Zeolites and Zeolitic Materials

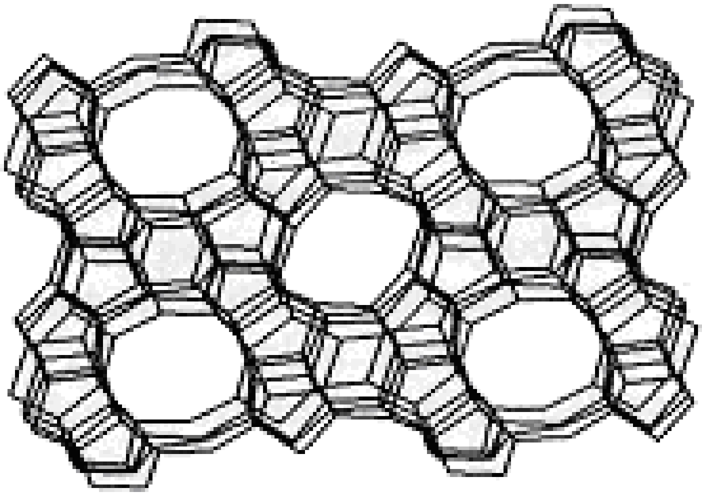
Molecular sieves = highly organized matrices of tunable pore shape, size, and polarity for separation, recognition, and organization of molecules with precision of about 1 Å.

detergent builders
adsorbents
size-shape selective catalysts
supramolecular chemistry
nanotechnology

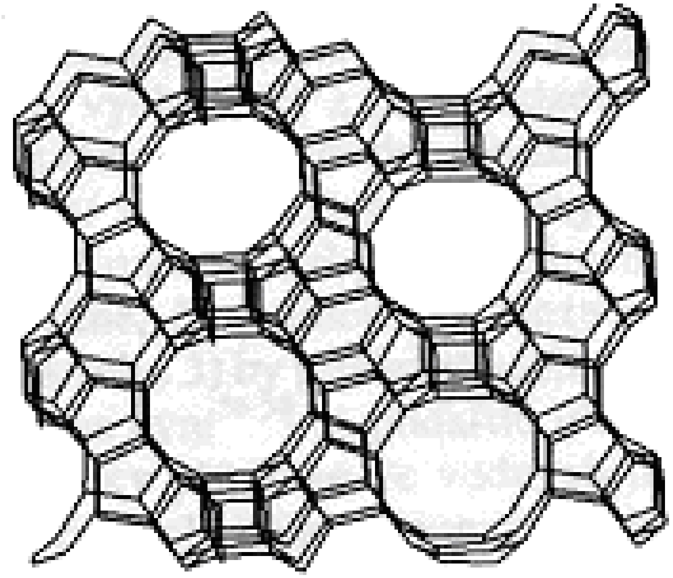
Chemical composition	
Silica	SiO_2
Aluminosilicates	$M_x{}^IAl_xSi_{2-x}O_4 \cdot nH_2O$
Aluminophosphates	$AlPO_4$ (isoelectronic with Si_2O_4)
Metallophosphates	MPO_4
Silicoaluminophosphates	$M_x{}^ISi_xAlP_{1-x}O_4$

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

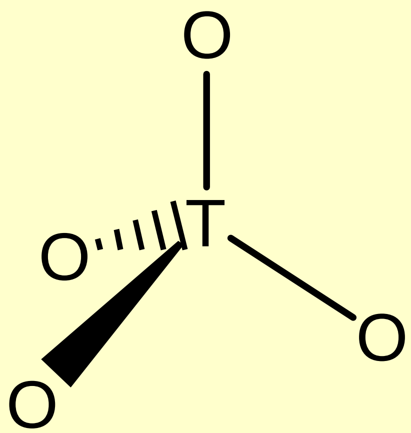
codes – AlPO4-5, 8, 11, ..., 54, ZSM-4, 18, 57, ...

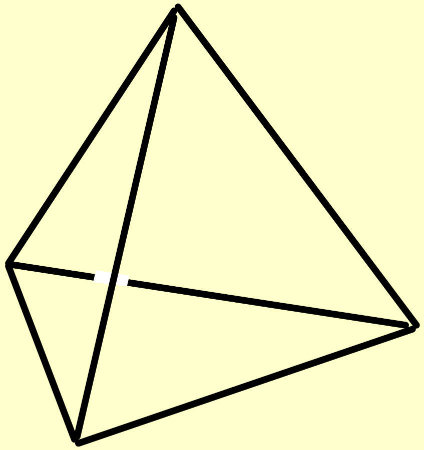
brand names – Linde A, D, F, L, N, Q , R, T, W, X, Y

university names
VPI-5 (Virginia Polytechnical Institute)
ULM (University Le Mans)

Zeolites and Zeolitic Materials

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

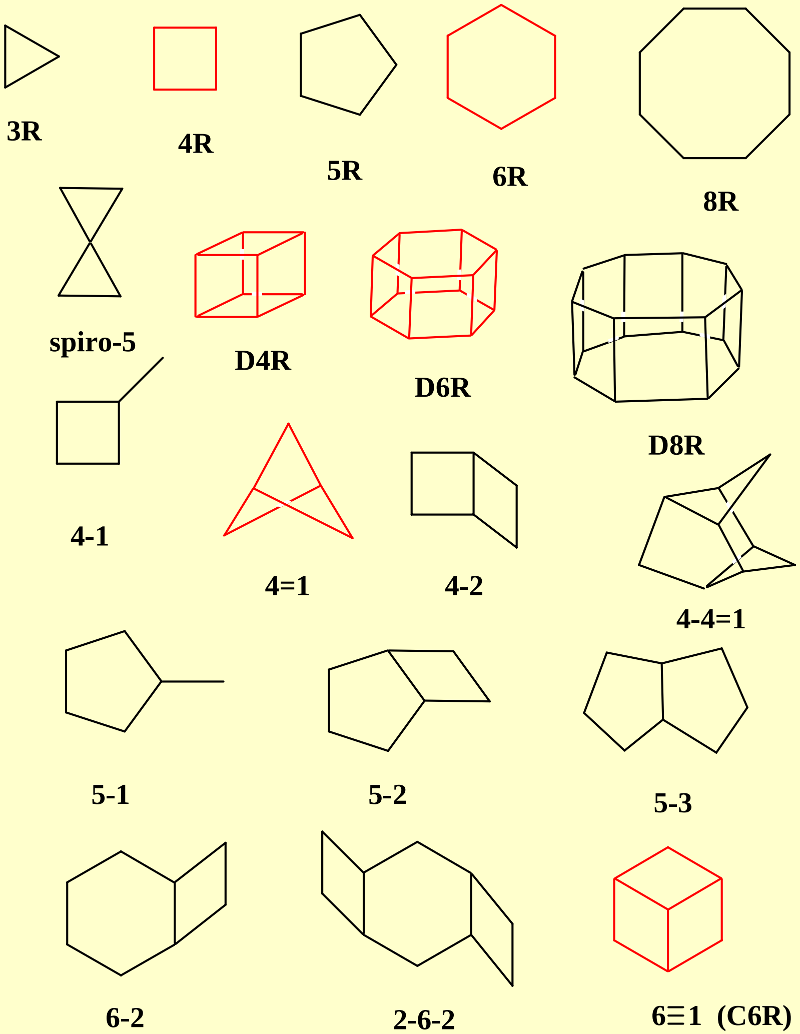


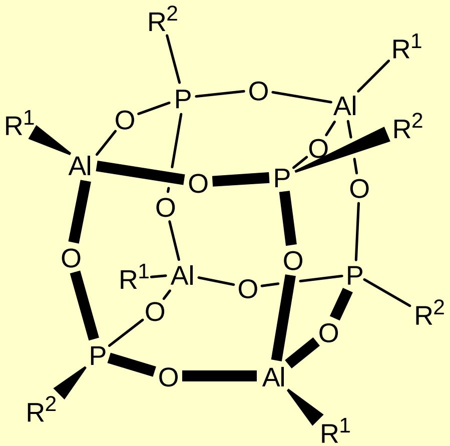


Isoelectronic relationship

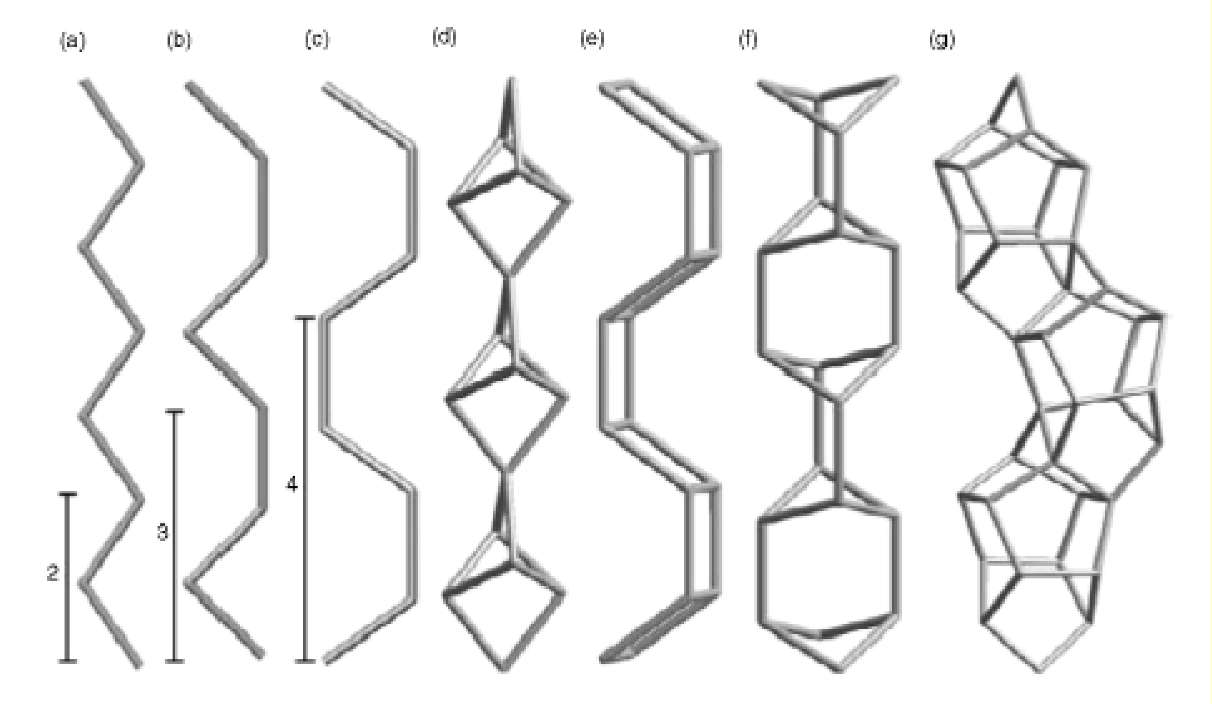
$(SiO_2)_2$ $[AlSiO_4]^-$ $AlPO_4$

Secondary (Structural) Building Units (SBU)



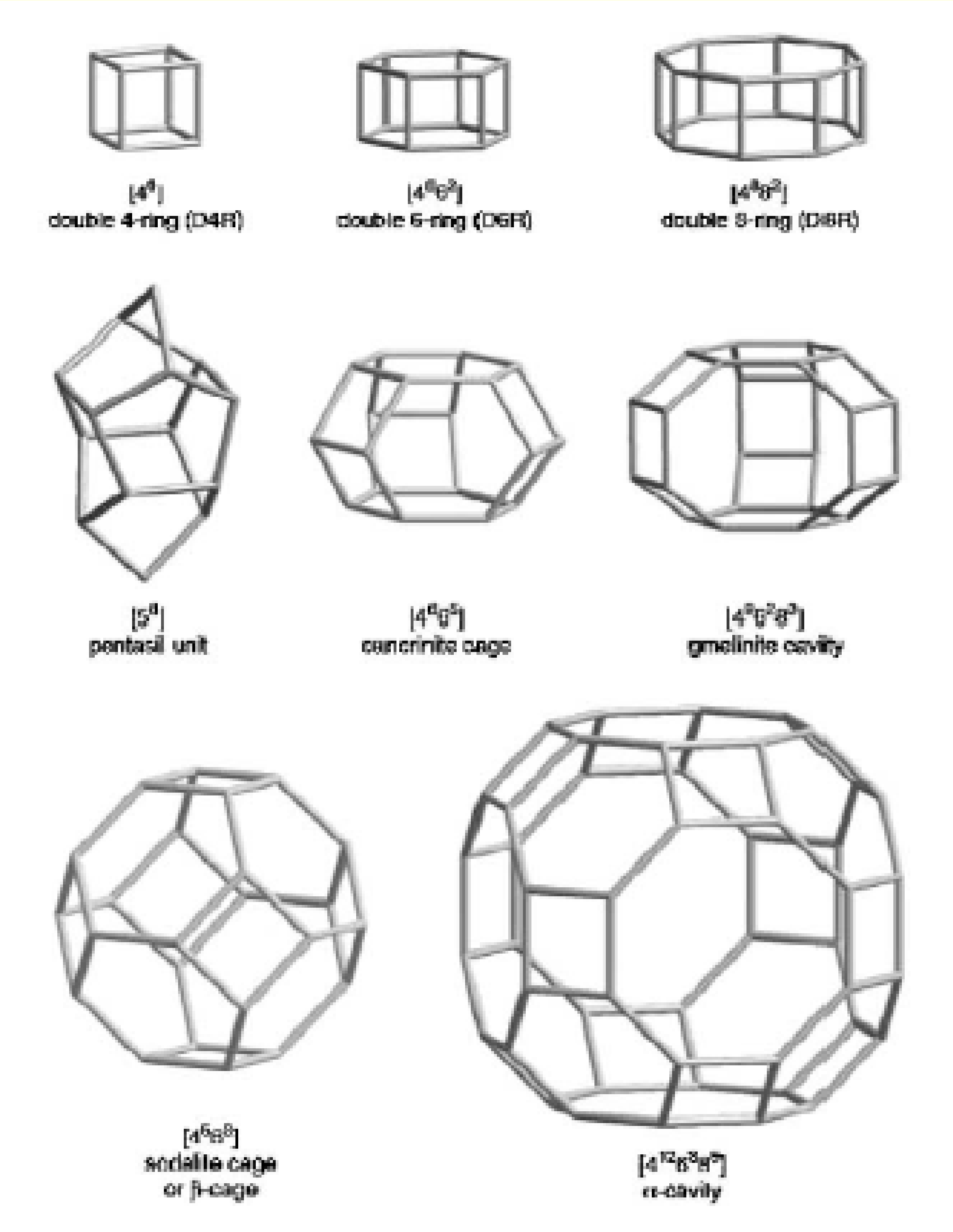


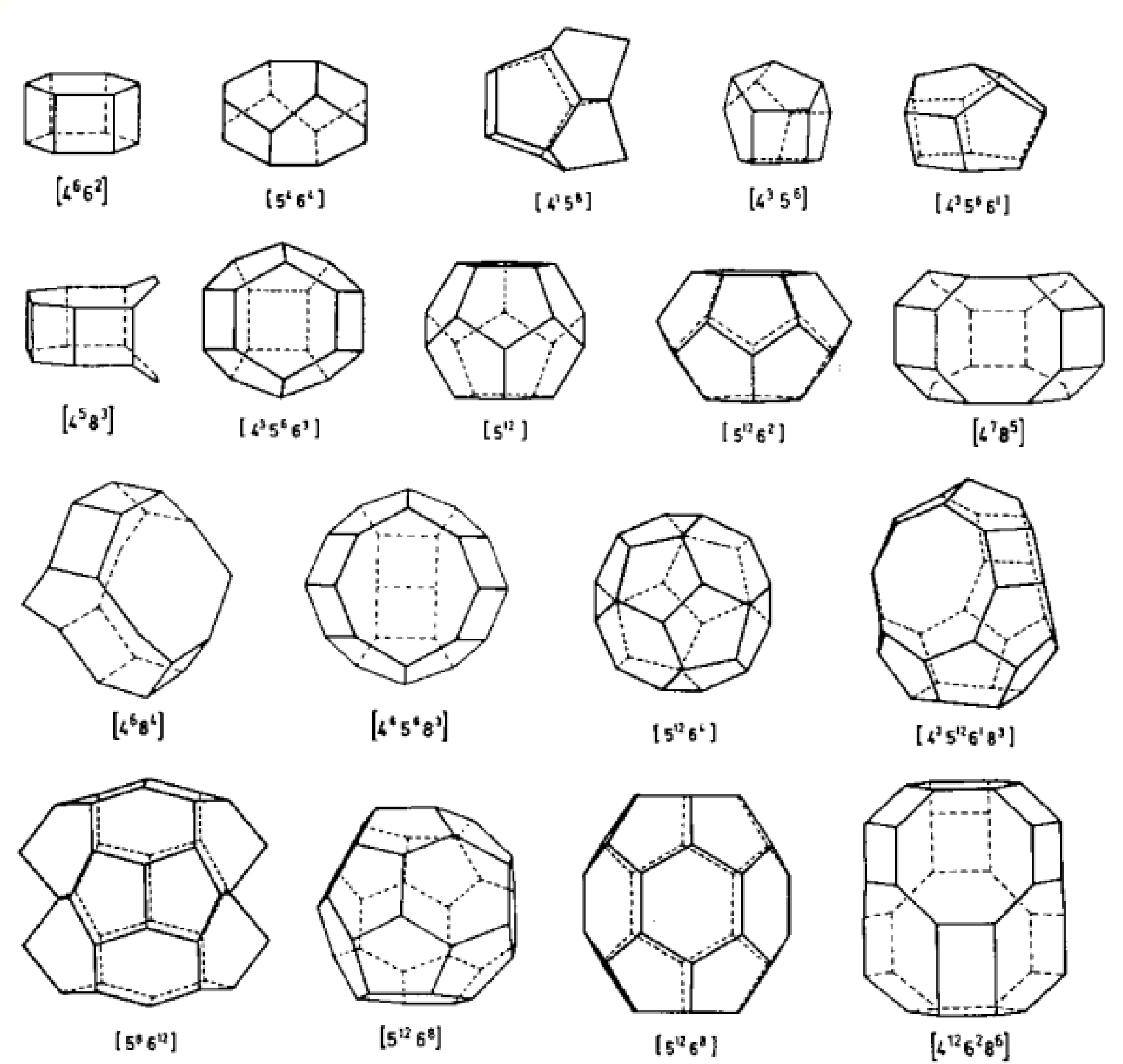
Chain composite building units



(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

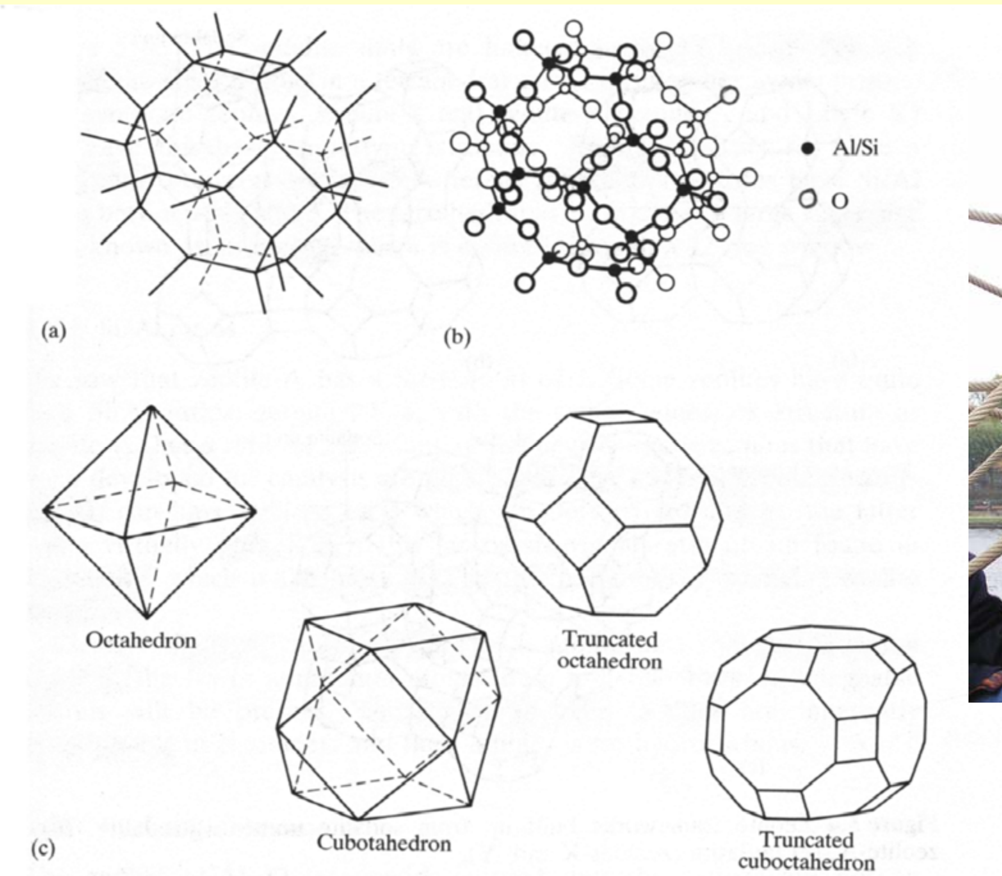




$[4^6 6^2]$
$[5^4 6^4]$
$[4^1 5^8]$
$[4^3 5^6]$
$[4^3 5^6 6^1]$
$[4^5 8^3]$
$[4^3 5^6 6^3]$
$[5^{12}]$
$[5^{12} 6^2]$
$[4^7 8^5]$
$[4^6 8^4]$
$[4^4 5^4 8^3]$
$[5^{12} 6^4]$
$[4^3 5^{12} 6^1 8^3]$
$[5^8 6^{12}]$
$[5^{12} 6^8]$
$[5^{12} 6^8]$
$[4^{12} 6^2 8^6]$

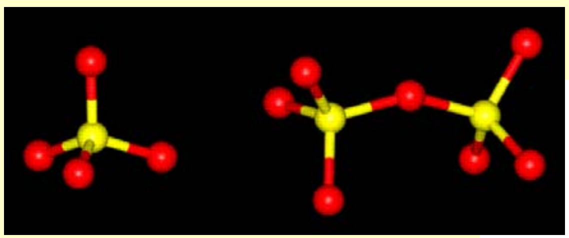
Sodalite Unit

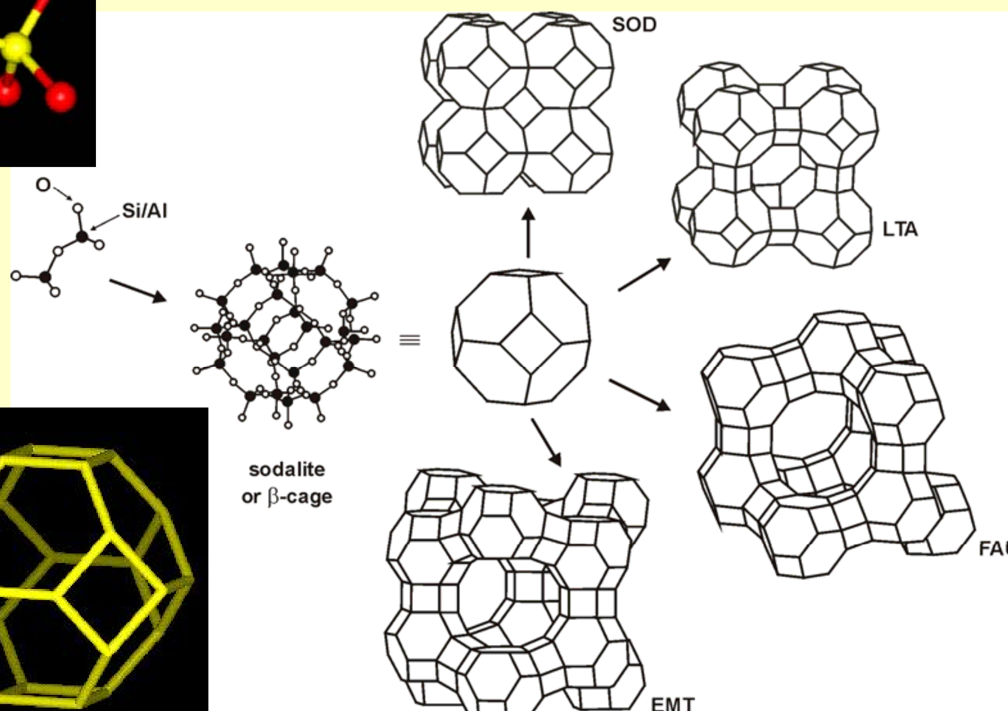
Truncated octahedron

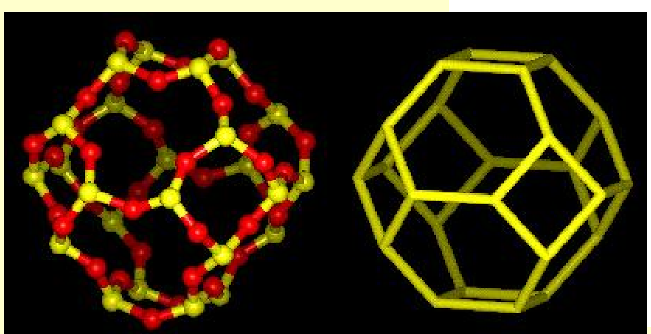


Sodalite Unit

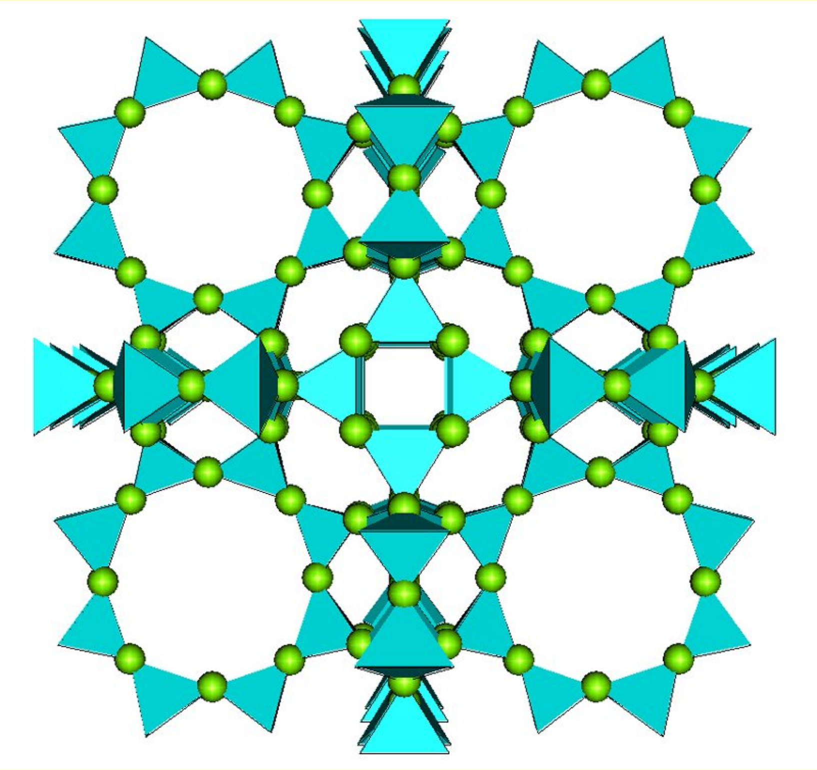
Packing of the sodalite units:
SOD – bcc, sharing of 4-rings
LTA – sc, 4-rings connected through O bridges
FAU (faujasite) – cubic diamond, 6-rings connected through O bridges
EMT – hexagonal diamond, 6-rings connected through O bridges

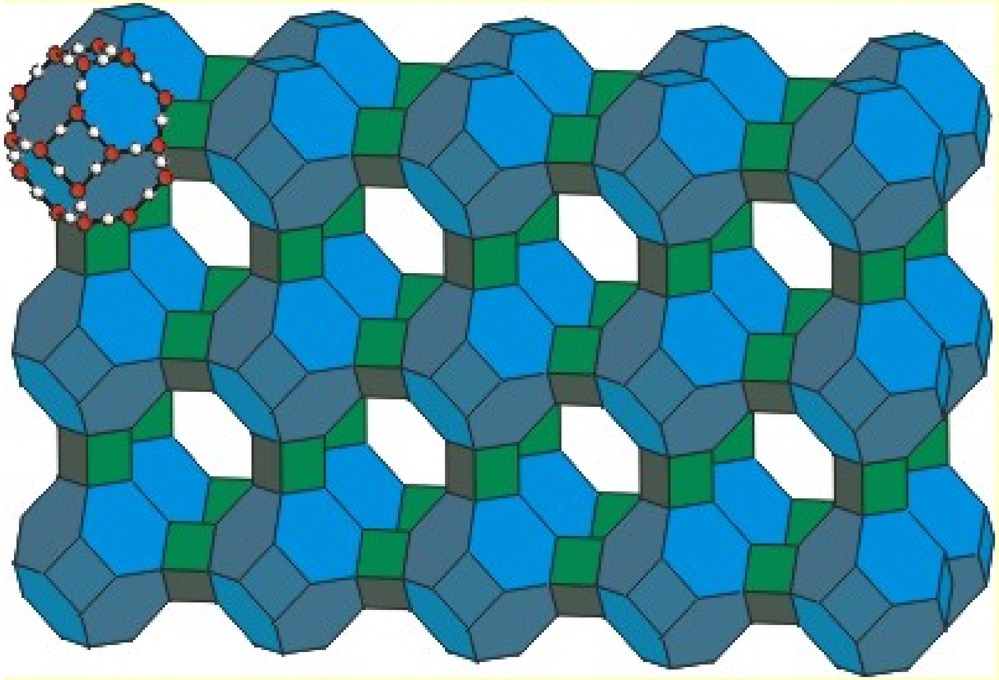




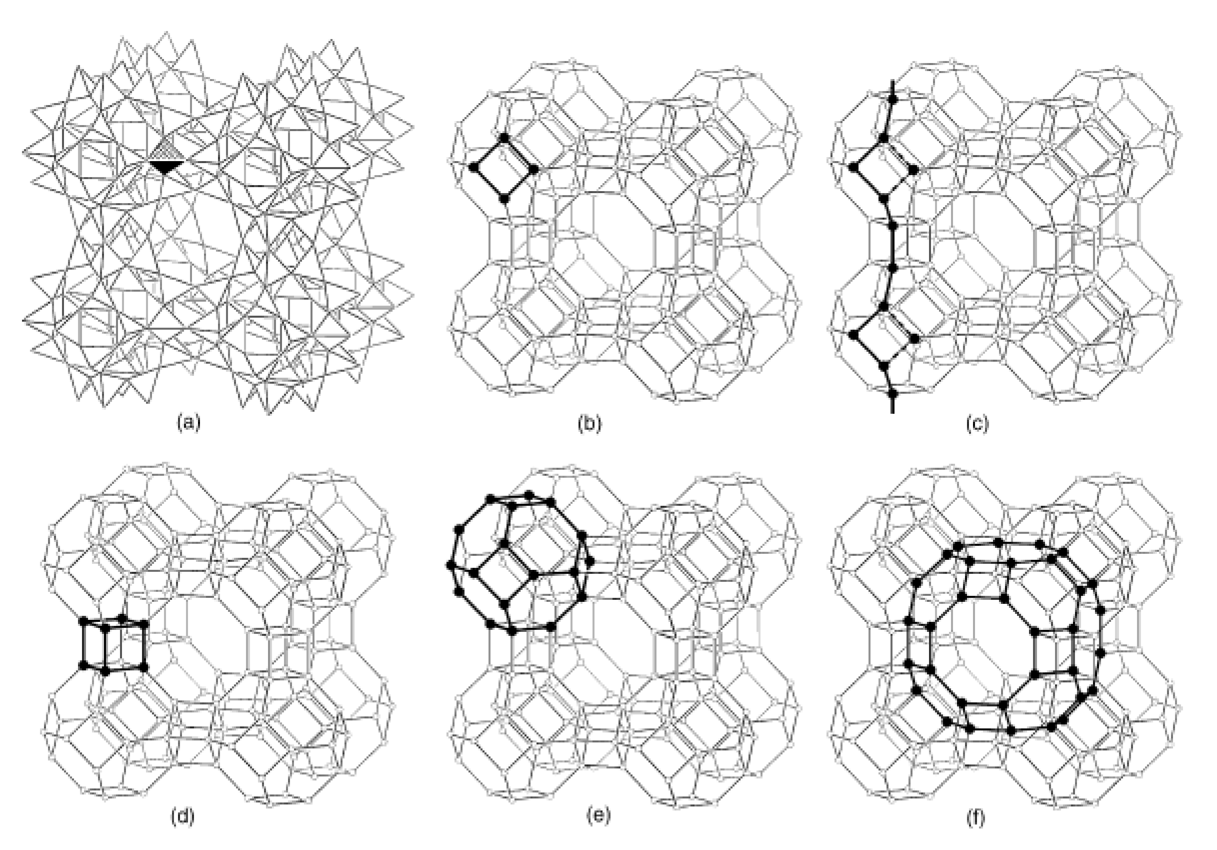


Zeolite LTA



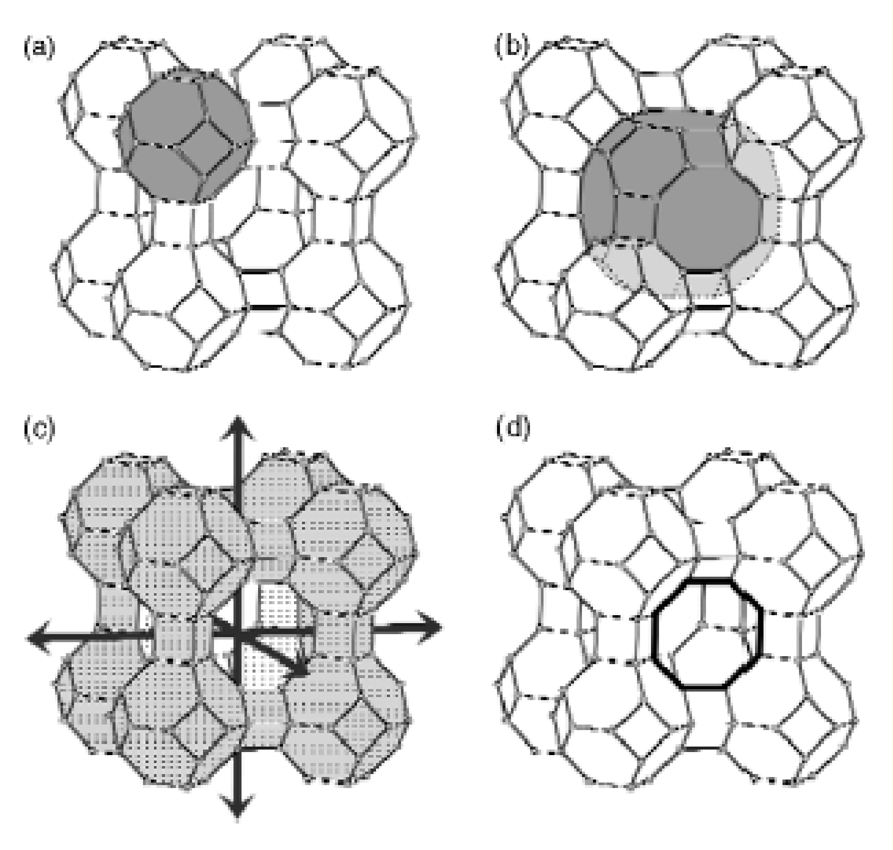


Zeolite A



(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)

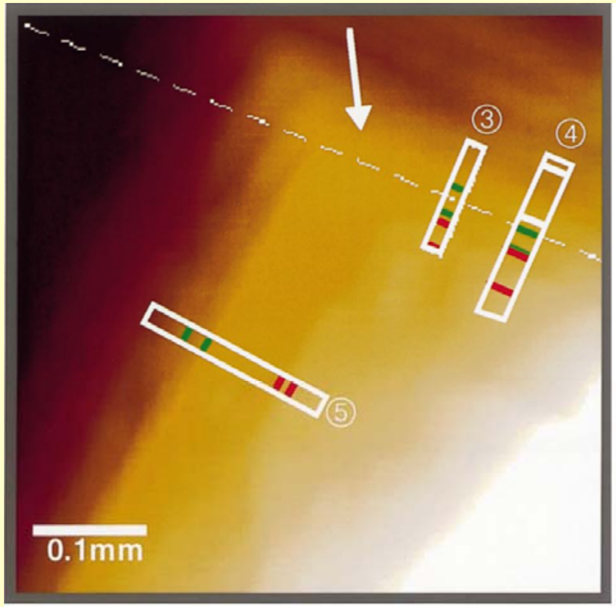


(a) the sodalite cage $[4^6 6^8]$

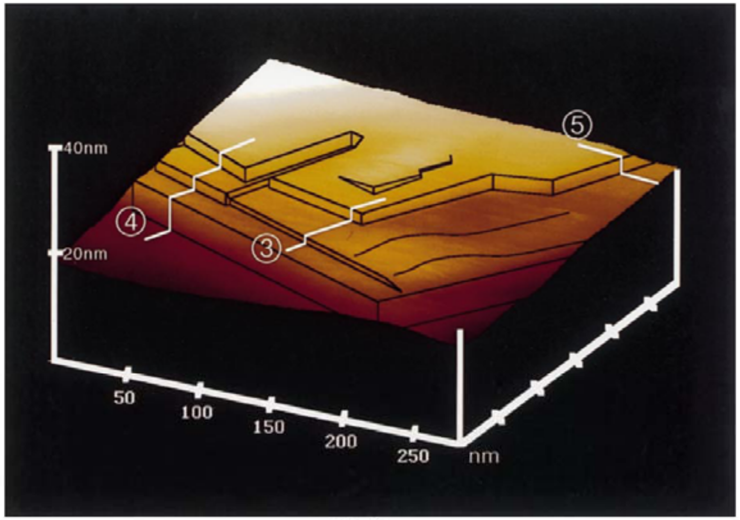
(b) the α-cavity $[4^{12} 6^8 8^6]$

(c) the 3-dimensional channel system

(d) the 8-ring defining the 0.41 nm effective channel width

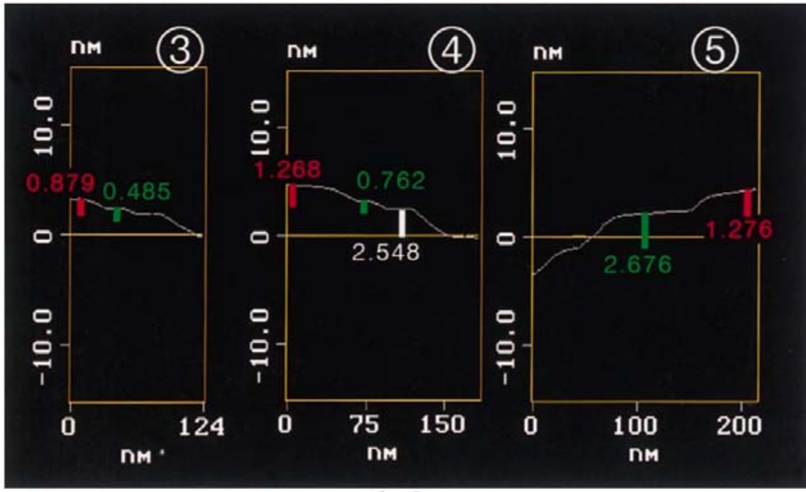


(a)



(b)

D4R

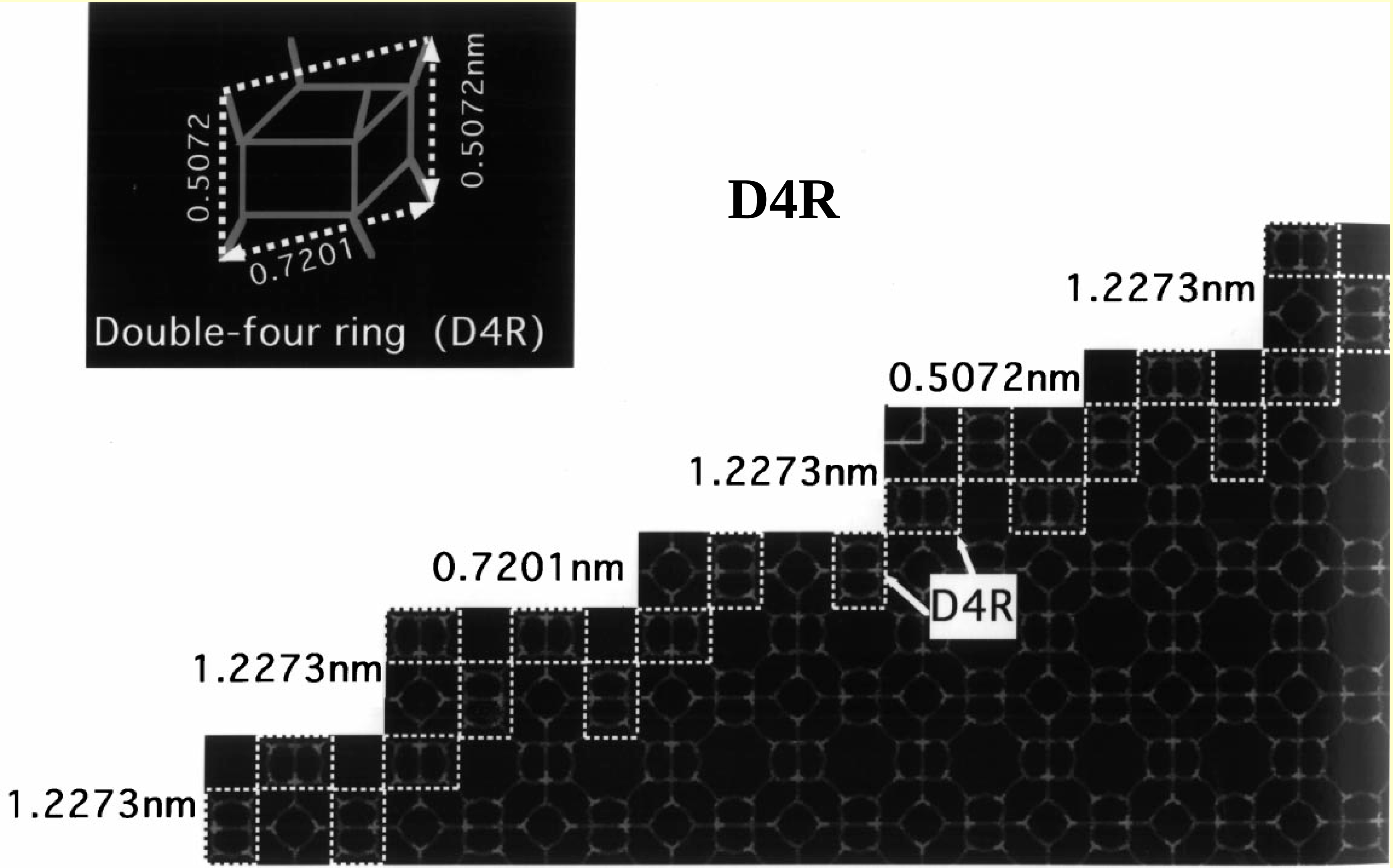


(c)

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

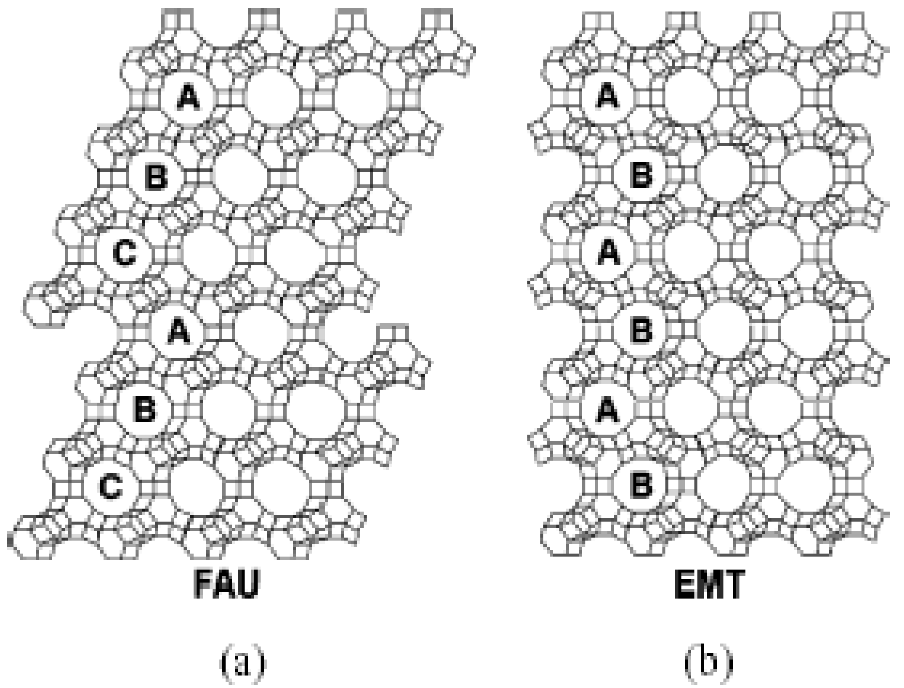


Fig. 1. Structure of zeolite Y: (a) cubic polymorph known as FAU with ABCABC… stacking, (b) hexagonal polymorph known as EMT with ABABAB… stacking.

	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

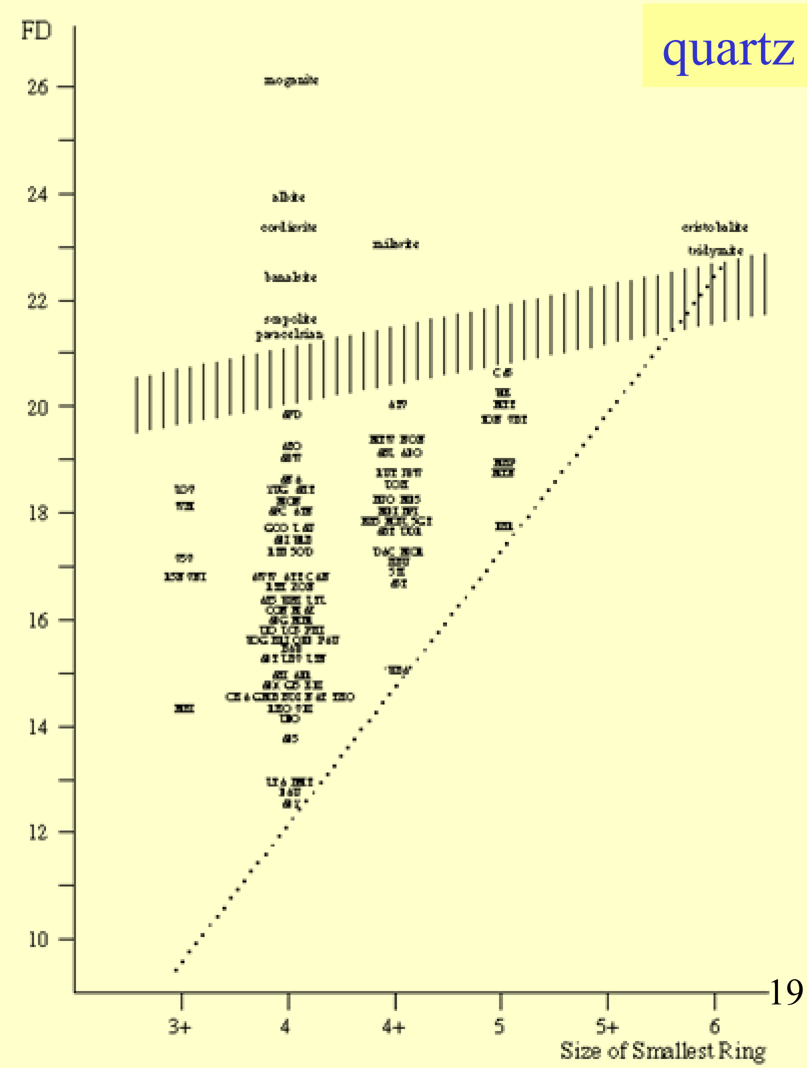
Framework Density

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



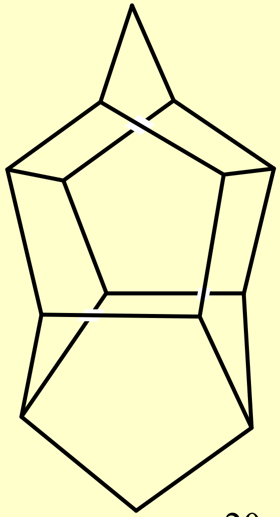
Pores
Various sizes (4 - 13 Å), shapes (circular, elliptical, cloverleaf-like), and connectivity (1-3D)
The size of the rings formed by the TO_4 tetrahedra ranges from 4 to 18 of the T-atoms and determines the pore aperture

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!

Templates

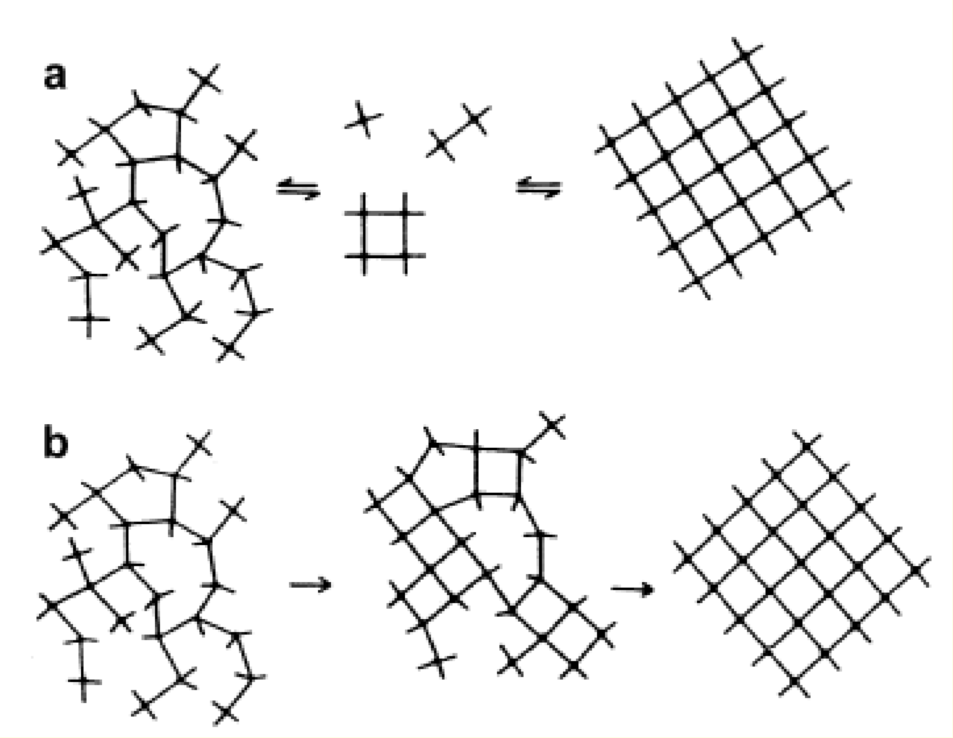
The ratio $TO_2/(C + N + O)$ is a measure of space-filling of the framework by the guest molecules, characteristic for a specific guest and structure.

Existence of primary and secondary units in a synthesis mixture

4R, 6R, 8R, D4R, D6R, 5-1, cubooctahedron

Zeolite Synthesis Mechanisms

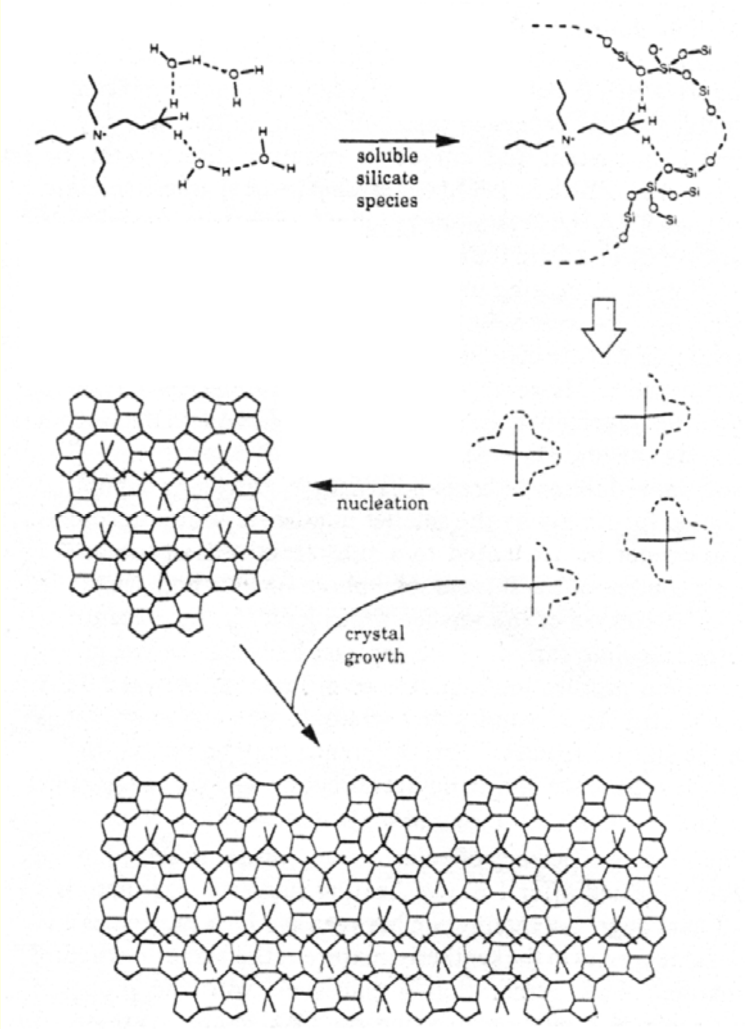
(a) gel dissolution and solution mediated crystallization (SBU in solution)



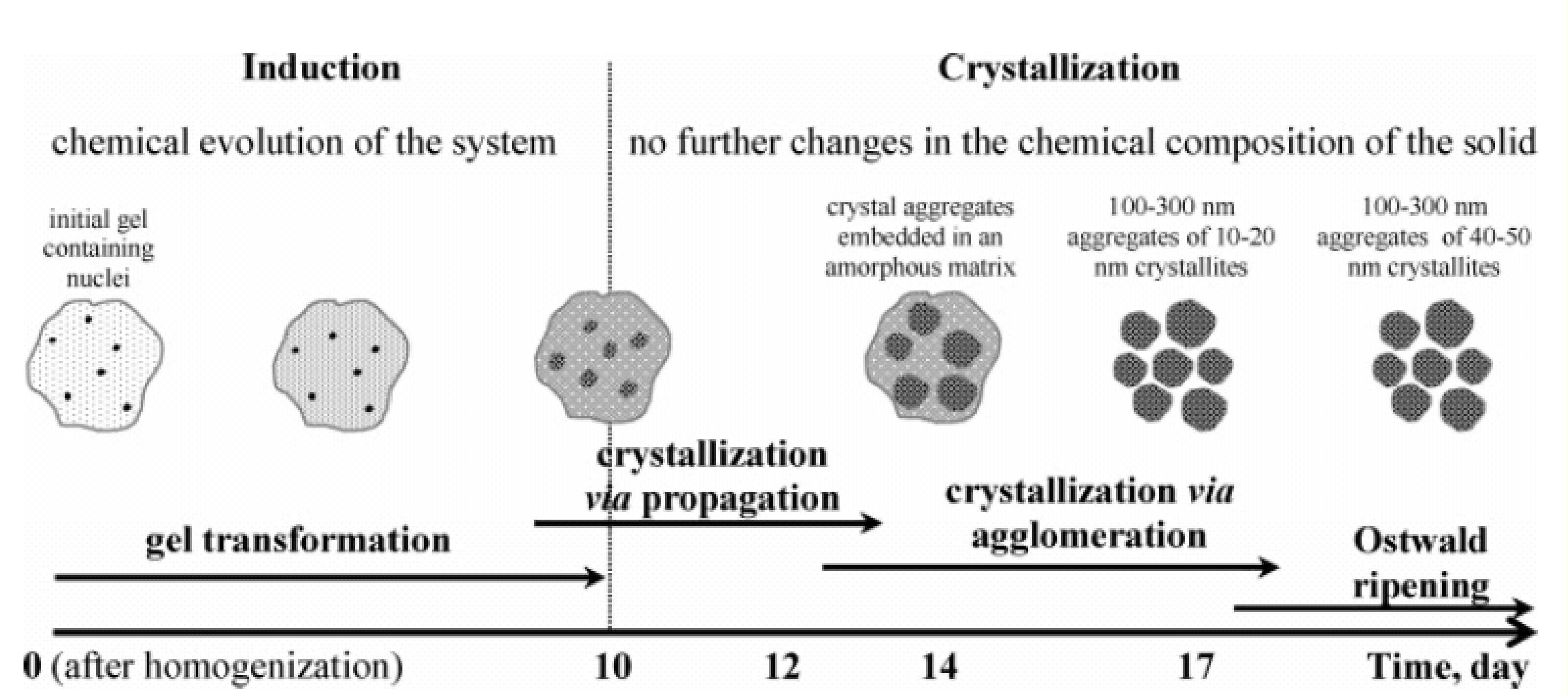
(b) “in situ” rearrangement of the gel

Zeolite Synthesis Mechanisms

Mechanism of structure-directing action of the TPA template



Crystallization Mechanism



crystallization mechanism of FAU-type zeolite under ambient conditions

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

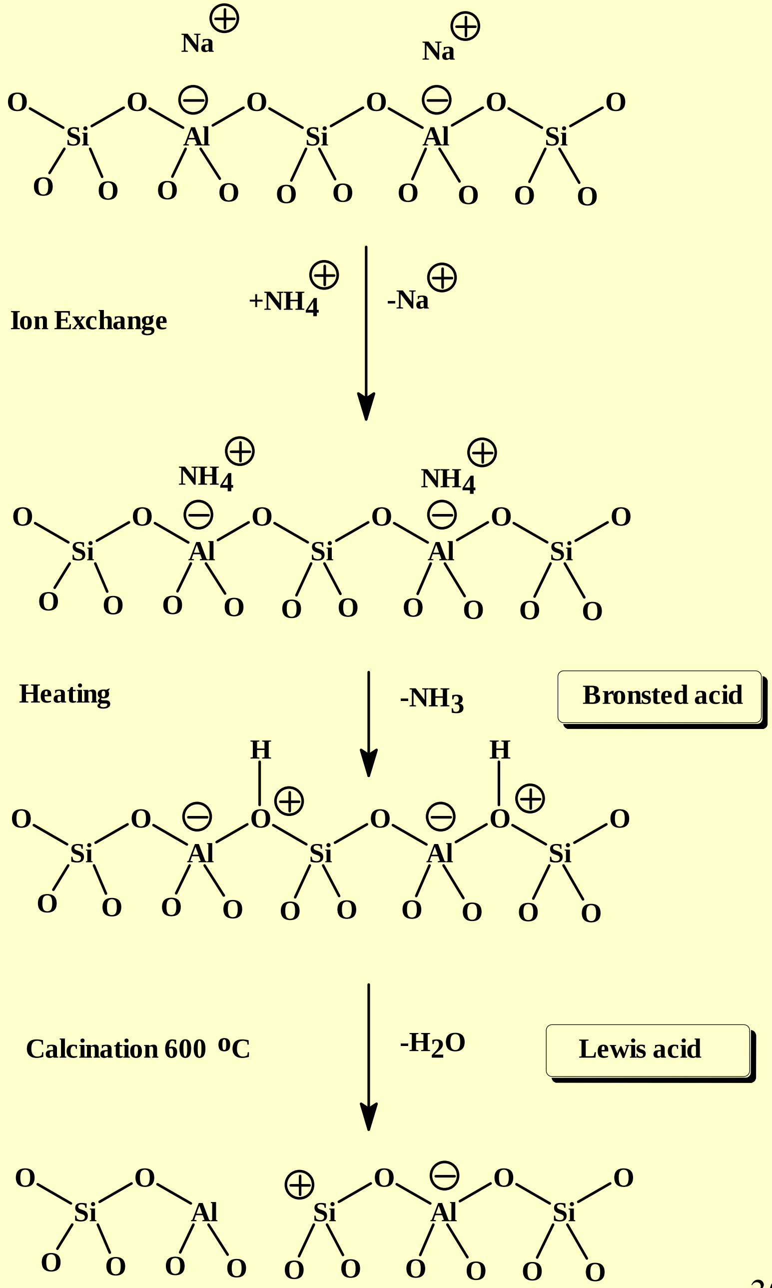
Brønsted Acidity

Tuning Bronsted acidity:

Ion exchange for NH_4^+
Pyrolysis to expel NH_3
Calcination to expel H_2O

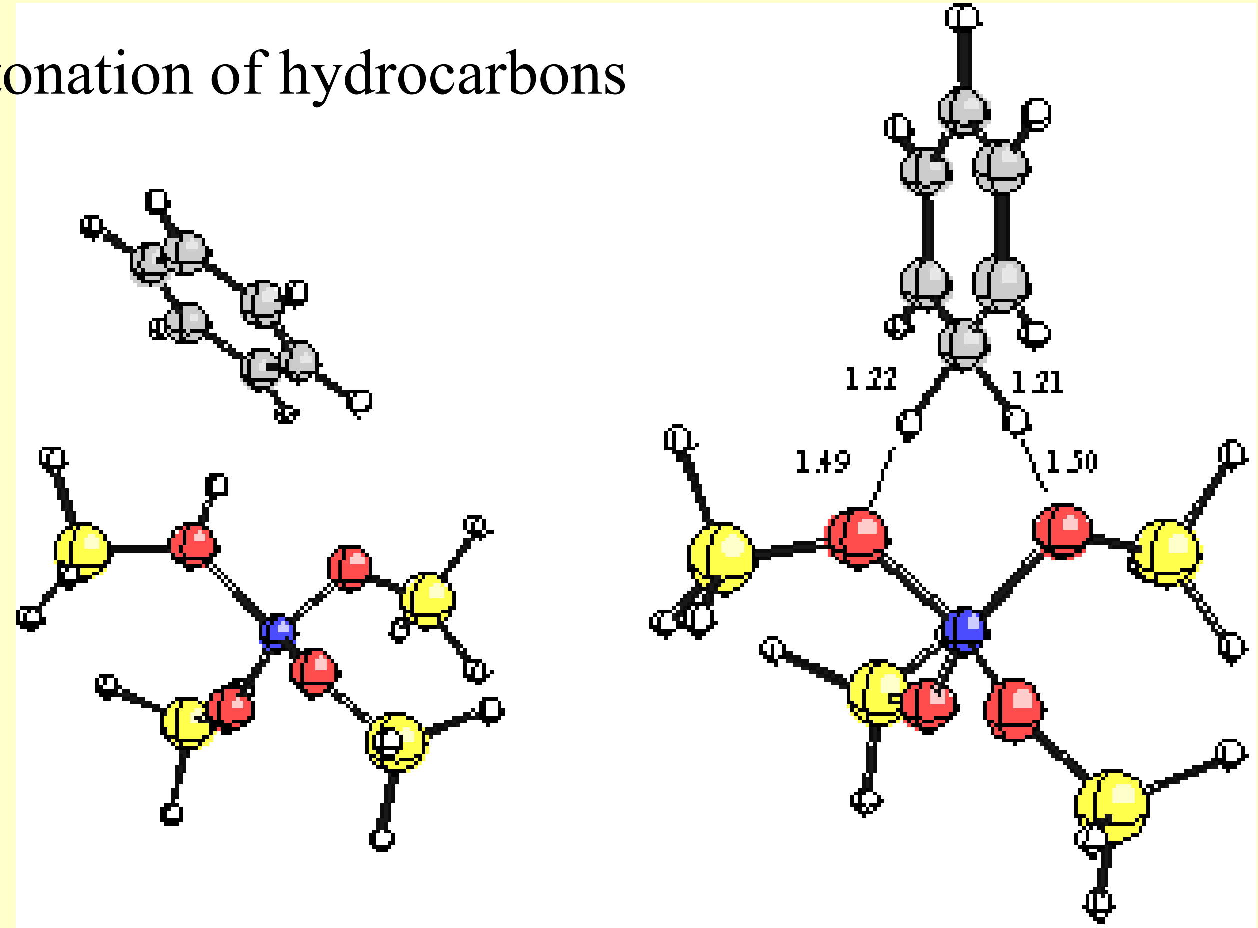
Solid acid for the hydrocarbon cracking

The larger the Si/Al ratio,the more acidic is the zeolite



Brønsted Acidity

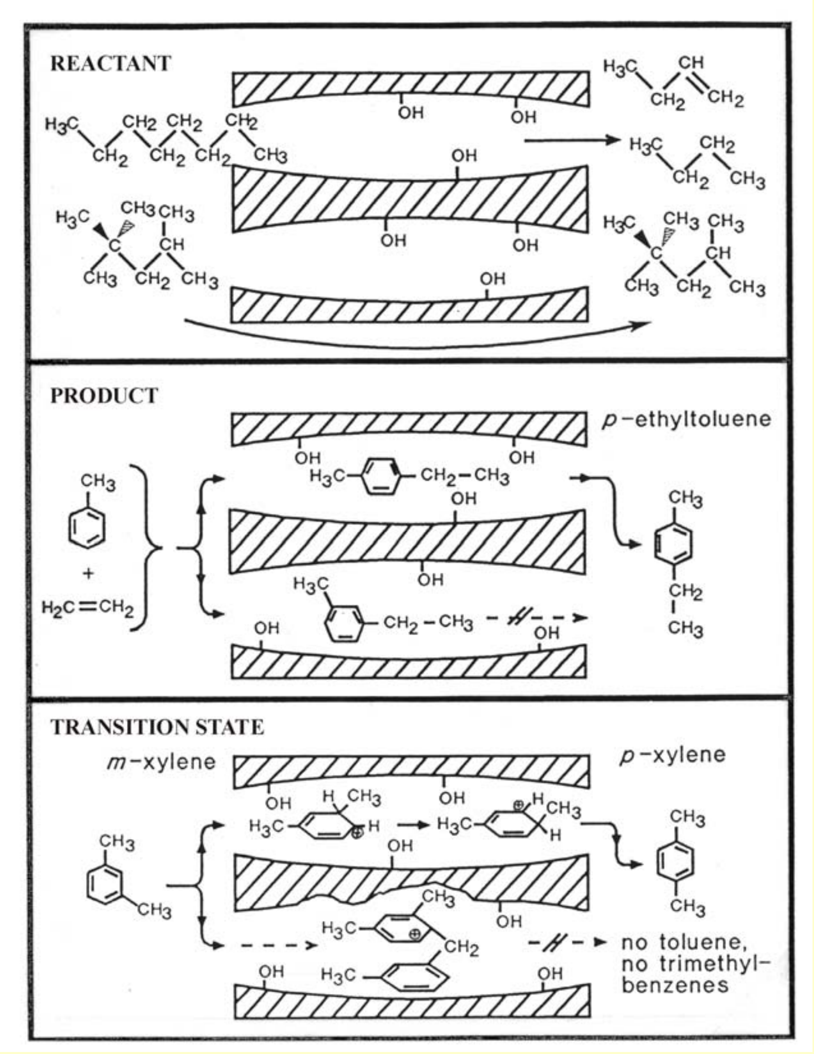
Protonation of hydrocarbons



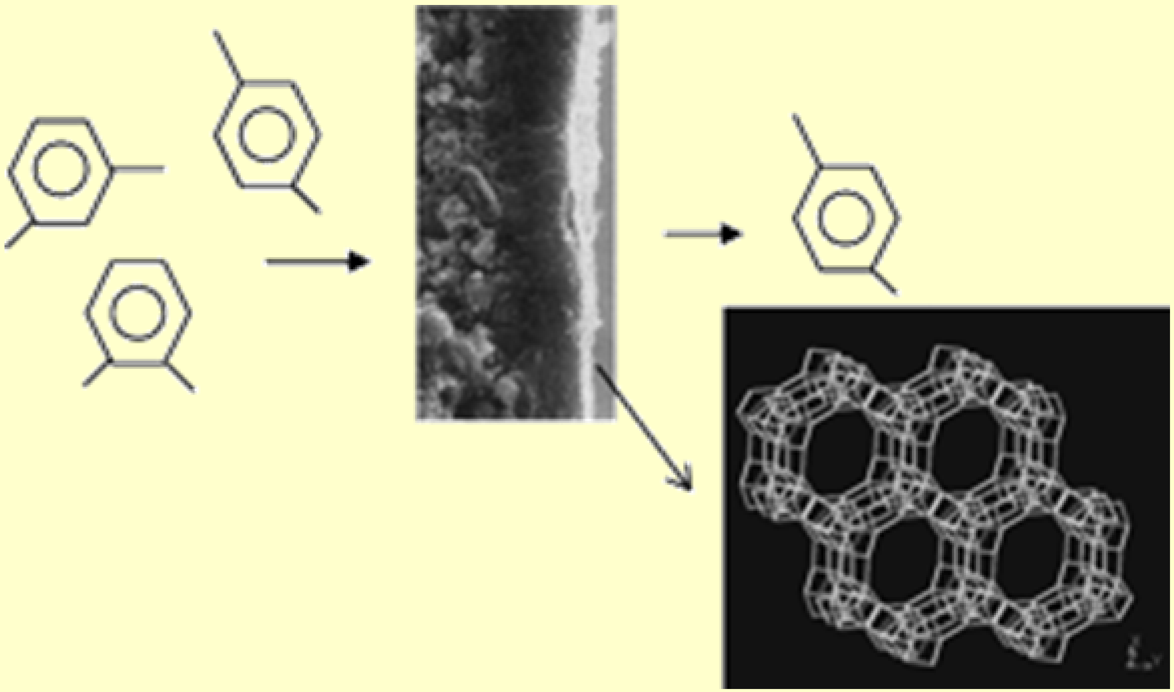
Size-Shape Selectivity

Size-shape selective catalysis, separations, sensing

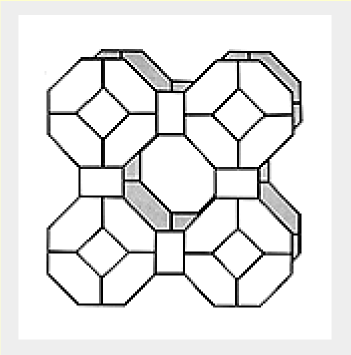
Selectivity at:
- **Reactants**
- **Products**
- **Transition state**



Separation of xylene isomers by pervaporation thru a MFI membrane



Zeolite Applications



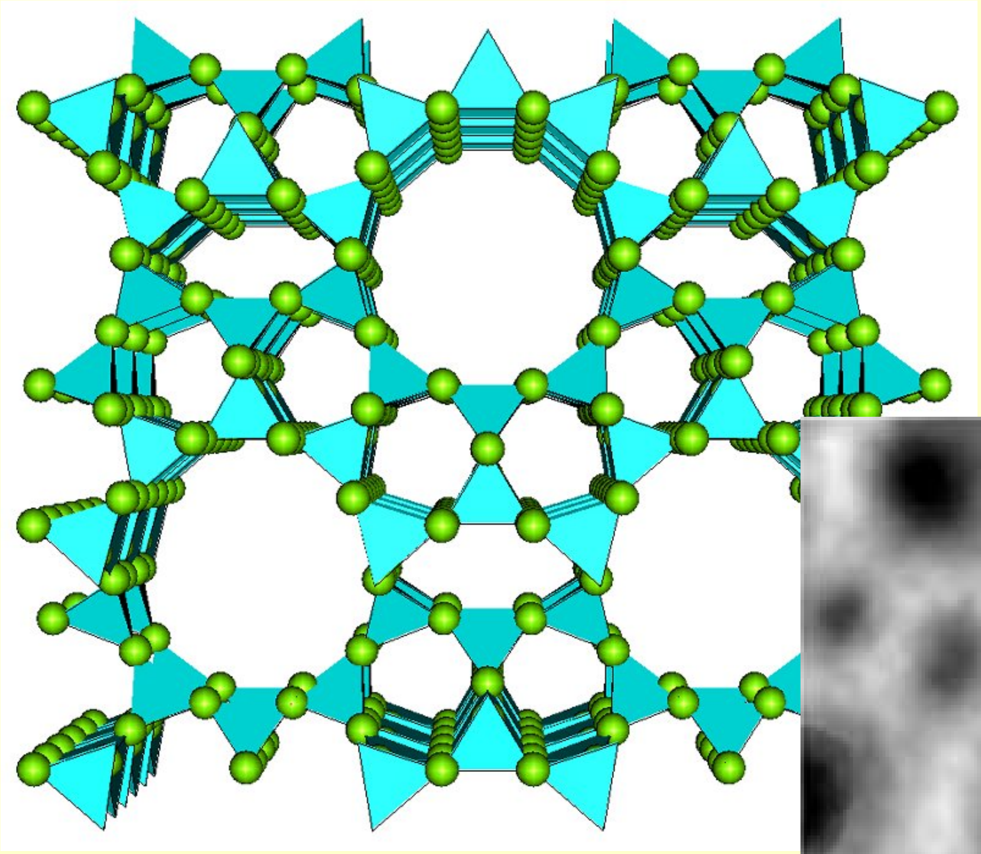
Odor control, adsorbents

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

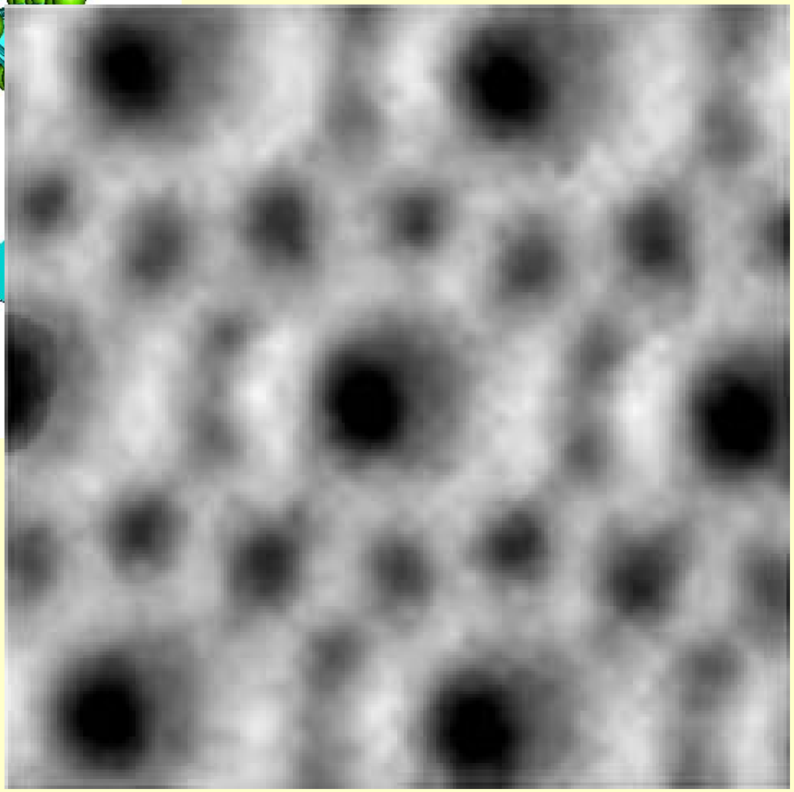
Host-guest inclusion, atoms, ions, molecules, radicals, organometallics, coordination compounds, clusters, polymers (conducting, insulating)

Nanoreaction chambers

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



HRTEM



Aquaculture
Ammonia filtration in fish hatcheries Biofilter media
Agriculture
Odor control Confined animal environmental control Livestock feed additives
Horticulture Nurseries, Greenhouses
Floriculture
Vegetables/herbs
Foliage
Tree and shrub transplanting
Turf grass soil amendment
Reclamation, revegetation, landscaping
Silviculture (forestry, tree plantations)
Medium for hydroponic growing

Household Products Household odor control Pet odor control

Industrial Products Absorbents for oil and spills Gas separations

Radioactive Waste Site remediation/decontamination

Water Treatment Water filtration Heavy metal removal Swimming pools

Wastewater Treatment Ammonia removal in municipal sludge/wastewater
Heavy metal removal Septic leach fields

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 $(AlO_2^-)(PO_2^+) = AlPO_4$

Aluminophosphates

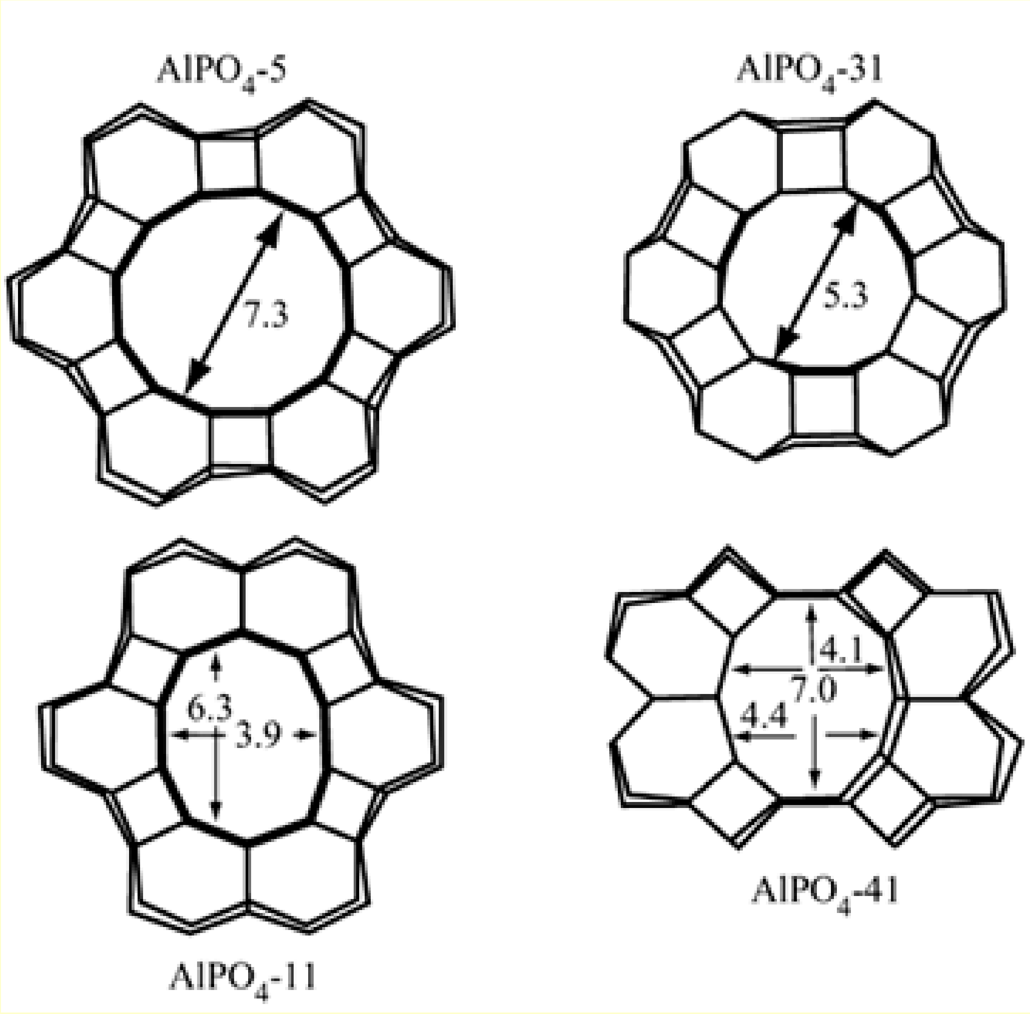
Some $AlPO_4$ structures are analogous to zeolites while other are novel and unique to this class of molecular sieves.

Only even-number rings = 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) 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.

Aluminophosphates



Aluminophosphate Synthesis

Aluminophosphates prepared by the hydrothermal synthesis
Source of Al: pseudoboehmite, Al(O)(OH), $Al(O\textit{i}\text{-}Pr)_3$

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

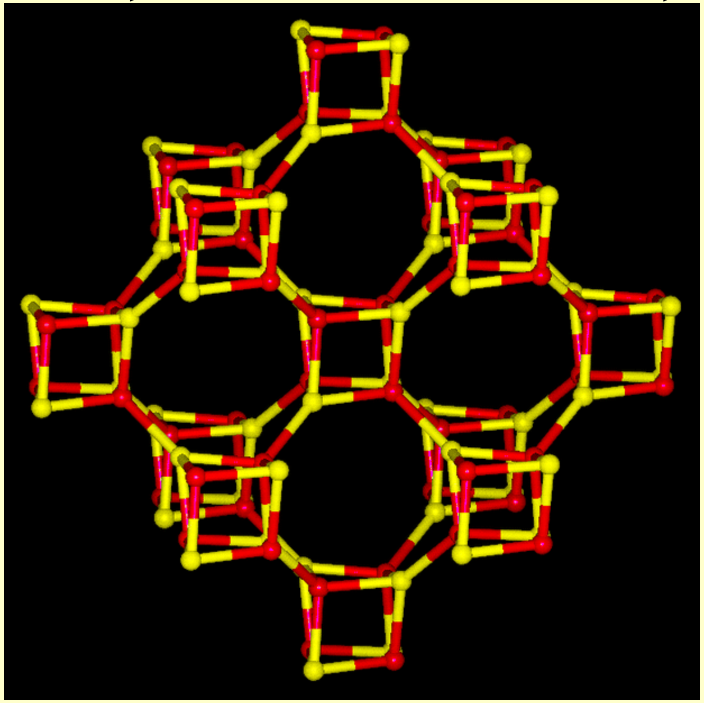
Cobalto-Aluminophosphate

ACP-1 (Co/Al 8.0)

bcc arrangement of the double 4-ring units (D4R)

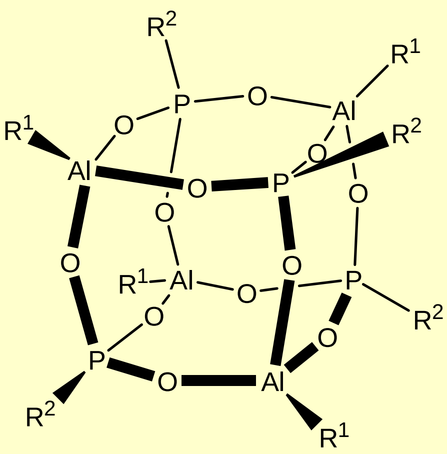
Ethylenediamine molecules are located inside 8-ring channels

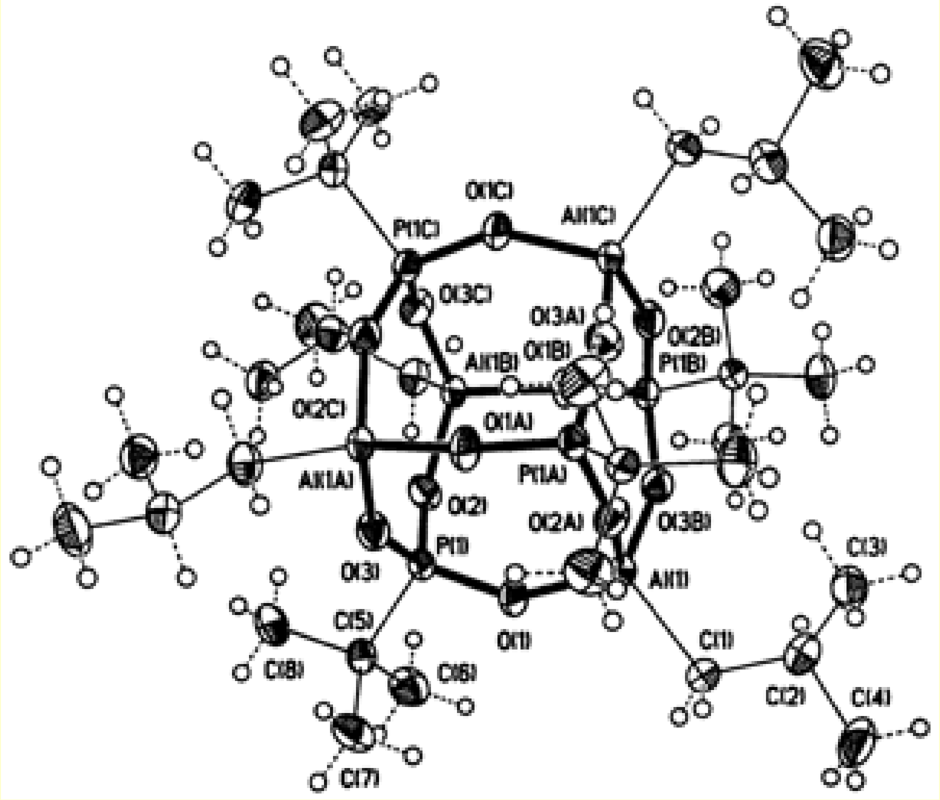
At the centre of each D4R, there is a water molecule, 2.31 Å away from four metal sites



$Al(O\text{-}iPr)_3$, $CoCO_3.H_2O$, 85% H_3PO_4, ethylene glycol, ethylenediamine, pH 8.4
Heated in a Teflon-coated steel autoclave at 180 °C for 4 d

Synthesis of Double 4-ring Units (D4R)





Metallo-Organic Framework (MOF) Structures

4000 structures known (2008), 1000 new per year

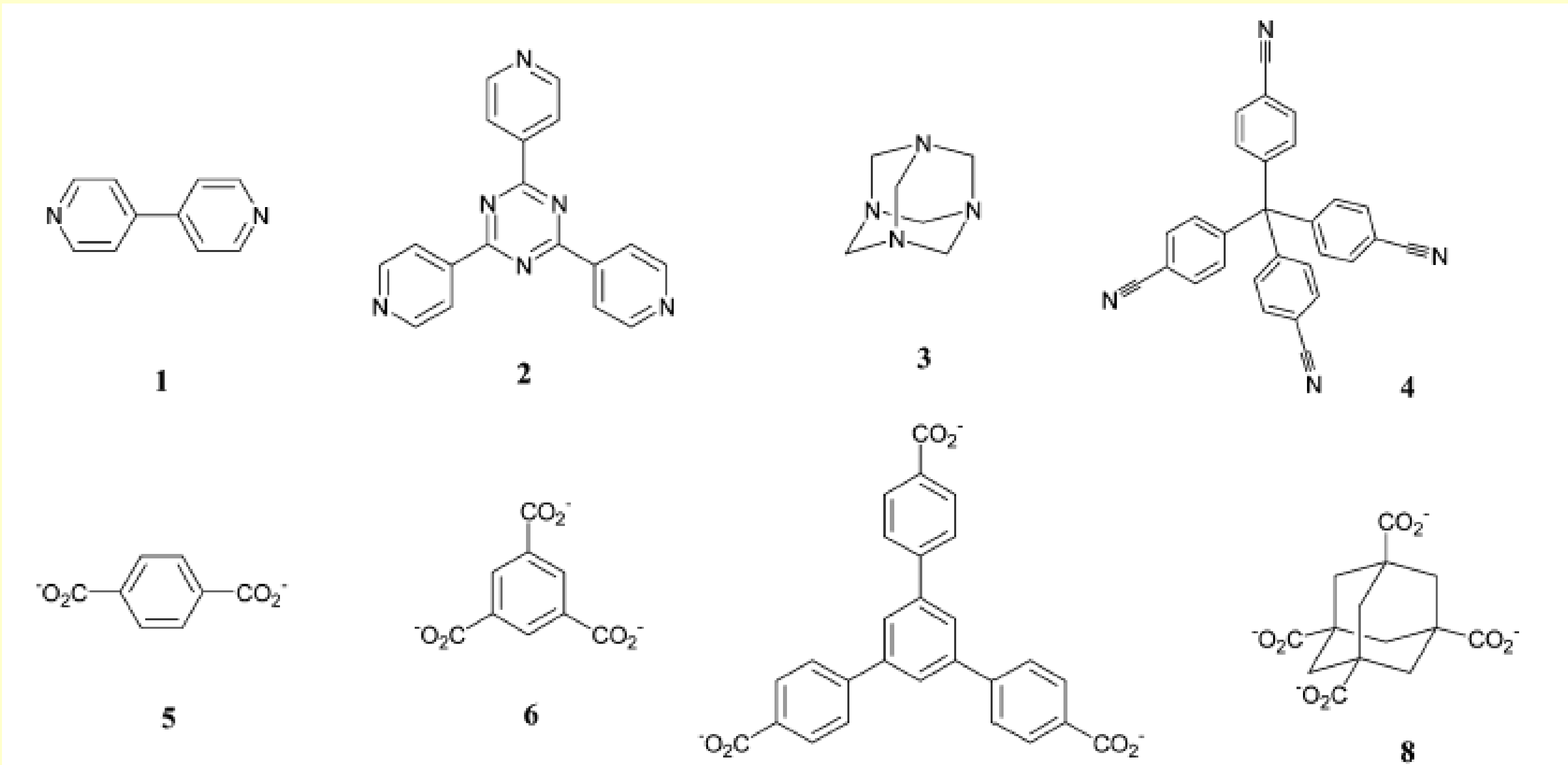
Metal centers

- **Coordiantive bonds**
- **Coordination numbers 3-6**
- **Bond angles**

Polytopic Ligands

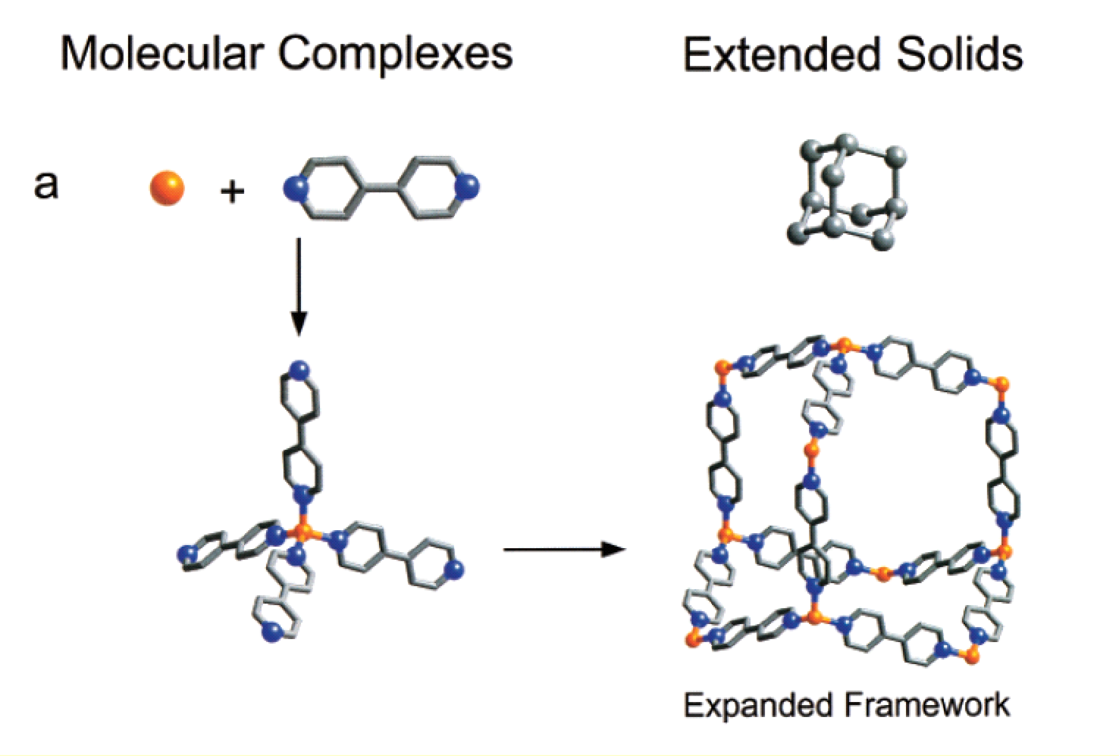
Organic spacers
Flexible – rigid
Variable length

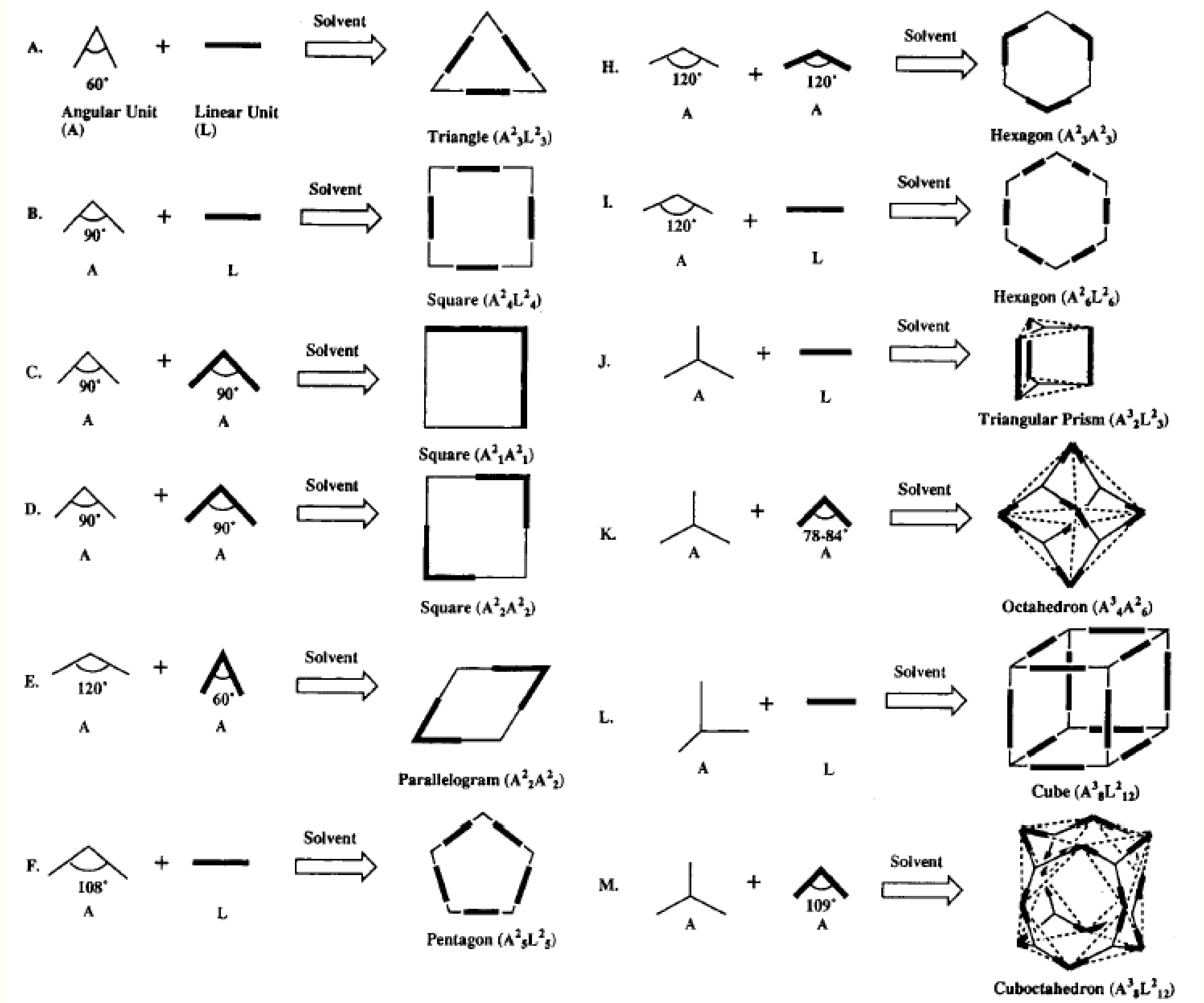
Polytopic Organic Linkers



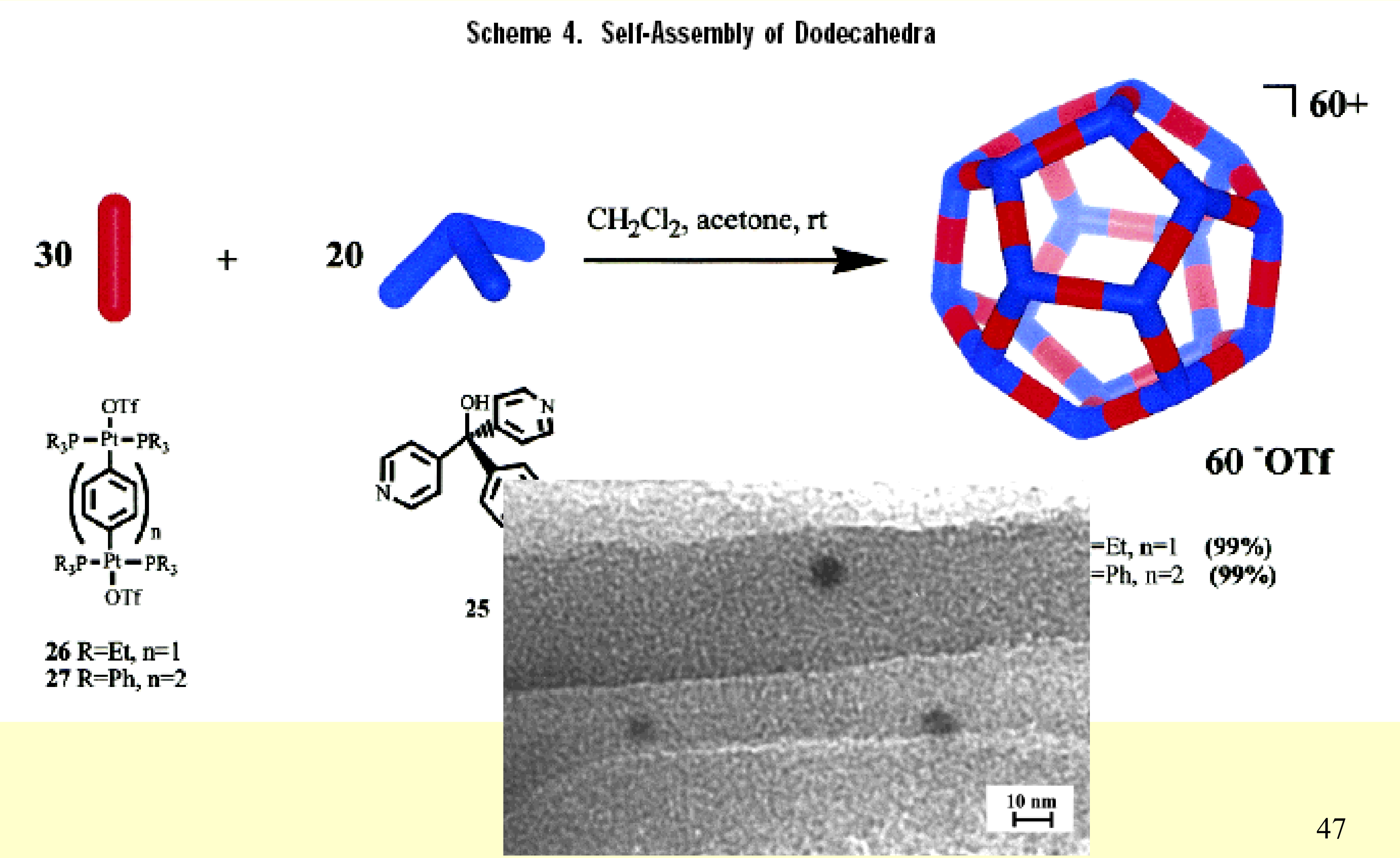
Polytopic N-bound Organic Linkers

Cationic framework structures
Evacuation of guests within the pores usually results in collapse of the host framework

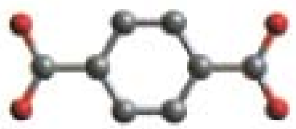



A.
60°
Angular Unit (A)
Linear Unit (L)
Solvent
Triangle (A²₃L²₃)
B.
90°
A
L
Solvent
Square (A²₄L²₄)
C.
90°
A
90°
A
Solvent
Square (A²₁A²₁)
D.
90°
A
90°
A
Solvent
Square (A²₂A²₂)
E.
120°
A
60°
A
Solvent
Parallelogram (A²₂A²₂)
F.
108°
A
L
Solvent
Pentagon (A²₅L²₅)
H.
120°
A
120°
A
Solvent
Hexagon (A²₃A²₃)
I.
120°
A
L
Solvent
Hexagon (A²₆L²₆)
J.
A
L
Solvent
Triangular Prism (A³₂L²₃)
K.
A
78-84°
A
Solvent
Octahedron (A³₄A²₆)
L.
A
L
Solvent
Cube (A³₈L²₁₂)
M.
A
109°
A
Solvent
Cuboctahedron (A³₈L²₁₂)

Metallo-Organic Framework Structures

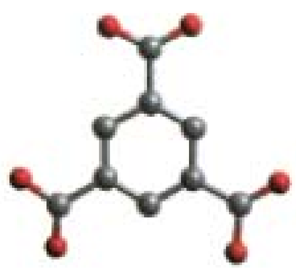


Polytopic carboxylate linkers

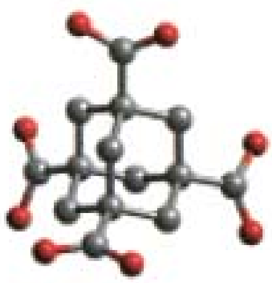


1,4-benzenedicarboxylate
(BDC)

1,4-azodibenzoate
(ADB)



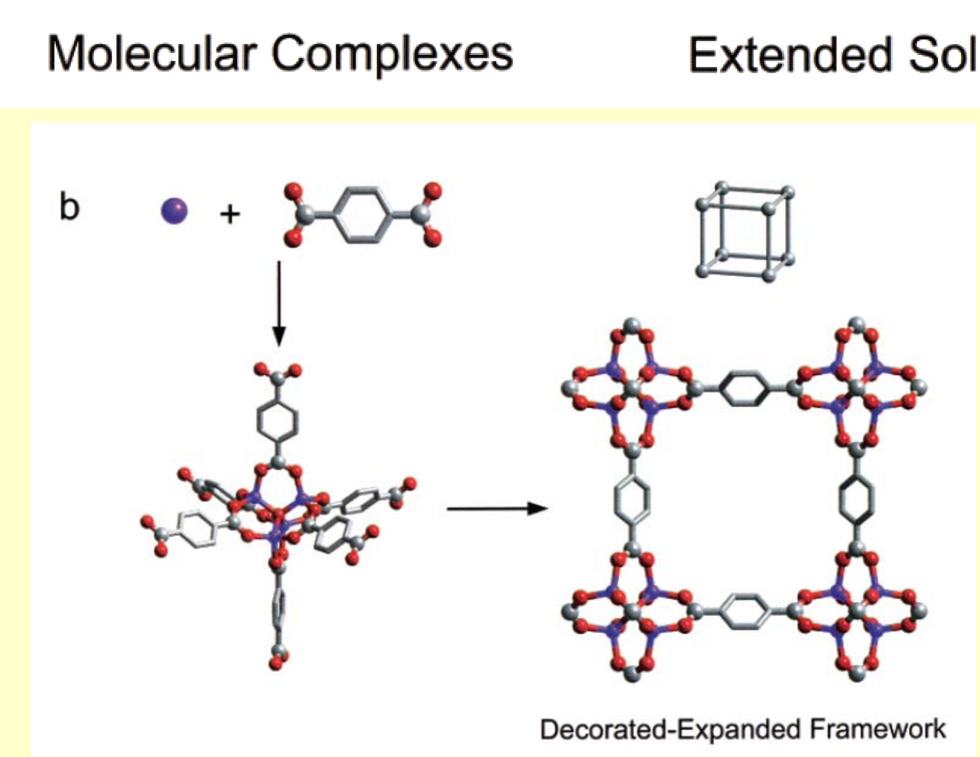
1,3,5-benzenetricarboxylate
(BTC)



1,3,5,7-adamantanetetracarboxylate
(ATC)

Polytopic Carboxylate Linkers

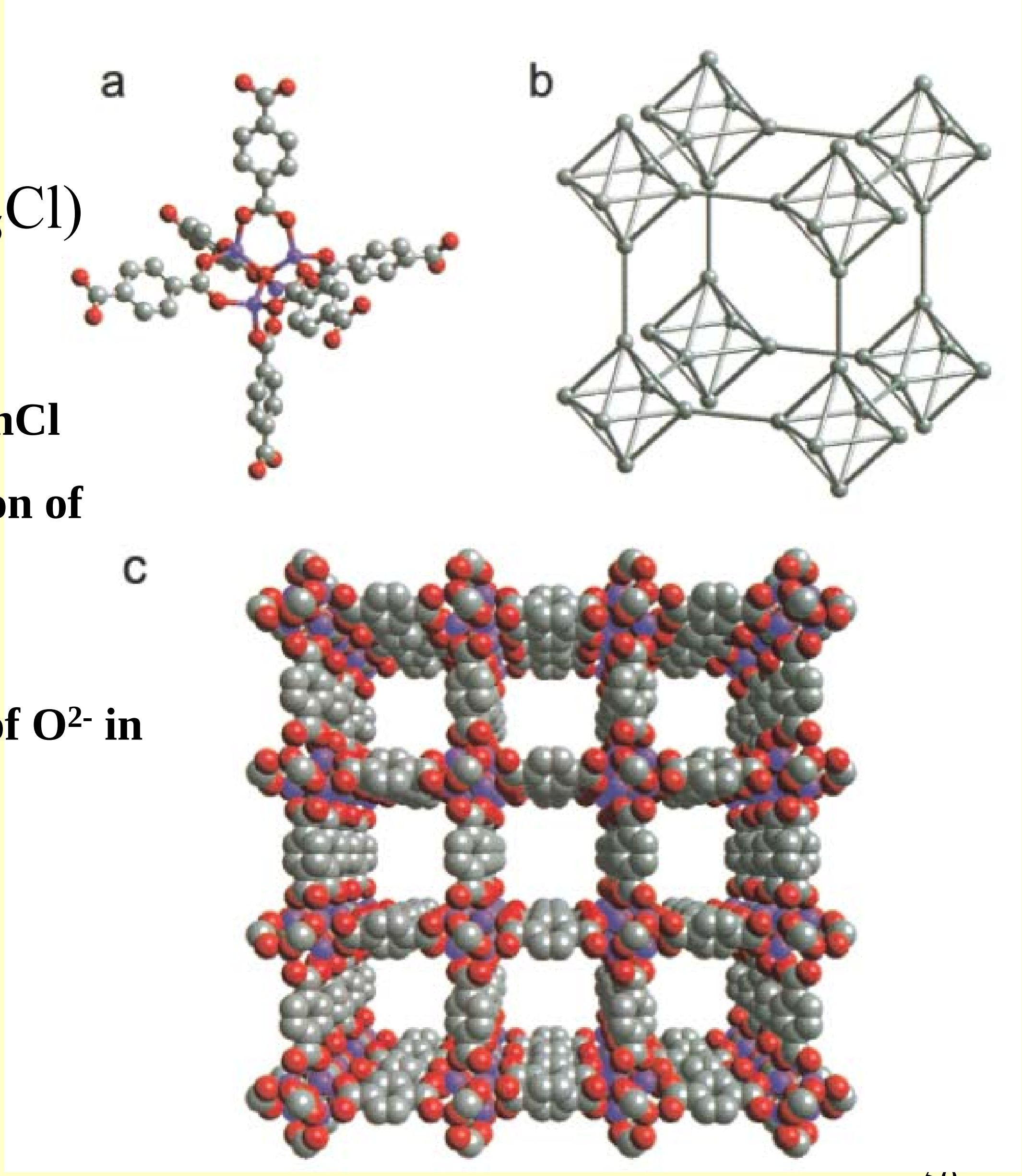
Aggregation of metal ions into M-O-C clusters
form more rigid frameworks
frameworks are neutral
no need for counterions



MOF-5

$Zn_4O(BDC)_3.(DMF)_8(C_6H_5Cl)$

- **$Zn(NO_3)_2$ + H_2BDC in DMF/PhCl**
- **Addition of TEA: deprotonation of H_2BDC**
- **Addition of Zn^{2+}**
- **Addition of H_2O_2: formation of O^{2-} in the cluster center**



Cavity diam. 18.5 Å

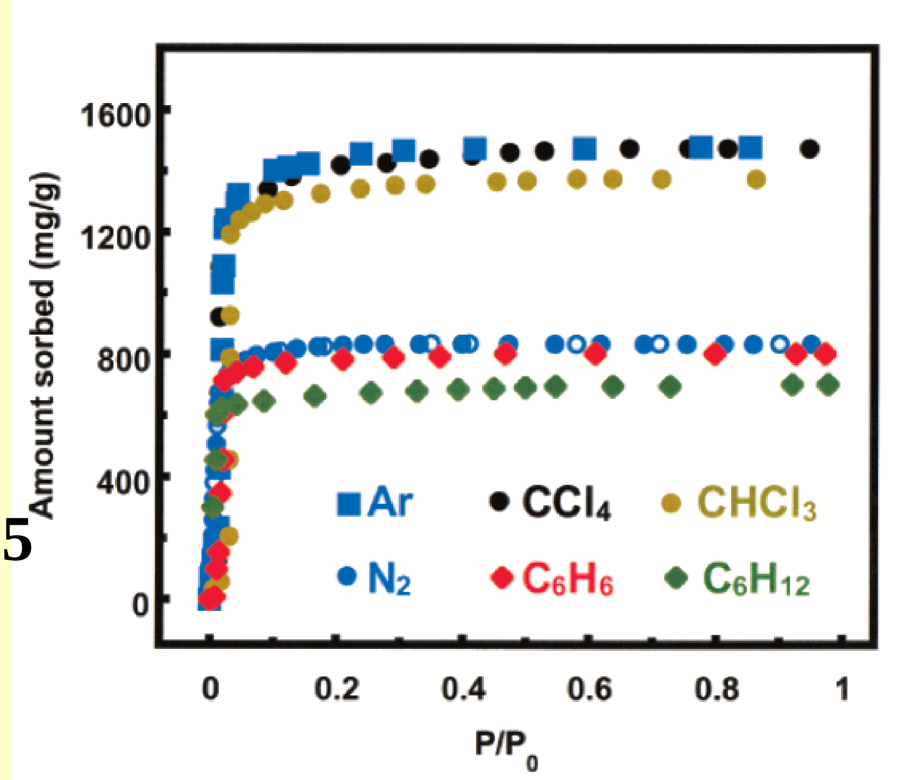
Nature, 1999, 402, 276

a primitive cubic lattice

MOF-5

MOF-5
Stable even after desolvation
at 300 °C in air

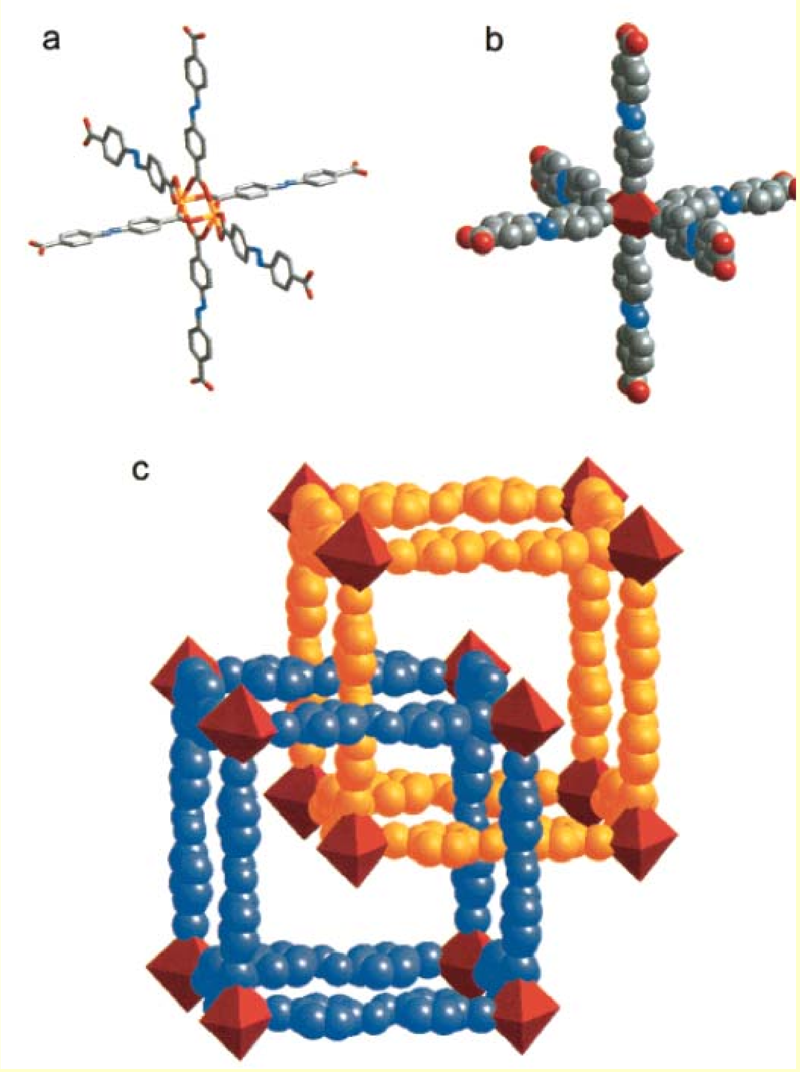
gas sorption isotherms for MOF-5



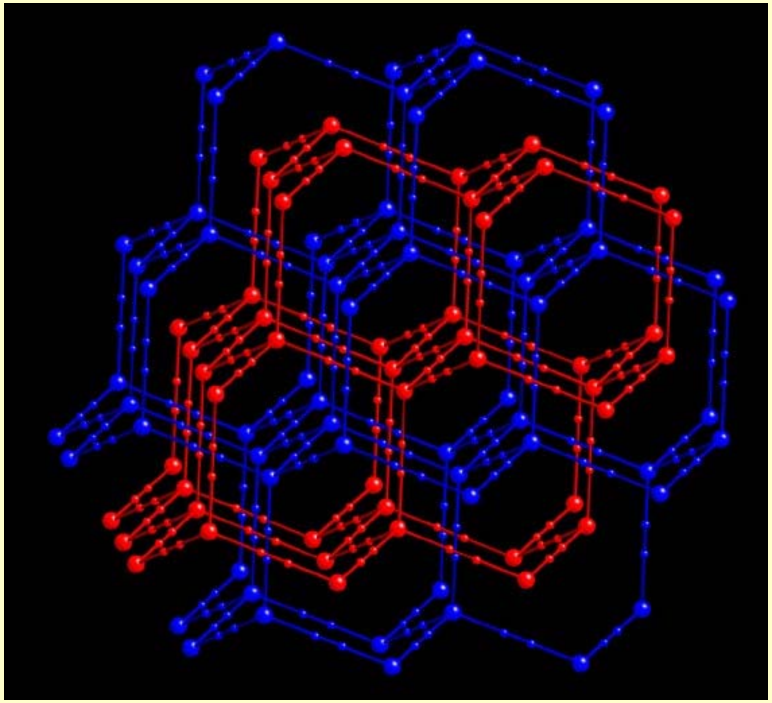
	MOF -2	MOF -3	MOF -4	MOF -5	MOF -6	MOF -9	MOF -11
pore diameter (Å)	7	8	14	12	4	8	7
surface area (m^2/g)	270	140		2900		127	560
pore volume (cm^3/g)	0.094	0.038	0.612	1.04	0.099	0.035	0.20

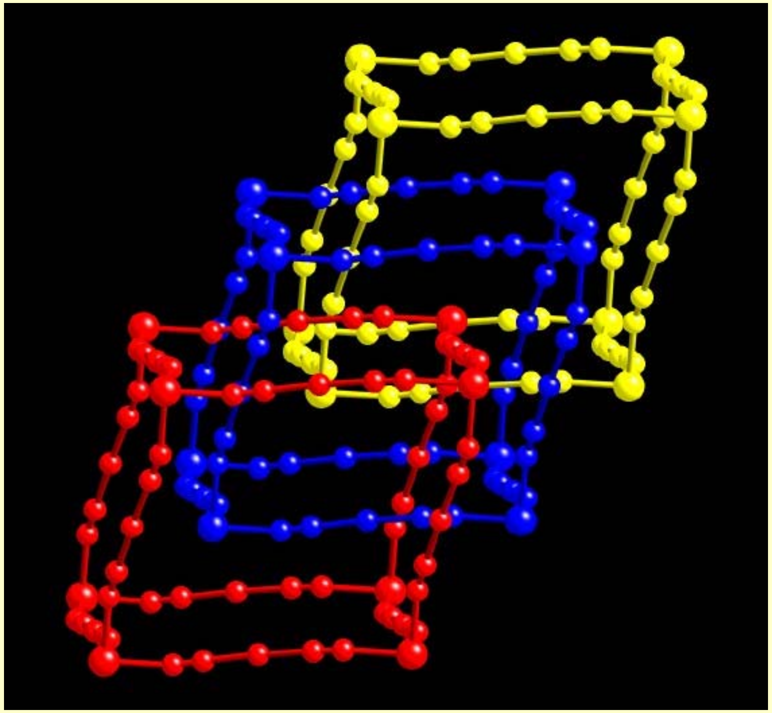
Interpenetration

MOF-9

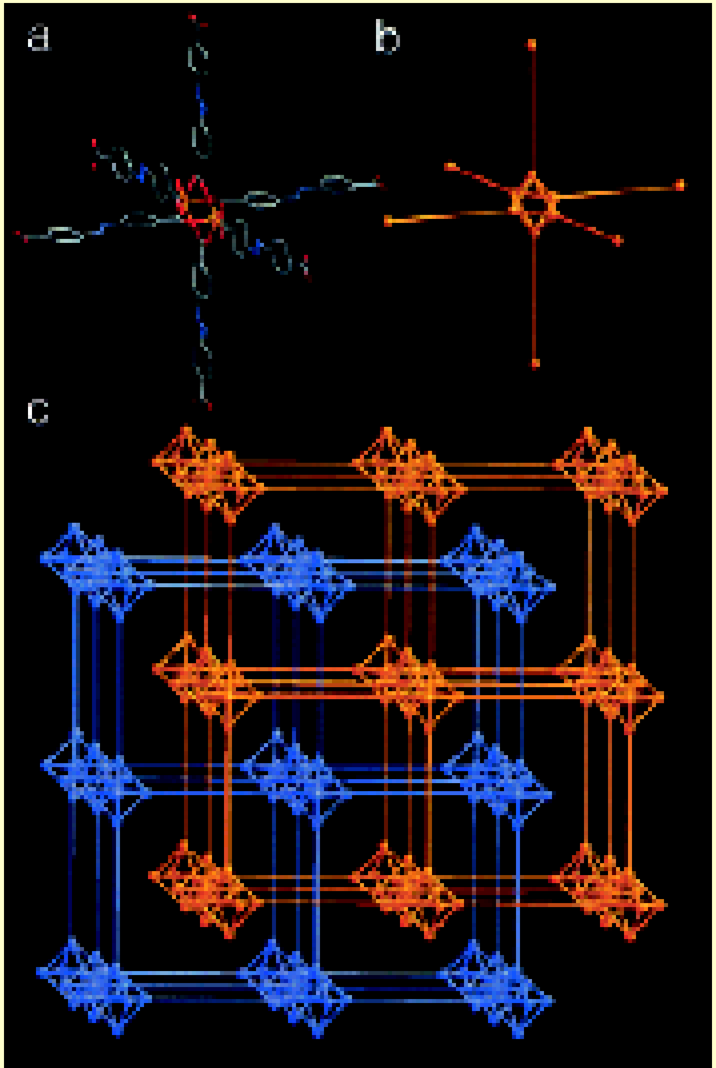


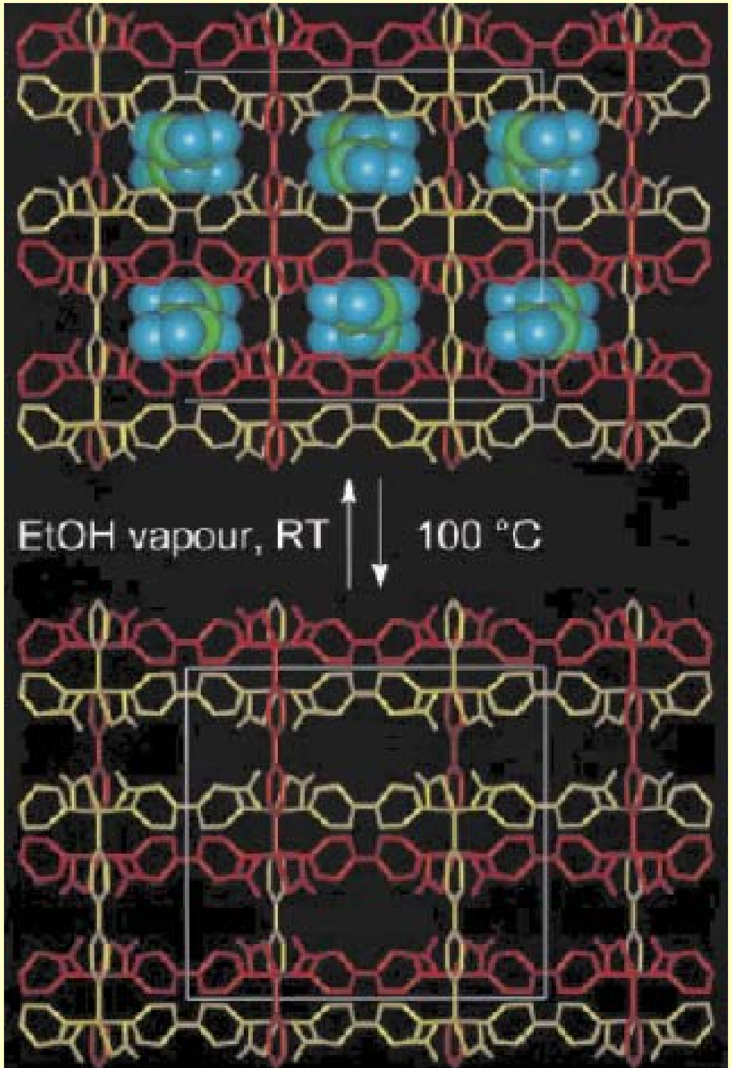
Interpenetration





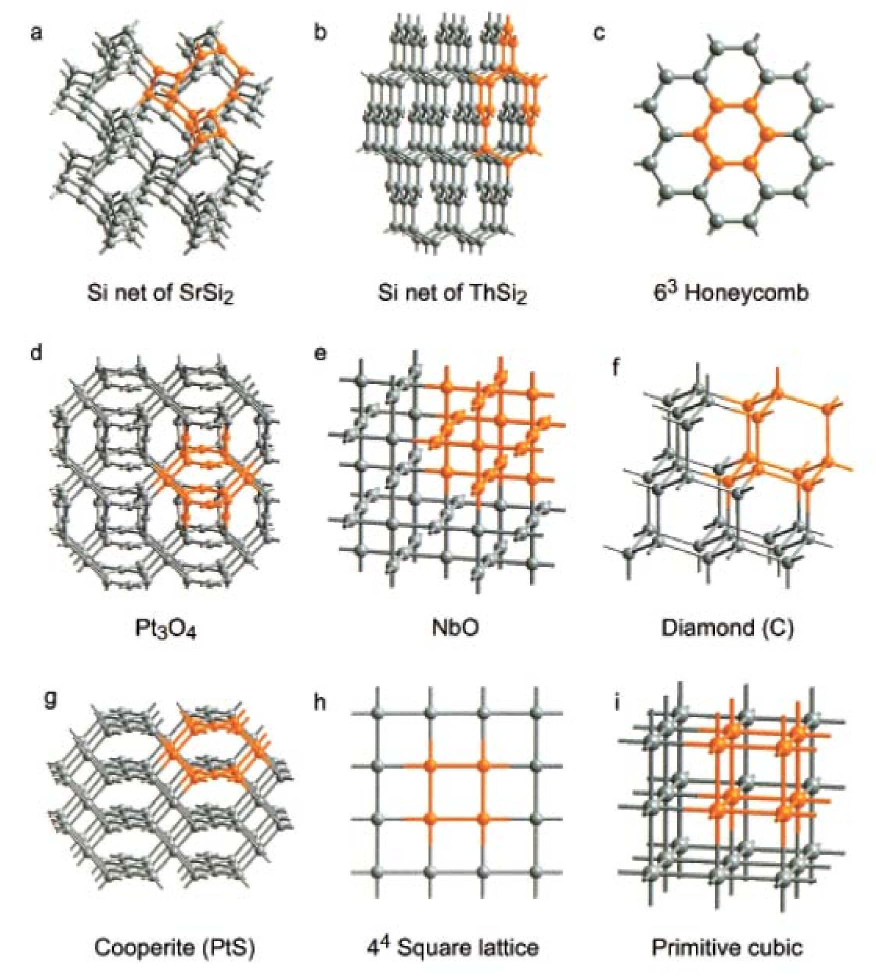
Metallo-Organic Framework Structures



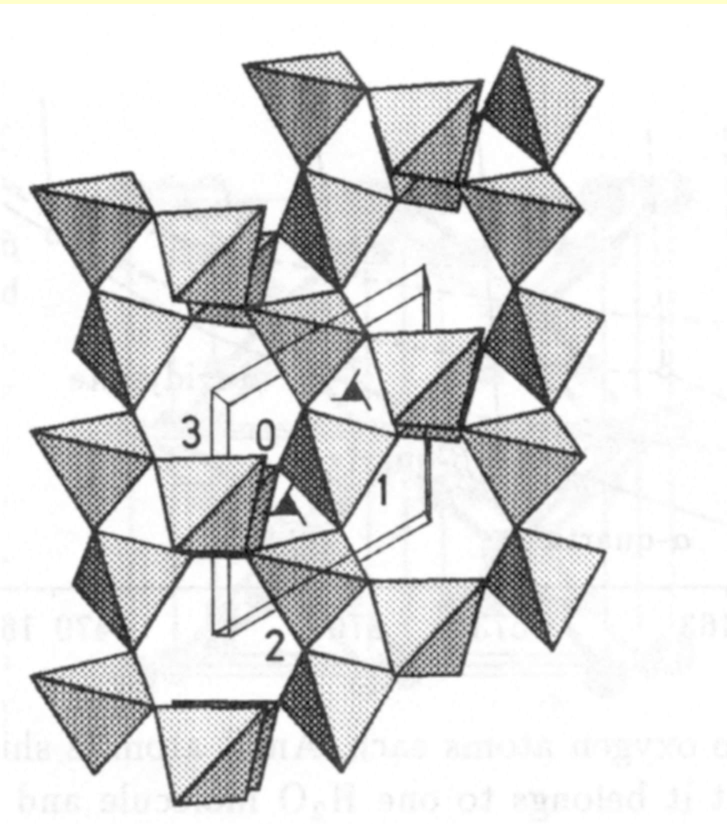


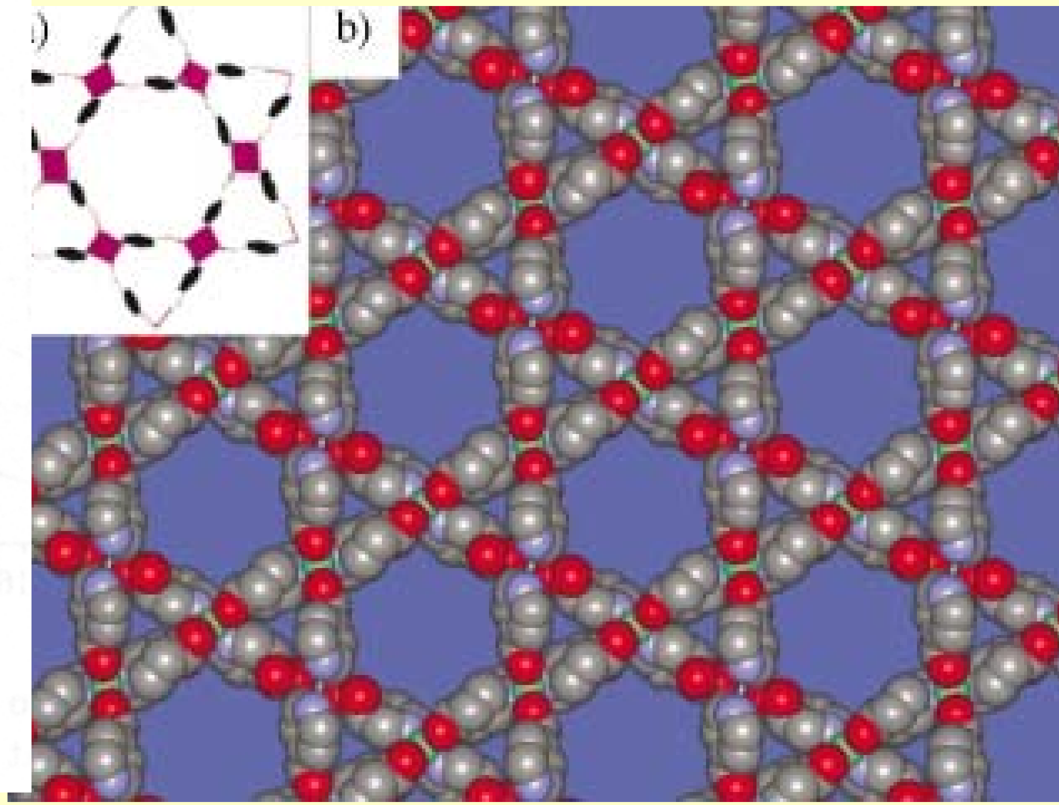
Basic Nets

coordination	coordination figures		net
3	triangle	triangle	$SrSi_2$
3	triangle	triangle	$ThSi_2$
3	triangle	triangle	6^3 honeycomb
3,4	triangle	square	Pt_3O_4
4	square	square	NbO
4	tetrahedron	tetrahedron	diamond (C)
4,4	square	tetrahedron	cooperite (PtS)
4	square	square	4^4 square lattice
6	octahedron	octahedron	primitive cubic
8	cube	cube	body-centered cubic

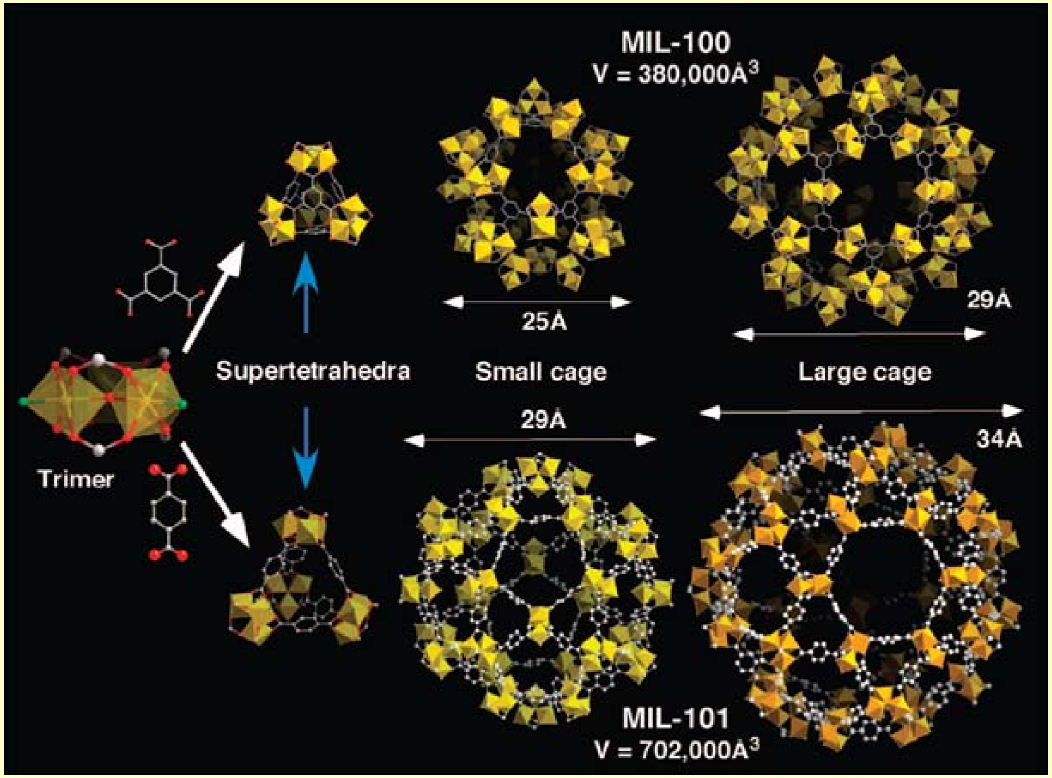


Inorganic and Metallo-Organic Quartz





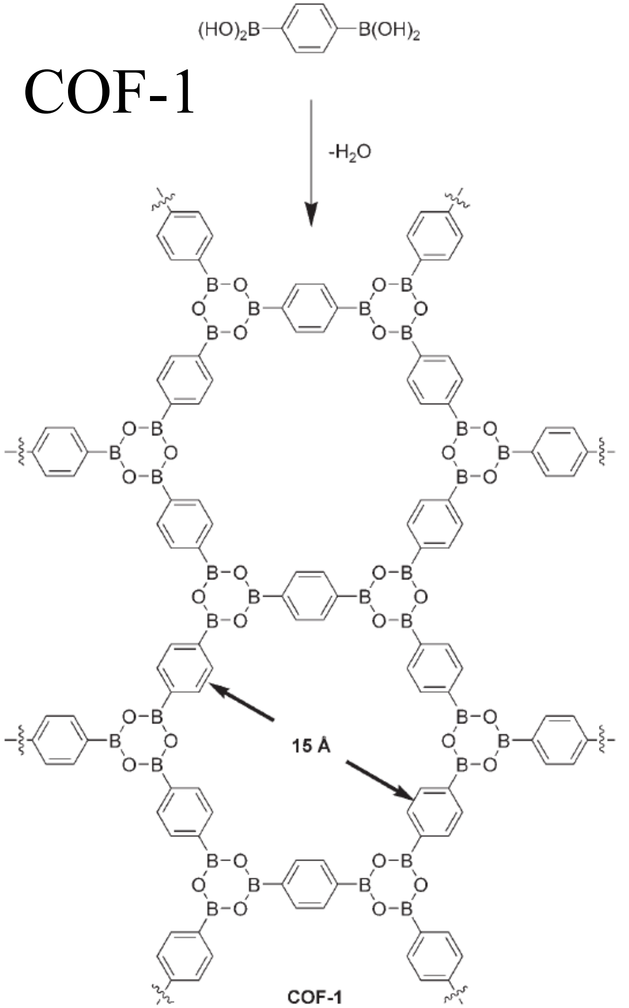
MIL-100 and MIL-101



MIL-101   Record Surface area 5 900 m^2/g

Covalent Organic Frameworks

COF-1



Solvents - reactants are poorly soluble (to slow down the reversible condensation)

sealed pyrex tubes

minimize defects by self-healing.

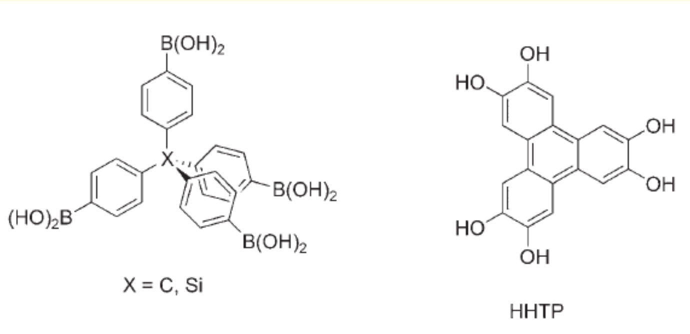
COF-1 = microcrystalline, high yield, high structural order by XRD

Solvent molecules are enclosed inside the pores, can be removed at 200 ^{o}C without collapse of the crystalline structure.

surface area of 711 m^2 g^{-1}

Covalent Organic Frameworks

3D frameworks
COF-102, COF-103, COF-105, and COF-108



COF-108 - bor structure
two different types of pores
diameters of 15.2 and 29.6 Å.
density 0.17 g cm^{-3}

surface area, m^2 g^{-1}
COF 102   3472
COF 103   4210