

CHAPTER III

THEORY

3.1 Molecular Sieves for Use in Catalysis

The history of a new class of inorganic materials, zeolites and molecular sieves, is reviewed from the finding of the first zeolite mineral in 1756 through the explosion in new molecular sieve structures and compositions in the 1980's [37]. The discovery result in an extending development of applications in many areas of catalysis, generating intense interest in these materials in industrial and academic laboratories [38-39]. As catalysts, zeolites exhibit high acid activity with shape-selective features not available in the compositionally equivalent amorphous catalysts. In addition, these materials can act as supports for numerous catalytically active metals.

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 of hydrophobicity and no ion exchange capacity.

3.2 Classification of Molecular Sieves

With the recent discoveries of molecular sieve 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. Therefore, all are molecular sieves though none but the aluminosilicates should carry the classical name, zeolite [39].

3.2.1 Zeolites

The crystalline solids of primary catalytic interest, called aluminosilicates, incorporate Al, Si, and O. Naturally occurring minerals and many solids prepared in the laboratory exemplify this class. Several of the more than 100 synthetic aluminosilicates find wide application as industrial catalysts [40].

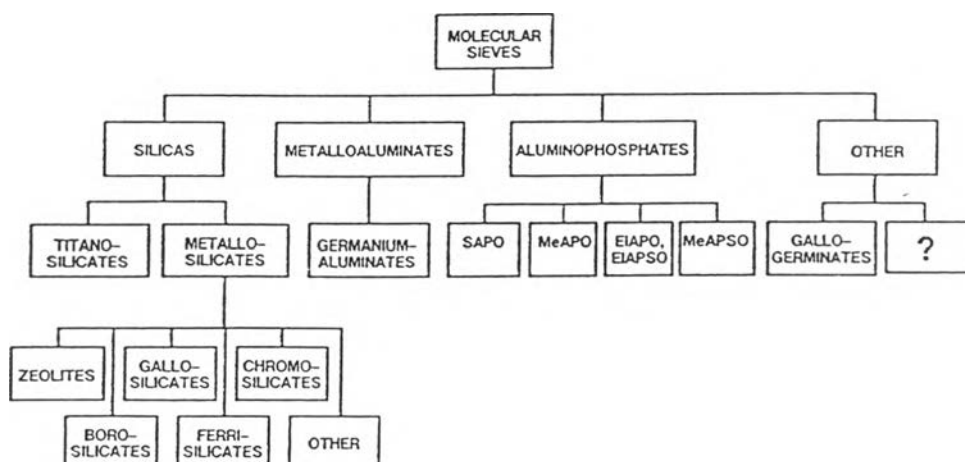


Figure 3.1 Classification of molecular sieve materials indicating extensive variation in composition. The zeolites occupy a subcategory of the metasilicates [39].

Zeolites are highly crystalline, hydrated aluminosilicates [38-42] that upon dehydration develop in the ideal crystal, an uniform pore structure having minimum channel diameter of from about 0.3 to 1.0 nm. The size depends primarily upon the type of zeolite and secondarily upon the cations present and the nature of treatments such as calcination and leaching. The zeolite 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 [41-42].

The structure of zeolites 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. The oxygen atoms are shared between adjoining tetrahedra (Figure 3.2), which can be present in various ratios and arranged in a variety of ways. The framework thus obtained contains pores, channels, and cages, or interconnected voids.

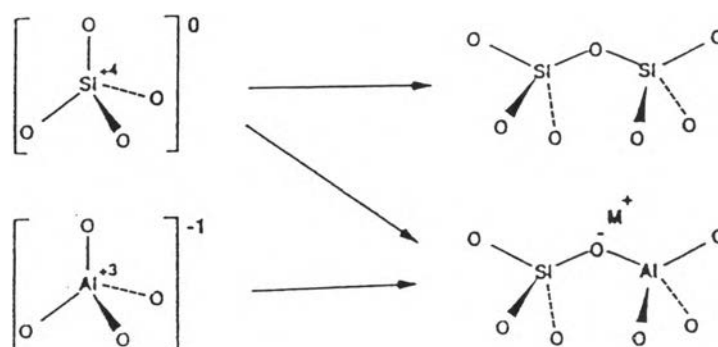
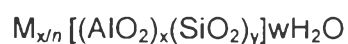


Figure 3.2 Basic building blocks of zeolites-molecular sieves [43].

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 [42]. M is a proton, the zeolite becomes a strong Bronsted acid, w is the number of water molecules per unit cell, and x , y are the total number of tetrahedra per unit cell [37]. As catalysts, zeolites are unique in their ability to discriminate between reactant molecular size and shape [44].

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 [45].

The frameworks of zeolites are used most frequently as adsorbent or catalyst. The Al or Si atoms are located at the intersection of lines that represent oxygen bridges. The X and Y zeolites are structurally and topologically related to the mineral faujasite and frequently referred to as

faujasite-type zeolites. The two materials differ chemically by their Si/Al ratios, which are 1-1.5 and 1.5-3.0 for X and Y zeolite, respectively. In faujasites, large cavities of 1.3 nm in diameter (supercages) are connected to each other through apertures of 1.0 nm.

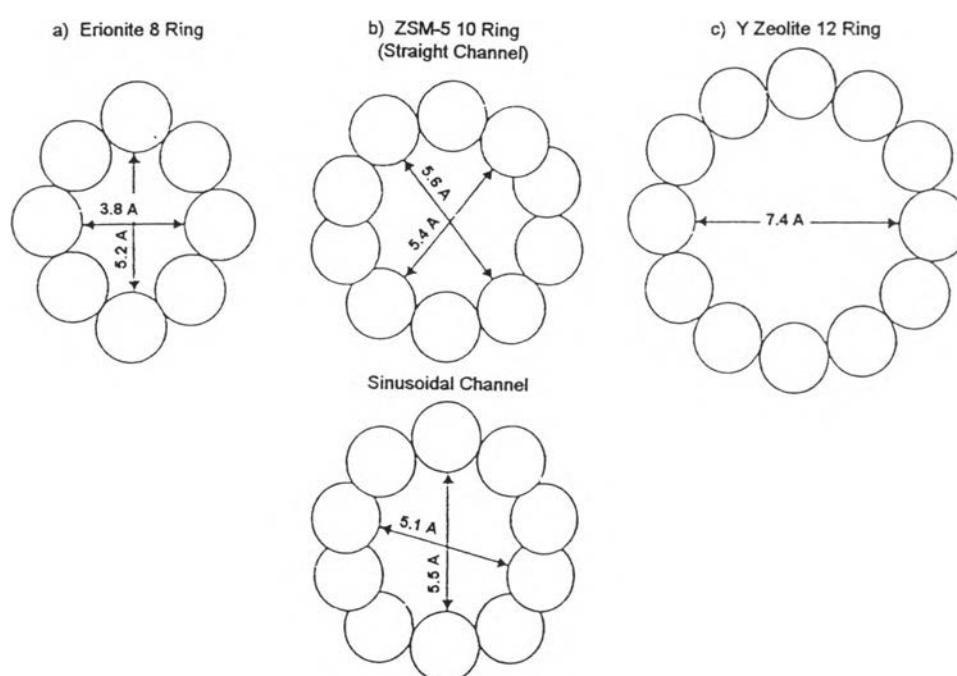


Figure 3.3 Typical zeolite pore geometries [39].

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 (0.6-0.7 nm) (Figure 3.3c) [42].

In silicalite and ZSM-5, the tetrahedra are linked to form the chain-type building block. The chains can be connected to form a layer, as shown in Figure 3.4. Rings consisting of five O atoms are evident in this

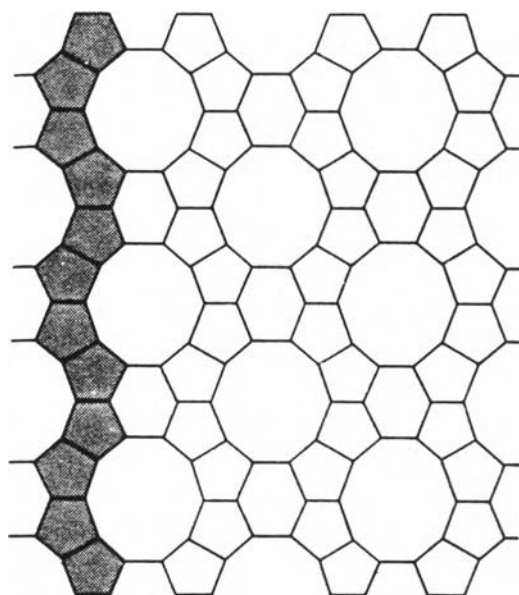


Figure 3.4 Schematic diagram of silicalite layers, formed by linking of the chains through sharing of oxygen in linked SiO_4 tetrahedra [40].

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 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.

The three-dimensional structure of silicalite (and ZSM-5) is represented in Figure 3.5a [40]. 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

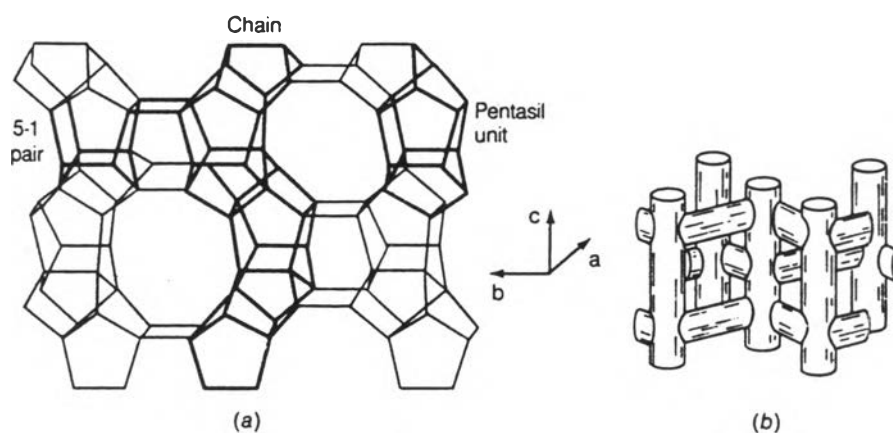


Figure 3.5 Three-dimensional structure of silicalite (ZSM-5) [40].

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

the former [42]. Many molecules are small enough to penetrate into this intracrystalline pore structure, where they may be catalytically converted.

The properties of a zeolite are depended 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 absorptive and catalytic properties of zeolites [46].

3.2.2 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 [39].

Current concepts of silicate structures are based on the principles governing the structures of complex ionic crystals as developed by Pauling. The fundamental unit is a tetrahedral complex consisting of a small cation, such as Si^{+4} , in tetrahedral coordination with four oxygens. The Al^{+3} ion commonly coordinates tetrahedrally as well as octahedrally with oxygen in silicates. This has a profound effect on aluminosilicate structures and their composition. Other ions in tetrahedral coordination include P^{+5} , Ga^{+2} , and Ge^{+4} . The complexity of silicate structures occurs because of the various ways in which the tetrahedral groups may link by the common sharing of oxygen ions to form polynuclear complexes. Considerable variations in chemical composition results from the substitution of cations in tetrahedral and octahedral sites.

The substitution of aluminum for a silicon produces a deficiency in electrical charge that must be locally neutralized by the presence of an additional positive ion (generally one of the alkali metals, R^{+} , or alkaline earths, R^{+2}) within the interstices of the structure. Different types of aluminosilicates result from differences in the way in which the tetrahedra may link in space in one, two, or three dimensions and from the types of other ions that substitute within the interstices [38].

3.3 Acidity of Zeolite

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 trigonally co-ordinated alumina atom is an electron deficient and can accept an electron pair, therefore behaves as a Lewis acid [44, 47].

In general, the increase in Si/Al ratio will increase acidic strength and thermal stability of zeolite [48]. 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, decrease 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 [47].

Recently it has been reported the mean charge on the proton was shifted regularly towards higher values as the Al content decreased [44]. Simultaneously the total number of acidic hydroxyls, governed by the Al atoms, were decreases. 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.

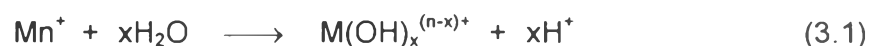
An improvement in thermal or hydrothermal stability has been ascribed to the lower density of hydroxyls groups which parallel to that of Al content [42]. A longer distance between hydroxyl groups decreases the probability of

dehydroxylation that generates defects on structure of zeolites.

3.4 Generation of Acid Centers

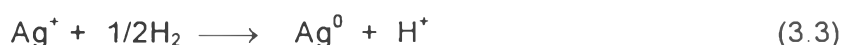
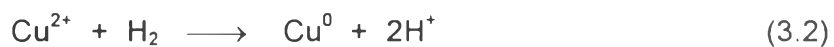
Protonic acid centers of zeolite are generated in various ways. Figure 3.6 depicts the thermal decomposition of ammonium exchanged zeolites yielding the hydrogen form [39].

The Bronsted acidity due to water ionization on polyvalent cations, described below, is depicted in Figure 3.7 [42].



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 noted to increase by reduction with hydrogen at 250-450 °C and to increase with the rise of the reduction temperature [42].



The formation of Lewis acidity from Bronsted sites is depicted in Figure 3.8 [42]. The dehydration reaction decreases the number of protons and increases that of Lewis sites.

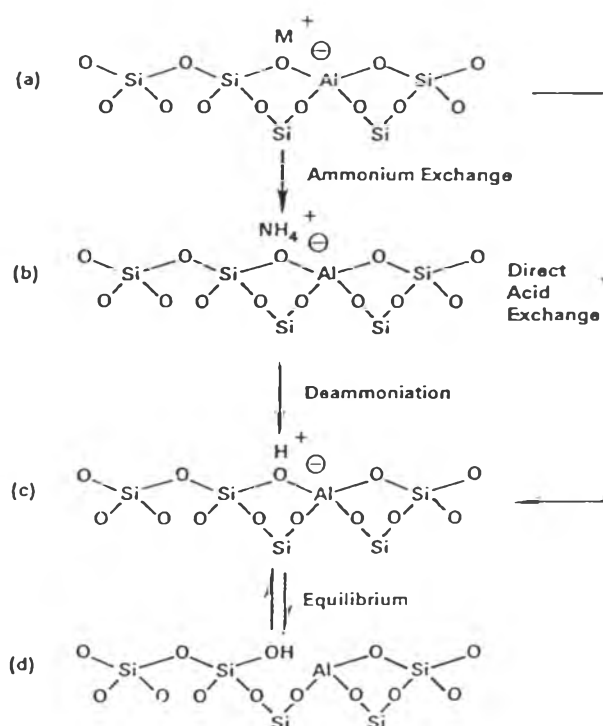


Figure 3.6 Diagram of the surface of a zeolite framework [39].

- 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.

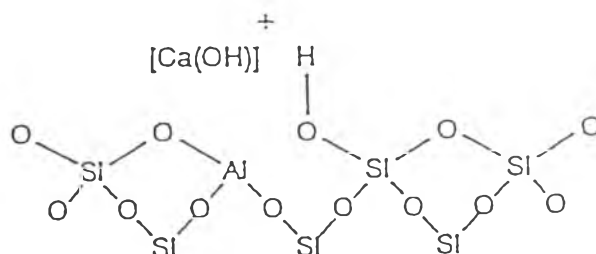


Figure 3.7 Water molecules coordinated to polyvalent cation are dissociated by heat treatment yielding Bronsted acidity [42].

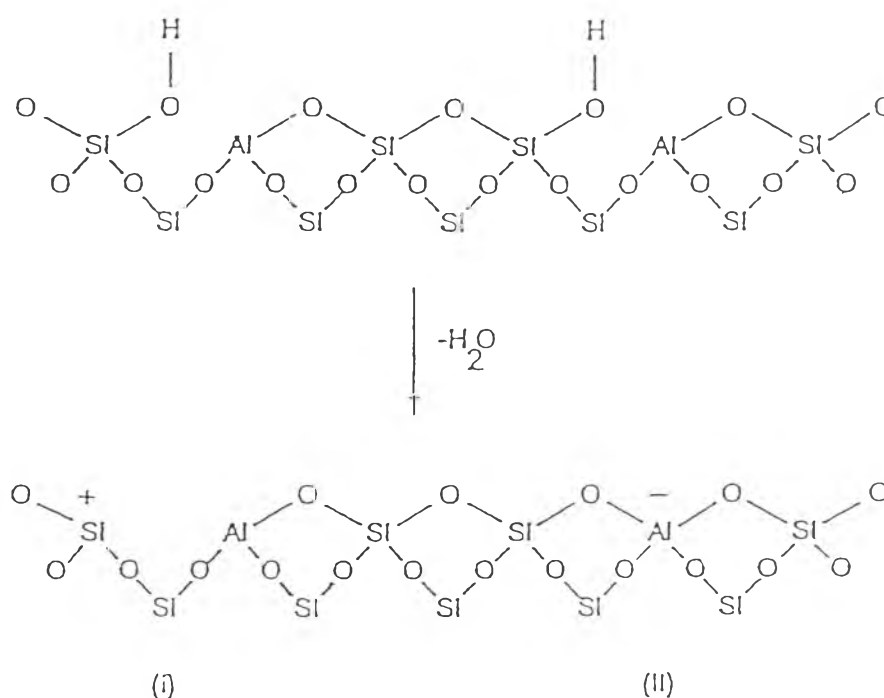


Figure 3.8 Lewis acid site developed by dehydroxylation of Bronsted acid site [42].

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

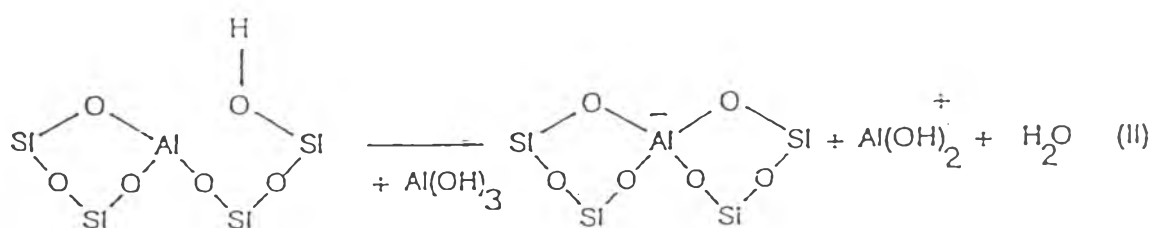
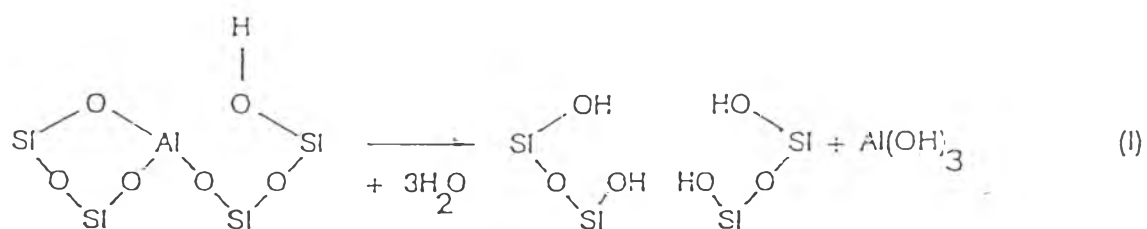


Figure 3.9 Steam dealumination process in zeolite [42].

The enhancement of the acid strength of OH groups is recently proposed to be pertinent to their interaction with those aluminum species sites are tentatively expressed in Figure 3.10 [42]. Partial dealumination might, therefore, yield a catalyst of higher activity while severe steaming reduces the catalytic activity.

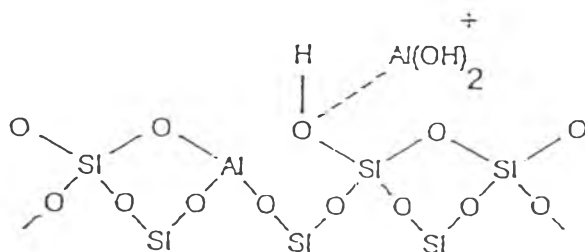


Figure 3.10 The enhancement of the acid strength of OH groups by their interaction with dislodged aluminum species [42].

3.5 Shape Selectivity

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 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 [43,49,50]. These type of selectivity are depicted in Figure 3.11 [43].

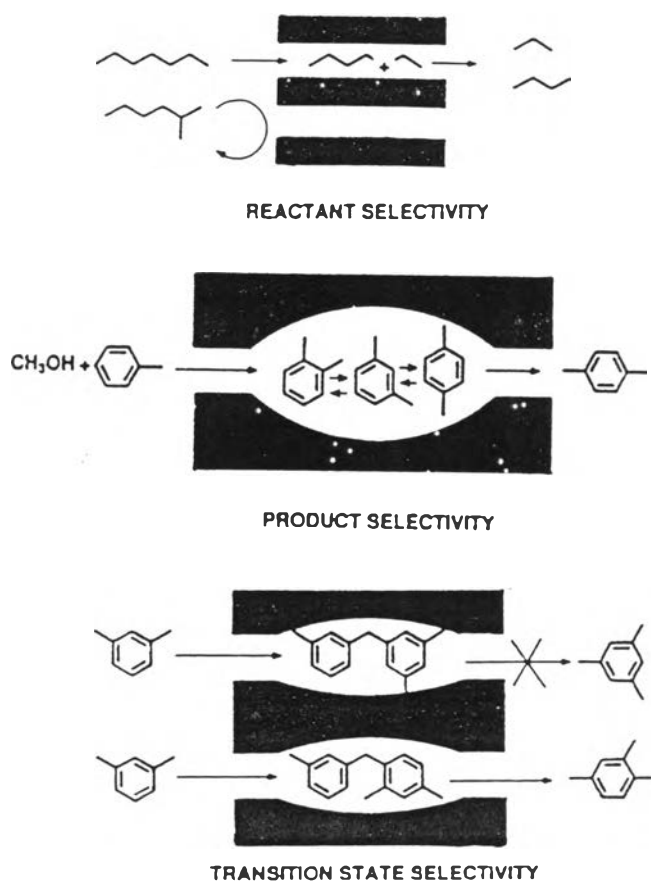


Figure 3.11 Diagram depicting the three type of shape selectivity exhibited by zeolites [43].

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.

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

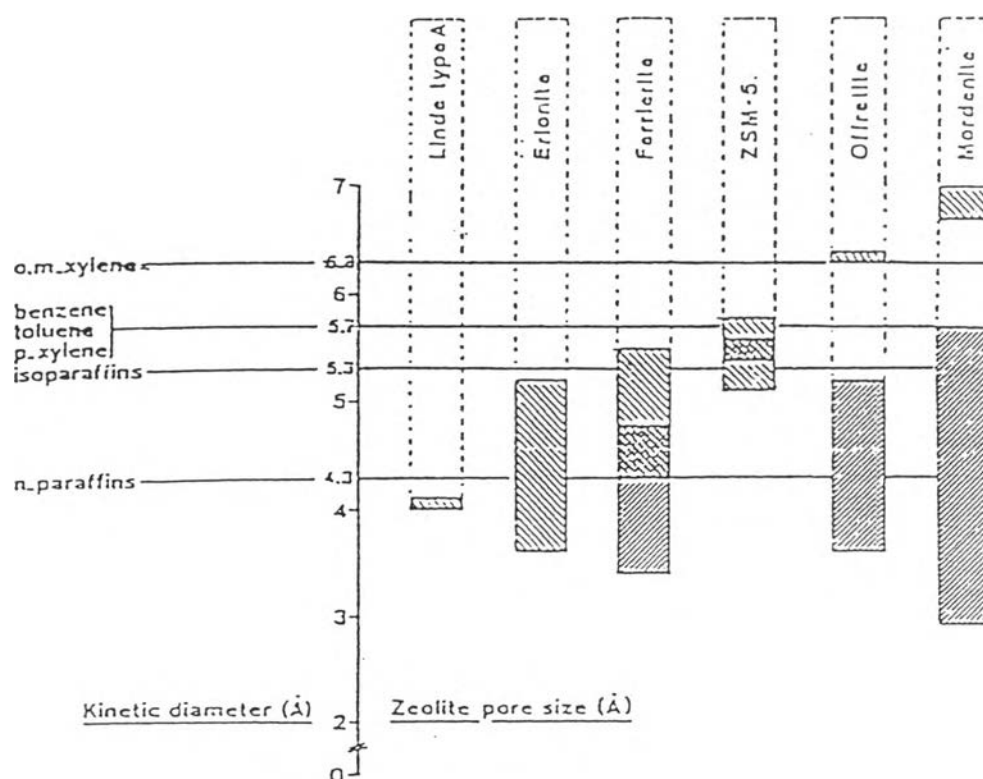


Figure 3.12 Correlation between pore size(s) of various zeolites and kinetic diameter of some molecules [49].

The critical diameter (as opposed to the length) of the molecules (Table 3.1) and the pore channel diameter of zeolites (Table 3.2) 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. Correlation between pore size(s) of zeolites and kinetic diameter of some molecules are depicted in Figure 3.12 [49].

Table 3.1 Kinetic diameters of various molecules based on the Lenard-Jones relationship [41]

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
<i>n</i> -C ₄ H ₁₀	4.3
Cyclopropane	4.23
<i>i</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 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 the crystallographic axis shown in brackets (e.g. $\langle 100 \rangle$) [39].

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	$4.2 \times 4.4[100]$ $2.8 \times 4.8[010]$ $3.3[001]$		
Rho	$3.9 \times 5.1 \langle 100 \rangle$		
Stilbite	$2.7 \times 5.7[101]$	$4.1 \times 6.2[100]$	
Thomsonite	$2.6 \times 3.9[101]$ $2.6 \times 3.9[010]$		
Yugawaralite	$3.1 \times 3.5[100]$ $3.2 \times 3.3[001]$		

3.6 Ion-exchange Reaction in Zeolites

The cation exchange property of zeolite minerals was first observed 100 years ago. The ease of cation exchange in zeolites and other minerals led to an early interest in ion exchange materials for use as water softening agents. Synthetic, noncrystalline aluminosilicate materials were primarily used; in more recent years, organic ion exchange resins are used. Crystalline zeolites have not been used commercially as water softeners.

The ion exchange behaviour of various inorganic exchangers and other types of crystalline silicates such as clay minerals and feldspathoids has been extensively reviewed. Because of their three-dimensional framework structure, most zeolites and feldspathoids do not undergo any appreciable dimensional change with ion exchange; clay minerals, because of their two-dimensional structure, may undergo swelling or shrinking with cation exchange. One application for commonly occurring zeolite minerals (such as clinoptilolite) is in the selective removal of radioactive ions from radioactive waste materials.

The cation exchange behaviour of zeolites depends upon (1) the nature of the cation species, the cation size, both anhydrous and hydrated, and cation charge; (2) the temperature; (3) the concentration of the cation species in solution; (4) the anion species associated with the cation in solution; (5) the solvent (most exchange has been carried out in aqueous solutions, although some work has been done in organic solvents); and (6) the structural characteristics of the particular zeolite. Cation selectivities in zeolites do not follow the typical rules that are evidenced by other inorganic and organic exchangers. Zeolite structures have unique features that lead to unusual types

of cation selectively and sieving. The recent structural analyses of zeolites form a basis for interpreting the variable cation exchange behaviour of zeolites.

Cation exchange in zeolite is accompanied by dramatic alteration of stability, adsorption behaviour and selectivity, catalytic activity and other important physical properties. Since many of these properties depend upon controlled cation exchange with particular cation species, detailed information on the cation exchange equilibria is important. Extensive studies of the ion exchange processes in some of the more important mineral and synthetic zeolites have been conducted [38].

3.7 X-ray Powder Diffraction

The first step in characterization of the solid isolated from the synthesis mixture is X-ray powder diffraction. The most significant information obtained about the solid is obtained from the diffraction pattern. This includes :

1. Successful (or unsuccessful) formation of a crystalline material.
2. Presence of a single phase or mixture of phases.
3. With the presence of sufficient peaks, the identification of the structure type or structure types comprising the mixture.
4. If standards are available, the level of crystallinity obtained from that synthesis batch.
5. Ultimately, with the proper techniques, determination of a new structure.

The X-ray powder diffraction pattern of the solid obtained from the zeolite synthesis mixture is generally taken between the values of $5^{\circ}2\theta$ and $40^{\circ}2\theta$. It is within this range that the most intense peaks characteristic of the

zeolite structure occur. The peaks at values higher than $40^\circ 2\theta$ are of significantly low intensity, and, depending on the level of crystallinity, may not be observable. Therefore, for most routine X-ray identification of zeolite phases, the range between $5^\circ 2\theta$ and $40^\circ 2\theta$ is examined.

A common occurrence in zeolite synthesis is the presence of a noncrystalline product from a given reaction mixture. An example of an X-ray diffraction pattern for a typical unsuccessful synthesis is shown in Figure 3.13(a). Beside the noncrystalline products possible from a given reactive mixture, crystalline but non-zeolite material may be obtained. The commonly observed crystalline phase obtained from an unsuccessful synthesis of the high-silica zeolites, for example, is cristobalite, a dense quartz phase. The cristobalite phase is a simple pattern to recognize, as it contains only one very intense line, between $5^\circ 2\theta$ and $40^\circ 2\theta$. A typical X-ray trace of cristobalite is shown in Figure 3.13(b). In some systems, mixtures are obtained. These can be readily identified if individual X-ray diffraction patterns of both components are already known. For example, in Figure 3.13(c), a mixture of cristobalite and ZSM-5 was produced from the reaction mixture. As both components are already well known, a comparison of these values with standard literature values for the X-ray diffraction patterns of cristobalite and ZSM-5 will confirm these components of the mixture. By changing the synthesis parameters, the zeolite phase can (in many cases) be optimized and the second phase suppressed, as shown in Figure 3.13(d). Here a sharp pattern for a well-crystallized ZSM-5 sample was obtained.

Many times in exploratory zeolite synthesis aimed at producing new structures, material are obtained with X-ray patterns that appear to indicate

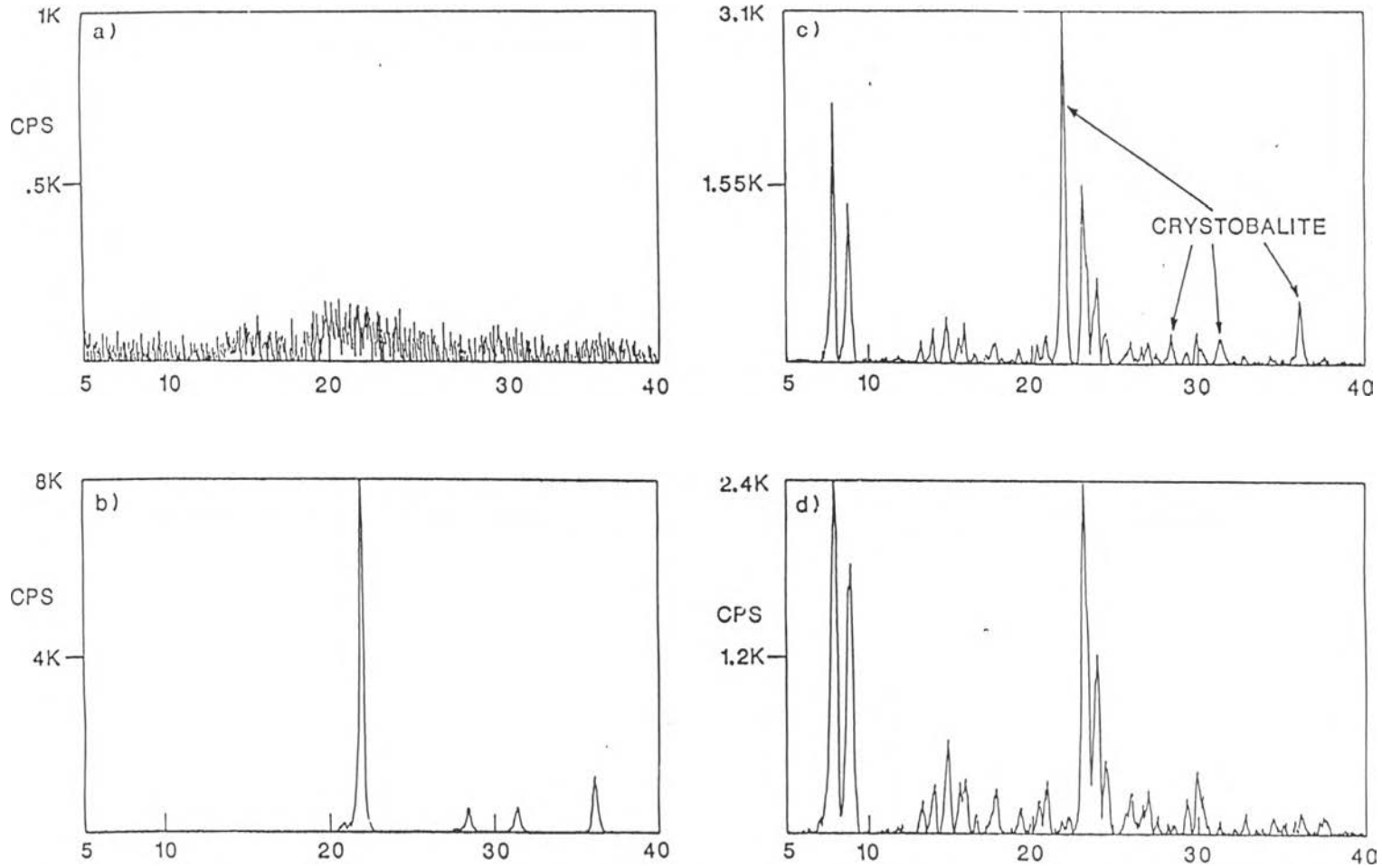


Figure 3.13 X-ray powder diffraction used to identify phases in synthesis of zeolites [39].

- a) Noncrystalline product b) crystalline but non-zeolitic phase (cristobalite shown in this example)
 c) mixture of phase (cristobalite and ZSM-5) d) pure single crystalline phase (ZSM-5)

a single phase and are already related in peak position to a known structure. However, in some cases the peak intensities are not in agreement. Changes in relative peak intensity have been to occur [39]:

1. Upon removal of an organic additive from the pores or changing the cations within the pores of the higher-silica-contain materials.
2. Upon changing the counter-ion.
3. When large crystals have a preferred orientation in the X-ray sample holder.
4. When other ions are substitute into the framework structure.

3.8 Structural Features from Infrared Spectroscopy

Infrared spectroscopy can yield information concerning structure details of the material. In addition, it can be used to confirm acid characteristics and isomorphous substitution, as well as to aid in relating different zeolite materials by their common structural features.

The IR spectrum of zeolites in the range of $300\text{-}1300\text{ cm}^{-1}$, mid-infrared region, contains the fundamental framework vibrations of the $\text{Si}(\text{Al})\text{O}_4$ groupings. In general, each zeolite structure has a characteristic infrared pattern; however, some common features are observed. These vibrations include the asymmetric and symmetric stretch, double ring vibrations, T-O bending modes, and possibly pore opening modes. The infrared spectrum can be classified into two groups of vibrations: (1) internal vibrations of the framework TO_4 , which are insensitive to structural vibration; and (2) vibrations related to the external linkage of the TO_4 units in the structure. The latter are sensitive to structural vibration. No distinction can be made between the SiO_4

and AlO_4 related vibrations, as the similarity in the mass of the two T atoms precludes separation. The general zeolite infrared assignments for the structure-insensitive (internal tetrahedra) and structure-sensitive (external linkages) vibrations are given in Table 3.3.

Table 3.3 Zeolite infrared assignments, cm^{-1} [39]

Internal tetrahedra :	
Asm. stretch	1250-950
Sym. stretch	720-650
T-O bend	420-500
External linkages :	
Double ring	650-500
Pore opening	300-420
Sym. stretch	750-820
Asym. stretch	1050-1150 (sh)

The infrared spectra of a number of 5-member ring zeolites and molecular sieves have been reported and listed in Table 3.4. Included in the listing are two zeolites with unknown structures, ZSM-34 and ZSM-35. The structure-sensitive vibrations near 1200 cm^{-1} and 550 cm^{-1} provide information on the differentiation of these zeolite types in addition to identifying some framework features of zeolites of undetermined crystal structures. For ZSM-5 structure, the external asymmetric stretching vibration around 1225 cm^{-1} is present in the spectra of structures containing four chains of 5-member rings arranged around a twofold screw axis. In the region near 550 cm^{-1} , absorption is attributed to another structure sensitive band caused by the double 5-member ring blocks of types A and B as depicted in Figure 3.14 [39].

Table 3.4 IR data between 1500 and 400 cm^{-1} of zeolites containing 5-member rings [39]

ZEOLITE TYPES	ASYM. STRETCH ^a		SYM. STRETCH ^a	
	EXTERNAL	INTERNAL	EXTERNAL	INTERNAL
Silicalite	1225(sh)	1093(s)	790(w)	—
ZSM-5	1225(sh)	1093(s)	790(w)	—
Boralite	1228(sh)	1096(s)	800(w)	—
ZSM-11	1225(sh)	1093(s)	790(w)	—
Mordenite	1223(sh)	1045(s)	800(w)	720(w)
Ferrierite	1218(sh)	1060(s)	780(w)	695(w)
Epistilbite	1175(sh)	1050(s)	795(w)	690(w)
Dachiardite	1210(sh)	1050(s)	775(w)	670(w)
Bikitaite	1105(sh)	968(s)	782(w)	680(w)
ZSM-39	—	1090(s)	790(w)	—
Melanophlogite	—	1118(s)	795(w)	—
ZSM-34	—	1060(s)	785(w)	—
ZSM-35	1232(sh)	1070(s)	790(w)	—
Aerosil	—	1100(s)	810(w)	—

ZEOLITE TYPES	DOUBLE RING ^{b,c}	T-O BEND ^b
Silicalite	550(m)	450(s)
ZSM-5	550(m)	450(s)
Boralite	550(m)	450(s)
ZSM-11	550(m)	450(s)
Mordenite	580, 560(w)	450(s)
Ferrierite	563(w)	455(s)
Epistilbite	563(w)	455(s)
Dachiardite	558(w)	440(s)
Bikitaite	—	460(s)
ZSM-39	—	460(s)
Melanophlogite	—	465(s)
ZSM-34	635, 580, 550(w)	465(s)
ZSM-35	590(m)	460(s)
Aerosil	—	468(s)

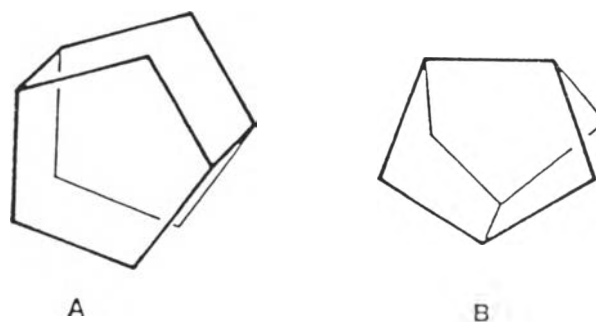


Figure 3.14 Types of 5-member ring blocks: (A) 5-5 block; (B) 5-3 block [39].