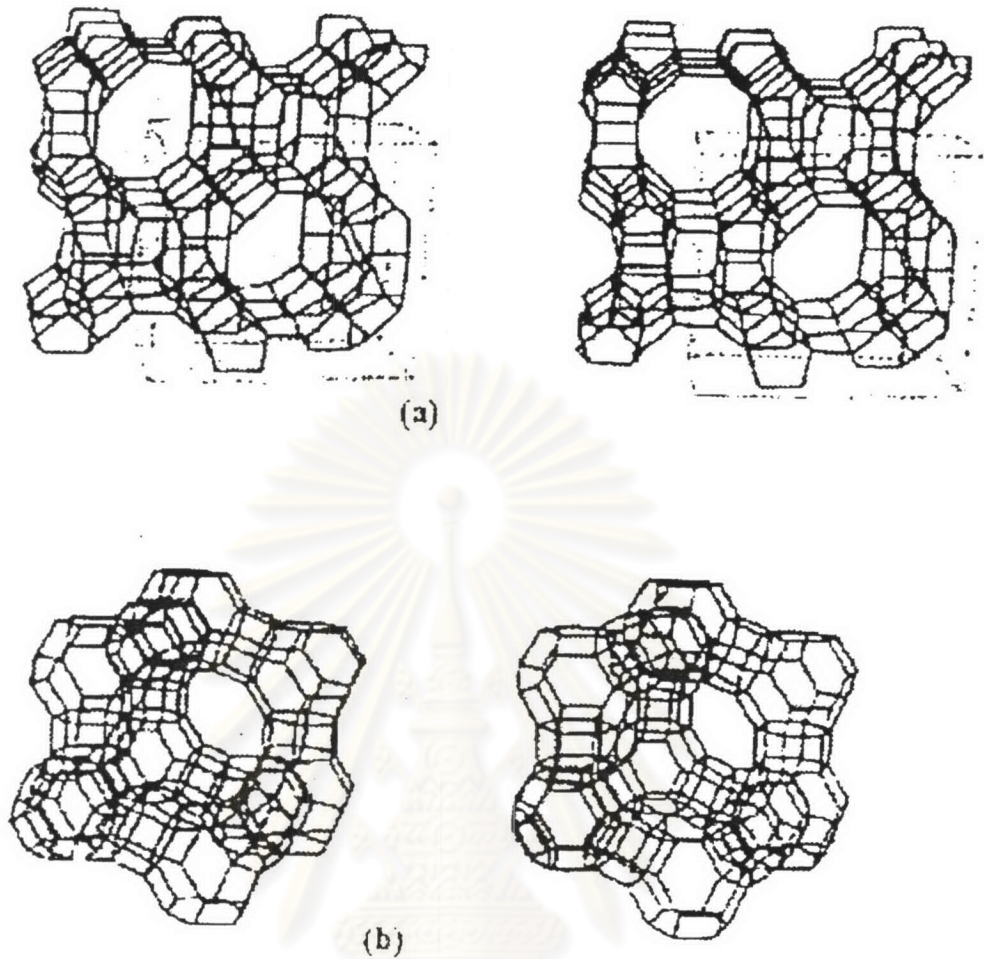


Figure 3.6 Large pore zeolite

(a) Mordenite framework

(b) Faujasite framework [54].

3.2.2 Silicalite and ZSM-5

In silicalite and ZSM-5, the tetrahedra are linked to form the chain-type building block in Figure 3.7. The chain can be connected to form a layer, as shown in Figure 3.8. Rings consisting of five O atoms are evident in this structure; the name *pentasil* is therefore used to describe it. Also evident in figure 3.8 are rings consisting of 10 oxygen atoms; these are important because they provide openings in the structure large enough for passage of 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, intermediate structures constitute the pentasil series.

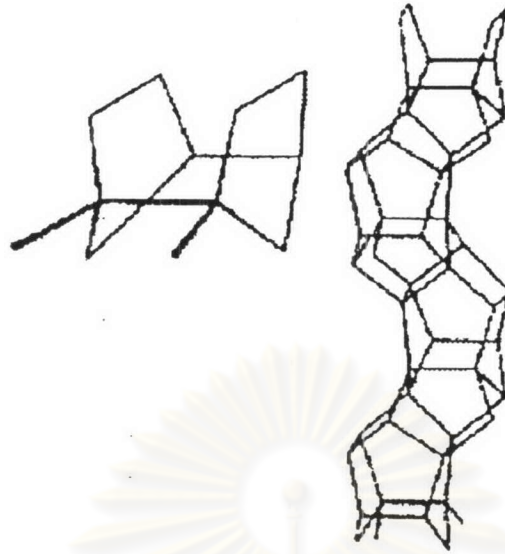


Figure 3.7 The chain-type building block formed from the secondary building units [55].

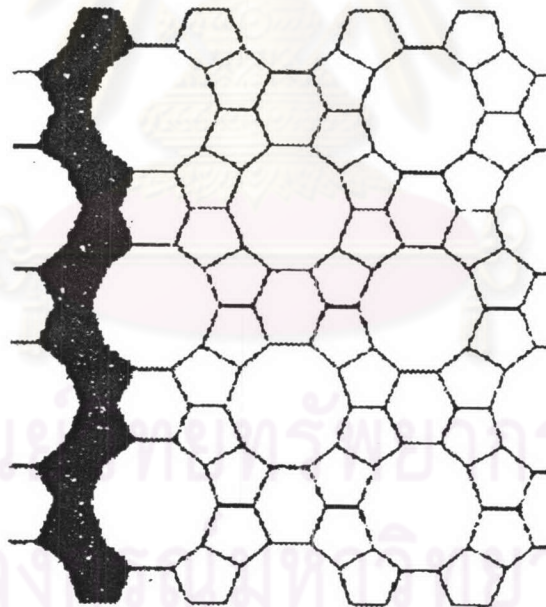


Figure 3.8 Schematic diagram of silicalite layer [55].

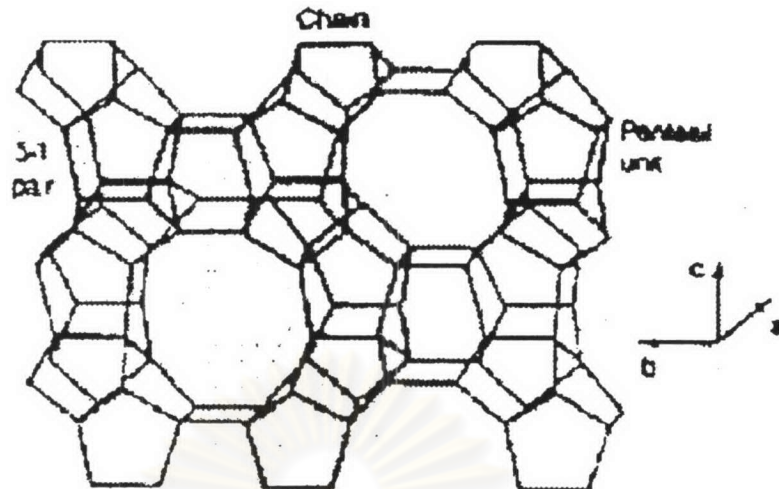


Figure 3.9 Three dimensional structure of silicalite (ZSM-5) [55]

The three dimensional structure of silicalite (and ZSM-5) is presented in Figure 3.9. The 10-membered rings provide access to a network of intersecting pores within the crystal. The pore structure is depicted schematically in Figure 3.5; there is a set of straight, parallel pores intersected by set of perpendicular zigzag pores. Many molecules are small enough to penetrate into this intracrystalline pore structure, where they may be catalytically converted.

3.3 Zeolites as Catalysts

The first use of zeolite as catalysts occurred in 1959 when zeolite Y was used as an isomerization catalyst by Union Carbide. More important was the first use of zeolite X as a cracking catalyst in 1962, based upon earlier work by plank and Rosinski. They noted that relatively small amounts of zeolites could usefully be incorporated into the then-standard silica/alumina or silica/clay catalysts. The use of zeolite in this way as promoters for petroleum cracking greatly improved their performance.

3.3.1 Potential versatility of zeolites as catalysts

Vaughan has graphically described zeolites as 'molecules boxes' which have variable dimensions suited to the encouragement of molecular rearrangements inside their confined geometry. The conditions inside the 'box', and of the 'box' itself, can

be controlled in a variety of ways based upon the unique properties of zeolite frameworks as summarized in Table 3.3 and described below.

Table 3.3 Correlation between zeolite properties and catalytic functionality [49].

Property	Catalytic functionality
Crystal voidage and Channels	Extensive internal surface to encourage catalytic processes
Variable pore size	Creates both reactant and product selectivity via molecules sieving
Ion exchange	Cations (I) control pore size, (ii) create high potential energy fields within voidage (active sites) and (iii) enable distribution of catalytically active metals on the zeolite substrate
Salt occlusion	Controls pore size, provide another method of metal incorporation and can improve thermal stability and poisoning resistance
Framework modification	Varies lattice charge (by synthesis or modification) to enhance active site production and thermal stability

3.3.1.1 Crystal voidage and channels

Although some heterogeneous reactions will take place at the external crystal surfaces, most practical zeolite catalysis takes place inside the framework. Here zeolites have the advantage of a very large internal surface, about 20 times larger than their external surface for the more open framework (e.g. zeolites X and Y). This internal capacity provides the appropriate surfaces at which catalytic transformations can take place. In the faujasite zeolites this is typically in the series of large cavities easily available via three-dimensional open-pore networks.

Further flexibility which is useful for planned catalytic uses arises in the more recently produced zeolites with subtly different cavity and channel systems. ZSM-5, for instance, has a three-dimensional system linked via intersections rather than cavities and mordenite catalysis seems to take place only in the largest channels.

3.3.1.2 Variable pore sizes

Given that catalysis take place largely within zeolite frameworks, access to this environment is patently controlled by oxygen windows. This is diffusion limited process, as is the egress of product molecules after transformations have taken place. This means that zeolites have very special practical advantages over the more traditional catalysts, in that they will admit only certain reactant molecules and that this can be potentially tailored to produced selected products. This selectivity is known as 'shape-selective catalysis' and controlled by 'configurational diffusion' this phrase was coined by Weiss to express a diffusion regime in which useful catalytic reactions and promoted by virtue of a matching of size, shape and orientation of the reactant product molecules to the geometry of zeolitic framework.

3.3.1.3 Ion exchange

Perhaps more relevant is the way in which ion exchange can be employed to place cations into very specific framework sites so as to create small volumes of high electrostatic field. These fields are 'active sites' to which an organic reactant molecule can be attracted thus promoting the bond distortion and rupture essential to molecular rearrangements.

Another feature of ion exchange is that it provides a route for the introduction of metal cations with a view to their subsequent reduction to metal particles. These exist in the so-called 'bifunctional' zeolite catalysts used to effect both hydrogenation and dehydrogenation reactions.

3.3.1.4 Exchangeability

Most zeolites are synthesized in the alkali cation form (mostly Na^+) in which the positively charged cations balance the negatively charged framework system. In aluminosilicates, these cations are readily exchanged by other mono-, di- and trivalent cations including NH_4^+ , H^+ , Ca^{2+} , and La^{3+} . Cations in ALPOs are not exchangeable. According to Ward [56] the rate and degree of cation exchange in zeolites depends on:

- the type of cation being exchanged, its diameter and charge;

- the nature of, size of and strength of cation coordination complex;
- ion exchange temperature;
- thermal treatment of the zeolite, before or after exchange;
- the structural properties of the zeolite and its Si:Al ratio;
- the locations of cations in the zeolite;
- the concentration of the cation exchange solution;
- any previous treatment of the zeolite.

H-sieves (hydrogen ion-exchanged sieves) are made by first ammonium ion exchange, followed by thermal decomposition.

3.3.1.5 Salt occlusion

The introduction of a salt molecule into a zeolite can be the first stage in the incorporation of a metal for subsequent reduction as mentioned above. It can also be used to enhance thermal stability. Yet another purpose is to 'pacify' zeolite cracking catalysts. The problem here is that crude oils contain metal cations (Ni, Cu, V, Fe) originating from the metal porphyrins thought to play an inherent part in the geological formation of oil. These metals create unwanted reactivity causing carbon (coke) formation and subsequent loss of catalytic properties. The occlusive introduction of stannates, bismuthates, or antimonates pacifies these metals to extend useful catalyst bed life. It enables the refinery to cope with a variety of crude oils from different oil fields and illustrates the flexible technology which can be achieved in zeolite catalysis.

Other salt treatments, via phosphates or fluorides, have been used to improve performance.

3.3.1.6 Framework modification

The electrostatic field a zeolite can be manipulated by isomorphous substitution into framework Si and Al sites. This can be done by synthetic or modification routes. When the Si : Al ratio is close to 1 the field strength is at its highest as is the cation content – i.e. the conditions of maximum negative charge on the framework. An increase of the Si:Al causes a greater separation of negative charge and hence higher field gradients (obviously also conditioned by cation position

and cation type). In this way catalytic activity can be controlled, and other parameters altered. A well – known example of these effects is the way in which the thermal and chemical stabilities of the synthetic faujastes can be critically altered by aluminium removal.

Framework substitution also can be created by the introduction of atoms other than Si and Al into tetrahedral sites via synthesis or modification. ZSM-5 can accept B and Ga into tetrahedral sites by simple salt treatment as mentioned earlier, although a similar reaction in other frameworks is by no means as facile.

3.4 Zeolite Active Sites

3.4.1 Active sites

The complex crystalline structure of each zeolite leads to a multiplicity of cation positions in the pores and supercages.

3.4.2 Acidity

Acidity in zeolites increases with decreasing Si:Al ratio, since acid sites are associated with Al ions; acidity is also a function of cation. H-sieves are strong acids but often too unstable for commercial use. Nevertheless, zeolites exchanged with di and trivalent ions are sufficiently acidic; for example, Ca^{2+} is thought to be present as $\text{Ca}(\text{OH})^+$ plus H^+ . ALPOs are mildly acidic relative to the aluminosilicates. The Bronsted and Lewis acidities of zeolites play important roles in their abilities to catalyze various hydrocarbon reactions, e.g. cracking and isomerization.

3.4.3 Acid Sites

Classical Bronsted and lewis acid models of acidity have been used to classify the active sites on zeolites. Bronsted acidity is proton donor acidity; a tridiagonally co-ordinated alumina atom is an electron deficient and can accept an electron pair, therefore behaves as a Lewis acid [53, 57].

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

Recently it has been reported the mean charge on the proton was shifted regularly towards higher values as the Al content decreased [53]. 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 is parallel to that of Al content [53]. A longer distance between hydroxyl groups decreases the probability of dehydroxylation that generates defects on structure of zeolites.

3.4.4 Generation of Acid Centers

Protonic acid centers of zeolite are generated in various ways. Figure 3.10 depicts the thermal decomposition of ammonium exchanged zeolites yielding the hydrogen form [50].

The Bronsted acidity due to water ionization on polyvalent cations, described below, is depicted in figure 3.11 [52].



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

Bronsted 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 [52].

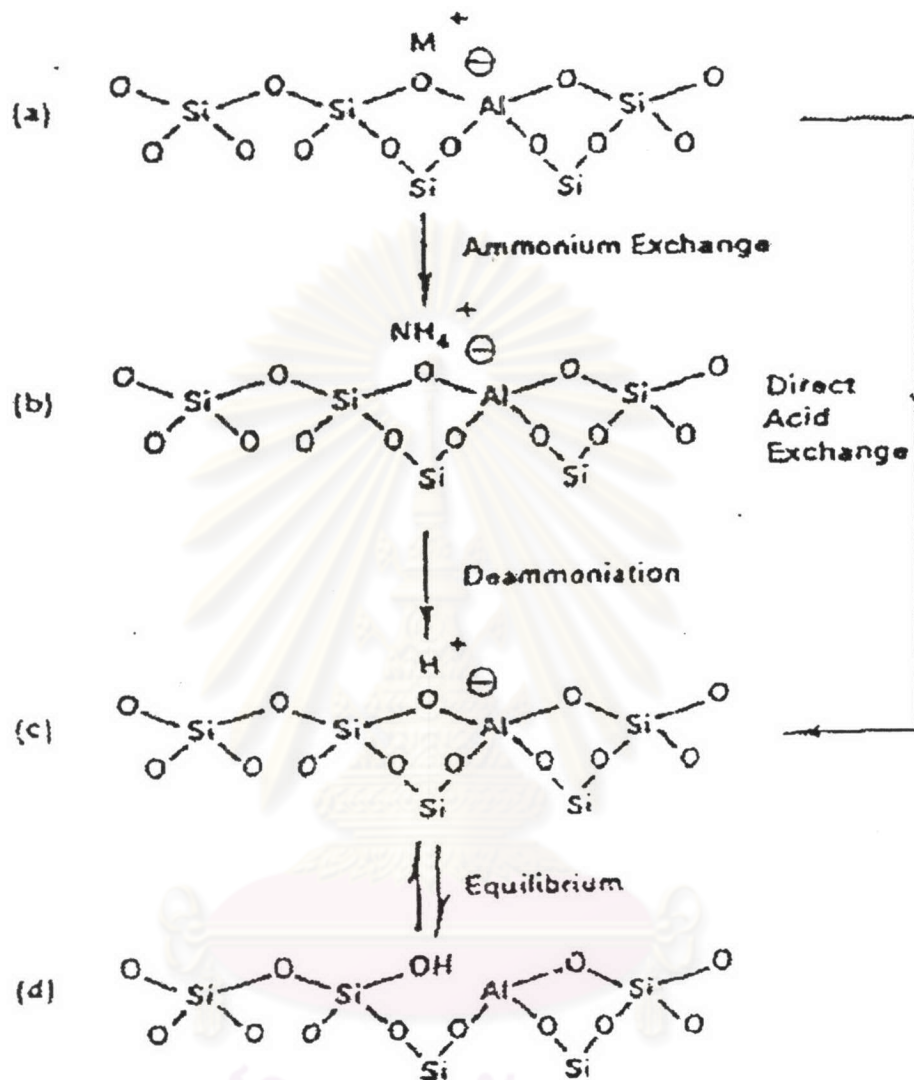


Figure 3.10 Diagram of the surface of a zeolite framework [50].

- In the as-synthesized form M^+ is either an organic cation or an alkali metal cation.
- Ammonium in exchange produces the NH_4^+ exchanged form.
- Thermal treatment is used to remove ammonia, producing the H^+ acid form.
- The acid form in (c) is in equilibrium with the form shown in (d), where there is a silanol group adjacent to a tricoordinate aluminum.

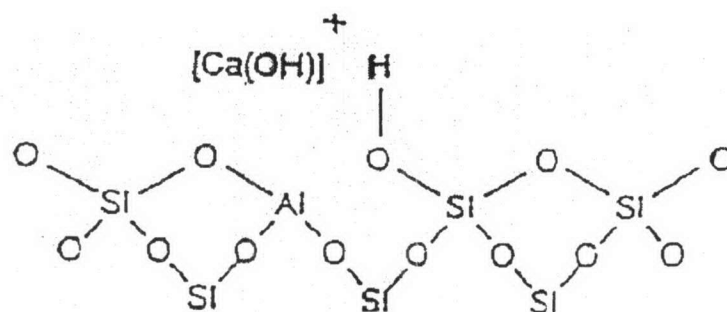
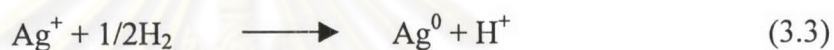
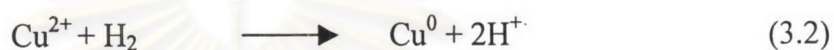


Figure 3.11 Water molecules co-ordinated to polyvalent cation are dissociated by heat treatment yielding Bronsted acidity [52].



The formation of Lewis acidity from Bronsted sites is depicted in Figure 3.12 [49]. The dehydration reaction decreases the number of protons and increases that of Lewis sites.

Bronsted (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.

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.

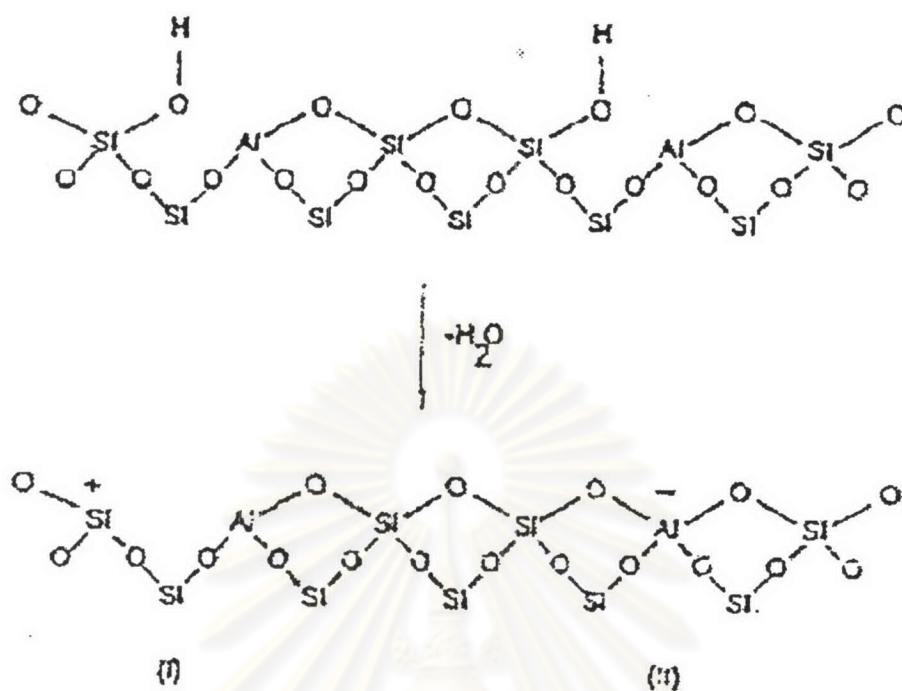


Figure 3.12 Lewis acid site developed by dehydroxylation of Bronsted acid site [52].

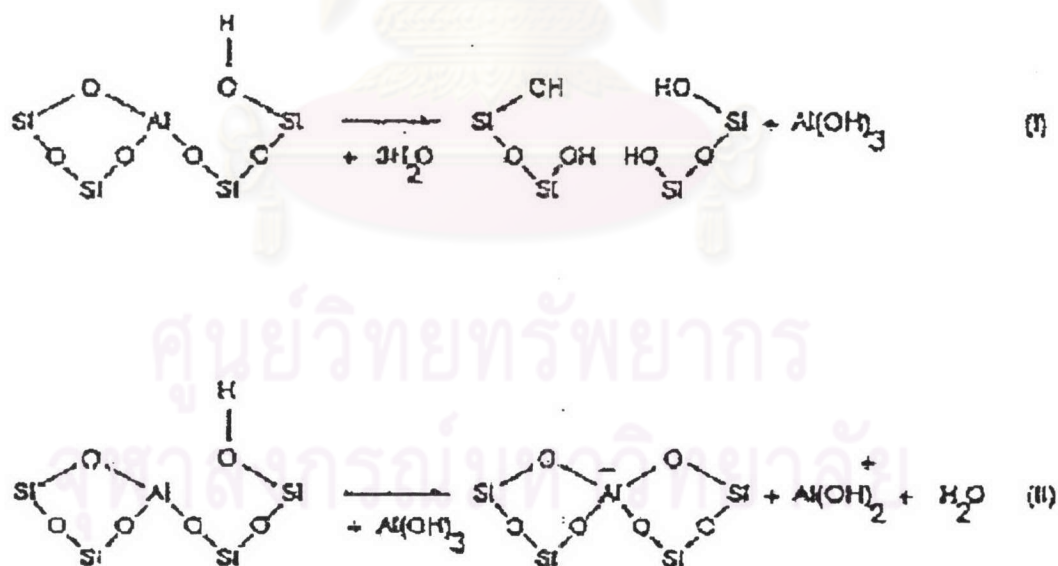


Figure 3.13 Steam dealumination process in zeolite [52].

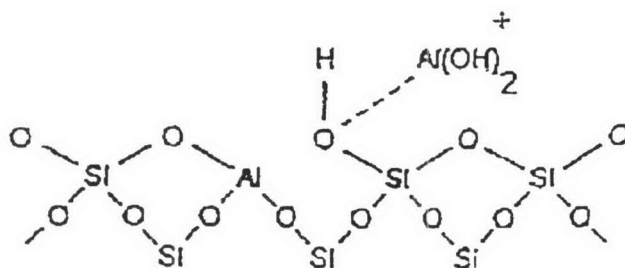


Figure 3.14 The enhancement of the acid strength of OH groups by their interaction with dislodged aluminum species [52].

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 3.14 [52]. Partial dealumination might therefore yield a catalyst of higher activity while severe steaming reduces the catalytic activity.

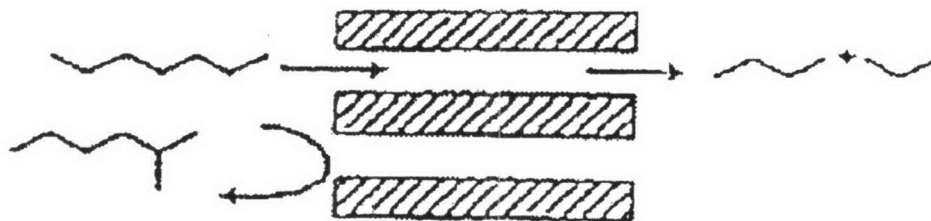
3.4.5 Basic Sites

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 has been shown to control the unimolecular cracking (*B*-scission). Feed radical mechanisms also contribute to surface catalytic reactions in these studies.

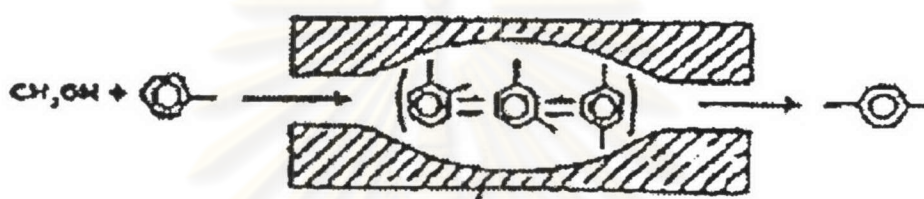
3.5 Shape-Selective Catalysis

Many reactions involving carbonium ions 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 spape 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 [50,59,60]. These type of selectivity are predicted in Figure 3.15 [50].

a) Reactants selectivity



b) Products selectivity



c) Transition states selectivity

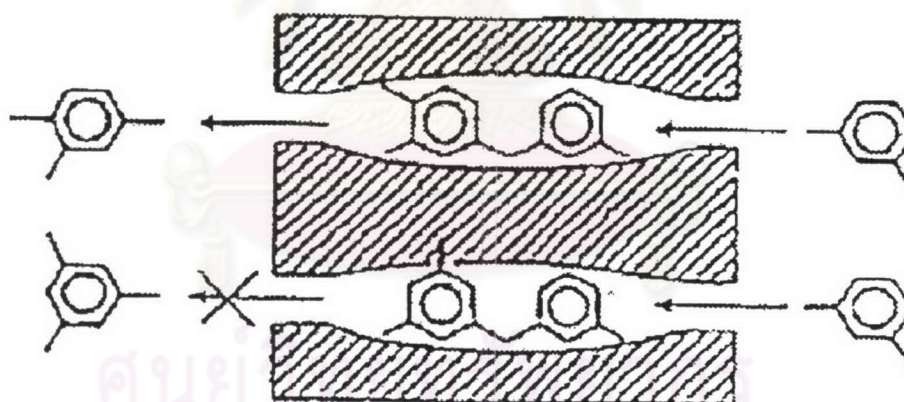


Figure 3.15 Diagram depicting the three type of selectivity [50].

Table 3.4 Kinetic diameters of various molecules based on the Lennard-Jones relationship [59].

	KINETIC DIAMETER (ANGSTROMS)
He	2.60
H ₂	2.89
O ₂	3.46
N ₂	3.43
NO	3.17
CO	3.76
CO ₂	3.30
H ₂ O	2.65
NH ₃	2.60
CH ₄	3.80
C ₂ H ₂	3.30
C ₂ H ₄	3.90
C ₃ H ₈	4.30
n-C ₄ H ₁₀	4.30
Cyclopropane	4.23
i-C ₄ H ₁₀	5.00
n-C ₅ H ₁₂	4.90
SF ₆	5.50
Neopentane	6.20
(C ₄ F ₉) ₃ N	10.20
Benzene	5.85
Cyclohexane	6.00
m-xylene	7.10
p-xylene	6.75
1,3,5 trimethylbenzene	8.50
1,3,5 triethylbenzene	9.20
1,3 diethylbenzene	7.40
1-methylnapthalene	7.90
(C ₄ H ₉) ₃ N	8.10

Reactant or 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.

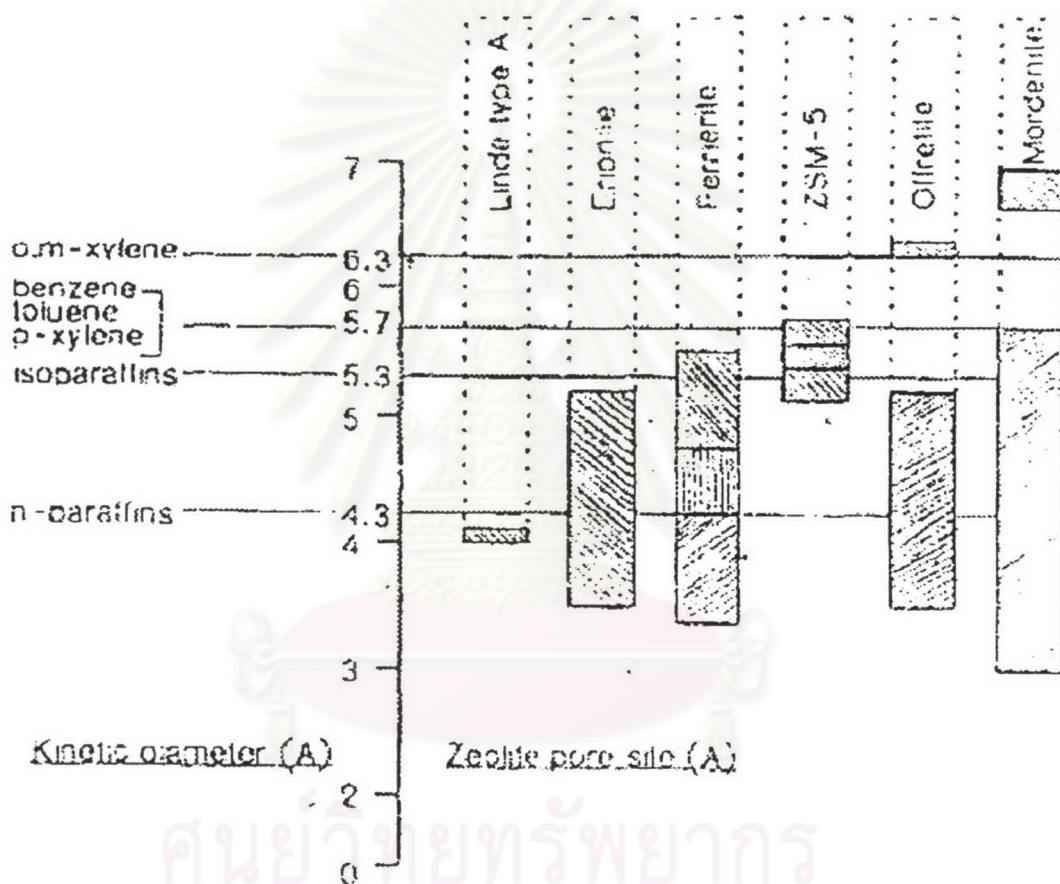


Figure 3.16 Correlation between pore size (s) of various zeolites and kinetic diameter of some molecules [61].

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 if the space required for formation of necessary transition state is restricted.

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.

Table 3.4 [62] presents values of selected critical molecular diameters and Table 3.5 [50] presents values of the effective pore size of various zeolites. Correlation between pore size(s) of zeolites and kinetic diameter of some molecules are depicted in Figure 3.16 [59].

Table 3.5 Shape of the pore mouth opening of known zeolite structures. The dimensions 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 crystallographic axis shown in brackets (e.g. $\langle 100 \rangle$ [63]).

STRUCTURE	4-MEMBER RING	10-MEMBER RING	12-MEMBER RING
Bikitaite	3.2×4.9[001]		
Brewsterite	2.3 × 5.0[100] 2.7 × 4.1[001]		
Cancrinite			6.2[001]
Chabazite	3.6 × 3.7[001]		
Dachiadite	3.6 × 4.8[001]	3.7 × 6.7[010]	
TMA-E	3.7 × 4.8[001]		
Edingtonite	3.5 × 3.9[110]		
Epistibite	3.7 × 4.4[001]	3.2 × 5.3[100]	
Erionite	3.6 × 5.2[001]		
Faujasite			7.4 $\langle 111 \rangle$
Ferrierite	3.4 × 4.8[010]	4.3 × 5.5[001]	
Gismondine	3.1 × 4.4[100] 2.8 × 4.9[010]		
Gmelinite	3.6 × 3.9[001]		7.0[001]

Table 3.5 Shape of the pore mouth opening of known zeolite structures. The dimensions 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 crystallographic axis shown in brackets (e.g. $\langle 100 \rangle$ [63]). (continued)

STRUCTURE	4-MEMBER RING	10-MEMBER RING	12-MEMBER RING
Heulandite	4.0 × 5.5[100] 4.1 × 4.7[001]		
ZK-5	3.9 $\langle 100 \rangle$		
Laumontite		4.0 × 5.6[100]	
Levyne	3.3 × 5.3[001]		
Type A	4.1 $\langle 100 \rangle$		
Type L			7.1[001]
Mazzite			7.4[001]
ZSM-11		5.1 × 5.5[100]	
Merlinoite	3.1 × 3.5[100] 3.5 × 3.5[010] 3.4 × 5.1[001] 3.3 × 3.3[001]		
ZSM-5		5.4 × 5.6[010] 5.1 × 5.5[100]	
Mordenite	2.9 × 5.7[010]		6.7 × 7.0[001]
Natrolite	2.6 × 3.9 $\langle 101 \rangle$		
Offretite	3.6 × 5.2[001]		6.4[001]
Paulingite	3.9 $\langle 100 \rangle$		
Phillipsite	4.2 × 4.4[100] 2.8 × 4.8[010] 3.3[001]		
Rho	3.9 × 5.1 $\langle 100 \rangle$		

Table 3.5 Shape of the pore mouth opening of known zeolite structures. The dimensions 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 crystallographic axis shown in brackets (e.g. $\langle 100 \rangle$ [63]). (continued)

STRUCTURE	4-MEMBER RING	10-MEMBER RING	12-MEMBER RING
Stibite	2.7 × 5.7[101]	4.1 × 6.2[100]	
Thomsonite	2.6 × 3.9[101] 2.6 × 3.9[010]		
Yugawaralite	3.1 × 3.5[100] 3.2 × 3.3[001]		

3.6 Non – aluminosilicate Molecular Sieves

Advances in the area of new molecular sieve materials have come in the preparation of zeolite – like structure containing framework components other than aluminum and silicon exclusively. The aluminosilicate zeolites offer the ion exchange properties, higher thermal stability, high acidity and shape-selective structural features desired by those working in the areas of adsorption and catalysis. However, modification and subsequent improvement of these properties have served as a driving force for changing the composition of these microporous materials.

It is well accepted that gallium can easily be substituted for aluminum and germanium for silicon in aluminosilicate system, as these elements are in the same family of the periodic table. Gallosilicate, gallogerminate and germanium aluminate analogs of the known zeolites have been hydrothermally synthesized under conditions comparable to the zeolite molecular sieves. Other elements were found not to substitute so easily. In the crystallization of many zeolite structures, the relative amounts of silicon and aluminum in the reacting gel strongly influenced the crystallization of a particular structure. Attempts to substitute vastly different elements for either aluminum or silicon resulted in suppression of crystallization. It was the discovery of the strong structure – directing properties of the cation organic

amine additives that fuelled new discoveries of different chemical compositions with zeolite – like structures. The graph in Figure 3.17 [50] show this explosion in new (non-zeolitic) molecular sieves patented relative to the reported new zeolite materials synthesized and the natural zeolite minerals known. The number of non – zeolite molecular sievers reported is far greater than the number of microporous aluminosilicate zeolite materials as shown in the graph.

In addition to the gallosilicates, germanium aluminates, and gallogerminates synthesized prior to the use of organic additives, materials containing zeolite – type structures crystallized in the presence of organic cation have been claimed to contain boron, iron. Chromium, cobalt, titanium, zirconium, zinc, beryllium, hafnium, manganese, magnesium, vanadium, and tin. Little characterization of the extent of incorporation has been presented for many of these materials. The most common structure claims to incorporate such elements is the ZSM-5 type framework.

However, it is well accepted that the ZSM-5 structure, strongly directed by the presence of the TPA cation, can easily crystallize in the pure silica form (silicate). Therefore, the possibility remain, without sufficient characterization to confirm incorporation, that this exclusively silica – containing structure could form metallosilicate reaction mixture, giving the characteristic X-ray diffraction pattern without incorporating the desired metal component into the structure. Boron, gallium, iron, and titanium have been sufficiently characterized to confirm structure incorporation.

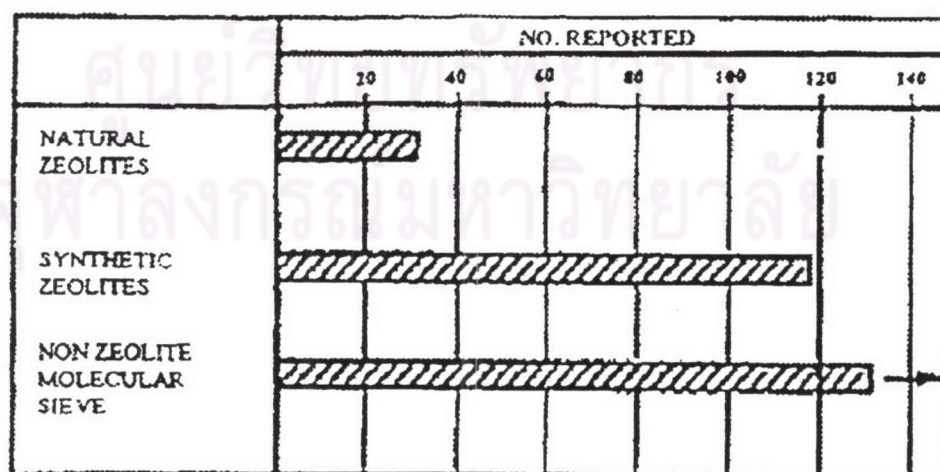


Figure 3.17 A comparison of the natural zeolites known and the number of zeolites synthesized within the last 30 years with the number of recently patented non-zeolite molecular sieves [50].

3.7 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. These 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 dichloride. 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 is structurally identical to that of ZSM-11) can be transformed into gallosilicate with its reaction with NaGaO_2 in an aqueous solution.

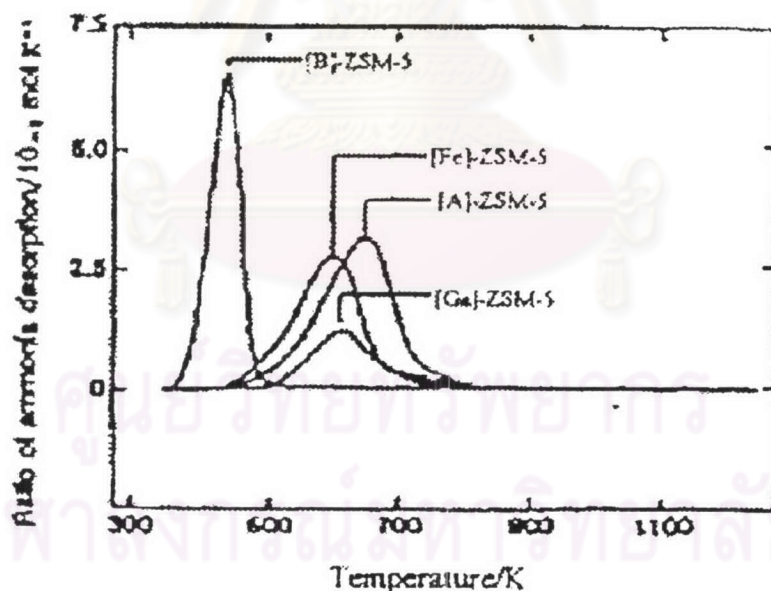


Figure 3.18 Temperature programmed desorption of ammonia from metallosilicate (Reported with permission by C. T – W. Chu, C. D. Chang, *J. Phys. Chem.*, 89, 1571(1985)) [52].

Figure 3.18 [52] shows the TPD spectrum of ammonia adsorbed on various metallosilicate. The acid strength of metallosilicate changes in decreasing order as follows:

[Al]-ZSM-5 > [Ga]-ZSM-5 > [Fe]-ZSM-5 > [B]-ZSM-5

The band position of OH groups changes in conformity with TPD spectra. Thus, the OH band appears at 3610, 3620, 3630, and 3725 cm^{-1} for [Al]-, [Ga]-, [Fe]-, and [B]-ZSM-5, respectively. 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 3.6 Product distribution of the conversion of 1-butene over H-ZSM-5, H-[B]-ZSM-5 and Zn-[B]-ZSM-5 [52].

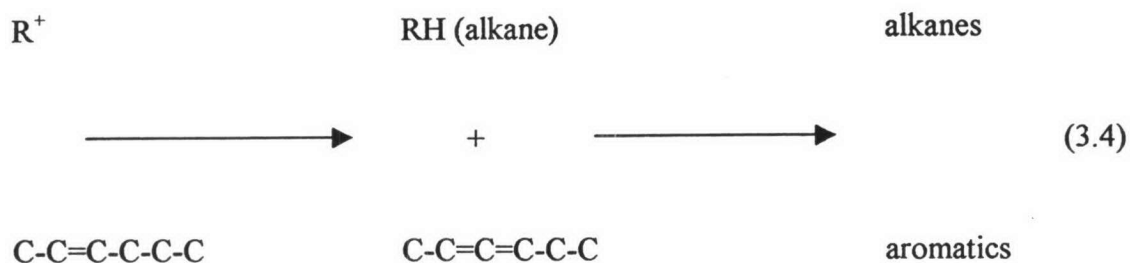
Catalyst	H-[Al]-ZSM-5	H-[B]-ZSM-5	Zn-[B]-ZSM-5
conversion/%	77.3	71.7	81.2
Products/% ^{††}			
C ₁ -C ₄ alkanes	41.3	5.1	6.3
C ₂ H ₄ +C ₃ H ₆	14.6	38.3	21.1
C ₄ H ₈ ^{†‡}	6.2	28.3	27.7
C ₅ ⁺	2.4	25.3	7.0
Aromatics	37.0	3.0	38.0

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

1-butene=23.0 kPa

^{††} carbon-number basis, ^{†‡} including 1-butene

Weaker acid strength of [B]-ZSM-5 is confirmed also by catalytic reactions. Table 3.6 [52] shows the product distributions 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 hydrocarbons, while over [B]-ZSM-5, lower alkenes are the main products. This indicates that the hydride transfer reactions from alkene to carbonium ion does not proceed over [B]-ZSM-5.



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

The yield of aromatic hydrocarbons greatly increases by introducing zine cations into [B]-ZSM-5 (Table 3.6). 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 zine 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 metnanol 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 aluminium 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 [52].

3.8 Thermal stability

The thermal stability of zeolited increases with increasing silica content and by exchange with rare earth cations. Most sieves are uncharged by dehydrating to 400 °C; high silica (ultrastabilized forms prepared by steam pre-treatment) and rare earth-exchanged sieves are stable to 700-800 °C. Generally, extensive dehydration causes loss of Bronsted acidity due to the removal of OH or silanol surface groups.

Thermal treatment of zeolites in the presence of water normally leads to dealumination. In fact, it is one of the recommended methods for preparing ultrastable zeolites. Moderate dealumination generally increases catalytic activity or leaves it unchanged, whereas advanced dealumination leads to a decrease in activity due to a loss of active sites and ultimately collapse of the zeolite structure. For example, dealumination of mordenite significantly changes important chemical and physical properties such as crystal structure, thermal stability, sorption capacity and acidity, as well as catalytic properties. Maximum thermal stability is reached for an $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of about 19. The sorption capacity towards water is highly reduced after dealumination because of the absence of strong polarizing cations which can dissociate water to strongly adsorbed hydroxy groups; accordingly, the number of Bronsted acid sites also decreases. Nevertheless, the hydrocarbon cracking activity of mordenite increases with increasing Si:Al ratio. For further details on zeolite stability, the reader is referred to the comprehensive review of McDaniel and Maher [64].



ศูนย์วิจัยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย