Microporous and mesoporous materials

Zeolites
Our hydrothermal synthesis

Hydrothermal:  
Synthesis from aqueous solutions above the boiling point

Solvothermal:  
Synthesis using other solvents above their boiling point

Preparation of large single crystals and synthesis of new materials
Natural zeolites

**Zeolites**

Zeolites are porous, hydrated aluminosilicates. They may be natural minerals or synthetic materials.

The general chemical composition of a zeolite is:

\[ \text{M}^{n+}_{x_n} \text{Si}_{1-x_n} \text{Al}_{x_n} \text{O}_2 \cdot y \text{H}_2\text{O} \]

Where M = e.g. Na\(^+\), K\(^+\), Li\(^+\), Ag\(^+\), NH\(_4^+\), H\(^+\), Ca\(^{2+}\), Ba\(^{2+}\)...

Characteristics of zeolites:

1) Tectosilicates, i.e. three dimensional structure built from tetrahedra. Some silicon atoms have been replaced by aluminium, i.e. the (Si+Al)/O = \(\frac{1}{2}\). (Tetrahedra usually denoted T-atoms.

2) Open framework structure built from TO4-tetrahedra, containing pores and voids. The structure and porosity is periodic (i.e. crystalline materials). The pores have molecular dimensions.
Zeolites

3) Counter ions (cations) are present in order to compensate for the negative framework charge created by aluminium substitution. The counter ions are situated in the pores and voids, and are usually mobile.

4) In the voids and pores are also water molecules (zeolitic water). One measure of the porosity is the amount of adsorbed water. The water molecules are also present in the pores and voids, and may (in many cases) be removed by heating and reabsorbed at lower temperatures.

5) Loewenstein's rule imposes a limit to the amount of aluminium which may be substituted into the framework: No Al-O-Al may be present in tectosilicates. This means that only half of the silicon atoms may be substituted by aluminium. For the general composition:

\[ \text{M}^{x+}_{x/n} \text{Si}_{1-x} \text{Al}_x \text{O}_2 \cdot y \text{H}_2\text{O} \]

This means that the Si/Al ratio is larger than 1 and that x is smaller than 0.5

This rule is not always obeyed! (High aluminium e.g. Si/Al = 0.5)

High silica and pure silica zeolites have been synthesised.
Zeolite stability fields

All zeolites are formed in aqueous solution. The water molecules act as “templates”, which are necessary in order to form a porous structure.

Most zeolites are formed from basic solution (exceptions are fluoride syntheses) which favours four-coordinated aluminium. Zeolites are formed in the low temperature end of the hydrothermal synthesis (70-300°C) due to the open structure and high water content. Higher temperatures often gives denser materials.

Zeolite types as a function of temperature
**Structure, porosity and building units**

One measure of porosity is the tetrahedra density, i.e. number of T-atoms in 1000Å³. For zeolites: between 12 and 20. Other tectosilicates: larger than 20 T/1000Å³.

**Primary building units:**
- TO₄-tetrahedron

**Secondary building units:**

**Tertiary building units,**
- e.g. the sodalite cage:
  - 6-ring: 6 T-atoms and 6 oxygen atoms

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**Structure, porosity and building units**

Representation of zeolite structures:

![Zeolite Structure Diagrams](image_url)
Building zeolites:

Three structures containing sodalite cages:

![Fig. 6a Sodalitstrukturen (SOD).](image1)

![Fig. 6b Zeolit A (LTA).](image2)

### Tab. 18.1. Examples of nanoporous aluminosilicates, giving the three letter IZA designations and a brief description of the pore systems.

<table>
<thead>
<tr>
<th>System</th>
<th>Pore System</th>
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<tbody>
<tr>
<td>Sodalite family (SOD) (e.g. mineral and synthetic sodalites)</td>
<td>3-dimensional; 6-ring channels</td>
</tr>
<tr>
<td>Zeolite A family (LTA) (e.g. zeolites A, ZK-4; no mineral analogue)</td>
<td>3-dimensional; 8-ring channels</td>
</tr>
<tr>
<td>Chabazites (CHA) (e.g. mineral chabazites, SSZ-13)</td>
<td>3-dimensional; 8-ring channels</td>
</tr>
<tr>
<td>ZSM-5 (MFI) (e.g. mineral mordenite, silicalite)</td>
<td>2-dimensional; 10-ring channels</td>
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<tr>
<td>Ferrierites (FER) (e.g. mineral and synthetic ferrierites)</td>
<td>2-dimensional; 10 &amp; 8-ring channels</td>
</tr>
<tr>
<td>Faujasites (FAU) (e.g. mineral faujasite, zeolites L5X, X, Y, US-Y)</td>
<td>3-dimensional; 12-ring channels</td>
</tr>
</tbody>
</table>

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Properties of zeolites

The properties of zeolites are closely related to both structure and chemistry.

Three main characteristic properties:

- Adsorption
- Ion exchange
- Catalytic activity

Adsorption (molecular sieve)

Adsorption in zeolites is significantly different from adsorption in e.g. silica gel or active coal, which have a broad size distribution of pore sizes, and where the size of the pores are in the range of 10 nm.

In zeolites the porosity is determined by the crystalline structure, i.e. the pores are arranged in a regular fashion with only one (or a few) discrete pore sizes. Also the pores have molecular dimensions.

The implication of this is the use of zeolites as adsorbants and molecular sieves.

Mainly used for water adsorption (very low equilibrium water vapour pressure)

Gas (hydrogen?) storage materials

Molecular sieving effect due to size limitation imposed by framework structure and cation size and position.

Also weaker interactions:

N₂-O₂ separation
**Ion exchange (ionic conductivity)**

The counter-cations in zeolites are mobile, and may easily be exchanged.

This results in ion exchange capability utilized e.g. in detergents and in waste water purification. Or pigs food…

**Catalysis**

One of the major uses of zeolites is as heterogeneous catalysts in the petrochemical industry. Cracking catalysts (H-form of zeolite Y, faujasite) is the largest use of zeolites.

They are used also e.g. for production of synthetic gasoline (ZSM-5) from methanol, and synthesis of fine chemicals.

Zeolite catalysts give high selectivity (shape selective) and their properties may be tailored by changing the chemistry, e.g. Si/Al ratio, and counter cations.
Microporous zeolite-like materials

Aluminophosphates, AlPO's III-V analogues of SiO₂; AlPO₄
E.g. Berlioniite structurally similar to α-quartz

Microporous aluminophosphates (Flannigan, Union Carbide)

AlPO-5

Tab. 11.2  Some important applications of aluminosilicate zeolites and other nonporous materials.

<table>
<thead>
<tr>
<th>Well-established:</th>
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<tbody>
<tr>
<td>Ion-exchange using hydrated zeolites</td>
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<tr>
<td>Detergency (e.g. zeolites Na-A and Na-Y)</td>
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<td>Water softeners</td>
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<td>Animal feeds</td>
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<tr>
<td>Radwaste immobilization (e.g. Cs, Sr with clinoptilolite)</td>
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<td>Molecular sieving using dehydrated zeolites</td>
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<td>Air separation (N₂ from O₂ with Li-LSX)</td>
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<td>Drying agents (e.g. double glazing, 4°C)</td>
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<td>Sulfur removal from natural gas</td>
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<td>Separation of HFCs (CFC substitutes)</td>
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<tr>
<td>Catalysis with dehydrated zeolites</td>
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<tr>
<td>Catalytic cracking (gasoline production) – zeolite-Y derivatives</td>
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<tr>
<td>Xylene isomerization (for polyesters) – H-ZSM-5</td>
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<tr>
<td>Butene isomerization – H-FER</td>
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<td>Methanol to gasoline – H-ZSM-5</td>
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<tr>
<td>Phenol to hydroquinone – Ti-zeosilicates</td>
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<tr>
<td>Denitration reactions – Cu-ZSM-5, Co-FER</td>
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</tbody>
</table>

Future possibilities include:
| Hydrogen storage |
| Nano-composites for optoelectronics |
| Sensors using zeolite thin films |
| Stereoselective polymerization |
| Contrast enhancement in MRI (e.g. Gd-Y) |
| Ship-in-bottle synthesis |
| Zeolite nanocrystals for delivery systems |

Fig. 11.1  The aluminophosphate AlPO₄. SiO₄ and PO₄ tetrahedra, which are strictly alternating, are represented in grey and water molecules have been omitted for clarity.
AlPO₄: Neutral framework
Synthesis at acidic conditions
More than 40 aluminophosphate based structures. Mainly alternating Al,P, i.e. no 5-ring structures...

Substitution of atoms with different valence into the framework creates lattice charge, important especially for use as catalysts:

SAPO: silicon substituted ALPO
MePO: Metal substituted aluminophosphates
MeAPSO: Metal substituted silicoaluminophosphates

Divalent cations which can adopt tetrahedral geometry, e.g. Mg²⁺, Mn²⁺, Fe²⁺, Co²⁺, Zn²⁺.

SAPO: Silicon substitutes only for P, e.g. HₓSiₓAlP₁₋ₓO₄
MAPO: divalent cations substitutes substitutes only for P, i.e. HₓAl₁₋ₓPO₄
MeAPSO: e.g. Hₓ₋y(SiₓMeᵧAl₁₋ₓP₁₋z)O₄

ALPO’s: higher coordination and interrupted frameworks

May form microporous framework structures with Al in higher coordination, V or VI.

Synthesis in non-aqueous solvents may result in low dimensional materials with a P/Al ratio larger than 1.

Anionic species e.g. hydroxyl, contribute to the coordination in non-bridging sites. When using fluoride in the synthesis, fluoride may participate in the framework, creating e.g. Al-F-Al bridges.
**Cloverite, 20-ring gallophosphate**

**Mixed coordination materials**

*Fig. 18.1.* The gallophosphate ULM-5. Gallium polyhedra are shown in gray and PIU tetrahedra are represented in light gray. Water molecules and the organic template have been omitted for clarity.

*Fig. 18.4.* The gallophosphate cloverite. Gallium polyhedra are shown in gray and PIU tetrahedra are represented in light gray. Water molecules and the organic template have been omitted for clarity.

*Fig. 18.5.* The vanadium phosphate $Cs_3[V_2O_7(PO_4)_2]$. Vanadium polyhedra are shown in gray and PIU tetrahedra are represented in light gray. Water molecules have been omitted for clarity.
Open framework iron phosphates

Fig. 18.6. The iron phosphate mineral cacoxenite, FeO₆ octahedra are shown in gray and AlO₆ and PO₄ tetrahedra are represented in light gray. Water molecules are omitted for clarity.

Molten salt flux; salts as templates in open framework materials

Fig. 18.7. The nickel phosphate VSR.1. NiO₆ octahedra are shown in gray and PO₄ tetrahedra are represented in light gray. Water molecules, extra-framework cations, and partial occupancy are omitted for clarity.
Microporous and mesoporous materials from soft building blocks

Escape from the zeolite prison

Microporous sulfides; microporous zeolite super building blocks

Figure 8.2  Schematic showing the crystal structure of a microporous sulfide material
(Reproduced with permission from Ref. [4])
Synthesis and Structure of MnGe$_4$S$_{10}$(C$_6$H$_{14}$N$_2$)$_2$·3H$_2$O: A Novel Sulfide Framework Analogous to Zeolite Li-A(BW)
Christopher L. Cahill and John B. Parise*

Figure 2. Structure of 

Zeolite Li-A(BW) analogue

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Supertetrahedra, Microporous sphalerite, ZnS

Figure 1. The principle of building supertetrahedra from the dense sphalerite structure: a) A part of the sphalerite structure limited to a large tetrahedron corresponding to an edge of ten primitive tetrahedra (in blue); b) assembly of T2 supertetrahedra with the same sphalerite topology (the supertetrahedron, in blue, contains four metal centers); c) assembly of T3 supertetrahedra built on the same principle; d) assembly of T4.

Flexibility in framework chemistry and structure:
Cationic, anionic or neutral frameworks

Figure 8.4 3D representation of a self-assembled metal sulfide cluster framework found to display remarkable ion conductivity
(Reproduced with permission from Ref. 20)
Metalorganic framework (MOF) materials
Hybrid (organic/inorganic) materials

BDC: 1,4-benzene-dicarboxylate Zn₄O(BDC)₃
Cubic structure, Surface area 2500-3000m²/g (BET), stable to 3-400°C
Hydrogen storage?: 78K: 4.5w% H₂, RT, 20 bar: 1w%
An example from UiO (Pascal Dietzel):

$\text{Ni}_2(\text{dhpt})(\text{H}_2\text{O})_2\cdot8\text{H}_2\text{O}$

dhpt: 2,5-dihydroxyterephthalic acid

Hydrated and anhydrous structure

1083 m$^2$ g$^{-1}$.  

Other materials: surface area of ~1700 m$^2$ g$^{-1}$.  
Orthorhombic crystal system

$a = b = 21.9078$ Å, $c = 37.1540$ Å, $V = 17832$ Å$^3$
Mesoporous materials, The MCM family

Figure 8.6 Supramolecular templating of mesoporous inorganics
Micelle formation in surfactant systems

![Micelle formation in surfactant systems](image)

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**Figure 8.7** TEM image of hexagonal mesoporous silica along with X-ray diffraction data demonstrating the hexagonal order. (Reproduced with permission from Ref. 36)
Transmission electron micrographs show, at left, the regular pattern of hexagonal channels in the ceramic material, and at right, the smooth distribution of iron oxide particles (dark spots) within the ceramic matrix.
Another length scale: Block copolymers templated mesoporous materials

Semiconducting mesoporous materials from germanium sulfide, adamantane-like clusters.

Figure 8.10 Modular self-assembly of adamantanoid $M_2S_{18}^{3-}$ clusters with $M^{3+}$ ions to form a mesocrystalline metal sulfide. (Reproduced with permission from Ref. 79)
Post treatment:
Recrystallization to ordered array of nanocrystals...

Figure 8.11 Nanocrystalline mesoporous nickel oxide yttria-stabilized-zirconia, oxide ion conductor used as the anode in a solid oxide fuel cell

Figure 8.12 Polyelectrolytes can be trapped in the silicate walls of a PMS, conferring to it additional function
(Reproduced with permission from Ref. 92)
Figure 8.13 Growth of polyferrocenylsilane within the channels of hexagonal mesoporous silica

Figure 8.14 Schematic showing the assembly of a periodic nanocrystal–silica composite. A TEM image is shown on the bottom left, highlighting the order of the material.
(Reproduced with permission from Ref. 114)