

# Zeolites and Zeolitic Materials

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

**detergent builders**

**adsorbents**

**size-shape selective catalysts**

**supramolecular chemistry**

**nanotechnology**

## **Chemical composition**

**Silica**



**Aluminosilicates**



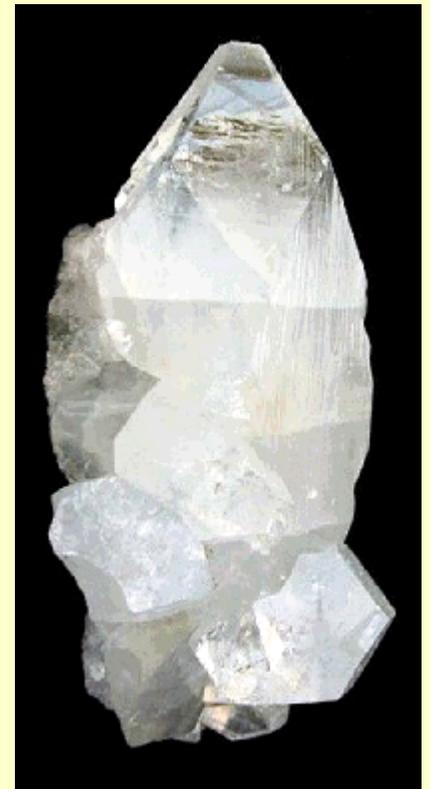
**Aluminophosphates**



**Metallophosphates**

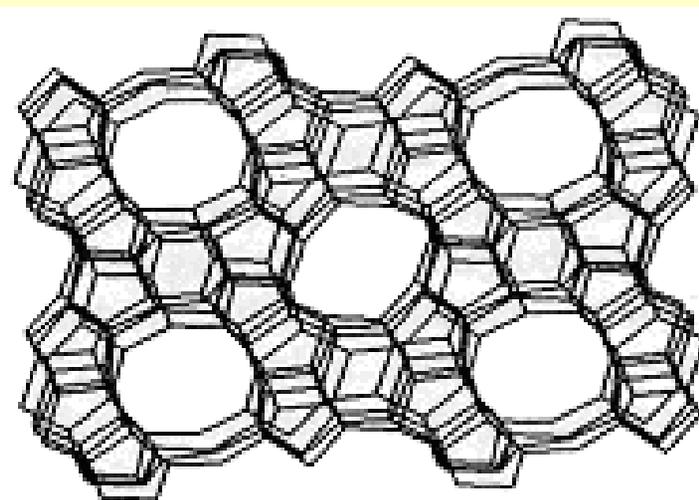


**Silicoaluminophosphates**

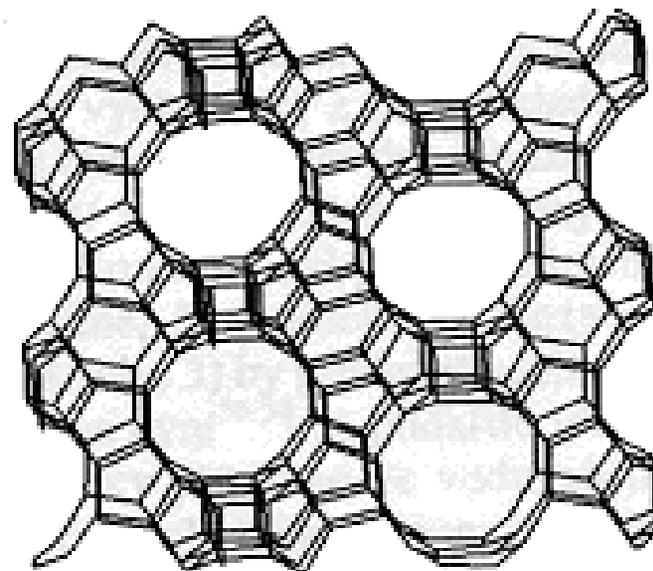


Pores

Channels



**ZSM-5[010]**



**Beta [100]**

# Zeolites and Zeolitic Materials

**>40 naturally occurring zeolites**

**>139 structure types**

**many hundreds of zeolite compounds**

**Nomenclature** [www.iza-structure.org/databases](http://www.iza-structure.org/databases)

**Structure types - three capital letter codes (Most well known zeolite archetypes: SOD, LTA, FAU, MOR, MFI )**

**Four-connected frameworks**

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

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

**Several zeolite compounds can belong to the same structure type:**

**FAU – faujasite, Linde X, Y, Beryllphosphate-X, SAPO-37,**

**Zincophosphate-X**

# **Zeolites and Zeolitic Materials**

## **Names of zeolite materials:**

**trivial names – Alpha, Beta, Rho**

**chemical names – Gallogermanate-A**

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

**codes – AlPO<sub>4</sub>-5, 8, 11, ..., 54, ZSM-4, 18, 57, ...**

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

**university names**

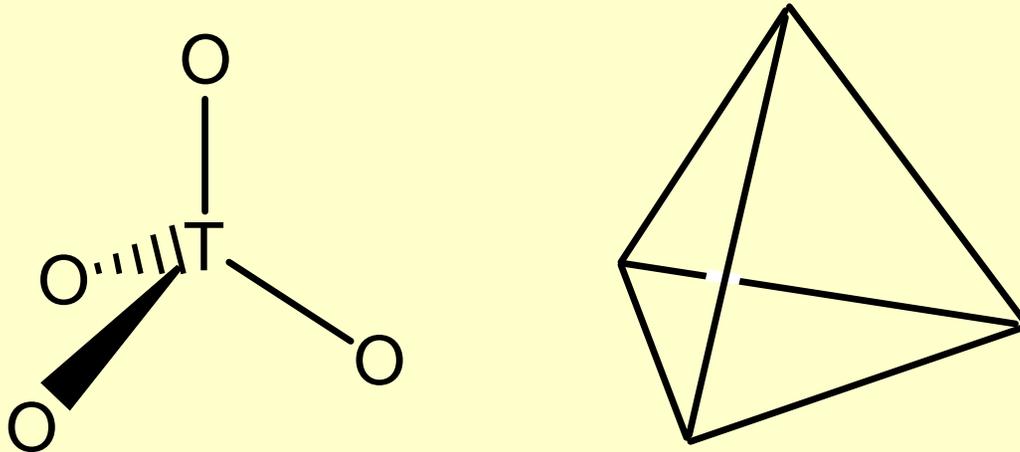
**VPI-5 (Virginia Polytechnical Institute)**

**ULM (University Le Mans)**

# Zeolites and Zeolitic Materials

Primary building units:

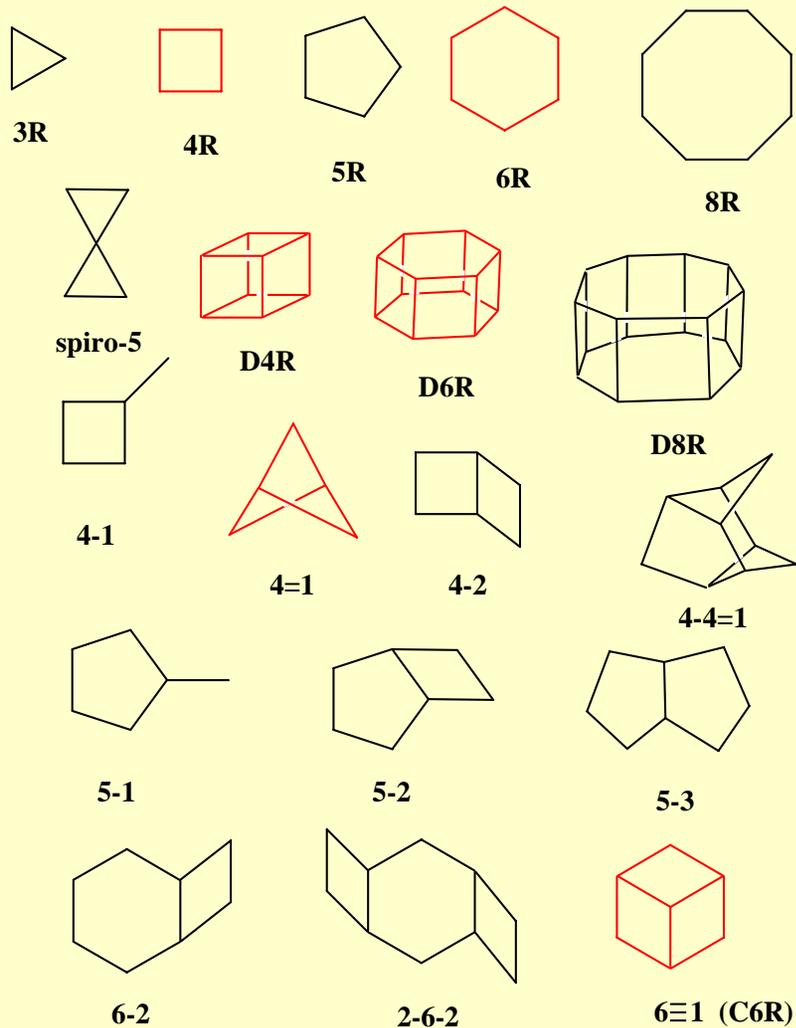
$\text{Al(III)O}_4$ ,  $\text{P(V)O}_4$  and  $\text{Si(IV)O}_4$  tetrahedra



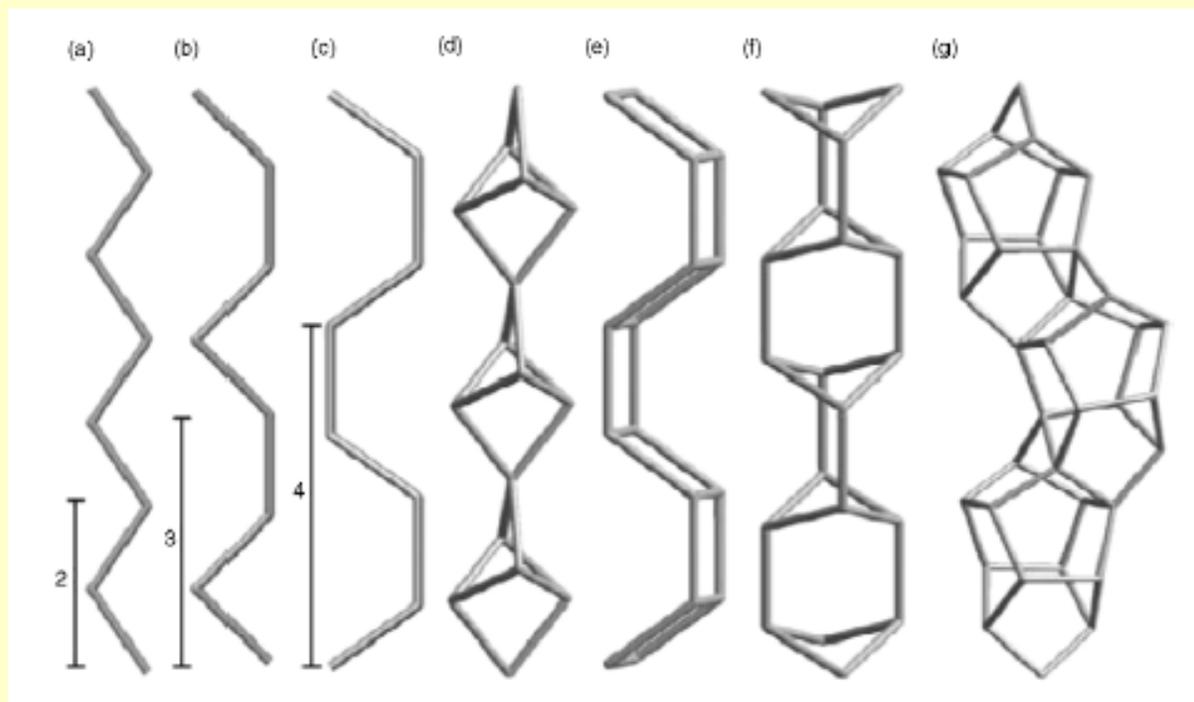
**Isoelectronic relationship**



# Secondary (Structural) Building Units (SBU)

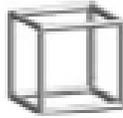


# Chain composite building units

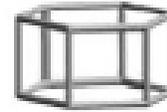


- (a) zig-zag unbranched single chain, periodicity of two
- (b) sawtooth unbranched single chain, periodicity of three
- (c) crankshaft unbranched single chain, periodicity of four
- (d) natrolite branched single chain
- (e) double crankshaft chain, an unbranched double chain
- (f) narsarsukite chain,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

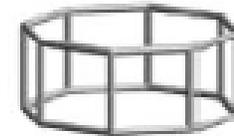
# Polyhedral composite building units



$[4^2]$   
double 4-ring (D4R)



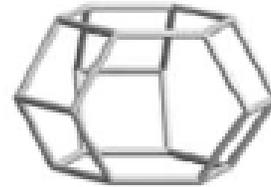
$[4^2 6^2]$   
double 6-ring (D6R)



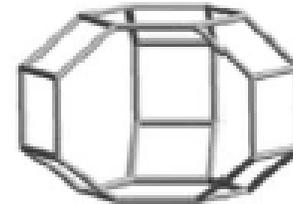
$[4^2 6^2]$   
double 8-ring (D8R)



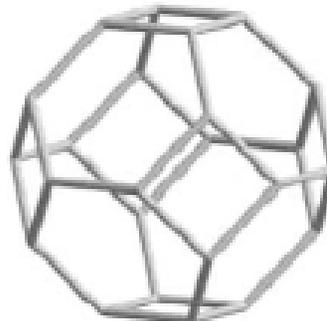
$[5^1]$   
pentasil unit



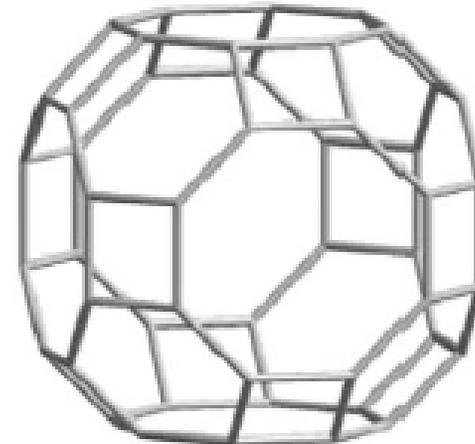
$[4^6 6^2]$   
cucurbitite cage



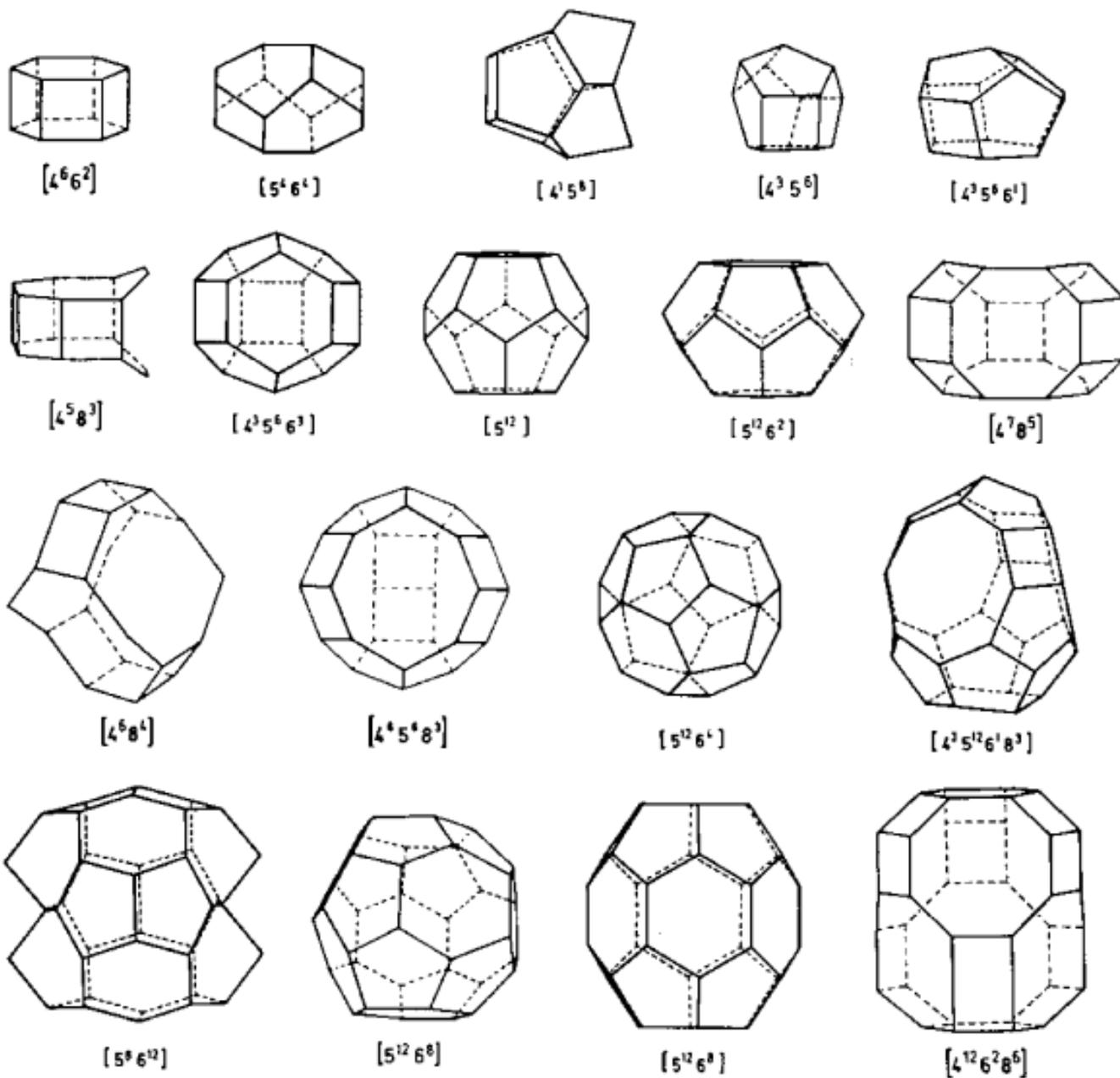
$[4^2 6^2 8^2]$   
gmelinite cavity



$[4^6 6^2]$   
sodalite cage  
or  $\beta$ -cage

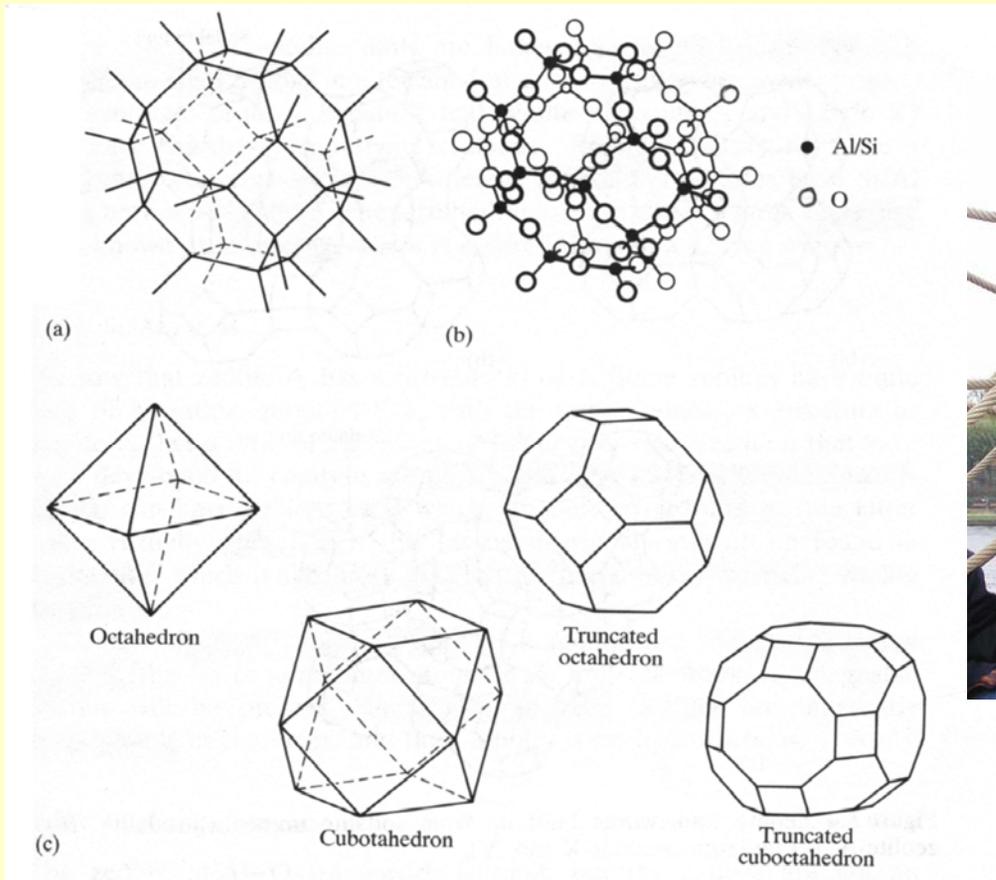


$[4^{12} 6^2 8^2]$   
 $\alpha$ -cavity



# Sodalite Unit

## Truncated octahedron



# Sodalite Unit

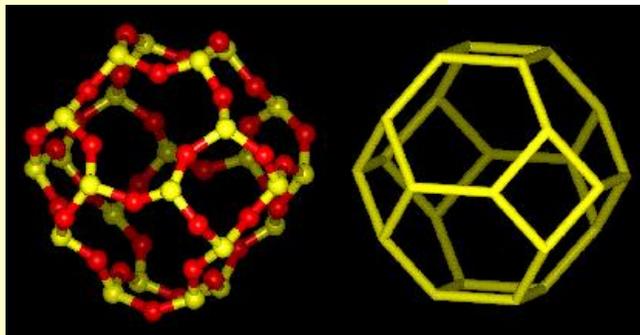
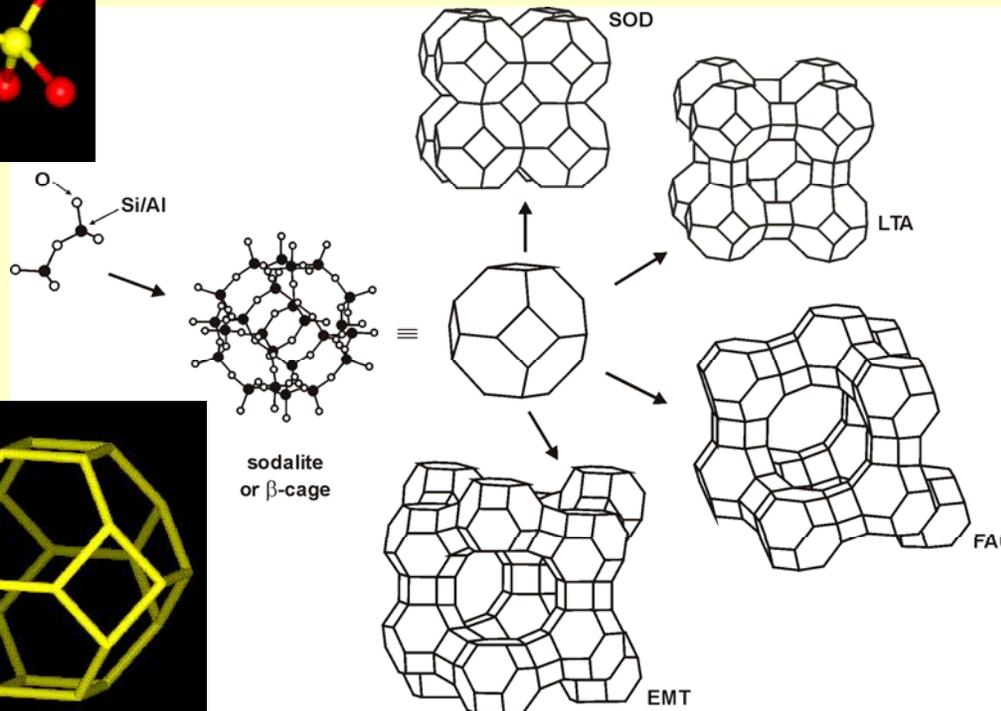
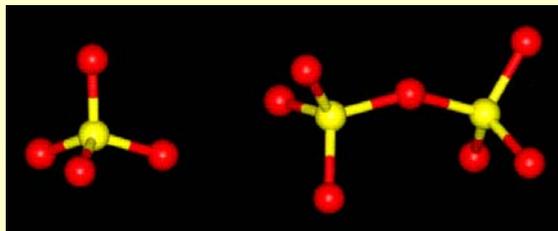
Packing of the sodalite units:

SOD – bcc, sharing of 4-rings

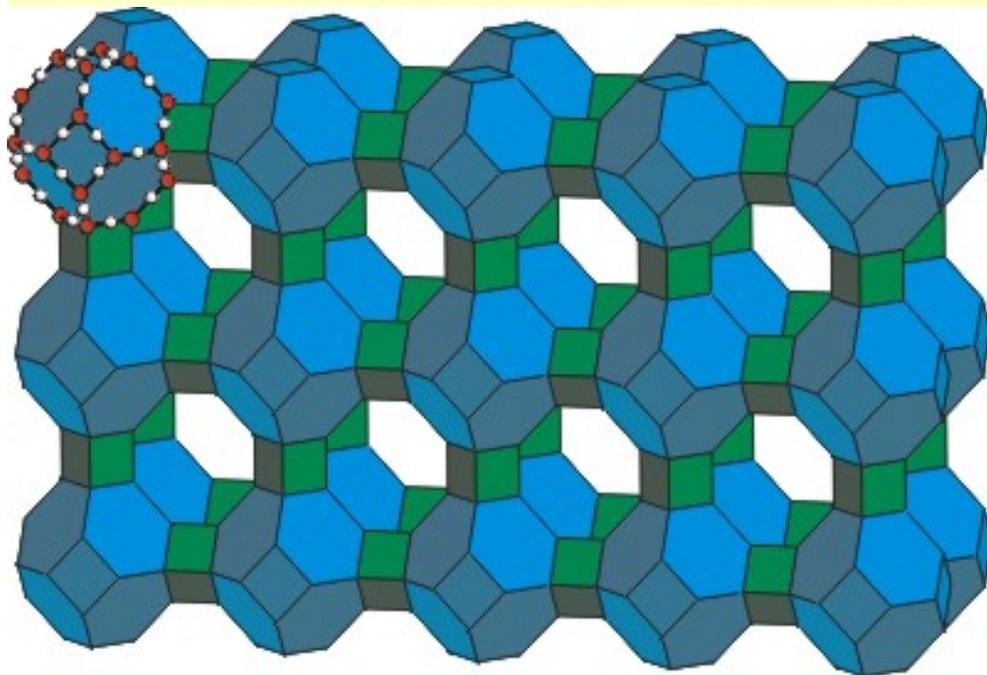
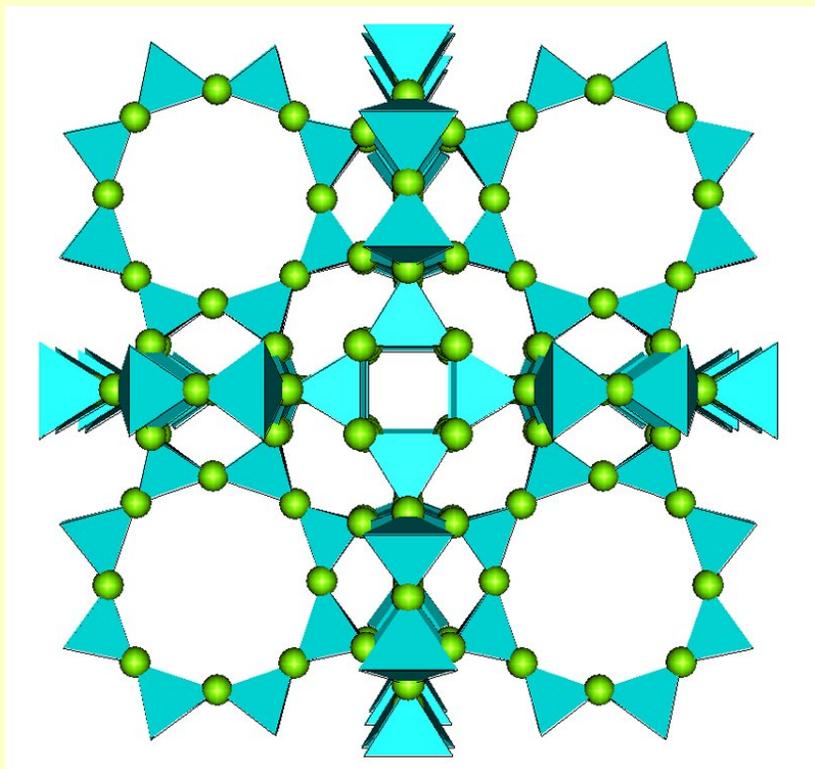
LTA – sc, 4-rings connected through O bridges

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

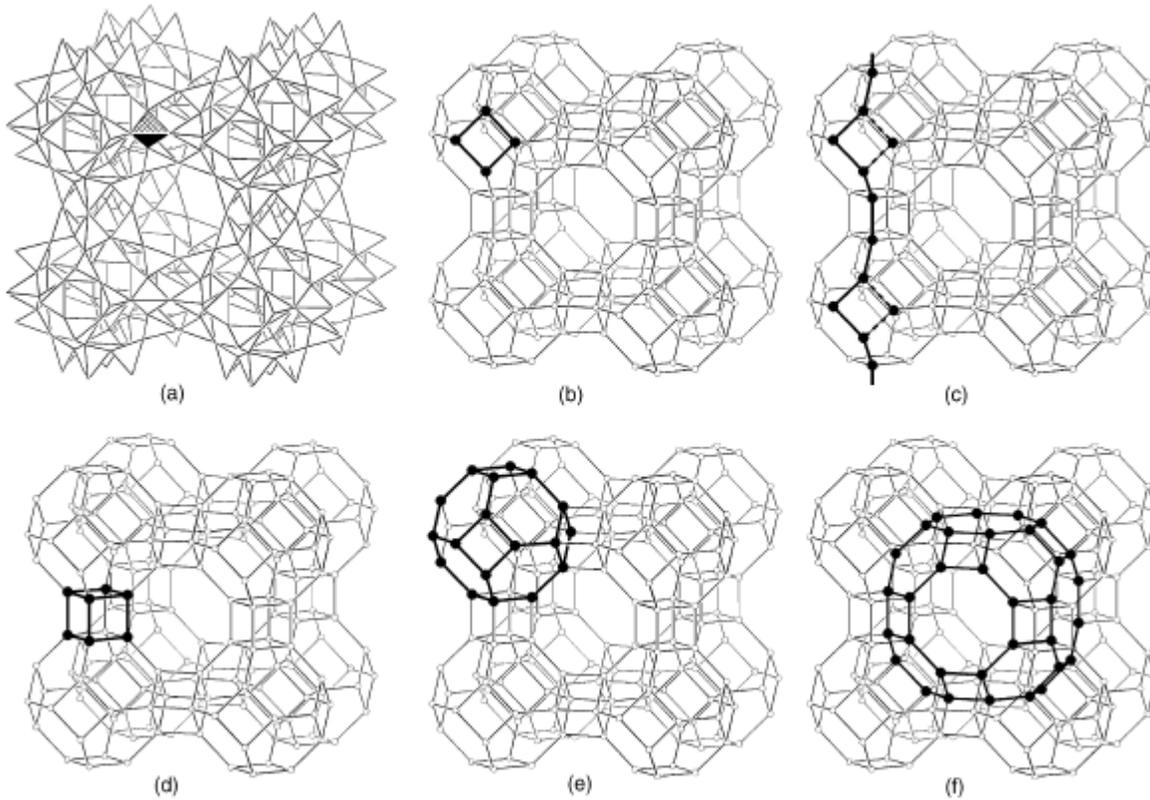
EMT – hexagonal diamond, 6-rings connected through O bridges



# Zeolite LTA

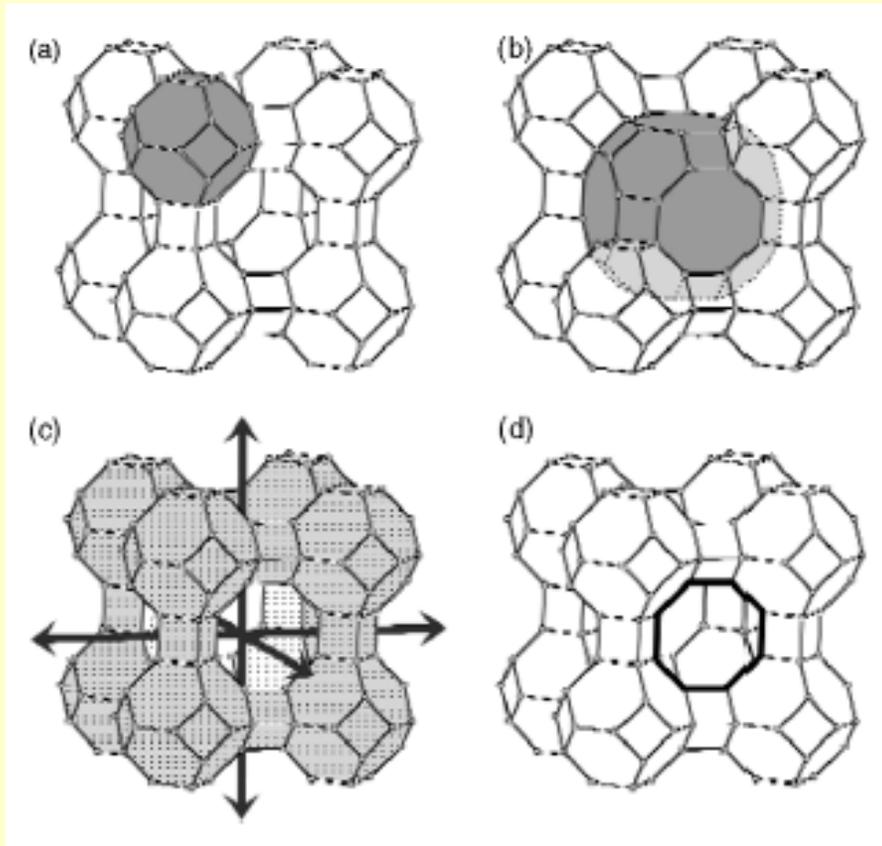


# Zeolite A

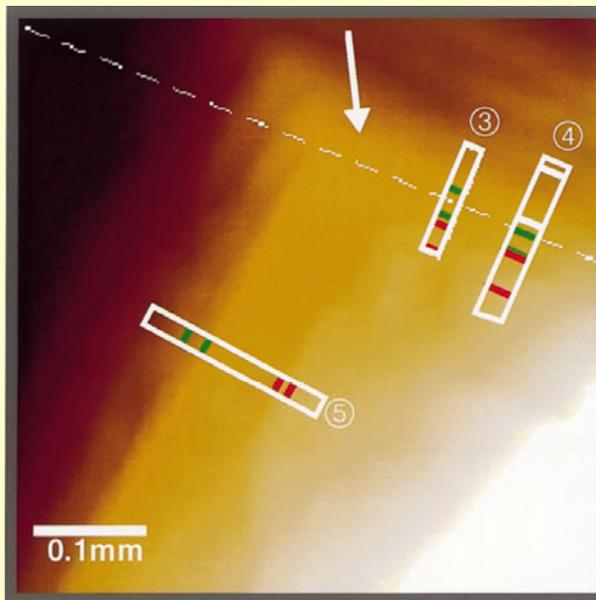


- (a) [TO<sub>4</sub>] tetrahedra as BBU
- (b) four-membered single rings
- (c) IB fuenfer chains
- (d) cubes [4<sup>6</sup>]
- (e) truncated octahedra [4<sup>6</sup>6<sup>8</sup>] (sodalite- or β-cages)
- (f) truncated cubeoctahedra [4<sup>12</sup>6<sup>8</sup>8<sup>6</sup>] (α-cavities)

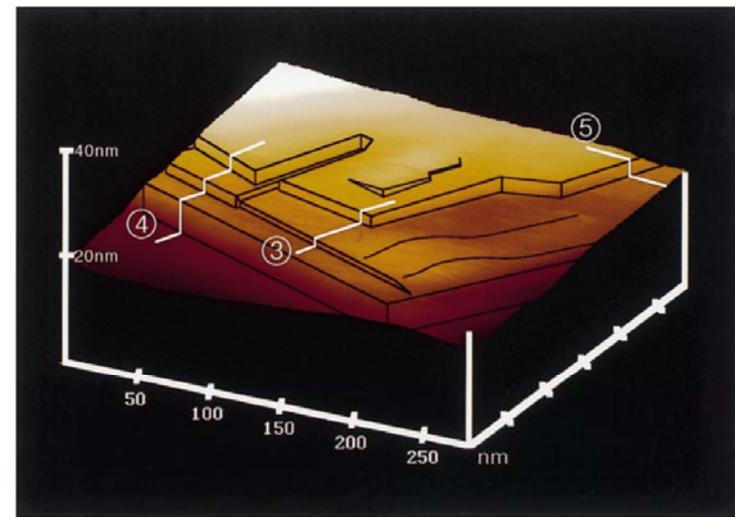
## Pores in Zeolite A (LTA)



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

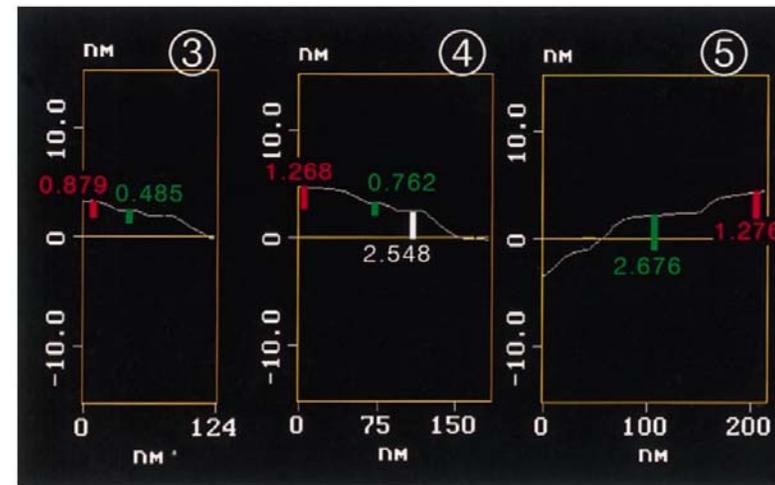


(a)



(b)

**D4R**



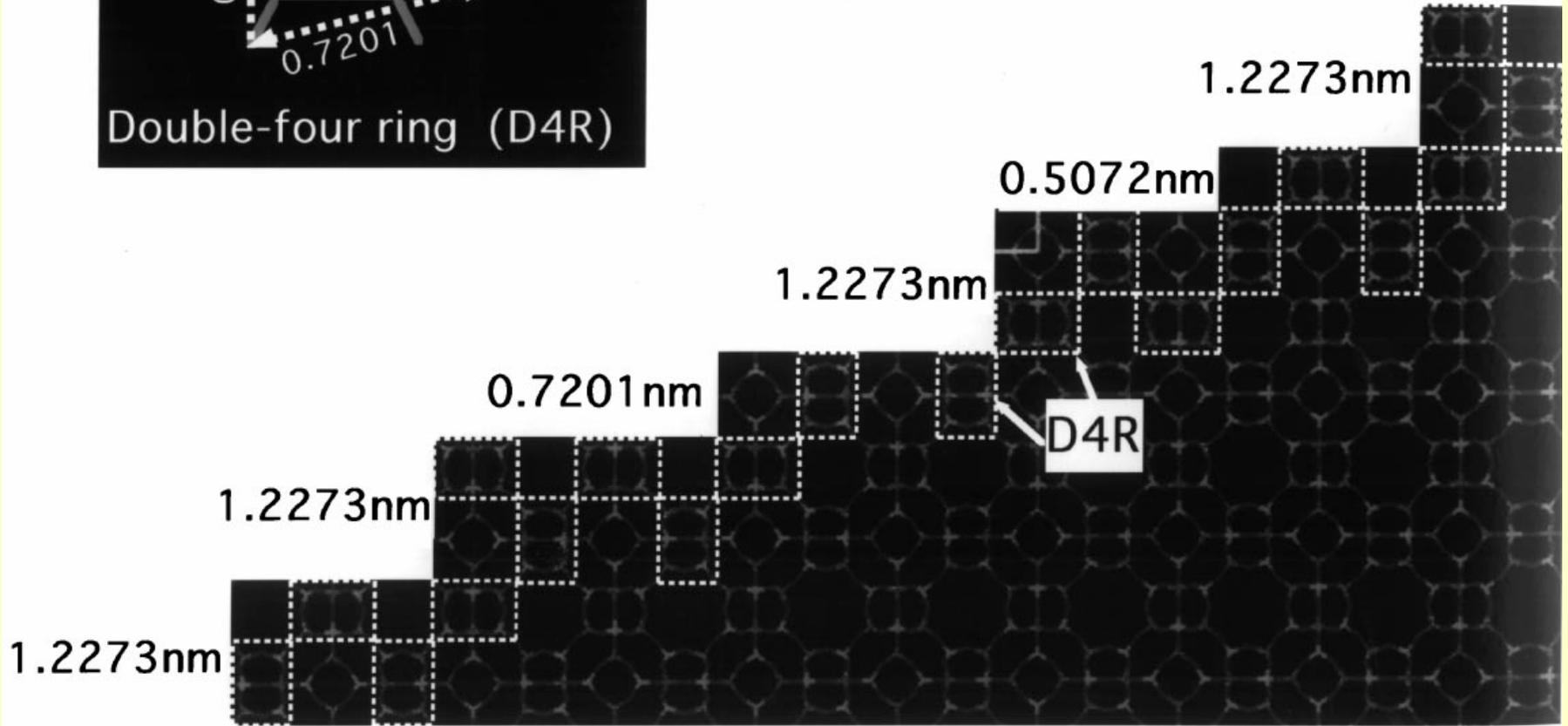
(c)

# AFM growth studies of LTA

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



# D4R



# Zeolite FAU (X and Y) and EMT

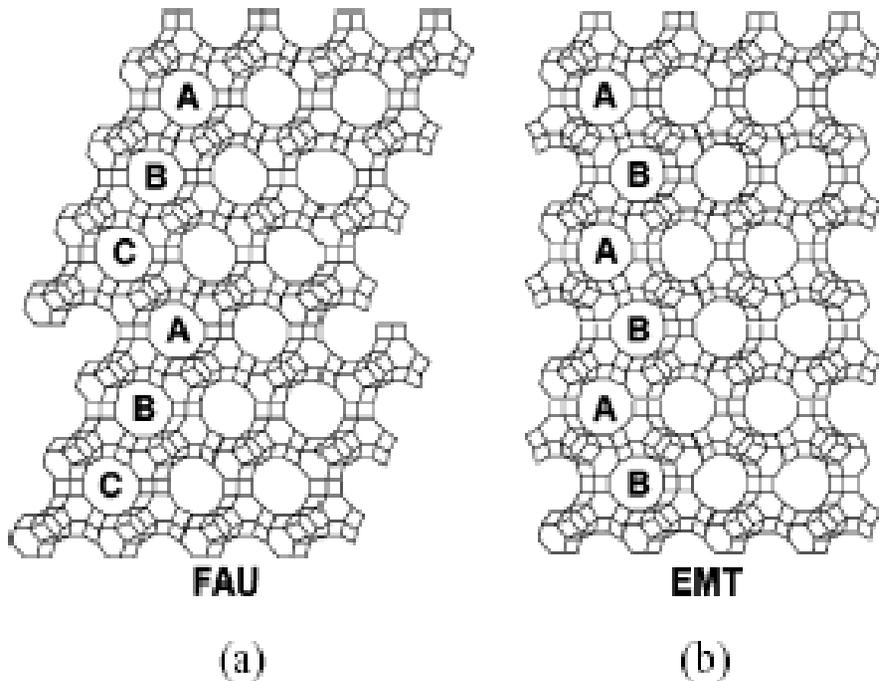


Fig. 1. Structure of zeolite Y: (a) cubic polymorph known as FAU with ABCABC... stacking, (b) hexagonal polymorph known as EMT with ABABAB... stacking.

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

## Molecular Sieves

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

Zeolite Y contains more Si

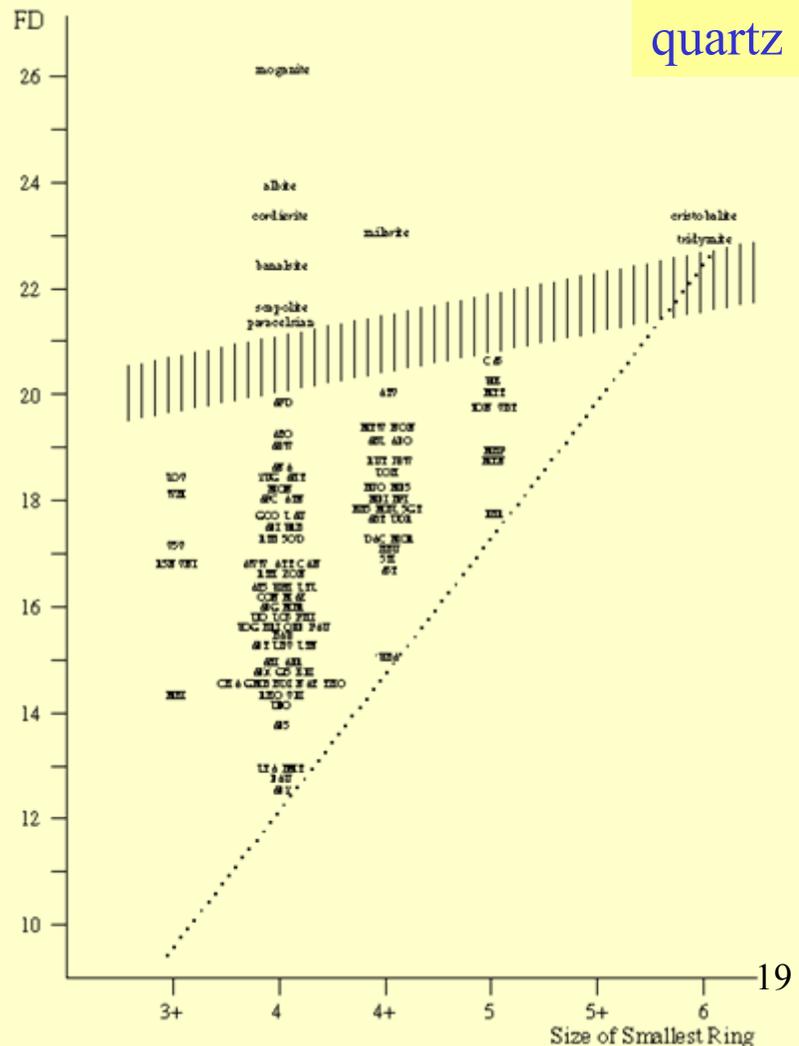
# Framework Density

## Framework density (FD)

Defined as the number of tetrahedral atoms (T-atoms) per cubic nanometer ( $1000 \text{ \AA}^3$ )

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  $\text{TO}_4$  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)       $\text{Si/Al} = 1$

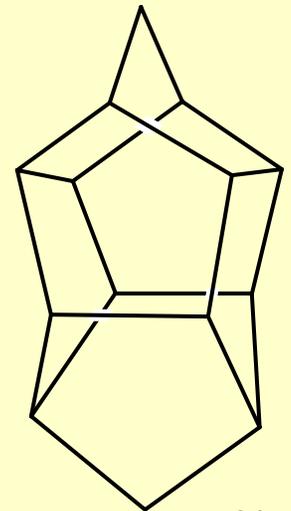
ZK-4 (LTA)         $\text{Si/Al} = 2.5$

ZSM-5               $\text{Si/Al} = 20 - \infty$

Pure  $\text{SiO}_2$          $\text{Si/Al} = \infty$

## Pentasil

ZSM-5



# Zeolite Synthesis

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

**Aluminosilicates – high pH**

🔔 **Mixing**

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

🔔 **Ageing**

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

🔔 **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  $25\text{-}500\text{ }^\circ\text{C}$  vacuum thermal  
dehydration

-template removal – calcination in  $\text{O}_2$  at  $400\text{-}900\text{ }^\circ\text{C}$  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

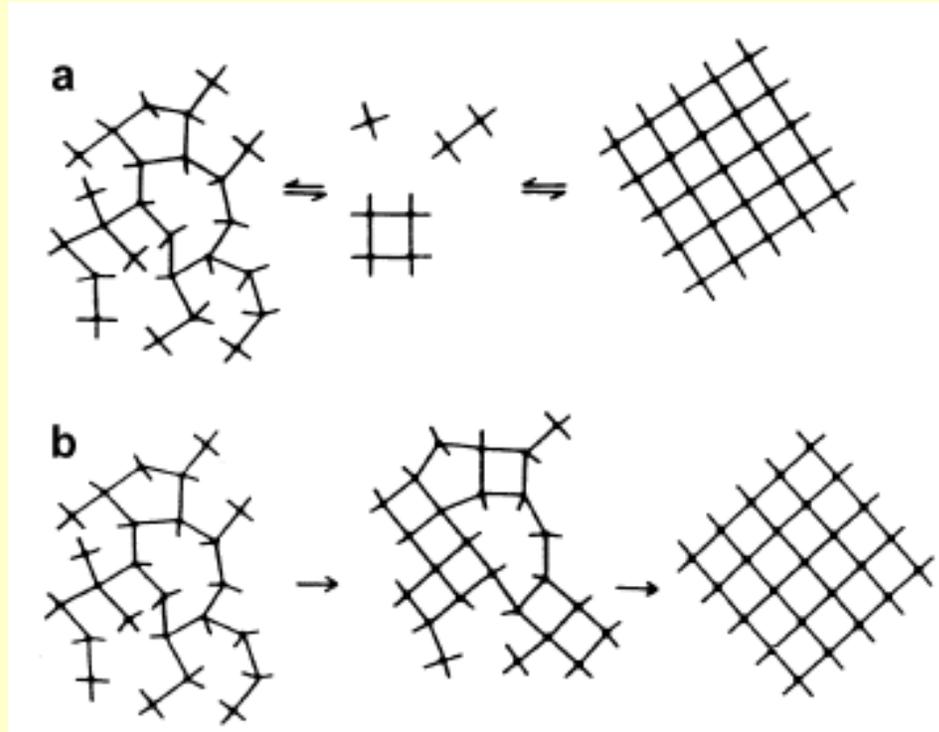
**The ratio  $\text{TO}_2/(\text{C} + \text{N} + \text{O})$  is a measure of space-filling of the framework by the guest molecules, characteristic for a specific guest and structure.**

**Existence of primary and secondary units in a synthesis mixture**

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

# Zeolite Synthesis Mechanisms

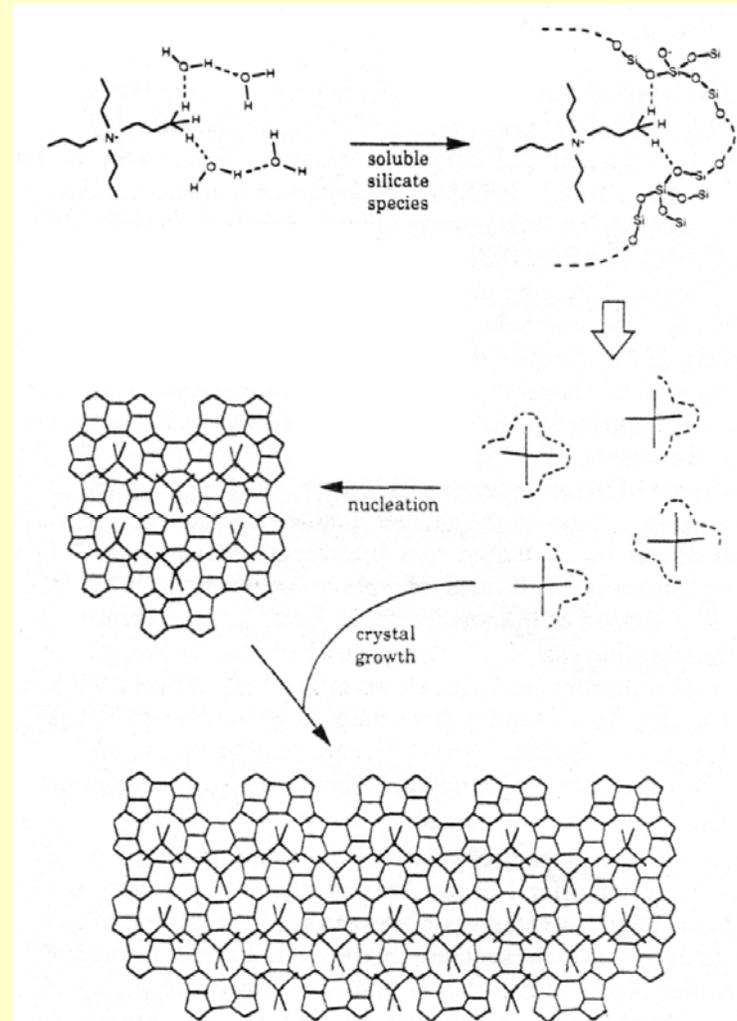
(a) gel dissolution and solution mediated crystallization (SBU in solution)



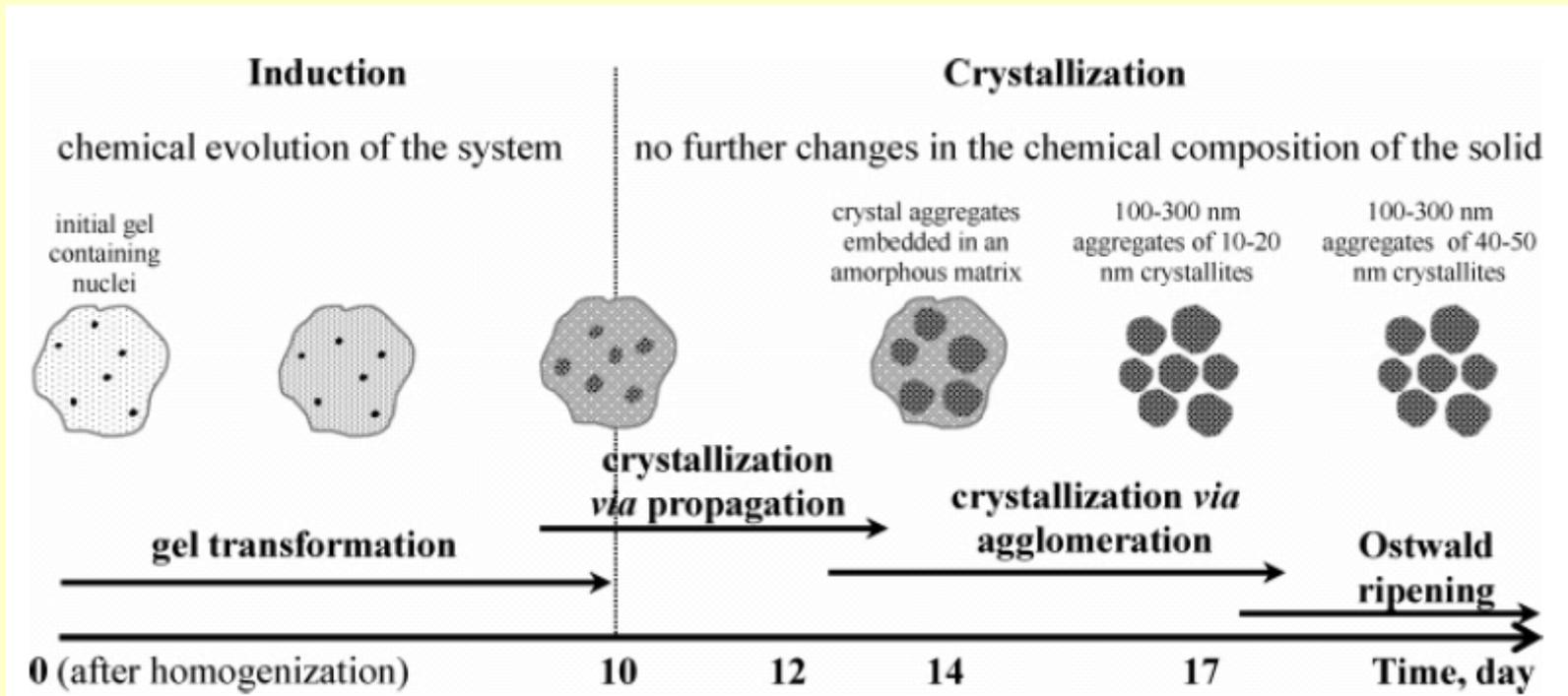
(b) "in situ" rearrangement of the gel

# Zeolite Synthesis Mechanisms

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



# Crystallization Mechanism



crystallization mechanism of FAU-type zeolite under ambient conditions

# Zeolites and zeolitic materials

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

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

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

✦ **Cation choice ( $\text{Ca}^{2+}$  exchanged for  $\text{Na}^+$ )**

✦ **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

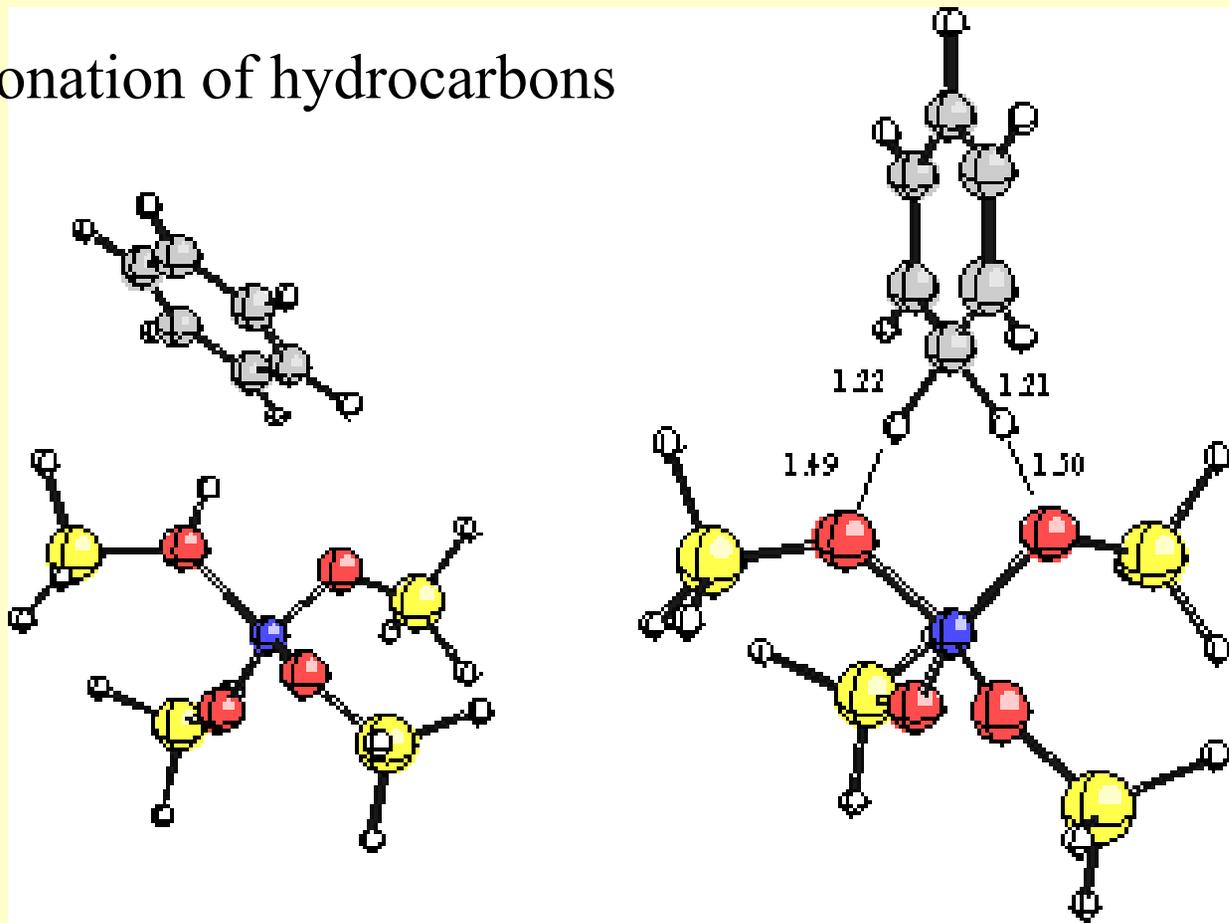
Al-O-Si-O-Al

NNN-principle



# Brønsted Acidity

Protonation of hydrocarbons

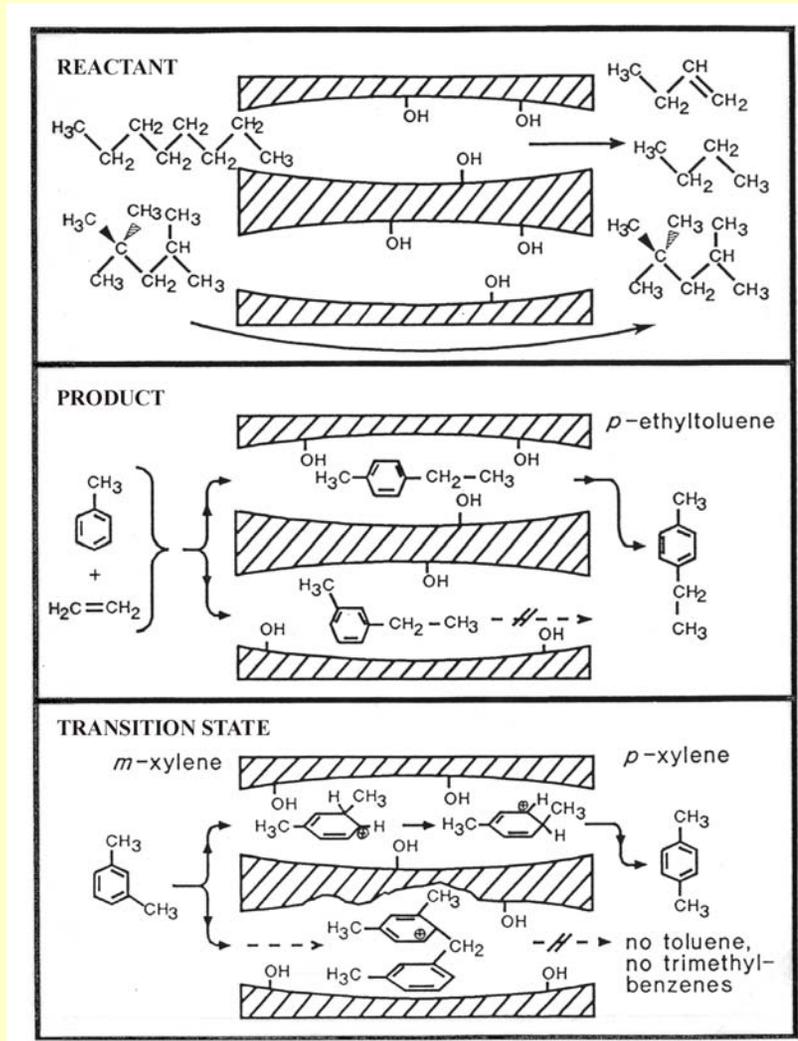


# Size-Shape Selectivity

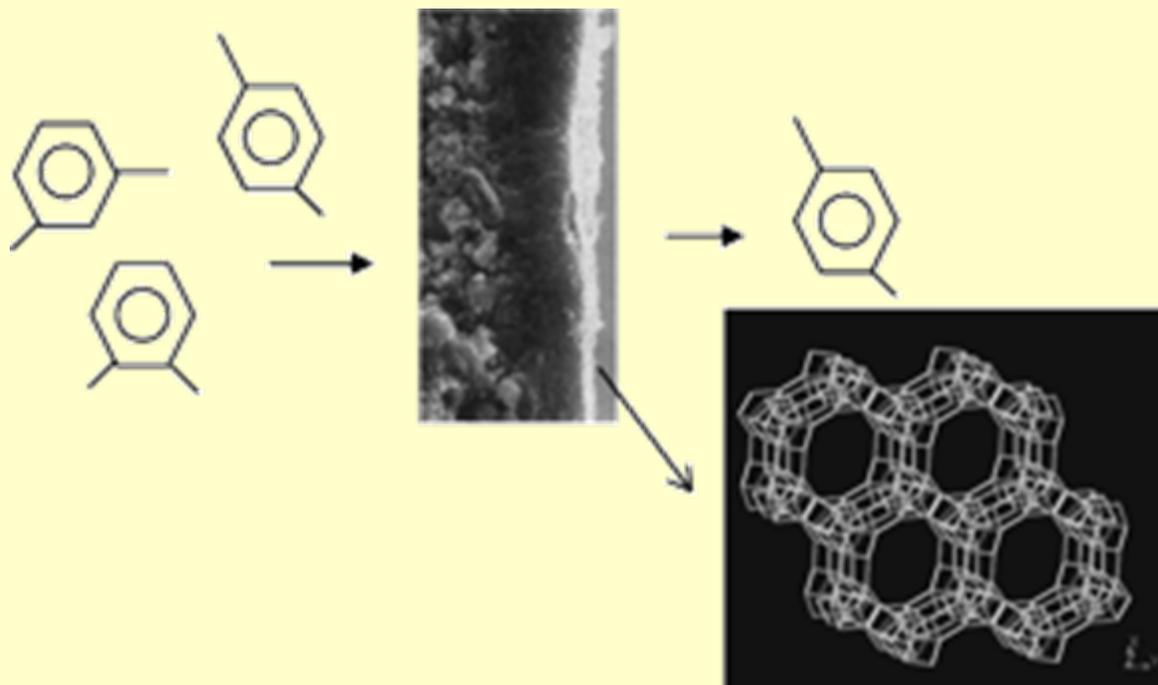
Size-shape selective catalysis, separations, sensing

Selectivity at:

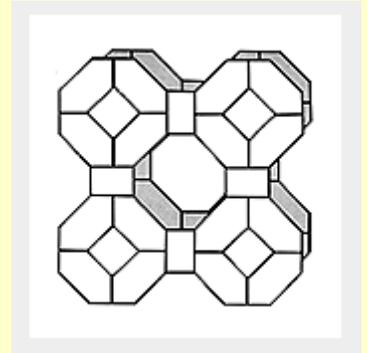
- Reactants
- Products
- Transition state



# Separation of xylene isomers by pervaporation thru a MFI membrane



# Zeolite Applications



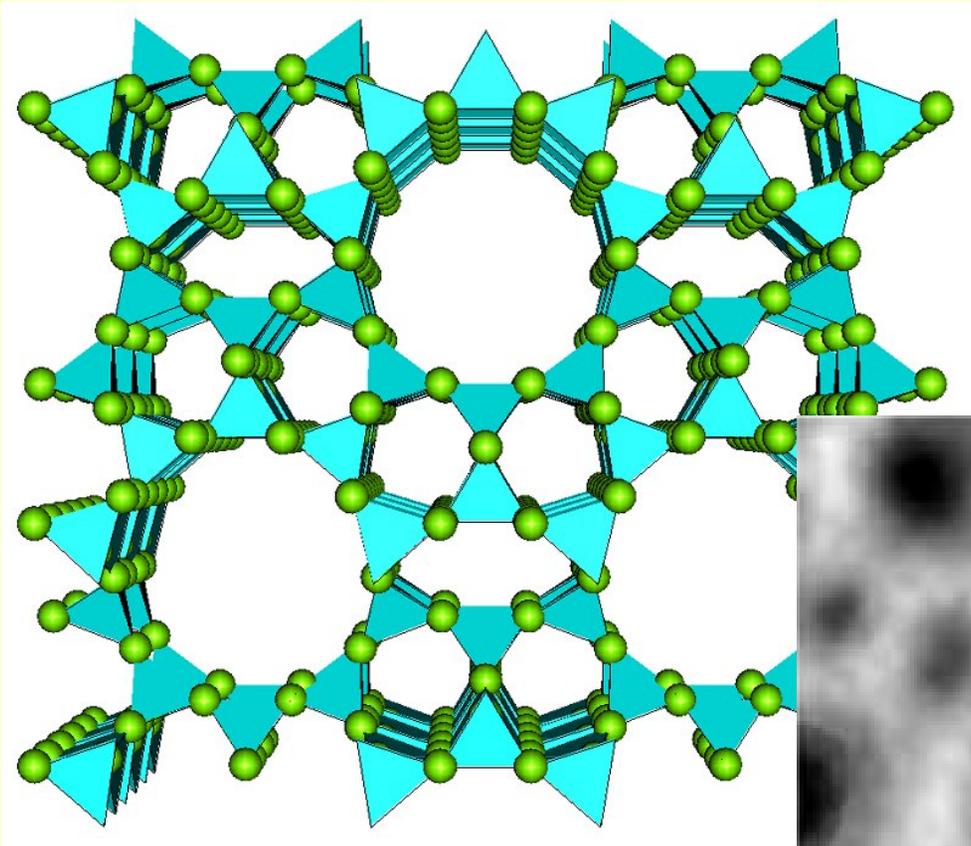
**Odor control, adsorbents**

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

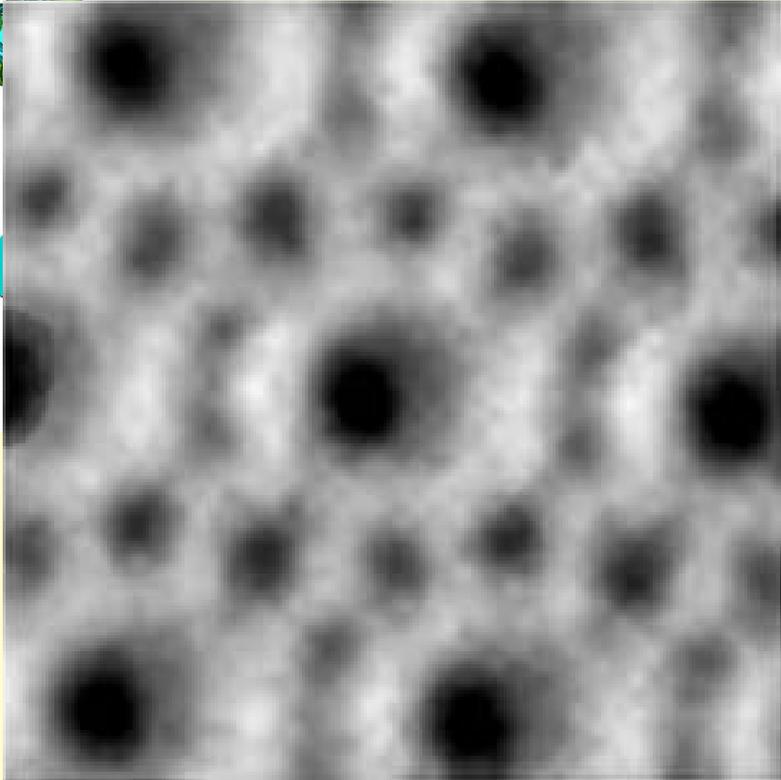
**Host-guest inclusion, atoms, ions, molecules, radicals, organometallics, coordination compounds, clusters, polymers (conducting, insulating)**

**Nanoreaction chambers**

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



HRTEM



Aquaculture

Ammonia filtration in fish hatcheries Biofilter media

Agriculture

Odor control Confined animal environmental control Livestock feed additives

Horticulture Nurseries, Greenhouses

Floriculture

Vegetables/herbs

Foliage

Tree and shrub transplanting

Turf grass soil amendment

Reclamation, revegetation, landscaping

Silviculture (forestry, tree plantations)

Medium for hydroponic growing

Household Products Household odor control Pet odor control

Industrial Products Absorbents for oil and spills Gas separations

Radioactive Waste Site remediation/decontamination

Water Treatment Water filtration Heavy metal removal Swimming pools

Wastewater Treatment Ammonia removal in municipal sludge/wastewater

Heavy metal removal Septic leach fields

# Aluminophosphates

✦ **Isoelectronic relationship of  $\text{AlPO}_4$  to  $(\text{SiO}_2)_2$**

✦ **Ionic radius of  $\text{Si}^{4+}$  (0.26 Å) is very close to the average of the ionic radii of  $\text{Al}^{3+}$  (0.39 Å) and  $\text{P}^{5+}$  (0.17 Å)**

**Many similarities between aluminosilicate and  $\text{AlPO}_4$  molecular sieves**

**Dense  $\text{AlPO}_4$  phases are isomorphous with the structural forms of  $\text{SiO}_2$ : 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  $\text{AlPO}_4$  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**

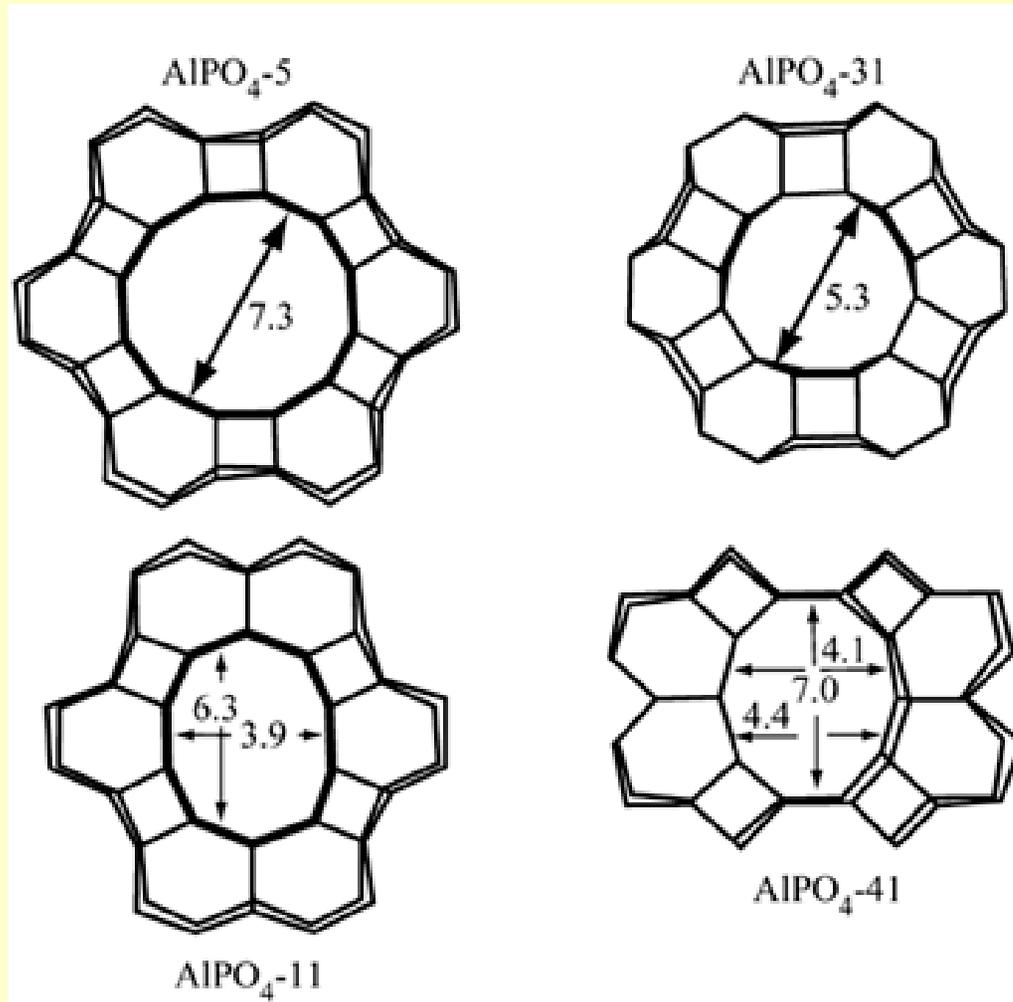
**Incorporation of elements such as Si, Mg, Fe, Ti, Co, Zn, Mn, Ga, Ge, Be, Li, As, and B into the tetrahedral sites of  $\text{AlPO}_4$  gives a vast number of element-substituted molecular sieves (MeAPO, MeAPSO, SAPO) important heterogeneous catalysts**

**$\text{M}^{1+}$ ,  $\text{M}^{2+}$ , and  $\text{M}^{3+}$  incorporate into the Al sites**

**$\text{M}^{5+}$  elements incorporate into the P sites**

**This substitution introduces a negative charge on these frameworks.  $\text{Si}^{4+}$ ,  $\text{Ti}^{4+}$ , and  $\text{Ge}^{4+}$  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,  $\text{Al(O)(OH)}$ ,  $\text{Al(Oi-Pr)}_3$**

**Mixing with aqueous  $\text{H}_3\text{PO}_4$  in the equimolar ratio – low pH !**

**Forms an  $\text{AlPO}_4$  gel, left to age**

**One equivalent of a guest compound = template**

**Crystallization in a reactor**

**Separated by filtration, washed with water**

**Calcination**

**Other zeolite materials**

**Oxide and non-oxide frameworks, sulfides, selenides**

**Coordination frameworks, supramolecular zeolites**

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

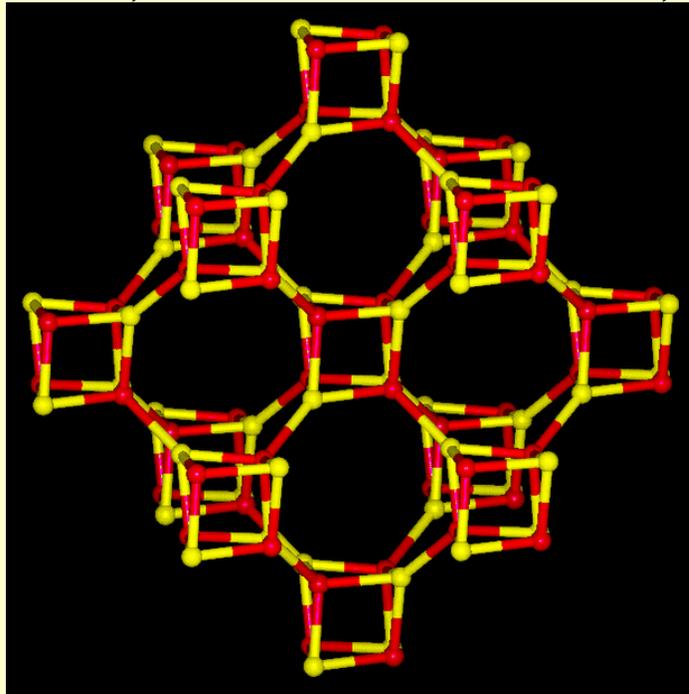
# Cobalto-Aluminophosphate

## ACP-1 (Co/Al 8.0)

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

Ethylenediamine molecules are located inside 8-ring channels

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



Al(O-*i*Pr)<sub>3</sub>, CoCO<sub>3</sub>·H<sub>2</sub>O, 85% H<sub>3</sub>PO<sub>4</sub>, ethylene glycol, ethylenediamine, pH 8.4  
Heated in a Teflon-coated steel autoclave at 180 °C for 4 d

# **Metallo-Organic Framework (MOF) Structures**

**4000 structures known (2008), 1000 new per year**

## **Metal centers**

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

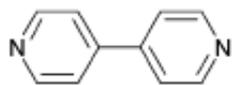
## **Polytopic Ligands**

**Organic spacers**

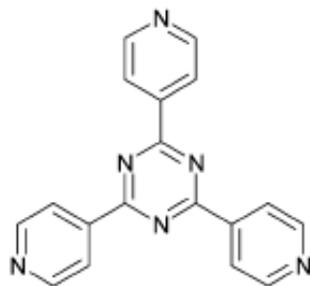
**Flexible – rigid**

**Variable length**

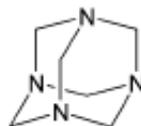
# Polytopic Organic Linkers



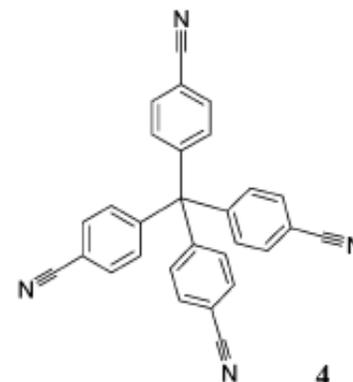
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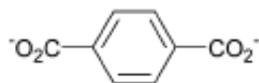
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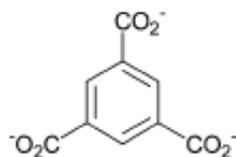
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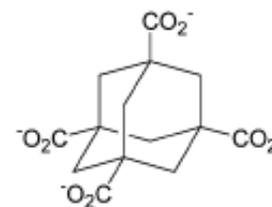
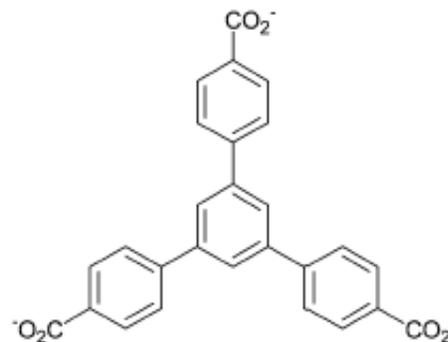
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5



6

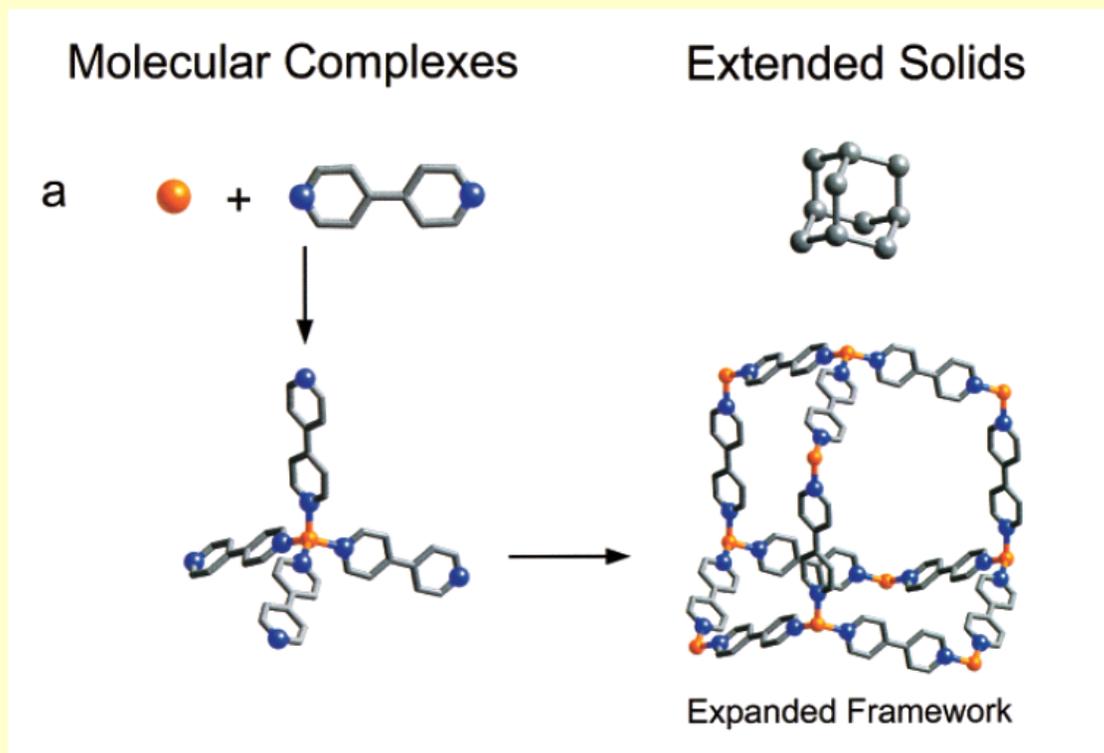


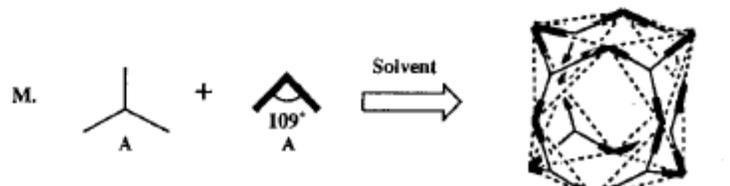
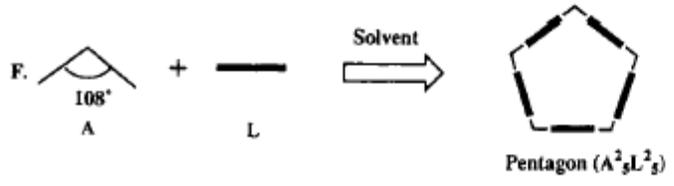
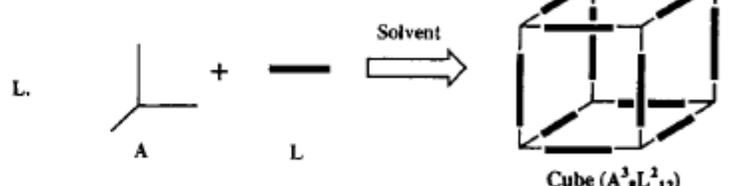
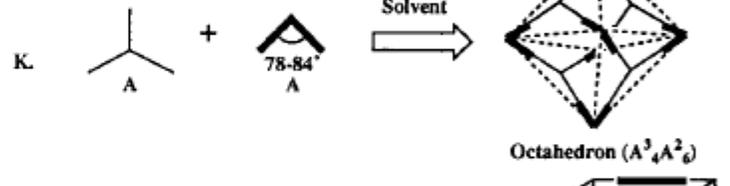
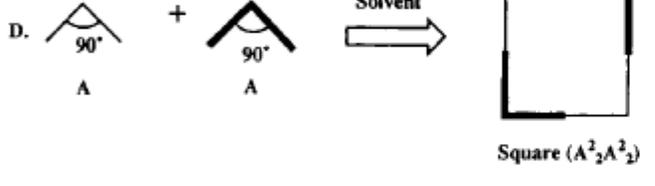
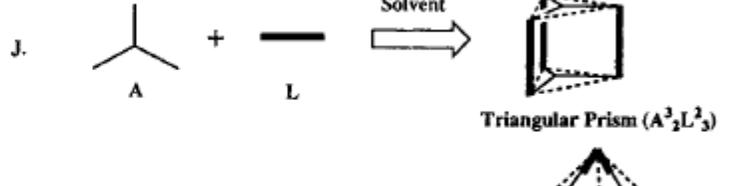
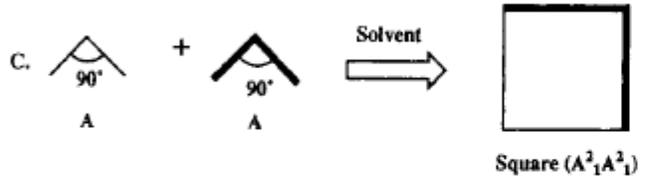
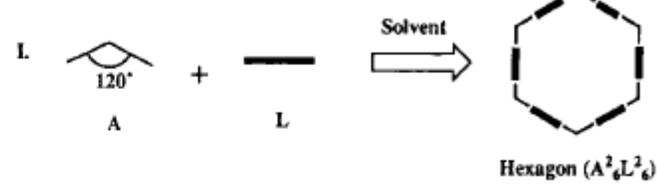
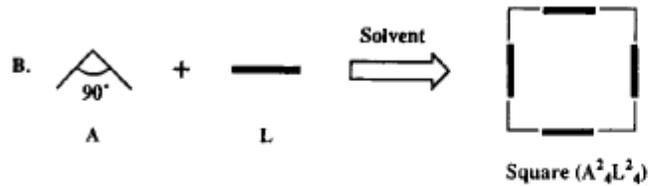
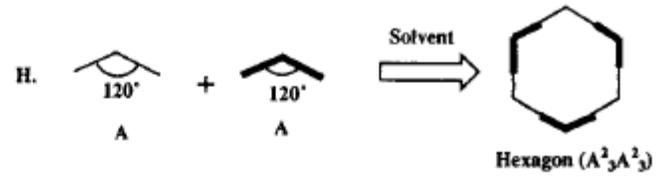
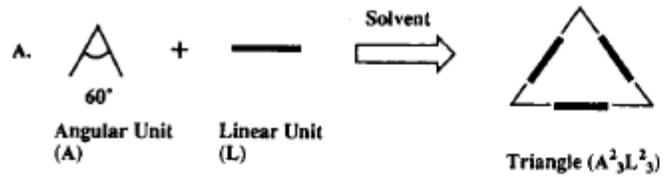
8

# Polytopic N-bound Organic Linkers

**Cationic framework structures**

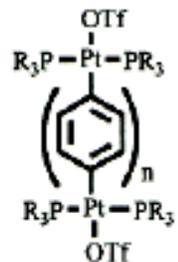
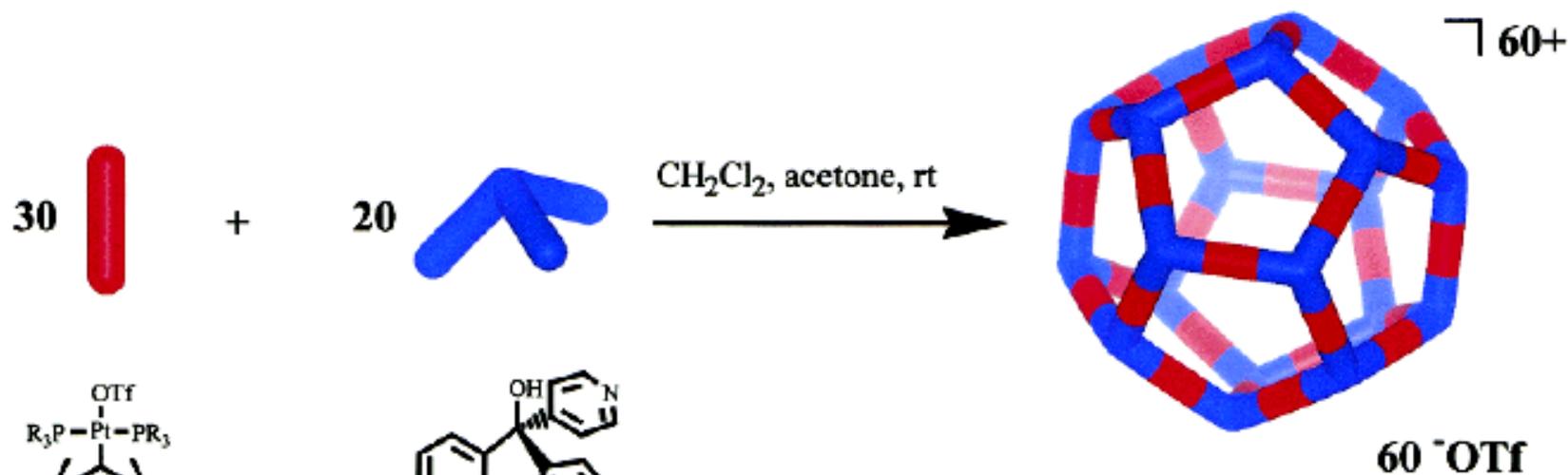
**Evacuation of guests within the pores usually results in collapse of the host framework**



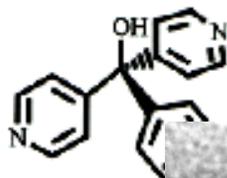


# Metallo-Organic Framework Structures

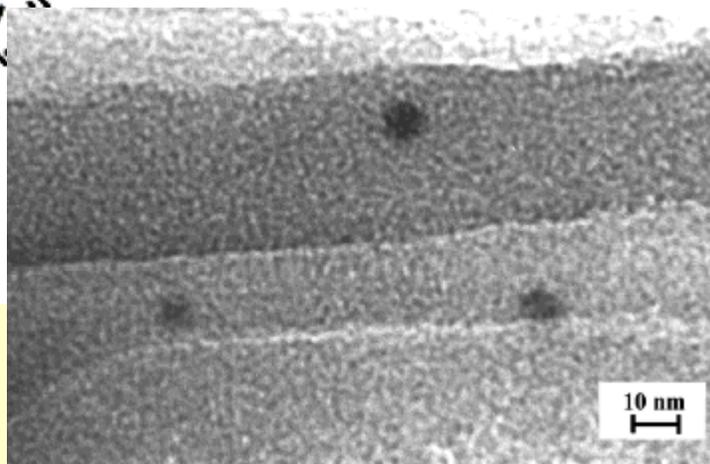
Scheme 4. Self-Assembly of Dodecahedra



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



25

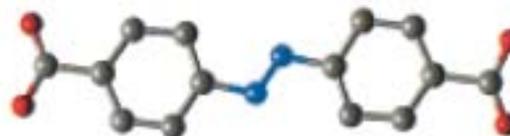


=Et, n=1 (99%)  
=Ph, n=2 (99%)

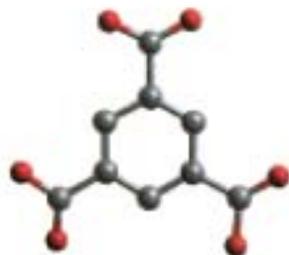
# Polytopic carboxylate linkers



1,4-benzenedicarboxylate  
(BDC)



1,4-azodibenzoate  
(ADB)



1,3,5-benzenetricarboxylate  
(BTC)



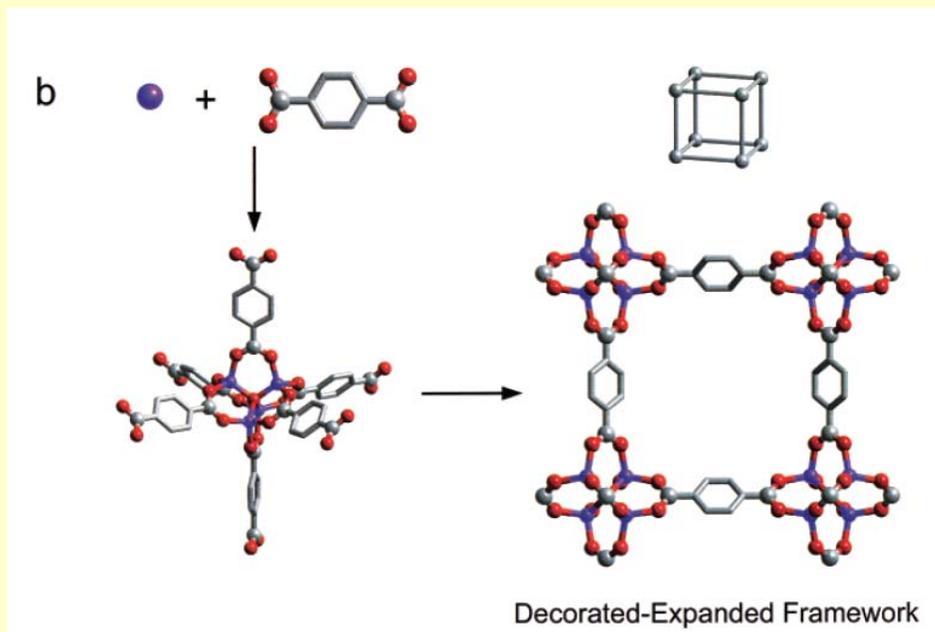
1,3,5,7-adamantanetetracarboxylate  
(ATC)

# Polytopic Carboxylate Linkers

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

Molecular Complexes

Extended Solids

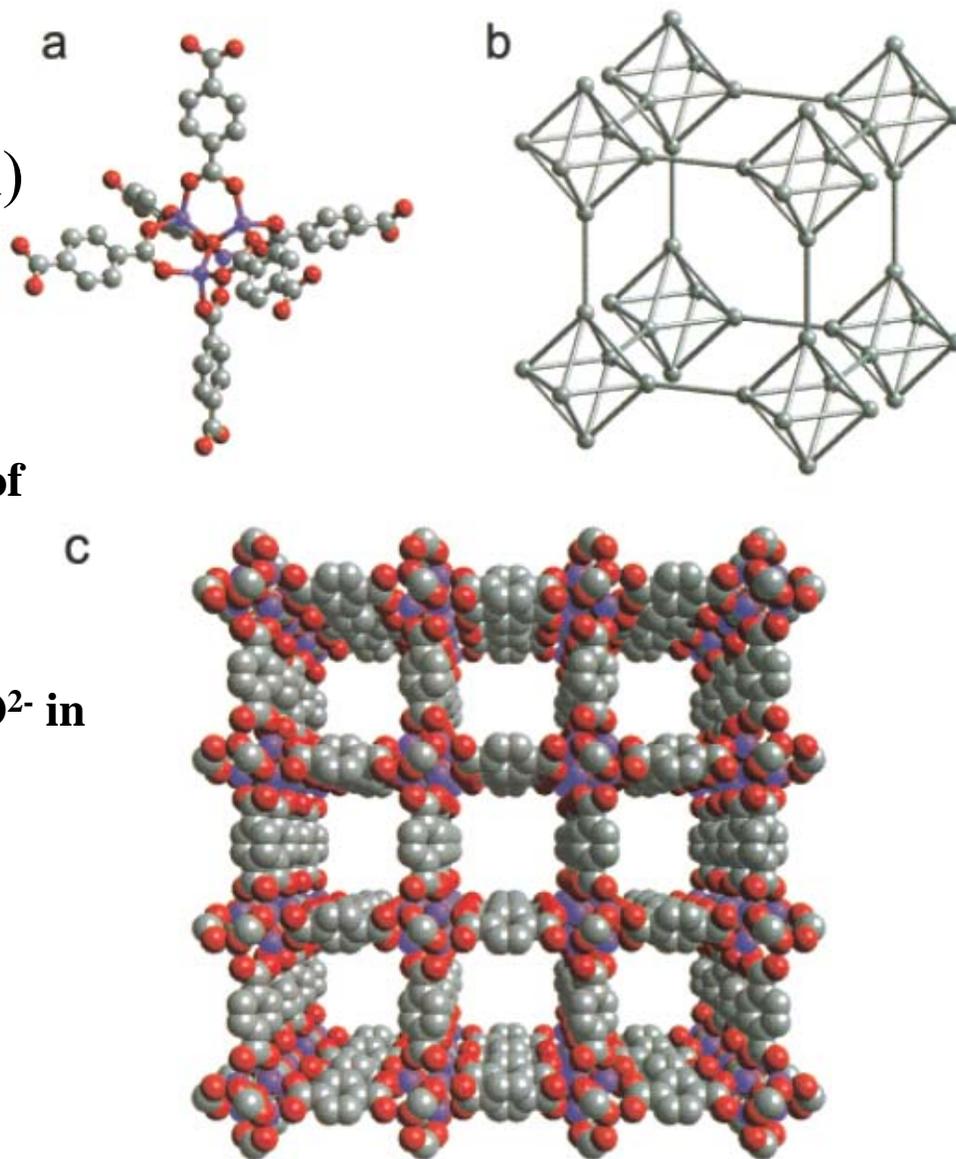


# MOF-5



- $\text{Zn}(\text{NO}_3)_2 + \text{H}_2\text{BDC}$  in DMF/PhCl
- Addition of TEA: deprotonation of  $\text{H}_2\text{BDC}$
- Addition of  $\text{Zn}^{2+}$
- Addition of  $\text{H}_2\text{O}_2$ : formation of  $\text{O}^{2-}$  in the cluster center

Cavity diam. 18.5 Å

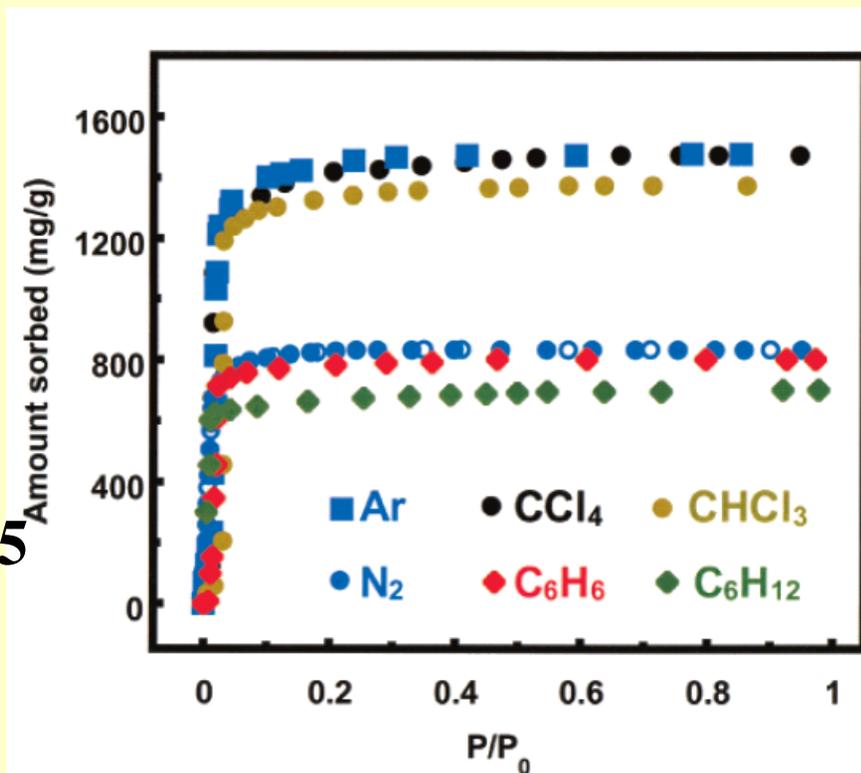


# MOF-5

MOF-5

Stable even after desolvation  
at 300 °C in air

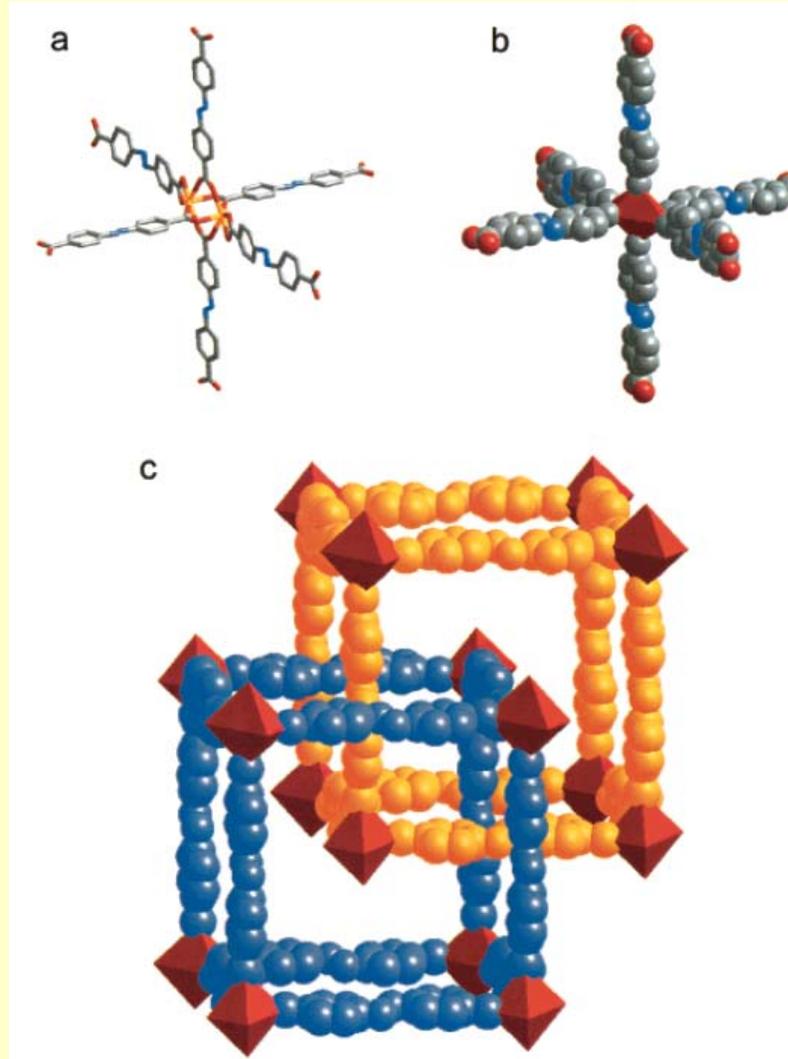
gas sorption isotherms for MOF-5



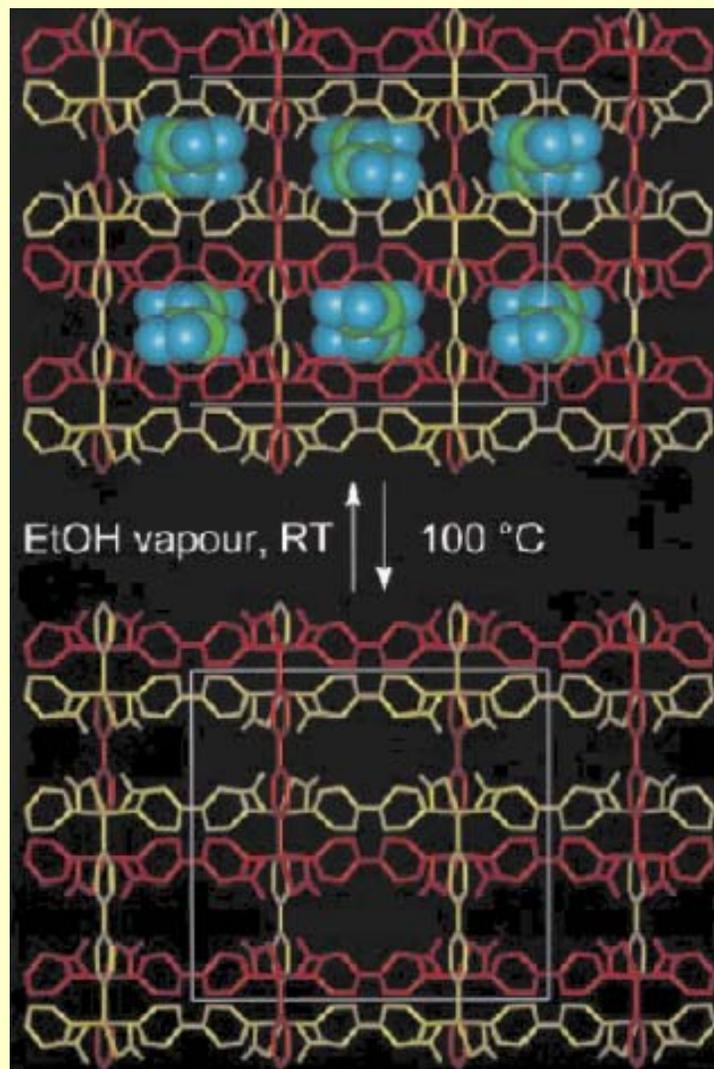
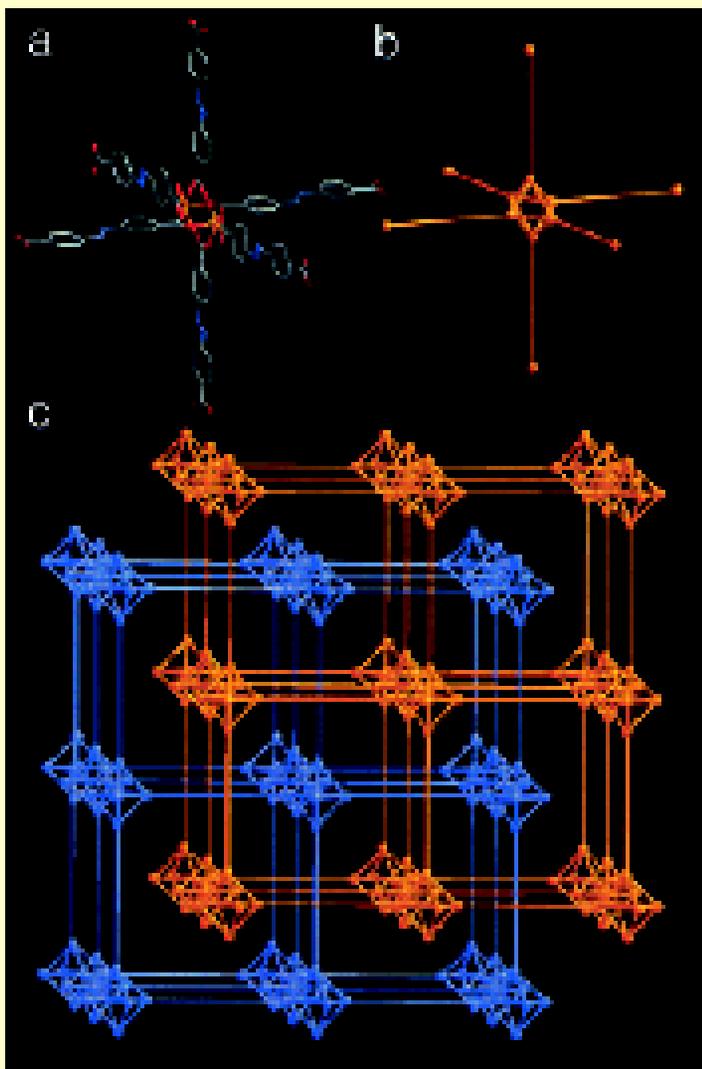
	MOF -2	MOF -3	MOF -4	MOF -5	MOF -6	MOF -9	MOF -11
pore diameter (Å)	7	8	14	12	4	8	7
surface area ( $\text{m}^2/\text{g}$ )	270	140		2900		127	560
pore volume ( $\text{cm}^3/\text{g}$ )	0.094	0.038	0.612	1.04	0.099	0.035	0.20

# Interpenetration

MOF-9

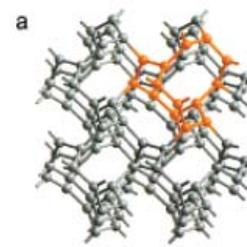


# Metallo-Organic Framework Structures

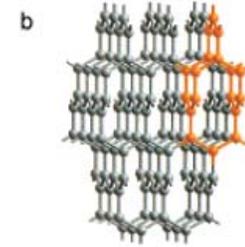


# Basic Nets

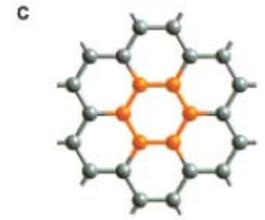
coordination	coordination figures		net
3	triangle	triangle	$\text{SrSi}_2$
3	triangle	triangle	$\text{ThSi}_2$
3	triangle	triangle	$6^3$ honeycomb
3,4	triangle	square	$\text{Pt}_3\text{O}_4$
4	square	square	$\text{NbO}$
4	tetrahedron	tetrahedron	diamond (C)
4,4	square	tetrahedron	cooperite (PtS)
4	square	square	$4^4$ square lattice
6	octahedron	octahedron	primitive cubic
8	cube	cube	body-centered cubic



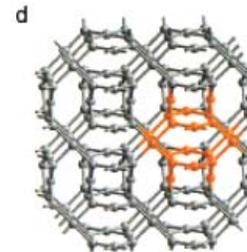
Si net of  $\text{SrSi}_2$



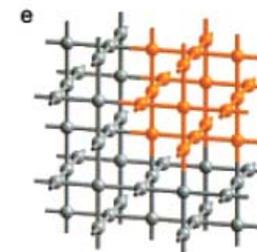
Si net of  $\text{ThSi}_2$



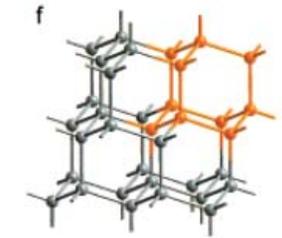
$6^3$  Honeycomb



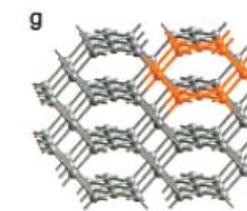
$\text{Pt}_3\text{O}_4$



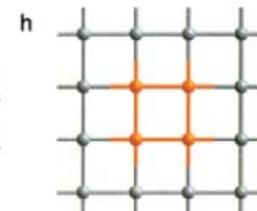
$\text{NbO}$



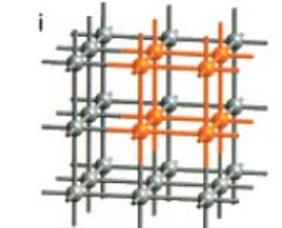
Diamond (C)



Cooperite (PtS)

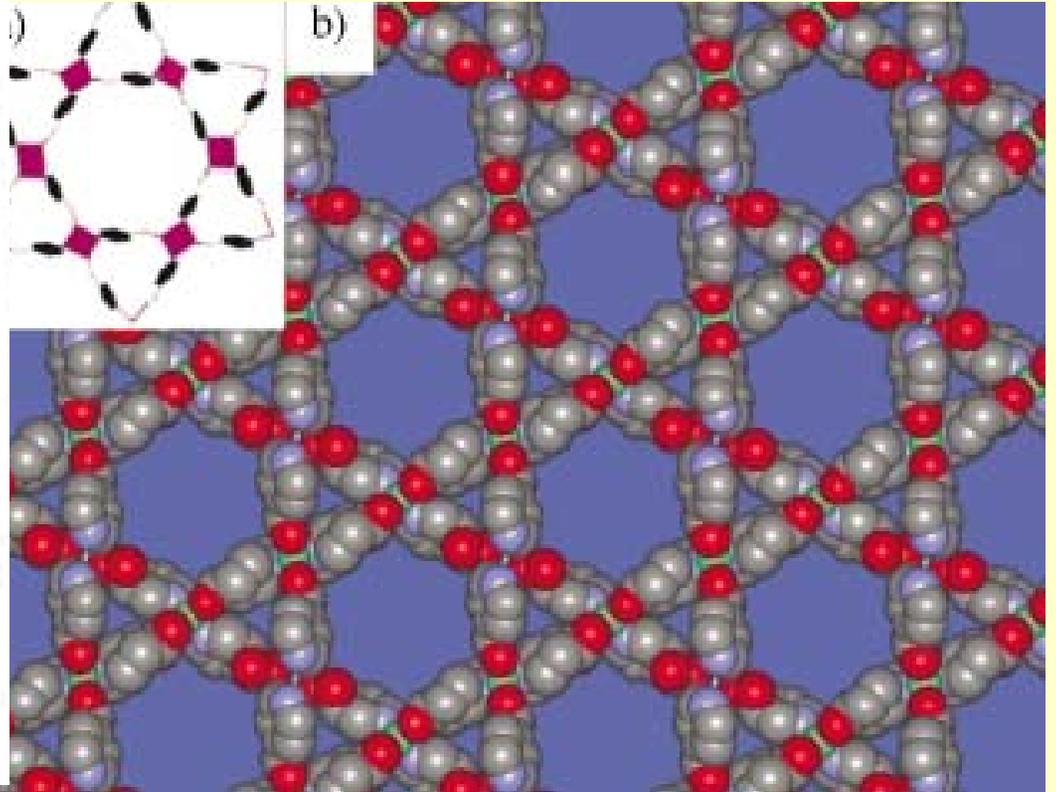
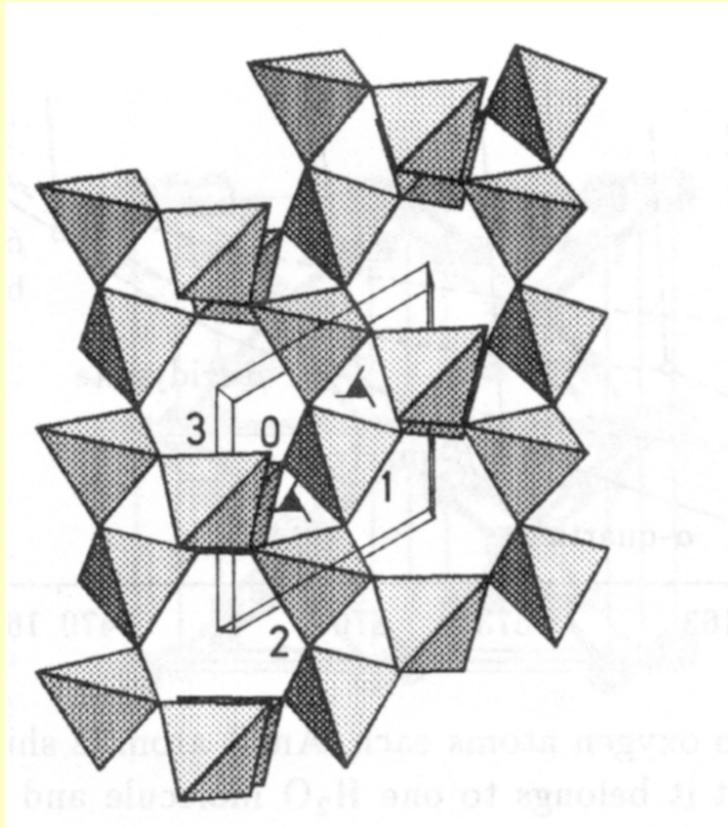


$4^4$  Square lattice

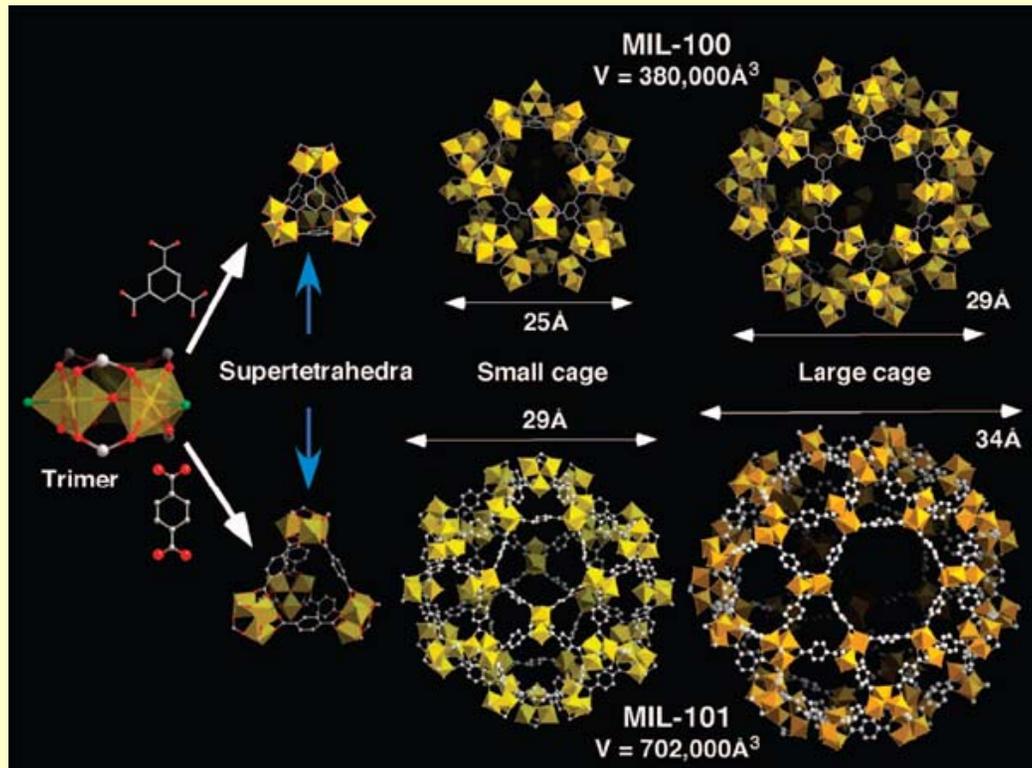


Primitive cubic

# Inorganic and Metallo-Organic Quartz



# MIL-100 and MIL-101



**MIL-101 Record Surface area 5 900 m<sup>2</sup>/g**