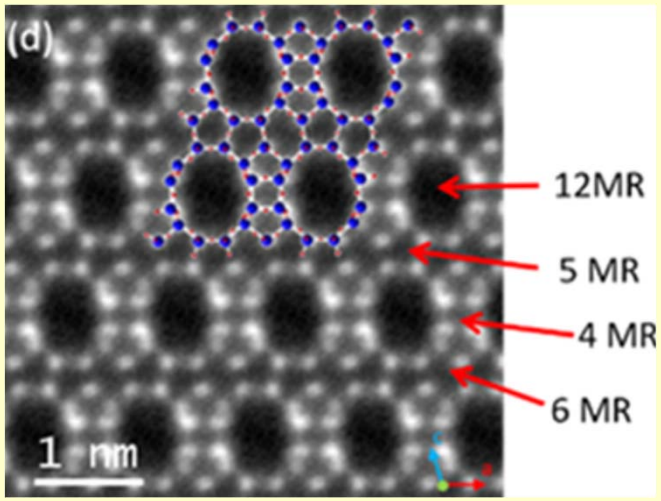
Zeolites and Zeolitic Materials

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

STEM ADF



IUPAC classification of porous materials

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

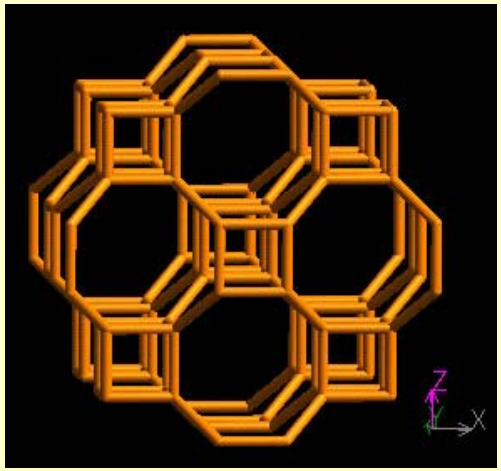
Applications: detergent builders, adsorbents, size-shape selective catalysts, supramolecular chemistry, nanotechnology

Chemical composition

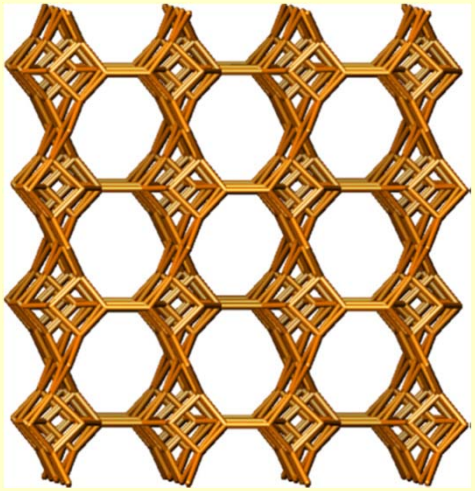
Silica	**SiO_2**
Aluminosilicates	**$M_x^I Al_x Si_{2-x} O_4 \cdot nH_2O$**
Aluminophosphates	**$AlPO_4$ (isoelectronic with Si_2O_4)**
Metallophosphates	**MPO_4**
Silicoaluminophosphates	**$M_x^I Si_x Al P_{1-x} O_4$**

Pores and Channels

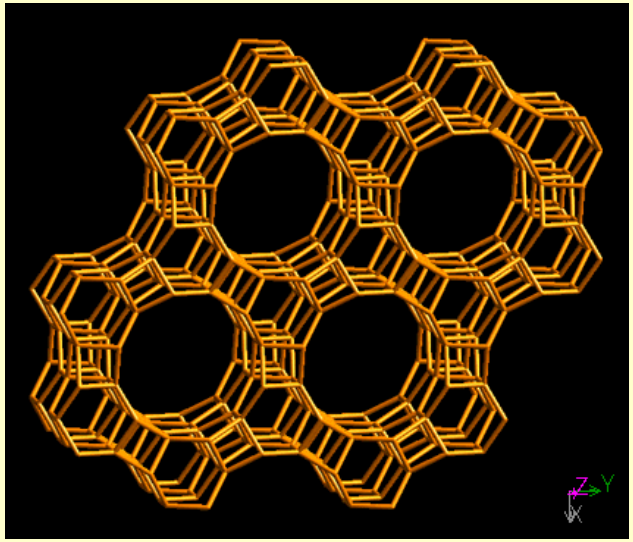
ACO



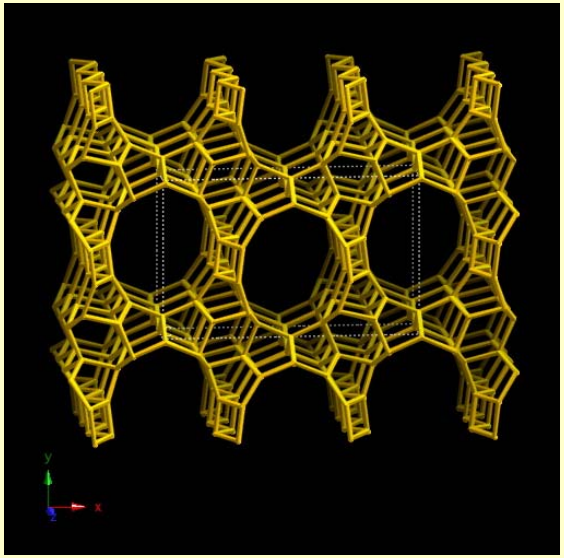
STI



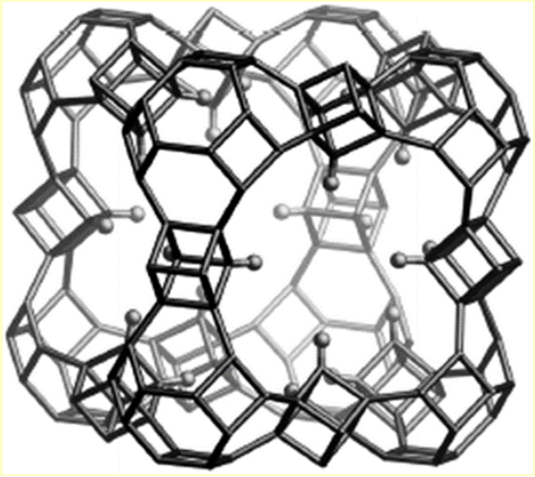
AFI



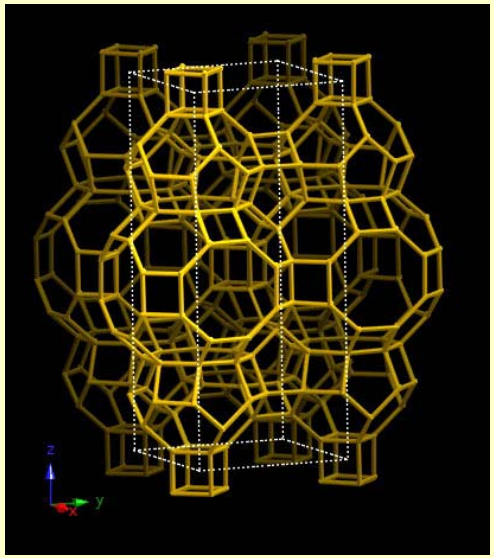
SSY



-CLO



UFI



Zeolite Types

>60 naturally occurring zeolites - large deposits of analcime, chabazite, clinoptilolite, erionite, mordenite and phillipsite
>253 zeolite framework types (IZA - 2020)
many hundreds of synthetic 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 (4c) frameworks (over 1 000 000 possible 4c frameworks)**
- **Interrupted frameworks (denoted by a hyphen: –CLO, cloverite)**

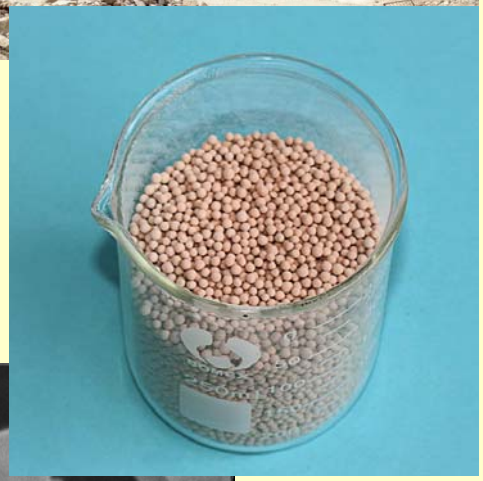
Structure types do not depend on: chemical composition, element distribution, cell dimensions, symmetry

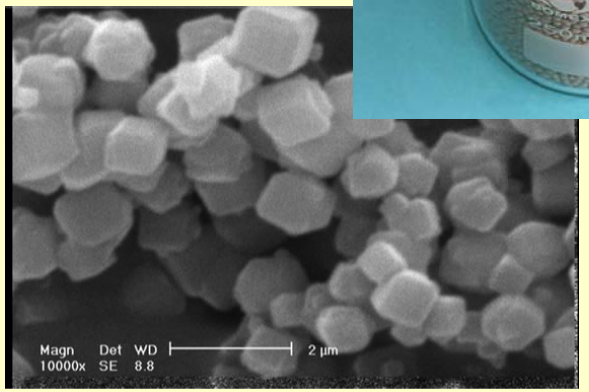
Several zeolite compounds can belong to the same structure type: FAU – faujasite, Linde X, Y, Beryllophosphate-X, SAPO-37, Zincophosphate-X

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-x (University Le Mans)
  - MU-n (Mulhouse, Université de Haute Alsace)

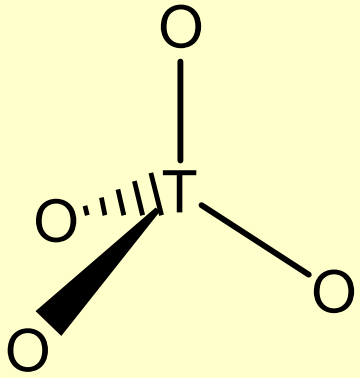


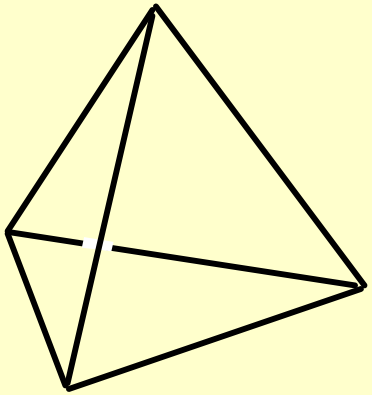


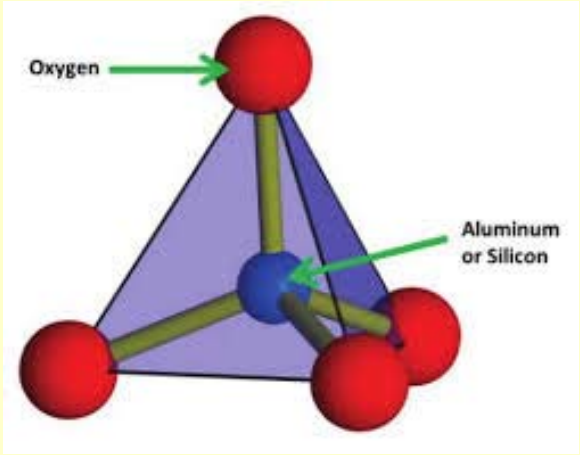
Zeolites Building Units

Primary building units = tetrahedra

$Al(III)O_4$, $P(V)O_4$, $Si(IV)O_4$ and MO_4





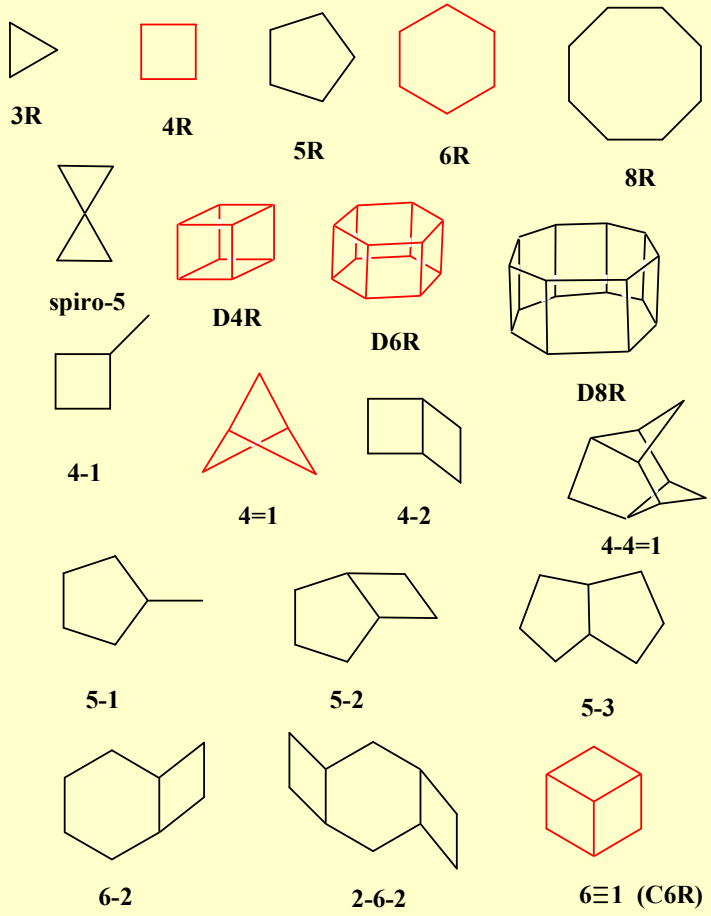


Isoelectronic relationship

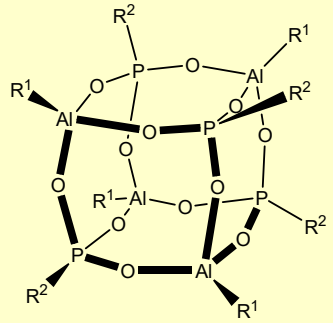
$(SiO_2)_2$ $[AlSiO_4]^-$ $AlPO_4$

Secondary (Structural) Building Units (SBU)

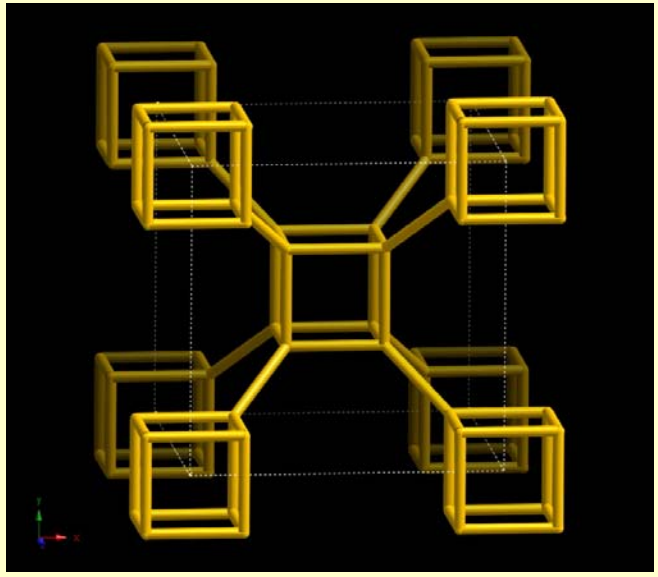
The whole network is constructed by connection a single type of SBU by oxygen bridges



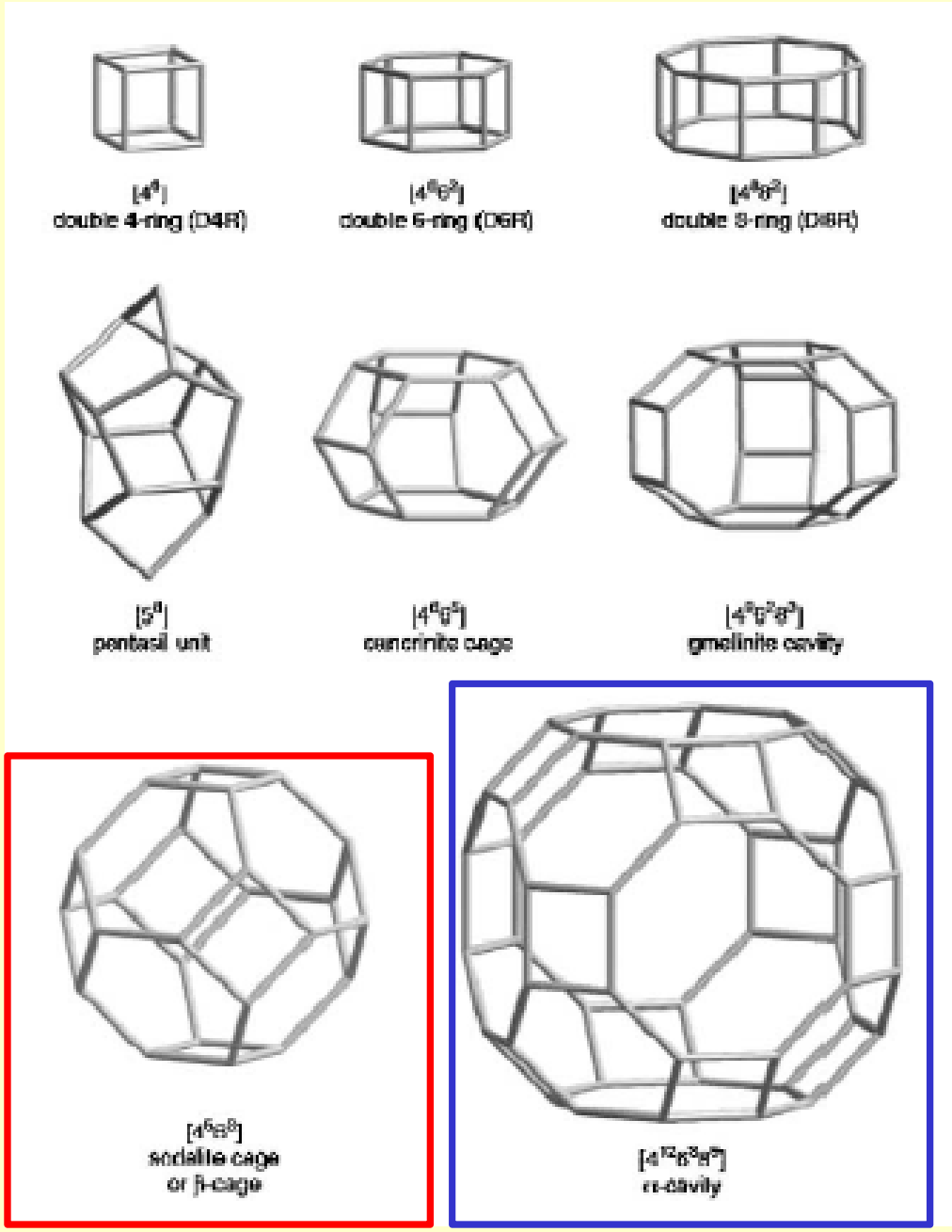
D4R = double four-ring
(= 8 T-atoms, Al, Si, P,…)



Framework Type ACO



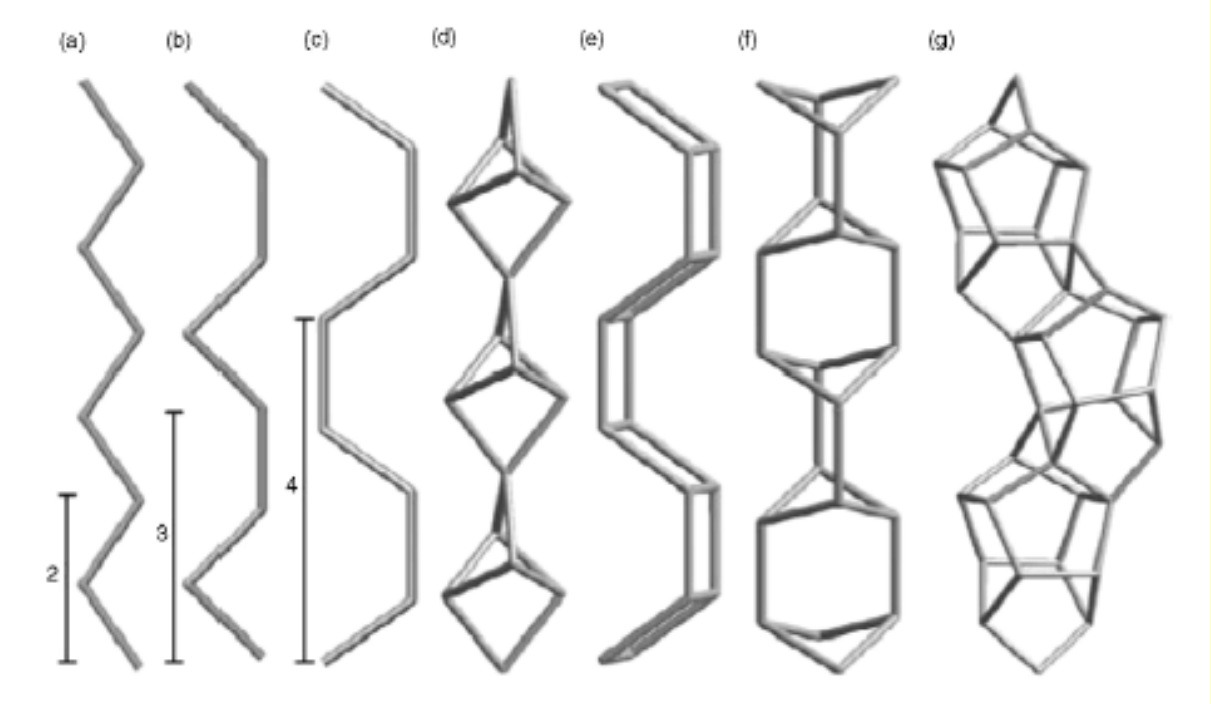
Polyhedral Composite Building Units



Truncated octahedra
[$4^6 6^8$] sodalite- or β-cages)

Truncated cubeoctahedra
[$4^{12} 6^8 8^6$] (α-cavities)

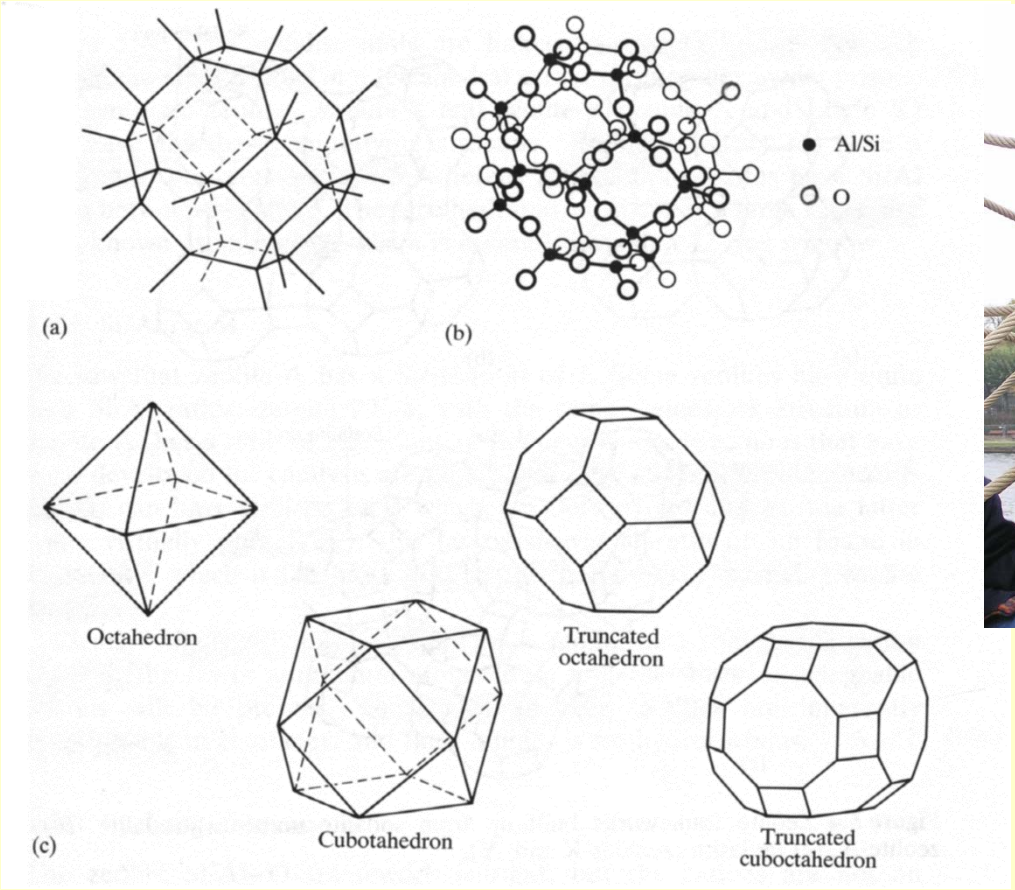
Chain Composite Building Units



(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

Sodalite cage = Truncated octahedron

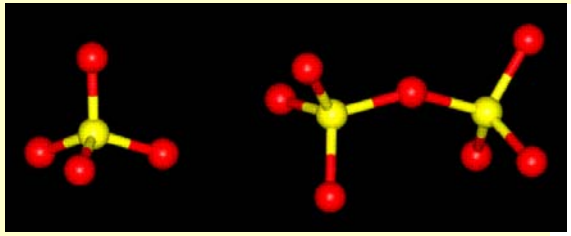


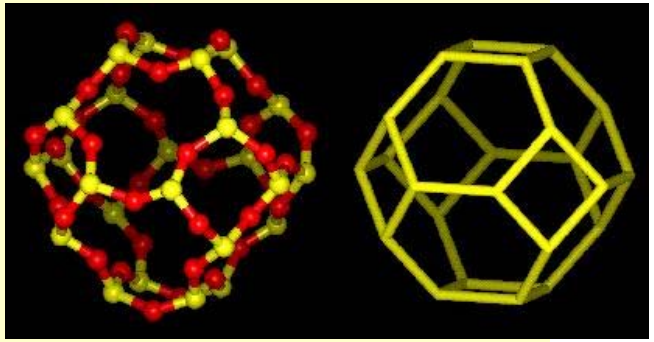
Truncated octahedra
[$4^6 6^8$] sodalite- or β-cages)

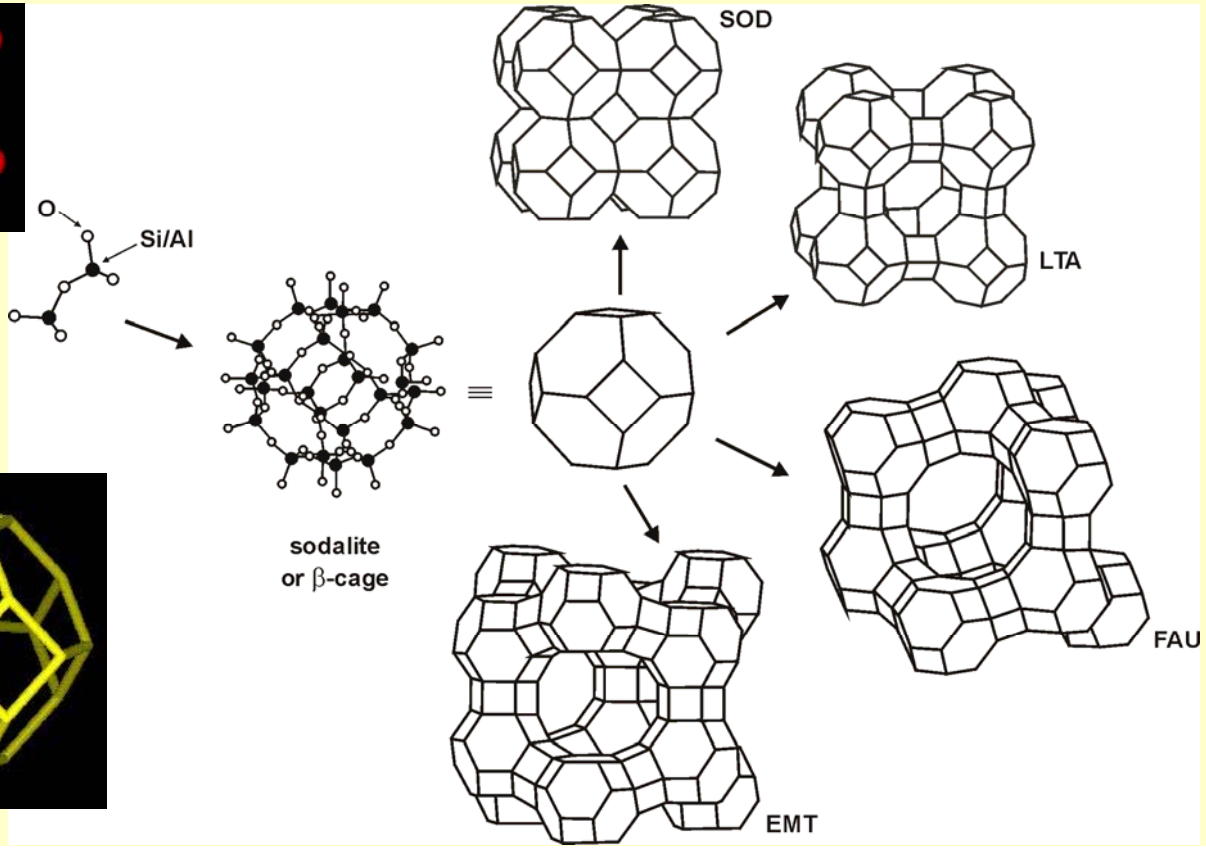
Truncated cubeoctahedra
[$4^{12} 6^8 8^6$] (α-cavities)

Sodalite Unit

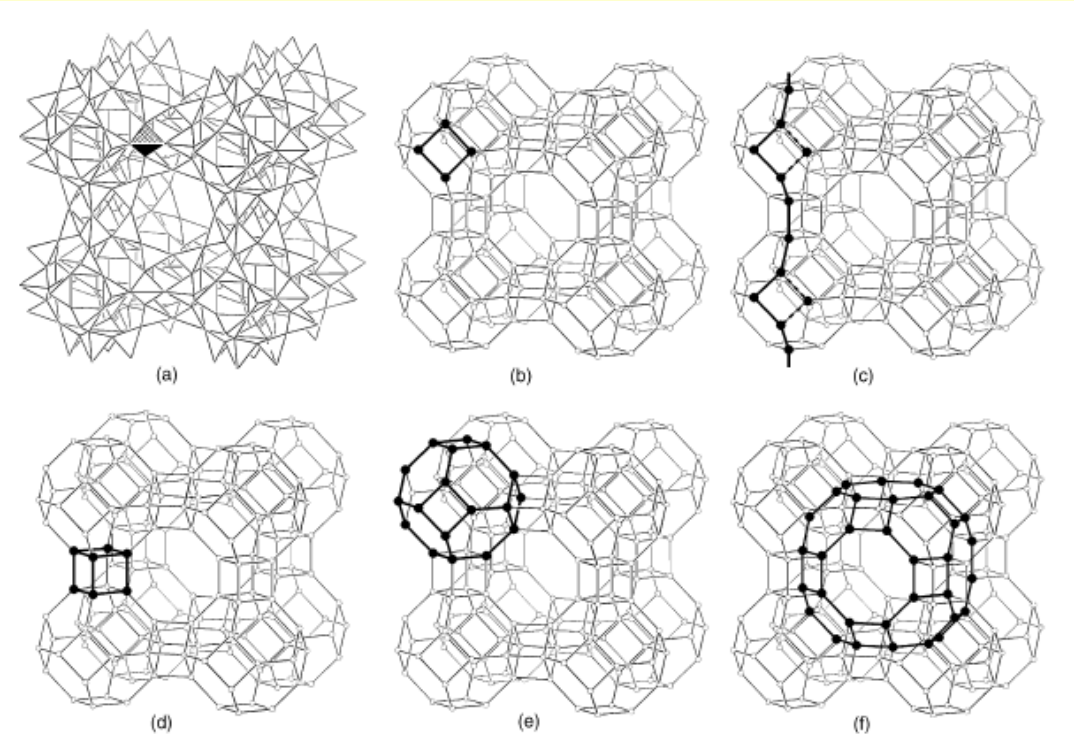
Packing of the sodalite (β-cage) units:
SOD – bcc, sharing of 4-rings
LTA – sc, 4-rings connected through O bridges
FAU (faujasite) – cubic diamond, 6-rings connected through O bridges
EMT – hexagonal diamond, 6-rings connected through O bridges

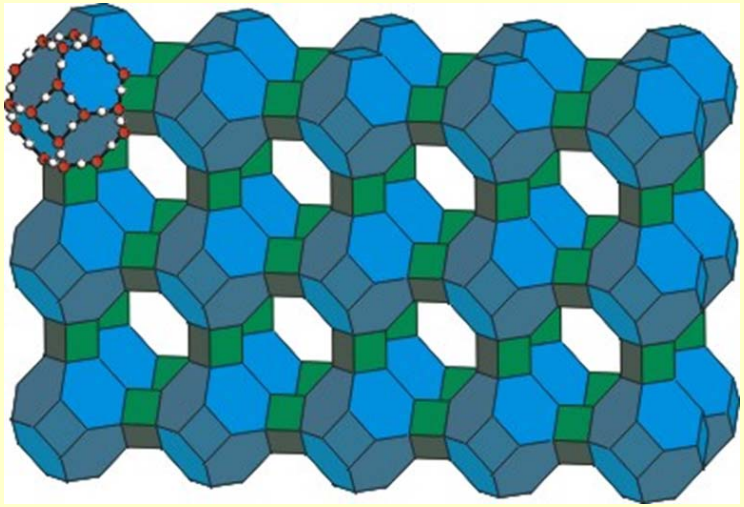


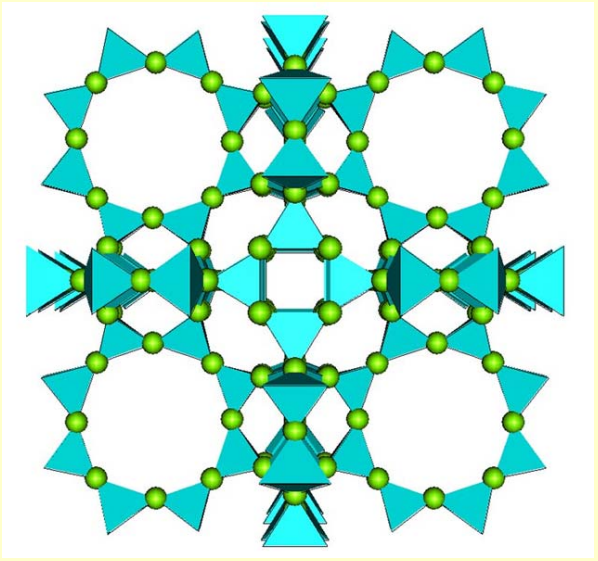




Building Units in Zeolite A (LTA)

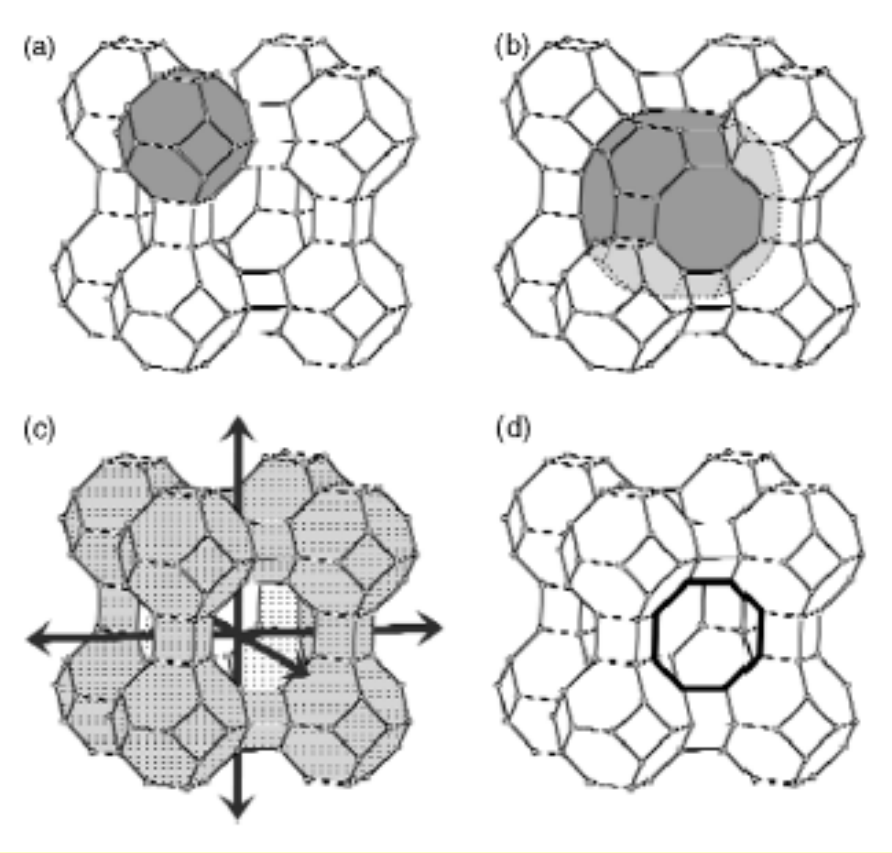






(a) [TO_4] tetrahedra as primary BU
(b) Four-rings 4R SBU
(c) IB fuenfer chains
(d) Cubes D4R [4^6] SBU
(e) Truncated octahedra [$4^6 6^8$] (sodalite- or β-cages)
(f) Truncated cubeoctahedra [$4^{12} 6^8 8^6$] (α-cavities)

Pores and Channels in Zeolite A (LTA)

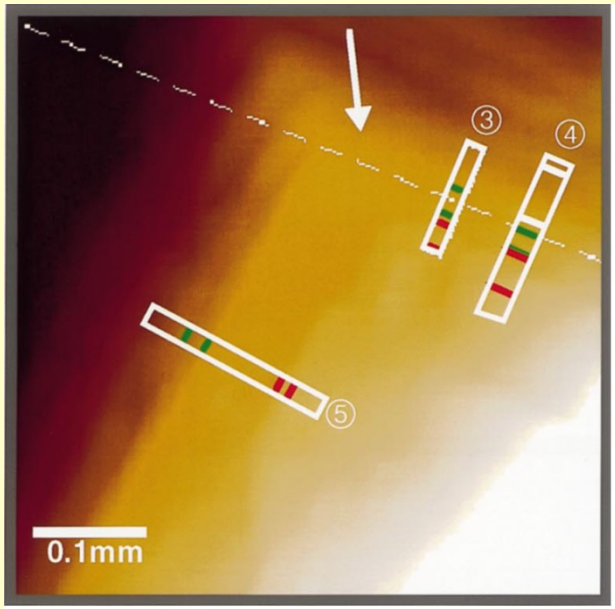


(a) the sodalite β-cage [$4^6 6^8$]

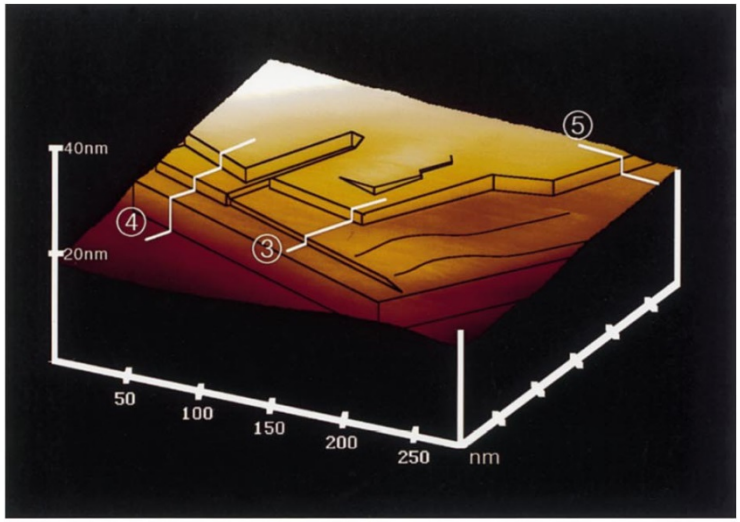
(b) the α-cavity [$4^{12} 6^8 8^6$]

(c) the 3-dimensional channel system

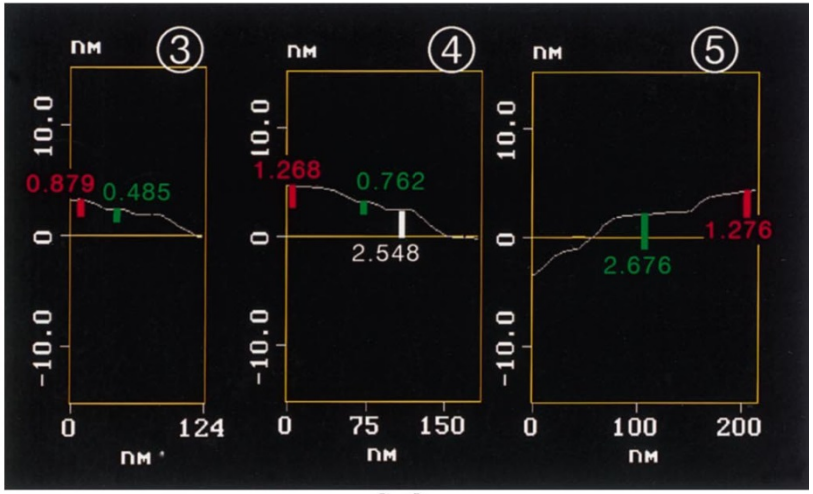
(d) the 8-ring defining the 0.41 nm effective channel width



(a)



(b)



(c)

Zeolite A (LTA)

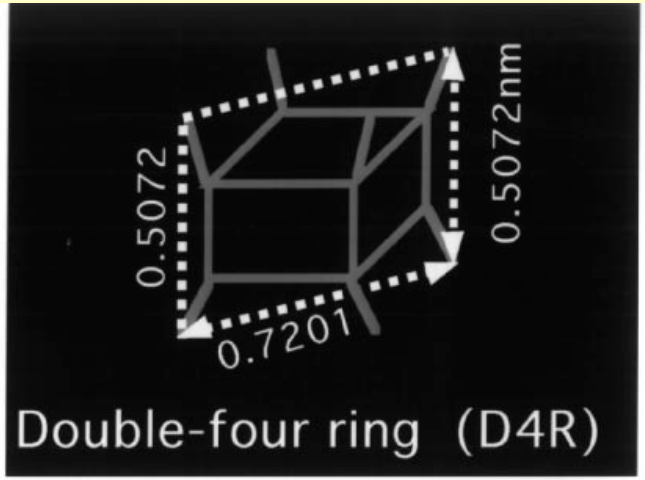
D4R

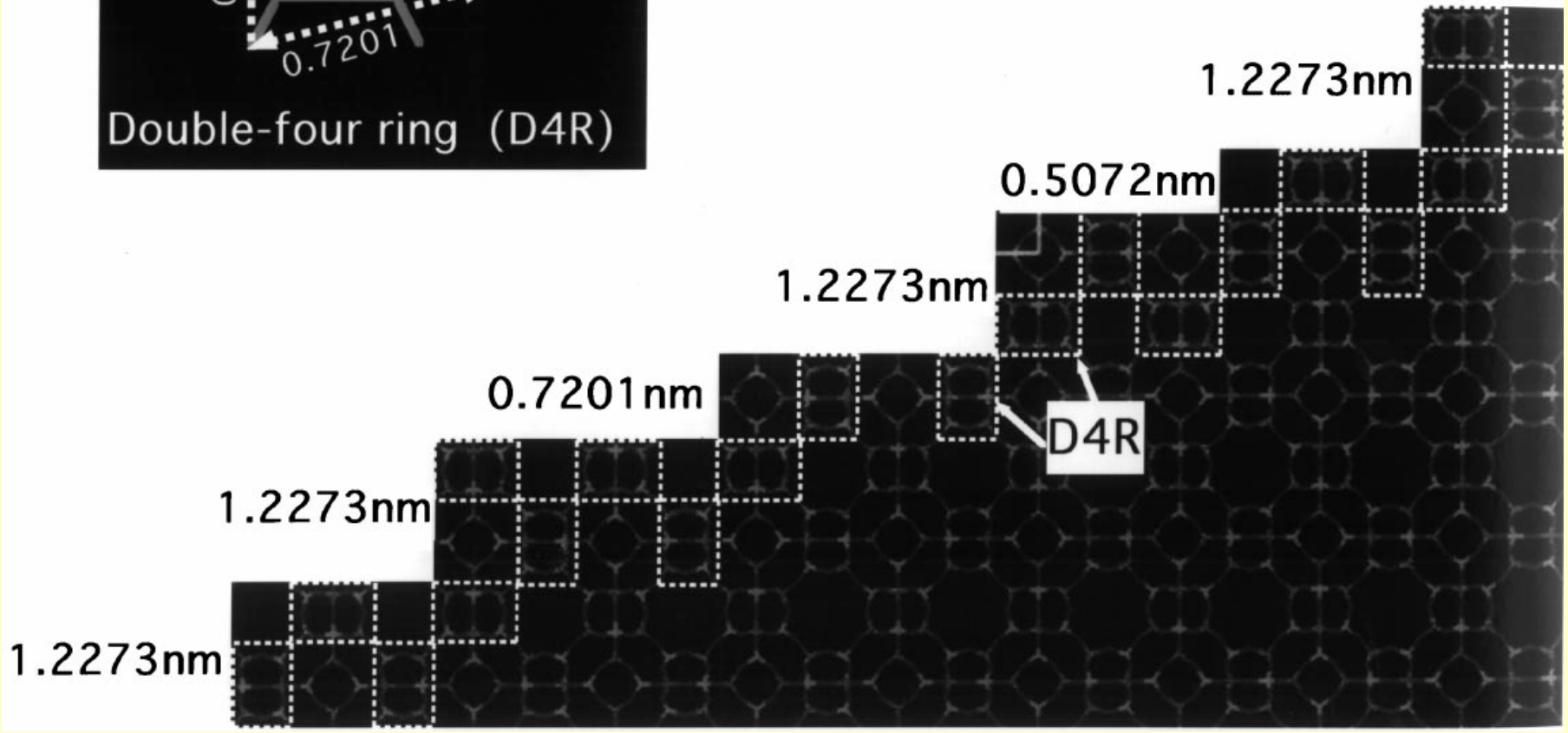
AFM growth studies of LTA

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

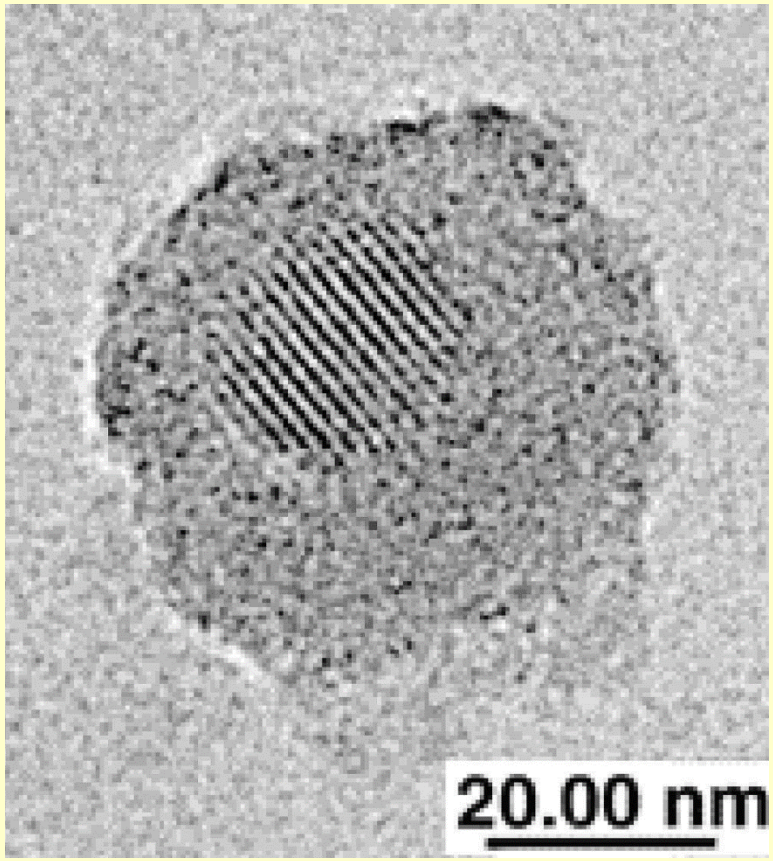
Zeolite A (LTA)

D4R





HRTEM of a Zeolite A (LTA) Crystal



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

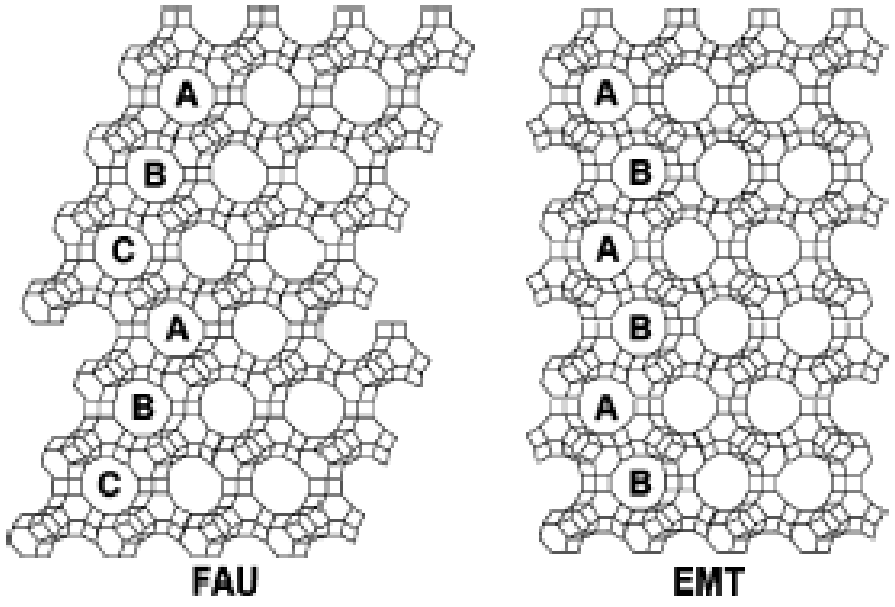
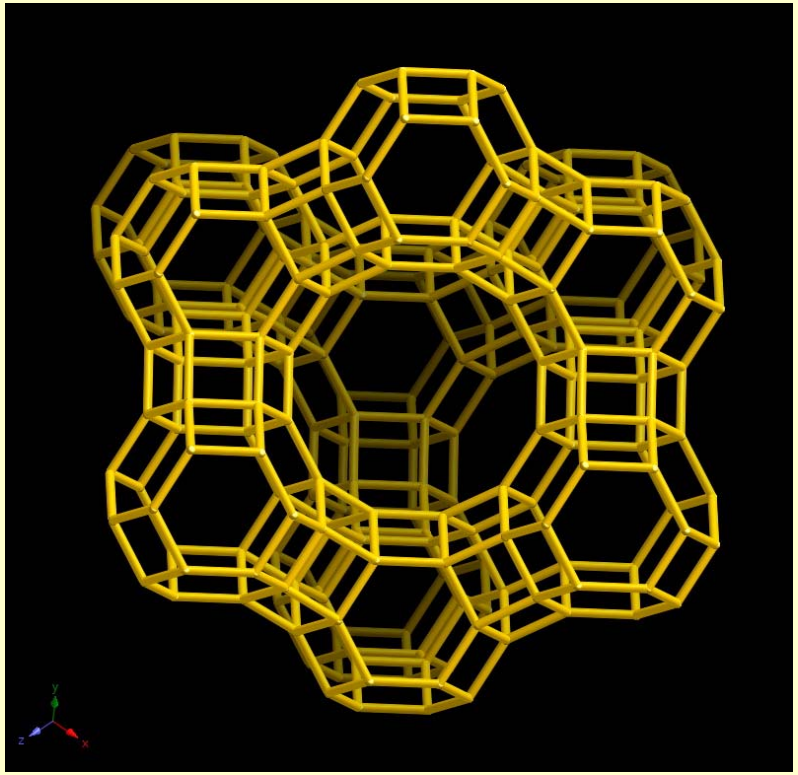


Fig. 1. Structure of zeolite Y: (a) cubic polymorph known as FAU with ABCABC... stacking, (b) hexagonal polymorph known as EMT with ABABAB... stacking.

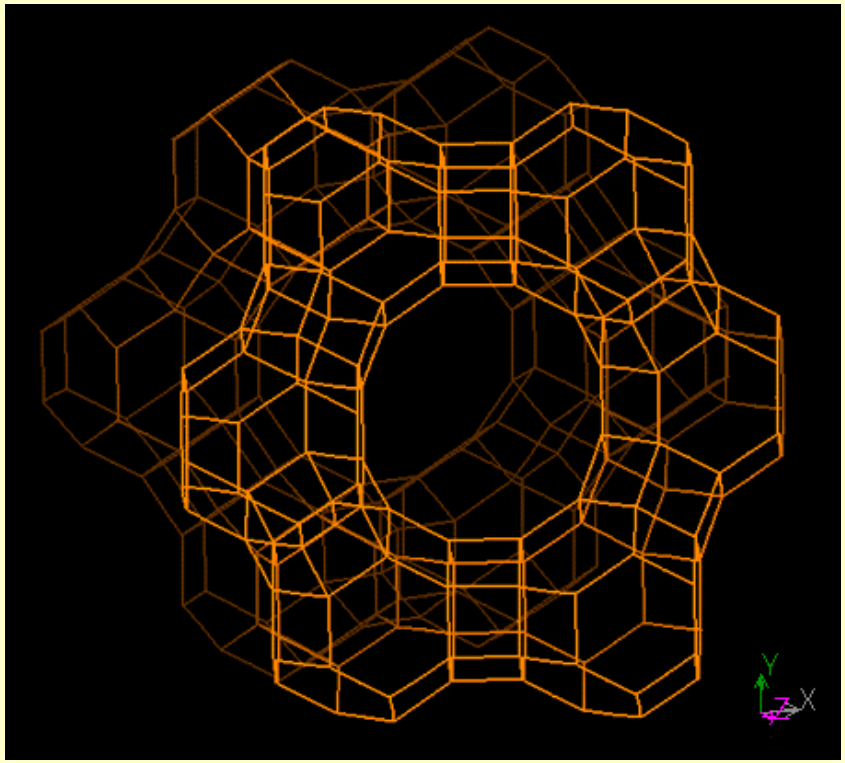
	FAU		
Cubic	ABCABC... stacking of layers agent	analagous to zinc blende	15-crown-5 structure directing agent
	EMT		
Hexagonal	ABABAB... stacking of layers	analagous to wurtzite	18-crown-6 structure directing agent

Zeolite FAU (X and Y) and EMT

Sodalite β-cage = carbon atom



Cubic diamond (sfalerite)

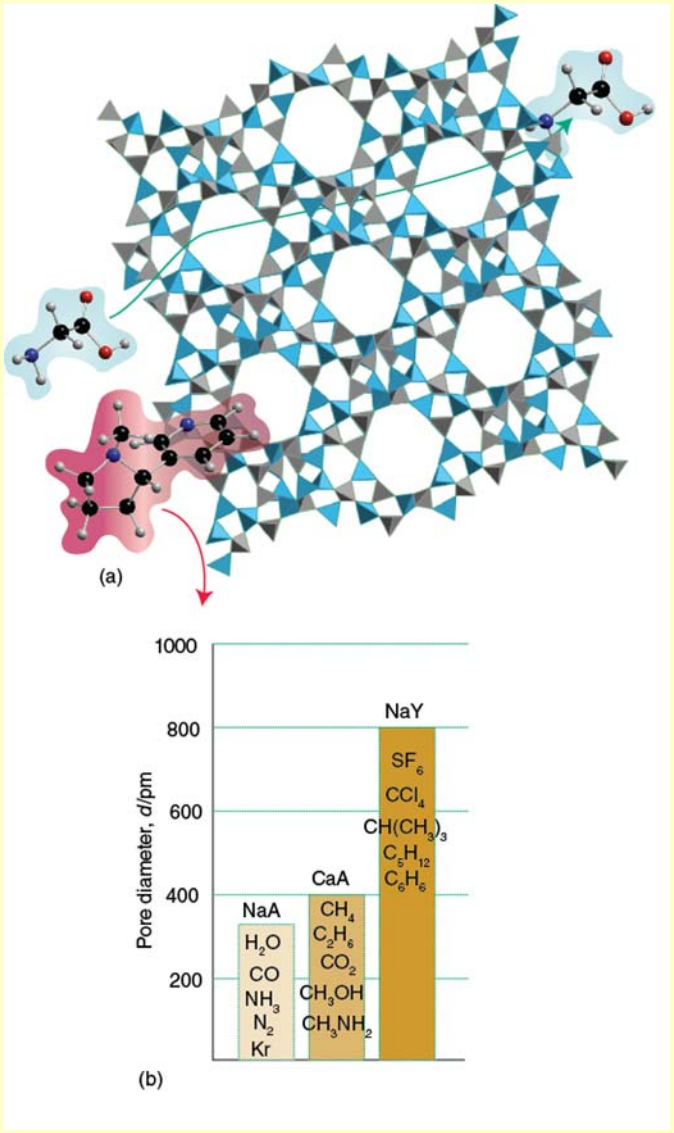


Hexagonal diamond (wurzite)

Molecular Sieves

Zeolite A = LTA
Zeolite X and Y = FAU

Zeolite	Cation	Code	Pore diameter
A	Na	4A	0.42 nm
	Ca	5A	0.48 nm
	Na, K	3A	0.38 nm
X	Na	13X	0.8-1.0 nm
	Ca	10X	0.7 nm
Y	as X, contains more Si		



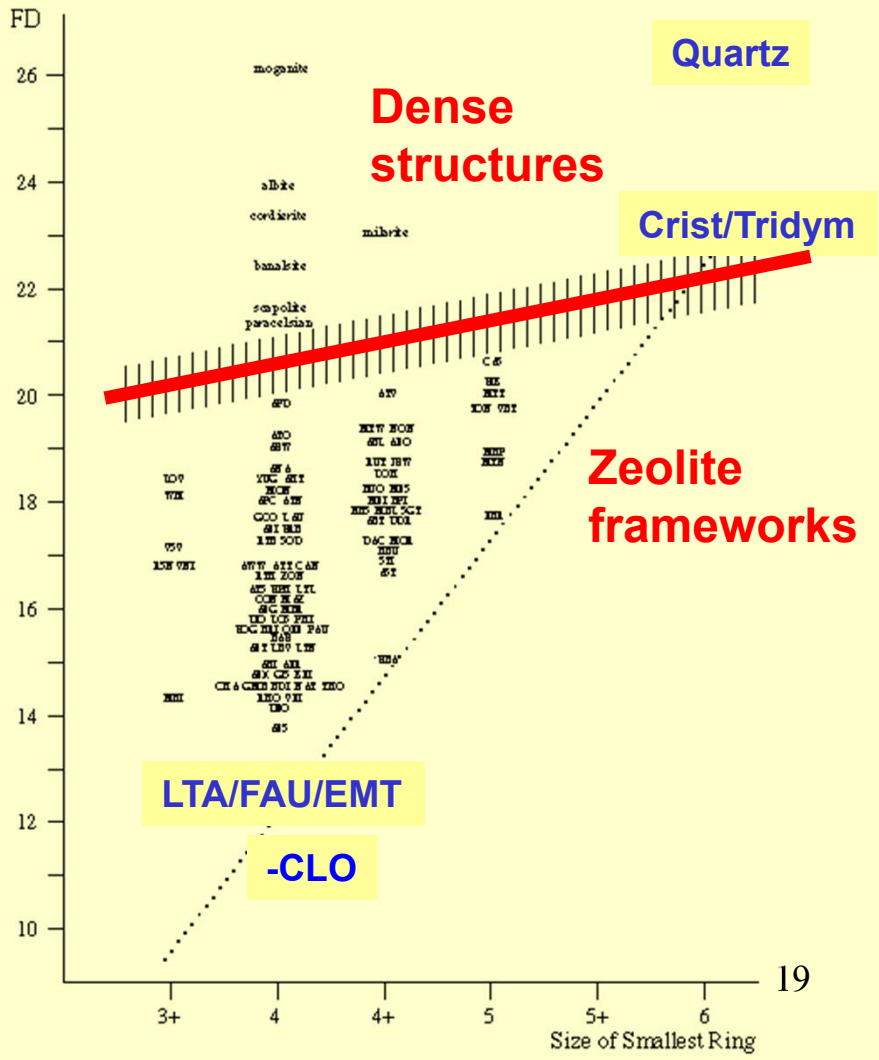
Framework Density

Framework density (FD)

FD = the number of tetrahedral atoms (T-atoms = Si, Al, P,…) per cubic nanometer (1000 Å^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



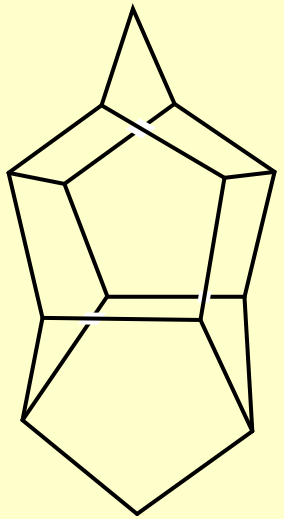
Pores

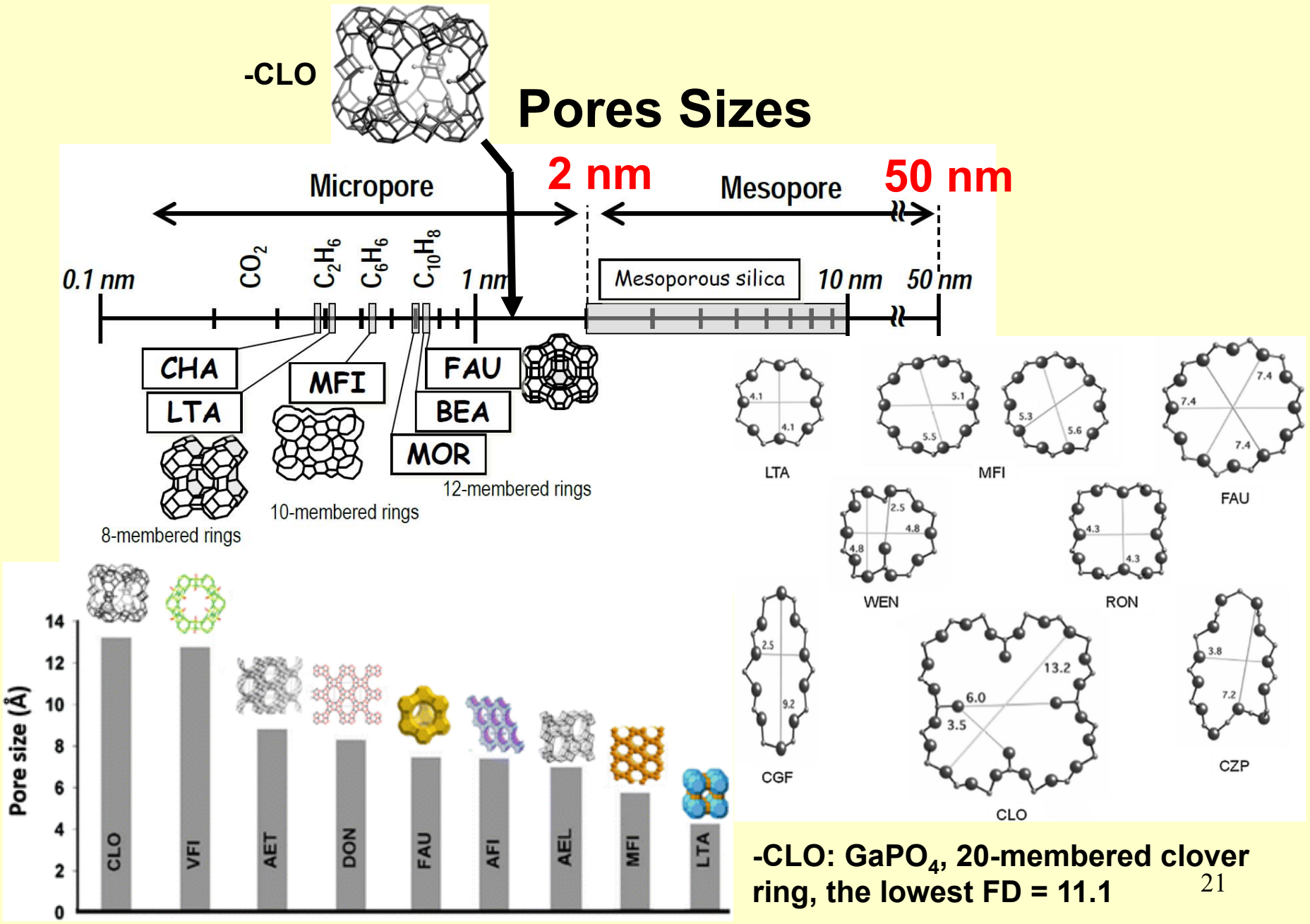
Various sizes (4 - 13 Å), shapes (circular, elliptical, cloverleaf-like), and connectivity (1-3D)
The size of the rings formed by the TO_4 tetrahedra ranges from 4 to 18 of the T-atoms and determines the pore aperture

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 = ∞**





-CLO: $GaPO_4$, 20-membered clover ring, the lowest FD = 11.1

Zeolite Synthesis

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

Aluminosilicates – at high pH

- **Mixing of precursors**

$NaAl(OH)_4(aq) + Na_2SiO_3(aq) + NaOH(aq)$, 25 °C

Condensation-polymerization, gel formation

- **Ageing of gel**

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

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

$Na_x(AlO_2)_x(SiO_2)_y.zH_2O$ (microcrystals)

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

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

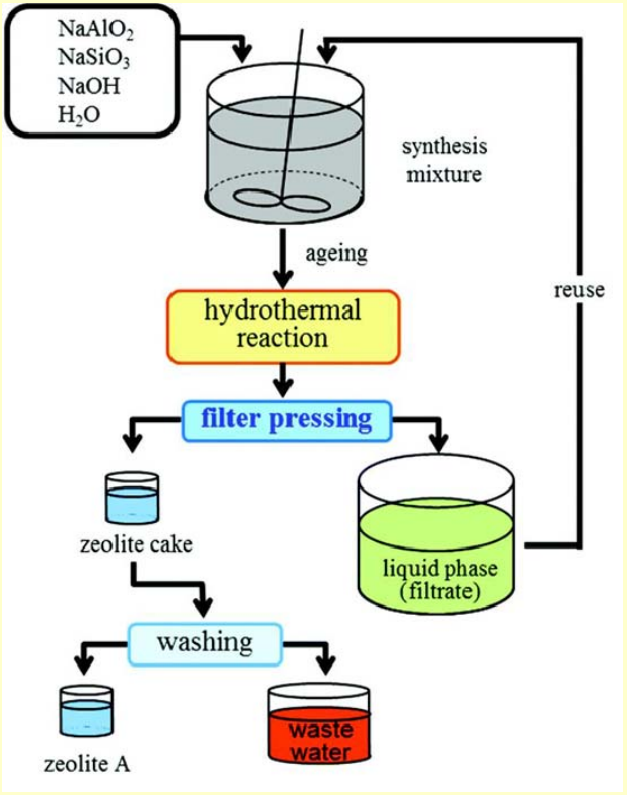
- template removal – calcination in O_2 at 400-900 °C removes the guest molecules from the framework without altering it

- **Extraction (neutral templates)**

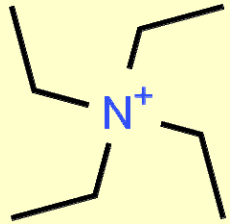
Zeolite Synthesis

Structure of the zeolite product depends on many reaction parameters:

- Composition, precursors
- 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: Inorganic cations (Na^+), organic cationic quaternary alkylammonium salts, alkylamines, aminoalcohols, crownethers, structure-directing, space-filling, charge-balancing

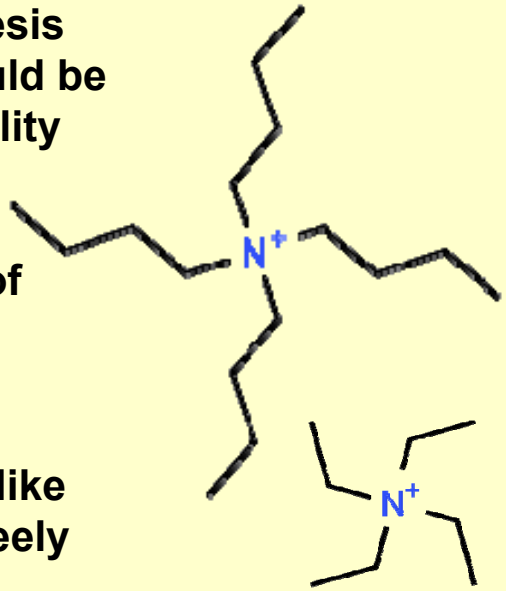


Templates

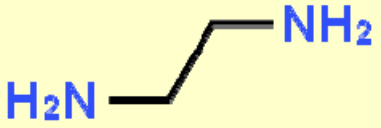
Templates or guest compounds – Structure directing agents (SDA)
Three levels of the guest action with increasing structure-directing specificity:

■ **Space-filling - the least specific, observed, e.g., in the synthesis of $AlPO_4$-5: 23 different, structurally unrelated compounds, could be employed, packing in the channels 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**



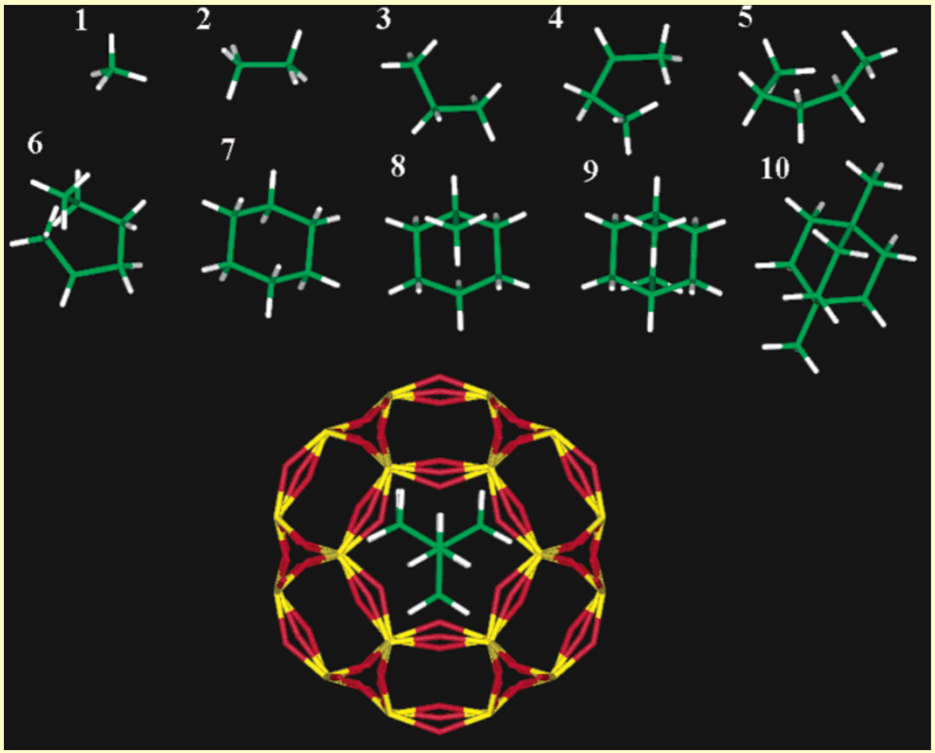
A curiosity: aluminophosphate VPI-5 does not require any guest for its formation!

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

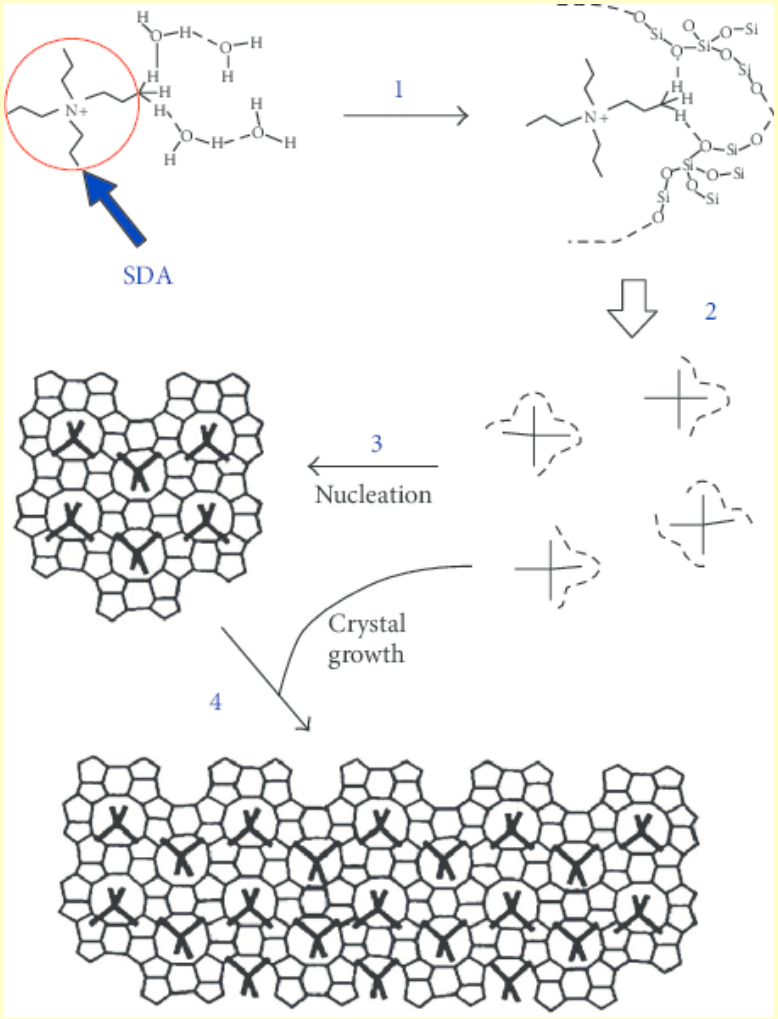
Structure directing agents (SDA)

(1) Formation of hydrogen bonds / charge attraction between the structure directing agent (SDA) and the silicates present in the synthesis solution

(2) Oligomerisation of silicates to primary units (2-3 nm)

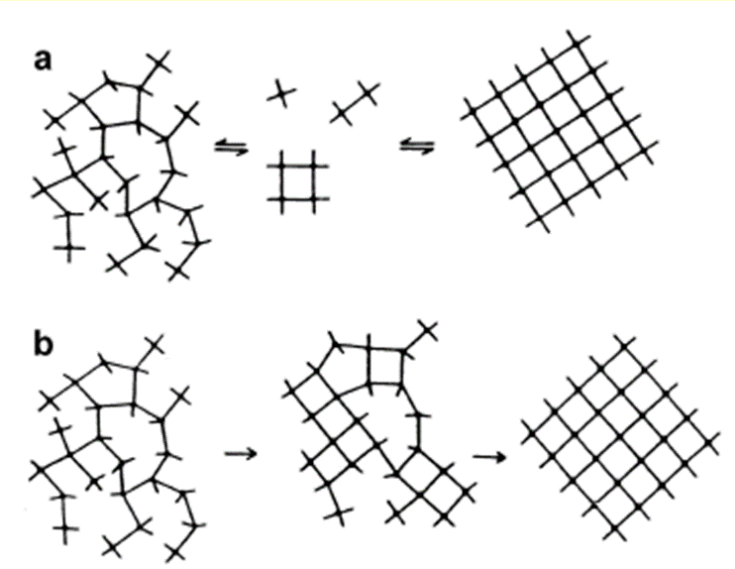
(3) Condensation of the silicate-SDA species to give the first stable crystalline nuclei (10 nm)

(4) Crystal growth (10-100 μm)

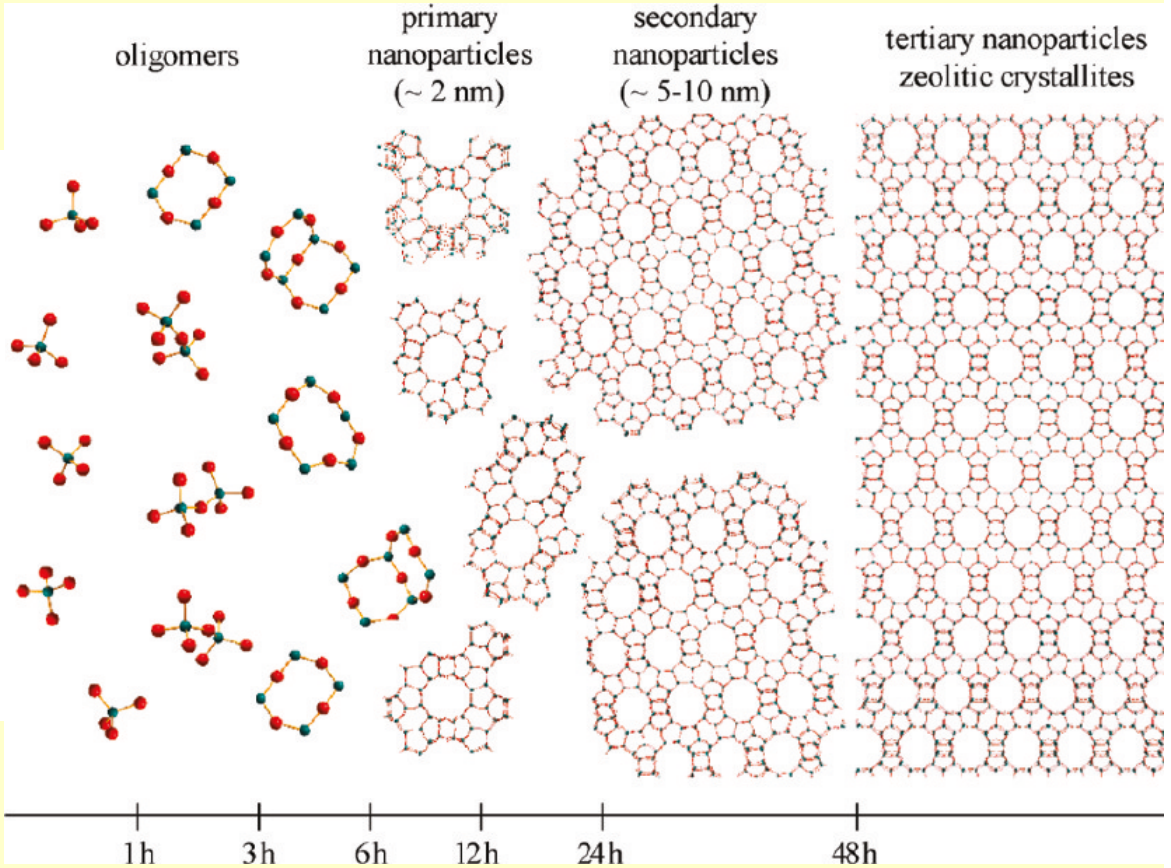


Zeolite Synthesis Mechanisms

Gel dissolution and solution mediated crystallization (SBU in solution)

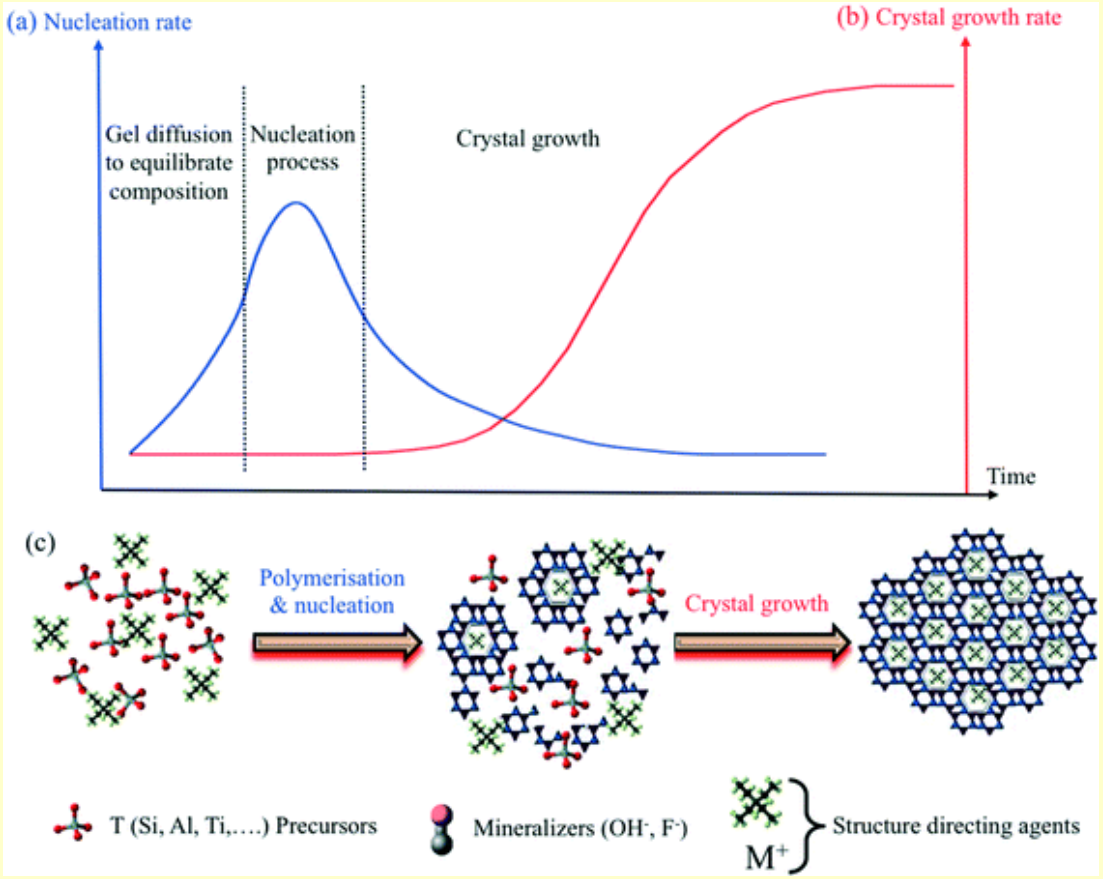


“In situ” rearrangement of the gel



Crystallization Mechanism

Crystallization kinetics of zeolite formation



Zeolites

Wide range of solid state characterization methods for zeolites: diffraction, microscopy, spectroscopy, thermal, gas adsorption

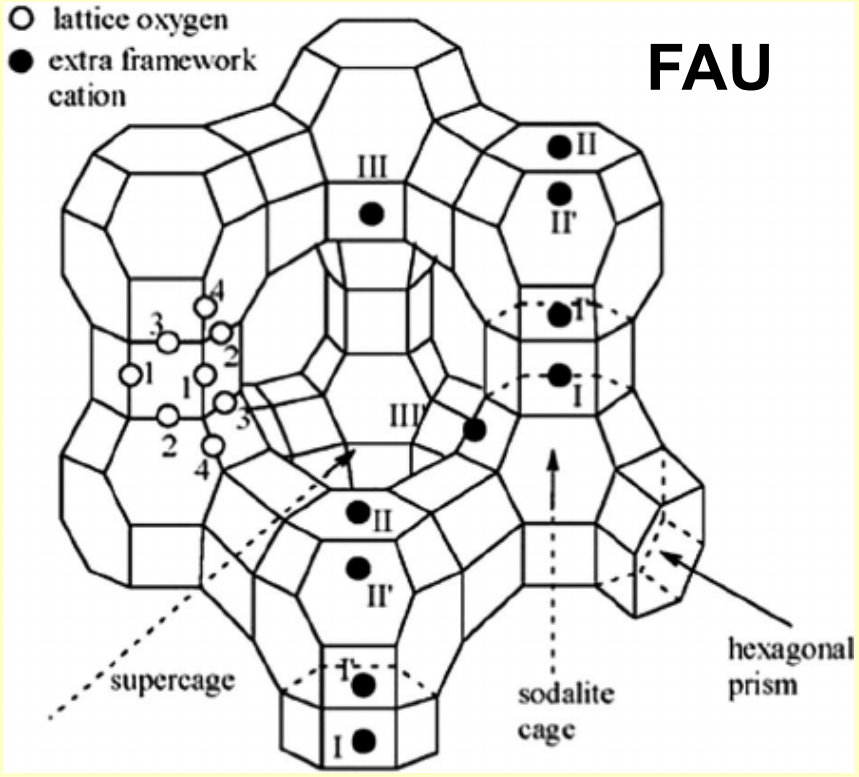
Zeolite post modification for controlling properties of zeolites

Tailoring channel, cage, window dimensions:

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

- Lőwenstein rule - the principle of aluminium avoidance: never Al-O-Al
- Dempsey rule: Al-O-Si-O-Si-O-Al is more stable than Al-O-Si-O-Al, negative charges at Al as far as possible
- NNN-principle: minimalization of Al-Al-next-nearest neighbor interactions

Cation Positions



Several extra framework sites are occupied by cations in faujasites (FAU)

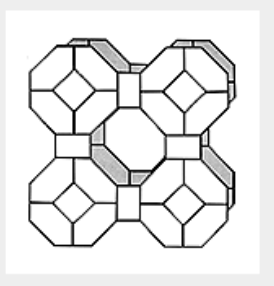
A standard nomenclature:

I at the center of the double 6-rings
I' in the sodalite cage, adjacent to a hexagonal ring shared by the sodalite cage and a double 6-ring
II in the supercage, adjacent to an unshared hexagonal face of a sodalite cage
II' in the sodalite cage, adjacent to an unshared hexagonal face
III is located on the walls of the supercage

Applications of Natural Mineral Zeolites

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

Applications of Synthetic Zeolite



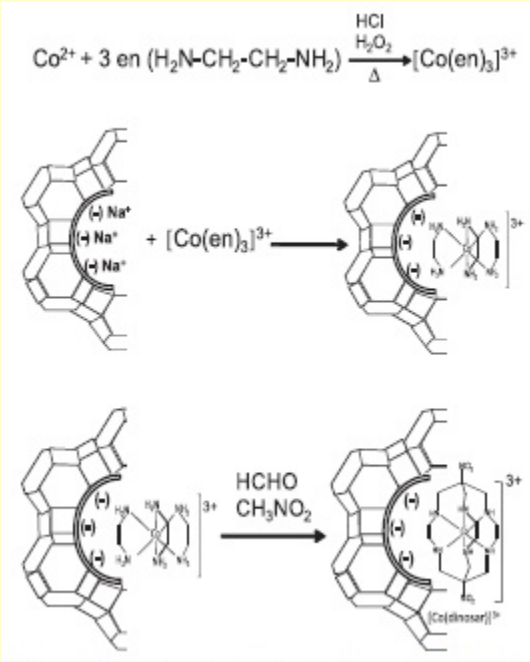
Production 1.6 million tons p.a. (about half that of natural zeolites)

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

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 (ship-in-a-bottle)



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

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

Brønsted Acidity

Solid acid catalysts for the hydrocarbon cracking

Introducing Bronsted acidity into zeolites:

(1) direct H^+-exchange of the charge-compensating metal cations

(2) NH_4^+ -exchange of the compensating metal cations followed by calcination to decompose the ammonium cation leaving a proton on the surface

(3) exchange with polyvalent cations that can generate H^+ via partial hydrolysis of H_2O molecules

(4) exchange by metal cations that can be reduced by H_2 to a lower valence state, generating protons on the surface

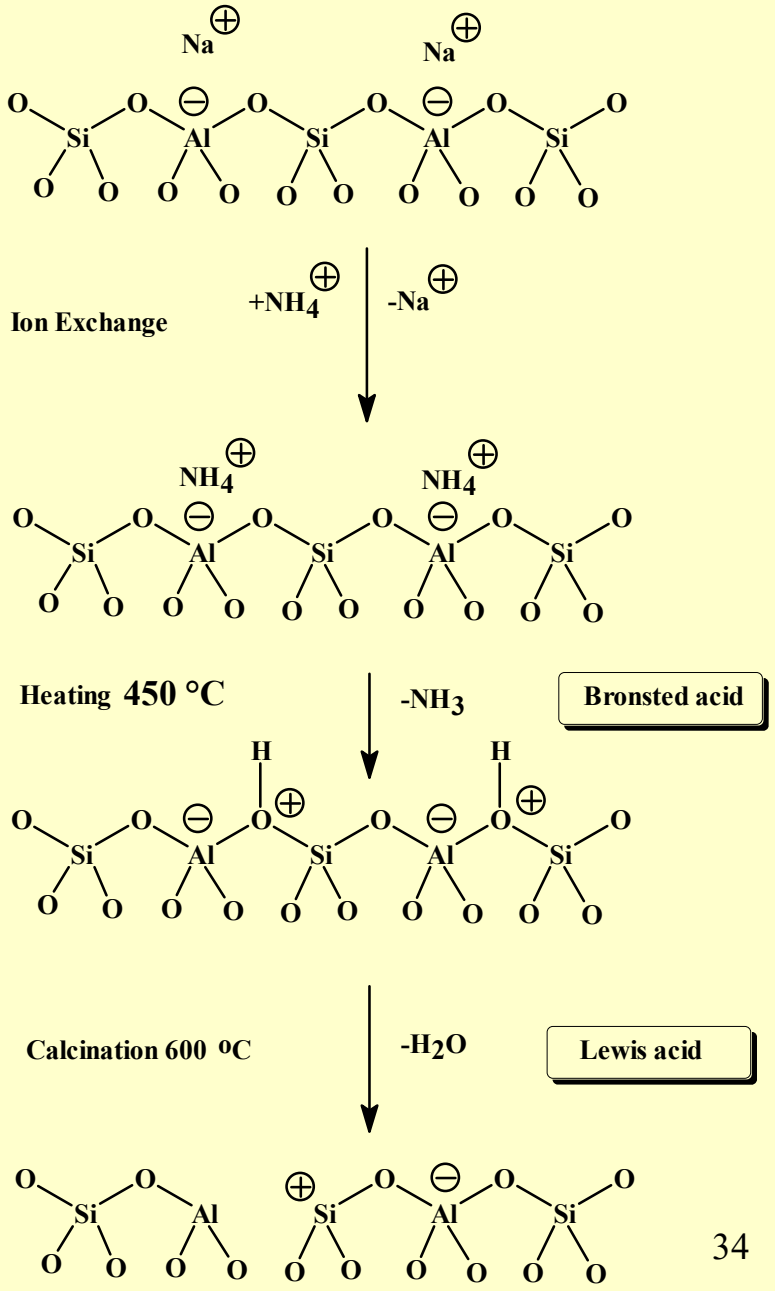
Brønsted Acidity

Tuning Brønsted acidity:

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

Solid acid for the hydrocarbon cracking

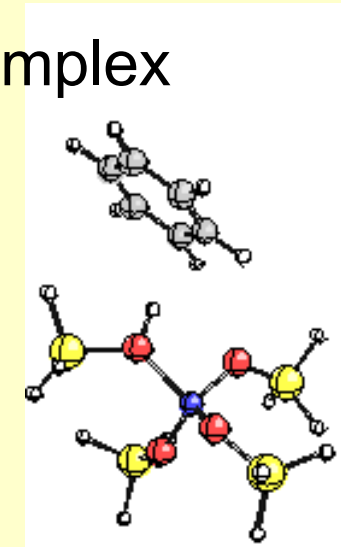
The larger the Si/Al ratio of a zeolite, the more Brønsted acidic is the OH, but the number of these sites decreases

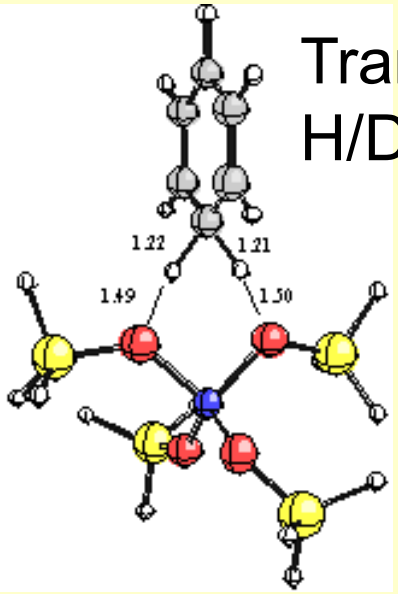


Strong Brønsted Acidity

Protonation of benzene

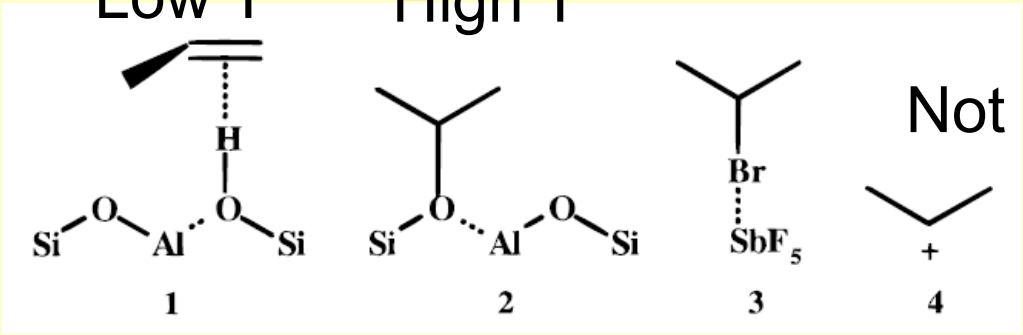
π-complex





Transition state for H/D exchange

Low T High T



Not present in zeolites

Brønsted Acidity

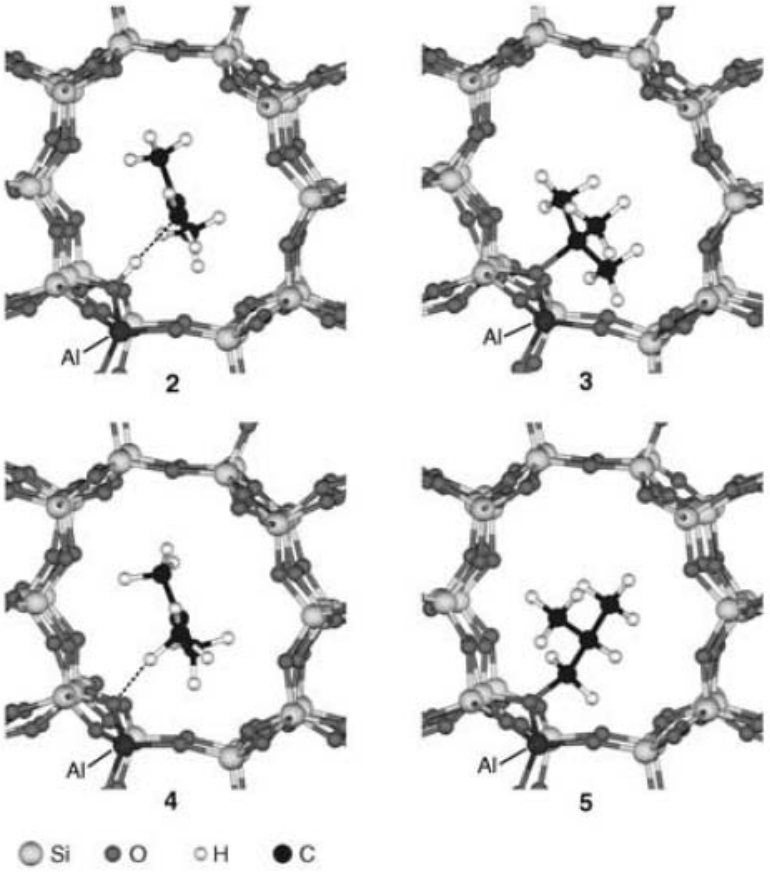
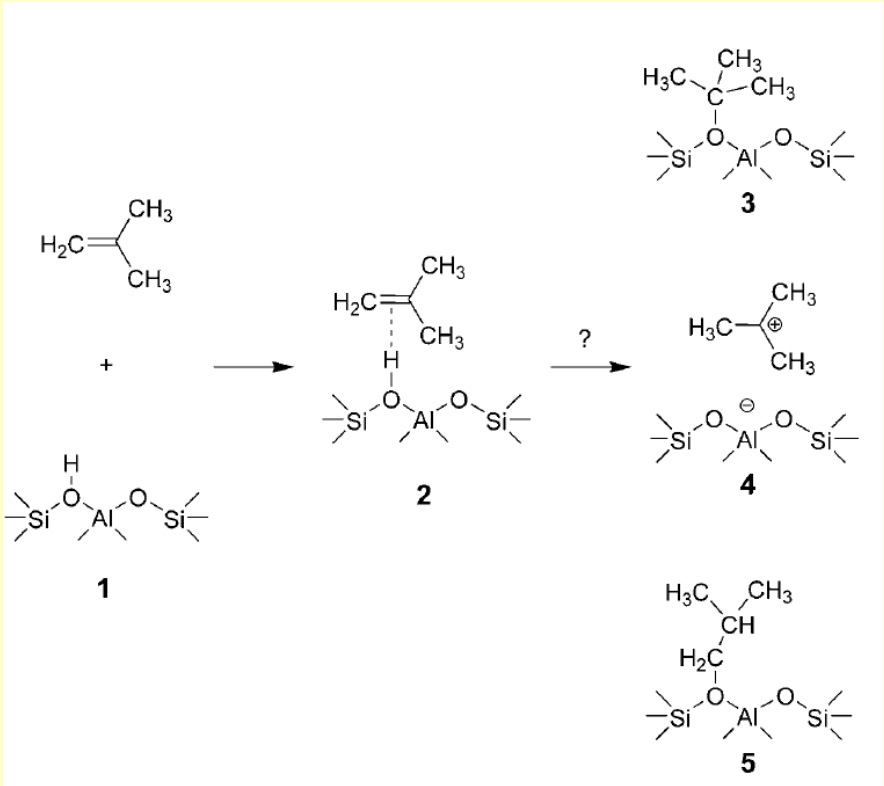
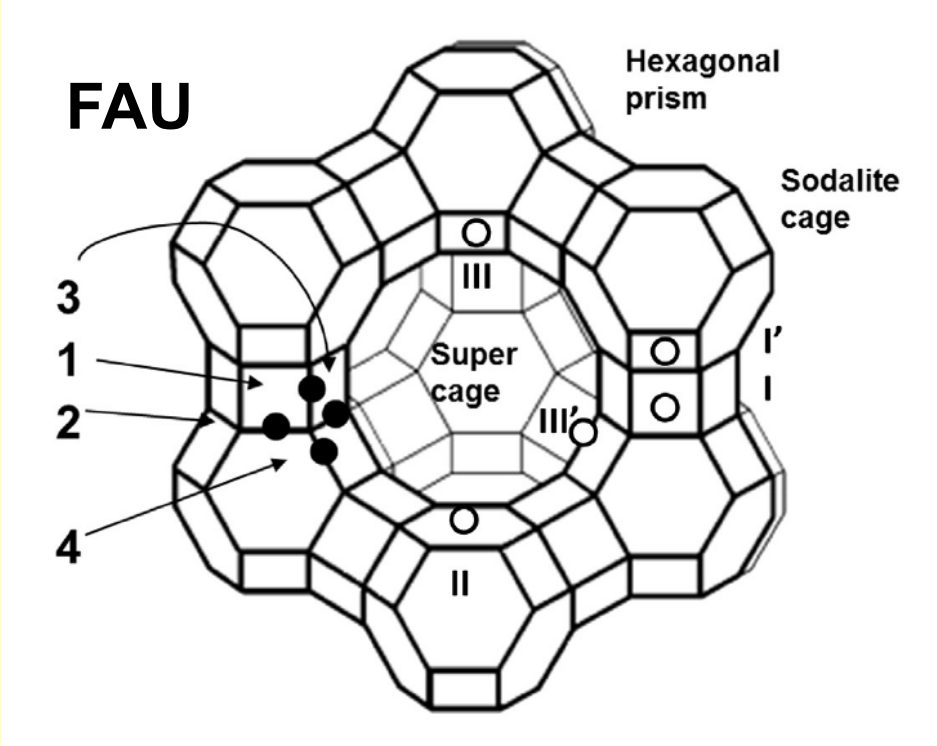
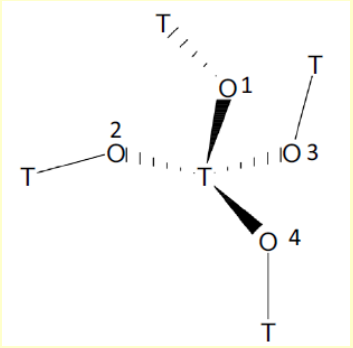


Figure 1. Portions of the structures calculated for the π complex of isobutene in ferrierite (**2**), for the *tert*-butyl cation in ferrierite (**4**), and for the *tert*-butoxide (**3**) and isobutoxide (**5**) of ferrierite.



Brønsted Acidity





IR vibrations for OH groups located at different sites in FAU

(● = lattice oxygens)

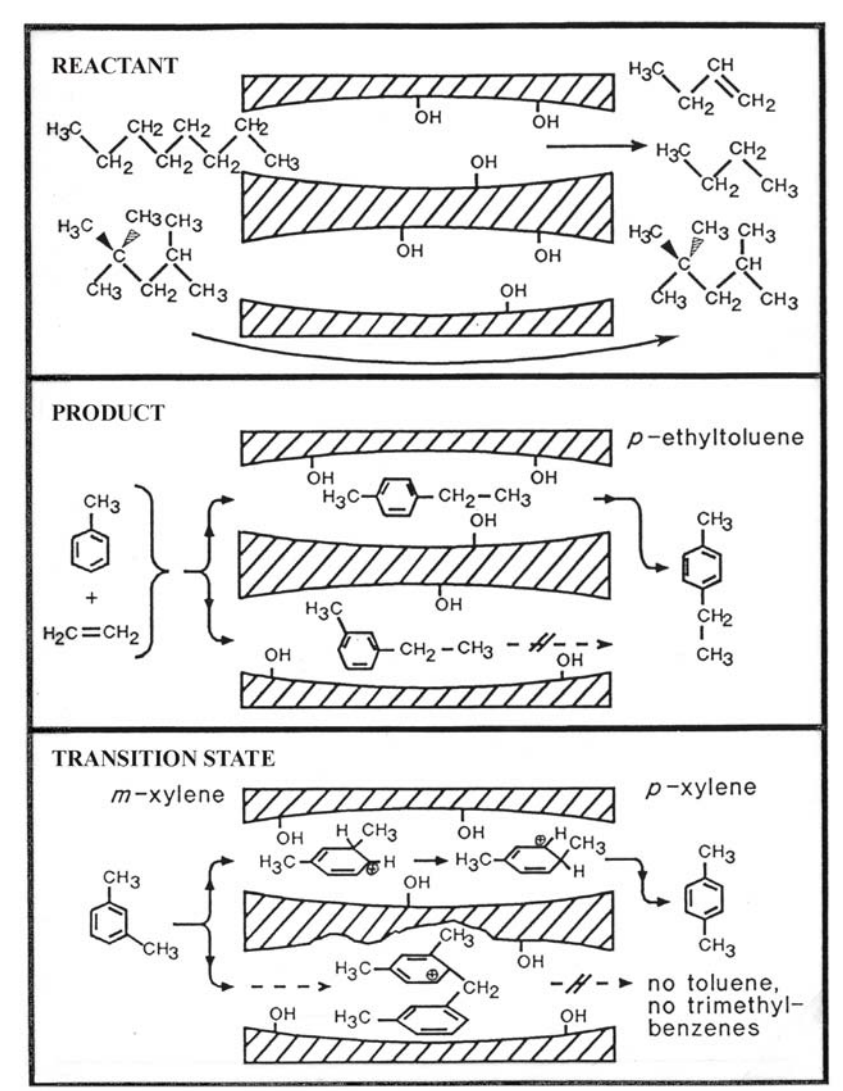
3648 cm^{-1} site 1 (pointing to the supercage)
3625 cm^{-1} site 1‘ or 4 (pointing to the supercage)
3571 cm^{-1} site 2 (pointing to the sodalite cage)
3526 cm^{-1} site 3 (pointing to the hexagonal prism)
3744 cm^{-1} free terminal OH at the external surface

Size-Shape Selectivity

Size-shape selective catalysis, separations, sensing

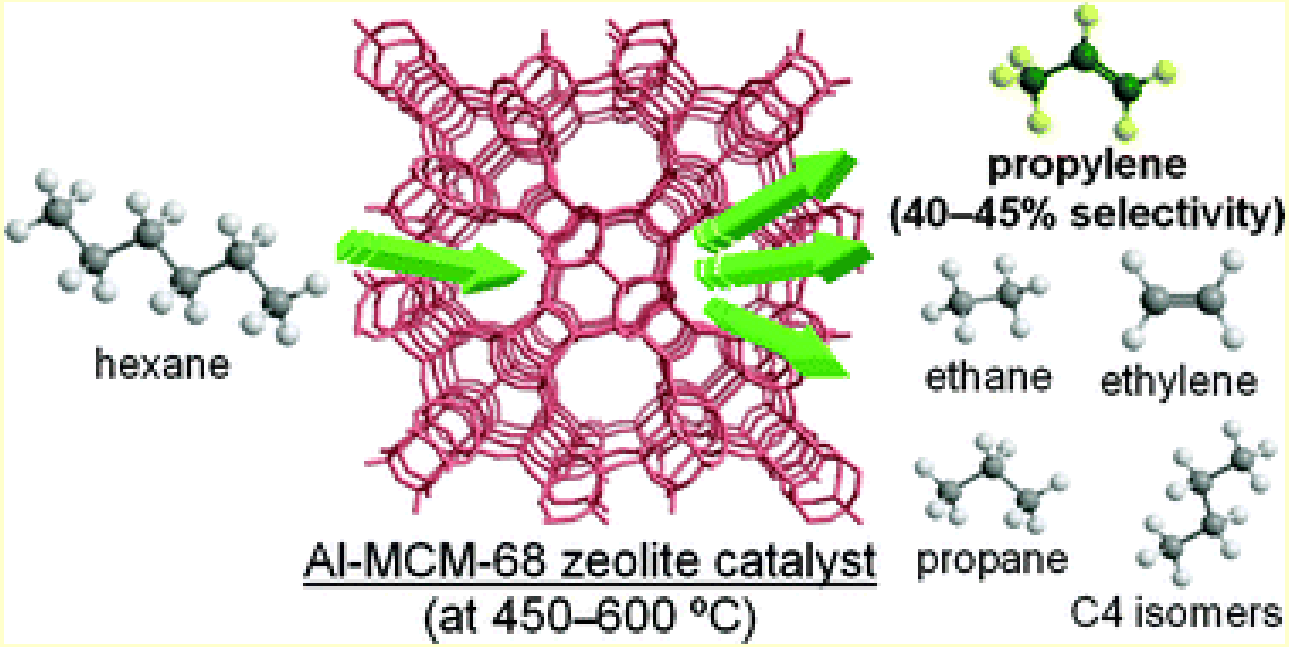
Selectivity at:

- **Reactants**
- **Products**
- **Transition state**



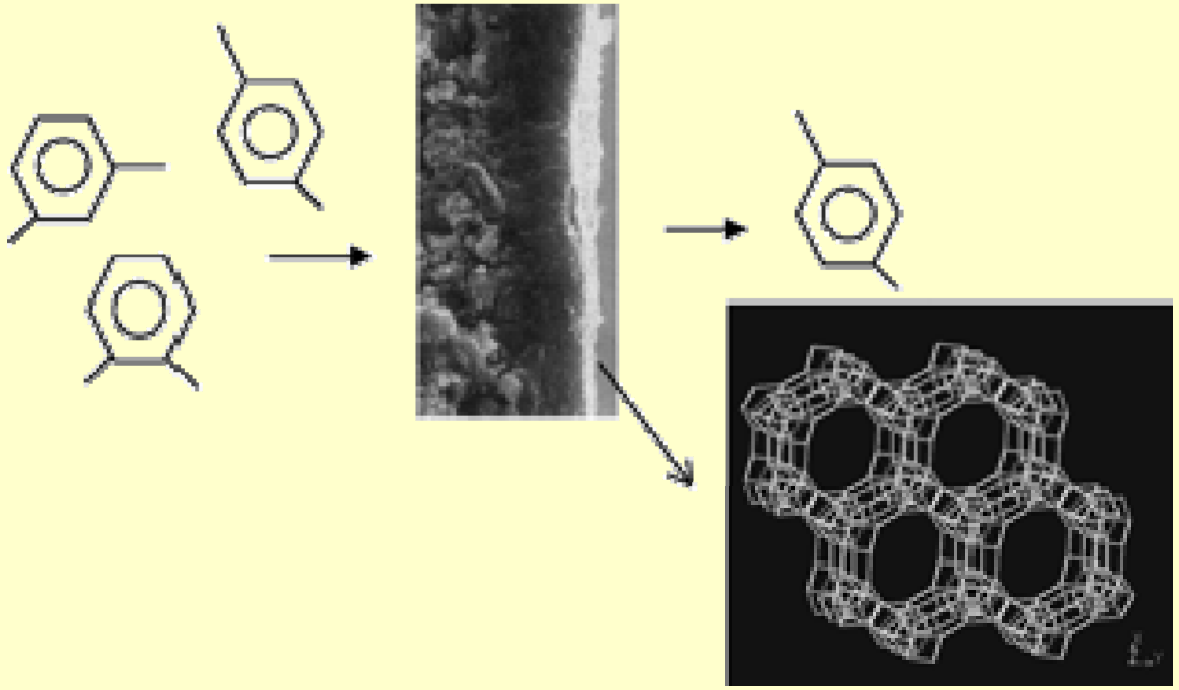
Fluid Catalytic Cracking (FCC)

Size-shape selective catalysis of hexane cracking
MSE zeolite - framework with 3-dimensional 10-MR or 12-MR micropores
Si/Al = 51
High selectivity to propylene, low coking



Gas Separation by Zeolites

Separation of xylene isomers by pervaporation through a MFI membrane



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

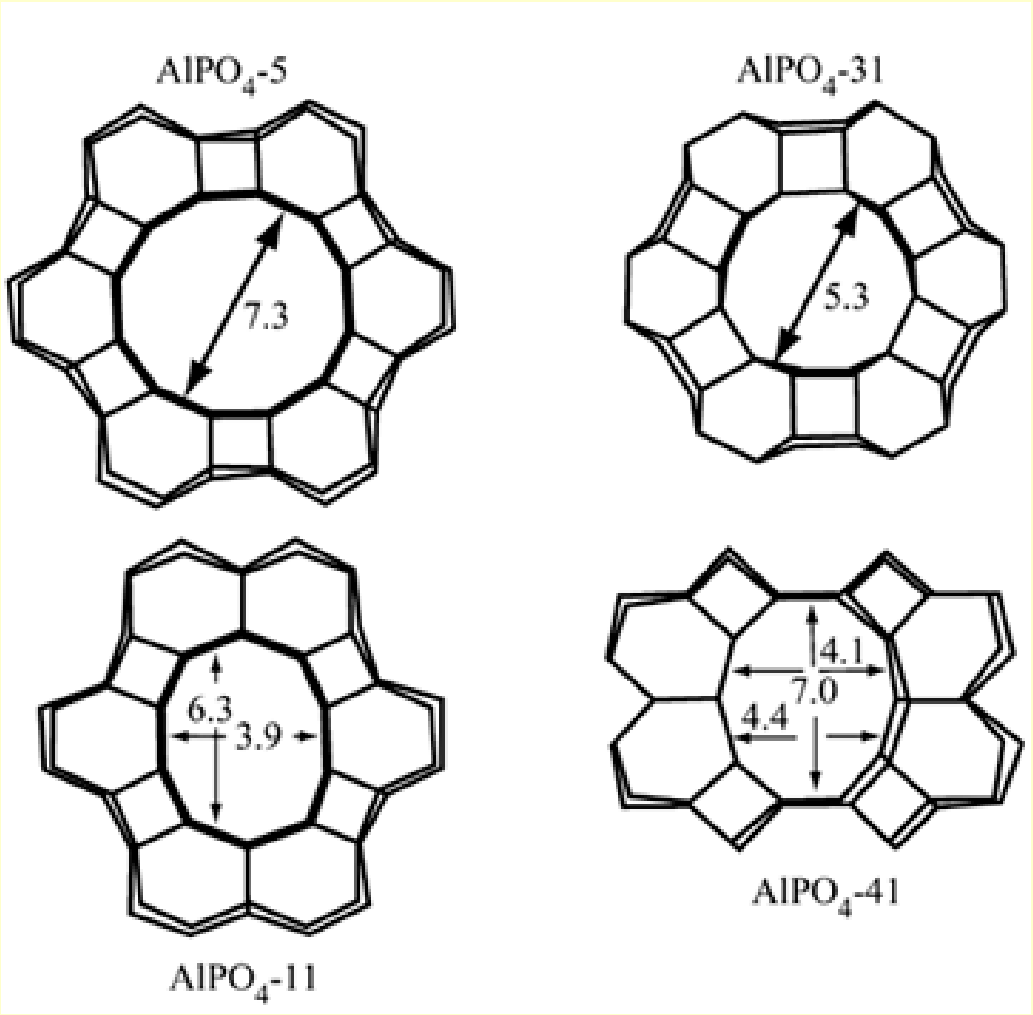
Incorporation of elements such as Si, Mg, Fe, Ti, Co, Zn, Mn, Ga, Ge, Be, Li, As, and B into the tetrahedral sites of $AlPO_4$ gives a vast number of element-substituted molecular sieves (MeAPO, MeAPSO, SAPO) important heterogeneous catalysts
M^{1+}, M^{2+}, and M^{3+} incorporate into the Al sites
M^{5+} 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

AFI(ve)

AEL(even)



ATO(three-one)

AFO(four-one)

Aluminophosphate Synthesis

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

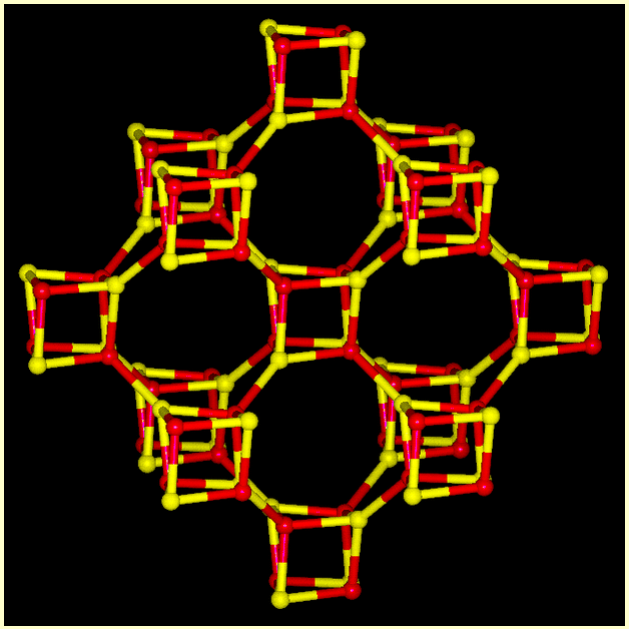
Mixing with aqueous H_3PO_4 in the equimolar ratio – low pH !
Forms an $AlPO_4$ gel, left to age
One equivalent of a guest compound = template
Crystallization in a reactor
Separated by filtration, washed with water
Calcination

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

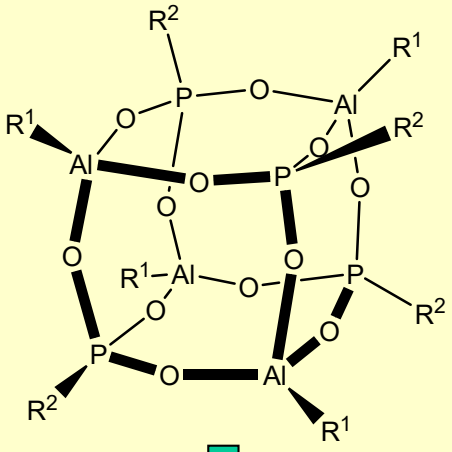


ACO

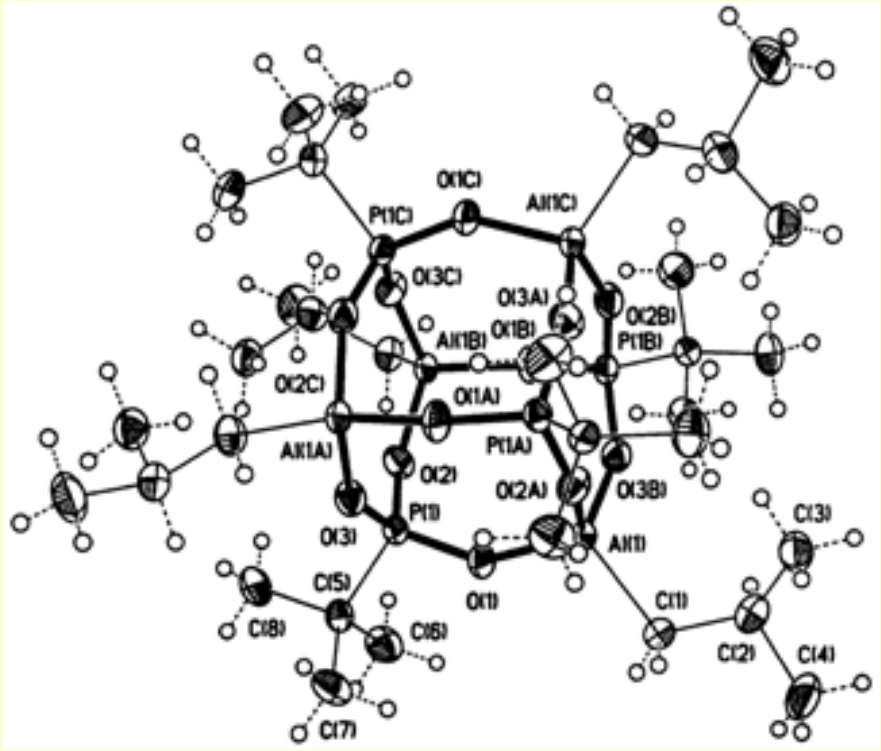
$Al(O\text{-}iPr)_3$, $CoCO_3.H_2O$, 85% H_3PO_4, ethylene glycol, ethylenediamine, pH 8.4
Heated in a Teflon-coated steel autoclave at 180 °C for 4 d

Synthesis of Double 4-ring Units (D4R)

Connect the double 4-ring units (D4R)



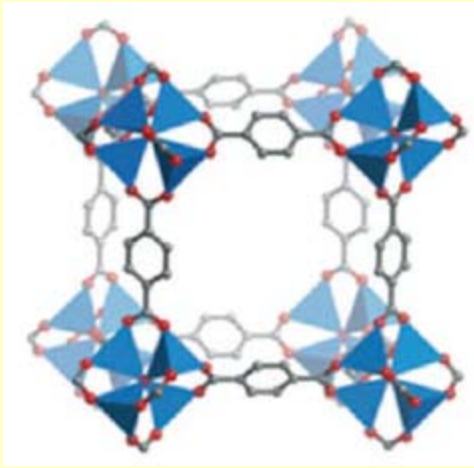
ACO



Metallo-Organic Framework (MOF) Structures

20 000 structures known (2019), 1000 new per year

Porous coordination polymers (PCP)

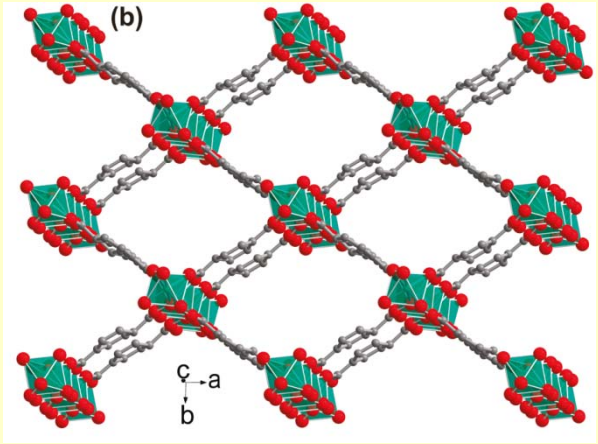


Metal centers

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

Polytopic Ligands

- Organic spacers
- Flexible – rigid
- Variable length
- Directionality



Reticular Chemistry

A building-block approach to the synthesis of nanostructured materials

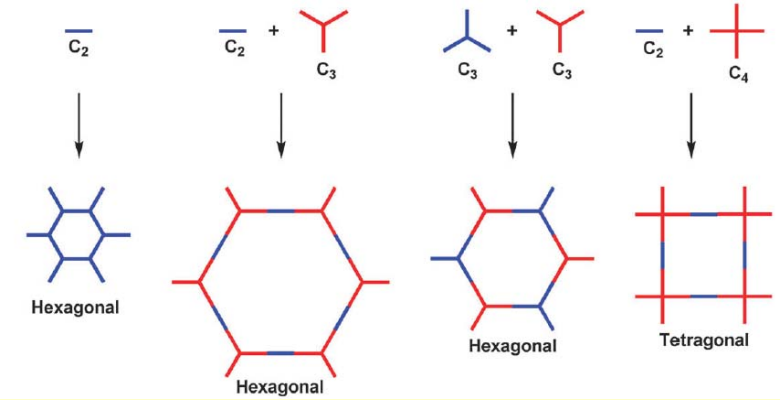
Materials formed by a bottom-up self-assembly of building blocks (reticuli) with predetermined symmetry

Targeted, predictable, and straightforward design and synthesis

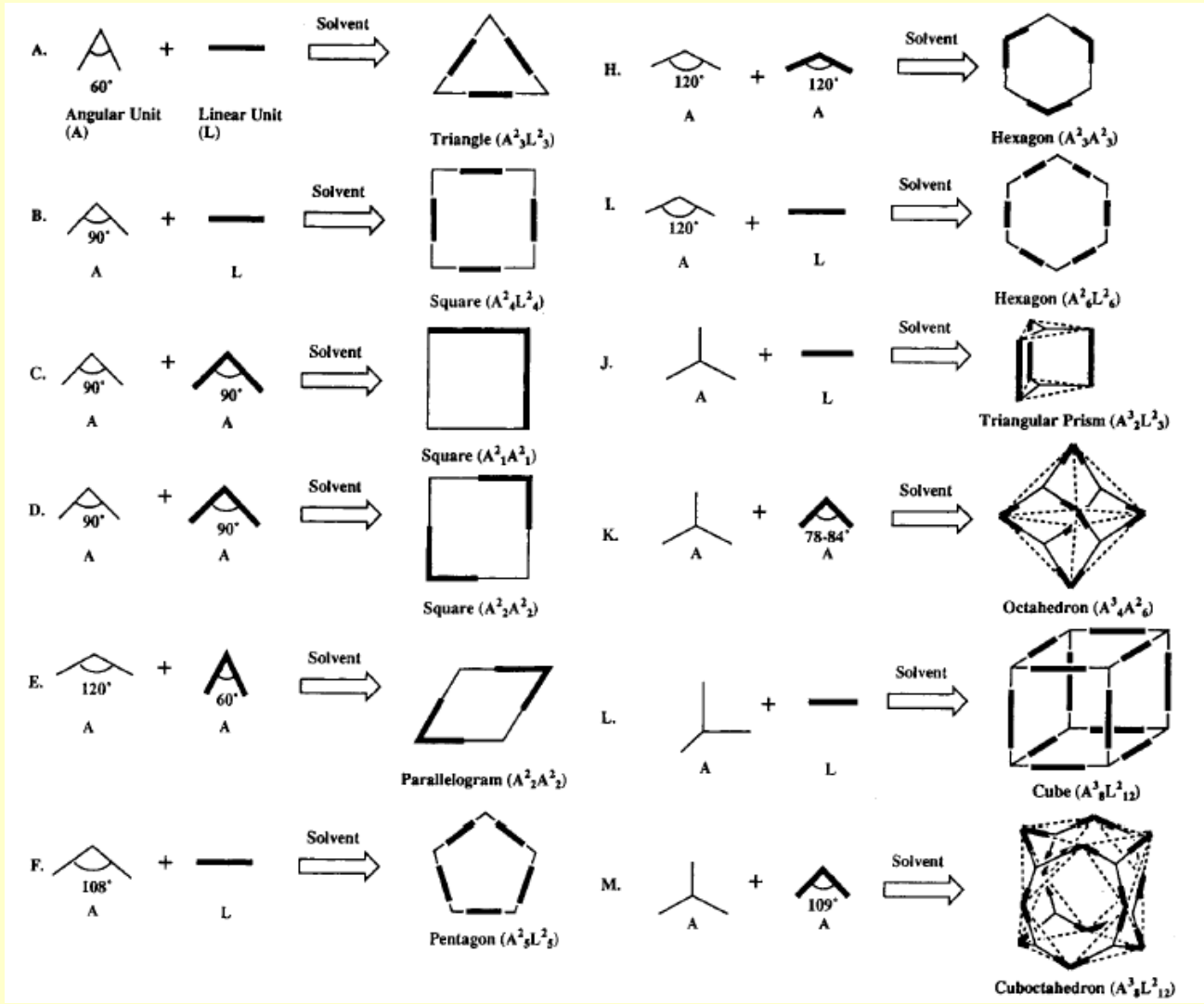
Chemistry of the self-assembly and the design should not interact

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**

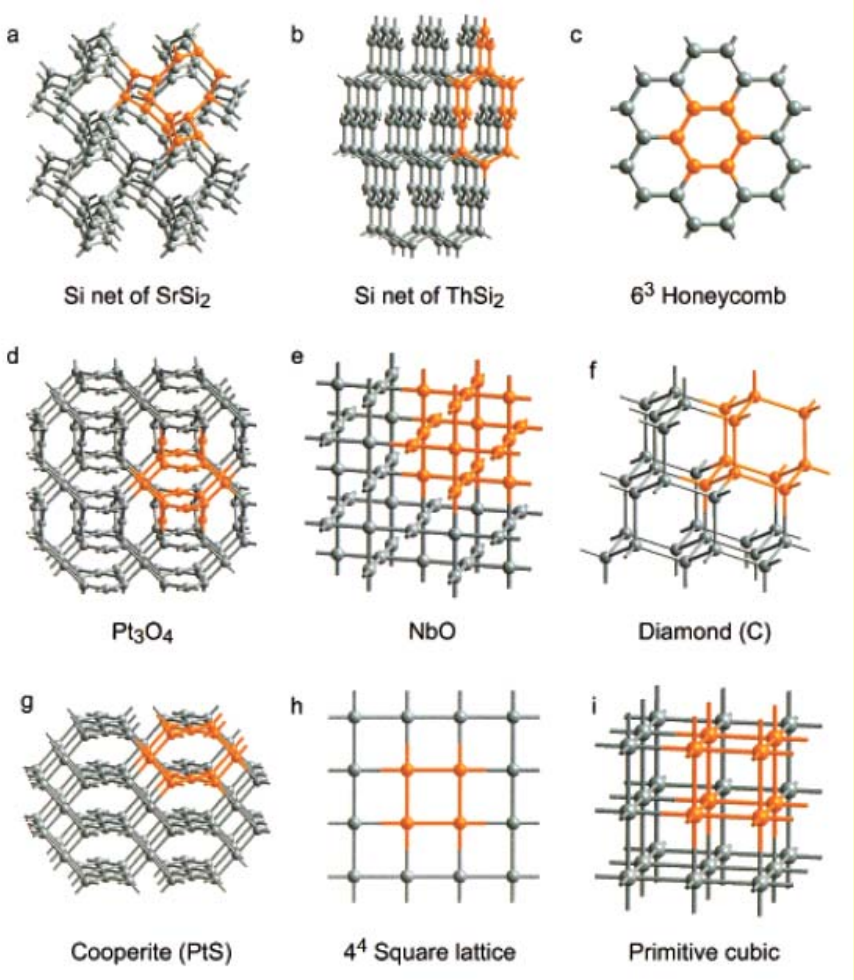


Reticular Chemistry



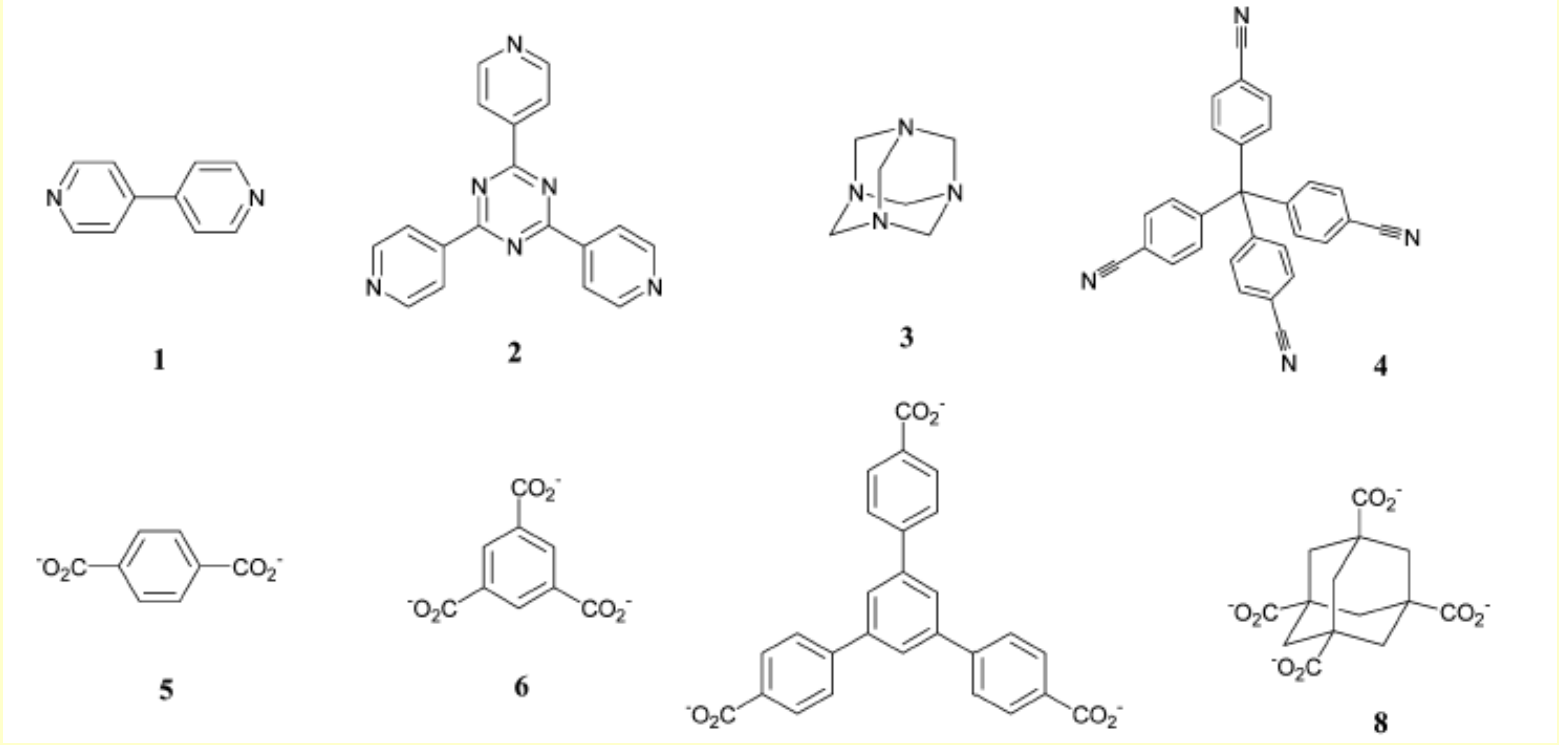
Basic Nets

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



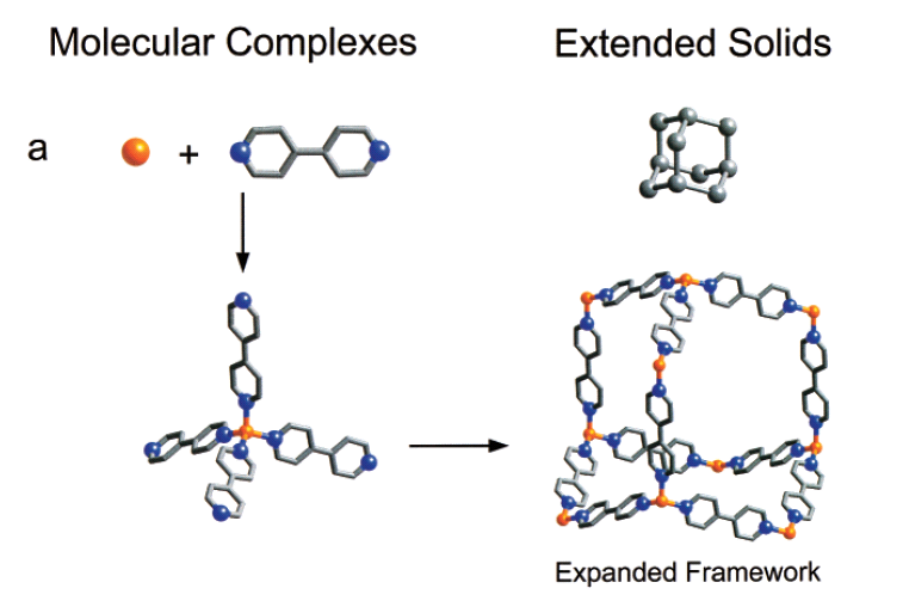
Polytopic Organic Linkers

- **N-based polydentate donors**
- **Carboxylates**



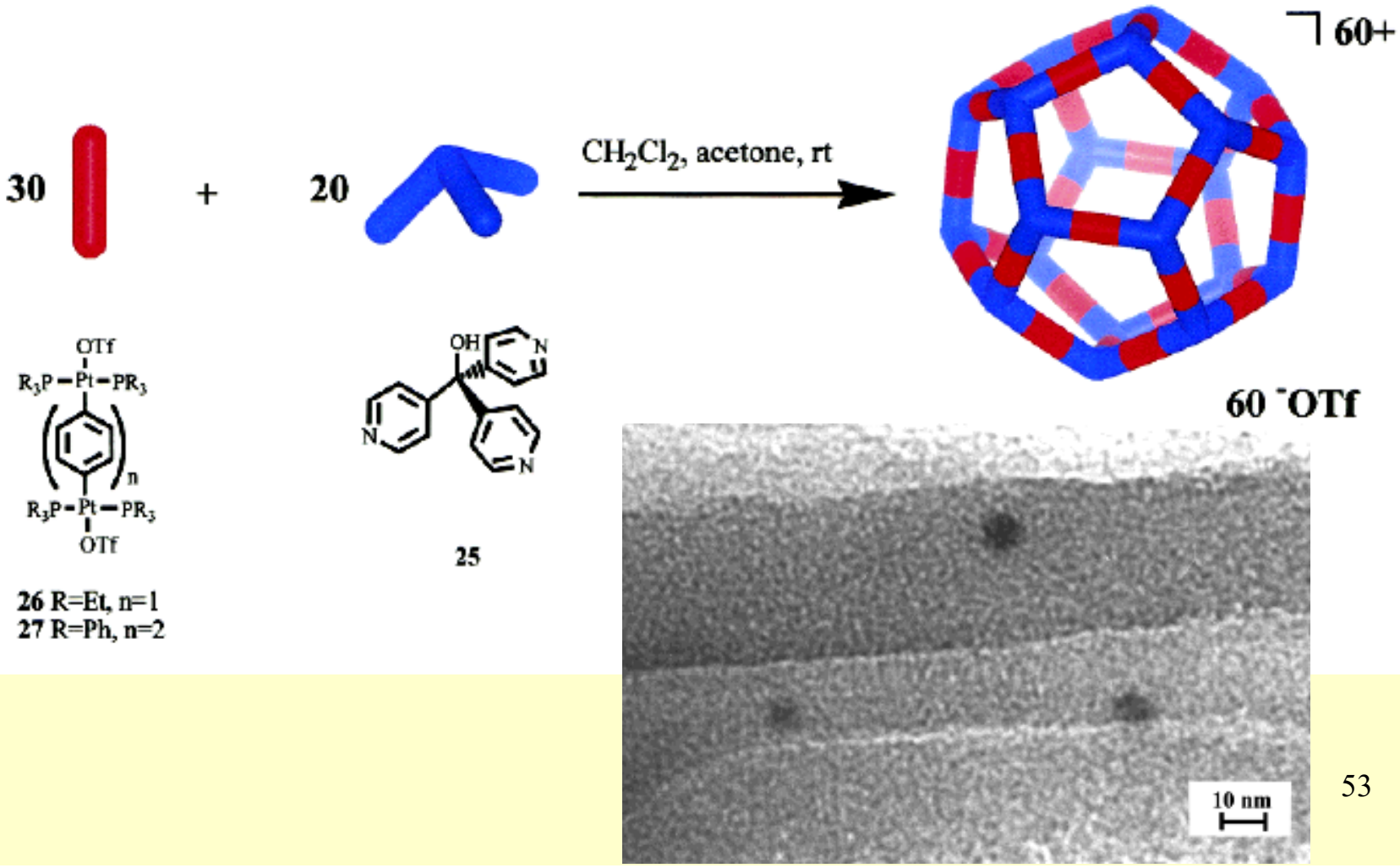
Polytopic N-bound Organic Linkers

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



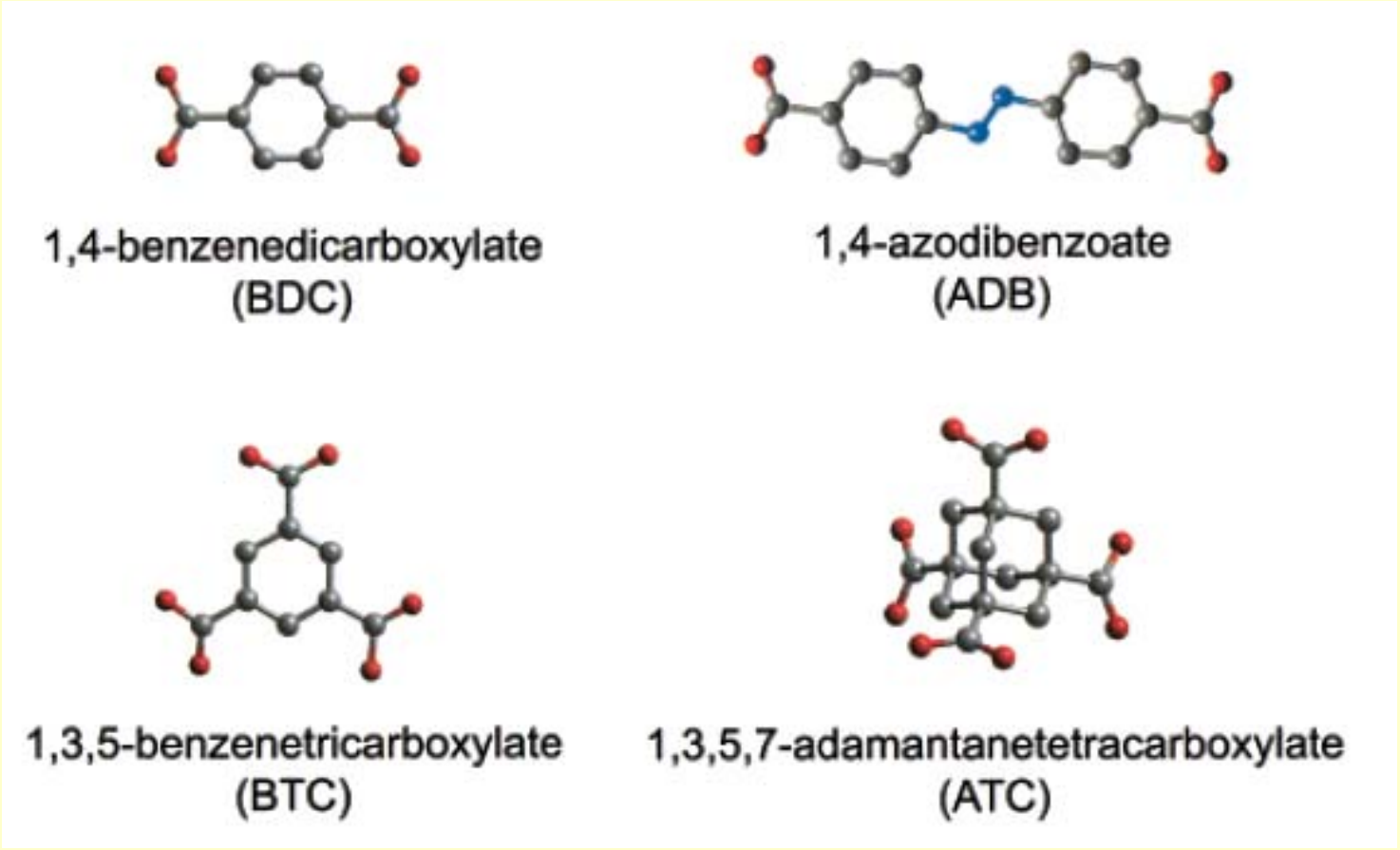
Metallo-Organic Framework Structures

Scheme 4. Self-Assembly of Dodecahedra



26 R=Et, n=1
27 R=Ph, n=2

Polytopic Carboxylate Linkers

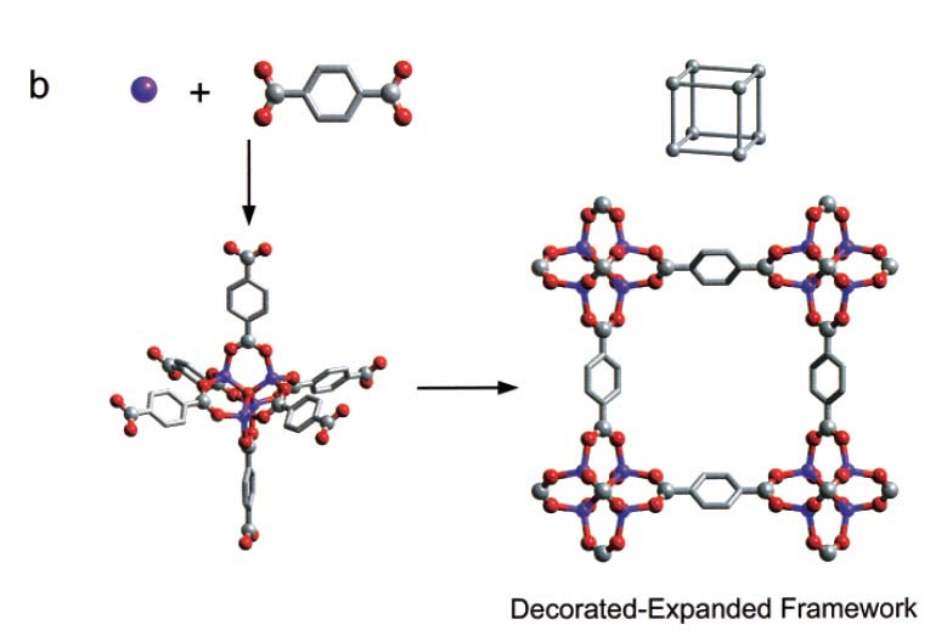


Polytopic Carboxylate Linkers

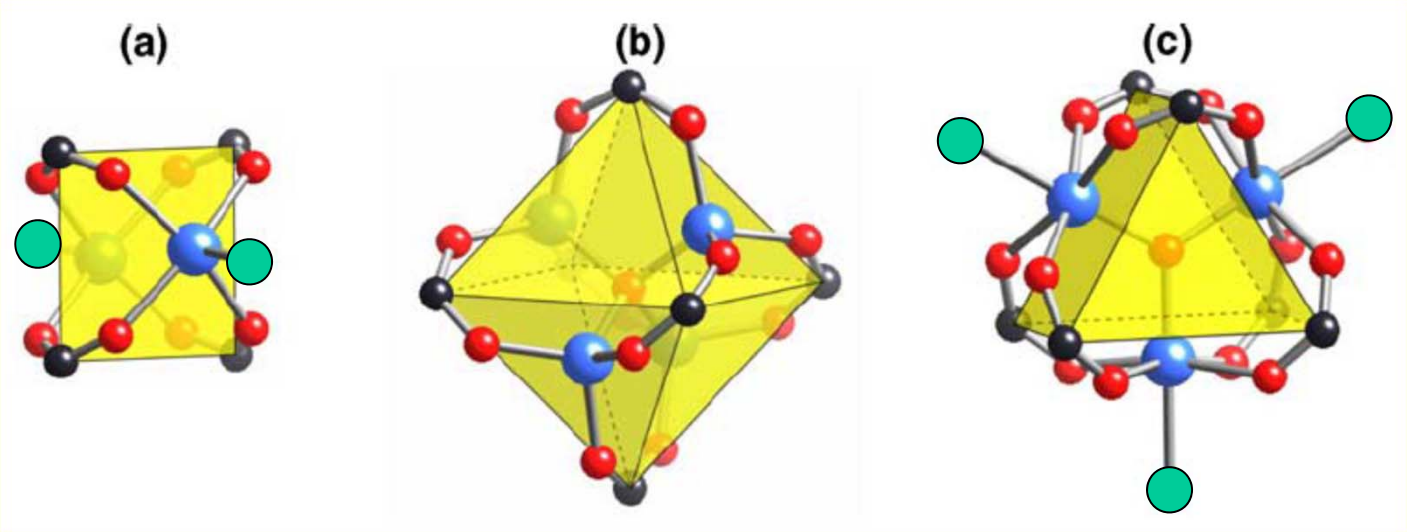
Aggregation of metal ions into M-O-C clusters

- **form more rigid frameworks**
- **frameworks are neutral**
- **no need for counterions**

Molecular Complexes Extended Solids



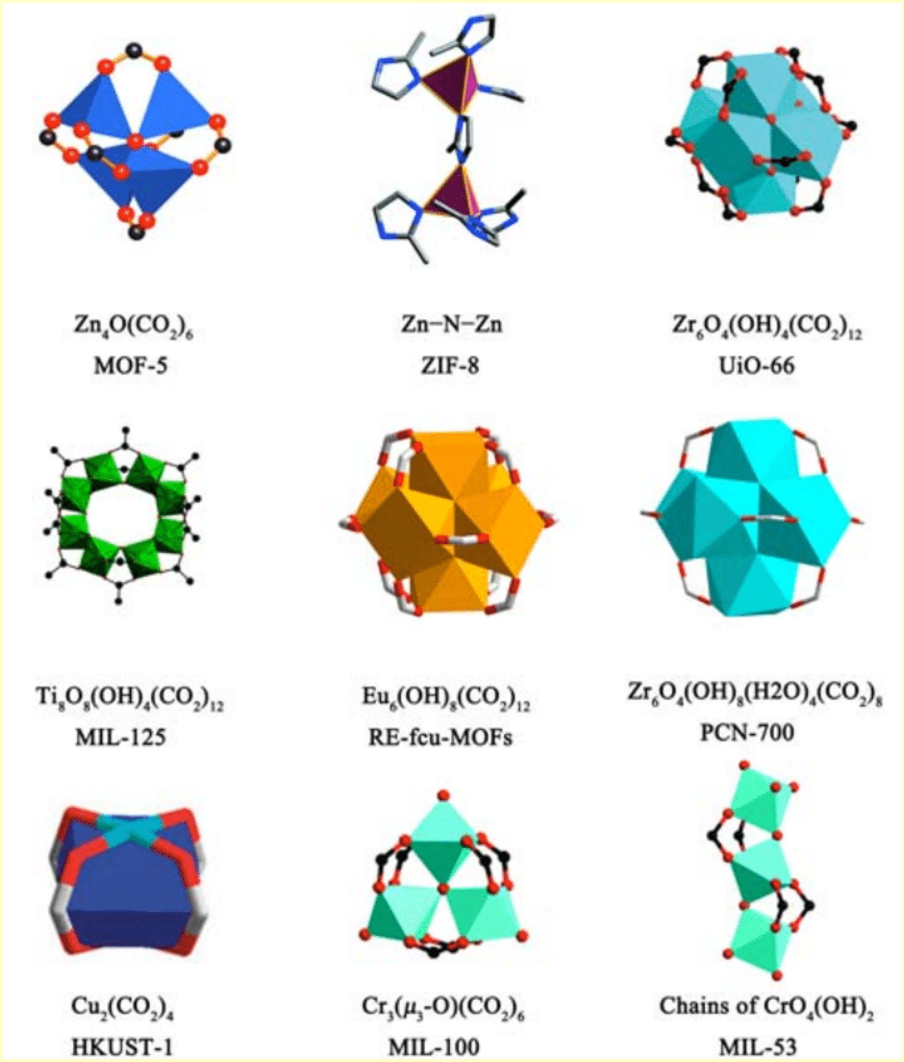
Inorganic Secondary Building Units (SBUs)



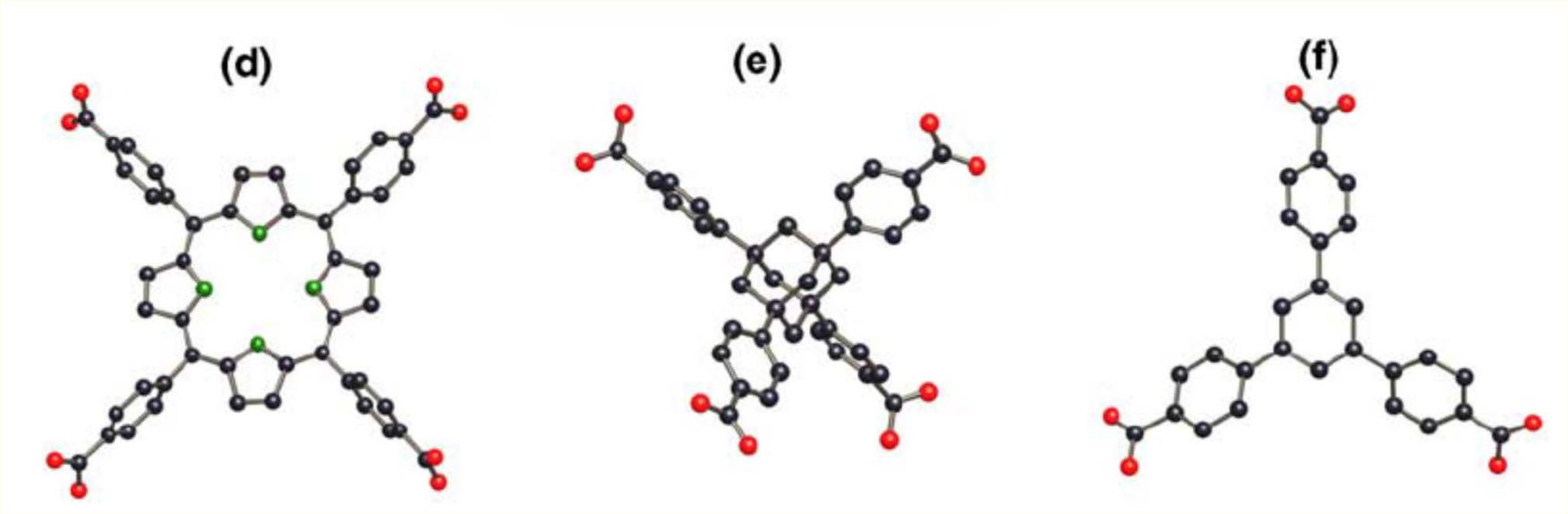
(a) the square "paddlewheel", with two terminal ligand sites
(b) the octahedral "basic zinc acetate" cluster
(c) the trigonal prismatic oxo-centered trimer, with three terminal ligand sites

The SBUs are reticulated into MOF by linking the carboxylate carbons with organic units or by replacement of the terminal ligands

Inorganic Secondary Building Units (SBUs)



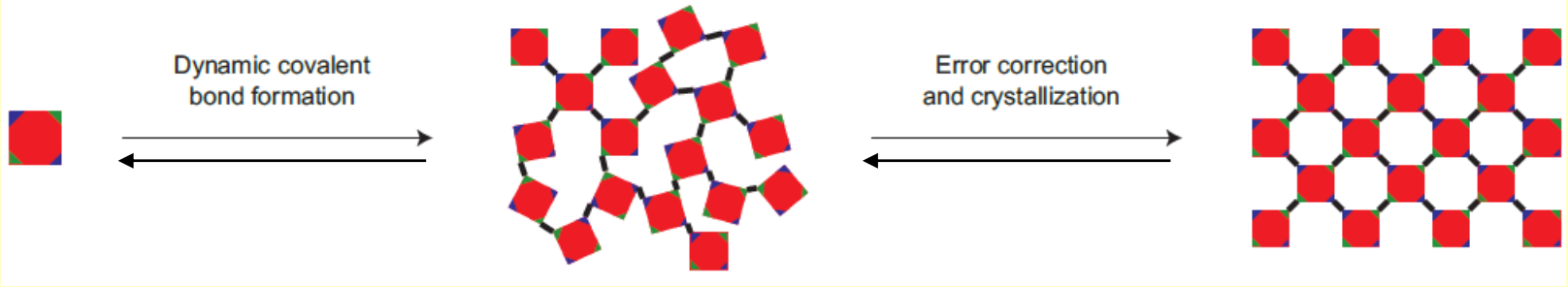
Organic Secondary Building Units (SBUs)



(d) square tetrakis(4-carboxyphenyl)porphyrin
(e) tetrahedral adamantane-1,3,5,7-tetracarboxylic acid
(f) trigonal 1,3,5-tris(4-carboxyphenyl)benzene

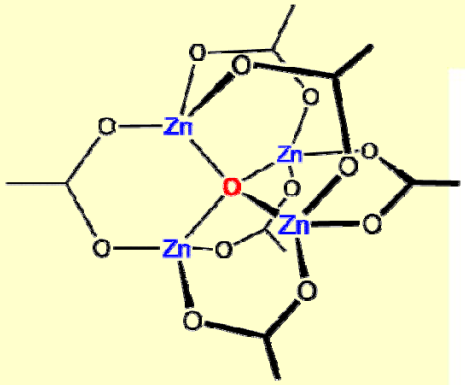
MOF Crystallization

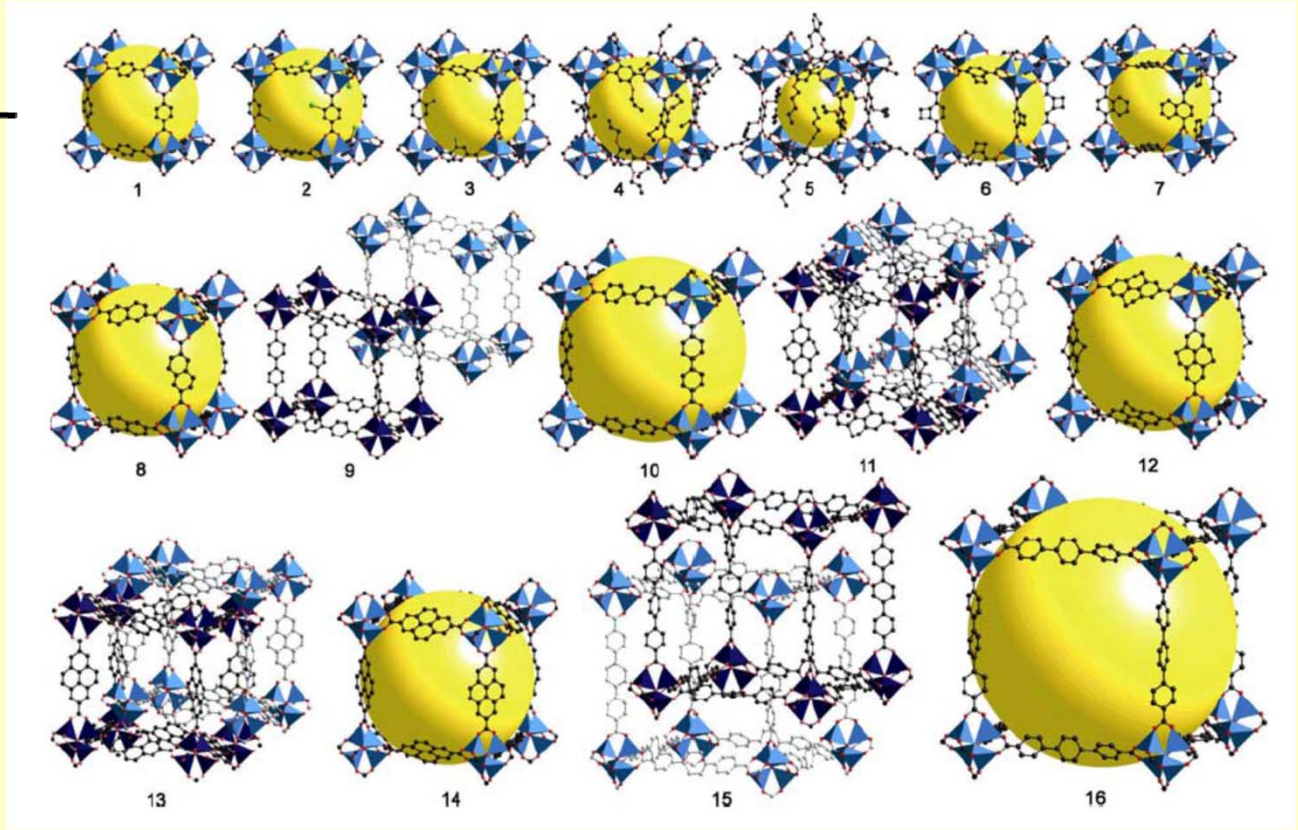
Entropy-driven errors in self-assembly
Mechanism for error correction required
The reaction should be reversible to allow for thermodynamic control
No side-reactions should exist (loss of reagents, contamination)
The building block rigidity, symmetry and discrete bonding direction decrease the incidence of errors
Solvothermal methods – control over p, T, μ – to establish equilibrium



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

Isoreticular Metal-Organic Frameworks (IRMOFs)

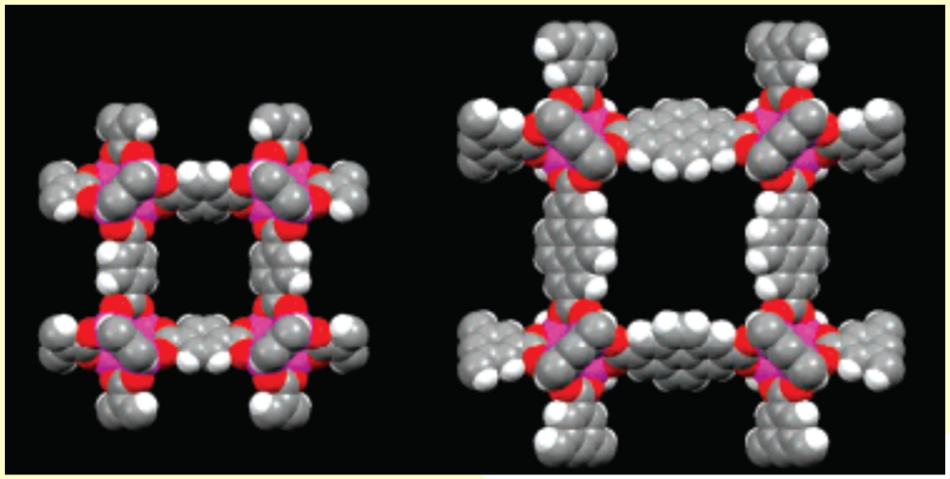




The same cubic topology, the links differ both in functionality (IRMOF-1 to -7) and in length (IRMOF-8 to -16), expansion of the links increases the internal voidspace (yellow spheres), it also allows the formation of catenated phases (IRMOF-9, -11, -13, and -15)

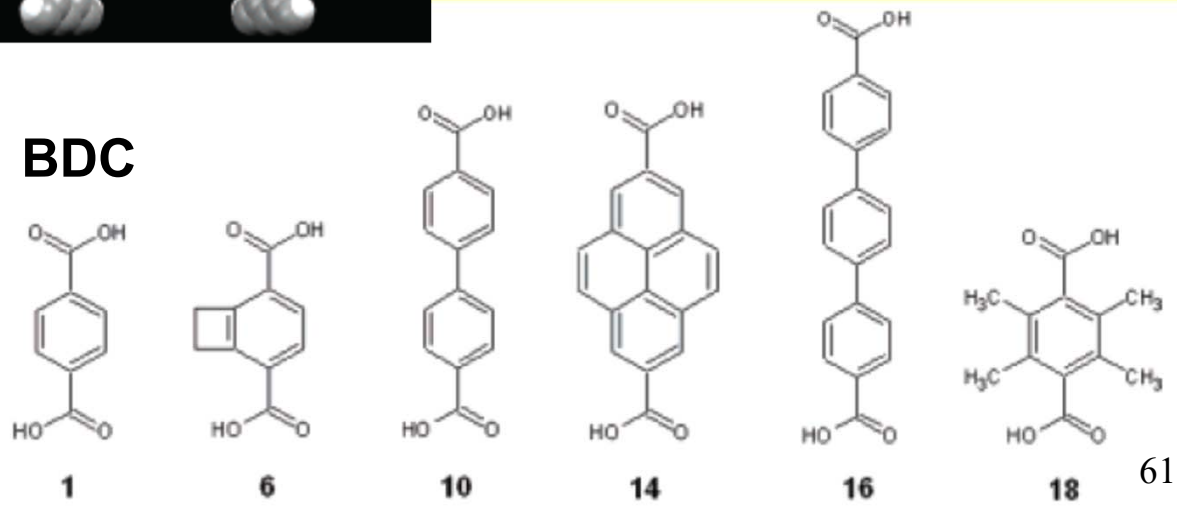
Isoreticular Metal-Organic Frameworks (IRMOFs)

IRMOF-1 **IRMOF-14**



Organic linkers for IRMOFs-X

BDC



MOF-5

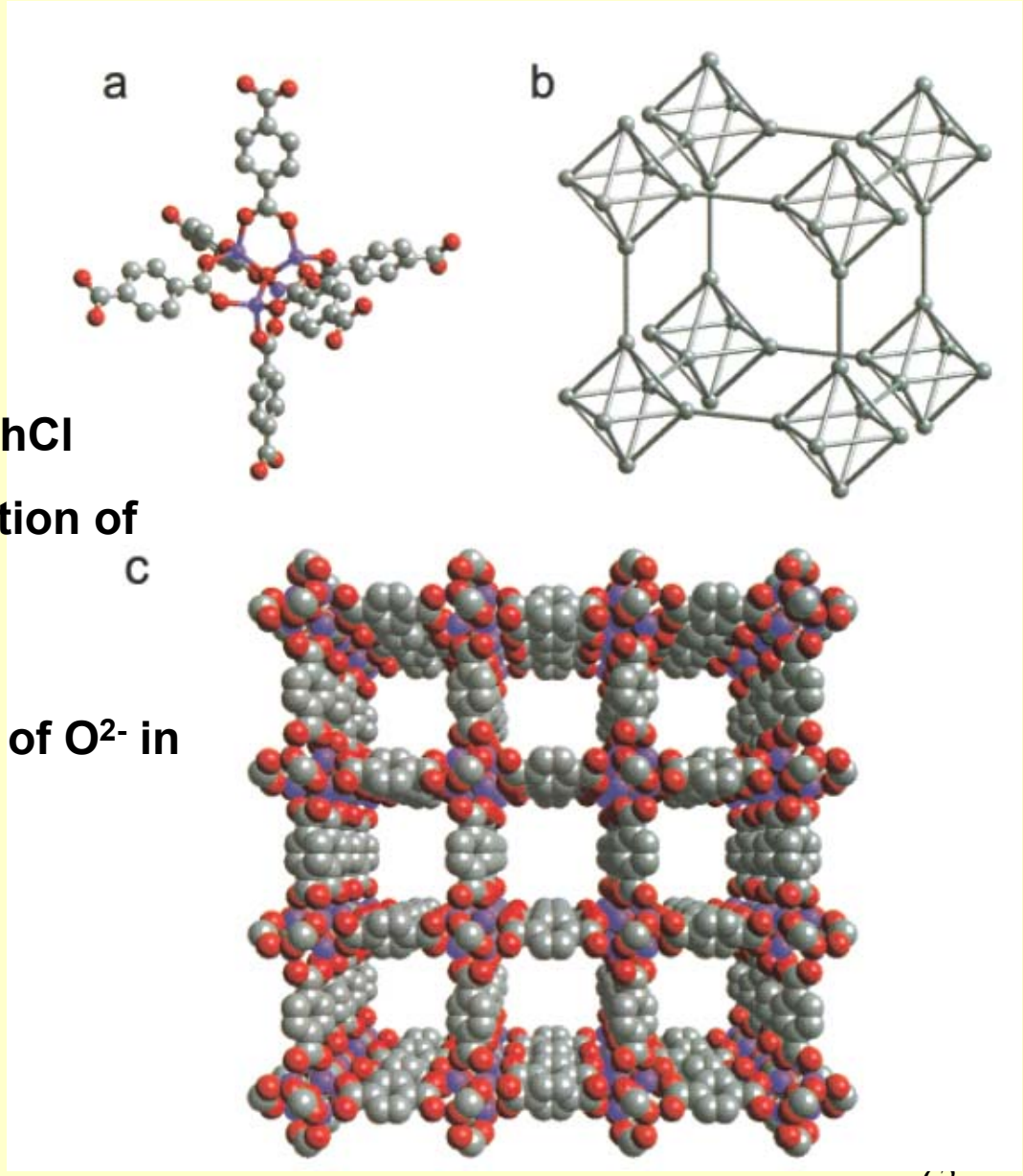
$Zn_4O(BDC)_3.(DMF)_8(C_6H_5Cl)$

Synthesis

- $Zn(NO_3)_2$ + 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

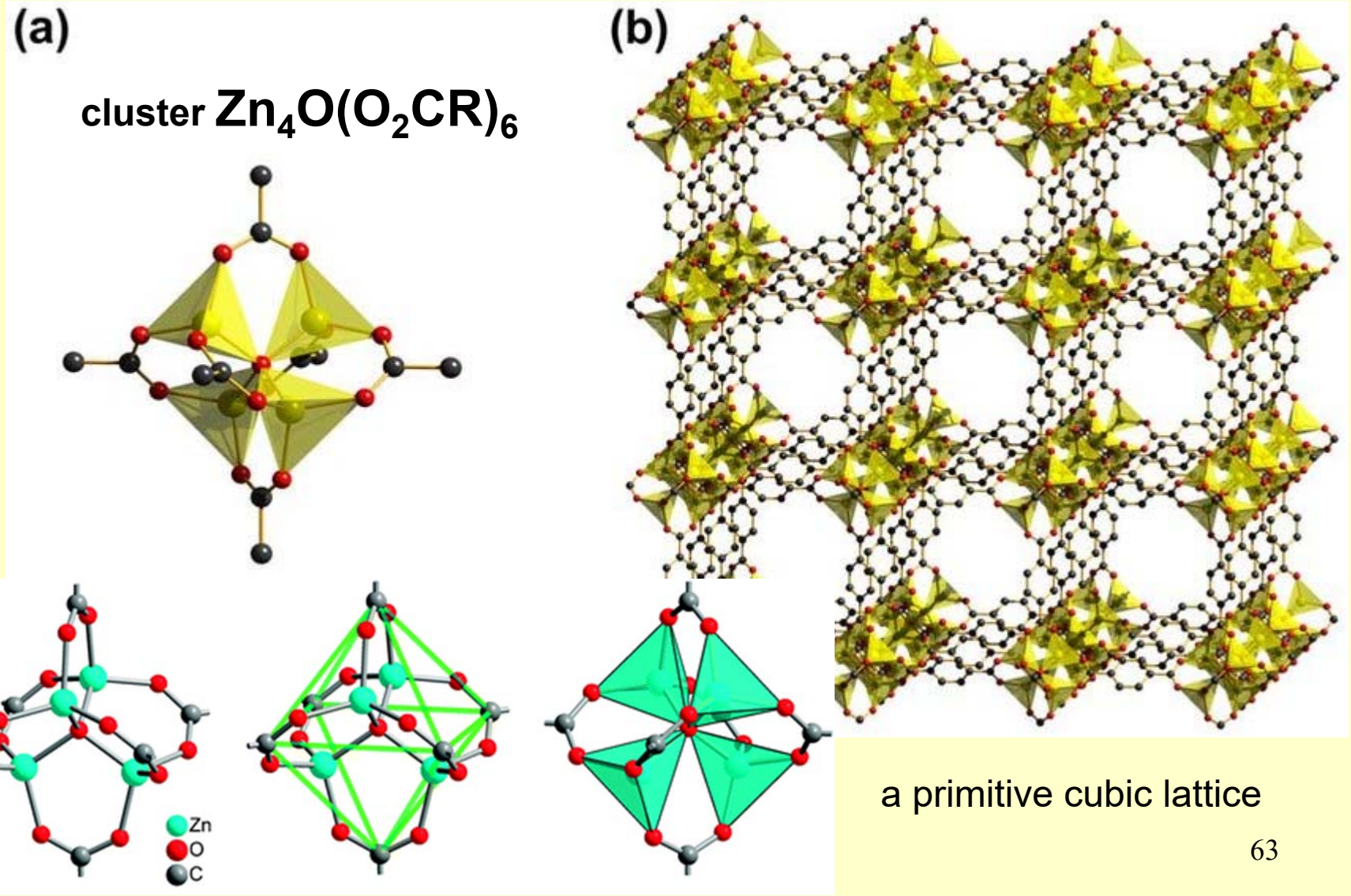
Cavity diam. 18.5 Å

Nature, 1999, 402, 276



a primitive cubic lattice

Metal-Organic Framework MOF-5



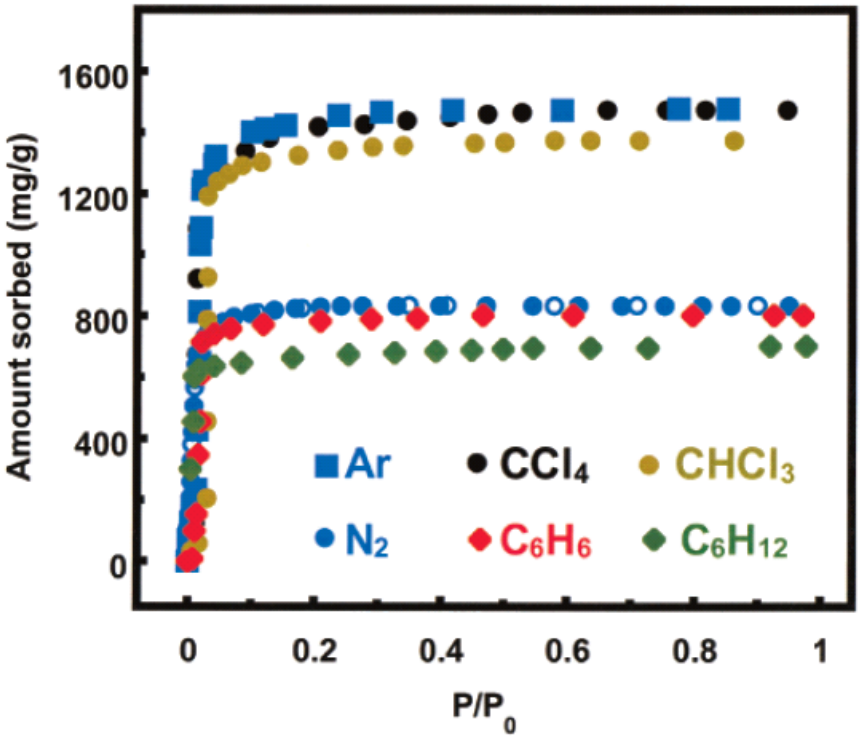
a primitive cubic lattice

Metal-Organic Framework MOF-5

MOF-5

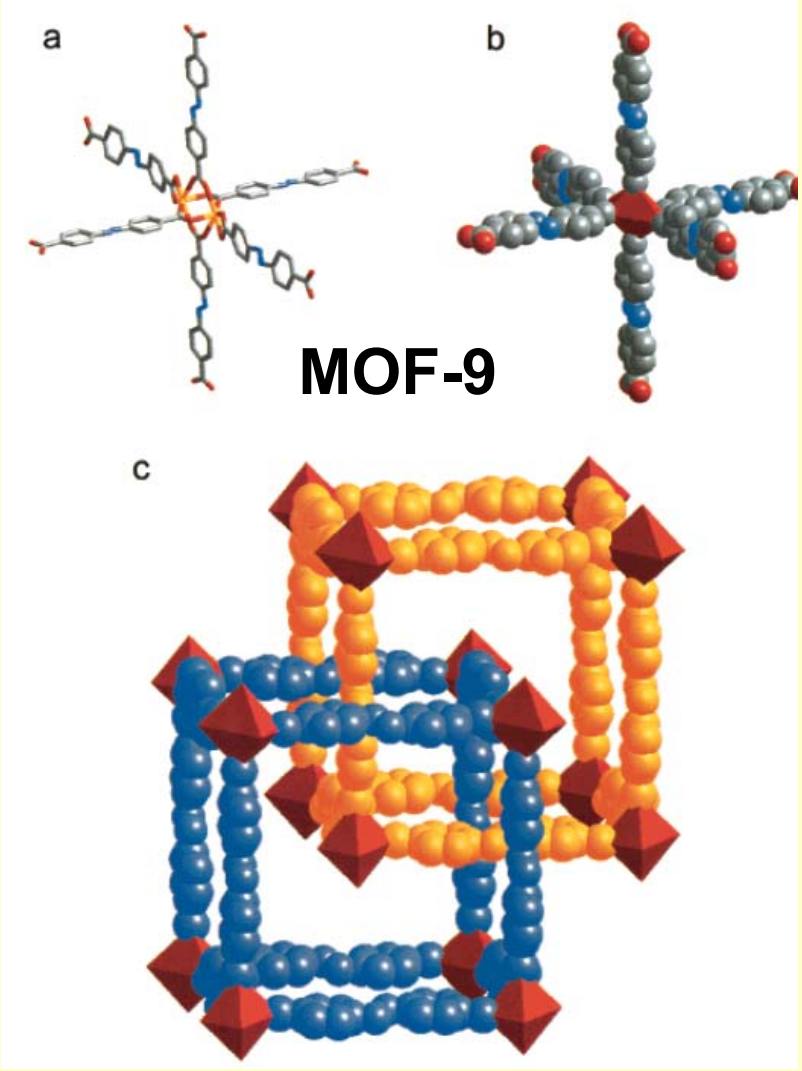
Stable even after desolvation at 300 °C in air

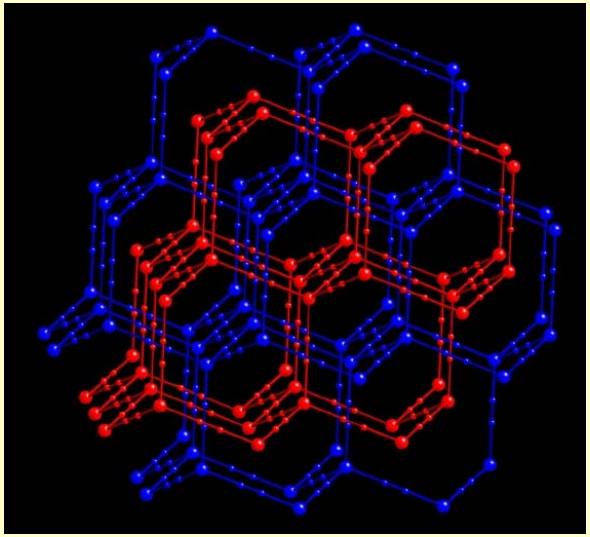
Gas sorption isotherms

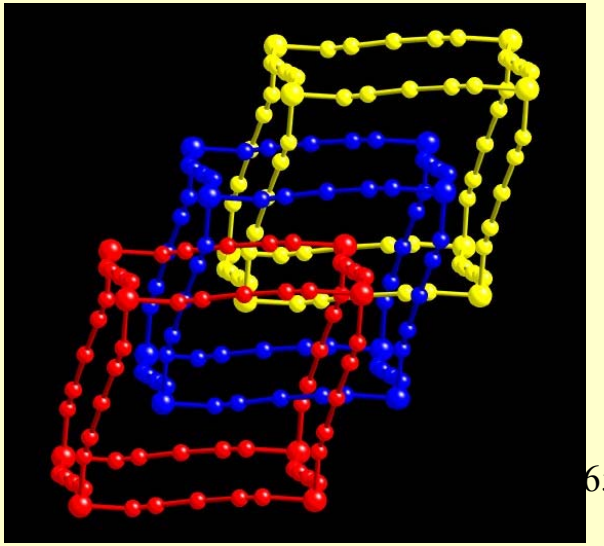


	MOF -2	MOF -3	MOF -4	MOF -5	MOF -6	MOF -9	MOF -11
pore diameter (Å)	7	8	14	12	4	8	7
surface area (m^2/g)	270	140		2900		127	560
pore volume (cm^3/g)	0.094	0.038	0.612	1.04	0.099	0.035	0.20

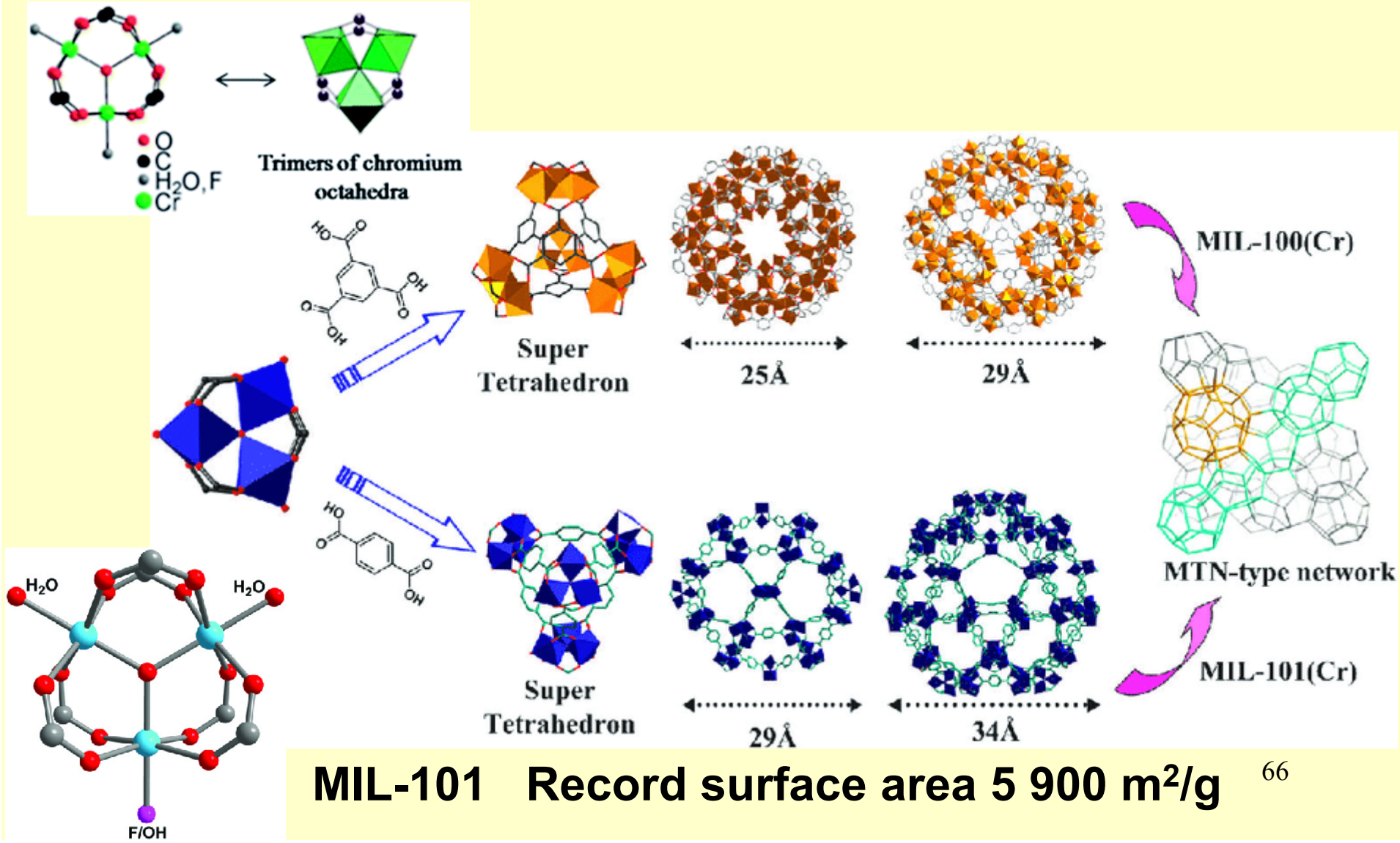
Interpenetration





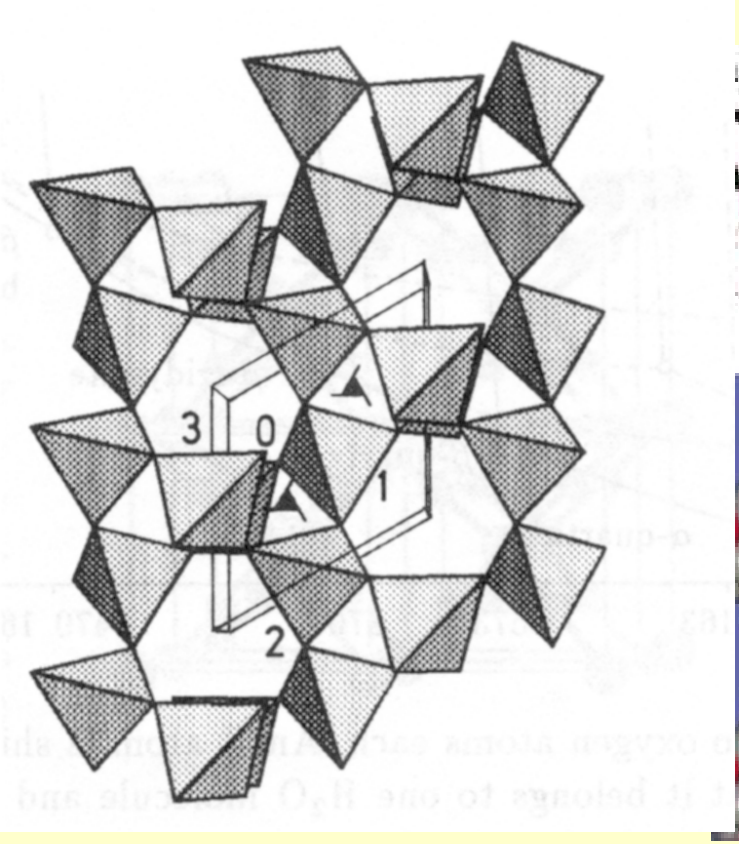


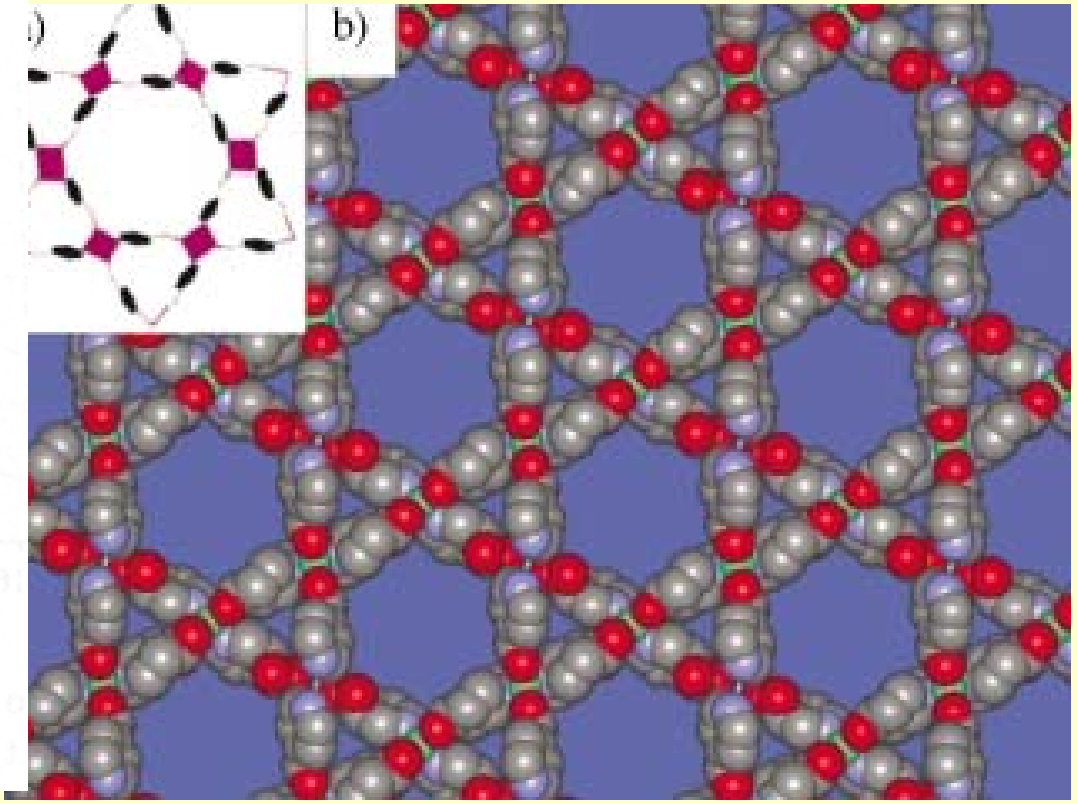
MIL-100 and MIL-101



MIL-101 Record surface area 5 900 m²/g

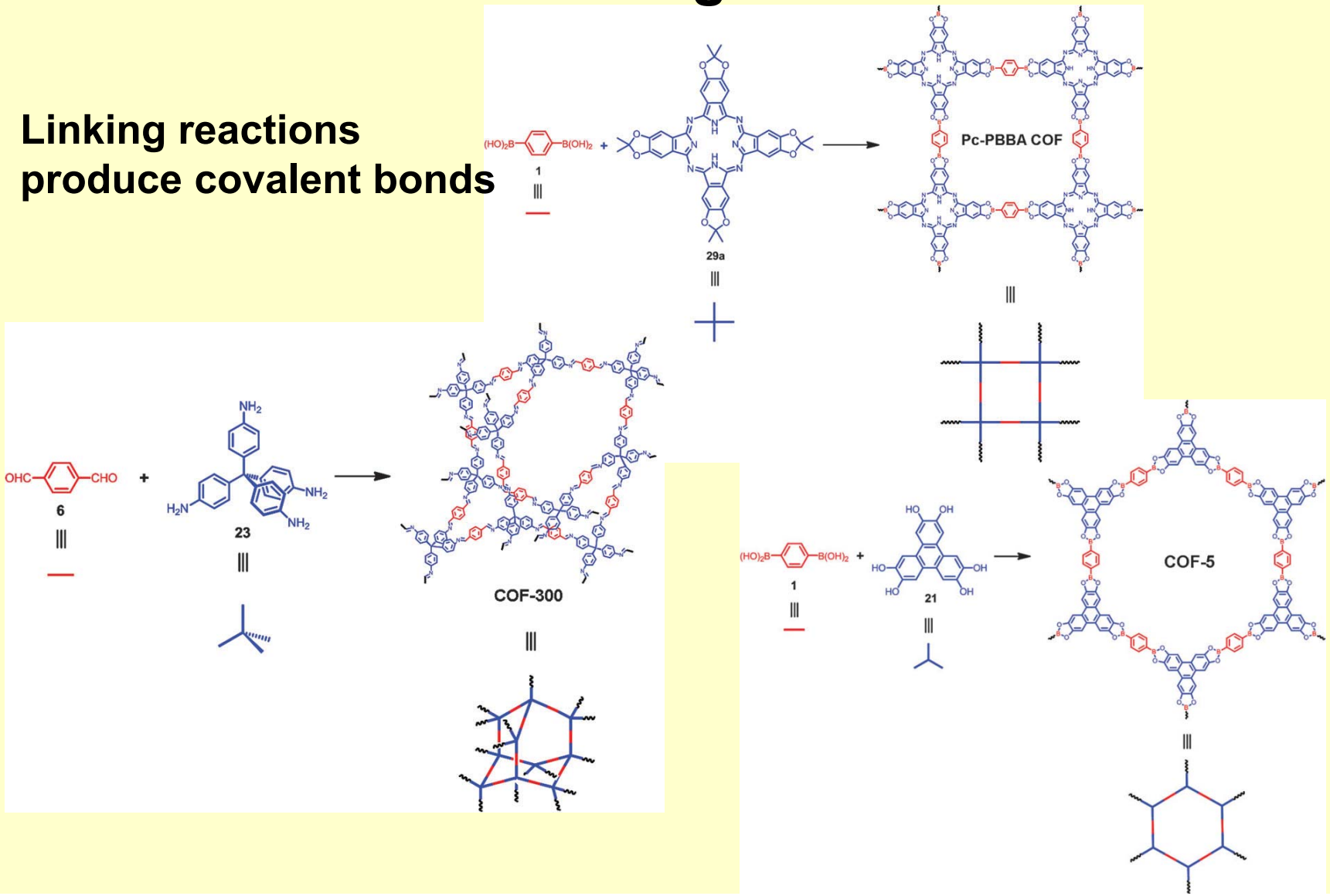
Inorganic and Metallo-Organic Quartz





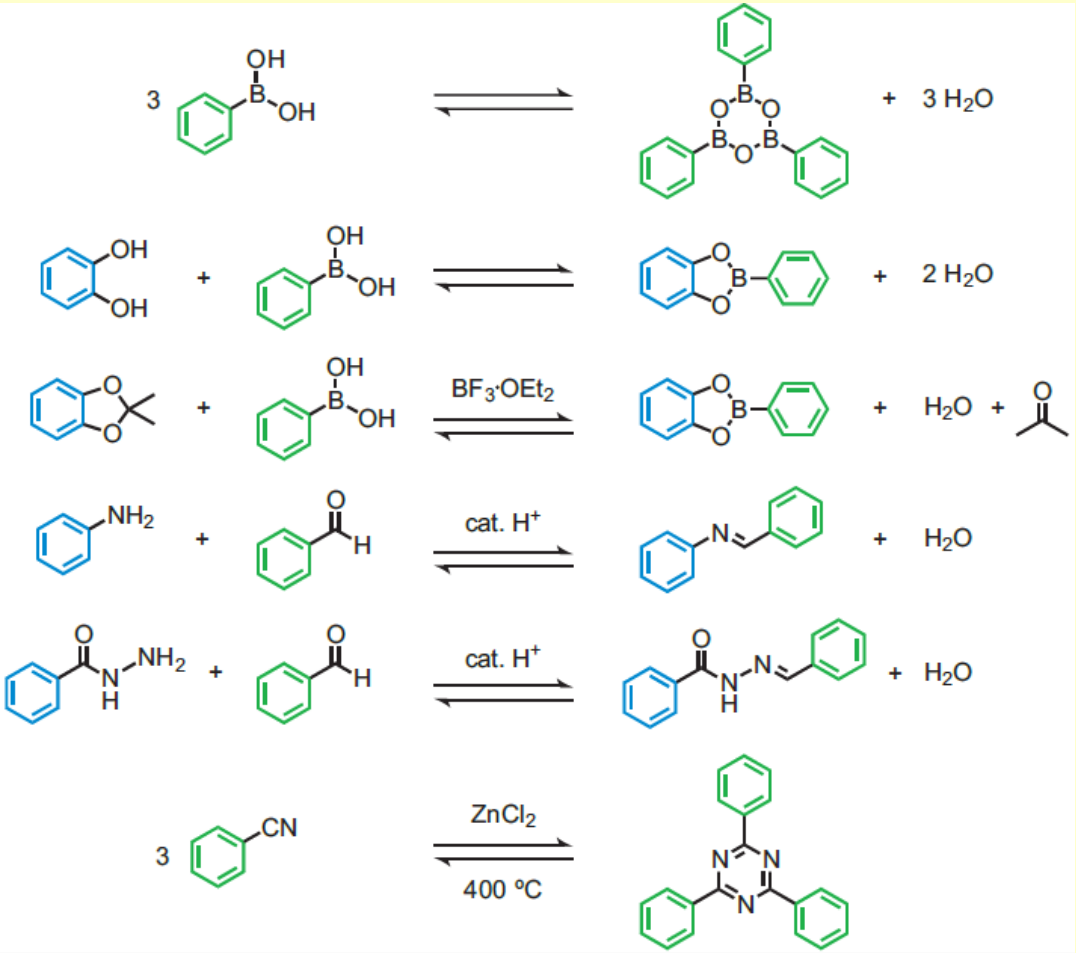
COF - Covalent Organic Frameworks

Linking reactions produce covalent bonds

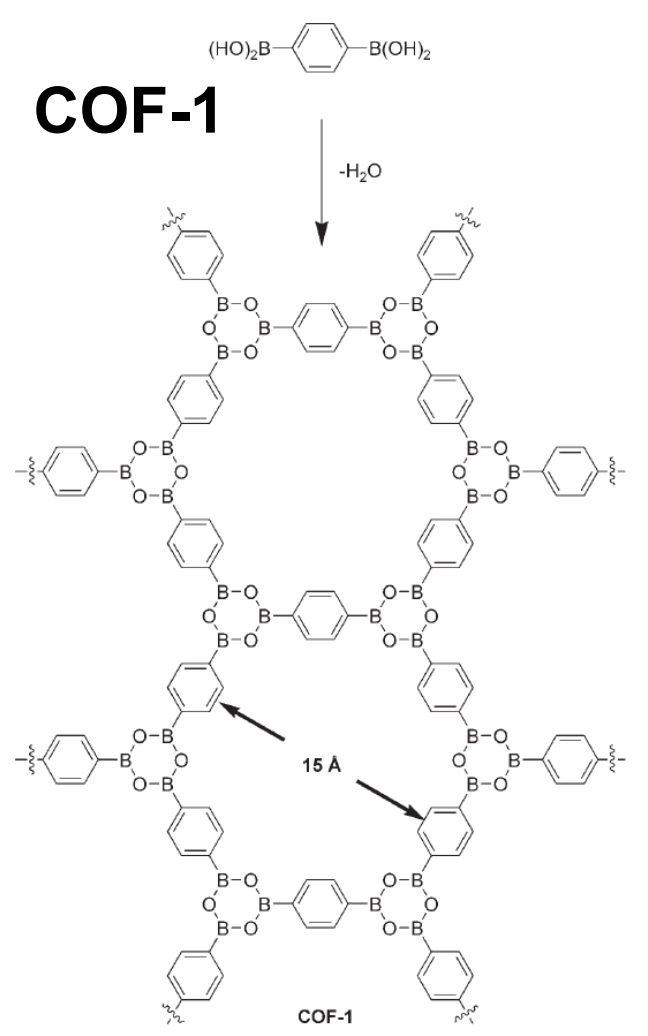


Covalent Organic Frameworks

Linking reactions



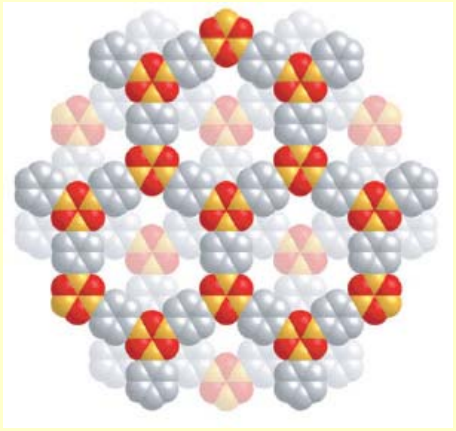
Covalent Organic Frameworks



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

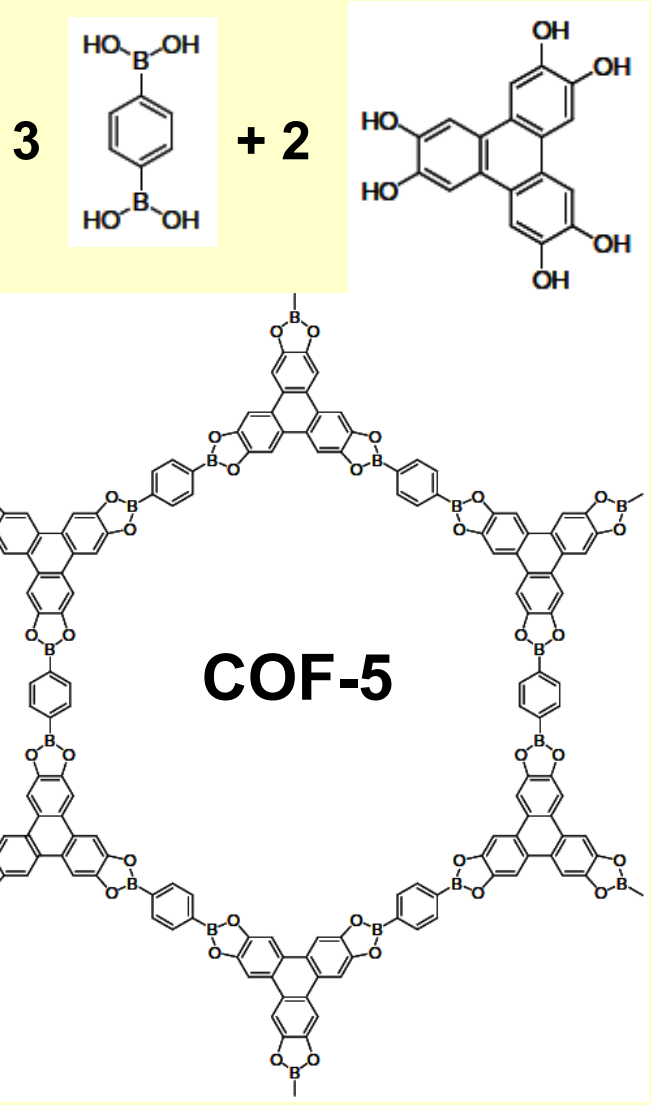
Sealed pyrex tubes, 110 °C, 72 h, minimize defects by self-healing

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

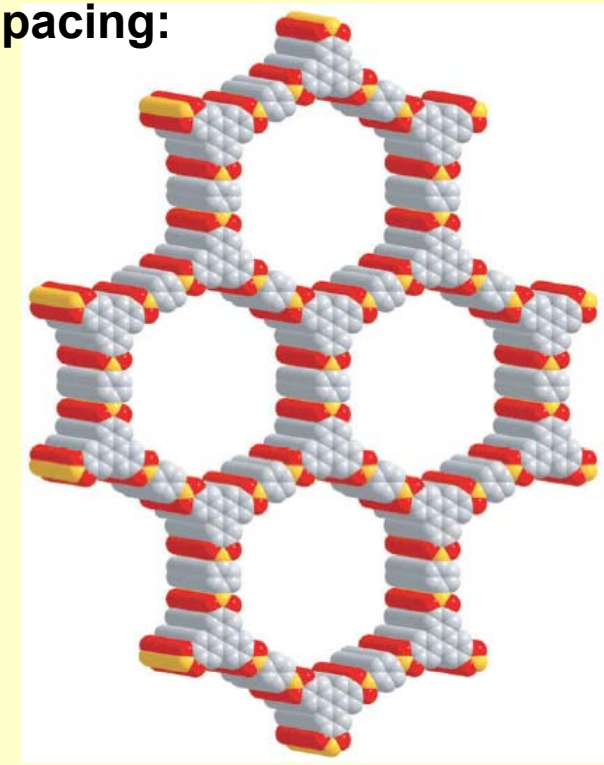
Covalent Organic Frameworks



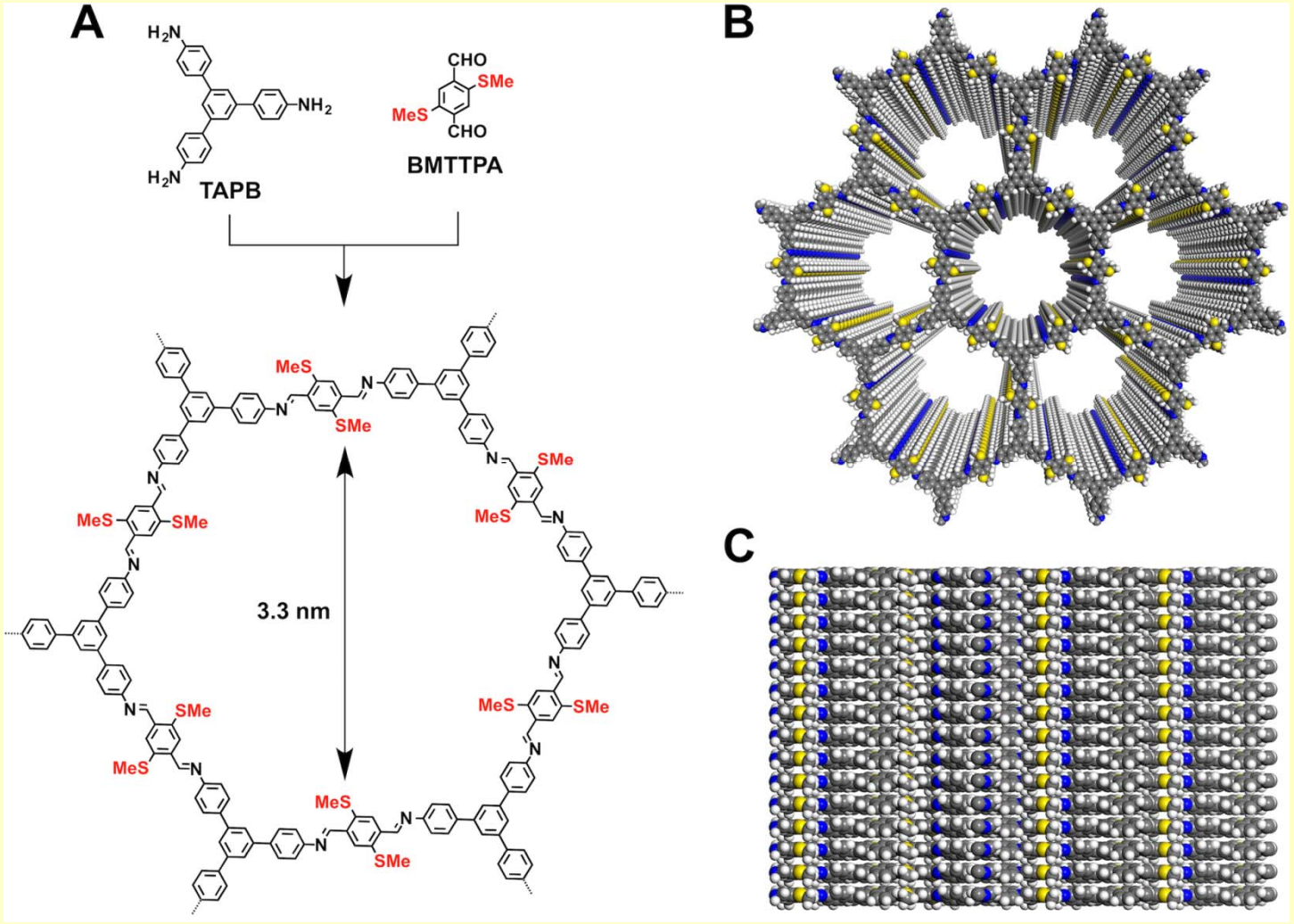
Surface area 1590 m^2/g

Pore size: 2.7 nm

Interlayer spacing: 0.346 nm

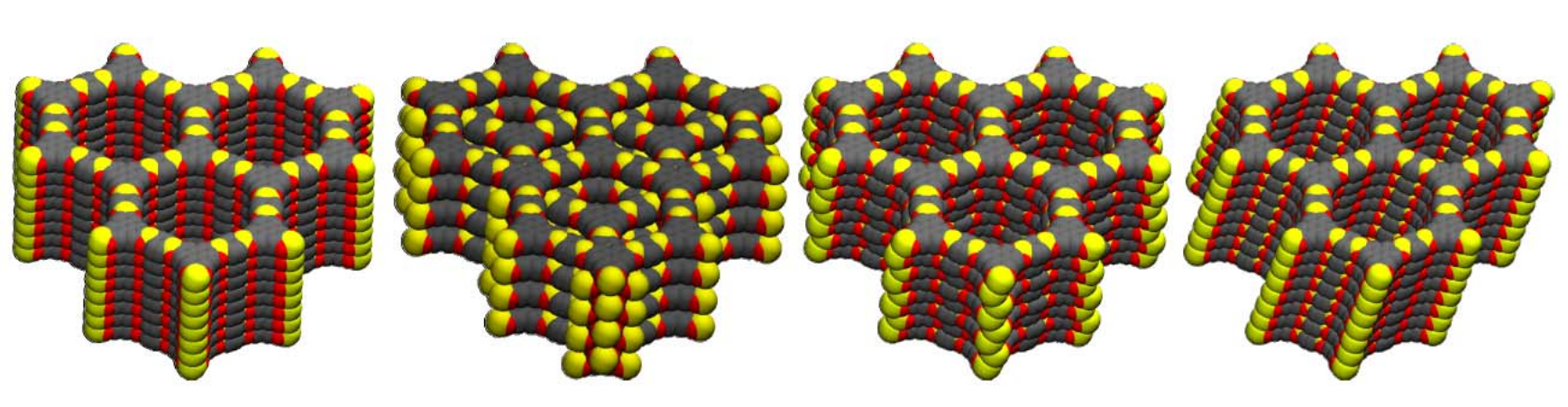


Covalent Organic Frameworks



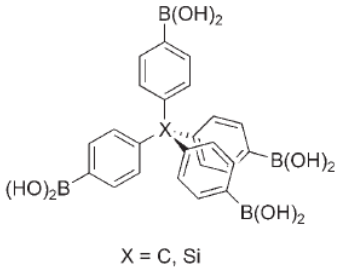
Covalent Organic Frameworks

Layer stackings: AA, AB, serrated and inclined

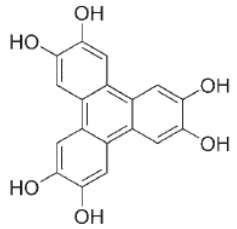


Covalent Organic Frameworks

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



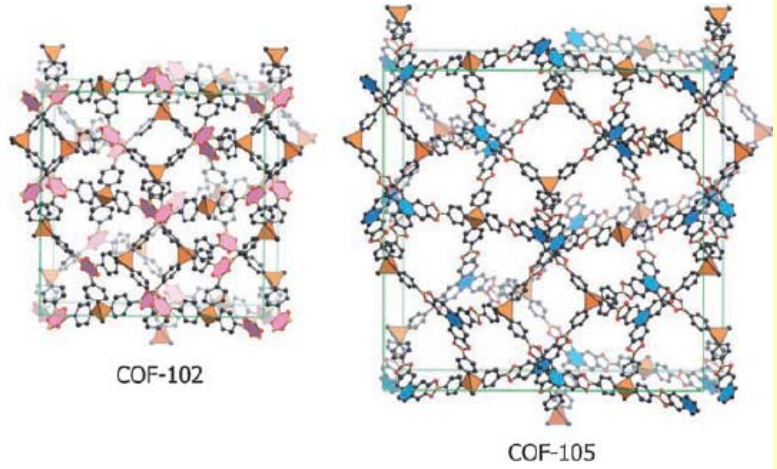
X = C, Si

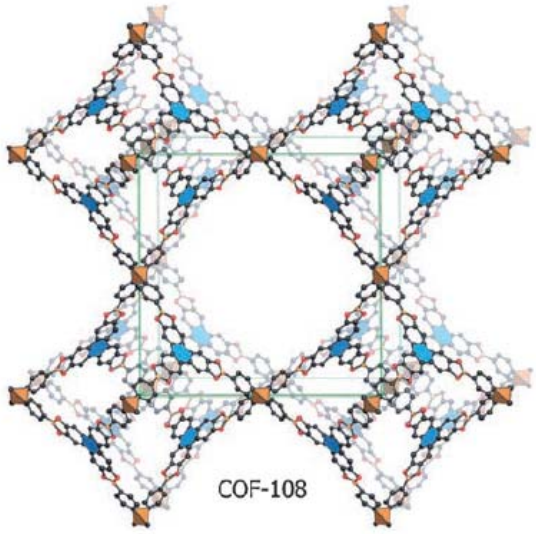


HHTP

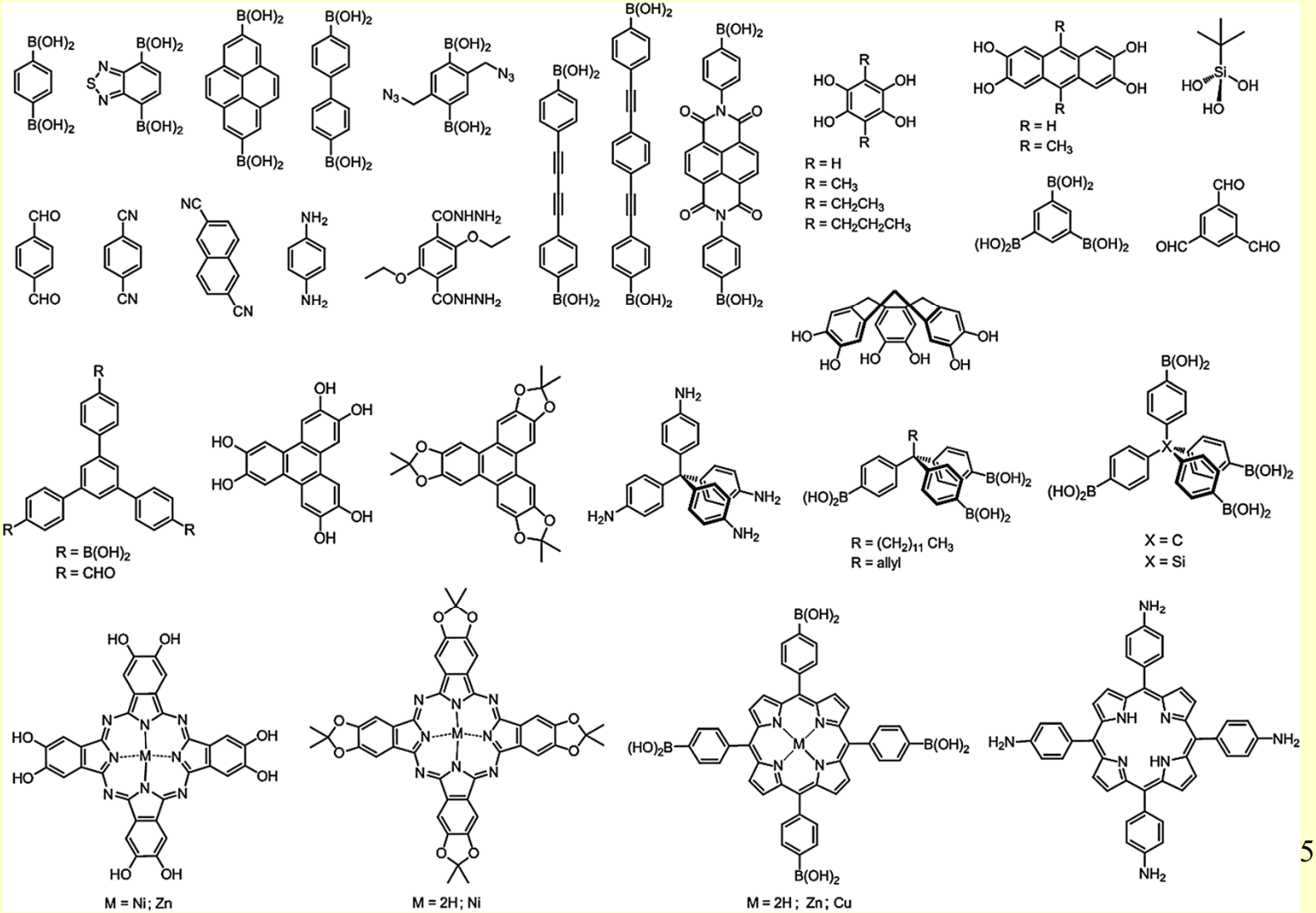
COF-108 - bor structure
two different types of pores
diameters of 15.2 and 29.6 Å
density 0.17 g cm^{-3}

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

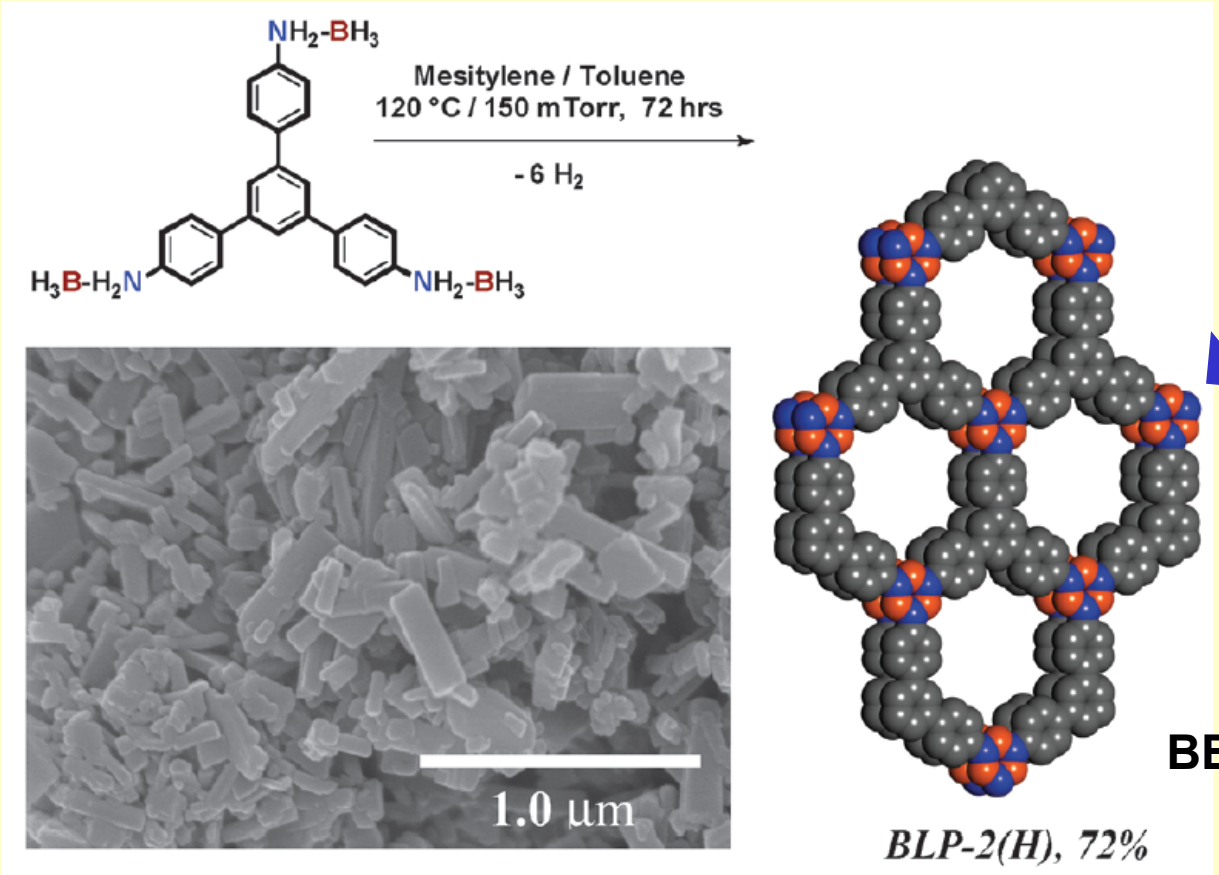


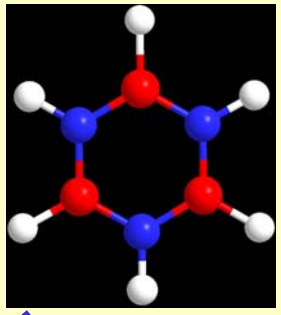


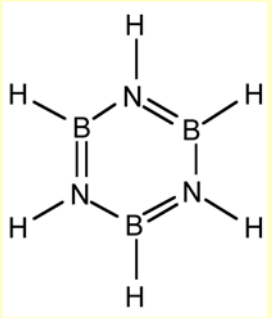
Covalent Organic Frameworks



Borazine COFs







BET: 1178 m^2/g

Pore size: 0.64 nm

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