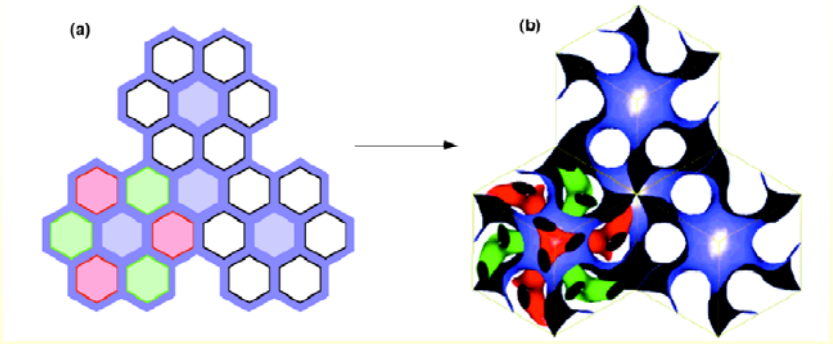
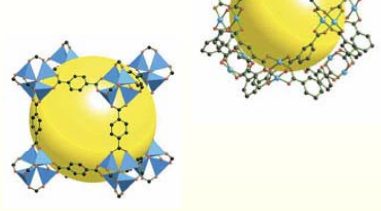
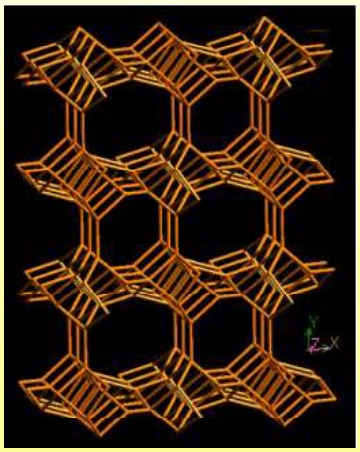
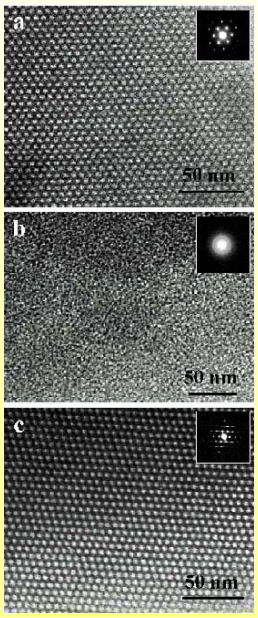
Microporous and mesoporous materials









Zeolites

Hydrothermal minerals

KJM3100 V2008

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

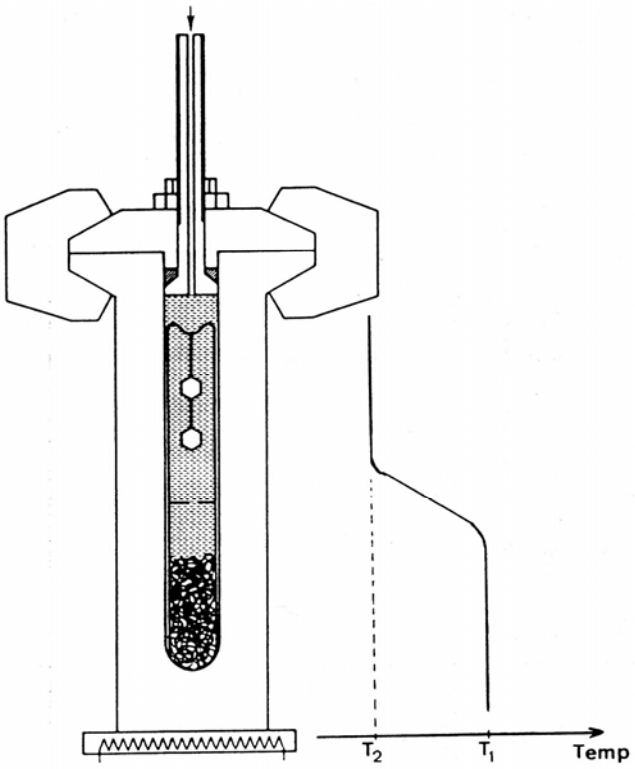


Fig. 2 Autoklave med temperaturgradient[5].
Nederste del af autoklaven har temperaturen T_1, og den øverste temperaturen T_2. Normalt stiger opløseligheden med temperaturen, og T_1 er større end T_2.

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Natural zeolites

Tabel 1 **Nogle naturligt forekommende zeolitter, med angivelse af opdagelsestidspunkt[5a].**

Stilbite	1756	Mordenite	1864
Natrolite	1758	Clinoptilolite	1890
Chabazite	1772	Offretite	1890
Harmotome	1775	Erionite	1890
Analcime	1784	Kehoeite	1893
Laumontite	1785	Gonnardite	1896
Thomsonite	1801	Dachiardite	1905
Scolecite	1801	Stellerite	1909
Heulandite	1801	Ferrierite	1918
Gmelinite	1807	Viseite	1942
Mesolite	1813	Yugawaralite	1952
Gismondine	1816	Wairakite	1955
Brewsterite	1822	Bikitaite	1957
Epistilbite	1823	Paulingite	1960
Phillipsite	1824	Garronite	1962
Levynite	1825	Mazzite	1972
Herschelite	1825	Barrerite	1974
Edingtonite	1825	Merlinoite	1976
Faujasite	1842		

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 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 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

Atlas of Zeolite Framework Types

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

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 atlas link

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 fourcoordinated 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.

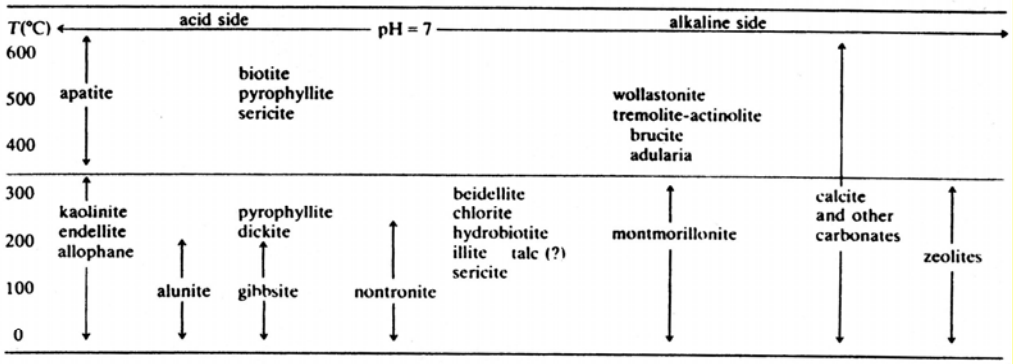


Fig. 1 Hydrotermale dannelsesbetingelser for nogle mineraler[15]. Sammenhæng mellem pH, temperatur og forekomst af nogle hydrotermalt dannede mineraler.

Zeolite types as a function of temperature

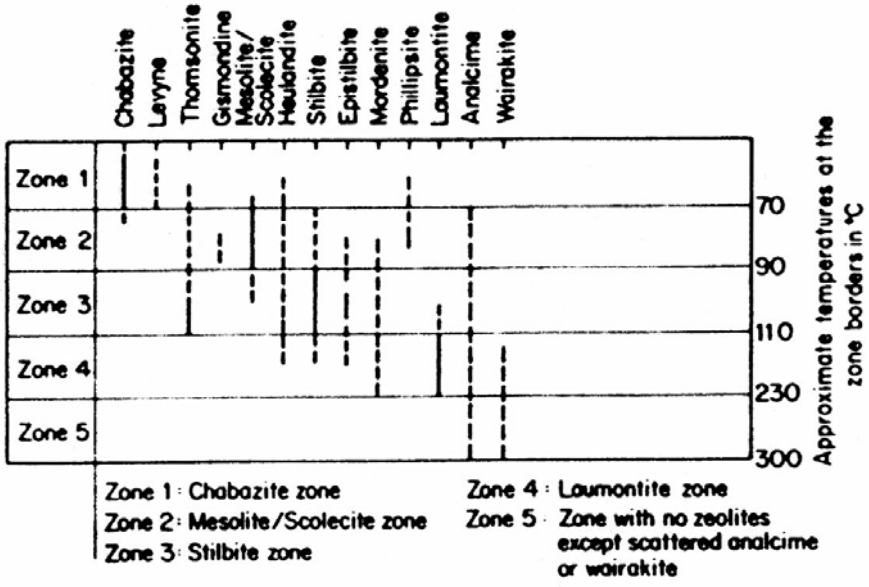
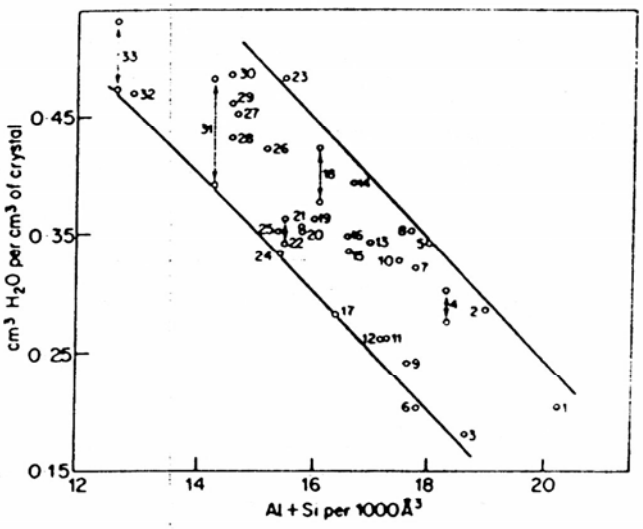


Fig. 2 Forekomst af zeolitter i forskellige temperaturzoner i varme kilder på Island[5].

Structure, porosity and building units

One measure of porosity is the tetrahedra density, i.e. number of T-atoms in 1000Å^3.
For zeolites: between 12 and 20.
Other tectosilicates: larger than 20 T/1000Å^3.

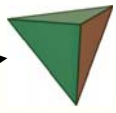


1. Bikitaite
2. Zeolite *ABW*
3. Analcime
4. Yugawaralite
5. Epistilbite
6. Natrolite
7. Thomsonite
8. Laumontite
9. Ferrierite
10. Brewsterite
11. Dachiardite
12. Mordenite
13. Sodalite and heulandite
14. Stilbite
15. Cancrinite
16. Edingtonite
17. Zeolite *LTL*
18. Mazzite
19. Merlinoite
20. Phillipsite
21. Zeolite *LOS*
22. Offretite
23. Paulingite
24. Zeolite *EAB*
25. Erionite
26. Levynite
27. Zeolite *KFI*
28. Gmelinite
29. Gismondine
30. Chabazite
31. Zeolite *RHO*
32. Zeolite *LTA*
33. Faujasite

Fig. 3 **Porevolumen angivet som funktion af tetraedertæthed for nogle zeolitter[5].**

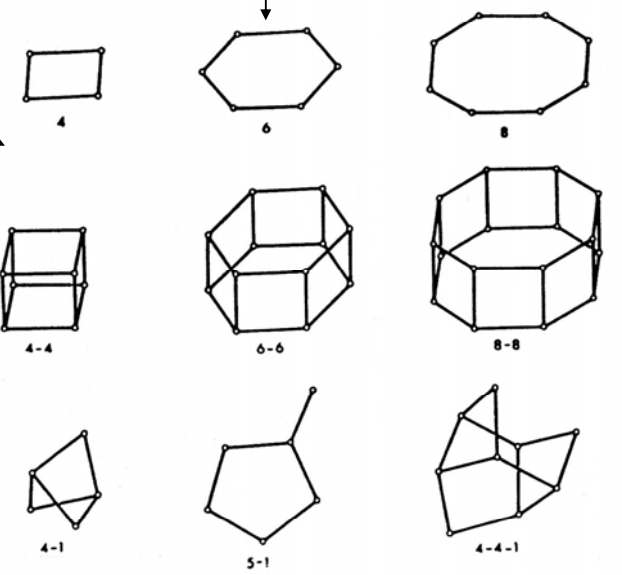
Structure, porosity and building units

Primary building units:
TO_4-tetrahedron



Secondary building units:

6-ring:
6 T-atoms and 6 oxygen atoms



Tertiary building units,
e.g. the sodalite cage::

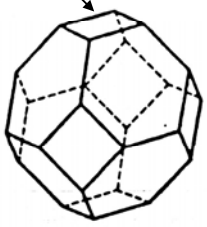


Fig. 5 **Kubooktaederet.**
Det afskårne oktaeder, også kaldet et sodalitbur.
En tertiær byggeenhed i flere zeolitter.

Fig. 4 **De sekundære byggeenheder for zeolitter[23].**
(Hertil kommer en enkelt 5-ring)

Structure, porosity and building units

Representation of zeolite structures:

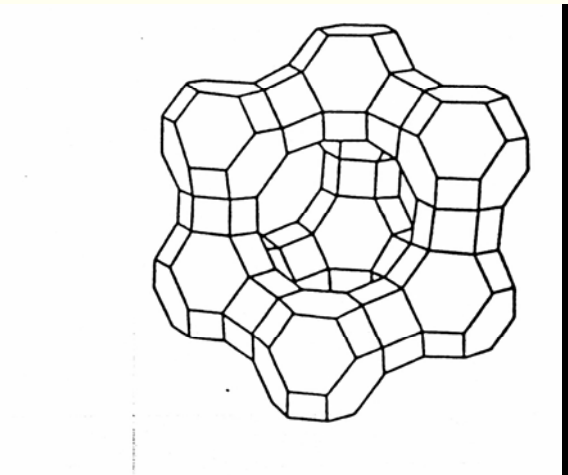
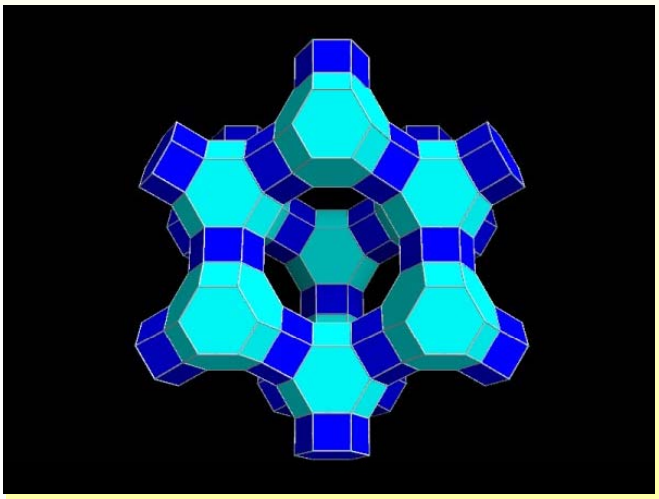


Fig. 6c Faujasitstruktur, Zeolit X og Y (FAU).



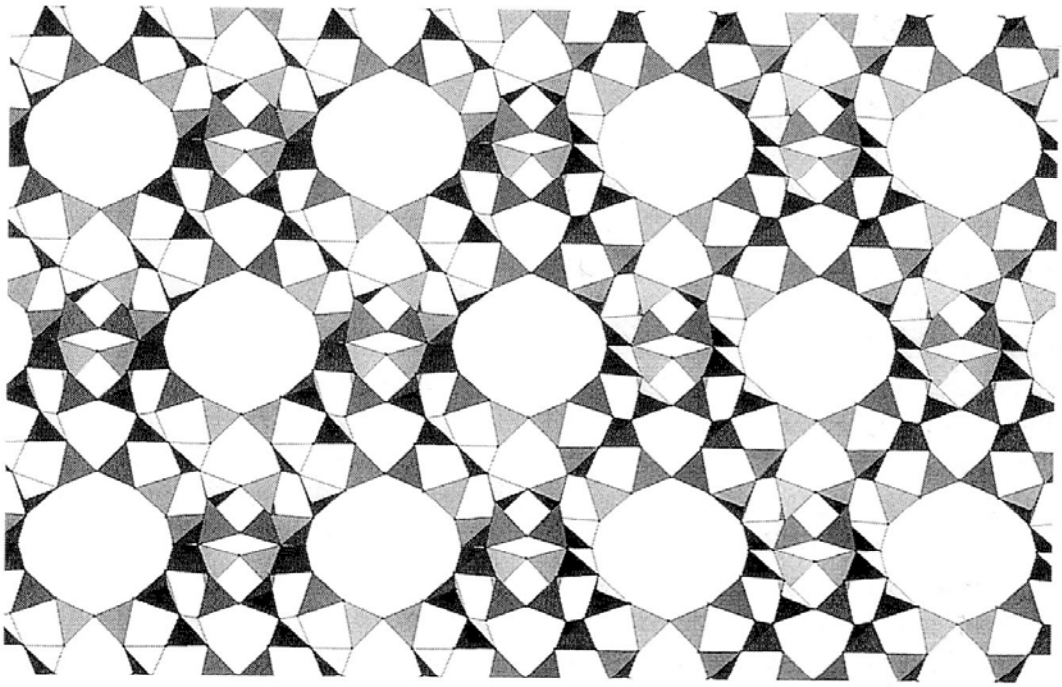
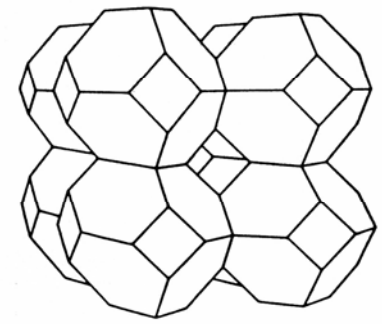


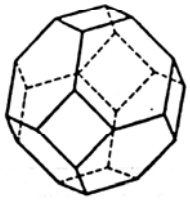
Fig. 18.1. The zeolite faujasite. SiO_4 tetrahedra are represented in gray, and water molecules and extra-framework cations have been omitted for clarity.

Zeolite atlas link

Building zeolites:

Three structures containing sodalite cages:





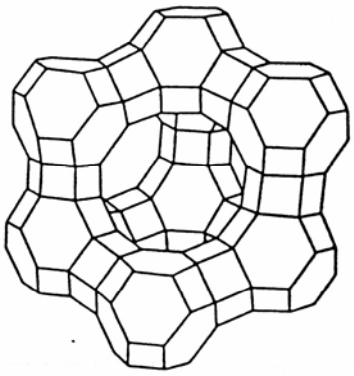


Fig. 6a Sodalitstrukturen (SOD).

Faujasitstruktur, Zeolit X og Y (FAU).

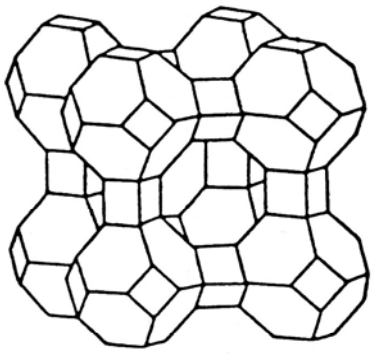


Fig. 6b Zeolit A (LTA).

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

System	*Pore System*
Sodalite family (SOD) (e.g. mineral and synthetic sodalites)	3-dimensional; 6-ring channels
Zeolite A family (LTA) (e.g. zeolites A, ZK-4; no mineral analogue)	3-dimensional; 8-ring channels
Chabazites (CHA) (e.g. mineral chabasites, SSZ-13)	3-dimensional; 8-ring channels
ZSM-5 (MFI) (e.g. mineral murataite, silicalite)	2-dimensional; 10-ring channels
Ferrierites (FER) (e.g. mineral and synthetic ferrierites)	2-dimensional; 10 & 8-ring channels
Faujasites (FAU) (e.g. mineral faujasite, zeolites LSX, X, Y, US-Y)	3-dimensional; 12-ring channels

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 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.

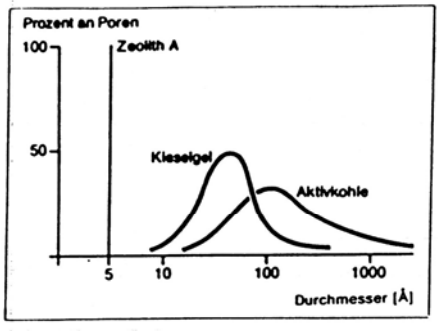


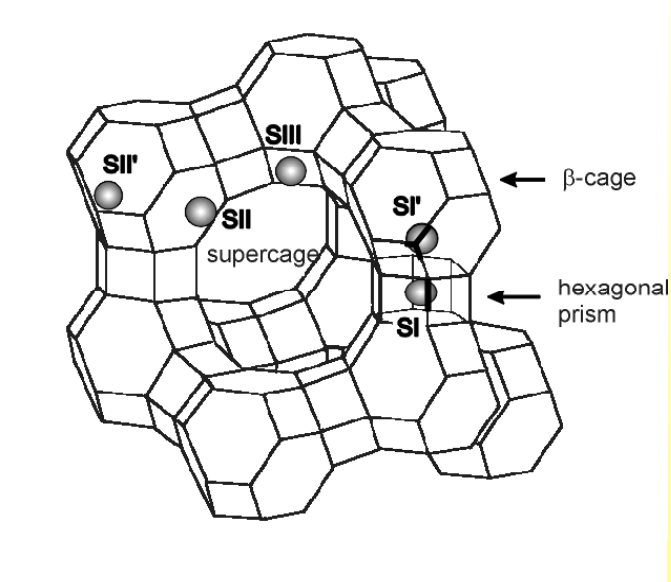
Fig. 7 Sammenligning af fordeling af porestørrelser i silikagel, aktivt kul og zeolit A.[19]

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…

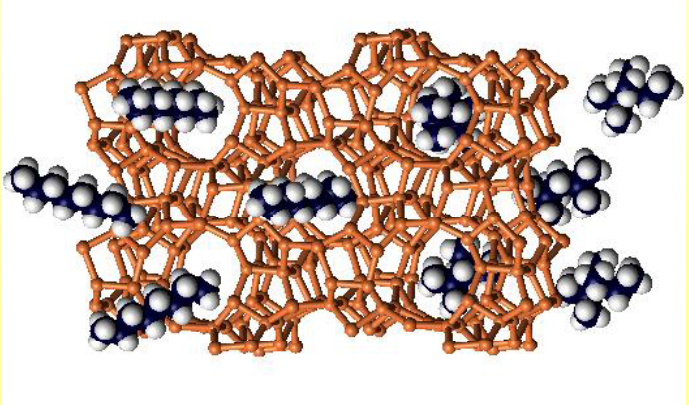


Catalysis

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.



Tab. 18.2. Some important applications of aluminosilicate zeolites and other nanoporous materials.

Well-established:

- Ion-exchange using hydrated zeolites
  - Detergency (e.g. zeolites Na-A and Na-P)
  - Water softeners
  - Animal feeds
  - Radwaste remediation (e.g. Cs, Sr with clinoptilolite)
- Molecular sieving using dehydrated zeolites
  - Air separation (N_2 from O_2 with Li-LSX)
  - Drying agents (e.g. double glazing, a/c)
  - Sulfur removal from natural gas
  - Separation of HFCs (CFC substitutes)
- Catalysis with dehydrated zeolites
  - Catalytic cracking (gasoline production) – xeolite-Y derivatives
  - Xylene isomerization (for polyesters) – H-ZSM-5
  - Butene isomerization – H-FER
  - Methanol to gasoline – H-ZSM-5
  - Phenol to hydroquinone – Titanosilicates
  - Denox reactions – Cu-ZSM-5, Co-FER

Future possibilities include:

- Hydrogen storage
- Nano-composites for optoelectronics
- Sensors using zeolite thin films
- Stereo-selective polymerization
  - Contrast enhancement in MRI (e.g. Gd-Y)
  - Ship-in-bottle synthesis
  - Zeolite nanocrystals for delivery systems

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-5

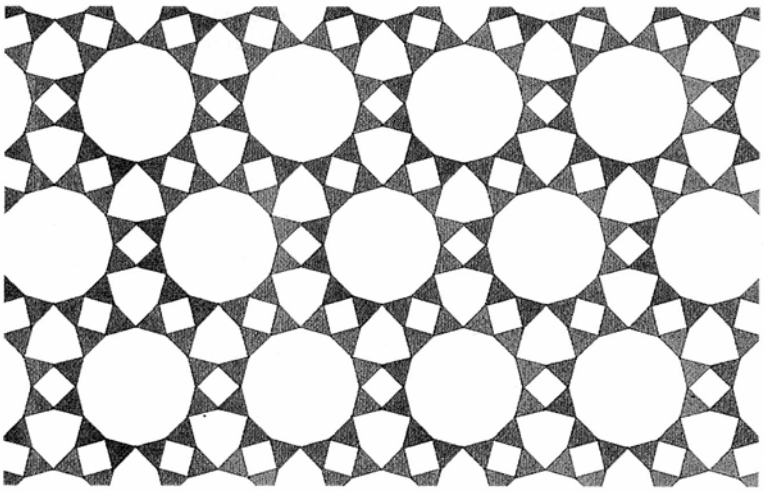


Fig. 18.2. The aluminophosphate AlPO-5. AlO_4 and PO_4 tetrahedra, which are strictly alternating, are represented in gray, and water molecules have been omitted for clarity.

$AlPO_4$: 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 substitutes only for P, i.e. $H_xAl_{1-x}PO_4$

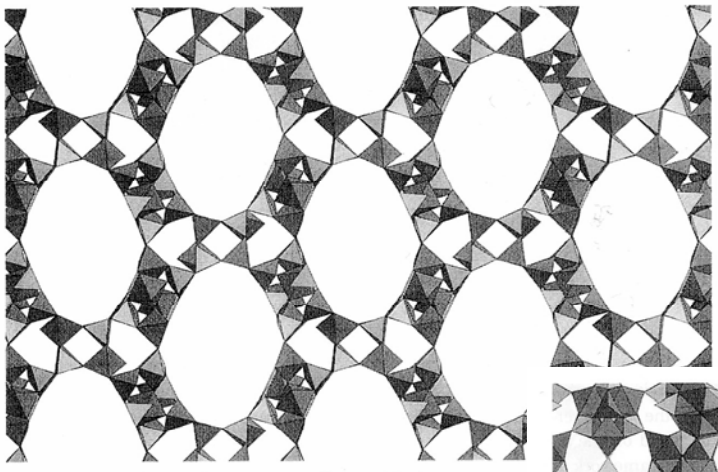
MeAPSO: e.g.. $H_{x+y}(Si_xMe_yAl_{1-y}P_{1-z})O_4$

ALPO's: higher coordination and interrupted frameworks

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

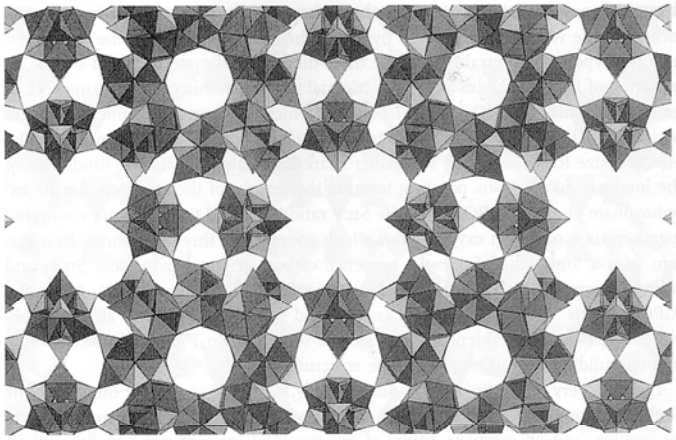
Synthesis in non-aqueous solvents may result in low dimensional materials with a P/Al ratio larger than 1.

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.



ULM-5, gallophosphate

Fig. 18.3. The gallophosphate ULM-5. Gallium polyhedra are shown in gray and PO_4 tetrahedra are represented in light gray. Water molecules and the organic template have been omitted for clarity.



Cloverite, 20-ring gallophosphate

Fig. 18.4. The gallophosphate cloverite. Gallium polyhedra are shown in gray and PO_4 tetrahedra are represented in light gray. Water molecules and the organic template have been omitted for clarity.

Mixed coordination materials

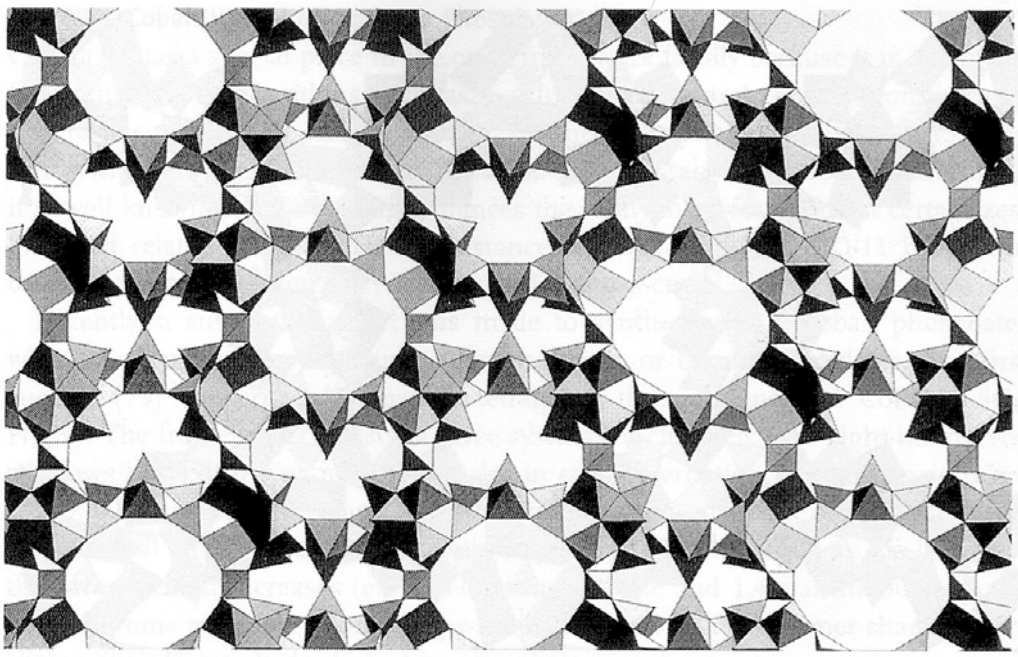


Fig. 18.5. The vanadium phosphate $Cs_3[V_5O_9(PO_4)_2]$. Vanadium polyhedra are shown in gray and PO_4 tetrahedra are represented in light gray. Water molecules have been omitted for clarity.

Open framework iron phosphates

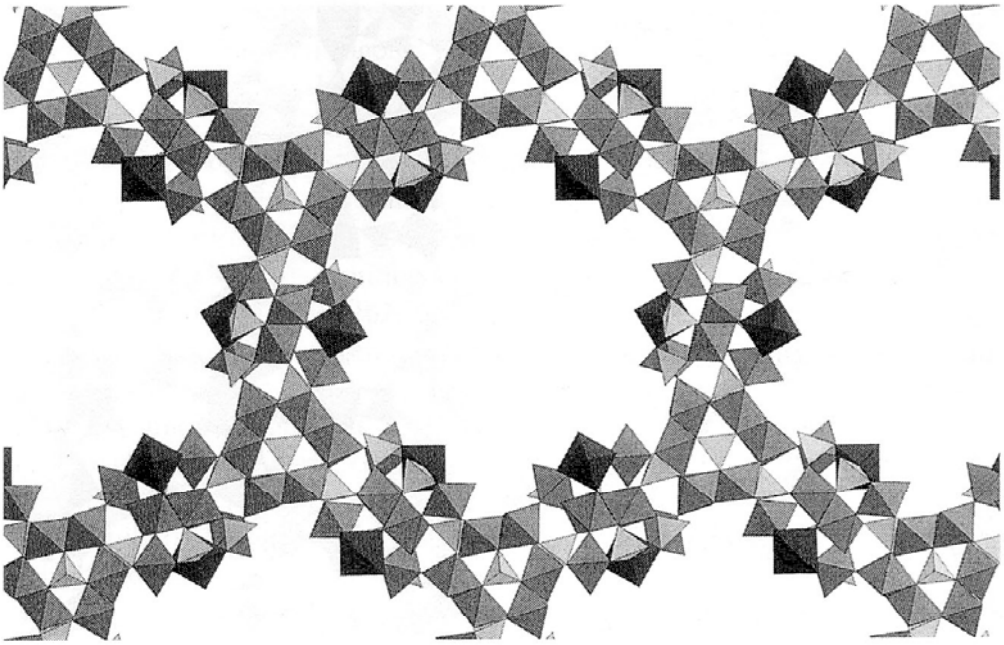


Fig. 18.6. The iron phosphate mineral cacoxenite. FeO_6 octahedra are shown in gray and AlO_4 and PO_4 tetrahedra are represented in light gray. Water molecules are omitted for clarity.

Molten salt flux; salts as templates in open framework materials

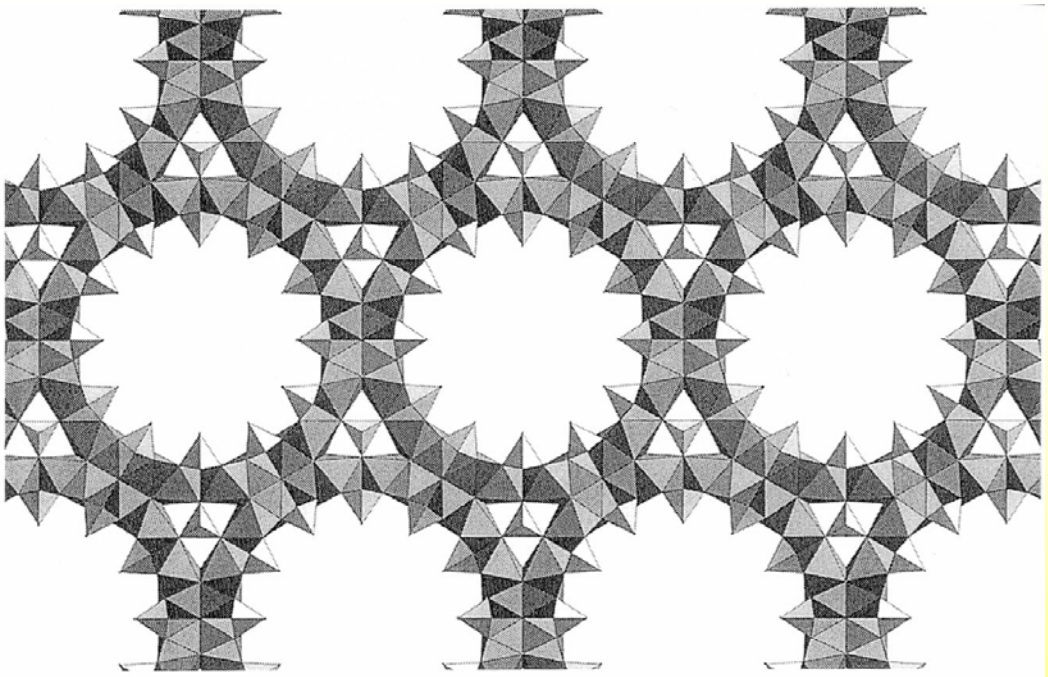


Fig. 18.7. The nickel phosphate VSB-1. NiO_6 octahedra are shown in gray and PO_4 tetrahedra are represented in light gray. Water molecules, extra-framework cations, and partial occupancy are omitted for clarity.

Microporous and mesoporous materials from soft building blocks

Escape from the zeolite prison

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.

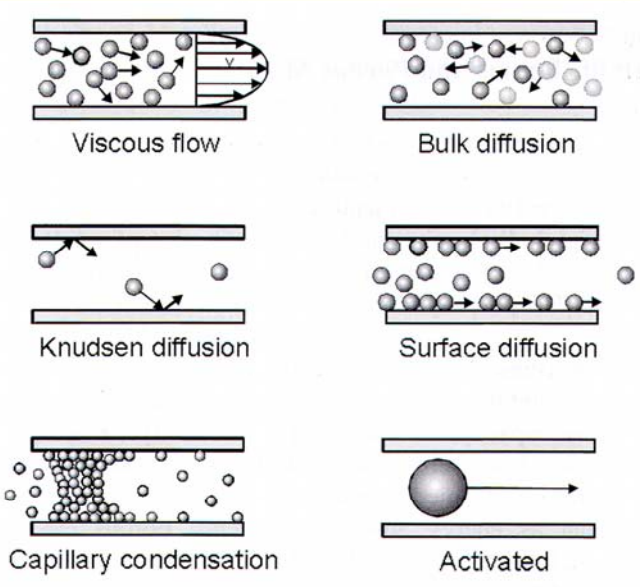


Figure 6-4. Transport mechanisms through pores.

Microporous sulfides; microporous zeolite super building blocks

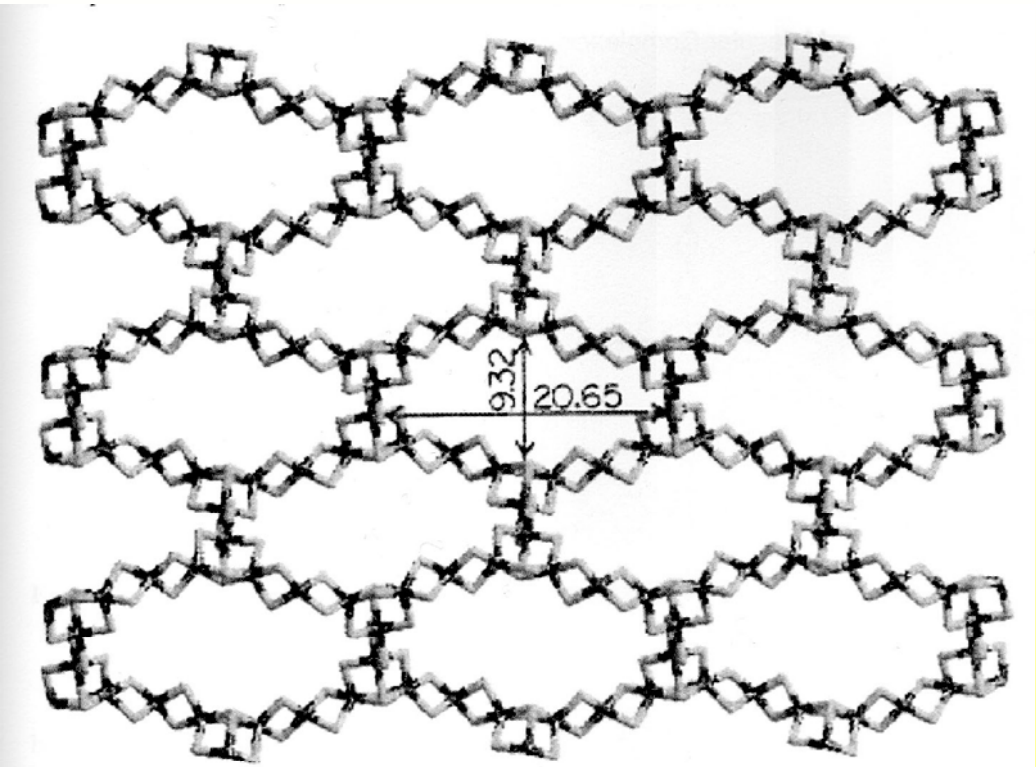


Figure 8.2 *Schematic showing the crystal structure of a microporous tin sulfide material* (Reproduced with permission from Ref. 14)

Synthesis and Structure of $MnGe_4S_{10}\cdot(C_6H_{14}N_2)\cdot 3H_2O$: A Novel Sulfide Framework Analogous to Zeolite Li-A(BW)

Christopher L. Cahill and John B. Parise*

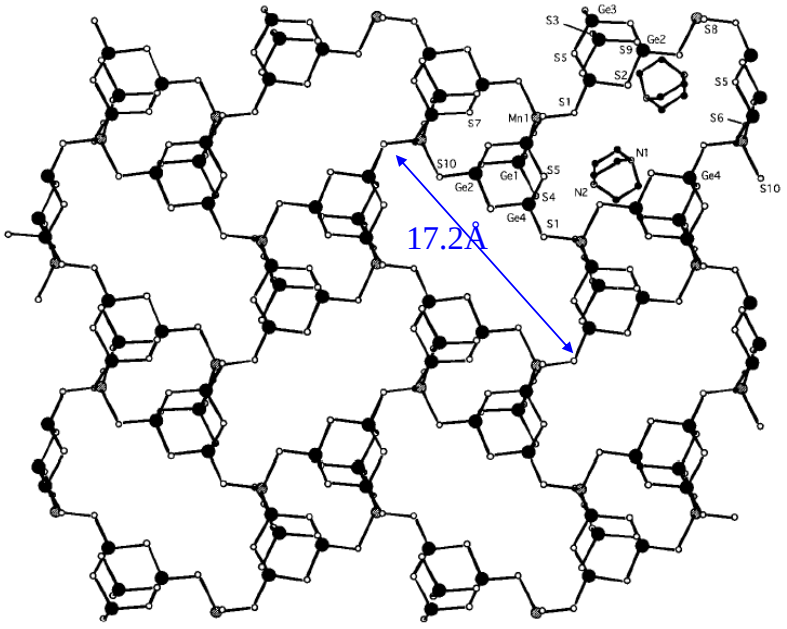
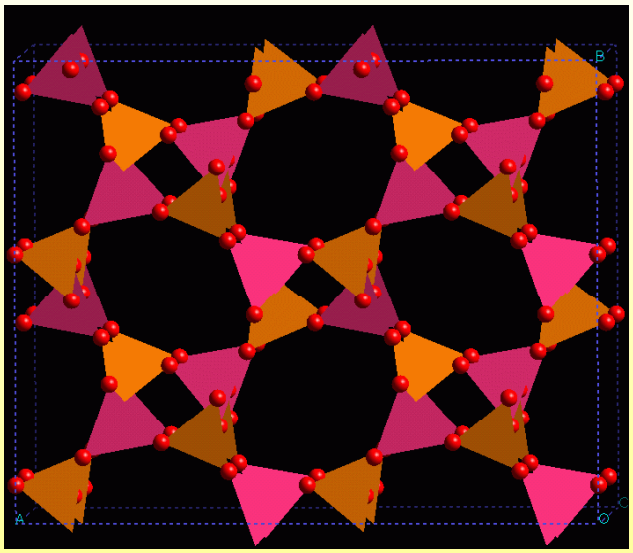
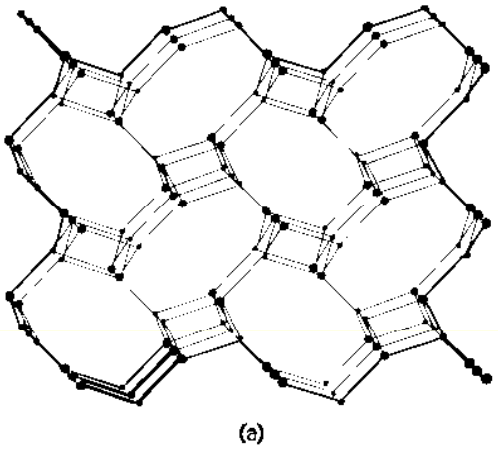


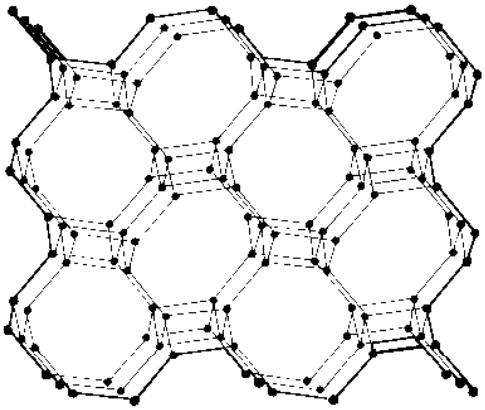
Figure 2. Structure of Dabco−MnGS−SB1 shown along [001]. Unlabeled small black circles are C. The H_2O molecules and hydrogen atoms have been omitted for clarity. Also for clarity, only one channel is shown to contain the Dabco.

Zeolite Li-A(BW) analogue





(a)



(b)

Supertetrahedra, Microporous sphalerite, ZnS

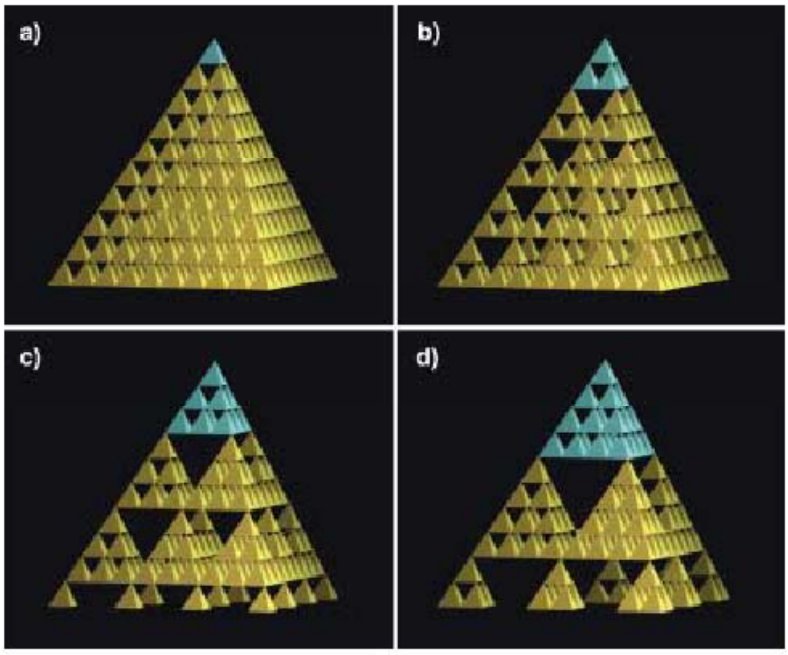


Figure 1. The principle of building supertetrahedra from the dense sphalerite structure: a) A part of the sphalerite structure limited to a large tetrahedron corresponding to an edge of ten primitive tetrahedra (in blue); b) assembly of T2 supertetrahedra with the same sphalerite topology (the supertetrahedron,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

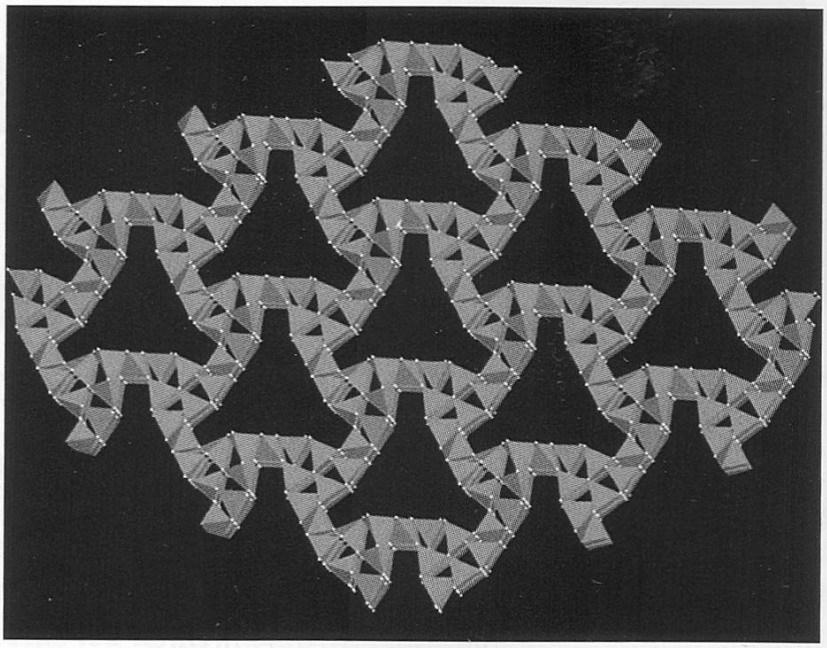


Figure 8.4 *3D representation of a self-assembled metal sulfide cluster framework found to display remarkable ion conductivity*
(Reproduced with permission from Ref. 20)

Metalorganic framework (MOF) materials Hybrid (organic/inorganic) materials

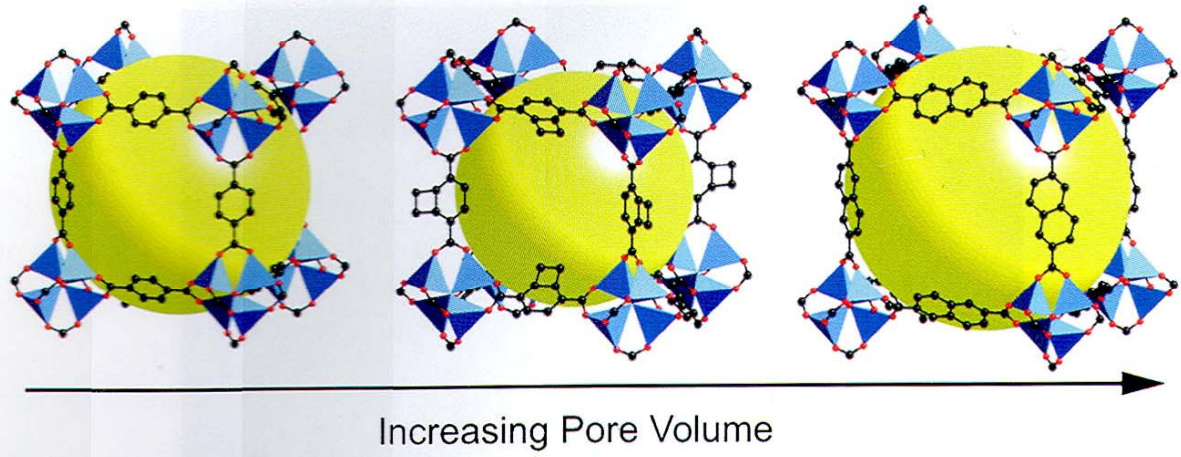
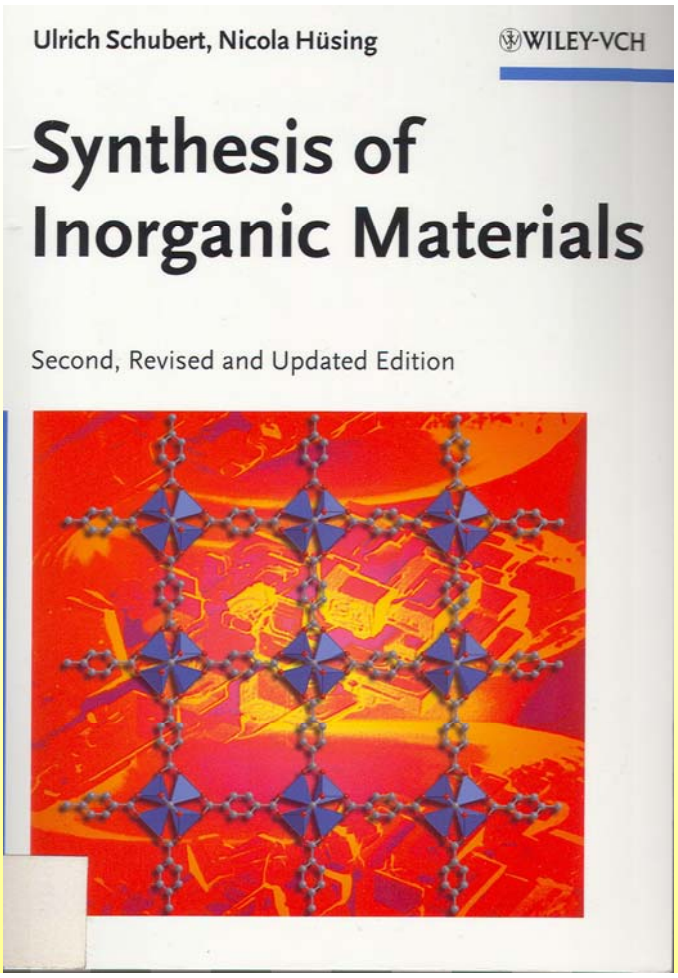


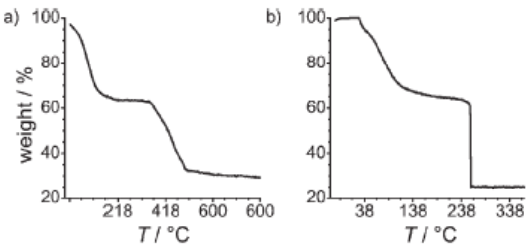
Figure 8.5 *Hydrogen storage metal–organic open-framework compound $Zn_4O(RDC)_3$*
(Reproduced with permission from Ref. 25)

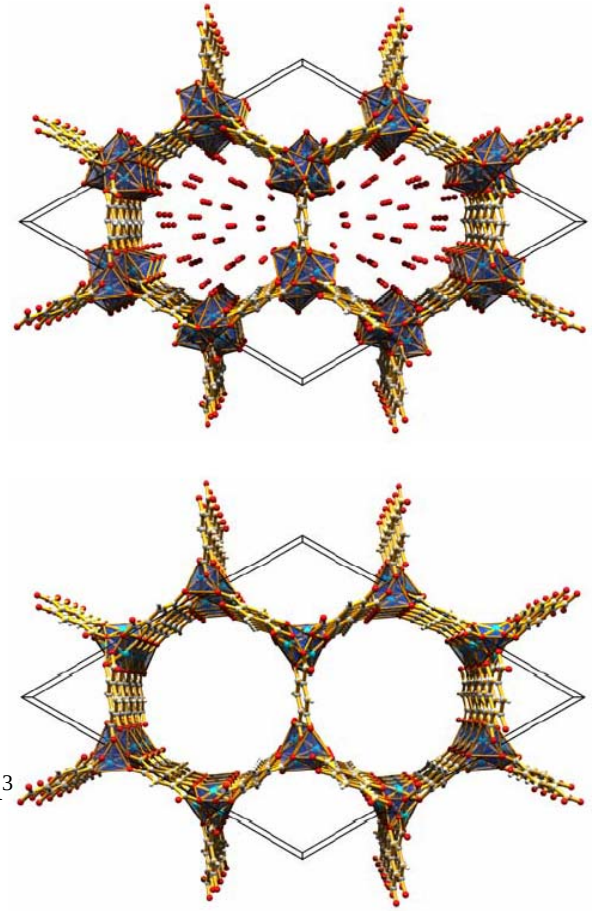
BDC: 1,4-benzene-dicarboxylate $Zn_4O(BDC)_3$
Cubic structure, Surface area 2500-3000m^2/g (BET), stable to 3-400ºC
Hydrogen storage?: 78K: 4.5w% H_2, RT, 20 bar: 1w%



An example from UiO (Pascal Dietzel):
$Ni_2(dhtp)(H_2O)2•8H_2O$
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, $V = 17832$ $Å^3$

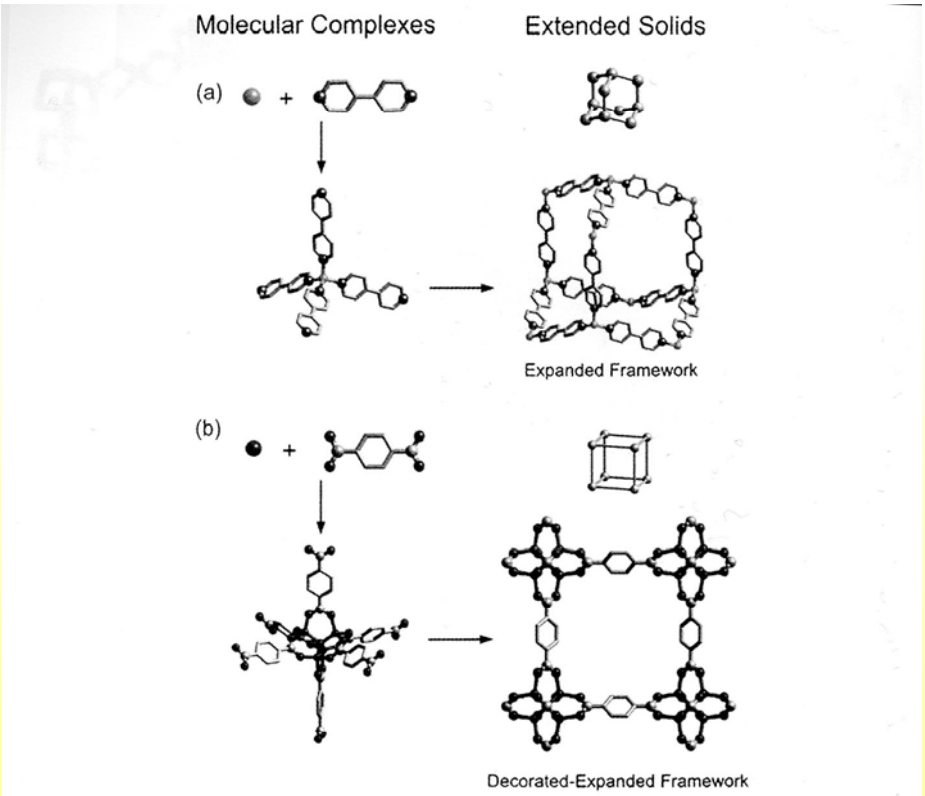


Figure 8.3 *Modular self-assembly of coordination open-framework materials. Linkers can be flexible, like metal–pyridine links above, or rigid, like metal–carboxylate links shown below*
(Reproduced with permission from Ref. 16)

Mesoporous materials, The MCM family

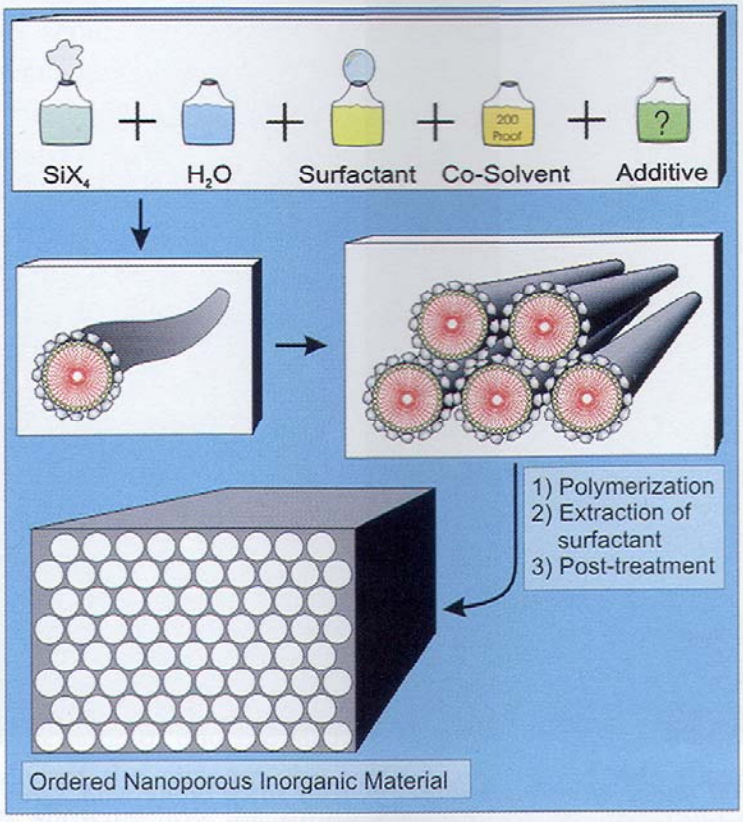
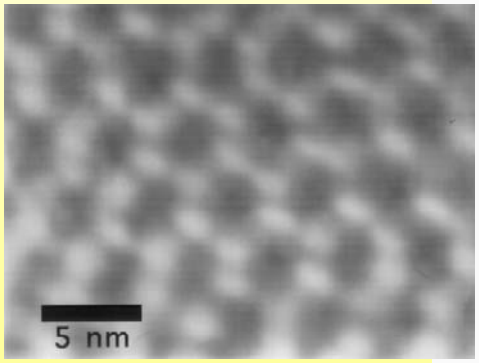
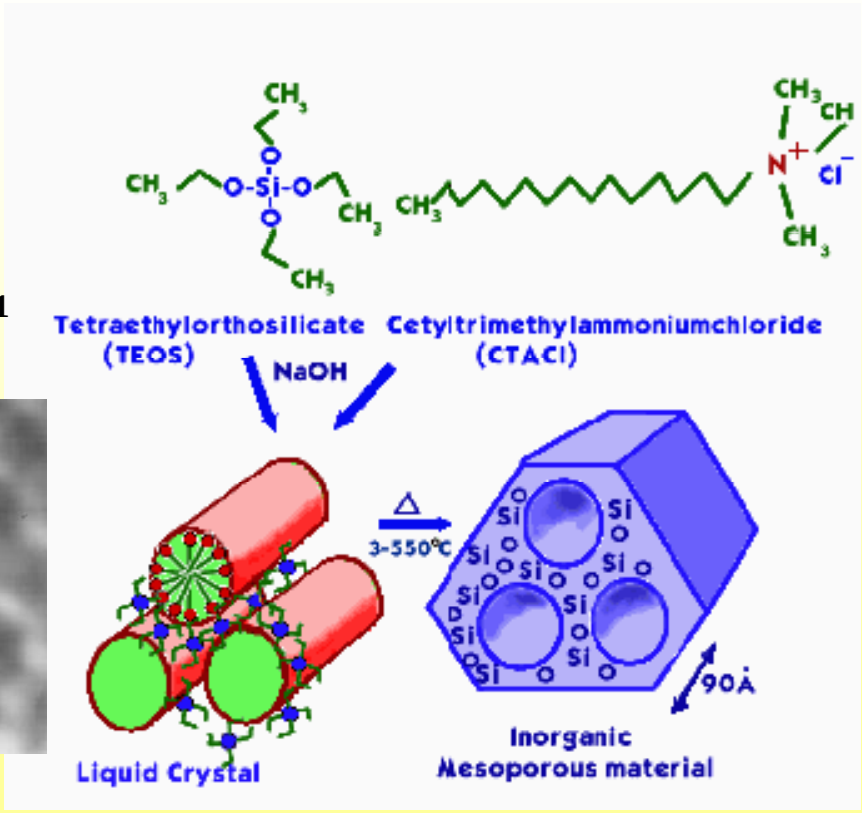


Figure 8.6 *Supramolecular templating of mesoporous inorganics*

Mesoporous materials, The MCM family

MCM-41





MCM-41

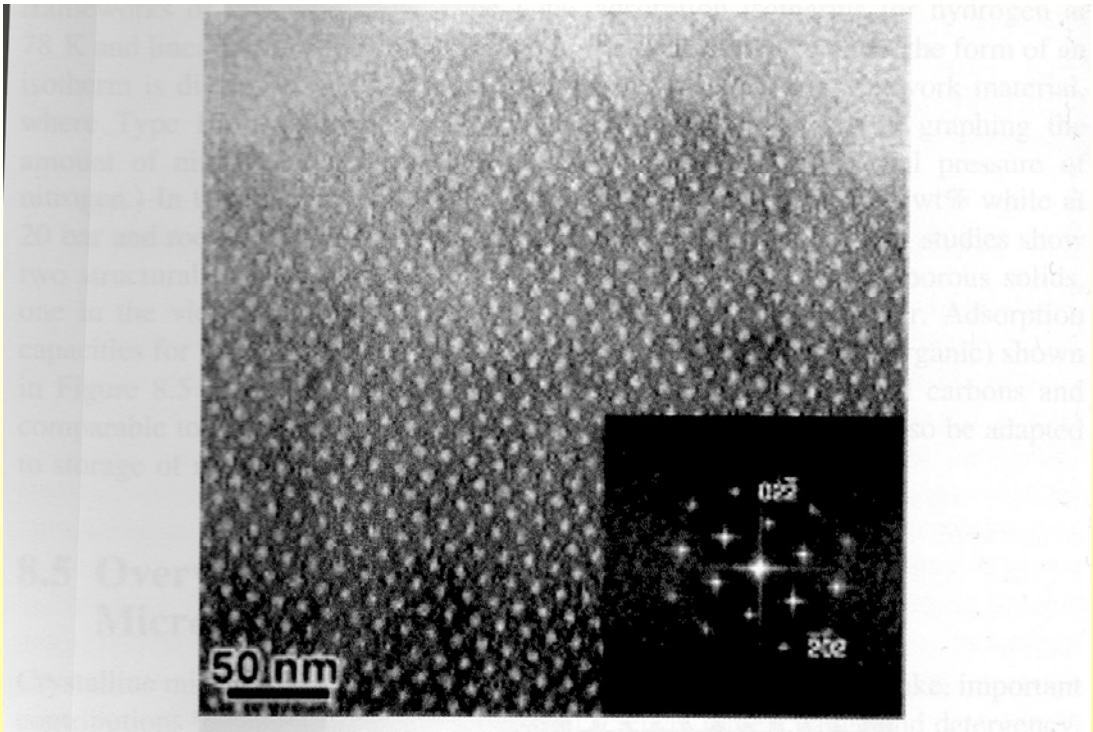
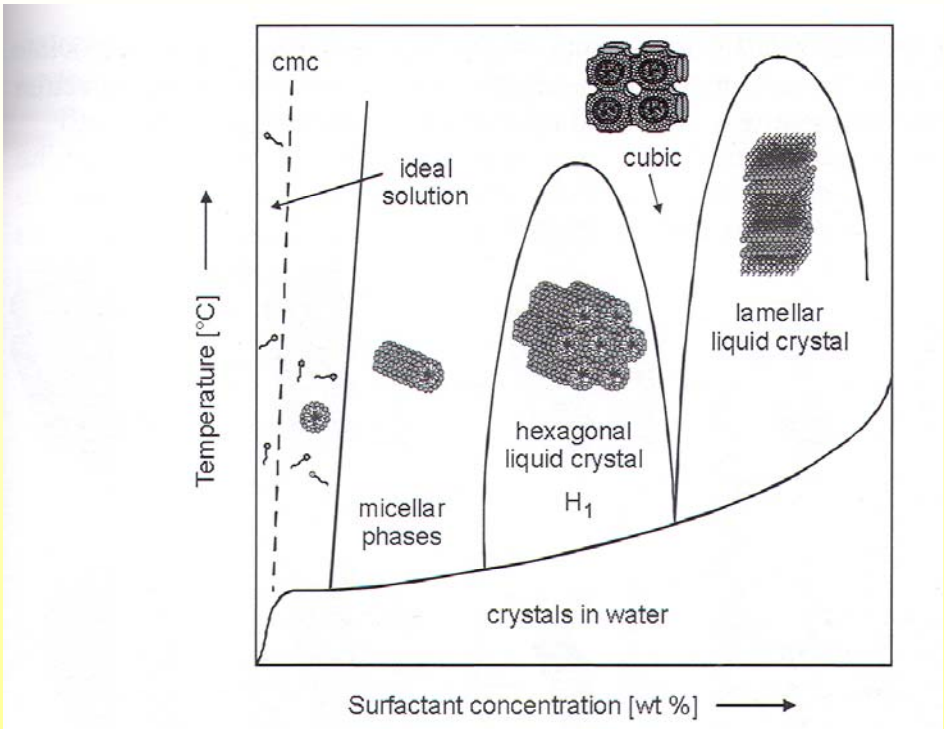


Figure 8.7 *TEM image of hexagonal mesoporous silica along with X-ray diffraction data demonstrating the hexagonal order*
(Reproduced with permission from Ref. 36)

Phase diagrams



KJM3100 V **Figure 6-34.** Schematic phase diagram for a surfactant in water.

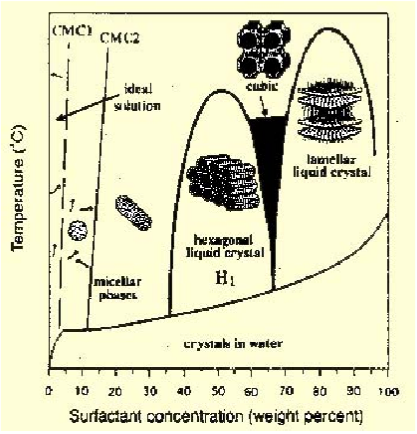
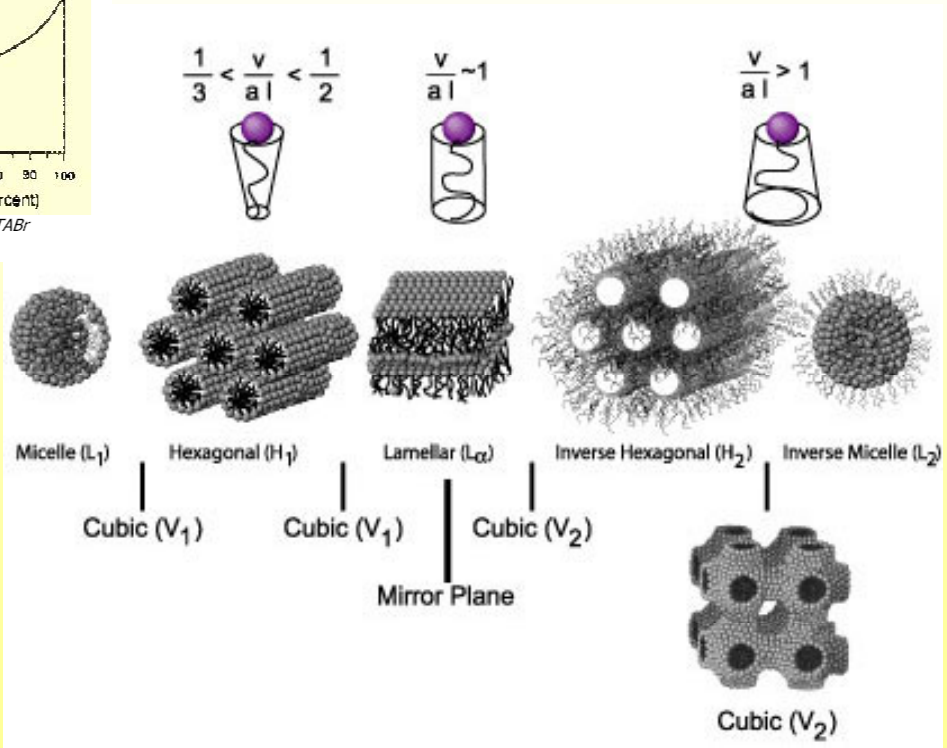
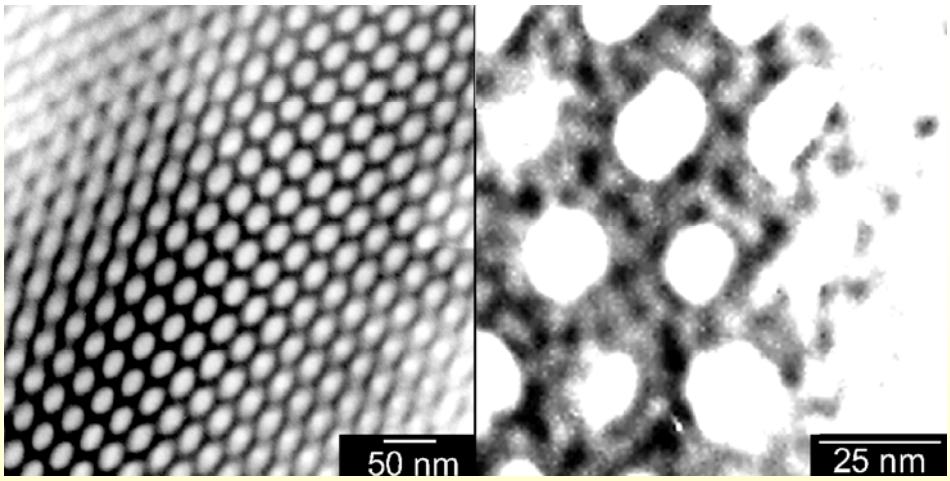


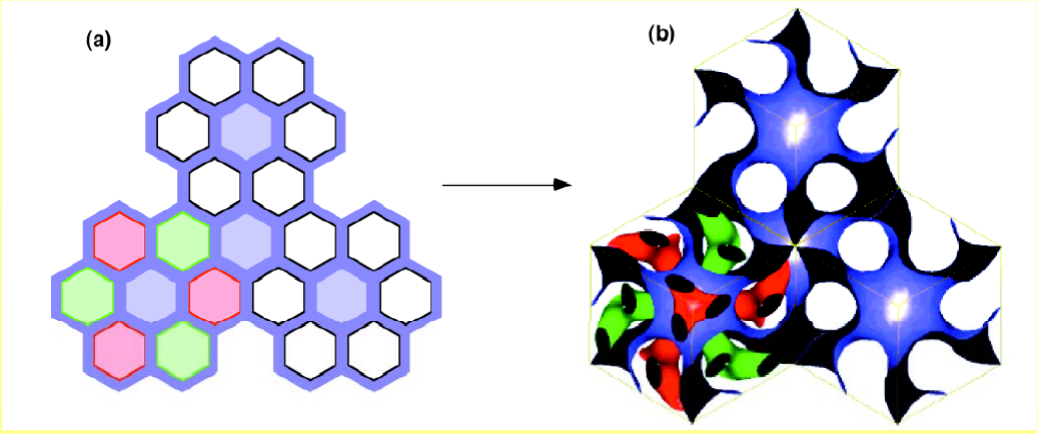
Fig. 2 Phase diagram of ionic surfactant CTABr in water.

Micelle formation in surfactant systems



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.





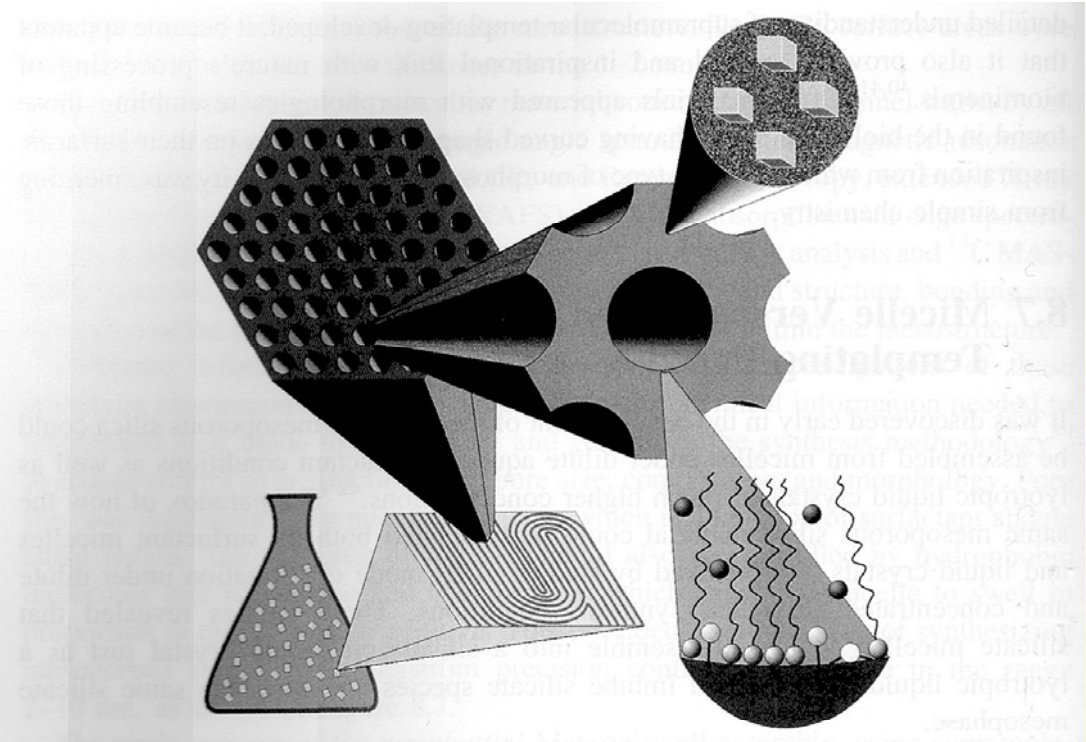
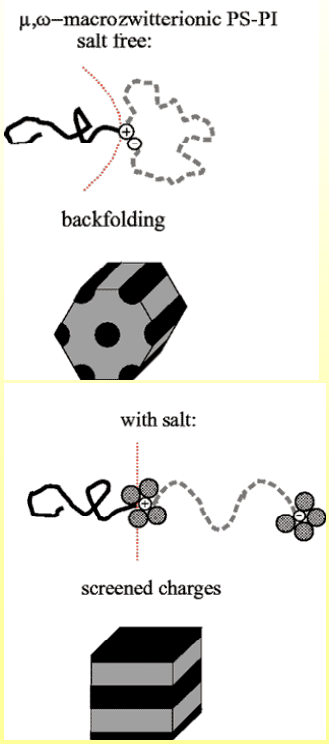


Figure 8.8 *Putting function into mesoporous materials at a hierarchy of length scales. Synthesized material displays hexagonal cylindrical order displaying defects like any liquid crystal. The composition and texture of the walls can be tuned, and the interior of the channels can be functionalized by a choice of surfactant, bridging or side-groups, and additives*

Another length scale: Block copolymers templated mesoporous materials



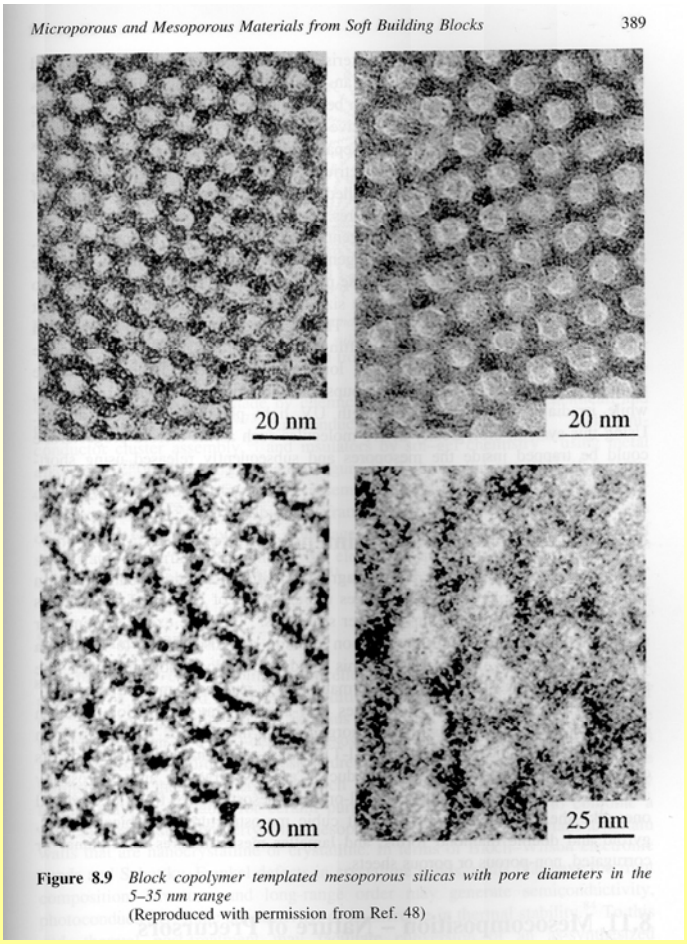


Figure 8.9 *Block copolymer templated mesoporous silicas with pore diameters in the 5–35 nm range*
(Reproduced with permission from Ref. 48)

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

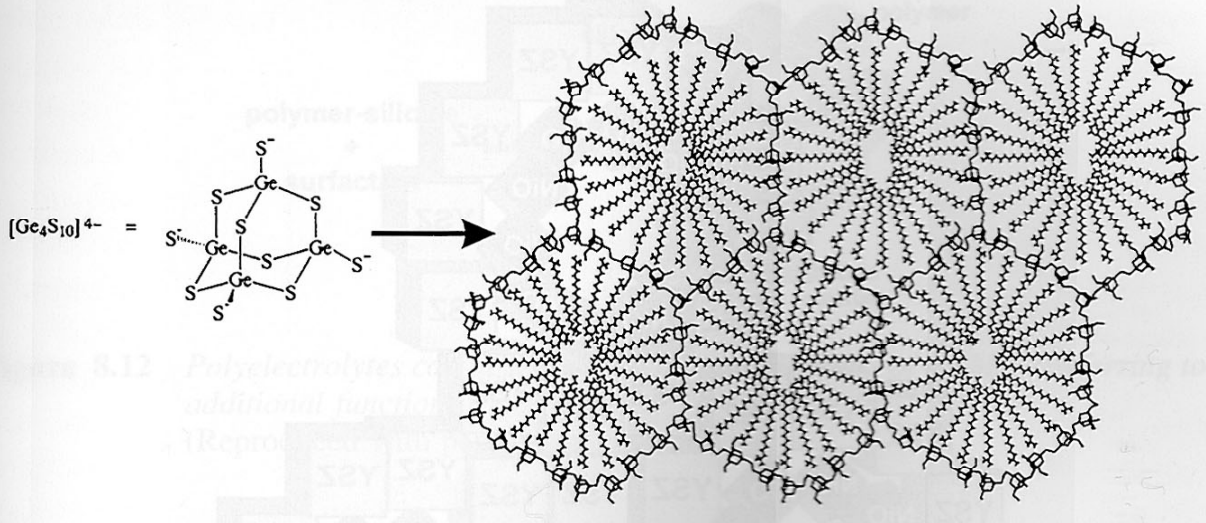


Figure 8.10 *Modular self-assembly of adamantanoid $M_4S_{10}^{4-}$ clusters with M^{2+} ions to form a mesostructured metal sulfide*
(Reproduced with permission from Ref. 79)

Post treatment:
Recrystallization to ordered array of nanocrystals…

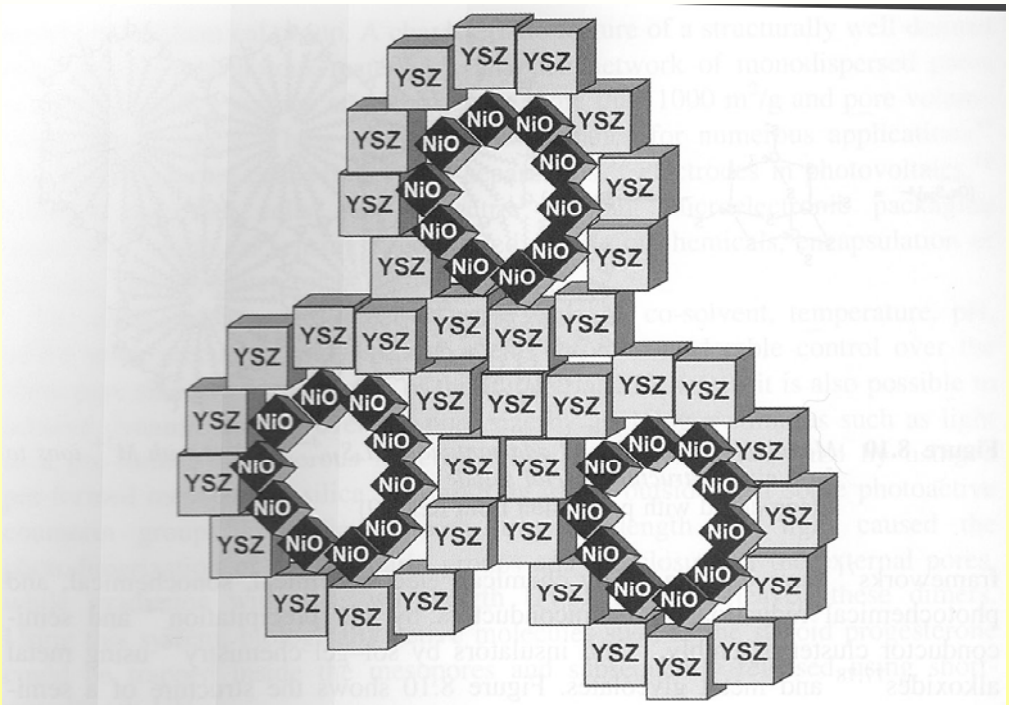


Figure 8.11 *Nanocrystalline mesoporous nickel oxide yttria-stabilized-zirconia, oxide ion conductor used as the anode in a solid oxide fuel cell*

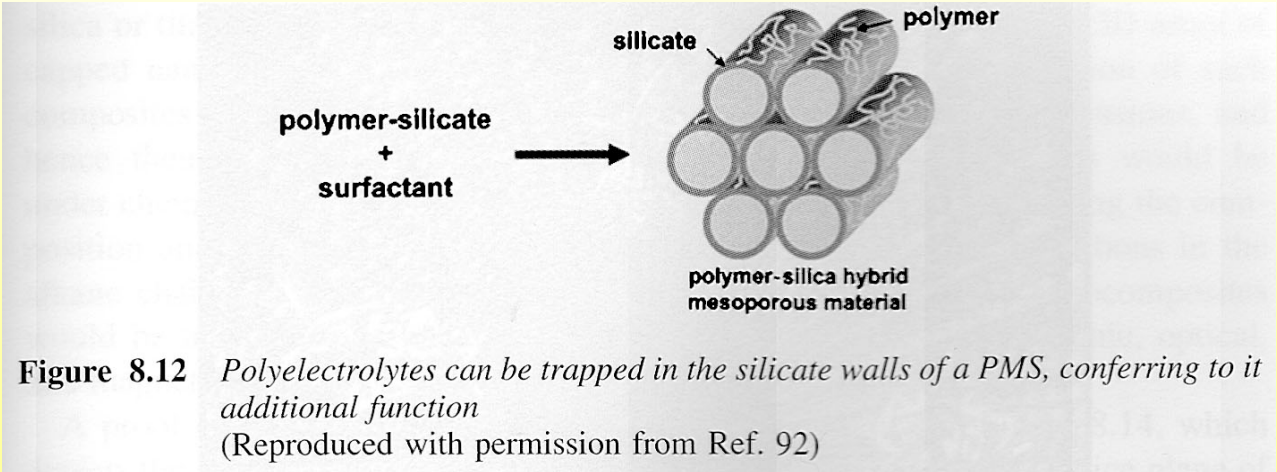


Figure 8.12 *Polyelectrolytes can be trapped in the silicate walls of a PMS, conferring to it additional function*
(Reproduced with permission from Ref. 92)

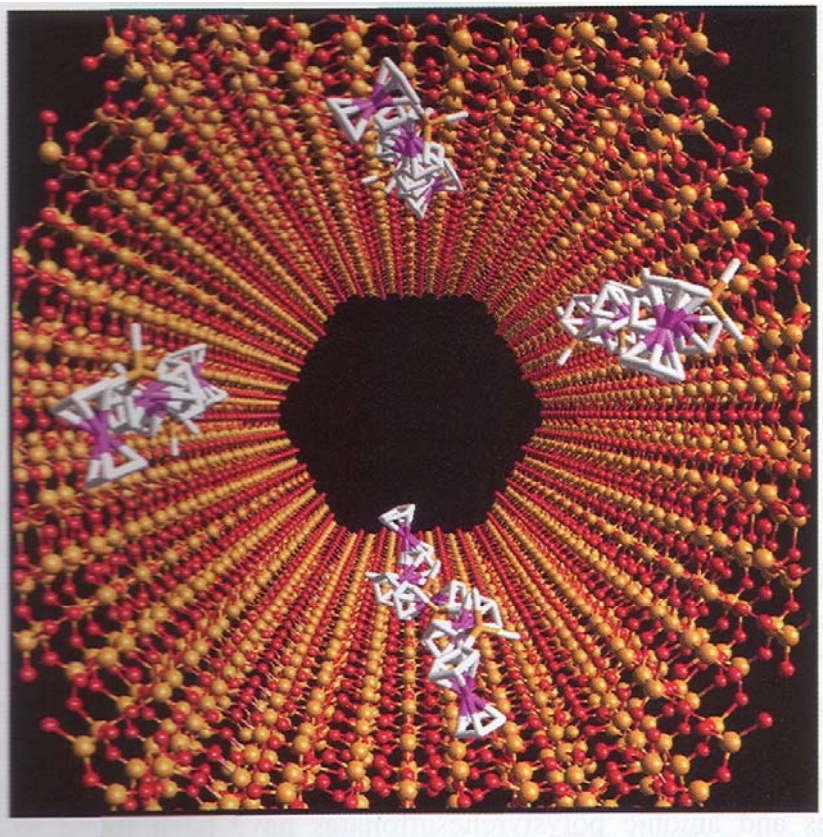


Figure 8.13 *Growth of polyferrocenylsilane within the channels of hexagonal mesoporous silica*

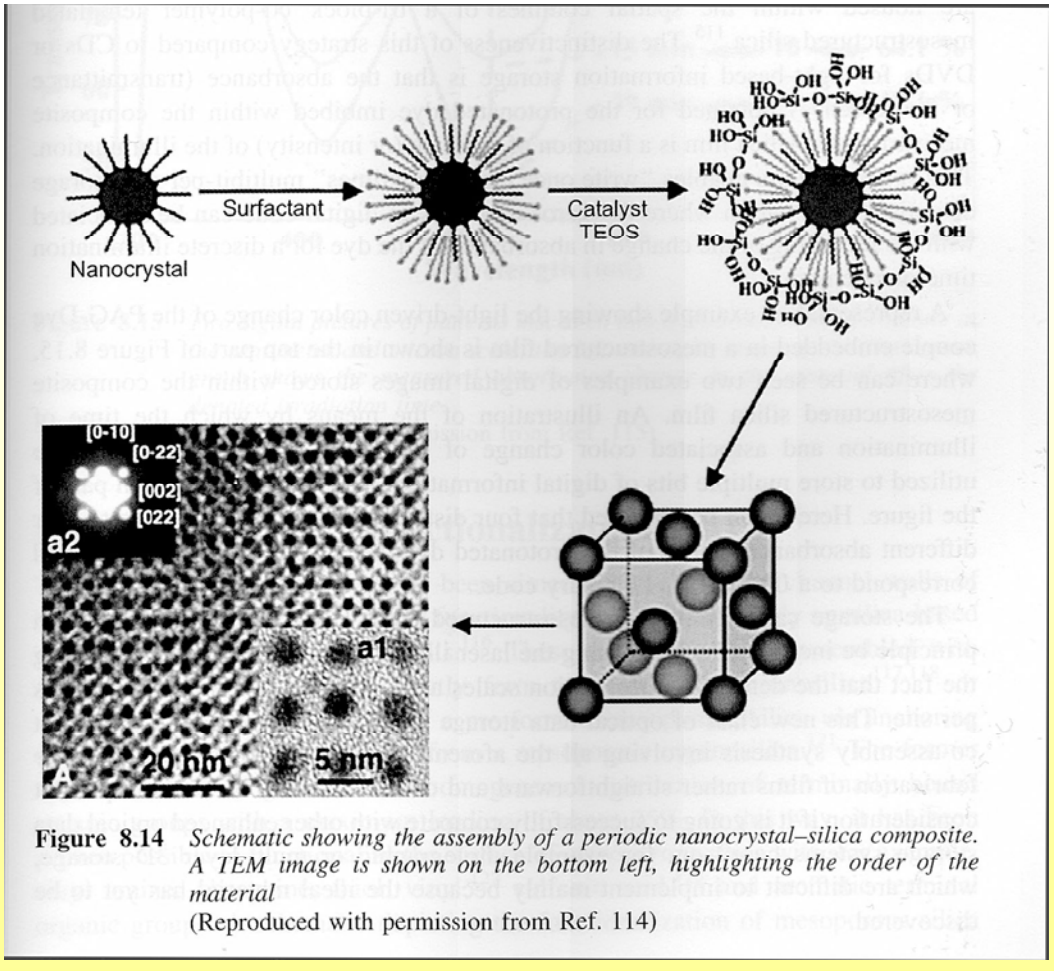
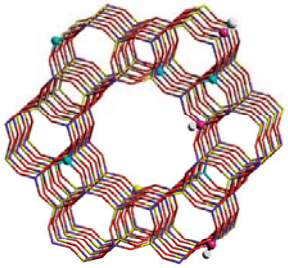
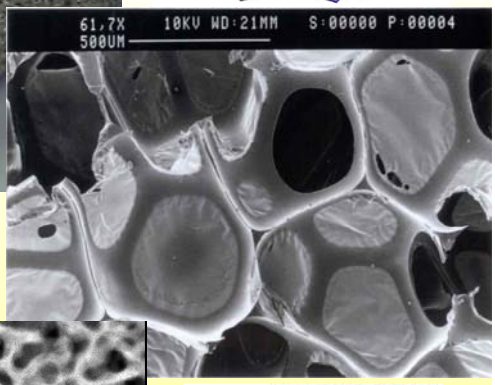
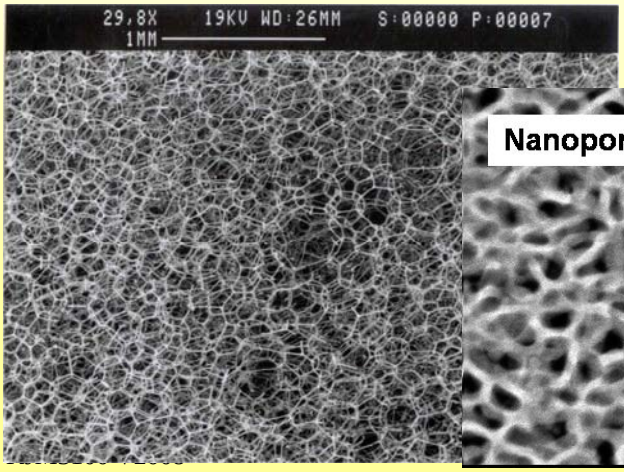


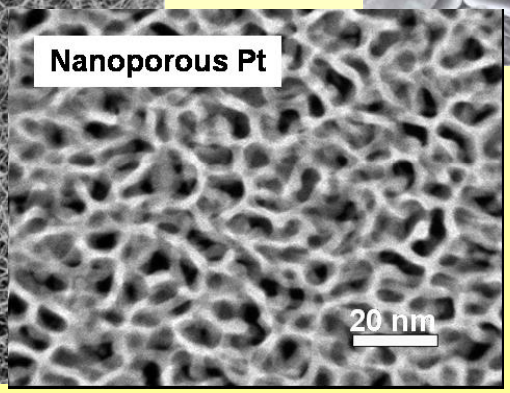
Figure 8.14 *Schematic showing the assembly of a periodic nanocrystal–silica composite. A TEM image is shown on the bottom left, highlighting the order of the material*
(Reproduced with permission from Ref. 114)

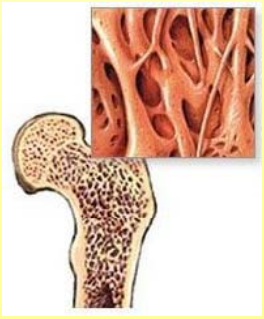
Porous materials











Cu and Mg gasars

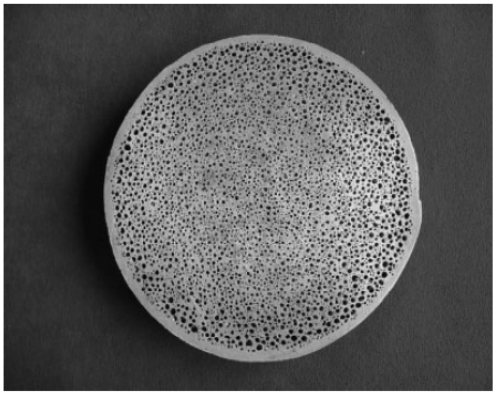
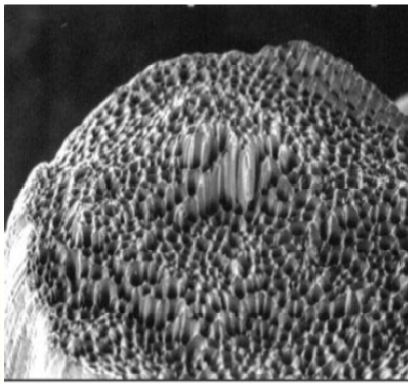


Fig. 4. Magnesium gasar with axial (left) and radial (right) pores.



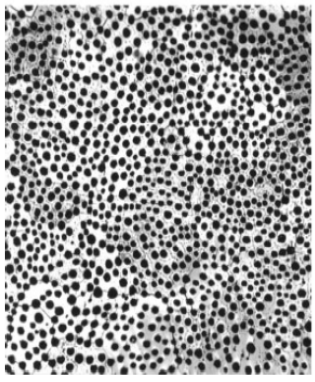


Fig. 2. General view of copper gasar on fracture surface.

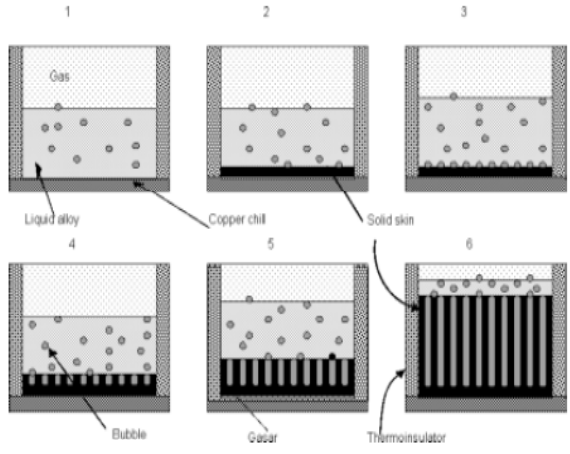


Fig. 3. Pores formation (schematic) on the surface of the native solidification front during unidirectional heat removal: 1–6 - consecutive gasar growth steps.

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

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.