

CHAPTER III



THEORY

3.1 Zeolite

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

In these crystalline materials we call zeolites, the metal atoms (classically, silicon or aluminium) are surrounded by four oxygen anions to form an appropriate tetrahedron consisting of a metal cation at the center and oxygen anions at the four apexes. The tetrahedral metals are called T-atoms for short, and these tetrahedra then stack in beautiful, regular arrays such that channels form. The possible ways for the stacking to occur is virtually limitless, and hundreds of unique structures are known. Graphical depictions of several representatives' types are given under “Representative Structures”

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

Since silicon typically exists in a 4+ oxidation state, the silicon-oxygen tetrahedra are electrically neutral. However, in zeolites, aluminum typically exists in the 3+ oxidation state so that aluminum-oxygen tetrahedra form centers that are

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

3.2 Structure of Zeolite

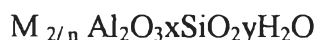
Zeolites are highly crystalline, hydrated aluminosilicates that upon dehydration develop in the ideal crystal a uniform pore structure having minimum channel diameters (aperture) of from about 0.3 to 1.0 nm. The size depends primarily on the type of zeolites and secondarily on the cations present and the nature of treatments such as calcination, leaching, and various chemical treatments. Zeolites have been of intense interest as catalysts for some three decades because of the high activity and unusual selectivity they provide, mostly in a variety of acid-catalyzed reactions. In many cases, but not all, the unusual selectivity is associated with the extremely fine pore structure, which permits only certain molecules to penetrate into the interior of the catalyst particles, or only certain products to escape from the interior. In some cases unusual selectivity seems to stem instead from constraints that the pore structure sets on allowable transition states, sometimes termed spacio – selectivity.

The structure of the zeolite consists of a three-dimensional framework of the SiO_4 and AlO_4 tetrahedra as presented in Figure 3.1, each of which contains a silicon or aluminum atom in the center. In 1982, Barrer defined zeolites as the porous tectosilicates, that is, three-dimensional networks built up of TO_4 tetrahedra where T is silicon or aluminum. The oxygen atoms are shared between adjoining tetrahedra,

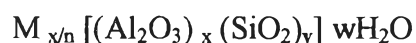
which can be present in various ratios and arrange in a variety of ways. The framework thus obtained pores, channels, and cages, or interconnected voids.

A secondary building unit (SBU) consists of selected geometric groupings of those tetrahedral. There are sixteen such building units, which can be used to describe all of known zeolite structures; for example, 4 (S4R), 6 (S6R), and 8 (S8R) – member single ring, 4-4 (D6R), 8-8 (D8R)-member double rings. The topologies of these units are shown in Figure 3.2 [22]. 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 list in Table 3.1. Both ZSM-5 zeolite 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 buildings. 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 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.

Zeolites may be represented by the empirical formula:



Or by a structural formula:



Where the bracketed term is the crystallographic unit cell. The metal cation (of valence n) is present it produces electrical neutrality science for each aluminum tetrahedron in the lattice there is an overall charge of – 1 [23]. Access to the channels is limited by aperture consisting of a ring of oxygen atoms of connected tetrahedral. There may be 4, 5, 6, 8, 10, or 12 oxygen atoms in the ring. In some cases an interior cavity exists of larger diameter in the aperture; in others, the channel is of uniform diameter like a tube.

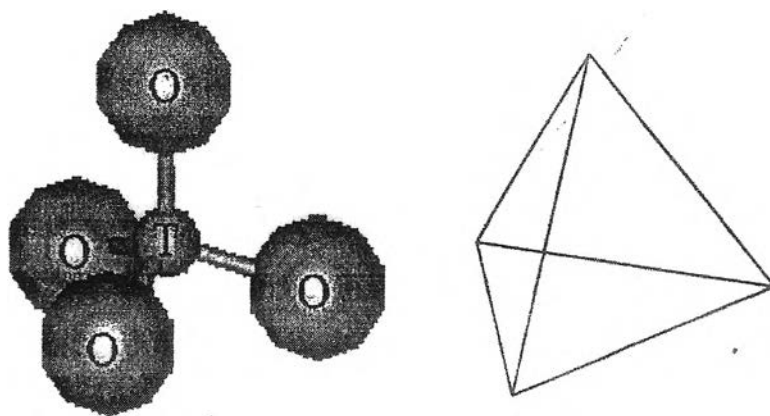


Figure 3.1 TO_4 tetrahedral (T=Si or Al)

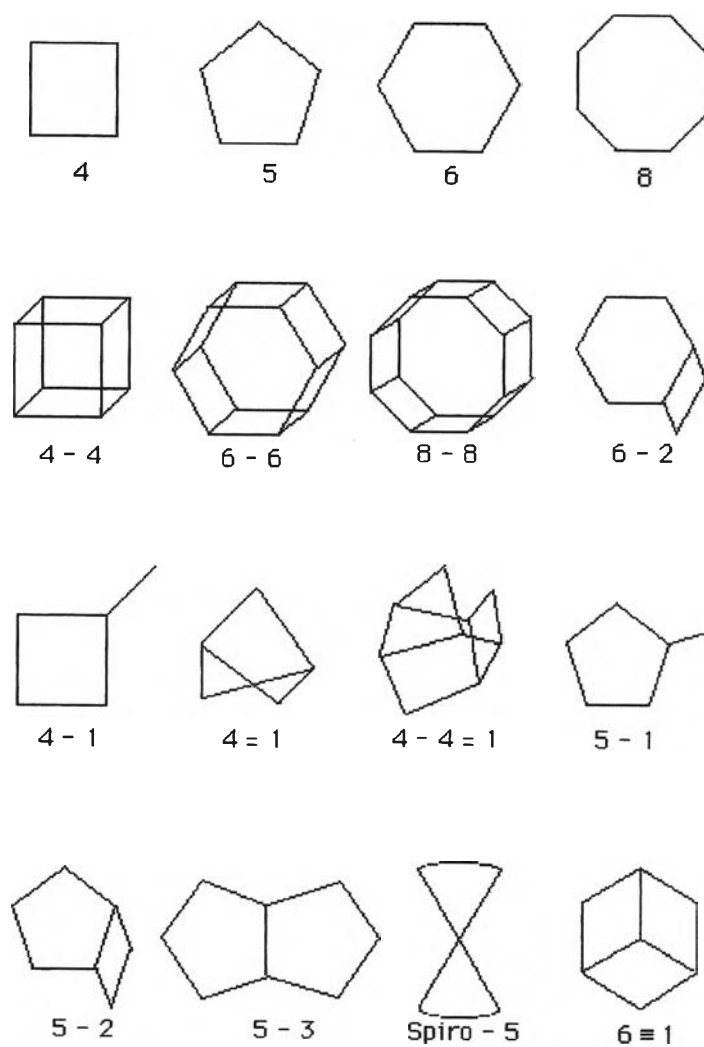


Figure 3.2 Secondary building units (SBU's) found in zeolite structures [22]

Table 3.1 Zeolites and their secondary building units. The nomenclature used is consistent with that presented in Figure 3.4 [24]

ZEOLITE	SECONDARY BUILDING UNITS							
	6	4	4-4	6-6	8-8	4-1	5-1	4-4=1
Bikilaite							X	
Li-A (BW)	X	X	X					
Analcime	X	X						
Yagawaralite	X		X					
<i>Episibite</i>							X	
ZSM-5							X	
ZSM-11							X	
Ferrierite							X	
Cachiardite							X	
Brewsterite	X							
Laumonite		X						
Modenite							X	
Sodalite	X	X						
Henulandite								X
Stibite								X
Natrolite						X		
Thomdonite						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							
Offeretite		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 Category of Zeolite

There are over 40 known natural zeolites and more than 150 synthetic zeolites have been reported [23]. The number of synthetic zeolites with new structure morphologies grows rapidly with time. Based on size of their pore opening, zeolites can be roughly divided into five major categories, namely 8-, 10-, and 12-member oxygen ring systems, dual pore systems and mesoporous systems [25]. Their pore structures can be characterized by crystallography, adsorption, measurements and/or through diagnostic reactions. One such diagnostic characterization test is the “constraint index” test. The concept of constraint index was defined as the ratio of the cracking rate constant of n-hexane to 3-methylpentane. The constraint index of a typical medium-pore zeolite usually ranges from 3 to 12 and those of the large-pore zeolites are the range 1-3. For materials with an open porous structure, such as amorphous silica alumina, their constraint indices are normally less than 1. On the index for erionite is 38.

A comprehensive bibliography of zeolite structures has been published by the International Zeolite Association. The structural characteristics of assorted zeolites are summarized in Table 3.2

Zeolite with 10-membered oxygen rings normally possesses a high siliceous framework structure. They are of special interest in industrial applications. In fact, they were the first family of zeolite that was synthesized with organic ammonium salts. With pore openings close to the dimensions of many organic molecules, they are particularly useful in shape selective catalysis. The 10-membered oxygen ring zeolites also possess other important characteristic properties including high activity, high tolerance to coking and high hydrothermal stability. Among the family of 10-membered oxygen ring zeolites, the MFI - type (ZSM-5) zeolite as presented in Figure 3.3 is probably the most useful one. ZSM-5 zeolite has two types of channel systems of similar sized, one with a straight channel of pore opening $5.3 \times 5.6 \text{ \AA}$ and the other with a tortuous channel of pore opening $5.1 \times 5.5 \text{ \AA}$. Those intersecting channels are perpendicular to each other, generating a three dimensional framework. ZSM-5 zeolites with a wide range of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio can easily be synthesized. High siliceous ZSM-5 zeolites are more hydrophobic and hydro thermally stable compared

with many other zeolites. Although the first synthetic ZSM-5 zeolite was discovered more than two decades ago (1972) new interesting applications are still emerging to this day. For example, its recent application in NO_x reduction, especially in the exhaust of lean-burned engine, has drawn much attention. Among various zeolite catalysts, ZSM-5 zeolite has the greatest number of industrial applications, covering from petrochemical production and refinery processing to environmental treatment.

Table 3.2 Structural characteristics of selected zeolites

Zeolite	Number of rings	Pore opening Å	Pore/Channel structure	Void volume (ml/g)	D _{Frame} ^a (g/ml)	CI ^b
<i>8-membered oxygen ring</i>						
Erionite	8	3.6x5.1	Intersecting	0.35	1.51	38
<i>10-membered oxygen ring</i>						
ZSM-5	10	5.3x5.6 5.1x5.5	Intersecting	0.29	1.79	8.3
ZSM-11	10	5.3x5.4	Intersecting	0.29	1.79	8.7
ZSM-23	10	4.5x5.2	One-dimensional	-	-	9.1
<i>Dual pore system</i>						
Ferrierite (ZSM-35, FU-9)	10,8	4.2x5.4 3.5x4.8	One-dimensional 10:8 intersecting	0.28	1.76	4.5
MCM-22	12	7.1	Capped by 6 rings	-	-	1-3
Mordenite	10	Elliptical				
	12	6.5x7.0	One-dimensional	0.28	1.70	0.5
	8	2.6x5.7	12:8 intersecting			
Omega (ZSM-4)	12	7.4	One-dimensional	-	-	2.3
	8	3.4x5.6	One-dimensional	-	-	0.6
<i>12membered oxygen ring</i>						
ZSM-12	12	5.5x5.9	One-dimensional	-	-	2.3
Beta	12	7.6x6.4 5.5x5.5	Intersecting	-	-	0.6
Faujasite (X,Y)	12	7.4	Intersecting	0.48	1.27	0.4
	12	7.4x6.5	12:12 intersecting			
<i>Mesoporous system</i>						
VPI-5	18	12.1	One-dimensional	-	-	-
MCM41-S	-	16-100	One-dimensional	-	-	-

^aFramework density

^bConstraint index

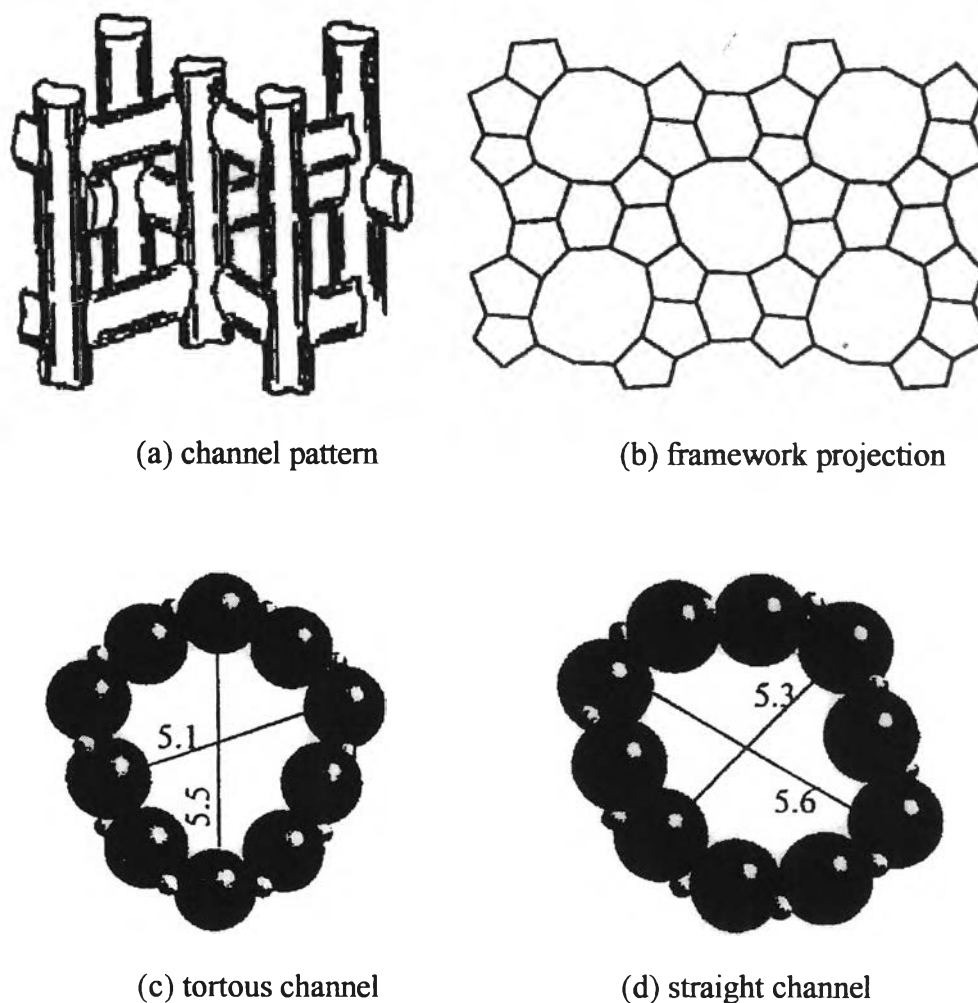
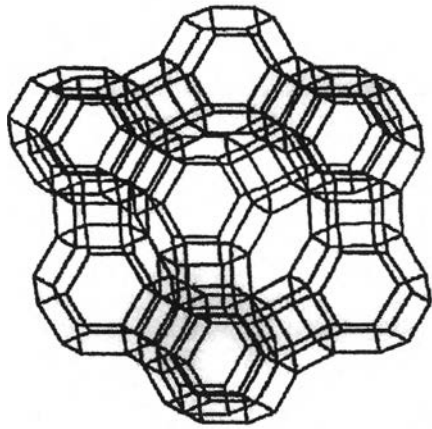
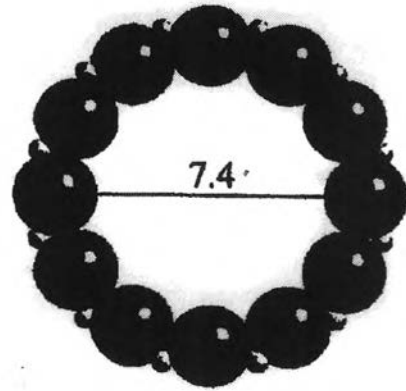


Figure 3.3 Structure of ZSM-5 [23]

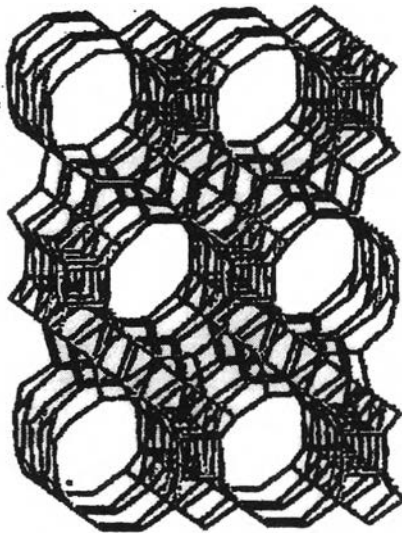
Although the 10-membered oxygen ring zeolite was found to possess remarkable shape selectivity, catalysis of large molecules may require a zeolite catalyst with a large-pored opening. Typical 12-membered oxygen ring zeolites, such as faujasite-type zeolites, normally have pore opening greater than 5.5 Å and hence are more useful in catalytic applications with large molecules, for example in trimethylbenzene (TMB) conversions. Faujasite (X or Y; Figure 3.4) zeolites can be synthesized using inorganic salts and have been widely used in catalytic cracking since 1960s. The framework structures of beta zeolite and ZSM-12 are shown in Figure 3.5 and 3.6, respectively.



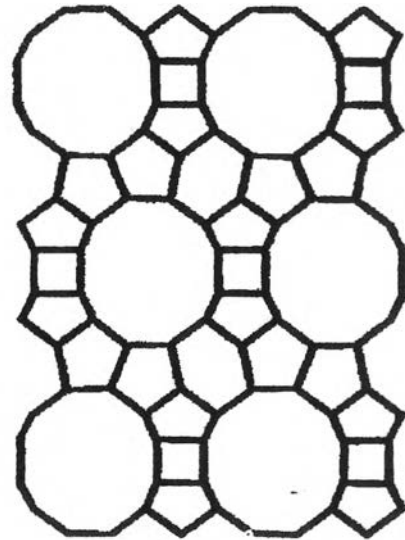
(a) framework structure



(b) pore opening

Figure 3.4 Structure of Faujasite [23]

(a) framework structure



(b) framework projection

Figure 3.5 Structure of beta zeolite [23]

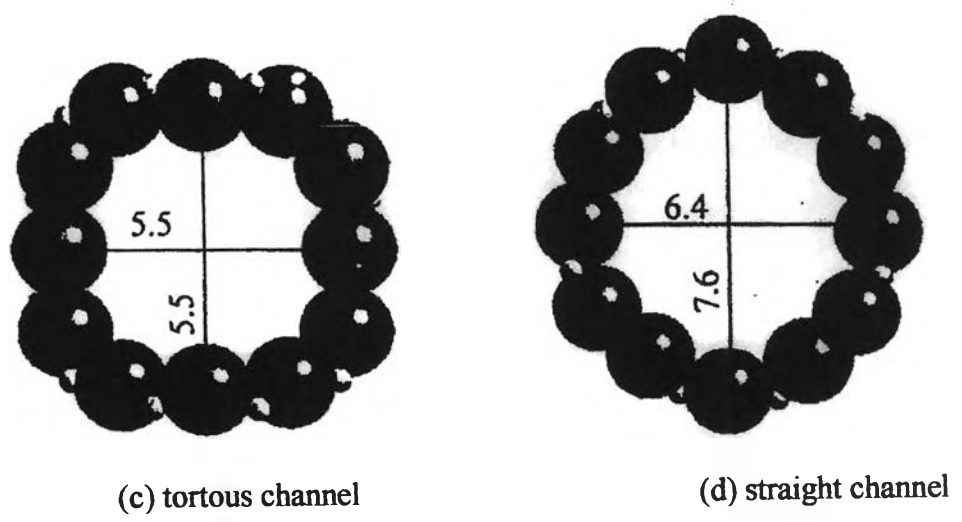


Figure 3.5 Structure of beta zeolite [23]

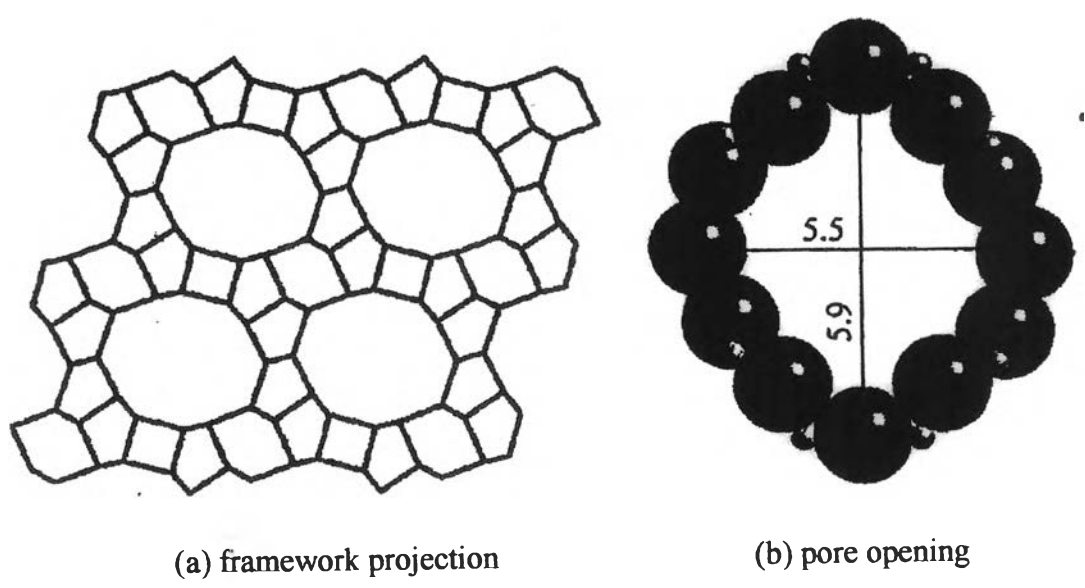


Figure 3.6 Structure of zeolite ZSM-12 [23]

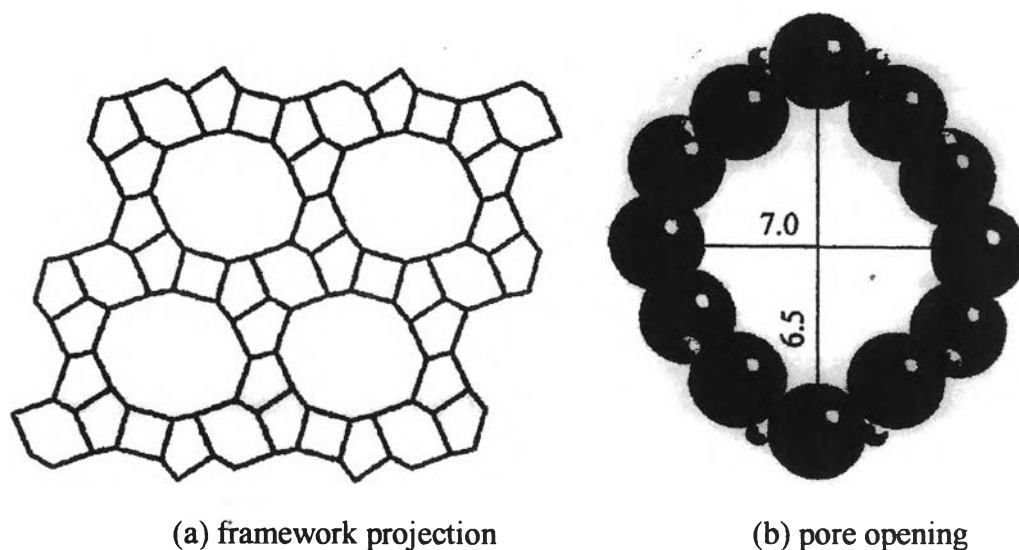


Figure 3.7 Structure of Mordenite [23]

Zeolites with a dual pore system normally possess interconnecting pore channels with two different pore opening sizes. Mordenite is a well-known dual pore zeolite having a 12-membered oxygen ring channel with pore opening $6.5 \times 6.7 \text{ \AA}$ which is interconnected to 8-membered oxygen ring channel with opening $2.6 \times 5.7 \text{ \AA}$ (Figure 3.7 [23]). MCM-22, which was found more than 10 years ago, also possesses a dual pore system. Unlike Mordenite, MCM-22 consists of 10- and 12-membered oxygen rings (Figure 3.8) and thus shows prominent potential in future applications.

In the past decade, many research efforts in synthetic chemistry have been invested in the discovery of large-pored zeolite with pore diameter greater than 12-membered oxygen rings. The recent discovery of mesoporous materials with controllable pore opening (from 12 to more than 100 \AA) such as VPI-5, MCM-41S undoubtedly will shed new light on future catalyst applications.

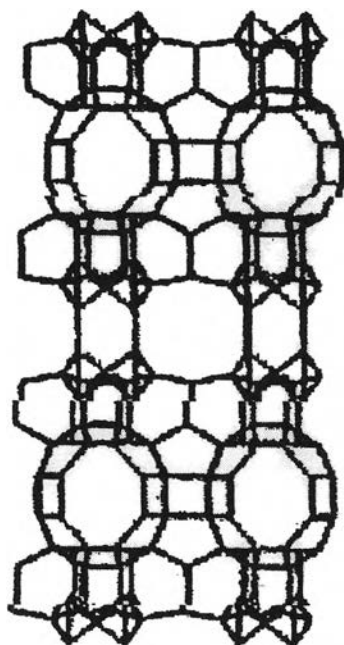


Figure 3.8 Framework structure of MCM-22 [23]

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 tridagonally coordinated alumina atom is an electron deficient and can accept an electron pair, therefore behaves as a Lewis acid [26].

In general, the increase in Si/Al ratio will increase acidic strength and thermal stability of zeolite. Since the numbers of acidic OH groups depend on the number of aluminium 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 increase Si/Al ratio. It was conceived that these phenomena are related to reduction of electrostatic interaction between framework sites, and possibly to

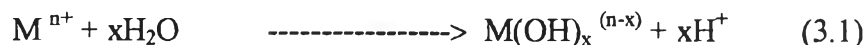
difference in the order of aluminum in zeolite crystal-the location of Al in crystal structure [27].

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. A longer distance between hydroxyl groups decreases the probability of dehydroxylation that generates defects on structure of zeolites.

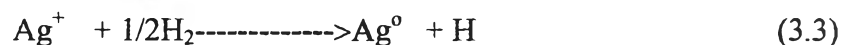
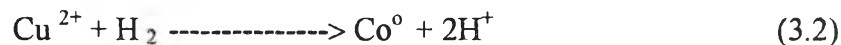
3.4.2 Generation of Acid Centers

Protonic acid centers of zeolite are generated in various ways. Figure 3.9 depicts the thermal decomposition of ammonium-exchanged zeolite yielding the hydrogen form [28].

The Brønsted acidity due to water ionization on polyvalent cations, described below, is depicted in Figure 3.10 [28].



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 noted to increase by hydrogen at 2.5 – 450 °C to increase with the rise of the reduction temperature.



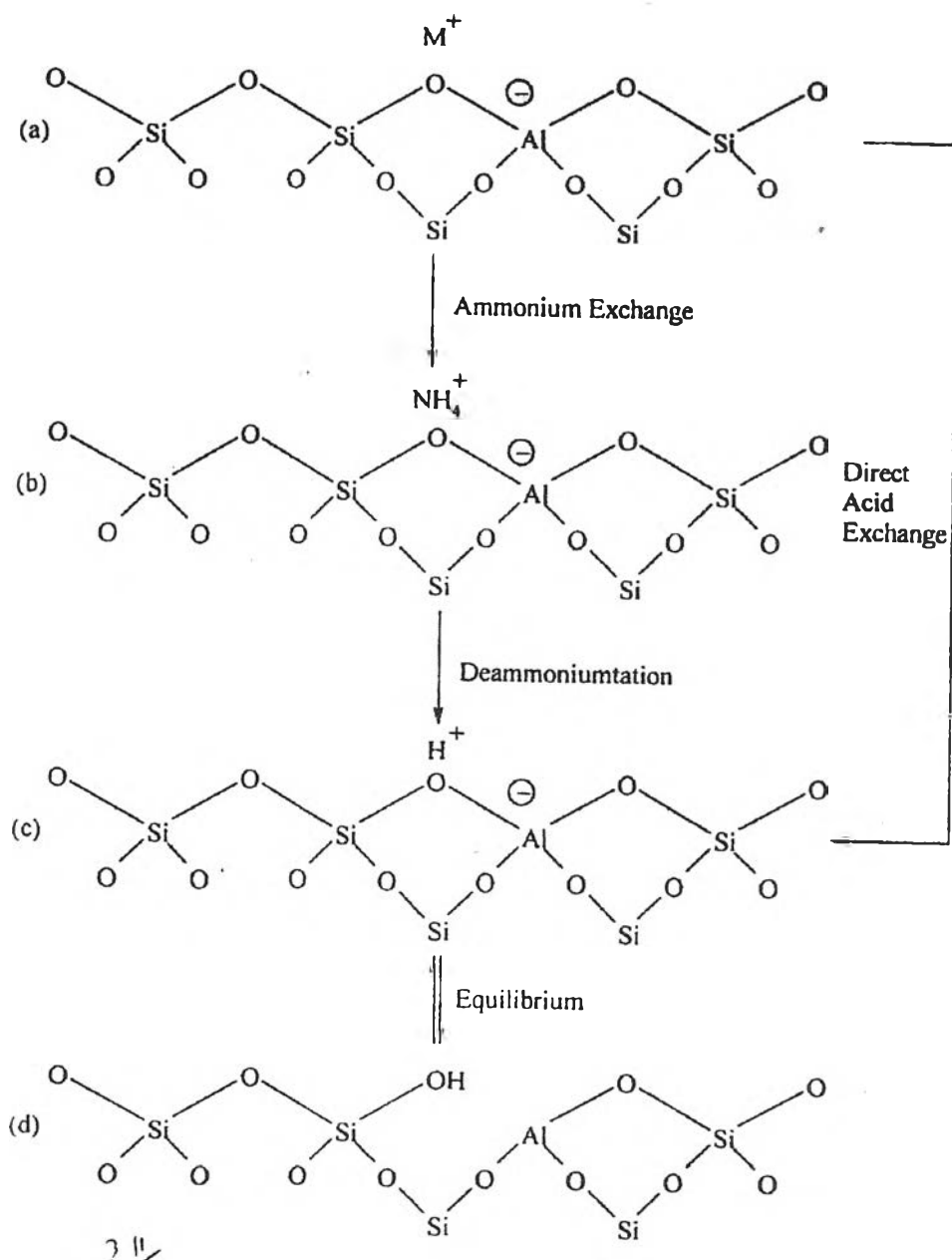


Figure 3.9 Diagram of the surface of a zeolite framework.

- In the as-synthesis form M^+ 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.

d) The acid form in (c) is in equilibrium with the shown in (d), where is a silanol group adjacent to tricoordinate aluminium.

The formation of Lewis acidity from Brønsted acid sites is depicted in Figure 3.11. The dehydration reaction decrease 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 at 500 °C and calcination at 800 to 900 °C produces irreversible dehydroxylation, which causes defection in crystal structure of zeolite.

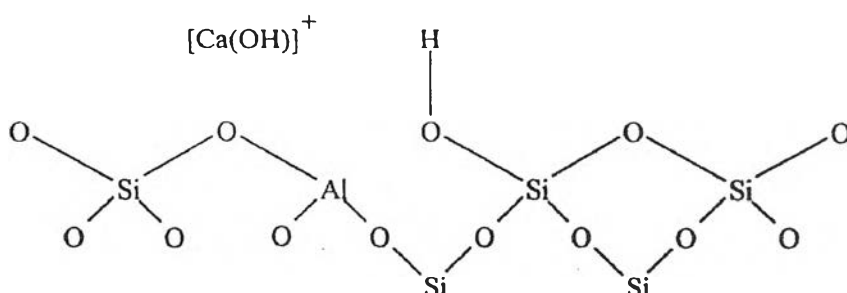


Figure 3.10 Water molecules co-ordinated to polyvalent cation are dissociated by heat treatment yielding Brønsted acidity

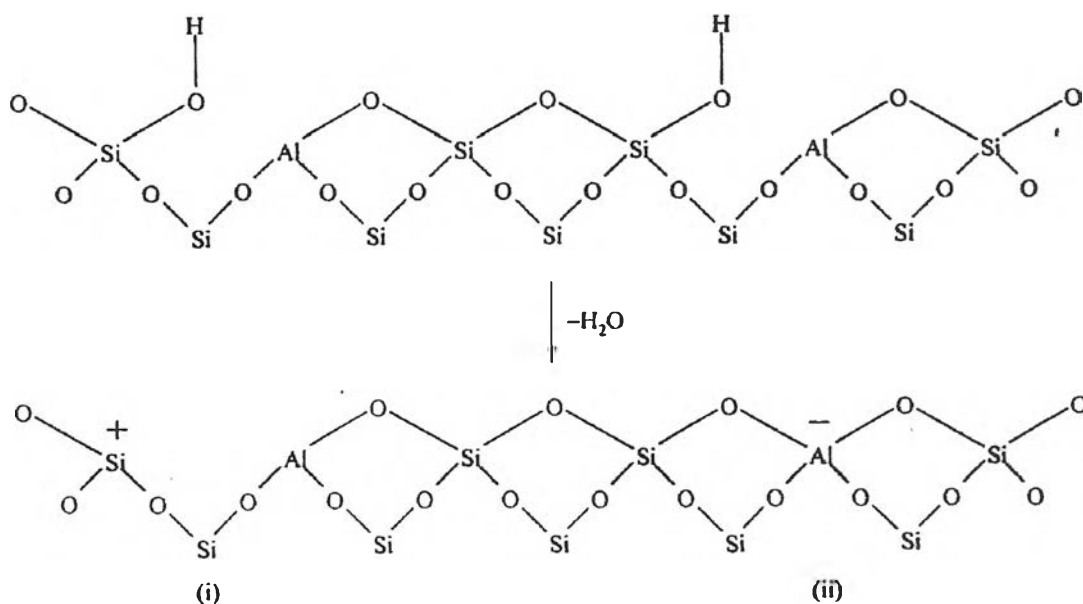


Figure 3.11 Lewis acid site developed by dehydroxylation of Brønsted acid site [28].

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

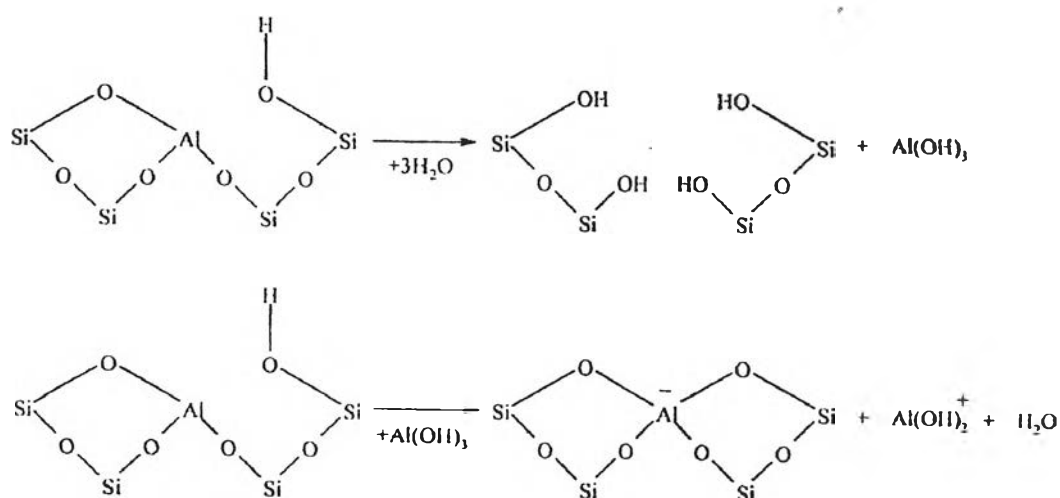


Figure 3.12 Steam dealumination process in zeolite

The enhancement of the acid strength of OH groups is recently proposed to be pertinent to their interaction with those aluminum species sites tentatively expressed in Figure 3.13. Partial dealumination might therefore yield a catalyst of higher activity while severe steaming reduces the catalytic activity.

3.4.3 Basic Sites

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

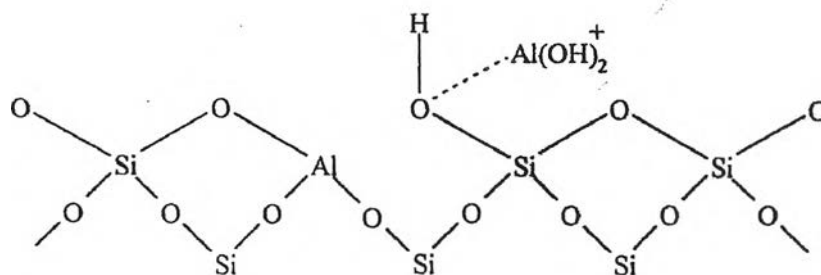


Figure 3.13 The enhancement of the acid strength of OH groups by their interaction with dislodged aluminum species .

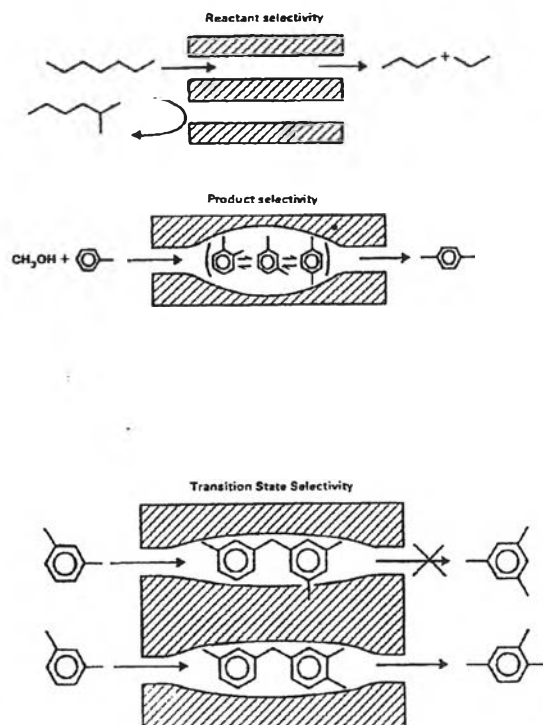
3.5 Shape Selective

Many reactions involving carbonium intermediates are catalyzed by acidic zeolite. With respects to a chemical standpoint the reaction mechanisms are nor fundamentally different with zeolites or with any the acidic oxides. What zeolite add is shape selectivity effect. The shape selective characteristics of zeolites influence their catalytic phenomena by three modes: shape selectivity, reactants shape selectivity, products shape selectivity and transition states shape selectivity. These types of selectivity are illustrated in Figure 3.14.

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 reaction. 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 from local environment around the active site, the rate constant for a certain reaction mechanism is reduced of the space required for formation of necessary transition state is restricted.

Figure 3.14 Diagram depicting the three type of selectivity



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 opening, which are smaller than their critical diameters. Hence, not only size but also the dynamics and structure of the molecules must be taken into account.

3.6 Zeolite Synthesis

Zeolites are generally synthesized by a hydrothermal process from a source of alumina (e.g., sodium aluminate or aluminium sulfate) and of silica (e.g., a silica sol, fumed silica, or sodium water glass) and an alkali such as NaOH, and/or a quaternary ammonium compound. An inhomogeneous gel is produced which gradually crystallizes, in some cases forming more than one type of zeolite in succession. Nucleation effects can be important, and an initial induction period at near ambient temperature may be followed by crystallization temperature that may range up to 200 °C or higher. The pressure is equal to the saturated vapor pressure of the water present.

The final product depends on a complex interplay between many variables including $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the starting medium, nucleating agents, temperature, pH, water content, aging, stirring, and the presence of various inorganic and organic cations. Much remains to be learned about how the initial reaction mixture forms the precursor species and how these arrange into the final crystalline products. A key concept is that the cations present give rise to a templating action, but clearly the process is more complex.

Bauer and coworkers in the early 1960s developed the use of reaction mixtures containing quaternary ammonium ions or other or other cations to direct the crystallization process. In their work and succeeding studies, a primary motivation was to attempt to synthesize zeolites with large apertures than X and Y. This did not occur, but instead organic species were found to modify the synthesis process in a variety of ways that led to the discovery of many new zeolites and new methods of synthesizing zeolite with structures similar to previously know zeolite.

The mechanism of action of the organic species is still controversial. It was originally thought to be primarily a templating effect, but later it was found that at least some of zeolites could be synthesized without an organic template. Further, organic species other than quaternary ammonium compounds had directing effects not readily ascribed to their size or shape. However, an important result was the zeolites of higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio than before could be synthesized. Previously, only structures with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of about 10 or less could be directly forms, but with organic additives, zeolites with ratio of 20 to 100 or more can be directly prepared.

After synthesis the zeolite are washed, dried, heated to remove water of crystallization, and calcined in air, e.g., at about 550 °C. Organic species are also thus removed. For most catalytic purpose, the zeolite is converted into acidic form. For some zeolites this can be achieved by treatment with aqueous HCl without significantly altering the framework structure. For other zeolites Na^+ is replaced with NH_4^+ via an ammonium compound such as NH_4OH , NH_4Cl or NH_4NO_3 . Upon heating NH_3 is driven off, leaving the zeolite in the acid form. For some reaction a hydrogenation component such as platinum or nickel is introduced by impregnation or ion exchange

3.6 ZSM-5 Zeolite

ZSM-5 zeolite has two types of channel systems of similar size, one with a straight channel of pore opening $5.3 \times 5.6 \text{ \AA}$ and the other with a tortuous channel of pore opening $5.1 \times 5.5 \text{ \AA}$. Those intersecting channels are perpendicular to each other, generating a three-dimensional framework. ZSM-5 zeolites with a wide range of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio can easily be synthesized. High siliceous ZSM-5 zeolites are more hydrophobic and hydrothermally stable compared to many other zeolites. Although the first synthetic ZSM-5 zeolite was discovered more than two decades ago (1972) new interesting applications are still emerging to this day. For example, its recent application in NO_x reduction, especially in the exhaust of lean-burn engine, has drawn much attention. Among various zeolite catalysts, ZSM-5 zeolite has the greatest number of industrial applications, covering from petrochemical production and refinery processing to environmental treatment.

3.7 Silver cluster

Several researches reported that Ag clusters were important active species for selective catalytic reduction of NO by hydrocarbon. Ag clusters increased NO conversion and increased the hydrocarbon combustion.

In 1989, A.Henglein *et al.* [6] studied Radiolytic reduction of Ag^+ ions in aqueous solution by γ -rays of a Co source and reduction by sodium borohydride in the presence of polyphosphate. And they suggested the mechanism of the formation of silver clusters in aqueous solution as follow.

The formation of silver cluster by Radiolytic was

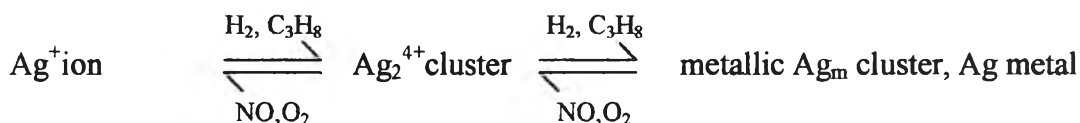


The Ag^+_2 ions dimerized



The absorption spectra of these species has also been observed at 360,310,275 nm assigned to Ag^0 , Ag_2^+ and Ag_4^{2+} respectively.

In 2003, Shibata *et al.* [3] studied Ag clusters appearing from the reduction of hydrogen on Ag-MFI under SCR $-\text{C}_3\text{H}_8$. They suggested the mechanism of the formation of silver clusters under SCR $-\text{C}_3\text{H}_8$ as follow.



They reported that the absorption of UV-Vis of Ag^+ ion were 210 and 235 nm. , of Ag_2^{4+} cluster were 260 and 285 nm., of metallic Ag_m cluster were 250 and 312 nm. and of Ag metal were from 350 – 480 nm..

Another research like Texter *et al.* reported that UV-absorption bands of Ag^+ ion were observed as a clear triplet (192, 210, and 225 nm.) in H_2O while the band intensity at 225 nm among the triplet was remarkably lower in ethanol. Considering their report, the disappearance of the band at 235 nm. may be attributed to absorption of gases (e.g., No_x and H_2O) on Ag^+ ion. Thus, the UV-Vis spectrum b indicates that Ag^+ ions are the predominant Ag species under C_3H_8 -SCR in the absence of H_2 . Then, by the addition of 0.5% H_2 for 30 min, new bands at 260 and 284 nm. were observed (spectrum c).Henglein and co workers assigned the absorption band around 280 nm. to Ag_4^{2+} in the studies on the pulse radiolytic reduction of Ag^+ ions in aqueous solutions . In a study on γ -irradiated Ag Cs-rho zeolites,

Michalik *et al.* [29] assigned the absorption band at 270 and 282 nm. to Ag_4^{2+} and Ag_4^{3+} , respectively. Gachard *et al.* [30] reported the formation of Ag_3^{2+} (265nm.) through γ - irradiation to AgNa-Y zeolites. Sato *et al.* [16] assigned the bands in the range of 238-272 and 275-326 nm. to Ag_n^+ and Ag_{n1} clusters, respectively