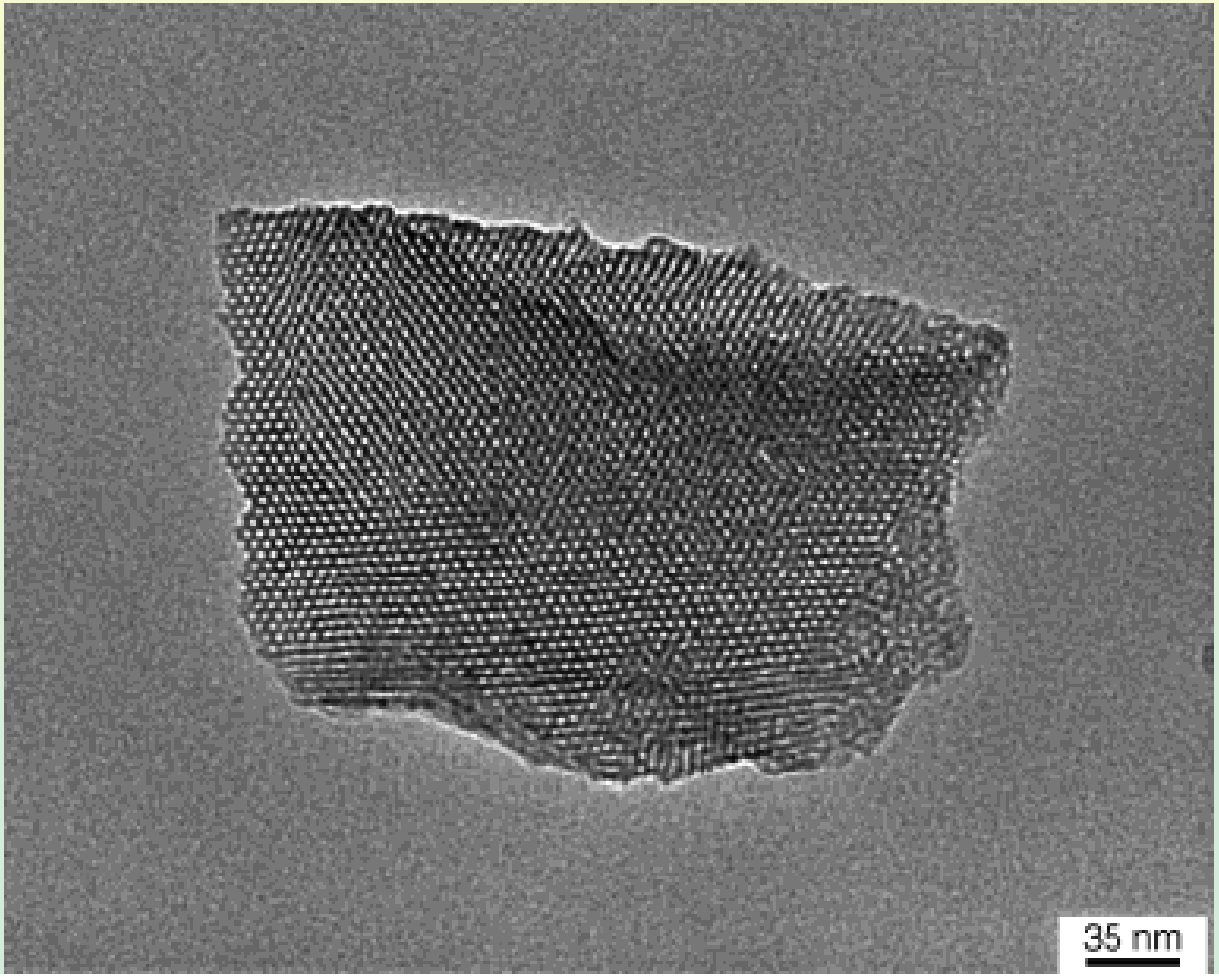
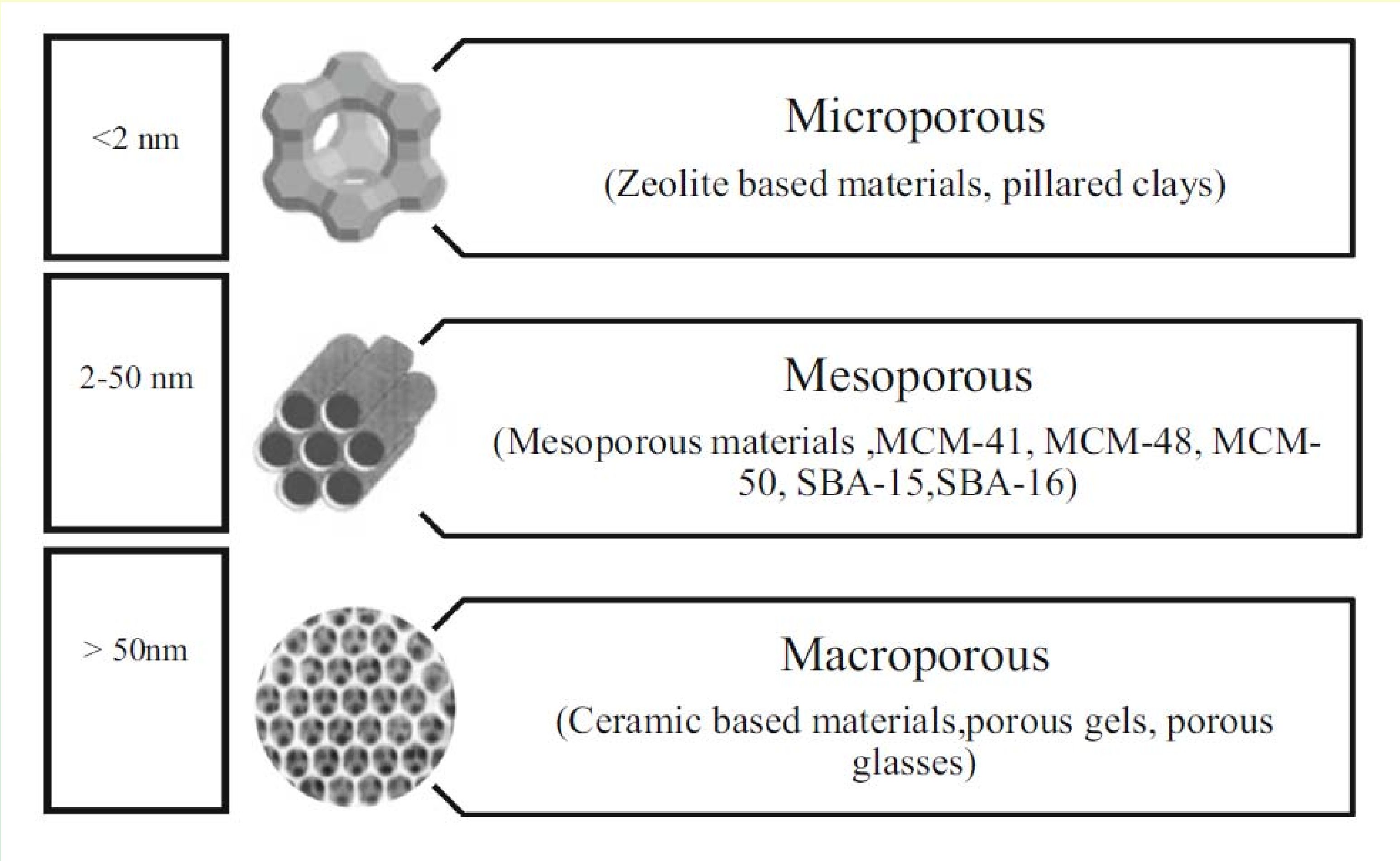
Mesoporous Materials

TEM image of the Pd-grafted mesoporous silicate material



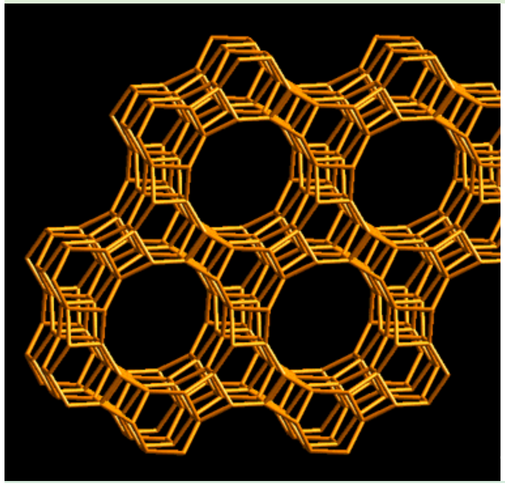
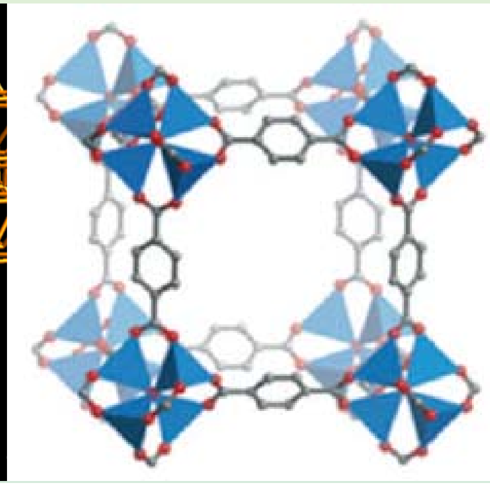
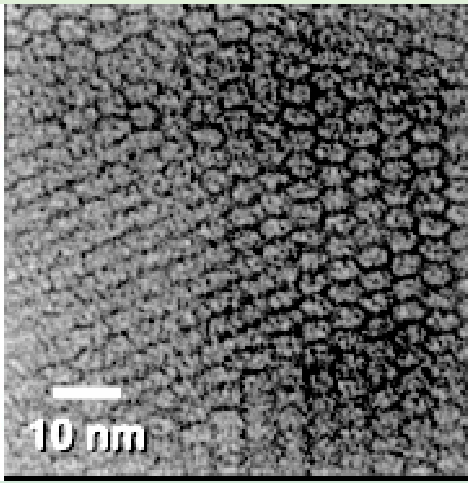
IUPAC Classification of Porous Materials

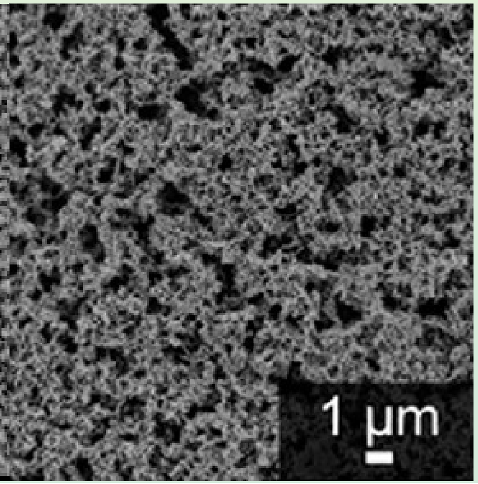


Mesoporous Materials

- **Disordered, amorphous - silica xerogels**
- **Ordered pores, amorphous walls (MCM, SBA)**

Pore diameter, ***d*** [nm]	Material	Example
$d > 50$	Macroporous	Aerogels, foams
$2 < d < 50$	Mesoporous	Xerogels, MCM-41, SBA-15
$d < 2$	Microporous	Zeolites, MOF, COF



Nomenclature of Mesoporous Materials

M41S - Group name of mesoporous MCM materials by Exxon Mobil (MCM = Mobil Crystalline Materials or Mobil Composition of Matter)

MMS - Mesoporous Molecular Sieves

OMS - Ordered Mesoporous Silicas

- **US pat. 1971 - forgotten**
- **Kuroda, Japan - 1990**
- **Independently rediscovered, pattented and published 1992 by Exxon Mobil**

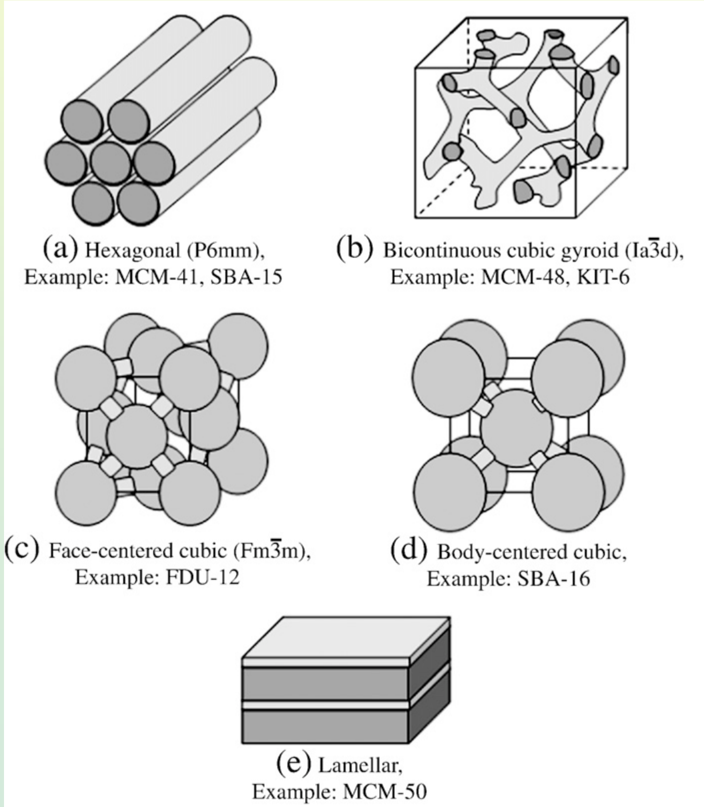
A - hexagonal 1D channels, MCM-41, SBA-15

B - cubic 3D channel structure (bicontinuous), MCM-48, KIT-6

C - FCC 3D channels, FDU-12

D - BCC 3D channels, SBA-16

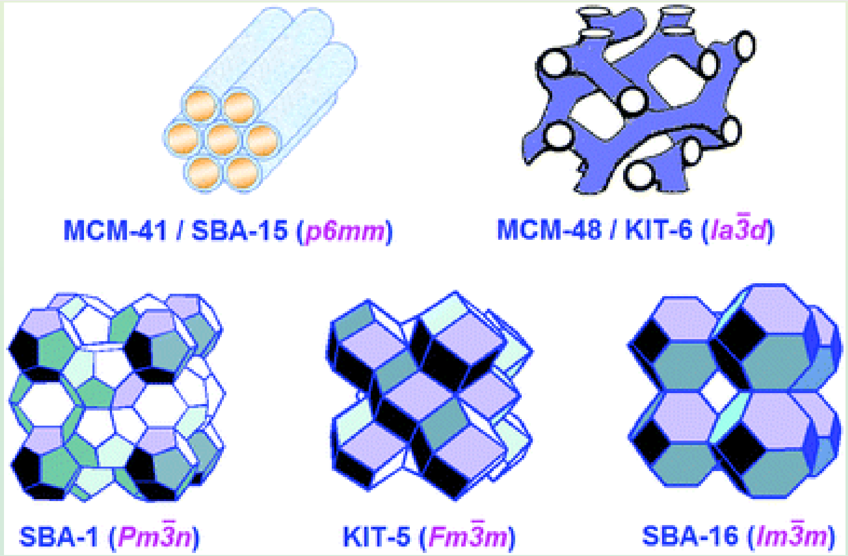
E - Lamellar, 2D layers, MCM-50



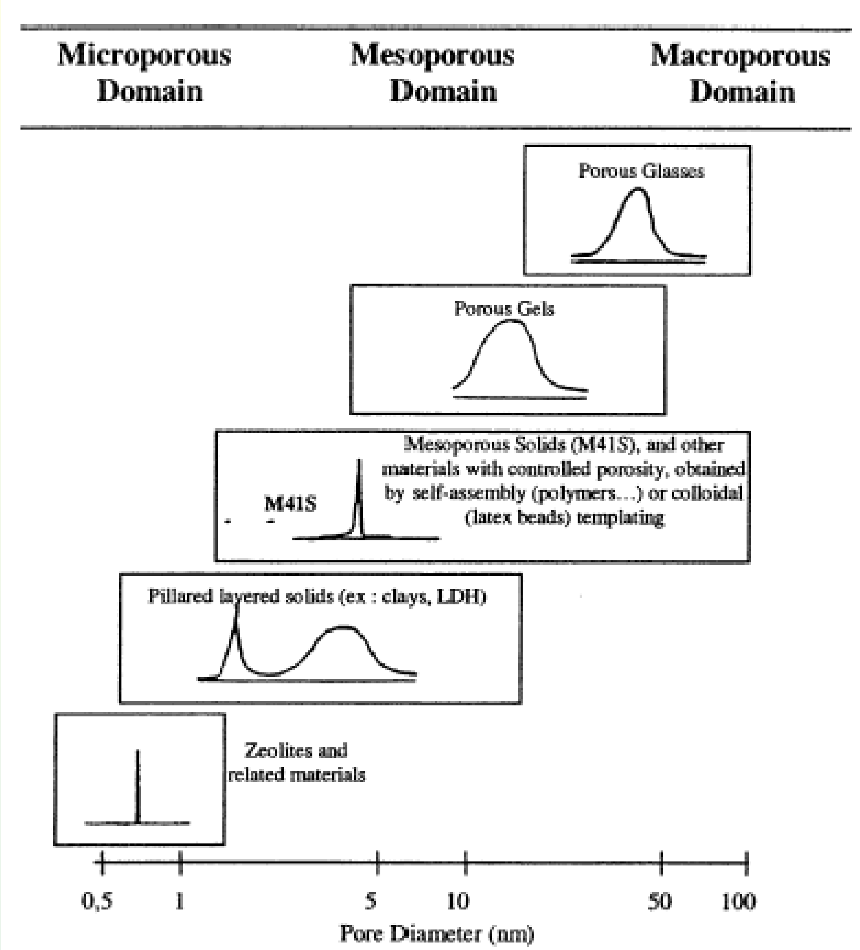
Nomenclature of Mesoporous Materials

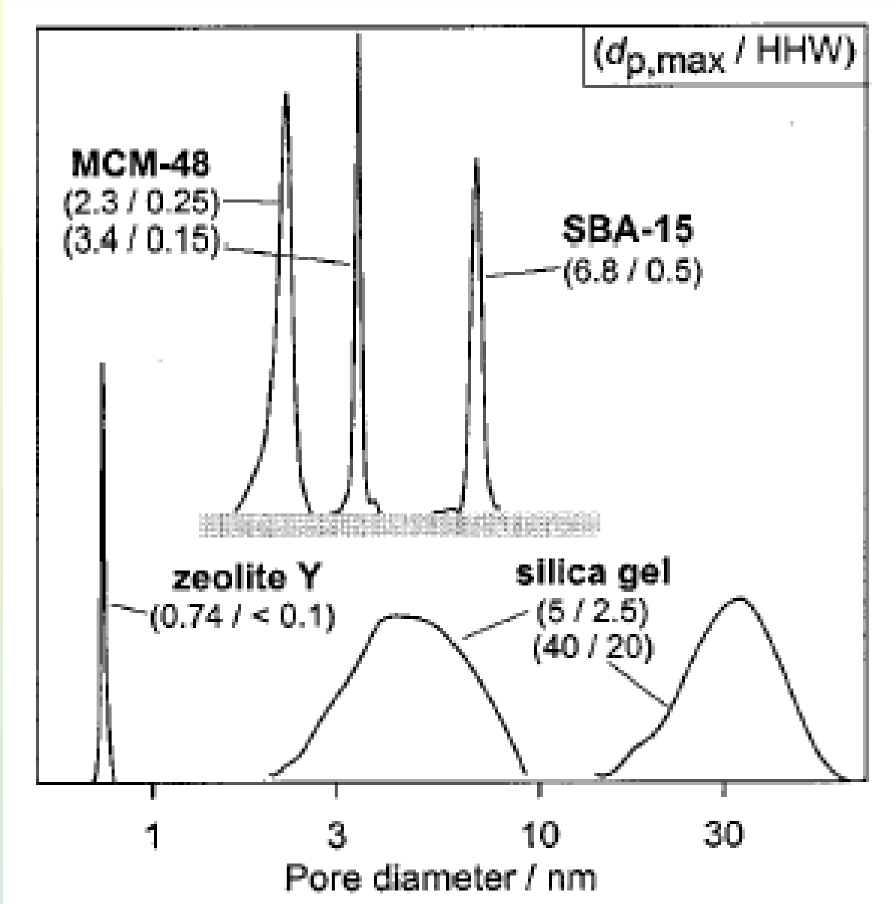
MSN Family	MSN Type	Pore Symmetry	Pore Size (nm)	Pore Volume (cm^3/g)
M41S	MCM-41	2D hexagonal $P6mm$	1.5–8	>1.0
	MCM-48	3D cubic $Ia3d$	2–5	>1.0
	MCM-50	Lamellar $p2$	2–5	>1.0
SBA	SBA-11	3D cubic $Pm3m$	2.1–3.6	0.68
	SBA-12	3D hexagonal $P6_3/mmc$	3.1	0.83
	SBA-15	2D hexagonal $p6mm$	6–0	1.17
	SBA-16	Cubic $Im3m$	5–15	0.91
KIT	KIT-5	Cubic $Fm3m$	9.3	0.45
COK	COK-12	Hexagonal $P6m$	5.8	0.45

MCM - Mobil Crystalline Materials
SBA - Santa Barbara Amorphous
KIT - Korea Advanced Institute of Science and Technology
COK - Centre for Surface Chemistry and Catalysis, Leuven
FDU - Fundan University
MSU - Michigan State University



Pore Size Distribution



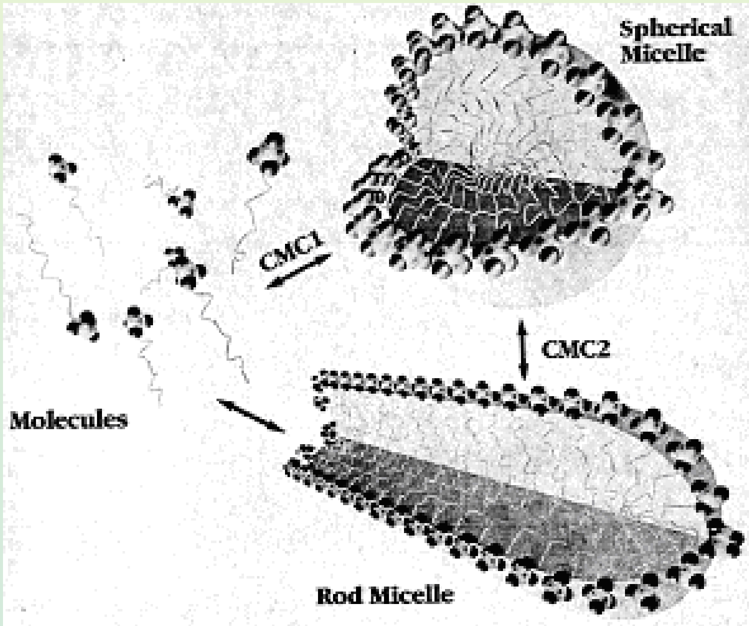


Micelles - Supramolecular Templates

In zeolitic materials, the template is a single molecule or ion – pores too small (micropores)

Self assembled aggregates of molecules or ions can also serve as templates – larger pores (mesopores)

Surfactants aggregate into a variety of structures depending on conditions (concentration, temperature, solvent,…)



Supramolecular Templating

Surfactants = amphiphilic molecules, polar (head group) and nonpolar (chain, tail) part

Lyophilic and lyophobic

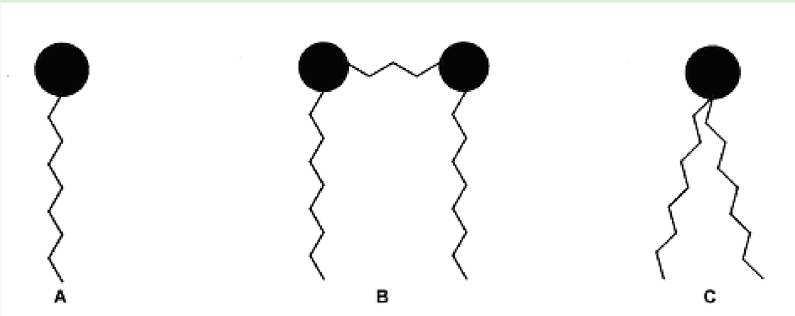
Ionic surfactants, cationic, anionic, zwitterionic

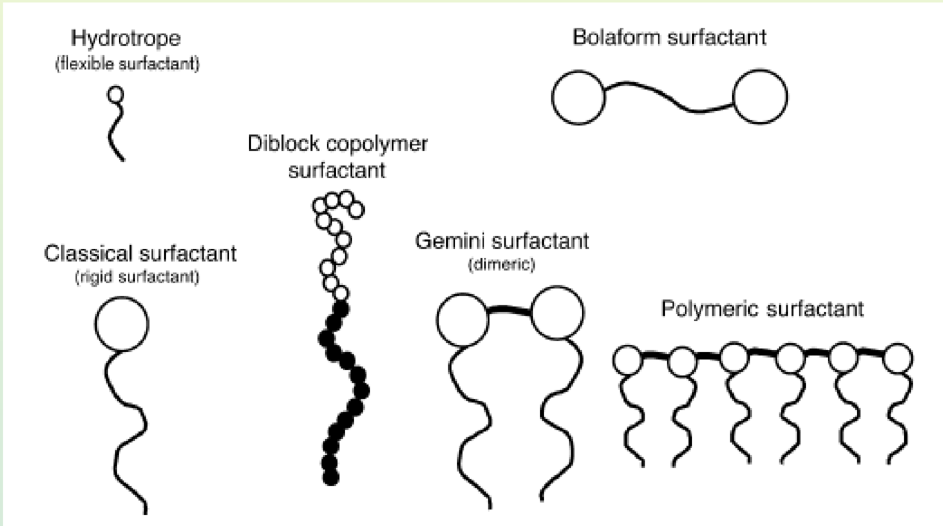
Nonionic amines, polyethyleneoxides

A - normal surfactant molecule

B - gemini

C - swallow tail





Types Surfactant Molecules

Cationic

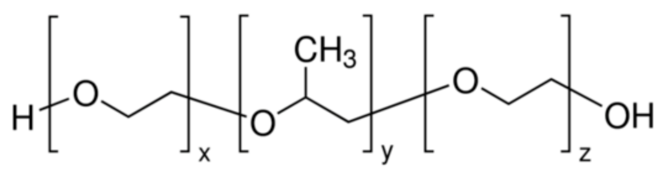
alkylammonium salts	$C_nH_{2n+1}(CH_3)_3NX$, X = OH, Cl, Br, HSO_4
dialkylammonium salts	$(C_{16}H_{33})_2(CH_3)_2N^+ Br^-$

Anionic

sulfates	$C_nH_{2n+1}OSO_3^- Na^+$
sulfonates	$C_nH_{2n+1}SO_3H$
phosphates	$C_nH_{2n+1}OPO_3H_2$
carboxylates	$C_nH_{2n+1}COOH$

Noionic

primary amines	$C_nH_{2n+1}NH_2$
polyethyleneoxides	$HO(CH_2CH_2O)_nH$
triblock copolymers	**Pluronic**



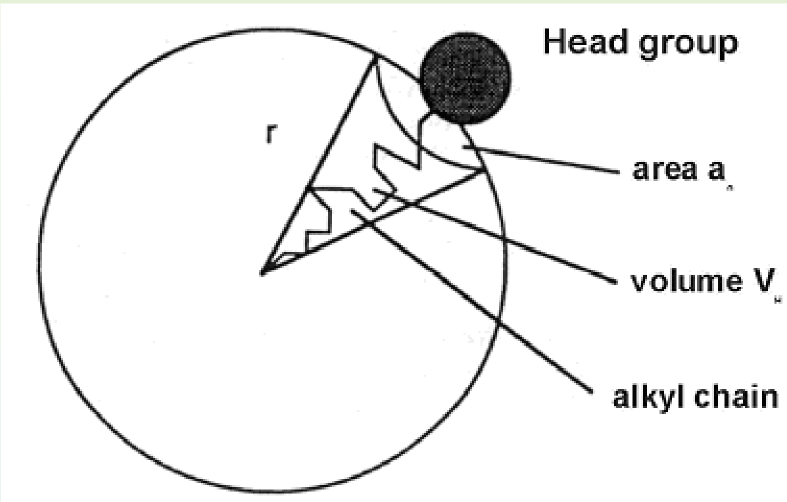
Surfactant Molecules

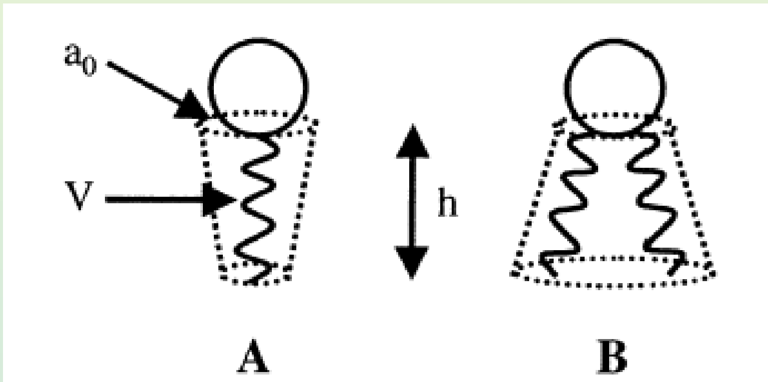
Critical packing parameter – CPP

$$\mathrm{CPP} = V_H / a_0\, l_c$$

V_H volume of the hydrophobic part, a_0 surface area of the hydrophilic part, l_c critical chain length:

$l_c \leq 1.5 + 1.265\, n$ [Å]
n number of carbon atoms, l_c depends on the chain shape

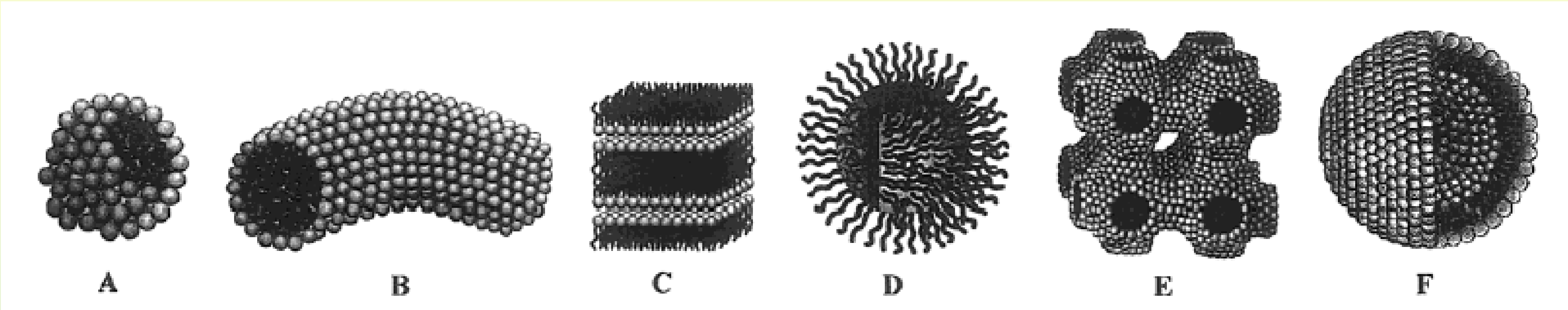




Conical (*icecream cone*, A)
Inverse conical (*champagne cork*, B)

Micellar Shapes

A) sphere, B) cylinder/rod, C) planar bilayer/ lamellar, D) reverse micelles, E) bicontinuous phase, F) liposomes)

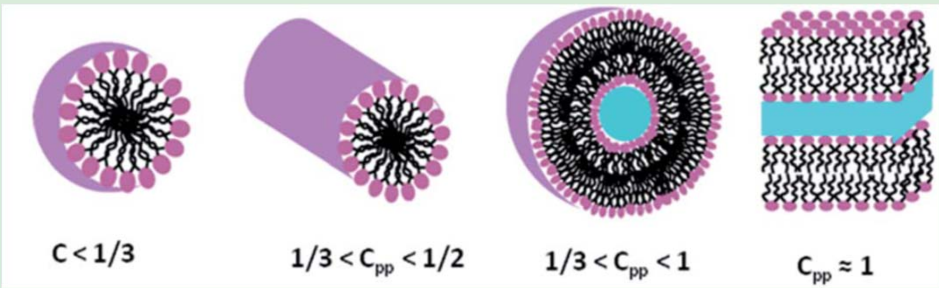


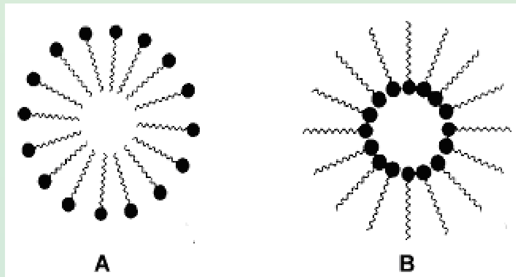
CPP	Surfactant	Micelle Shape
< 0.33	linear chain, large head	spherical
0.33 - 0.5	linear chain, small head	cylindrical
0.5 - 1.0	two chains, large head	bilayers

Micelles in media

A - normal, in polar solvent, H_2O

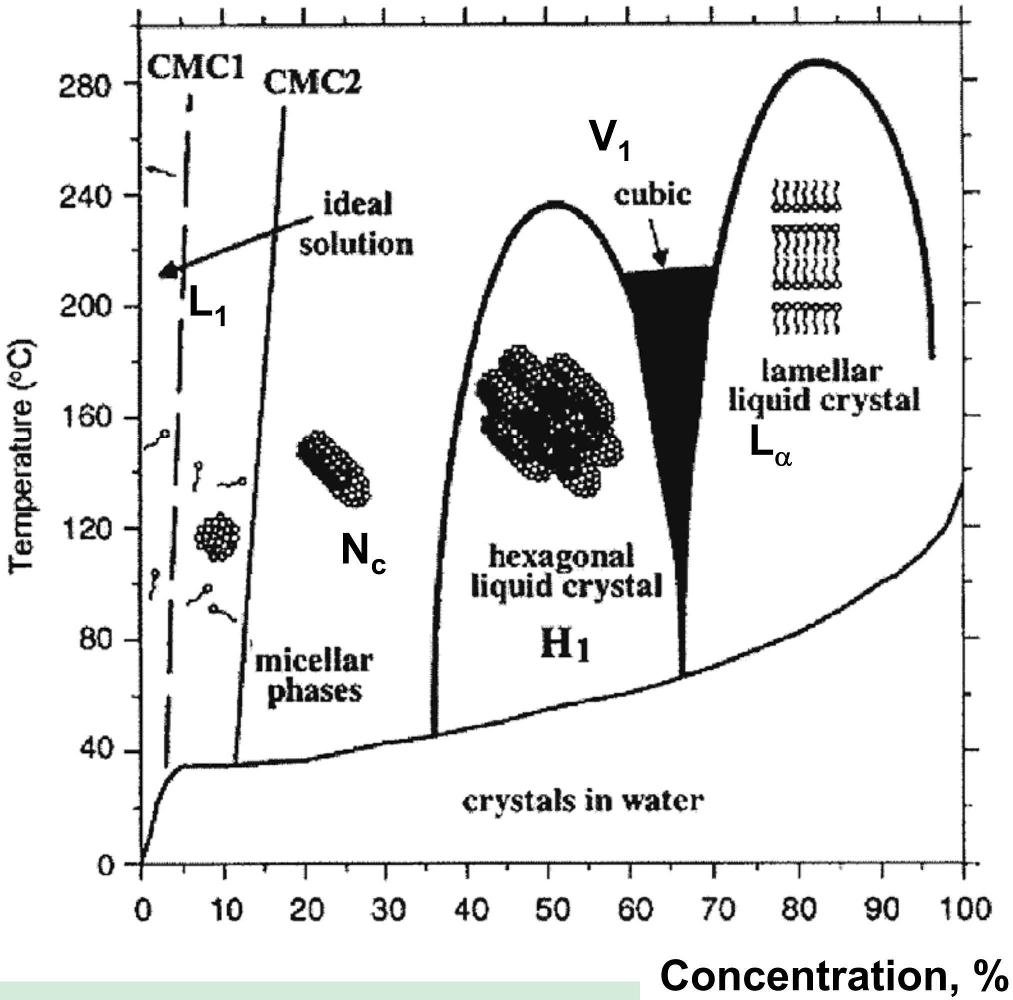
B - inverse, in nonpolar solvent, organics





Supramolecular Templating

Phase diagram of $[(C_{16}H_{33})N(CH_3)_3]Br$ cetyltrimethylammonium bromide (CTAB)



L_1 = micellar solution

N_c = nematic phase

H_1 = hexagonal liquid crystal phase (MCM-41; SBA-15)

V_1 = bicontinuous cubic liquid crystal phase (MCM-48)

L_α = lamellar phase (MCM-50)

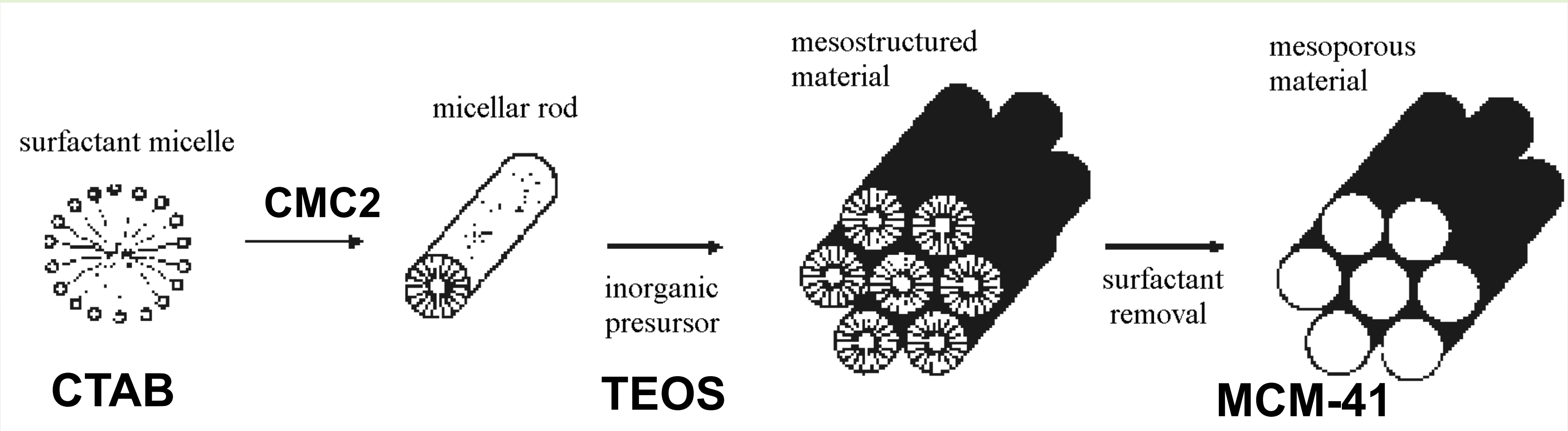
CMC1 = critical spherical micelle conc.

CMC2 = critical rod-like micelle conc.

Mechanism of the Mesoporous Material Formation

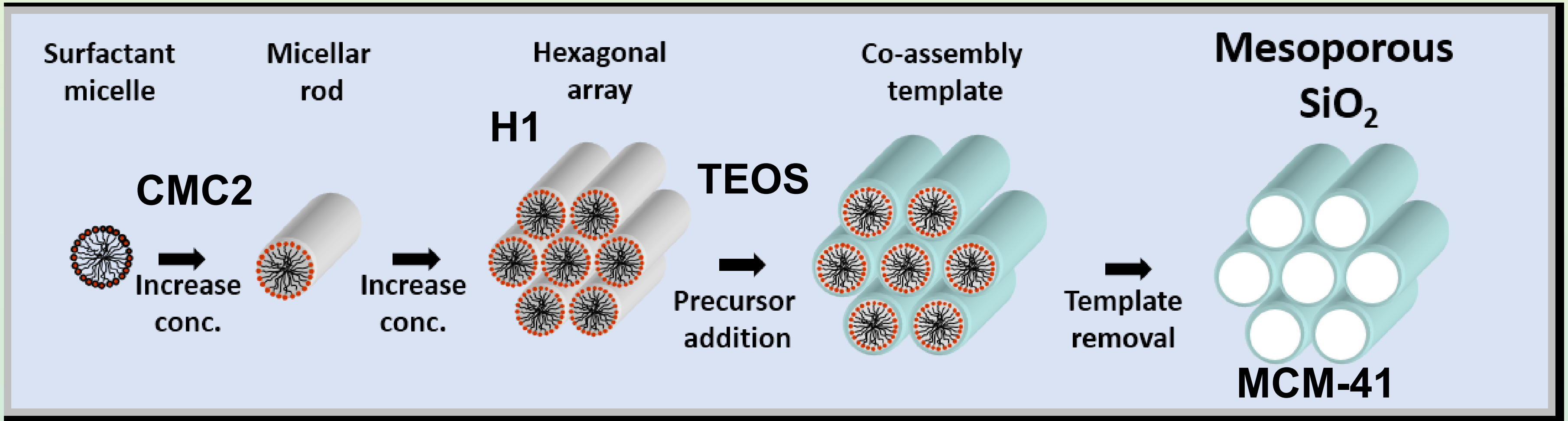
Hexagonal MCM-41

- **Liquid Crystal Templating (LCT)**
- **Silicate Rod Assembly**
- **Silicatropic Liquid Crystals (SLC)**
- **Lamellar to Hexagonal Transformation**



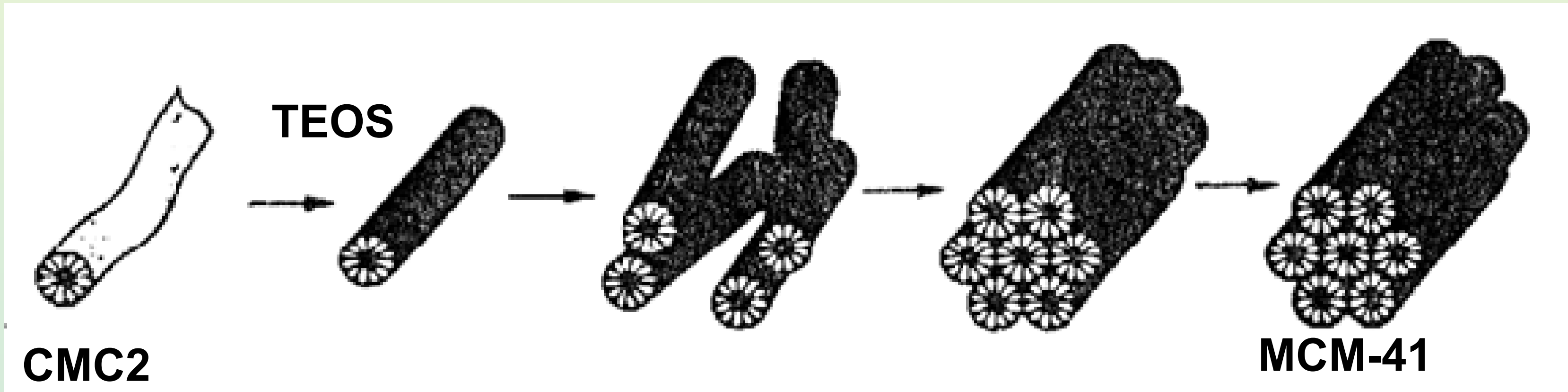
Liquid Crystal Templating (LCT) Mechanism

- **Formation of rod-like micelles (above CMC2)**
- **Assembly of rod-like micelles into hexagonal liquid crystal phase H1**
- **TEOS deposition in between rod-like micelles**
- **Hydrolysis and condensation to form solid amorphous walls of silica**
- **Template removal to form MCM-41**



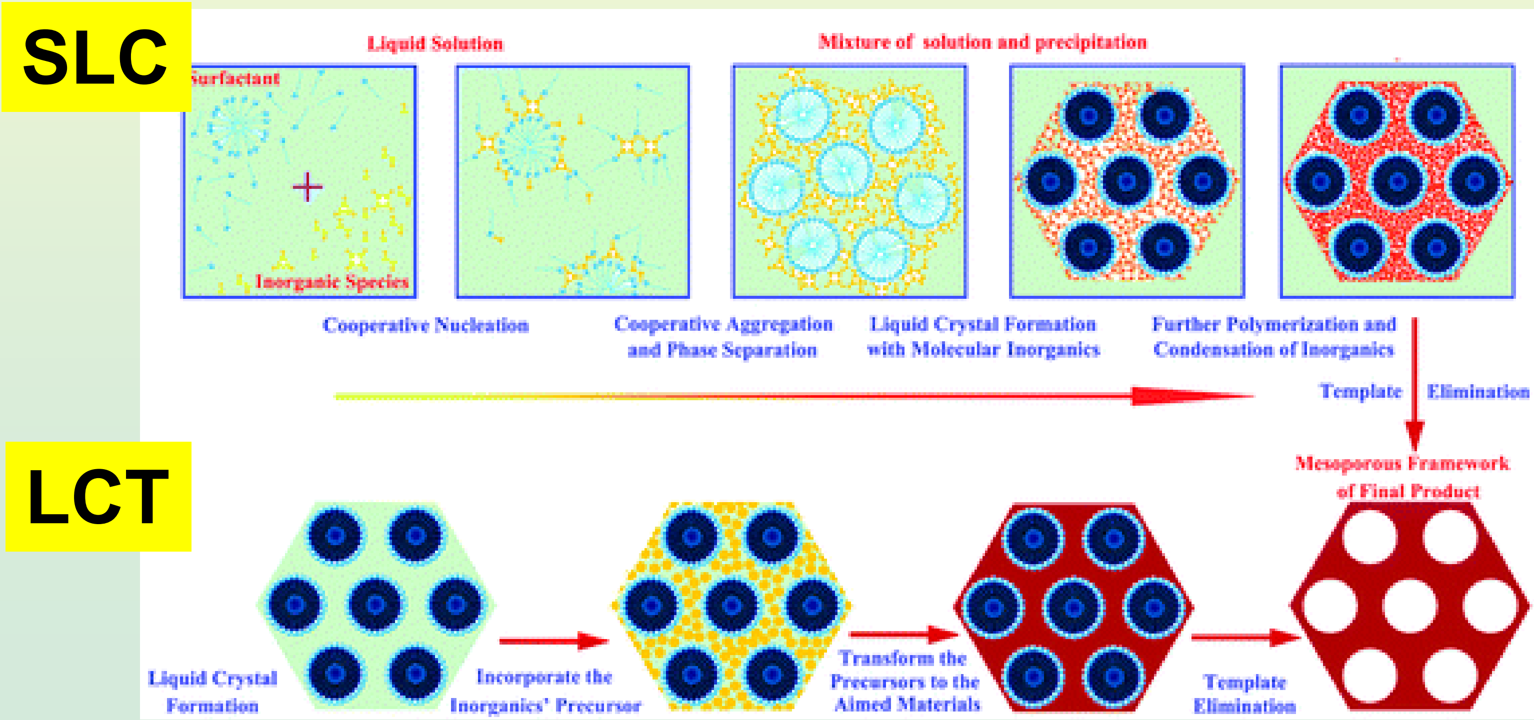
Silicate Rod Assembly Mechanism

- Formation of rod-like micelles (above CMC2)
- Silicate deposition on the surface of micelles
- Silica/surfactant rods assemble to hexagonal arrays
- Silica condensation to solid amorphous walls
- Template removal to MCM-41



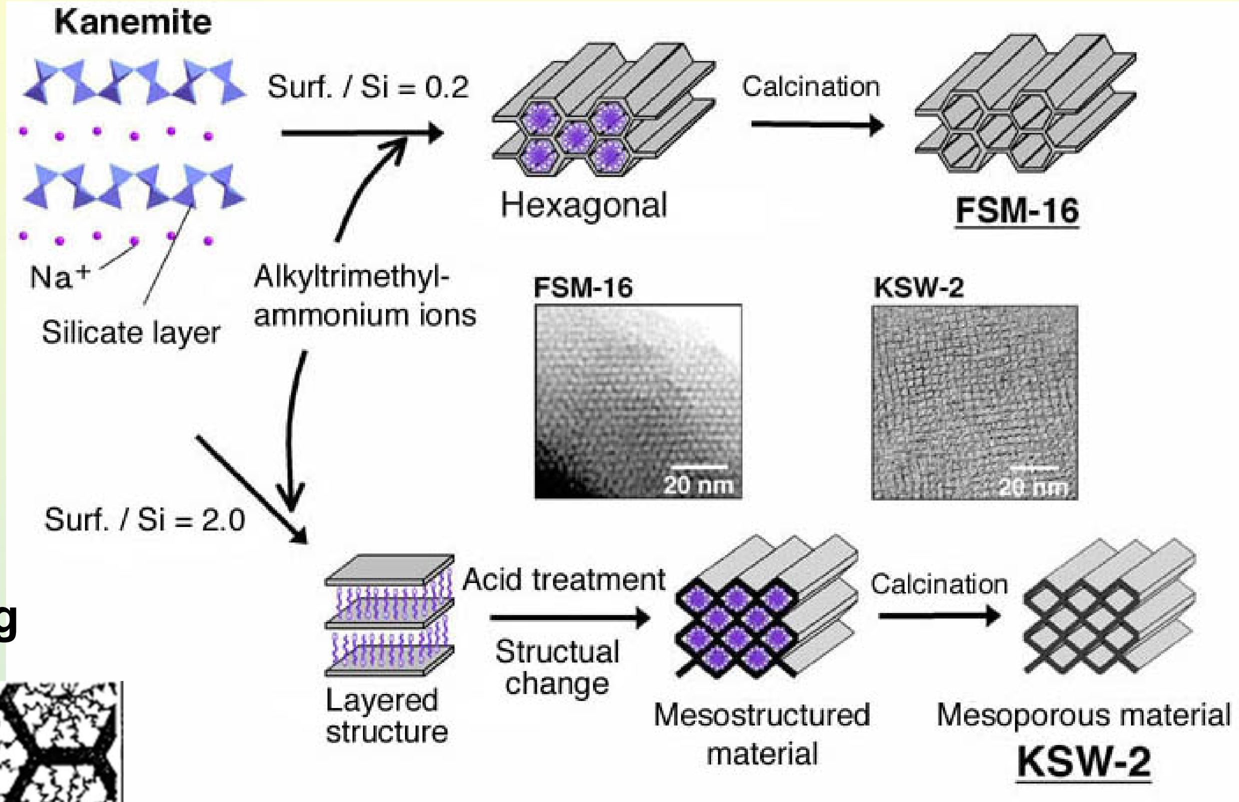
Silicatropic Liquid Crystals (SLC) Mechanism

- **Interaction/ion-exchange of surfactant and inorganic precursors**
- **Cooperative self-assembly of silicate/surfactant micelles below CMC2 !!**
- **Assembly to hexagonal liquid crystal phase**
- **Silica condensation to solid amorphous walls**

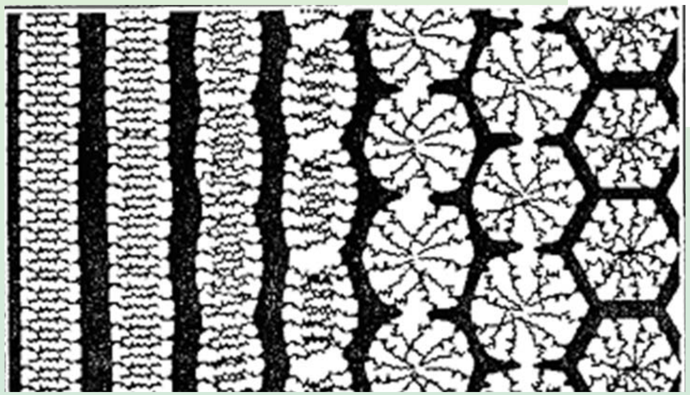


Lamellar to Hexagonal Transformation

- **Ion Exchange of Na^+ for surfactant**
- **Folding of silicate layers**



Charge Density Matching



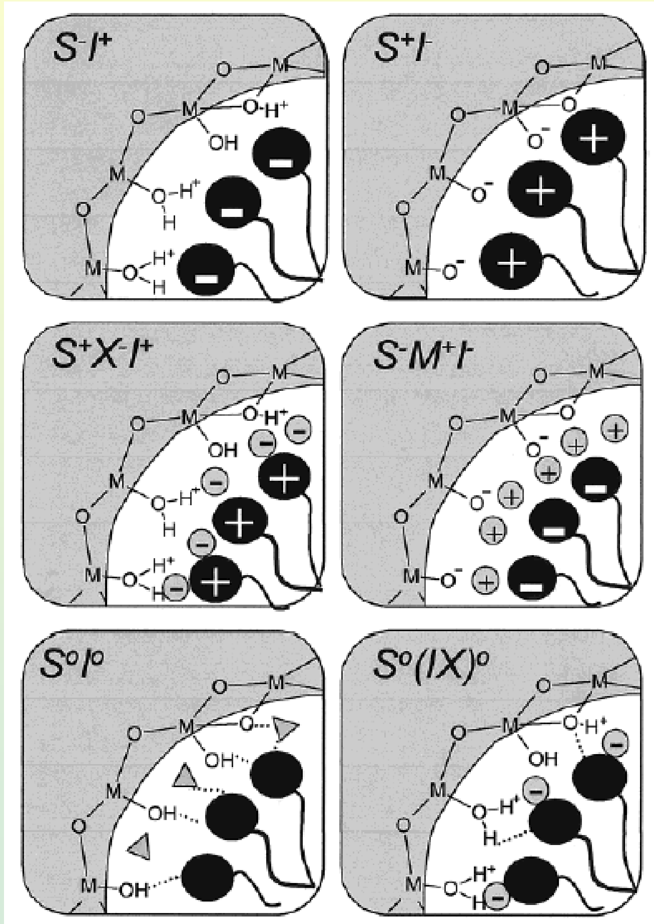
As condensation proceeds the charge on the silicate layer decreases

Si–O⁻ → Si–O–Si

Precursor-Micelle Interactions

Electrostatic Interactions

a) $S^+ I^-$	**I = silicate (Si-O^-)** **S = trimethylammonium**
b) $S^- I^+$	**I = Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Mg^{2+}, Mn^{2+}, Pb^{2+}, Al^{3+}** **S = sulfonate**
c) $S^+ X^- I^+$	**I = silicate – positive charge** **X = Cl^-** **S = trimethylammonium**
d) $S^- M^+ I^-$	**I = aluminate** **M = Na^+** **S = phosphate**

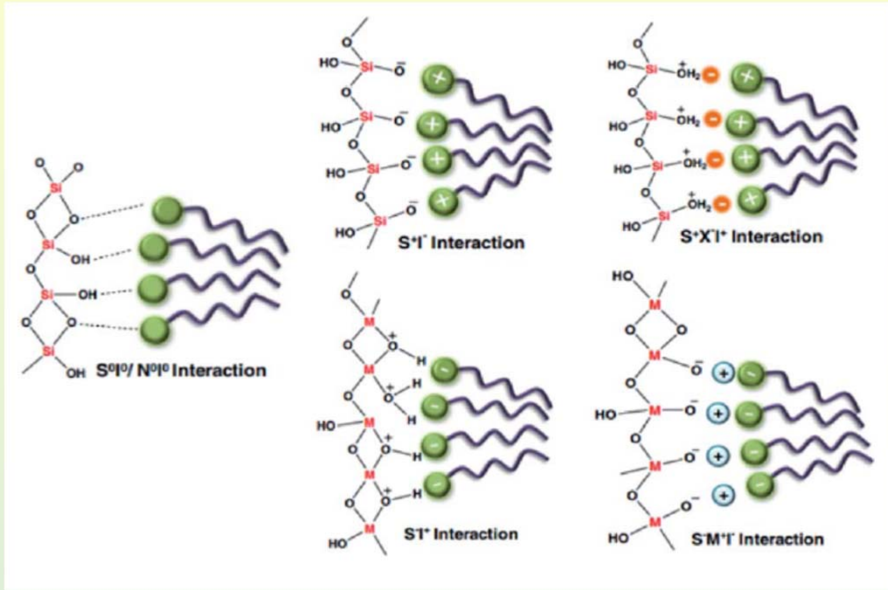


Precursor-Micelle Interactions

Hydrogen Bond

a) S^0 I^0 — **I = silicate at IEP**
S = ammine

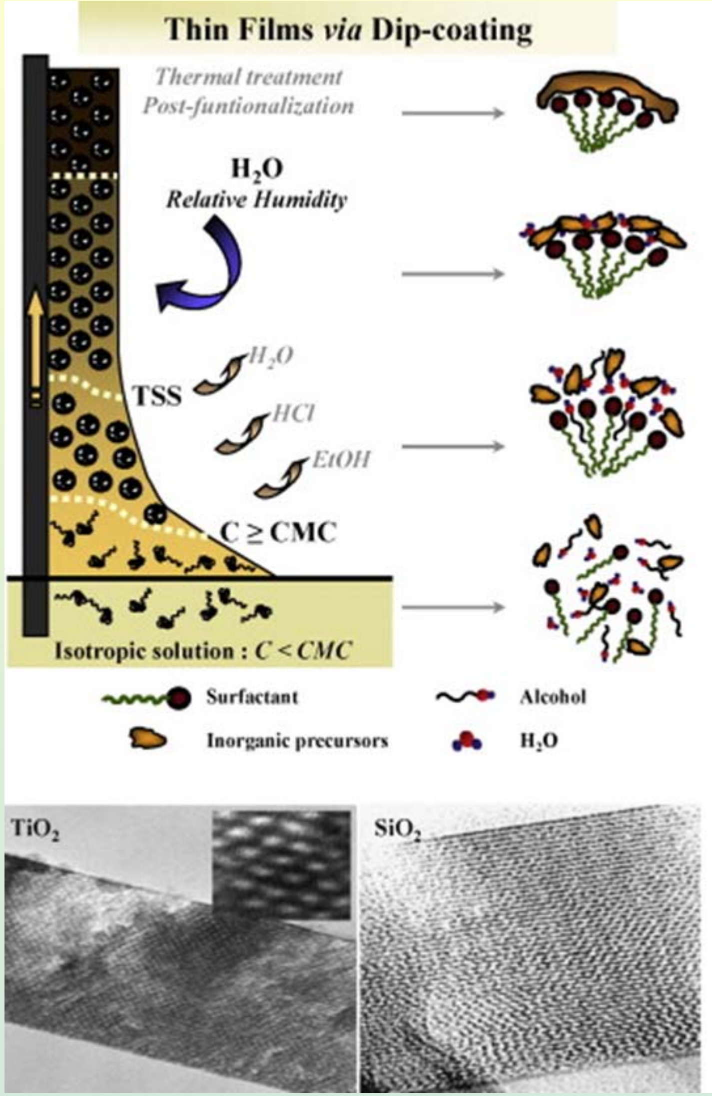
b) N^0 I^0 — **I = silicate**
N = polyethylenoxide



Covalent Bond

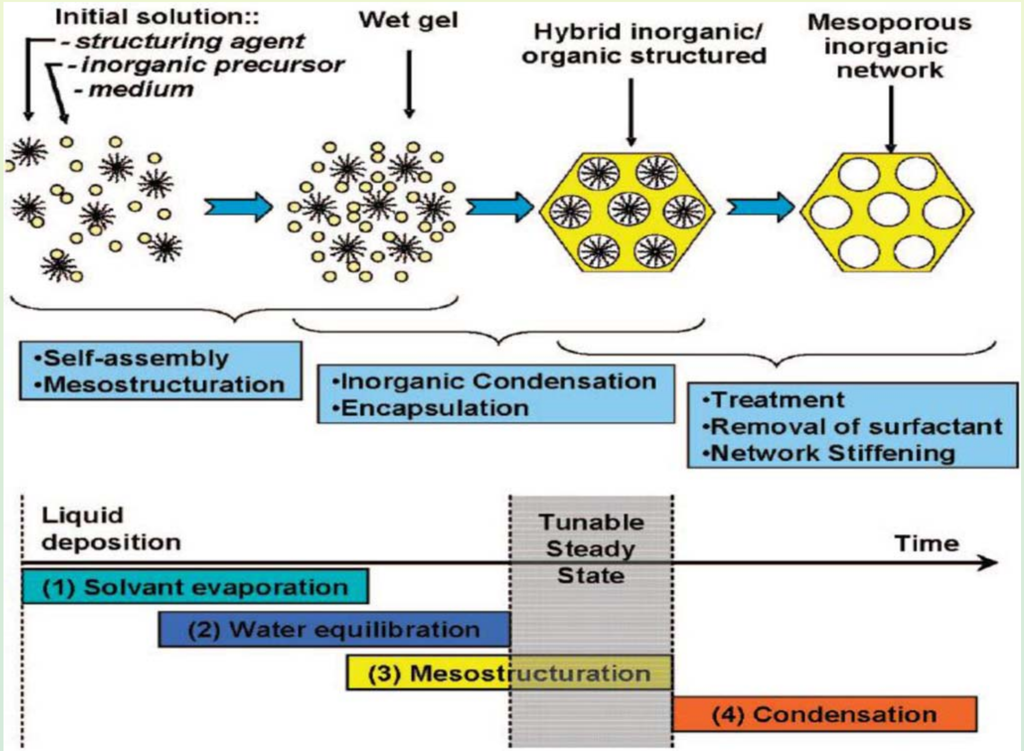
a) S-I — **I = niobate, tantalate**
S = ammine

EISA = Evaporation-Induced Self-Assembly



Critical parameters

- **Molar ratio of Surfactant/Inorganic precursor**
- **Amount of water**
- **Volatile cosolvent content (EtOH, THF,…)**
- **Temperature**
- **Relative humidity**



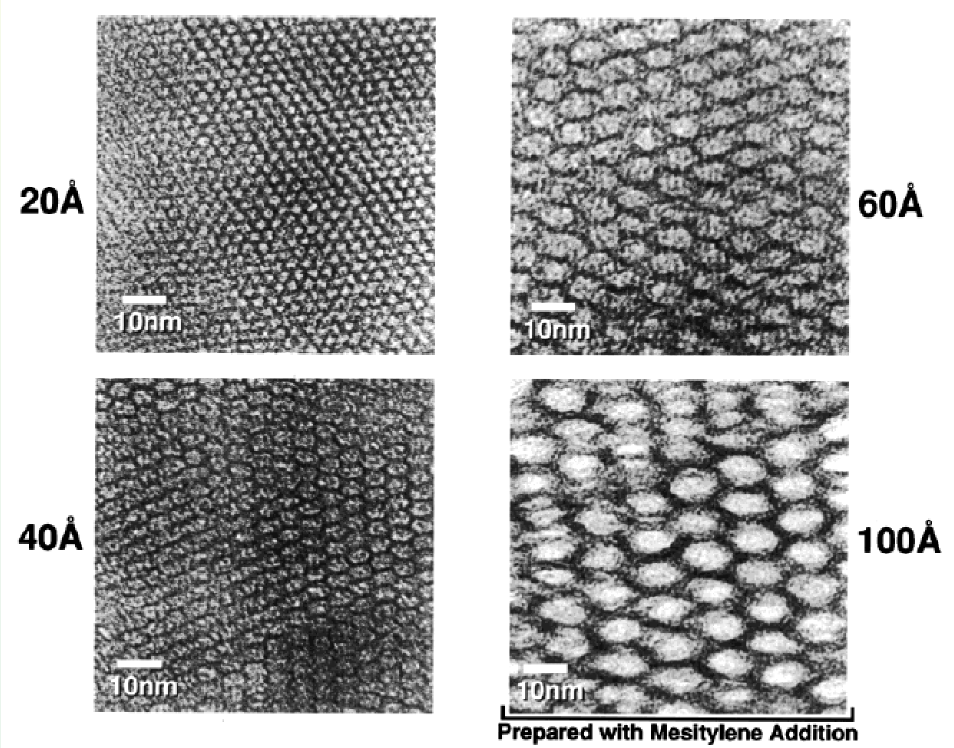
Control of Pore Size

Surfactant chain length - increasing the chain length = bigger pores

Swelling agents – an organic additive, such as trimethylbenzene, enters the surfactant assembly (micelle) = bigger pores

Post synthetic modification - after a material has been made the pore size can be reduced by modifying the interior surface = smaller pores

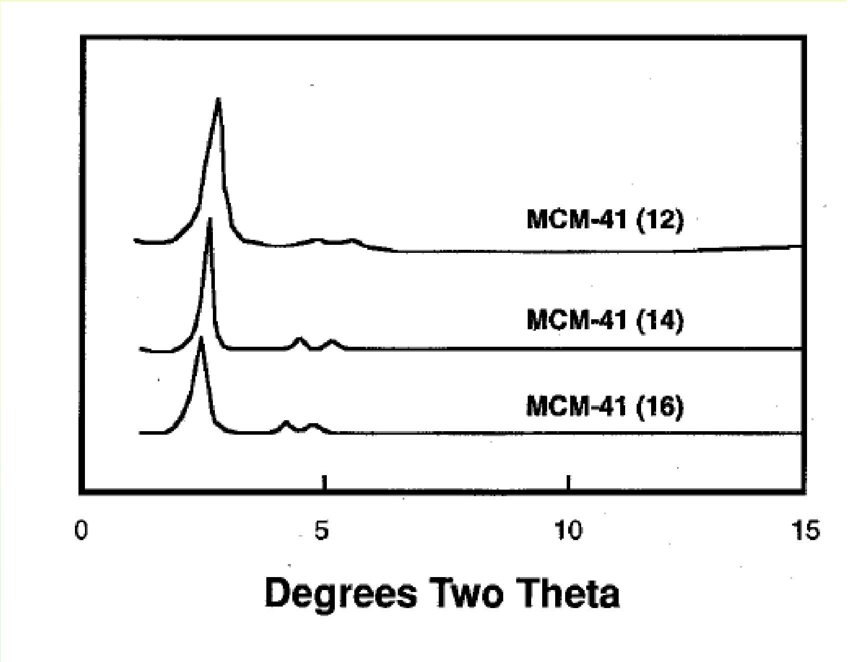
MCM-41



Control of Pore Size

Surfactant chain length - increasing the chain length = bigger pores

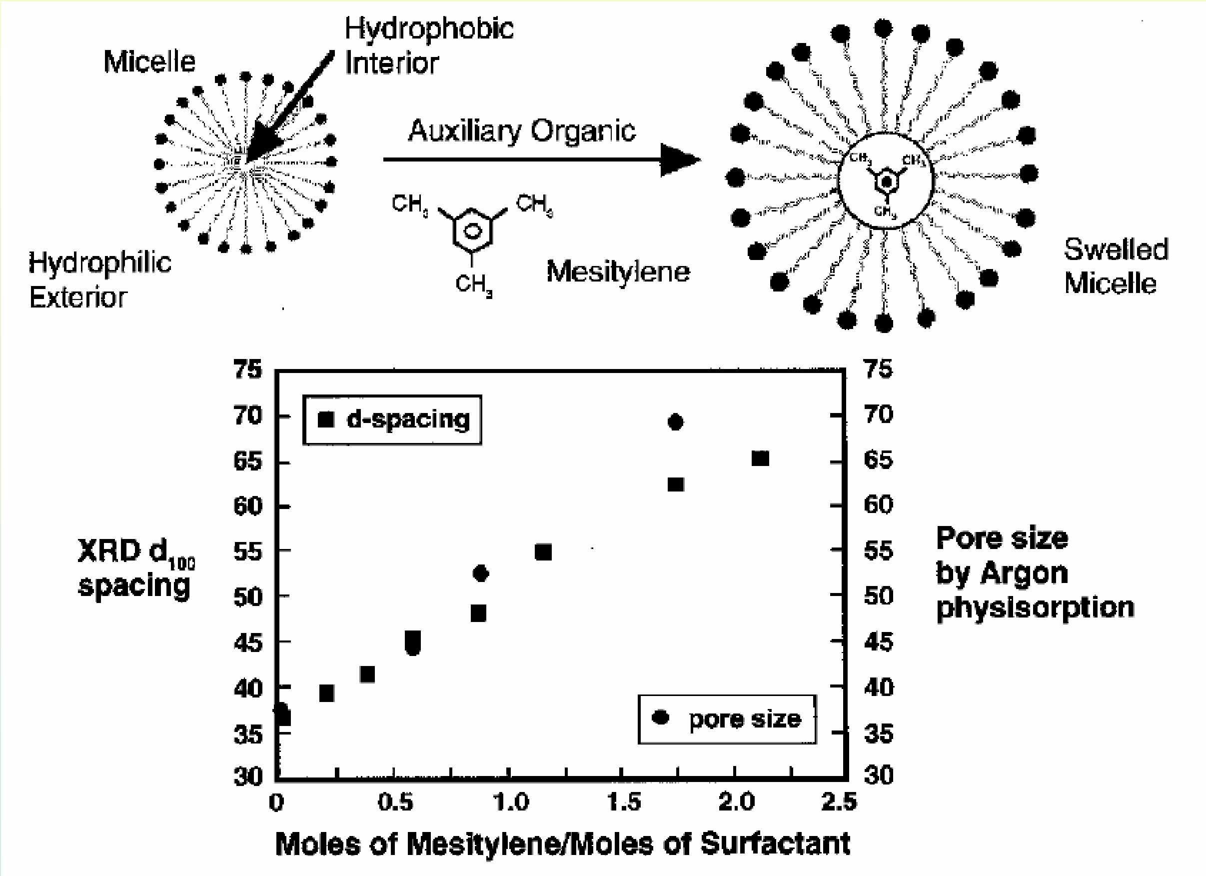
XRD



Surfactant chain length n $C_nH_{2n+1}NMe_3^+$	Lattice constant (Å)	Ar pore size (Å)	Maximum benzene uptake at 50 torr (wt%)
8	31	18	16
9	32	21	37
10	33	22	32
12	33	22	36
14	38	30	54
16	40	37	64

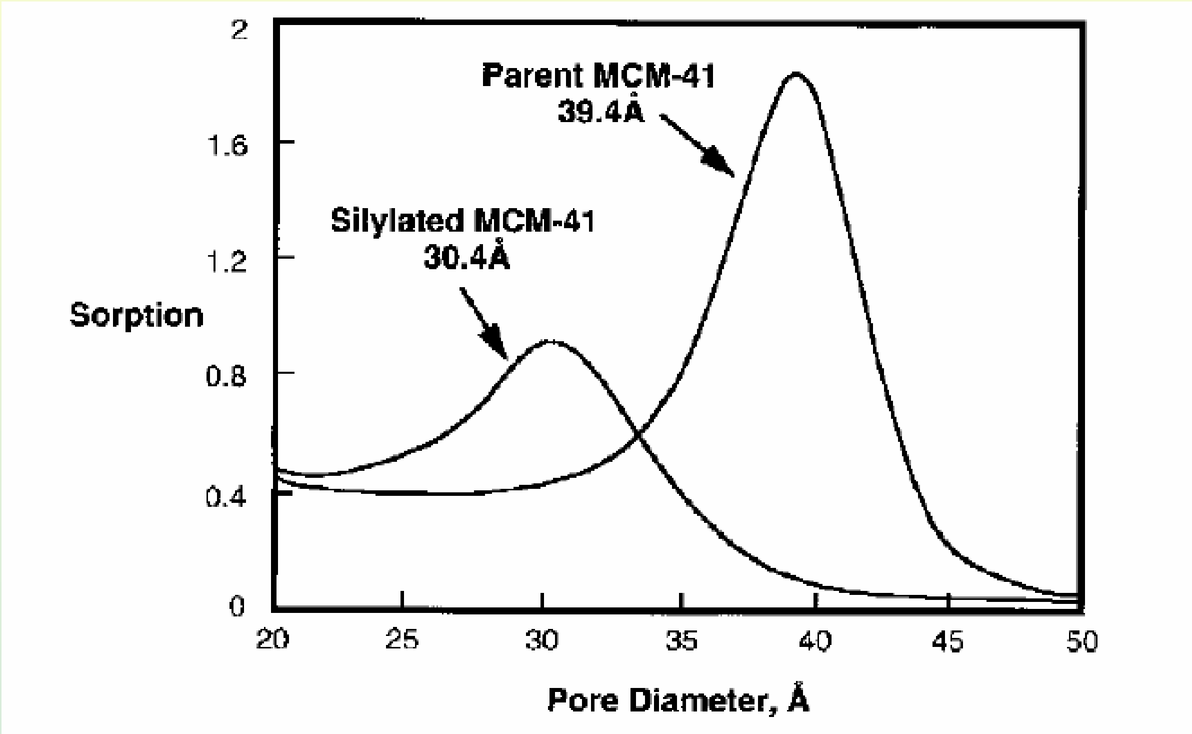
Control of Pore Size

Swelling agents – an organic additive, such as trimethylbenzene, enters the surfactant assembly (micelle) = bigger pores



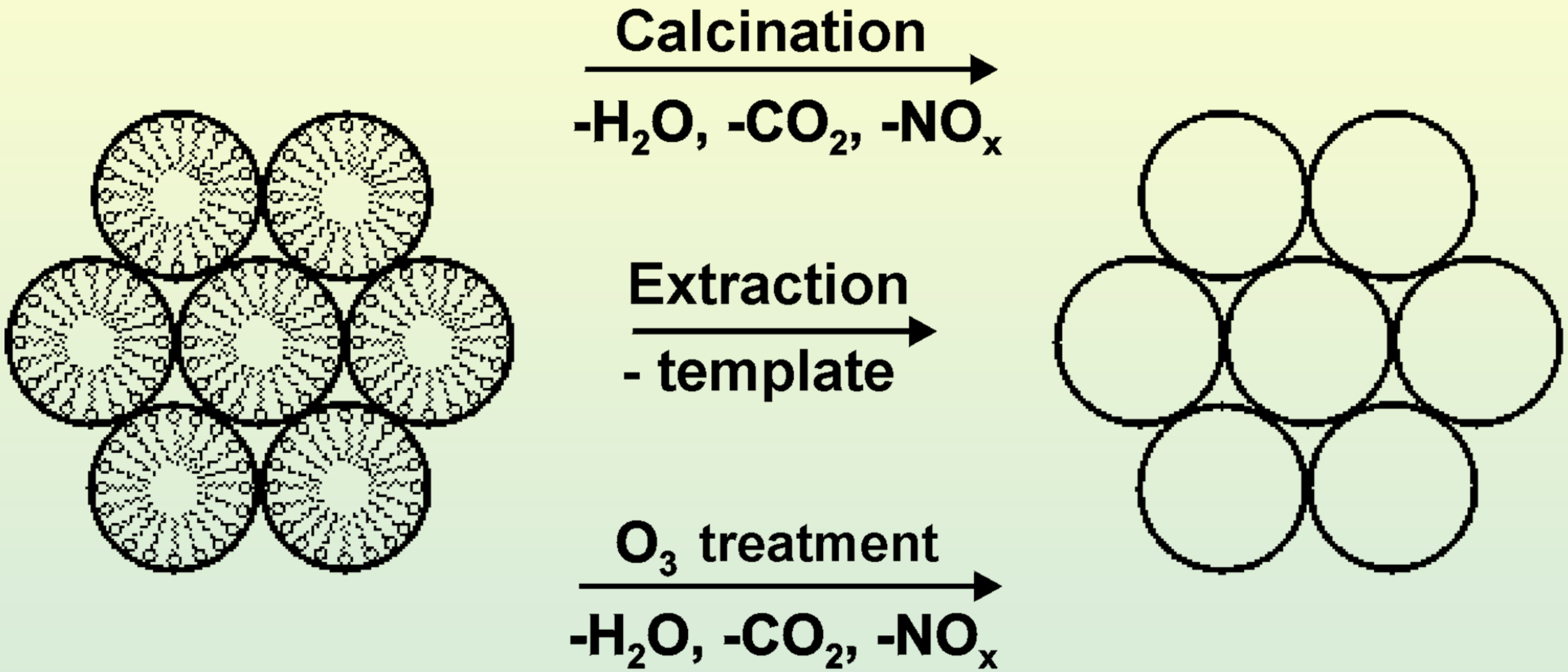
Control of Pore Size

Post synthetic modification - after a material has been made the pore size can be reduced by modifying the interior surface = smaller pores



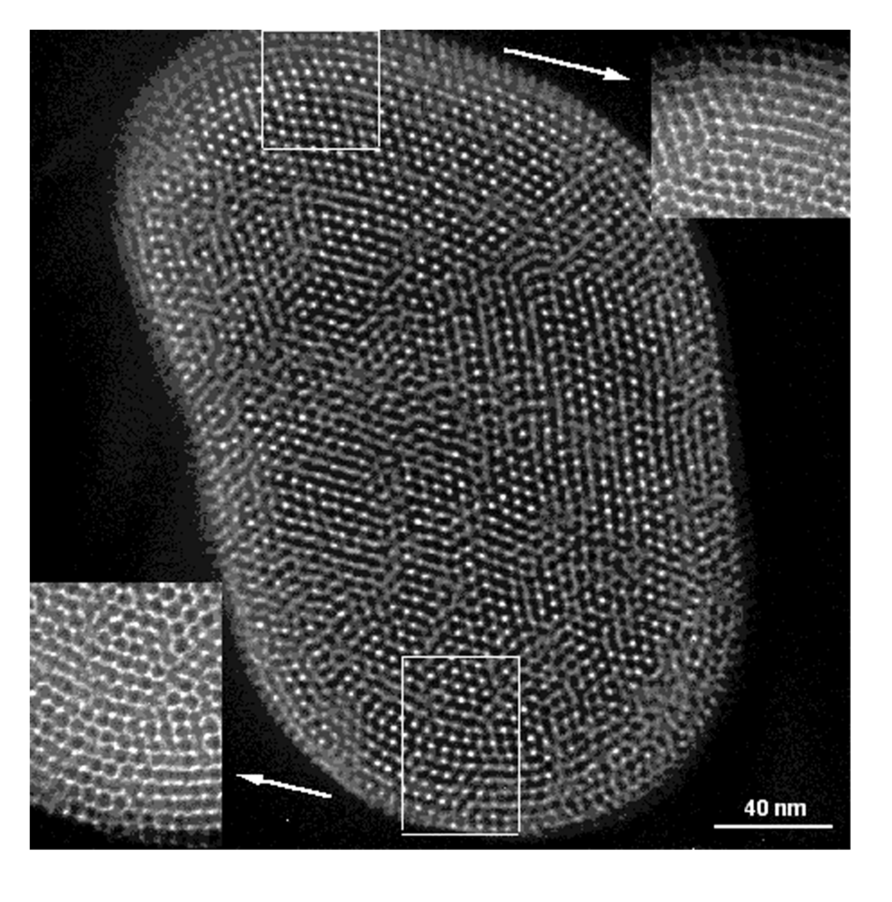
Silylation of hydroxyl groups in MCM-41 by Me_3SiCl reduces the effective pore size

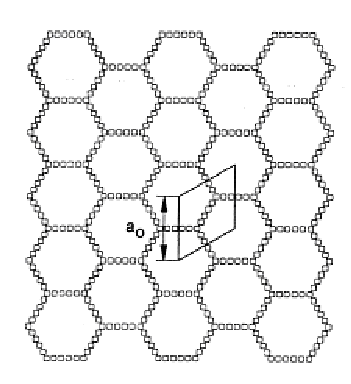
Template Removal

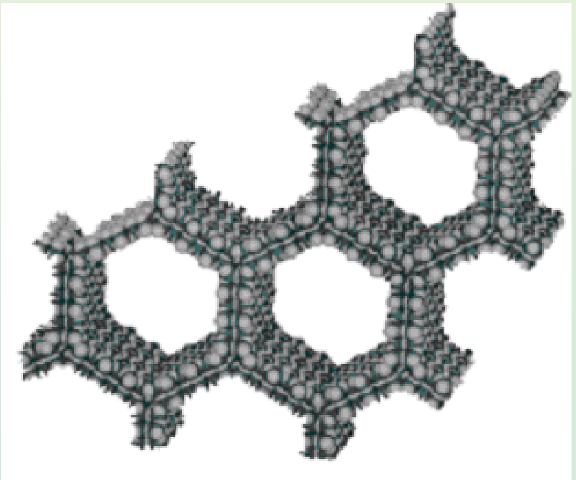


Characterization of Mesoporous Materials

TEM micrograph of hexagonal molecular sieve



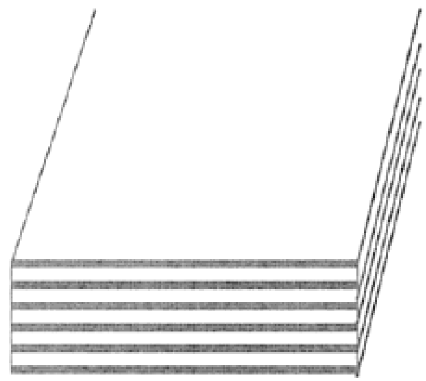


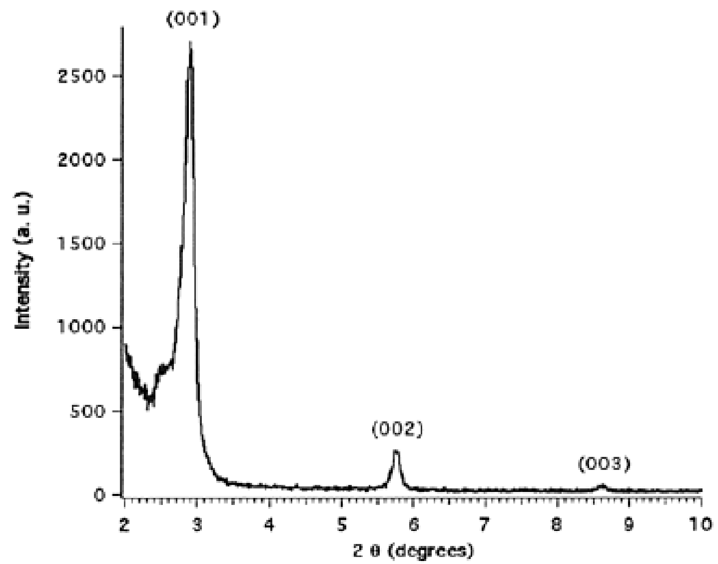


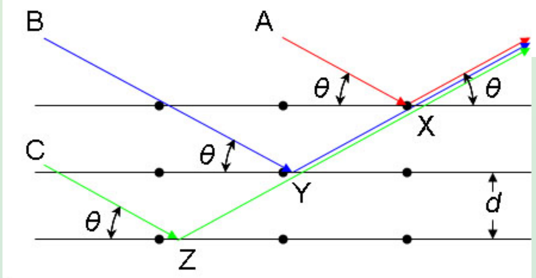
Characterization of Mesoporous Materials

XRD of Lamellar MCM-50

Only (00l) diffractions observed



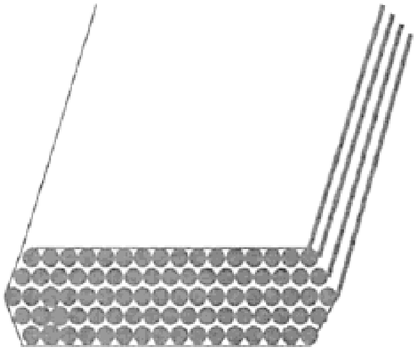


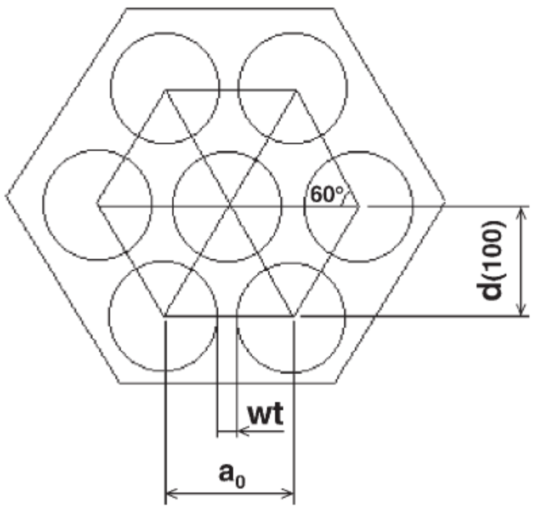


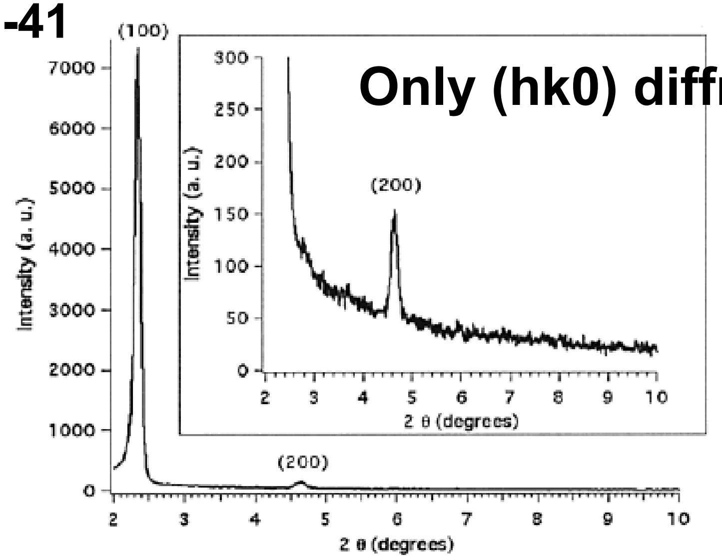
Bragg's Law $n\lambda = 2d \sin \theta$

Characterization of Mesoporous Materials

XRD of Hexagonal MCM-41







Only (hk0) diffractions observed

wt = wall thickness
d(100) = interplanar distance in the (100) plane
a_0 = mesoporous parameter

$$a_0 = \frac{2d_{100}}{\sqrt{3}}$$

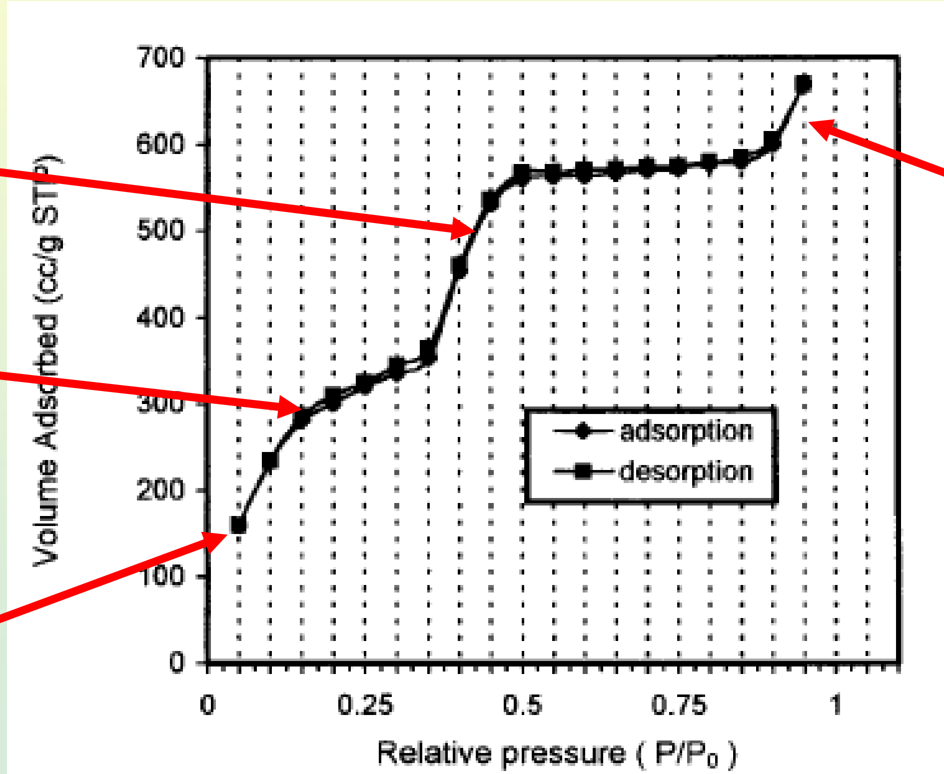
Characterization of Mesoporous Materials

Gas Adsorption Isotherms (N_2 at 77 K)

Mesopore filling

BET
Surface area

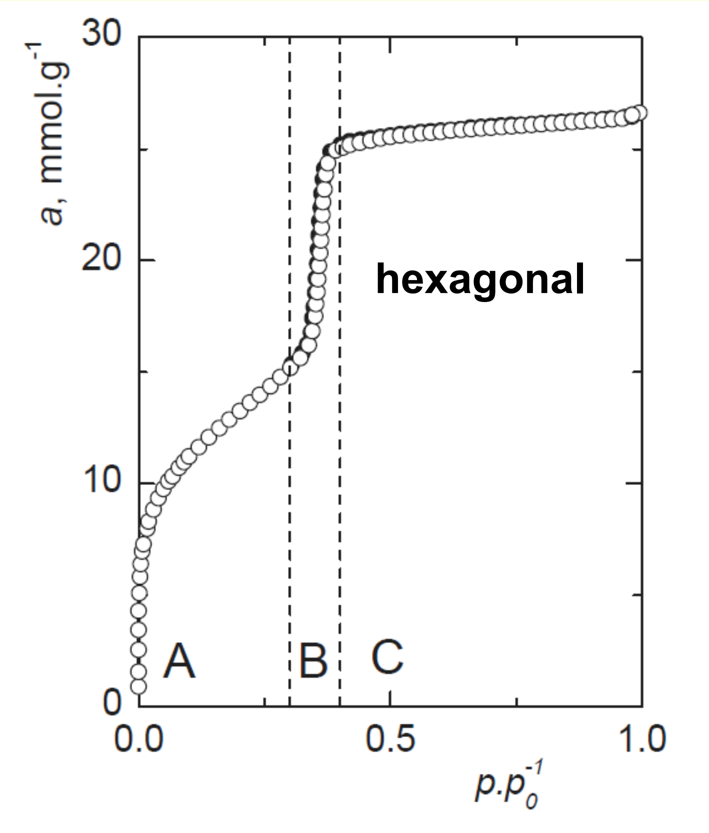
Micropore filling

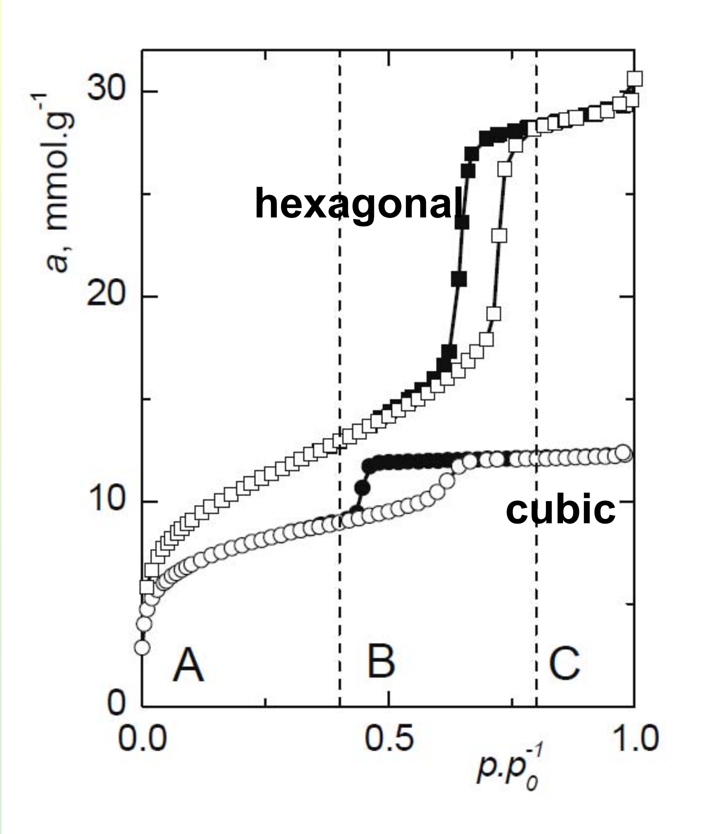


Pores filled with liquid N_2
Pore volume

Characterization of Mesoporous Materials

ads.-des. N_2 at 77 K





MCM-41 Pore size 3.4 nm, no Kelvin capillary condensation below 3.6–3.8 nm - no hysteresis, sharp inc-decr at B

SBA-15 (□ = ads., ■ = des.) 6.5 nm Kelvin capillary cond. - hysteresis SBA-16 (○ = ads., ● = des.) spherical pores 6 nm with windows 4 nm

Mesoporous Platinum Metal

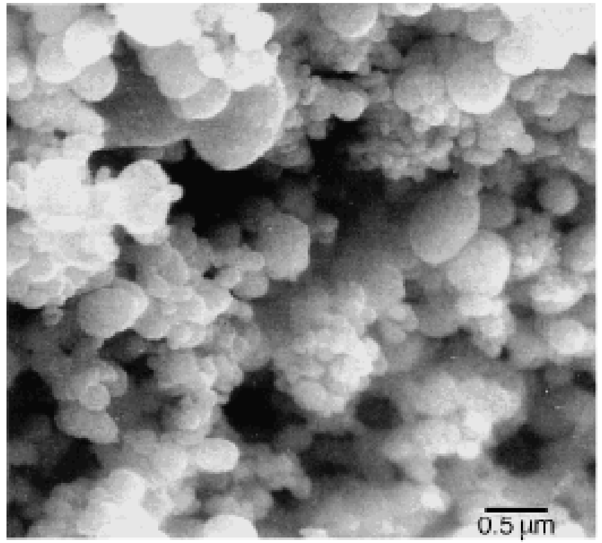
$H_2[PtCl_6]$ or $(NH_4)_2[PtCl_6]$

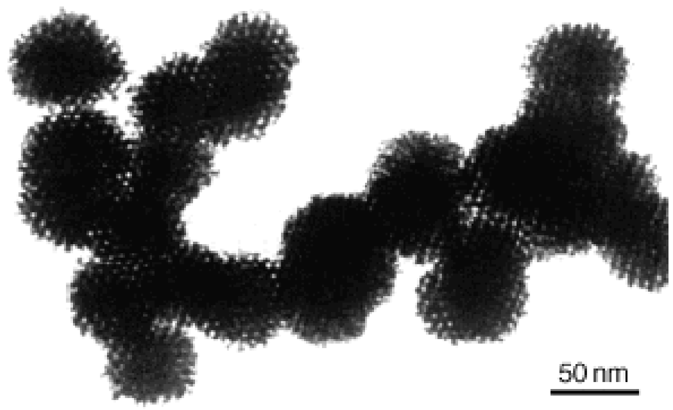
$C_{16}(EO)_8$

Assembly of liquid crystalline phase

Reductants: Fe, Zn, Hg, NH_2NH_2

Washed with acetone, water, HCl

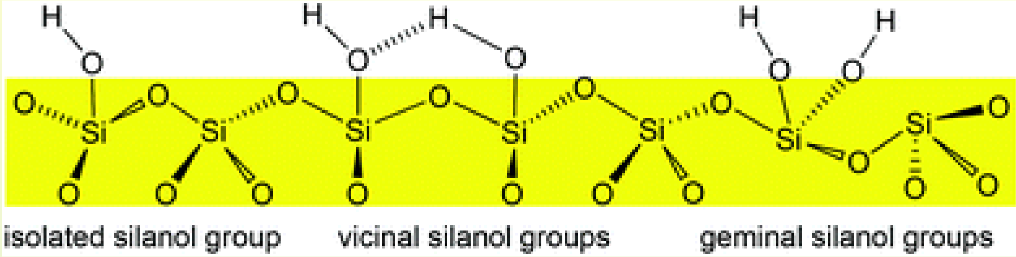


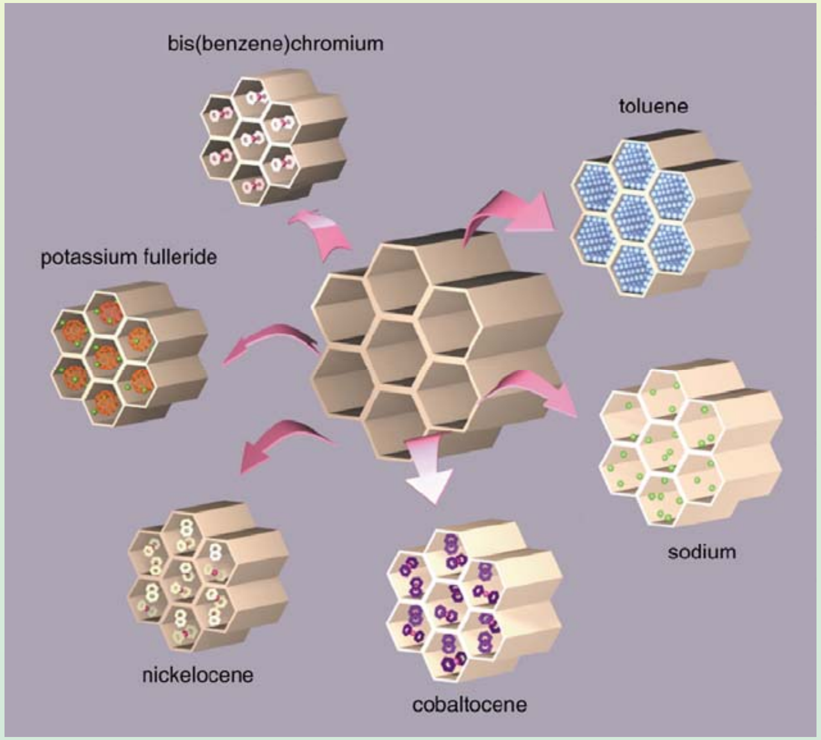


SEM (upper) and TEM (lower) images of mesoporous Pt metal show particles 90-500 nm in diameter and a pore diameter of 30 Å and a pore wall thickness of 30 Å

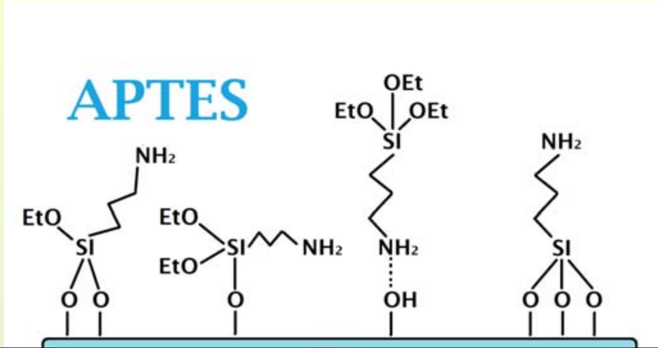
Chemistry inside the Pores

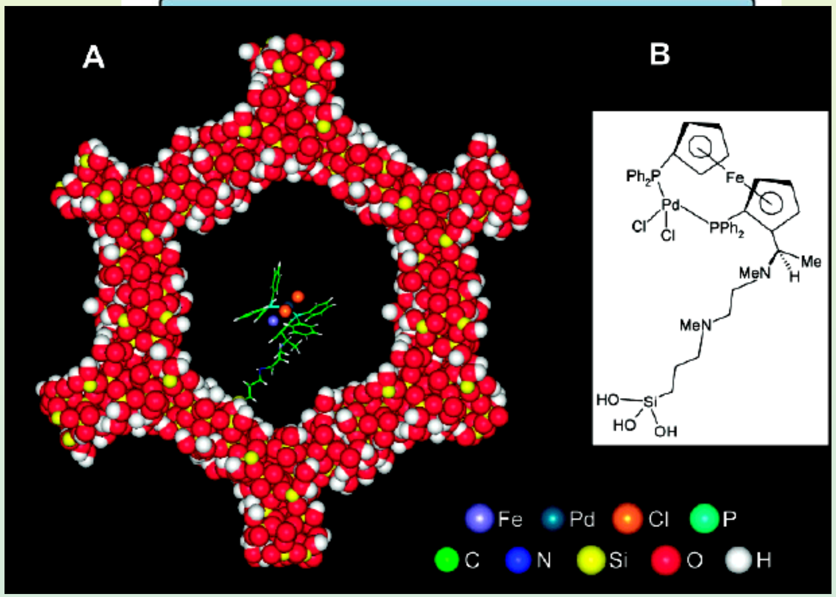
Surface silanols in MCM-41 pores



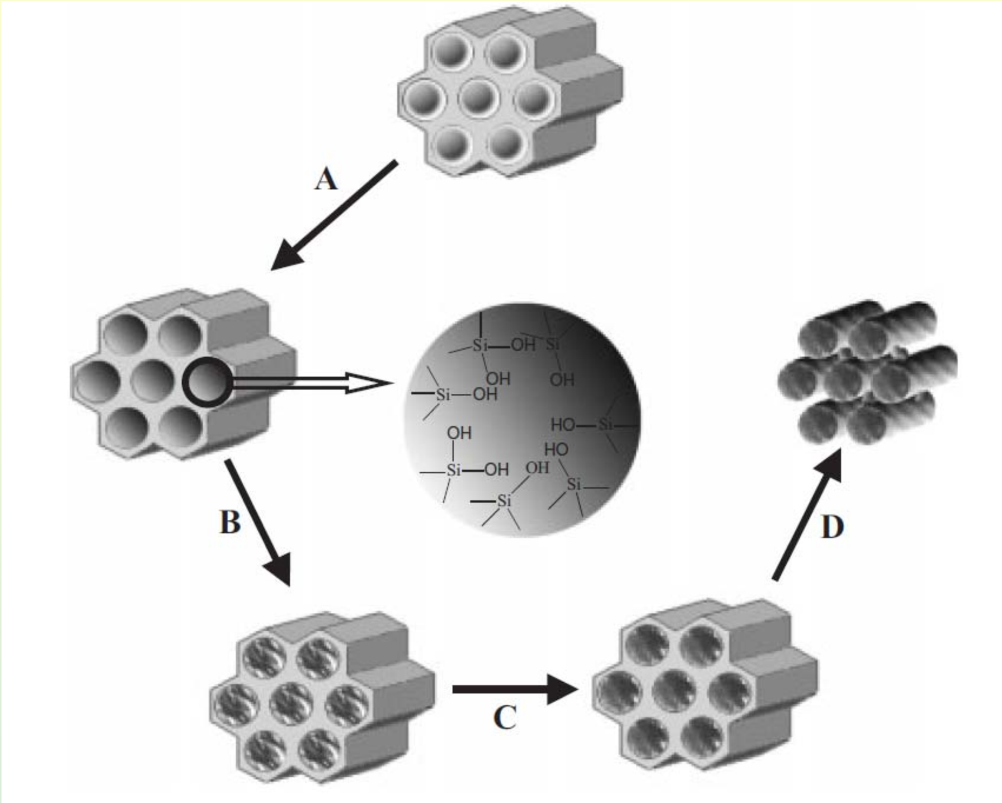


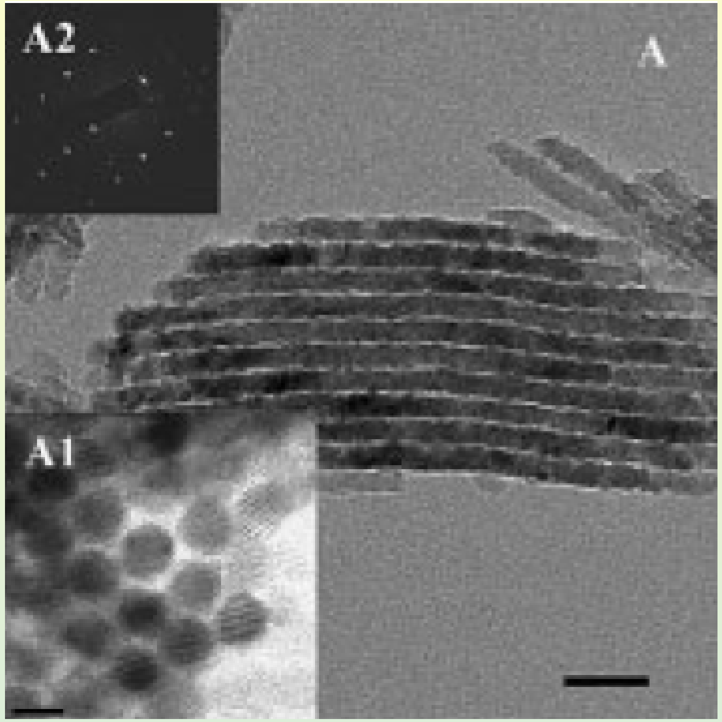
(3-Aminopropyl)triethoxysilane





Hard Tempalting





Cr_2O_3 crystalline nanowires
(bar = 25 nm for A, 10 nm for A1)

A = microwave digestion - template removal
B = introduction of metal salt solution
C = calcination
D = dissolution of SiO_2 in HF or NaOH

Hard Tempalting