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

Zeolites and zeolitic materials

Chemical composition
Silica \( \text{SiO}_2 \)
Aluminosilicates \( M_x^1 \text{Al}_x \text{Si}_{2-x} \text{O}_4 \cdot n\text{H}_2\text{O} \)
Aluminophosphates \( \text{AlPO}_4 \) (isoelectronic with \( \text{Si}_2\text{O}_4 \))
Metallophosphates \( \text{MPO}_4 \)
Silicoaluminophosphates \( M_x^1 \text{Si}_x \text{AlP}_{1-x} \text{O}_4 \)
Pores
Channels
Zeolites and zeolitic materials

>40 naturally occurring zeolites
>139 structure types
many hundreds of zeolite compounds

Nomenclature  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, Beryllophosphate-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 – AlPO₄-5, 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)
Zeolites and zeolitic materials

Primary building units: Al(III)O₄, P(V)O₄ and Si(IV)O₄ tetrahedra

Isoelectronic relationship

\[(\text{SiO}_2)_2 \quad [\text{AlSiO}_4 ]^- \quad \text{AlPO}_4\]
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
Sodalite unit
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
LTA
(a) $[\text{TO}_4]$ tetrahedra as BBU
(b) four-membered single rings
(c) IB fuenfer chains
(d) cubes $[4^6]$ 
(e) truncated octahedra $[4^66^8]$ (sodalite- or $\beta$-cages)
(f) truncated cubeoctahedra $[4^{12}6^88^6]$ ($\alpha$-cavities)
Pores in zeolite A (LTA)

(a) the sodalite cage \([4^66^8]\]
(b) the \(\alpha\)-cavity \([4^{12}6^88^6]\]
(c) the 3-dimensional channel system
(d) the 8-ring defining the 0.41 nm effective channel width
AFM growth studies of LTA
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.
## Molecular sieves

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Cation</th>
<th>Code</th>
<th>Pore diameter</th>
</tr>
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<tbody>
<tr>
<td>Zeolite A:</td>
<td>Na</td>
<td>4A</td>
<td>0.42 nm</td>
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<tr>
<td></td>
<td>Ca</td>
<td>5A</td>
<td>0.48 nm</td>
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<td></td>
<td>Na, K</td>
<td>3A</td>
<td>0.38 nm</td>
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<td>Zeolite X:</td>
<td>Na</td>
<td>13X</td>
<td>0.8-1.0 nm</td>
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<tr>
<td></td>
<td>Ca</td>
<td>10X</td>
<td>0.7 nm</td>
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</tbody>
</table>

Zeolite Y contains more Si
Framework density

**Framework density (FD)**

Defined as the number of tetrahedral atoms (T-atoms) per cubic nanometer (1000 Å³)

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 TO₄ 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 Si/Al ≥ 1
Linde A (LTA) Si/Al = 1
ZK-4 (LTA) Si/Al = 2.5
ZSM-5 Si/Al = 20 - ∞
Pure SiO₂ Si/Al = ∞

Pentasil
ZSM-5
Zeolite Synthesis

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

Aluminosilicates – high pH

라도 Mixing
NaAl(OH)$_4$(aq) + Na$_2$SiO$_3$(aq) + NaOH(aq), 25 °C, condensation-polymerization, gel formation

라도 Ageing
Na(H$_2$O)$_n$ + template effect → Na$_a$(AlO$_2$)$_b$(SiO$_2$)$_c$·NaOH·H$_2$O(gel) → 25-175 °C

라도 Hydrothermal crystallization of amorphous gel, 60-200 °C
Na$_x$(AlO$_2$)$_x$(SiO$_2$)$_y$.zH$_2$O(crystals)

라도 Separation of the solid product by filtration

라도 Calcination
- occluded water, removed by 25-500 °C vacuum thermal dehydration
- template removal — calcination in O$_2$ at 400-900 °C removes the guest molecules from the framework without altering it
- extraction (neutral templates)
Zeolite Synthesis

Structure of the zeolite product depends on:
- Composition
- Concentrations and reactant ratios
- Order of mixing
- Temperature
- Ageing time (hours to weeks)
- Crystallization time (days to weeks, kinetics of the structure-directing process is slow)
- pH
- Stirring/no stirring
- Pressure
- Seeding
- Reactor material (PTFE, glass, steel)
- Templates

Templates: Organic cationic quaternary alkylammonium salts, alkylamines, aminoalcohols, crownethers, structure-directing, space-filling, charge-balancing
Vary the template - discover new structures!
Templates

Template or guest compounds
Three levels of the guest action with increasing structure-directing specificity:

- **Space-filling** - the least specific, observed, for example, in the synthesis of AIPO₄-5, 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 AIPO₄-20
  - 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!
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, cubo-octahedron
The zeolite synthesis mechanism

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

(b) “in situ” rearrangement of the gel
Mechanism of structure-directing action of the TPA template
Zeolites and zeolitic materials

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

Zeolite post modification for controlling properties of zeolites

Tailoring channel, cage, window dimensions:
- Cation choice (Ca$^{2+}$ exchanged for Na$^+$)
- Larger Si/Al
decreases unit cell parameters, window size
decreases number of cations, free space
increases hydrophobicity
- Reaction temperature, higher T, larger pores
Stability Rules

Löwenstein rule: never Al-O-Al

Dempsey rule: Al-O-Si-O-Si-O-Al
is more stable than
Al-O-Si-O-Al

NNN-principle
Tuning Bronsted acidity:

Solid acid for the hydrocarbon cracking
The larger the Si/Al ratio, the more acidic is the zeolite
Brønsted acidity
ZEOLITES and ZEOLITIC MATERIALS

Size-shape selective catalysis, separations, sensing
Reactant, product, transition state selectivity:
Separation of xylene isomers by pervaporation thru a MFI membrane
ZEOLITES and ZEOLITIC MATERIALS

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
ZEOLITES and ZEOLITIC MATERIALS

Aluminophosphates

▲ Isoelectronic relationship of AlPO₄ to (SiO₂)₂
▲ Ionic radius of Si⁴⁺ (0.26 Å) is very close to the average of the ionic radii of Al³⁺ (0.39 Å) and P⁵⁺ (0.17 Å)

Many similarities between aluminosilicate and AlPO₄ molecular sieves
Dense AlPO₄ phases are isomorphic with the structural forms of SiO₂: quartz, tridymite, and cristobalite

Aluminosilicate framework charge balanced by extraframework cations
Aluminophosphate frameworks neutral \((\text{AlO}_2^-)(\text{PO}_2^+) = \text{AlPO}_4\)
ZEOLITES and ZEOLITIC MATERIALS

Some of the AlPO₄ microporous structures are analogous to zeolites while other are novel and unique to this class of molecular sieves.

Only even-number rings because of 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 AlPO₄ gives a vast number of element-substituted molecular sieves (MeAPO, MeAPSO, SAPO) which are important heterogeneous catalysts.

M¹⁺, M²⁺, and M³⁺ incorporate into the Al sites
M⁵⁺ elements incorporate into the P sites
This substitution introduces a negative charge on these frameworks.
Si⁴⁺, Ti⁴⁺, and Ge⁴⁺ 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.
ZEOLITES and ZEOLITIC MATERIALS

Aluminophosphates prepared by the hydrothermal synthesis

Source of Al: pseudoboehmite, Al(O)(OH), Al(O-i-Pr)_3
Mixing with aqueous H_3PO_4 in the equimolar ratio – low pH!
Forms an AlPO_4 gel, left to age
One equivalent of a guest compound = template
Crystallization in a reactor
Separated by filtration, washed with water
Calcination

Other zeolite materials

Oxide and non-oxide frameworks, sulfides, selenides
Coordination frameworks, supramolecular zeolites

The quest for larger and larger pore sizes
Metallo-Organic Framework Structures
Metallo-Organic Framework Structures

Scheme 4. Self-Assembly of Dodecahedra

30 + 20 → CH₂Cl₂, acetone, rt → 60+ 60°OTf

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

(99%)

10 nm
Metallo-Organic Framework Structures
Inorganic and Metallo-Organic Quartz