Zeolites and porous materials: synthesis and applications

UE LS 205
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Silicates and zeolites
Silicates

wt. % in earth crust:

O: 47 %  
Si: 28 %  
Al: 5 %  
Fe: 5 %  
Ca: 3.5 %  
Na: 2.8 %  
K: 2.6 %  
Mg: 2 %  
.....

silicates and aluminosilicates

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

NESOSILICATES  
SOROSILICATES  
CYCLOSILICATES  
INOSILICATES  
PHYLLOSILICATES  
TECTOSILICATES

the basic structural unit: \( \text{SiO}_4^{4-} \) linked by vertices (only...)

\( \chi(\text{Al}) \sim \chi(\text{Si}) \)

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

CN(Al): 4 or 6!
Neso- and sorosilicates

«isolated» $\text{SiO}_4^{4-}$ units: nesosilicates

$\text{Mg}_2\text{SiO}_4$: Forsterite  
$\text{(Mg,Fe)}_2\text{SiO}_4$: Olivine

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

other examples: garnets, Portland cement...

$X_3Y_2(\text{SiO}_4)_3$

«isolated» $\text{Si}_2\text{O}_7^{6-}$ units: sorosilicates

$\text{Sc}_2(\text{Si}_2\text{O}_7)$: Thortveitite  
$\text{Zn}_4(\text{Si}_2\text{O}_7)(\text{OH})_2.\text{H}_2\text{O}$: Hemimorphite

other units (rare!): $\text{Si}_3\text{O}_{10}^{8-}$, $\text{Si}_4\text{O}_{13}^{10-}$

$\text{SiO}_2$, $\text{Ag}_2\text{O}$, $T \sim 600^\circ\text{C}$, $P(\text{O}_2) \sim 4.5$ kBar

$\text{Ag}_{10}(\text{Si}_4\text{O}_{13})$
Cyclosilicates

Cycles including 3, 4, 6 or 8 silicate units: \((\text{Si}_n\text{O}_{3n})^{2n-}\) (n = 3, 4, 6, 8)

\[\text{Si}_6\text{O}_{18}^{12-}\]

\[\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18} : \text{Beryl or... emerald!}\]

\[(\text{Na, Ca})(\text{Li, Mg, Al})_3(\text{Al, Fe, Mn})_6(\text{OH})_4(\text{BO}_3)_3\text{Si}_6\text{O}_{18} : \text{Tourmaline}\]
Inosilicates

- **Pyroxenes**: \((\text{Si}_3\text{O}_9)^2^-\) properties of fibers
- **Amphiboles**: \((\text{Si}_4\text{O}_{11})^6^-\)
Phyllosilicates

Kaolinite (or Antigorite)

\[(\text{Si}_4\text{O}_{10})^{4-}\]
\[-(\text{Al}_2(\text{OH})_2)^{4+}\]
[or \((\text{Mg}_3(\text{OH})_2)^{4+}\)]

Muscovite (or Biotite)

\[-(\text{Al}_2(\text{OH})_2)^{4+}\]
\[-(\text{Mg}_3(\text{OH})_2)^{4+}\]

Pyrophyllite (or Talc)

\[(\text{Si}_4\text{O}_{10})^{4-}\]
\[-(\text{Al}_4(\text{OH})_4)^{8+}\]
[or \((\text{Mg}_6(\text{OH})_4)^{8+}\)]

Chlorite

\[(\text{Al}_2\text{Si}_3\text{O}_{10})^{5-}\]
\[-(\text{Mg}_3(\text{OH})_2)^{4+}\]
\[-(\text{Mg}_2\text{Al}(\text{OH})_6)^{+}\]

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

plastic properties
Tectosilicates

\((\text{SiO}_2)_n\) or \((\text{Si,Al,C}^+)_n\text{O}_{2n}\)

silica
Feldspaths
zeolites

\{ porosity? \}

Feldspath (plagioclase)

a typical zeolite structure
Hierarchical porosity

porous materials

nanoporous
$\varnothing < 2$ nm

mesoporous
$2 < \varnothing < 50$ nm

macroporous
$50$ nm $< \varnothing$

zeolites

MCM

foams
Zeolites

discovered by Baron A. Von Kronstedt

**ZEO:** to boil
**LITHOS:** stone

(1756)

 characteristics...
- exchangeable cations (neutrality)
- rigid anionic networks
- cavities and channels
- guest molecules (water...)

\[ M^{n+} \left[ (AlO_2)_y (SiO_2)_z \right] \cdot mH_2O \]
Natural zeolites

Faujasite

Natrolite

Anacilme

~ 40 natural zeolites
The *sodalite cage*

**Sodalite**, a mineral: $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$

- 24 linked tetrahedra (Si or Al)

**the sodalite entity**

- Sodalite (mineral)
- *Lapis-lazuli*
- Linde-A (synthetic)

**octahedron**

**truncated octahedron**

**Faujasite (mineral)**

$\text{NaCa}_{1.5}(\text{Al}_2\text{Si}_5\text{O}_{14}).10\text{H}_2\text{O}$
Some characteristics of zeolites

A- the Si/Al ratio

- Linde-A: Si/Al = 1
- Mordenite (mineral): Si/Al = 5.5
- ZSM: $20 < \text{Si/Al} < \infty$ (hydrophobic)

B- exchangeable cations

various accessible sites

C- cavities and tunnels

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<th>tetrahedra</th>
<th>$\Theta$ (pm)</th>
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<td>ZSM-5</td>
<td>10</td>
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<td>Faujasite</td>
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<td>740</td>
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<td>Mordenite</td>
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<td>$670 \times 700$</td>
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Synthetic zeolites: the ZSM family

Zeolite Socony Mobil (~ 1975)

«Pentasil» unit
(five-membered rings)

planes

3D architecture

ZSM-5

ZSM-5

ZSM-11

ZSM-18
Interconnected channels: structural dependence

ZSM-5

Faujasite
More and more porosity!

~ 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

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Secondary Building Units (SBU)

D4R type SBU

ACO type
Mimicking SBU: Al-O-P clusters

T. Azaïs

3 (S3R)  4 (S4R)  6 (S6R)  8 (S8R)

4-1  4=1  4-2  4-4=1

5 (S5R)  5 (S5R)  5 (S5R)

6 (S6R)  2-6-2  6=1

SPIRO-5  4-4 (D4R)  6-6 (D6R)  8-8 (D8R)

AlCl₃, AlBr₃

EDI type

AlCl₃, AlBr₃

OH OH OH

P

Φ

OH

O

O

P

P

Al
Cluster structures

S4R

D4R

new!

T. Azaïs, Paris 6
Exotic solid state NMR: \(^1\text{H}\) and \(^{35}\text{Cl}\)

\[
\begin{align*}
\text{LW} &= 330\text{Hz} \\
\omega_r / 2\pi &= 2.14 \text{ kHz} \\
\nu_{1H} &= 14 \text{ kHz, } 300 \text{ MHz} \\
\eta_Q &= 0.96 \\
C_Q &= 5.86 \text{ MHz}
\end{align*}
\]

SIMPSON:
- CT and sat.
- 2\(^{nd}\) order
- finite pulses

\[
\begin{align*}
\text{Exp} &\quad \text{Sim}
\end{align*}
\]
Synthesis of zeolites: general approach

- Solution of silicates and aluminates (high pH)
- Co-condensation: gel
- Templating agent
- $\text{OH}^-$ or $\text{F}^-$
- Hydrothermal condition ($T$, $P$)
- Characterization (XRD..)
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
\([\text{N8C42.656]} \text{[Al25Zn7P32O128]}\)
Applications
Molecular sieves

- Catalysis (8%)
- Separation (3%)
- Cationic exchange (89%)

The concept...

Keywords:
- Adsorption
- Ion or molecule exchange
- Substances removal
- Catalysis
**Catalysis**

$$\text{CH}_3\text{OH} + \text{toluene} \rightarrow \text{distilled compounds}$$
Characterizing Zeolite Acidity by Spectroscopic and Catalytic Means: A Comparison

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Adsorption of H₂, N₂, and CO on four different protonated zeolites—H-ZSM-5, H-β, 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

some organic ligands...

inorganic SBU’s linked by organic bridges


1,4-benzenedicarboxylate (BDC)

1,3,5-benzenetricarboxylate (BTC)
An example
Crystal «sponges» - MOF-5

- Organic links
- Inorganic vertices (Zn₄)

- $d \sim 20 \, \text{Å}$
- $S \sim 3000 \, \text{m}^2\cdot\text{g}^{-1}$ (?)
- $\text{cell} > 700,000 \, \text{Å}^3$
Storage of CH$_4$, CO$_2$, H$_2$

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


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, the 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 m²/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.
The chemical nature of surfactant
Pluronic® P123 Block Copolymer Surfactant

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

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

Self assembly of surfactant

Condensation of silica source

Silica source
Surfactant

Removal of surfactant

Surfactant
Catalyst
Temperature
pH
Concentration
Precursor
Template removal
Aging conditions
Mesoporous silica and other oxides

- Hydrolysis of TEOS
- Ordered network of pores
- Pores from 2 to 50 nm

Boissière, Chem. Mater., 2006
Applications towards a new chemistry...

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

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

M=UO$_2^{2+}$
sensors with optical detection
Drug delivery

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

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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, 13C, and 29Si 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).