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.

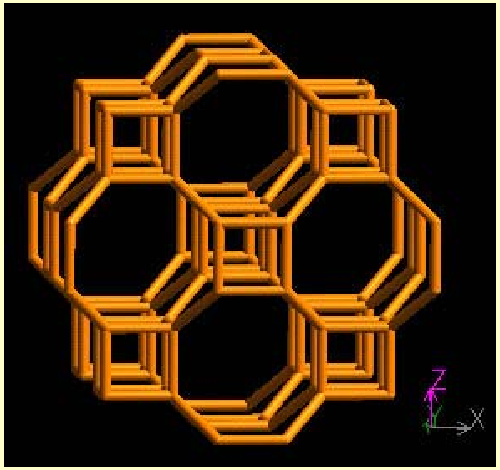
Macroporous > 50 nm
Mesoporous 2–50 nm
Microporous < 2 nm
Ultramicroporous < 0.7 nm

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

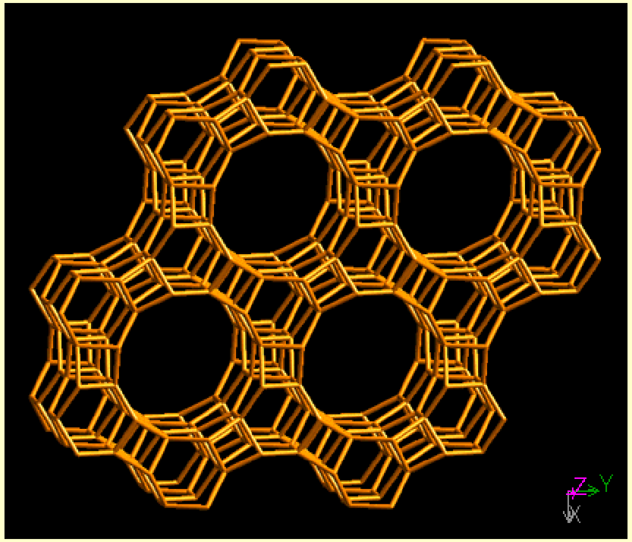
Chemical composition	
Silica	SiO_2
Aluminosilicates	$M_x^I Al_x Si_{2-x} O_4 . nH_2O$
Aluminophosphates	$AlPO_4$ (isoelectronic with Si_2O_4)
Metallophosphates	MPO_4
Silicoaluminophosphates	$M_x^I Si_x AlP_{1-x} O_4$

Pores and Channels

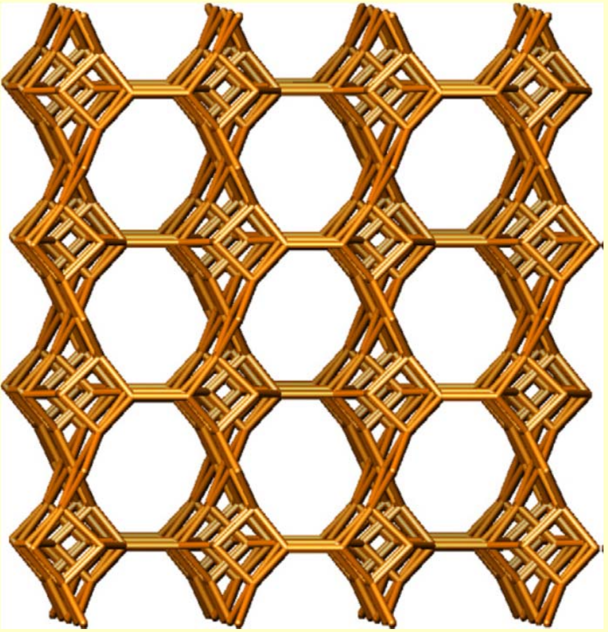
ACO



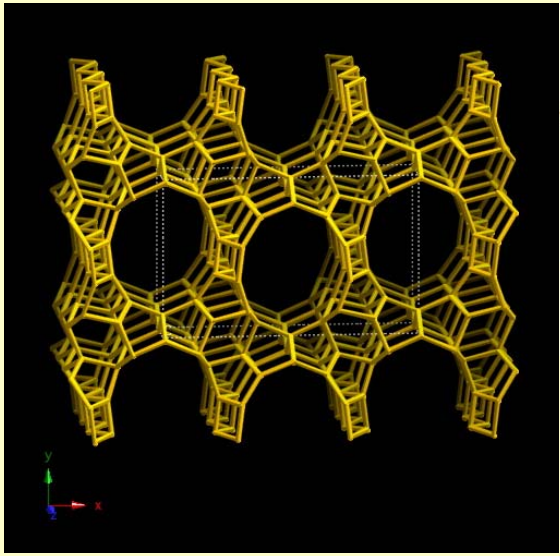
AFI



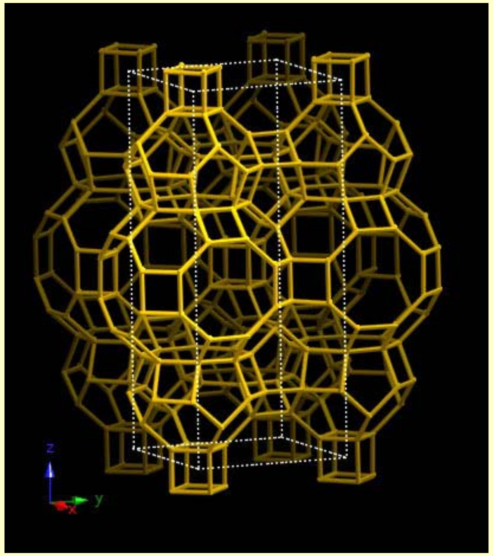
STI



SSY



UFI



Zeolite Types

>60 naturally occurring zeolites - large deposits of analcime, chabazite, clinoptilolite, erionite, mordenite and phillipsite
>232 zeolite framework types (IZA - 2017)
many hundreds of zeolite compounds

Nomenclature http://www.iza-structure.org/
Structure types - three capital letter codes
Most well known zeolite archetypes: SOD, LTA, FAU, MOR, MFI
Aluminium Cobalt Phosphate - 1 (One) = ACO

- **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

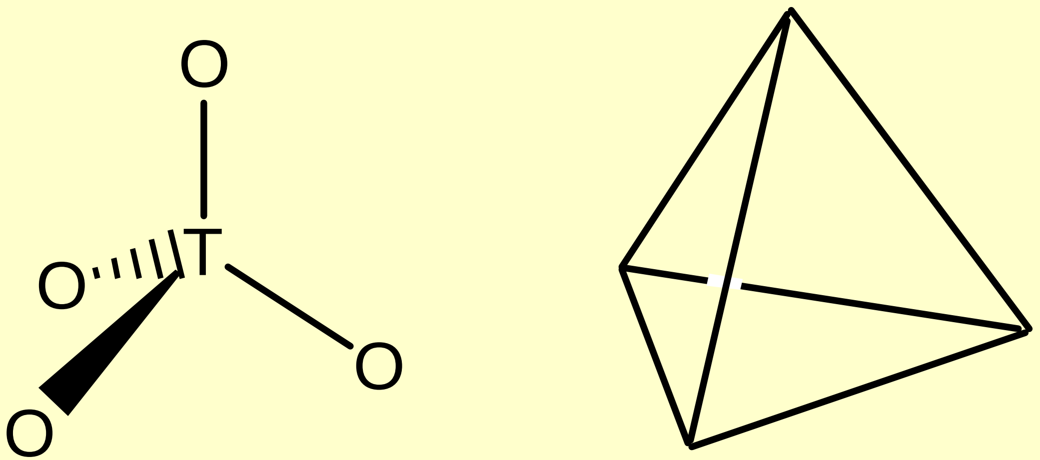
Zeolite Names

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)**
  - **MU-n (Mulhouse, Université de Haute Alsace)**

Zeolites Building Units

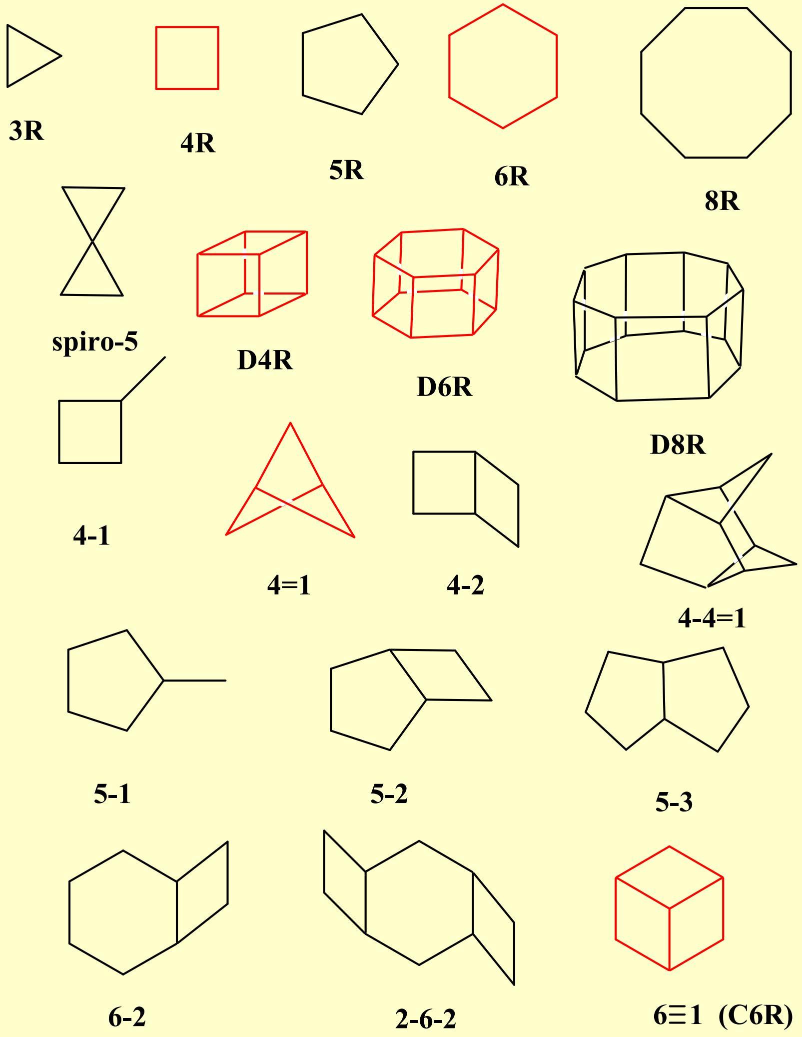
Primary building units:
Al(III)O_4, P(V)O_4 and Si(IV)O_4 tetrahedra

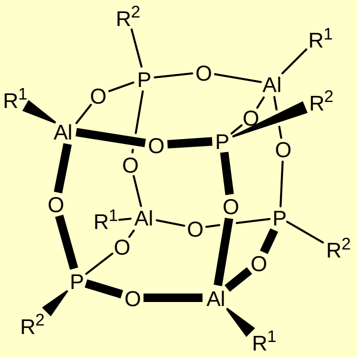


Isoelectronic relationship

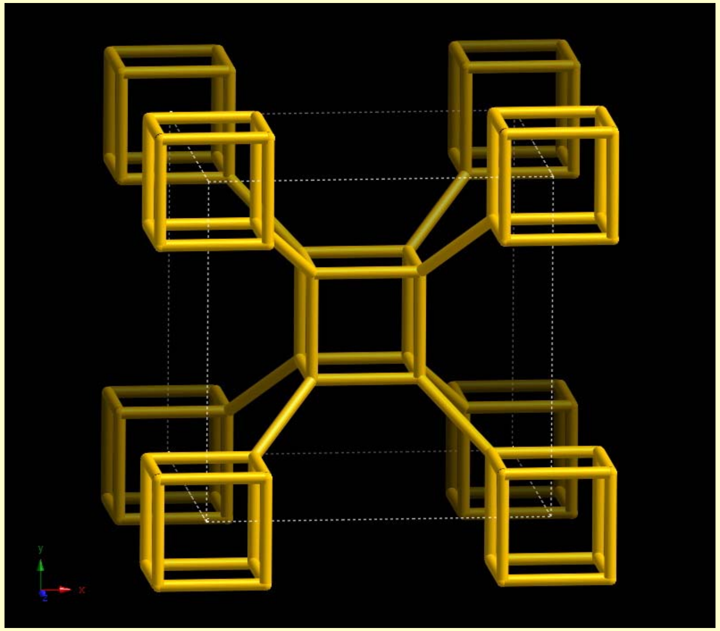
$(SiO_2)_2$ $[AlSiO_4]^-$ $AlPO_4$

Secondary (Structural) Building Units (SBU)

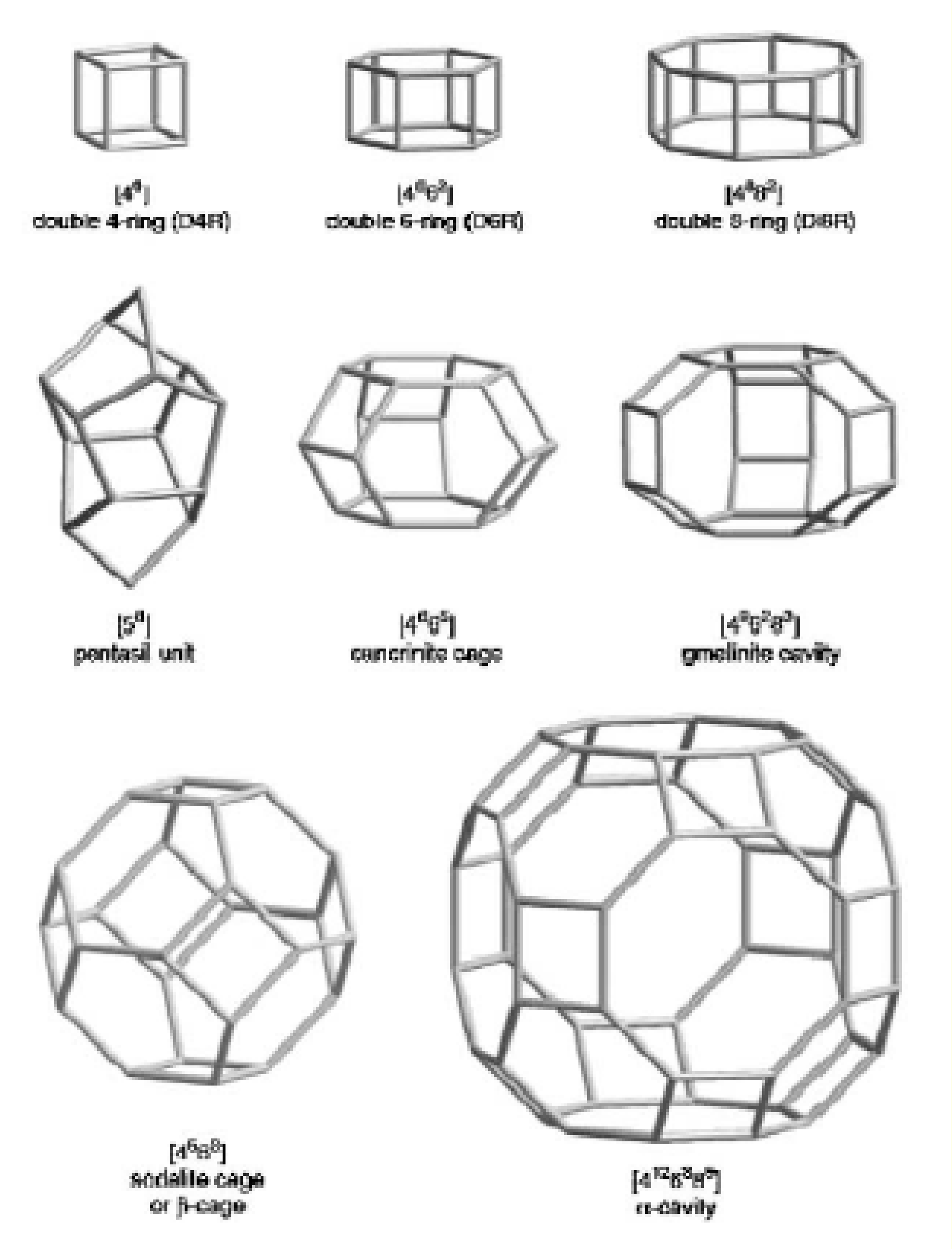




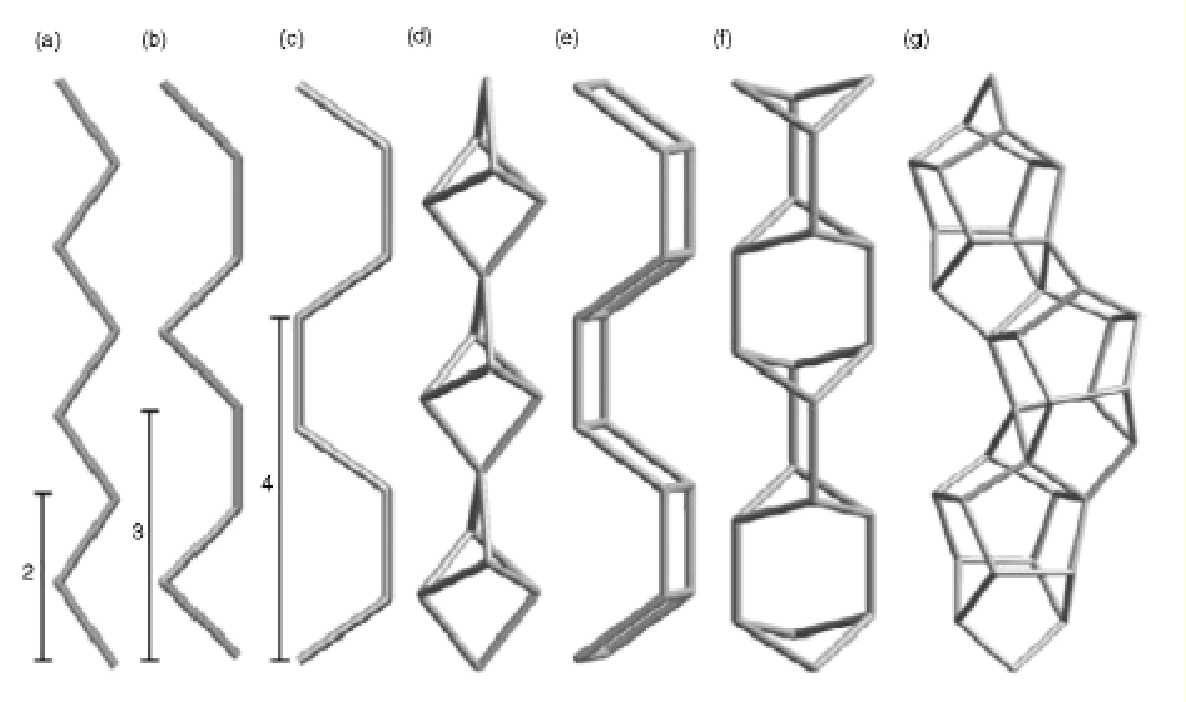
Framework Type ACO



Polyhedral composite building units



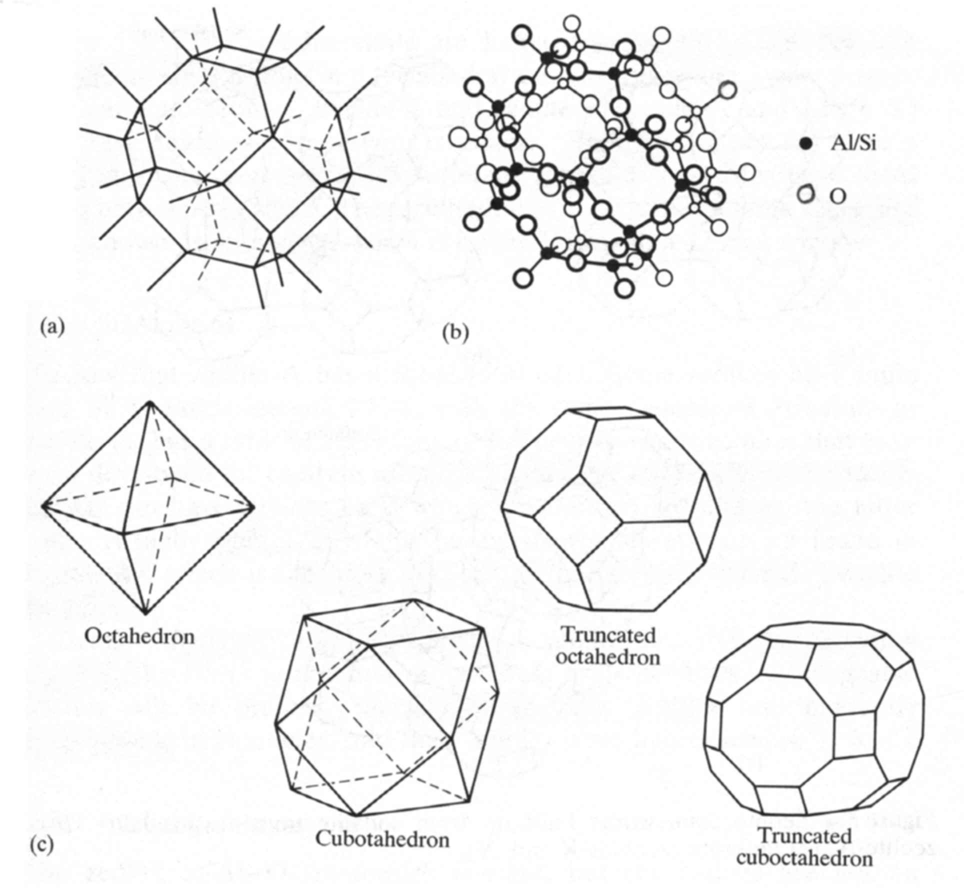
Chain composite building units



(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

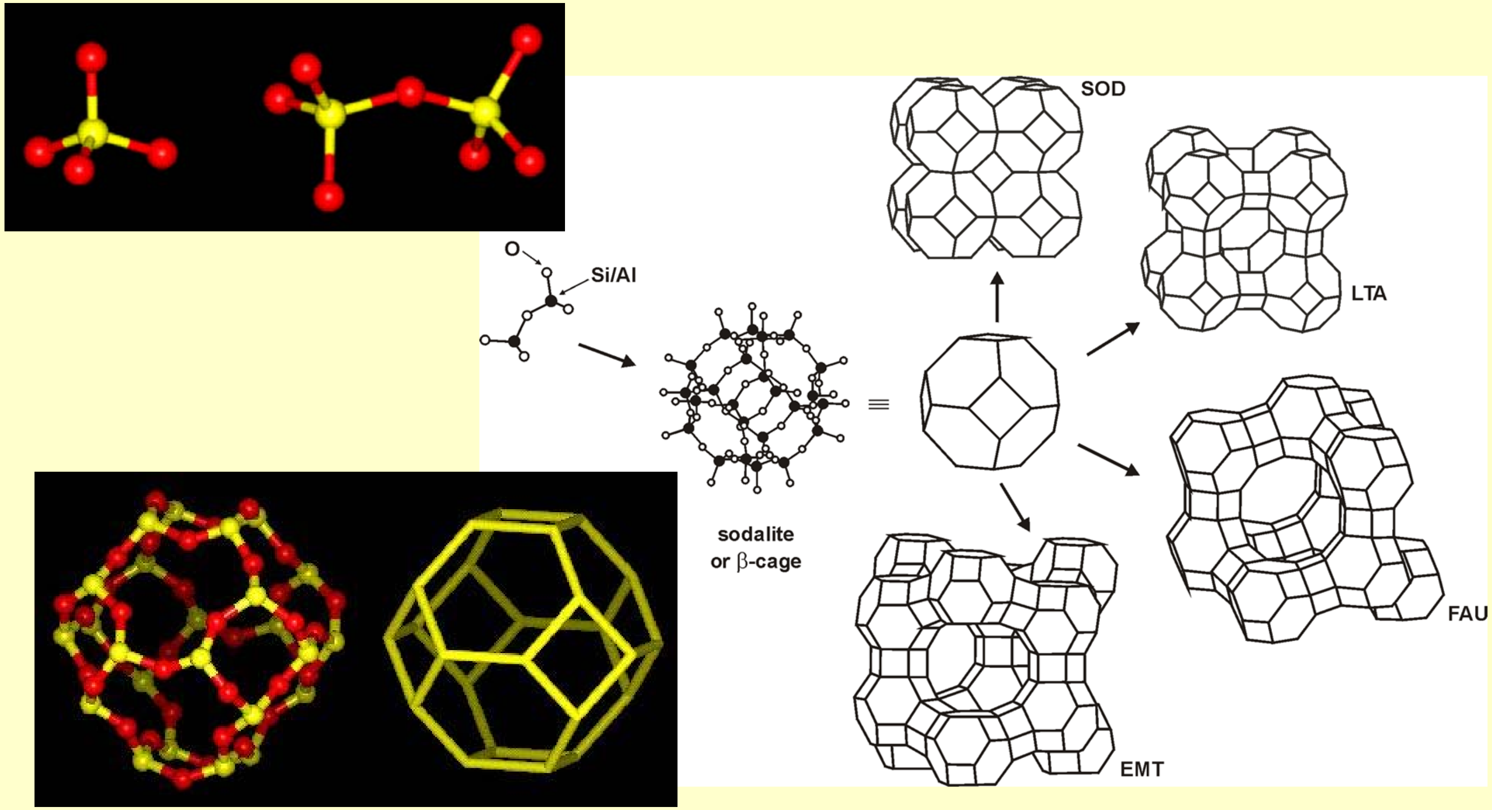
Sodalite Unit

Truncated octahedron

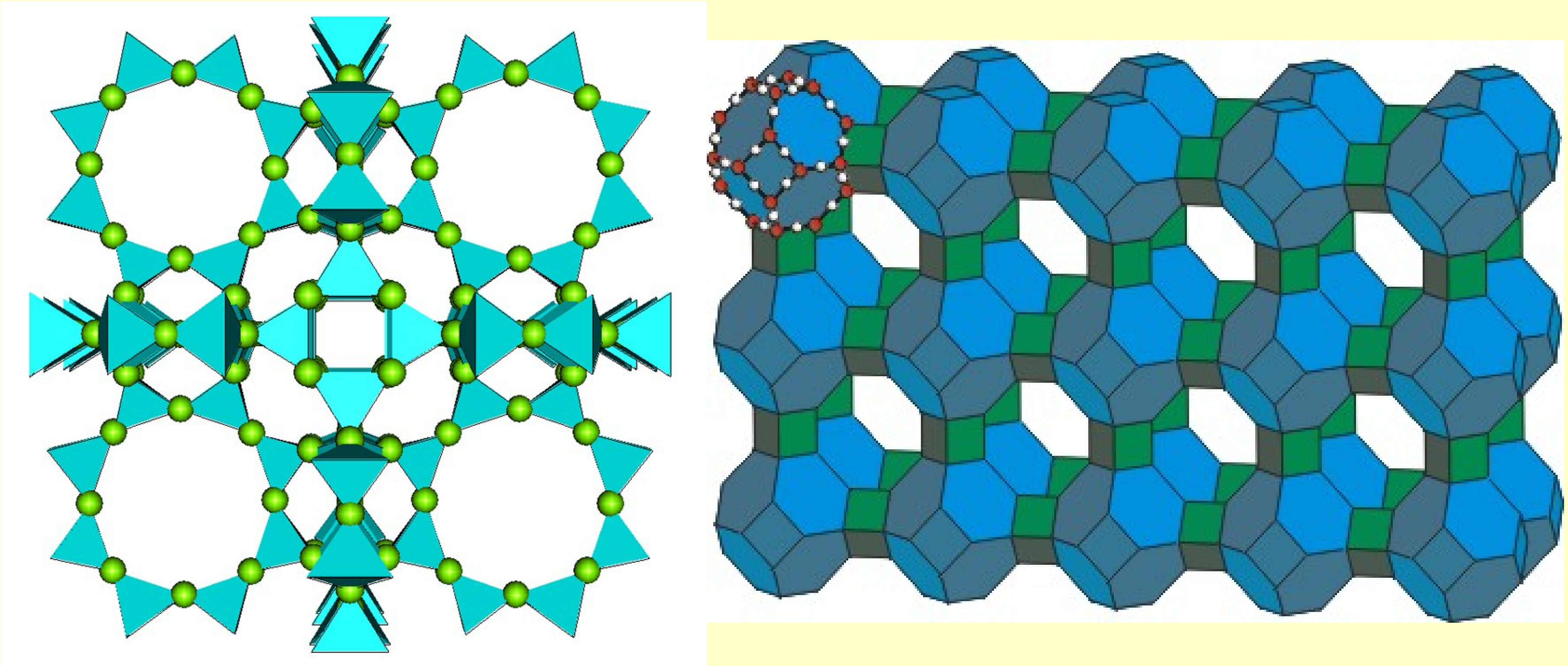


Sodalite Unit

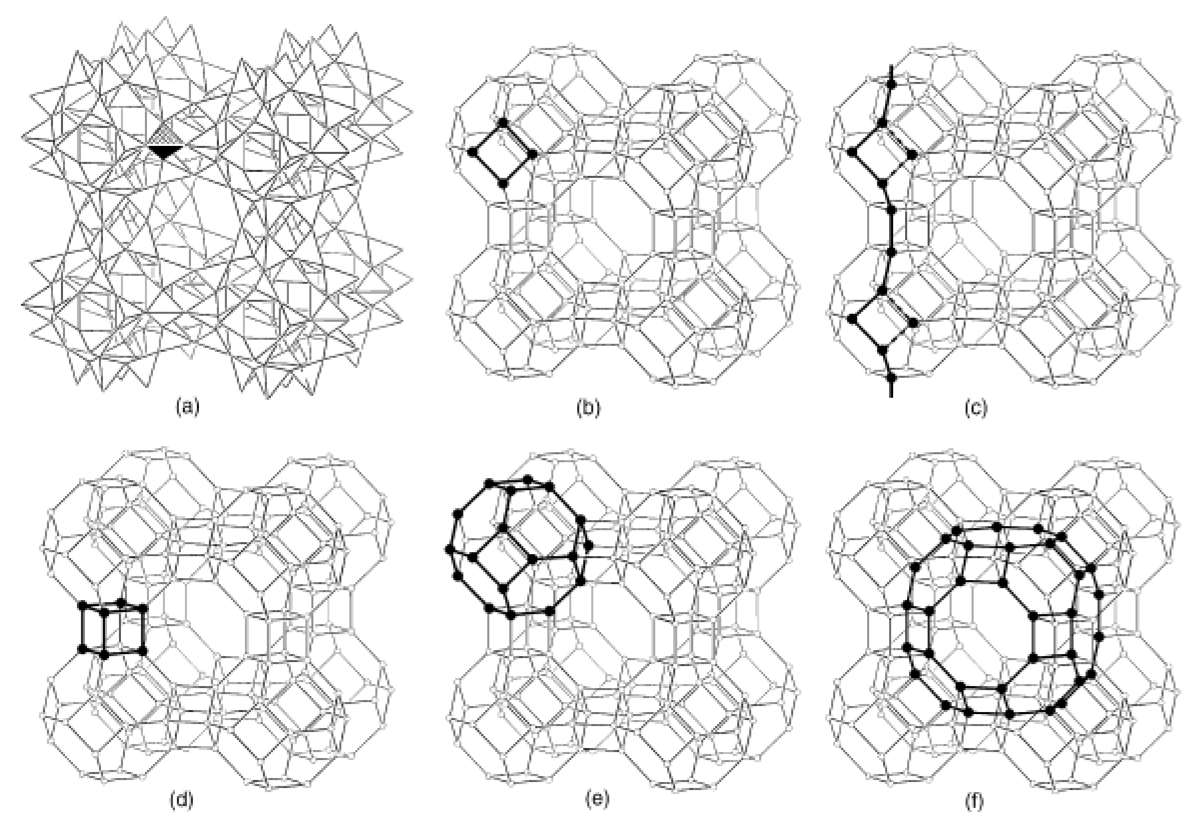
Packing of the sodalite units:
SOD – bcc, sharing of 4-rings
LTA – sc, 4-rings connected through O bridges
FAU (faujasite) – cubic diamond, 6-rings connected through O bridges
EMT – hexagonal diamond, 6-rings connected through O bridges



Zeolite LTA

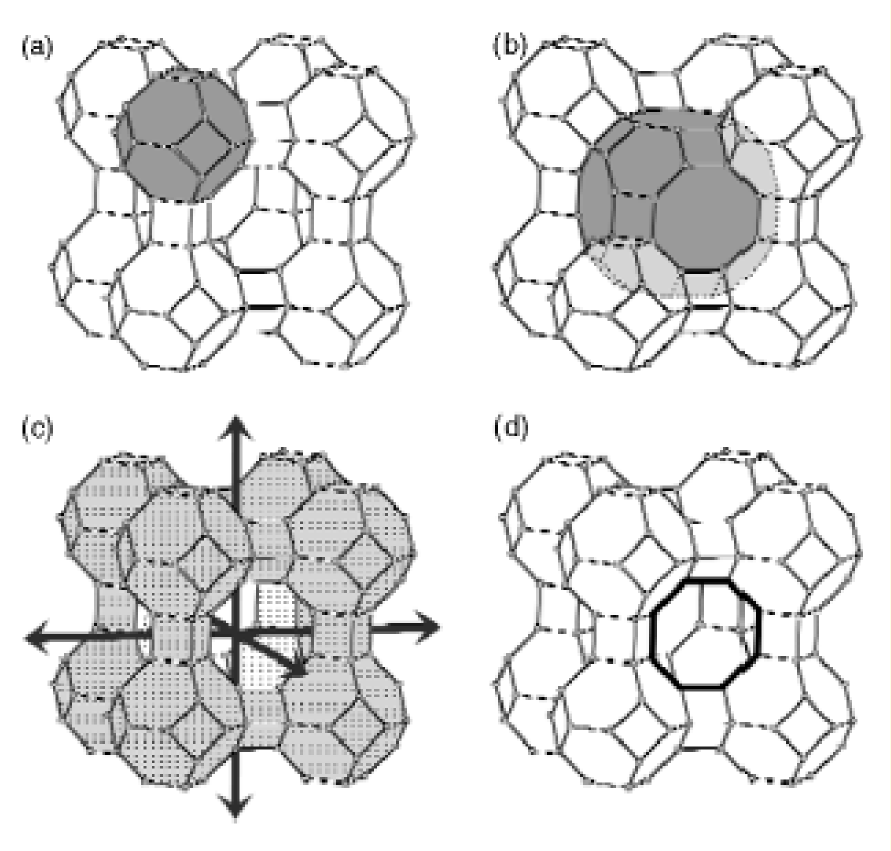


Zeolite A

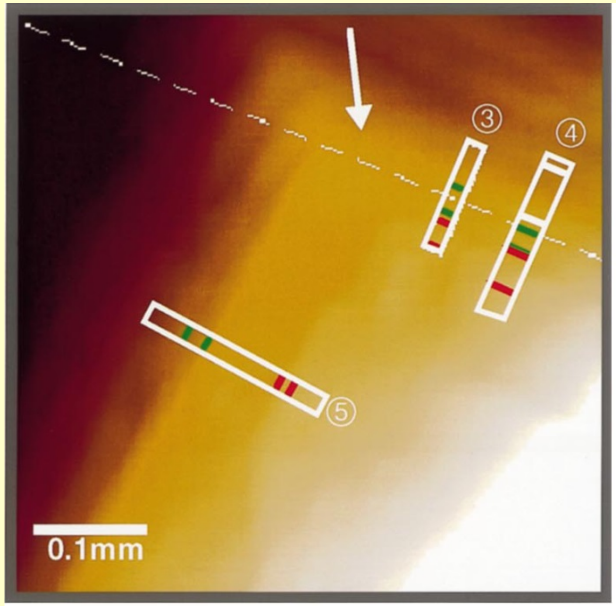


(a) [TO_4] tetrahedra as BBU
(b) four-membered single rings
(c) lB fuenfer chains
(d) cubes [4^6]
(e) truncated octahedra [$4^6 6^8$] (sodalite- or β-cages)
(f) truncated cubeoctahedra [$4^{12} 6^8 8^6$] (α-cavities)

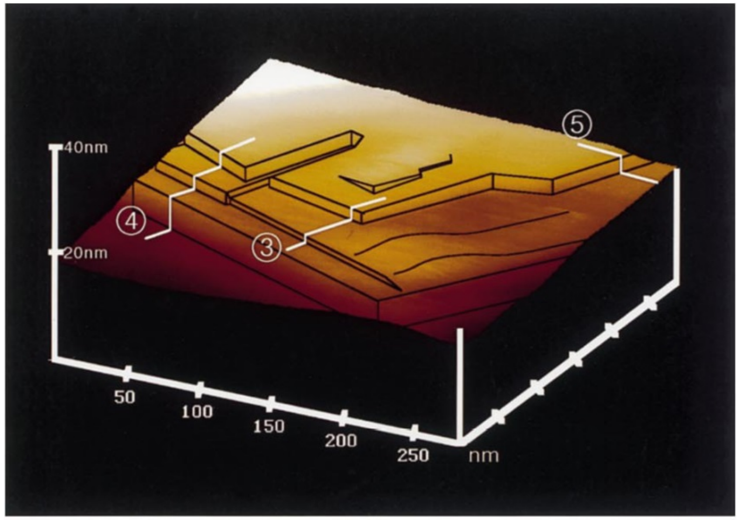
Pores in Zeolite A (LTA)



(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

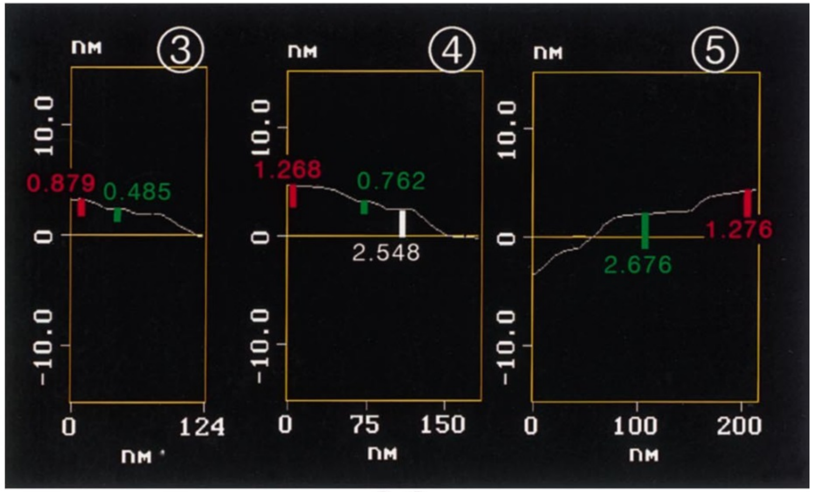


(a)



(b)

D4R

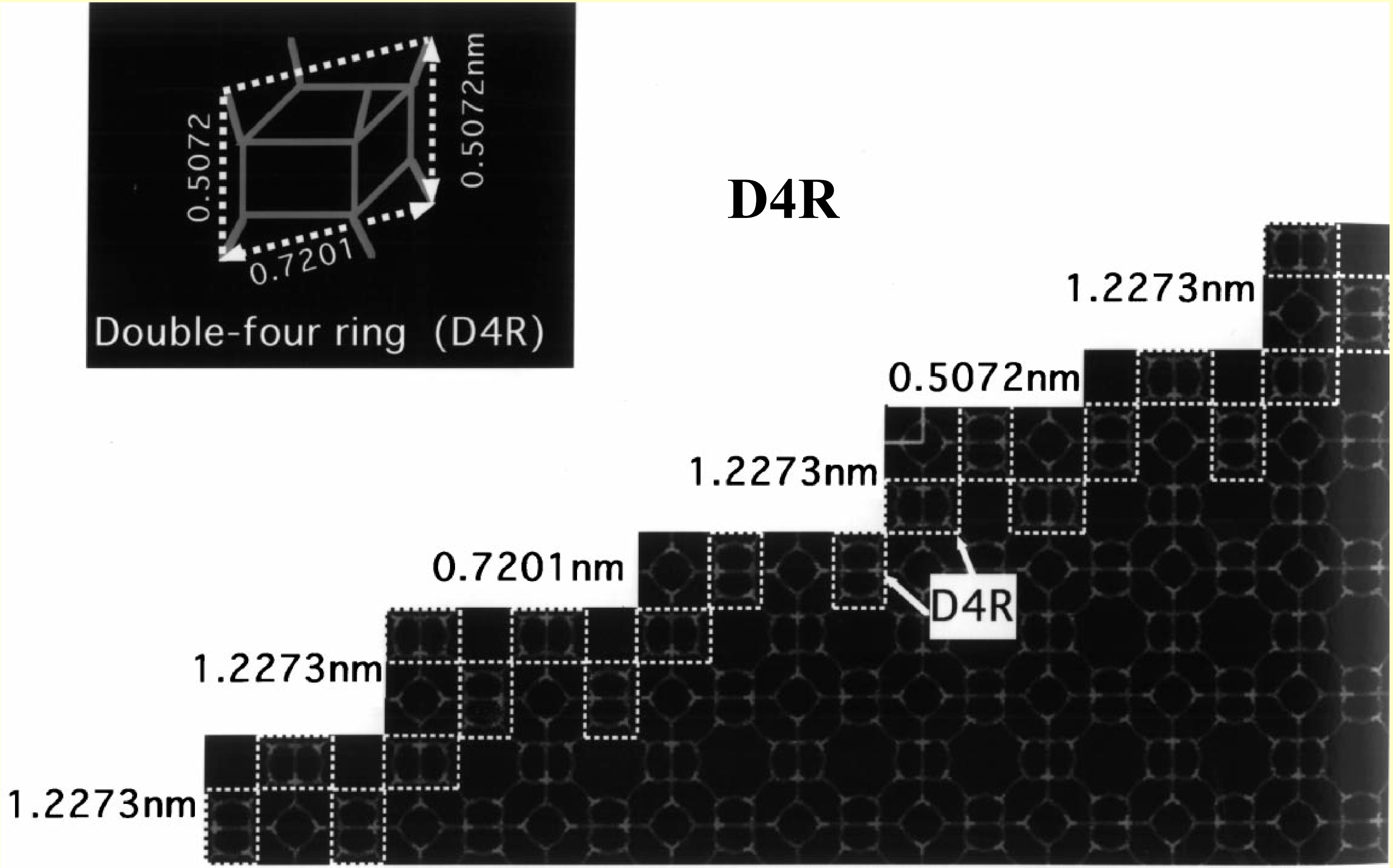


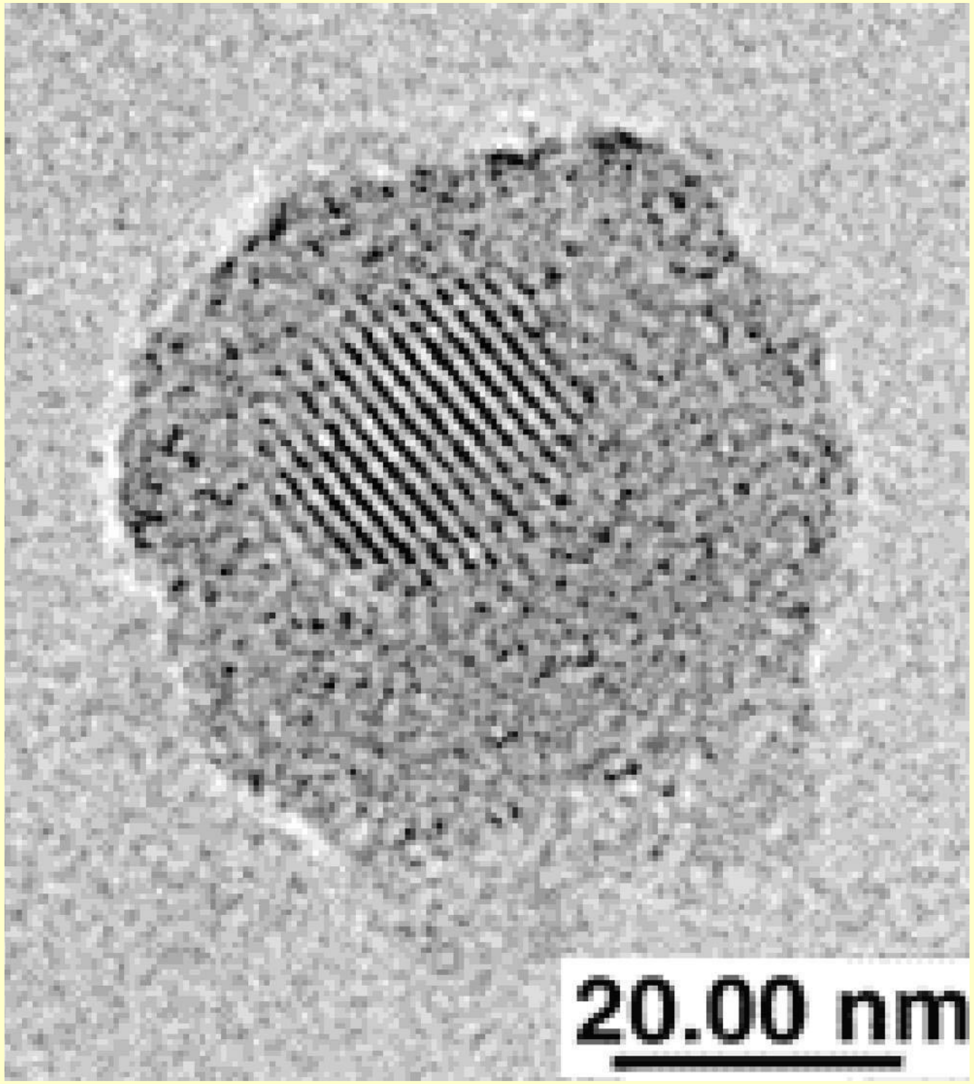
(c)

AFM growth studies of LTA

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

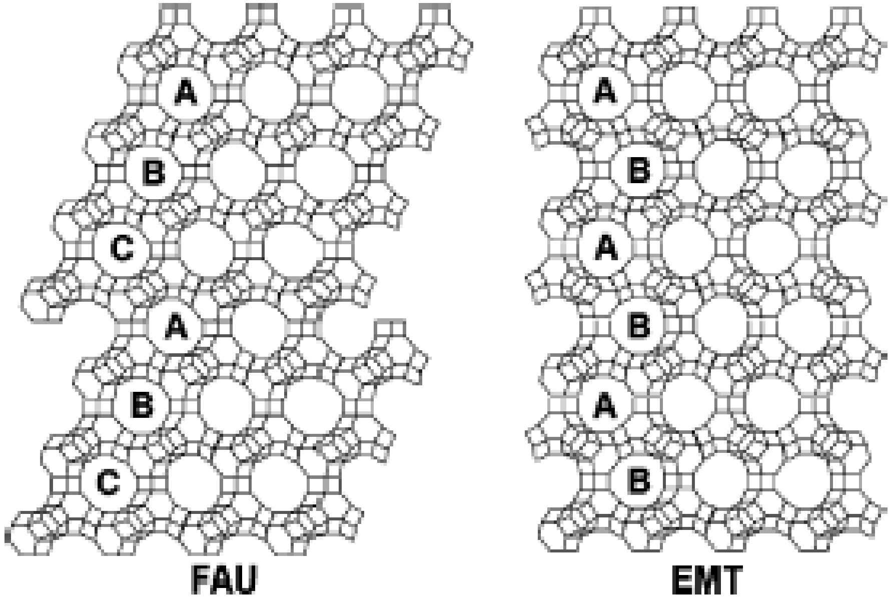
D4R


0.5072
0.5072nm
0.7201
Double-four ring (D4R)
1.2273nm
0.5072nm
1.2273nm
0.7201nm
D4R
1.2273nm
1.2273nm



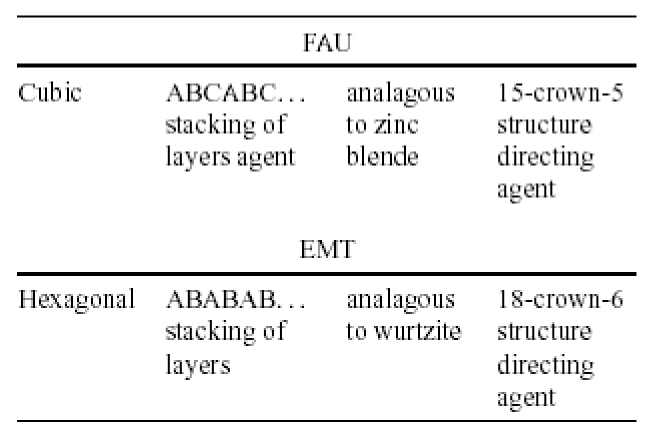
Zeolite A crystal in an amorphous gel particle after a synthesis time of 3 days at room temperature

Zeolite FAU (X and Y) and EMT



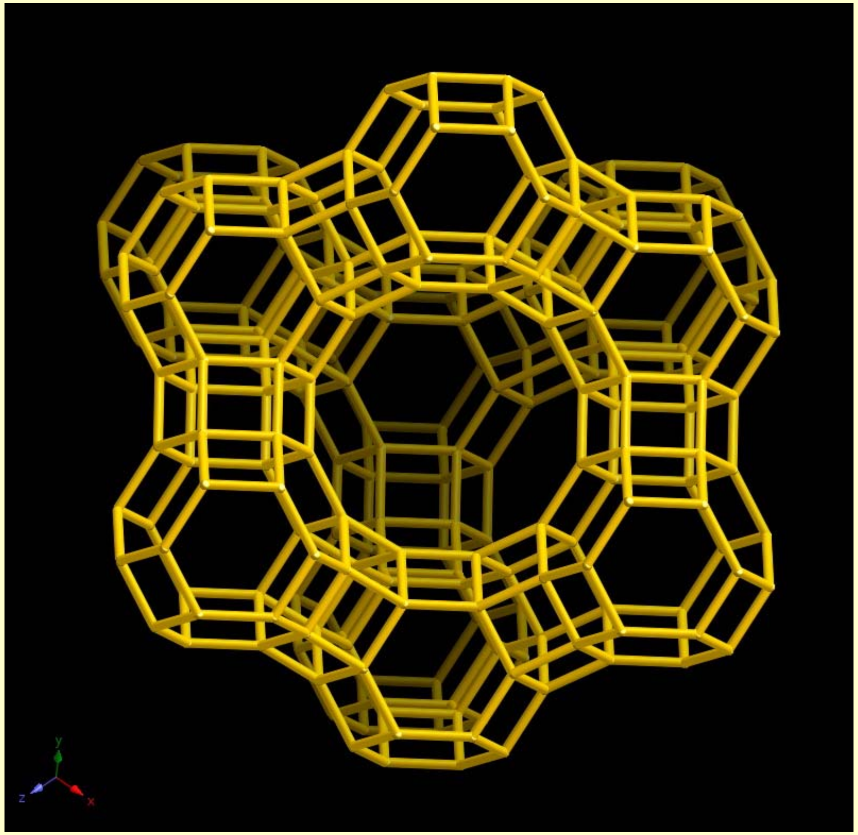
(a) (b)

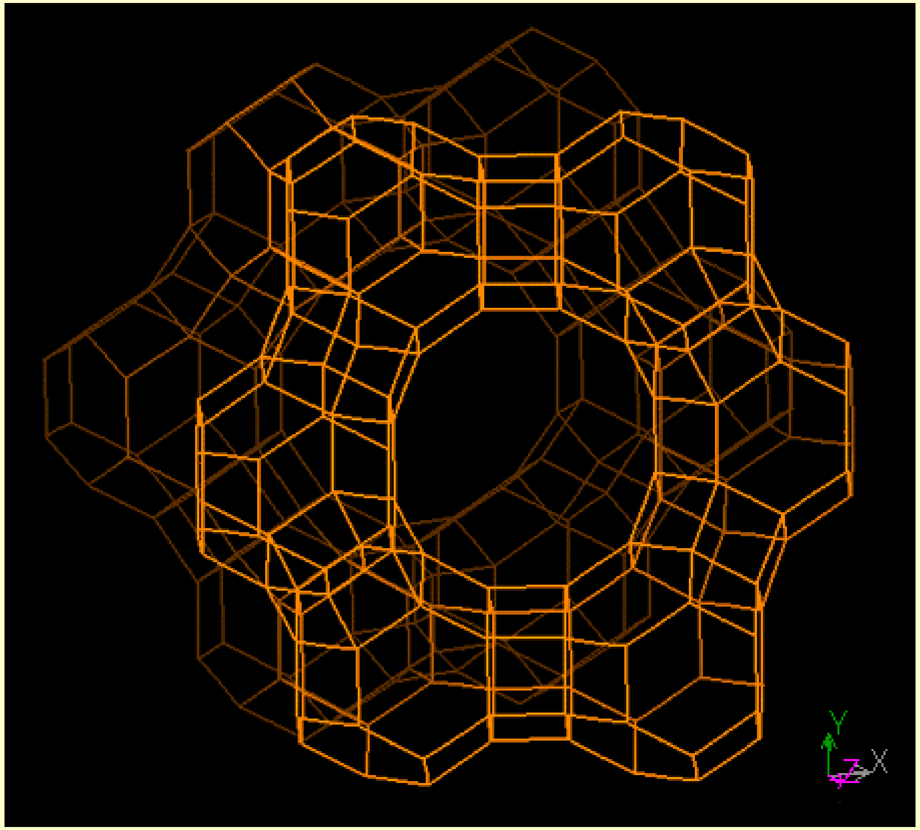
Fig. 1. Structure of zeolite Y: (a) cubic polymorph known as FAU with ABCABC… stacking, (b) hexagonal polymorph known as EMT with ABABAB… stacking.



	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

Zeolite FAU (X and Y) and EMT





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

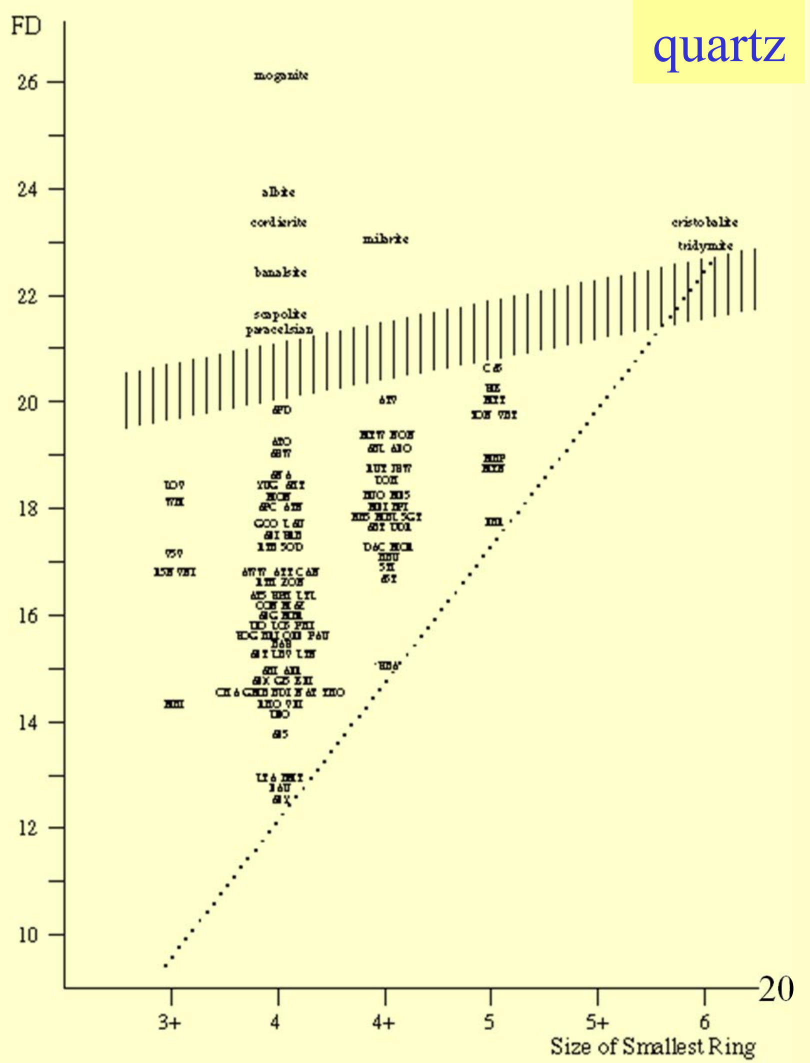
Framework Density

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

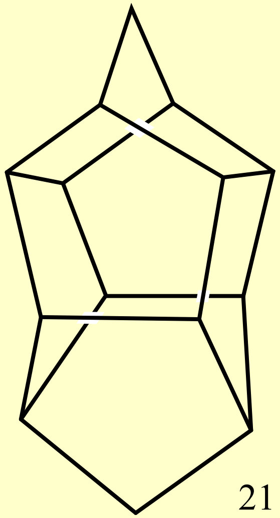
Löwenstein rule:

absence of the Al-O-Al moieties, in aluminosilicates $Si/Al > 1$

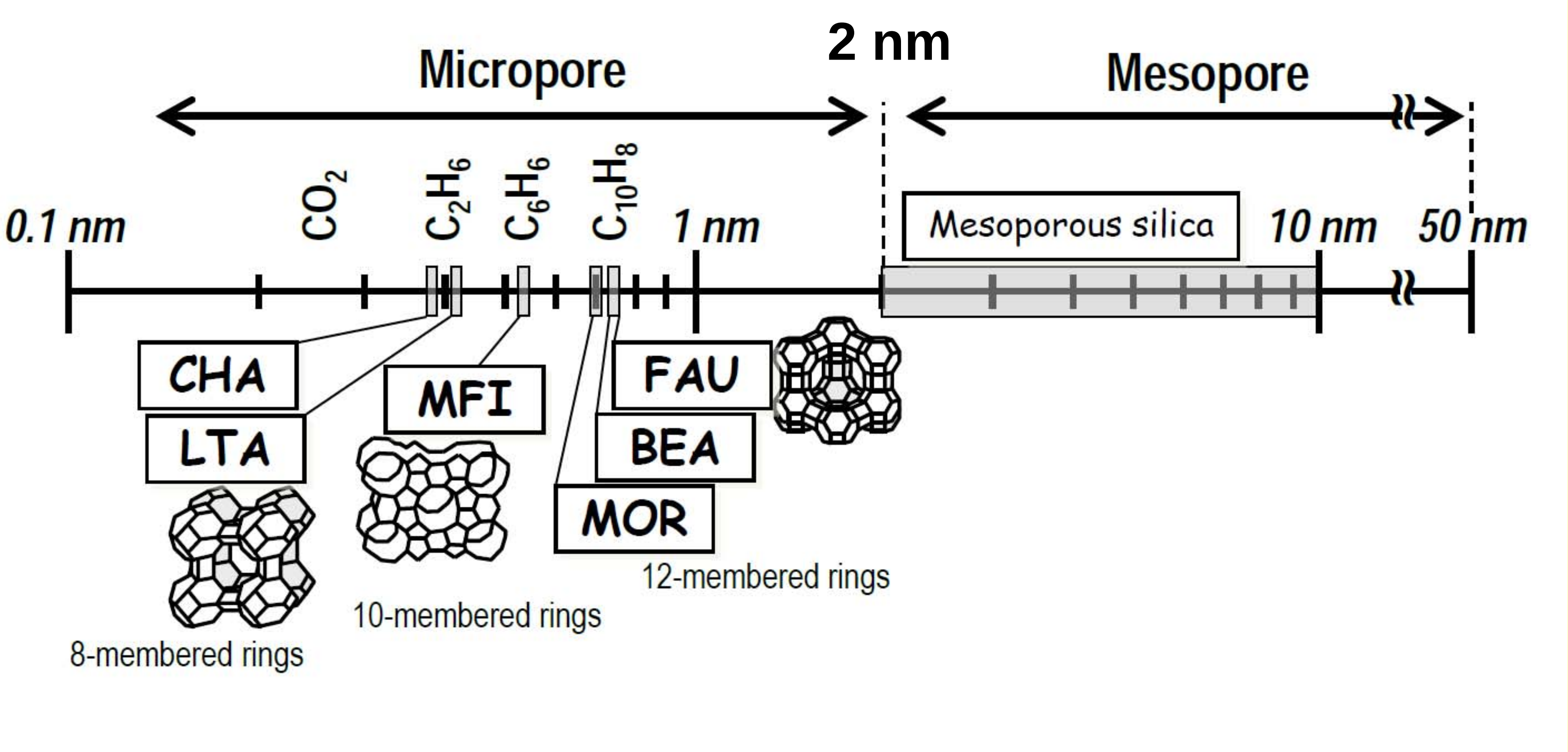
Linde A (LTA)	**$Si/Al = 1$**
ZK-4 (LTA)	**$Si/Al = 2.5$**
ZSM-5	**$Si/Al = 20 - \infty$**
Pure SiO_2	**$Si/Al = \infty$**

Pentasils

ZSM-5



Pores


2 nm
Micropore
Mesopore
CO_2
C_2H_6
C_6H_6
$C_{10}H_8$
0.1 nm
1 nm
Mesoporous silica
10 nm
50 nm
CHA
LTA
MFI
FAU
BEA
MOR
12-membered rings
10-membered rings
8-membered rings

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 → $Na_a(AlO_2)_b(SiO_2)_c.NaOH.H_2O(gel)$ → 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)

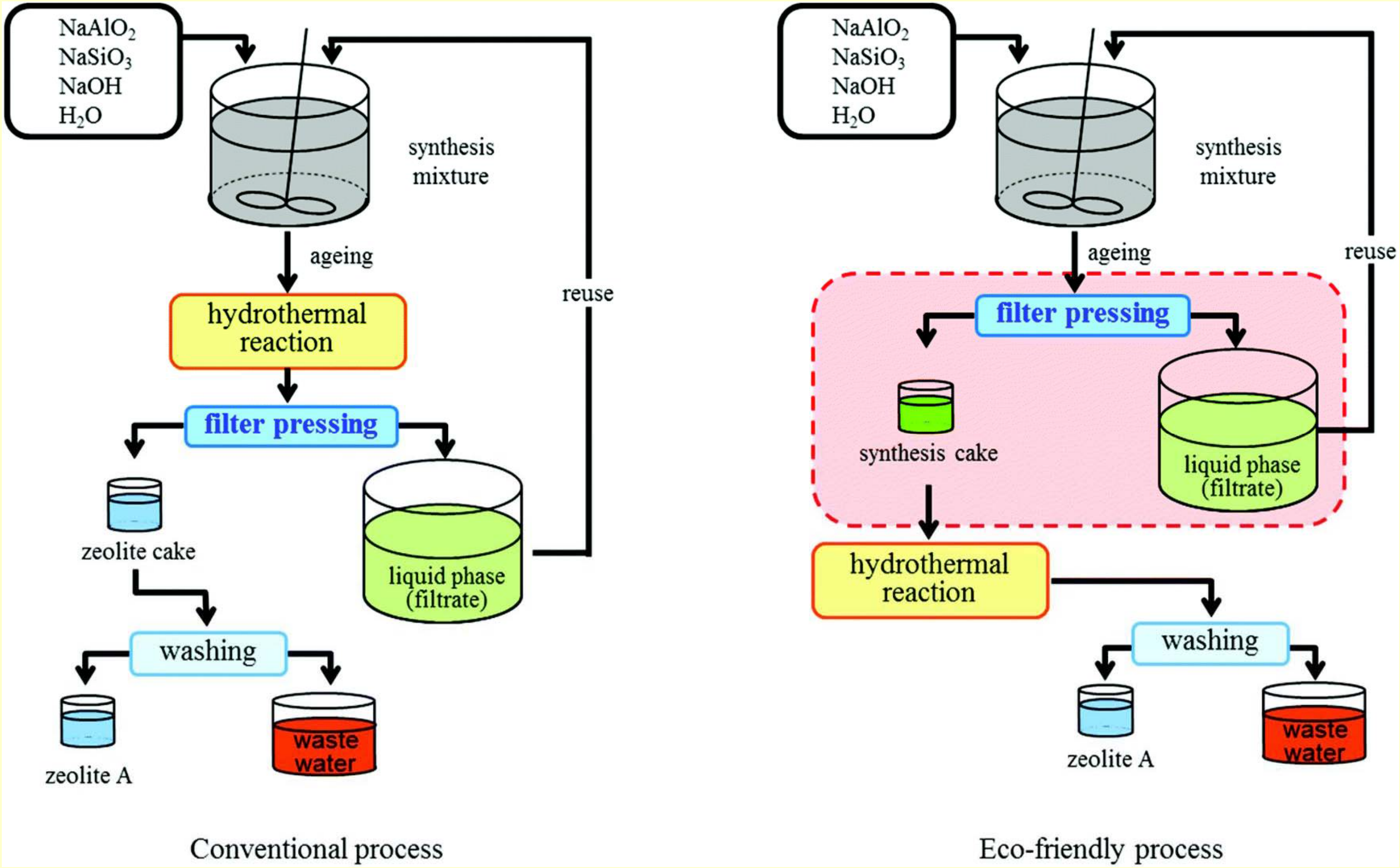
Zeolite Synthesis

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 !

Zeolite Synthesis



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

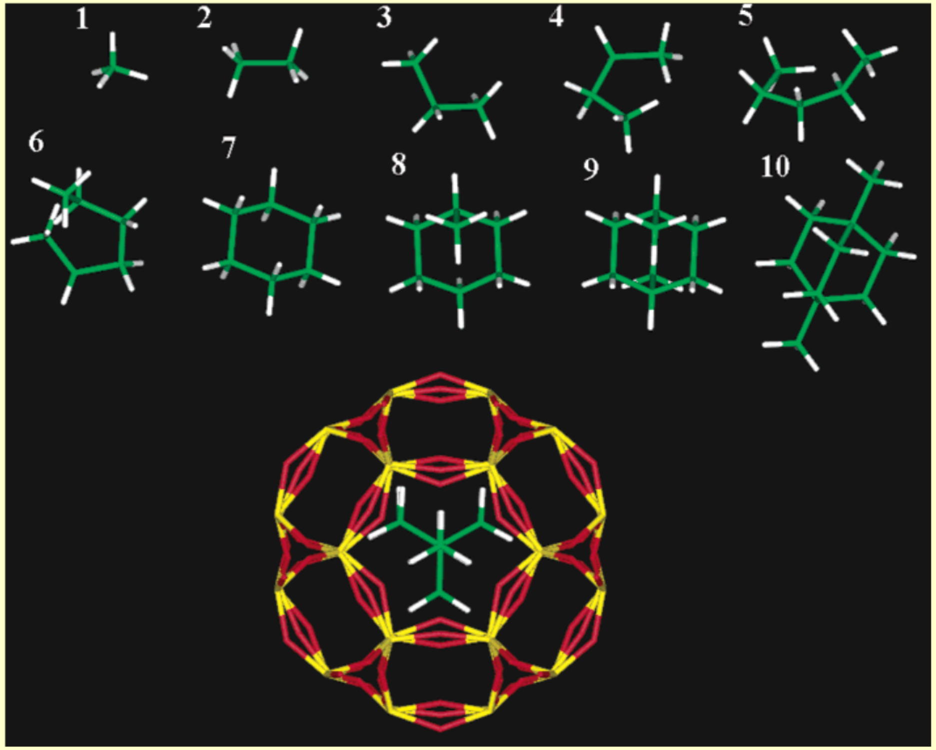
A curiosity: aluminophosphate VPI-5 does not require any guest for its formation!

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.

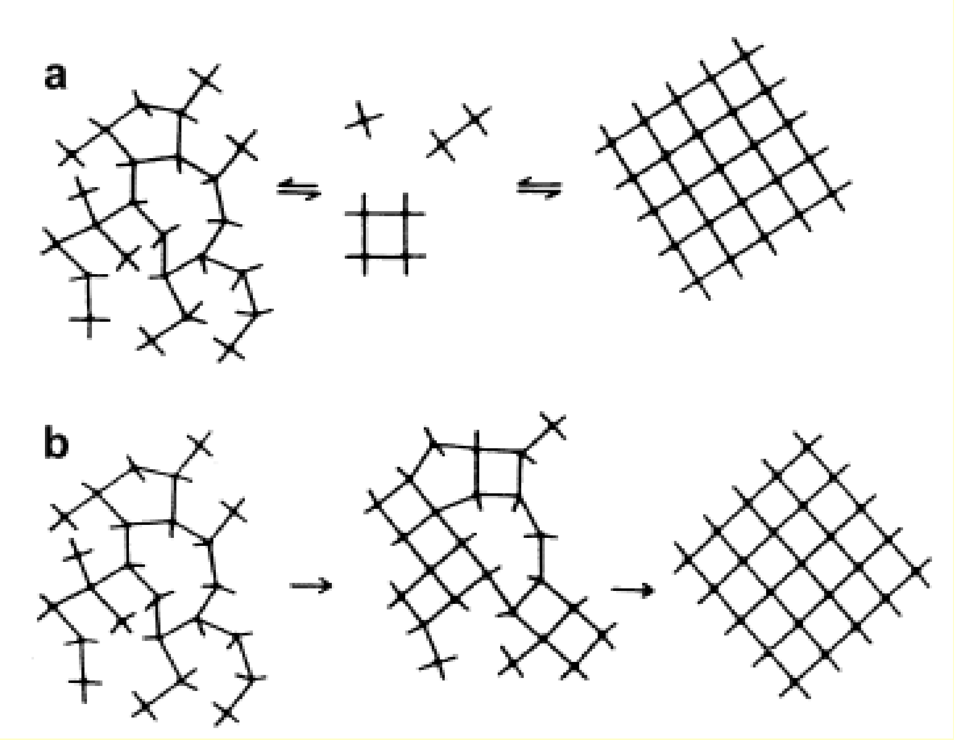
Existence of primary and secondary units in a synthesis mixture

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



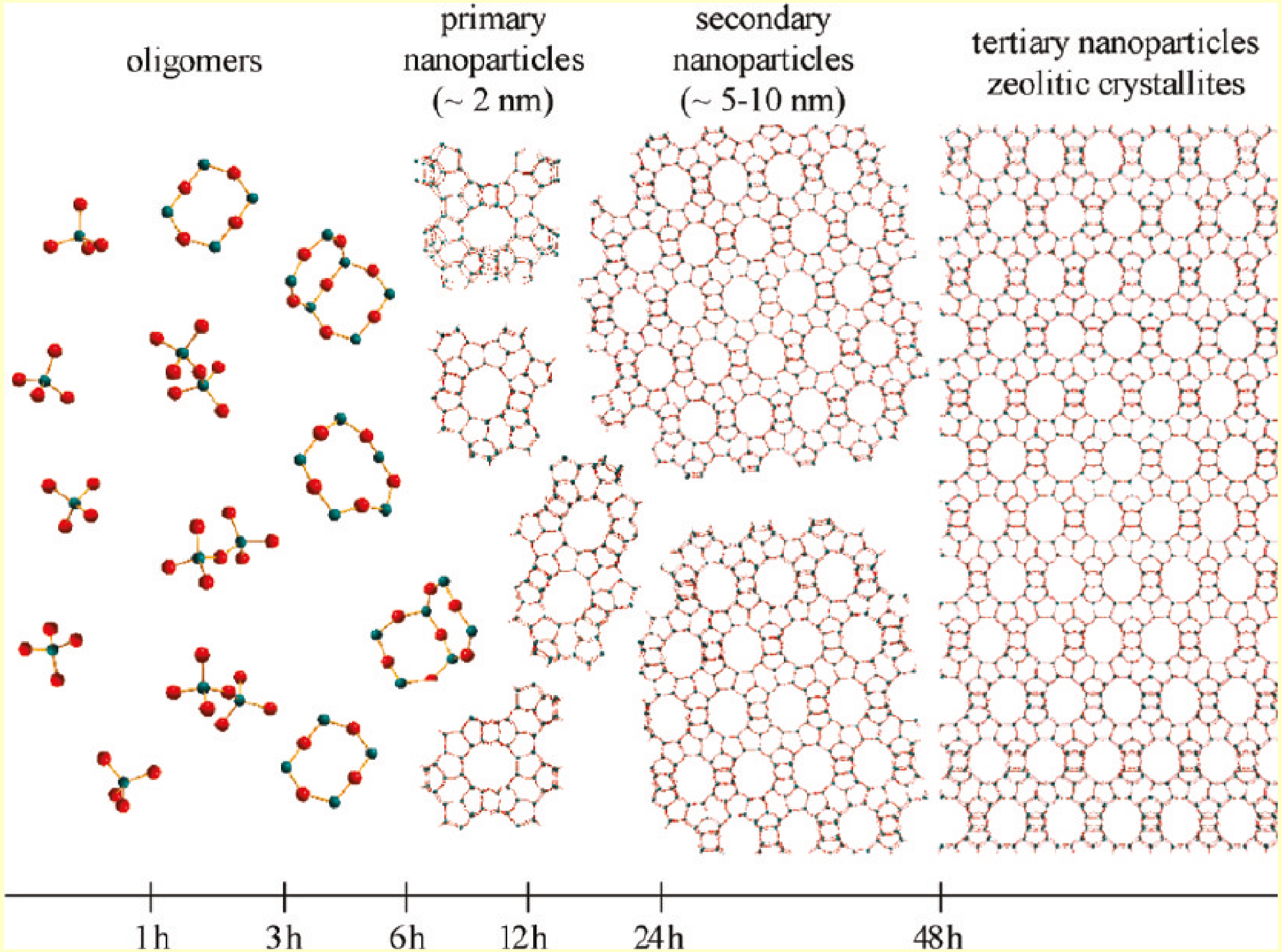
Zeolite Synthesis Mechanisms

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

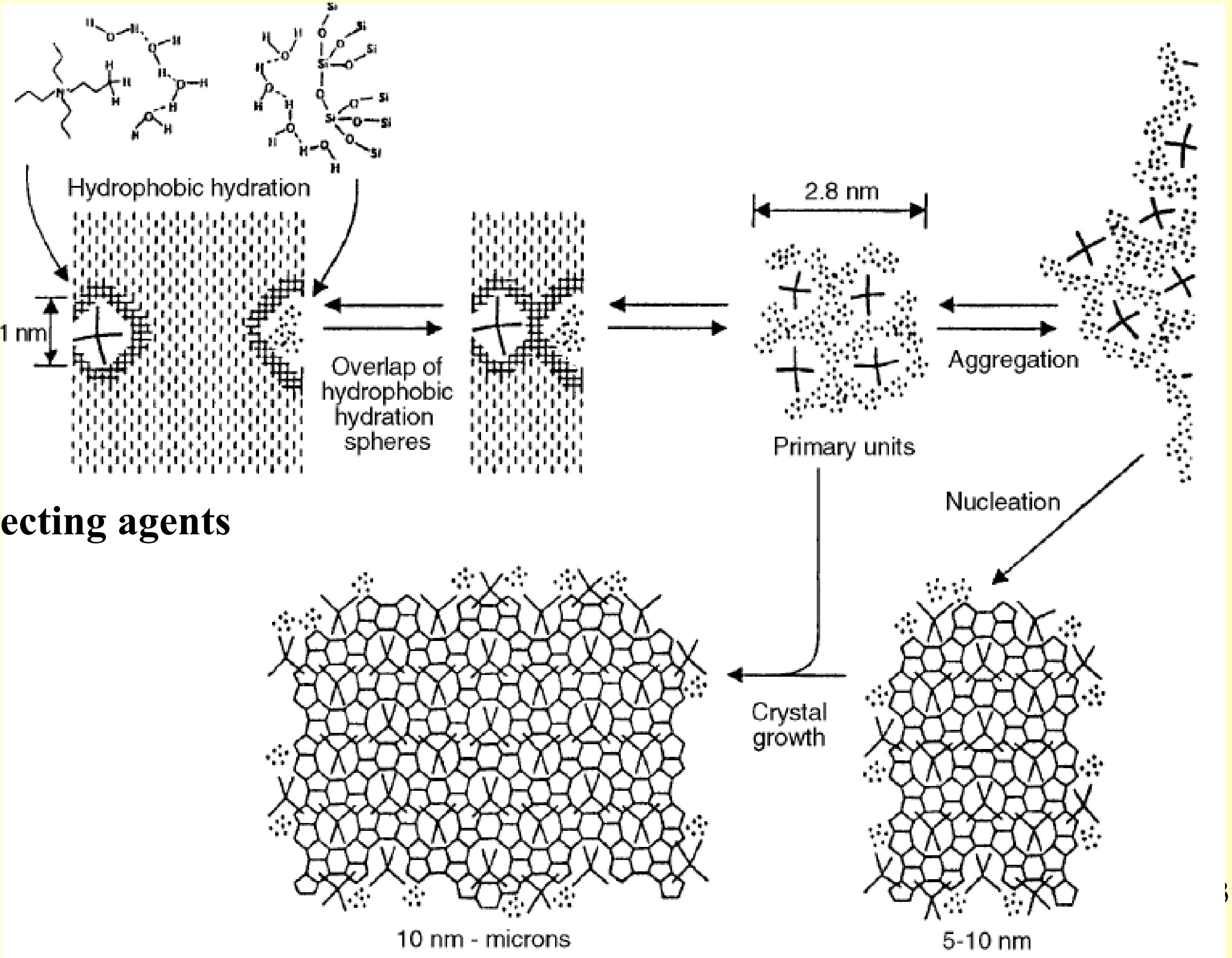


(b) "in situ" rearrangement of the gel

Zeolite Synthesis Mechanisms

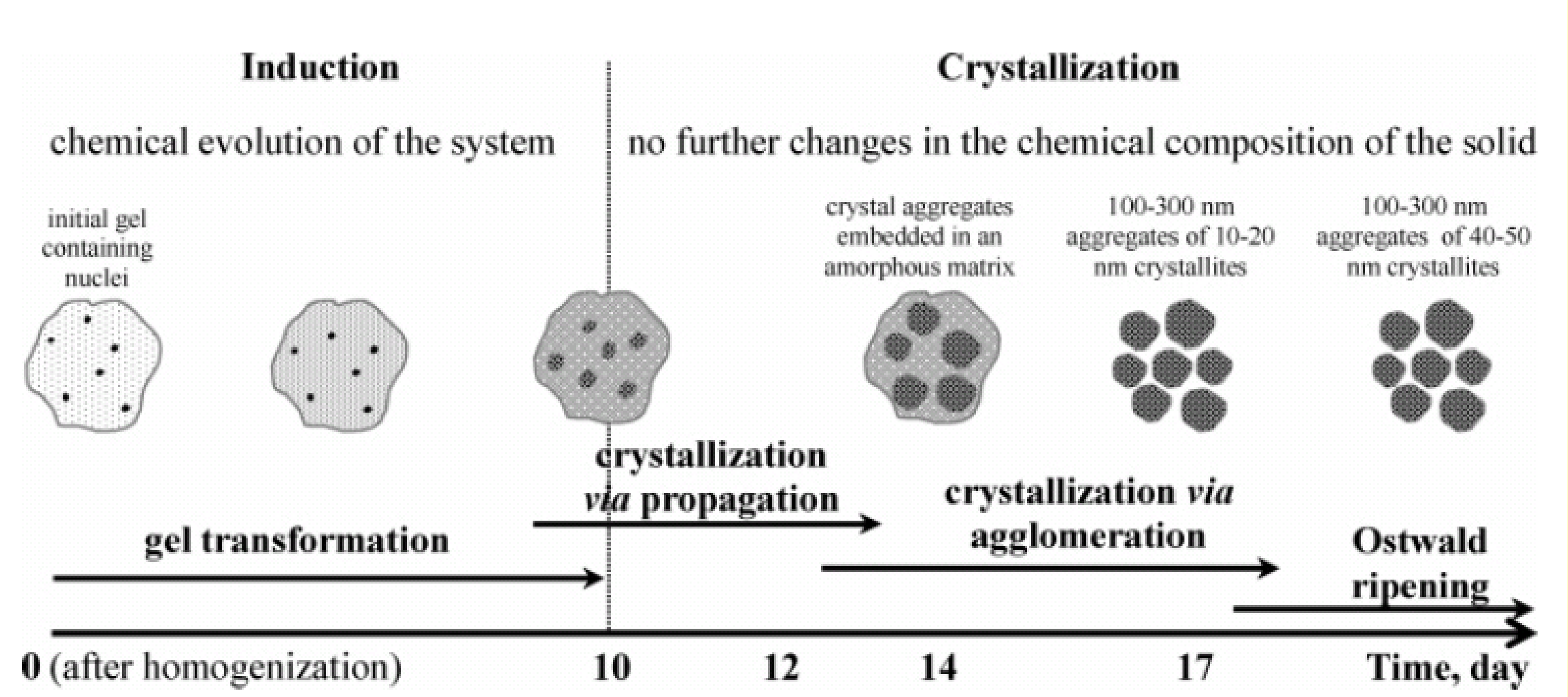


Zeolite Synthesis Mechanisms



Structure directing agents

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

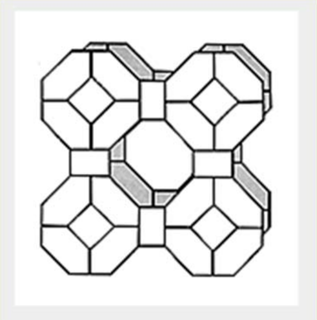
Lőwenstein rule: never Al-O-Al

Dempsey rule: Al-O-Si-O-Si-O-Al

is more stable than

Al-O-Si-O-Al

NNN-principle



Synthetic Zeolite Applications

Production 1.6 million tons p.a. (about half that of natural zeolites)

Detergent - water softening by ion exchange (82%) - zeolites A and X

Catalysis (8%) - zeolite Y (faujasite, 96 wt.%), mordenite, ZSM-5, zeolite Beta

Desiccants/absorption (5%) - zeolites A, X, Y and mordenite

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

Mineral zeolites - odor control

Natural Mineral Zeolite Applications

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

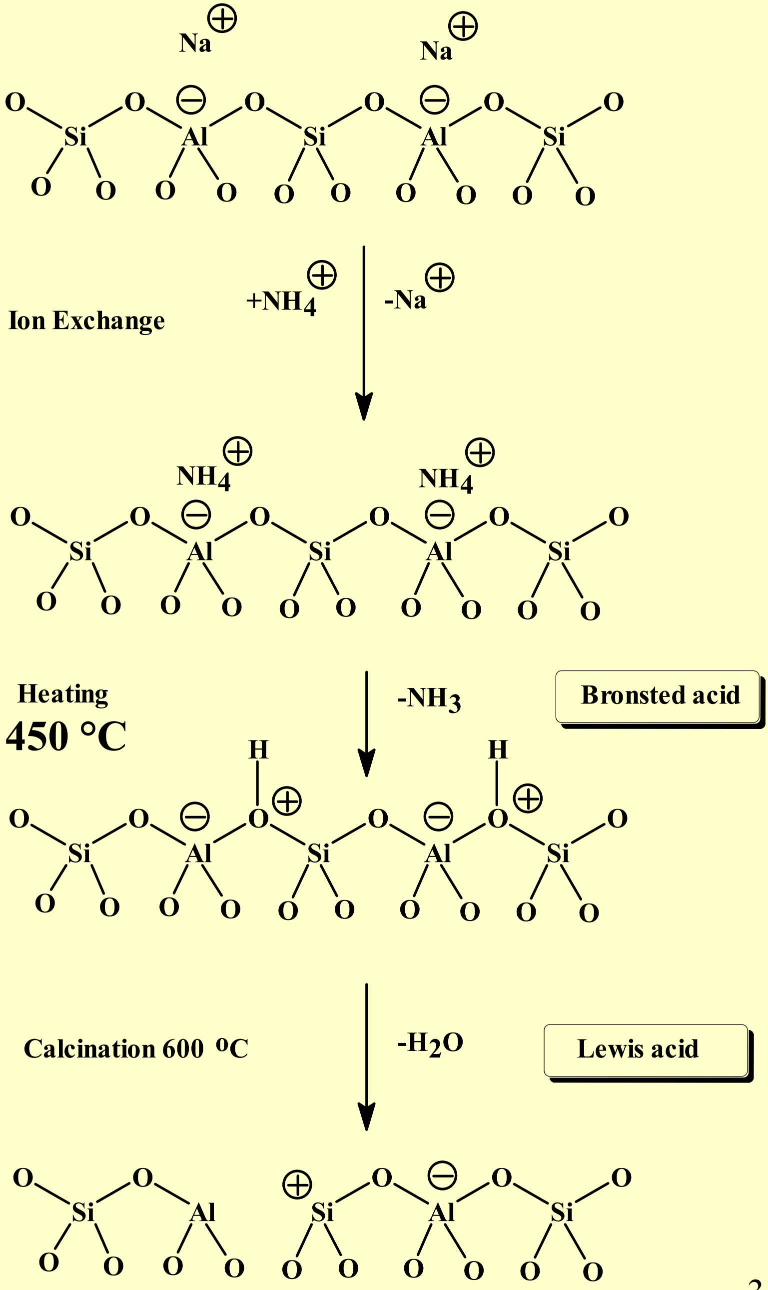
Brønsted Acidity

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

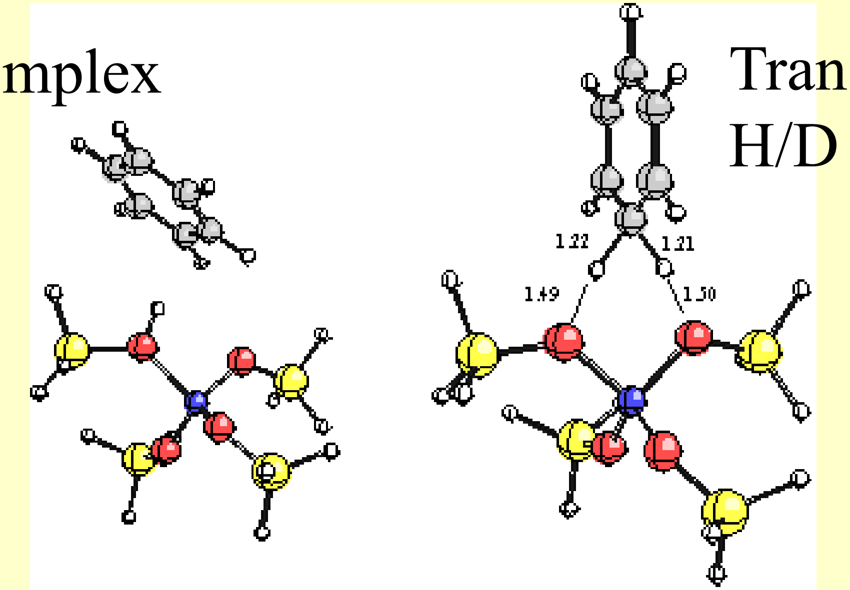


Strong Brønsted Acidity

Protonation of benzene

π-complex

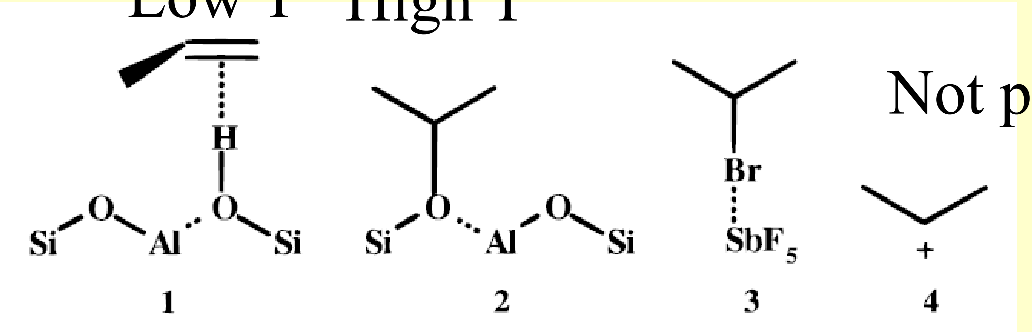
Transition state for H/D exchange



Low T

High T

Not present in zeolites



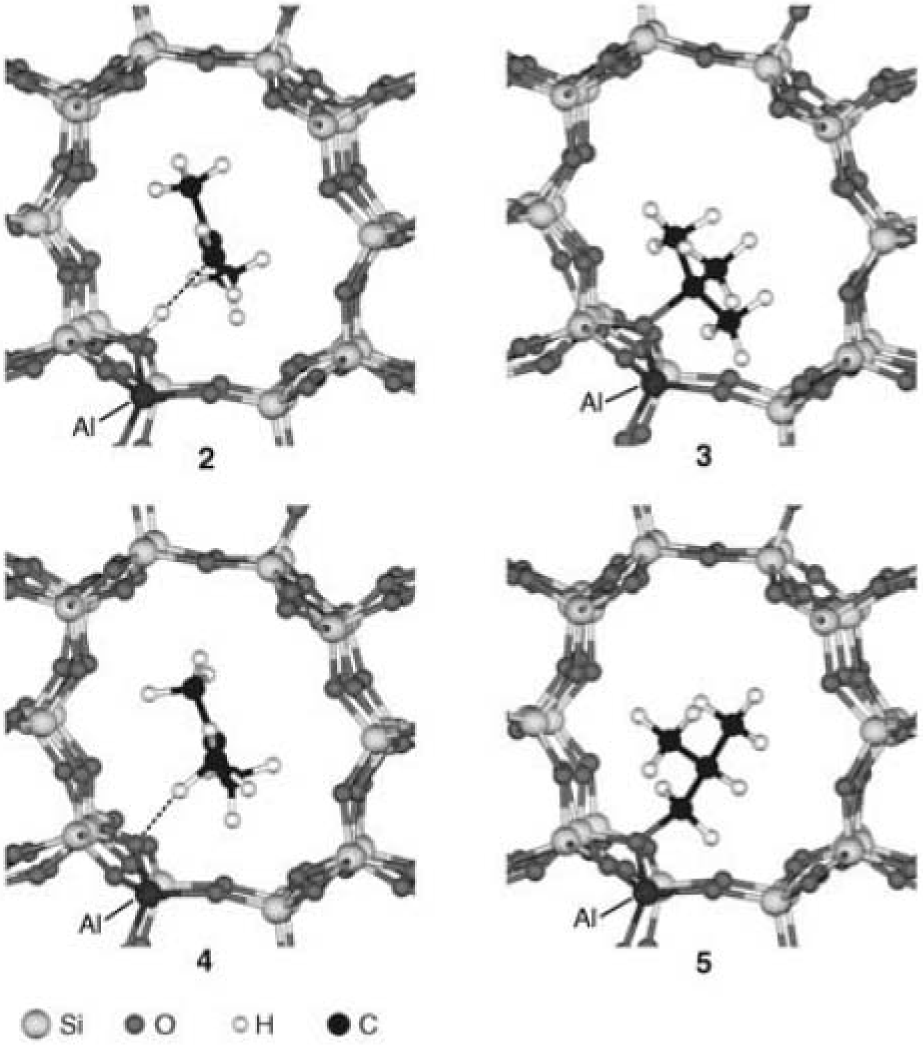
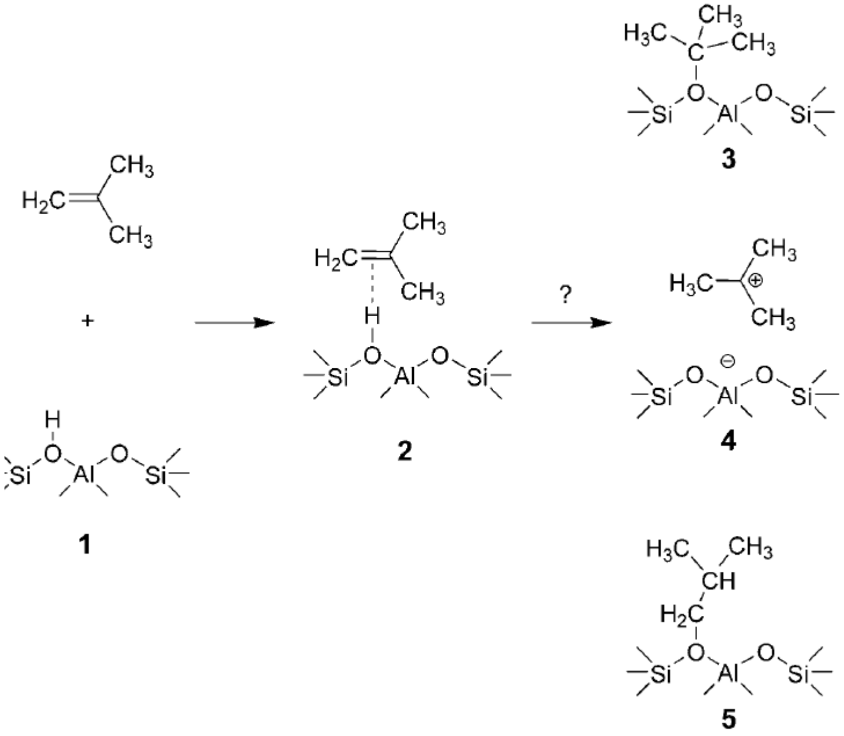


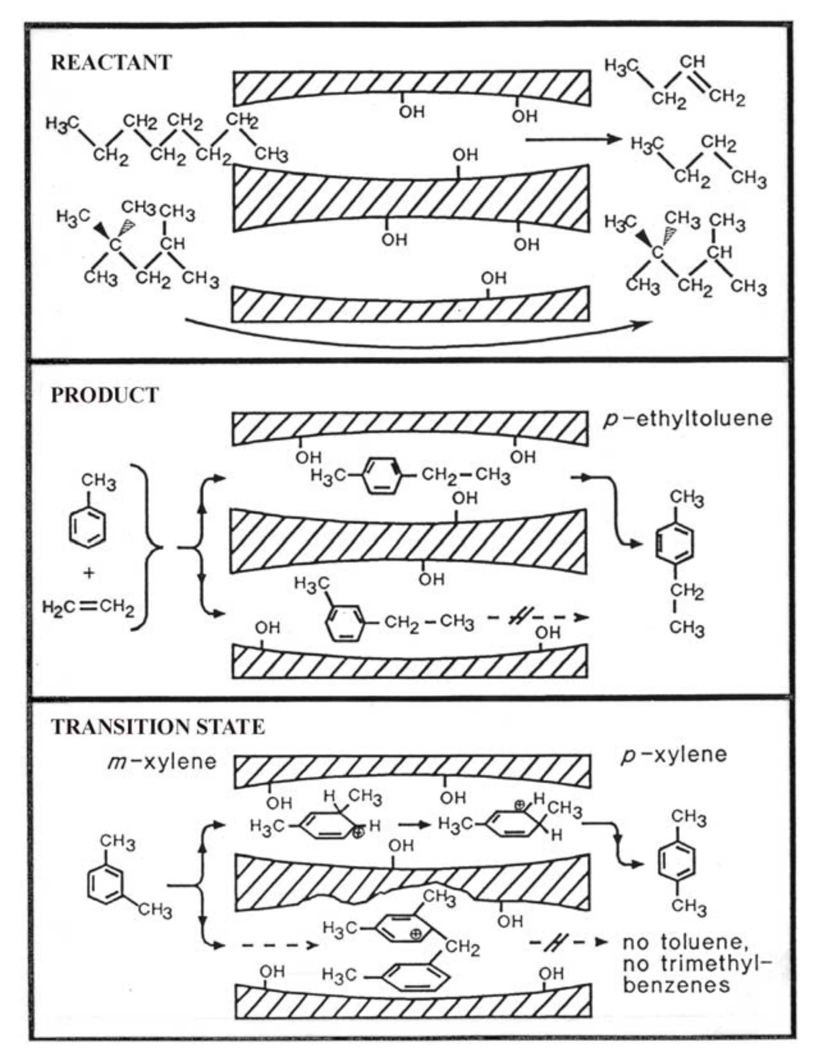
Figure 1. Portions of the structures calculated for the π complex of isobutene in ferrierite (**2**), for the *tert*-butyl cation in ferrierite (**4**), and for the *tert*-butoxide (**3**) and isobutoxide (**5**) of ferrierite.



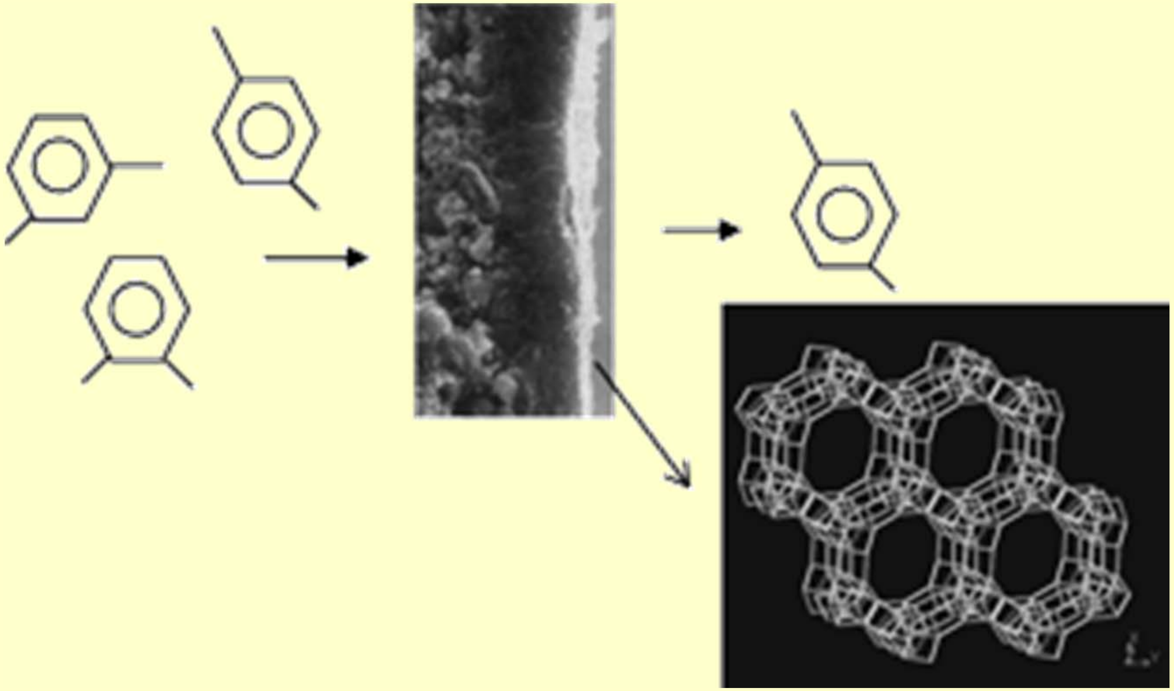
Size-Shape Selectivity

Size-shape selective catalysis, separations, sensing

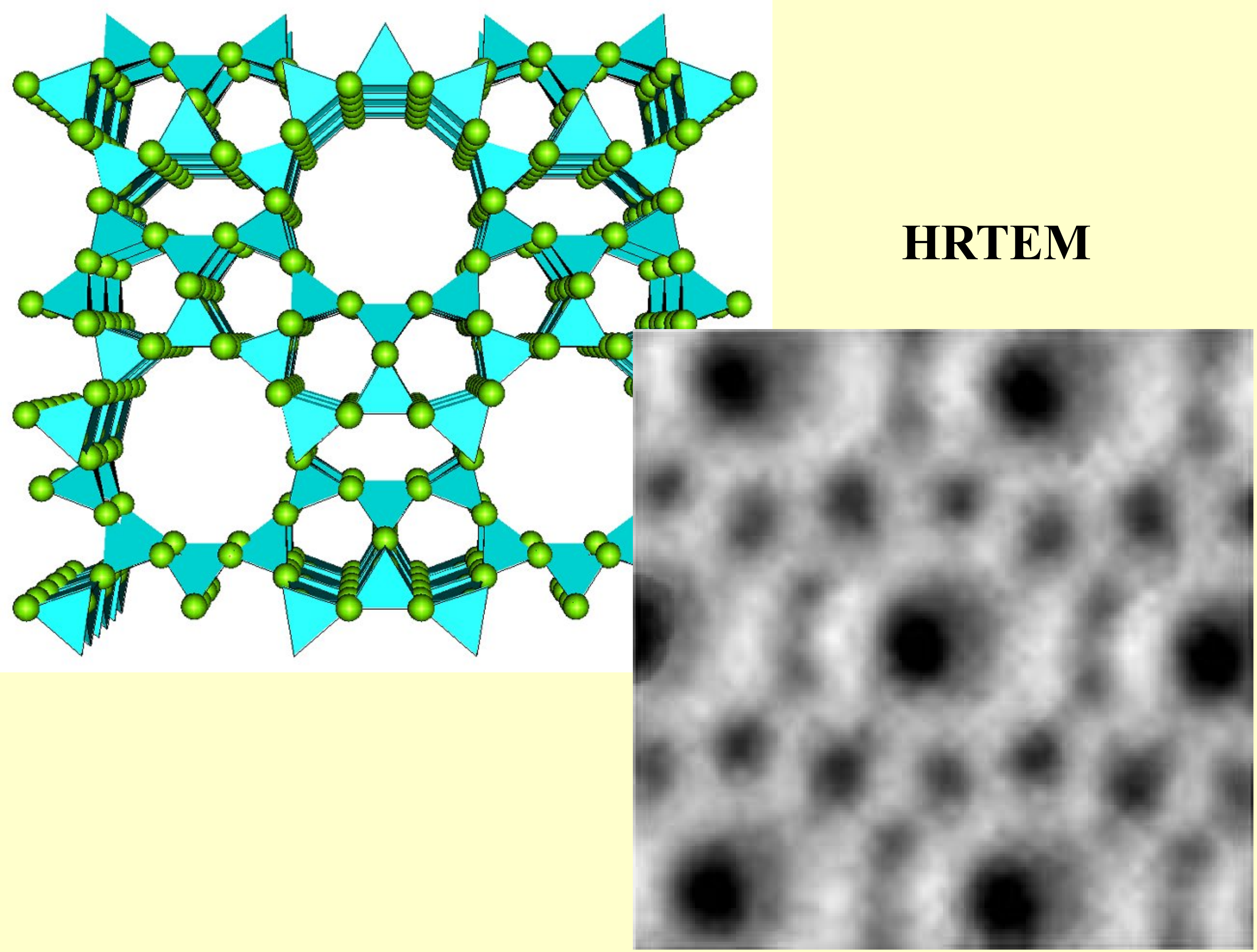
Selectivity at:
- Reactants
- Products
- Transition state



Separation of xylene isomers by pervaporation through a MFI membrane



HRTEM



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

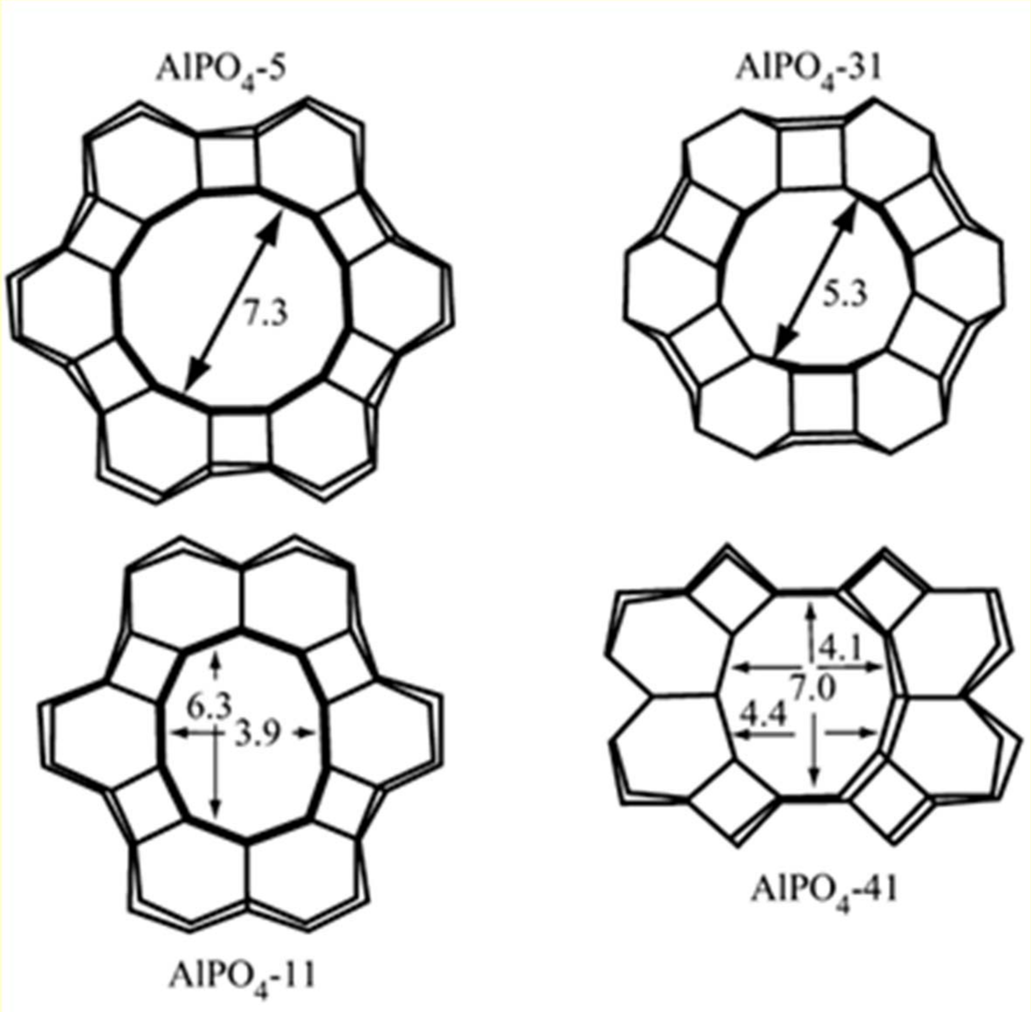
Some $AlPO_4$ structures are analogous to zeolites while other are novel and unique to this class of molecular sieves.

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*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

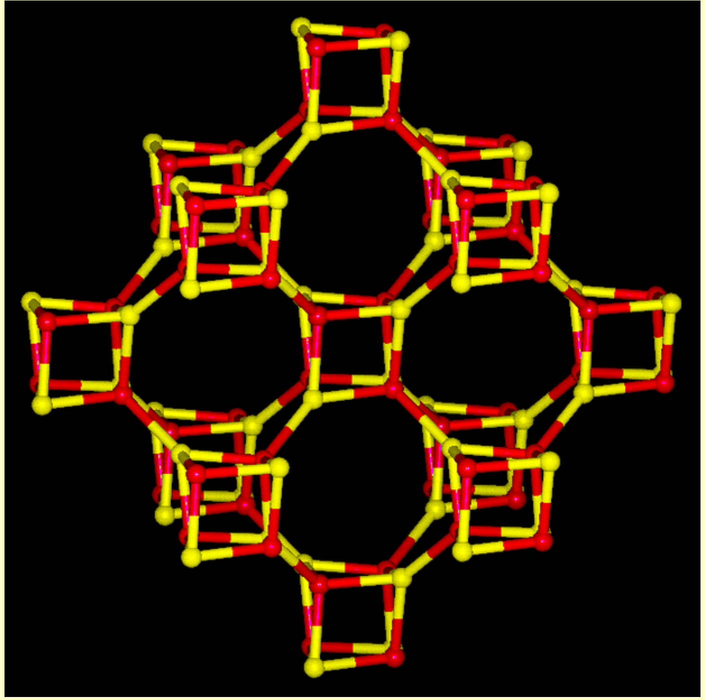
Cobalto-Aluminophosphate

ACP-1 (Co/Al 8.0)

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

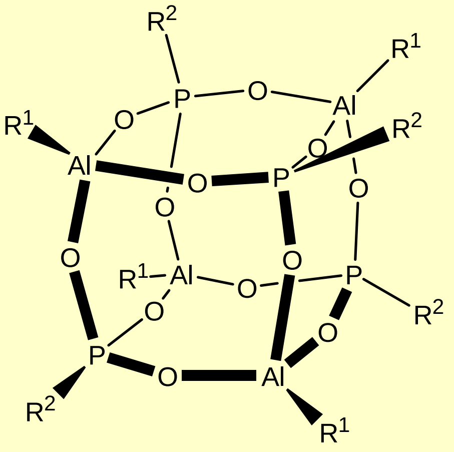
Ethylenediamine molecules are located inside 8-ring channels

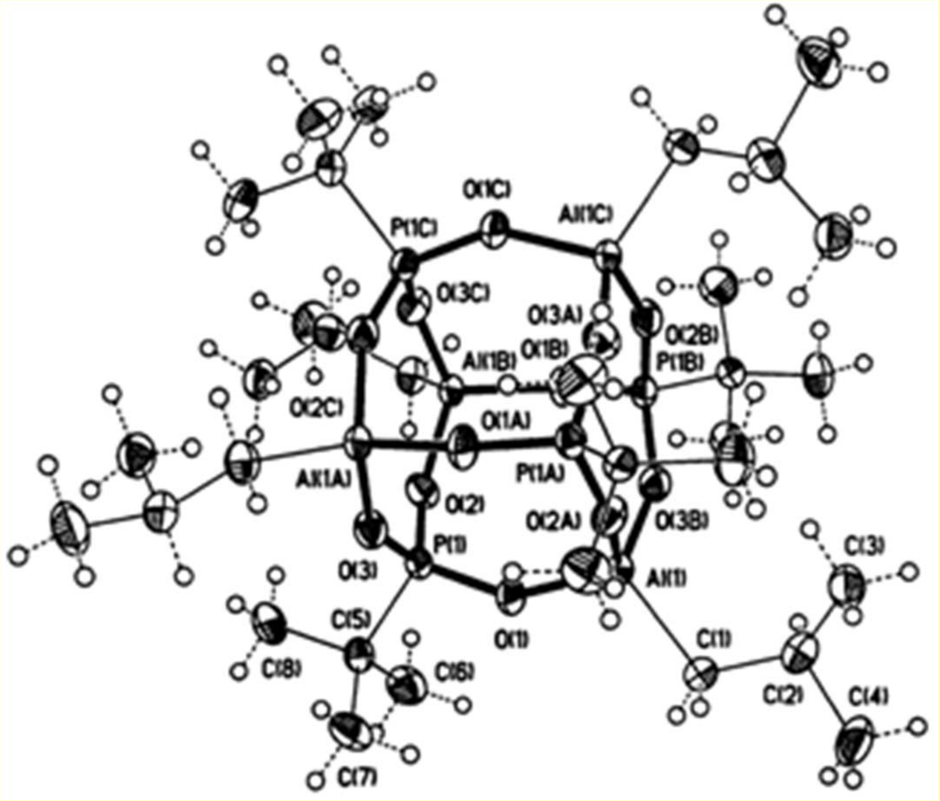
At the centre of each D4R, there is a water molecule, 2.31 Å away from four metal sites



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

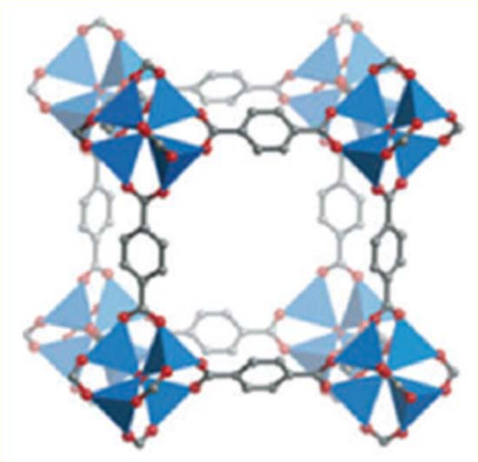
Synthesis of Double 4-ring Units (D4R)





Metallo-Organic Framework (MOF) Structures

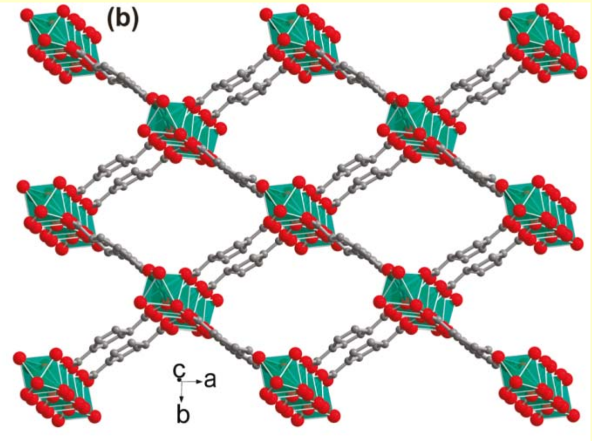
4000 structures known (2008), 1000 new per year



Porous coordination polymers (PCP)

Metal centers

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



Polytopic Ligands

- Organic spacers
- Flexible – rigid
- Variable length

Reticular Chemistry

A building-block approach to the synthesis of nanostructured materials

Materials formed by a bottom-up self-assembly of building blocks (reticuli) with predetermined symmetry

Targeted, predictable, and straightforward design and synthesis

Chemistry of the self-assembly and the design should not interact

Building blocks:

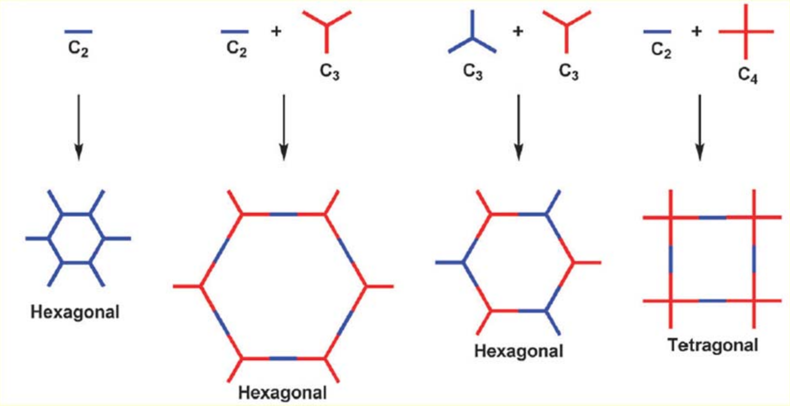
Discrete symmetry: C_∞, C_2, C_3, C_4, T_d, …

Rigid, inert

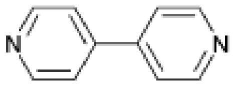
Functional groups for linking

Suitable linking reaction

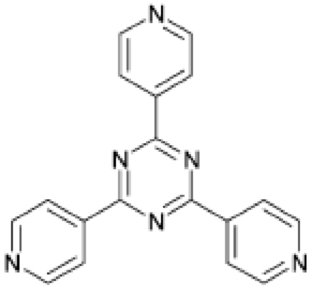
Discrete bonding direction



Polytopic Organic Linkers



1



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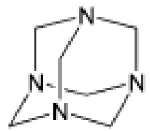

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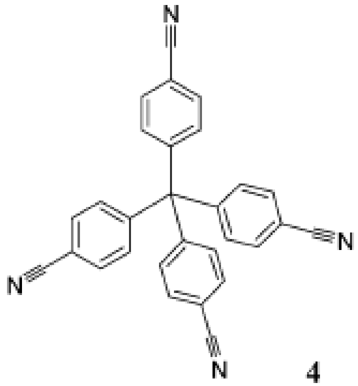
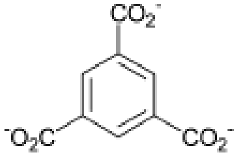


4

5



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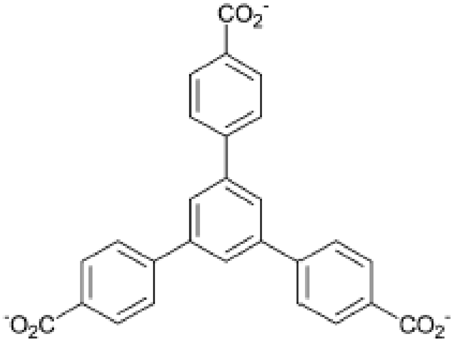
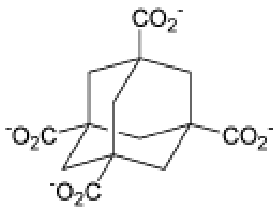


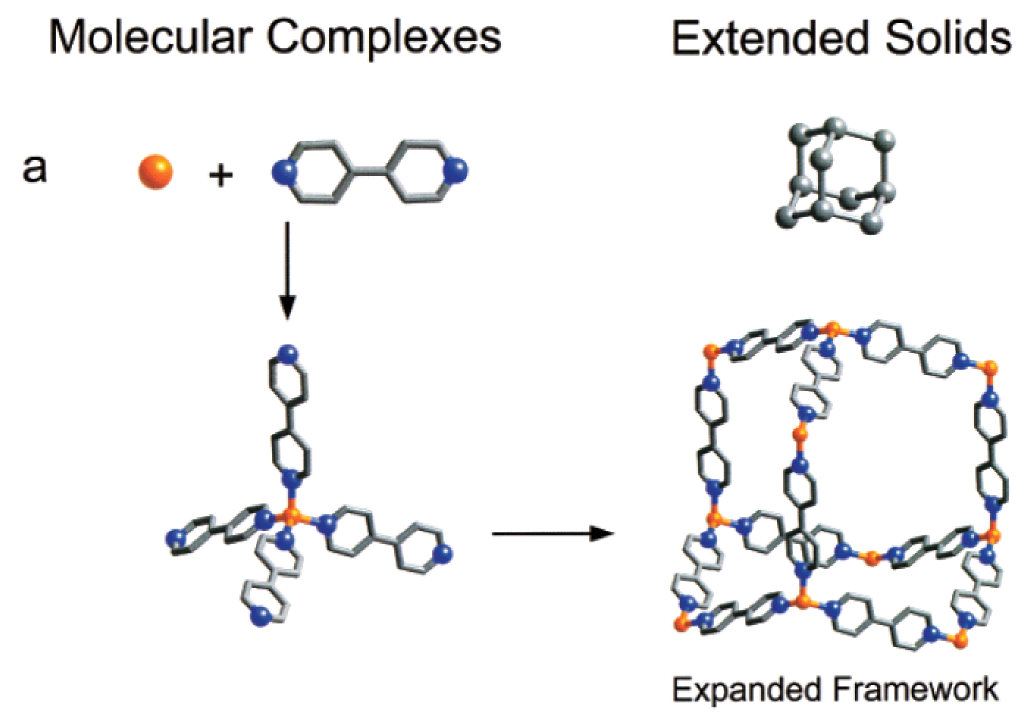


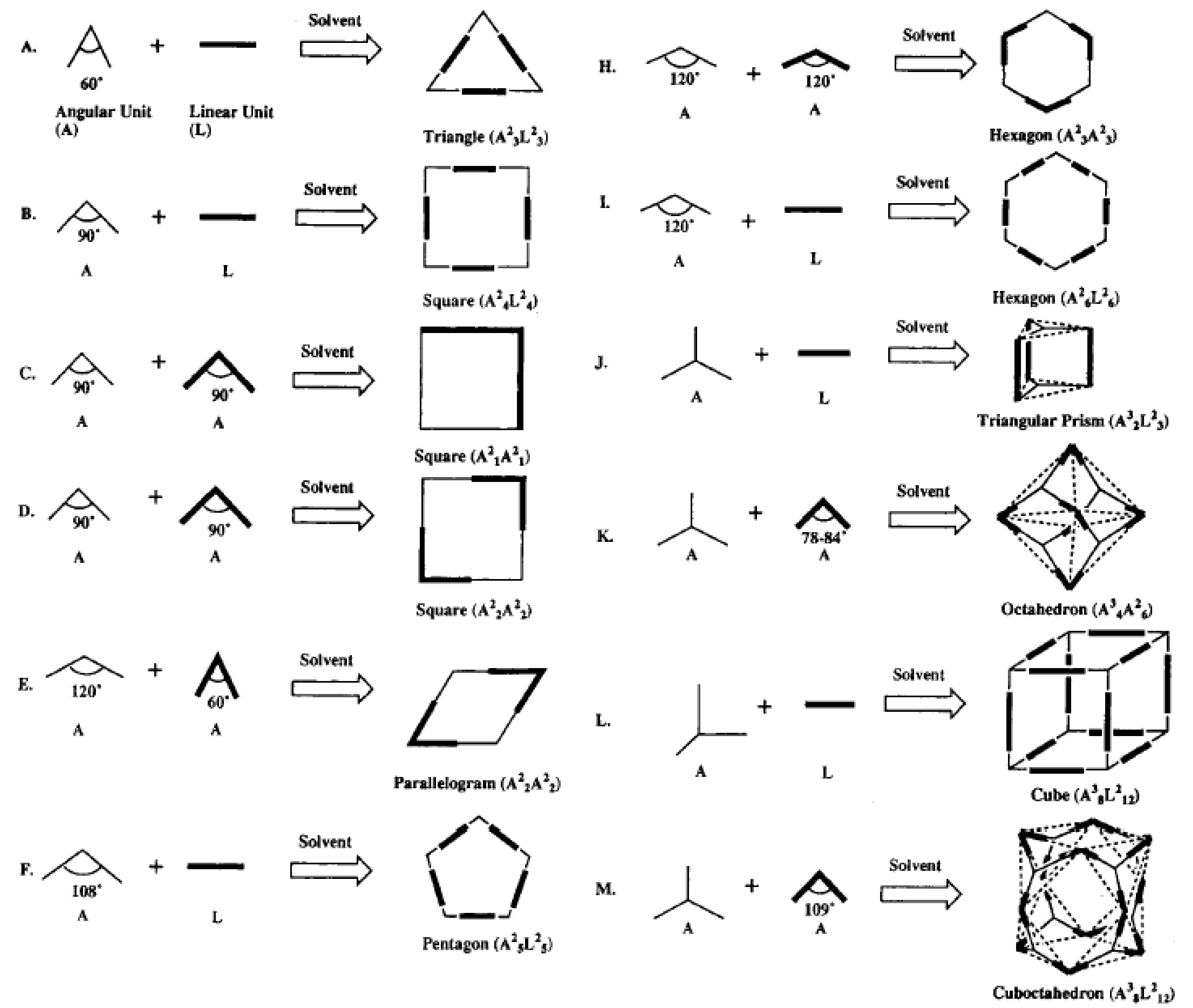
8

Polytopic N-bound Organic Linkers

Cationic framework structures

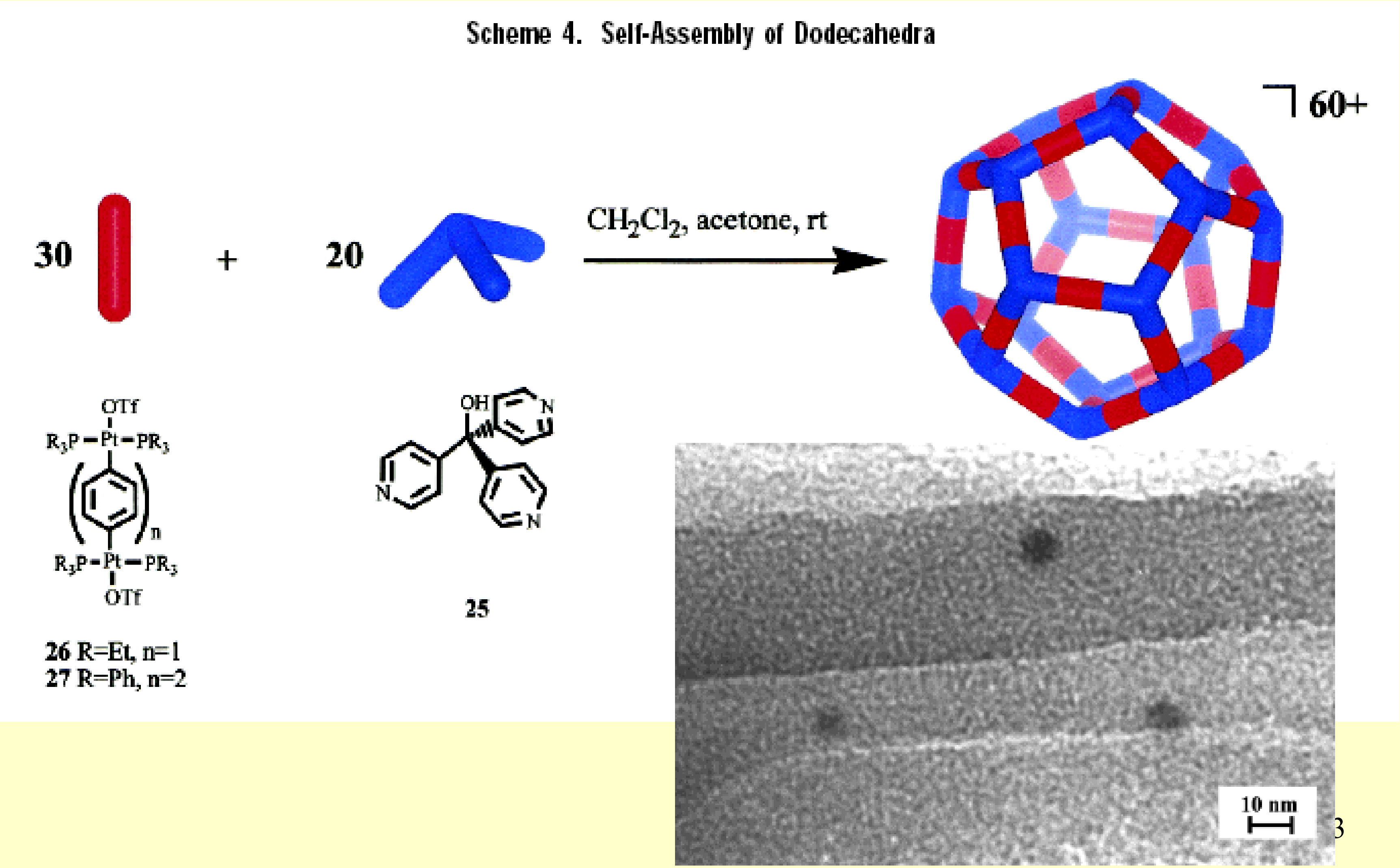
Evacuation of guests within the pores usually results in collapse of the host framework




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

Metallo-Organic Framework Structures

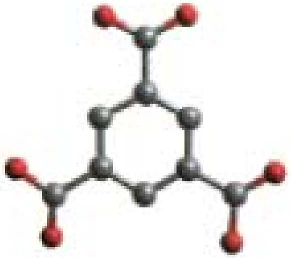
Scheme 4. Self-Assembly of Dodecahedra



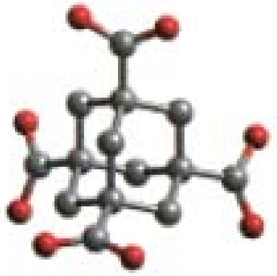
Polytopic carboxylate linkers

1,4-benzenedicarboxylate
(BDC)

1,4-azodibenzoate
(ADB)



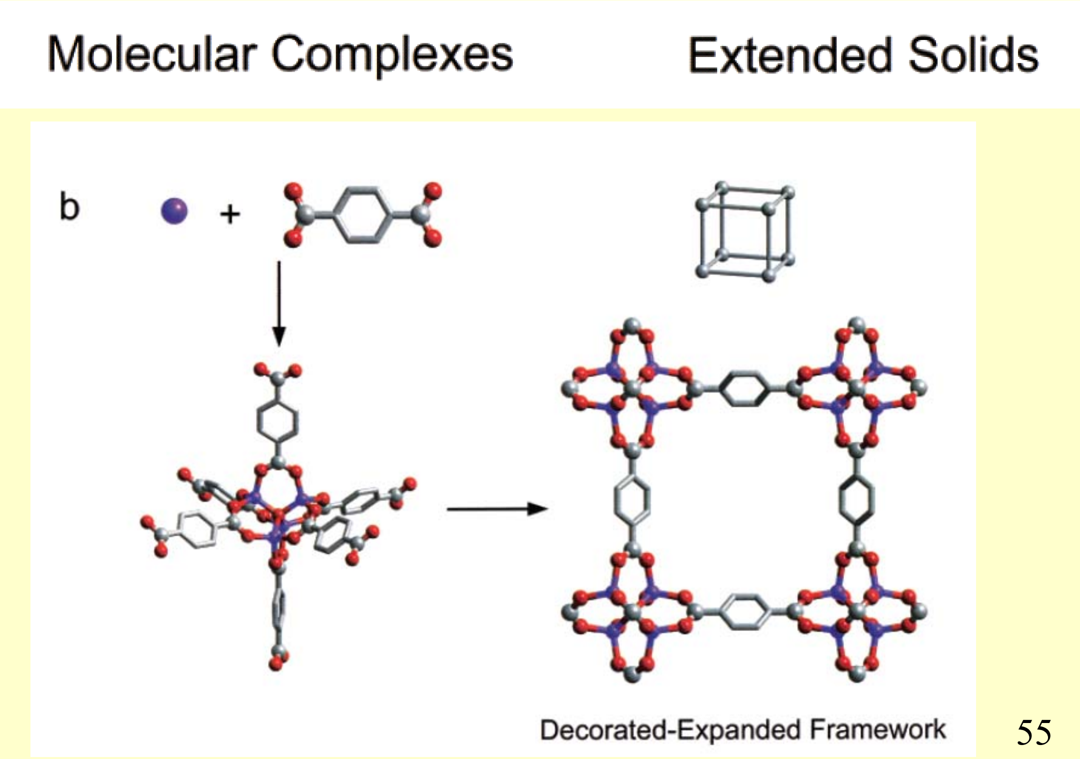
1,3,5-benzenetricarboxylate
(BTC)



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 Crystallization

Entropy-driven errors in self-assembly

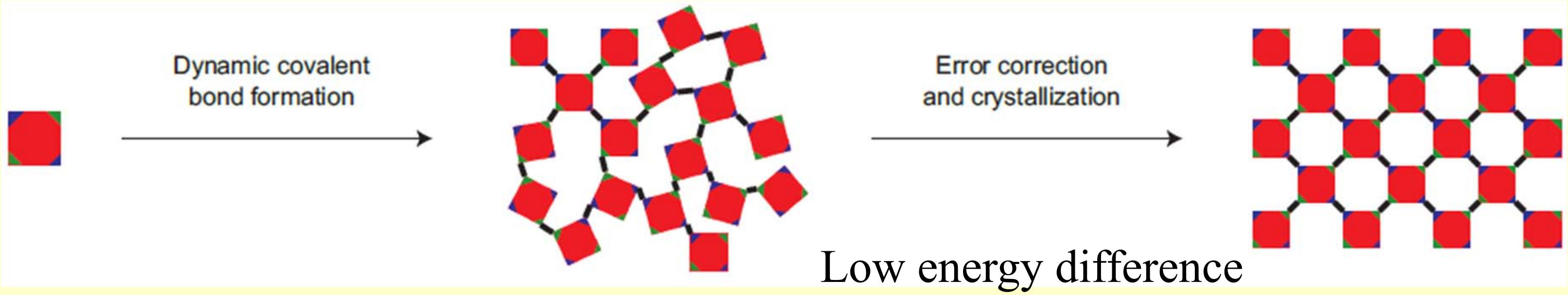
Mechanism for error correction required

The reaction should be reversible to allow for thermodynamic control

No side-reactions should exist (loss of reagents, contamination)

The building block rigidity, symmetry and discrete bonding direction decrease the incidence of errors

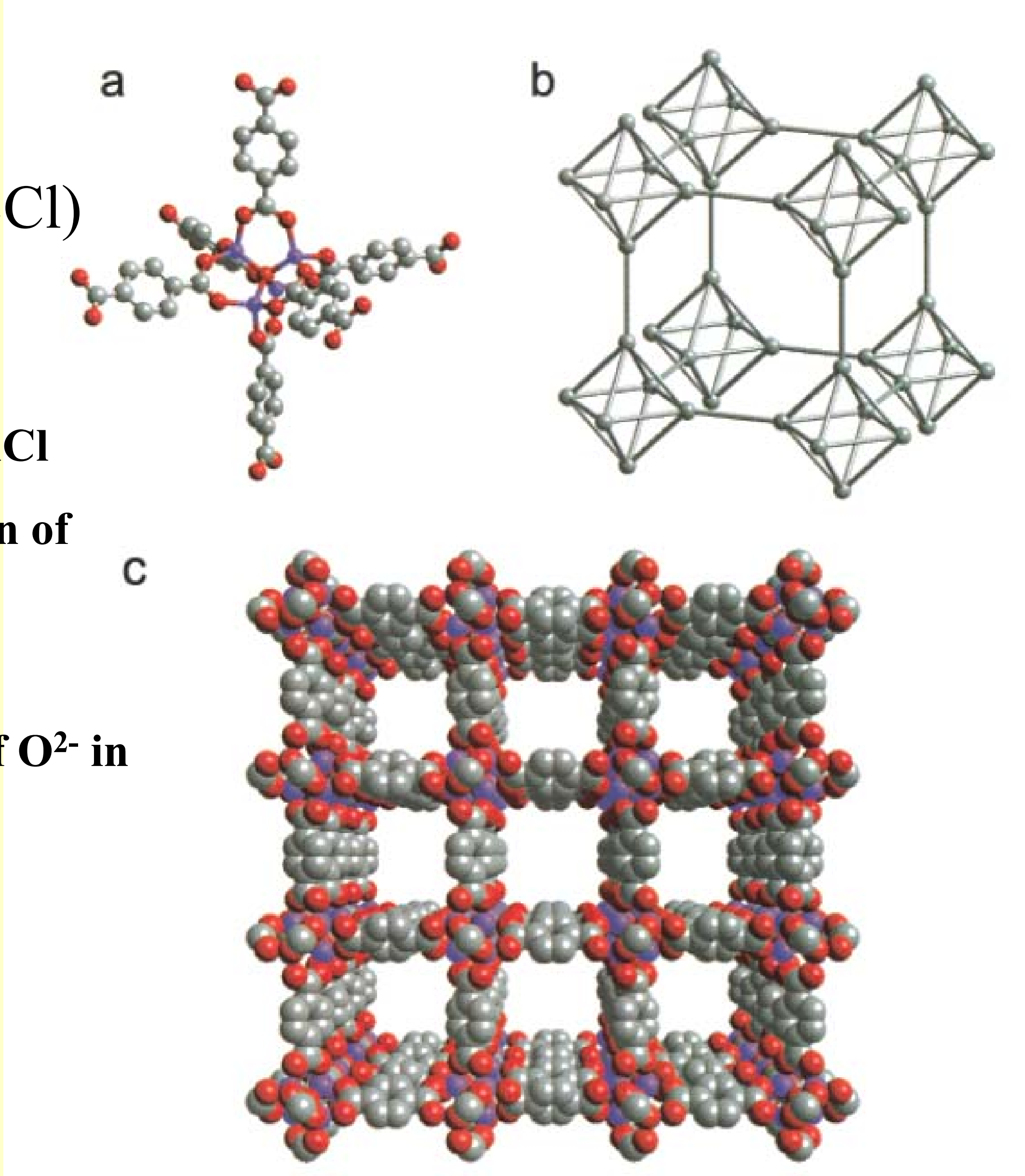
Solvothermal methods – control over p, T, μ to establish equilibrium



Low energy difference
($\Delta H < -T\Delta S$)

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** Zn_4O

Cavity diam. 18.5 Å

Nature, 1999, 402, 276

a primitive cubic lattice

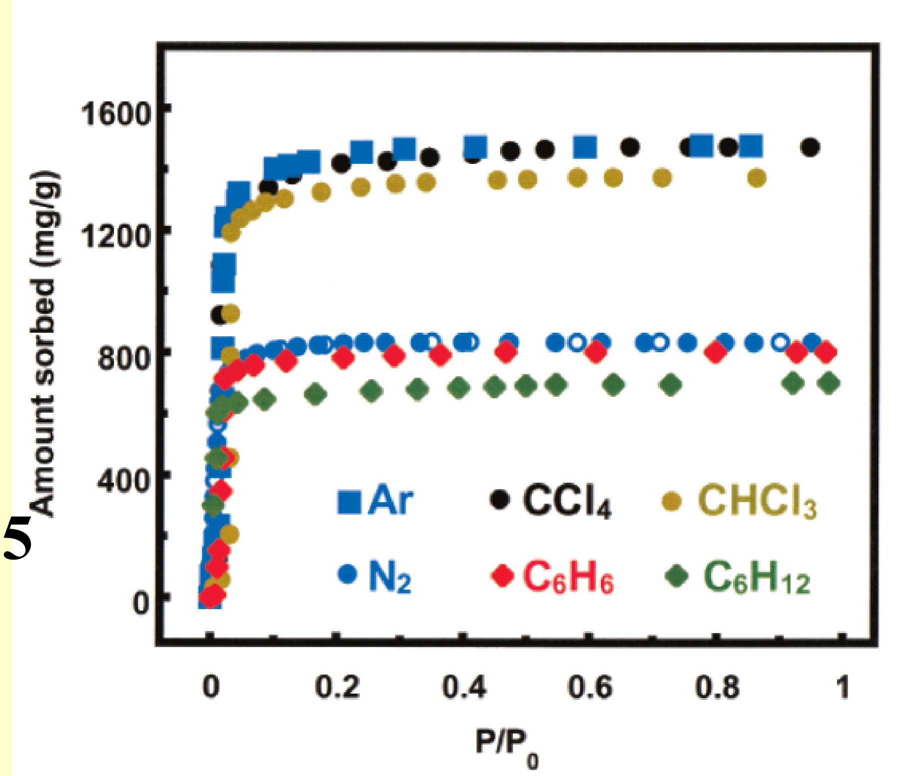
MOF-5

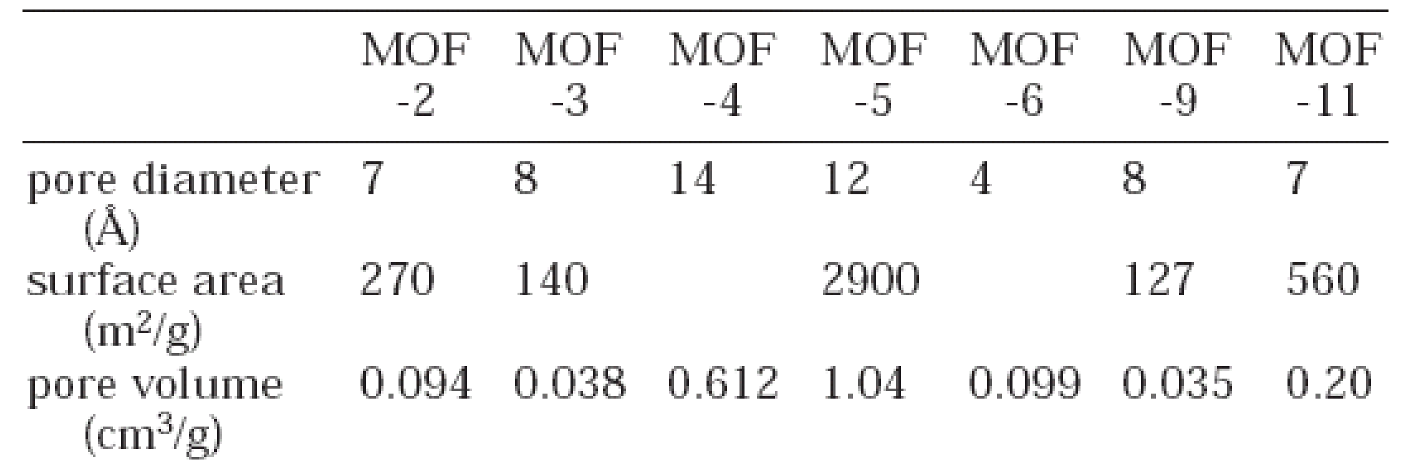
MOF-5

Stable even after desolvation

at 300 °C in air

gas sorption isotherms for MOF-5

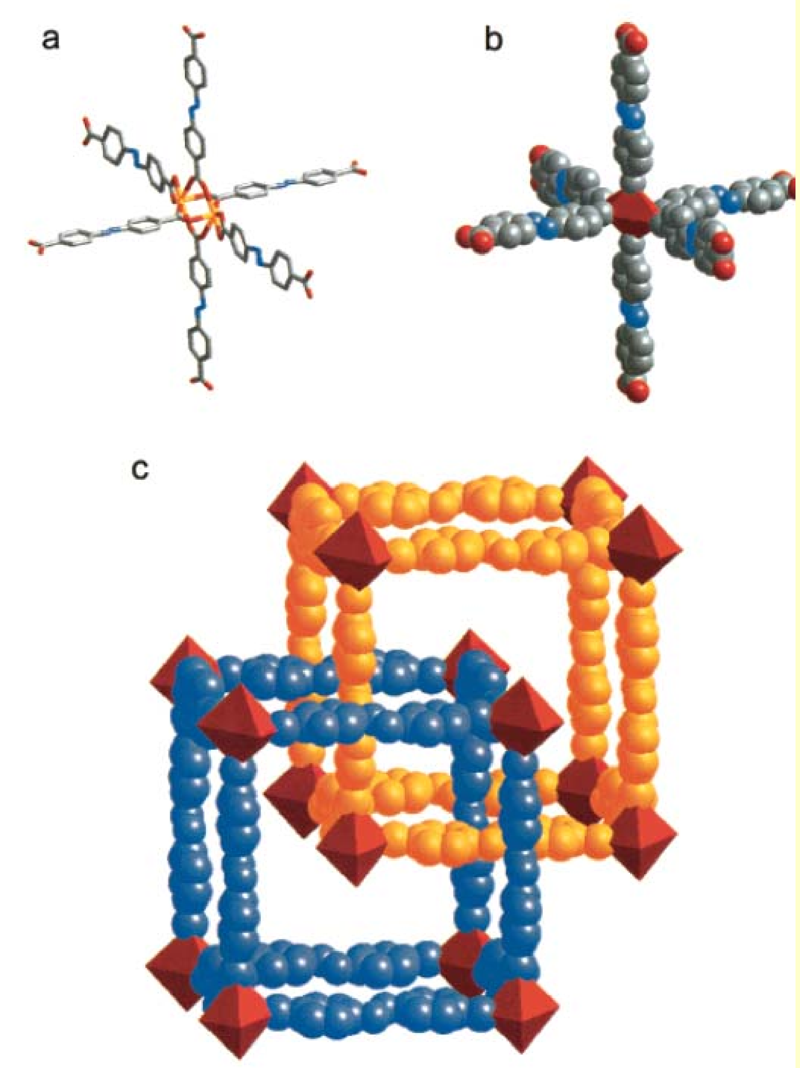




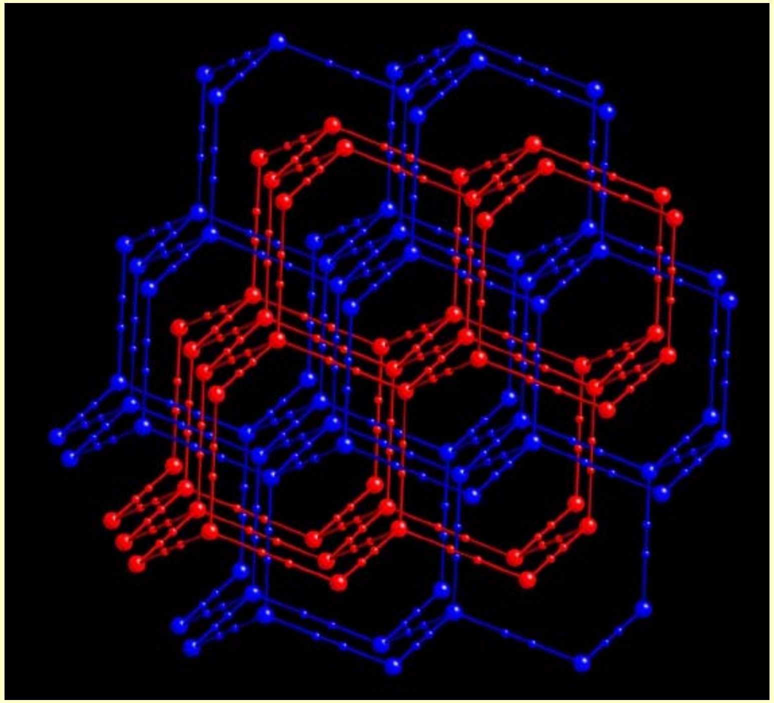
	MOF -2	MOF -3	MOF -4	MOF -5	MOF -6	MOF -9	MOF -11
pore diameter (Å)	7	8	14	12	4	8	7
surface area (m^2/g)	270	140		2900		127	560
pore volume (cm^3/g)	0.094	0.038	0.612	1.04	0.099	0.035	0.20

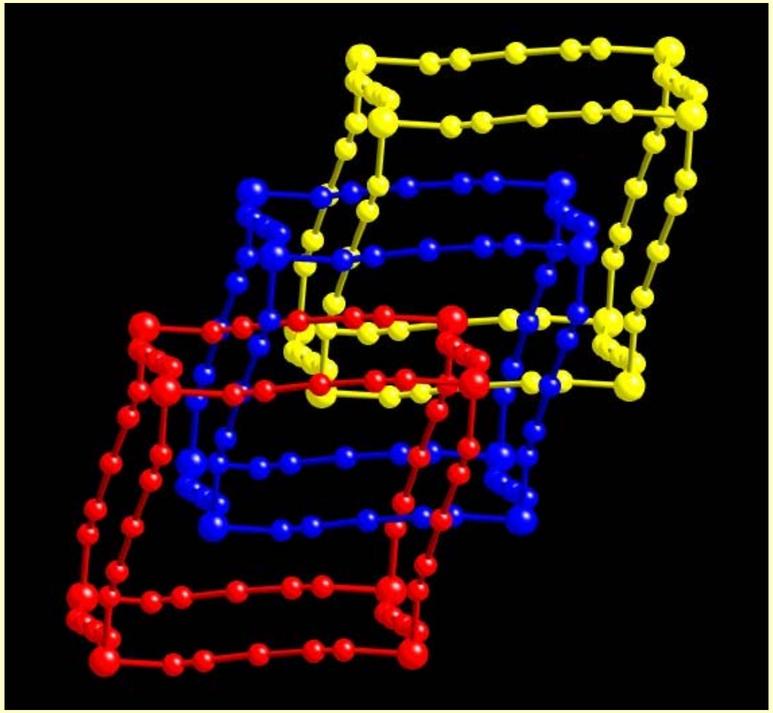
Interpenetration

MOF-9

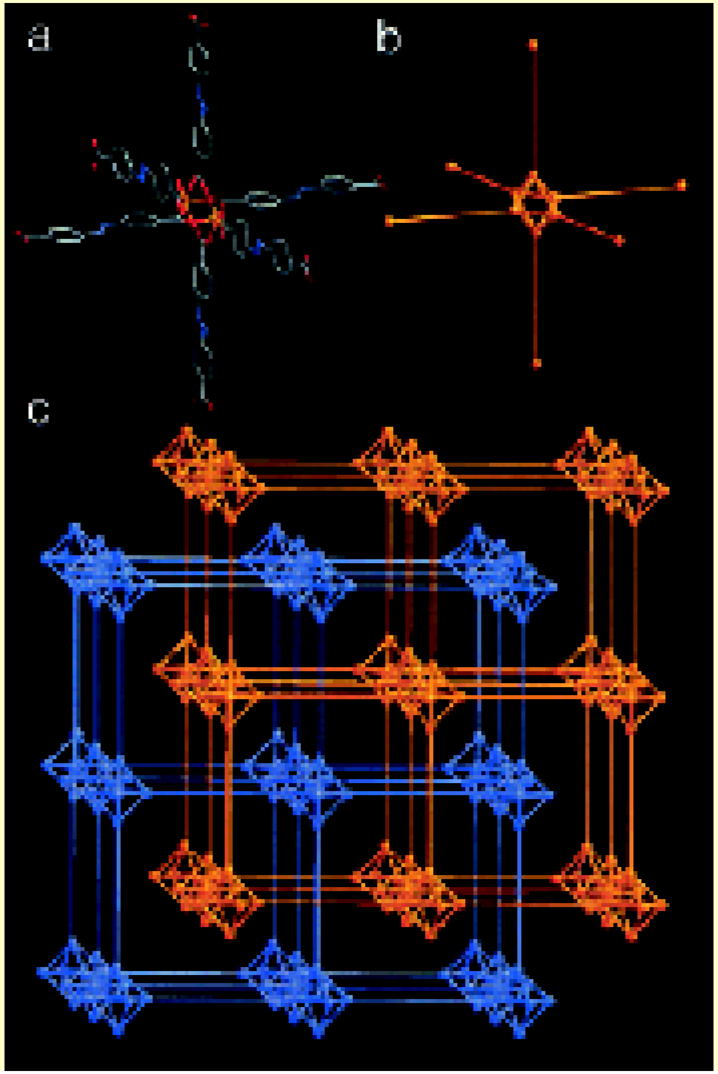


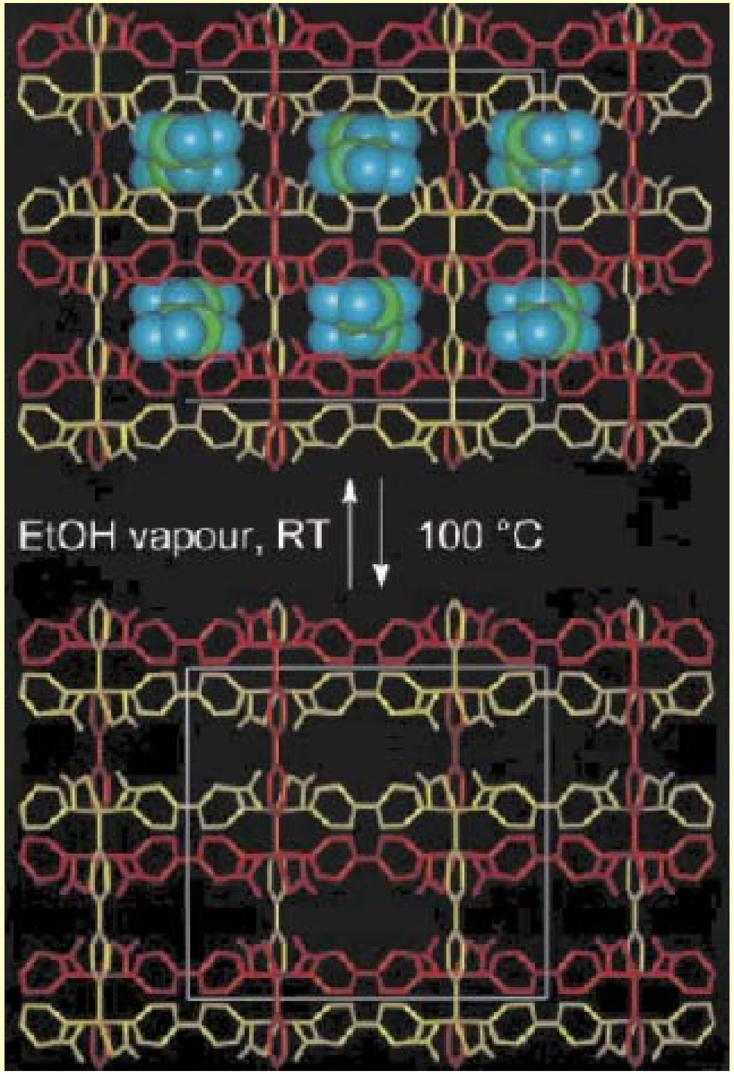
Interpenetration





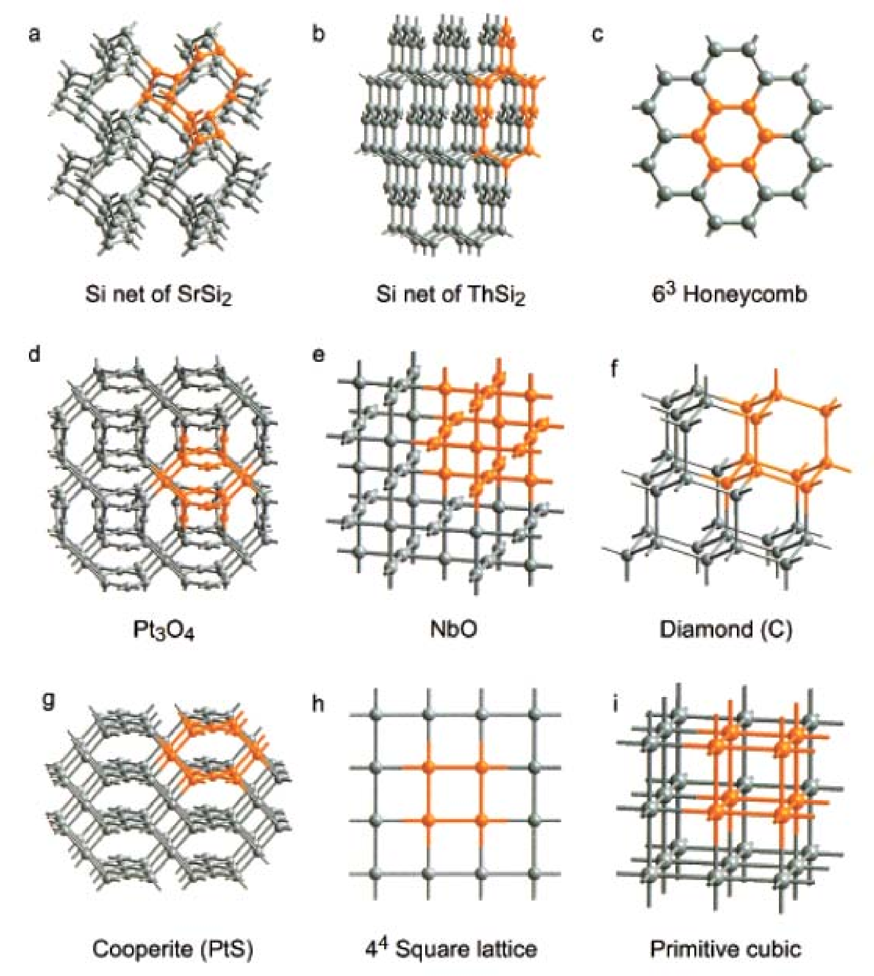
Metallo-Organic Framework Structures



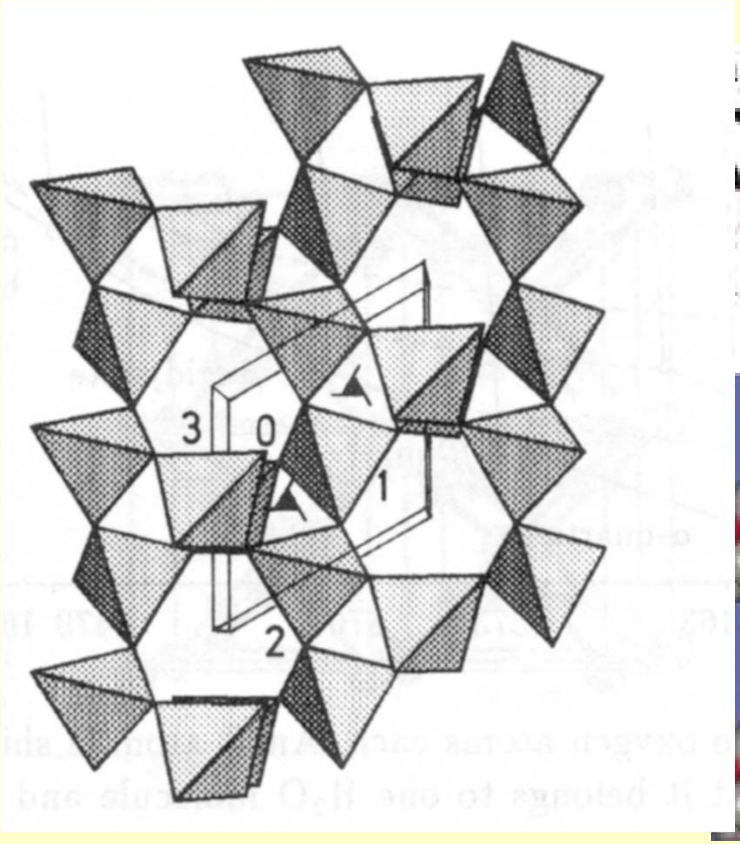


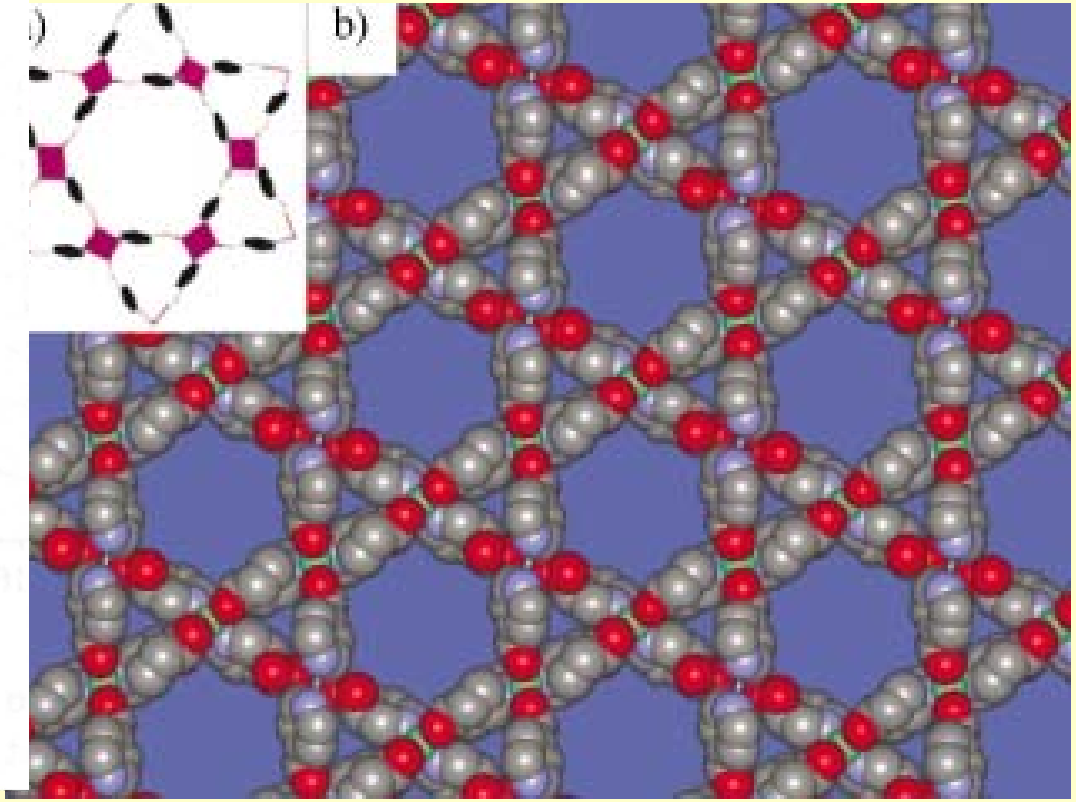
Basic Nets

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

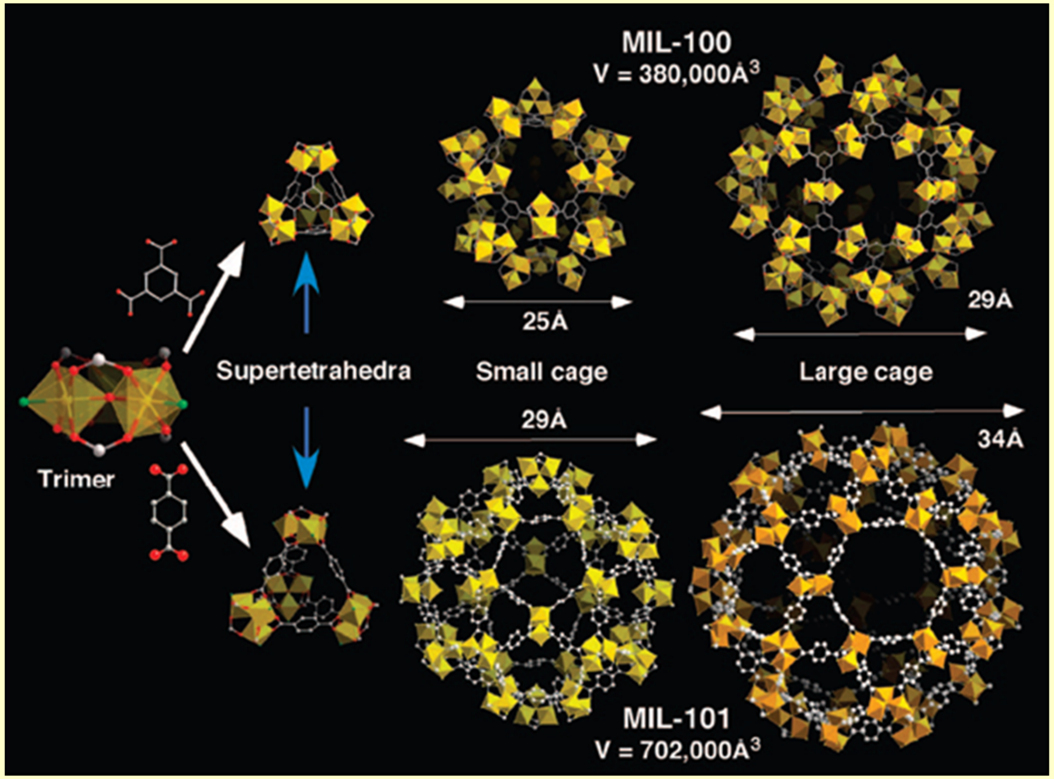


Inorganic and Metallo-Organic Quartz





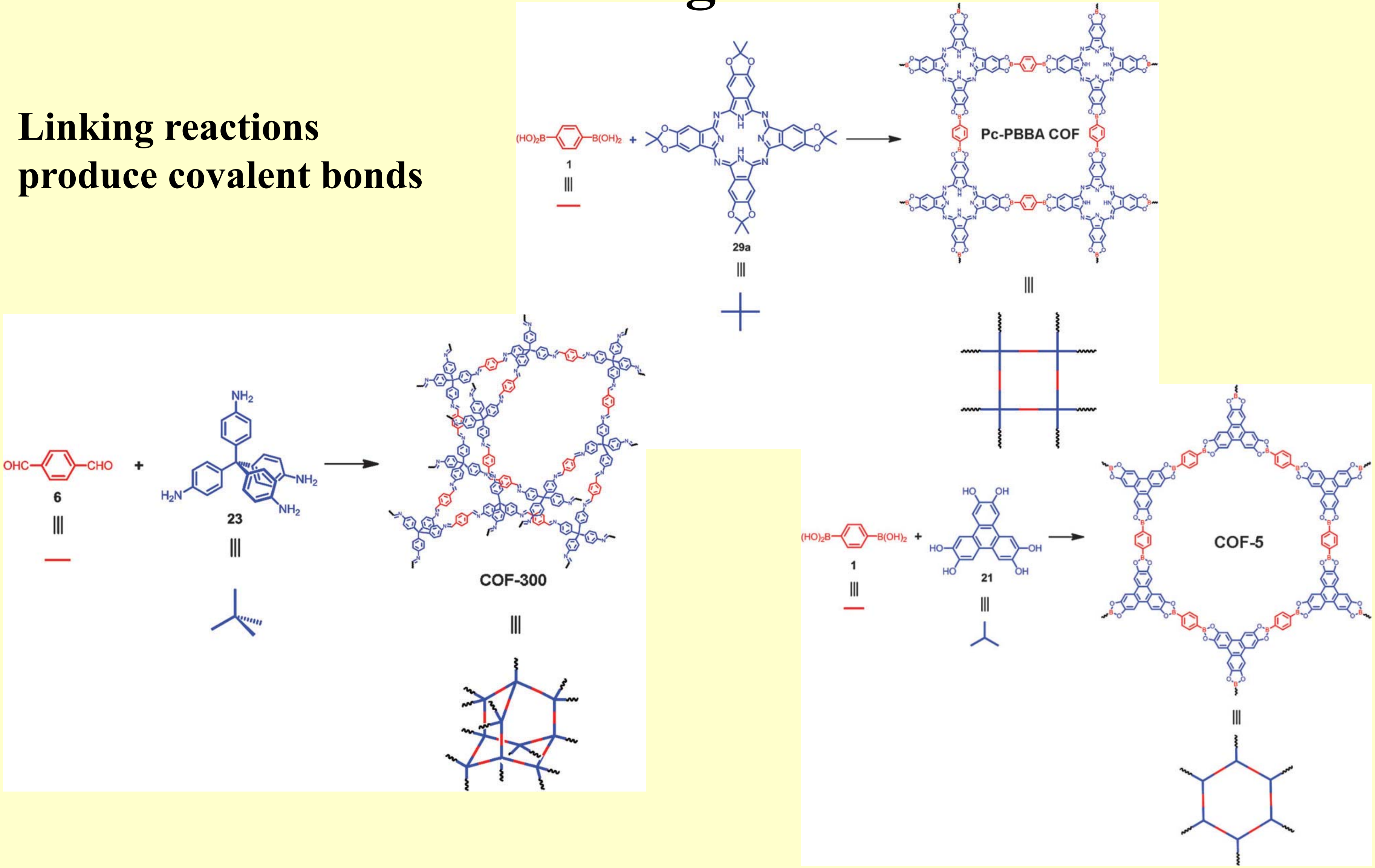
MIL-100 and MIL-101



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

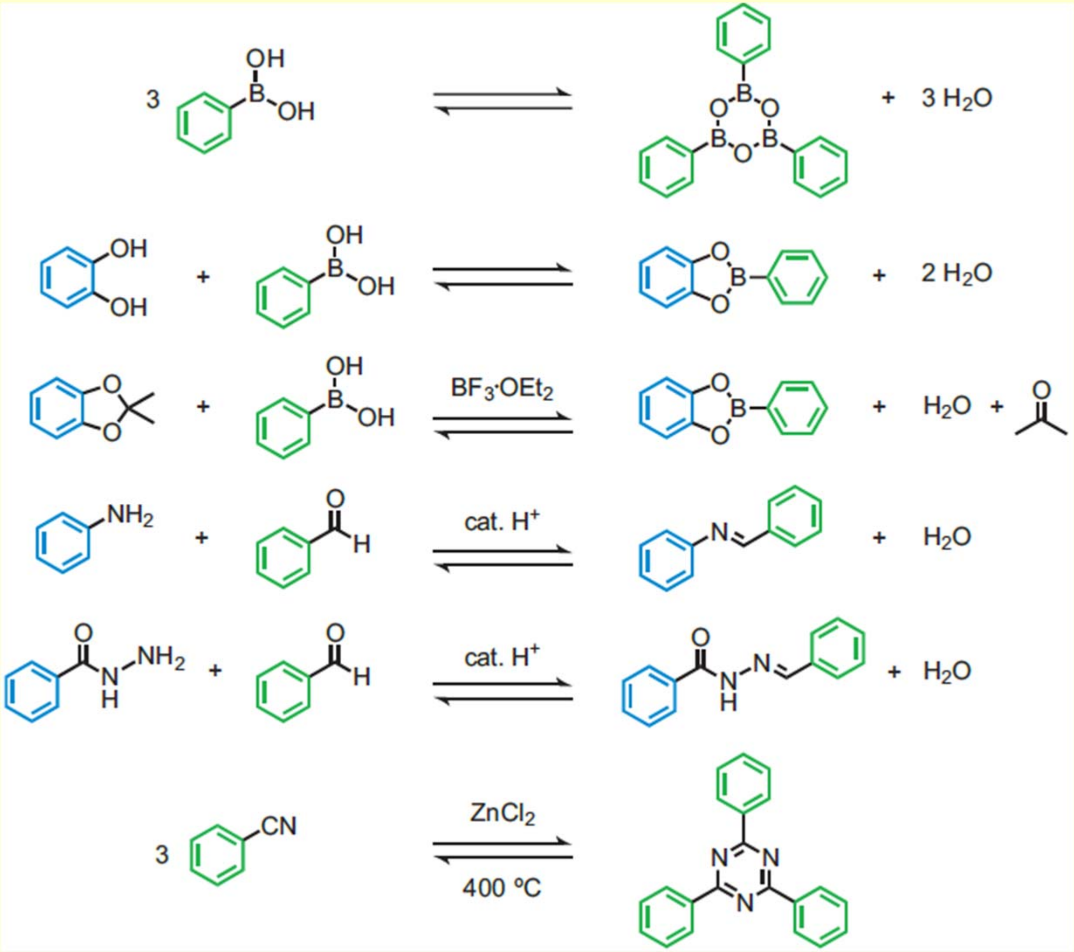
COF - Covalent Organic Frameworks

Linking reactions produce covalent bonds



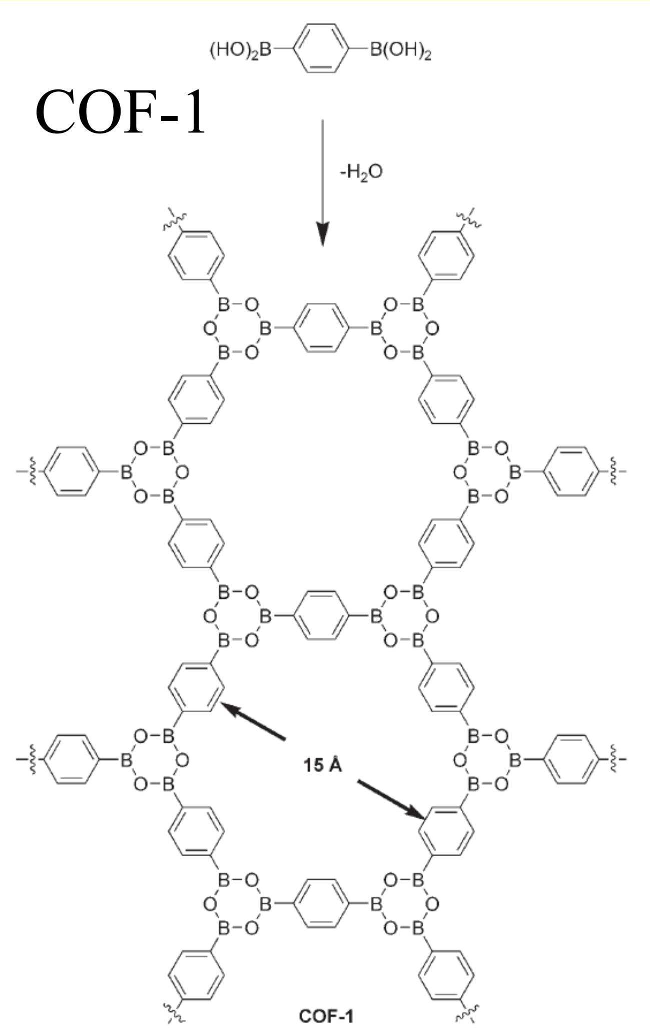
Covalent Organic Frameworks

Linking reactions



Covalent Organic Frameworks

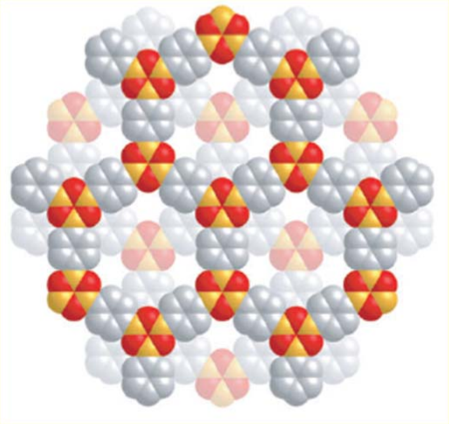
COF-1



Solvents - reactants are poorly soluble (to slow down the reversible condensation) mesitylene-dioxane (1:1)

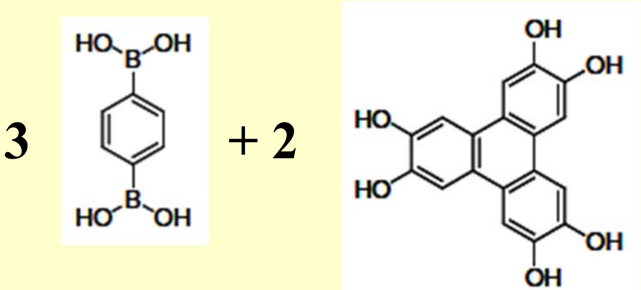
Sealed pyrex tubes, 110 °C, 72 h, minimize defects by self-healing

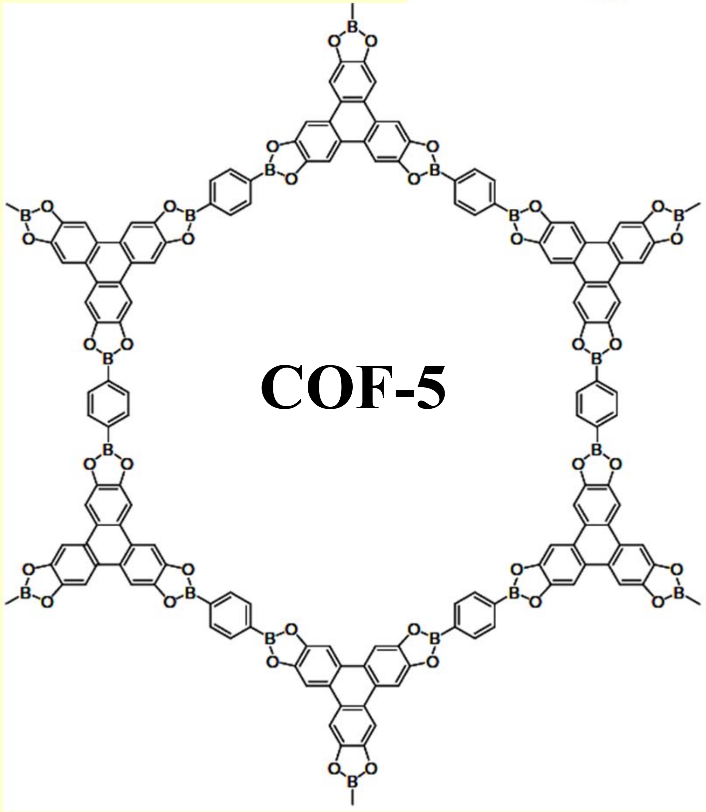
COF-1 = microcrystalline, high yield, high structural order by XRD
Solvent molecules are enclosed inside the pores, can be removed at 200 ºC without collapse of the crystalline structure
Surface area of 711 m^2 g^{-1}, pore size 0.7 nm



Interlayer spacing: 0.333 nm

Covalent Organic Frameworks



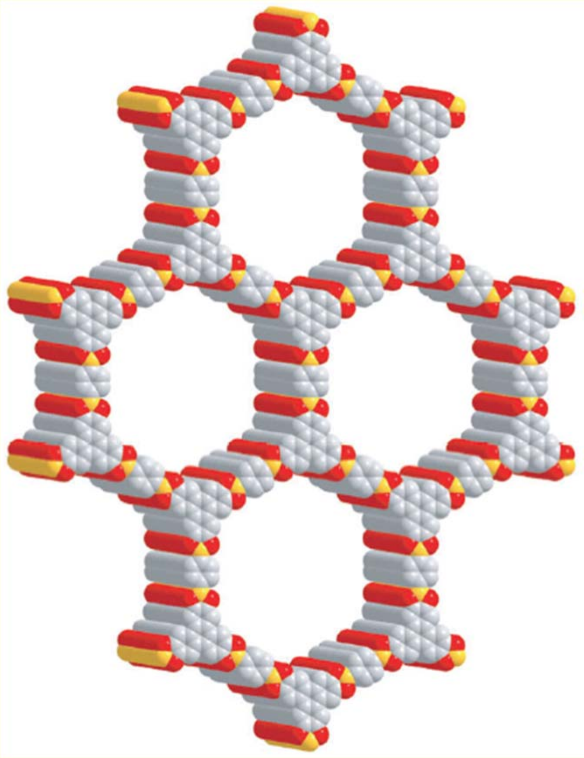


COF-5

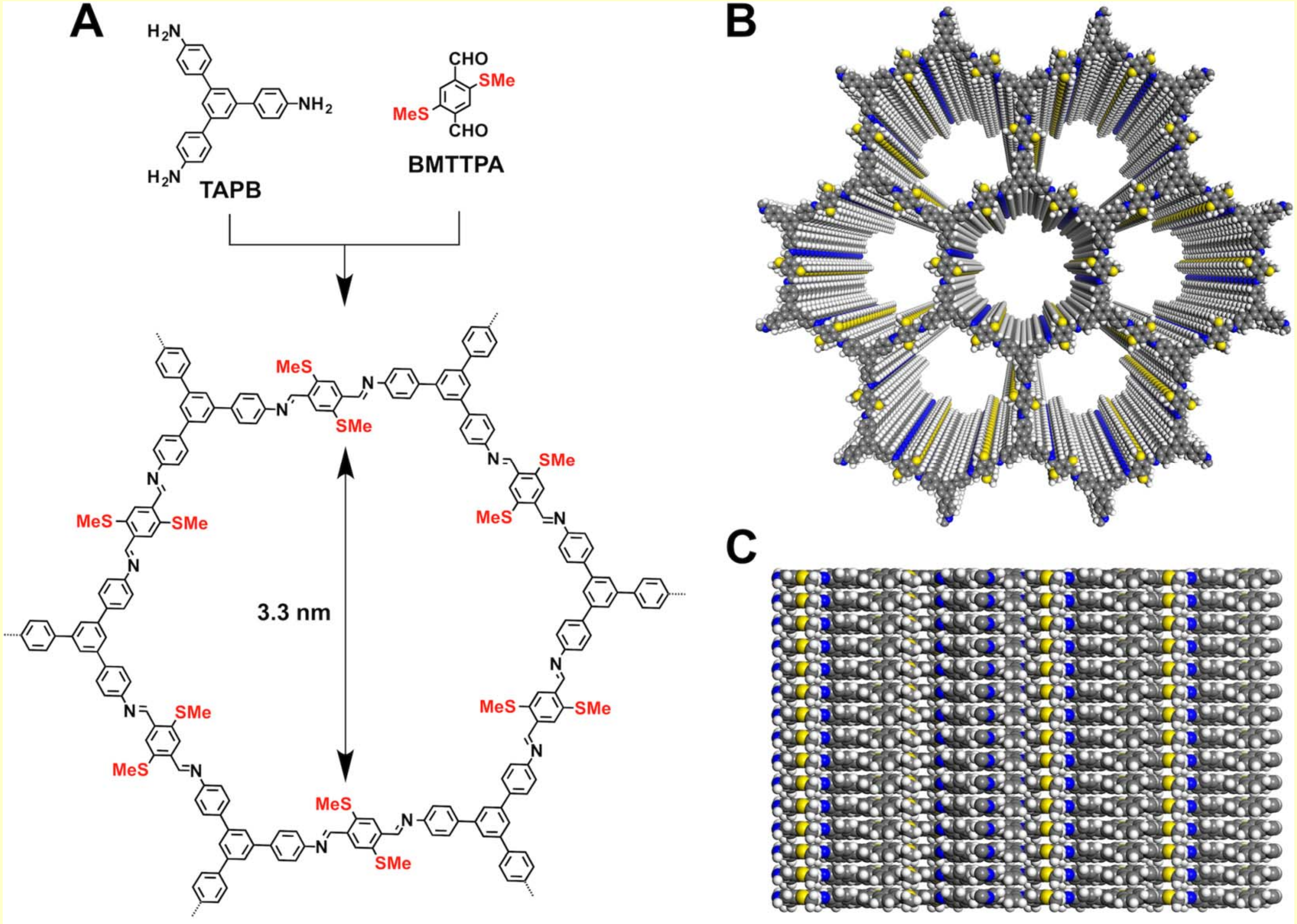
Surface area 1590 m^2/g

Pore size: 2.7 nm

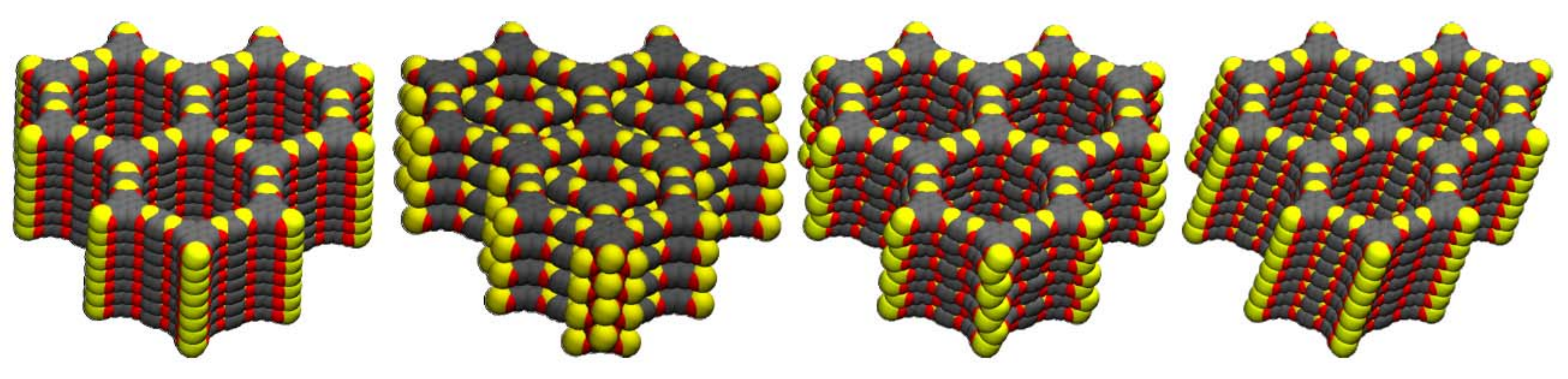
Interlayer spacing: 0.346 nm



Covalent Organic Frameworks



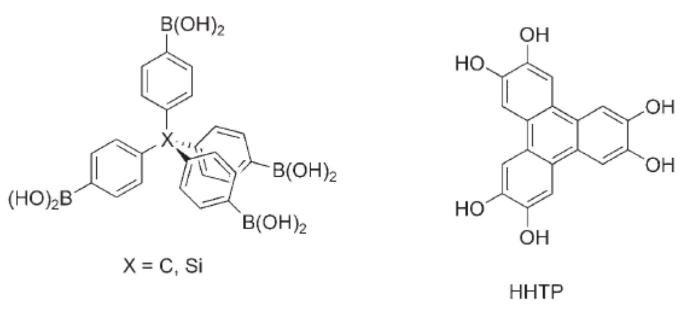
Covalent Organic Frameworks

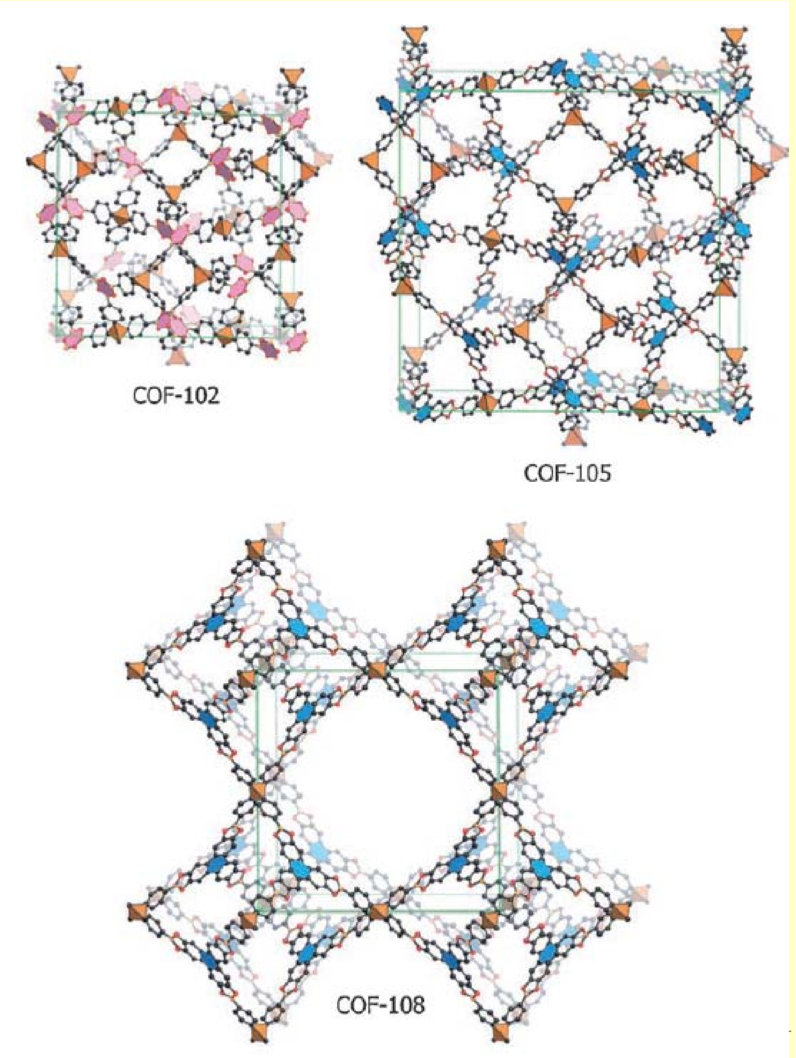


Layer stackings: AA, AB, serrated and inclined

Covalent Organic Frameworks

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

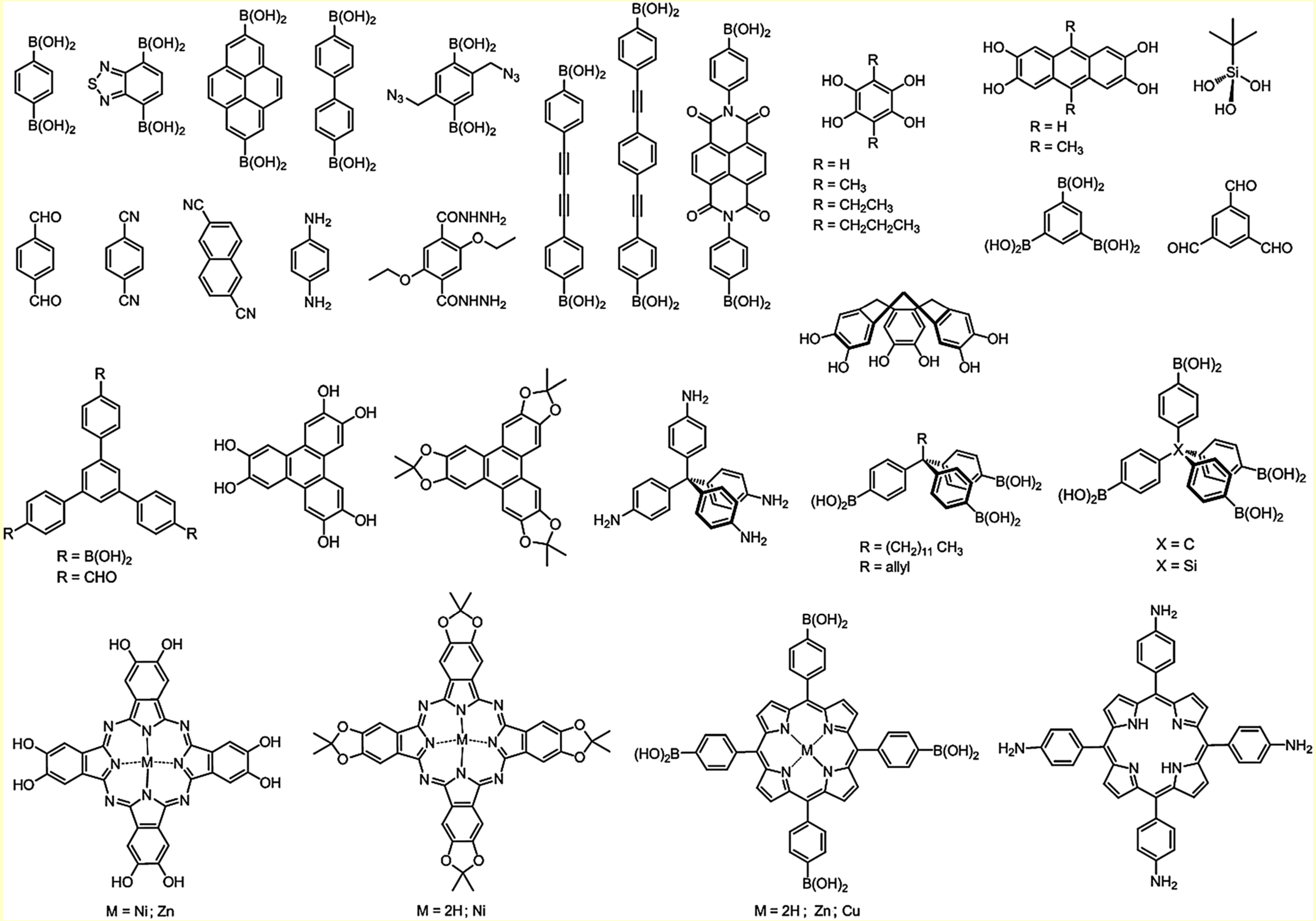




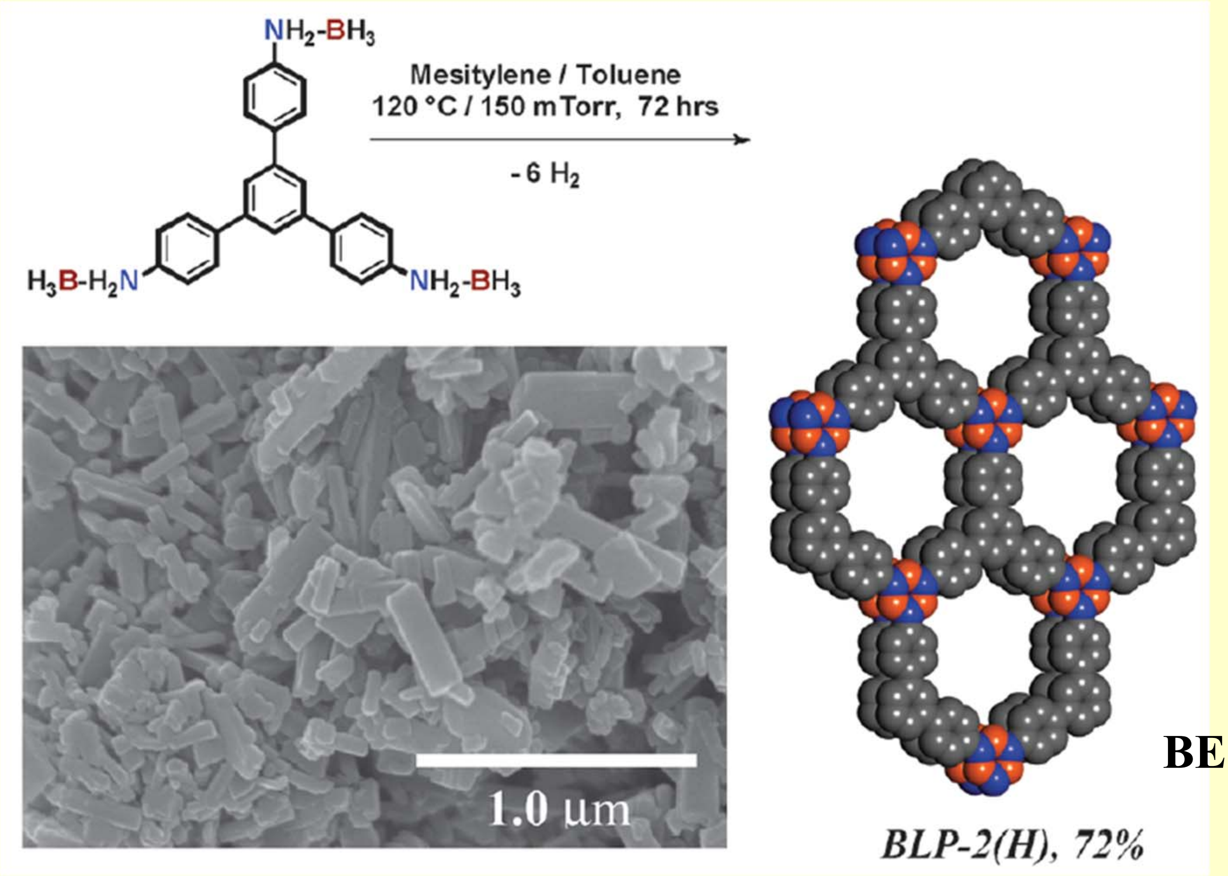
COF-108 - bor structure
two different types of pores
diameters of 15.2 and 29.6 Å.
density 0.17 g cm^{-3}

surface area, m^2 g^{-1}

COF 102	**3472**
COF 103	**4210**


B(OH)2
B(OH)2
NC
CN
NH2
CONHNHNH2
N3
R = H
R = CH3
R = CH2CH3
R = CH2CH2CH3
HO
OH
CHO
OHC
R = B(OH)2
R = CHO
R = (CH2)11 CH3
R = allyl
X = C
X = Si
H2N
(HO)2B
M = Ni; Zn
M = 2H; Ni
M = 2H ; Zn ; Cu

Borazine COFs



BET: 1178 m^2/g

Pore size: 0.64 nm

Jackson K., Reich T., *Chem. Commun.*, **2012**, 48, 8823–8825