

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

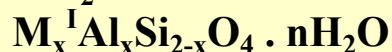
detergent builders, adsorbents, size-shape selective catalysts, supramolecular chemistry, nanotechnology

Chemical composition

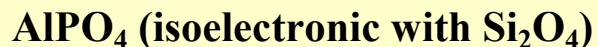
Silica



Aluminosilicates



Aluminophosphates



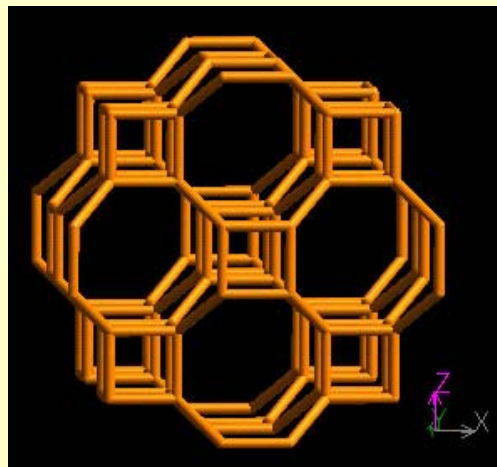
Metallophosphates



Silicoaluminophosphates

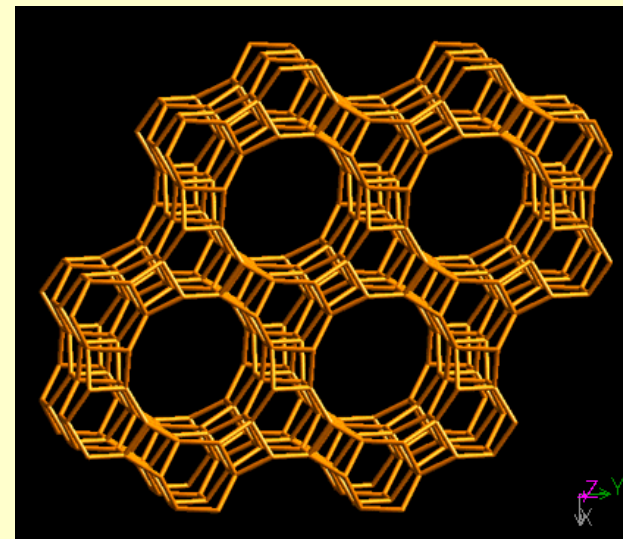


ACO

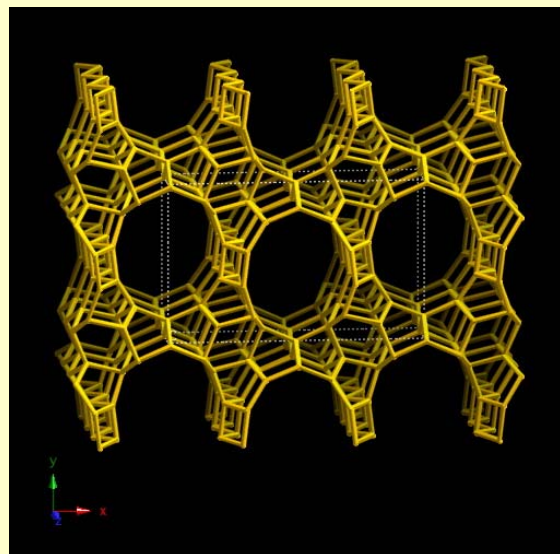


Pores and Channels

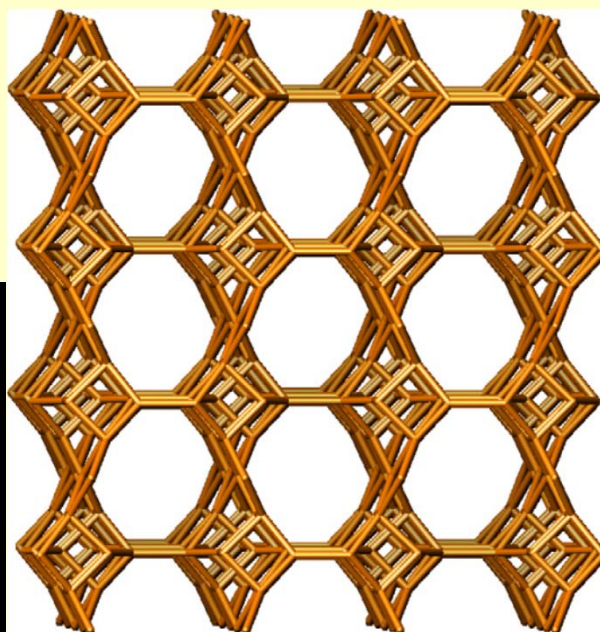
AFI



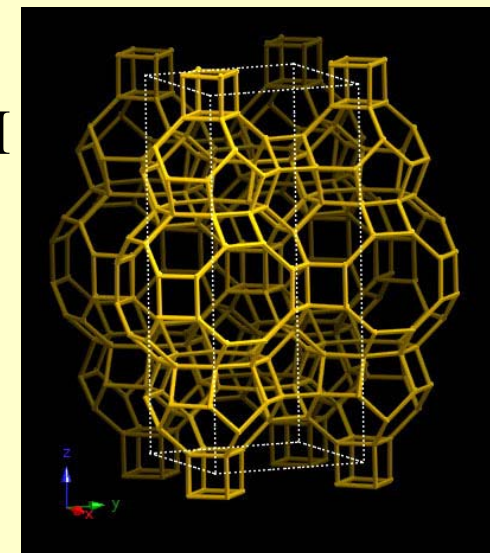
SSY



STI



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)

- 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, Beryllphosphate-X, SAPO-37,
Zincophosphate-X**

Zeolite Names

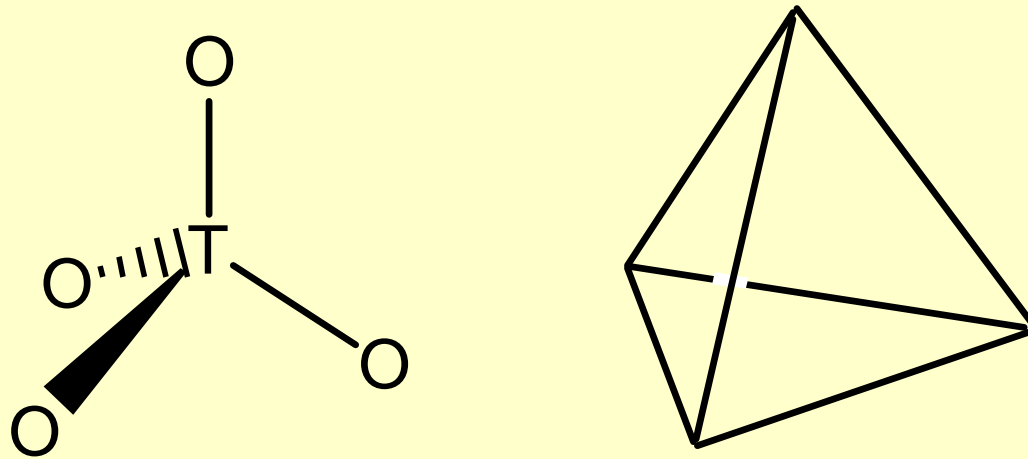
Names of zeolite materials:

- **trivial names – Alpha, Beta, Rho**
- **chemical names – Gallogermanate-A**
- **mineral names – Chabazite, Mordenite, Stilbite, Sodalite**
- **codes – AIPO4-5, 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)**

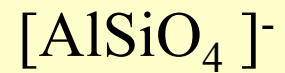
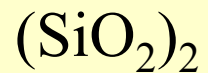
Zeolites Building Units

Primary building units:

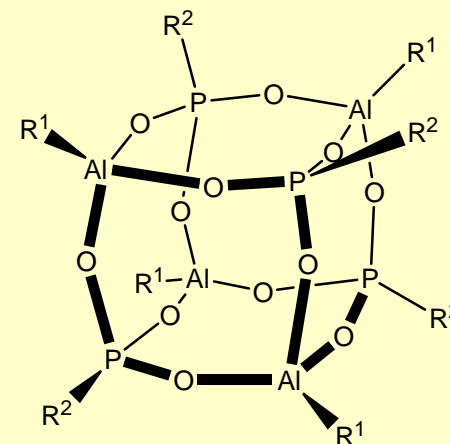
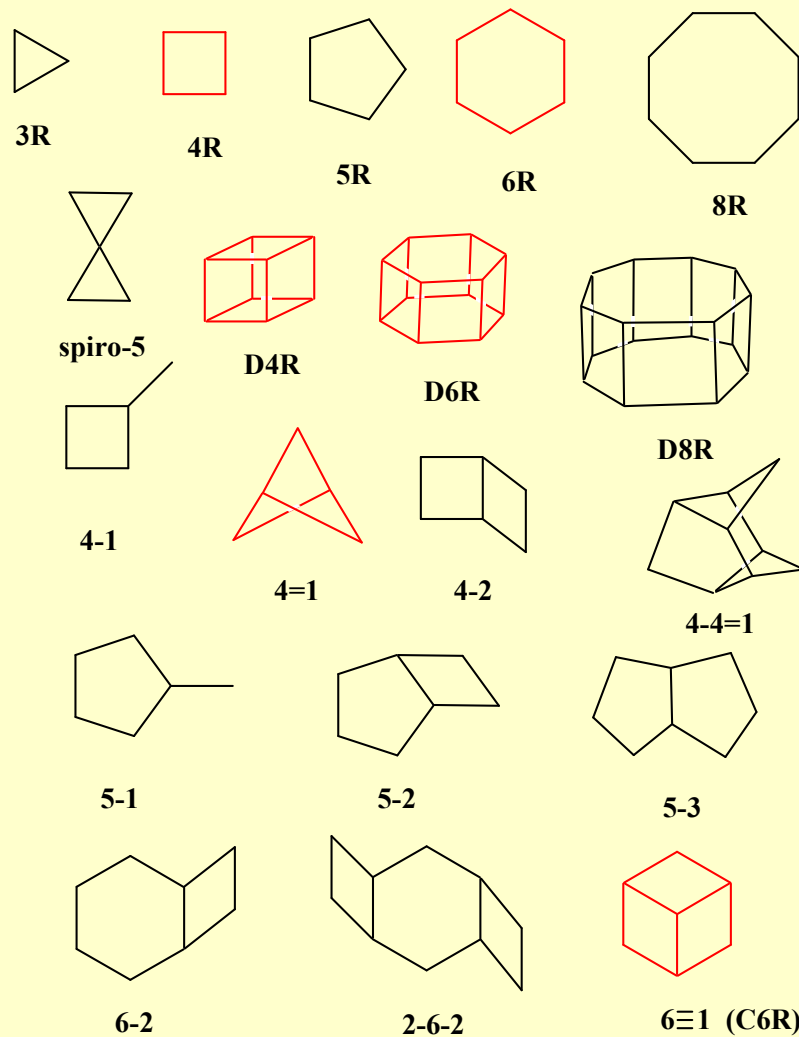
Al(III)O_4 , P(V)O_4 and Si(IV)O_4 tetrahedra



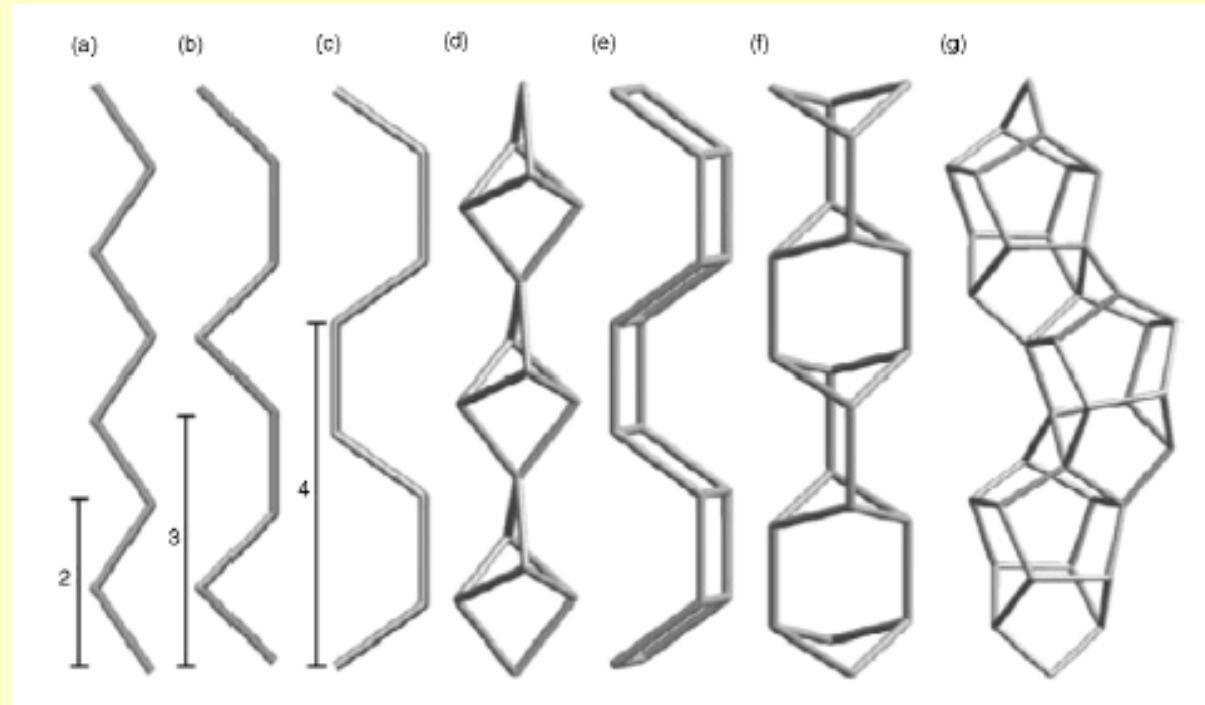
Isoelectronic relationship



Secondary (Structural) Building Units (SBU)

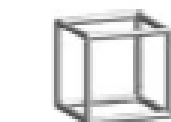


Chain composite building units

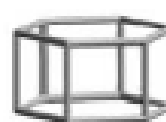


- (a) zig-zag unbranched single chain, periodicity of two**
- (b) sawtooth unbranched single chain, periodicity of three**
- (c) crankshaft unbranched single chain, periodicity of four**
- (d) natrolite branched single chain**
- (e) double crankshaft chain, an unbranched double chain**
- (f) narsarsukite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

Polyhedral composite building units



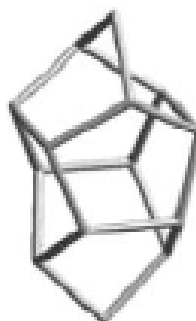
$[4^4]$
double 4-ring (D4R)



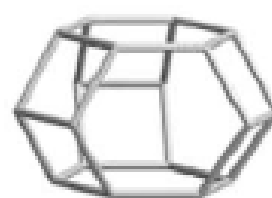
$[4^6 6^2]$
double 6-ring (D6R)



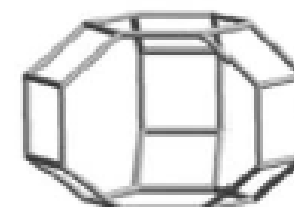
$[4^8 8^2]$
double 8-ring (D8R)



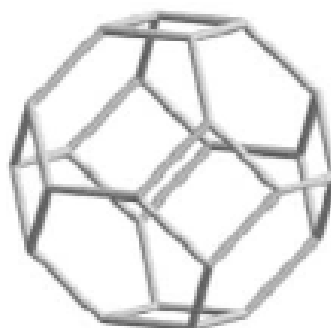
$[5^5]$
pentasil unit



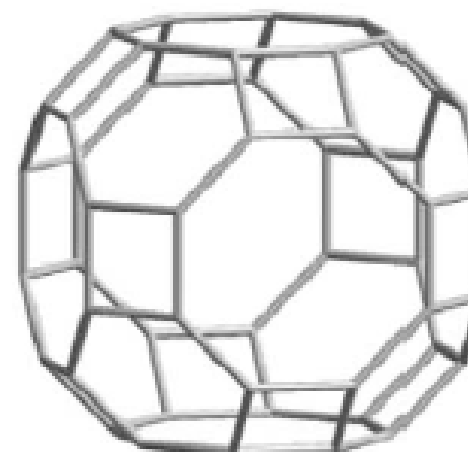
$[4^6 5^6]$
cancrinite cage



$[4^4 5^4 6^4 8^2]$
gmelinite cavity



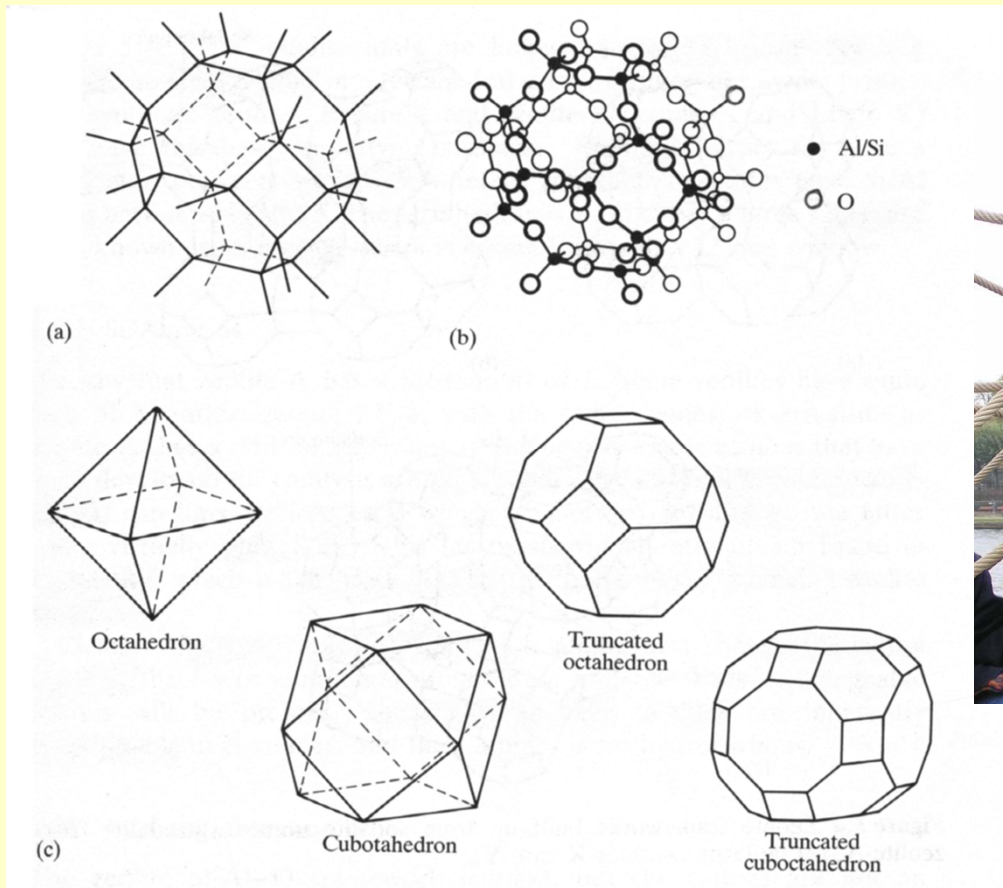
$[4^4 5^4 6^4 8^2]$
sodalite cage
or β -cage



$[4^4 5^4 6^4 8^2]$
 α -cavity

Sodalite Unit

Truncated octahedron



Sodalite Unit

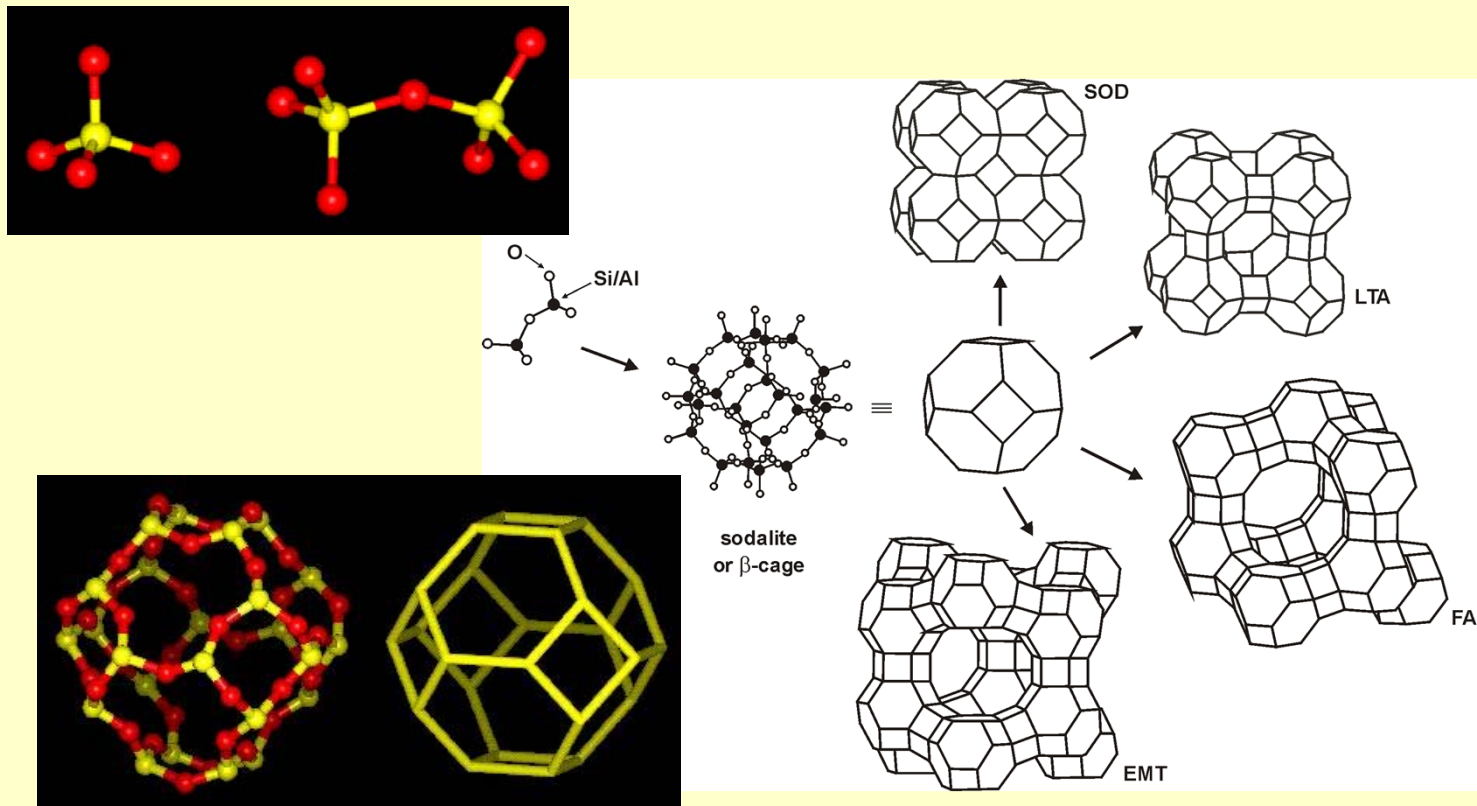
Packing of the sodalite units:

SOD – bcc, sharing of 4-rings

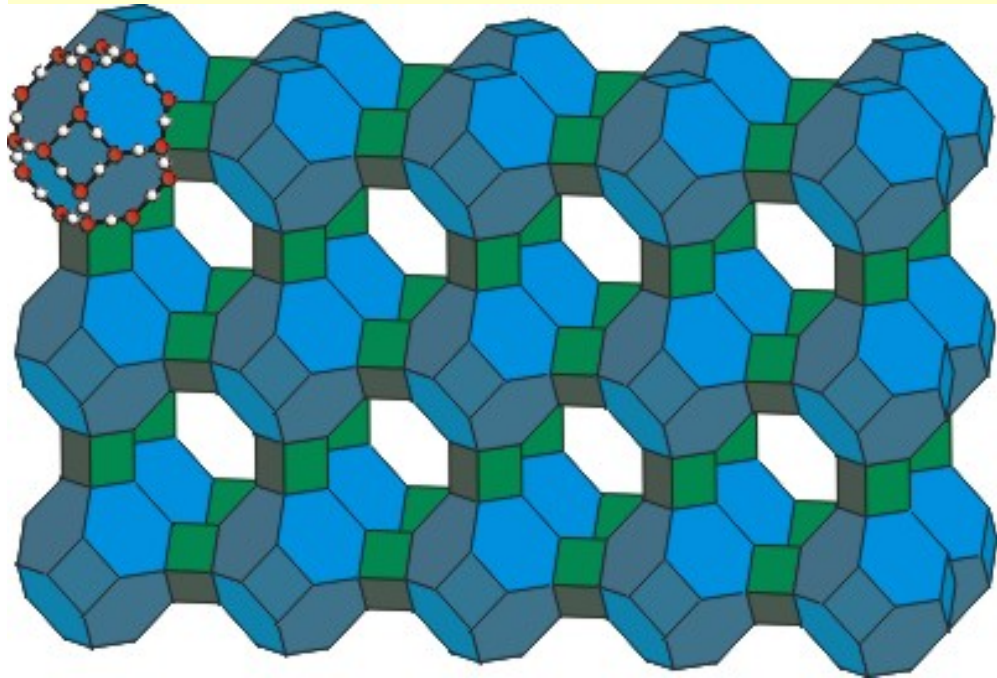
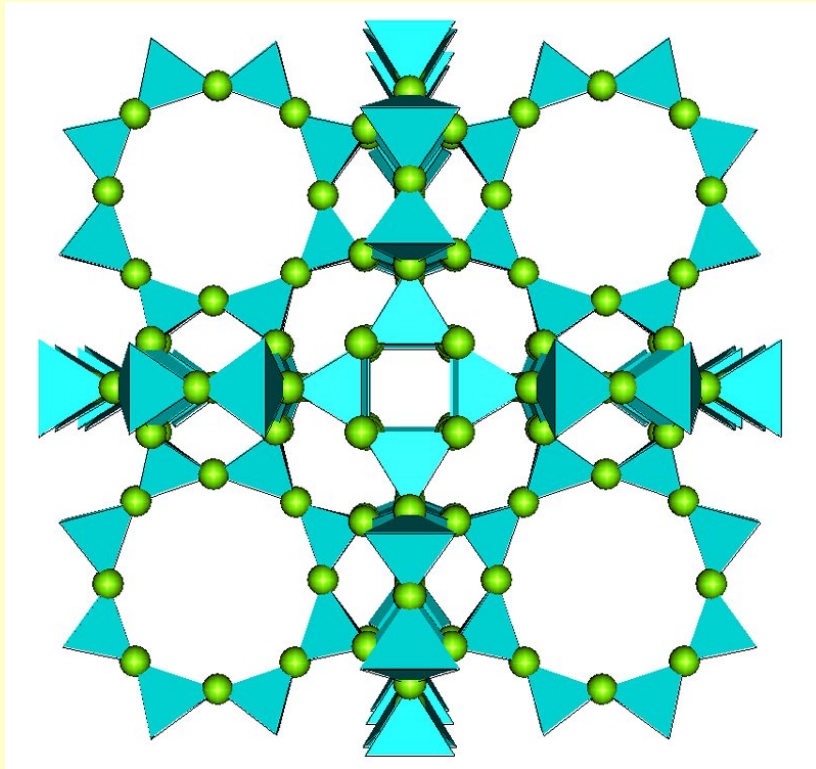
LTA – sc, 4-rings connected through O bridges

FAU (faujasite) – cubic diamond, 6-rings connected through O bridges

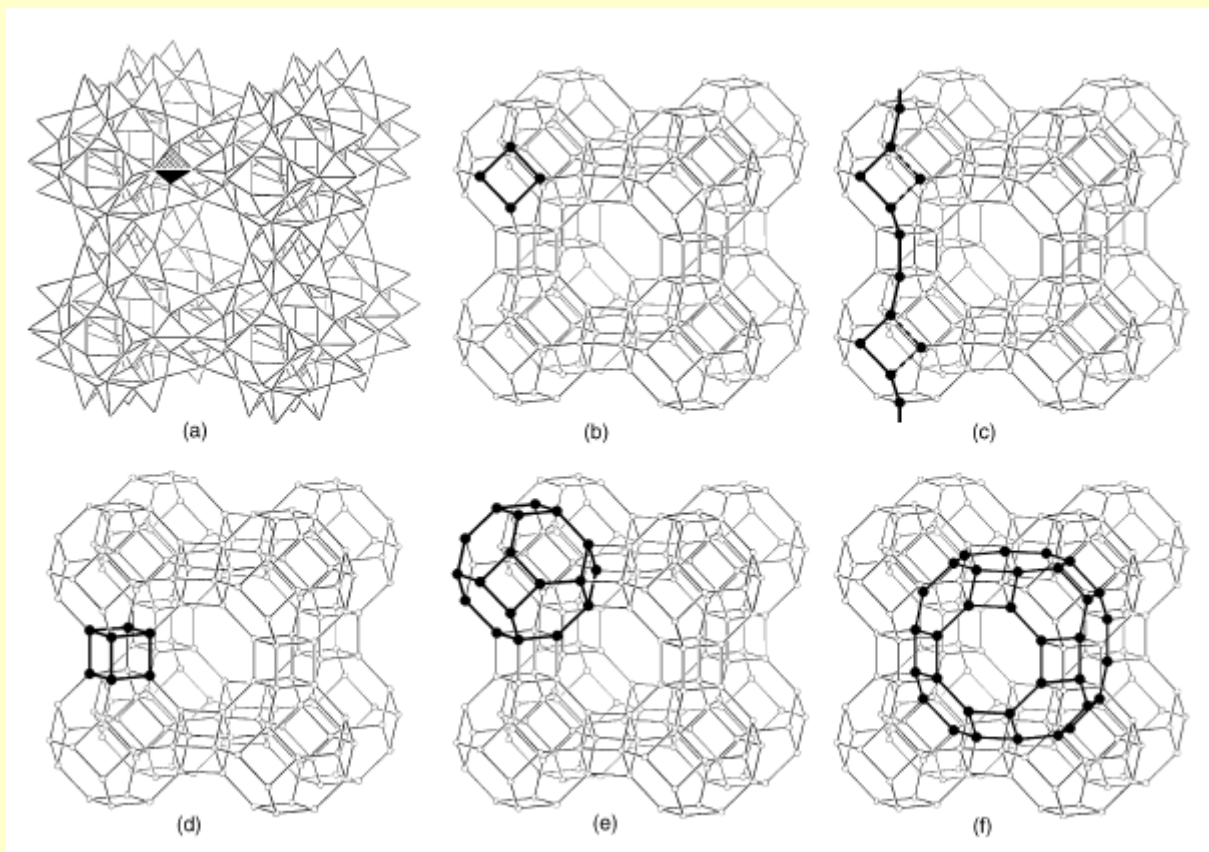
EMT – hexagonal diamond, 6-rings connected through O bridges



Zeolite LTA

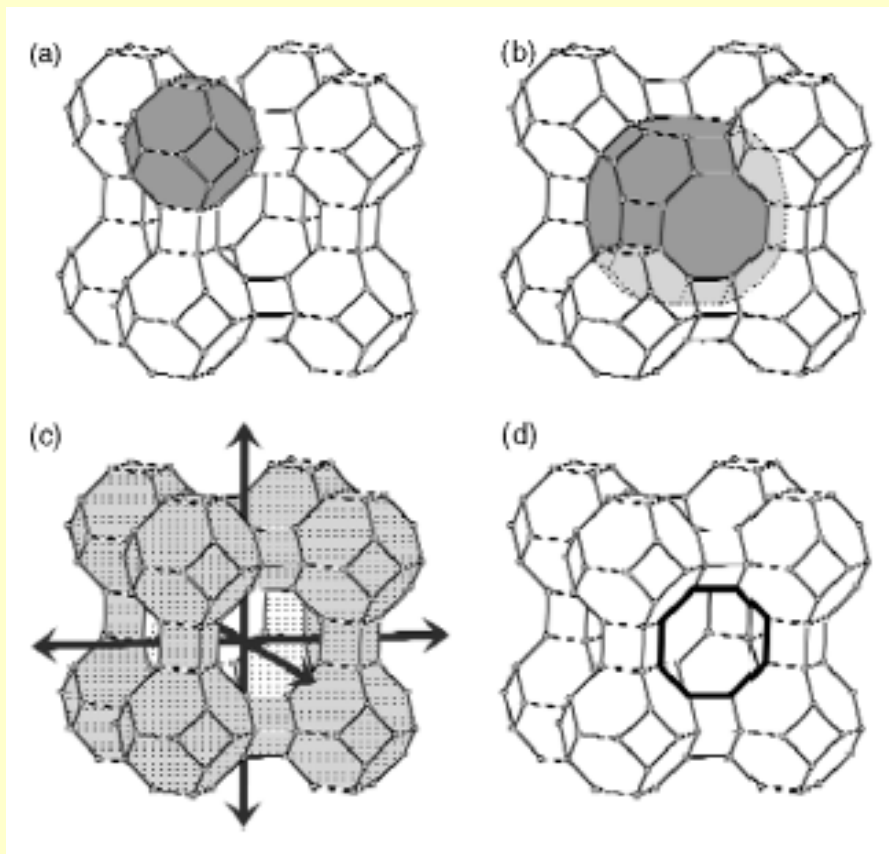


Zeolite A



- (a) $[TO_4]$ tetrahedra as BBU
- (b) four-membered single rings
- (c) IB fuenfer chains
- (d) cubes $[4^6]$
- (e) truncated octahedra $[4^66^8]$ (sodalite- or β -cages)
- (f) truncated cubeoctahedra $[4^{12}6^88^6]$ (α -cavities)

Pores in Zeolite A (LTA)

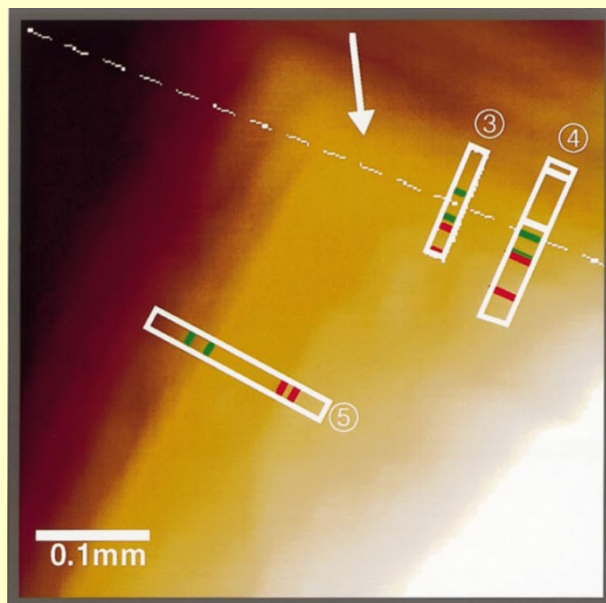


(a) the sodalite cage $[4^66^8]$

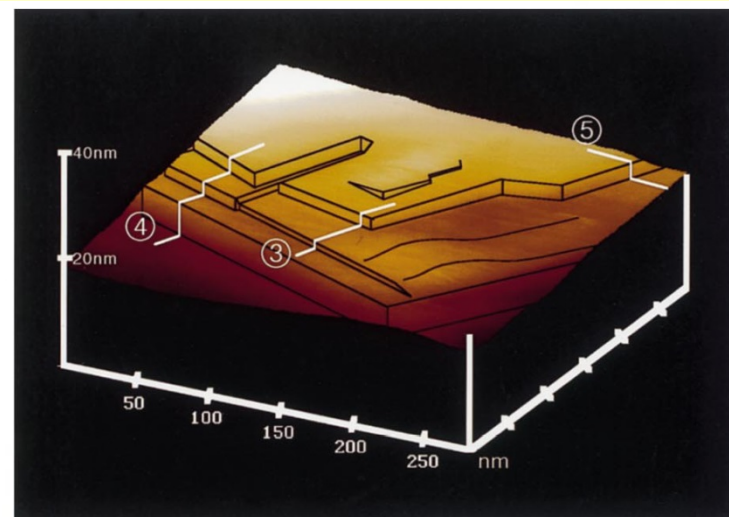
(b) the α -cavity $[4^{12}6^88^6]$

(c) the 3-dimensional channel system

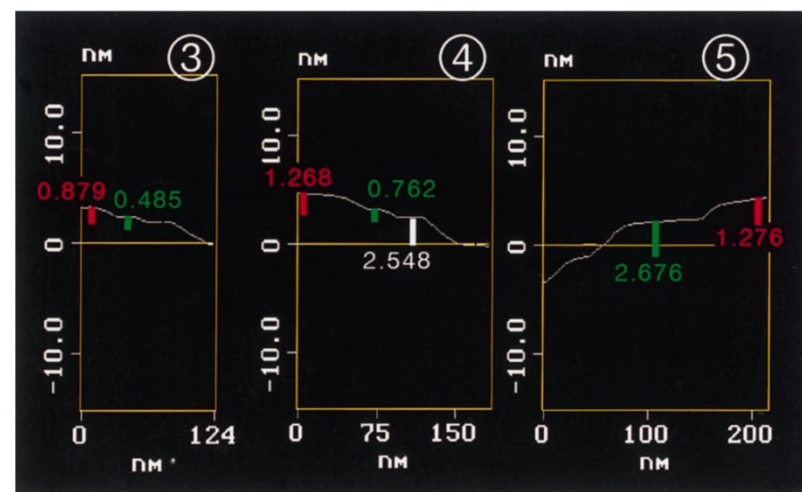
(d) the 8-ring defining the 0.41 nm effective channel width



(a)



(b)



(c)

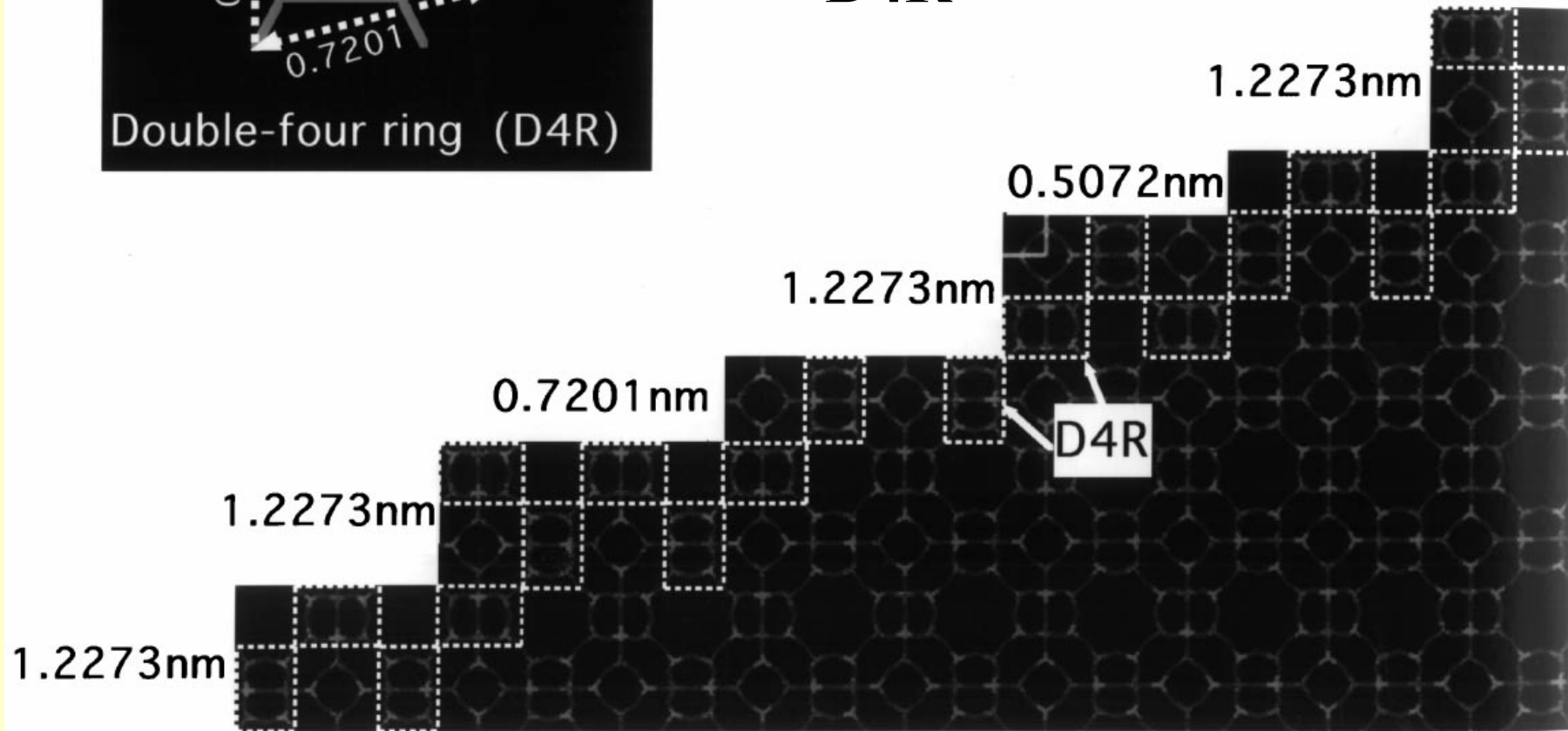
D4R

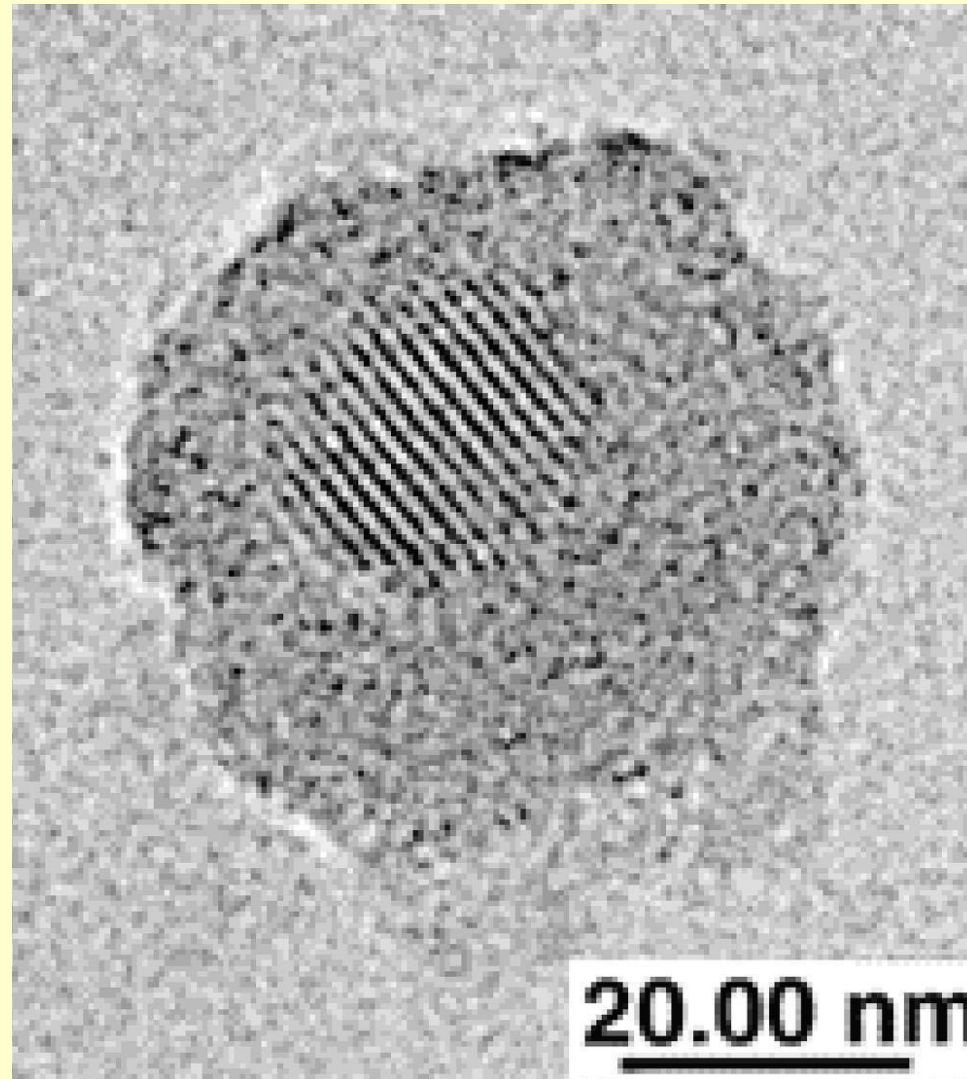
AFM growth studies of LTA

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



D4R





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

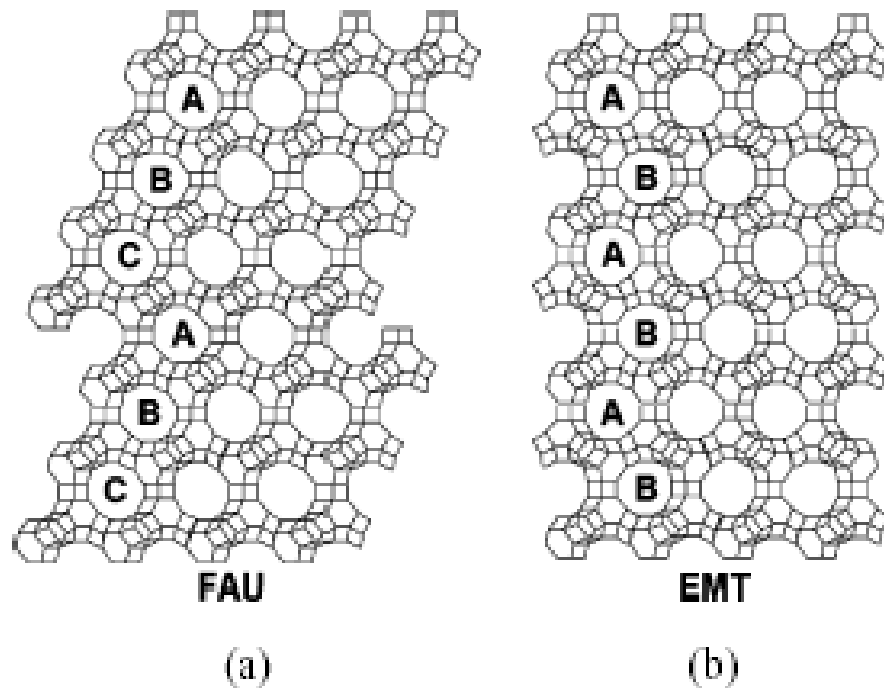
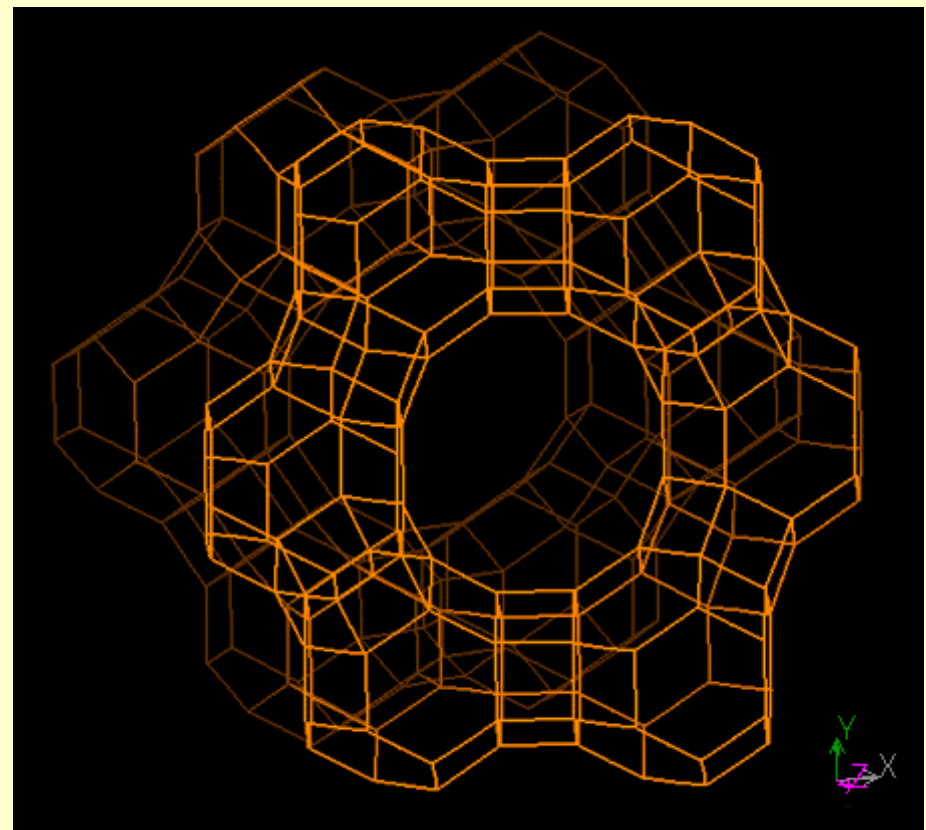
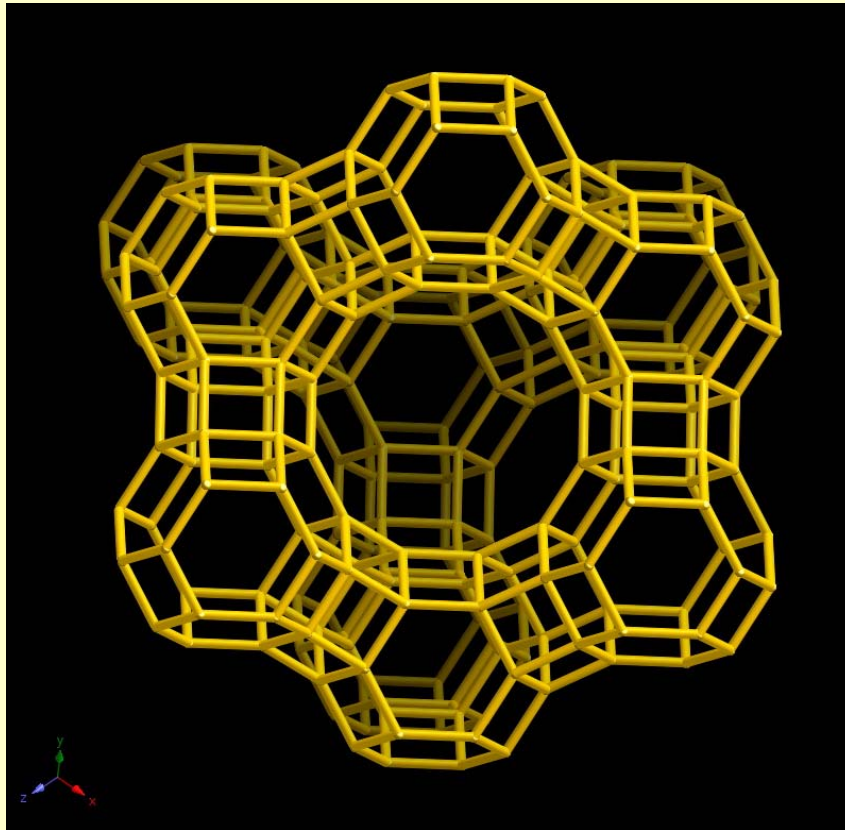


Fig. 1. Structure of zeolite Y: (a) cubic polymorph known as FAU with ABCABC... stacking, (b) hexagonal polymorph known as EMT with ABABAB... stacking.

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



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

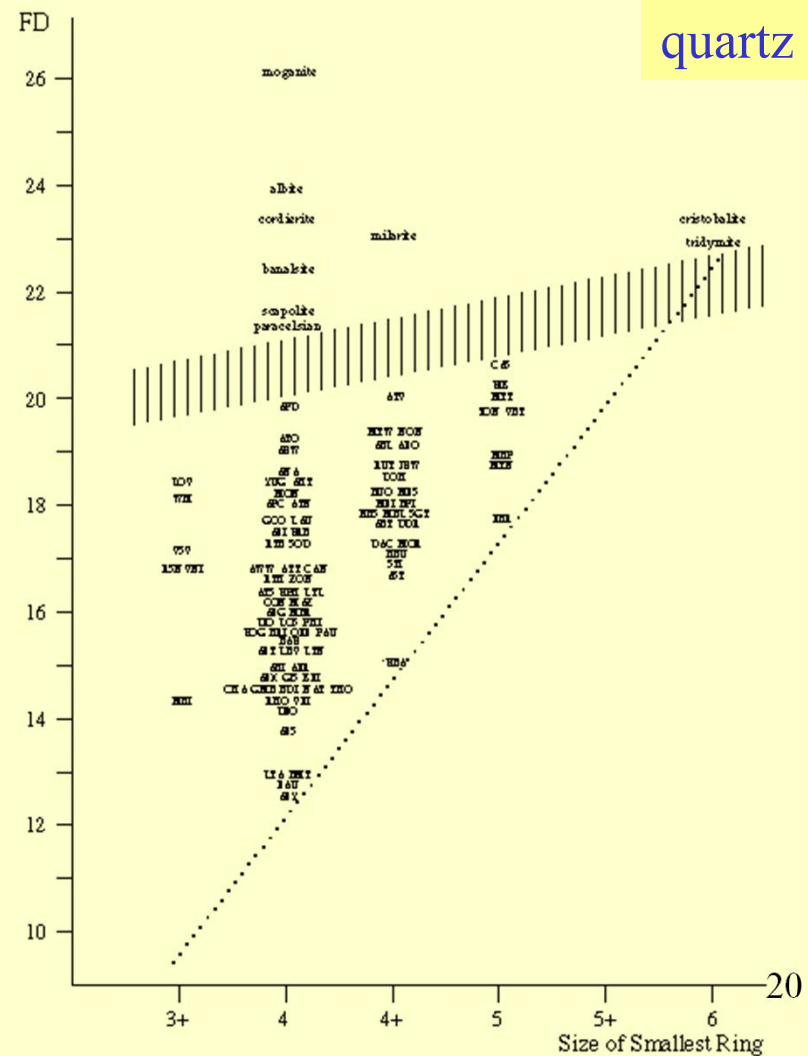
Framework Density

Framework density (FD)

Defined as the number of tetrahedral atoms (T-atoms) per cubic nanometer (1000 \AA^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

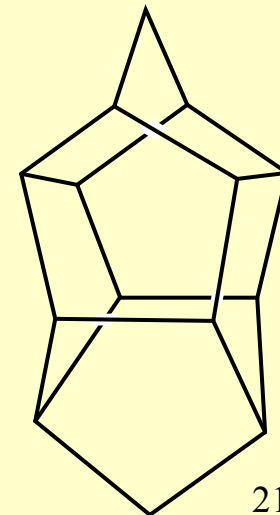
Influences cation content, hydro-phobicity/-philicity, acidity

Löwenstein rule:

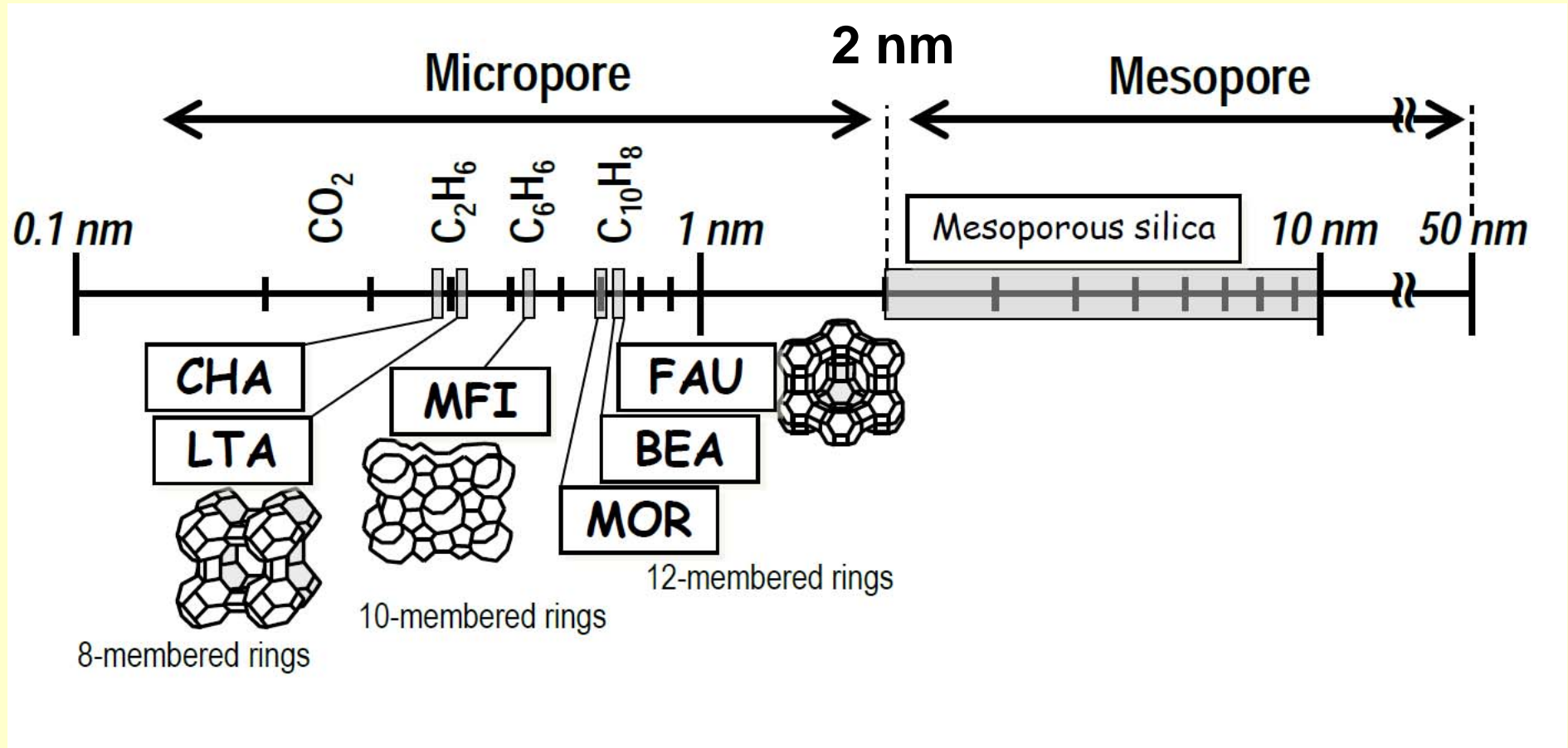
absence of the Al-O-Al moieties, in aluminosilicates $\text{Si/Al} > 1$

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

Pentasil
ZSM-5



Pores



Zeolite Synthesis

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

Aluminosilicates – high pH

🔔 **Mixing**

$\text{NaAl(OH)}_4(\text{aq}) + \text{Na}_2\text{SiO}_3(\text{aq}) + \text{NaOH}(\text{aq}), 25\text{ }^\circ\text{C}$,
condensation-polymerization, gel formation

🔔 **Ageing**

$\text{Na(H}_2\text{O)}_n^+$ template effect $\rightarrow \text{Na}_a(\text{AlO}_2)_b(\text{SiO}_2)_c \cdot \text{NaOH} \cdot \text{H}_2\text{O}(\text{gel}) \rightarrow$
25-175 °C

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

$\text{Na}_x(\text{AlO}_2)_x(\text{SiO}_2)_y \cdot z\text{H}_2\text{O}(\text{crystals})$

🔔 **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 $\text{AlPO}_4\text{-5}$, 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 $\text{AlPO}_4\text{-20}$

-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

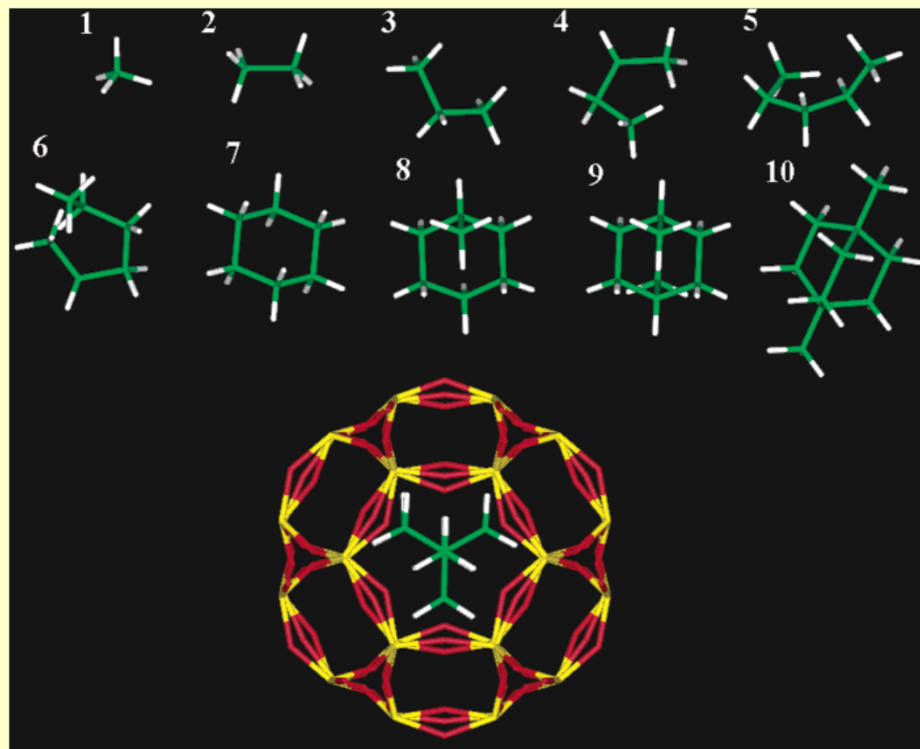
A curiosity: aluminophosphate VPI-5 does not require any guest for its formation!

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.

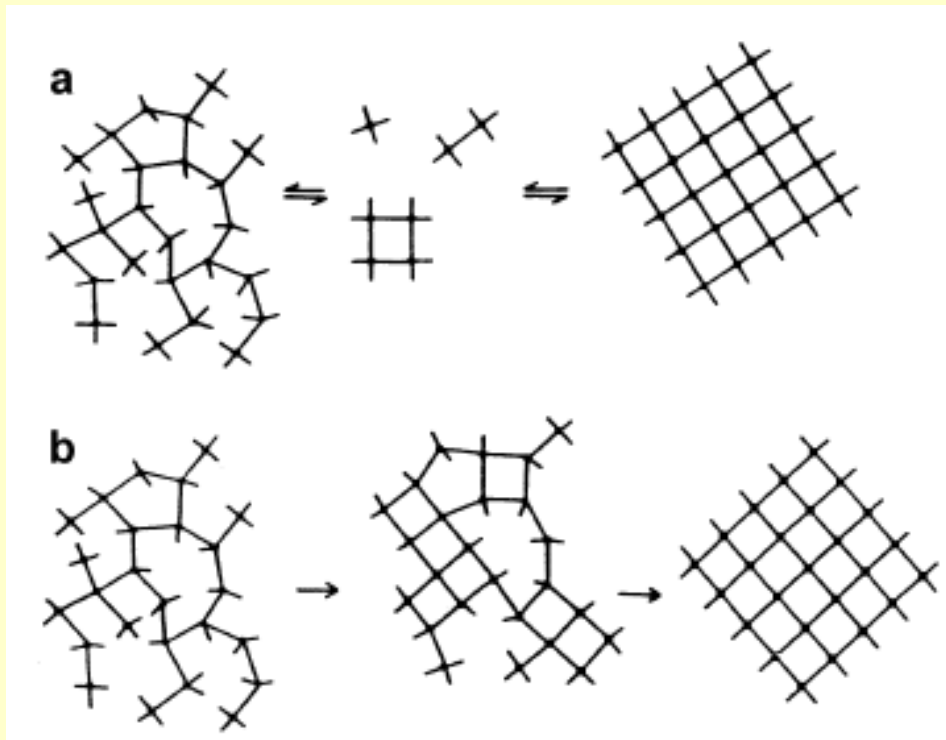
Existence of primary and secondary units in a synthesis mixture

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



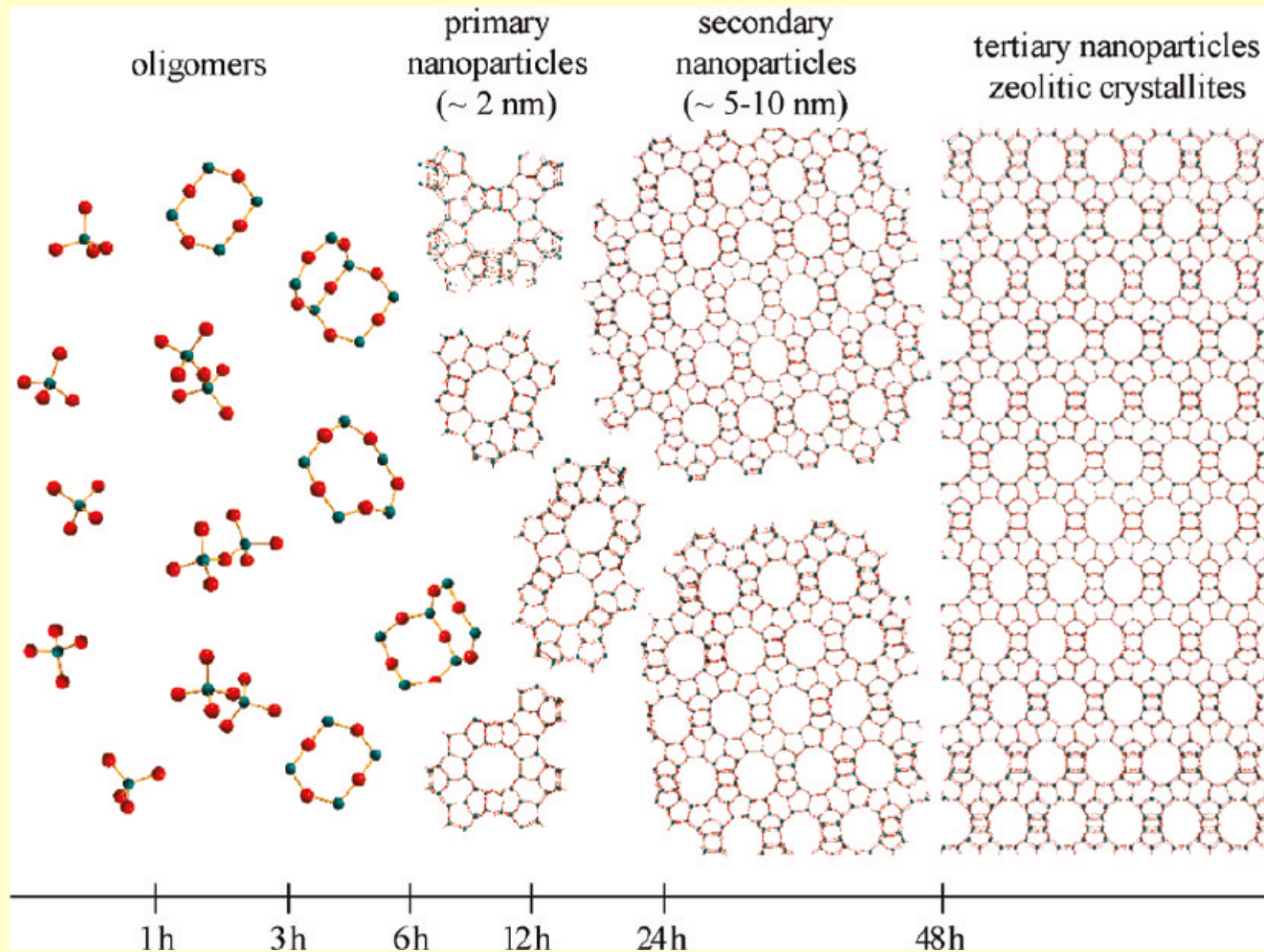
Zeolite Synthesis Mechanisms

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

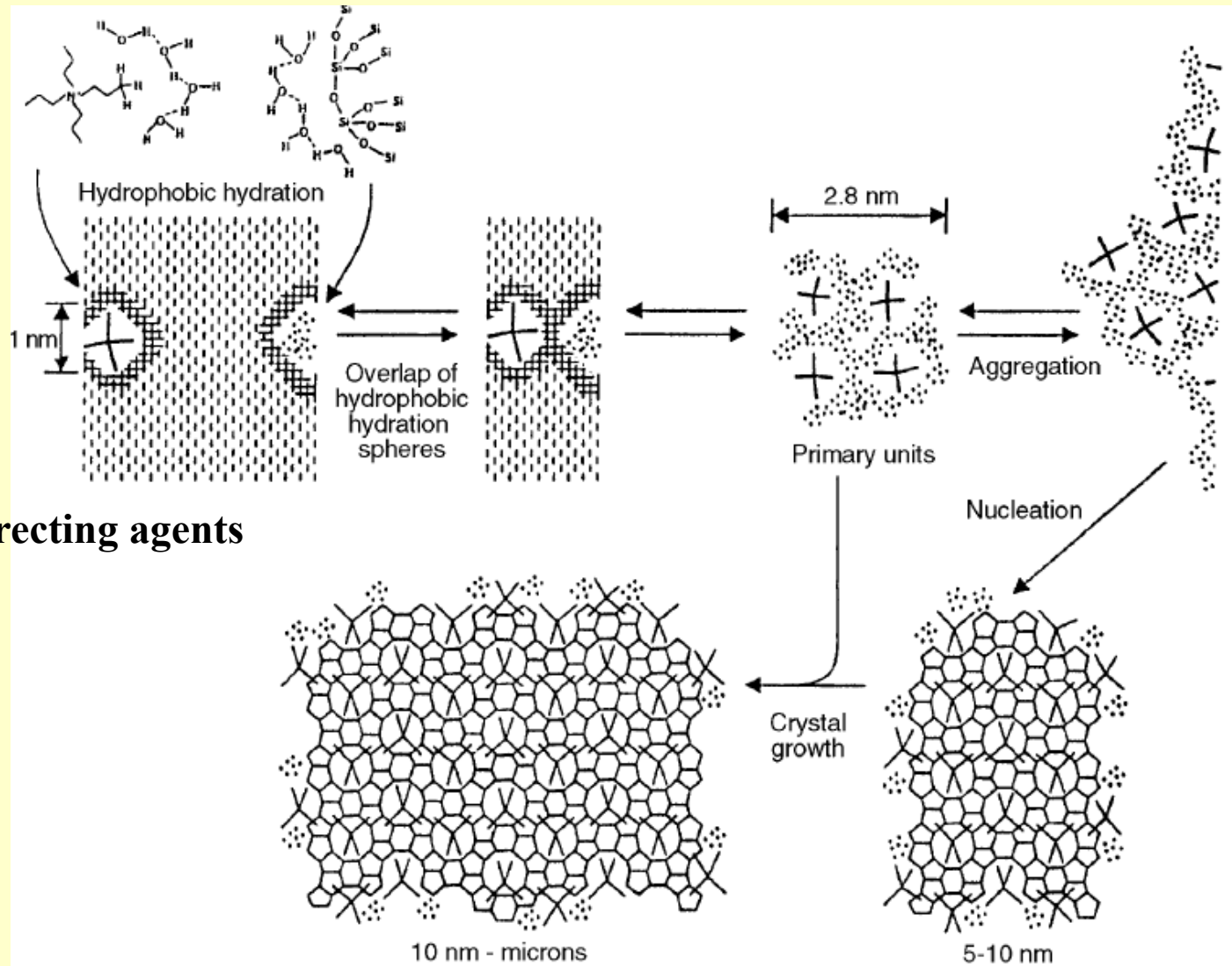


(b) "in situ" rearrangement of the gel

Zeolite Synthesis Mechanisms

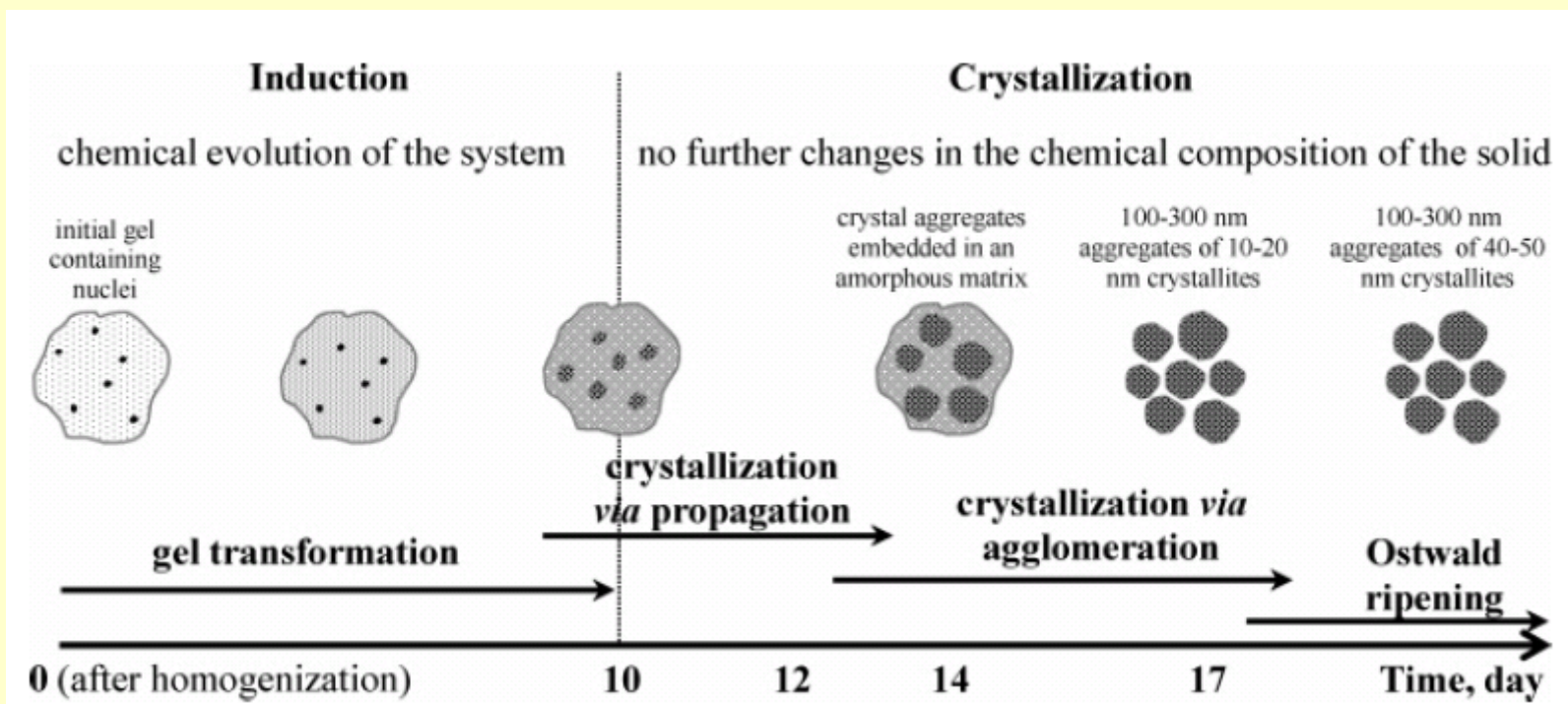


Zeolite Synthesis Mechanisms



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 parameters, window size

decreases number of cations, free space

increases hydrophobicity

✦ Reaction temperature, higher T, larger pores

Stability Rules

Löwenstein rule: never Al-O-Al

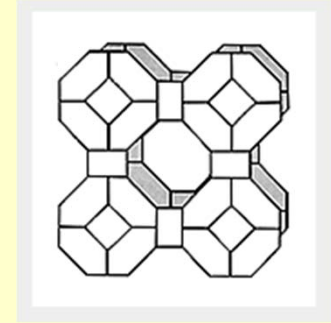
Dempsey rule: Al-O-Si-O-Si-O-Al

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

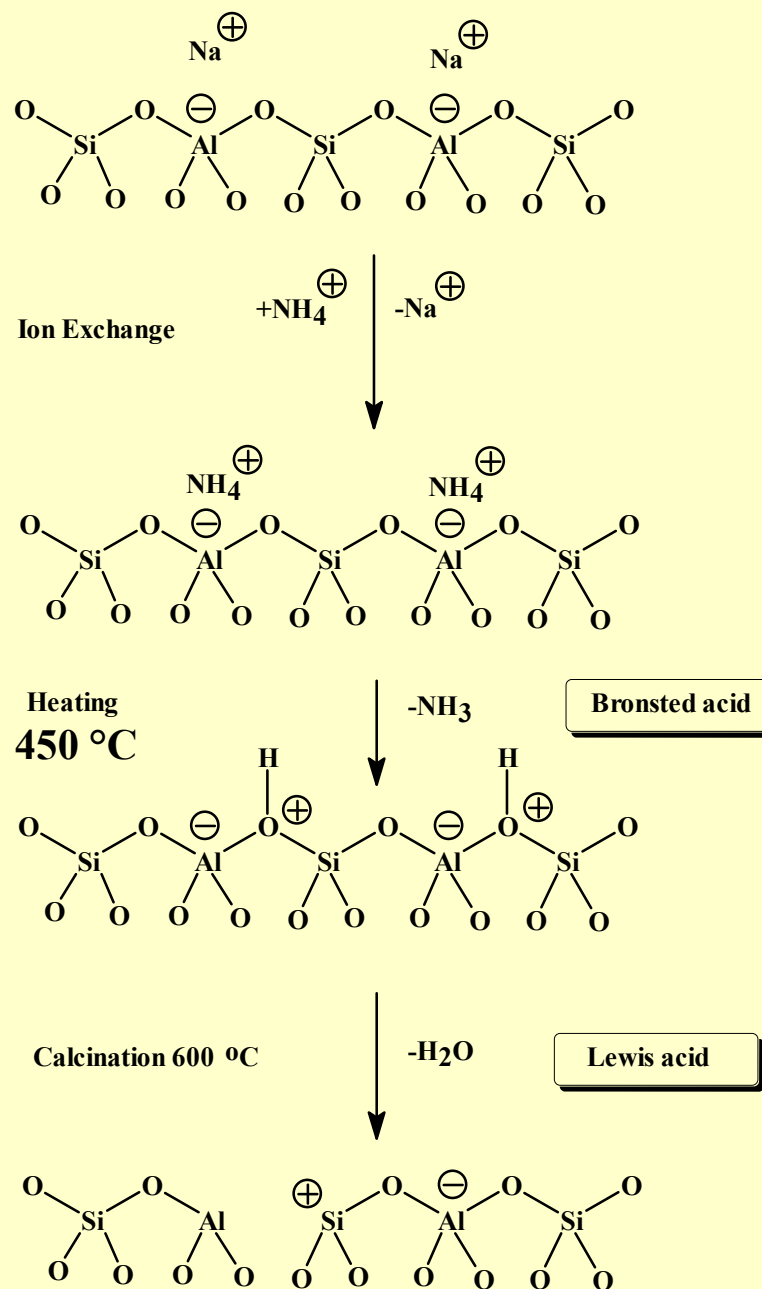
Brønsted Acidity

Tuning Brønsted acidity:

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

Solid acid for the hydrocarbon cracking

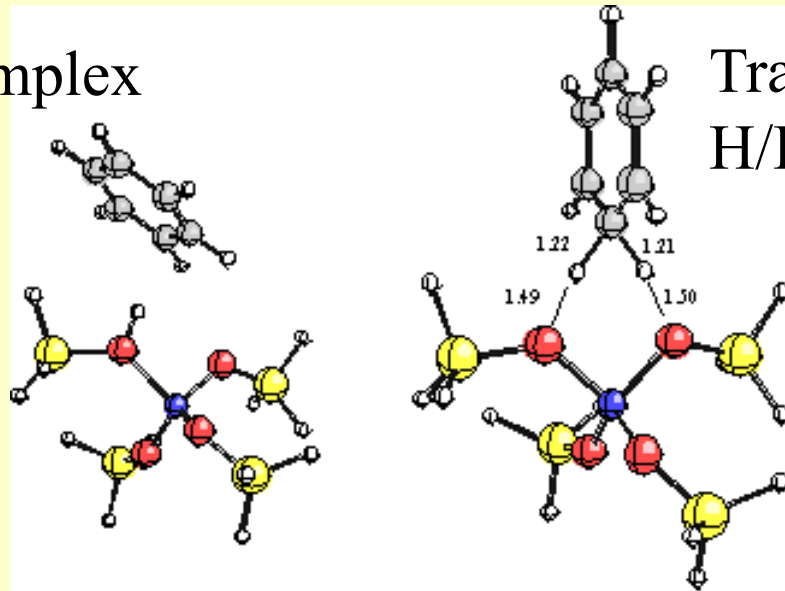
The larger the Si/Al ratio, the more acidic is the zeolite



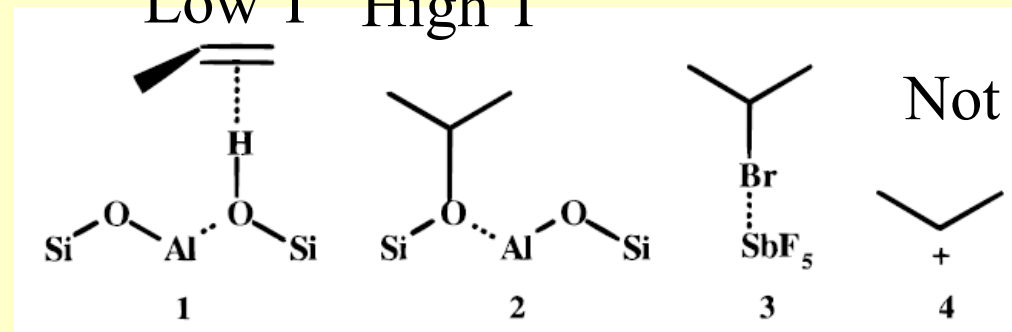
Strong Brønsted Acidity

Protonation of benzene

π -complex



Low T High T



Not present in zeolites

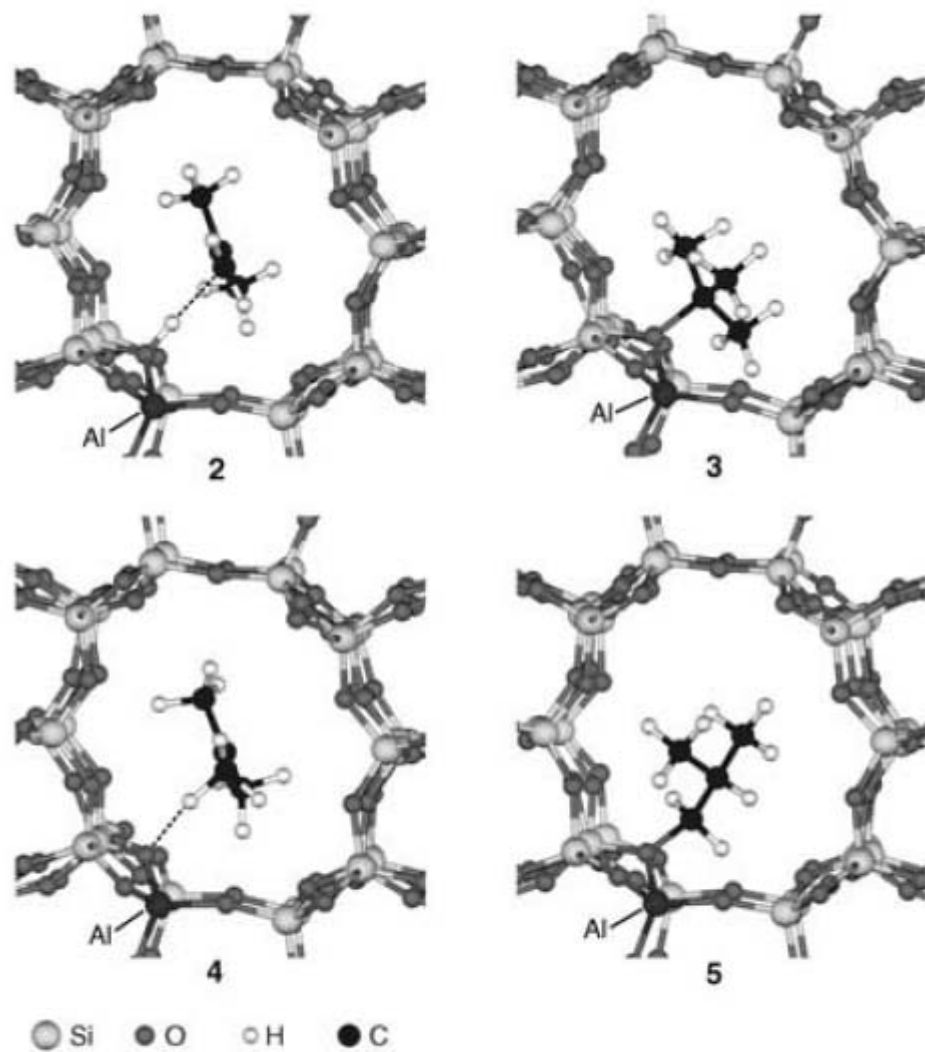
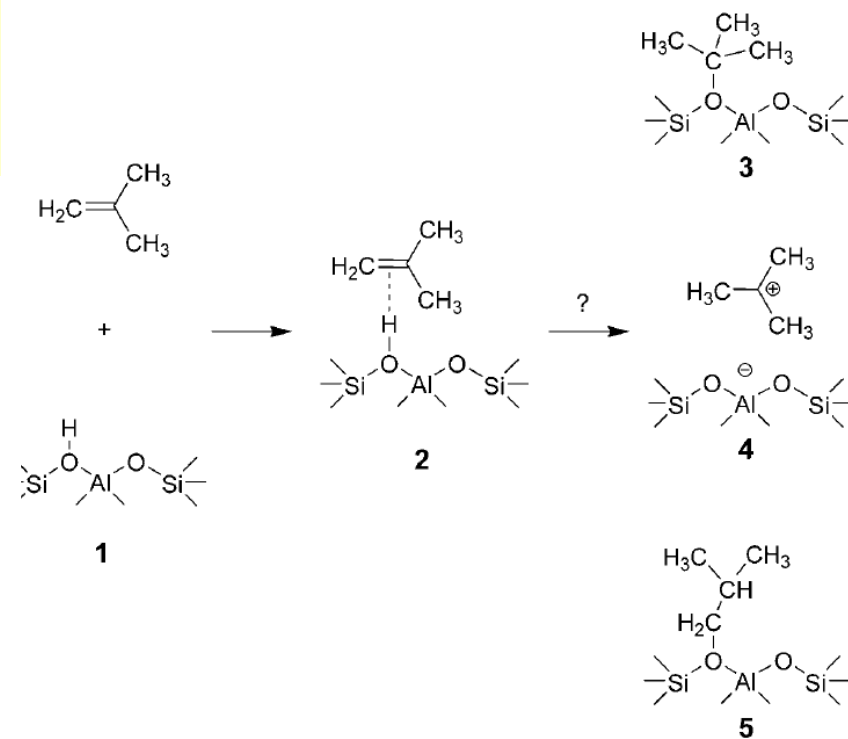


Figure 1. Portions of the structures calculated for the π complex of isobutene in ferrierite (2), for the *tert*-butyl cation in ferrierite (4), and for the *tert*-butoxide (3) and isobutoxide (5) of ferrierite.

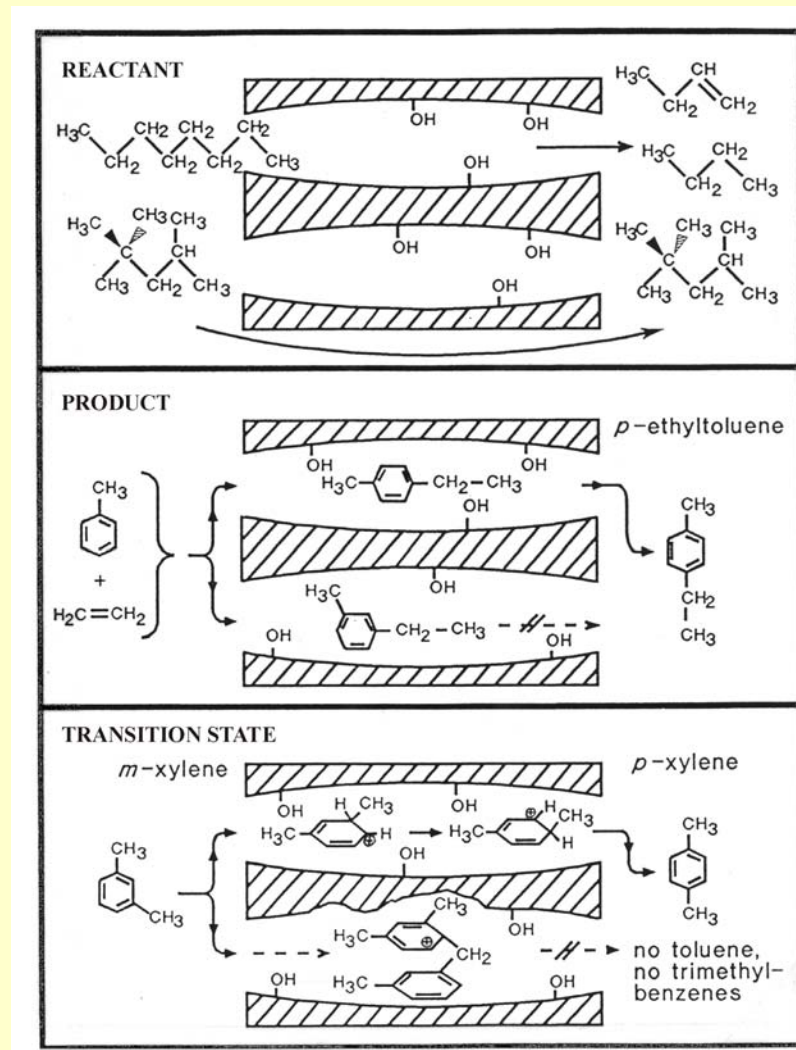


Size-Shape Selectivity

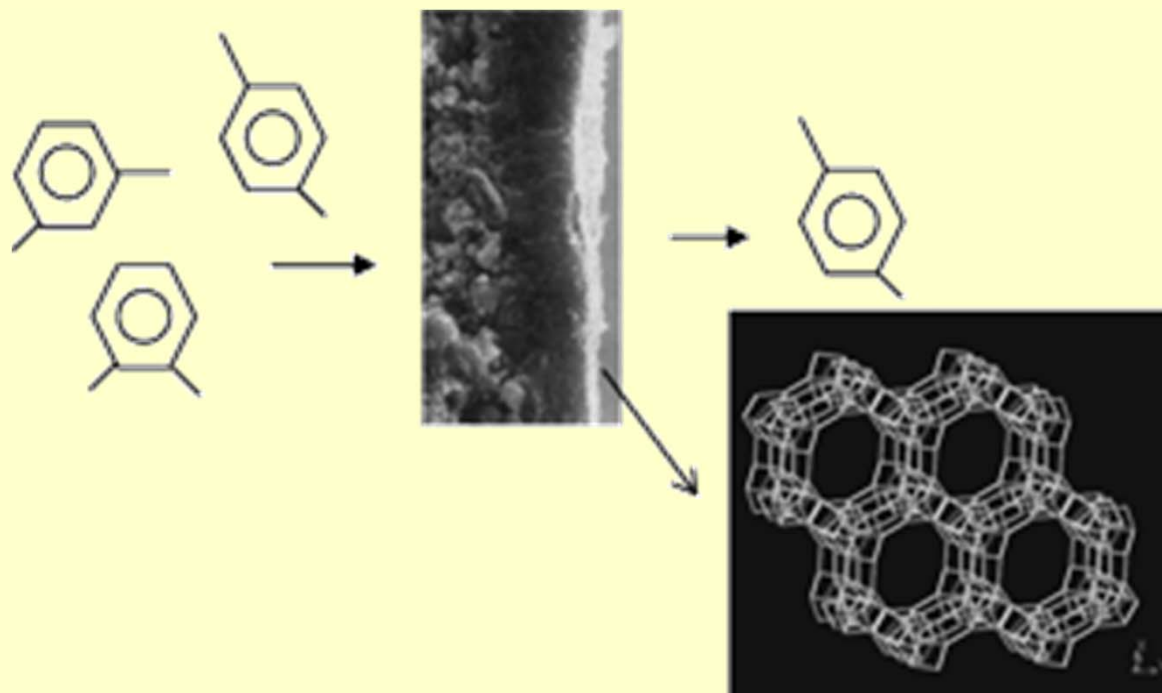
Size-shape selective catalysis, separations, sensing

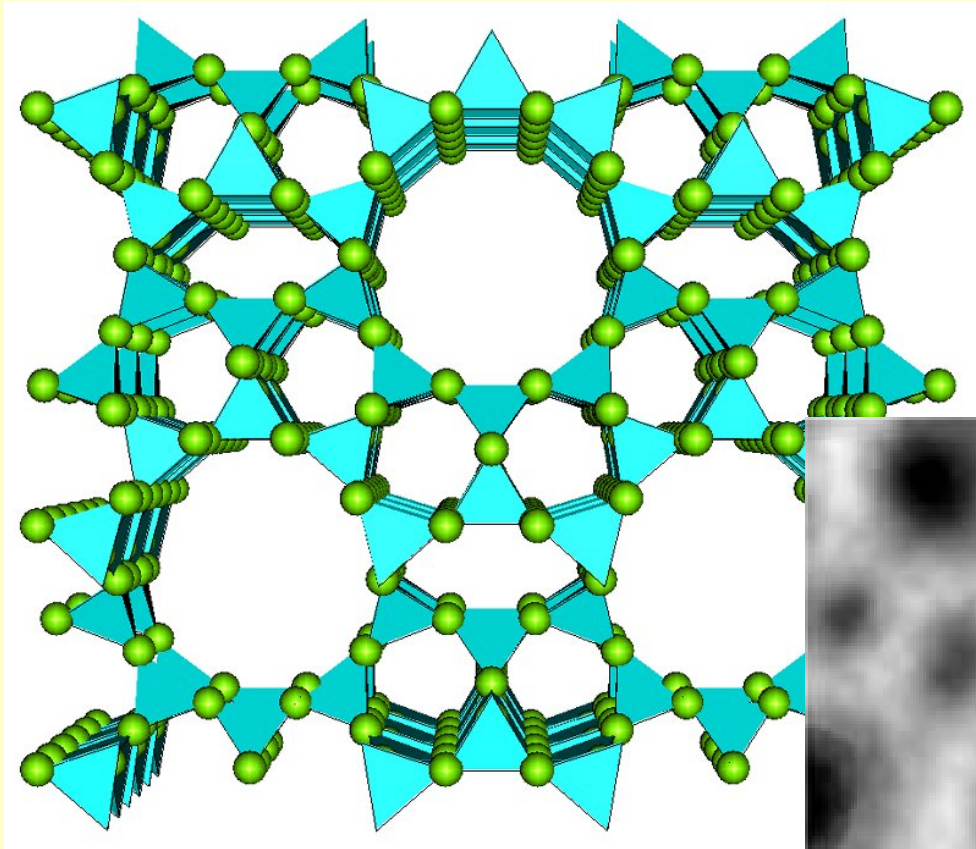
Selectivity at:

- Reactants
- Products
- Transition state

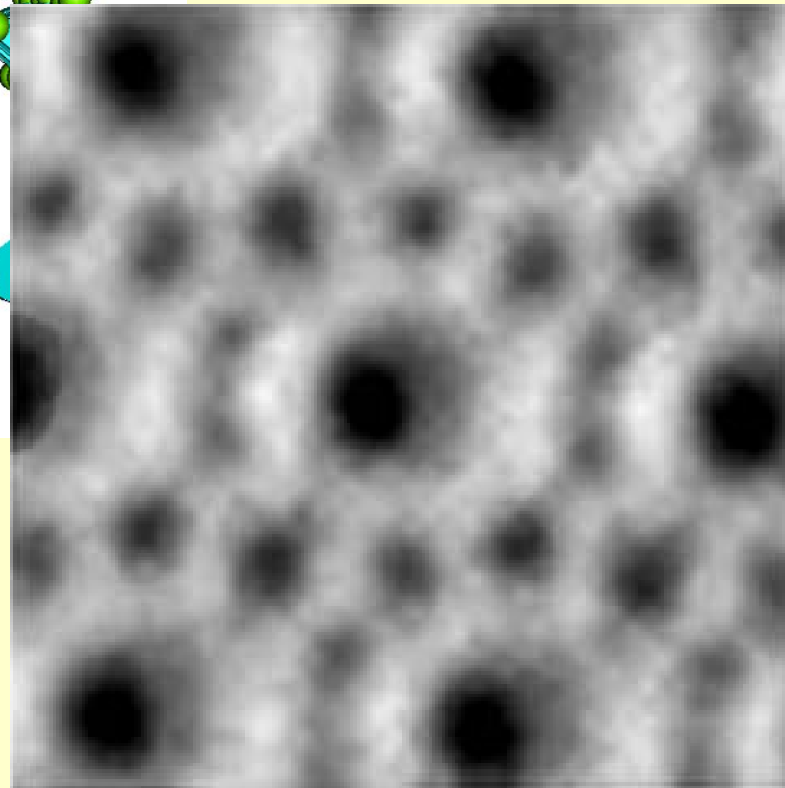


Separation of xylene isomers by pervaporation through a MFI membrane





HRTEM



Aluminophosphates

✦ Isoelectronic relationship of AlPO_4 to $(\text{SiO}_2)_2$

✦ 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 $(\text{AlO}_2^-)(\text{PO}_2^+) = \text{AlPO}_4$

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

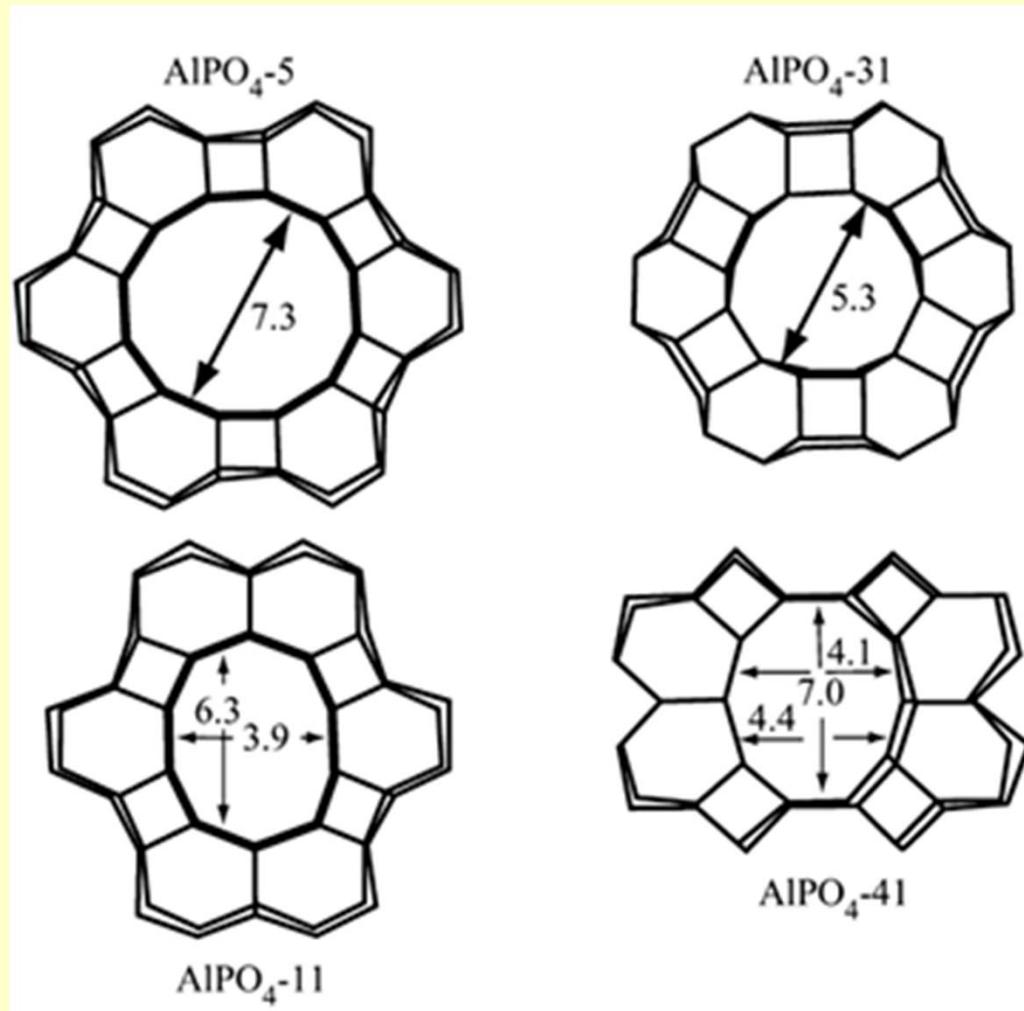
M^{1+} , M^{2+} , and M^{3+} incorporate into the Al sites

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, $\text{Al}(\text{O})(\text{OH})$, $\text{Al}(\text{O}i\text{-Pr})_3$

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

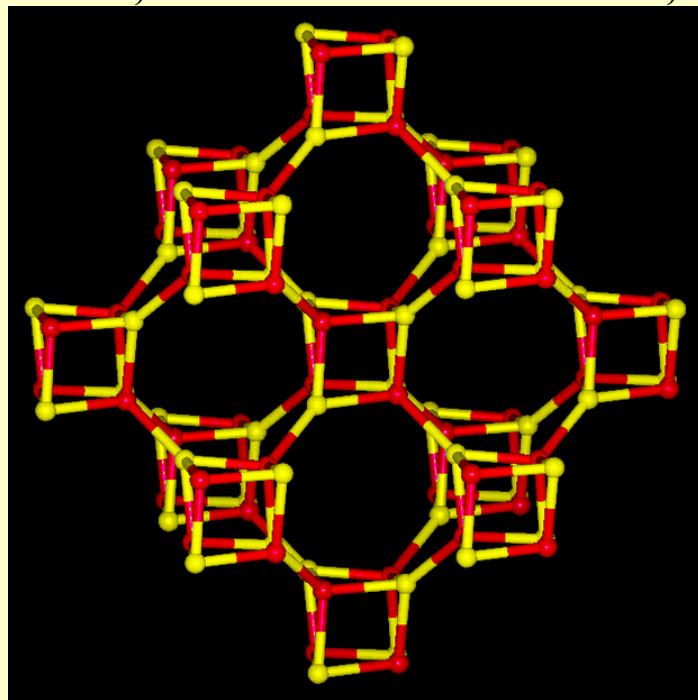
Cobalto-Aluminophosphate

ACP-1 (Co/Al 8.0)

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

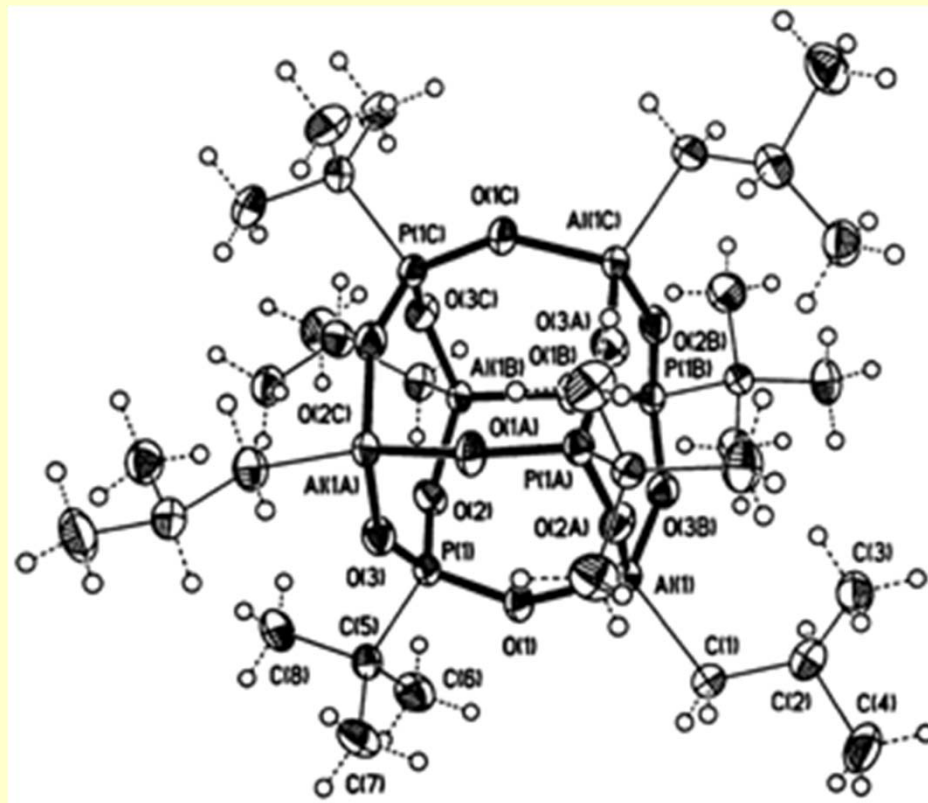
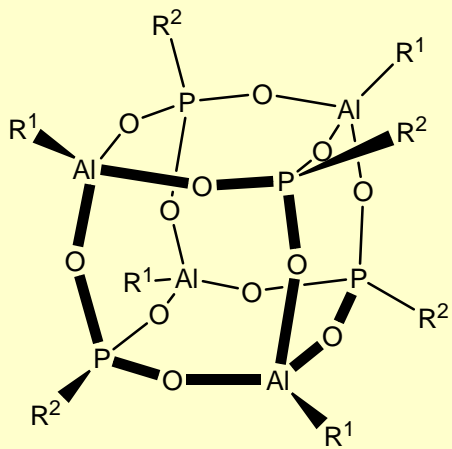
Ethylenediamine molecules are located inside 8-ring channels

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



$\text{Al}(\text{O}-i\text{Pr})_3$, $\text{CoCO}_3 \cdot \text{H}_2\text{O}$, 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)



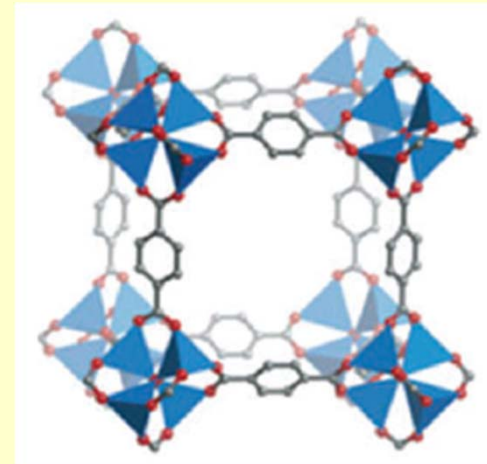
Metallo-Organic Framework (MOF) Structures

4000 structures known (2008), 1000 new per year

Porous coordination polymers (PCP)

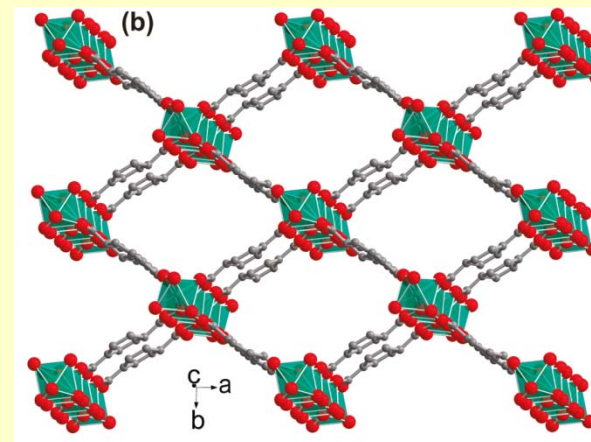
Metal centers

- Coordinative 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:

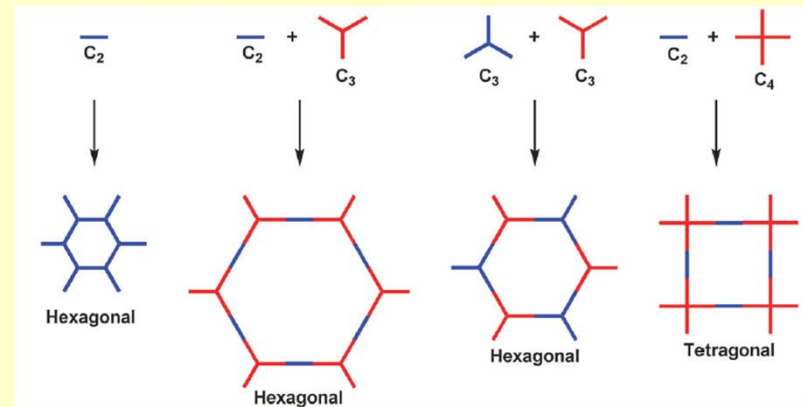
Discrete symmetry: C_∞ , C_2 , C_3 , C_4 , T_d , ...

Rigid, inert

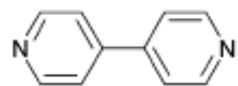
Functional groups for linking

Suitable linking reaction

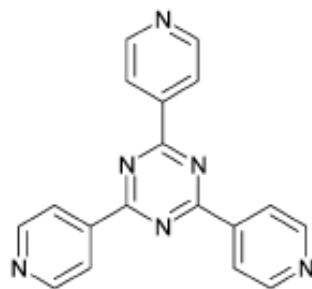
Discrete bonding direction



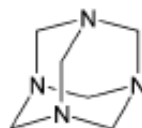
Polytopic Organic Linkers



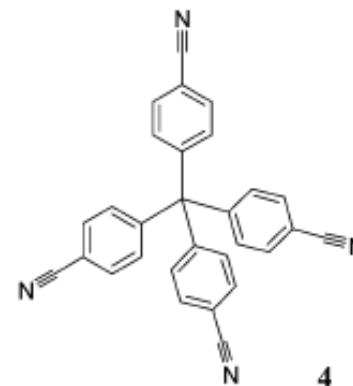
1



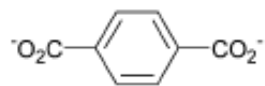
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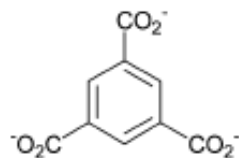
3



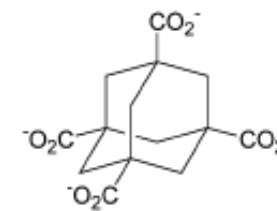
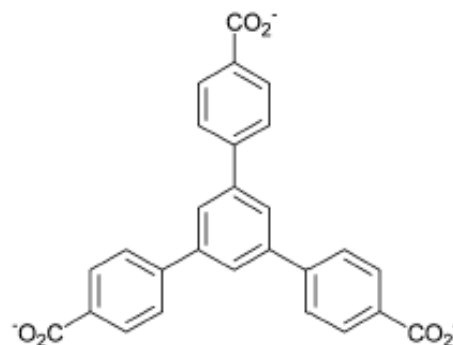
4



5



6

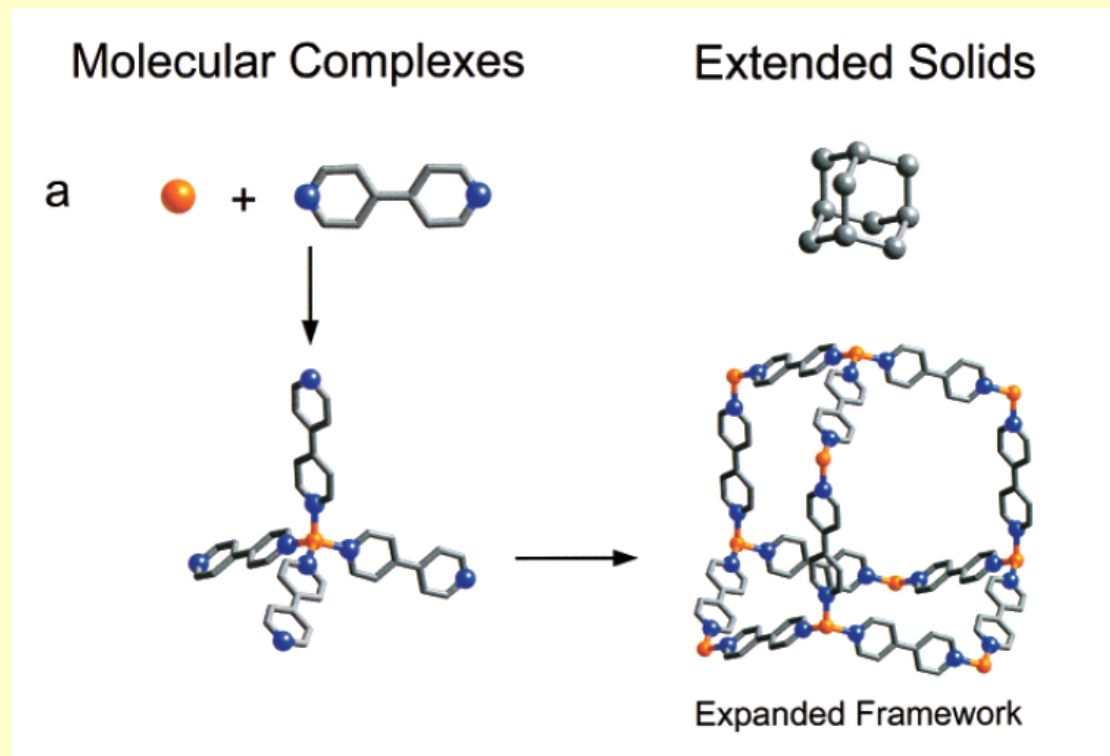


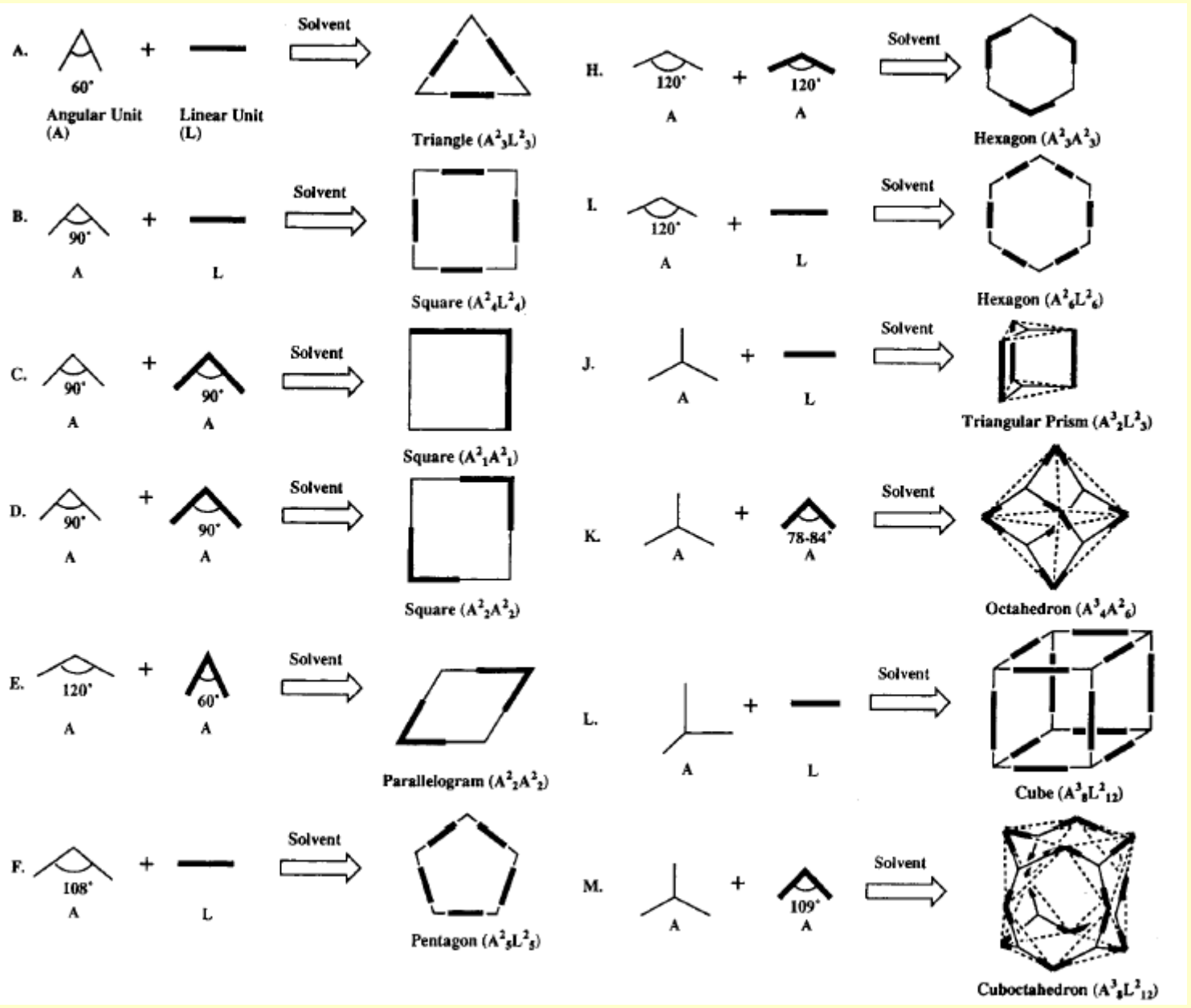
8

Polytopic N-bound Organic Linkers

Cationic framework structures

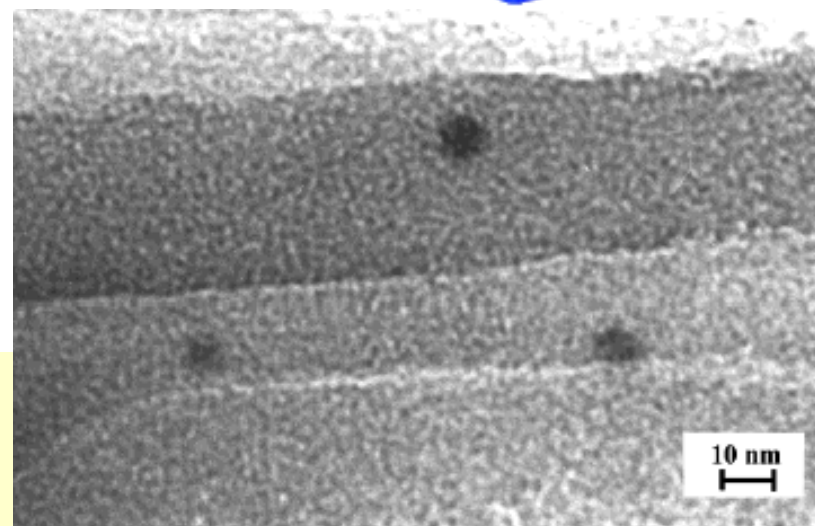
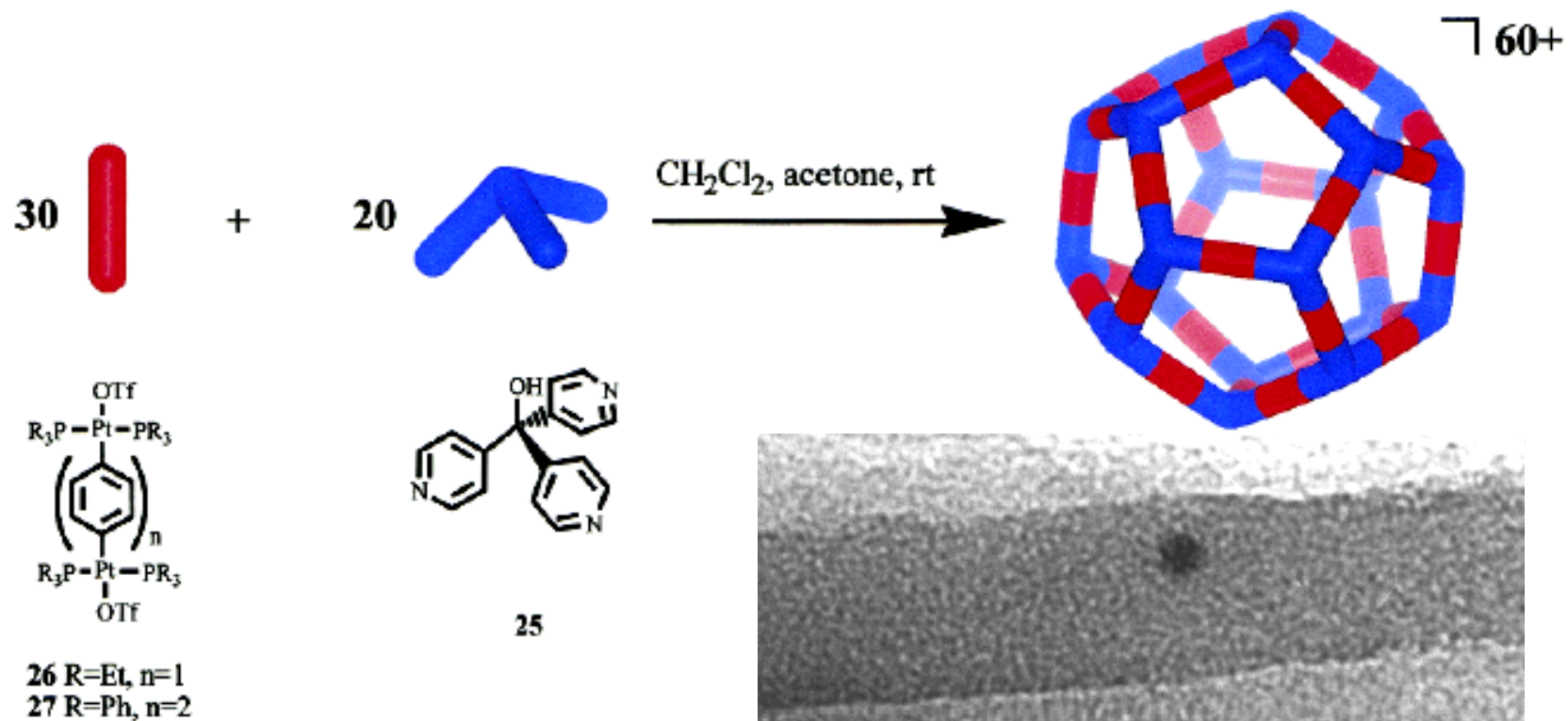
Evacuation of guests within the pores usually results in collapse of the host framework





Metallo-Organic Framework Structures

Scheme 4. Self-Assembly of Dodecahedra



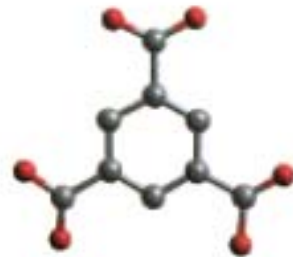
Polytopic carboxylate linkers



1,4-benzenedicarboxylate
(BDC)



1,4-azodibenzoate
(ADB)



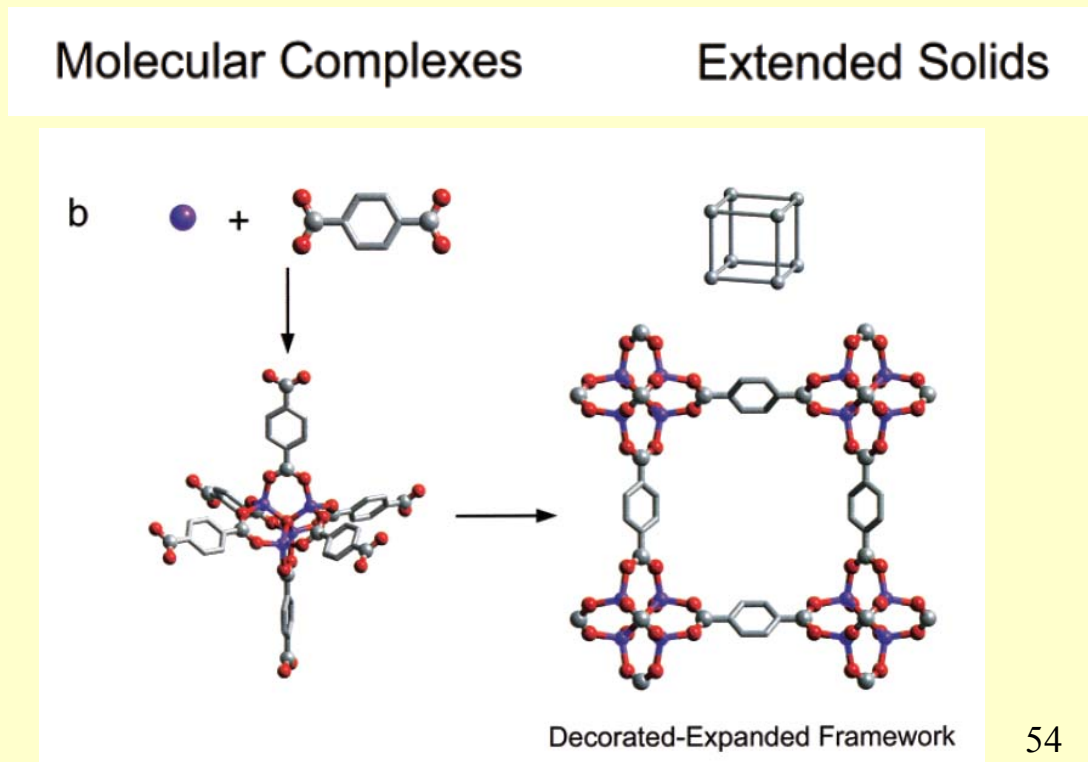
1,3,5-benzenetricarboxylate
(BTC)



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

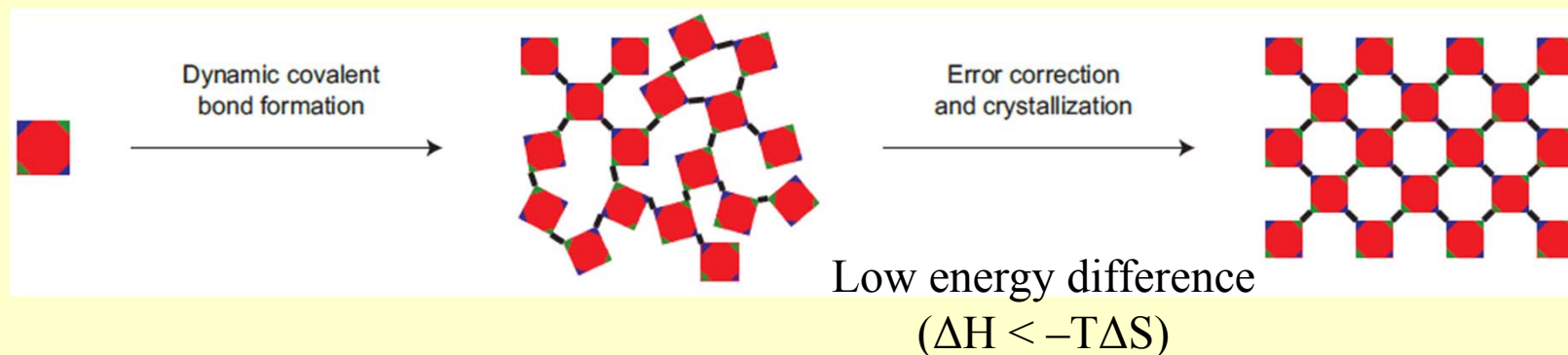
Mechanism for error correction required

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



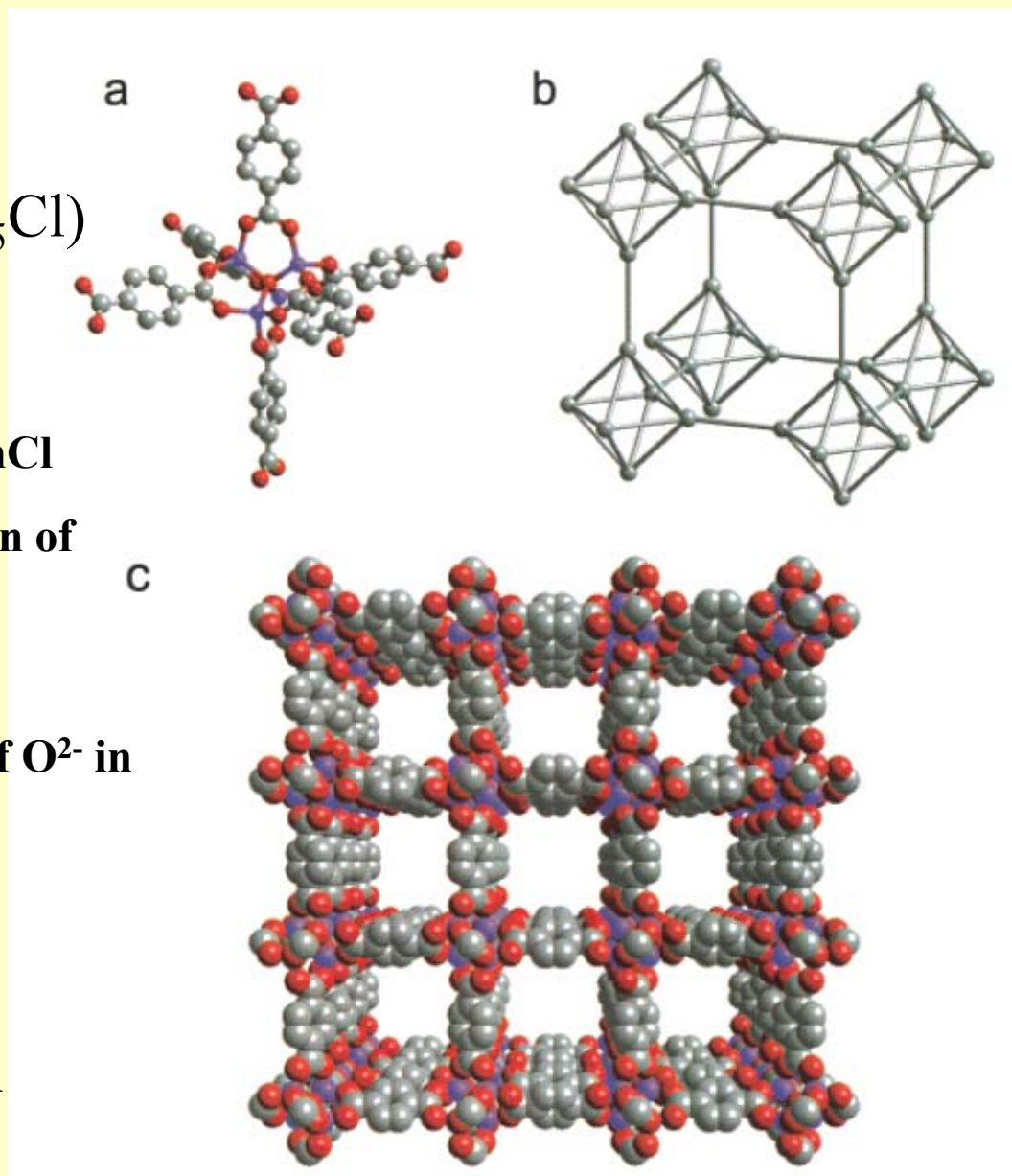
MOF-5



- $\text{Zn}(\text{NO}_3)_2 + \text{H}_2\text{BDC}$ 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



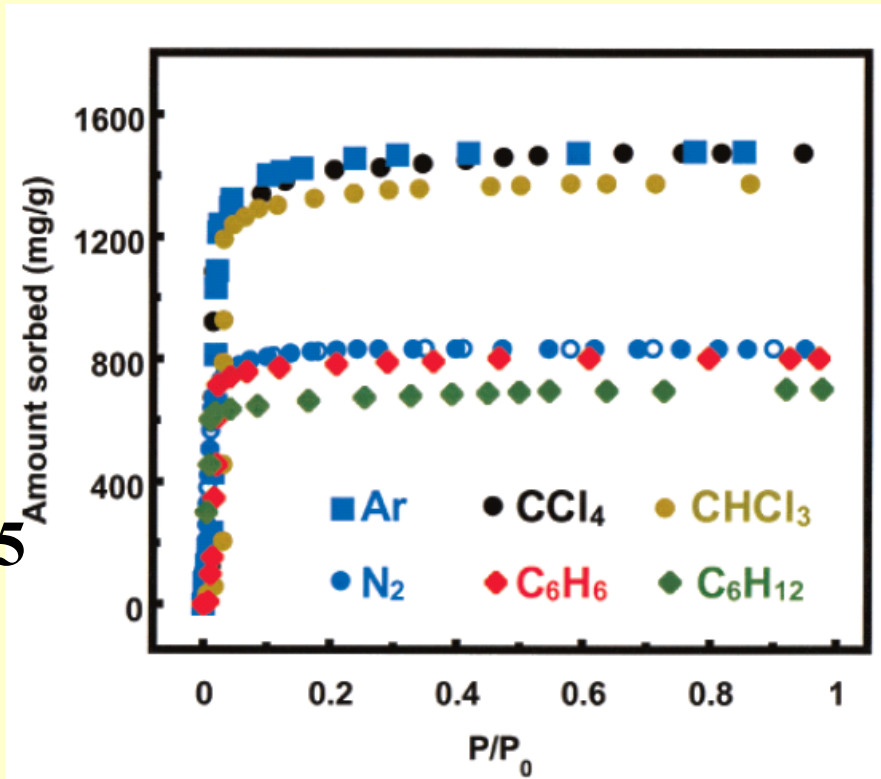
a primitive cubic lattice

MOF-5

MOF-5

Stable even after desolvation
at 300 °C in air

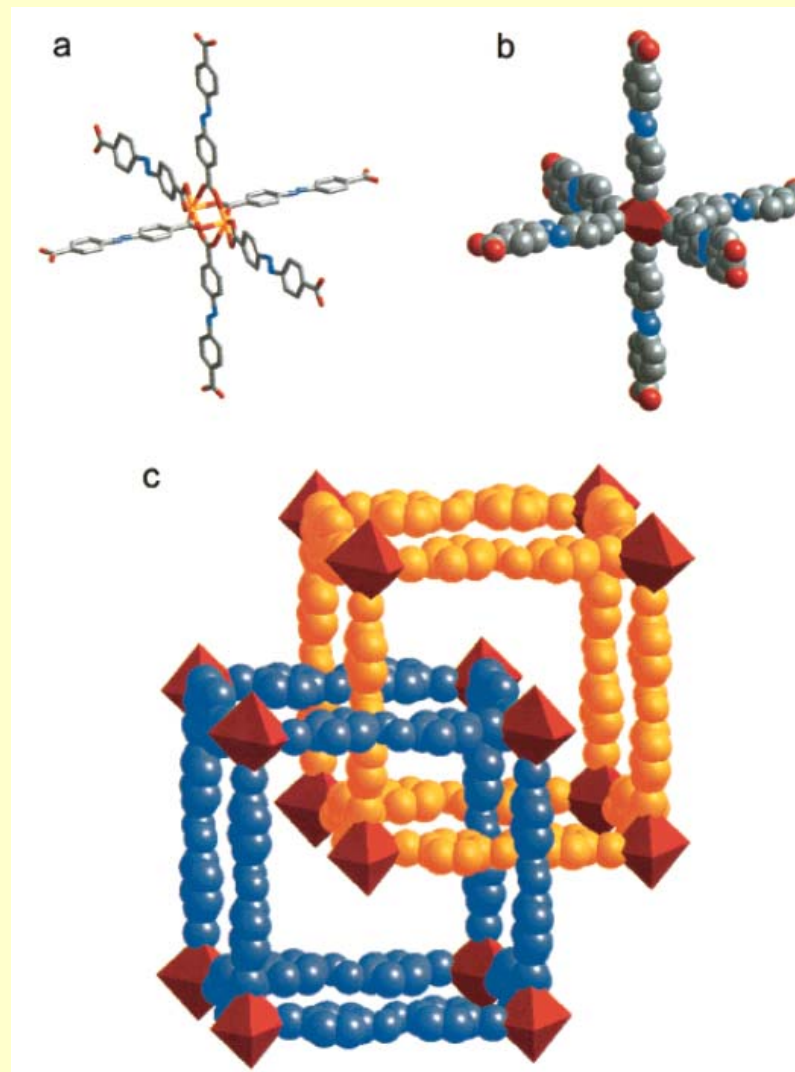
gas sorption isotherms for MOF-5



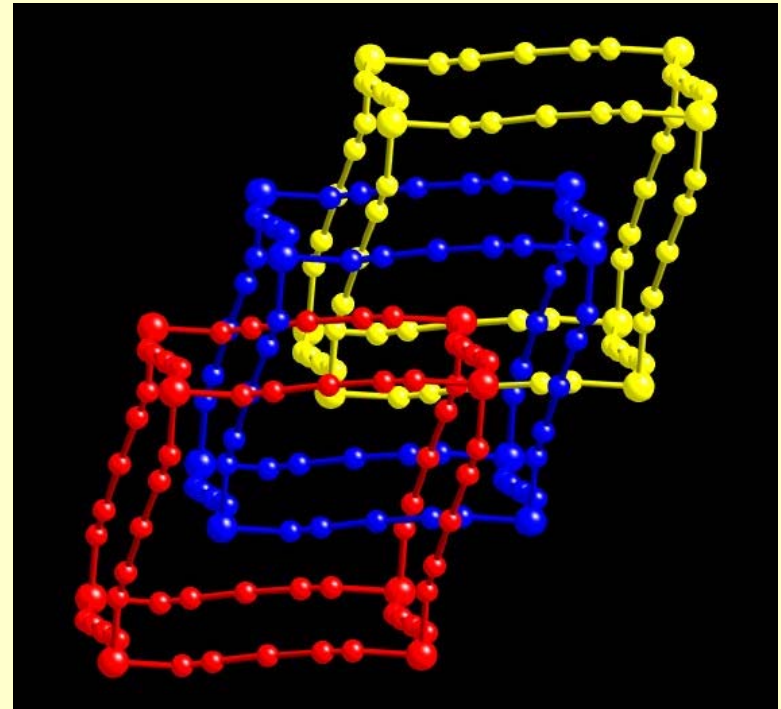
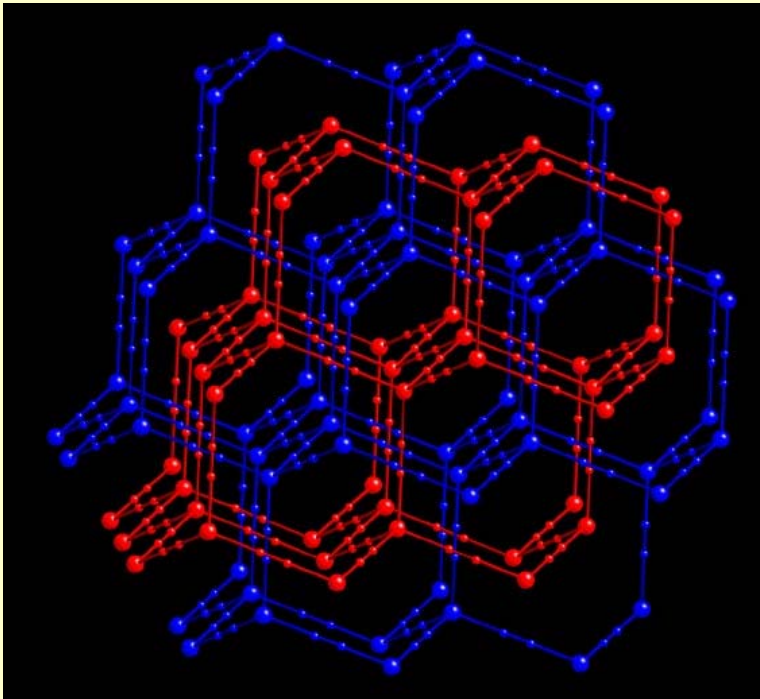
	MOF -2	MOF -3	MOF -4	MOF -5	MOF -6	MOF -9	MOF -11
pore diameter (Å)	7	8	14	12	4	8	7
surface area (m ² /g)	270	140		2900		127	560
pore volume (cm ³ /g)	0.094	0.038	0.612	1.04	0.099	0.035	0.20

Interpenetration

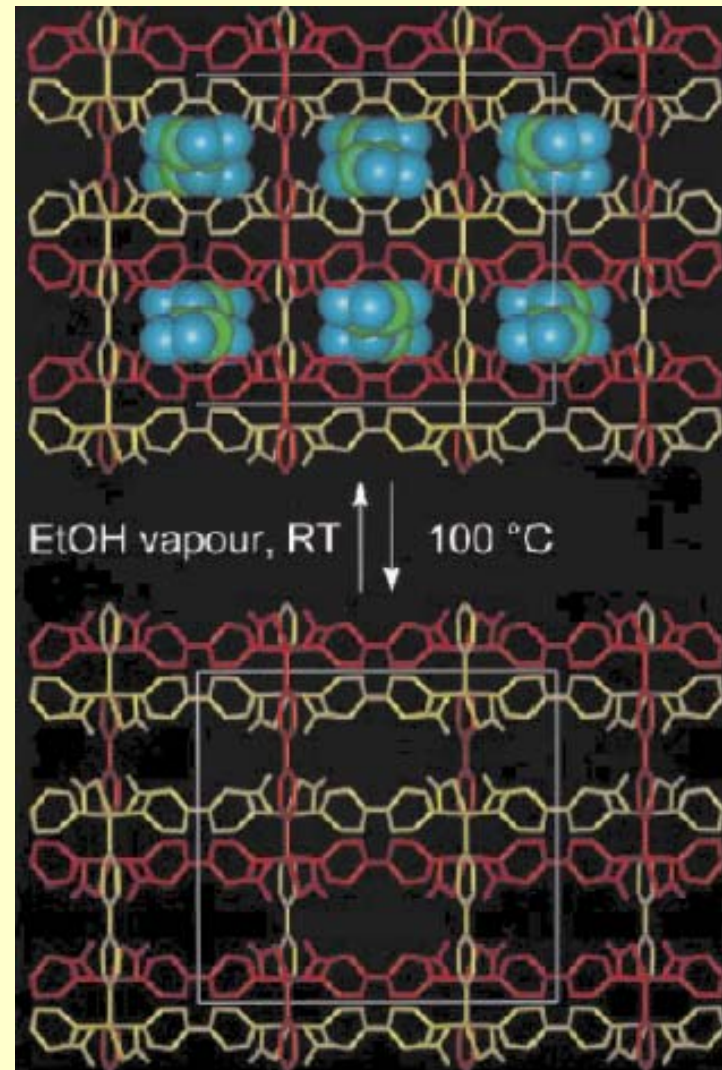
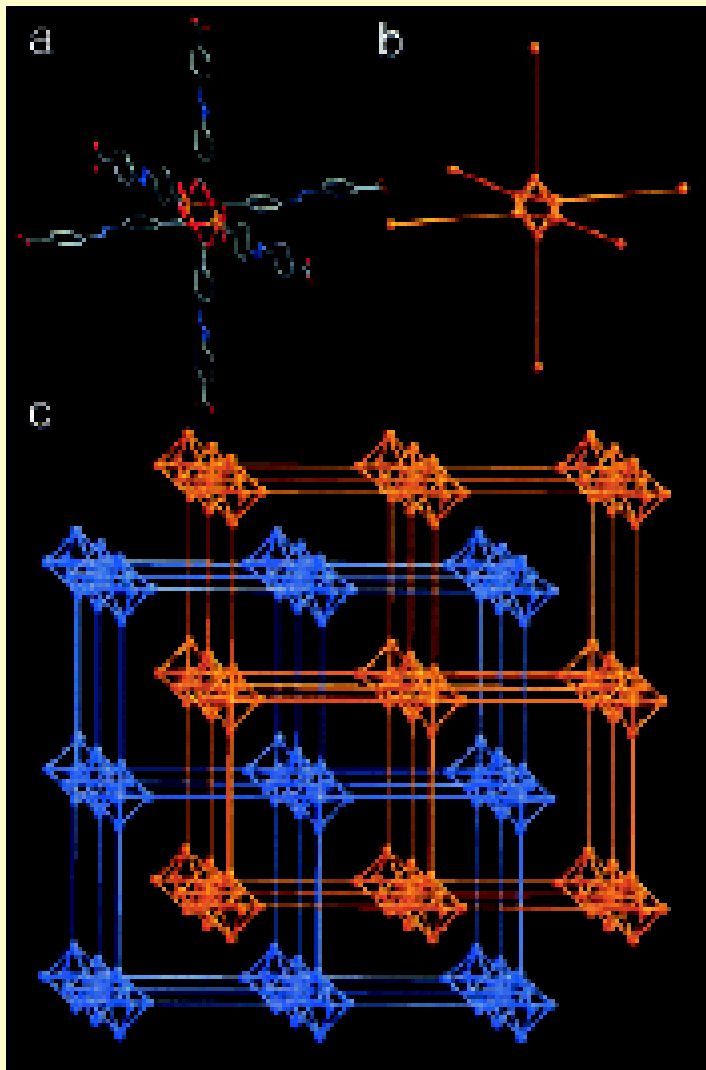
MOF-9



Interpenetration

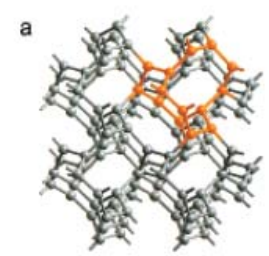


Metallo-Organic Framework Structures

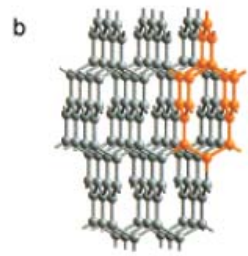


Basic Nets

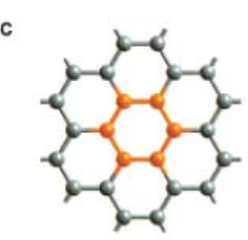
coordination	coordination figures		net
3	triangle	triangle	SrSi_2
3	triangle	triangle	ThSi_2
3	triangle	triangle	6^3 honeycomb
3,4	triangle	square	Pt_3O_4
4	square	square	NbO
4	tetrahedron	tetrahedron	diamond (C)
4,4	square	tetrahedron	cooperite (PtS)
4	square	square	4^4 square lattice
6	octahedron	octahedron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



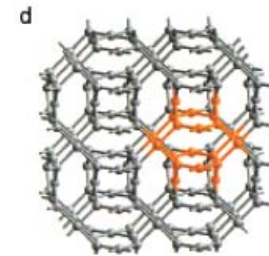
Si net of SrSi_2



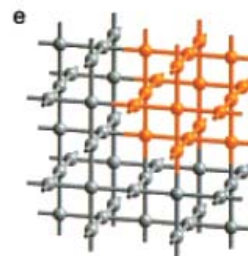
Si net of ThSi_2



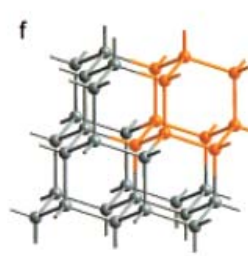
6^3 Honeycomb



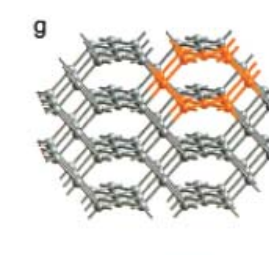
Pt_3O_4



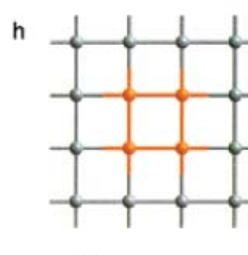
NbO



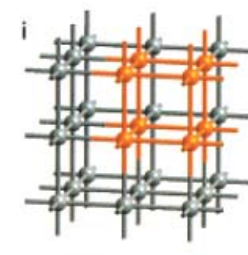
Diamond (C)



Cooperite (PtS)

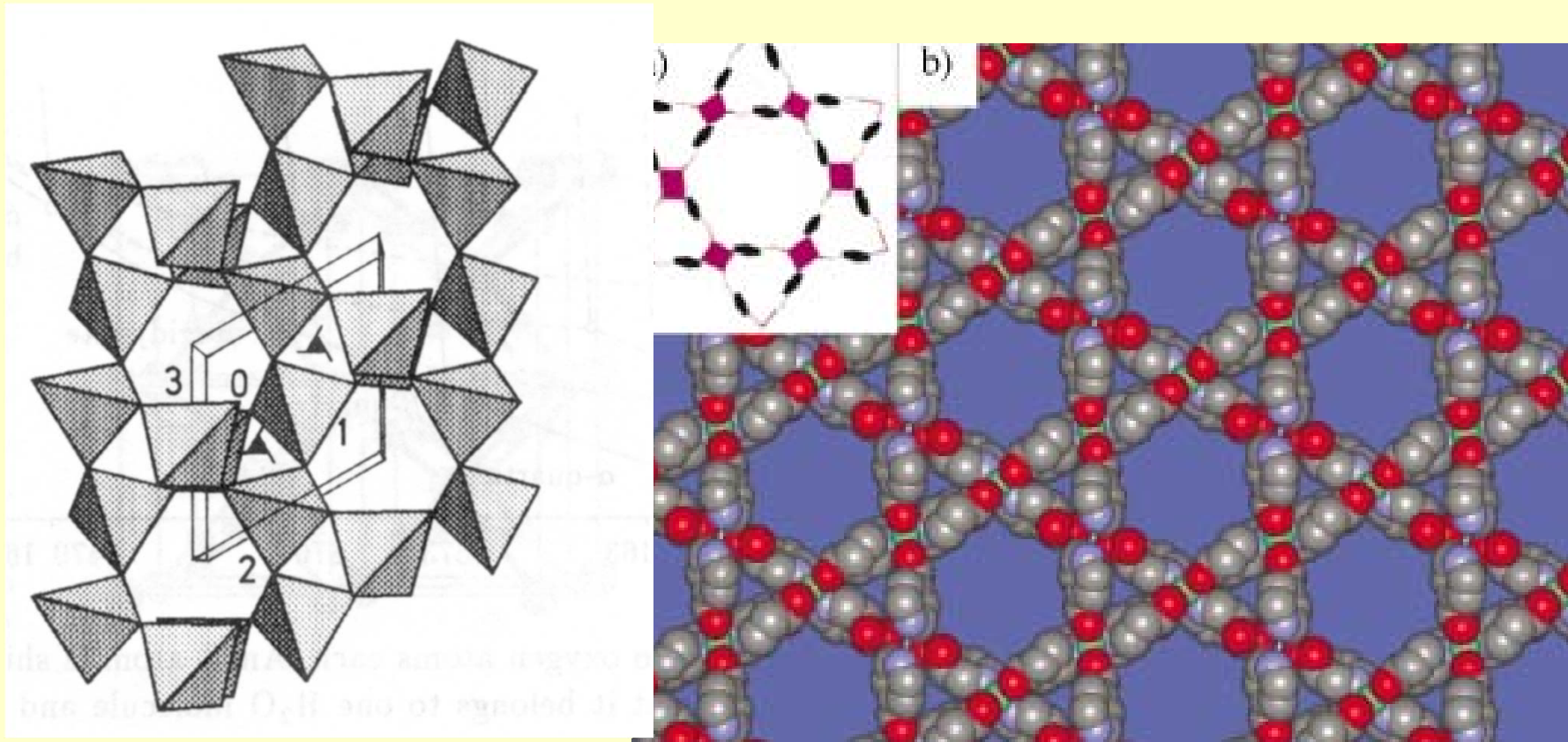


4^4 Square lattice

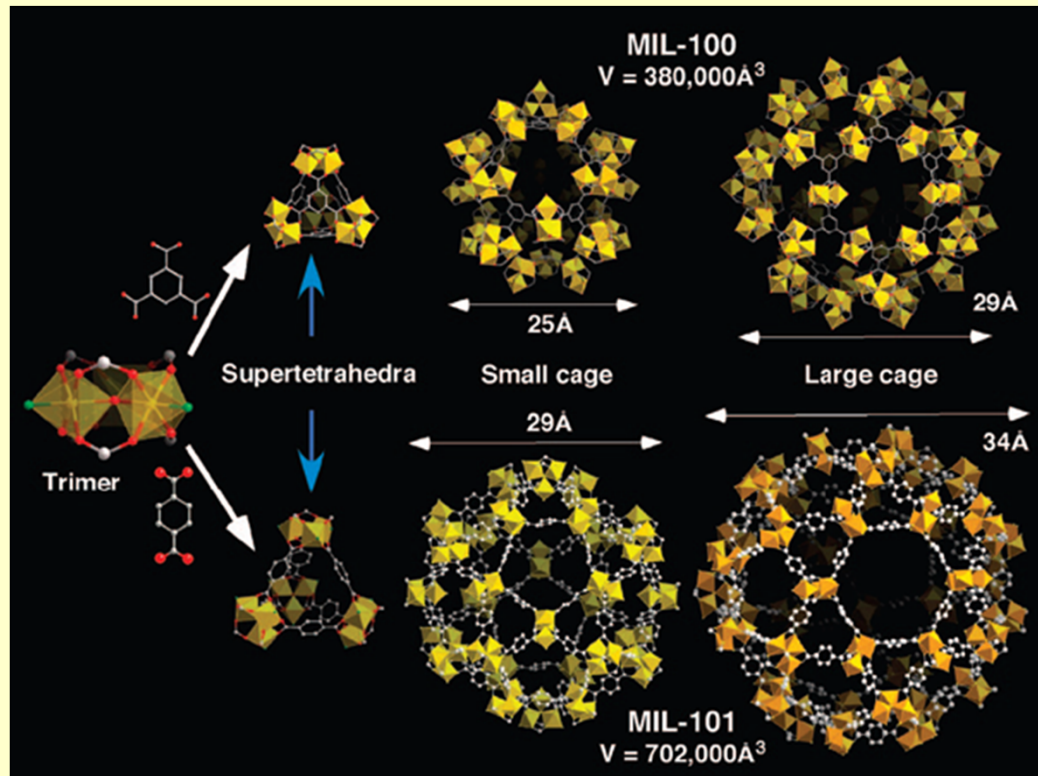


Primitive cubic

Inorganic and Metallo-Organic Quartz



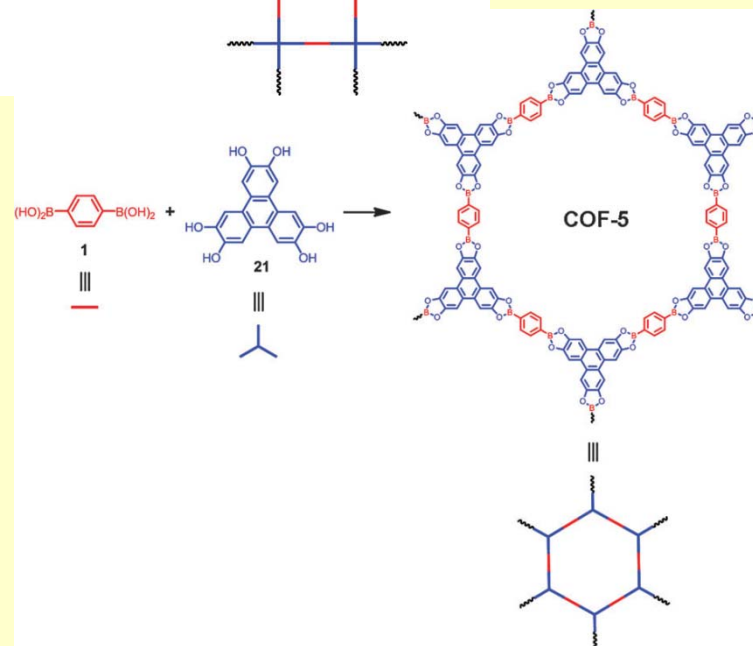
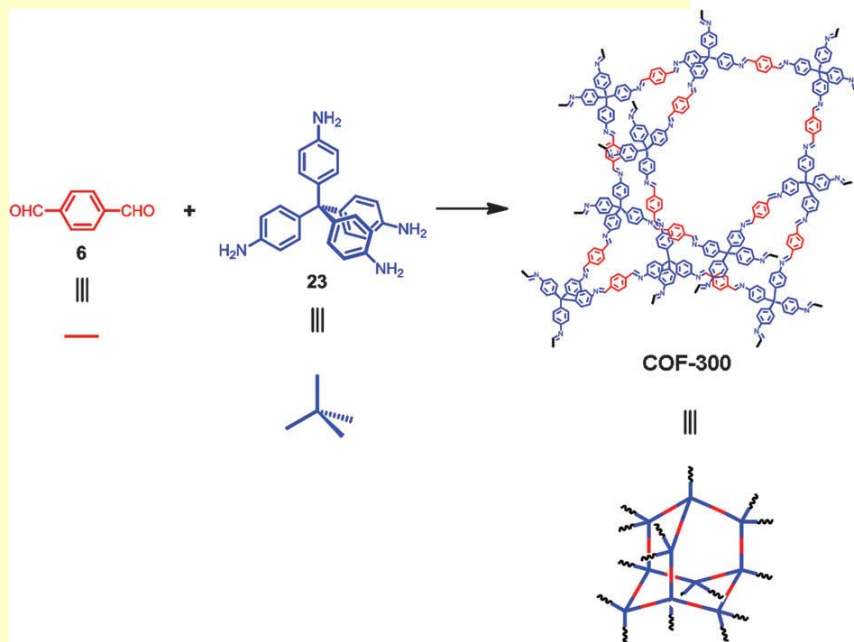
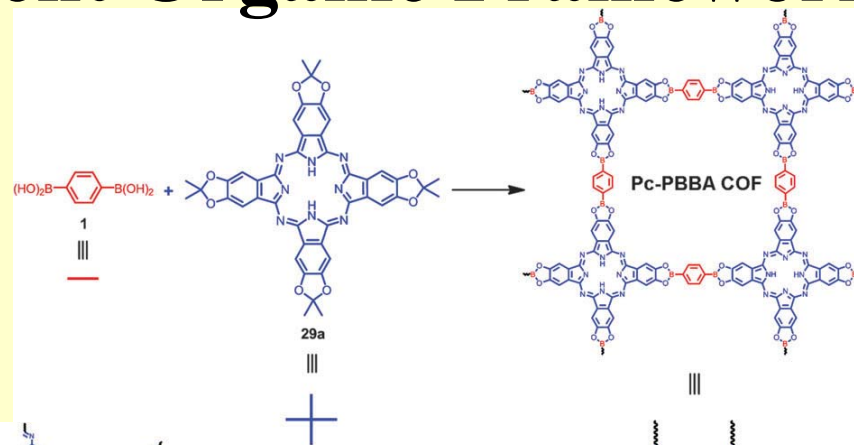
MIL-100 and MIL-101



MIL-101 Record Surface area 5 900 m²/g

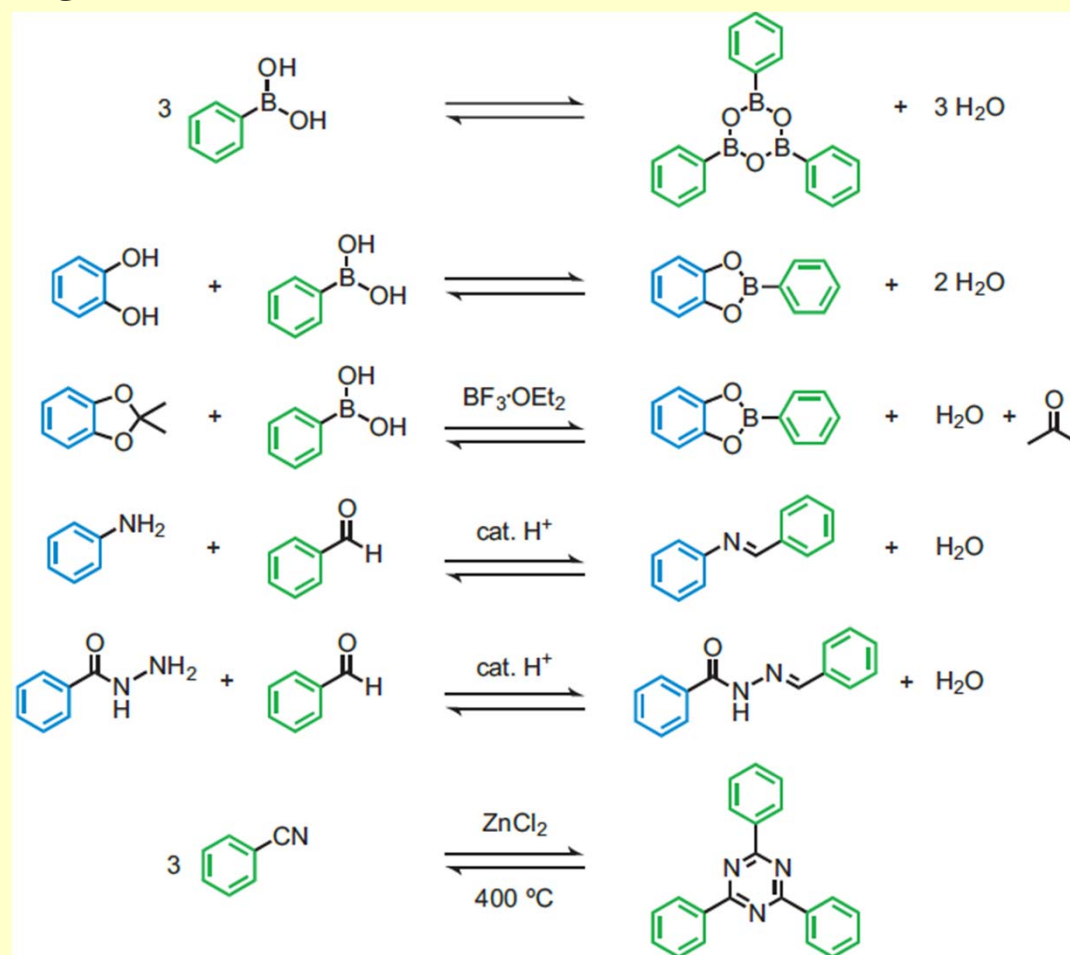
COF - Covalent Organic Frameworks

Linking reactions
produce covalent bonds

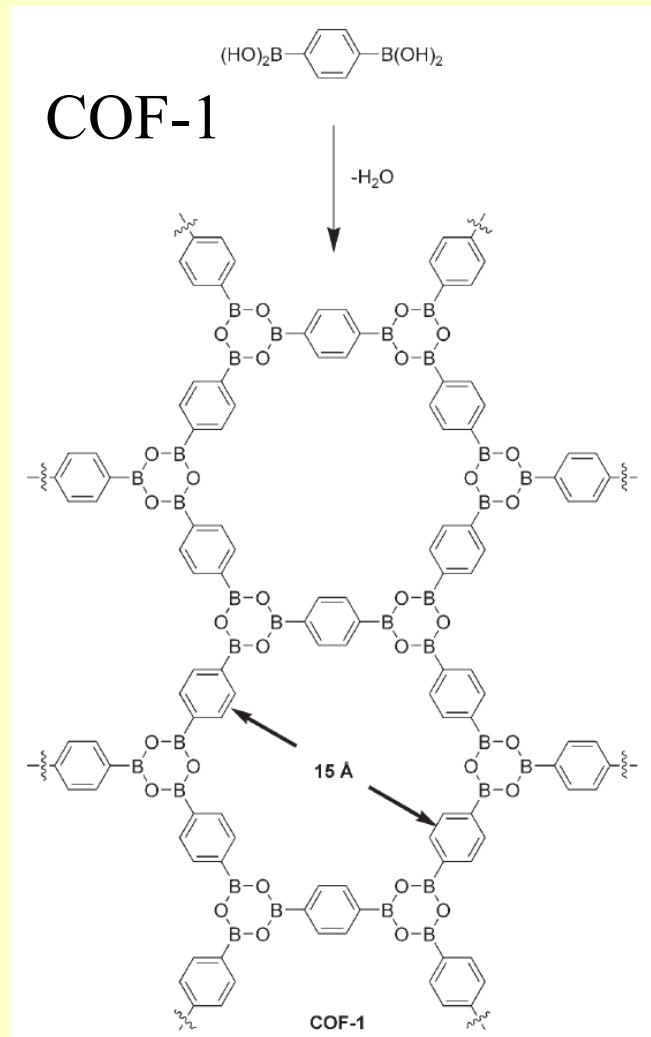


Covalent Organic Frameworks

Linking reactions



Covalent Organic Frameworks



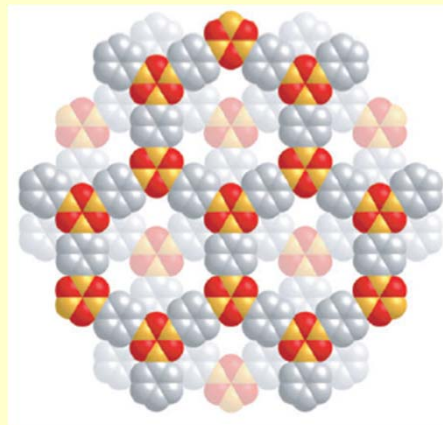
**Solvents - reactants are poorly soluble
(to slow down the reversible condensation)
mesitylene-dioxane (1:1)**

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

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

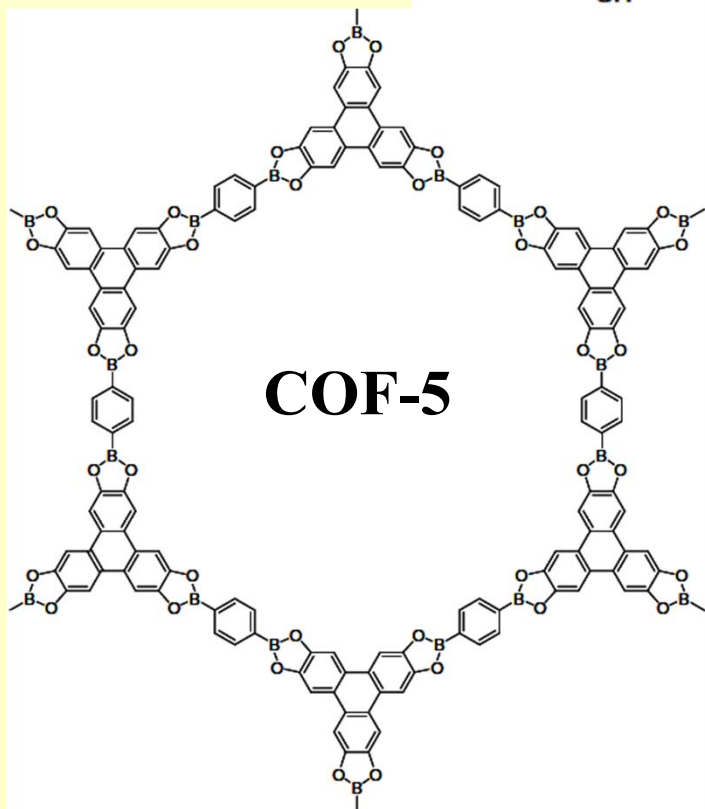
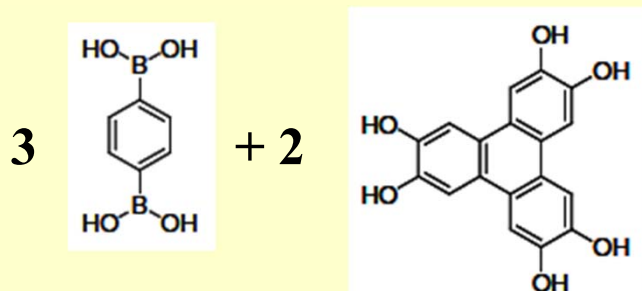
Solvent molecules are enclosed inside the pores, can be removed at 200 °C without collapse of the crystalline structure

Surface area of 711 m² g⁻¹, pore size 0.7 nm



Interlayer spacing: 0.333 nm

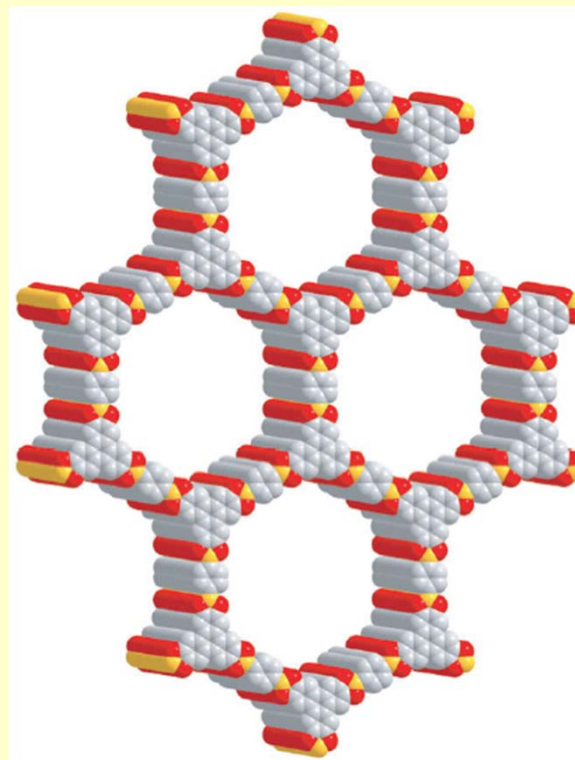
Covalent Organic Frameworks



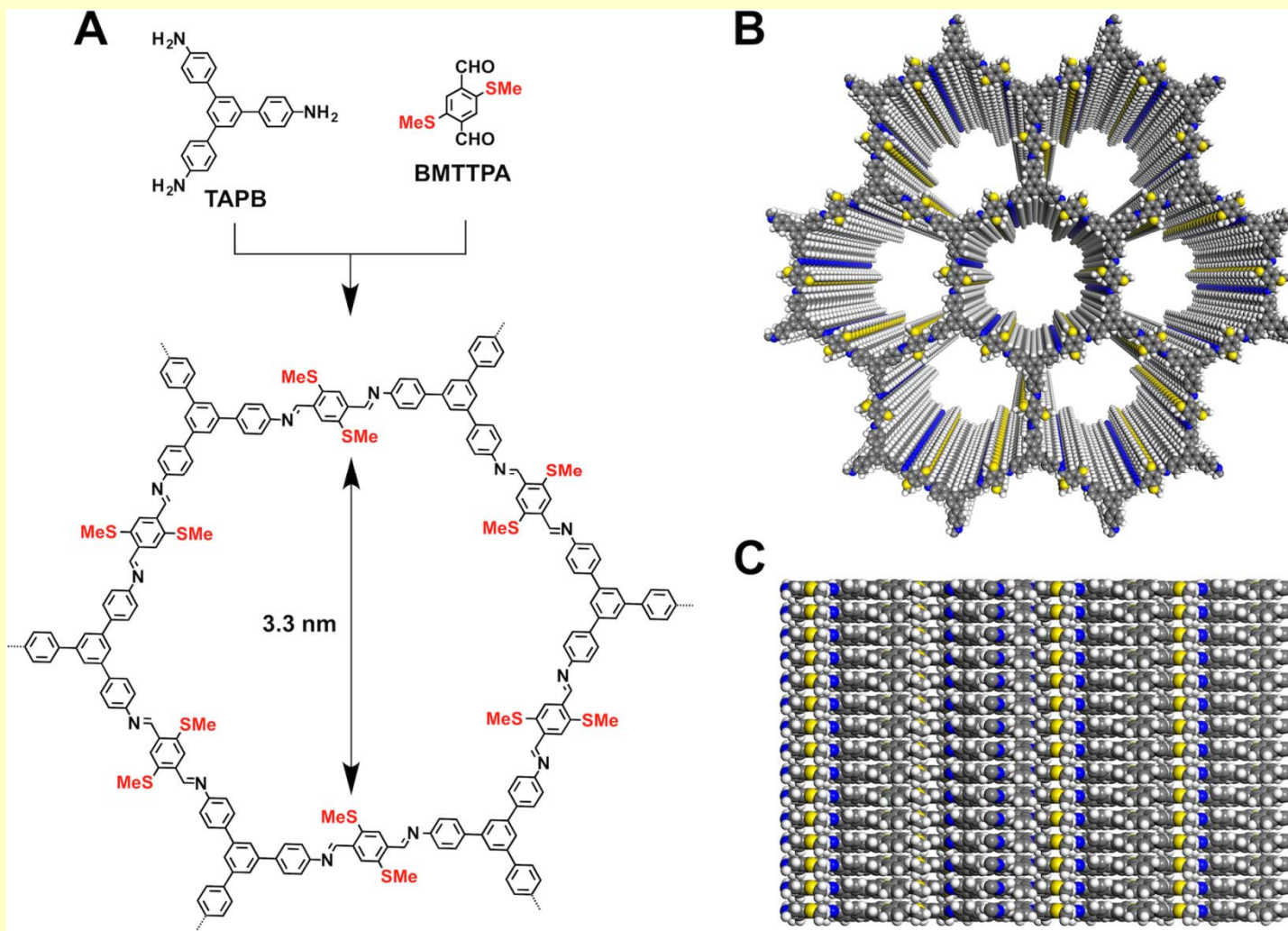
Surface area 1590 m²/g

Pore size: 2.7 nm

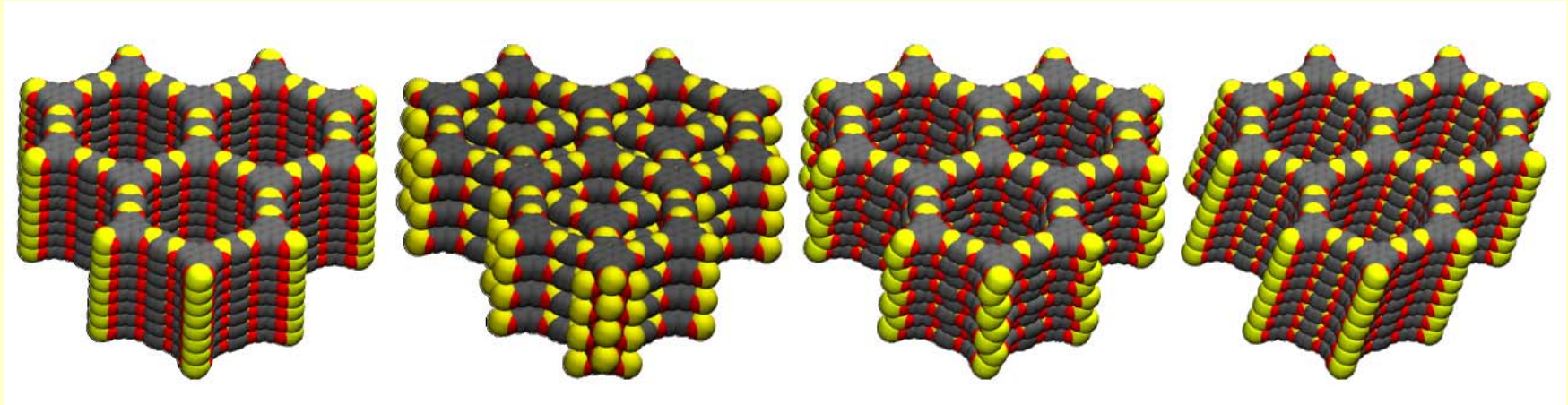
Interlayer spacing:
0.346 nm



Covalent Organic Frameworks



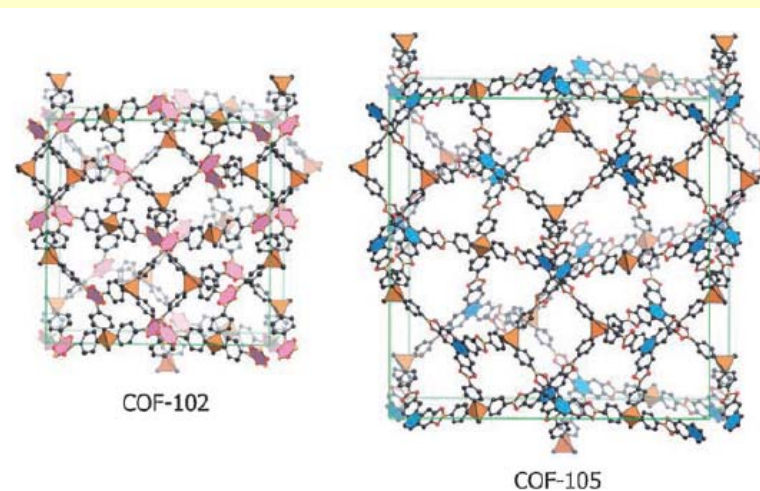
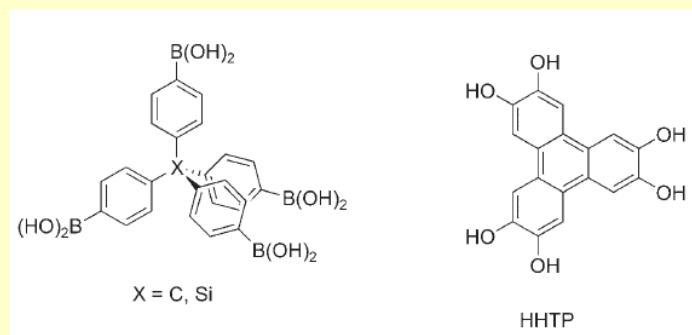
Covalent Organic Frameworks



Layer stackings: AA, AB, serrated and inclined

Covalent Organic Frameworks

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

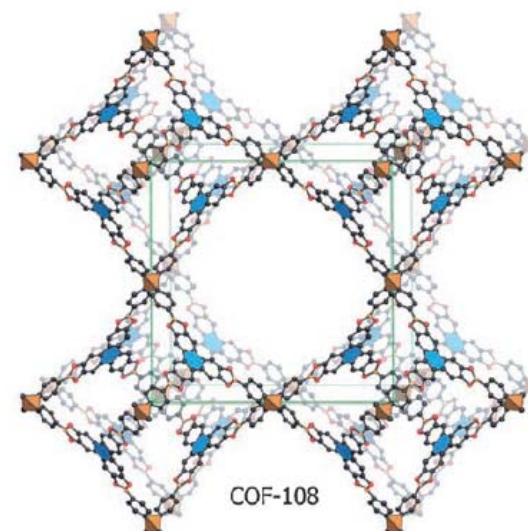


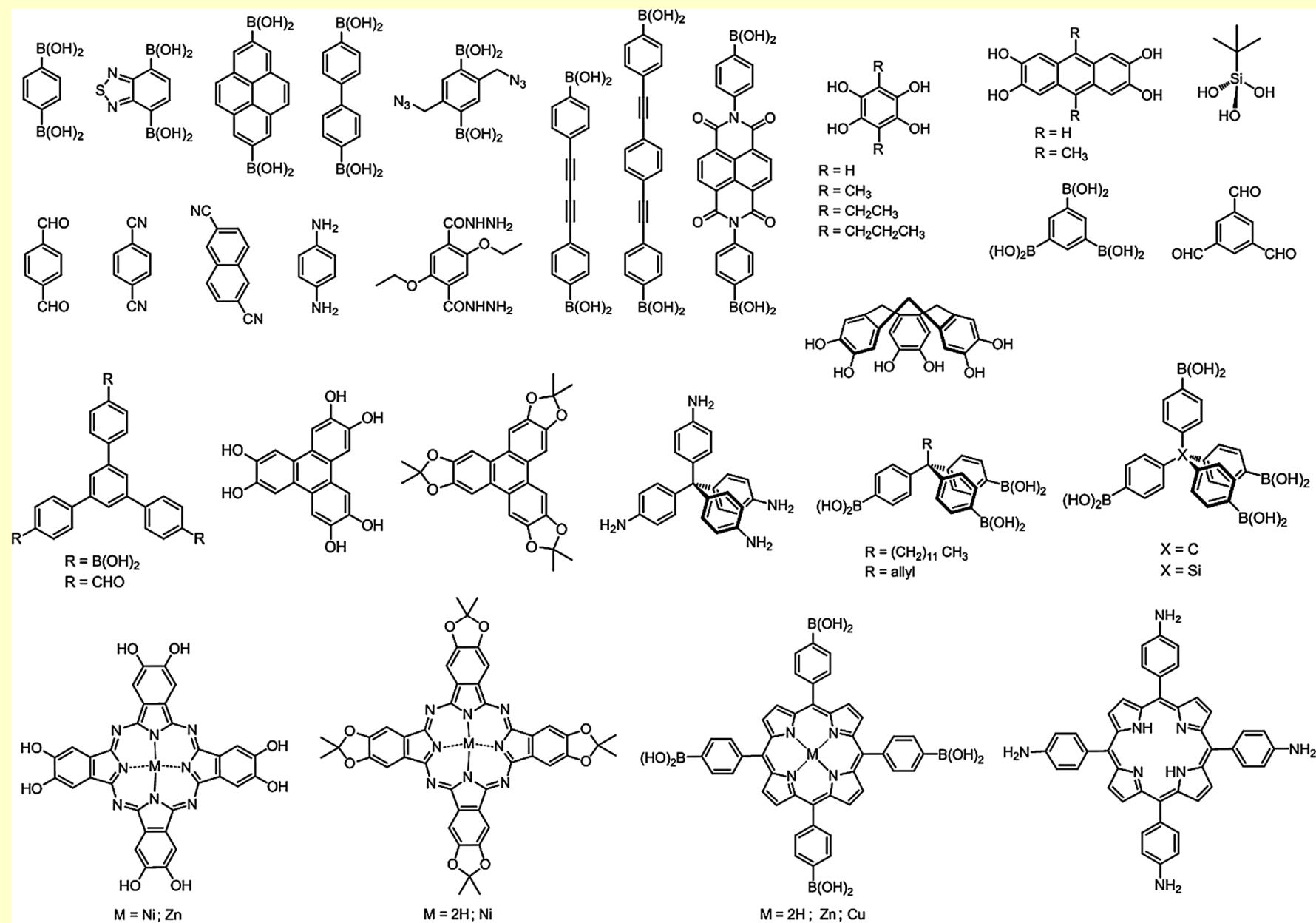
COF-108 - bor structure
two different types of pores
diameters of 15.2 and 29.6 Å.
density 0.17 g cm⁻³

surface area, m² g⁻¹

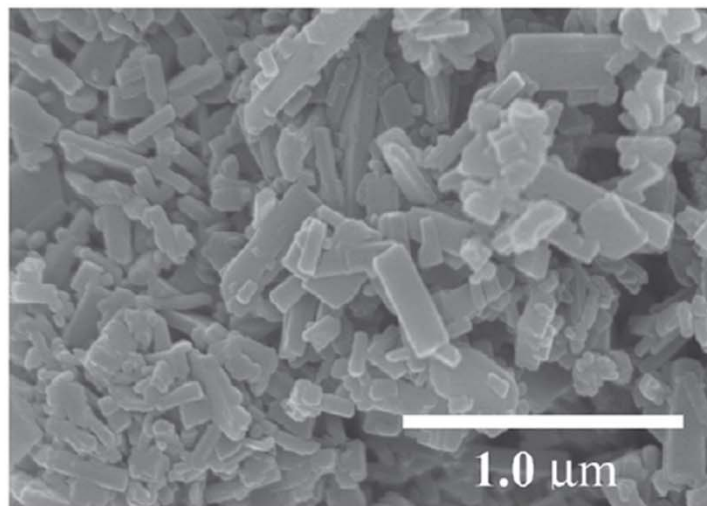
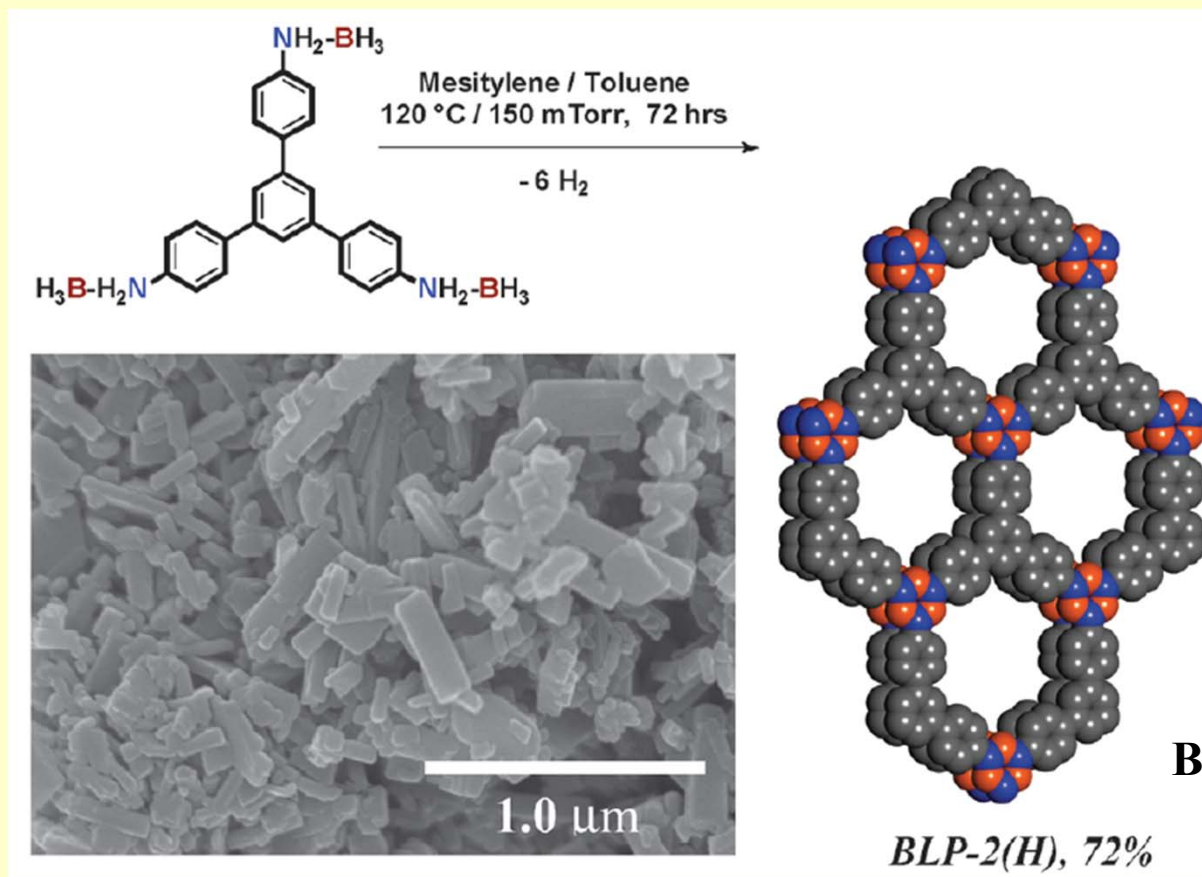
COF 102 3472

COF 103 4210





Borazine COFs



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

Pore size: 0.64 nm