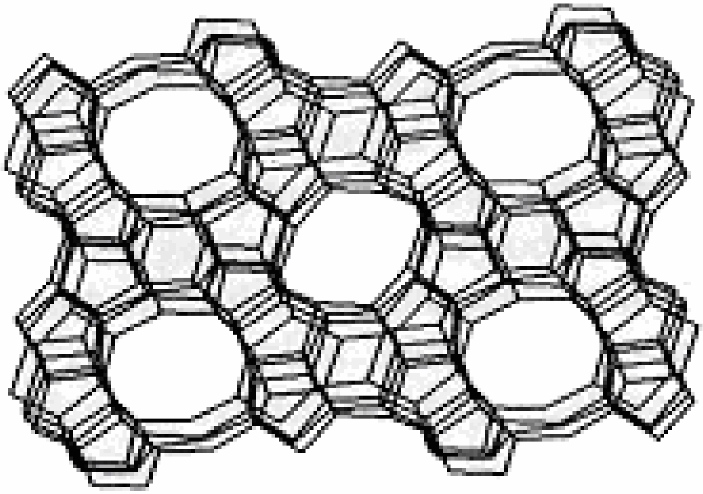
# Zeolites and zeolitic materials

**Molecular sieves = highly organized matrices of tunable pore shape, size, and polarity for separation, recognition, and organization of molecules with precision of about 1 Å.**

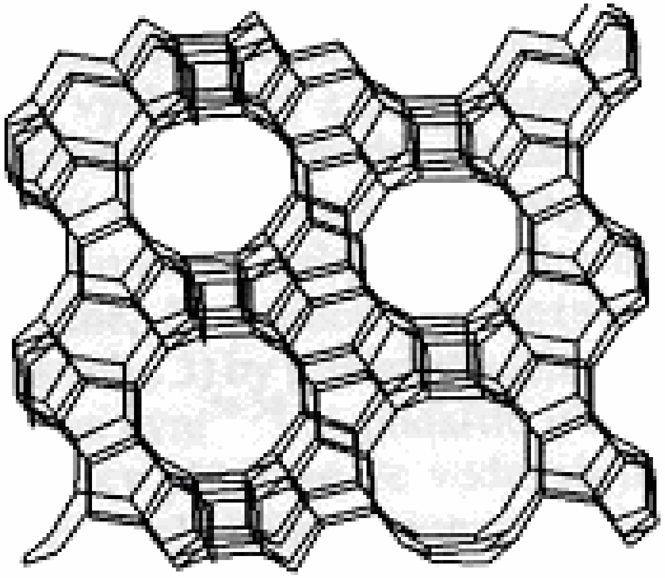
**detergent builders**
**adsorbents**
**size-shape selective catalysts**
**supramolecular chemistry**
**nanotechnology**

| | |
|---|---|
| **Chemical composition** | |
| **Silica** | $SiO_2$ |
| **Aluminosilicates** | $M_x^{I}Al_xSi_{2-x}O_4 \cdot nH_2O$ |
| **Aluminophosphates** | $AlPO_4$ (isoelectronic with $Si_2O_4$) |
| **Metallophosphates** | $MPO_4$ |
| **Silicoaluminophosphates** | $M_x^{I}Si_xAlP_{1-x}O_4$ |

Pores
Channels



ZSM-5[010]



Beta [100]

# Zeolites and zeolitic materials

**>40 naturally occurring zeolites**
**>139 structure types**
**many hundreds of zeolite compounds**

**Nomenclature** www.iza-structure.org/databases
**Structure types - three capital letter codes (Most well known zeolite archetypes: SOD, LTA, FAU, MOR, MFI )**

**Four-connected frameworks**
**Interrupted frameworks (denoted by a hyphen: –CLO, cloverite)**

**Structure types do not depend on: chemical composition, element distribution, cell dimensions, symmetry**

**Several zeolite compounds can belong to the same structure type: FAU – faujasite, Linde X, Y, Beryllophosphate-X, SAPO-37, Zincophosphate-X**

# Zeolites and zeolitic materials

**Names of zeolite materials:**

**trivial names – Alpha, Beta, Rho**

**chemical names – Gallogermanate-A**

**mineral names – Chabazite, Mordenite, Stilbite, Sodalite**

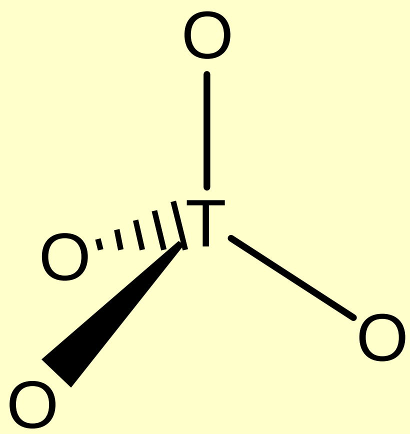
**codes – $AlPO_4$-5, 8, 11, ..., 54, ZSM-4, 18, 57, ...**

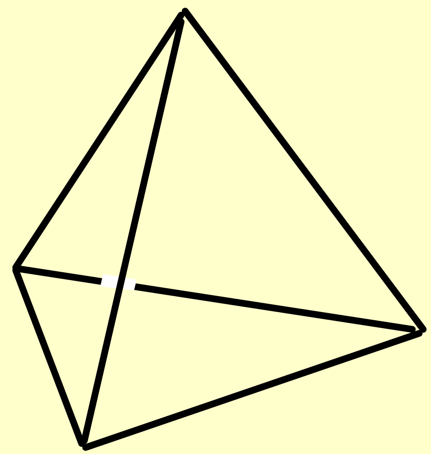
**brand names – Linde A, D, F, L, N, Q , R, T, W,  X, Y**

**university names – VPI-5 (Virginia Polytechnical Institute)**

# Zeolites and zeolitic materials

☞ **Primary building units: Al(III)$O_4$, P(V)$O_4$ and Si(IV)$O_4$ tetrahedra**

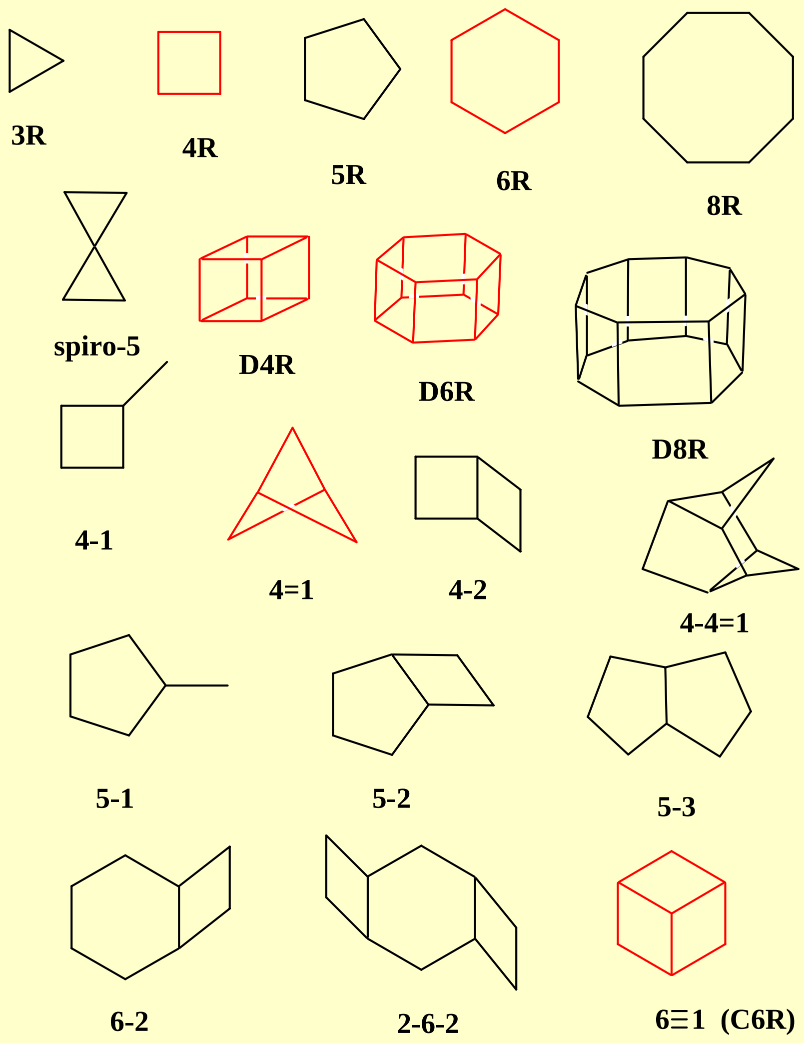


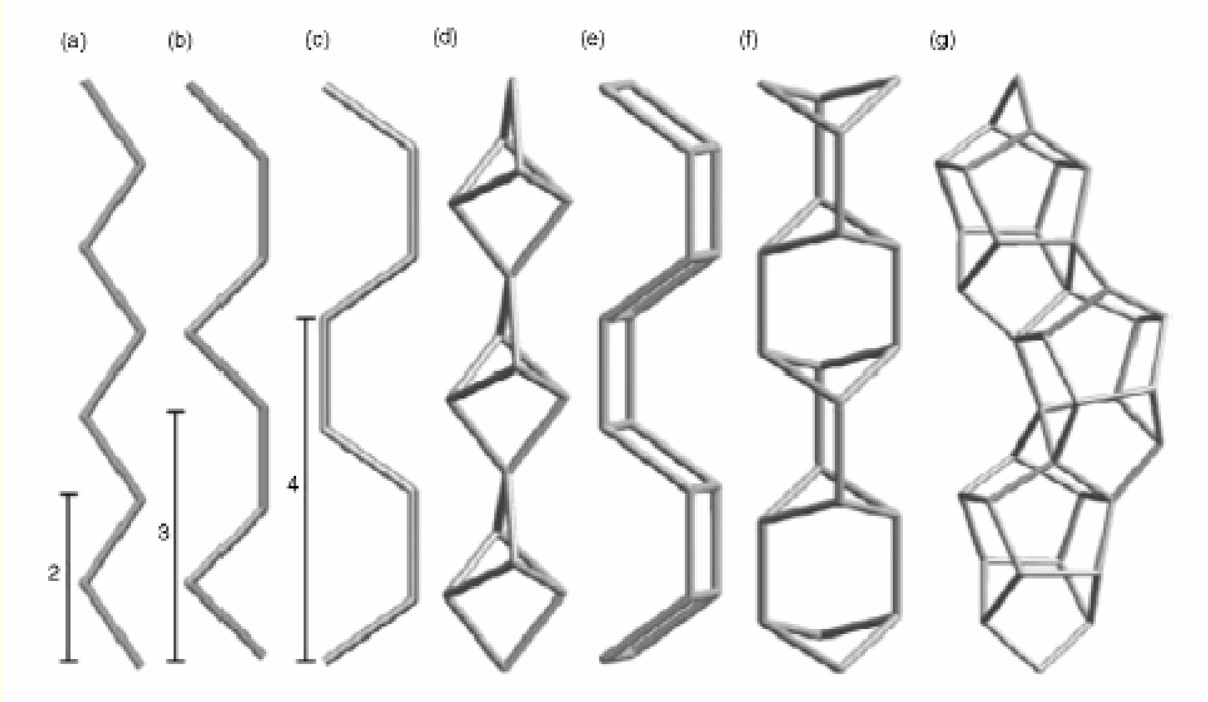
Isoelectronic relationship

$(SiO_2)_2$ $[AlSiO_4]^-$ $AlPO_4$

# Secondary (Structural) Building Units (SBU)

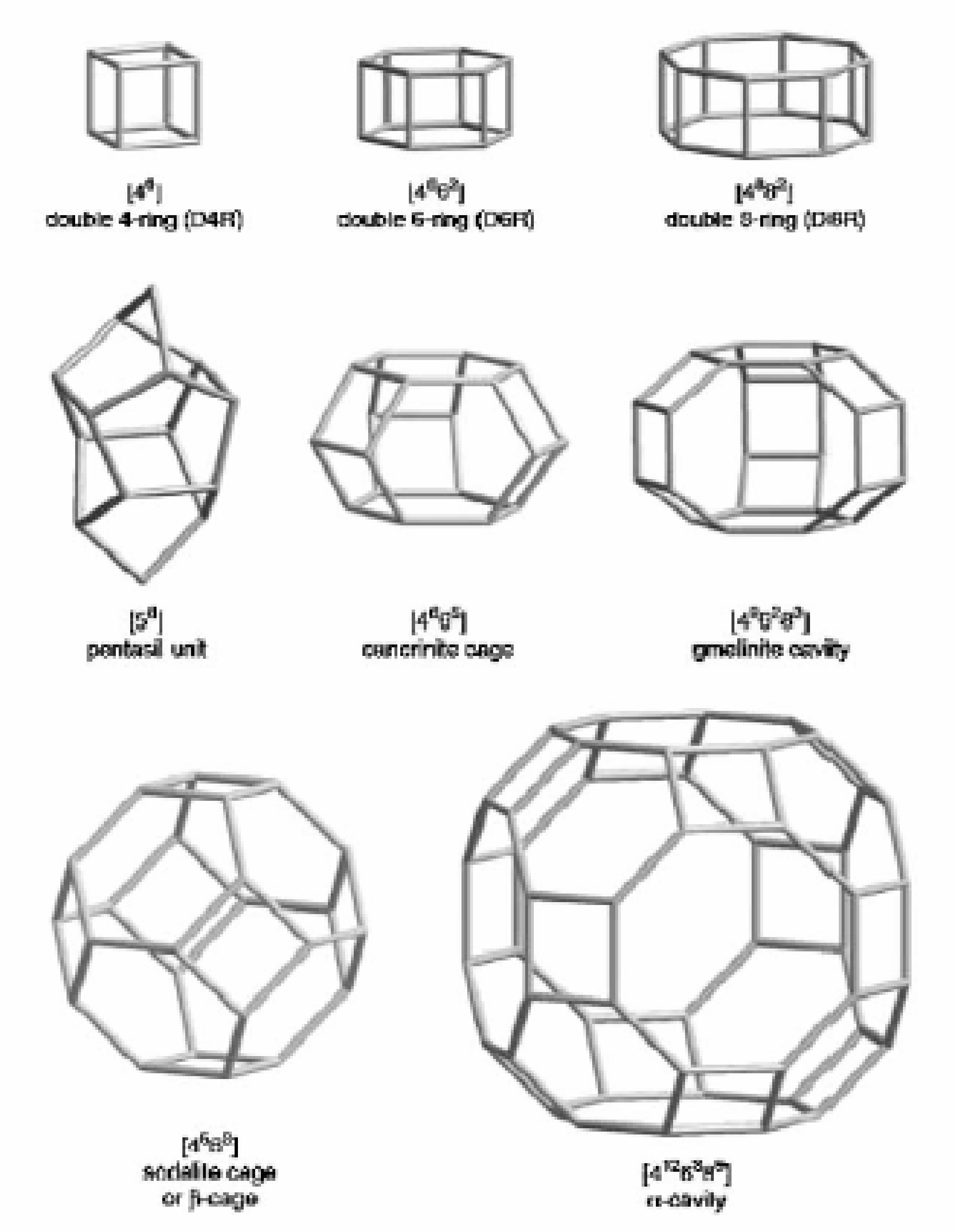


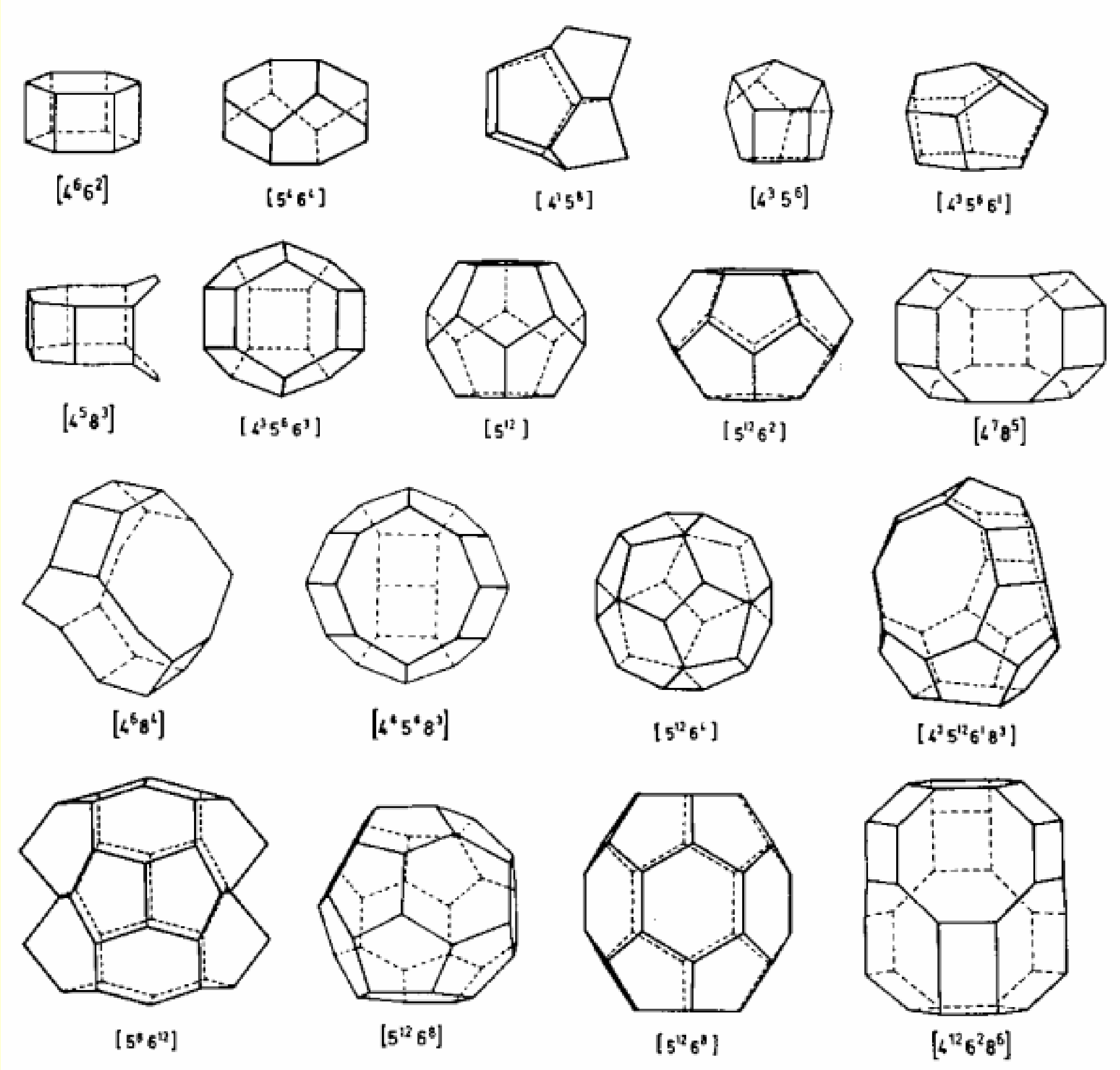
# Chain composite building units



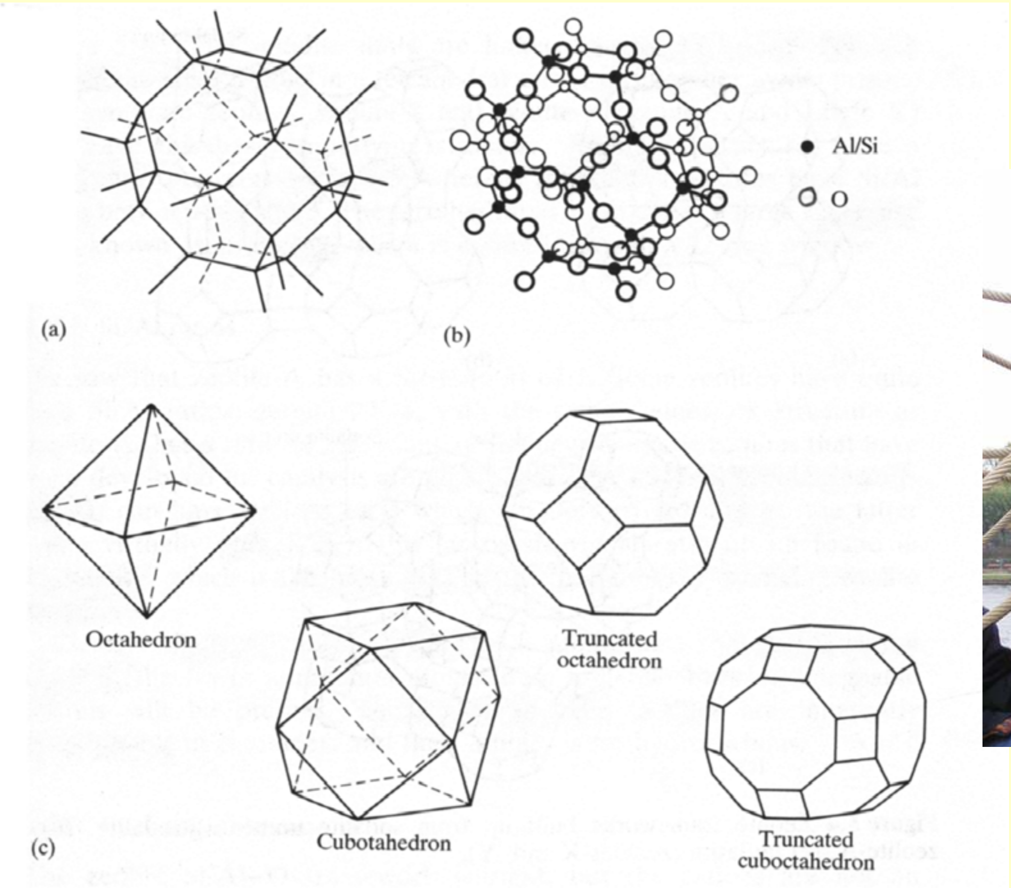

**(a) zig-zag unbranched single chain, periodicity of two**
**(b) sawtooth unbranched single chain, periodicity of three**
**(c) crankshaft unbranched single chain, periodicity of four**
**(d) natrolite branched single chain**
**(e) double crankshaft chain, an unbranched double chain**
**(f) narsarsukite chain, a branched double chain**
**(g) a pentasil chain**

**Polyhedral composite building units**



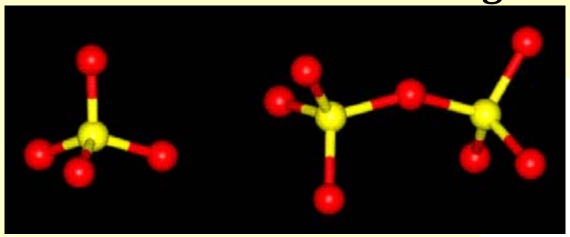

[4^6 6^2]
[5^4 6^4]
[4^1 5^8]
[4^3 5^6]
[4^3 5^6 6^1]
[4^5 8^3]
[4^3 5^6 6^3]
[5^12]
[5^12 6^2]
[4^7 8^5]
[4^6 8^4]
[4^4 5^4 8^3]
[5^12 6^4]
[4^3 5^12 6^1 8^3]
[5^8 6^12]
[5^12 6^8]
[5^12 6^8]
[4^12 6^2 8^6]

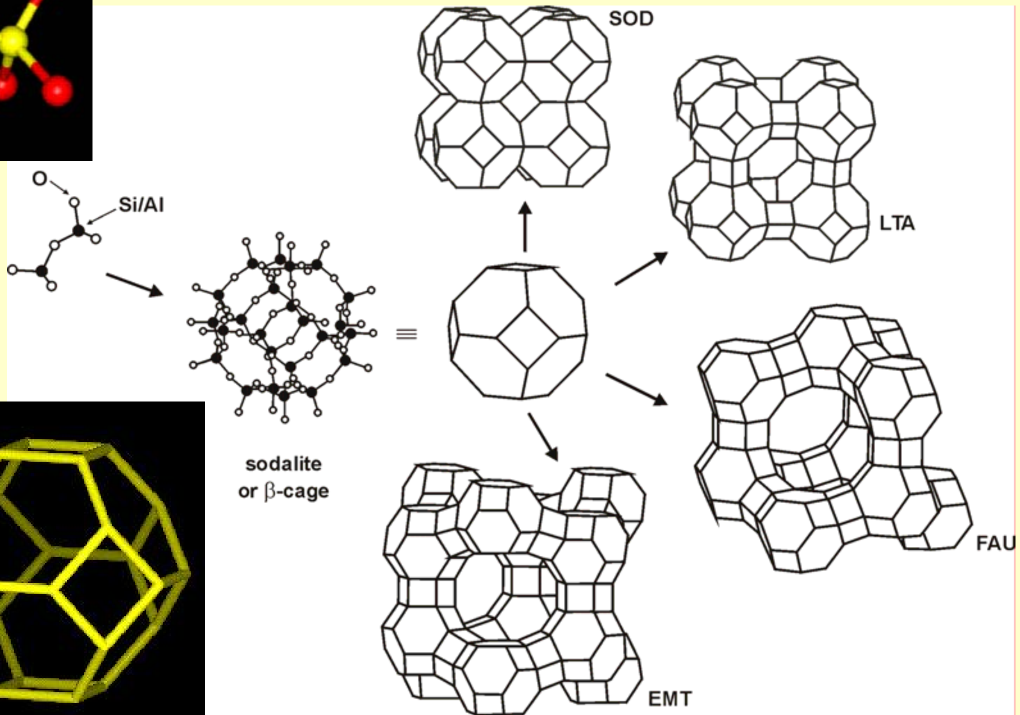
# Sodalite unit

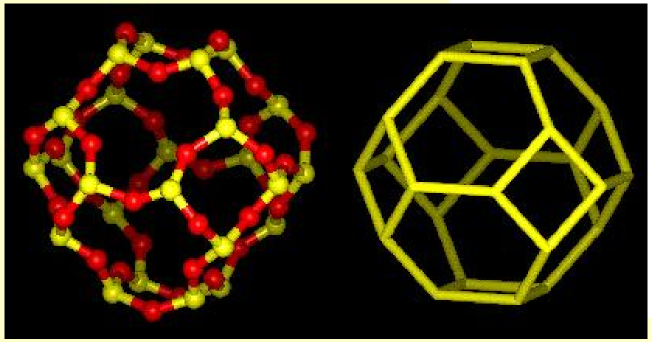



# Sodalite unit

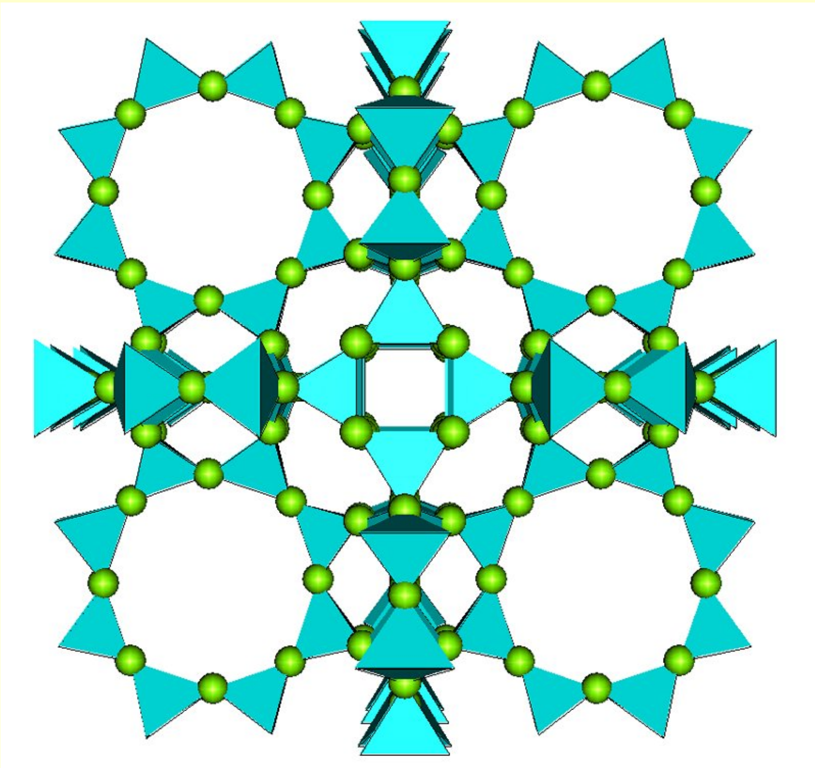
**Packing of the sodalite units:**
**SOD – bcc, sharing of 4-rings**
**LTA – sc, 4-rings connected through O bridges**
**FAU (faujasite) – cubic diamond, 6-rings connected through O bridges**
**EMT – hexagonal diamond, 6-rings connected through O bridges**

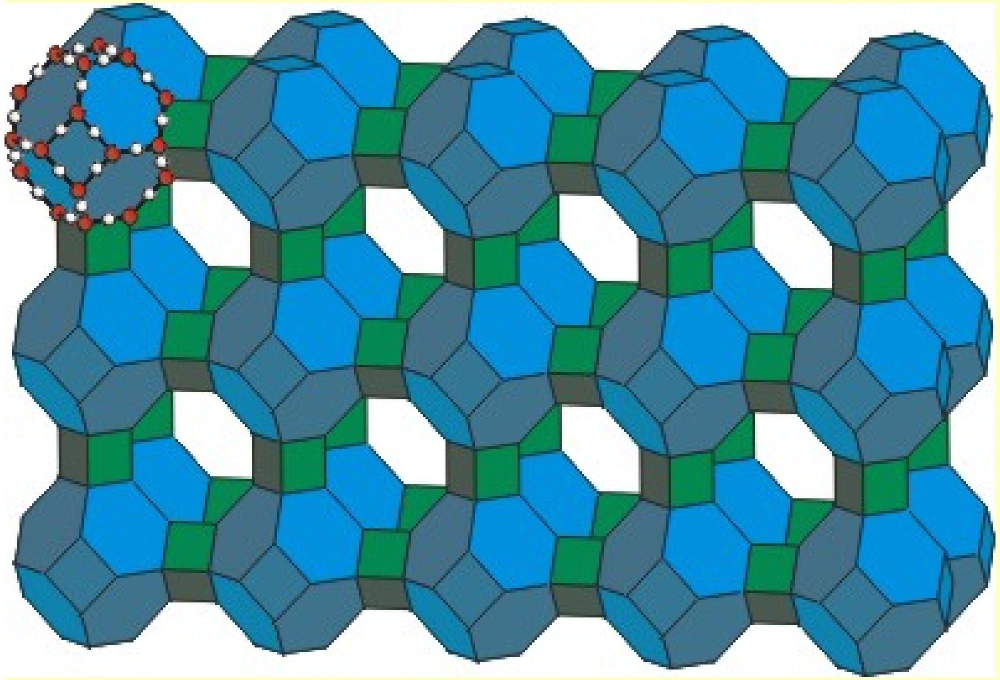




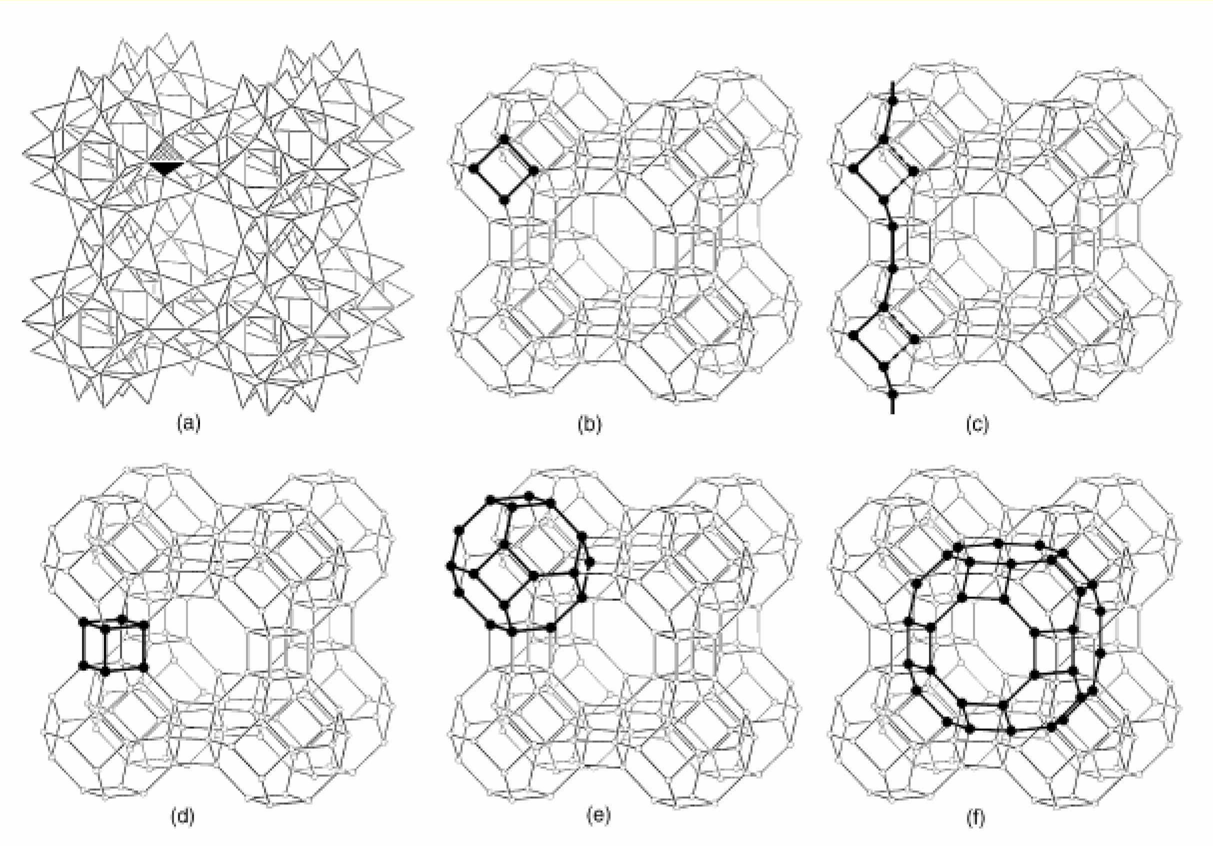



# LTA



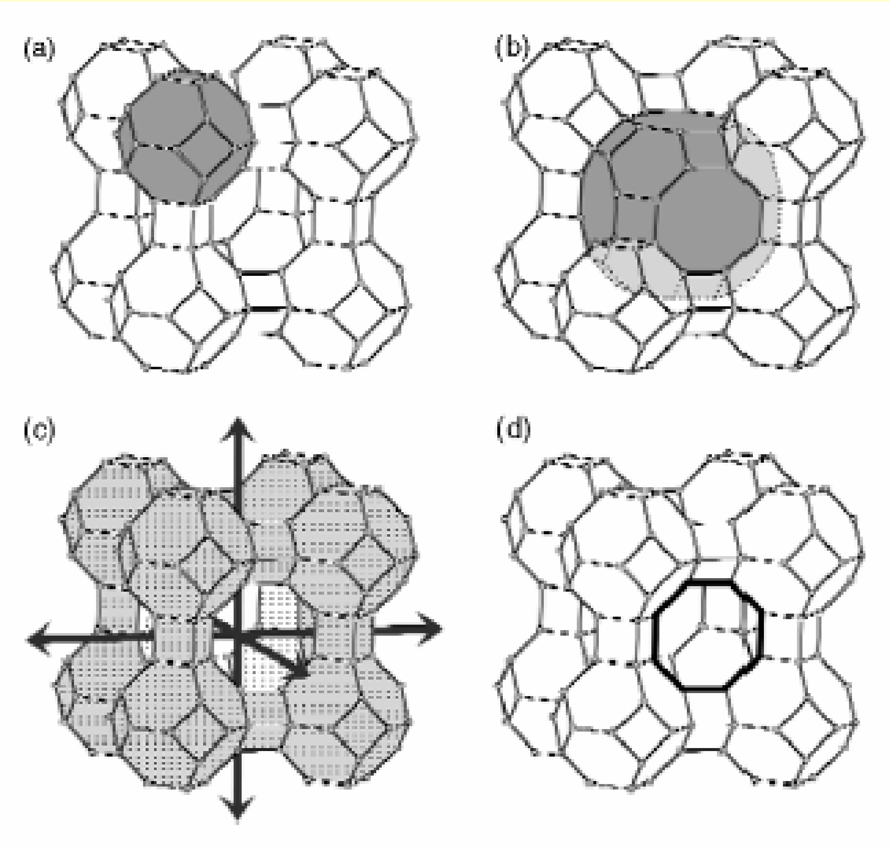


# Zeolite A

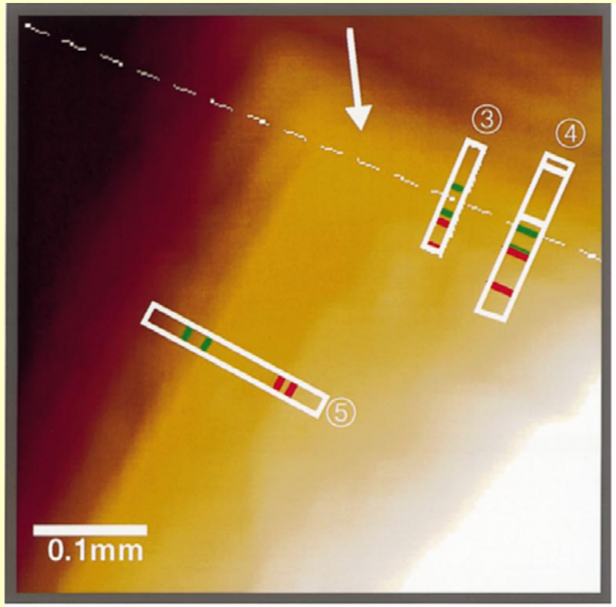



**(a) $[TO_4]$ tetrahedra as BBU**
**(b) four-membered single rings**
**(c) lB fuenfer chains**
**(d) cubes $[4^6]$**
**(e) truncated octahedra $[4^6 6^8]$ (sodalite- or β-cages)**
**(f) truncated cubeoctahedra $[4^{12} 6^8 8^6]$ (α-cavities)**

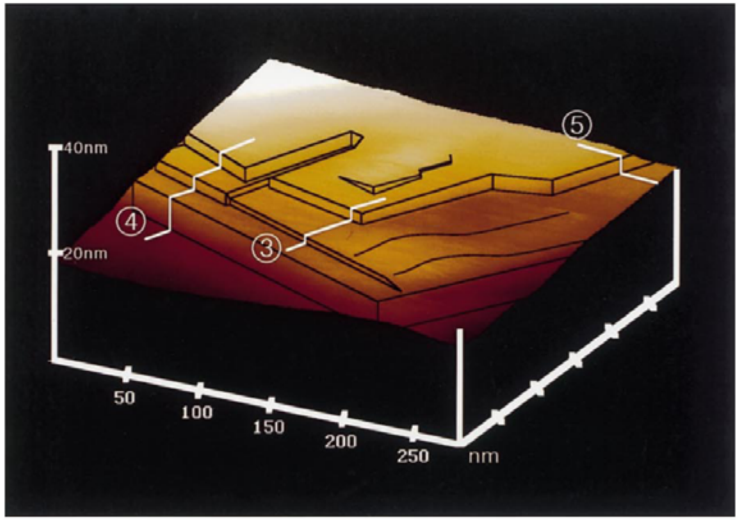
# Pores in zeolite A (LTA)




(a) the sodalite cage $[4^6 6^8]$
(b) the α-cavity $[4^{12} 6^8 8^6]$
(c) the 3-dimensional channel system
(d) the 8-ring defining the 0.41 nm effective channel width

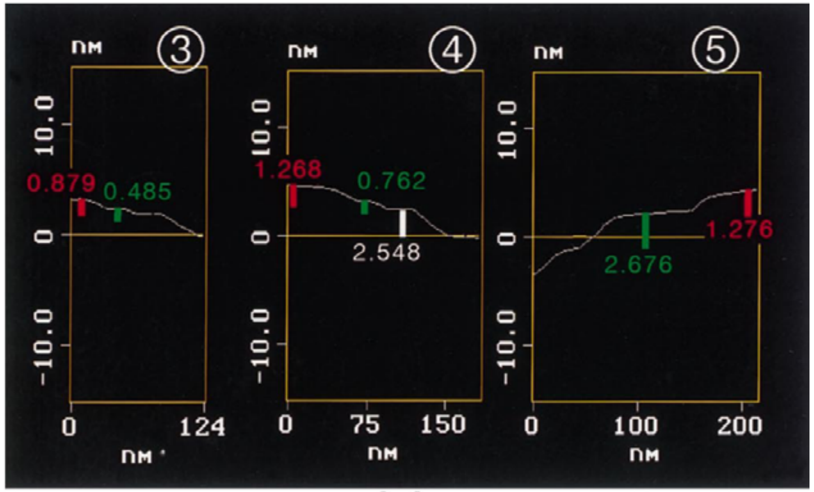



(a)




(b)

D4R



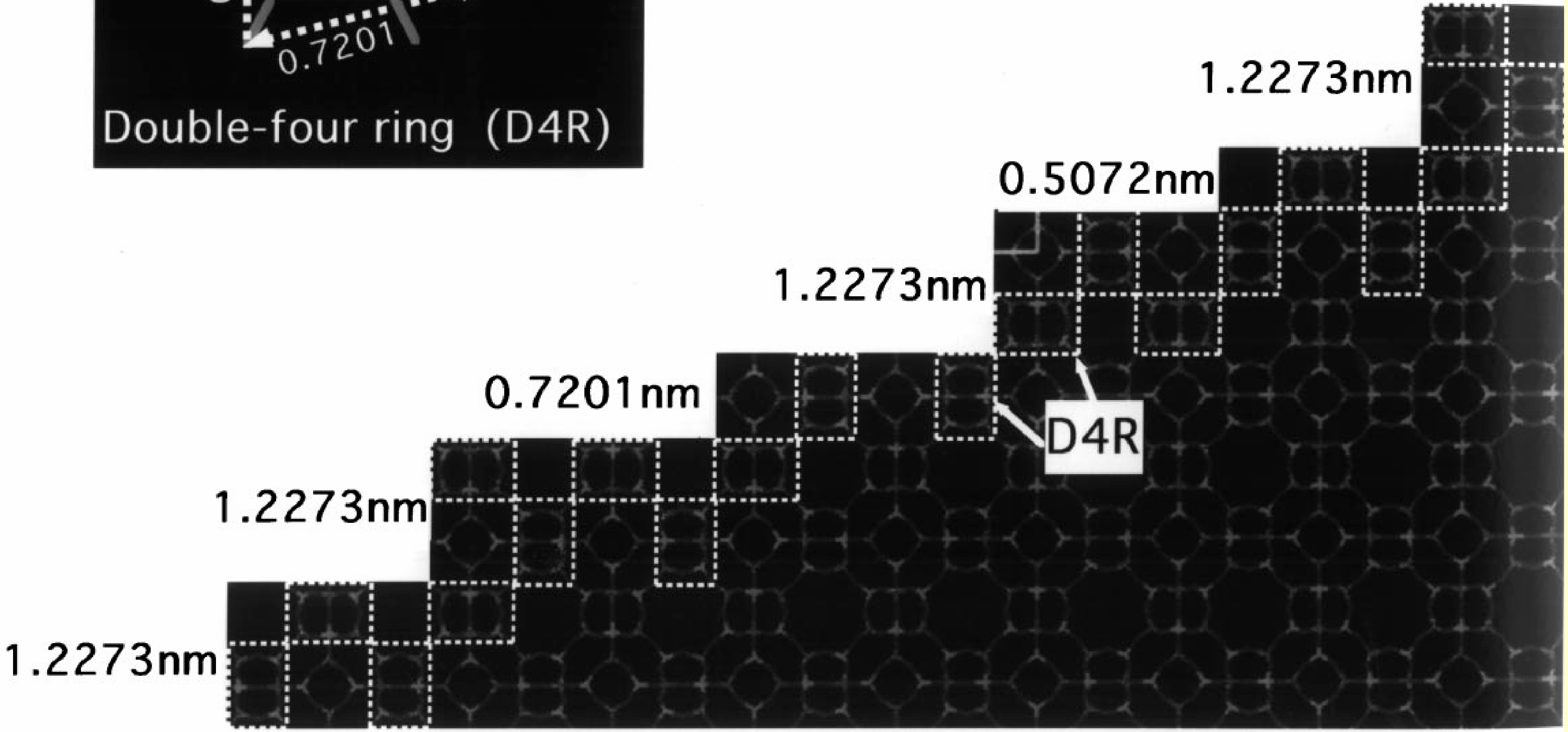

(c)

# AFM growth studies of LTA

S. Sugiyama et. al. Microporous and Mesoporous Materials 28 (1999) 1–7

# D4R


0.5072
0.5072nm
0.7201
Double-four ring (D4R)


1.2273nm
0.5072nm
1.2273nm
0.7201nm
D4R
1.2273nm
1.2273nm

# Zeolite FAU (X and Y) and EMT

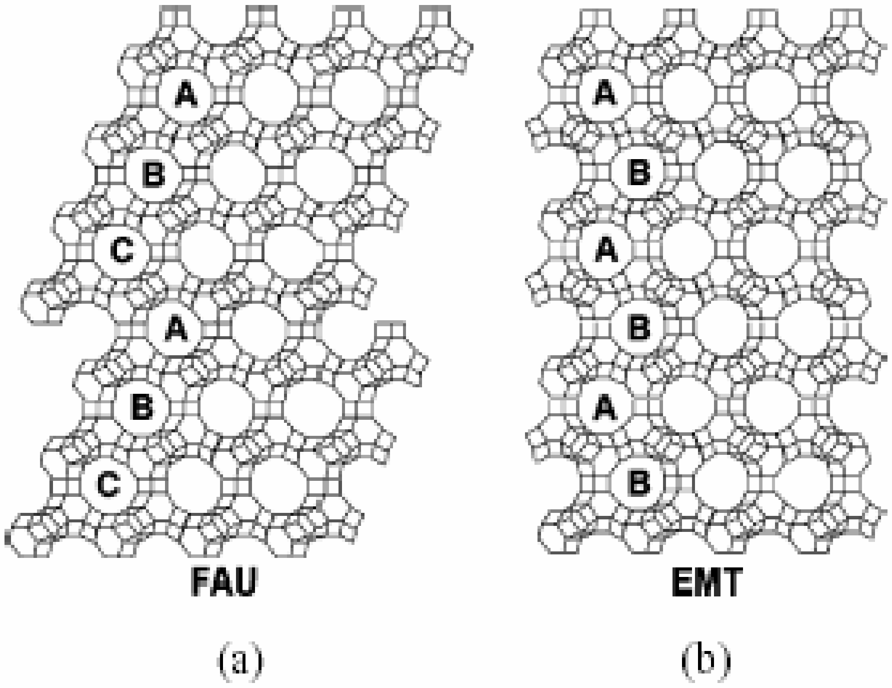



Fig. 1. Structure of zeolite Y: (a) cubic polymorph known as FAU with ABCABC… stacking, (b) hexagonal polymorph known as EMT with ABABAB… stacking.

| | | | |
|---|---|---|---|
| FAU | | | |
| Cubic | ABCABC… stacking of layers agent | analagous to zinc blende | 15-crown-5 structure directing agent |
| EMT | | | |
| Hexagonal | ABABAB… stacking of layers | analagous to wurtzite | 18-crown-6 structure directing agent |

# Molecular sieves

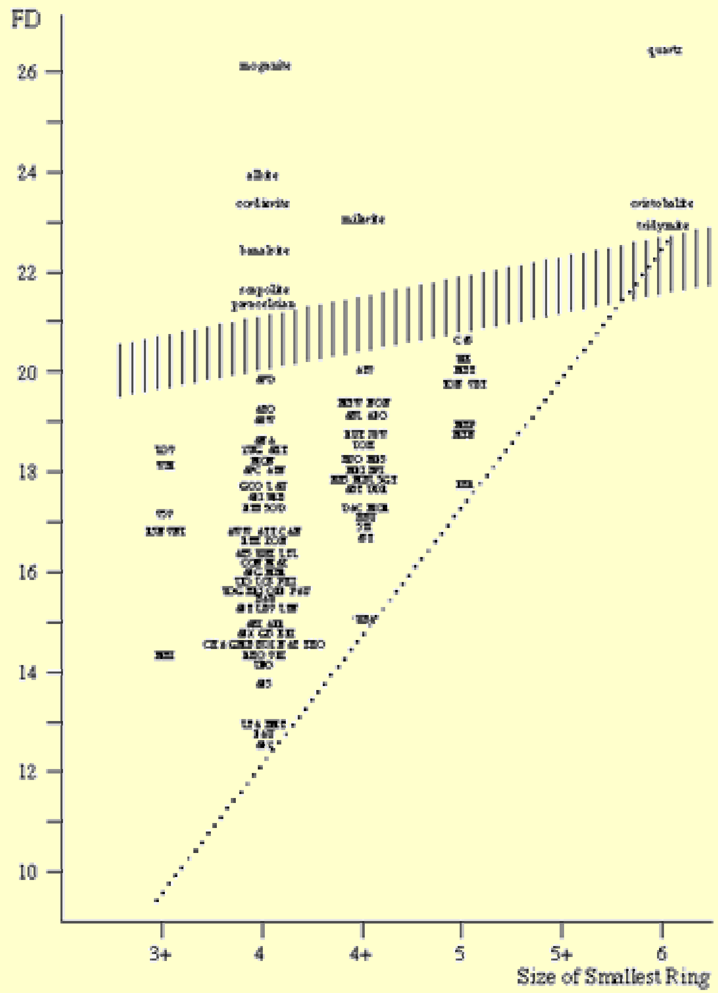
| Zeolite | Cation | Code | Pore diameter |
|---|---|---|---|
| Zeolite A: | Na | 4A | 0.42 nm |
| | Ca | 5A | 0.48 nm |
| | Na, K | 3A | 0.38 nm |
| Zeolite X: | Na | 13X | 0.8-1.0 nm |
| | Ca | 10X | 0.7 nm |

Zeolite Y contains more Si

# Framework density

**Framework density (FD)**

**Defined as the number of tetrahedral atoms (T-atoms) per cubic nanometer (1000 A$^3$)**
**FD is related to the void volume of the crystal: as the FD value decreases, the void volume and capacity for adsorption increases FD < 20 are characteristic of microporous structures, the minimum known FD is 12.5 with the void occupying just over half of the crystal volume**



➢**Pores**

**Various sizes (4 - 13 Å), shapes (circular, elliptical, cloverleaf-like), and connectivity (1-3D)**
**The size of the rings formed by the $TO_4$ tetrahedra ranges from 4 to 18 of the T-atoms and determines the pore aperture**

➢**Extraframework charge-balancing cations**

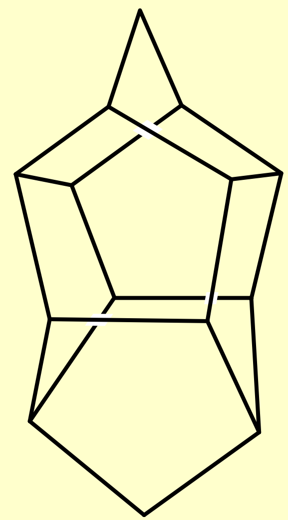
**Ion-exchangeable, size, charge, positions, distribution, ordering, coordination number**

➢**Si-to-Al ratio**

**Influences cation content, hydro-phobicity/-philicity, acidity**
**Löwenstein rule:**
**absence of the Al-O-Al moieties ⇒ in aluminosilicates Si/Al ≥ 1**

| | |
|---|---|
| **Linde A (LTA)** | **Si/Al = 1** |
| **ZK-4 (LTA)** | **Si/Al = 2.5** |
| **ZSM-5** | **Si/Al = 20 - ∞** |
| **Pure $SiO_2$** | **Si/Al = ∞** |

**Pentasils**
**ZSM-5**



# Zeolite Synthesis

**Synthesis - an empirical and heuristic process, new phases are often discovered by serendipity**

**Aluminosilicates – high pH**

- **Mixing**

**$NaAl(OH)_4(aq) + Na_2SiO_3(aq) + NaOH(aq)$, 25 °C, condensation-polymerization, gel formation**

- **Ageing**

**$Na(H_2O)_n^+$ template effect $\rightarrow$ $Na_a(AlO_2)_b(SiO_2)_c.NaOH.H_2O(gel) \rightarrow$ 25-175 °C**

- **Hydrothermal crystallization of amorphous gel, 60-200 °C**

**$Na_x(AlO_2)_x(SiO_2)_y.zH_2O$(crystals)**

- **Separation of the solid product by filtration**
- **Calcination**

**- occluded water, removed by 25-500 °C vacuum thermal dehydration**

**-template removal – calcination in $O_2$ at 400-900 °C removes the guest molecules from the framework without altering it**

**– extraction (neutral templates)**

# Zeolite Synthesis

**Structure of the zeolite product depends on:**

**- Composition**
**- Concentrations and reactant ratios**
**- Order of mixing**
**- Temperature**
**- Ageing time (hours to weeks)**
**- Crystallization time (days to weeks, kinetics of the structure-directing process is slow)**
**- pH**
**- Stirring/no stirring**
**- Pressure**
**- Seeding**
**- Reactor material (PTFE, glass, steel)**
**- Templates**

**Templates: Organic cationic quaternary alkylammonium salts, alkylamines, aminoalcohols, crownethers,**
**structure-directing, space-filling, charge-balancing**
**Vary the template - discover new structures !**

# Templates

**Template or guest compounds**
**Three levels of the guest action with increasing structure-directing specificity:**

■ **Space-filling - the least specific, observed, for example, in the synthesis of $AlPO_4$-5, 23 different, structurally unrelated compounds, could be employed, they pack in the channels of the structure thereby increasing its stability.**

■ **Structure-directing - a higher degree of specificity, only tetramethylammonium hydroxide is effective in the synthesis of $AlPO_4$-20**
**-elongated molecules, such as linear diamines, initiate the formation of channels**
**-nondirectional-shaped guests leads to the formation of cage-like cavities, the size of these cavities correlates with the size of freely rotating guests**

■ **True templating - very rare, it requires even more precise host-guest fit which results in the cessation of the free guest-molecule rotation**

**A curiosity: aluminophosphate VPI-5 does not require any guest for its formation!**

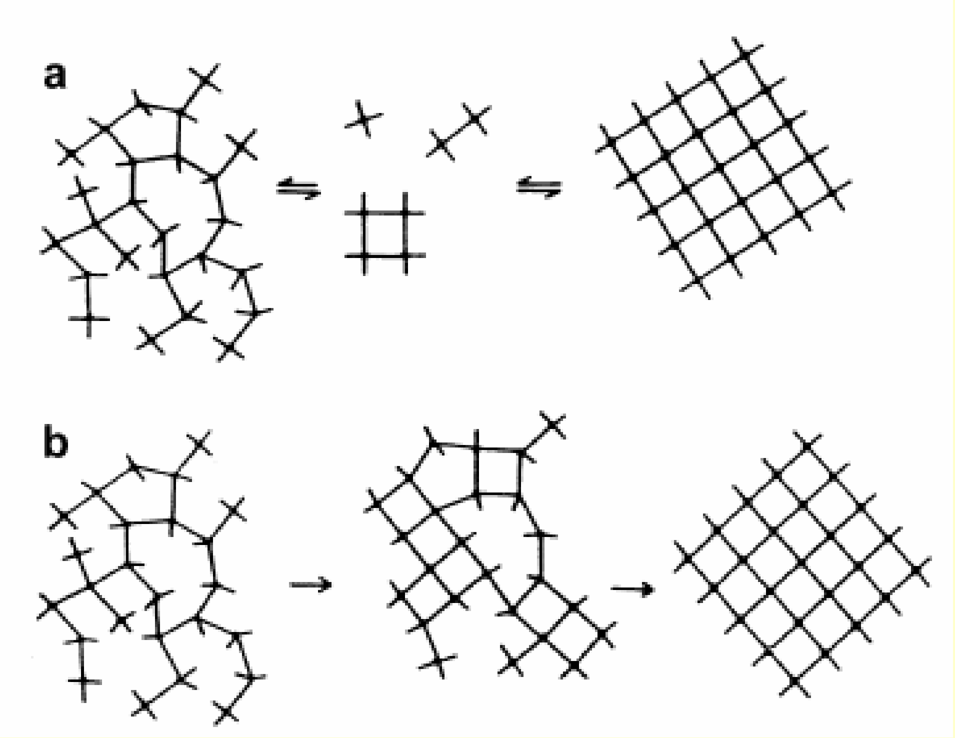
# ZEOLITES and ZEOLITIC MATERIALS

**The ratio $TO_2/(C + N + O)$ is a measure of space-filling of the framework by the guest molecules, characteristic for a specific guest and structure.**

**Existence of primary and secondary units in a synthesis mixture, 4R, 6R, 8R, D4R, D6R, 5-1, cubooctahedron**

# The zeolite synthesis mechanism

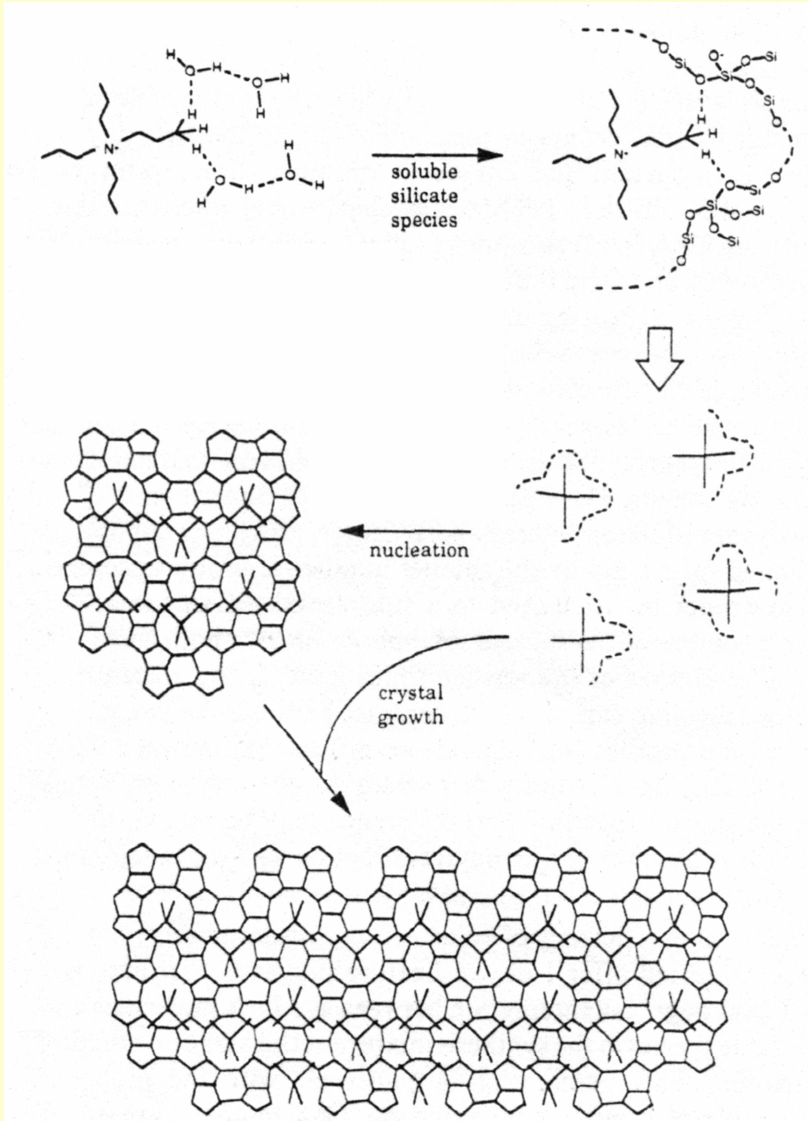
(a) gel dissolution and solution mediated crystallization (SBU in solution)




(b) “in situ” rearrangement of the gel

# ZEOLITES and ZEOLITIC MATERIALS

**Mechanism of structure-directing action of the TPA template**



# Zeolites and zeolitic materials

**Wide range of solid state characterization methods for zeolites: diffraction, microscopy, spectroscopy, thermal, adsorption and so forth**

**Zeolite post modification for controlling properties of zeolites**

**Tailoring channel, cage, window dimensions:**

- **Cation choice ($Ca^{2+}$ exchanged for $Na^{+}$)**
- **Larger Si/Al**
  - **decreases unit cell parametrs, window size**
  - **decreases number of cations, free space**
  - **increases hydrophobicity**
- **Reaction temperature, higher T, larger pores**

# Stability Rules

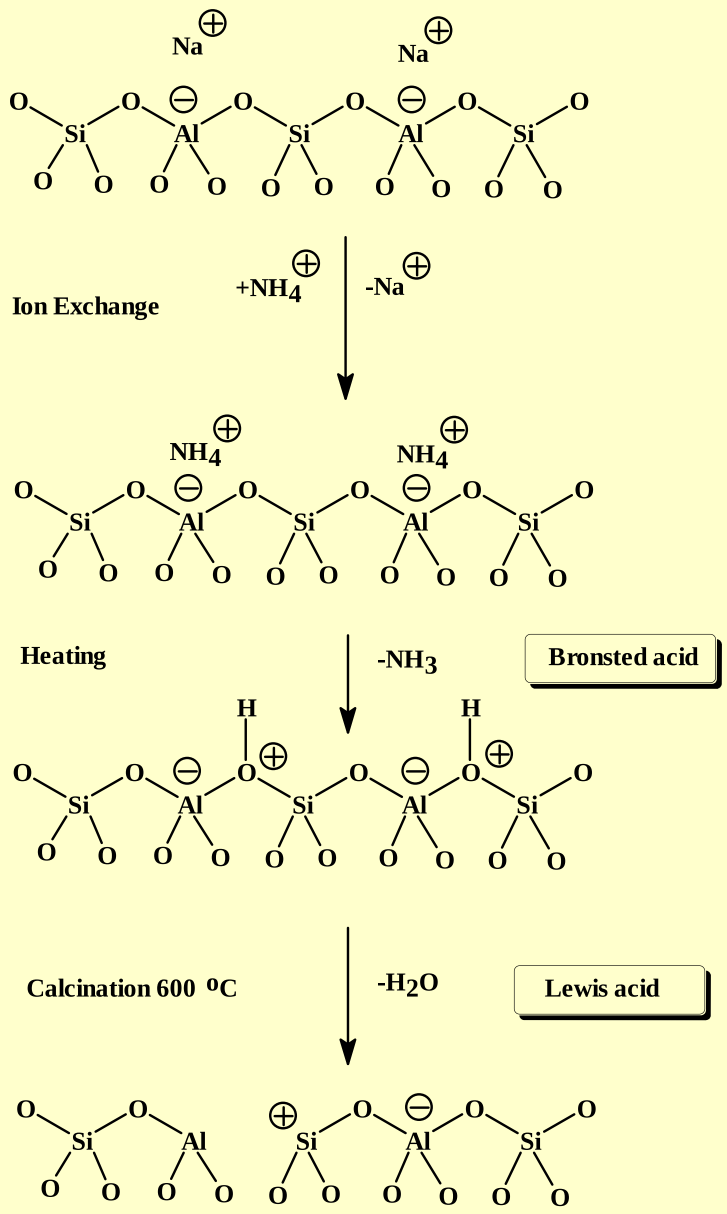
Lőwenstein rule: never Al-O-Al

Dempsey rule: Al-O-Si-O-Si-O-Al
is more stable than
Al-O-Si-O-Al

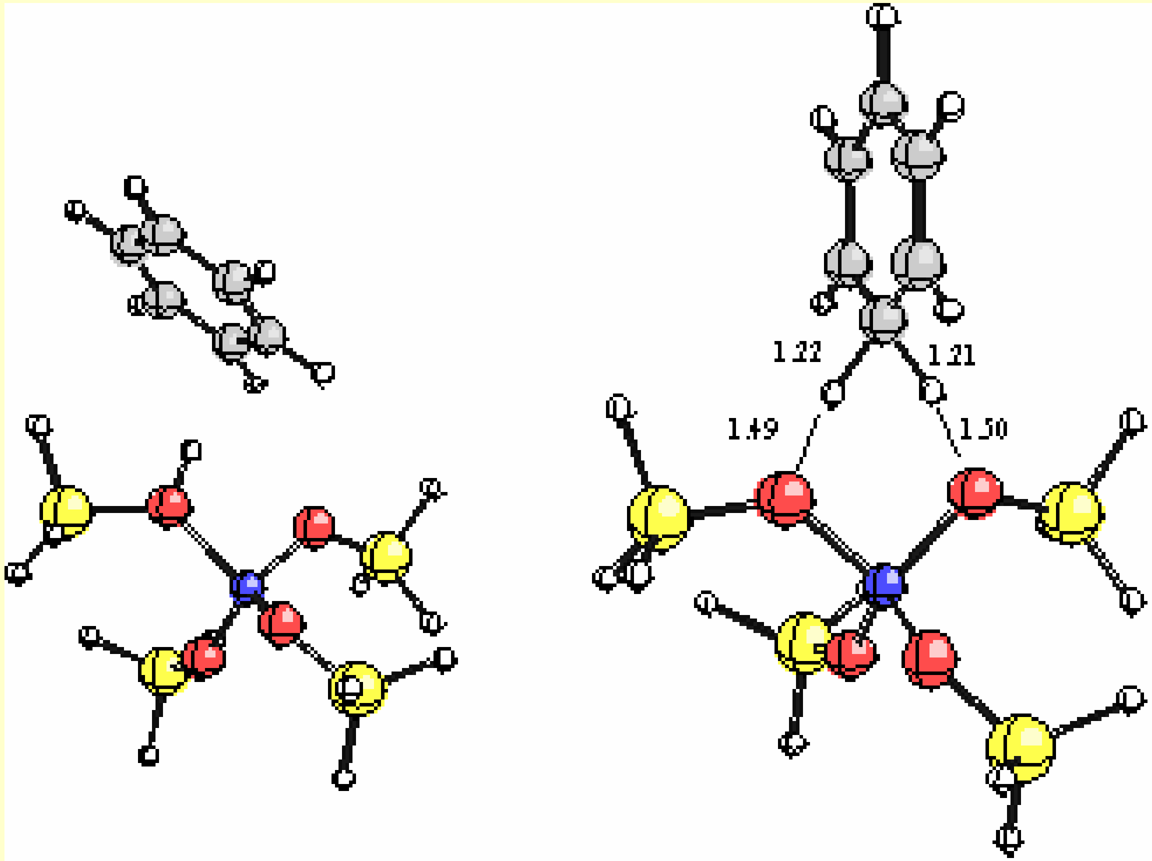
NNN-principle

**Tuning Bronsted acidity:**

**Solid acid for the hydrocarbon cracking**
**The larger the Si/Al ratio,the more acidic is the zeolite**

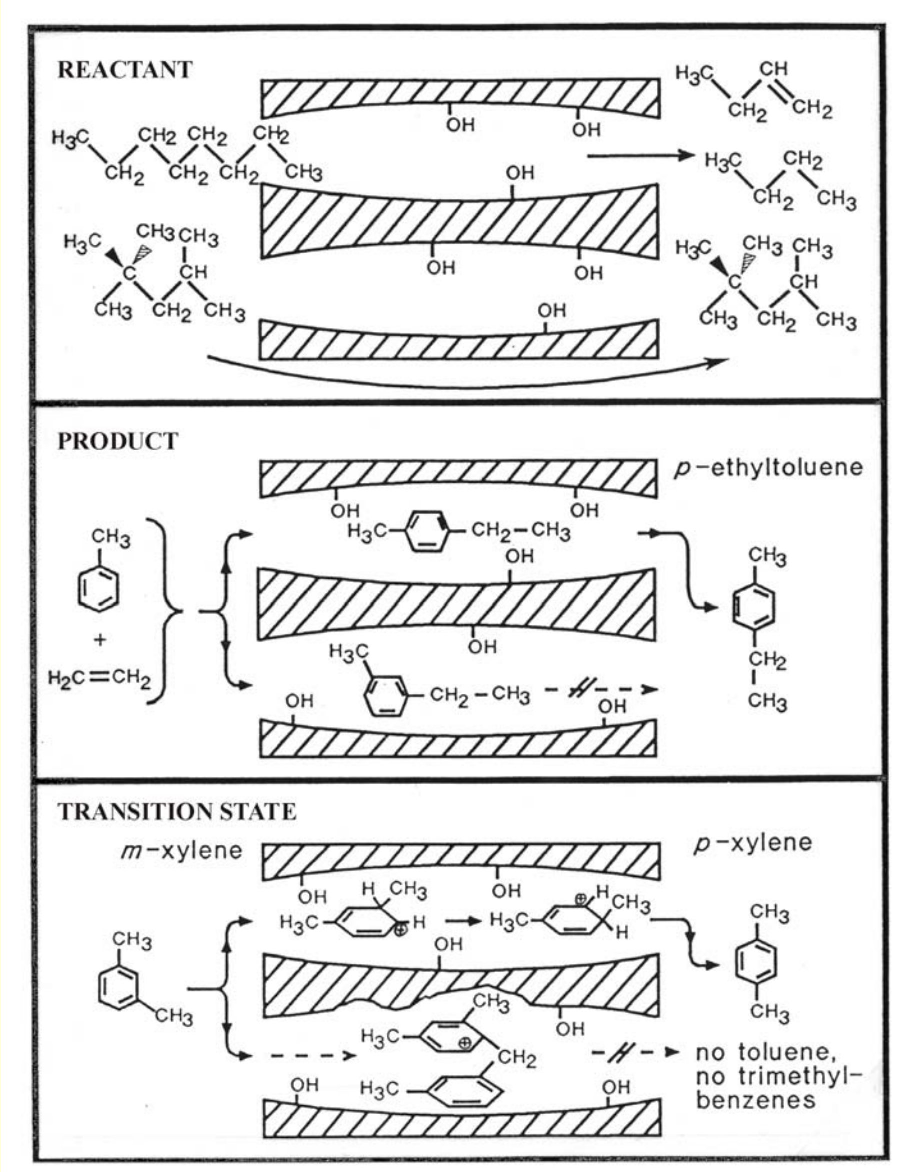


# Brønsted acidity

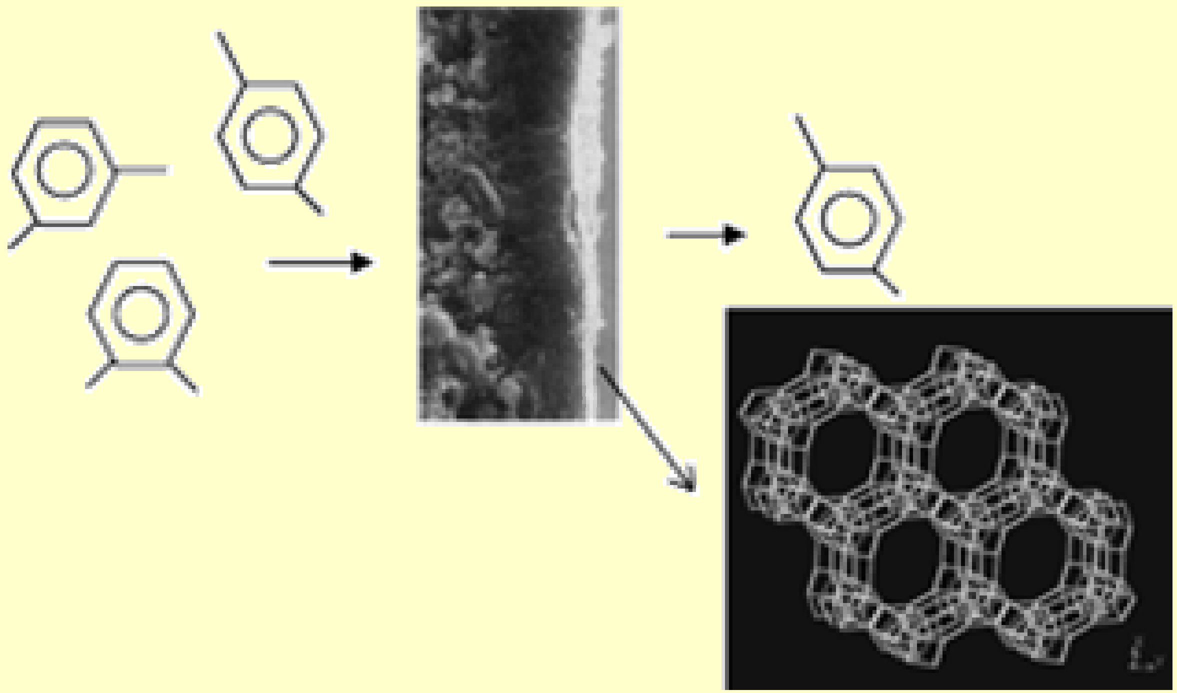


# ZEOLITES and ZEOLITIC MATERIALS

**Size-shape selective catalysis, separations, sensing**
**Reactant, product, transition state selectivity:**



# Separation of xylene isomers by pervaporation thru a MFI membrane



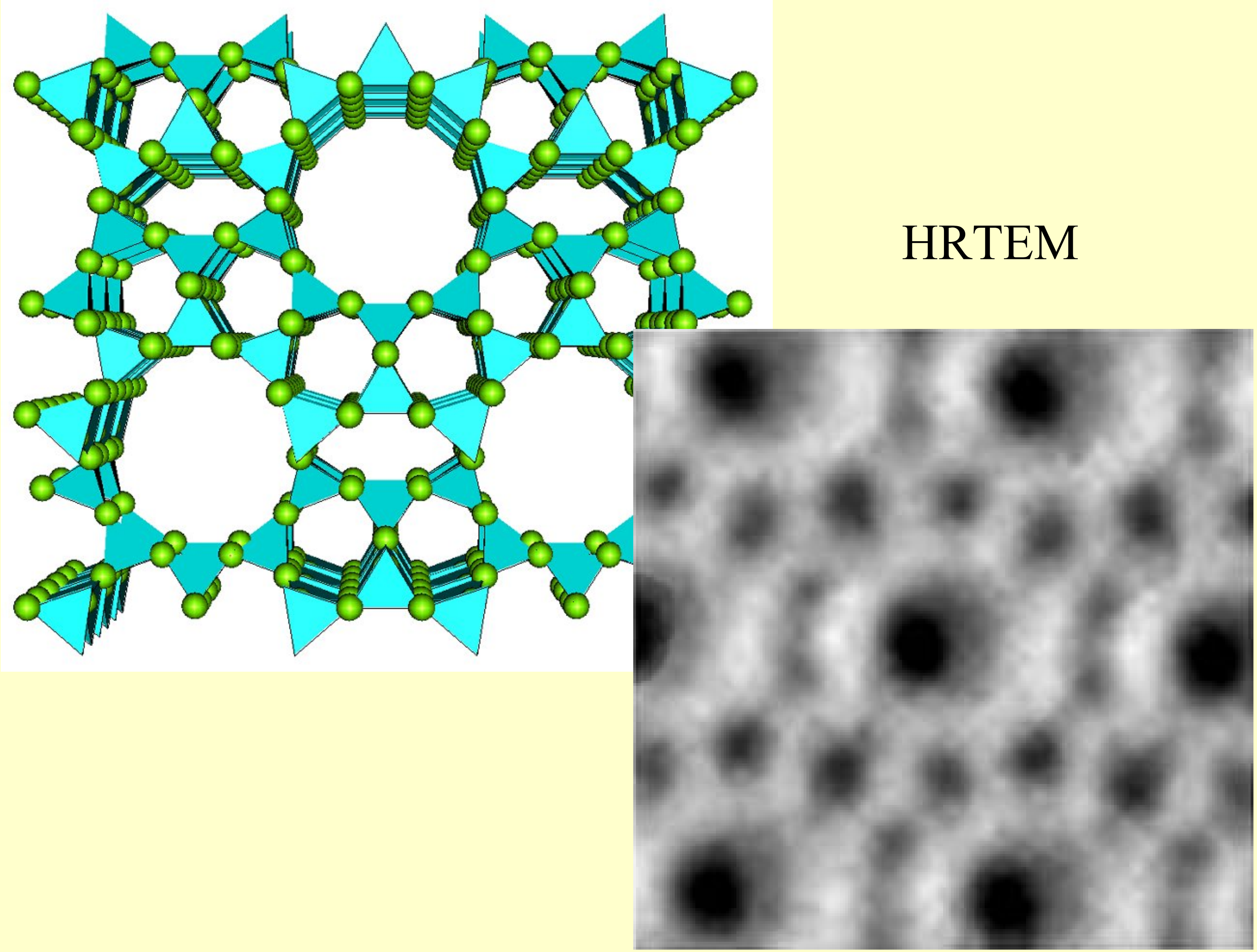
# ZEOLITES and ZEOLITIC MATERIALS

**Ion exchange capacity, water softening, detergents (25wt% zeolite)**

**Host-guest inclusion, atoms, ions, molecules, radicals, organometallics, coordination compounds, clusters, polymers (conducting, insulating)**

**Nanoreaction chambers**

**Advanced zeolite devices, electronic, optical, magnetic applications, nanoscale materials, size tunable properties, QSEs**



HRTEM

# ZEOLITES and ZEOLITIC MATERIALS

## Aluminophosphates

♠Isoelectronic relationship of $AlPO_4$ to $(SiO_2)_2$
♠Ionic radius of $Si^{4+}$ (0.26 Å) is very close to the average of the ionic radii of $Al^{3+}$ (0.39 Å) and $P^{5+}$ (0.17 Å)

Many similarities between aluminosilicate and $AlPO_4$ molecular sieves
Dense $AlPO_4$ phases are isomorphic with the structural forms of $SiO_2$: quartz, tridymite, and cristobalite

Aluminosilicate framework charge balanced by extraframework cations
Aluminophosphate frameworks neutral $(AlO_2^-)(PO_2^+) = AlPO_4$

## ZEOLITES and ZEOLITIC MATERIALS

**Some of the $AlPO_4$ microporous structures are analogous to zeolites while other are novel and unique to this class of molecular sieves.**

**Only even-number rings because of the strict alternation of Al and P atoms.**
**Incorporation of elements such as Si, Mg, Fe, Ti, Co, Zn, Mn, Ga, Ge, Be, Li, As, and B into the tetrahedral sites of $AlPO_4$ gives a vast number of element-substituted molecular sieves (MeAPO, MeAPSO, SAPO) which are important heterogeneous catalysts.**

**$M^{1+}$, $M^{2+}$, and $M^{3+}$ incorporate into the Al sites**
**$M^{5+}$ elements incorporate into the P sites**
**This substitution introduces a negative charge on these frameworks.**
**$Si^{4+}$, $Ti^{4+}$, and $Ge^{4+}$ can either replace P and introduce a negative charge or a pair of these atoms can replace an Al/P pair and retain the charge neutrality.**

# ZEOLITES and ZEOLITIC MATERIALS

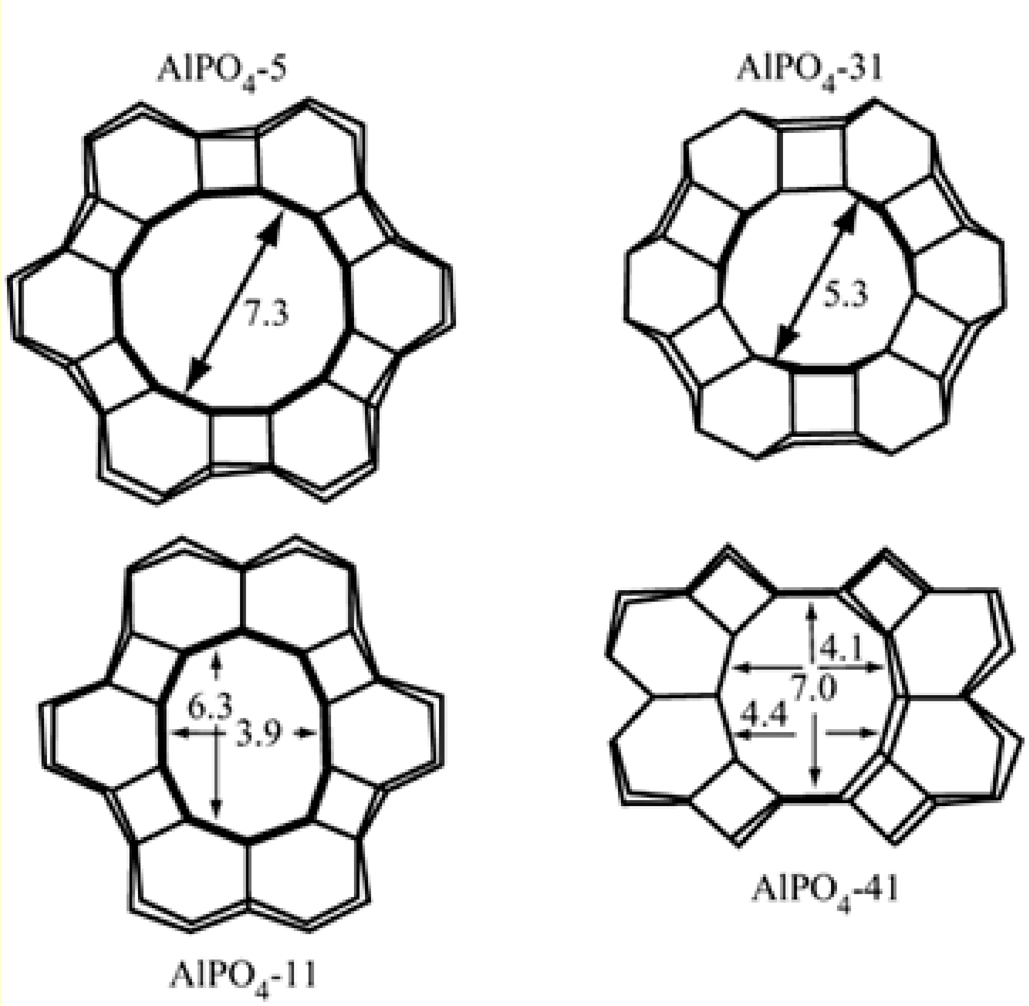
**Aluminophosphates prepared by the hydrothermal synthesis**

**Source of Al: pseudoboehmite, Al(O)(OH), Al(O*i*-Pr)$_3$**
**Mixing with aqueous $H_3PO_4$ in the equimolar ratio – low pH !**
**Forms an $AlPO_4$ gel, left to age**
**One equivalent of a guest compound = template**
**Crystallization in a reactor**
**Separated by filtration, washed with water**
**Calcination**

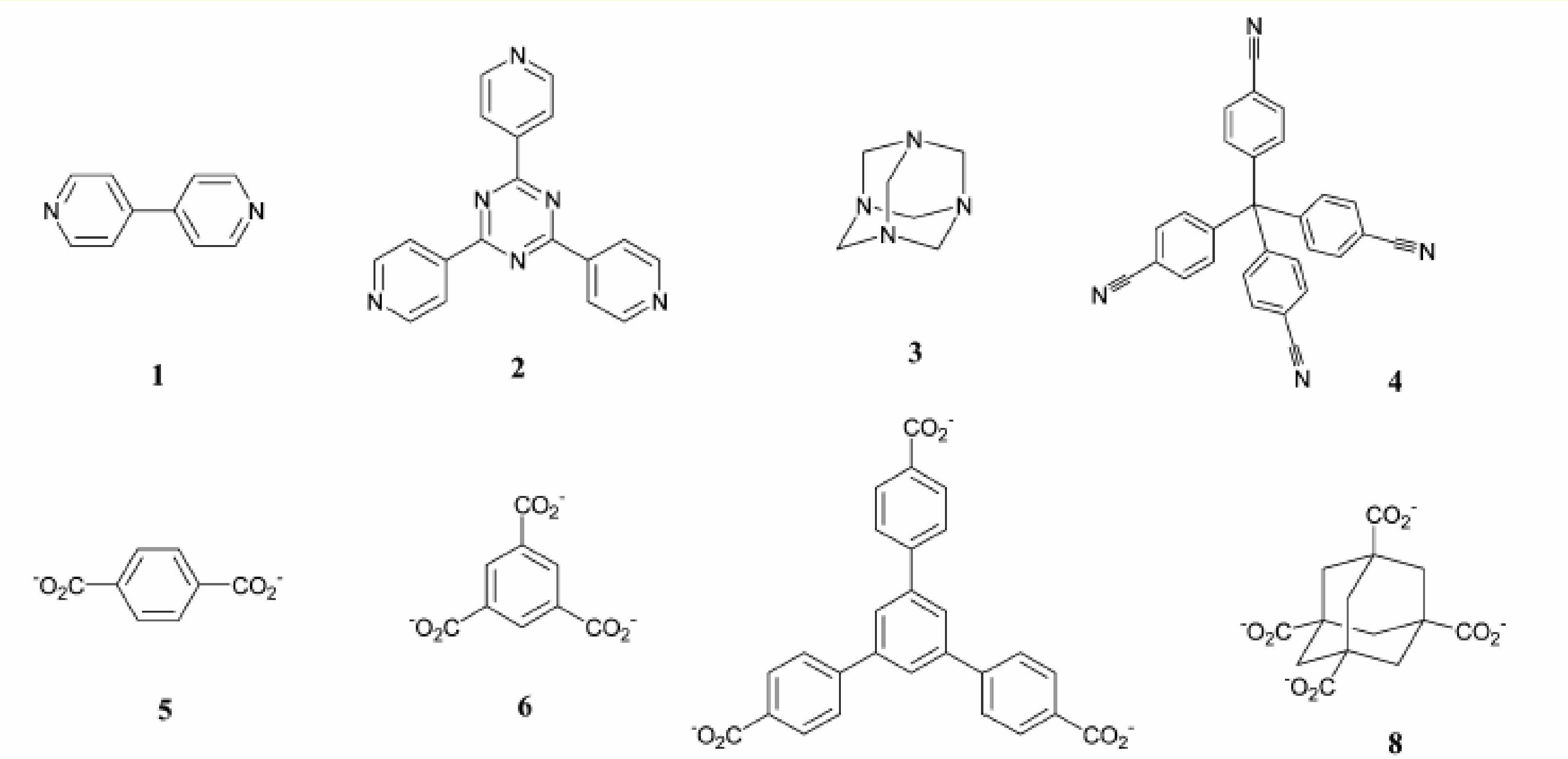
**Other zeolite materials**

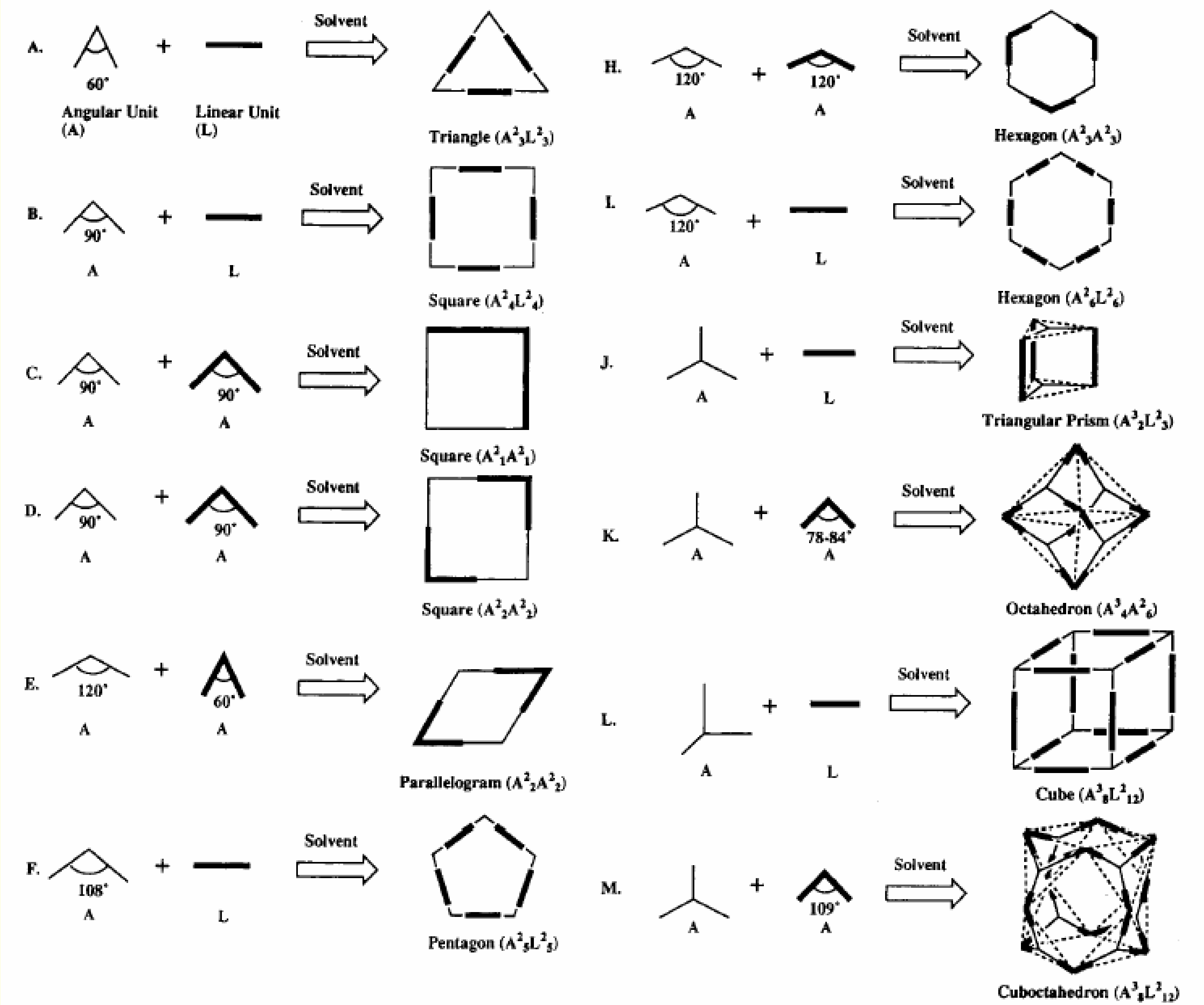
**Oxide and non-oxide frameworks, sulfides, selenides**
**Coordination frameworks, supramolecular zeolites**

**The quest for larger and larger pore sizes**


AlPO4-5
7.3
AlPO4-31
5.3
6.3
3.9
AlPO4-11
4.1
7.0
4.4
AlPO4-41

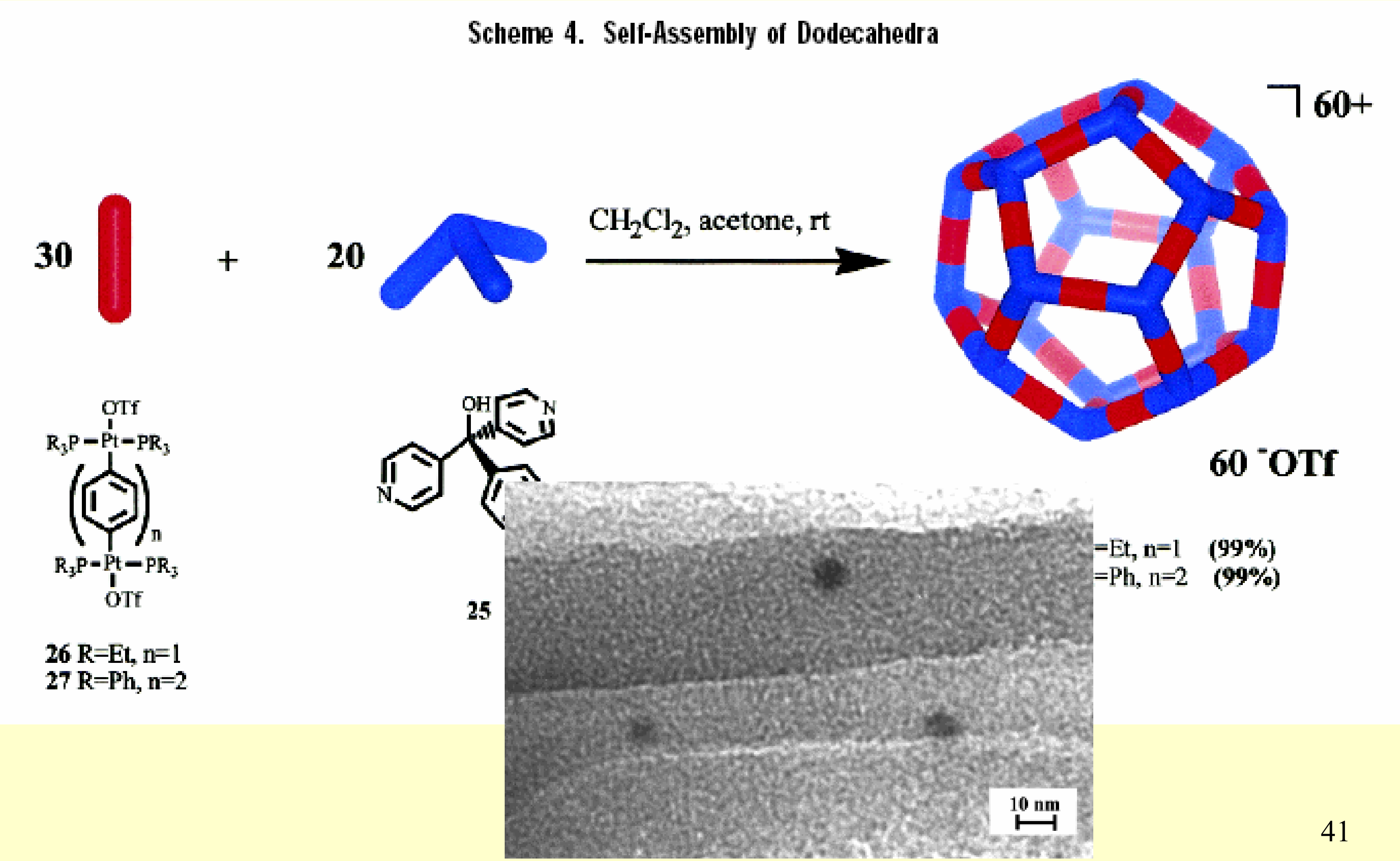
# Metallo-Organic Framework Structures





A.
60°
Angular Unit (A)
Linear Unit (L)
Solvent
Triangle ($A^2_3L^2_3$)
H.
120°
A
120°
A
Solvent
Hexagon ($A^2_3A^2_3$)
B.
90°
A
L
Solvent
Square ($A^2_4L^2_4$)
I.
120°
A
L
Solvent
Hexagon ($A^2_6L^2_6$)
C.
90°
A
90°
A
Solvent
Square ($A^2_1A^2_1$)
J.
A
L
Solvent
Triangular Prism ($A^3_2L^2_3$)
D.
90°
A
90°
A
Solvent
Square ($A^2_2A^2_2$)
K.
A
78-84°
A
Solvent
Octahedron ($A^3_4A^2_6$)
E.
120°
A
60°
A
Solvent
Parallelogram ($A^2_2A^2_2$)
L.
A
L
Solvent
Cube ($A^3_8L^2_{12}$)
F.
108°
A
L
Solvent
Pentagon ($A^2_5L^2_5$)
M.
A
109°
A
Solvent
Cuboctahedron ($A^3_8L^2_{12}$)

# Metallo-Organic Framework Structures



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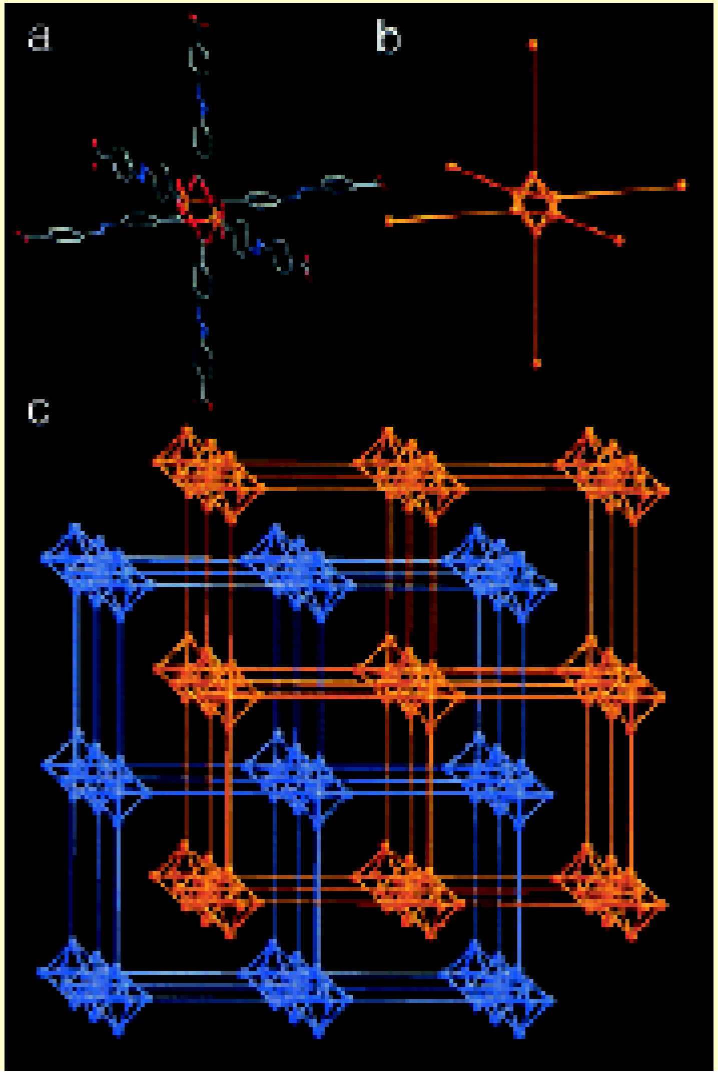


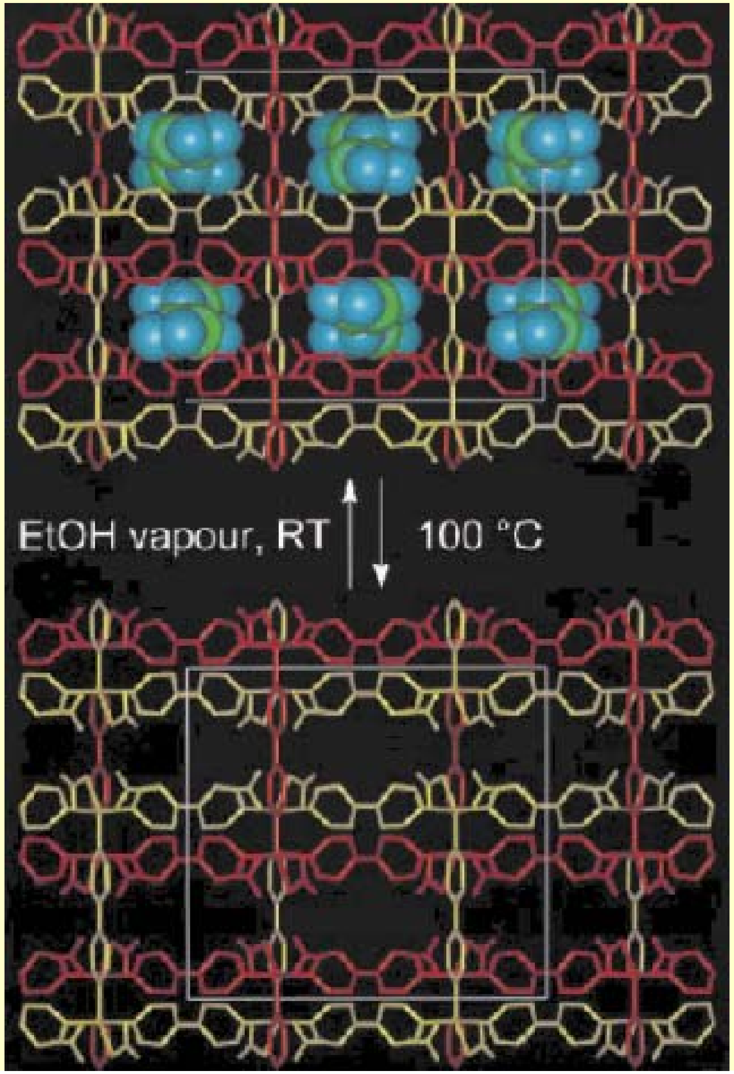

# Inorganic and Metallo-Organic Quartz