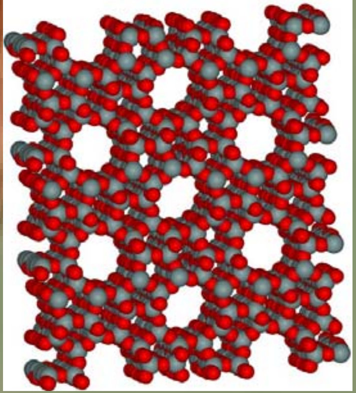
# Zeolites and porous materials: synthesis and applications

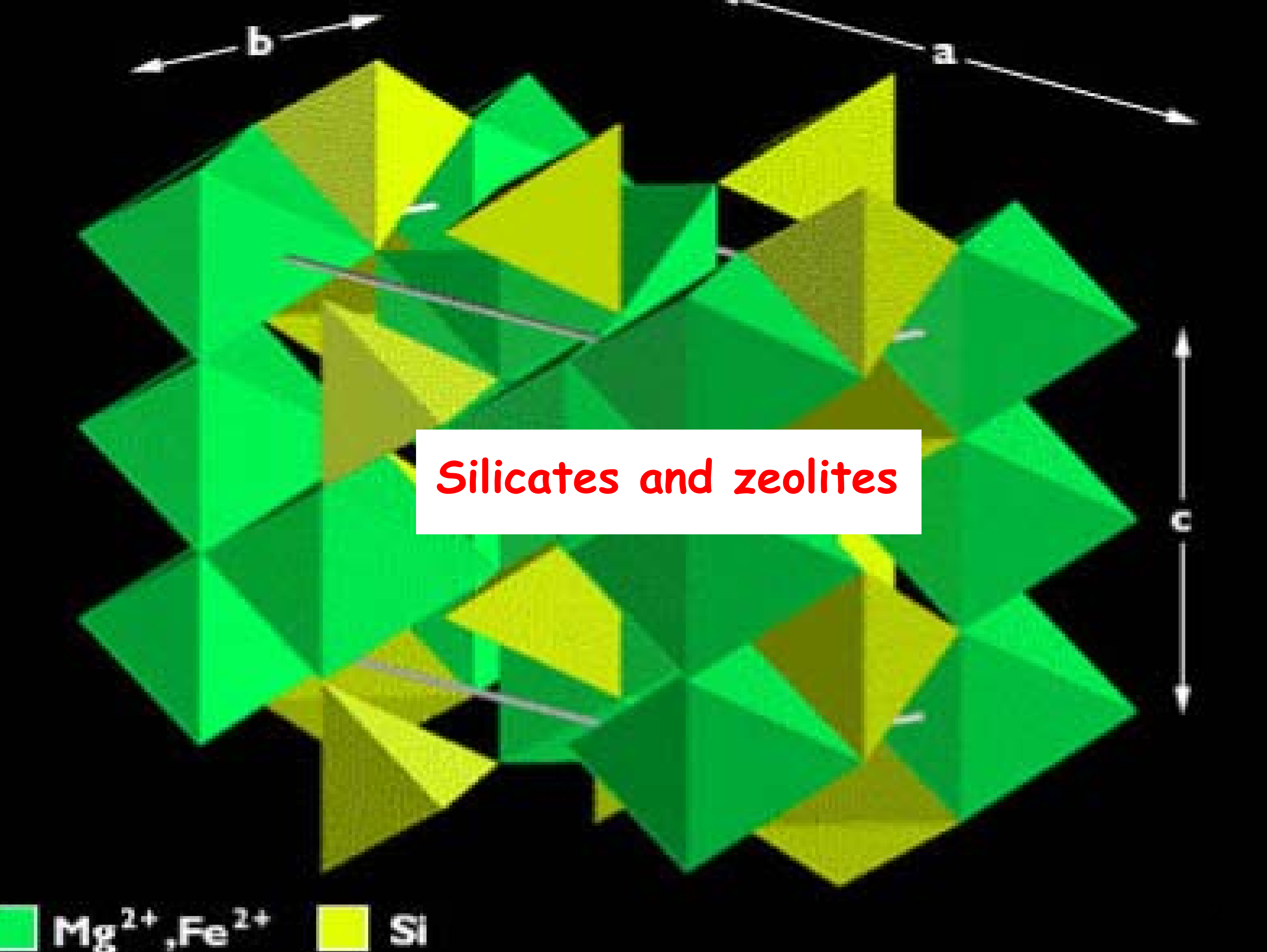


UE LS 205

C. Bonhomme, Professor

Université P. et M. Curie, Paris 6

# Silicates and zeolites



# Silicates

**wt. % in earth crust:**

O: 47 %
Si: 28 %
Al: 5 %

silicates and aluminosilicates

Fe: 5 %
Ca: 3.5 %
Na: 2.8 %
K: 2.6 %
Mg: 2 %
.....

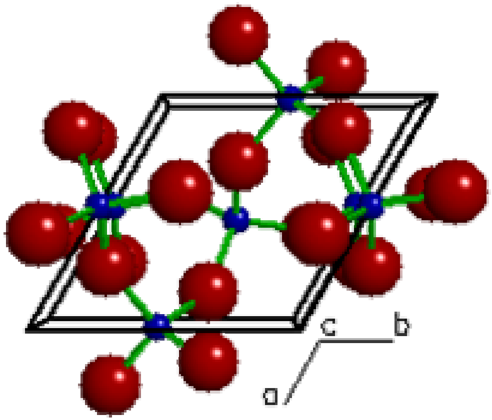
$\chi(\mathrm{Al}) \sim \chi(\mathrm{Si})$

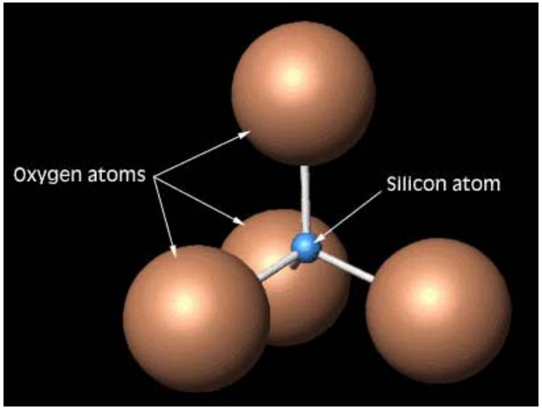
$r(\mathrm{Al}^{3+})/r(\mathrm{O}^{2-}) \sim 0.43$

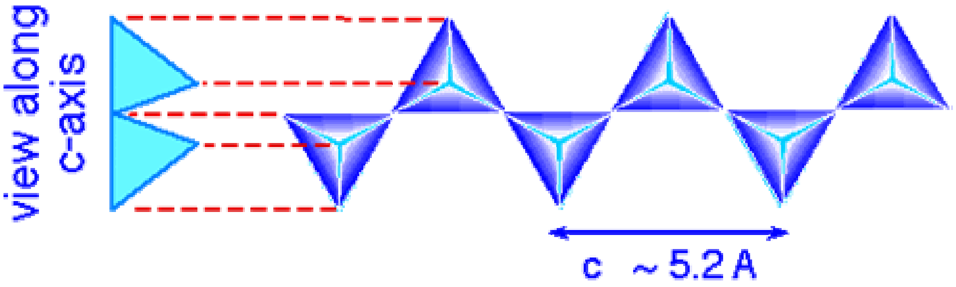
CN(Al): 4 or 6!

but... a very large variety of structures!...

NESOSILICATES
SOROSILICATES
CYCLOSILICATES
INOSILICATES
PHYLLOSILICATES
TECTOSILICATES



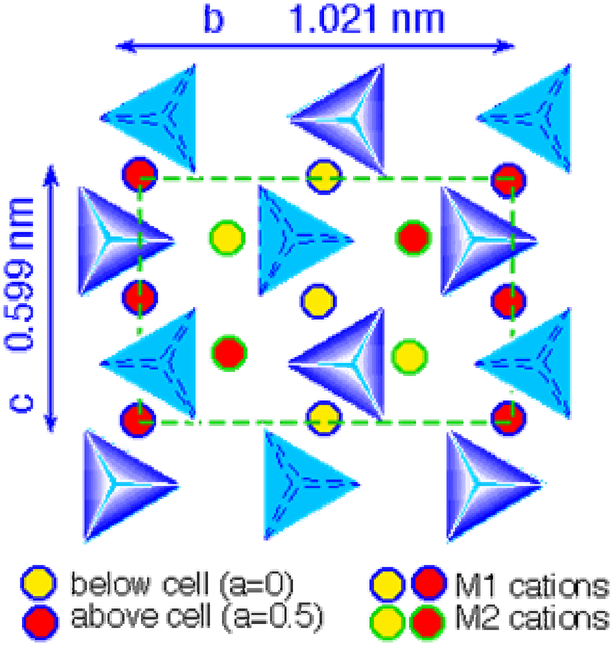




the basic structural unit: $\mathrm{SiO_4^{4-}}$ ➡ linked by vertices (only...)

# Neso- and sorosilicates

## «isolated» $SiO_4^{4-}$ units: nesosilicates



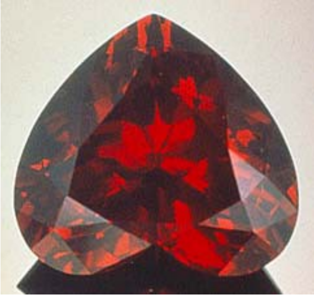
$Mg^{2+}$, $Fe^{2+}$

$Mg_2SiO_4$: Forsterite

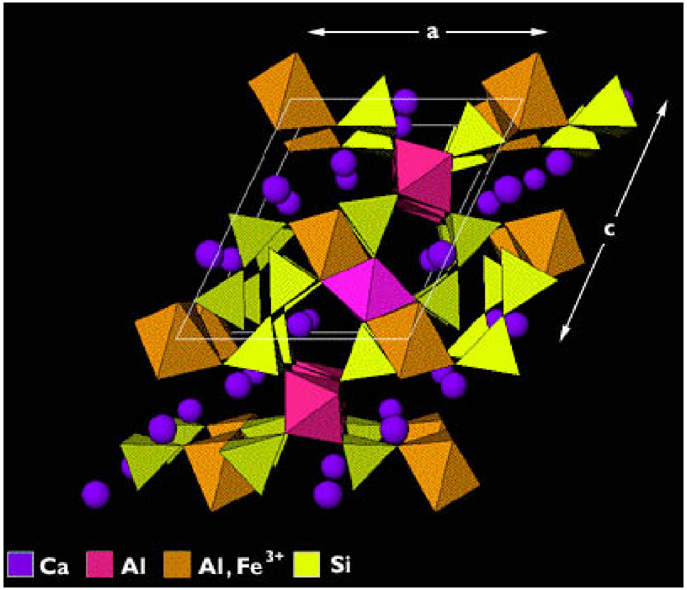
$(Mg,Fe)_2SiO_4$: Olivine

other examples: garnets, Portland cement...

$X_3Y_2(SiO_4)_3$



## «isolated» $Si_2O_7^{6-}$ units: sorosilicates



$Sc_2(Si_2O_7)$: Thortveitite

$Zn_4(Si_2O_7)(OH)_2,H_2O$: Hemimorphite

other units (rare!): $Si_3O_{10}^{8-}$, $Si_4O_{13}^{10-}$

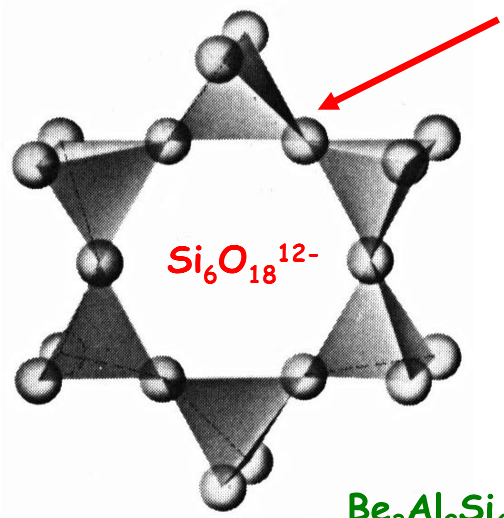
$$SiO_2,\ Ag_2O,\ T \sim 600°C,\ P(O_2) \sim 4.5\ kBar$$

$$\Downarrow$$

$$Ag_{10}(Si_4O_{13})$$

# Cyclosilicates

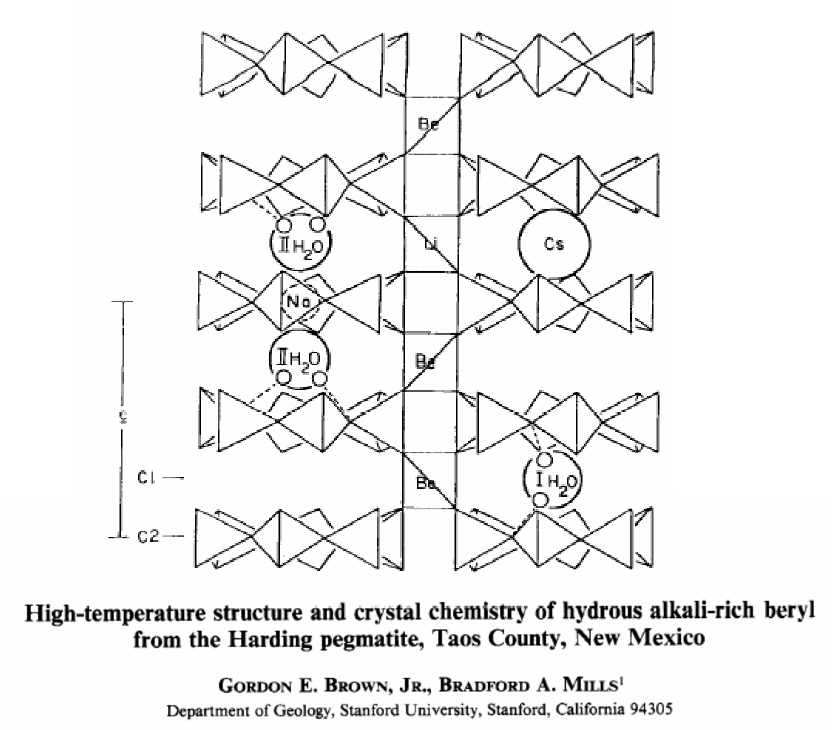
Cycles including 3, 4, 6 or 8 silicate units: $(Si_nO_{3n})^{2n-}$ (n = 3, 4, 6, 8)



shared vertex

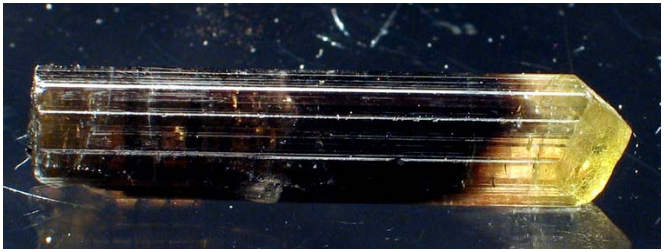
$Si_6O_{18}^{12-}$

$Be_3Al_2Si_6O_{18}$: Beryl
or...emerald!



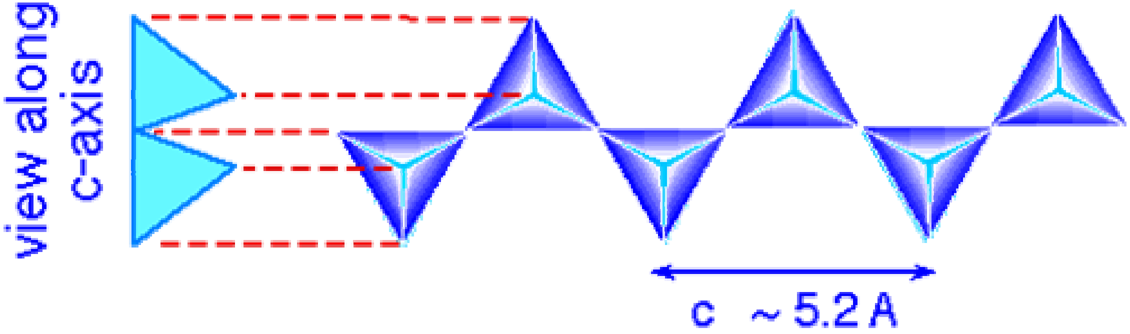
**High-temperature structure and crystal chemistry of hydrous alkali-rich beryl from the Harding pegmatite, Taos County, New Mexico**

GORDON E. BROWN, JR., BRADFORD A. MILLS[1]
Department of Geology, Stanford University, Stanford, California 94305



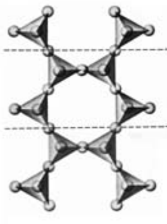
$(Na,Ca)(Li,Mg,Al)_3(Al,Fe,Mn)_6(OH)_4(BO_3)_3Si_6O_{18}$: Tourmaline

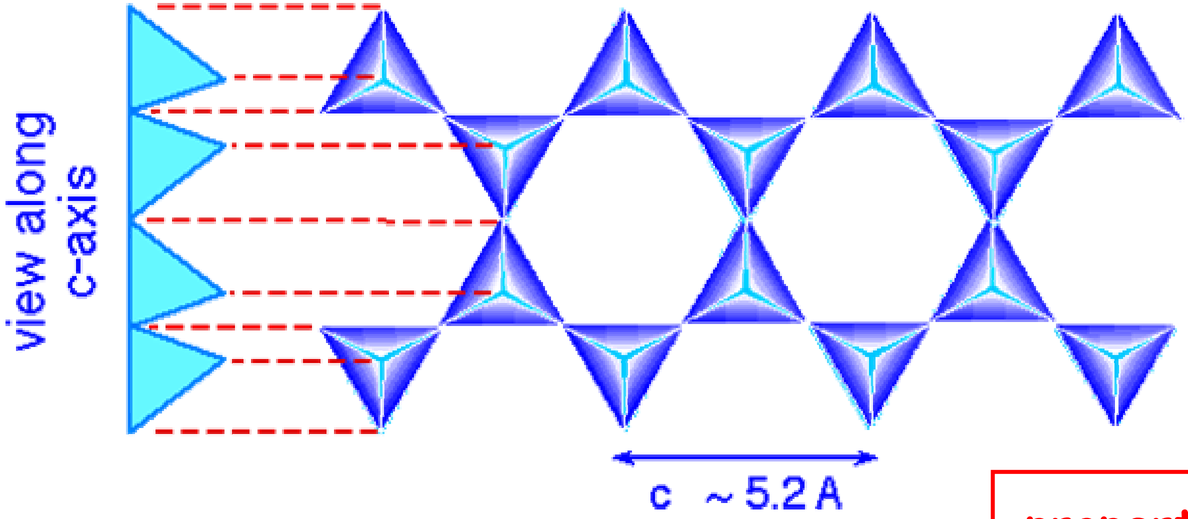
# Inosilicates



$(SiO_3)^{2-}$

**pyroxenes**





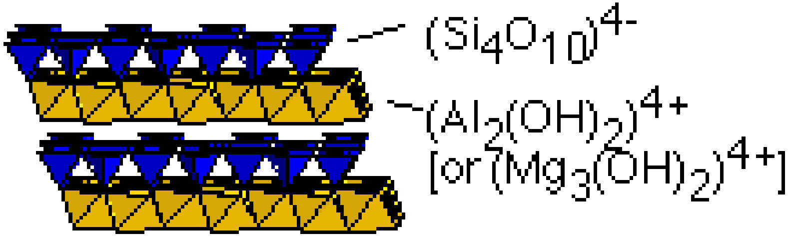
$(Si_4O_{11})^{6-}$

**amphiboles**

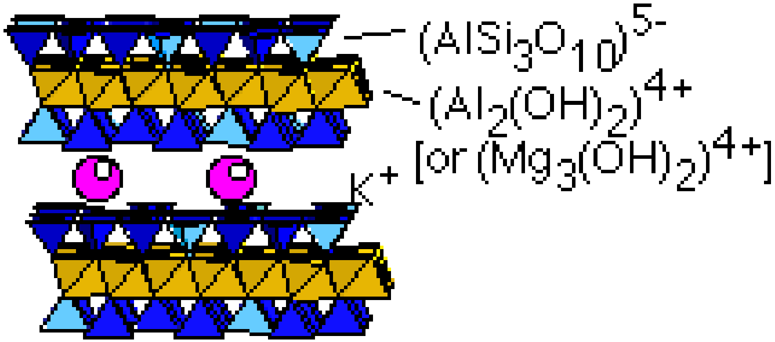
properties of fibers

# Phyllosilicates

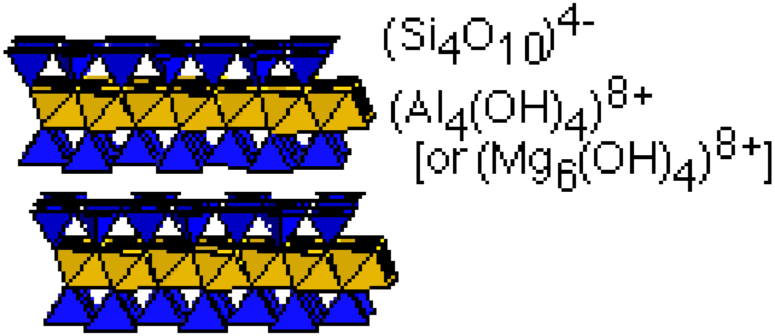
Kaolinite (or Antigorite)



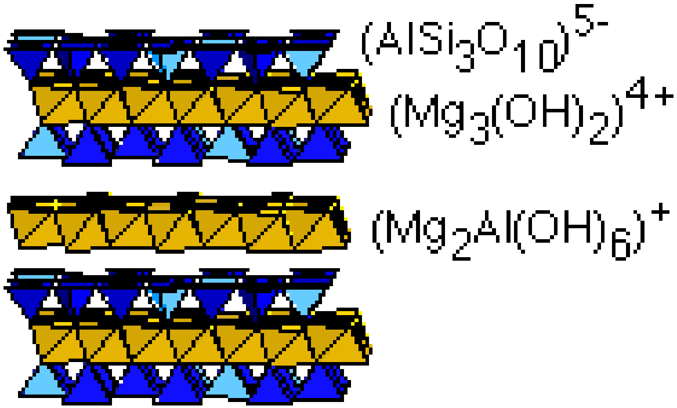
Muscovite (or Biotite)



Pyrophyllite (or Talc)



Chlorite

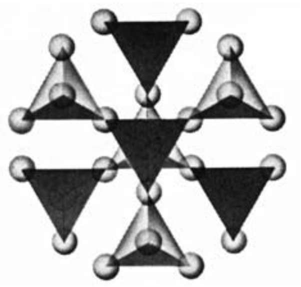


**but also...clays! (intercalation of water molecules)**

**(montmorillonite...)**

**plastic properties**

# Tectosilicates

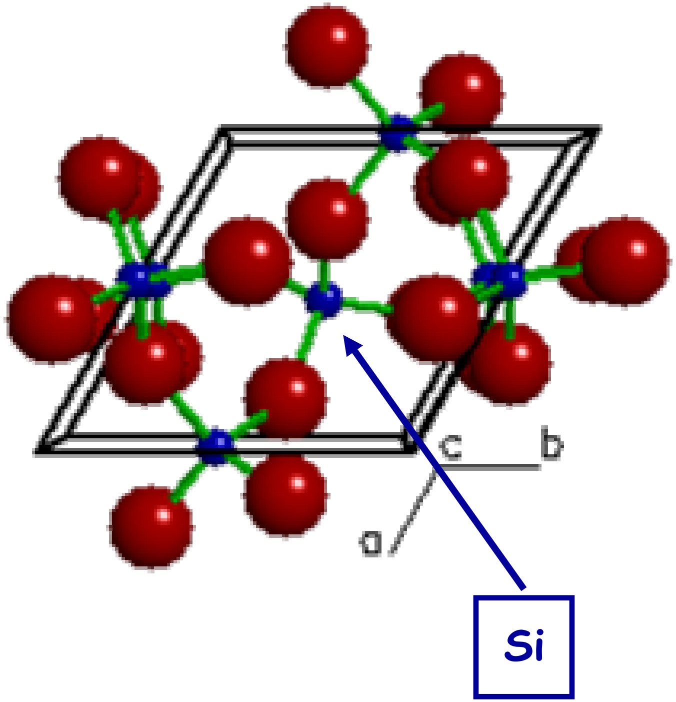


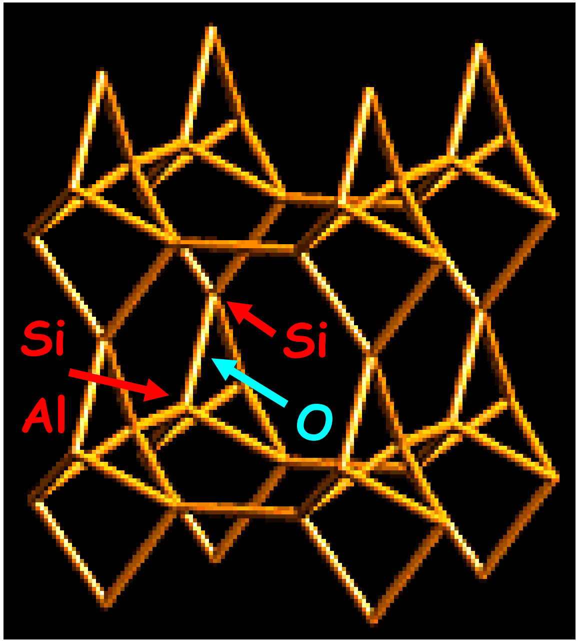
$(SiO_2)n$ or $(Si,Al,C^+)_nO_{2n}$

- silica
- Feldspaths
- zeolites

porosity?

Feldspath (plagioclase)





a typical zeolite structure

# Hierarchical porosity

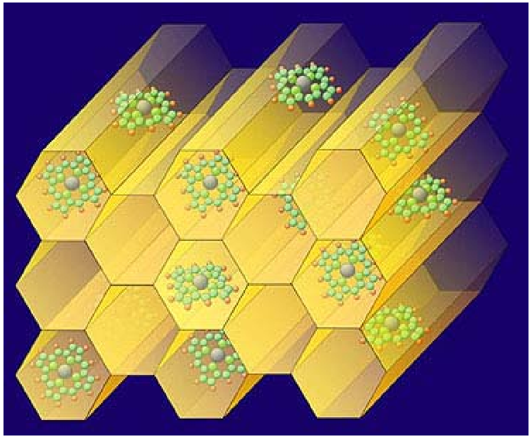
## porous materials

**nanoporous**
ø < 2 nm

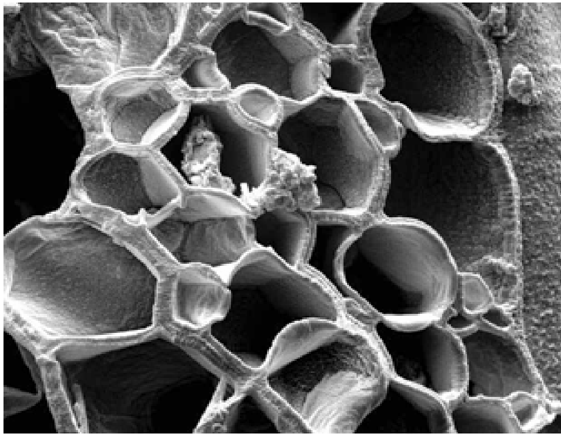
**mesoporous**
2 < ø < 50 nm

**macroporous**
50 nm < ø

zeolites



MCM



foams

# Zeolites

dicovered by Baron A. Von Kronstedt

*ZEO*: to boil

*LITHOS*: stone

(1756)

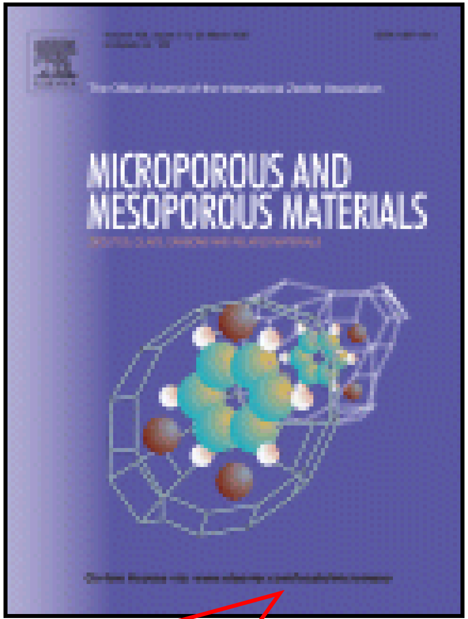
characteristics...

- exchangeable cations

  (neutrality)

$M_x [ (AlO_2)_y (SiO_2)_z ], mH_2O$

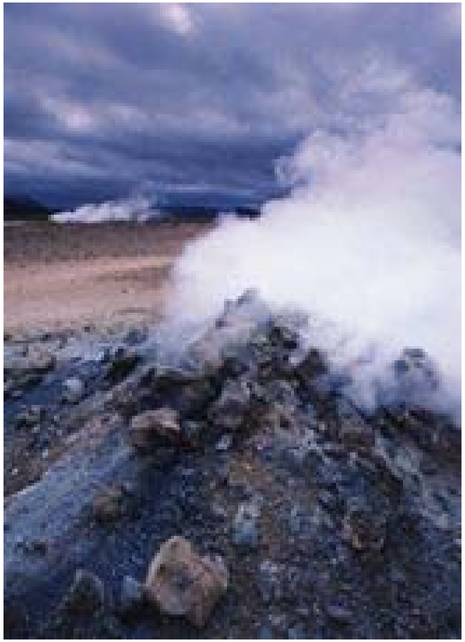
- rigid anionic networks
- cavities and channels
- guest molecules (water...)

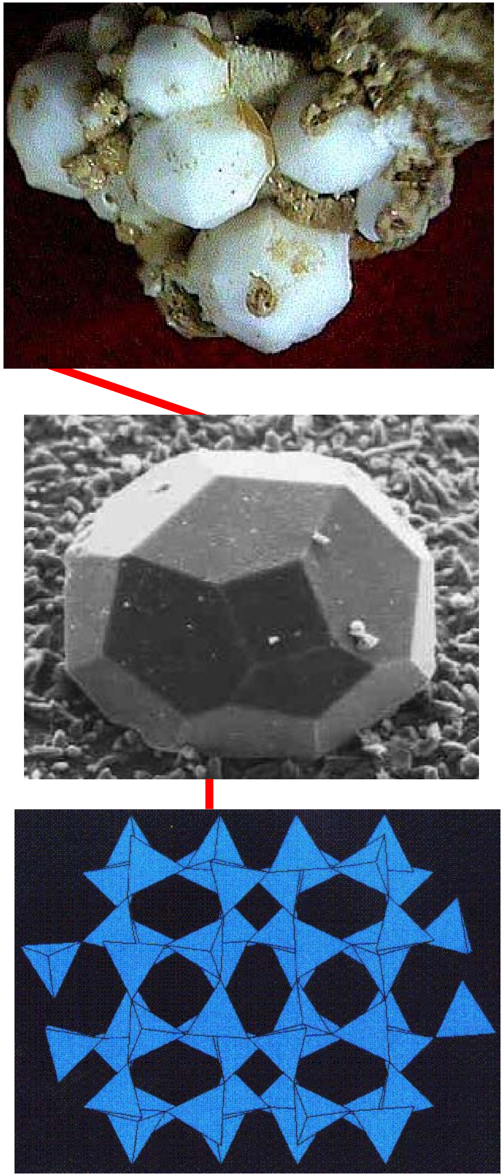


MICROPOROUS AND MESOPOROUS MATERIALS

official journal of the international zeolite association

# Natural zeolites





~ 40 natural zeolites

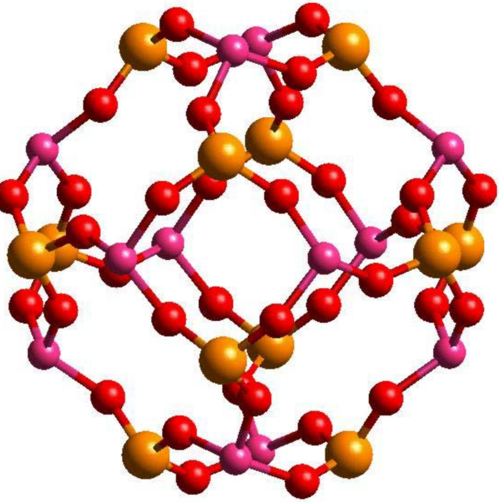
**Natrolite**

**Faujasite**

**Anacilme**

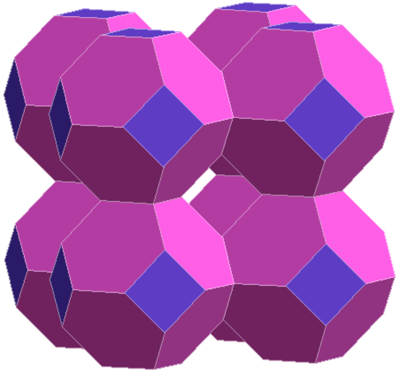
# The *sodalite* cage

*Sodalite*, a mineral: $Na_8Al_6Si_6O_{24}Cl_2$



24 linked tetrahedra (Si or Al)

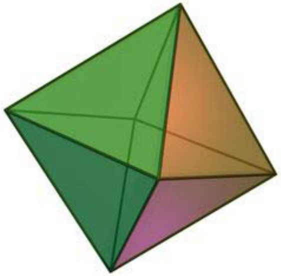
the *sodalite* entity



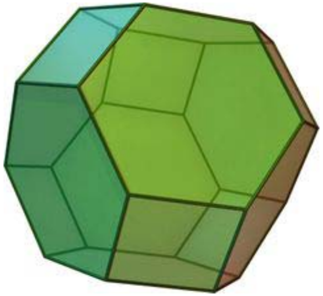
Sodalite (mineral)

*Lapis-lazuli*

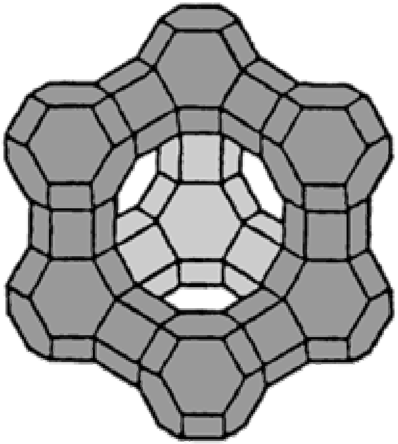
Linde-A (synthetic)



octahedron



truncated octahedron



Faujasite (mineral)

$NaCa_{1.5}(Al_2Si_5O_{14}).10H_2O$

# Some characteristics of zeolites

## A- the Si/Al ratio

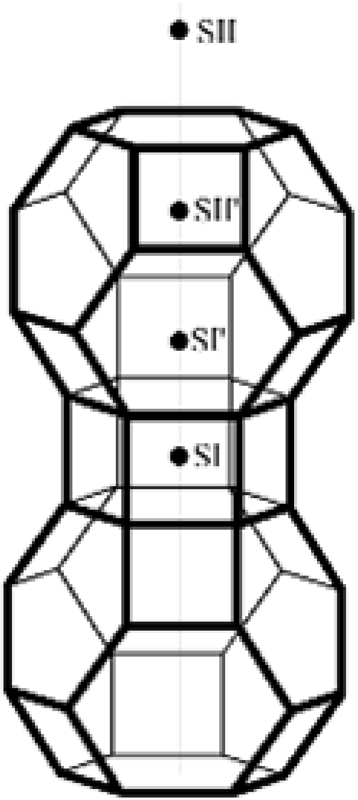
Linde-A: Si/Al =1

Mordenite (mineral): Si/Al = 5.5

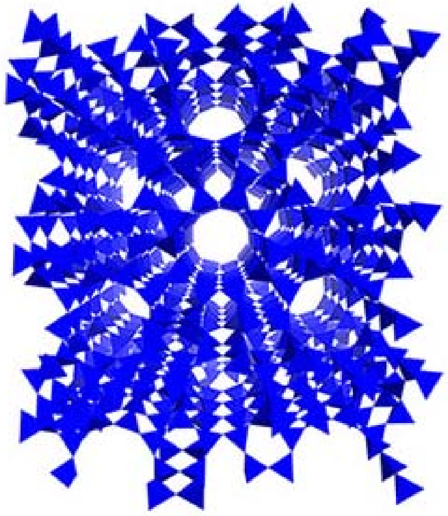
ZSM: 20 < Si/Al < ∞! (hydrophobic)

## B- exchangeable cations

various accessible sites



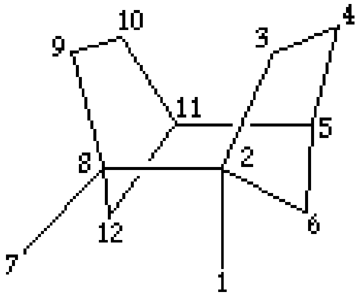
## C- cavities and tunnels



| Zeolithe | tetrahedra | Ø (pm) |
|---|---|---|
| Sodalite | 4 | 260 |
| Linde-A | 8 | 410 |
| ZSM-5 | 10 | 510 × 560 |
| Faujasite | 12 | 740 |
| Mordenite | 12 | 670 × 700 |

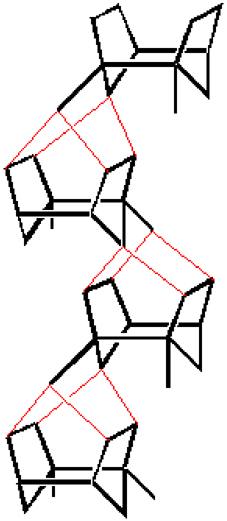
# Synthetic zeolites: the ZSM family

**Zeolite Socony Mobil (~ 1975)**

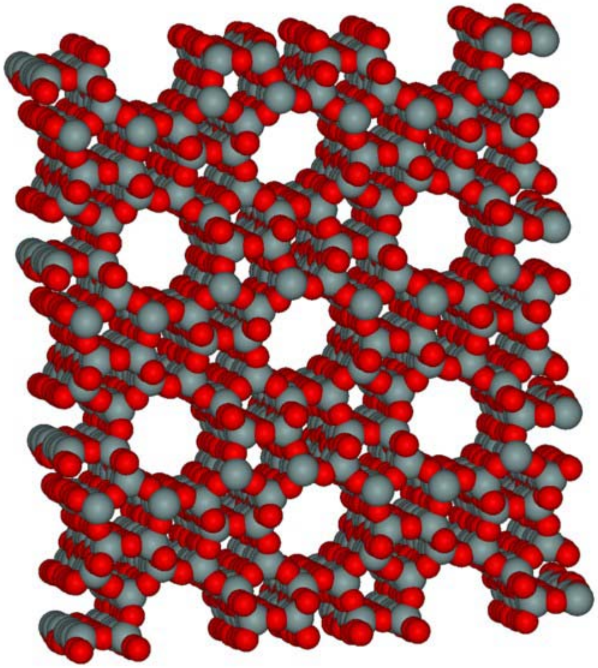


«Pentasil» unit

(five-membered rings)

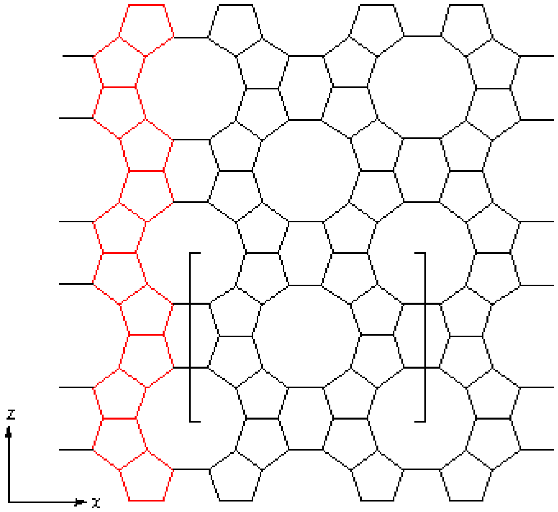


chains

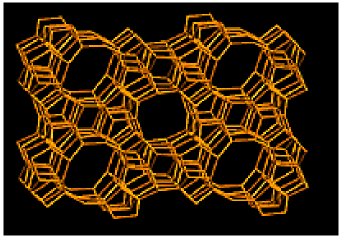


3D architecture

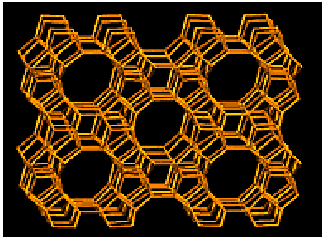
**ZSM-5**



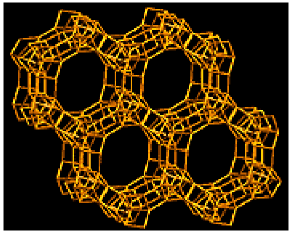
planes



**ZSM-5**

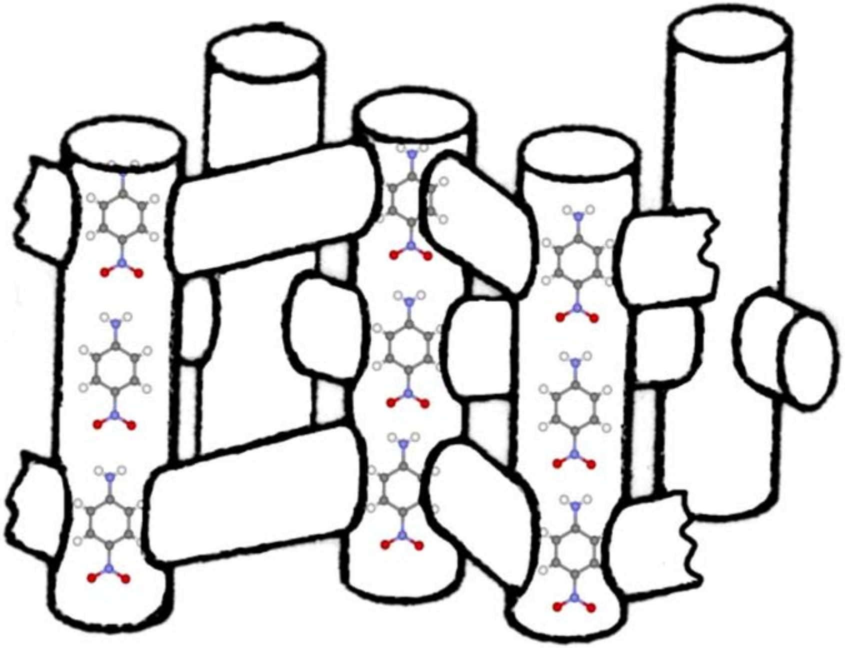


**ZSM-11**

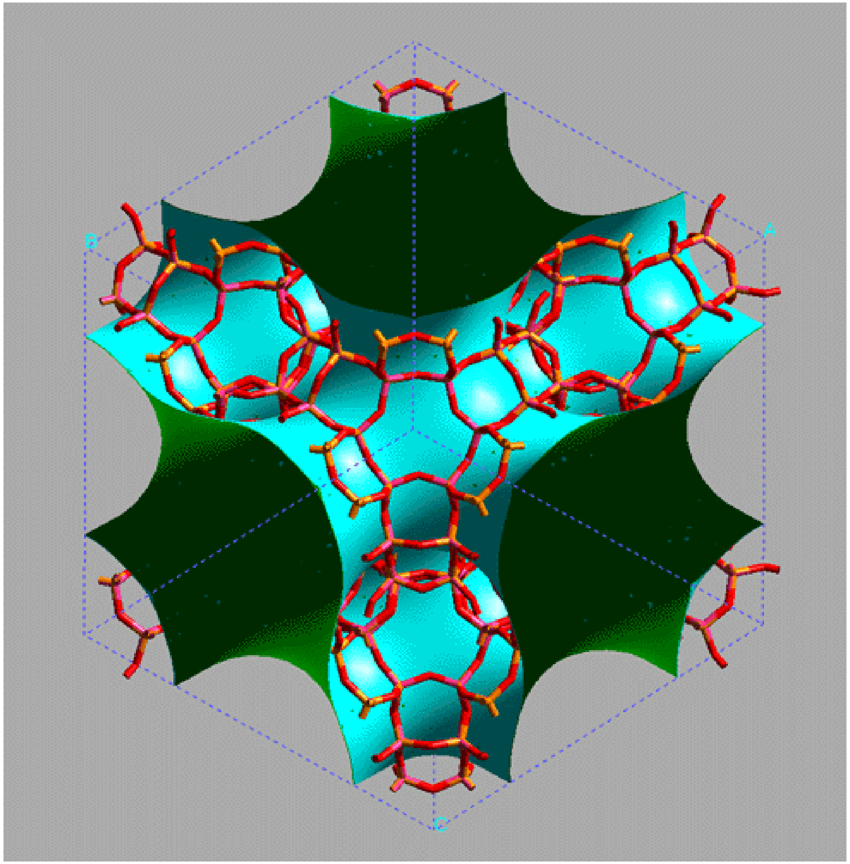


**ZSM-18**

# Interconnected channels: structural dependence

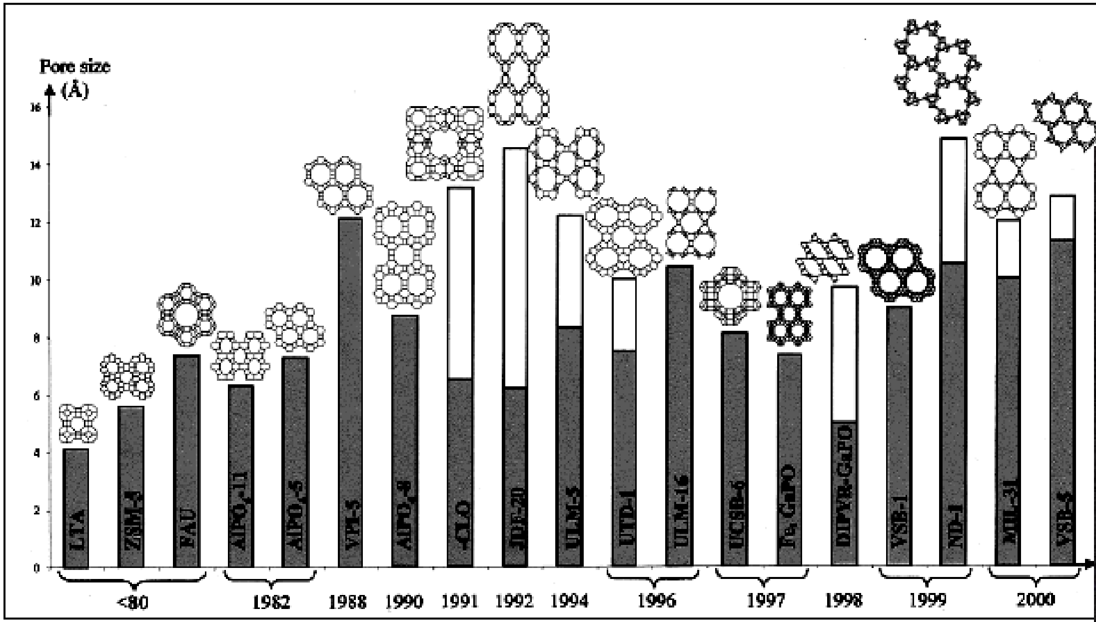


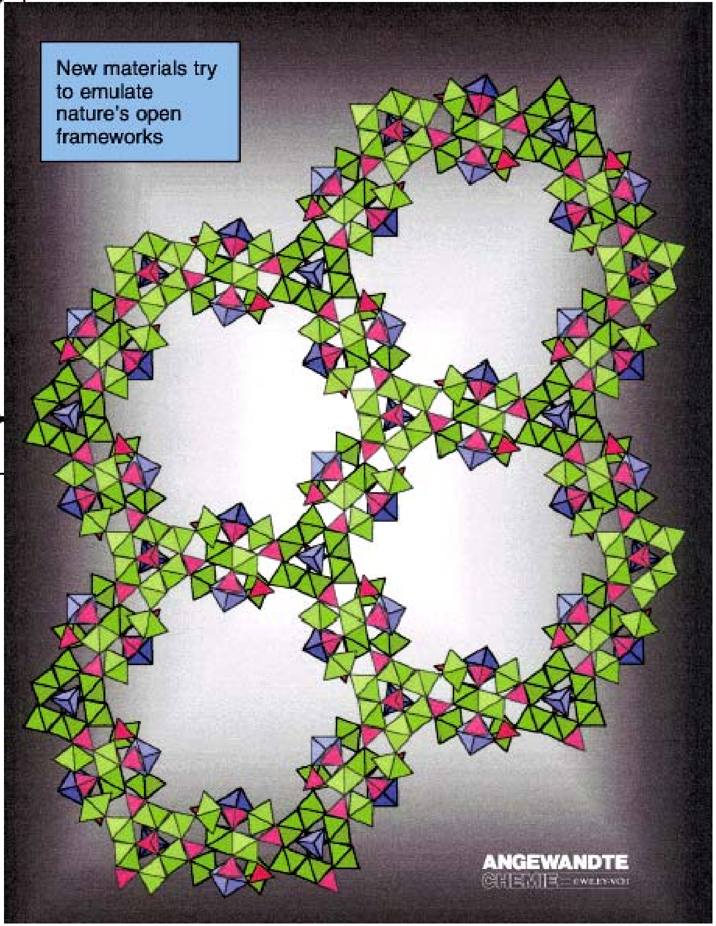
**ZSM-5**



**Faujasite**

# More and more porosity!




New materials try to emulate nature's open frameworks

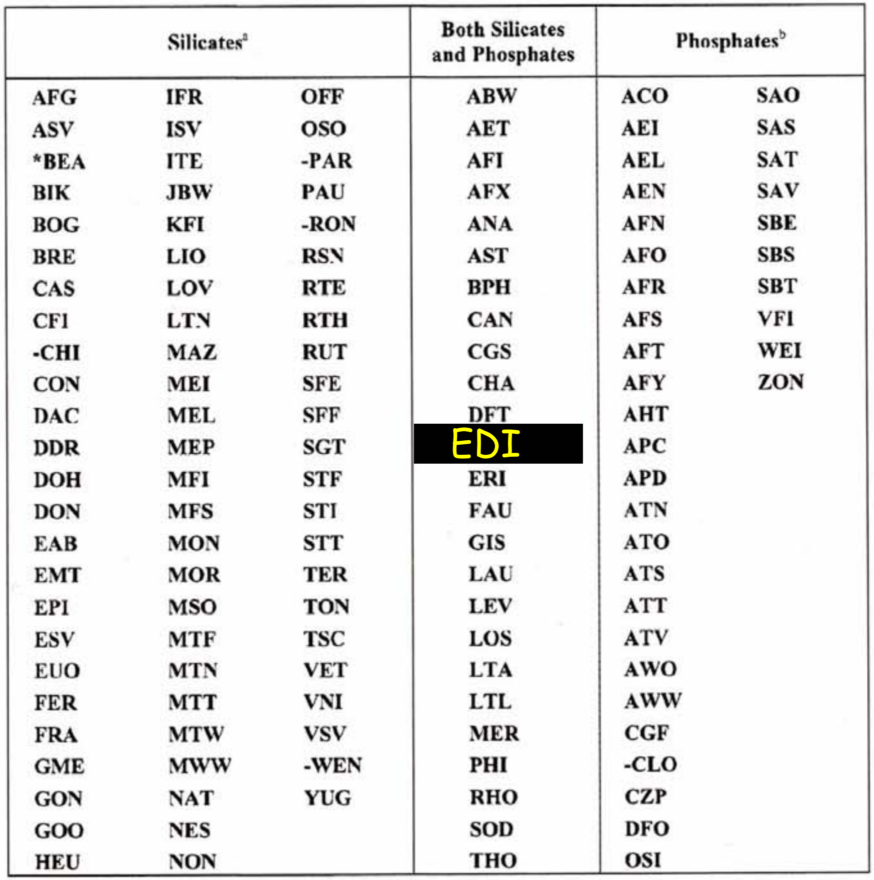
~ 200 synthetic zeolites!

# Classification of zeolites

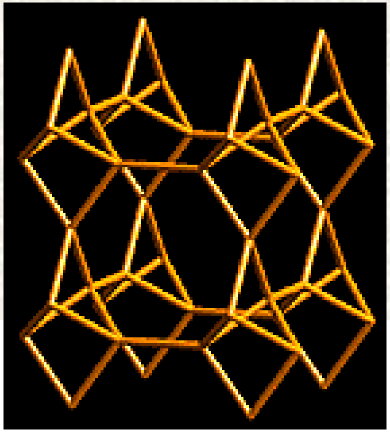
## Zeolite Type Categories and Framework Type Groups

- Zeolite type categories
  - Silicates
  - Phosphates
- Framework type groups
  - Silicates
  - Phosphates
  - Both, silicates and phosphates

Si (Si,P) P

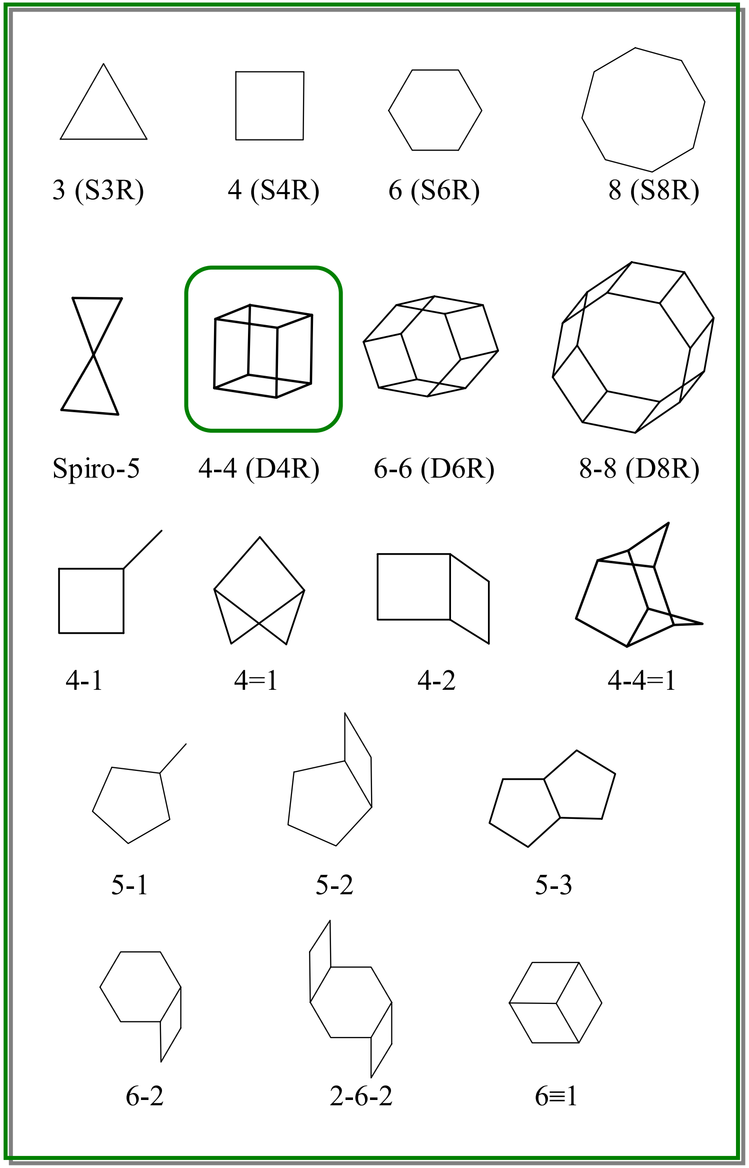


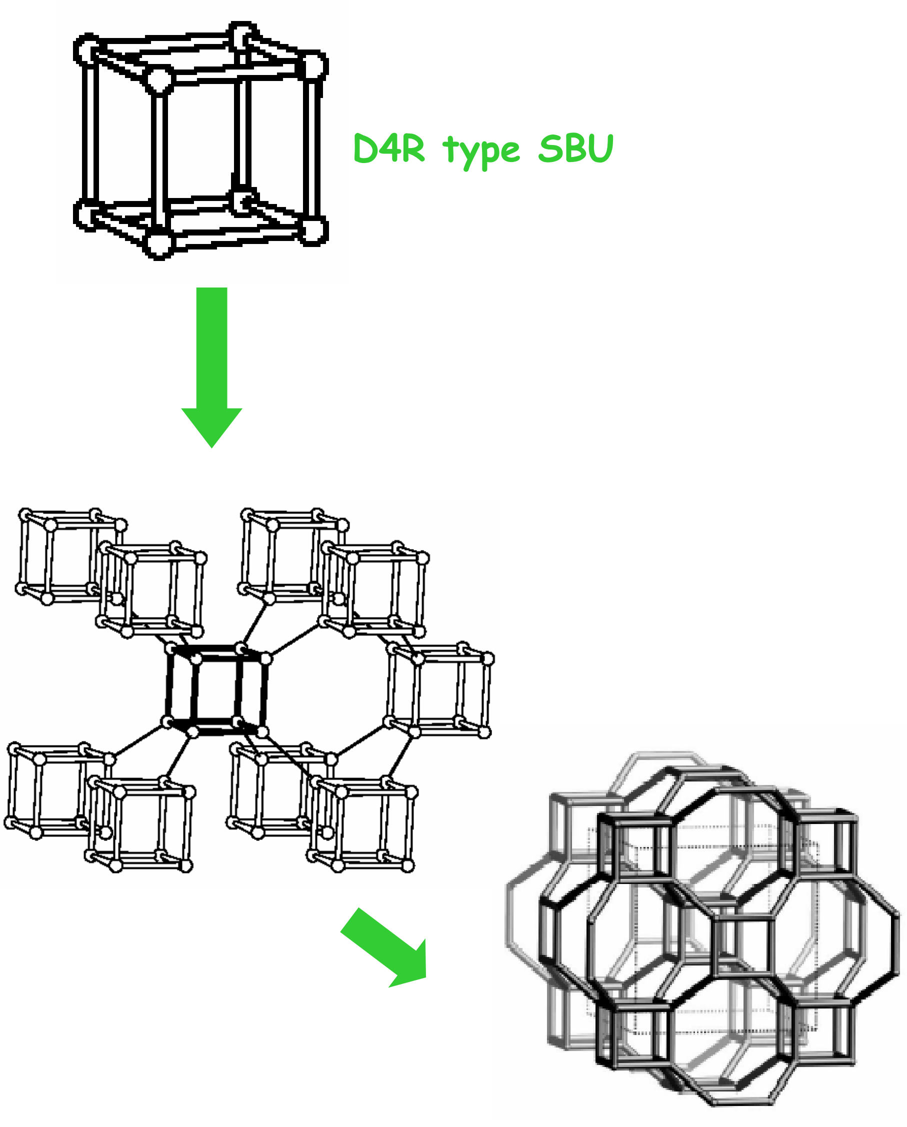
| Silicates[a] | | | Both Silicates and Phosphates | Phosphates[b] | |
|---|---|---|---|---|---|
| AFG | IFR | OFF | ABW | ACO | SAO |
| ASV | ISV | OSO | AET | AEI | SAS |
| *BEA | ITE | -PAR | AFI | AEL | SAT |
| BIK | JBW | PAU | AFX | AEN | SAV |
| BOG | KFI | -RON | ANA | AFN | SBE |
| BRE | LIO | RSN | AST | AFO | SBS |
| CAS | LOV | RTE | BPH | AFR | SBT |
| CFI | LTN | RTH | CAN | AFS | VFI |
| -CHI | MAZ | RUT | CGS | AFT | WEI |
| CON | MEI | SFE | CHA | AFY | ZON |
| DAC | MEL | SFF | DFT | AHT | |
| DDR | MEP | SGT | EDI | APC | |
| DOH | MFI | STF | ERI | APD | |
| DON | MFS | STI | FAU | ATN | |
| EAB | MON | STT | GIS | ATO | |
| EMT | MOR | TER | LAU | ATS | |
| EPI | MSO | TON | LEV | ATT | |
| ESV | MTF | TSC | LOS | ATV | |
| EUO | MTN | VET | LTA | AWO | |
| FER | MTT | VNI | LTL | AWW | |
| FRA | MTW | VSV | MER | CGF | |
| GME | MWW | -WEN | PHI | -CLO | |
| GON | NAT | YUG | RHO | CZP | |
| GOO | NES | | SOD | DFO | |
| HEU | NON | | THO | OSI | |



EDI

# Secondary Building Units (SBU)



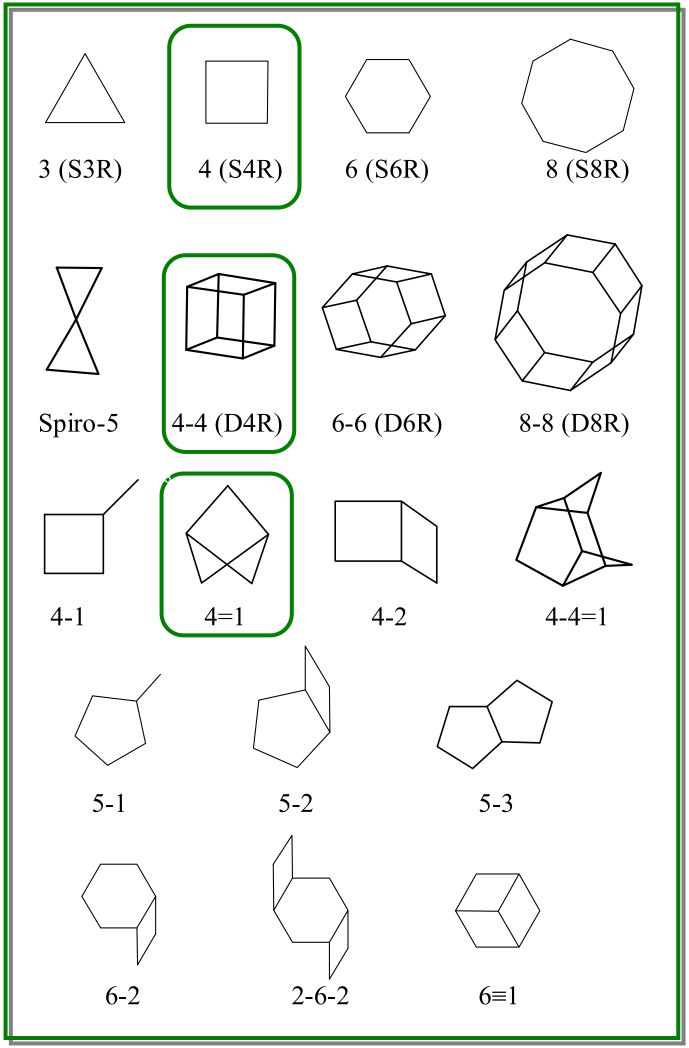


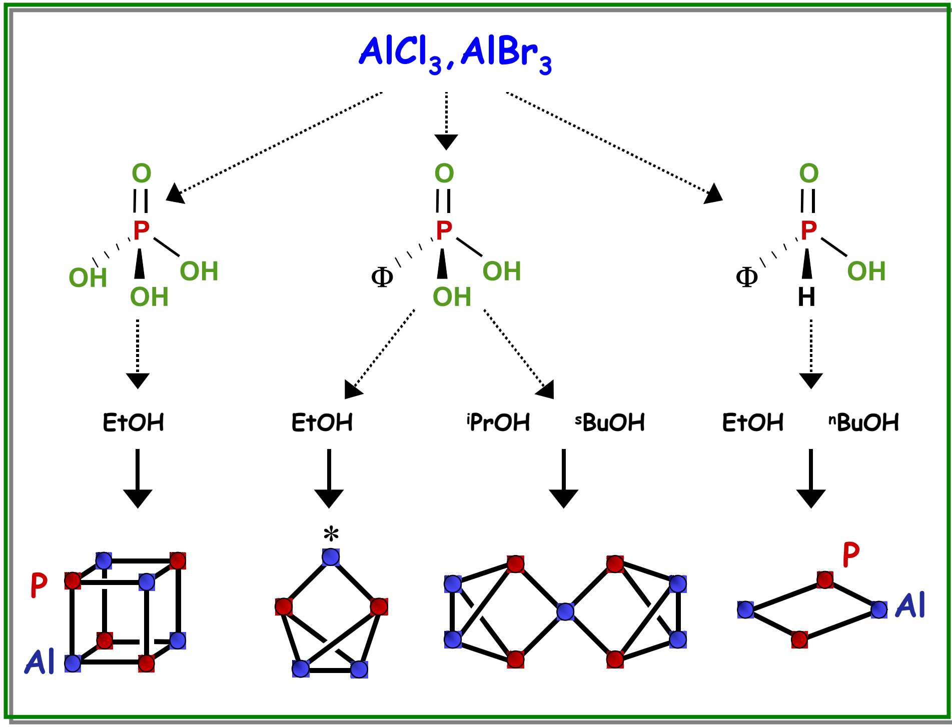
D4R type SBU

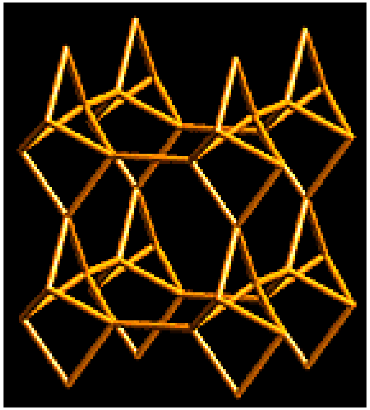
ACO type

# Mimicking SBU: Al-O-P clusters

T. Azaïs

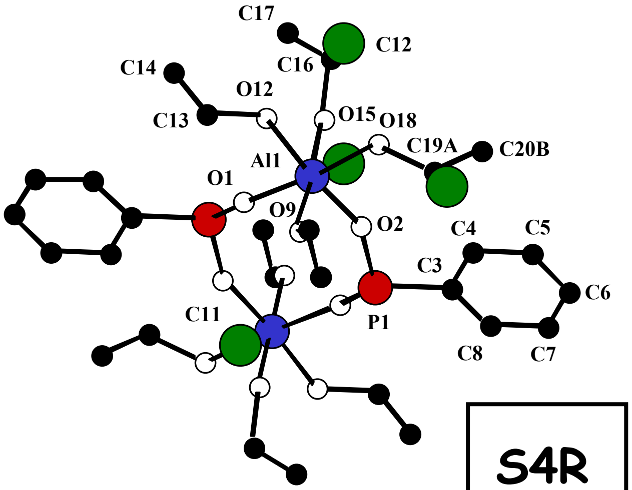






EDI type

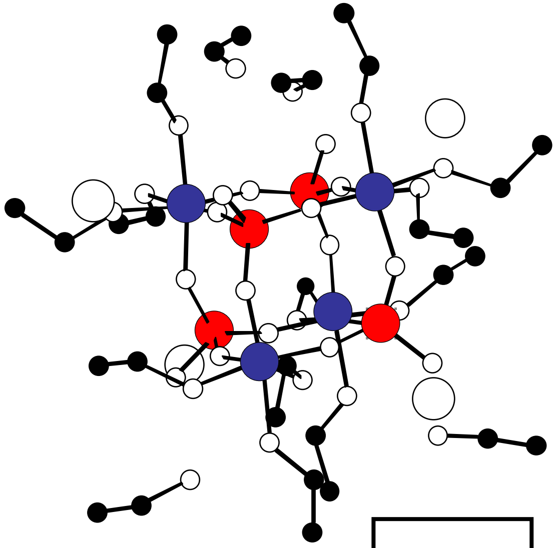
# Cluster structures



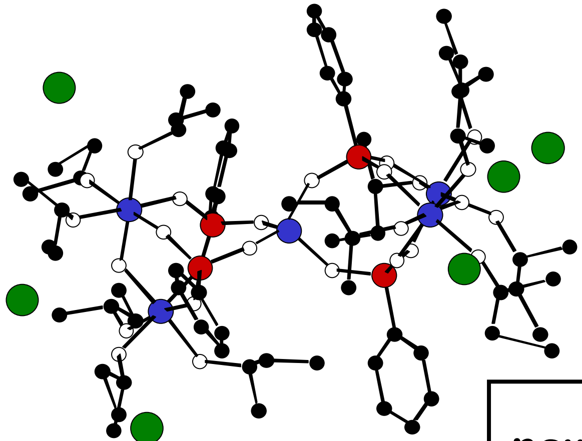
S4R

🔵 Al

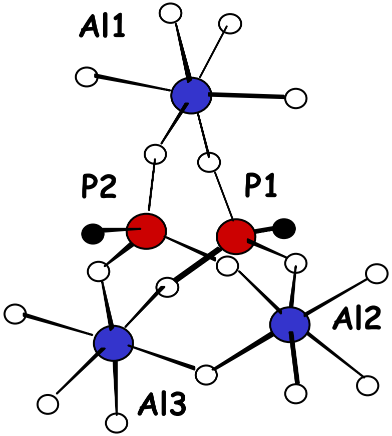
🔴 P



D4R

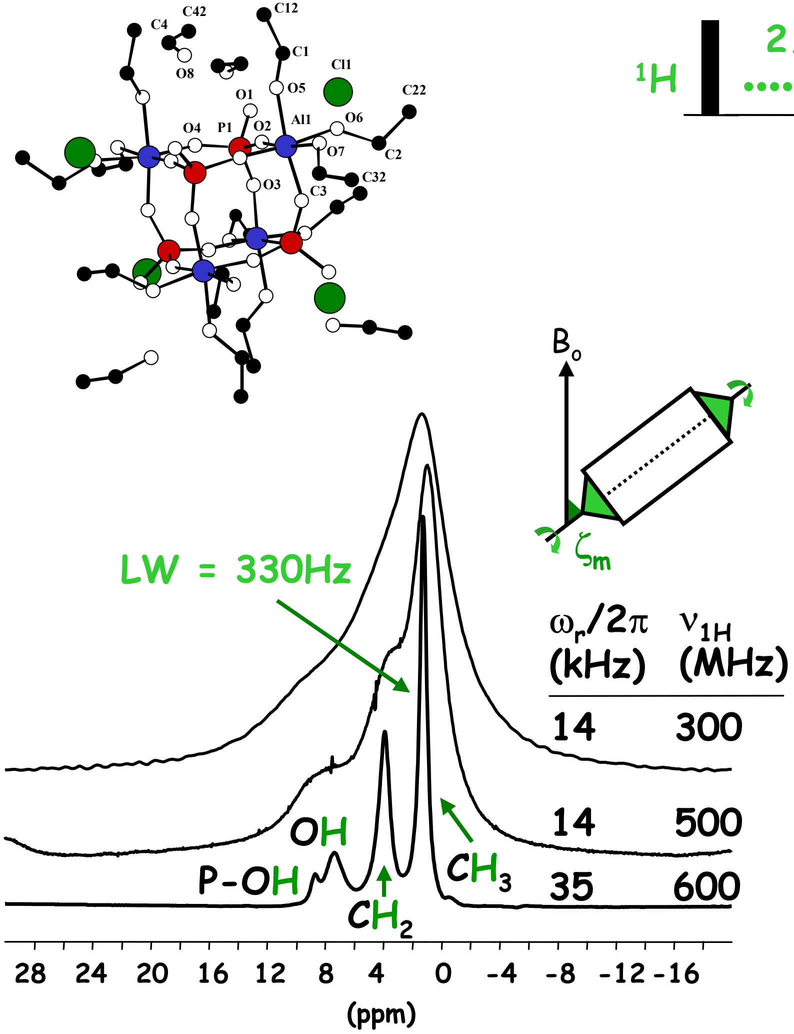


new!



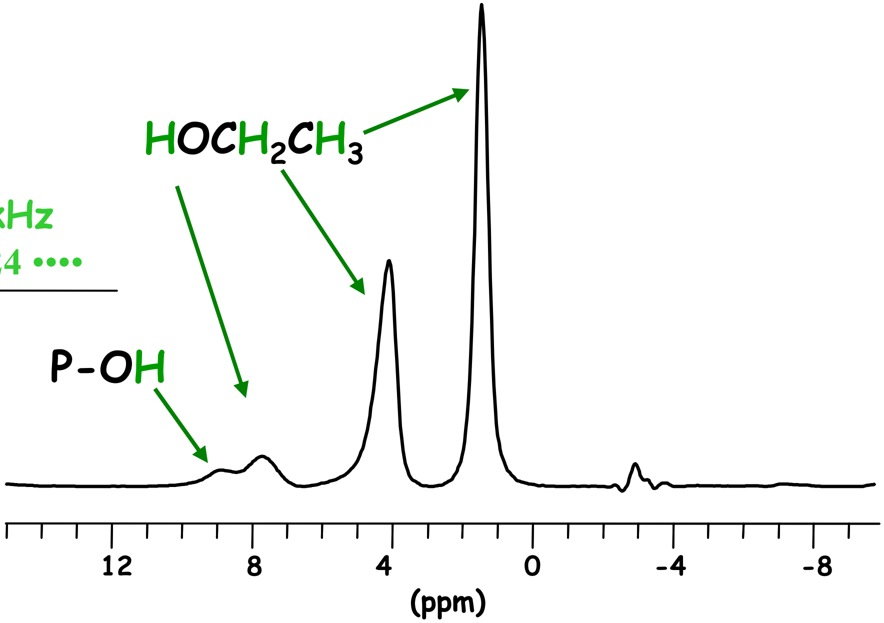
4=1

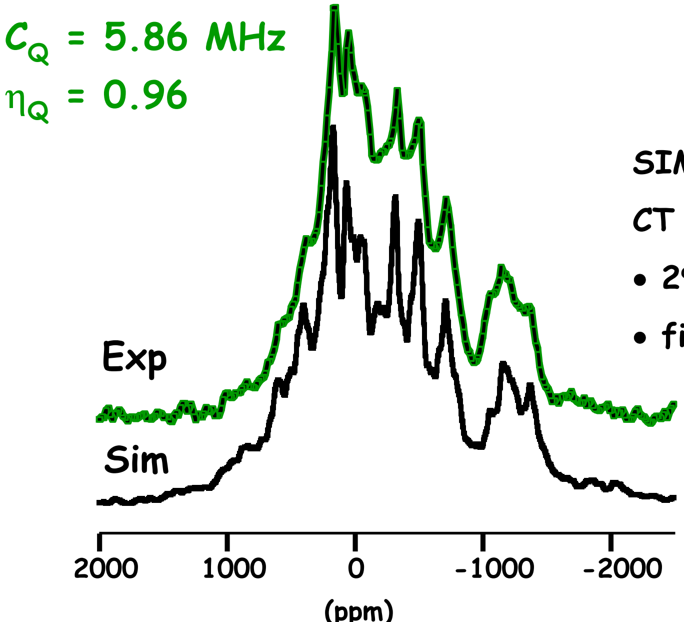
# Exotic solid state NMR: $^{1}H$ and $^{35}Cl$



| $\omega_r/2\pi$ (kHz) | $\nu_{1H}$ (MHz) |
|---|---|
| 14 | 300 |
| 14 | 500 |
| 35 | 600 |

$^{1}H$ 2.14 kHz ····BR-24 ····





SIMPSON:

CT and sat.

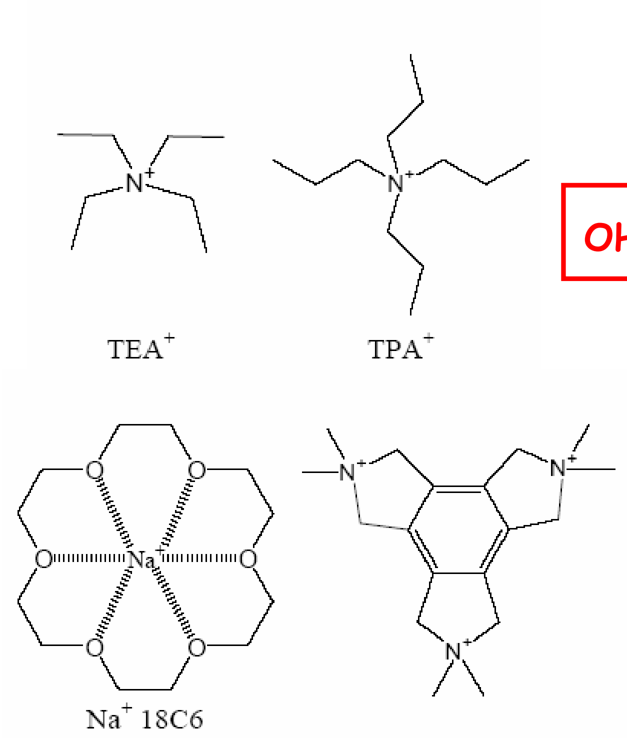
- 2d order
- finite pulses

# Synthesis of zeolites: general approach

solution of silicates and aluminates
(high pH)

co-condensation: gel

templating agent


TEA$^+$

TPA$^+$

Na$^+$ 18C6

OH$^-$ or F$^-$

hydrothermal condition
( T, P )

characterization (XRD..)

# The zeolite web site: www.iza-structure.org

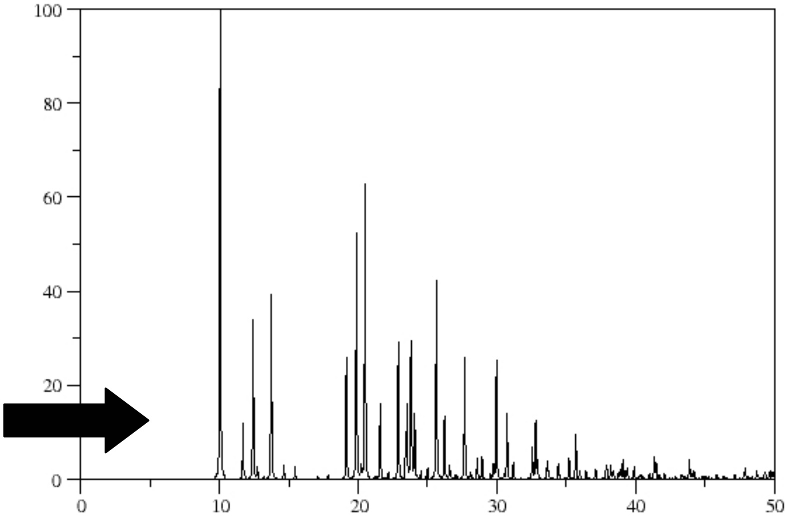
**Welcome to the Database of Zeolite Structures**

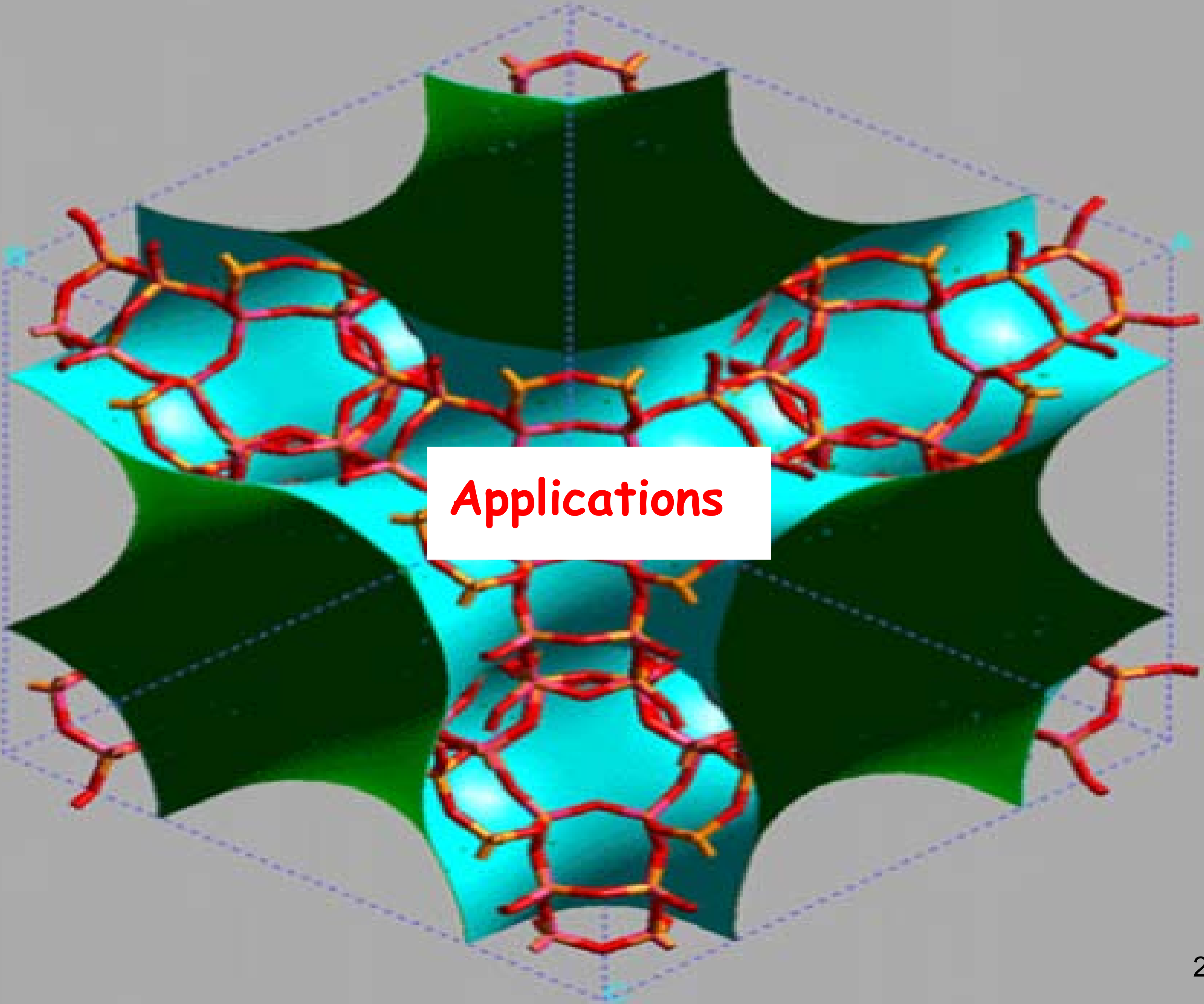
- **Atlas of Zeolite Framework Types**
- **Catalog of Disordered Zeolite Structures**
- **PDF Files of IZA Publications**
- **Collection of Simulated XRD**
- **Powder Patterns of Zeolites**

…

Tetramethylammonium ZAPO-M1

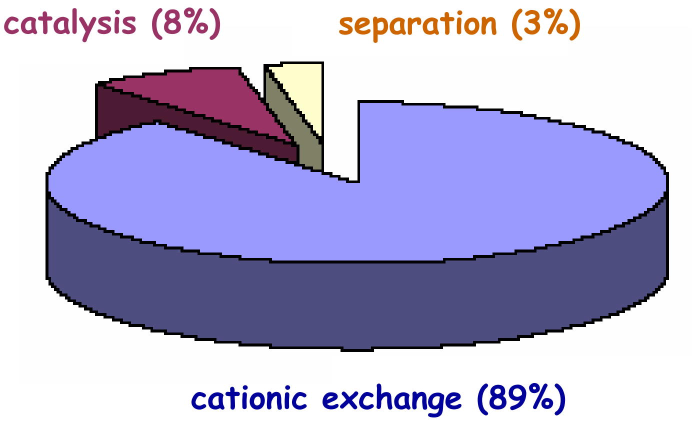
|N8C42.656| [Al25Zn7P32O128]



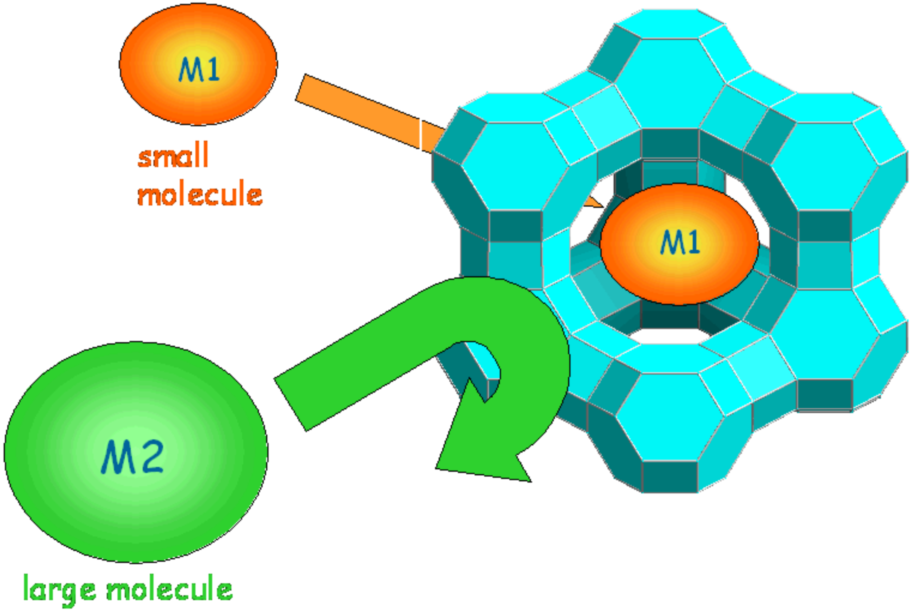


# Applications

# Molecular sieves

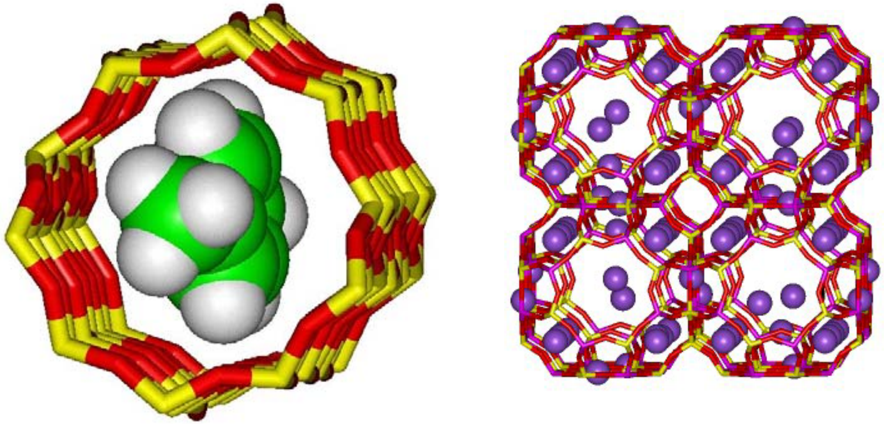


## the concept...

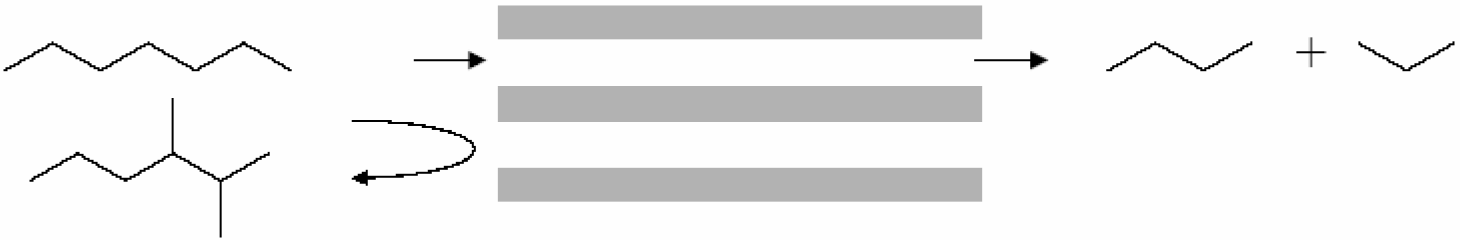


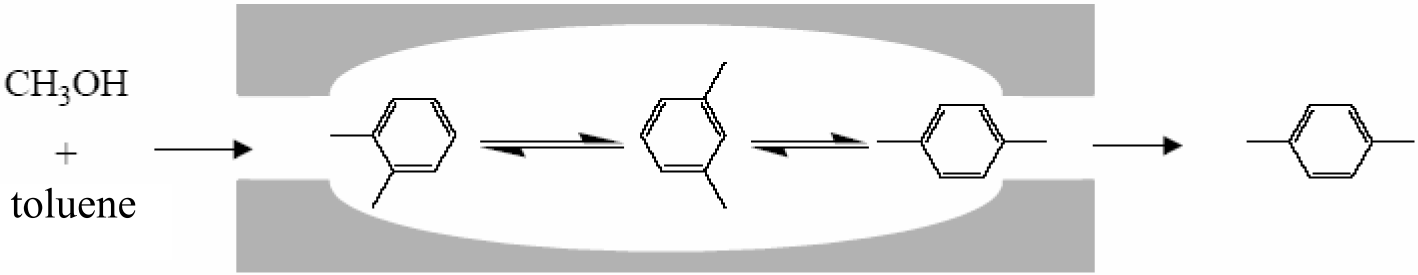
*keywords*:

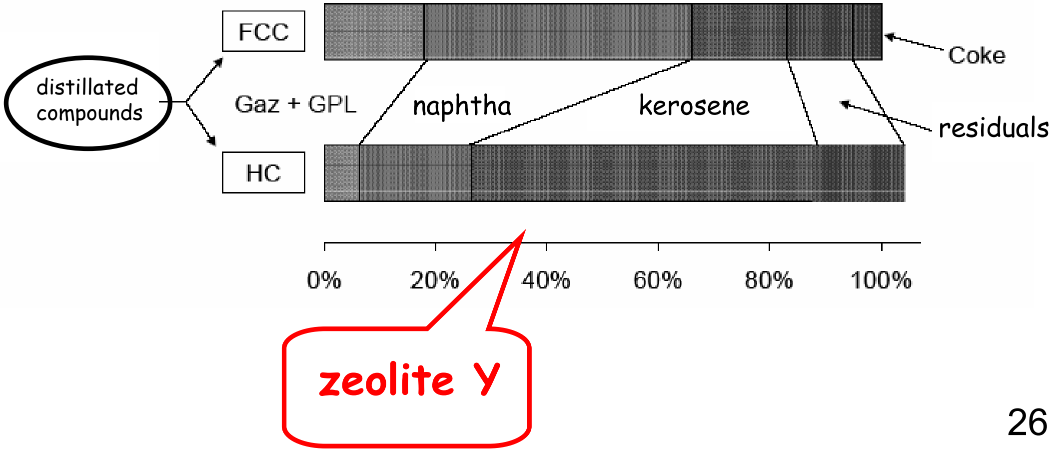
- adsorption
- ion or molecule exchange
- substances removal
- catalysis



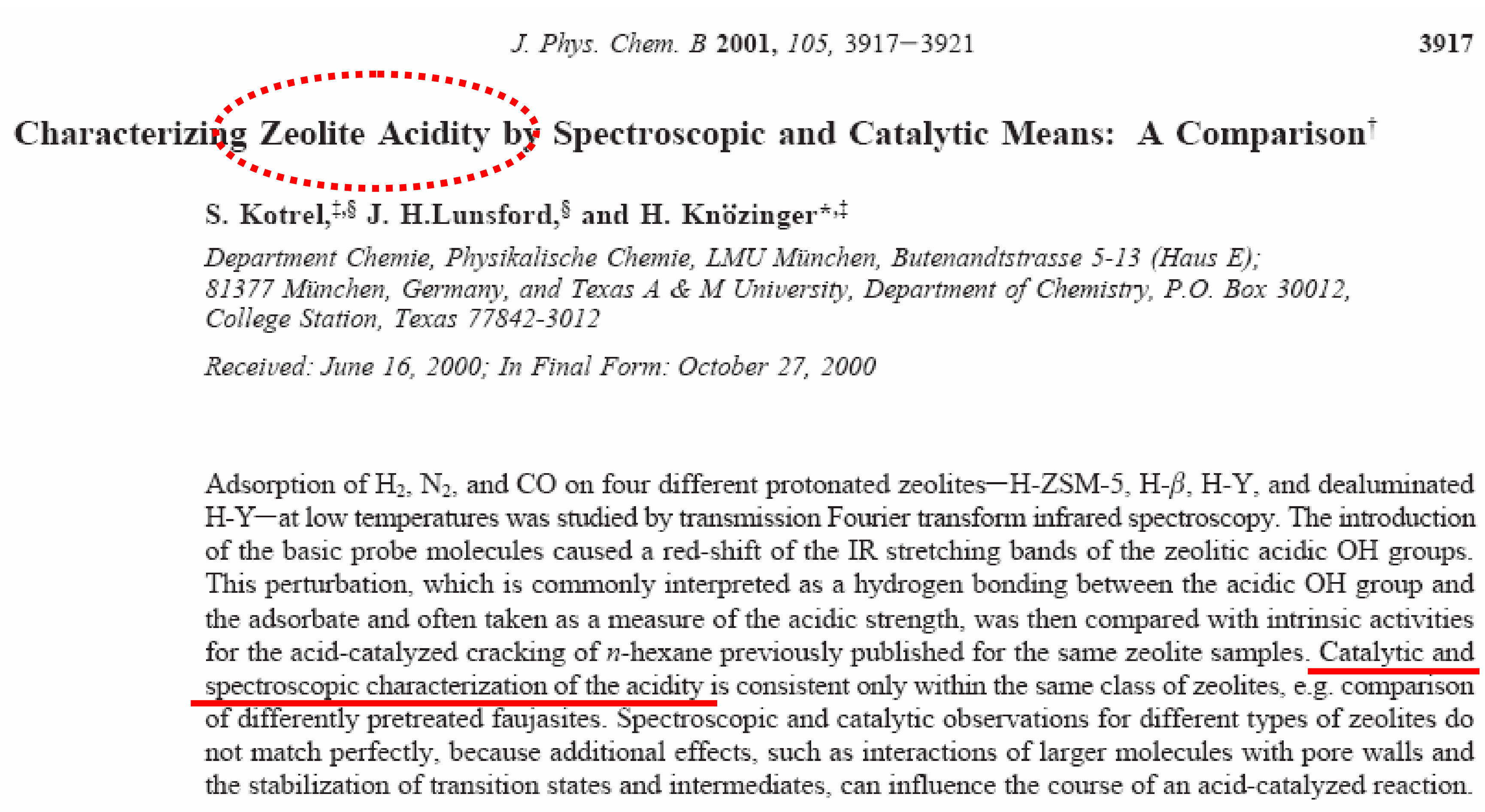
# Catalysis




$CH_3OH$
+
toluene


distillated compounds
FCC
HC
Gaz + GPL
naphtha
kerosene
Coke
residuals
0%
20%
40%
60%
80%
100%
zeolite Y

# A key concept: zeolite acidity



*J. Phys. Chem. B* **2001,** *105,* 3917−3921 **3917**

## Characterizing Zeolite Acidity by Spectroscopic and Catalytic Means: A Comparison†

**S. Kotrel,‡,§ J. H.Lunsford,§ and H. Knözinger*,‡**

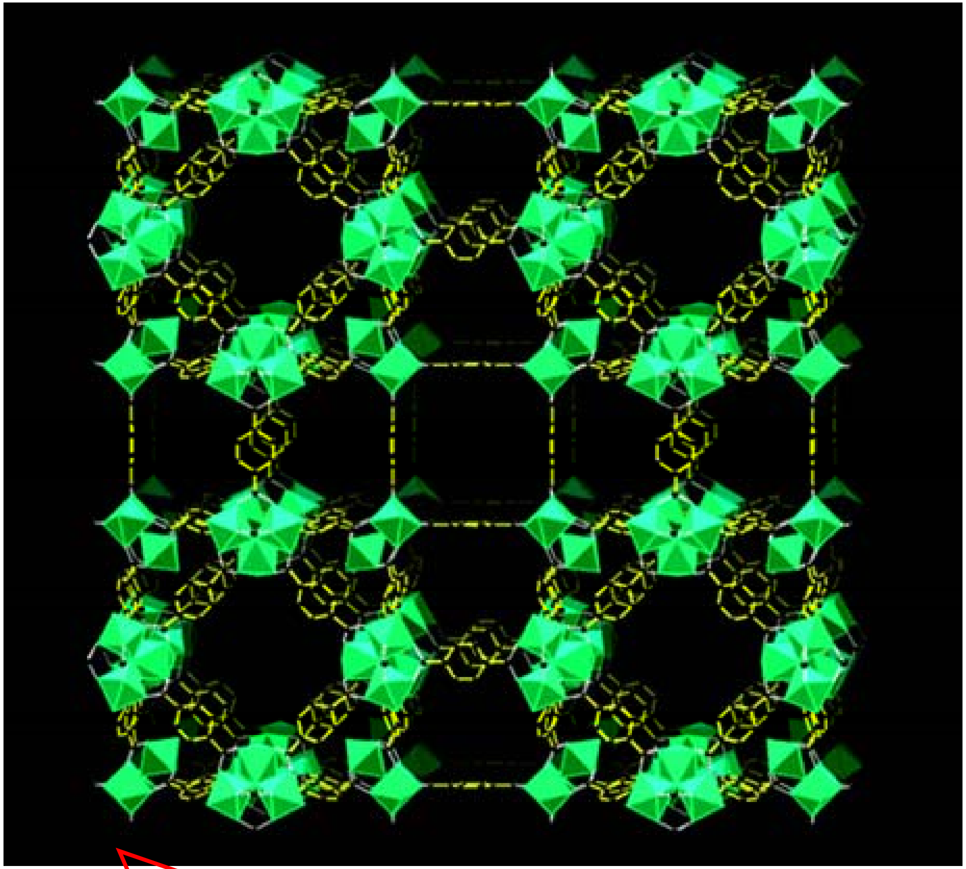
*Department Chemie, Physikalische Chemie, LMU München, Butenandtstrasse 5-13 (Haus E);*
*81377 München, Germany, and Texas A & M University, Department of Chemistry, P.O. Box 30012,*
*College Station, Texas 77842-3012*

*Received: June 16, 2000; In Final Form: October 27, 2000*

Adsorption of $H_2$, $N_2$, and CO on four different protonated zeolites—H-ZSM-5, H-$\beta$, H-Y, and dealuminated H-Y—at low temperatures was studied by transmission Fourier transform infrared spectroscopy. The introduction of the basic probe molecules caused a red-shift of the IR stretching bands of the zeolitic acidic OH groups. This perturbation, which is commonly interpreted as a hydrogen bonding between the acidic OH group and the adsorbate and often taken as a measure of the acidic strength, was then compared with intrinsic activities for the acid-catalyzed cracking of *n*-hexane previously published for the same zeolite samples. Catalytic and spectroscopic characterization of the acidity is consistent only within the same class of zeolites, e.g. comparison of differently pretreated faujasites. Spectroscopic and catalytic observations for different types of zeolites do not match perfectly, because additional effects, such as interactions of larger molecules with pore walls and the stabilization of transition states and intermediates, can influence the course of an acid-catalyzed reaction.

# Metal Organic Frameworks (MOFs)

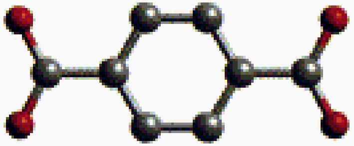
porous hybrid organic/inorganic solids



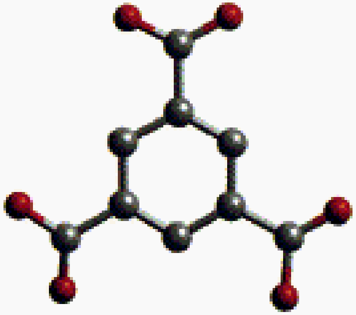
inorganic SBU's linked by organic bridges

O. M. Yaghi, G. Férey (~ 2000)

some organic ligands...

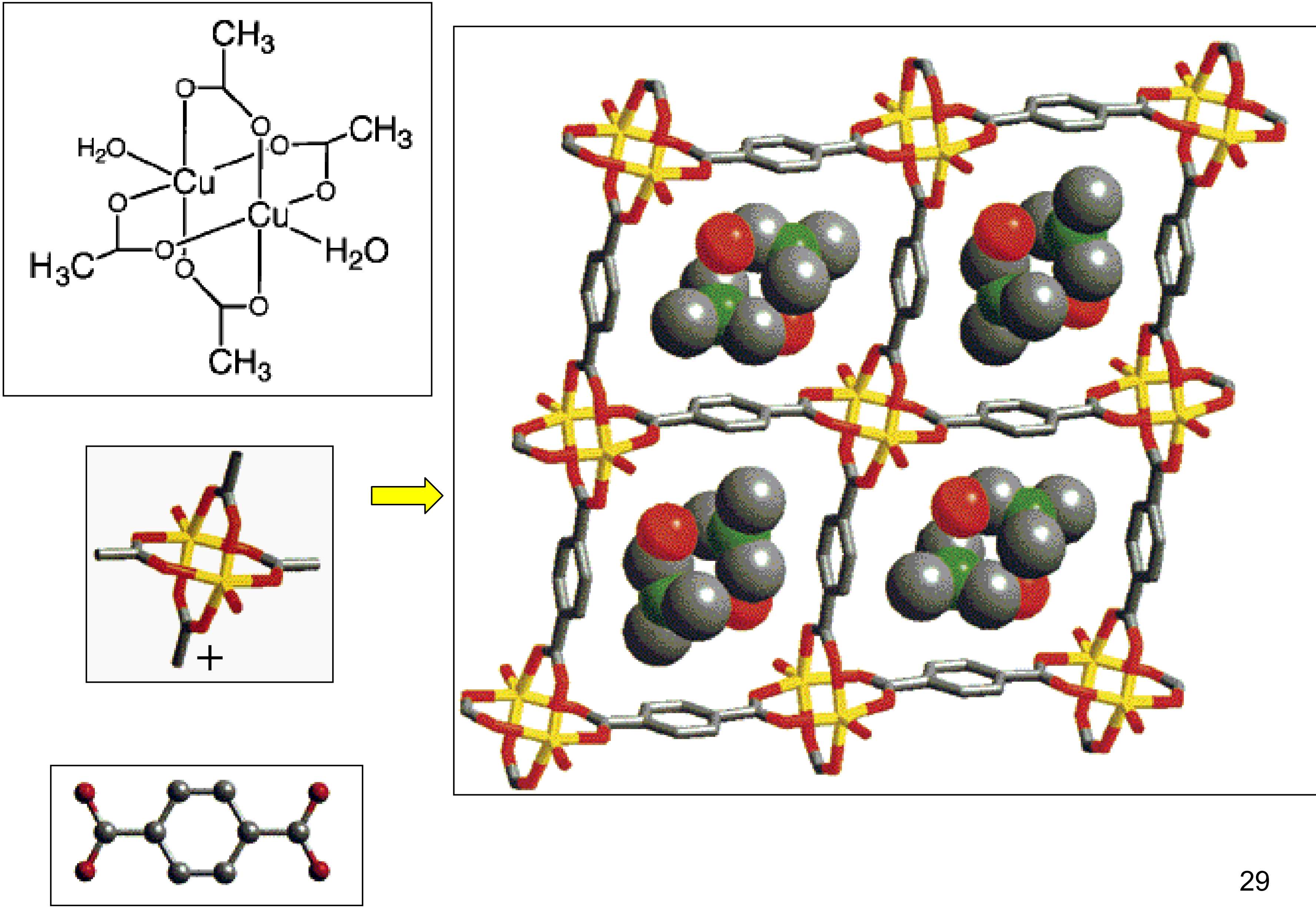


1,4-benzenedicarboxylate
(BDC)

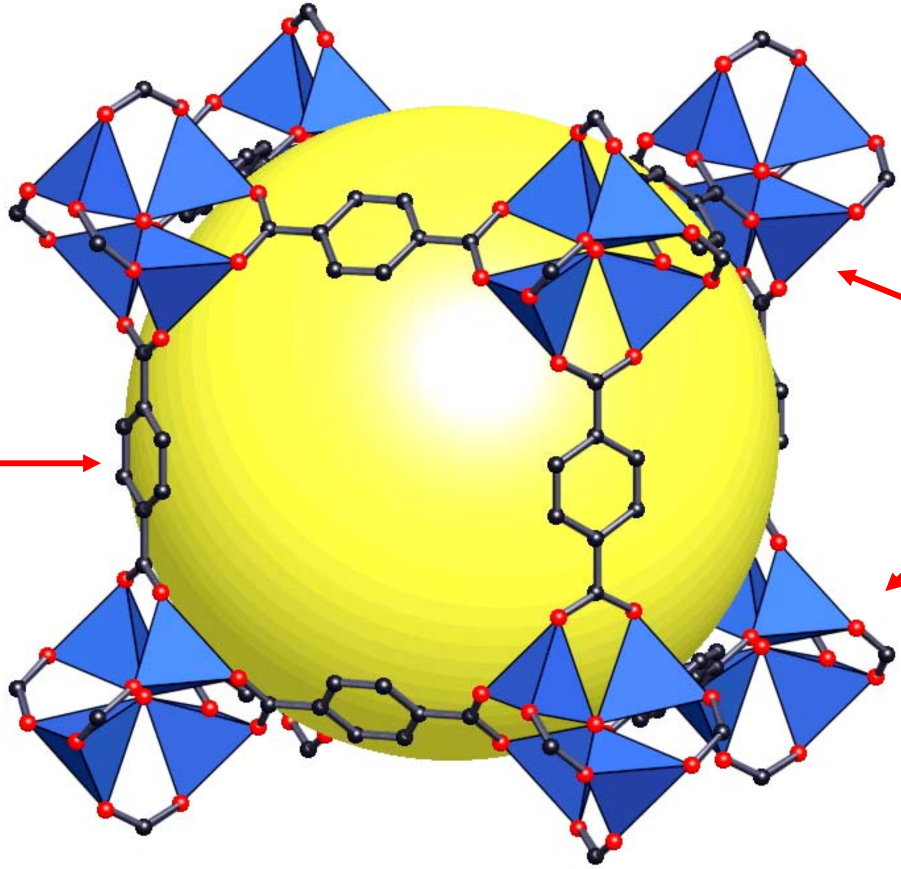


1,3,5-benzenetricarboxylate
(BTC)

# An example



# Crystal «sponges» - *MOF-5*



organic links

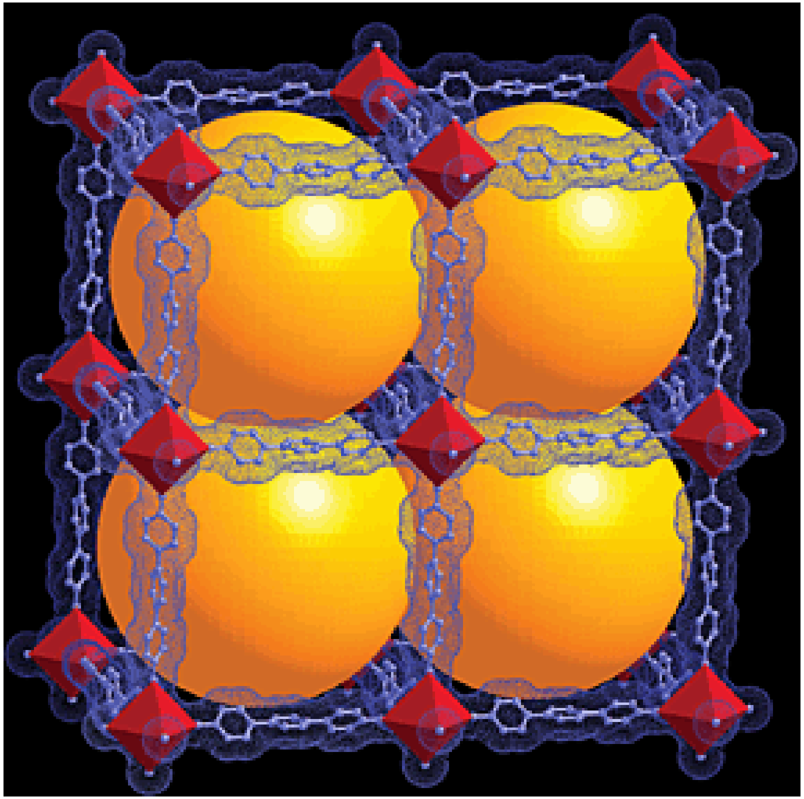
inorganic vertices ($Zn_4$)

d ~ 20 Å

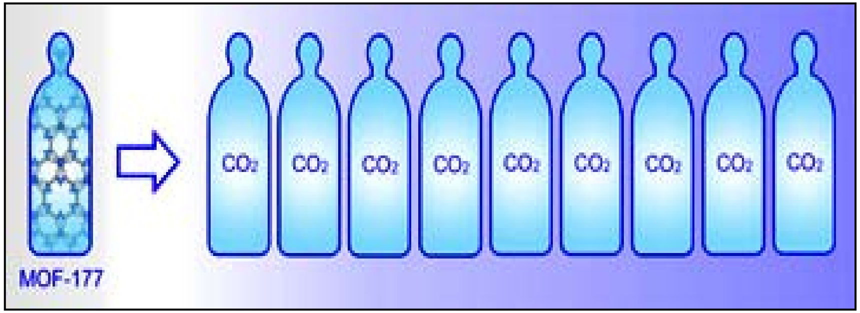
S ~ 3000 $m^2.g^{-1}$ (?)

cell > 700.000 $Å^3$

# Storage of $CH_4$, $CO_2$, $H_2$



**MOF-177**



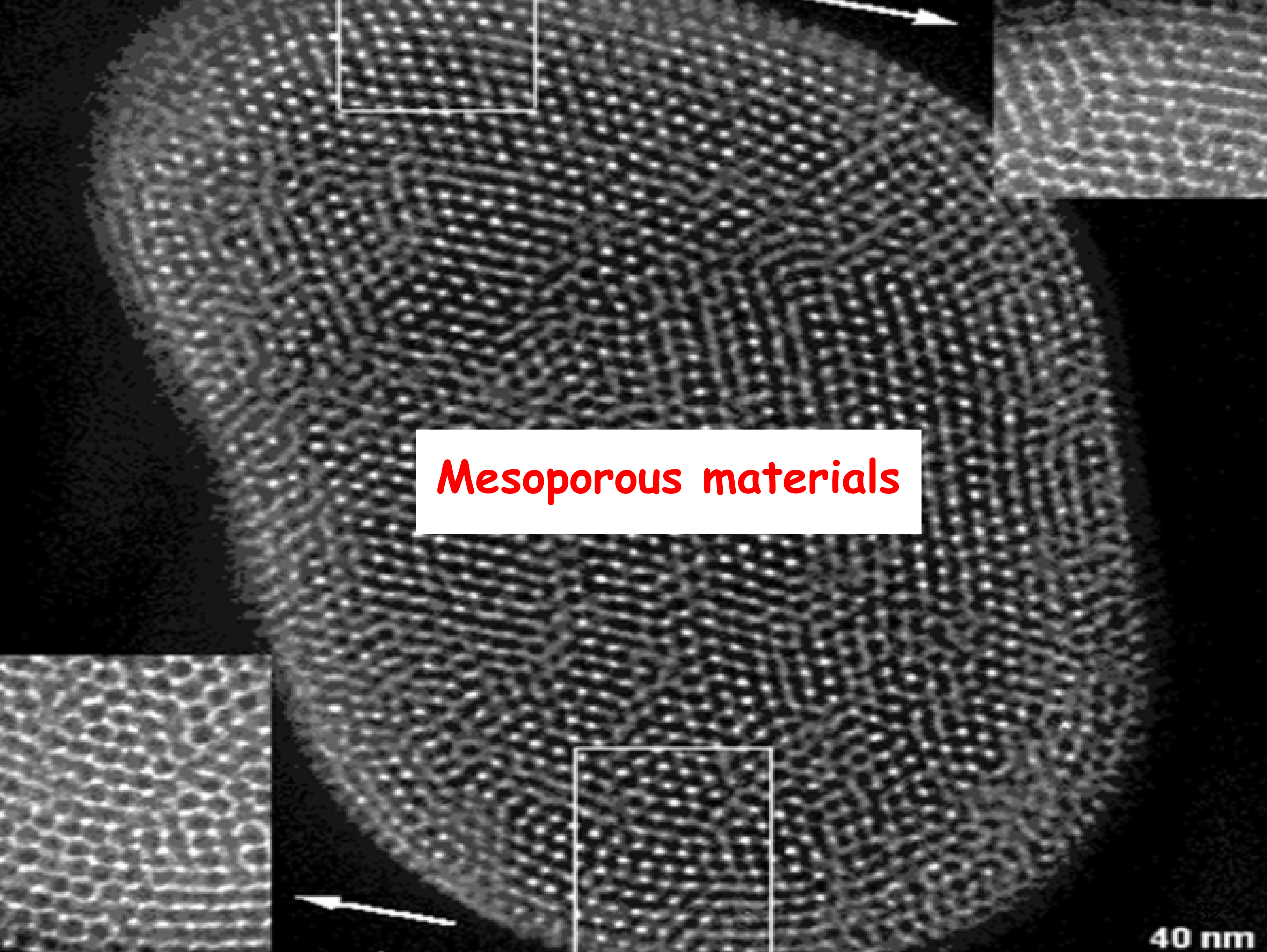
*1* container with MOF-177 ~ *9* empty containers

*other applications...*

◊ drug delivery

◊ magnetic properties

◊ rare earths and luminescence...



Mesoporous materials

# Hierarchical porosity

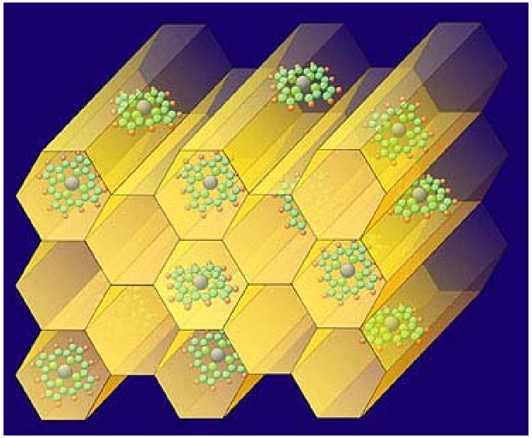
## porous materials

**nanoporous**
$\varnothing < 2$ nm

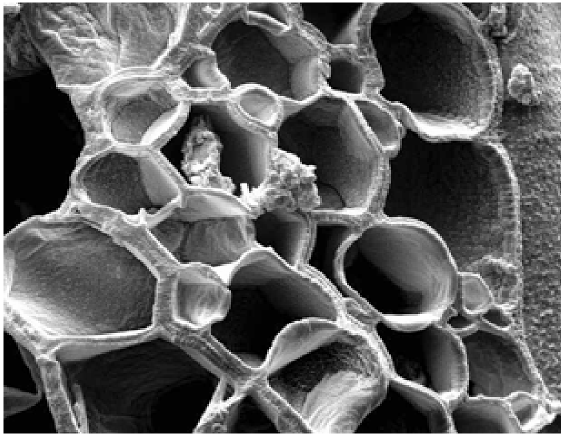
**mesoporous**
$2 < \varnothing < 50$ nm

**macroporous**
$50$ nm $< \varnothing$

zeolites

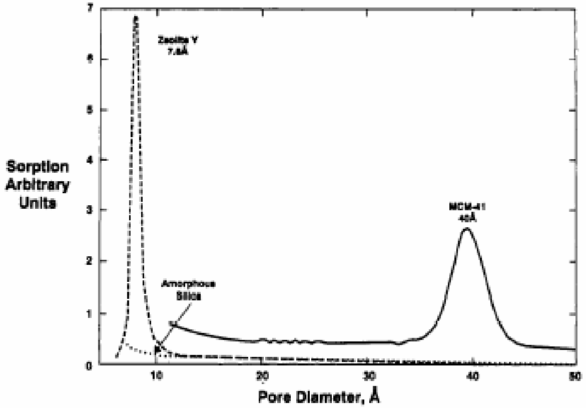


MCM



foams

# 1992: «the» breakthrough!



## A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates

**J. S. Beck,*,† J. C. Vartuli,*,† W. J. Roth,*,‡ M. E. Leonowicz,*,‡ C. T. Kresge,*,‡ K. D. Schmitt,† C. T-W. Chu,‡ D. H. Olson,† E. W. Sheppard,† S. B. McCullen,† J. B. Higgins,† and J. L. Schlenker†**

*Contribution from the Mobil Research and Development Corporation, Central Research Laboratory, Princeton, New Jersey 08543, and Paulsboro Research Laboratory, Paulsboro, New Jersey 08066.* *Received June 30, 1992*

**Abstract:** The synthesis, characterization, and proposed mechanism of formation of a new family of silicate/aluminosilicate mesoporous molecular sieves designated as M41S is described. MCM-41, one member of this family, exhibits a hexagonal arrangement of uniform mesopores whose dimensions may be engineered in the range of ~15 Å to greater than 100 Å. Other members of this family, including a material exhibiting cubic symmetry, have been synthesized. The larger pore M41S materials typically have surface areas above 700 m$^2$/g and hydrocarbon sorption capacities of 0.7 cc/g and greater. A templating mechanism (liquid crystal templating—LCT) in which surfactant liquid crystal structures serve as organic templates is proposed for the formation of these materials. In support of this templating mechanism, it was demonstrated that the structure and pore dimensions of MCM-41 materials are intimately linked to the properties of the surfactant, including surfactant chain length and solution chemistry. The presence of variable pore size MCM-41, cubic material, and other phases indicates that M41S is an extensive family of materials.

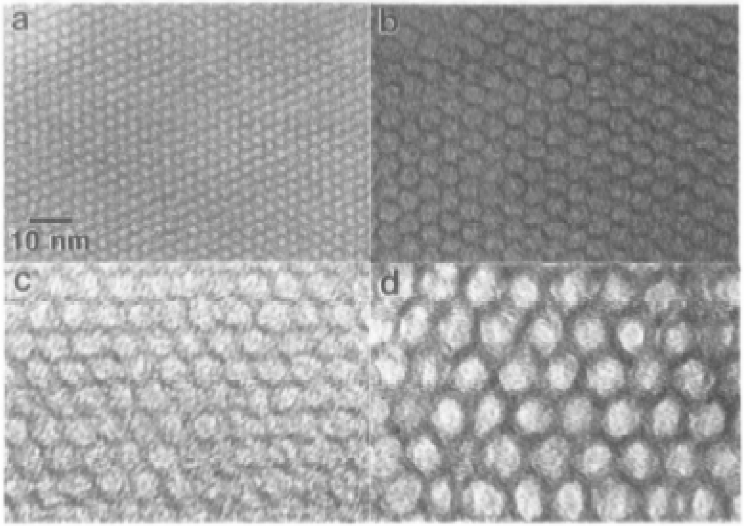


Figure 2. Transmission electron micrographs of several MCM-41 materials having Ar pore sizes of (a) 20, (b) 40, (c) 63, and (d) 100 Å.

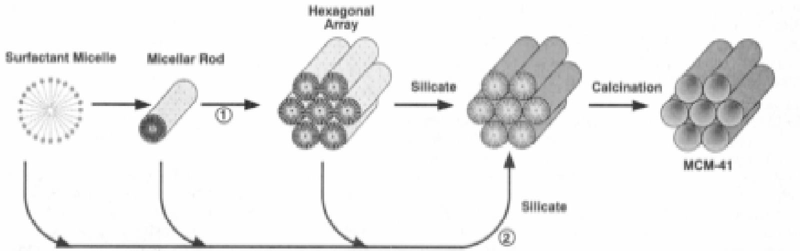
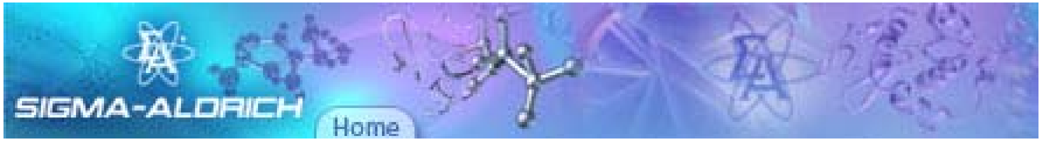
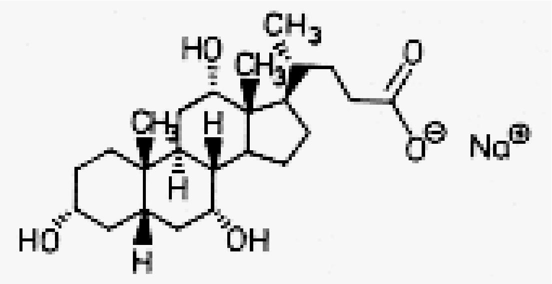


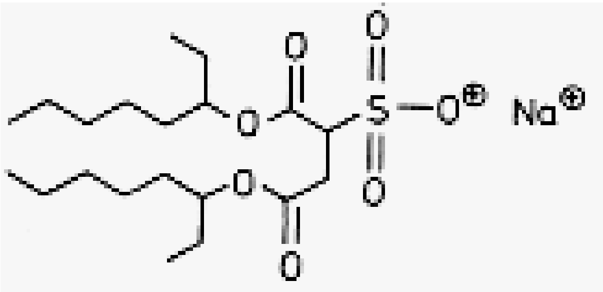
Figure 14. Possible mechanistic pathways for the formation of MCM-41: (1) liquid crystal phase initiated and (2) silicate anion initiated.

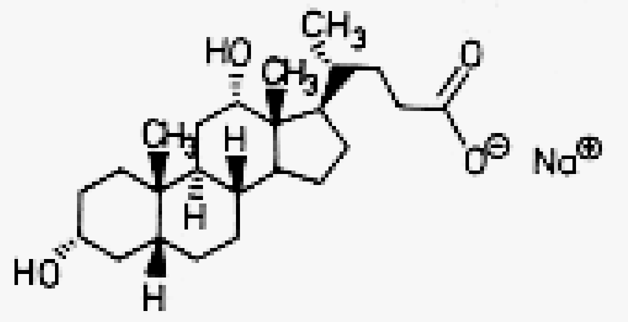
citations: 5367!

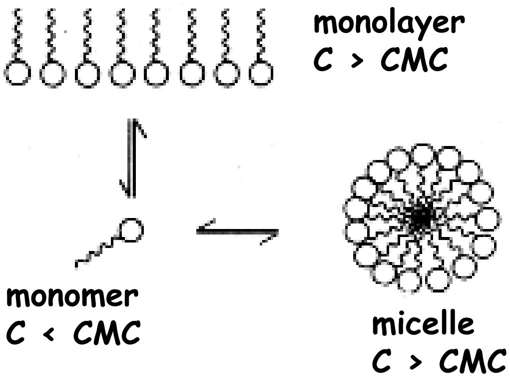
# The chemical nature of surfactant





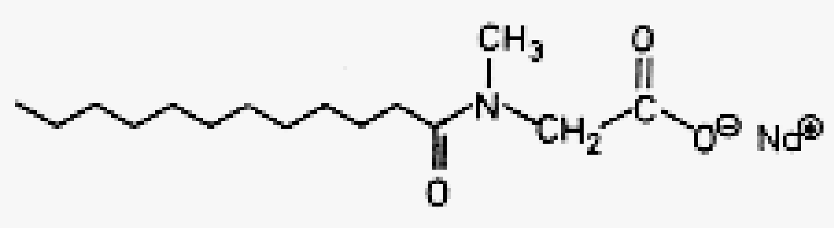






○ denotes hydrophilic portion

〰 denotes hydrophobic portion



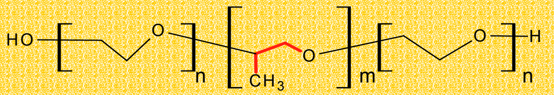
CTAB

# Block copolymers

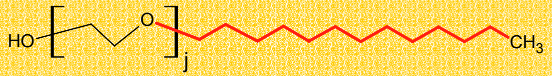
## Pluronic® P123 Block Copolymer Surfactant

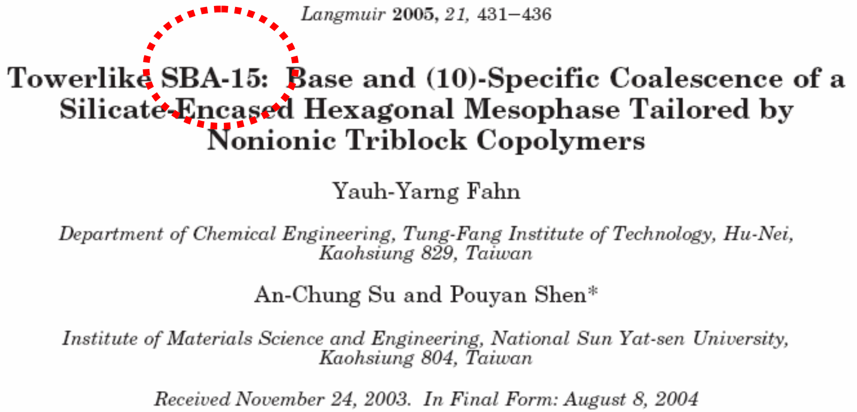
**BASF**

**Pluronics :**



**Brij :**





*Langmuir* **2005,** *21,* 431−436

### Towerlike SBA-15: Base and (10)-Specific Coalescence of a Silicate-Encased Hexagonal Mesophase Tailored by Nonionic Triblock Copolymers

Yauh-Yarng Fahn

*Department of Chemical Engineering, Tung-Fang Institute of Technology, Hu-Nei, Kaohsiung 829, Taiwan*

An-Chung Su and Pouyan Shen*

*Institute of Materials Science and Engineering, National Sun Yat-sen University, Kaohsiung 804, Taiwan*

*Received November 24, 2003. In Final Form: August 8, 2004*

*Towerlike SBA-15*

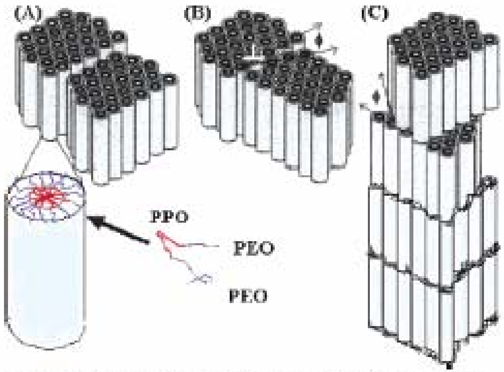


Figure 8. Proposed model for the hydrothermal mixing of $EO_{20}$-$PO_{70}EO_{20}$ and TEOS under optimized HCl dosage: (A) original hexagonal column particulates with silicatropic rodlike micelles of $EO_{20}PO_{70}EO_{20}$ inset; (B) {10}-specific yet imperfect impingement of the column to form edge dislocations at the interface; (C) imperfect base attachment to form faulting with tubules offset and dislocations decorated at the suture zone.

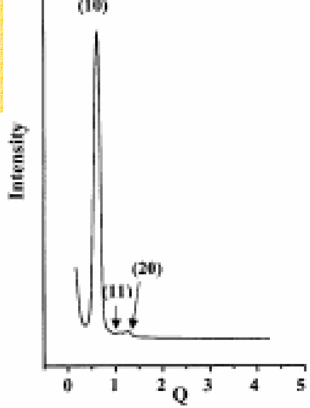


Figure 1. Small-angle X-ray scattering trace of the SBA-15 sample prepared by reacting $EO_{20}PO_{70}EO_{20}$ and TEOS under an optimized 2 M HCl dosage (pH − 0.3) at 35 °C for 24 h followed by overnight aging at 80 °C and then template removal using ethanol. The (10), (11), and (20) peaks of 2-D hexagonal structure ($a = 11.73$ nm, with corresponding $d$ spacing values of 10.16, 5.86, and 5.08 nm, respectively) were indexed according to a 2-D plane group scheme. The abscissa $Q = 2\pi/d$ is in inverted nanometers.

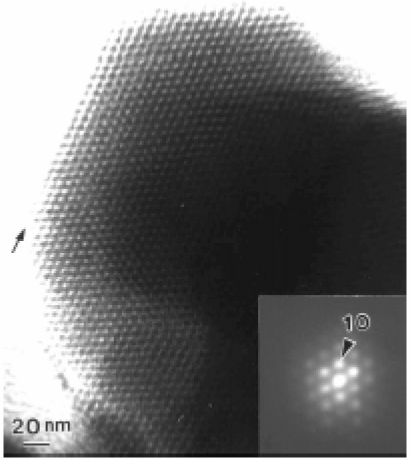
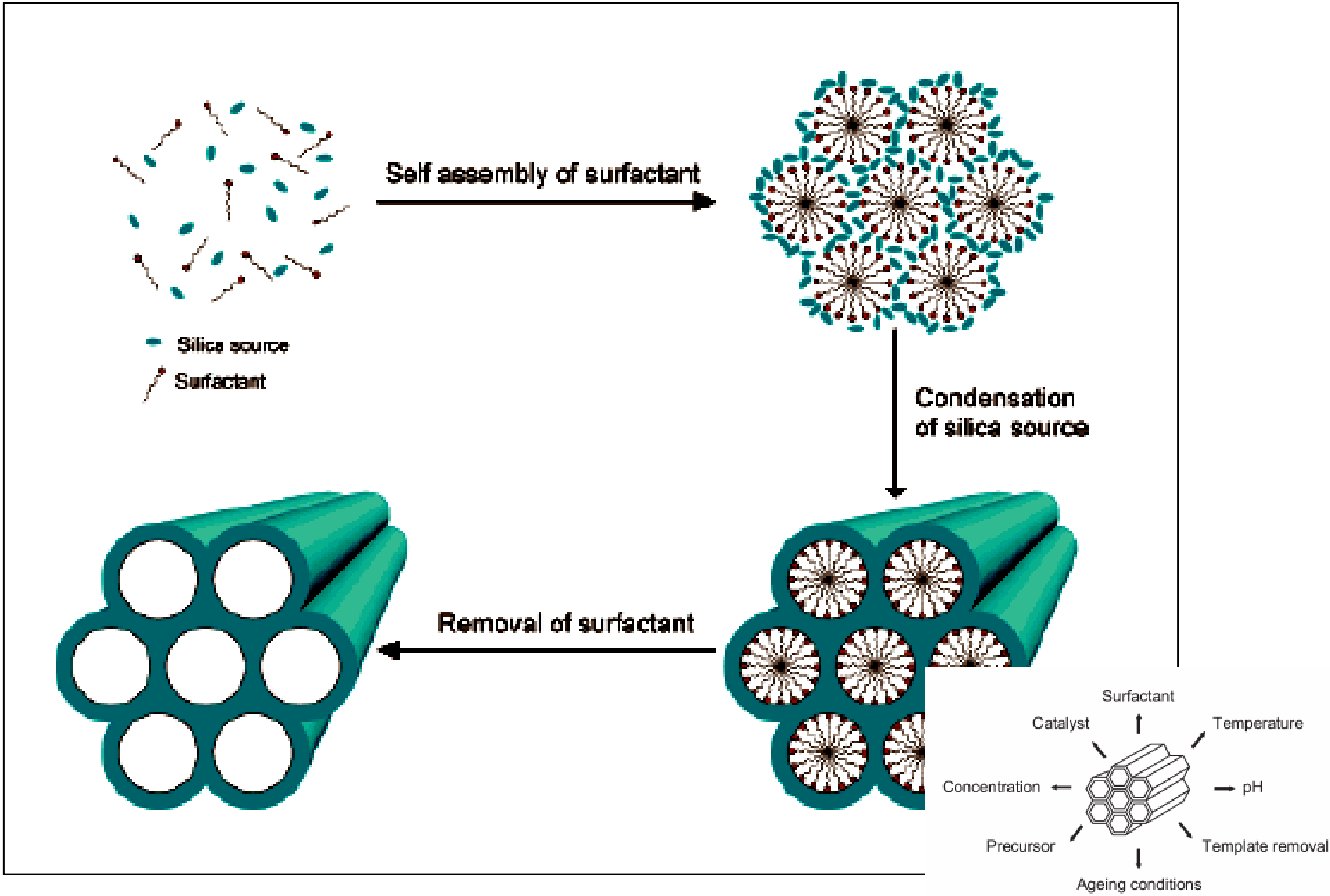
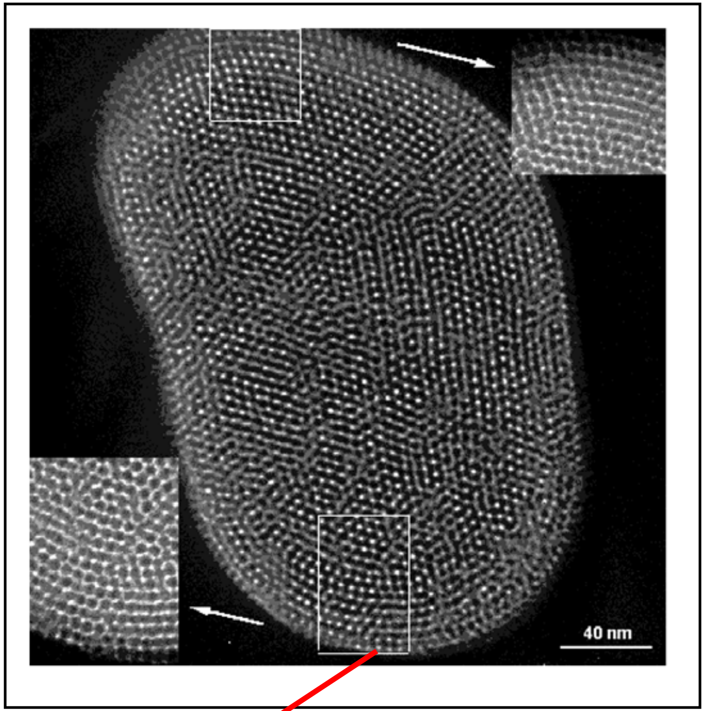


Figure 3. TEM photograph with an inset electron diffraction pattern of platelike SBA-15 hexagons (top view) showing a defect-free single domain with a well-developed {10} surface more or less with steps and a curved micelle wall (arrow). Note the hexagon has a rather flat base for uniform diffraction contrast.

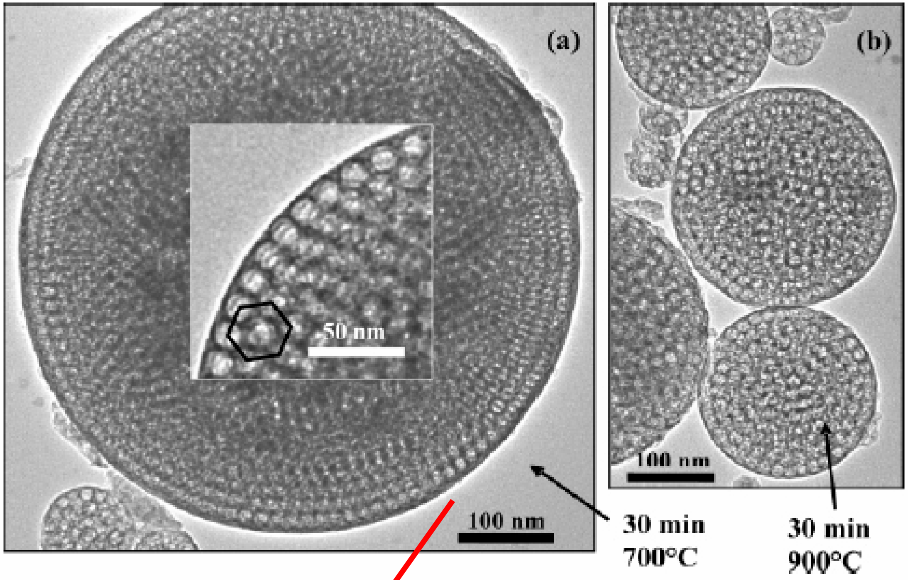
# Mesoporous materials



# Mesoporous silica and other oxides

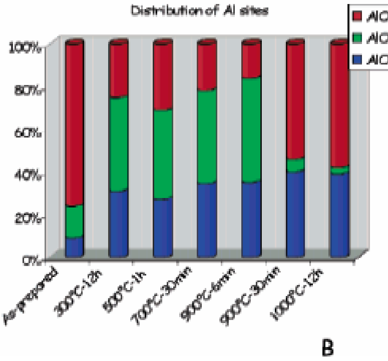


$SiO_2$



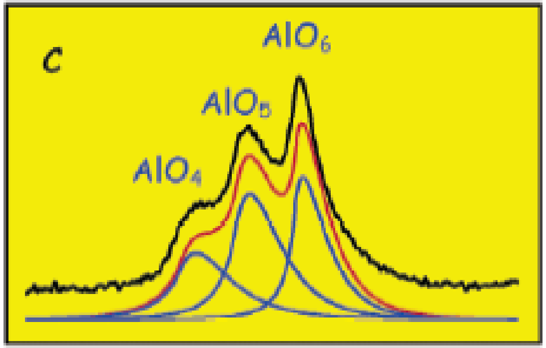
$Al_2O_3$

Boissière, Chem. Mater., 2006



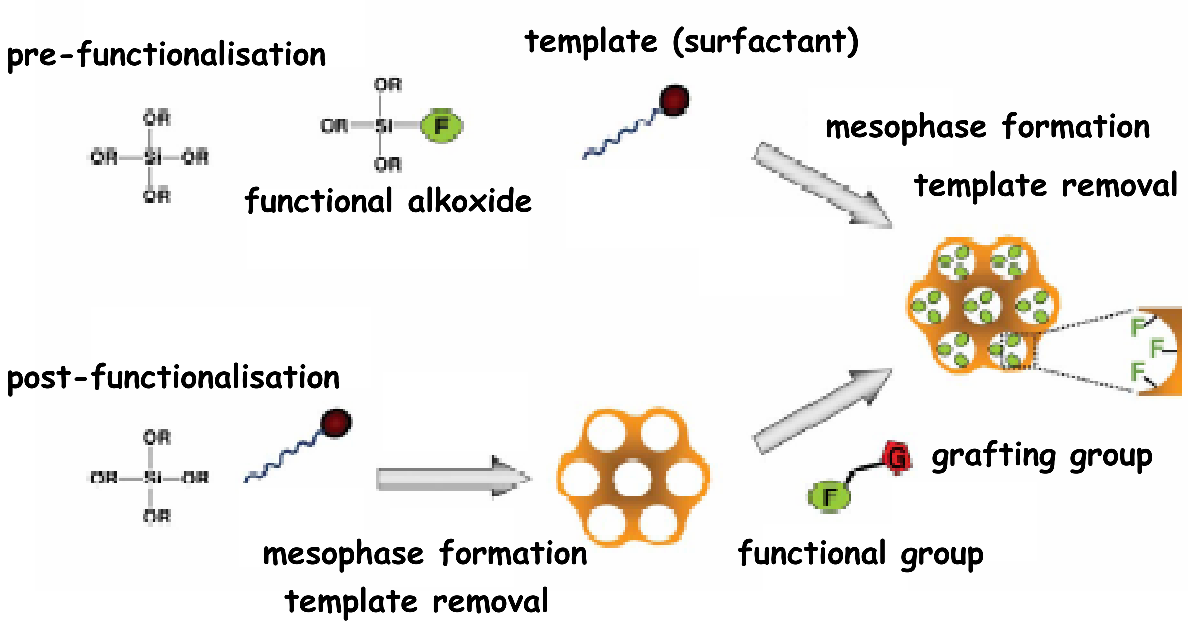
hydrolysis of TEOS

- ordered network of pores
- pores from 2 to 50 nm

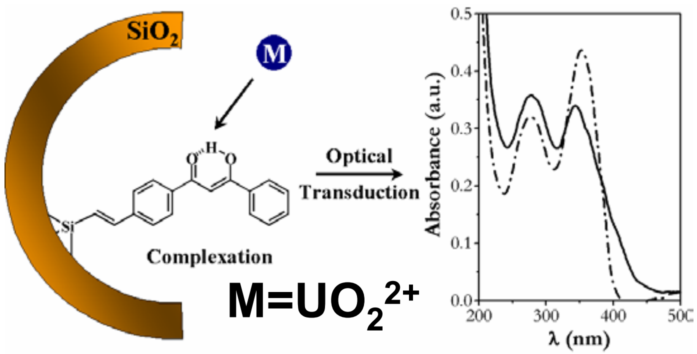


# Applications

## towards a new chemistry...



L. Nicole, J. Mater. Chem., 2005



sensors with optical detection

- ◇ organic functionalized silicas
- ◇ thin films
- ◇ surface grafting
- ◇ polymer hybrids
- ◇ nanocasting
- ◇ bioencapsulation
- ◇ adsorption applications
- ◇ sensors, photoresponse
- ◇ ...

# Drug delivery

## Solid-State NMR Study of Ibuprofen Confined in MCM-41 Material

Thierry Azaïs,[*,†] Corine Tourné-Péteilh,[‡] Fabien Aussenac,[§] Niki Baccile,[†] Cristina Coelho,[†]
Jean-Marie Devoisselle,[*,‡] and Florence Babonneau[†]

*Université Pierre et Marie Curie—Paris 6, UMR 7574, Laboratoire Chimie de la Matière Condensée de Paris, Paris F-75005, France, Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, UMR 5618/ENSCM/Université Montpellier 1, 8 rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France, and Bruker Biospin, 34 rue de l'industrie, 67166 Wissembourg, France*

*Received July 5, 2006. Revised Manuscript Received October 20, 2006*

Ibuprofen (an anti-inflammatory drug that is a crystalline solid at ambient temperature) has been encapsulated in MCM-41 silica matrices with different pore diameters (35 and 116 Å). Its behavior has been investigated by magic angle spinning (MAS) $^1H$, $^{13}C$, and $^{29}Si$ solid-state NMR spectroscopy at ambient and low temperature. This study reveals an original physical state of the drug in such materials. At ambient temperature, ibuprofen is not in a solid state (crystalline or amorphous) and is extremely mobile inside the pores, with higher mobility in the largest pores (116 Å). The interaction between ibuprofen and the silica surface is weak, which favors fast drug release from this material in a simulated intestinal or gastric fluid. The quasi-liquid behavior of ibuprofen allows the use of NMR pulse sequences issued from solution-state NMR, such as the INEPT sequence, to characterize these solid-state samples. The solid-state MAS NMR study shows that the proton of the carboxylic acid group of ibuprofen is in a chemical exchange at ambient temperature. Furthermore, at low temperature (down to 223 K), NMR spectroscopy results show that ibuprofen is able to crystallize inside the largest pores (116 Å), whereas a glassy state is obtained for the smallest ones (35 Å).