

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 aluminium, 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 absorption 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 sieve were known when McBain put forth his definition; the zeolite 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 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 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 sieve

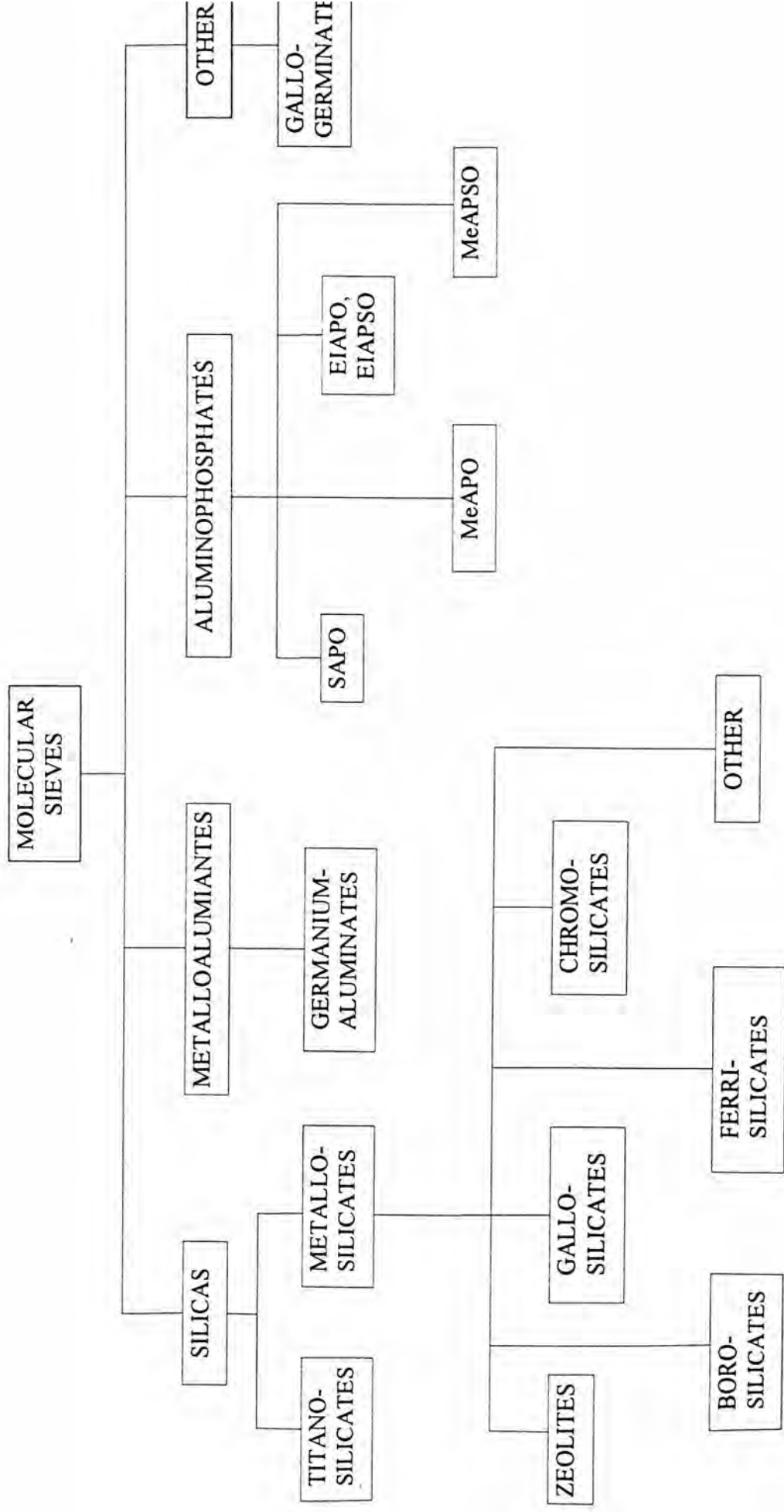


Figure 3.1 Classification of molecular sieve materials [27].

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 [27].

3.2 Zeolites

Zeolites were first identified by Constredt in 1756 [28]. 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 catalysts 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, in addition, provides a novel means of obtaining high dispersions of these metals within the constrained pores of industrially interesting catalyst material.

3.2.1 Structure of Zeolite

Zeolites are porous, crystalline aluminosilicate that develop uniform pore structure having minimum channel diameter of 0.3-0.1 nm. This size depends primarily upon the type of 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 3.2). 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.

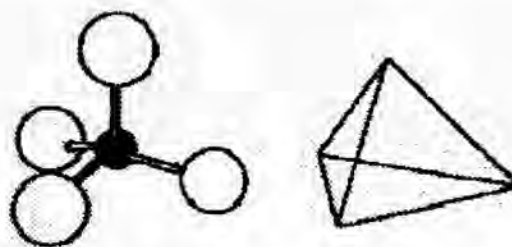
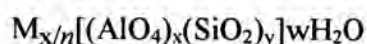


Figure 3.2 SiO_4 or AlO_4 tetrahedra [33]

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(D6R), 8-8(D8R)-member double rings, and 4-1, 5-1 and 4-4-1 branched rings [27]. The topologies of these units are shown in figure 3.3. 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 [27]. Both zeolite ZSM-5 and ferrierite are described by their 5-1 building units. Offertile, zeolite L, cancrinite, and erionite are generated using only single 6-member rings. Some zeolite structures can be described by several building units. The sodalite framework can be built from either the single 6-member ring or the single 4-member ring. Faujasite (type X or type Y) and zeolite A can be constructed using 4 ring or 6 ring building units. Zeolite A can also be formed using double 4 ring building units, whereas faujasite cannot.

Zeolite may be represented by the general formula,



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 [29]. M is a proton, the zeolite becomes a strong Brønsted acid. As a catalyst, zeolite becomes a strong Brønsted acid. As catalysts, zeolites are unique in their ability to discriminate between reactant molecular size and shape [30].

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 3.4 [31].

3.2.1.1 Small pore zeolites

Structures of some of the small pore zeolites are illustrated in Figure 3.5. The erionite structure, Figure 3.5 (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 3.5 (b), the double 6 rings layer sequence is ABCABC, and the double 6 rings units are linked together through tilted 4 ring units. The framework contains large ellipsoidal cavities, Figure 3.4 (c), each entered through six 8 ring units. These cavities are joined together via their 8 ring units, forming a 3 dimensional channel system.

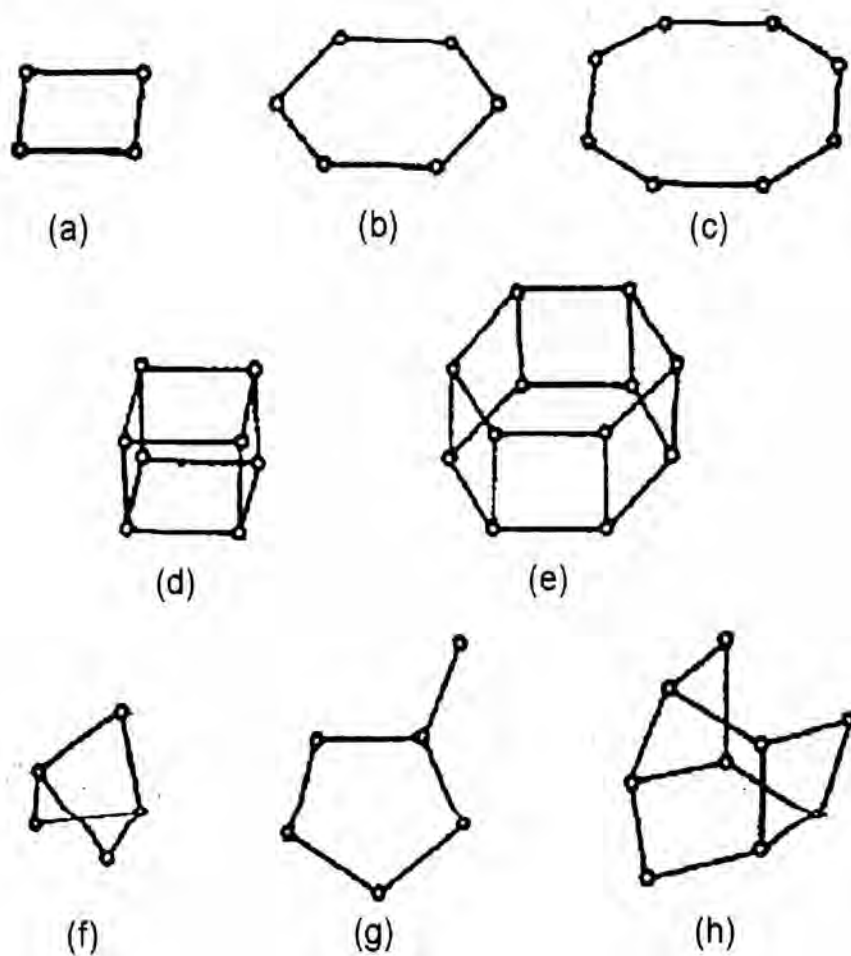


Figure 3.3 Secondary building units (SBU's) found in zeolite structures [32].

Erionite 8 Ring

ZSM-5 10 Ring
(Straight Channel)

Y Zeolite 12 Ring

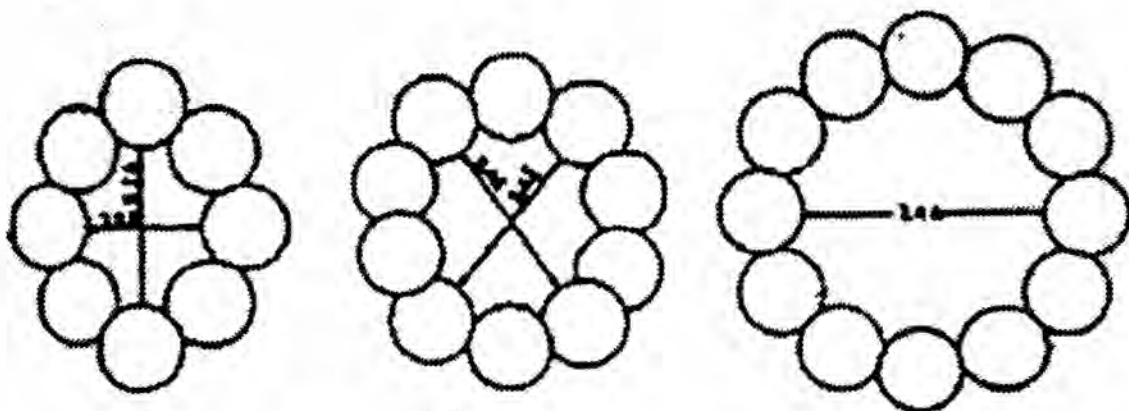


Figure 3.4 Typical Zeolite pore geometries [31].

3.2.1.2 Medium pore zeolites

The channel system of zeolite ZSM-5, presented in Figure 3.6, 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 $5.4 \times 5.6 \text{ \AA}$ (straight channel) and $5.1 \times 5.4 \text{ \AA}$ (sinusoidal channel) based on oxygen radii 1.35 \AA .

3.2.1.3 Large pore zeolite

The faujasite structure, Figure 3.7 (a), is built up of truncated octahedra interconnected via double 6 ring units. Faujasite contains extremely large supercages (~13 Å diameter) entered through 12 oxygen ring.

Mordinite, Figure 3.7 (b), is characterized by a one dimensional system of parallel elliptical channels, defined by 12 oxygen ring.

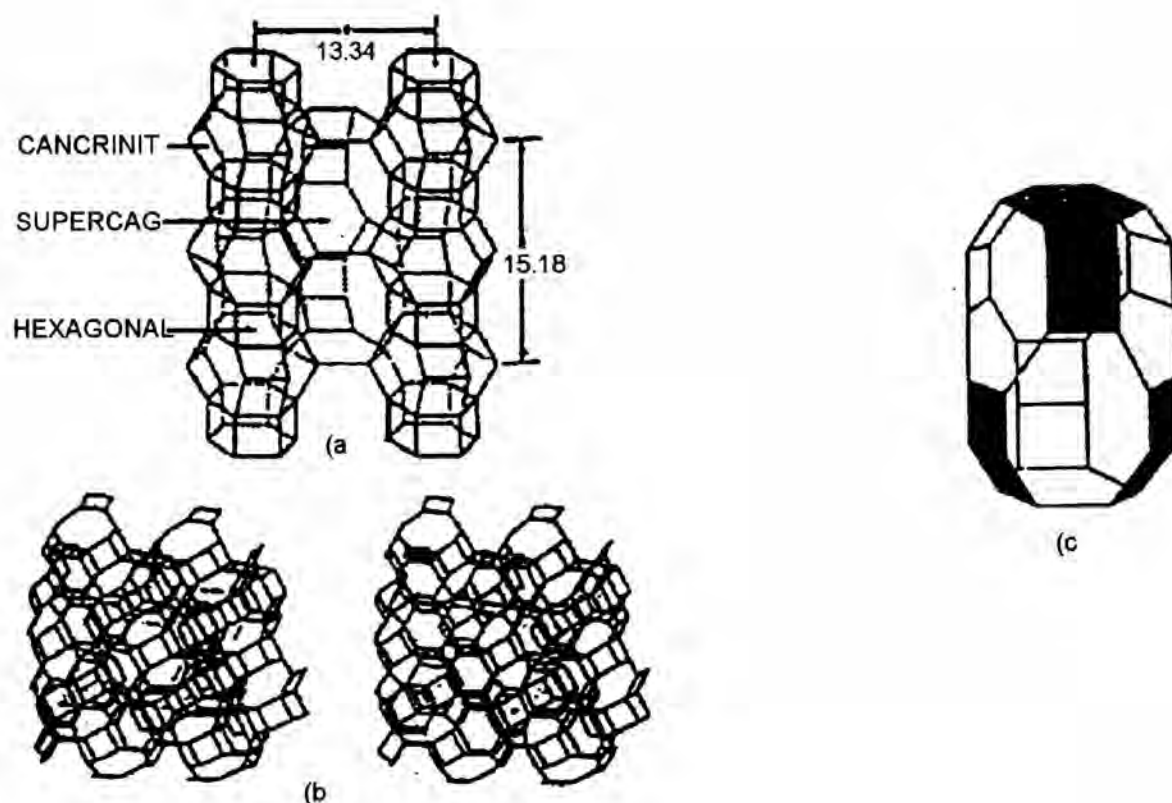


Figure 3.5 Small pore zeolites (a) Erionite framework (b) chabazite framework (c) Chabazite cavity [31].

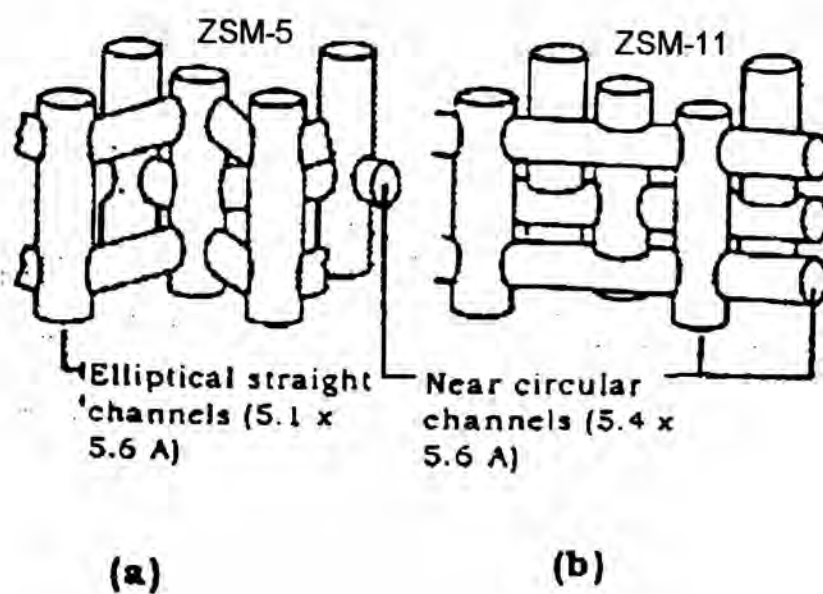


Figure 3.6 ZSM-5 and ZSM-11 channel system [31].

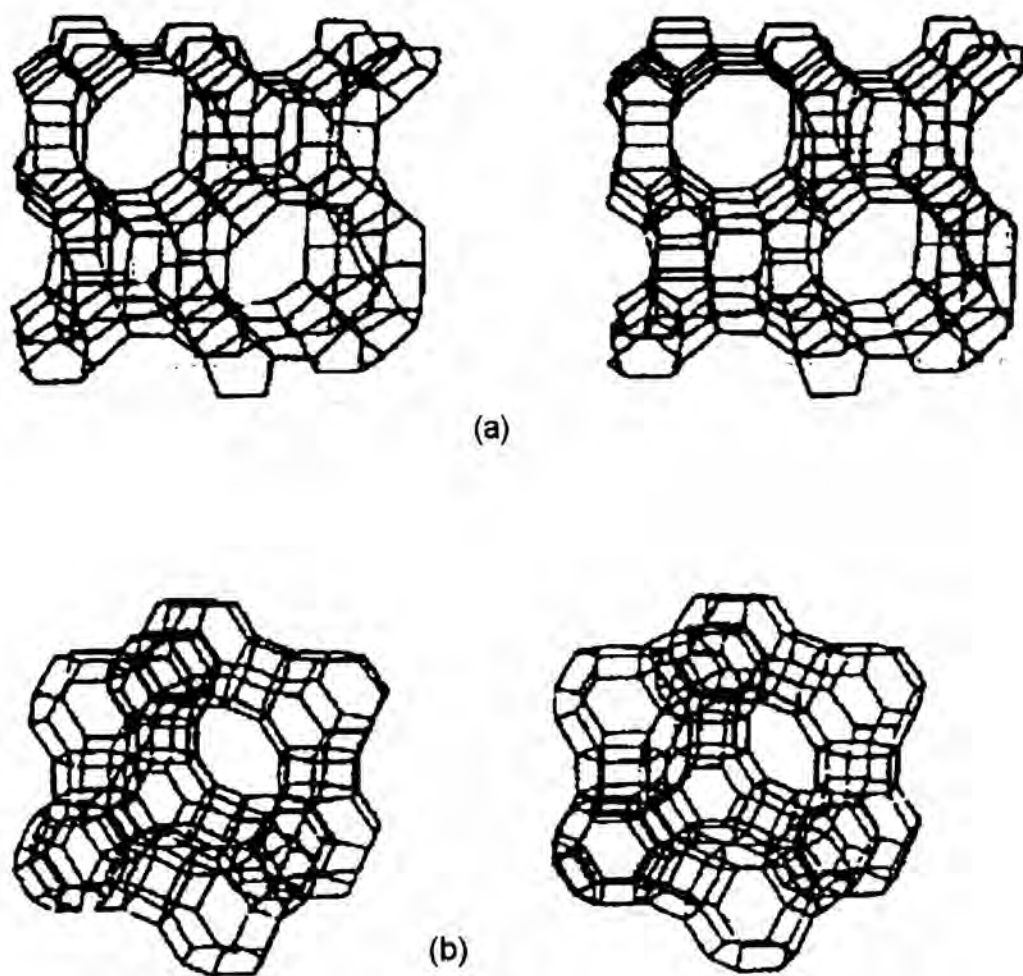


Figure 3.7 Large pore zeolites

(a) Mordenite framework

(b) Faujasite framework [31].

Table 3.1 Zeolites and their secondary building units. The nomenclature used is consistent with that presented in Figure 3.3 [27].

ZEOLITE	SECONDARY BUILDING UNITS								
	4	6	8	4-4	6-6	8-8	4-1	5-1	4-4-1
Bikitaite								X	
Li-A (BW)	X	X	X						
Analcime	X	X							
Yugawaralite	X		X						
Episitbite								X	
ZSM-5								X	
ZSM-11								X	
Ferrierite								X	
Dachiardite								X	
Brewsterite	X								
Laumonite		X							
Mordenite								X	
Sodalite	X	X							
Henulandite									X
Stibite									X
Natrolite							X		
Thomsonite							X		
Edingtonite							X		
Cancrinite		X							
Zeolite 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				

3.3 Zeolites as Catalyst

The first use of zeolites 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 racking 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 3.2 and described below.

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 transformation can take place. In the faujasites this is typically in the series of large cavities easily available via three-dimensional Open-pore networks.

Table 3.2 Correlation between zeolite properties and catalytic functionality [33].

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 in the zeolite substrate
Salt occlusion	Controls pore size, provide another method of metal incorporation and can improve thermal stability and poisoning resistance
Framework modification	Varied lattice charge (by synthesis or modification) to enhance active site production and thermal stability

Further flexibility which is useful for planned catalytic uses arises in the more recently produced zeolites with subtly different cavity and channels systems. ZSM-5, for instance, has a three-dimensional system linked via intersections rather than cavities and mordenite catalysts 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 produce 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 are 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 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.

3.3.1.5 Framework modification

The electrostatic field of 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 Si : Al causes a greater separation of negative charge and hence higher

field gradients (obviously also conditioned by cation position and cation style). 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 faujasites 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 on other frameworks is by no means so facile.

3.4 Zeolite Active Sites

3.4.1 Acid sites

Classical Brønsted and Lewis acid models of acidity have been used to classify the active sites on zeolites. Brønsted acidity is proton donor acidity; a tridimensionally co-ordinated aluminum atom is an electron deficient and can accept an electron pair, therefore behaves as a Lewis acid [30, 34].

In general, the increase in Si/Al ratio will increase acidic strength and thermal stability of zeolites [35]. Since the number of acidic OH groups depend on the number of aluminum in zeolites framework, decrease in Al content is expected to reduce catalytic activity of zeolite. If the effect of increase in the acidic centers, increase in Al content, shall result in enhancement of catalytic activity.

Based on electrostatic consideration, the charge density at a cation site increase 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 [34].

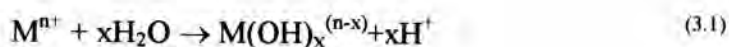
Recently it has been reported the mean charge on the proton was shifted regular towards higher values as the Al content decreased [30]. Simultaneously the total number of acidic hydroxyls, governed by the Al atoms, were decreased. This evidence emphasized that the entire acid strength distribution (weak, 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 hydroxyl groups which is parallel to that of Al content [30]. A longer distance between hydroxyl groups decreases the probability of dehydroxylation that generates defects on structure of zeolites

3.4.2 Generation of Acid Centers

Protonic acid centers of zeolite are generated in various ways. Figure 3.8 depicts the thermal decomposition of ammonium exchanged zeolites yielding the hydrogen form [27].

The Brønsted acidity due to water ionization on polyvalent cations, described below, is depicted in figure 3.9 [29].



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

Brønsted acid sites are also generated by the reduction of transition metal cations. The concentration of OH groups of zeolite containing transition metals was note to increase by hydrogen at 250-450 °C to increase with the rise of the reduction temperature [29].



The formation of Lewis acidity from Brønsted sites is depicted in Figure 3.10 [29]. 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.

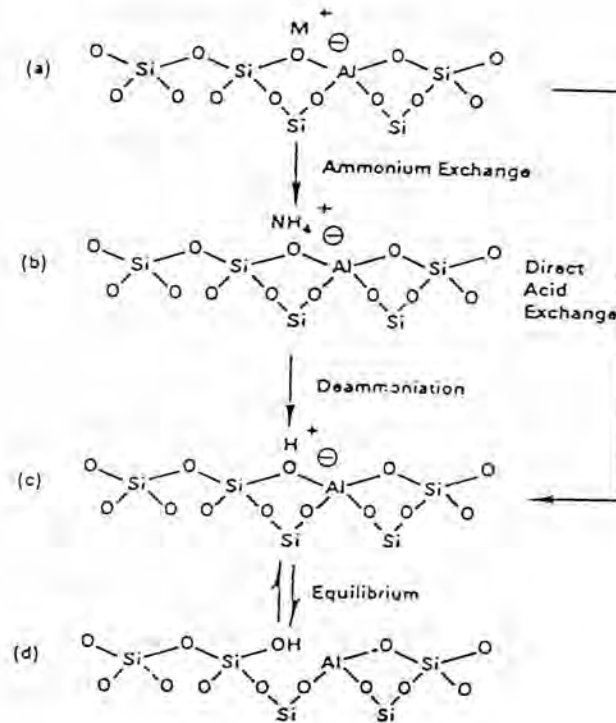


Figure 3.8 Diagram of the surface of a zeolite framework [27].

- In the as-synthesis 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, from.
- 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.

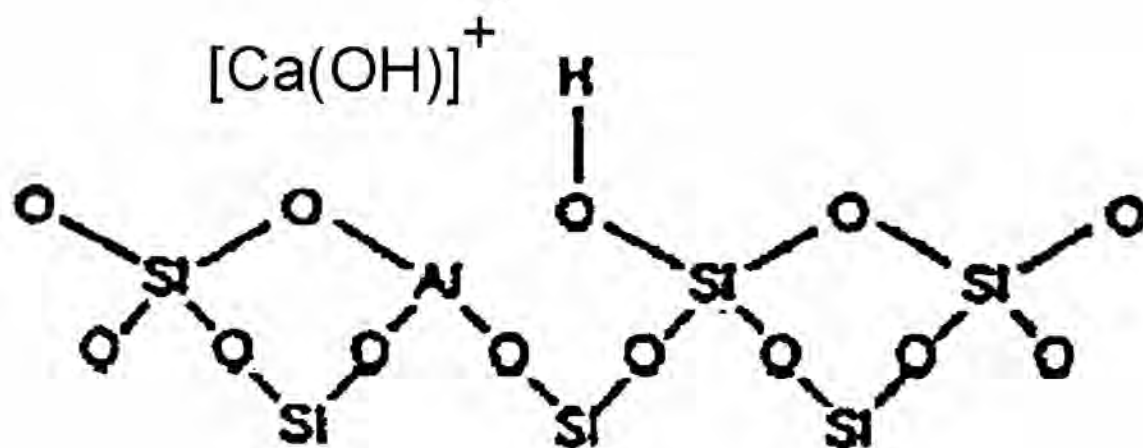


Figure 3.9 Water molecules co-ordinated to polyvalent cation are dissociated by heat treatment yielding Brønsted acidity [29].

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

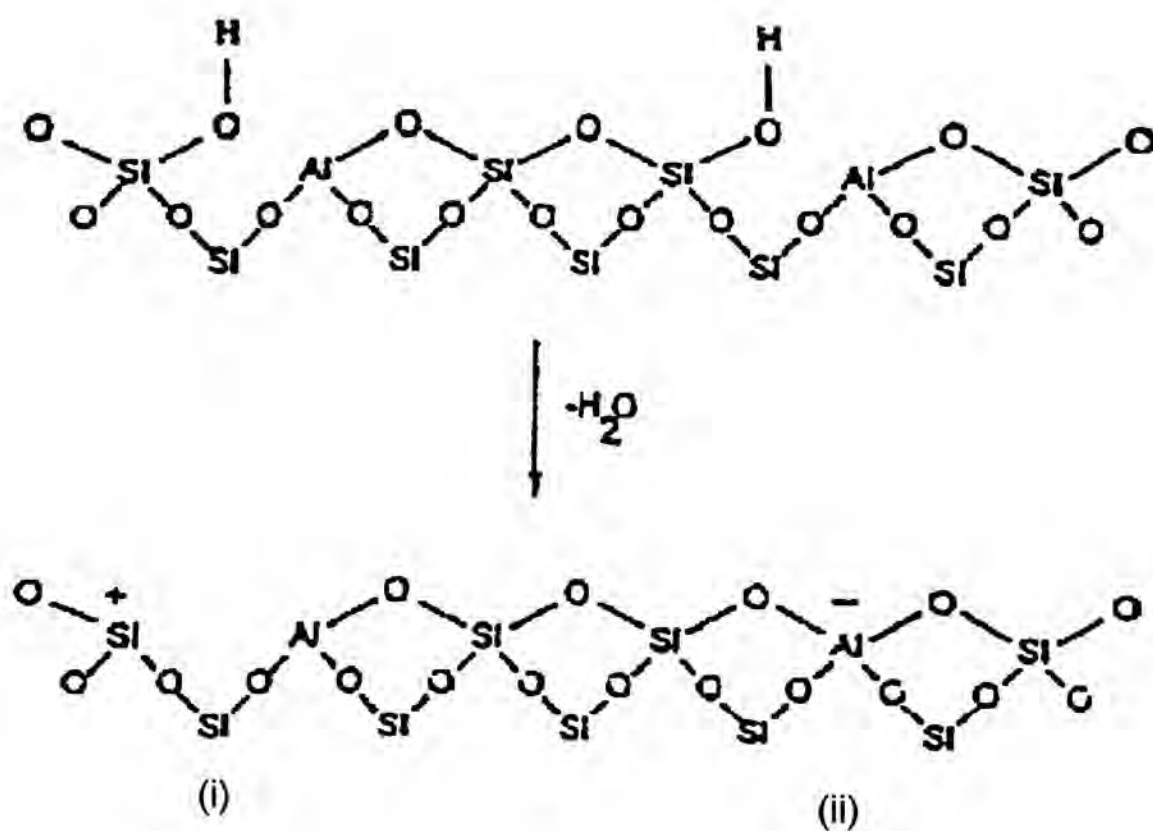


Figure 3.10 Lewis acid site developed by dehydroxylation of Brønsted acid site [29].

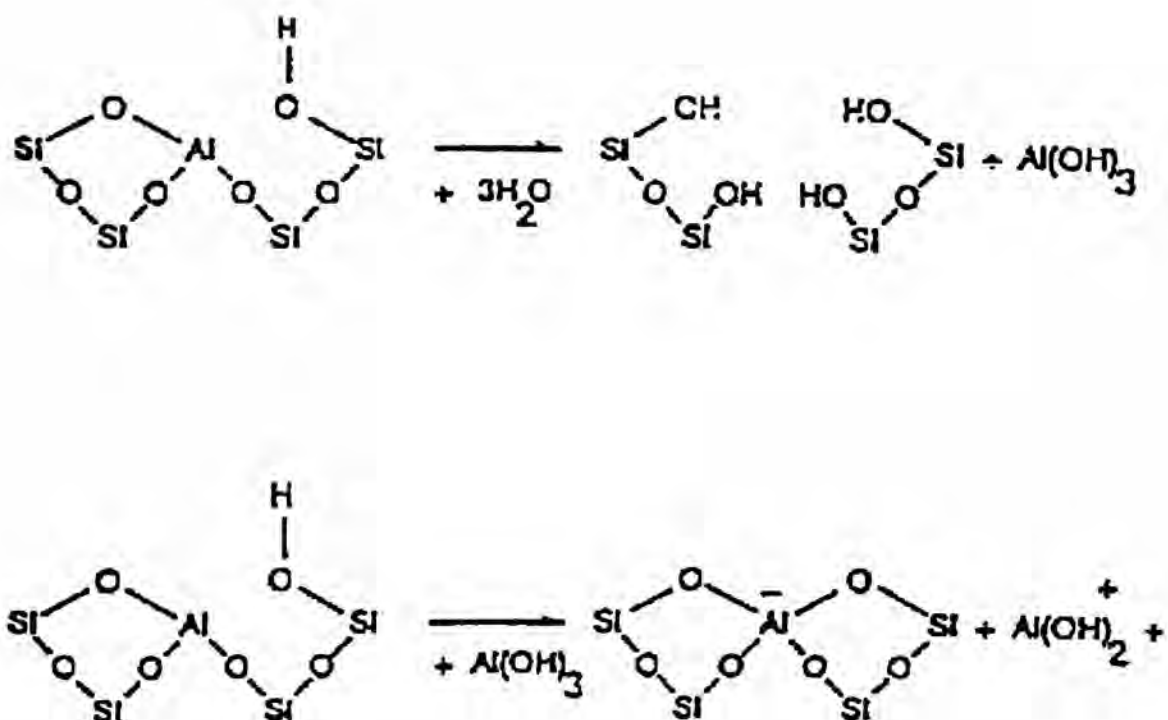


Figure 3.11 Steam dealumination process in zeolite [29].

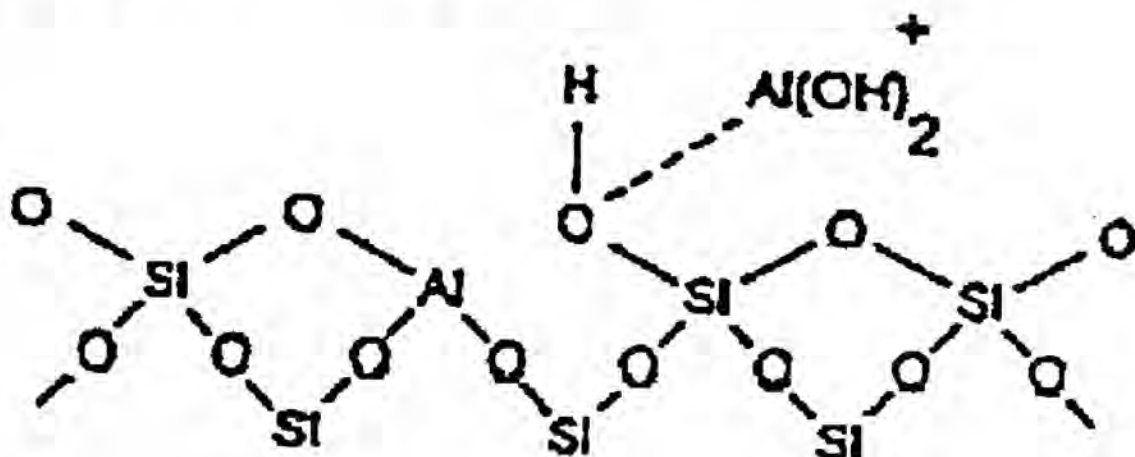


Figure 3.12 The enhancement of the acid strength of OH groups by their interaction with dislodged aluminum species [29].

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 3.12 [29]. Partial dealumination might therefore yield a catalyst of higher activity while severe steaming reduces the catalytic activity.

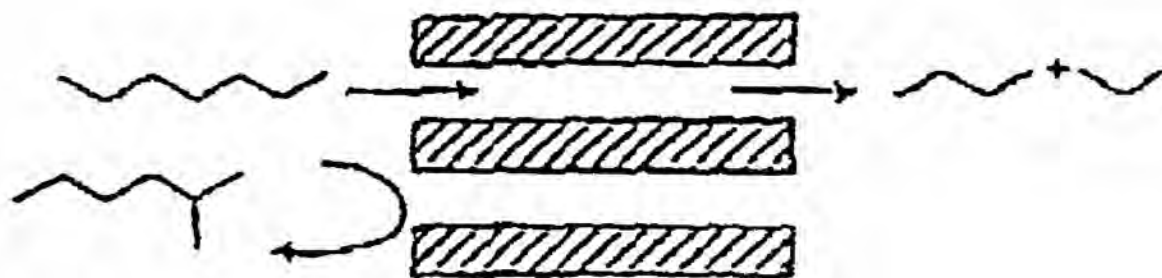
3.4.3 Basic Sites

In certain instances reactions have been shown to be catalyzed at basic (cation) sites in zeolite without any influences from acid sites. The best characterized example of this is that K-Y which splits n-hexane isomers at 500 °C. The potassium cations has been shown to control the unimolecular cracking (β -scission). Free radical mechanisms also contribute to surface catalytic reactions in these studies.

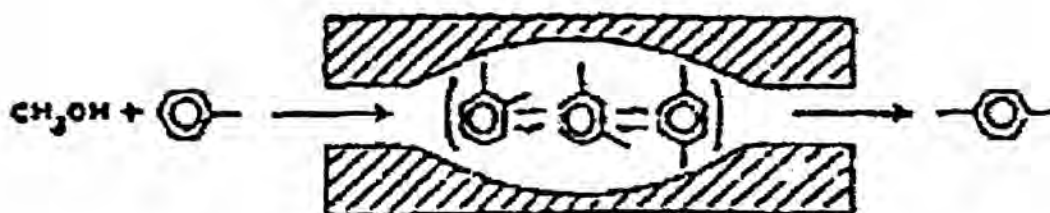
3.5 Shape-Selective Catalysis

Many reactions involving carbonium intermediates are catalyzed by acidic zeolites. With respect to a chemical standpoint the reaction mechanisms are not fundamentally different with zeolites or with any other acidic oxides. What zeolite add is shape selectivity effect. The shape selective characteristics of zeolites influence their catalytic phenomena by three modes; reactants shape selectivity, products shape selectivity and transition states shape selectivity [27, 36, 37]. These type of selectivity are predicted on Figure 3.13 [27].

a) Reactants selectivity



b) Products selectivity



c) Transition states selectivity

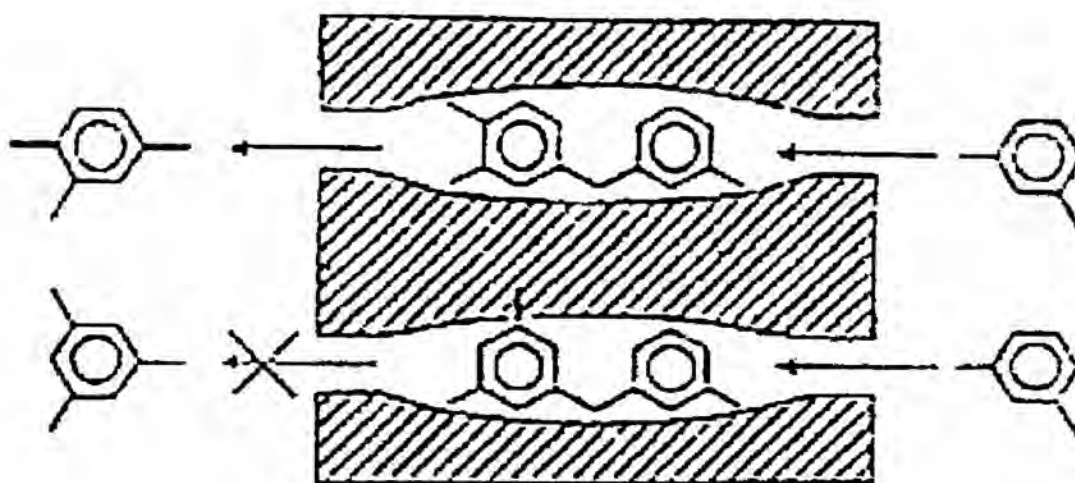


Figure 3.13 Diagram depicting the three type of selectivity [27].

Reactants of charge selectivity results from the limited diffusibility of some of the reactants, which cannot effectively enter and diffuse inside crystal pore structures of the zeolites.

Product shape selectivity occurs as slowly diffusing product molecules cannot escape from the crystal and undergo secondary reactions. This reaction path is established by monitoring changes in product distribution as a function of varying contact time.

Restricted transition state shape selectivity is a kinetic effect arising from local environment around the active site, the rate constant for a certain reaction mechanism is reduced 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 3.3 [38] presents values of selected critical molecular diameters and Table 3.4 [27] presents values of the effective pore size of various zeolites.

Table 3.3 Kinetic diameters of various molecules based on the Lennard-Jones relationship [36].

	KINETICS 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

Table 3.4 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 channels. The channels are parallel to the crystallographic axis shown in brackets (e.g. $\langle 100 \rangle$) [39].

STRUCTURE	4 -MR	10-MR	12-MR
Bikitaite	3.2×4.9[001]		
Brewsterite	2.3×5.0[100] 2.7×4.1[001]		
Cancrinite			6.2[100]
Chabazite	3.6×3.7[001]		
Dachiarite	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]
Heulandite	4.0×5.5[100] 4.1×4.7[001]	4.4×7.2[001]	
ZK-5	3.9 $\langle 100 \rangle$		
Laumonite		4.0×5.5[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 $\langle 100 \rangle$		
Sibite	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 Beta Zeolite

Beta zeolite was initially synthesized by Wadling et al. [40] using tetraethylammonium hydroxide as an organic template. The structure of Beta zeolite was described by Treacy and Newsam [41] and Higgins et al. [42]. Beta zeolite is an intergrowth hybrid of two distinct but closely related structures [9,41,42] which have tetragonal and monoclinic symmetry. In both systems, straight 12-membered-ring channels are present in two crystallographic directions perpendicular to [001], while the 12-membered-ring in the third direction, parallel to the c axis, is sinusoidal. The sinusoidal channels have circular openings (5.5\AA), and the straight channels have elliptical openings. The only difference between the two polymorphs is in the pore dimension of the straight channels. In tetragonal system, the straight channels have openings of $6.0\times 7.3\text{\AA}$, whereas in the monoclinic system they are $6.8\times 7.3\text{\AA}$.

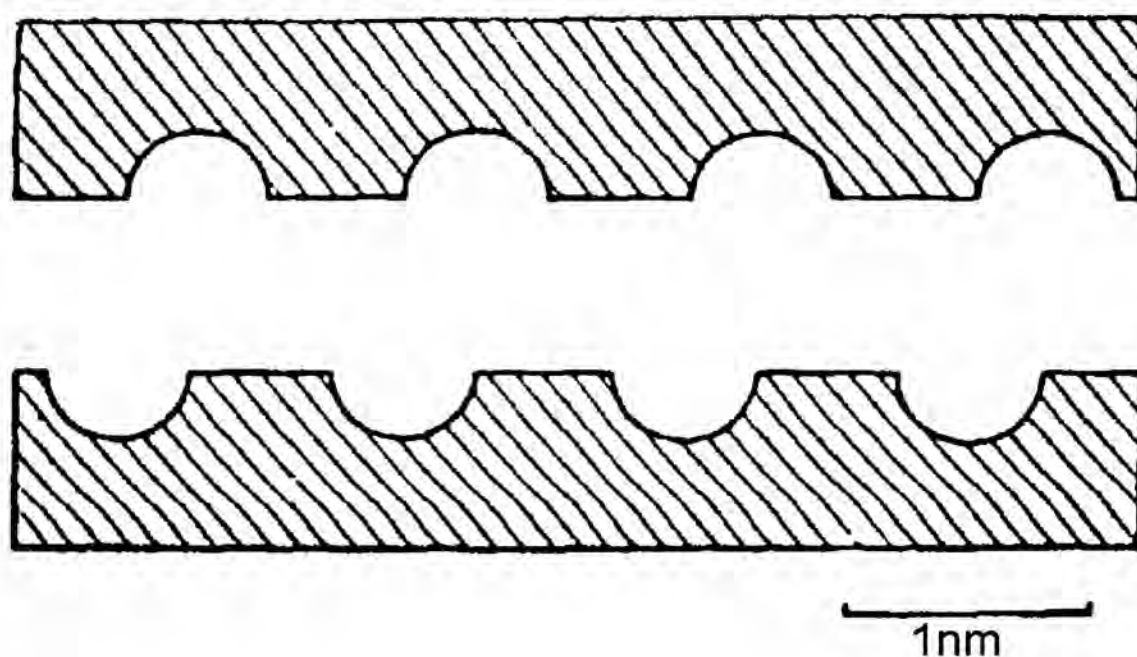


Figure 3.14 Cross section of the linear channels of the tetragonal and monoclinic polymorphs of zeolite

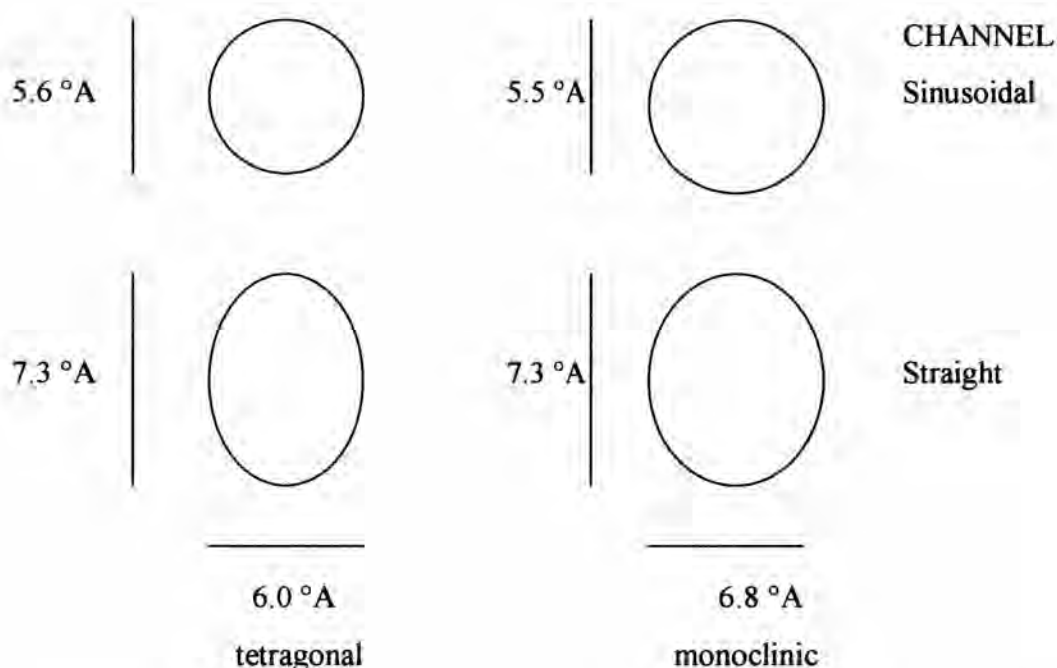


Figure 3.15 Pore openings of the sinusoidal and straight channels of the tetragonal and monoclinic analogs of zeolite β .

This zeolite may offer interesting opportunities as a catalyst, since it combines three important characteristics: large pores, high silica-to-alumina synthesis ratio, and a tridirectional network of pores. In addition, the dimensions of one type of pores (5.5 \AA) can give a certain level of shape selectivity. This has been shown to apply to the isomerization and transalkylation of xylenes [9,12], to the alkylation of toluene by methanol [13], and to the condensation of benzene and formaldehyde [10]. Recently, it has been claimed that zeolite- β can be used to catalyze the isomerization of Light Strain Run [11], or combined with BF_3 it can be used to alkylate *i*-butane with alkenes to obtain alkylate gasolines [14,15].

Effect of reaction temperature on nucleation and crystallization

In order to study the effect of reaction temperature on the nucleation and crystallization rate, a reactant mixture with molar ratios 4.6 (TEA)₂O-Na₂O-Al₂)₂-27.2 SiO₂-440 H₂O was tested at various temperatures. The results, shown in Figure 4, indicate that the rate of nucleation and crystallization increases remarkably with increasing temperature. In all the experiments performed, zeolite β was the only crystalline phase found, and no phase transformation was observed. Figure 5 shows the Arrhenius plot of rates of crystallization and nucleation. The apparent activation energy for nucleation, E_n, can be determined by using the relationship [43,44] :

$$\frac{d \ln(1/\theta)}{d (1/T)} = \frac{-E_n}{R}$$

where θ is the induction time, and T the reaction temperature. Similarly, the apparent activation energy for crystal growth, E_c, can be determined by using the Arrhenius equation [43].

$$\frac{d \ln W_c}{d (1/T)} = \frac{-E_c}{R}$$

where W_c is the maximum rate of conversion for each temperature. Accordingly E_n and E_c were calculated to be 7.0 kcal/mol and 16.2 kcal/mol, respectively. Sand et al. Also reported that the activation energies for nucleation and crystallization of ZSM-5 in TPA system were 9.6 and 15.6 kcal/mol, respectively [45].

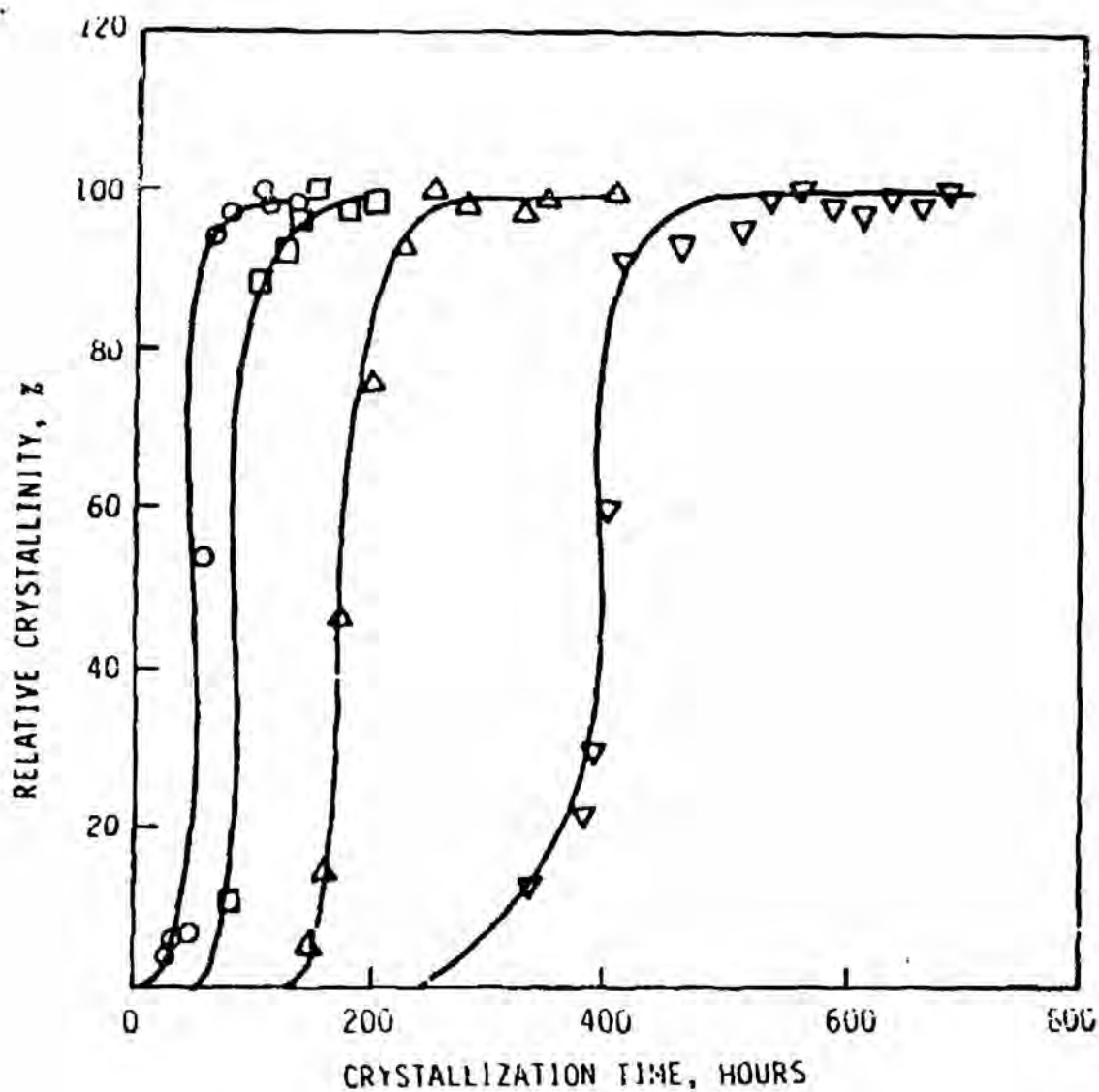


Figure 3-16 Effect of reaction temperature on the crystallization of zeolite β ; $4.6 (\text{TEA})_2\text{O}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-27.2 \text{SiO}_2-440 \text{H}_2\text{O}$. (O) 438 K, (□) 421 K, (ρ) 403 K, (σ) 387 K.

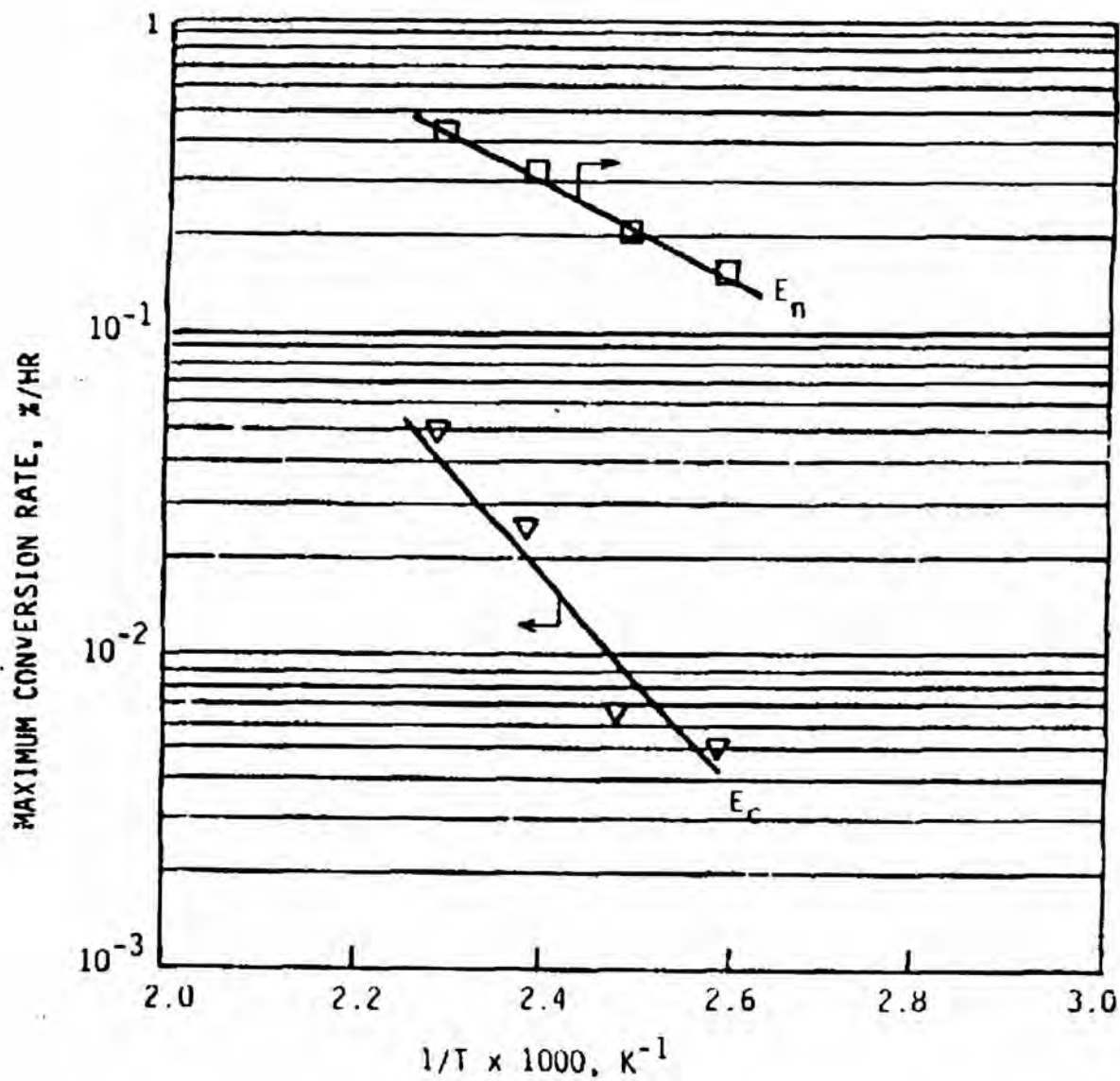
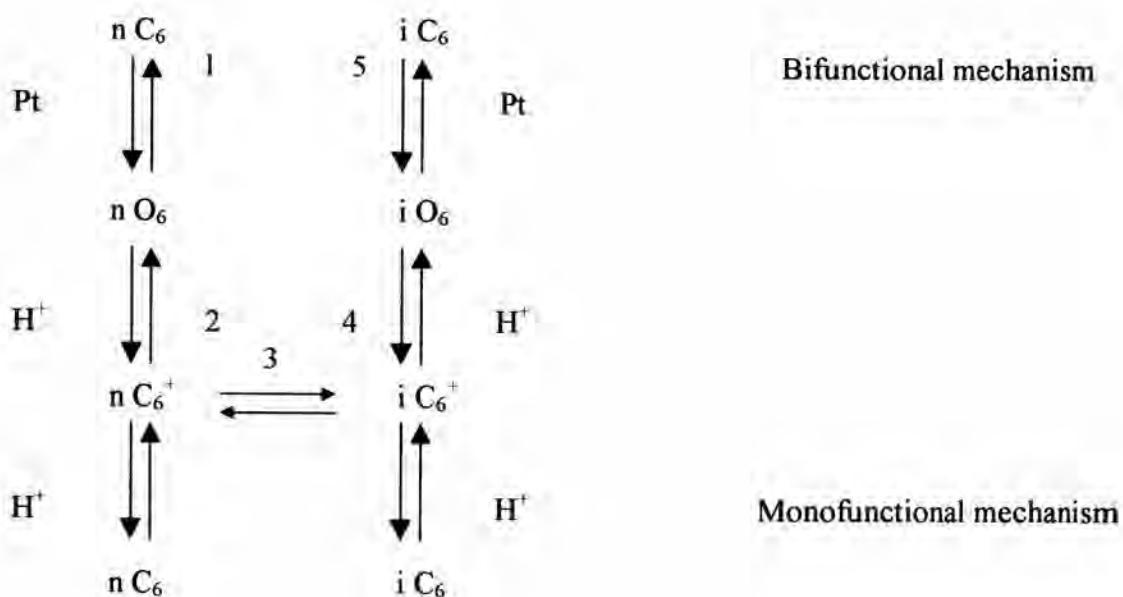


Figure 3-17 Arrhenius plots of crystallization rate and nucleation rate as a function of reaction temperature.

3.7 Reaction mechanisms of n-hexane hydroisomerization

The mechanisms of hydroisomerization of n-hexane on metal acid bifunctional catalysts are as follows.

Weisz [46] proposed a mechanism as described below



If the mechanism is purely acid the formation of the carbonium ion is the rate-determining step.

The C₆⁺ is formed through the hydrogen transfer between the n-paraffin and a carbonium ion previously present or by a reaction on the Brønsted or Lewis sites of the zeolite [47].

For low metal contents, the hydrogenation and dehydrogenation reactions are the limiting step, the isomerization activity being proportional to the metal content. If the hydrogenating activity is high, which happens for higher metal content, the limiting step will be the skeletal isomerization of olefins on acid sites and the activity depends only on the acidity of the zeolitic catalysts [48].

At low conversion, and neglecting the external and internal diffusional limitations, the isomerization rate of n-hexene can be expressed, according to the

bifunctional mechanism, in which the limiting step is the acid isomerization of olefins, as follows:

$$r = k_3 C_m K_2 K_1 \frac{P_{nc6}}{p_{H_2} + K_1 K_2 P_{nc6}} \quad [49]$$

Where k_3 is the isomerization rate constant of carbonium ions, C_m the concentration of Brønsted sites of the zeolite K_1 and K_2 the equilibrium constants of the dehydrogenation of n-hexene and of the carbonium ion formation.

The validity of this equation, and consequently of the bifunctional mechanism was tested [49] for the hydroisomerization of n-hexene on Pt/H-Y (6.0 wt %) under a total pressure of 40 bars, and a good agreement was found with the experimental values.

Kinetics studies of the n-hexene isomerization carried out by Braun and co-workers [50] have shown that no significant mass transfer limitations on the external and internal surface of pellets of Pt/H-mordenite (0.5% wt Pt) occur. The experimental values obtained for effectiveness factors corresponding to pellet diameters in the range of 0.5 to 4 mm and at a temperature of 270 °C, lie between 0.9 and 1.0.