2. Structure of Zeolites

Structurally zeolites are framework aluminosilicates consisting of infinitely extending three-dimensional networks of AlO_4 and SiO_4 tetrahedra which are linked to each other by sharing all of the oxygens. The aforementioned tetrahedra are called the primary building units of the zeolite structure. The structural formula of a zeolite is expressed by the empirical formula for the crystallographic unit cell:

$$M_{\frac{x}{n}} \{(AlO_2)_x \ (SiO_2)_y\} \cdot wH_2O$$

M is the cation of valence n.

w is the number of water molecules.

$\frac{y}{x}$ usually has values of 1 to 5 depending on the structure.

The sum x + y is the total number of tetrahedra in the unit cell.

That portion of the composition residing between the square brackets represents the framework composition.

Groups of primary building units can be arranged to form polymeric subunits known as secondary building units. The secondary building units shown in Figure 20a[97] are charac-

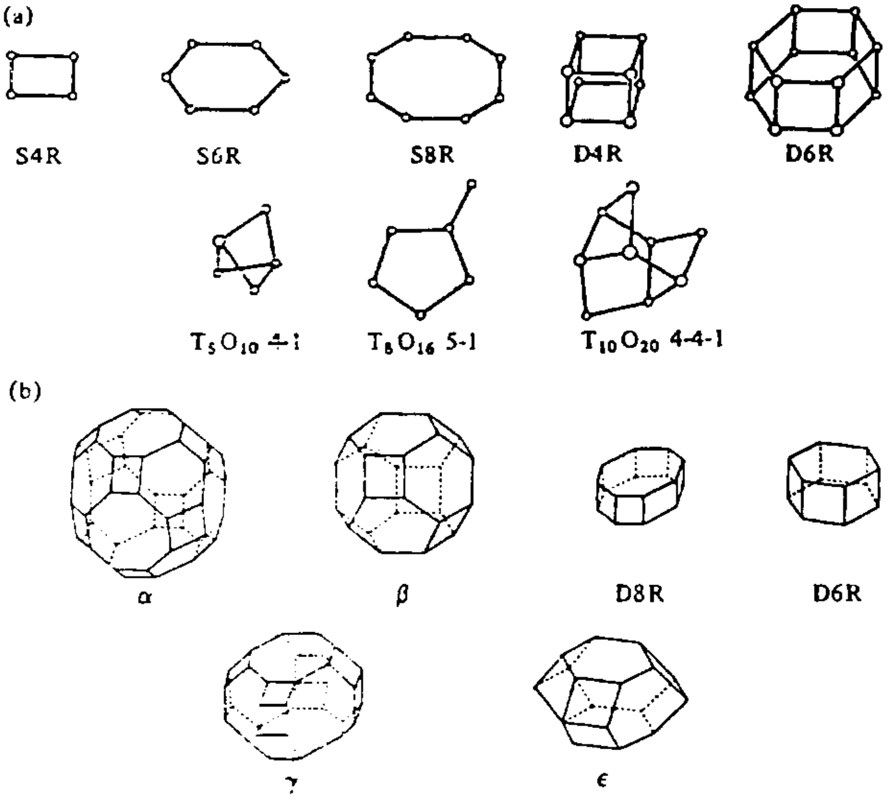


Figure 20a and b. Structure of Zeolites.[97]

teristic configurations of tetrahedra known to be recurrent in many zeolite structures. In this Figure the atoms drawn are the tetrahedral (T) atoms (the oxygens are not shown). Secondary building units can be combined to form larger polyhedra which are often cage-like in structure. Figure 20b[97] shows some of the complex polyhedra found in zeolite structures. The secondary building units comprising the structure of various zeolites are given by Meier as shown in Table 8.[98]

	Single Rings			Double Rings		Complex Units		
	4	6	8	4	6	4-1	5-1	4-4-1
Analcime	+	+						
Natrolite						+		
Thomsonite						+		
Edingtonite						+		
Gmelinite	+	+	+		+			
Chabazite	+	+	+		+			
Erionite	+	+						
Levynite	+	+						
Cancrinite	+	+						
Sodalite	+	+						
Phillipsite	+		+					
Gismondine	+		+					
Barrer's P	+		+	+				
Brewsterite	+							
Heulandite								+
Stilbite								+
Mordenite							+	
Dachiardite							+	
Epistilbite							+	
Ferrierite							+	
Bikitaite							+	
Faujasite	+	+	+		+			
Linde A	-	+	+	+				
ZK-5	-	+	+		+			
Paulingite	-		+					

Table 8. Secondary building units involved in zeolite groups.[98]

3. Classification of Zeolites

Zeolites have been classified in accordance with their morphological characteristics, effective port diameter, crystal structure, chemical composition and natural occurrence. The effective port diameter is dependent on the number of tetrahedra resident in the ring aperture which circumscribes the pore. The maximum dimension of the ring aperture in angstroms as a function of the number of tetrahedra in the ring is shown in Table 9.[99] Barrer classfied zeolites into five groups based upon their effective adsorbtion port diameter.[100] Structural classification of zeolites have been proposed by Smith,[101] Fischer and Meier,[98] and Breck.[102] Table 10 represents the structural classification of zeolites described by Meier.[98] Sand[103] presented a classification of zeolites categorizing them into small port, intermediate port, and large port varieties.as is shown in Table 11.

No. of Tetrahedra in Ring	*Maximum Free Dimension (A)*
4	1.6
5	1.5
6	2.8
8	4.3
10	6.3
12	8.0
18 (proposed but not observed)	15

Table 9. Apertures Formed by Rings of Tetrahedra Found in Zeolite Structures.[99]

Species	Crystal System and Space Group	Secondary Building Units
1. Analcime group		Interconnected 4- and 6-membered rings
Analcime	cubic Ia3d	
2. Natrolite group		Chains of tetrahedra with 6.6 Å repeat distance
Natrolite	orthorhombic Fdd2	
Thomsonite	orthorhombic Pnn2	
Edingtonite	orthorhombic $p2_12_12$	
3. Chabazite group		Parallel 6-, or double 6-membered rings
Chabazite	trigonal $R\bar{3}m$	
Erionite	hexagonal $P6_3/mmc$	
Levynite	trigonal $R\bar{3}m$	
Gmelinite	hexagonal $P6_3/mmc$	
Cancrinite hydrate	hexagonal $P6_3$	
Sodalite hydrate	cubic $P\bar{4}3n$	
4. Phillipsite group		Approximately parallel 4-membered rings
Phillipsite	orthorhombic B2mb	
Gismondine	monoclinic $P2_1/c$	
Barrer's P	cubic Im3m	
5. Heulandite group		Characteristic configurations with 4-, or 5-membered rings
Heulandite	monoclinic Cm	
Brewsterite	monoclinic $P2_1/m$	
Stilbite	monoclinic C2/m	
6. Mordenite group		Each tetrahedron of the framework belongs to at least one 5-membered ring
Mordenite	orthorhombic Cmcm	
Ferrierite	orthorhombic Immm	
Dachiardite	monoclinic C2/m	
Epistilbite	monoclinic C2/m	
Bikitaite	monoclinic $P2_1$	
7. Faujasite group		Frameworks based on polyhedral cages of cubic or or near-cubic symmetry
Faujasite	cubic Fd3m	
Linde A	cubic $Fm\bar{3}c$	
ZK-5	cubic Im3m	
Paulingite	cubic Im3m	

Table 10. Structural Classification of Zeolites.[98]

Small Port 8-membered ring	Intermediate Port 10-membered ring	Large Port 12-membered ring
Zeolite A*	dachiardite	Zeolite X
clinoptilolite	ferrierite	Zeolite Y
ZK-4	epistilbite	Zeolite ω
ZK-5		Mordenite
mordenite		Offretite
chabazite		Zeolite L
erionite		
phillipsite		
gismondine		

*Synthetic zeolites are capitalized, natural zeolites are not.

Table 11. Classification of Zeolites.[103]

B. Zeolite ZSM-5

1. Structure of Zeolite ZSM-5

ZSM-5 is an abbreviation for Zeolite Socony-Mobil-5 which is a silica-rich synthetic porotecto silicate of the Pentasil type. The term Pentasil was proposed by Kokotailo and Meier[104] to designate the group of structures having secondary building units similar to those which form ZSM-5. The framework of ZSM-5 is made up of a unique configuration of silica and/or alumina tetrahedra consisting of eight 5-membered rings which are shown in Figure 21a.[105] This structural unit is repetitively linked through its edges to form the chain configurations shown in Figure 21b.[105] A skeletal diagram of the ZSM-5 unit cell is shown in Figure 22a which depicts the (010)-face.[105] Figure 22b is a skeletal diagram of the (100)-face.[105] The 10-membered ring apertures shown in Figure 21a are parallel to the (010) crystallographic direction and are elliptical in nature. The nearly circular 10-membered ring apertures shown in Figure 22b are the entrances to the sinusoidally dispersed channels which extend parallel to the (100) crystallographic direction. The channel system of ZSM-5 consists of zig zag

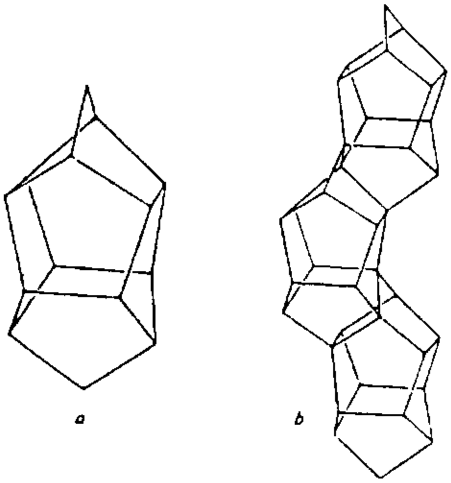


Figure 21 a and b. Characteristic configuration (a) and its linkage within chains (b) in ZSM-5. These chains run parallel to (001). Only T-atoms (Si, Al) are shown.[105]

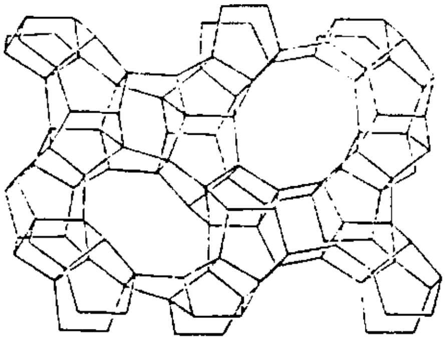
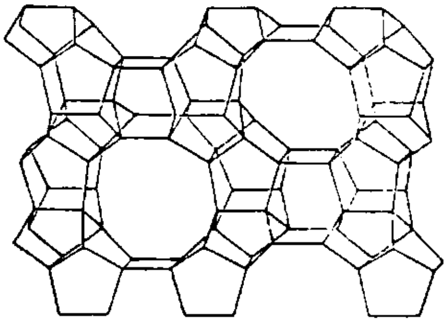


Figure 22a. Skeletal diagram of the (010)-face of the ZSM-5 unit cell.[105]



b. Skeletal Diagram of the (100)-face of the ZSM-5 unit cell.[105]

sinusoidally dispersed channels parallel to (100) which interconnect with straight channels parallel to (010) as shown in Figure 23.[105] ZSM-5 crystals are orthorhombic with space group Pnma and have lattice constants A = 20.1, B = 19.9, and C = 13.4 angstroms.[105] Recent evidence from solid state magic-angle-spinning NMR suggest that $Pn2_1a$ or $P2_{1/n}$ space groups might be more appropriate than Pnma for 24 distinct tetrahedral locations were observed when only 12 would be possible in the Pnma space group.[106]

The composition of the unit cell of Na-ZSM-5 is $Na_n Al_n Si_{96-n} O_{196} \cdot \sim 16\ H_2O$ where $n<27$ and is typically approximately 3. In this empirical formula n is constant for a bulk composition of unit cells but varies from the center to the surface of the zeolite crystallite Von Ballmoos[107] and Von Ballmoos and Meier[108] reported

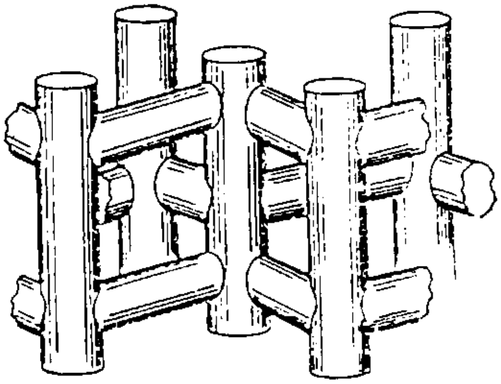


Figure 23. The Channel Structure in ZSM-5.[105]

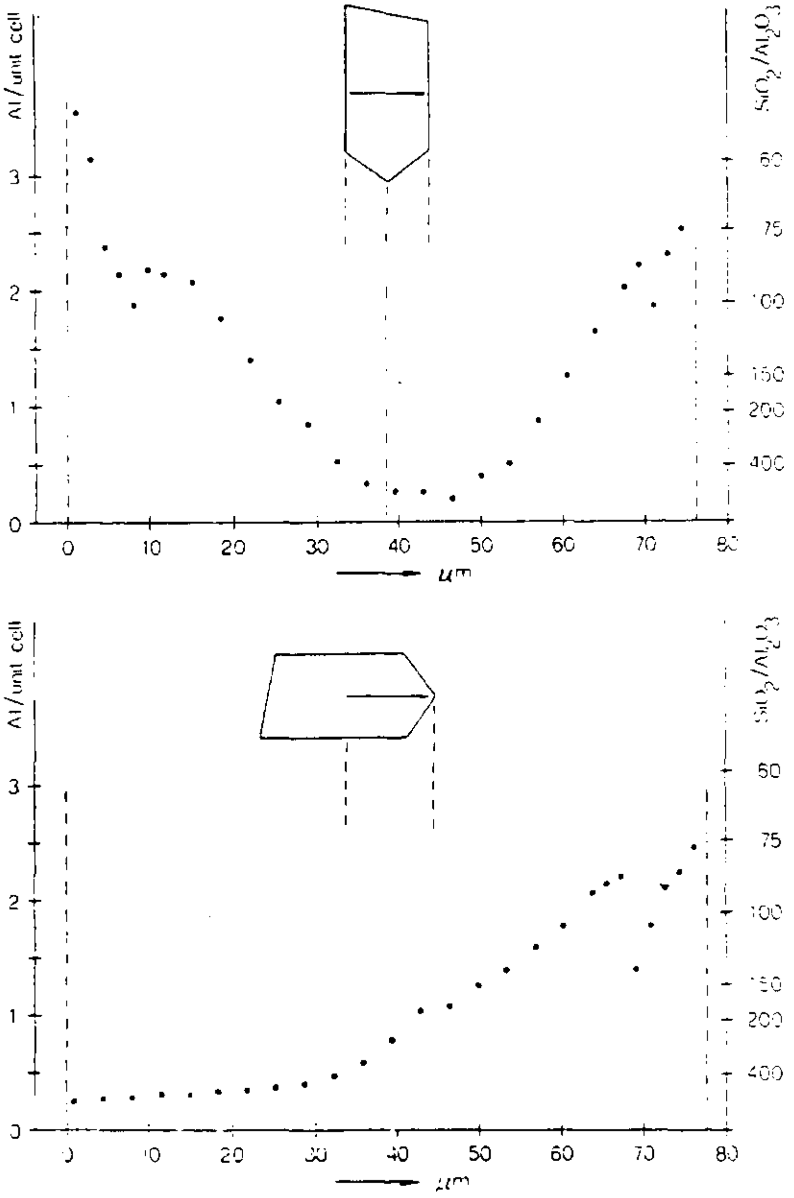


Figure 24. Variation in Aluminum Concentration

Zoned aluminum distribution in ZSM-5 crystals. Al and Be coated section parallel to the c-axis of an as-synthesized crystal (sample no. 147 G). Figs. 22 a (top) and b (bottom, half of the crystal only) are perpendicular to each other. The sudden decrease in the Al concentration near the rim is noteworthy.

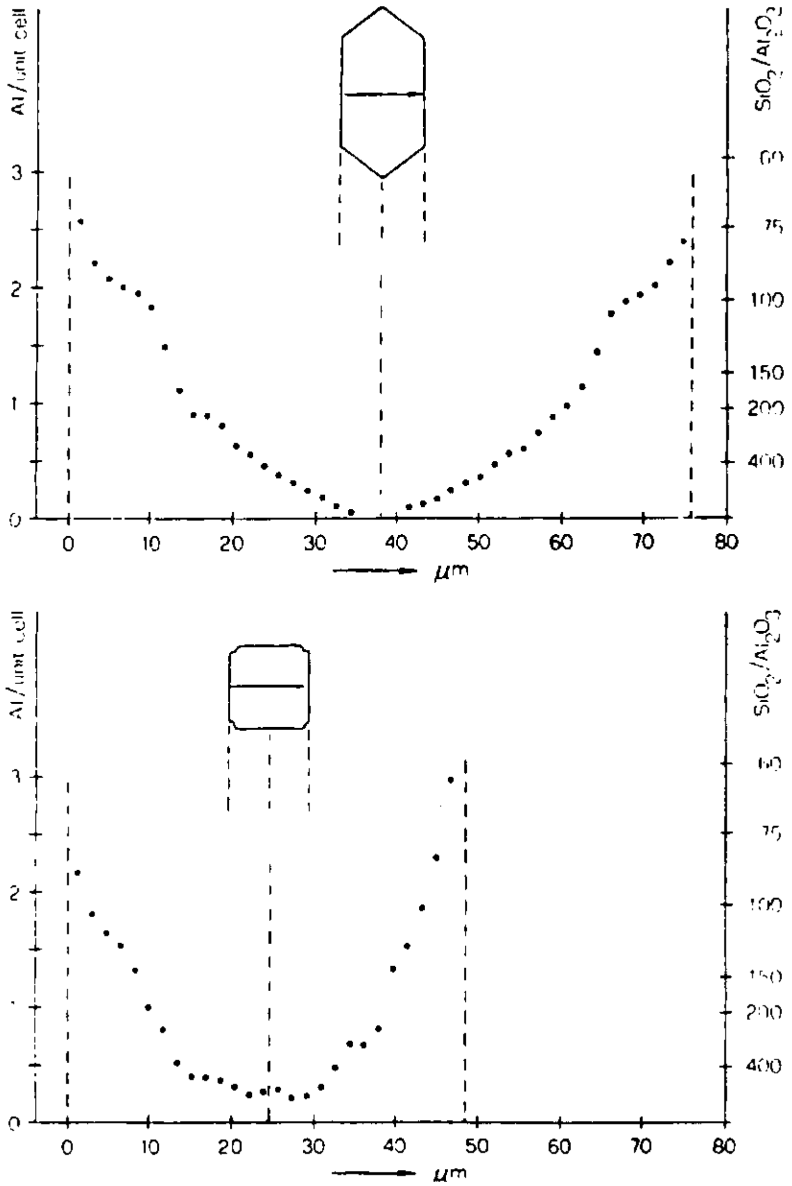


Figure 25. Variation in Aluminum Concentration[107]

Zoned aluminum distribution in ZSM-5 crystals (sample no. 147 D). Polished sections parallel (Fig. 23 a, top) and perpendicular (Fig. 23 b, bottom) to the c-axis, coated with Be only. Fig. 23 a shows a very low Al-concentration in the core and rim concentrations greater by a factor of over ten. The profile of Fig. 23 b contains some residual Al in the core. The flanks are very steep in this case.

strong compositional zoning across cross-sections of ZSM-5 single crystals. Figures 24 and 25[107] show the variation in aluminum concentration (Al/unit cell) determined by the electron microprobe analysis of cross sections of the ZSM-5 crystal. Barrer suggests that the reason for this compositional variation is that aluminum free ZSM-5 nucleates more readily than ZSM-5 richer in aluminum content as the silica is rapidly consumed during ZSM-5 synthesis. The silica to alumina ratio of the hydrothermal magma decreases and due to the depleted availability of silicon larger amounts of aluminum enter the framework.[109] Lyman et al.[110] found three types of chemical profiles across Na-ZSM-5 crystallites in the size range of 0.1 to 2 microns.

2) Synthesis of ZSM-5

ZSM-5 was first synthesized by Argauer and Landolt in the Na-TPA (Tetrapropylammonium hydroxide) system.[111] Where $(R_4N)^+$ is a quaternary ammonium ion and M is an alkali-metal cation of valence n the composition of the systems from which ZSM-5 is crystallized is:

$$(R_4N)_2\,O\text{-}M_{2/n}O\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$$

The quaternary ammonium ion can be selected from the group tetramethylammonium (TMA), tetraethyl ammonium (TEA), tetrapropylammonium (TPA), and tetrabutylammonium (TBA) ions. The broad, preferred, and particularly preferred ranges of compositions of reaction mixtures which yield the ZSM-5 phase are shown in Table 12.[111] This range of batch compositions is presented graphically in the $(TPA, Na)_2O$-Al_2O_3-SiO_2 ternary diagram shown in Figure 26.[111] The composition of the ZSM-5 phase synthesized from these batch compositions is reported to be:

$$(0.9 \pm 0.2)\ M_{2/n}\,O\text{-}Al_2O_3\text{-}(5\text{-}100)\ SiO_2\text{-}(0\text{-}40)\ H_2O.$$

The range of product compositions is also shown in the ternary phase diagram of Figure 26. ZSM-5 is prepared by heating

	Range		
Ratio	Broad	Preferred	Particularly Preferred
$\frac{OH^-}{SiO_2}$	0.07- 10.0	0.1- 0.8	0.2- 0.75
$\frac{TPA^+}{TPA^+ + Na^+}$	0.2 - 0.95	0.3- 0.9	0.4- 0.9
$\frac{H_2O}{OH^-}$	10 -300	10 -300	10 -300
$\frac{SiO_2}{Al_2O_3}$	5 -100	10 - 60	10 - 40

Table 12. Preferred Ranges of Compositions of Reaction Mixtures Which Yield the ZSM-5 Phase.[111]

the reaction mixture in a batch reactor to a temperature of 100 to 175 C for 6 hours to 60 days, respectively. The preferred temperature range is 150 to 175 C for a period of time ranging from 12 hours to 8 days. The ZSM-5 crystals are separated from the reaction solution by filtering. They are then washed and dried at 230 F for 8 to 24 hours. The batch composition can be generated through adding the appropriate amounts of Na-aluminate, Na-silicate, silicagel, fumed silica, silicic acid, silica hydrosol, alumina, Na-hydroxide and the hydroxide or bromide of tetrapropylammonium.

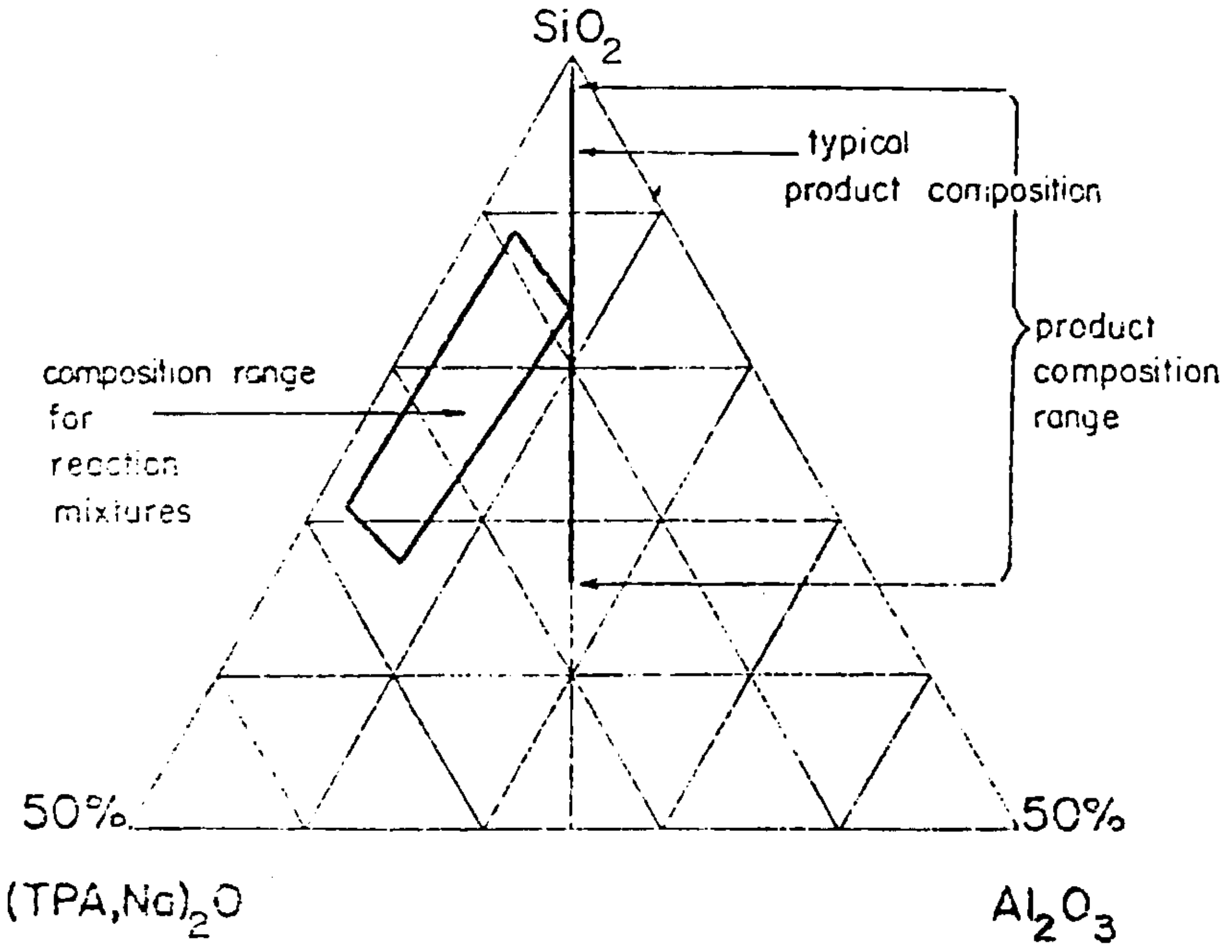


Figure 26. Range of Product Compositions For the Crystallization of ZSM-5.[111]

ZSM-5 has also been prepared in systems substituting for TPA, tetraurea-cobalt (II)[112] or amines and diamines.[113] Grose and Flanigen[114] also report the synthesis of ZSM-5 in TPA free systems containing Na, Na-lithium, Barium Na. Other recent works in the synthesis of ZSM-5 include Mostowicz and Sand[115] and Erdem and Sand.[116]

3. Properties and Uses of ZSM-5

a) Adsorption

ZSM-5 is a silica-rich zeolite which has been synthesized with greatly differing SiO_2/Al_2O_3 ratios from approximately 20 to infinity. ZSM-5, therefore, constitutes a substitutional series whose sorption chracteristics are dependent on both structure and composition. Chen[117,118] demonstrated that HZSM-5 is hydrophobic and that the degree of hydrophobicity increases linearly with the silica to alumina ratio. The equilibrium sorption capacity for water on ZSM-5 with varying silica to alumina ratios is presented by Olson et al[119] in Figure 27.

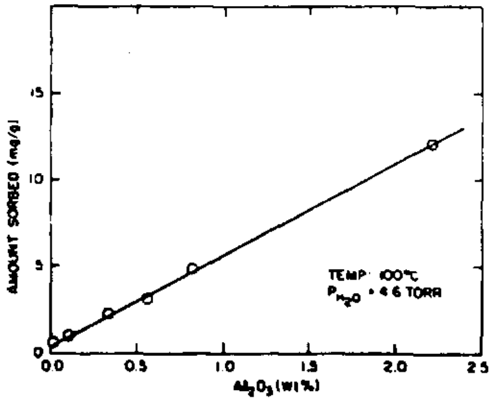


Figure 27. Effect of alumina content on water sorption of HZSM-5 at $P/P_0 = 0.006$.[119]

Extrapolating his results to 0 aluminum content the sorption capacity is 0.3 mg/G. He attributes this small sorption value at 0 aluminum to the interaction of water molecules with surface hydroxyls. The amount of water adsorbed on aluminum deficient HZSM-5 is considerably below the pore capacity which is shown in the water adsorption isotherms shown in Figure 28.[120]

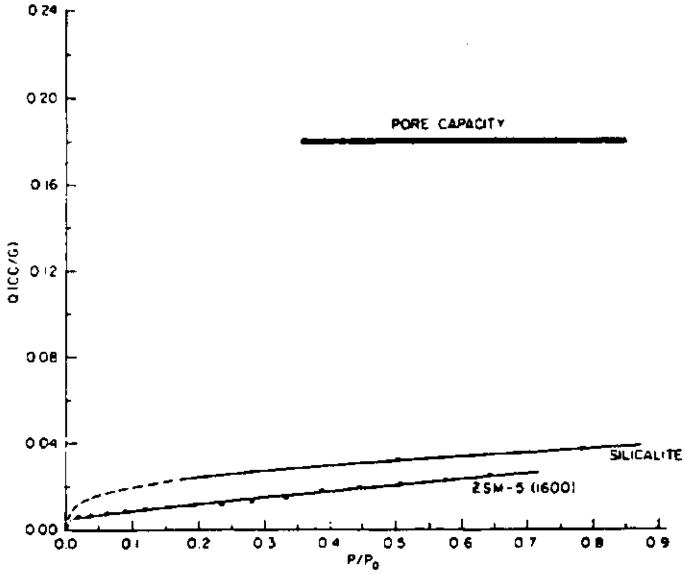


Figure 28. Water adsorption isotherms for HZSM-5[120]

With a channel size intermediate between small pore zeolites (8-ring) and large pore (12-ring) zeolites the sorption and diffusion properties of ZSM-5 are unique due to its 10-membered ring pore system. While 8-ring zeolites limit hydrocarbon adsorption to the normal parafins, ZSM-5 can adsorb molecules as large as 1,2,4-trimethyl benzene (6.9 angstroms) and 12-membered ring zeolite molecules as large as tributylamine (9.1 angstroms).[121] Slightly larger molecules such as 1,3,5-trimethyl benzene (7.8 angstroms) are completely excluded by the ZSM-5 pore system. Zeolites typically exhibit type 1 isotherms[122] where the hydrocarbon capacity of the pore system is reached at the plateau region of the isotherm. The amount adsorbed at this plateau region reflects the zeolite pore volume.

The hydrophobicity of ZSM-5 and silicalite (the high silica end member) and its high affinity for normal alkanes make it potentially attractive for the separation of certain hydrocarbons from aqueous media. The pore dimensions of its 10-membered ring pore system give it the capacity to adsorb or desorb paraxylene and exclude ortho and metaxylenes. This capability combined with the nearly identical match between the pore diameter and the kinetic diameter of benzene make ZSM-5 useful industrially significant catalytic processes. The degree of hydrophobicity of Pentasil materials is quantitatively expressed by the relative adsorbtion index (RAI). The relative adsorbtion index values are empirically determined by the volume ratio of adsorbed n-hexane to adsorbed water.

b) Ion-Exchange

ZSM-5 can have its original ions replaced with a wide variety of other metallic cations in a process known as ion-exchange.[111] Ion-exchange is accomplished through contacting ZSM-5 with a salt solution which contains a large excess of the desired cations. Ion-exchange usually involves an aqueous solution containing the chloride, nitrate, or sulfate salt of the desired cation. If ZSM-5 is to be changed from its sodium form to its hydrogen form two approaches can be utilized. The first is the simple ion-exchange of sodium by hydrogen from acidic solution. The second approach involves the replacement of sodium by ammonium from solutions of ammonium hydroxide or ammonium chloride followed by the thermal decomposition of ammonium ion into hydrogen ion and ammonia gas. The latter method is usually preferred for it does not result in the dealuminization of ZSM-5 which is known to occur in the former. If transition metals are present on the ZSM-5 support at the time of ion-exchange it is preferrable to use ammonium hydroxide over ammonium chloride for the chloride ion can be strongly adsorbed by the surface of the transition metal which can permanently alter its catalytic activity. Olson et al[119] showed that the ion-exchange capacity of ZSM-5 was in good stoichiometric agreement with the concentration of framework aluminum. As shown in Figure 29 [119] the amount of cesium ion exchanged is directly related to the aluminum content of the ZSM-5 framework.

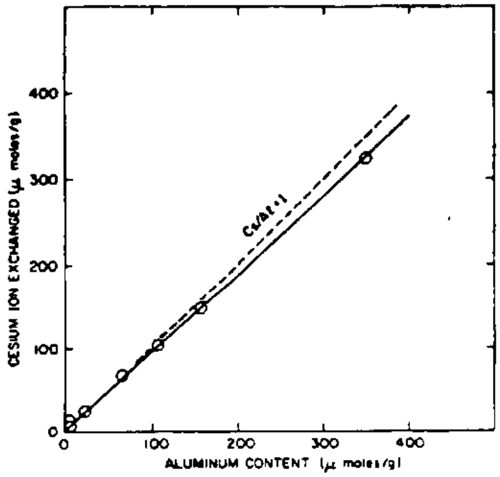


Figure 29. Effect of Aluminum Content of ZSM-5 Materials on Ion-Exchange Capacity.[119]

c) Catalytic Properties and Surface Chemistry

Zeolites have played an increasingly important role in industrial catalytic processes since the early 1950s. In zeolites tetrahedral aluminum replaces silicon in certain lattice sties. The -1 charge associated with tetrahedral aluminum requires the presence of a cation in the general vicinity of this anion to preserve the electrical neutrality of the lattice. Three of the four types of active sites found in zeolites are associated with and attributable to the substitution of aluminum for certain silicon sites in the framework. If the charge compensating cation associated with tetrahedral aluminum is hydrogen the zeolite surface obtains the capacity to act as a proton donor and, therefore, can serve as a Bronsted acid. If the zeolite is heated to 550 C scission of the Si-O-Al bond occurs resulting in the formation of a Lewis (electron pair accepting) acid site. According to the model of Ward[123] two Bronsted acid sites are destroyed in the formation of a single Lewis acid site. If by conventional ion-exchange techniques transition metal ions are introduced into the zeolite pore system, a third type of active site is generated. The fourth type of active site is the 0 valent metal atom produced in the zeolite pore system through the reduction of metal cations or the decomposition of metal complexes.

All four types of active sites in zeolites are intracrystalline and reside on the internal surfaces of the zeolite pores and cavities. As a consequence, the molecules which can be exposed to the intracrystalline catalytically active centers are determined by the shape and size of the penetrant molecules. From the catalytic view point the most significant properties of zeolites as presented by Vaughan[124] are:

1. The high density of active sites.
2. Ingress-Egress control-stereospecificity.
3. Sites for occluded species.
4. Controllable potential energy fields.

The intracrystalline pore-cavity system in zeolites called the zeolitic surface is strongly influenced by the zeolite crystal field which surrounds it. Because Si-O-Si bonds are covalent the ionic character of the zeolite crystal field is controlled by the alumina content of the framework. Depending on the aluminum content zeolites range from weak to very strong electrolytes. Molecules adsorbed by zeolites particularly polar or strongly polarizable ones will be polarized by the zeolite and will themselves exert a similar effect on the zeolite crystal. The overall interaction between a zeolite and an adsorbate must tend to minimize the free energy of the zeolite adsorbate system.[125] The simplist way to forecast thermodynamically favored reactions in zeolites is, therefore, to evaluate their effect on the stability of the zeolite crystal.[125]

All important industrial applications of zeolite catalysts to date are based on carbonium ion chemistry. Carbonium ions are produced by the strong acid hydroxyl groups on the zeolitic surface.[125] All industrially significant catalytic applications of zeolites rely on the shape selective effects generated by the pore dimensions of the intracrystalline channels. Five types of shape selectivity have been reported in the literature; i.e., reactant selectivity, product selectivity, cage or concentration effects, restricted transition state selectivity, and molecular traffic control. Reactant selectivity occurs when only certain reactants have dimensions sufficiently small to enter the zeolite pore system to be exposed to the active sites. This type of selectivity is used in catalytic dewaxing where normal parafins are cracked and branched parafins left to remain intact. Product selectivity occurs when only certain products have dimensions allowing them to exit the pore system. Product selectivity is used to produce paraxylene via the paraselective alkalation of toluene. Cage and concentration effects are caused by the increased reactant density within the zeolite pore system attributable to the electrostatic field interactions with the adsorbed molecule. The result of this form of selectivity is an increase in bimolecular reactions over unimolecular reactions. Restricted transition state selectivity, as the name implies, results in the elimination of certain reaction pathways because the transition state leading to those pathways is larger than can be accommodated by the zeolite pore or cavity. These forms of selectivity were recently reviewed by Csicseri.[126] The last form of shape selectivity known as molecular traffic control is throught to occur in zeolites such as ZSM-5 which have interconnecting pore systems in two directions which are slightly different in pore diameter. Reactant molecules being smaller than product molecules can enter the smaller pore system, be converted to product, and diffuse out the larger pore system. Counter diffusion is thereby minimized.

The pore dimensions of ZSM-5 have made it applicable for acid catalysis in a wide variety of industrially importhant reactions. It has been utilized in the conversion of methanol and other oxygenates into high octane gasoline.[127,128] It has been employed for the alkalation of toluene into paraxylene.[129,130] It has also been used for the hydrodewaxing of oils[131] and the isomerization of xylenes.[132] All these applications are acid catalyzed reactions which are carried out over the hydrogen exchange form of ZSM-5. The extreme strength of the Bronsted acid sites on the zeolitic surface of HZSM-5 combined with its intermediate 10-membered ring pore dimensions create the extreme versatility of this catalyst. Its use and the mechanisms involved in its application to synthesize gasoline from methanol and in upgrading Fischer-Tropsch products will be discussed in the following section.