



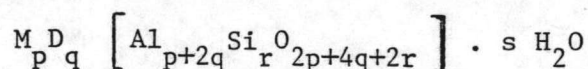
CHAPTER 3

THE SYNTHESIS AND TOPOLOGY OF ZEOLITE FAMILIES

3.1 Introduction :

Zeolites (molecular sieves) are crystalline aluminosilicates composed of SiO_4 and AlO_4 tetrahedra arranged in various geometric patterns (13). The framework structure consists of cornerlinked tetrahedra in which small atoms (collectively denoted T atoms) lie at the centers of tetrahedra and oxygen atoms lie at the corners. The T sites of all natural zeolites are dominated by Al and Si atoms. The large ions in the cavities of natural zeolites are mono- or divalent, and the principal species (Na, K, Ca, Mg, and Ba) reflect the geochemical abundance and the competition with other minerals during geochemical differentiation.

The ideal formula of a Zeolite is (14) :



where

M = mono-valent metal ion

D = divalent metal ion

p, q, r are number of charged of monovalent, divalent and Si respectively.

s is number of hydrate

The finite corner-sharing of tetrahedra requires that there are twice as many framework oxygens as T atoms, while charge balance requires that the number of trivalent Al ions equals the sum of

p (mono-valent) ions and twice q (divalent) ions.

Table 3.1 Properties of Selected Zeolites and Feldspathoids (14).

Name	Crystallographic Data	Selected Chemical Composition
A	isometric : a 12.3 A Pm3m (Pseudo)	$\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot 27 \text{H}_2\text{O}$
cancrinite	hexagonal : a 12.7, c 5.1 A P6 ₃	$\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24} \cdot \text{CaCO}_3 \cdot 2 \text{H}_2\text{O}$
chabazite	rhombohedral : a 9.4 A 94.5°, R3m	$(\text{Ca}, \text{Na}_2)_2 \text{Al}_4\text{Si}_8\text{O}_{24} \cdot 13 \text{H}_2\text{O}$
erionite	hexagonal: a 13.3 c 15.1A P6 ₃ /mmc	$(\text{Ca}, \text{K}_2, \text{Na}_2)_4 \text{Al}_8\text{Si}_{28}\text{O}_{72} \cdot 27 \text{H}_2\text{O}$
faujasite	isometric: a 24.7A; Fd3m	$\text{Na}_{13}\text{Ca}_{11}\text{Mg}_9\text{K}_2\text{Al}_{55}\text{Si}_{137}\text{O}_{384} \cdot 235 \text{H}_2\text{O}$
X	isometric : a 25.0	$\text{Na}_{86}\text{Al}_{86}\text{Si}_{106}\text{O}_{384} \cdot 264 \text{H}_2\text{O}$
Y	isometric : a 24.7	$\text{Na}_{56}\text{Al}_{56}\text{Si}_{136}\text{O}_{384} \cdot 250 \text{H}_2\text{O}$
gmelinite	hexagonal : a 13.7c 10.0A P6 ₃ /mmc	$(\text{Na}, \text{etc})_8 \text{Al}_8\text{Si}_{16}\text{O}_{48} \cdot 24 \text{H}_2\text{O}$
L	hexagonal : 18.4c 7.5A P6/mmm	$\text{K}_9\text{Al}_9\text{Si}_{27}\text{O}_{72} \cdot 22 \text{H}_2\text{O}$
mazzite	hexagonal : 18.4c, 7.6A P6 ₃ /mmc do but a 18.2	$\text{K}_{2.5}\text{Mg}_{2.1}\text{Ca}_{1.4}\text{Na}_{0.3}\text{Al}_{10}\text{Si}_{26}\text{O}_{72} \cdot 28 \text{H}_2\text{O}$ $(\text{Na}, \text{etc})_8 \text{Al}_8\text{Si}_{28}\text{O}_{72} \cdot 21 \text{H}_2\text{O}$
mordenite	orthorombic : a 18.1 b 20.5 c 7.5A Cmc	$\text{Na}_8\text{Al}_8\text{Si}_{40}\text{O}_{96} \cdot 24 \text{H}_2\text{O}$
offretite	hexagonal: a 13.3 c 7.6A P6m2	$\text{KCaMgAl}_5\text{Si}_{13}\text{O}_{36} \cdot 15 \text{H}_2\text{O}$
sodalite	isometric: a 8.9; P43n	$\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24} \cdot 2 \text{NaCl}$
ZK-5	isometric: a 18.7A; Im3m	$\text{Na}_{30}\text{Al}_{30}\text{Si}_{66}\text{O}_{192} \cdot 98 \text{H}_2\text{O}$

From Table 3.1, those with proper names occur as natural minerals. The synthetic zeolites X and Y have the same framework topology as faujasite while Ω is probably related to mazzite. For two felsphathoids - cannerinite and sodalite - are included because their framework are topologically related to the zeolite framework.

3.2 Topology of Zeolite Framework (14)

The only item of a zeolite structure which can be precisely specified is the topology of the aluminosilicate framework. All other items, such as the distribution of atoms on the crystallographically equivalent sites, are complex and uncertain. For mathematical description of the topology, it is desirable to reduce the atomic pattern to the simplest features. Instead of using the chemical concept of four large oxygen anions (radius 1.35 \AA) lying at the vertices of a tetrahedron occupied by a small cation (Al or Si), it is convenient to envisage merely the center position ($1 \text{ \AA} = 0.1 \text{ nm}$). Linked tetrahedra can be presented by joining the centers of adjacent tetrahedra. A zeolite framework thus becomes represented by a four-connected three-dimensional network. The oxygen atoms lie near but not at the midpoints of each branch. Having reduced the silicate framework to a four-connected net, it is now possible to recognize polygons or polyhedra as subunits.

Figure 3.1 shows three levels of abstraction for part of a framework actually the sodalite unit. Diagram (a) shows the centers of the oxygen and T atoms by open and filled circles, respectively (the T atoms are about the correct size, but the O atoms have only one-third the proper ionic radius.) Diagram (b) shows imaginary silicate tetrahedra with shared corners, while (c) shows merely the T-T linkages. At this final stage of abstraction, the T-T linkages

outline a truncated octahedron which is one of the Archimedean semi-regular solids.

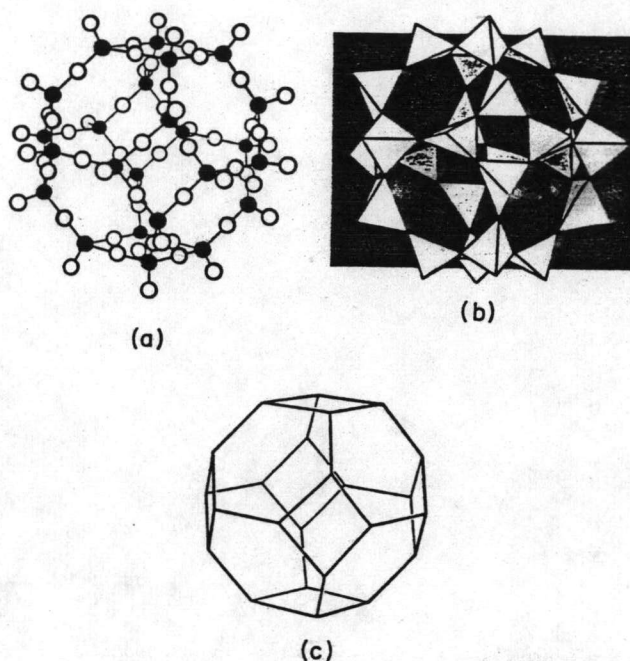


Figure 3.1 *Three ways of depicting the truncated octahedron (or sodalite unit) in aluminosilicate frameworks (14)*

Six of the materials in Table 3.1 have structures related by crosslinking of parallel 6-rings (cancrinites, sodalite, offretite, gmelinite, chabazite, and erionite). For cancrinite, Figure 3.2 and Figure 3.3, can be constructed from 4- and 6- rings. Looking perpendicular to Figure 3.2 (i.e. down the hexagonal axis of the unit cell), the 6-rings are linked by tilted 4-rings. The 6-rings lie at different heights and can be labeled as in Figure 3.3 (upper left) in which the increment of height are 2.5 Å. In projection, one set of hexagonal rings superimposes at heights 0, 2, 4, etc and the other set at 1, 3, 5, etc. Another way of describing the structure utilizes the unit shown in Figure 3.3 (upper right) the "cancrinite cage". This consists of two planar 6-rings and three pairs of adjacent 4-rings. In addition, the cancrinite cage has three boat-shaped 6-rings which complete the 11-sided irregular polyhedron.

Imagine the position of the oxygen atoms which lie near the centers of edges. Remembering that the T-T distances for an

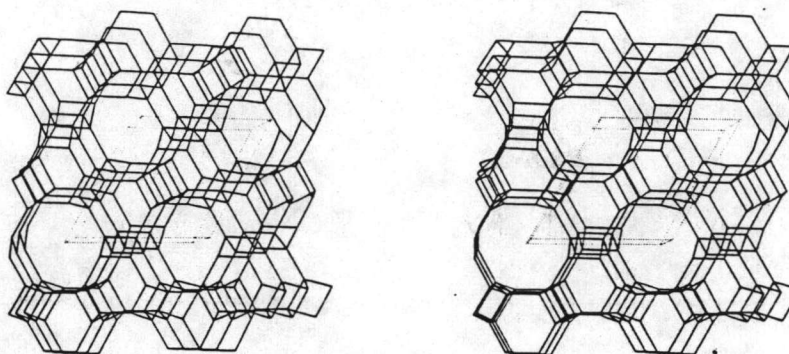


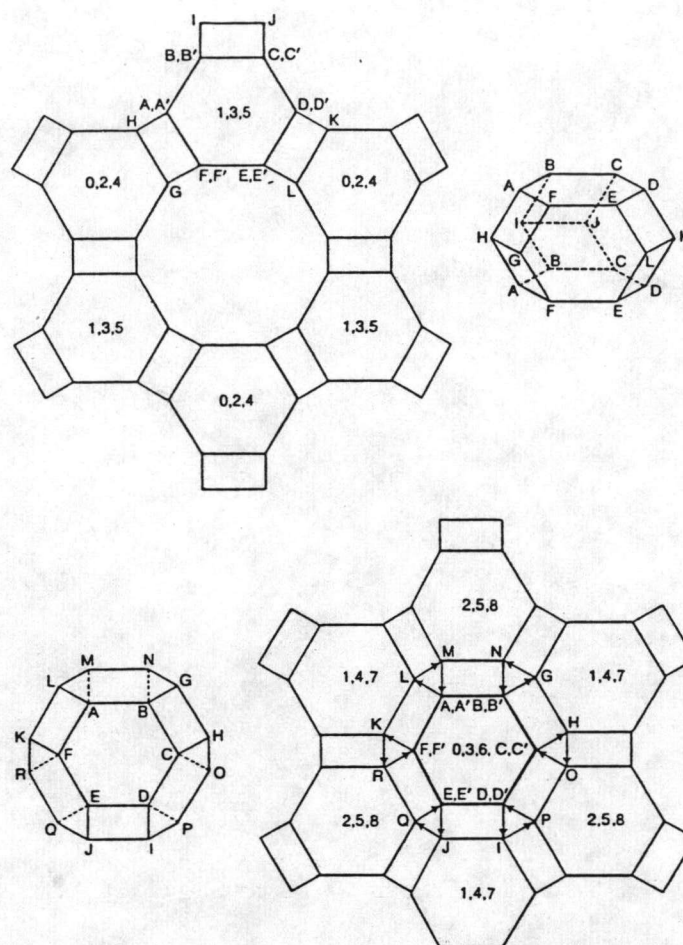
Figure 3.2 *Stereodiagram of framework topology of cancrinite. The dotted lines show one unit cell (14).*

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aluminosilicate are near 3.1 Å and that the radius for an oxygen anion is about 1.35 Å, one can begin to appreciate the amount of space available for the exchangeable cations and water molecules.

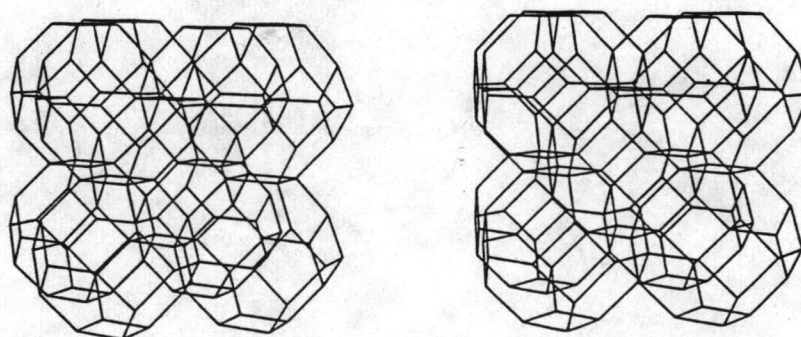
Indeed the projection in Figure 3.3 can be obtained by looking along any of the body diagonals of Figure 3.4. The cubic and hexagonal close packing of spheres is analogous with the linkage of 6-rings of sodalite and cancrinite.

In offretite (Figure 3.5) the pattern of the 6-rings is more complicated. Around the vertical sides of the hexagonal unit cell, the 6-rings lie at heights 1,2,4,5,7,8,etc. forming columns of alternate hexagonal prisms and cancrinite cages. These columns of alternate hexagonal prisms and cancrinite cages. These column are joined by another type of column composed of offretite cages which share parallel 6-rings at the top and bottom. Each offretite cages which share parallel 6-rings at the top and bottom. Each offretite cage also has three triplets of adjacent 4-rings plus three boat-shaped



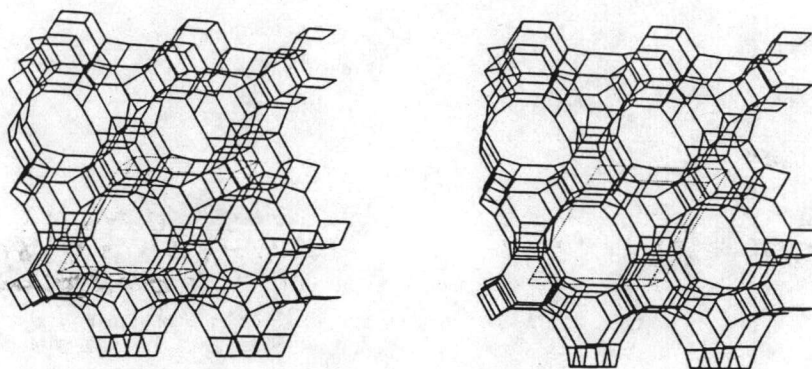
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Figure 3.3 Two-dimensional projections of three-dimensional frameworks of cancrinite and sodalite. In cancrinite (upper left) hexagonal rings superimpose in projection at heights 0, 2, 4, etc. or at 1, 3, 5, etc. The edges of the rings form tilted squares which project as rectangles. A cancrinite cage formed from the labeled intersections of *A* is shown at upper right. In sodalite (lower right), the hexagonal rings superimposed at 0, 3, 6, etc., 1, 4, 7, etc., and 2, 5, 8, etc., form truncated octahedra as shown at lower left. The upper hexagonal face of a truncated octahedron is emphasized at lower right and descending lines are shown by arrows (14)



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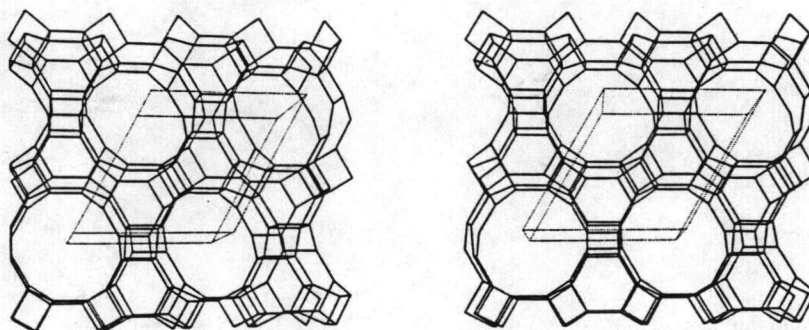
Figure 3.4 Stereodiagram of framework topology of sodalite (14)



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Figure 3.5 Stereodiagram of framework topology of offretite (14)

8-rings.

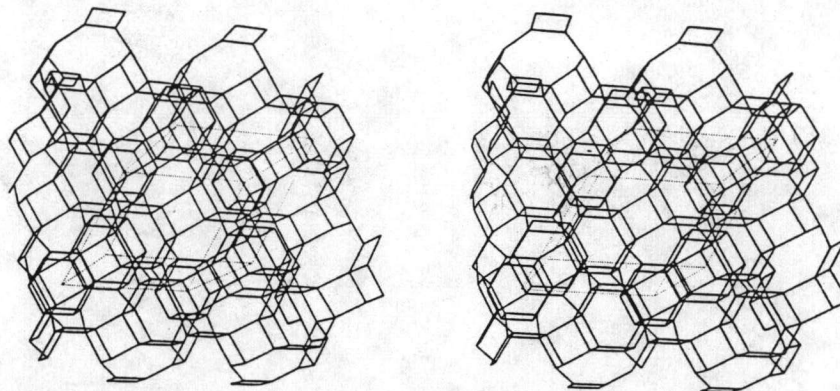
Gmelinite (Figure 3.6) is composed of column of hexagonal prisms alternating with offretite cages. Note that each hexagonal prism shares its 6-rings with offretite cages instead of the offretite structure.



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Figure 3.6 Stereodiagram of framework topology of gmelinite (14)

In both gmelinite and offretite, the hexagonal prisms share 4-rings with offretite cages. The gmelinite structure has 6-rings with offretite cages. The gmelinite structure has 6-rings at height 1, 2, 5, 6, 9, 10, etc and 3, 4, 7, 8, etc. in adjacent columns.

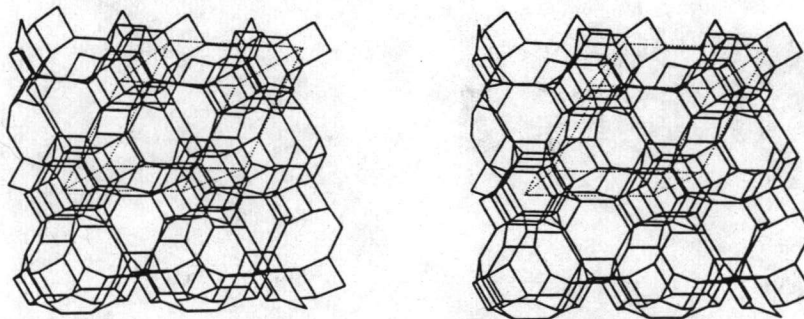
Chabazite is derivable from gmelinite by the same trick : its 6 rings (Figure 3.7) lie in three column at 1, 2, 7, 8, 13,14 etc and 5, 6, 11, 12, 17, 18, etc. The unit cell is now a rhombohedron instead of the



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Figure 3.7 Stereodiagram of framework topology of chabazite (14)

hexagonal prism of gmelinite, and the structure can be obtained merely by placing a hexagonal prism at each corner of the unit cell and linking them by 4-rings. The dotted lines in Figure 3.7 outline the triply primitive hexagonal unit cell. To obtain the primitive rhombohedral cell, connect the centers of adjacent hexagonal prisms.

Finally for this group of zeolites, Figure 3.8 shows the framework topology of erionite. Centered on the vertical edges of the hexagonal unit cell are alternating hexagonal prisms and canorinite



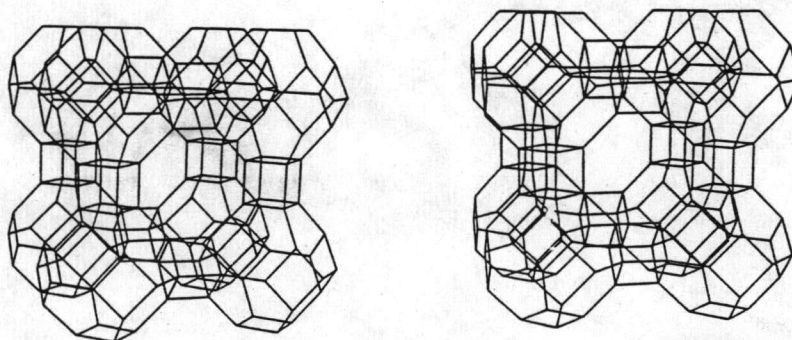
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Figure 3.8 Stereodiagram of framework topology of erionite (14)

units which are crosslinked by 4-rings and single 6-rings to form a complex pore system interconnected by 8-rings.

The possible stacking arrangements this group can be systematized as follows :

Packing type	name
AB	cancrinite
ABC	sodalite
AAB	offretite
AABB	gmelinite
AABBCC	chabazite
AABAAC	erionite
etc.	

The next group has framework whose T atoms are related to Archimedean polyhedra. The A-Zeolite (Figure 3.9) is obtained by replacing each 4-ring of the sodalite cage at the corner of the unit cell by a cube. Each sodalite cage at the body center of the unit cell transforms into a truncated cuboctahedron with twelve 4-rings, eight 6-rings, and six 8-rings. The truncated cuboctahedra form a



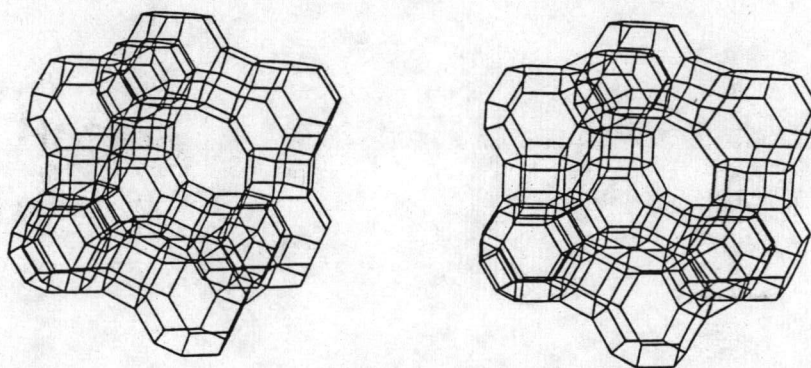
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Figure 3.9 Stereodiagram of framework topology of type A (14)

system of pores linked in three directions by windows of 8-rings. The sodalite units are separated from each other, and access to

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them is via 6-rings.

The topology of faujasite (and of the related X and Y zeolites) is obtained by linking sodalite units with hexagonal prisms. Each sodalite unit (Figure 3.10) is linked to four sodalite units in a tetrahedral configuration by hexagonal prisms which are attached to four of the eight hexagonal faces. There are two ways of linking sodalite units by a hexagonal prism : in faujasite, the 4-rings bordering on the hexagonal prism alternate it give an axis of inverse three-fold symmetry. The framework of faujasite is very open and encloses a system of large cages linked by four windows of 12-rings

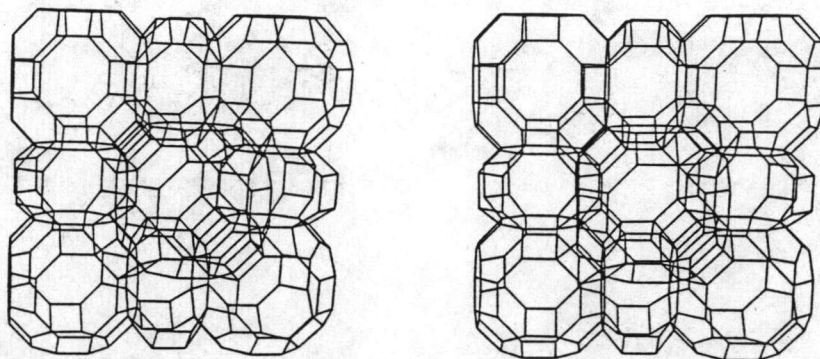


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Figure 3.10 Stereodiagram of framework topology of faujasite (14)

to adjacent pores. Each of the faujasite cages is bounded by eighteen 4-ring, four 6-ring and four 12 rings.

Returning to the A-structure (Figure 3.9), it can be envisaged as the linkage of truncated cuboctahedra by cubes. The ZK5 structure (Figure 3.11) consists of the linkage of truncated cuboctahedra by hexagonal prisms. The remaining volume is occupied by a polyhedron consisting of twelve 4-rings, four boat shaped 8-rings, and two planar 8-rings. The pore system is interconnected in three dimensions with access controlled by the 8-rings.

The framework of mazzite, on the basis of X-ray powder patterns, probably applies also to the synthetic zeolite Ω . This framework (Figure 3.12) is related to that of offretite (Figure 3.5) in that both contain infinite chains of offretite cages sharing hexagonal faces.



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Figure 3.11 Stereodiagram of framework topology of ZK-5 (14)

However, these chains are crosslinked by hexagonal prisms in offretite and by strips of 5-rings in mazzite. Each 5-ring is composed of an edge from three offretite cages plus two horizontal joins shared with adjacent 5-rings. Large cylindrical channels are bounded by the 12-rings and walled by a continuous linkage of 4- and 5- rings. Between the offretite cages there are irregular flattened spaces permitting

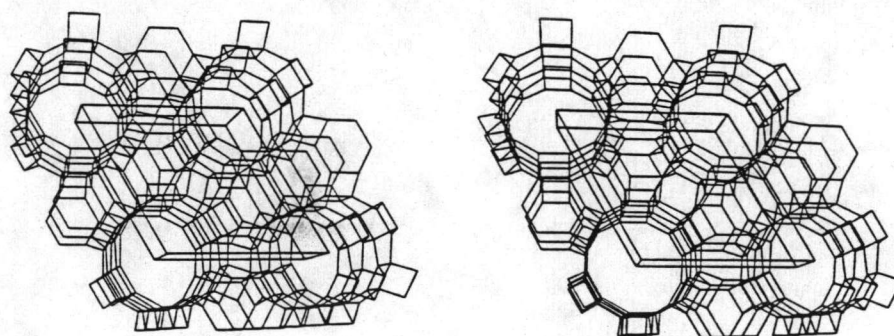
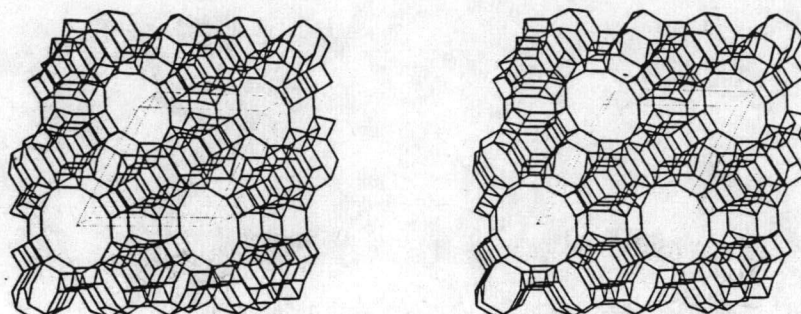


Figure 3.12 Stereodiagram of framework topology of mazzite (prepared by R. Rinaldi and J. J. Pluth) (14)

access by non-planar 8-rings. The pore system is therefore extremely complex with one dimensional tubes bounded by 12-rings separated by

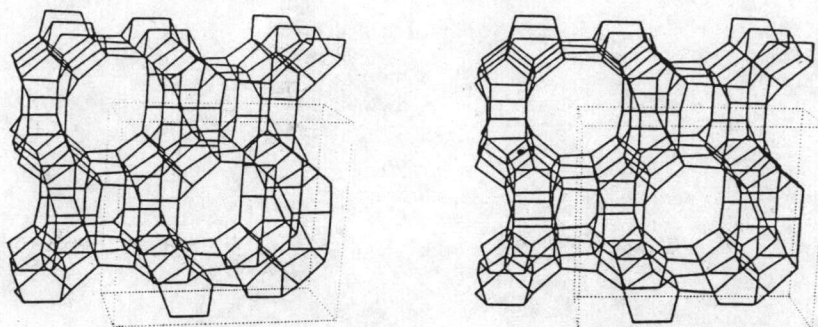
the walls of 4- and 5- rings from the irregular three-dimensional system of linked offretite cages.

The framework of L (Figure 3.13) consists of columns of alternating cancrinite cages and hexagonal prisms as in erionite (Figure 3.8); however the crosslinkages are single horizontal joins instead of hexagons. Large cylindrical channels are bounded by 12-rings and walled by boat-shaped 8-rings and triple 4-rings, the former providing access into the spaces between the cancrinite cages.



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Figure 3.13 Stereodiagram of framework topology of type L (14)

Mordenite (Figure 3.14) is a complex structure composed of horizontal 4-rings interspersed by pairs of tilted 5-rings sharing an edge. These combine together to form twisted 12-rings which span vertical, near-cylindrical channels. The walls of these channels system contain 5-, 6-, and 8- membered rings, the latter providing access through zig-zag passages between adjacent cylinders. The pairs of tilted 5-rings are connected up and down to other pairs of 5-rings to form vertical strips of high rigidity. These strips can be cross-linked in different ways to form other members of the mordenite group of zeolites.



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Figure 3.14 Stereodiagram of framework topology of mordenite (14)

3.3 Zeolite Synthesis with Organic Reagents

Since the work of Barrer and Kerr (15-16), a variety of organic cations have been used in zeolite synthesis. These organic cations are usually found in the following families;

Alkylammonium (R_4N^+)

Alkylphosphonium (R_4P^+)

Organic complexes

More alkylammonium organic cations are used in zeolite synthesis than phosphonium cations. Also, it should be noted that some of the more complex structures are slightly larger than the alkylammonium and phosphonium cations.

The initial driving force for the use of organic cations was to synthesize a zeolite material with a larger intracrystalline pore channel system than X- or Y- type zeolite (8). A wider pore zeolite would crack more of the heavy end of the petroleum barrel because the carbon molecules of the larger hydrocarbon can more easily react at the active site located in the large intracrystalline pore channel

system. A second objective was to synthesize a zeolite material with a high silicon-to-aluminum ratio (Si/Al). As the Si/Al ratio increases, the thermal, hydrothermal, and acid stability also increases. The application of unique organic templates in zeolite synthesis should continue to evolve in the future.

3.4 Framework Substitutes in Zeolite Synthesis

Attempts to synthesize zeolites by replace aluminum and/or silicon in the framework of zeolites can be probably be attributed to early observations of phosphorous in tetrahedral PO_4 units in the rare zeolites, kehoeite and viseite. For obvious reasons, much effort has been directed toward introducing other atoms into the framework of known zeolites such as A,X,Y and mordenite. Such efforts could result not only in new zeolites structures with unique pore channel and cage systems, but also in the synthesis of new catalytic systems with unusual substrate-zeolite "solvent" framework interactions. Such substrate-zeolite solvent framework interaction could lead to highly selective reaction pathways.