Porous materials

Nanoporous Pt

20 nm

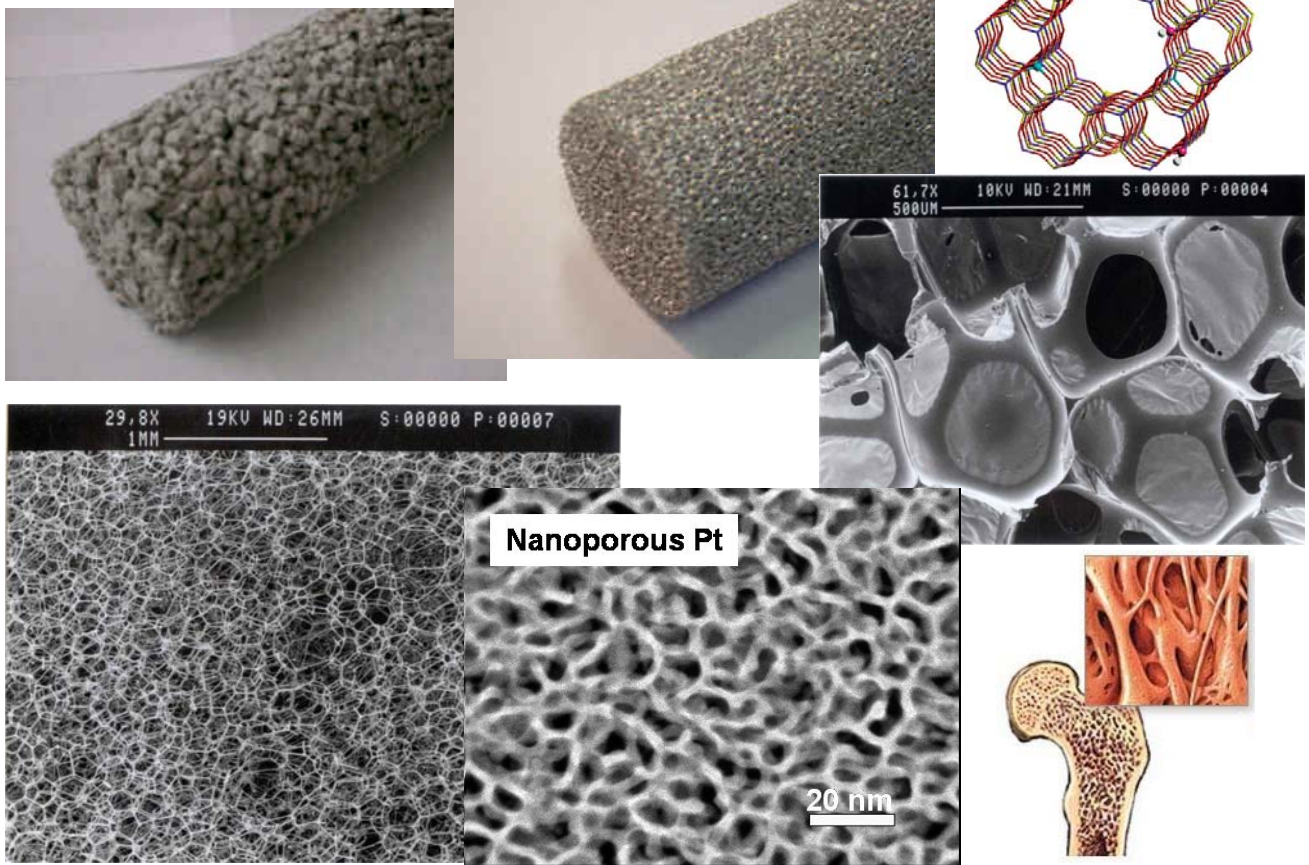
Porous materials

Classically porous materials are organic materials, polymeric foams…
A large number of inorganic porous materials have been developed, e.g. for insulation, cushioning, impact protection, catalysis, membranes, construction materials…

- Materials with different pore sizes (from nanometer to millimeter)
- Ordered or irregular arrangement of pores
- Various chemical compositions (metal, oxides…)
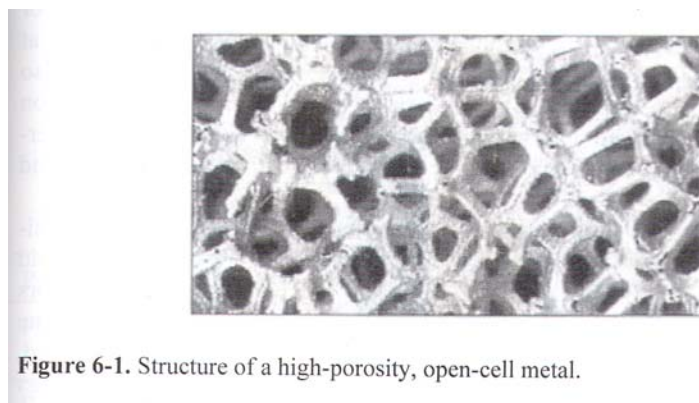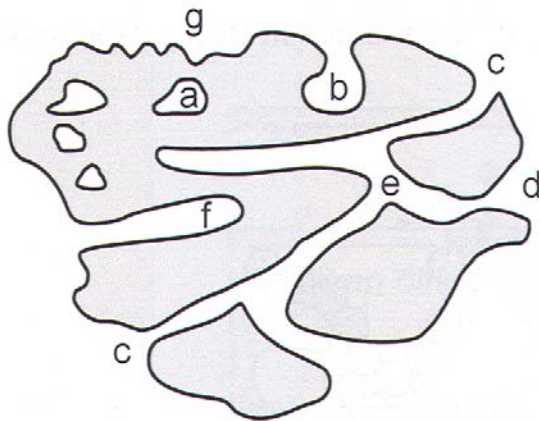- Different preparative approaches.

Figure 6-1. Structure of a high-porosity, open-cell metal.

Porosity

Porous:
Contain pores (cavities, channels, interstices) which are deeper than they are wide.

Either describe the pores, or describe the cell/pore walls

Accessibility:
a: closed pores
b,c,d,e,f: open pores
b, f: blind pores (dead-end or saccate)
e: through pores
Shape:
c:Cylindrical open
f:Cylindrical blind
b: ink-bottle-shaped
d: funnel shaped
g: roughness

Figure 6-2. Different types of pores.

Some definitions

Table 6-1. Definition of terms used to characterize porous solids.

| Density	true density	density of a material excluding pores and interparticle voids (density of the solid network)
	apparent density	density of a material including closed and inaccessible pores
	bulk density	density of the material including pores and interparticle voids (mass per total volume, with volume = solid phase + closed pores + open pores)
Pore volume	V_p	volume of the pores
Pore size		also called pore width (diameter): the distance of two opposite walls of the pore
Porosity		ratio of the total pore volume V_p to the apparent volume V of the particle or powder
Surface area		the accessible (or detectable) area of solid surface per unit mass of material

Measuring porosity

The measured value depends on the method.
Some detects only open pores, e.g. adsorption of molecules.
(Open pore and accessibility is then defined by the probe molecule)
Other may probe also closed pores, e.g. spectroscopy, diffraction, scattering.
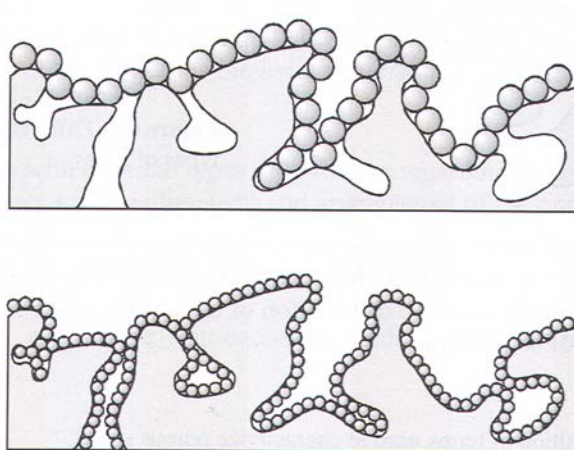
Figure 6-3. Schematic of gas adsorption on a porous material by gases of different molecular size. The surface area, when measured with large molecules, is smaller than when smaller molecules are used.

Pore size

Pore size is important for applications.
IUPAC, three pore size regimes, associated with transport mechanisms:

- *Microporous*, smaller than 2 nm
- *Mesoporous*, between 2 and 50 nm
- *Macroporous*, larger than 50 nm

Macropores: larger than typical mean free path length of typical fluid. Bulk diffusion and viscous flow.

Mesopores: same order or smaller than the mean free path length. Knudsen diffusion and surface diffusion. Multilayer adsorption and capillary condensation ay contribute.

Micropores: pore size comparable to the molecules. Activated transport dominates.
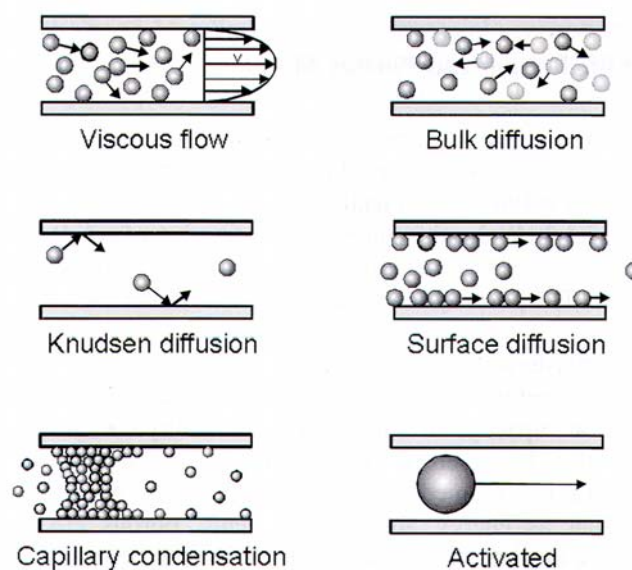
Figure 6-4. Transport mechanisms through pores.

Metallic foams and porous metals

May be seen as composite materials consisting of a solid and a gaseous phase.
Porous metals: high bulk density, independent, distributed voids
Metallic foams: Low bulk density, interconnected voids.
Porosity: 30-98 vol% (pore volume/apparent volume, V_P/V)

Impact energy adsorption, air and water permeability, acoustical properties, low thermal conductivity.

Energy absorbing systems, porous electrodes, sound absorbers, filters, insulating materials, heat exchangers, construction materials, electromagnetic shielding, membrane and membrane support.

Figure 6-5. Aluminum foam components for different applications.
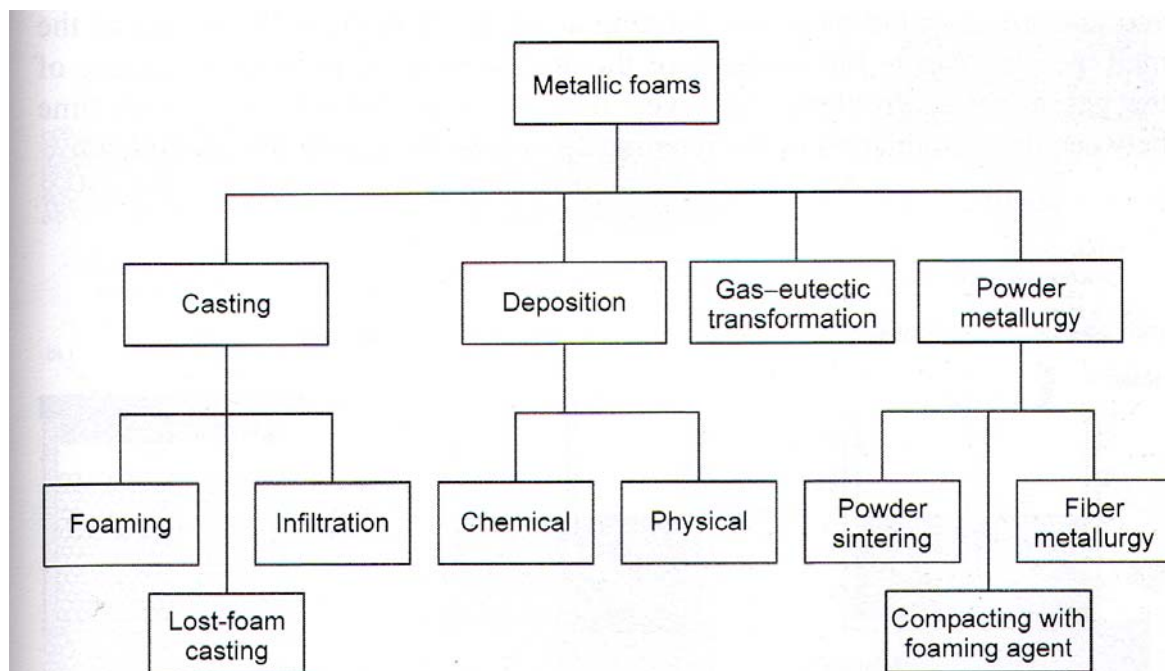
7

Metallic foam production

Figure 6-6. Summary of methods for the synthesis of porous metallic structures.

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Casting techniques

Foaming: a blowing agent (e.g. a metal hydride) is added to the molten metal.
Decomposition creates gas, which expands and foams the metal.
Difficulties: to obtain small bubbles distributed uniformly throughout the material.
High speed mixing, viscosity increasing agents.
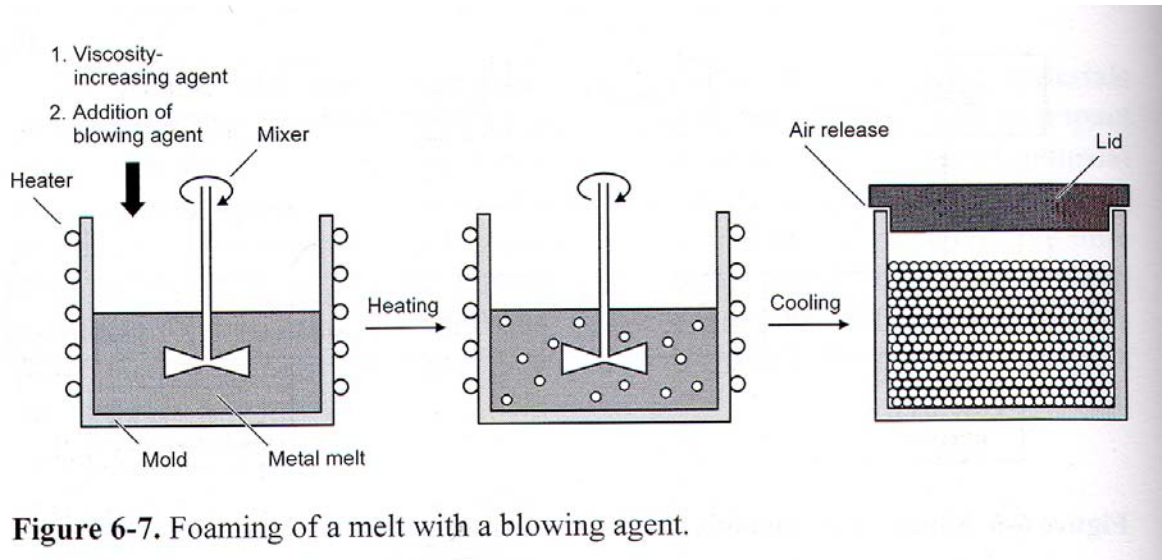High porosity, 60-97%, Closed-cell materials.

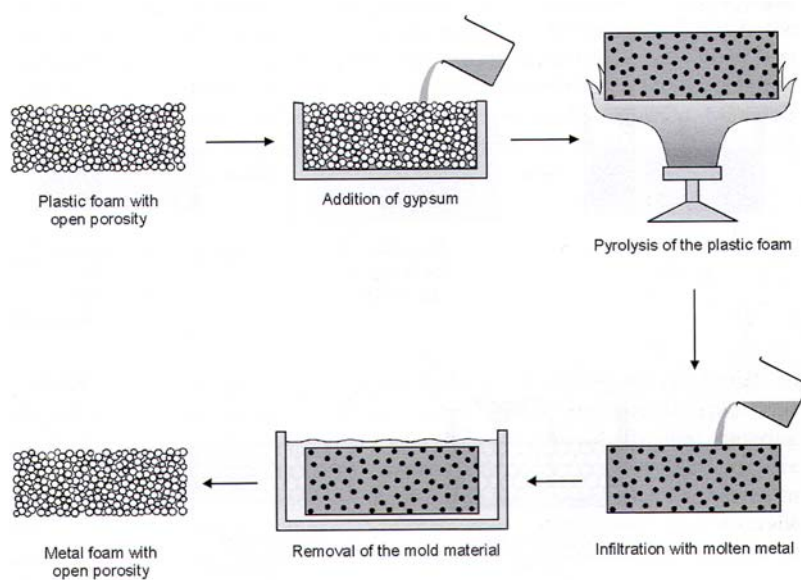**Figure 6-7.** Foaming of a melt with a blowing agent.

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"Lost-foam casting"

Organic foam is filled by an inorganic castable material, e.g. gypsum.
Combustion of organics result in porous inorganic material.
This is used as a mold for the metal (solidified in pores)
The inorganic matrix is then removed selectively.

Used e.g. for low melting metals and alloys, e.g. Cu, Al, Pb, Sn, Zn
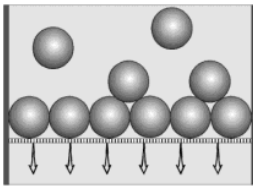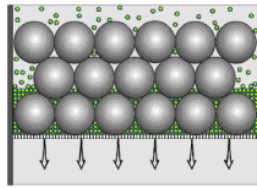
Up to 95% porosity

Figure 6-8. Principle of lost-foam casting.
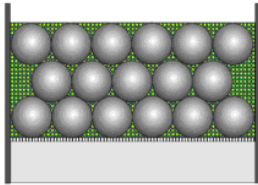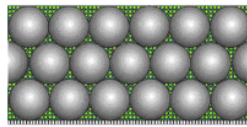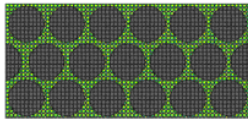
10

Porous gold

Latex Crystal Deposition

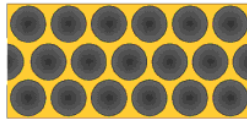Infusion with gold

Latex/Gold Layer Dried

Gold/Latex Composite

Solvent or Oxidizer

300° C
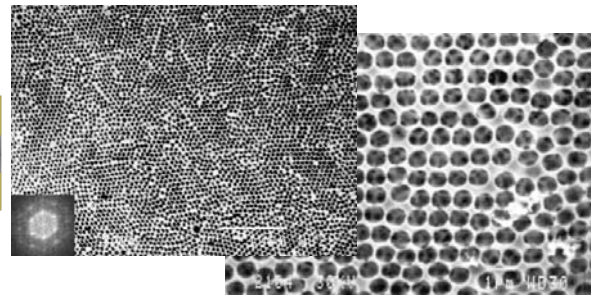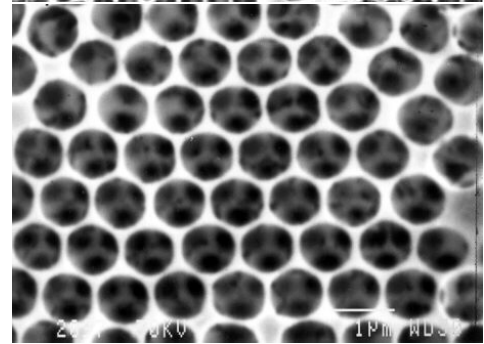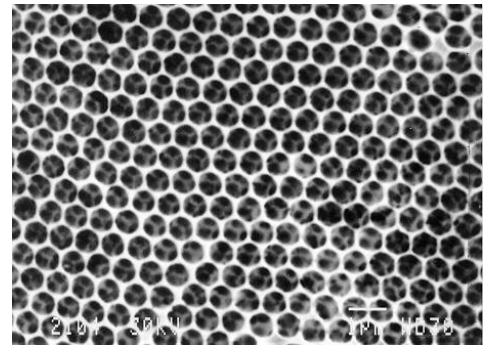
Meso/Macro Porous Gold

Macroporous Gold

Infiltration

Casting metal around densely packed granular material (template)
Interconnected sponge-like materials are obtained, porosity ca. 70%
The template materials should be soluble, but heat resistant. E.g. sodium chloride, expanded clays, glass spheres, hollow corundum spheres…

Infiltration with metal

Removal of the template by rinsing

Material with open-porous structure

Hollow spheres

Infiltration with metal

Material with closed-porous structure
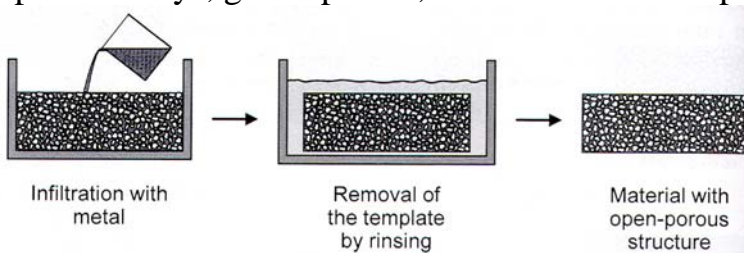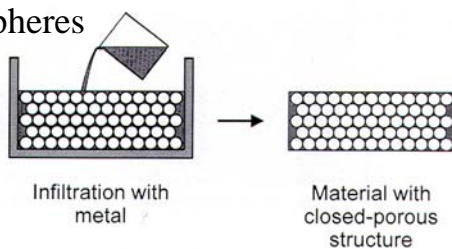
Alternatively: stirring of granular materials into the melt.

Figure 6-9. Process of casting metals around templates. Upper row: two-step process in which the template is removed after infiltration of the metal; lower row: one-step process using hollow spheres.

Gas-eutectic transformation

Mainly metal-hydrogen systems based on saturating the molten metal with gas.

1. Charging the melt with hydrogen to reach the eutectic composition
2. Solidification of the melt, whereby the saturated melt decomposes into a solid and a gas phase.
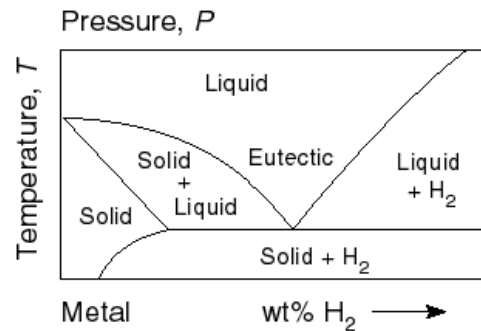
No foaming is observed, gas evolution as the metal solidifies.

Process parameters: hydrogen level in the melt, gas pressure above the melt, direction and rate of heat removal, chemical composition.
Porosity ca. 70%, pore size 10 μm – 10 mm

Gasars. (abbreviation of the Russian term for gas-reinforced.)

a) Metal - Hydrogen Binary Phase Diagram

Cu and Mg gasars
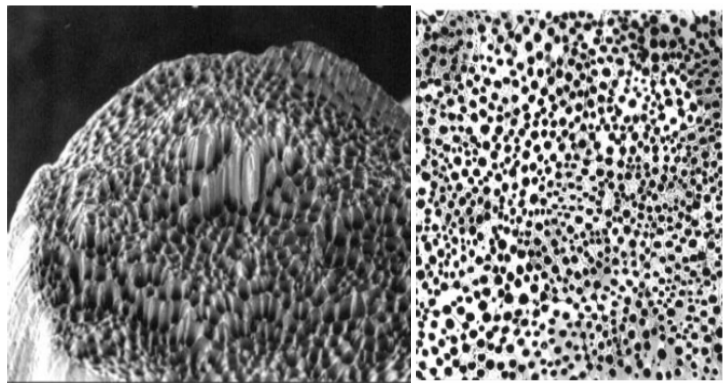
Fig. 2. General view of copper gasar on fracture surface.

Fig. 3. Pores formation (schematic) on the surface of the native solidification front during unidirectional heat removal: 1–6 - consecutive gasar growth steps.

10 cm

10 cm

Fig. 4. Magnesium gasar with axial (left) and radial (right) pores.

V. Shapovolov and L. Boyko, Adv. Eng. Mater. 2004, 407

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Powder metallurgy

Powder sintering or loose powder sintering:
Fill the loose powder into a form and heat. Sintering by forming contacts between grains. Porous metals formed, porosity 40-60%.
Pore forming or spacing agents may be added. Decompose or evaporate during sintering. May give porosities of 90%.

Dense packing of spheres
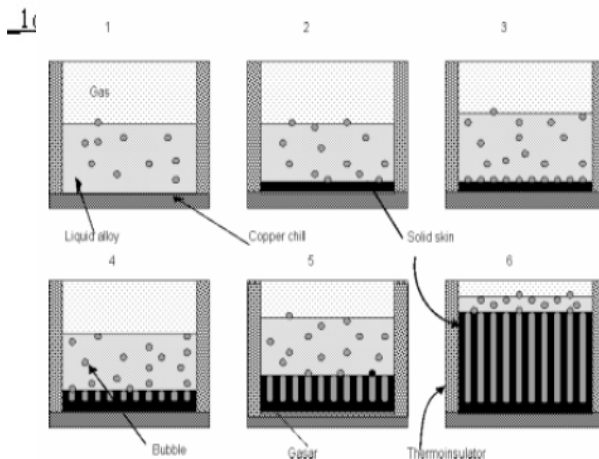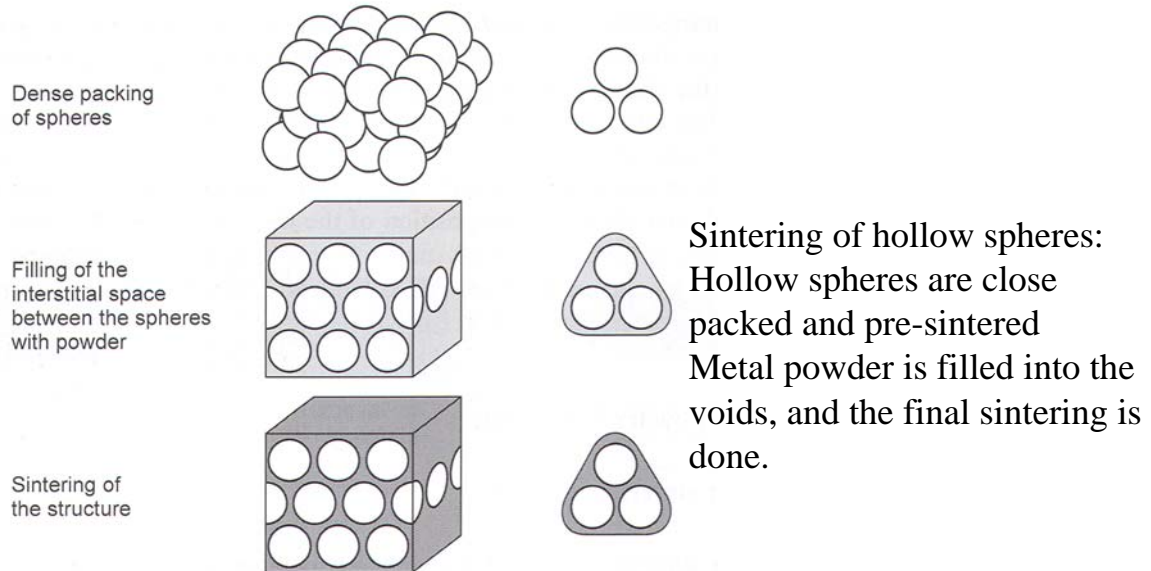
Filling of the interstitial space between the spheres with powder

Sintering of the structure

Sintering of hollow spheres:
Hollow spheres are close packed and pre-sintered
Metal powder is filled into the voids, and the final sintering is done.

Figure 6-10. Principle of sintering with hollow spheres.

Fiber metallurgy

Metal fibers are used instead of powder.
•The porosity may be controlled from 0-95vol%, while maintaining constructional properties.
•High strength and ductility may be obtained.

Metal fibers are produced e.g. by machining or drawing.
Compacted and sintered
May be coated by a low-melting agent to improve bonding.
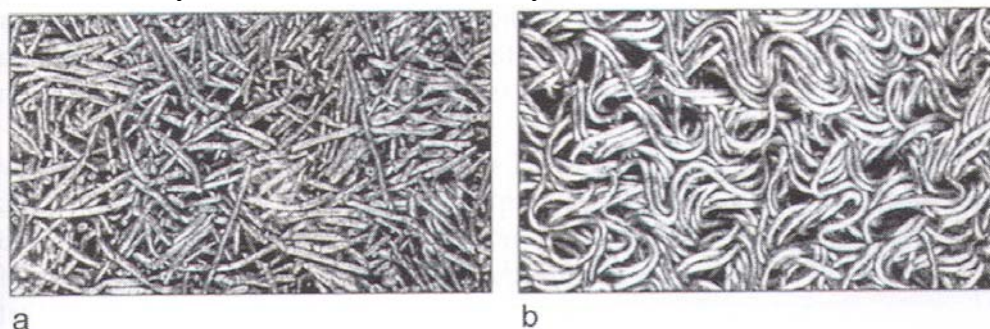The structure may be ordered or randomly oriented.

a   b

Figure 6-11. The structure of porous metals produced by a) sintering of short straight fibers; b) sintering of long crimped fibers.

Metal deposition

CVD, electrochemical, PVD methods may be used.

Electrochemically deposited on porous organic substrates. (ca. 90% porous)
PVD on cold substrate, which is then removed (up to 95% porosity)

Porous silicon by anodization. Si-wafer in a solution of hydrofluoric acid, ethanol and water. Anodized for a short time using an electric current. Interconnected network of pores, ca. 10nm. The density is 1/10 of silicon, but the material is crystalline.
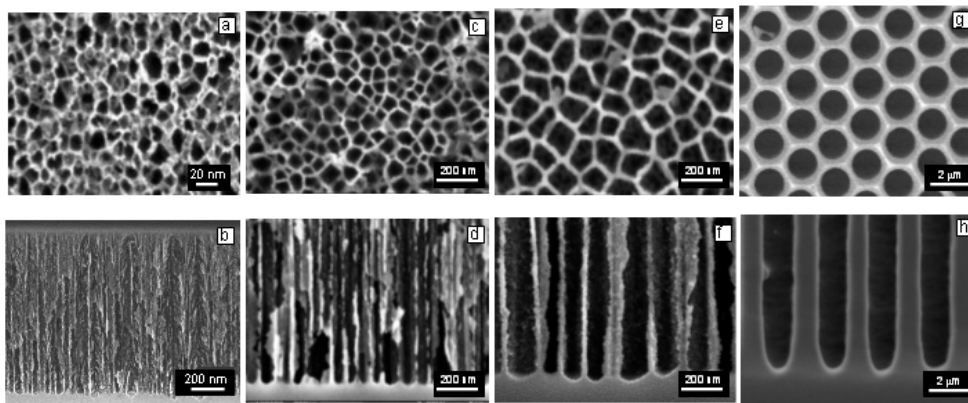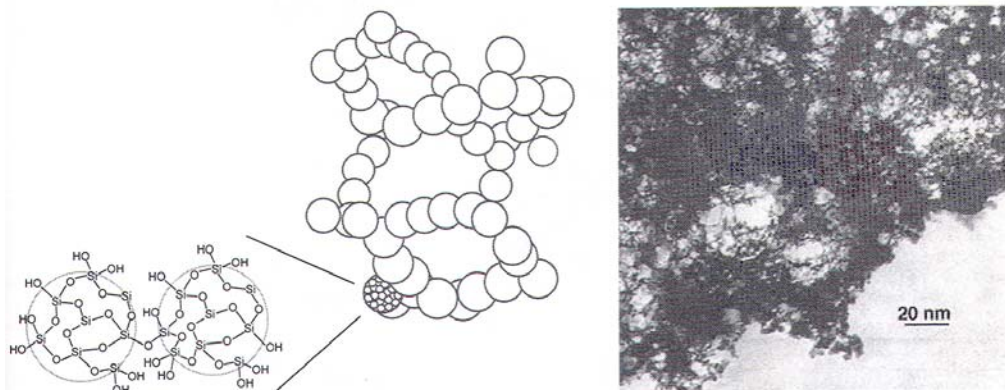
Aerogels

Supercritical drying of a gel.
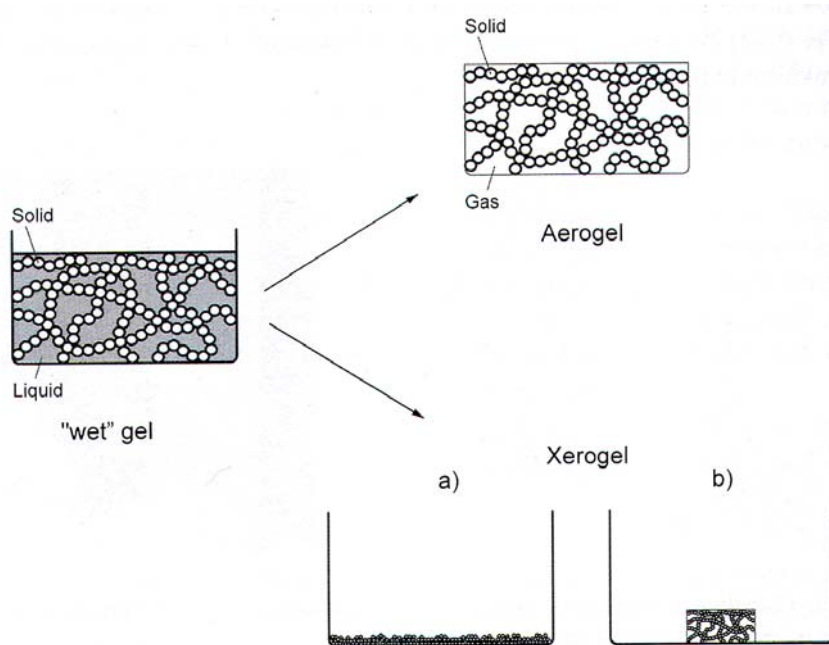Pores in the mesoporous range, 2-50 nm.
Built from e.g. nanometer sized silica spheres forming a three dimensional network. Bulk densities 0.004 – 0.5 g/cm^3. (Air: 0.00129 g/cm^3)

Figure 6-12. Silica aerogel; left: Schematic of the structure; right: a transmission electron microscopy (TEM) image.
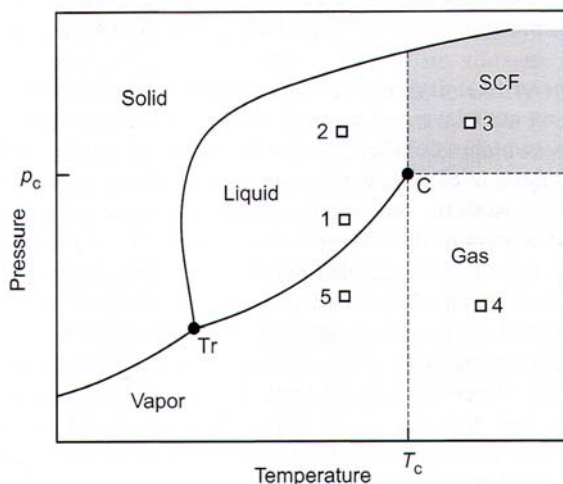
Drying

Figure 6-13. Top: Drying of a wet gel body to give an aerogel (the volume of the body remains approximately constant). Bottom: Conventional drying to give a xerogel powder (a) or monolith (b), associated with large shrinkage of the gel body.

Supercritical drying

Table 6-2. Comparison of some physical properties of gases, liquids and supercritical fluids.

Property	Gas	Liquid	Supercritical fluid
Density [$g \cdot cm^{-3}$]	10^{-4}–10^{-3}	0.6–1.4	0.1–1
Diffusion coefficient [$cm^2 \cdot s^{-1}$]	10^{-1}	10^{-5}	10^{-3}–10^{-4}
Solvency	No	Yes	Yes
Compressibility	Yes	No	Yes

A supercritical fluid is a gas, not a vapour.

Supercritical drying; follow the path 1-2-3-4-5.

Figure 6-14. Schematic pressure–temperature diagram for a pure compound. The shaded area represents the supercritical fluid region (SCF), where C is the critical point. Tr represents the triple point, and 1 to 5 are random points in the phase diagram (see text).

Table 4-4. Critical constants of some solvents.

Solvent	Critical temperature [°C]	Critical pressure [bar]
H_2O	374.1	221.2
NH_3	132.3	111.0
Cl_2	144	77.1
HCl	51.4	83.2
CO_2	31.3	73
SO_2	157.8	78.7
H_2S	100.4	90.1
CS_2	279	79
C_2H_5OH	243	63.8
CH_3NH_2	156.9	40.7
CH_3OH	240	81
$HCOOH$	308	–

Ambient pressure drying
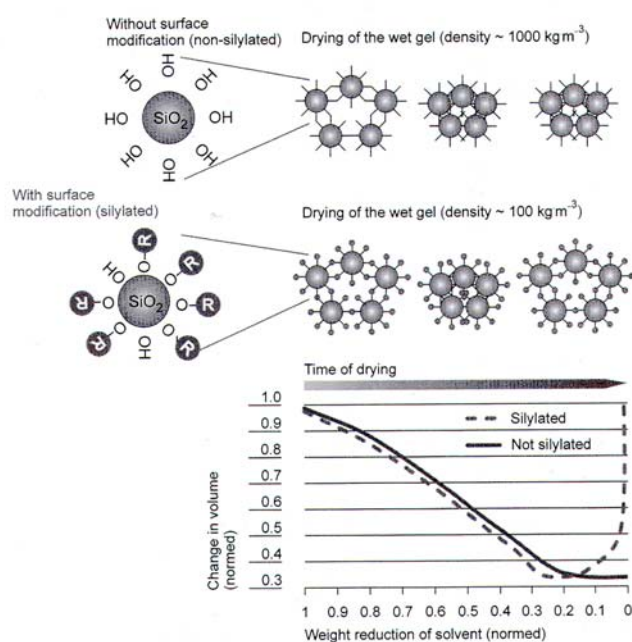
Figure 6-15. Ambient pressure drying; top: irreversible shrinking of an unmodified silica gel; middle: reversible shrinking of a silica gel modified by organic groups; bottom: volume change of unmodified and modified gels upon ambient pressure drying.

Capillary forces are the main reason for collapse of the gel during drying. Solutions:
Strengthen the network
and/or
Modify the contact angle between liquid and solid. (modifying the surface and variation of solvent properties)

Exchange the solvent with a water free solvent.
Silylate the Si-OH group (e.g. by chlorotrimethylsilane) (hydrophobic)
Wash and dry.
Shrink, then expand (spring-back)
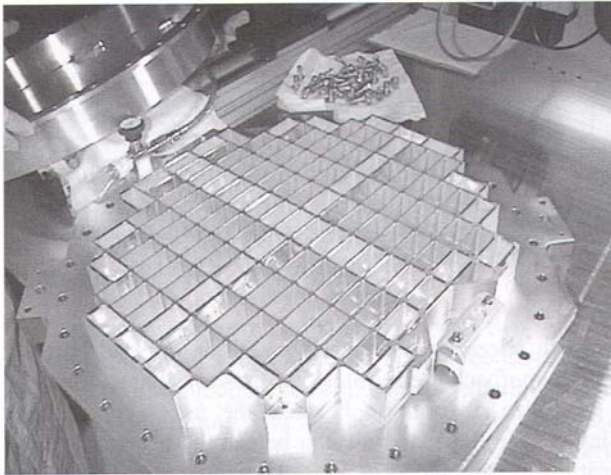
22

Applications

STARDUST
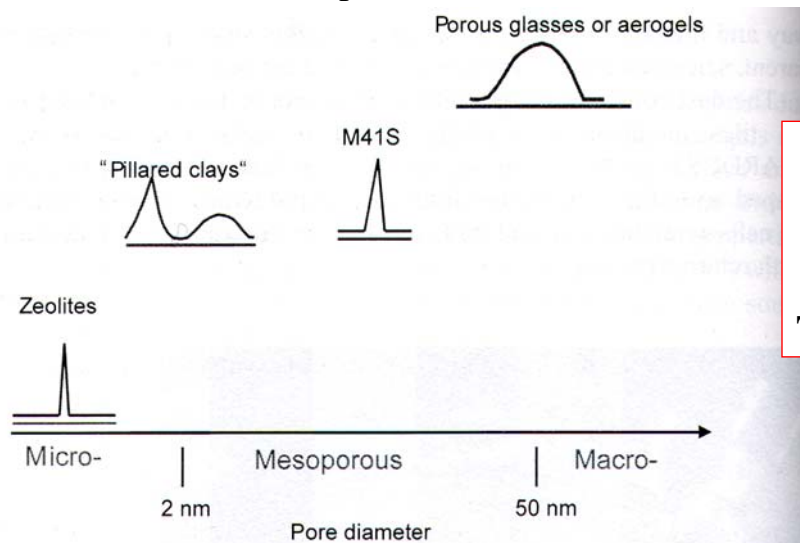

Figure 6-16.
Aerogel collector
for cosmic dust.

Porous solids with an ordered porosity

Templating approach to ordered porous solids: pores are arranged in a regular pattern with a narrow pore size distribution.
Zeolites: microporous
MCM /M41S) materials: mesoporous

Figure 6-17. Simplified picture of representative porous materials with different pore sizes and the corresponding pore size distributions.

Synthesis

Drying

Template removal

Microporous crystalline solids
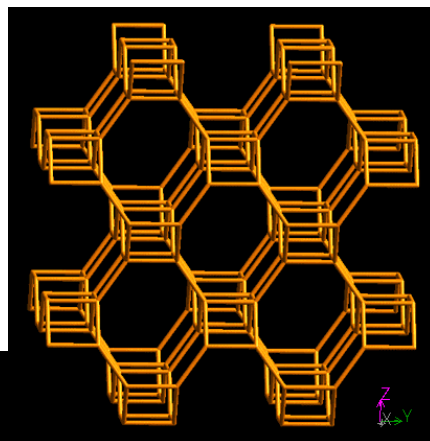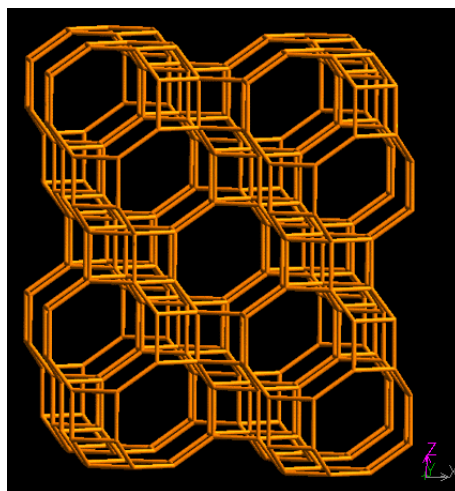
Microporous inorganic solids:
Zeolites
Zeotypes
(microporous aluminophosphates,
chlatrasils…)

Catalysts
Molecular sieves
Sorption
Ion exchange

Natural zeolites

Zeolites

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

The general chemical composition of a zeolite is:

$$M^n_{x/n}Si_{1-x}Al_xO_2 \cdot yH_2O$$

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 = ½. (Tetrahedra usually denoted T-atoms.

2) Open framework structure built from TO_4-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 readsorbed at lower temperatures.

5) Loewensteins 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:

$$M^n_{x/n}Si_{1-x}Al_xO_2 \cdot yH_2O$$

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

Microporous zeolite-like materials

Aluminophosphates, AlPO's III-V analogues of SiO_2: $AlPO_4$
E.g. Berlionite structurally similar to α-quartz

Microporous aluminophosphates (Flannigan, Union Carbide)

$AlPO_4$: 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. Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{+2}, Zn^{2+}.
SAPO: Silicon substitutes only for P, e.g. $H_xSi_xAlP_{1-x}O_4$
MAPO: divalent cations substitutes only for Al, i.e. $H_xM_xAl_{1-x}PO_4$
MeAPSO: e.g.. $H_{x+y}(Si_xMe_yAl_{1-y}P_{1-z})O_4$

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 arrnged 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.
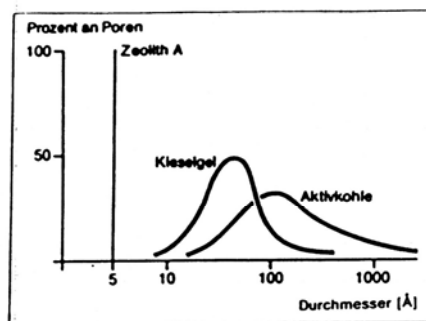

Fig. 7 Sammenligning af fordeling af porestørrelser i silikagel, aktivt kul og zeolit A.[19]
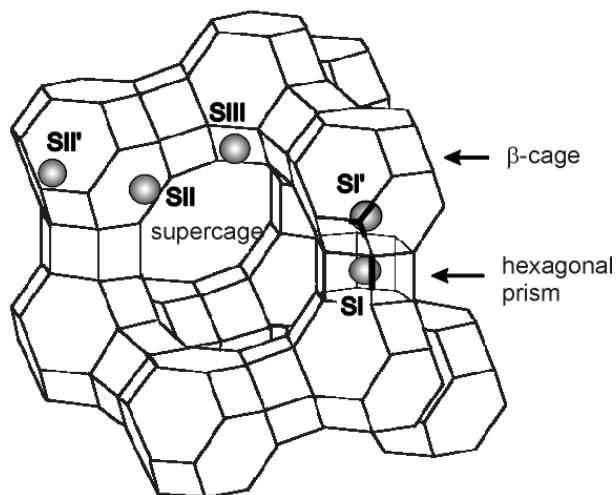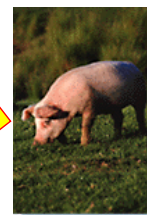
Also weaker interactions:
N_2-O_2 separation

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…
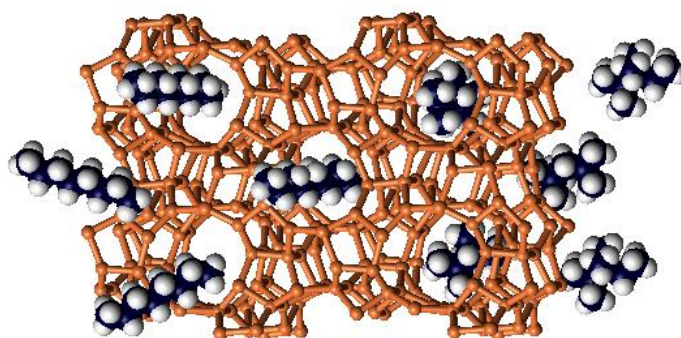

Catalysis

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.

Atlas of Zeolite Framework Types

http://www.iza-structure.org/databases/

ABW	ACO	AEI	AEL	AEN	AET	AFG	AFI	AFN	AFO	AFR	AFS
AFT	AFX	AFY	AHT	ANA	APC	APD	AST	ASV	ATN	ATO	ATS
ATT	ATV	AWO	AWW	BCT	*BEA	BEC	BIK	BOG	BPH	BRE	CAN
CAS	CDO	CFI	CGF	CGS	CHA	-CHI	-CLO	CON	CZP	DAC	DDR
DFO	DFT	DOH	DON	EAB	EDI	EMT	EON	EPI	ERI	ESV	ETR
EUO	FAU	FER	FRA	GIS	GIU	GME	GON	GOO	HEU	IFR	IHW
ISV	ITE	ITH	ITW	IWR	IWW	JBW	KFI	LAU	LEV	LIO	-LIT
LOS	LOV	LTA	LTL	LTN	MAR	MAZ	MEI	MEL	MEP	MER	MFI
MFS	MON	MOR	MOZ	MSO	MTF	MTN	MTT	MTW	MWW	NAB	NAT
NES	NON	NPO	NSI	OBW	OFF	OSI	OSO	OWE	-PAR	PAU	PHI
PON	RHO	-RON	RRO	RSN	RTE	RTH	RUT	RWR	RWY	SAO	SAS
SAT	SAV	SBE	SBS	SBT	SFE	SFF	SFG	SFH	SFN	SFO	SGT
SOD	SOS	SSY	STF	STI	STT	TER	THO	TON	TSC	UEI	UFI
UOZ	USI	UTL	VET	VFI	VNI	VSV	WEI	-WEN	YUG	ZON	

Zeolite synthesis

The first laboratory synthesis of a zeolite is attributed to Deville, who in 1862 synthesized levyne (levynite) $Ca_9 [Al_{18}Si_{36}O_{108}] \cdot 50 H_2O$ by heating potassium silicate and sodium aluminate in a glass ampoule.

A large increase in synthesis of zeolites was seen after 1940 when X-ray diffraction became a common tool for analysis.

http://www.iza-online.org/synthesis/default.htm

Usually synthesized from a basic medium (sol or gel) under mild to medium hard hydrothermal conditions (70-350˚C). Mainly obtained as powder ar very small crystals.

Contains: Water, silica source, alumina source, pH-regulators, templates, (catalysts, nucleation centers…)

reaction ordinate (time / temperature)

E

SiO$_2$ (am)

E_a'

zeolite

E_a"

quartz
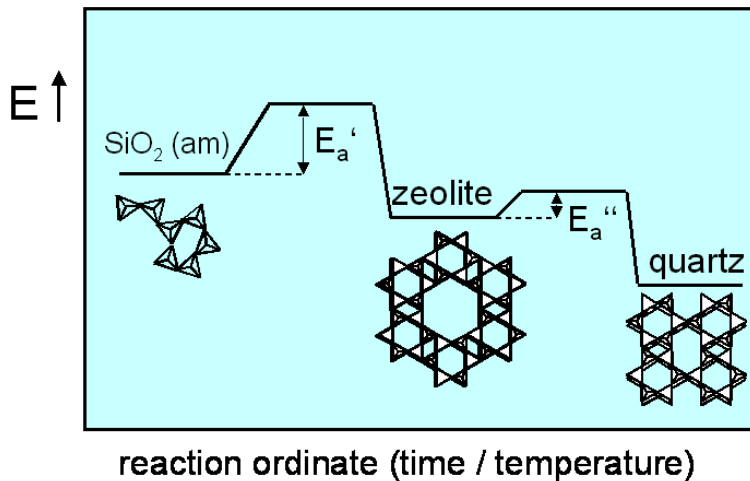
Parameters:

- **Composition**
- **Temperature**
- **pH**
- **temperature ramps**
- **ageing conditions**
- **stirring rate**
- **order of mixing**
etcetcetc

Low silica content →
low synthesis temperature, 70-100˚C

More siliceous → hydrothermal

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Zeolite synthesis is still mainly done by trial and error. And some knowledge and experience.

Some rules-of-thumb for zeolite synthesis:

Table 6-3. Influence of different components of the reaction mixture on the zeolite structure.

Reaction mixture composition	Primary influence
SiO_2/Al_2O_3 ratio	framework composition
H_2O/SiO_2 ratio	rate; crystallization mechanism
OH^-/SiO_2 ratio	silicate molecular weight
inorganic cations/SiO_2 ratio	structure; cation distribution
organic additives/SiO_2 ratio	structure; framework Al content

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Templates

Cations (and hydrated cations) acts as counterions, but also have a templating effect. Templates stabilize the open framework by filling the empty space.
Added templates, e.g. amines and quaternary ammonium ions
Goal: targeted synthesis of microporous structures by template control.
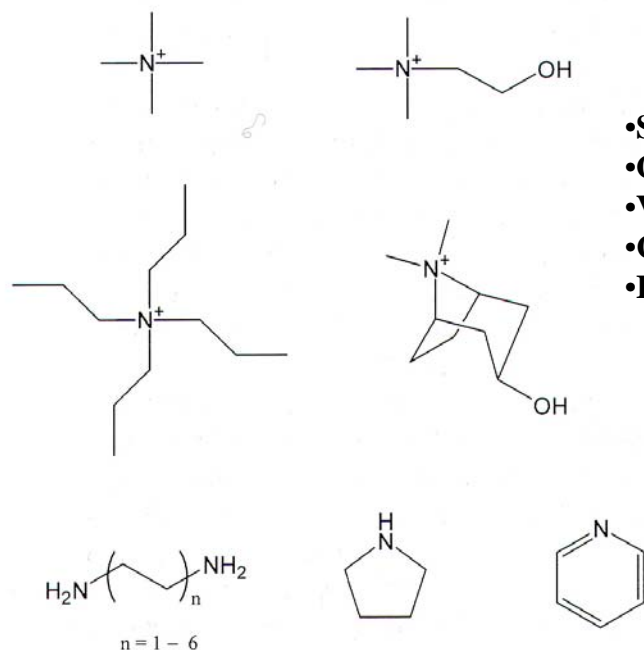
•**Structure directing or templating agent**
•**Gel modifier (e.g. influencing Si/Al ratio)**
•**Void filler**
•**Change the formation and aging of gels**
•**Influence the crystallization process**

Figure 6-19. Some representative ammonium or amino compounds used as organic additives in zeolite syntheses.

n = 1 – 6

Templates as structure directing agents

TPA⁺ → ZSM-5

TEA⁺, EDA, ethanolamine, propanolamine, alcohol, glycerin, morpholine, hexanediol, TPA⁺ → ZSM-5

TMA⁺ → A, X, Y, Sodalith, P, S, R, ZSM-6, ZSM-47, Omega
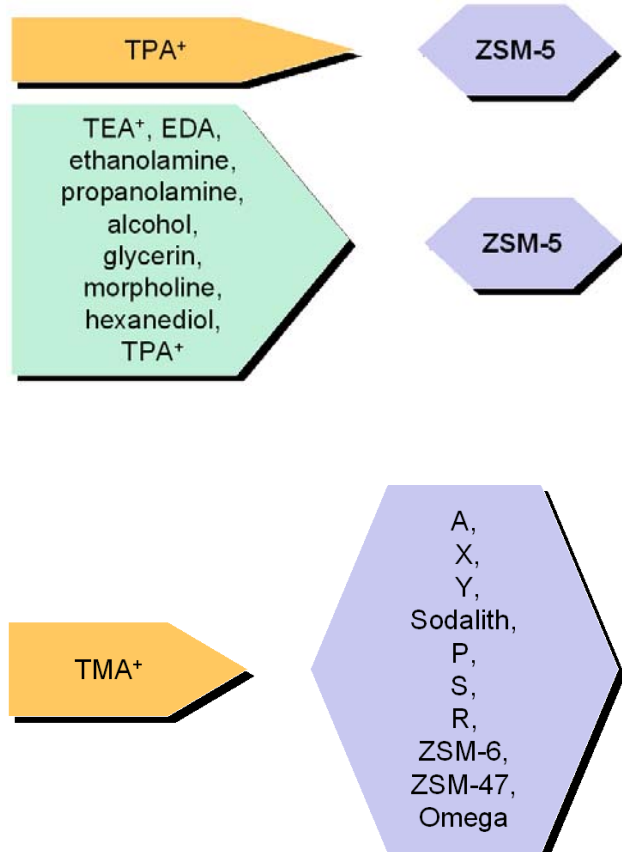
Addition of other templates have increased the number of zeolite type structures prepared by leading to hitherto unknown zeolites and other microporous materials.
Also, it has made it possible to synthesize zeolites with various Si/Al ratios, e.g. zeolite LTA with a Si/Al ratio > 1.
Clearly the template has a structure directing effect. But the templating effect is still not understood, and it is not possible to predict which zeolite structure is produced by a certain template.

Combinatorial approach (SINTEF)
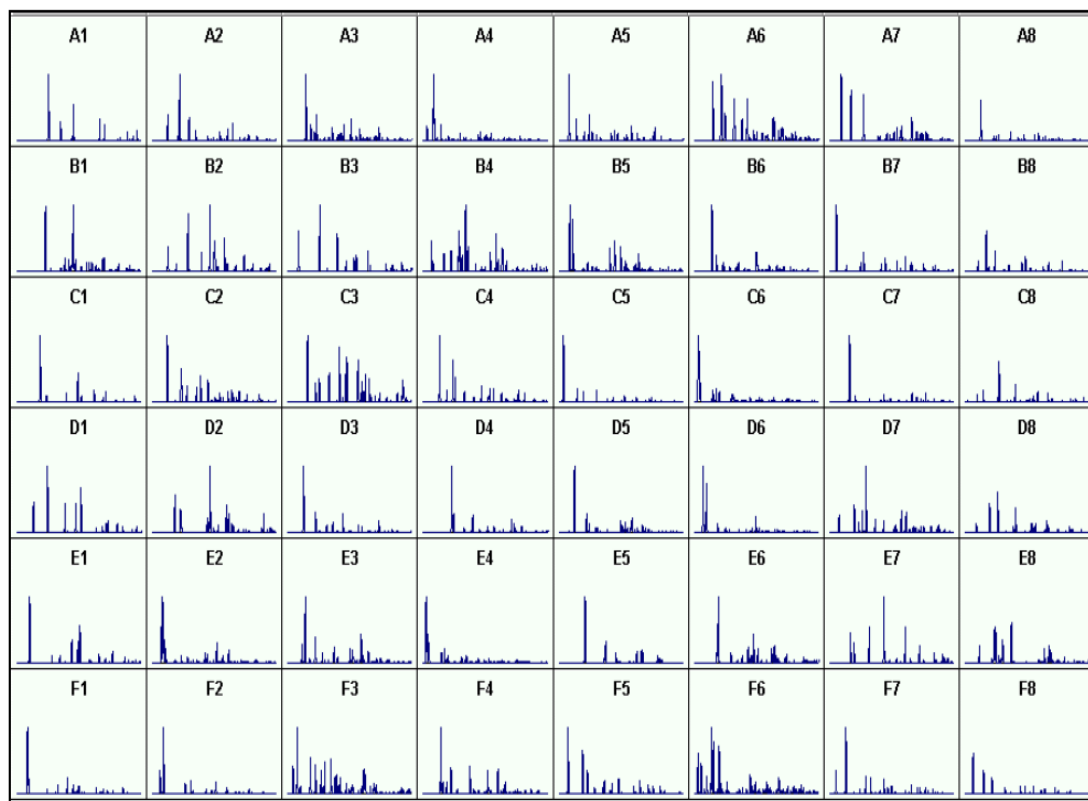
In-situ studies; understanding nucleation and crystallization in hydrothermal synthesis of microporous materials.
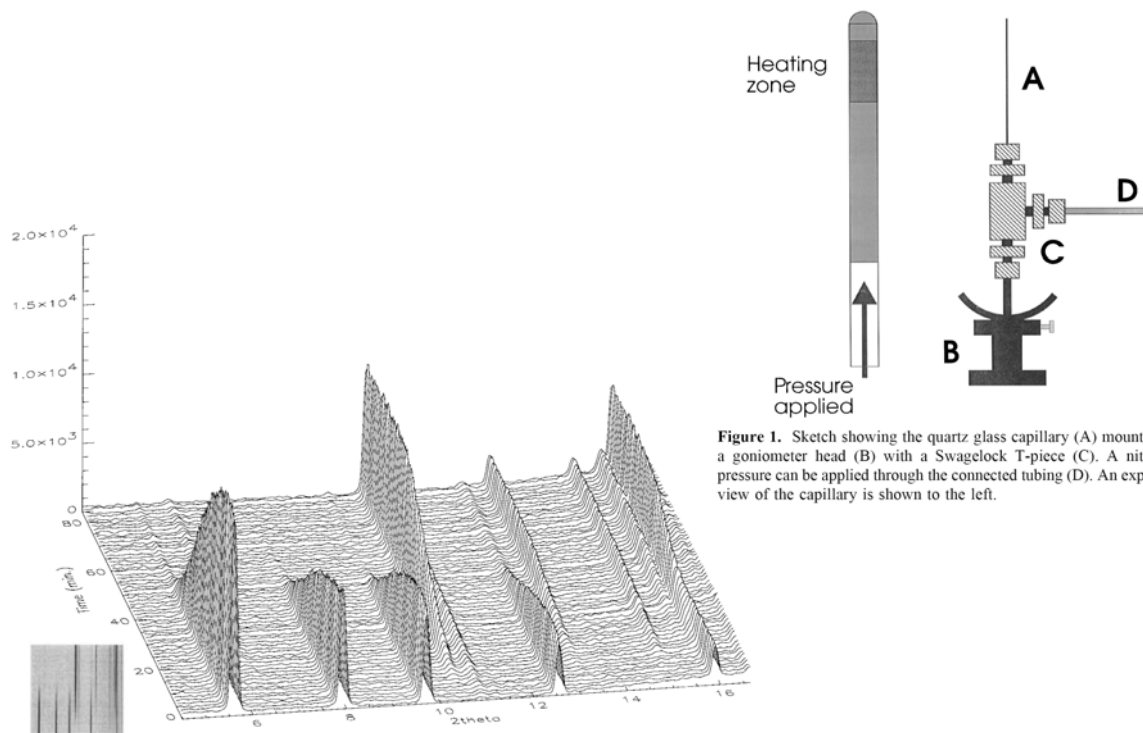
Figure 1. Sketch showing the quartz glass capillary (A) mounted on a goniometer head (B) with a Swagelock T-piece (C). A nitrogen pressure can be applied through the connected tubing (D). An exploded view of the capillary is shown to the left.

Figure 4. 3-Dimensional plot of powder diffraction profiles as a function of time during the hydrothermal conversion of zeolite Li/Na-LTA to zeolite Li-A(BW). The wavelength used was 1.1727(2) Å. The temperature was ramped to 200 °C in 5 min and kept at that temperature.

Zeolite (zeotype) structure

Figure 6-20. Six-membered ring structure of [SiO$_4$] and [AlO$_4$] tetrahedra (left) that can be found in zeolites, and its schematic representation as a CBU (right).

Representation of a six membered ring of TO$_4$-tetrahedra
(Contains 6 Si and 6 O)
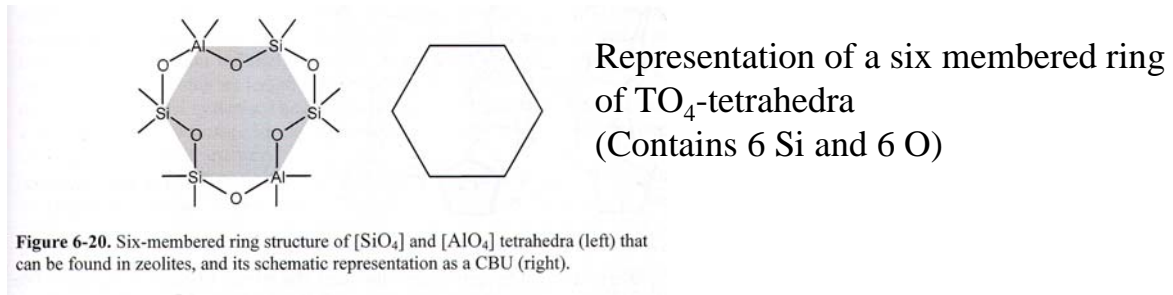
- The basic (primary) building blocks are tetrahedra
- All tetrahedra share corners
- The arrangement of the building blocks is periodic (crystalline)

Building units:
- Primary or basic building units (BBU): Tetrahedron
- Secondary or composite building units (CBU): polymeric structures (rings, prisms etc.)
- Tertiary building units: Larger cages

The flexibility of the T-O-T bond angle (120-180°) allows a large number of CBUs to exist, and results in a wealth of different structures to be constructed

---

CBUs

Zeolite structures may be seen as built from CBUs. For instance the ZSM-5 framework may be built from 5-1 units.

It is important not to assume that the synthesis of zeotype materials occur via assembly of CBUs floating around in the synthesis mixture.
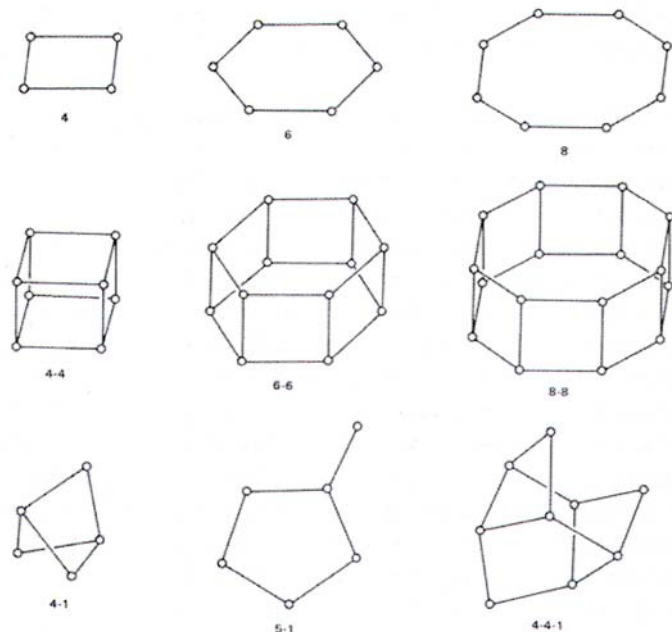
Figure 6-21. Composite building units (CBUs) found in zeolite structures.

Figure 6-22. Network structure of ZSM-5.

Rings and pore size

Figure 6-23. Examples of three types of pore openings in zeolites: Erionite (left) contains an 8-ring pore opening, ZSM-5 (center) a 10-ring system, and type Y zeolite (right) a 12-ring pore system (the diameters are given in Å).
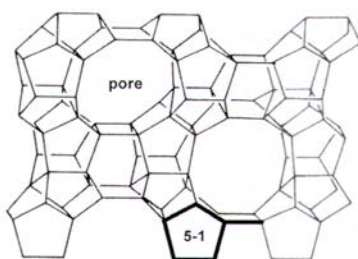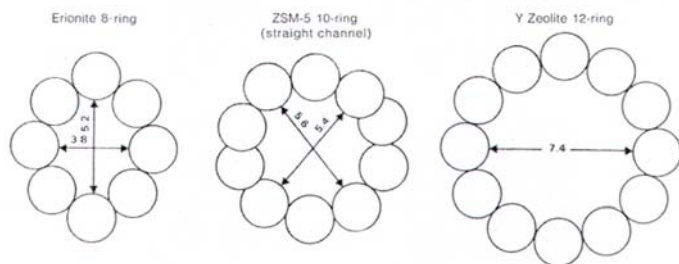
Pore openings or rings in zeolites. 8-, 10-, and 12-rings shown as connecting spheres.
The openings may have various shapes, influencing the kinetic diameter.

Analcime 8-ring
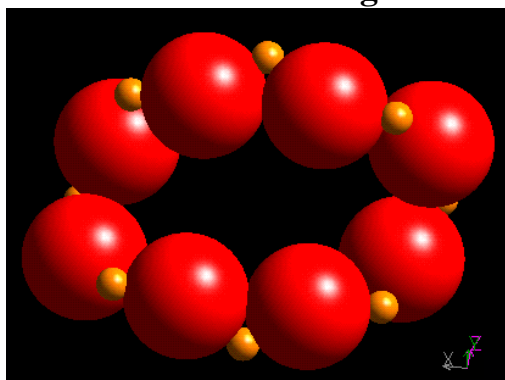
Edingtonite 8-ring
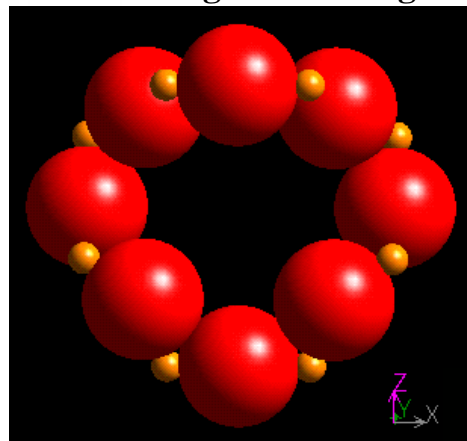
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Cages and channels

Zeolite LTA. May be seen as built from the CBUs: 8, 4-4, 6-2, 6, 1-4-1, 4
May be seen as built from interconnected sodalite cages (β-cages)
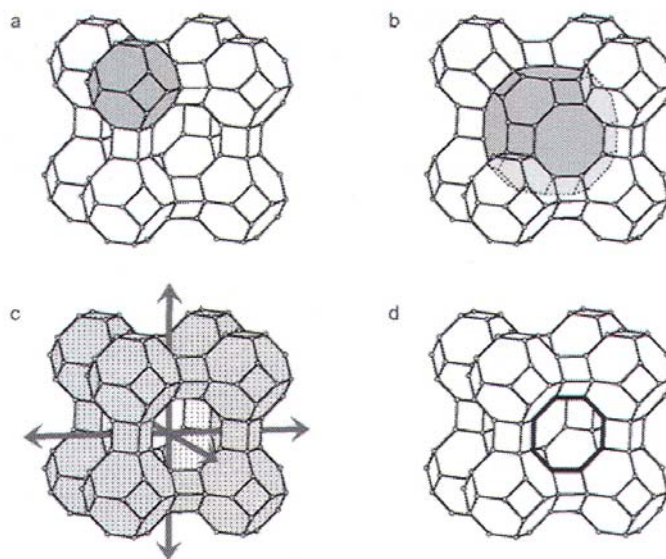
Figure 6-24. Features of the pores in zeolite A: a) the sodalite cage, b) the α-cavity, c) the three-dimensional channel system, and d) the 8-membered ring defining the effective channel width.

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Linking CBUs, composite building units
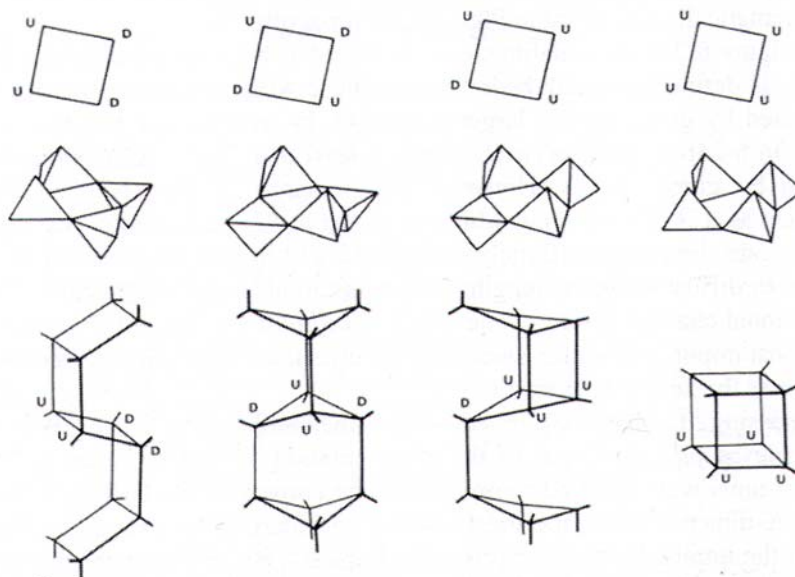
cancrinite
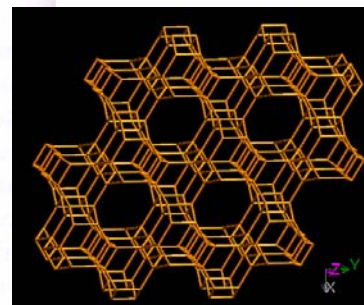
Figure 6-25. Possible linkages for the 4-membered ring CBU. Upper row: schematic representation of the CBU; U = up and D = down. Center row: the tetrahedral view. Bottom row: chain sequences formed from the differently oriented CBUs.

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Dimensionality
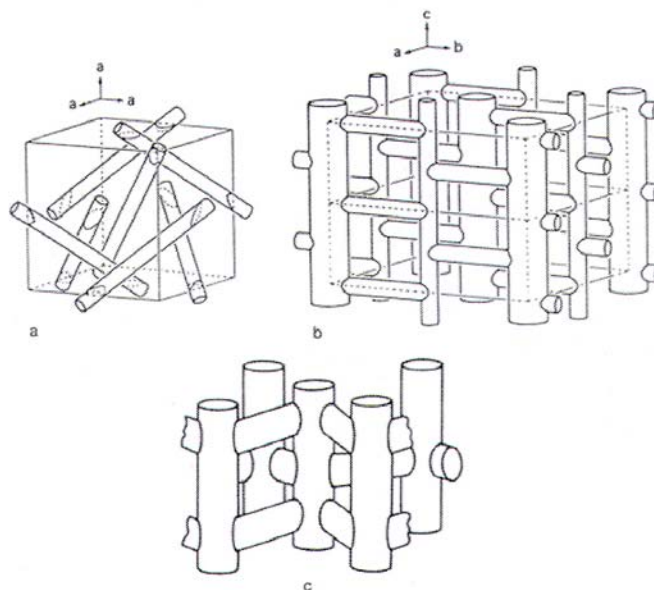
Figure 6-26. Channel representation for examples of one-, two-, and three-dimensional systems; a) analcime; b) mordenite; c) ZSM-5.

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Metal-organic framework materials (MOFs)
Porous three dimensional coordination polymers
Hybrid materials

A new class of ordered microporous materials
are the metalorganic framework materials.
These are built by linking inorganic parts
(connector) (metal ions, clusters…) using
organic linkers.
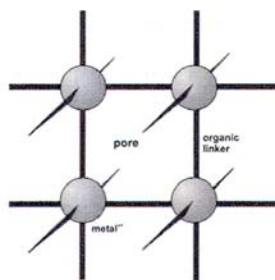
Figure 6-27. Schematic representation of a MOF.
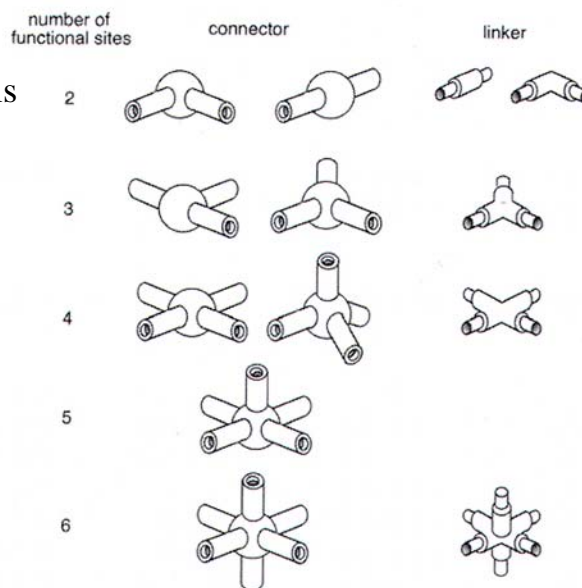
Figure 6-28. Basic building units (BBUs) of coordination polymers.

Connectors and linkers

- The connectors are mostly transition
  metal or lanthanoid ions. Coordination
  number varies. May also be polynuclear
  clusters.

- The linkers are organic (or inorganic) bi-
  or multidentate.

- The interaction between connectors and
  linkers are coordinative or ionic (not
  covalent as in zeolites)

  Popular linkers may contain
  nitrogen or oxygen donor atoms,
  e.g. 4,4'-bipyridine, benzene-1,4-
  dicarboxylate (terephthalate).
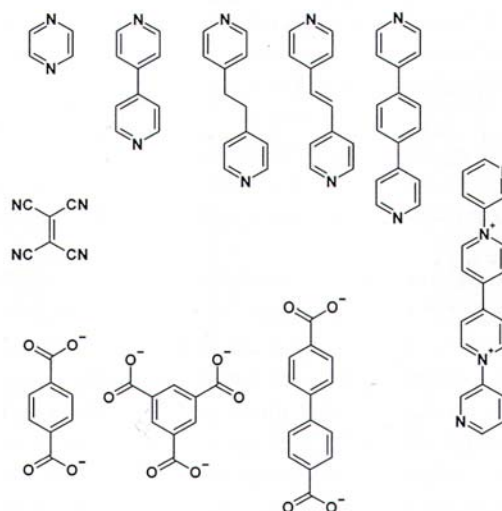
Figure 6-29. Examples of linkers used in MOFs

Synthesis

The variety of different connectors and linkers makes it possible to construct a variety of 1-, 2- and 3-dimensional structures. The design of linkers is especially efficient in attempting to form new structure types.

Standard coordination chemistry methods are used, where metal ions are reacted with an organic ligand. The conditions are low temperature and hydrothermal/solvothermal synthesis.
This may be seen as "self-assembly" of basic building units. The products are usually not kinetically but thermodynamically determined.
The flexibility/rigidity of the linker is important for the properties, e.g. the possibility of forming porous materials. Most used linker are fairly rigid.
Also during formation the rigidity of the linkers are important; a very flexible linker may enable several possible conformations, resulting in poorly crystalline materials.

Frameworks

Frameworks obtained by using various connectors linked by linear linkers.

3-D MOF materials are among those with the largest pores for crystalline materials. When synthesized the pores will be filled by guest or template molecules. In order to obtain porosity it is necessary to remove the guest species. This is difficult due to a generally low thermal stability of the materials. (May also fill space by forming e.g. two interpenetrating frameworks). Also exceptionally high surface areas may be obtained. (several thousand square meters per gram)
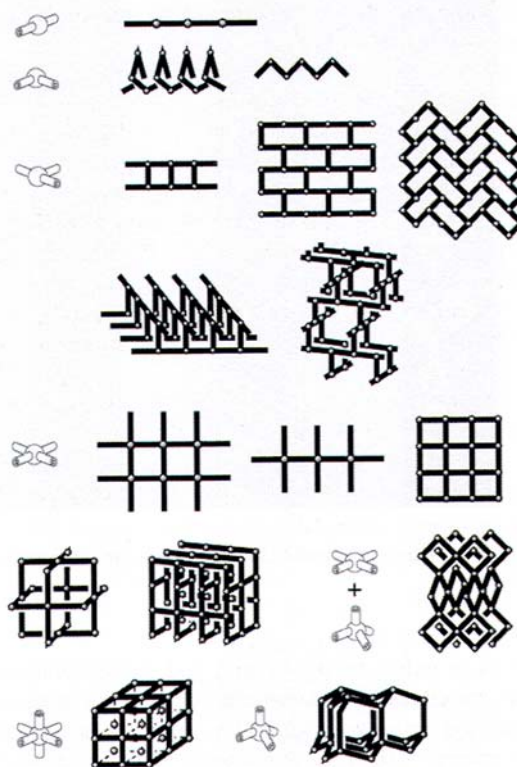
Figure 6-30. Examples for structural frameworks that can be constructed from 2–6 coordinated connectors and linear linkers.

Zn$_4$O(terephthalate) (Yaghi)
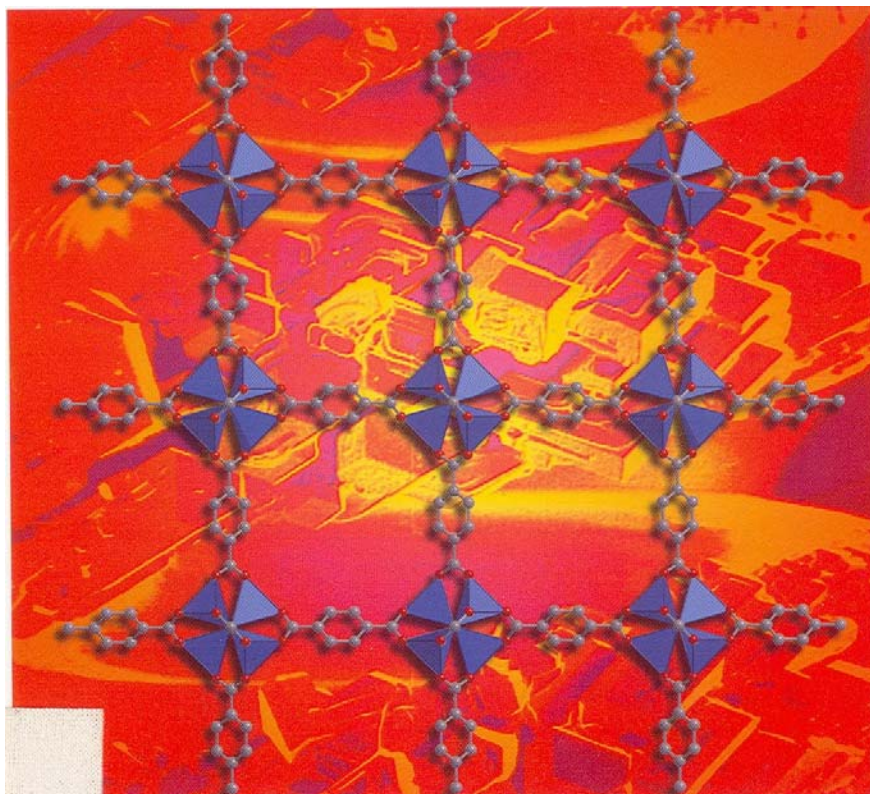
Very low density: (0.59g/cm^3)

Framework stable up to 300˚C.

Very high surface area.

Classification

- 1st generation: The framework is only maintaines with the guest molecules present, and collapses upon removal of the guests.
- 2nd generation: The framework is stable and robust, and have porosity when removing the guest species.
- 3rd generation: the framework is flexible and dynamic and responds to external stimuli.

2nd and 3rd generation materials may be used for gas storage or as catalysts.

Advantages:

- In principle the dimensions and shape of the channels are easily tunable by changing the organic linkers.
- Functionality may be built into the linkers.
- The materials are light weight, making it possible to obtain large surface areas.

Mesoporous solids with ordered porosity.

Pore size is important for applications.
IUPAC, three pore size regimes, associated with transport mechanisms:

- *Microporous*, smaller than 2 nm
- *Mesoporous*, between 2 and 50 nm
- *Macroporous*, larger than 50 nm

New development in 1992 by Mobil: ordered mesoporous materials were made by using supramolecular species as templates instead of solvated cations or organic molecules.

Amphiphilic surfactant molecules (lyotropic liquid crystals) were used.
- **Pore range from 2 to 10 nm.**
- **Large specific surface area**
- **Large pore volume**
- **Monomodal narrow distribution of of pore sizes.**

Pore walls are amorphous (not crystalline)

M41S

The M41S family are of interest e.g. as catalysts, catalyst supports, adsorbents, host structures for nanometer sized guest compounds.
MCM (Mobil Composition of Matter)
MCM-41: One dimensional, hexagonal ordered, channel structure
MCM-48: Cubic three-dimensional channel structure (bicontinuous)
MCM-50: Lamellar two dimensional. Silica layers, surfactant bilayers

MCM-41   MCM-48   lamellar
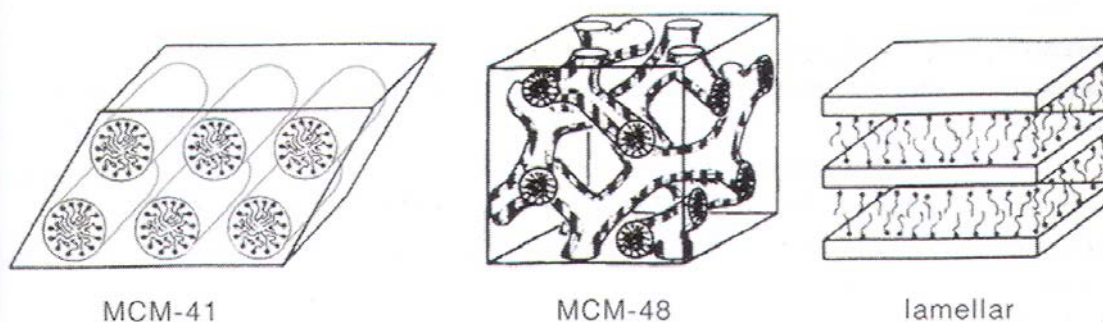
Figure 6-32. Different structural types of the M41S family: hexagonal MCM-41; bicontinuous cubic MCM-48; lamellar MCM-50.

Synthesis

Ingredients for MCM synthesis:
Water, an amphophilic molecule, a soluble inorganic precursor and a catalyst
(Why a catalyst??)

Figure 6-33.
Amphiphilic surfactant
molecule.

Synthesis conditions from -14 to 180°C.

Synthesis:
- **Formation of supramolecular arrangement of molecules,**
- **Templating**
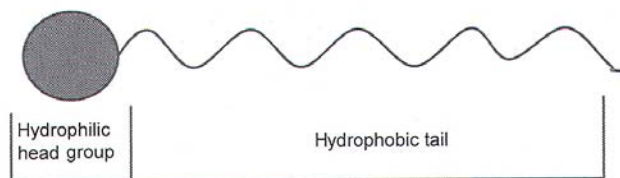- **Removal of template**

Supramolecular arrangements

The surfactants may arrange themselves in supramolecular arrays, e.g. micelles.

e.g. CTAB: cetyltrimethylamonium bromide, $CH_3(CH_2)_{15}N(CH_3)_3N^+Br^-$
Forms spherical micelles.

Size, extent, shape of micelles and aggregation into liquid crystals depends on
the concentration and temperature.

Low concentration: individual molecules
Increasing concentration:
- Small spherical micelles above the micelle concentration (cmc)
- Micelles coalesce into elongatede cylindrical micelles
- Liquid crystals form at slightly higher concentrations:
    - Hexagonal close packed cylinders
    - Bicontinous cubic arrangement
    - Lamellar arrangement
- At even higher concentrations inverse phases may exist.
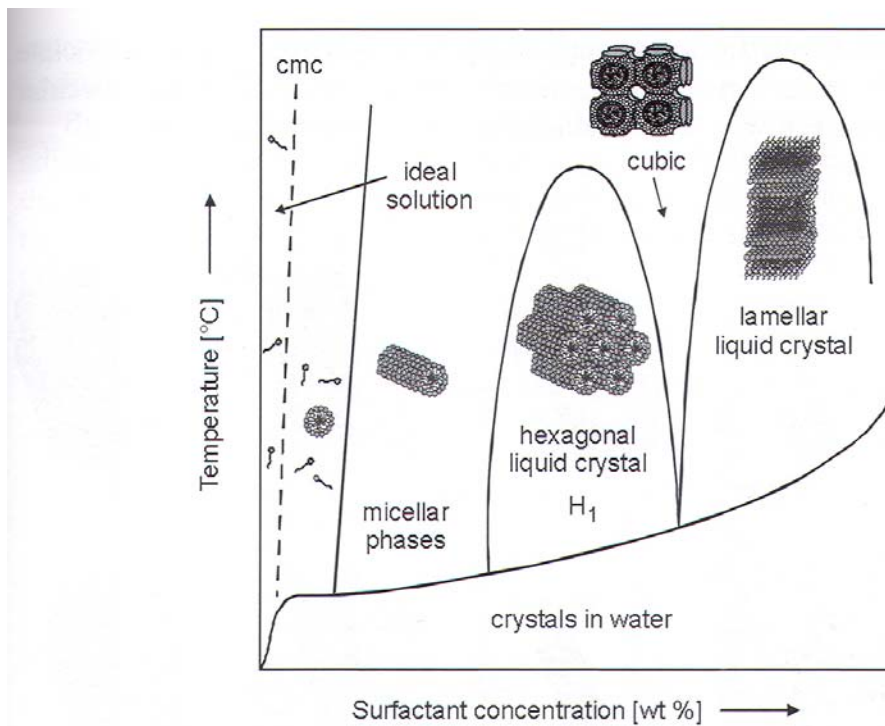
Phase diagrams

Figure 6-34. Schematic phase diagram for a surfactant in water.

Templating

MCM-41 synthesized under hydrothermal conditions using CTAB
Two mechanisms were proposed:

1) Liquid crystal initiated pathway: Organization of the surfactant molecules (independent of the polycondensation). Followed by formation of the siliceous framework around the aggregates,
2) Silicate anion-initiated pathway: The siliceous species associate with the surfactant molecules, and then it organizes into a supramolecular array.

Pathways

Figure 6-35. Possible mechanistic pathways for the formation of MCM-41; the gray shading represents the silica.

Tuning
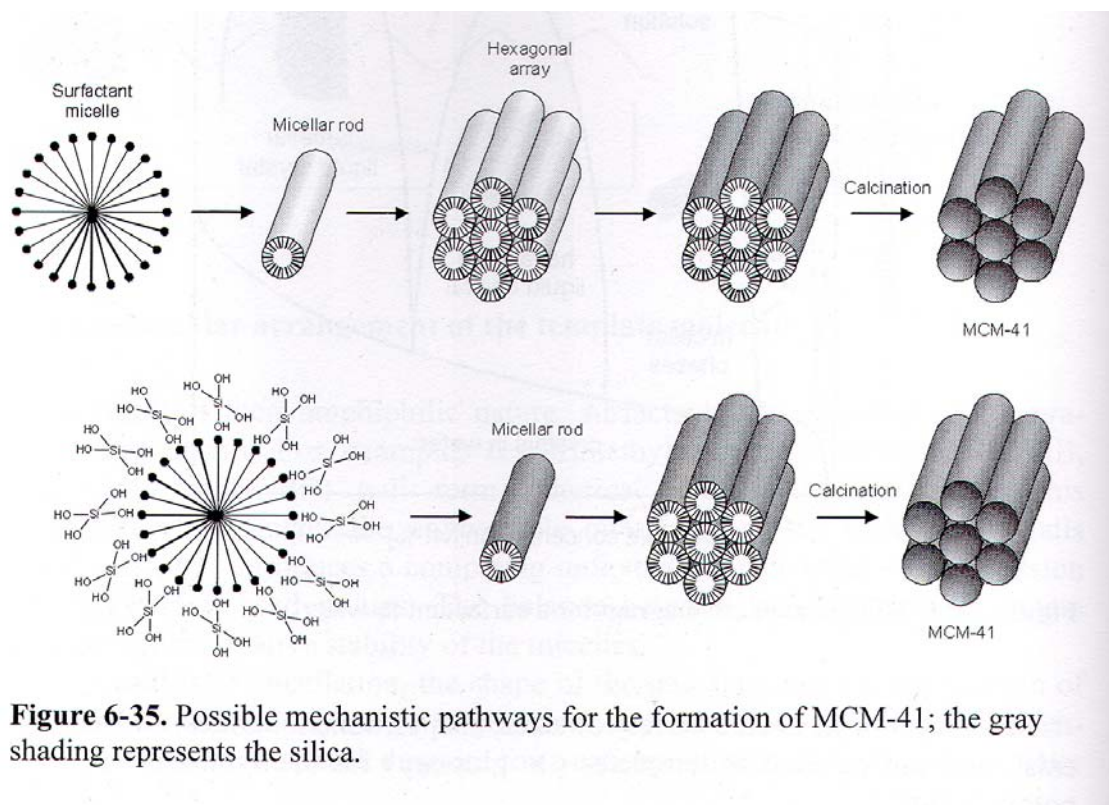
Synthesis by electrostatic templating procedure: surfactants with cationic head groups and anionic inorganic building units: S^+I^-.
Other combinations are possible, e.g.
Reversed charge: S^-I^+
Counter ion mediated: $S^+X^-I^+$ or $S^-M^+I^-$ (X^- e.g. halide, M^+ e.g. alkali)
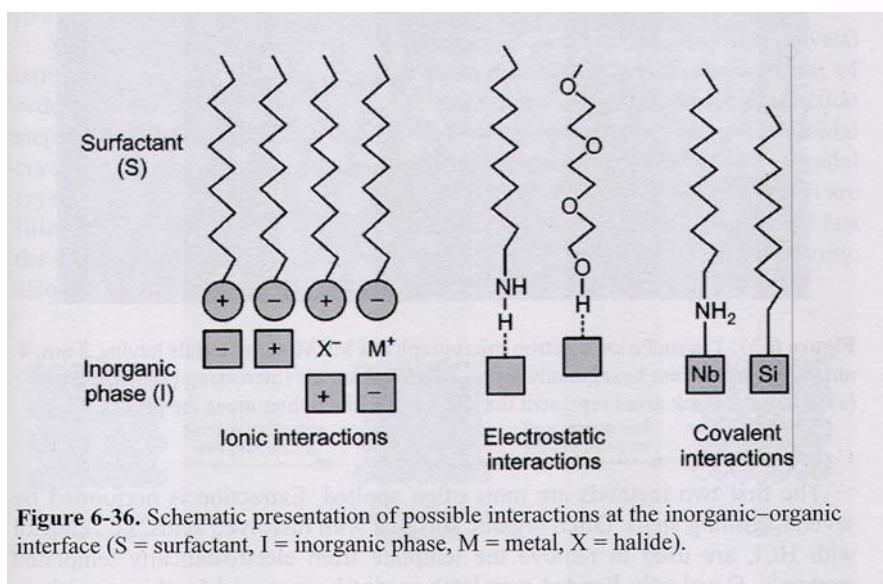
Figure 6-36. Schematic presentation of possible interactions at the inorganic–organic interface (S = surfactant, I = inorganic phase, M = metal, X = halide).

Removal of template

In order to create porosity the template must be removed.
Several different ways are possible:

- Solvent extraction
- Calcination
- Oxygen plasma treatment
- Supercritical drying

Extraction often with organic solvents with dissolved acids. (e.g. EtOH w. HCl)
(Cannot remove covalently bonded molecules)
Calcination typically at 4-600˚C in e.g. N_2 or air.

Framework structures (hexagonal or cubic MCM phases) may survive template removal. Lamellar phases collapse.

Design of mesoporous ordered materials with dieerent pore sizes is possible by tuning the template molecules.
Mesoporous materials containing elements other than Si have been produced.

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MCM-41, TEM images
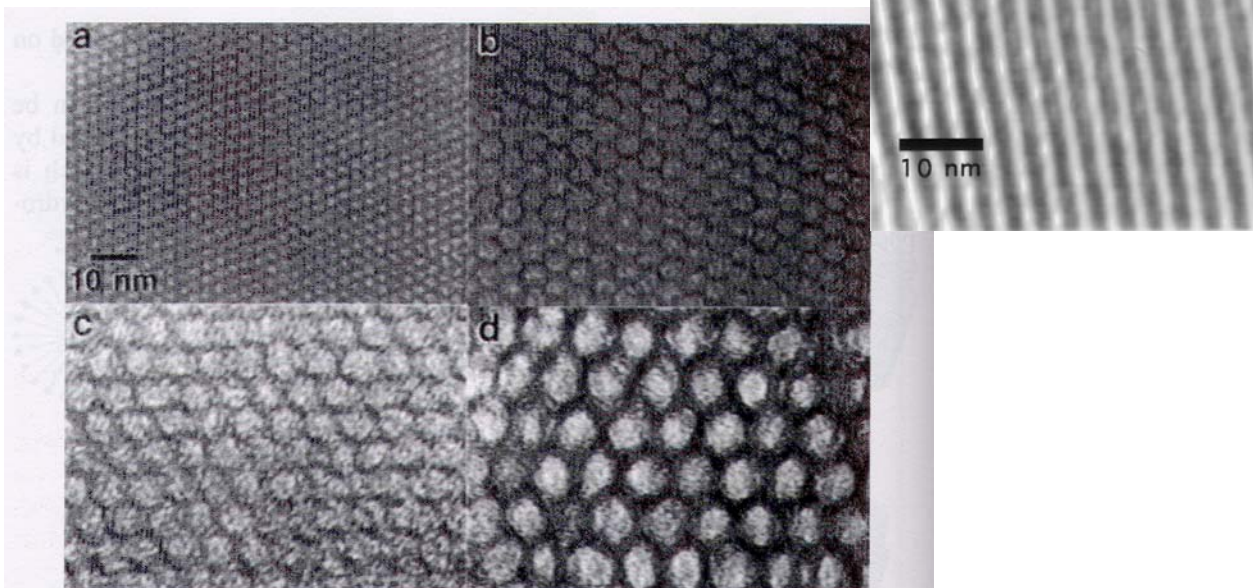
Figure 6-37. Transmission electron micrographs of MCM-41 materials having 2 nm, 4 nm, 6 nm, and 10 nm hexagonally arranged pore channels (increasing pore size from (a) to (d); the black areas represent the silica walls, the lighter areas the pores).

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Macroporous solids with ordered porosity

Prepared by e.g. packing of solid materials. (as described with metal foams)

Colloidal crystal packing:
1) Colloidal crystal formed by closed packed monodisperse spheres (e.g. latex or silica) (Similar to Opals)
2) The interstitial space is filled with a liquid precursor
3) The precursor solidifies
4) The template is removed

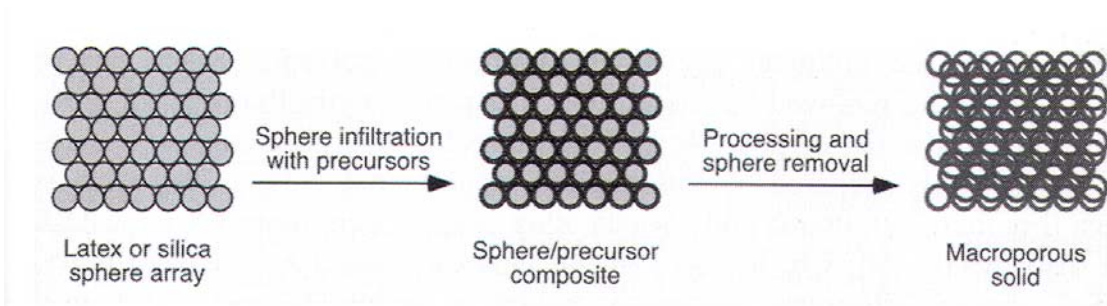Inverse replica of the template array (also called inverse opal)

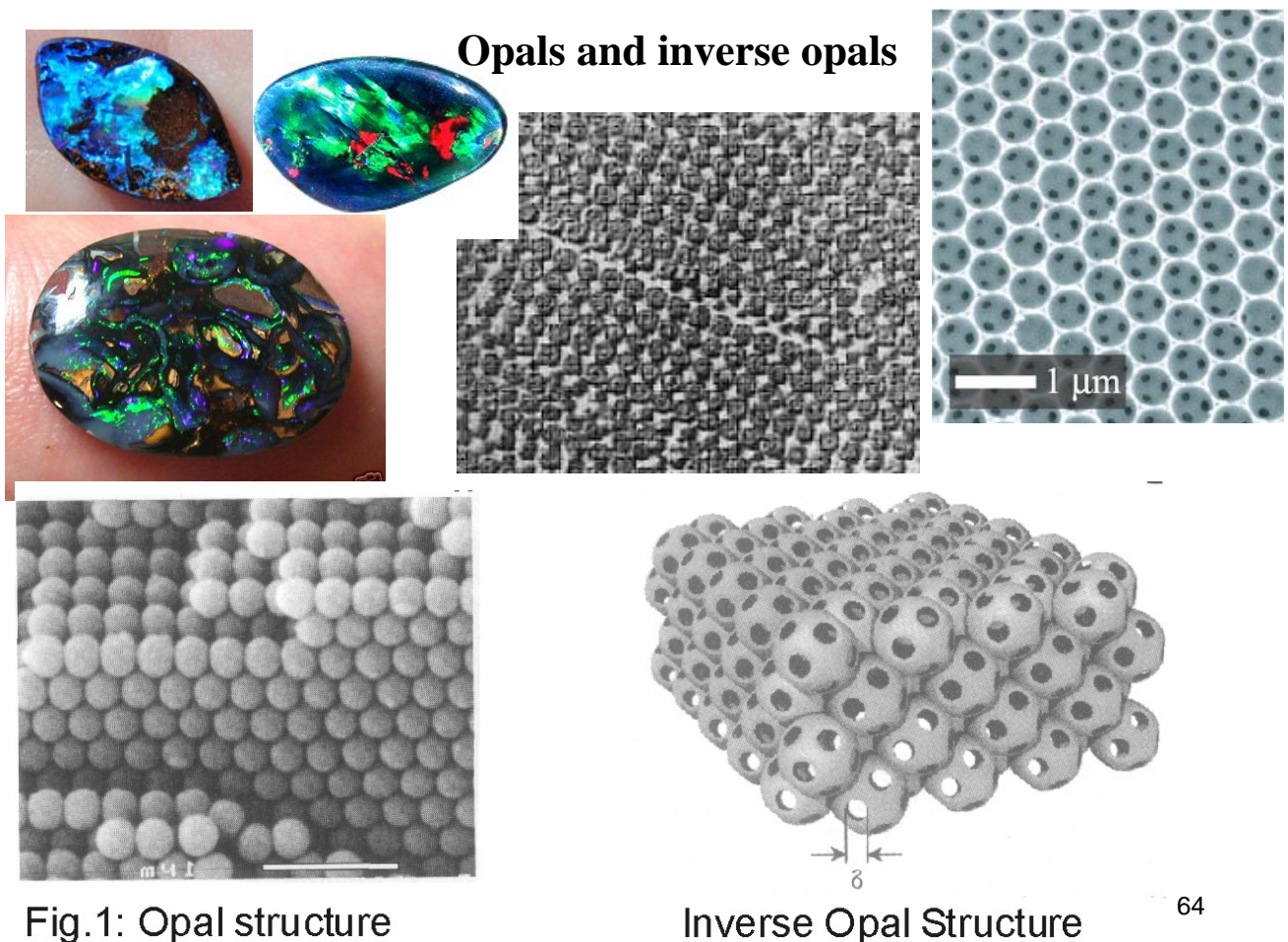Figure 6-38. General synthesis scheme for periodic macroporous solids.

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Opals and inverse opals

Fig.1: Opal structure

Inverse Opal Structure

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Spheres

Spheres for packing into either fcc or hcp. Requirements:
- The template must be removable
- Must be compatible with process conditions
- The precursor solution must wet the particles
- Must have a narrow size distribution.

Narrow it down to two classes:
- Silica spheres prodused by the Stöber process (50 nm – 2 μm)

Organic polymer spheres produced from emulsion polymerization.

Stöber process:
TEOS is reacted at high pH (ammonia solution) with large excess of water. Monodisperse silica spheres between 0.1 and 1 μm.

Impregnating

Impregnating with a low viscodity liquid, solutions, dispersions.
Metal alkoxides, molten metals, salt solutions, colloidal gold nanoparticles, vapours (Precursors for CVD)

Removal of the template by extraction (e.g. HF for silica) or calcination (may be simultaneous with the solidification step)
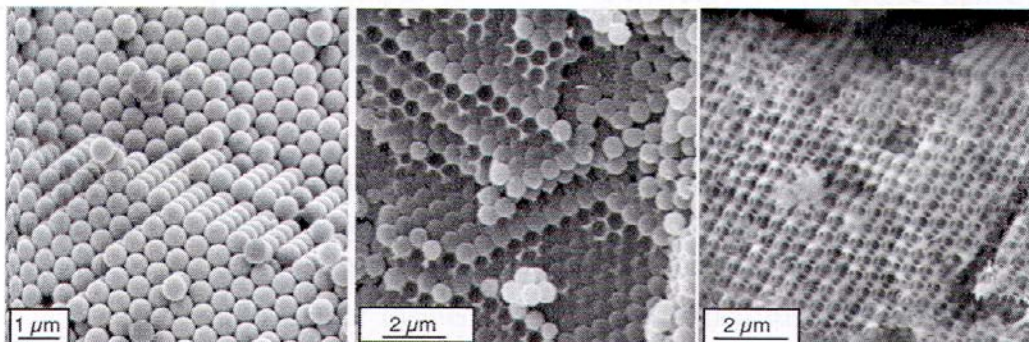
Figure 6-39. Scanning electron micrographs of the different processing steps of a periodic macroporous silica material prepared from a colloidal crystal polystyrene template.

Functional groups incorporated into porous materials
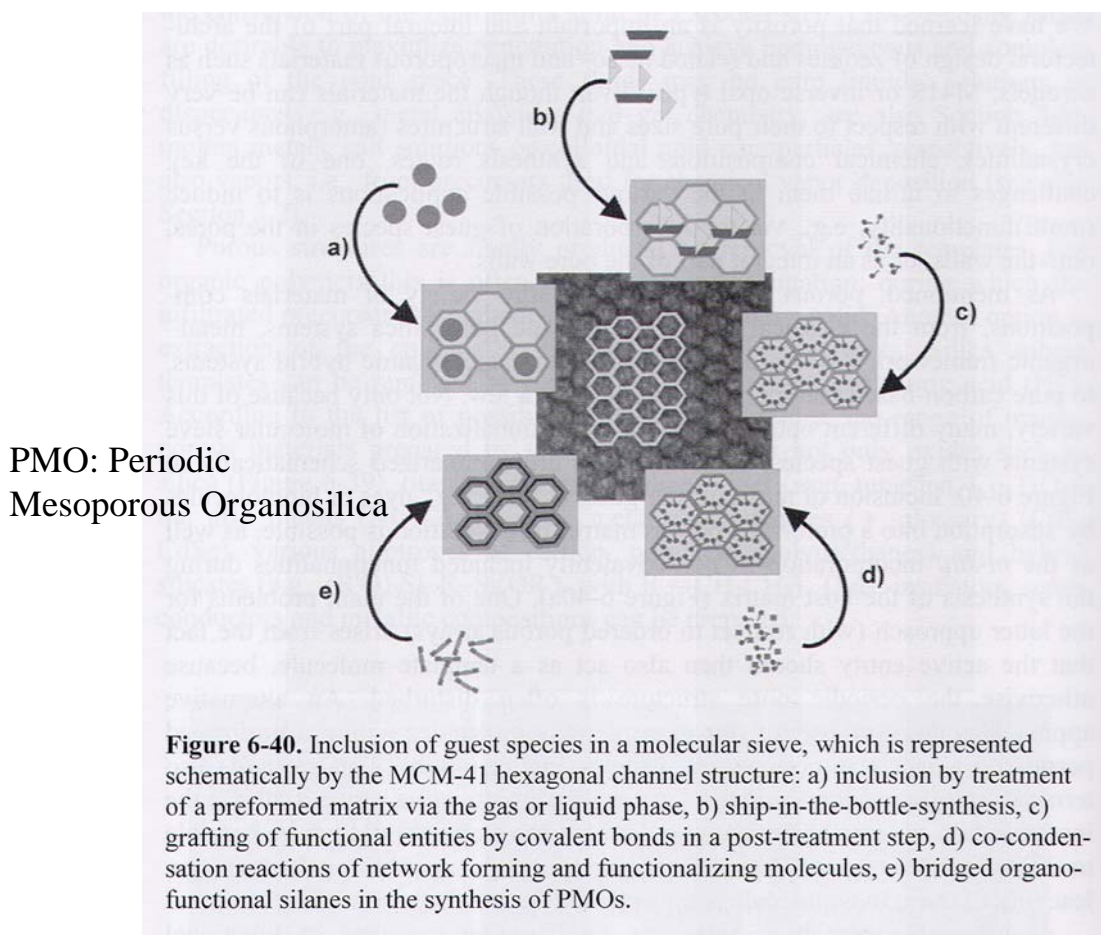
Functionalizing porous materials is important for many applications.

Functionalization may be done by introducing guest species in the pores, attached to the walls or by building functionality into the walls.

E.g. dyes or biomolecules, catalysts, optical active molecules, functional organic groups (e.g. adsorption)…

Molecules may be introduced by adsorption, by co-synthesis (templates), "ship-in-a-bottle" synthesis, condensation (covalently attached) by grafting, or co-condensation.

PMO: Periodic
Mesoporous Organosilica

Figure 6-40. Inclusion of guest species in a molecular sieve, which is represented schematically by the MCM-41 hexagonal channel structure: a) inclusion by treatment of a preformed matrix via the gas or liquid phase, b) ship-in-the-bottle-synthesis, c) grafting of functional entities by covalent bonds in a post-treatment step, d) co-condensation reactions of network forming and functionalizing molecules, e) bridged organo-functional silanes in the synthesis of PMOs.