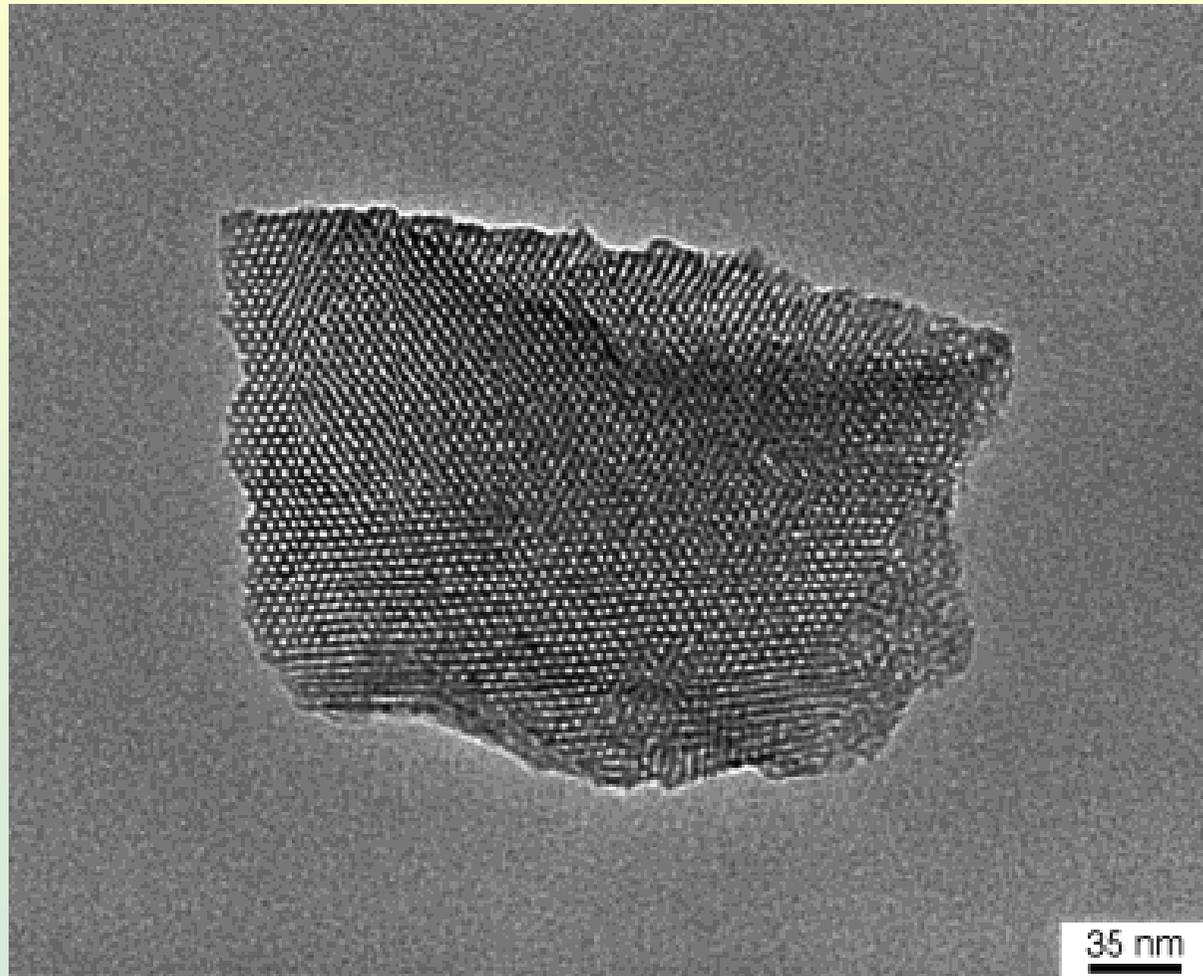


TEM image of the Pd-grafted mesoporous silicate material



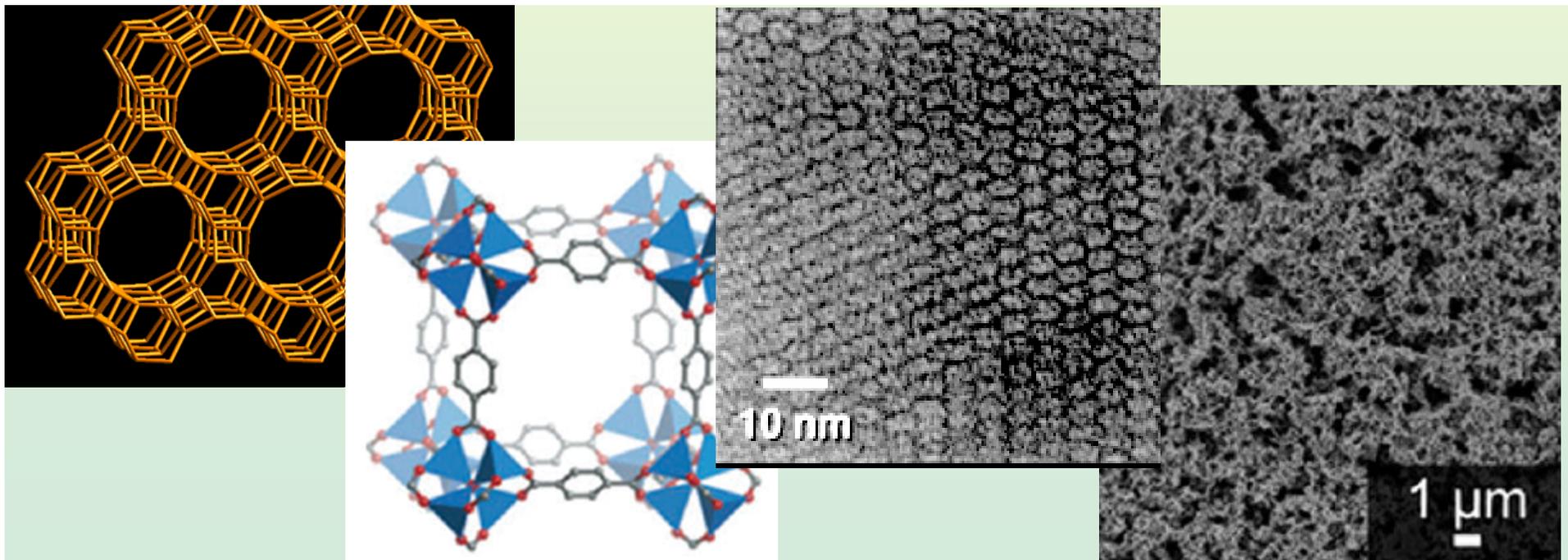
Mesoporous Materials

- Amorphous, disordered - silica xerogels
- Ordered pores, amorphous walls

Pore diameter, d [nm]	Material	Example
$d > 50$	Macroporous	Aerogels
$2 < d < 50$	Mesoporous	Xerogels
$d < 2$	Microporous	Zeolites

Mesoporous Materials

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



Mesoporous Materials

MMS mesoporous molecular sieves

MCM-n Mobil Composition of Matter

M41S

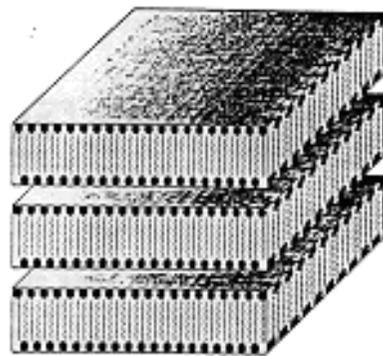
Discovered 1992

A - lamellar, 2D layers, MCM-50

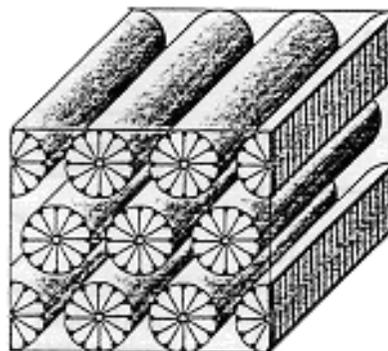
B - hexagonal order, 1D channels, MCM-41

C - cubic, 3D channel structure (bicontinuous), MCM-48

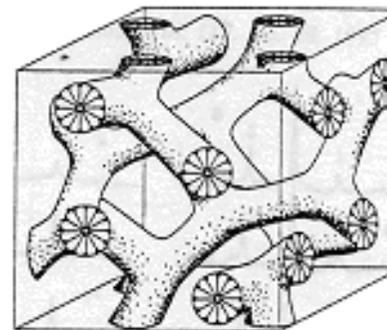
Inverse hexagonal



A

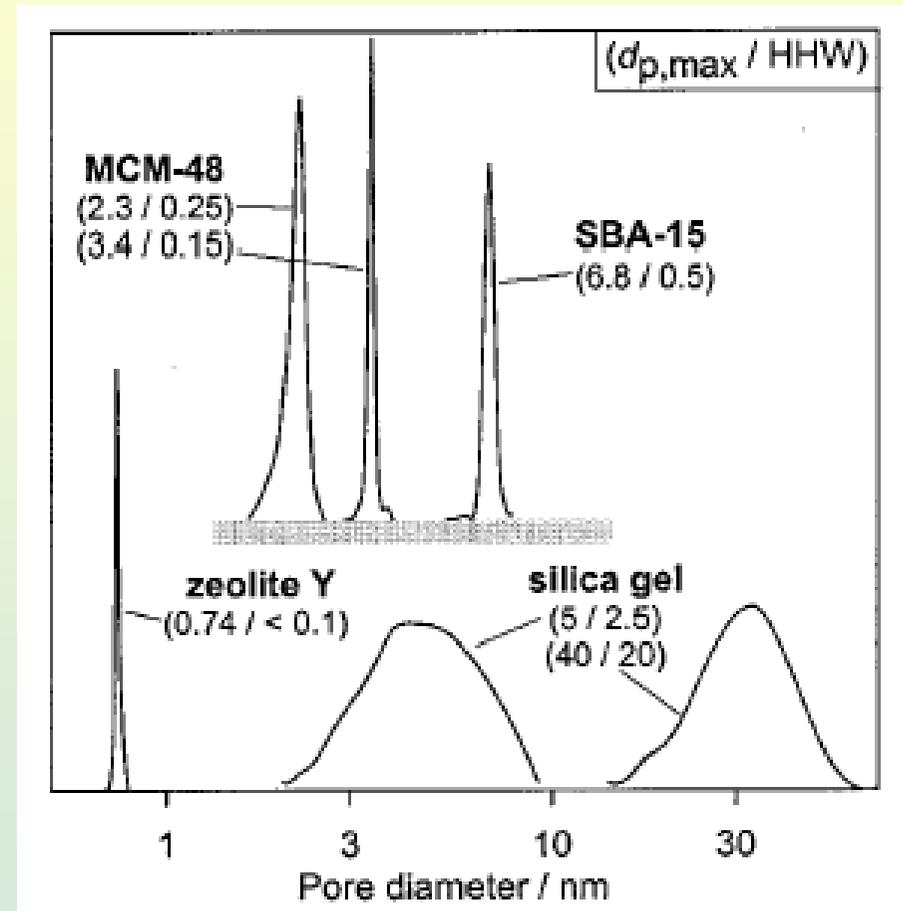
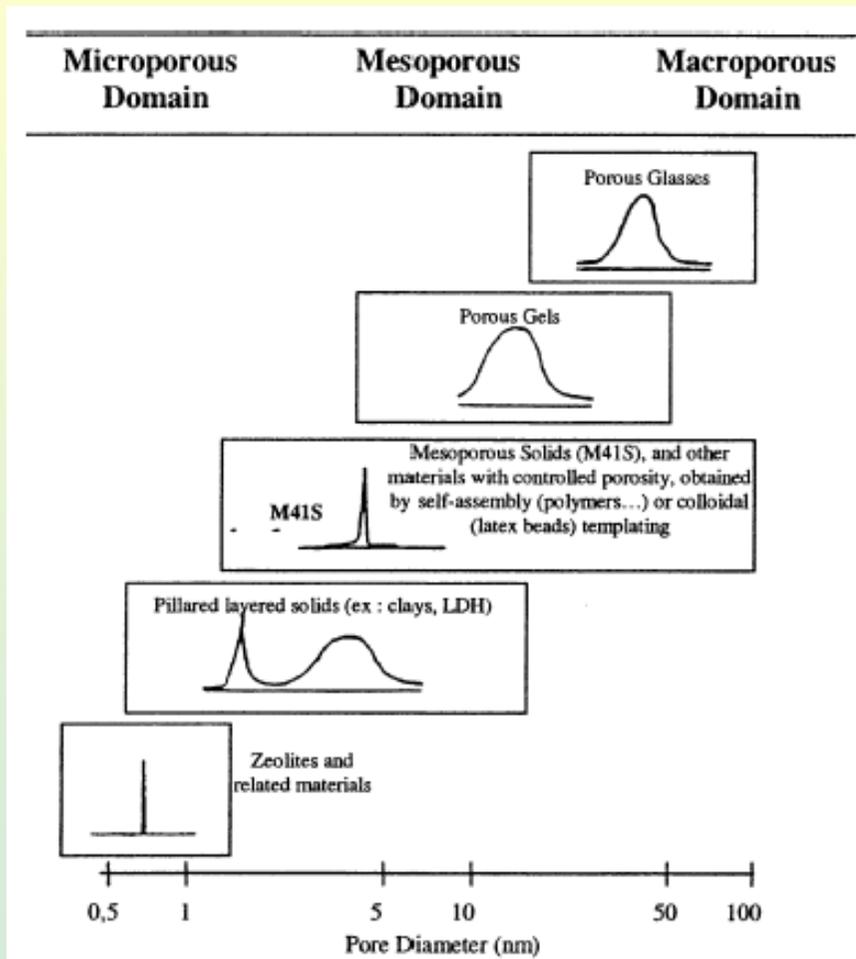


B



C

Pore size distribution

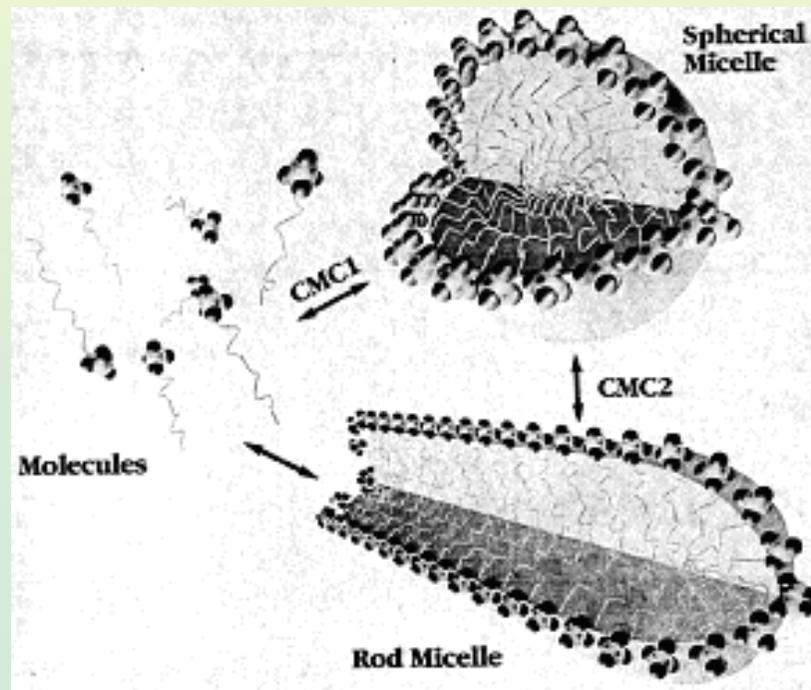


Micelles - Supramolecular Templates

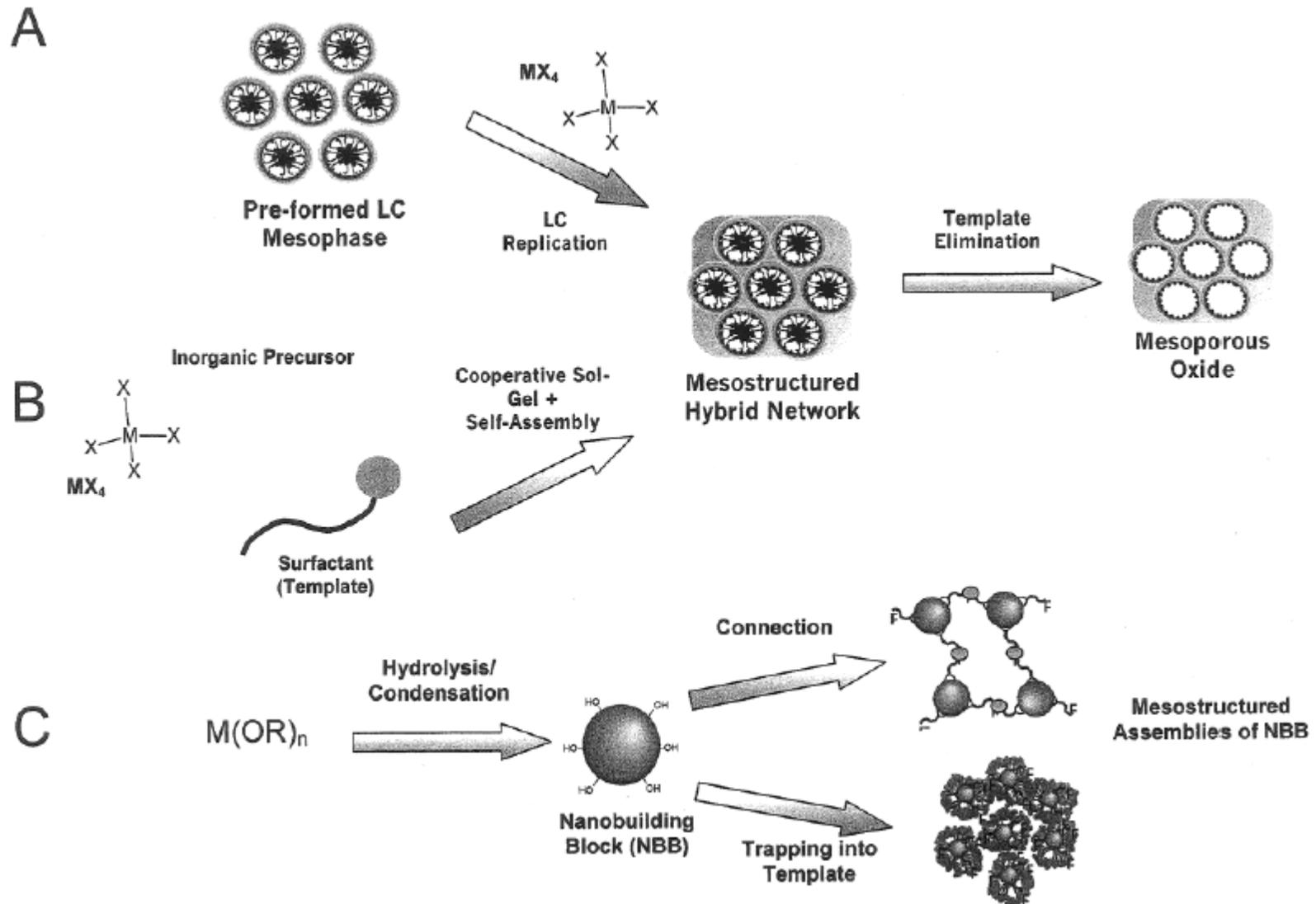
In zeolitic materials the template is a single molecule or ion

Self assembled aggregates of molecules or ions can also serve as templates

Surfactants aggregate into a variety of structures depending on conditions



Mesostructure Assembly



Supramolecular Templating

Surfactants - amphiphilic molecules, polar (head group) and nonpolar (chain, tail) part
lyophilic, lyophobic

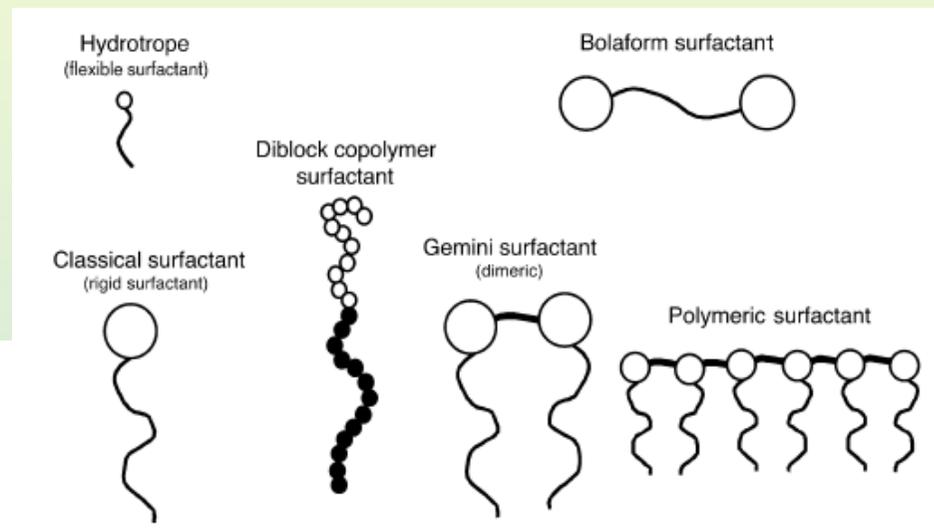
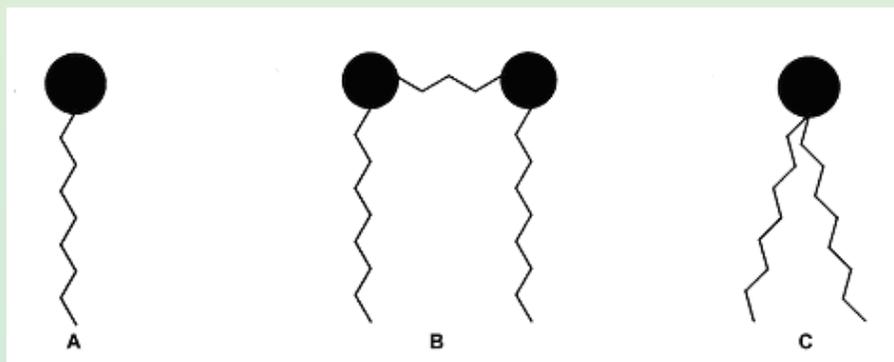
Ionic surfactants, cationic, anionic, zwitterionic

Nonionic amines, polyethyleneoxides

A - normal surfactant molecule

B - gemini

C - swallow tail



Surfactants

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*: $C_nH_{2n+1}COOH$

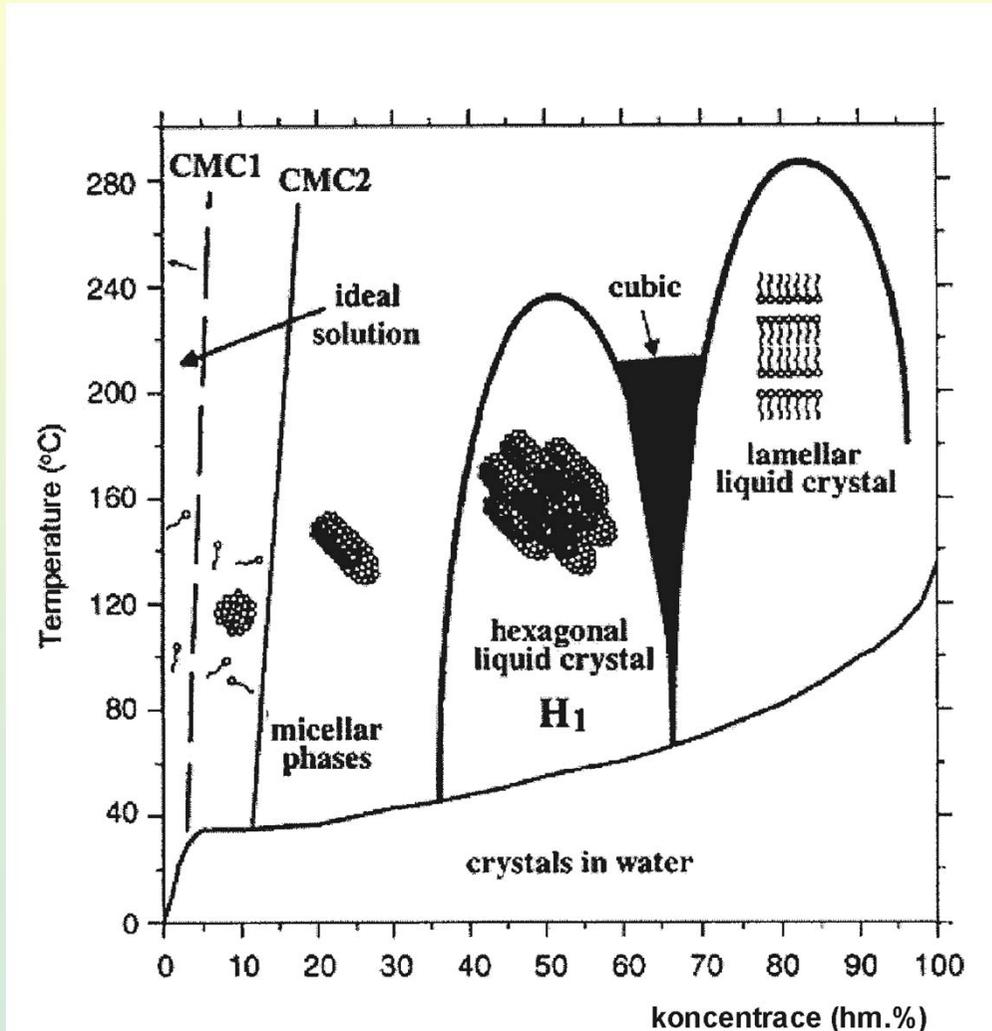
Cationic

- *alkylammonium salts*: $C_nH_{2n+1}(CH_3)_3NX$ X = OH, Cl, Br, HSO₄
- *dialkylammonium salts*: $(C_{16}H_{33})_2(CH_3)_2N^+Br^-$

Noionic

- *primary amines*: $C_nH_{2n+1}NH_2$
- *polyethyleneoxides*: $HO(CH_2CH_2O)_nH$

Supramolecular Templating



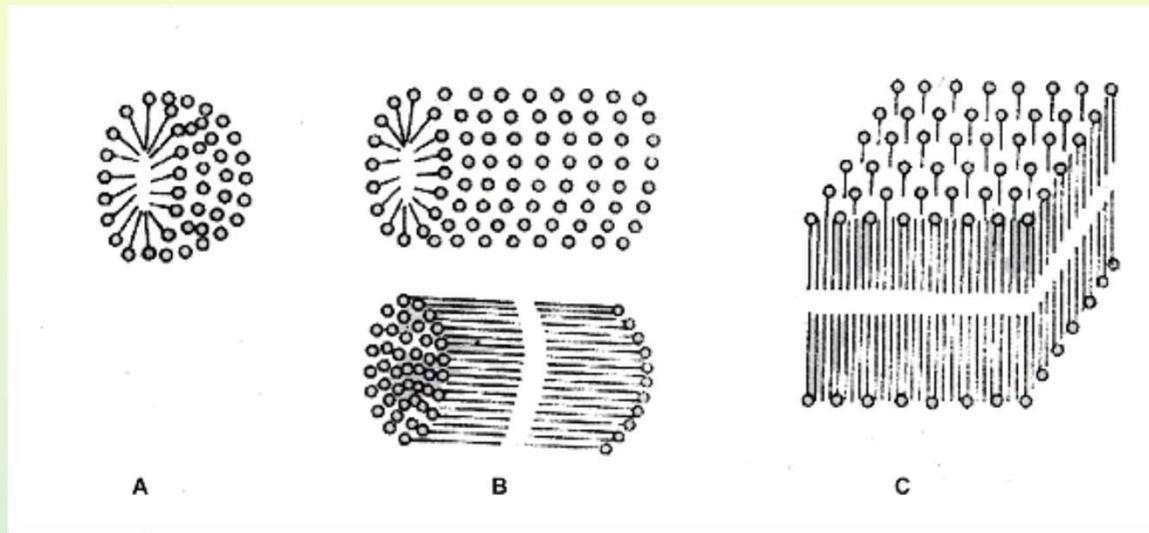
Phase diagram of C₁₆TMABr

CMC = critical micelle conc.

Micellar Shapes

Micellar shapes

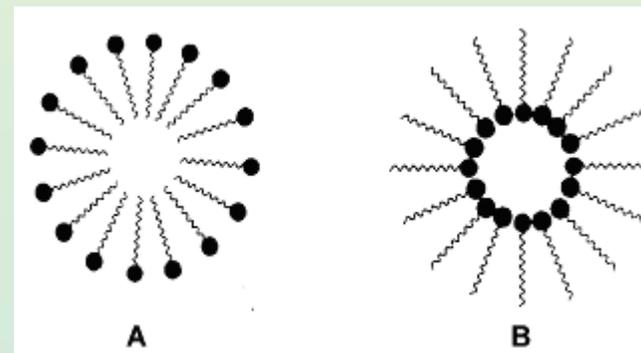
A - spherical, B - rod-like, C - lamellar



Micelles in media

A - normal, in polar solvent, H_2O

B - inverse, in nonpolar solvent, organics



Surfactant Molecules

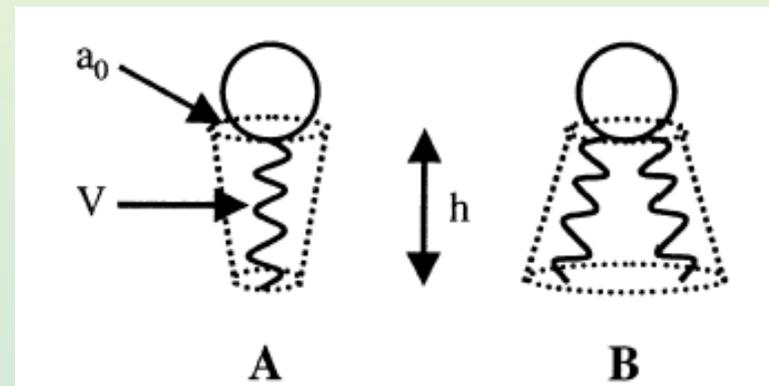
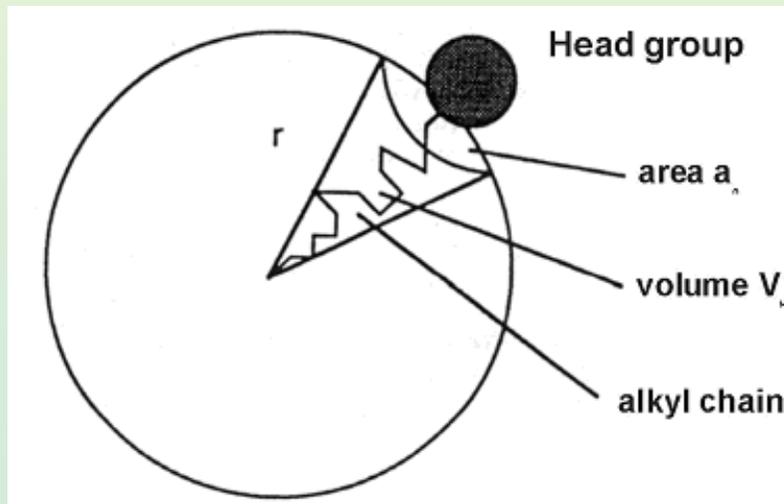
Critical packing parameter – CPP

$$\text{CPP} = V_H / a_0 l_c$$

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

$$l_c \leq 1.5 + 1.265 n \quad [\text{\AA}]$$

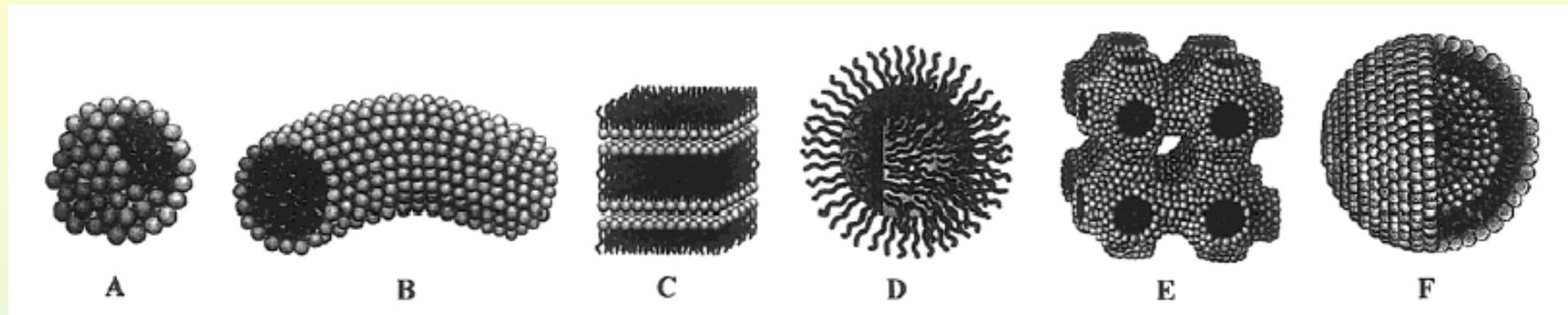
n number of carbon atoms. l_c depends on the chain shape.



Conical (*icecream cone*, A)

Inverse conical (*champagne cork*, B)

Micellar Shapes

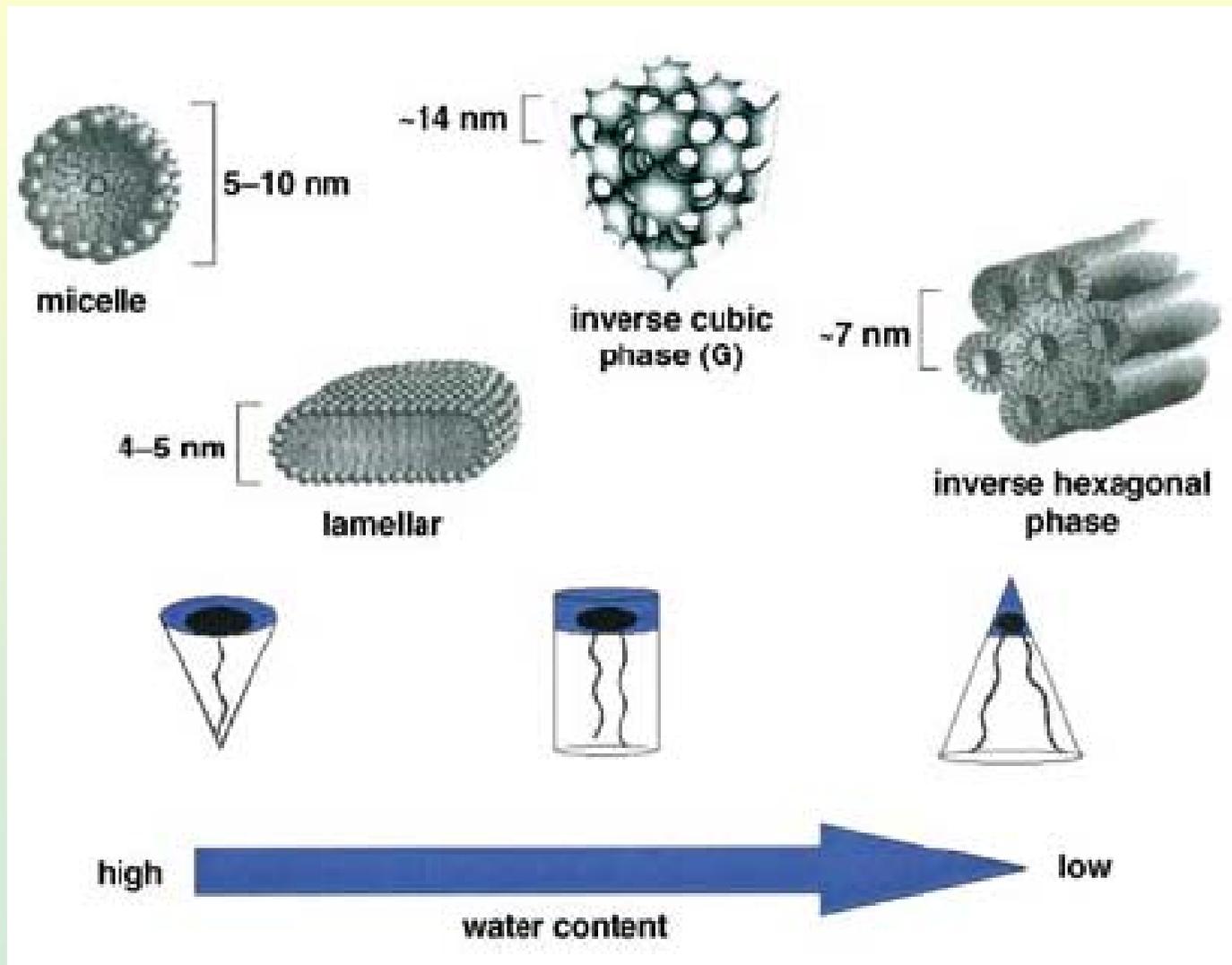


Micellar structures

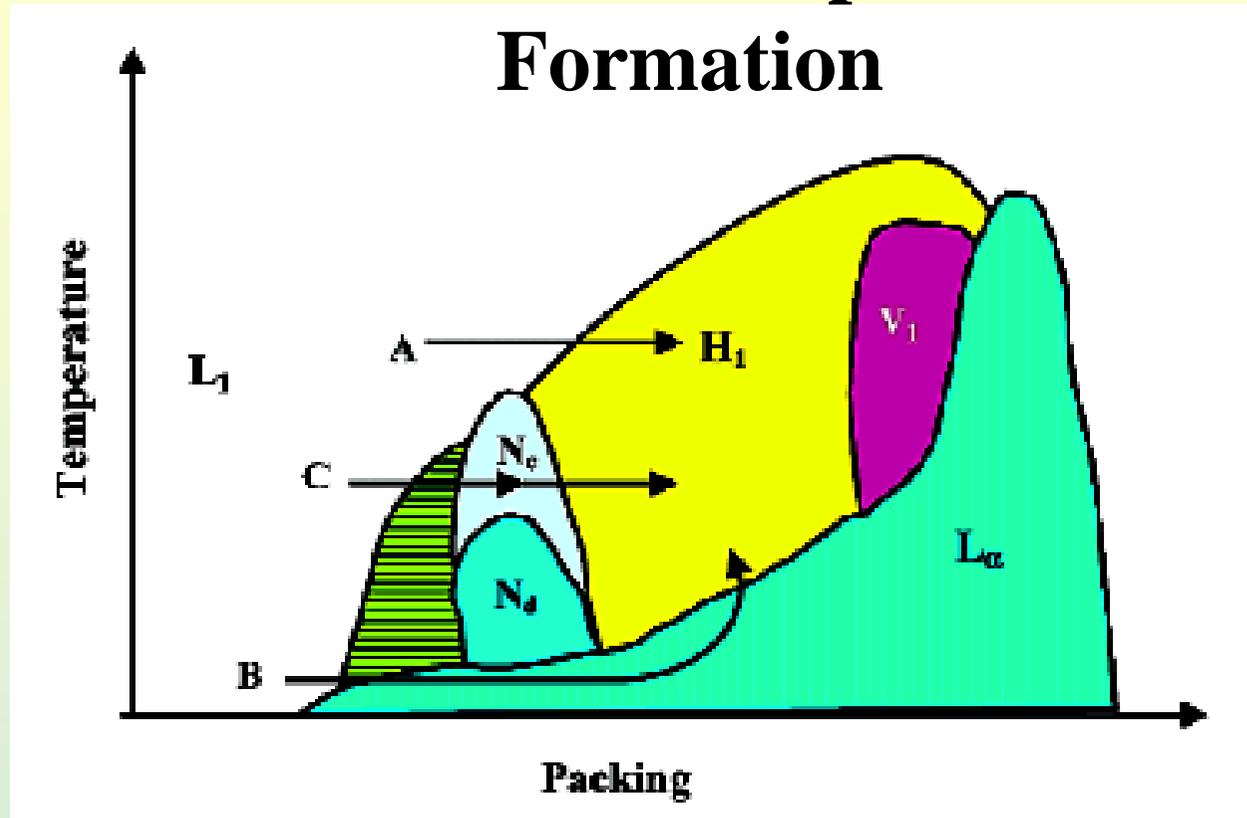
A) sphere, B) cylinder, C) planar bilayer, D) reverse micelles, E) bicontinuous phase, F) liposomes).

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

Surfactant Molecules



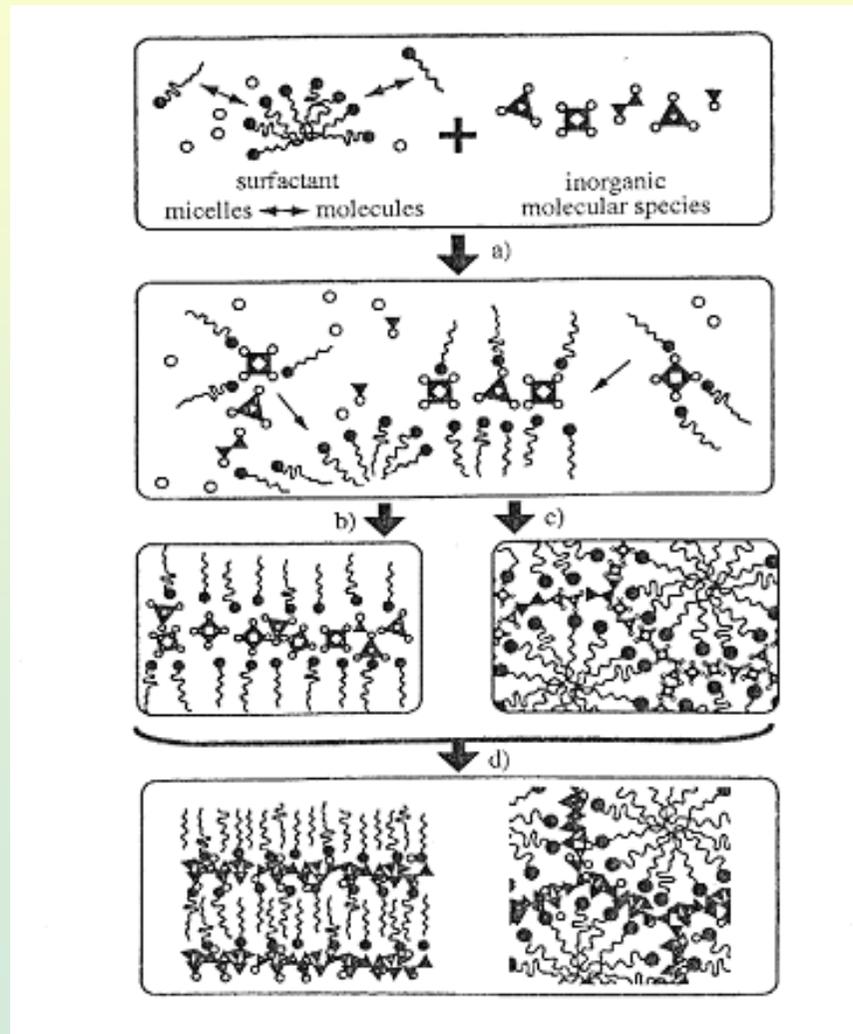
Mechanism of the Mesoporous Material Formation



L_1 = micellar solution; N_c = nematic phase; H_1 = normal hexagonal phase (MCM-41; SBA-15);
 V_1 = normal bicontinuous cubic phase (MCM-48); L_α = lamellar phase (MCM-50)

path A, the micellar solution route
path B, the lamellar phase route
path C, the nematic phase route

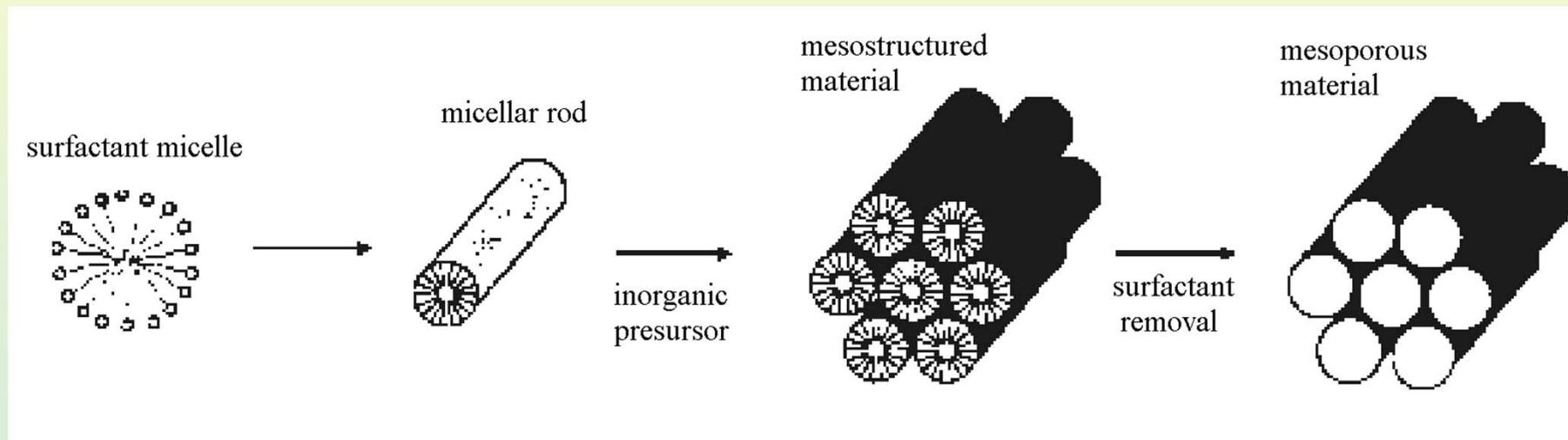
General Liquid Crystal Templating (LCT) Mechanism



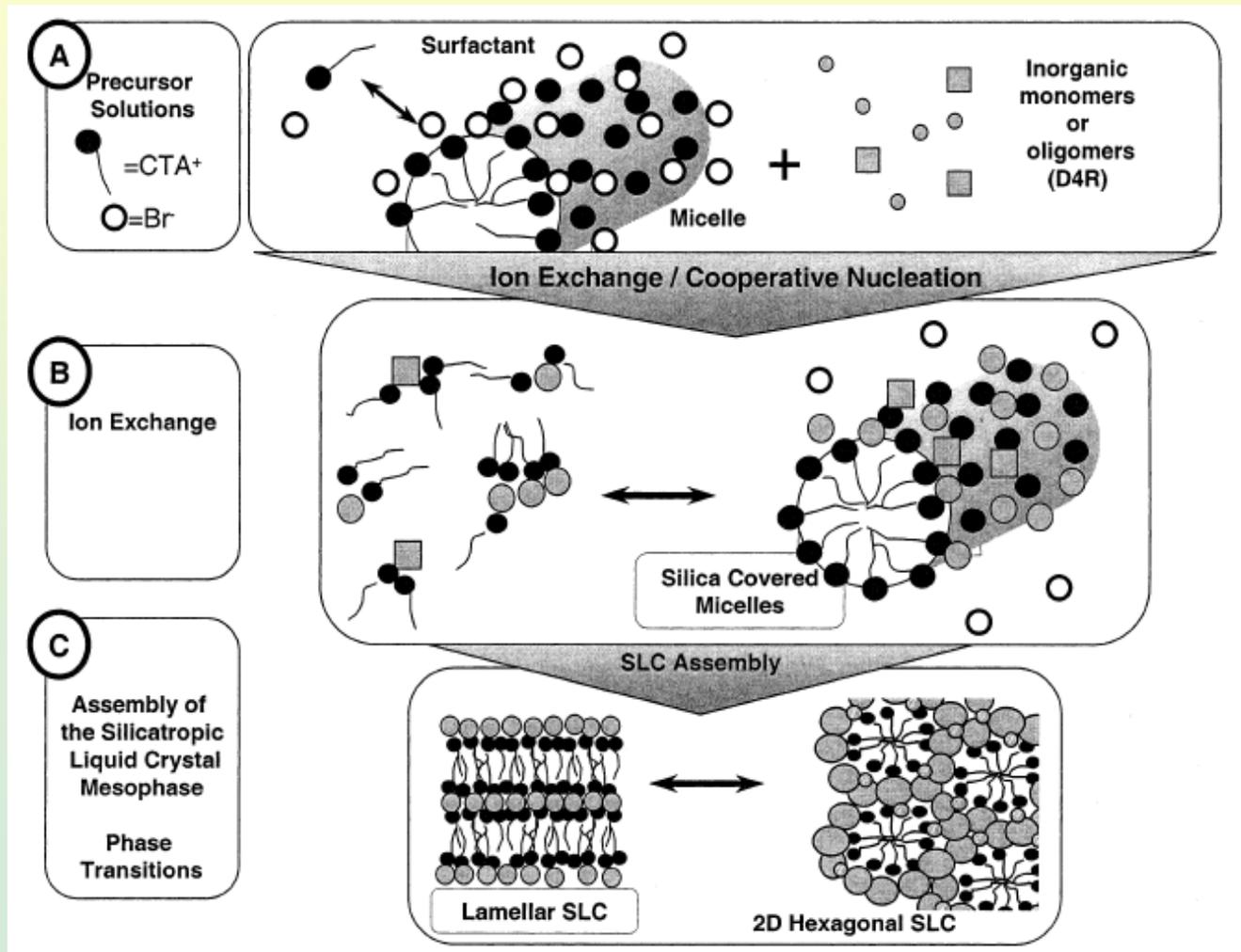
Mechanism of the Mesoporous Material Formation

Hexagonal, MCM-41

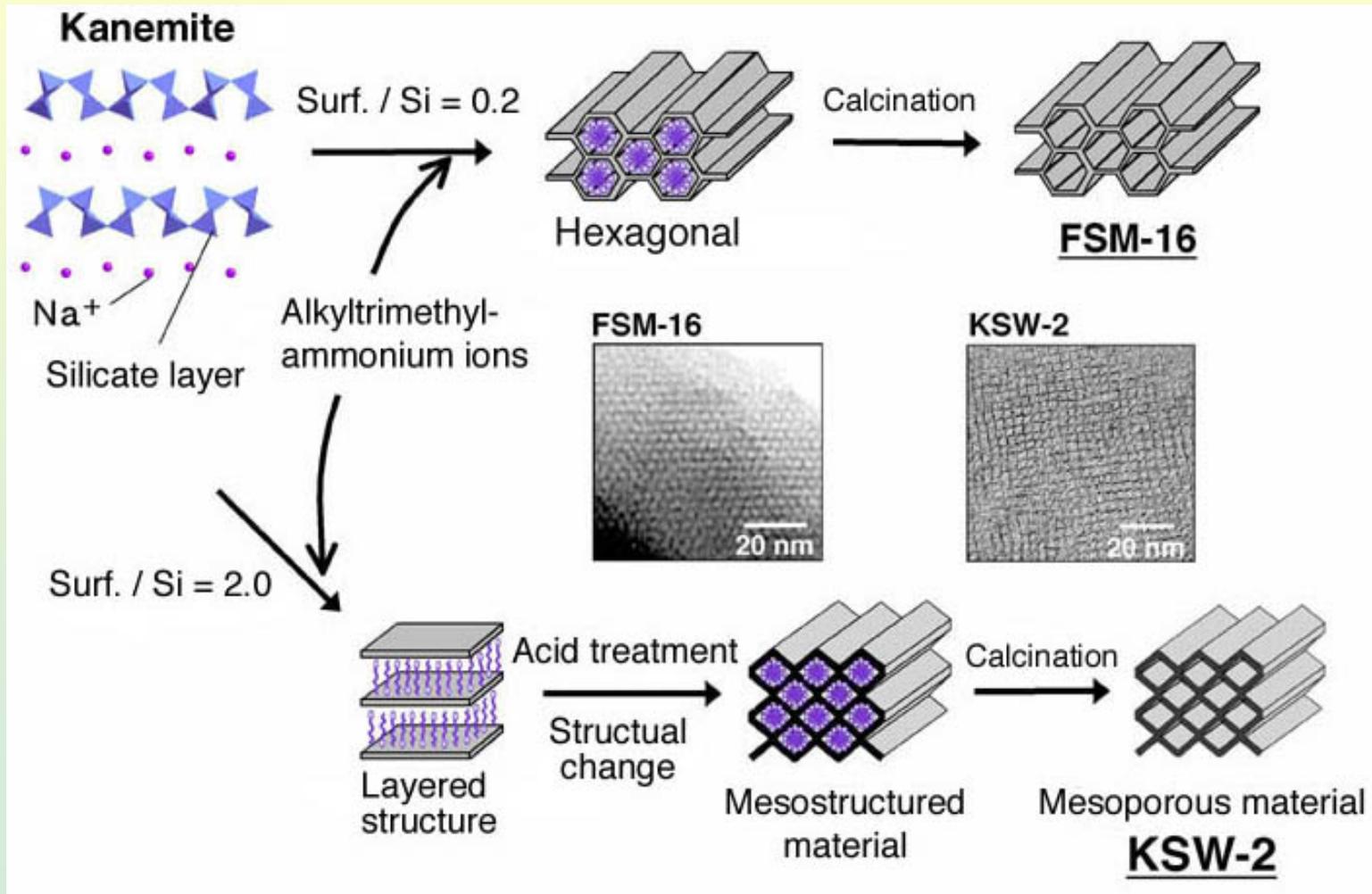
LCT Liquid Crystal Templating



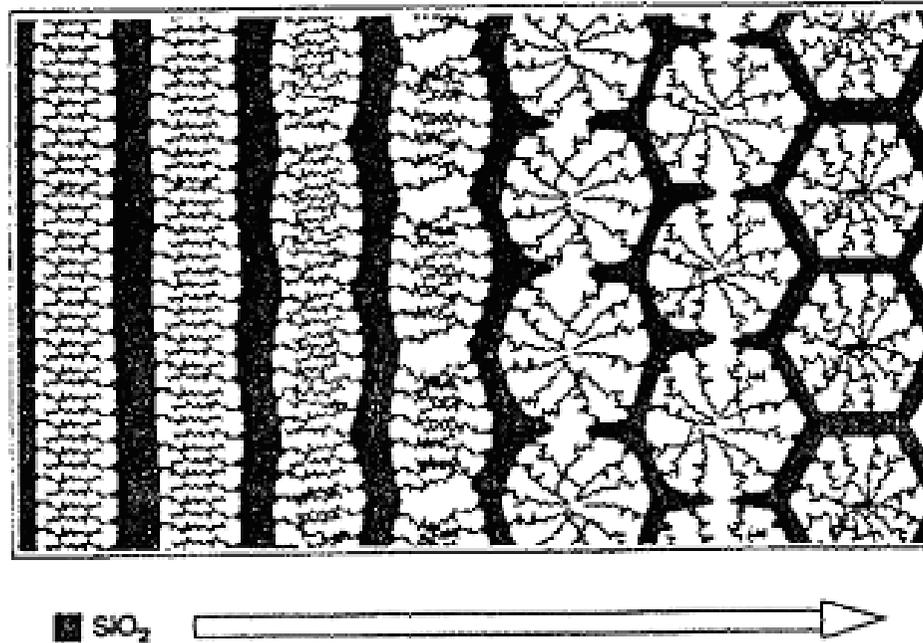
SLC Silicatropic Liquid Crystals Mechanism



Lamellar to Hexagonal Transformation

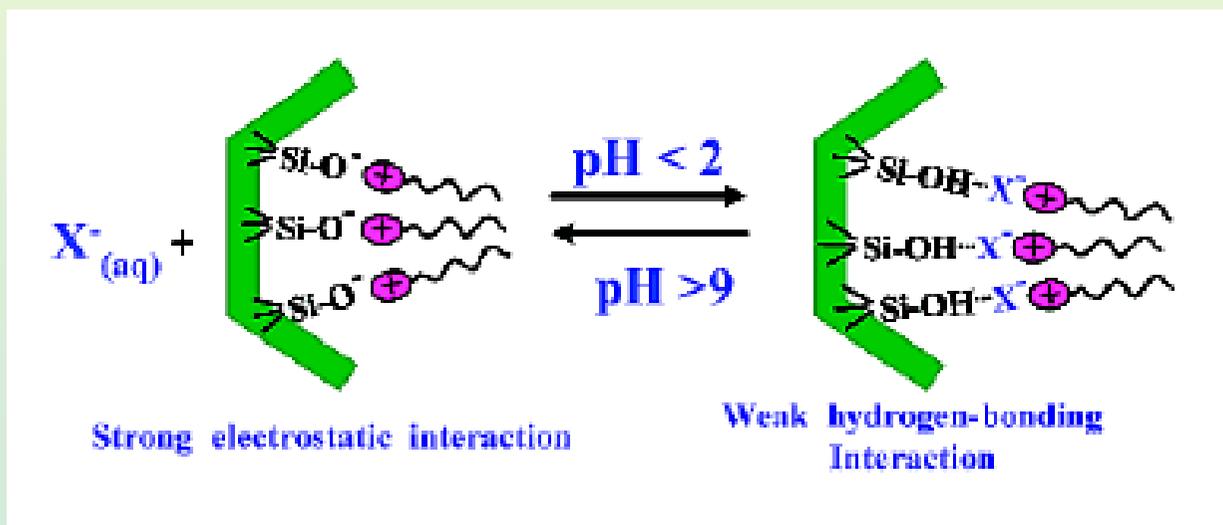
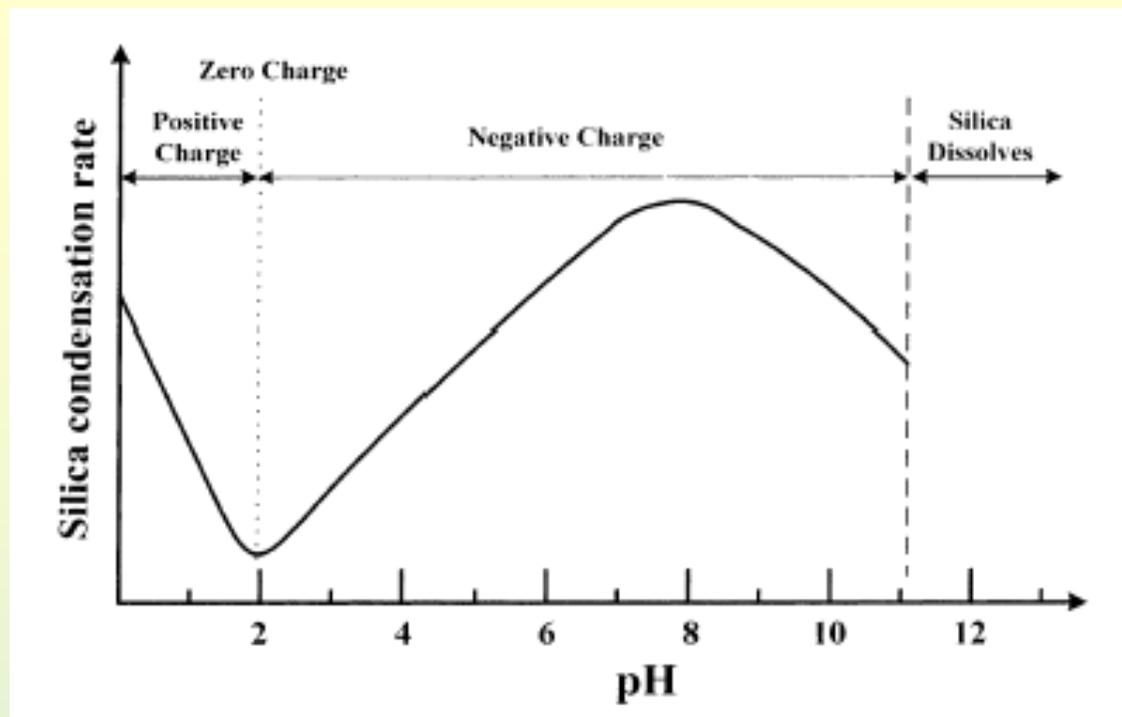


Charge Density Matching



As condensation proceeds the charge on the silicate layer decreases





• **Electrostatic interactions**

a) S^+I^-



I = silicate

S = trimethylammonium

b) ST^+



I = Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} ,

Mg^{2+} , Mn^{2+} , Pb^{2+} , Al^{3+}

S = sulfonane

c) S^+XI^+



I = silicate – polyelectrolyte
positive charge

X = Cl

S = trimethylammonium

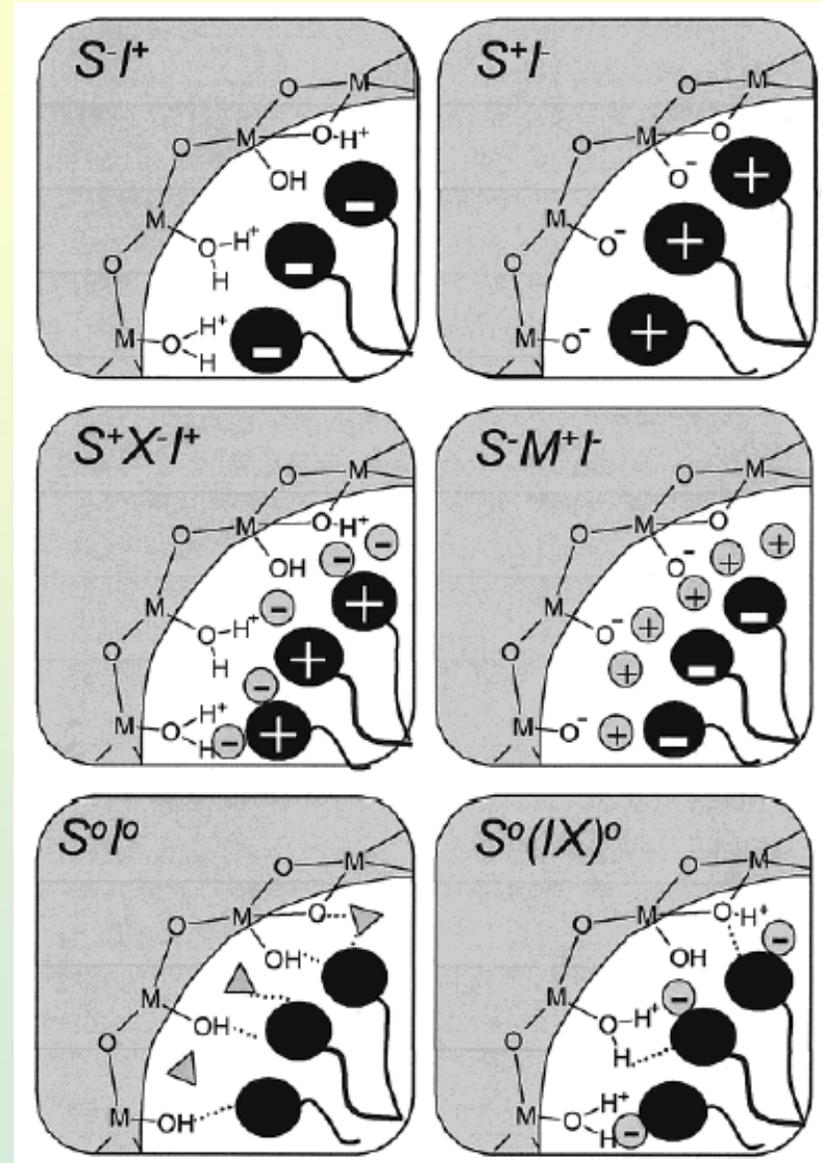
d) $S^+M^+I^-$



I = aluminate

M = Na

S = phosphate



- **Hydrogen Bond**

a) **S⁰I⁰**



I = silicate

S = ammine

b) **N⁰I⁰**



I = silicate

N = polyethylenoxide

- **Covalent Bond**

a) **S-I**



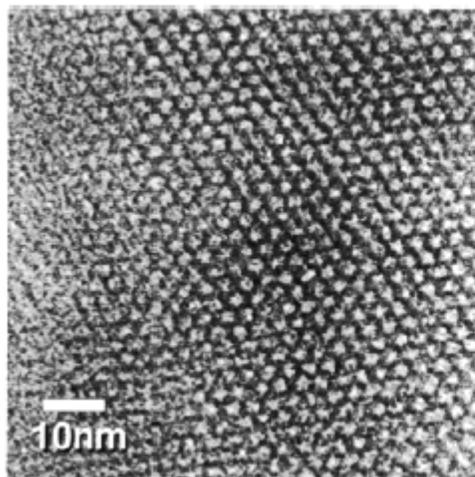
I = niobate, tantalate

S = ammine

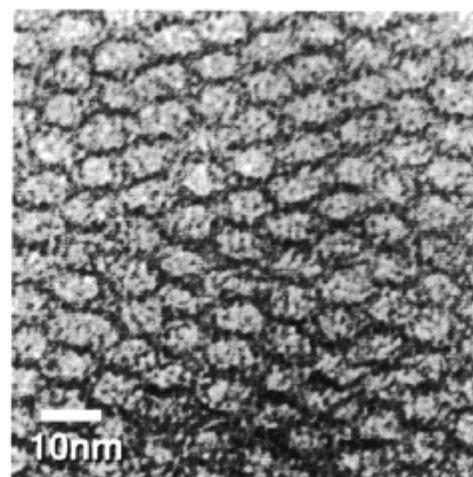
Control of Pore Size

MCM-41

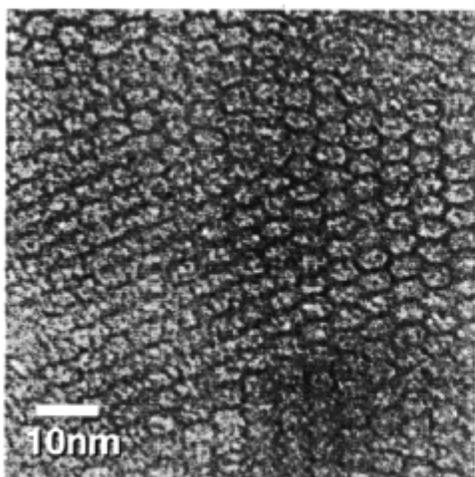
20Å



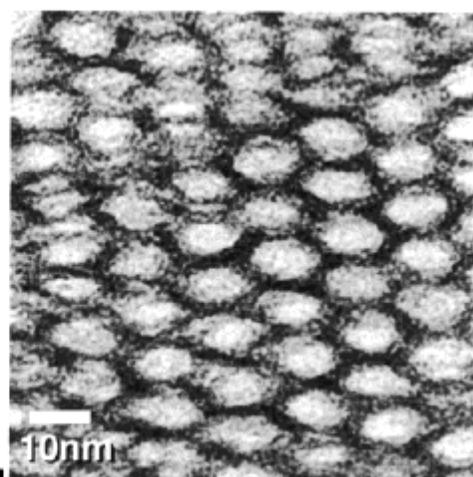
60Å



40Å



100Å



Prepared with Mesitylene Addition

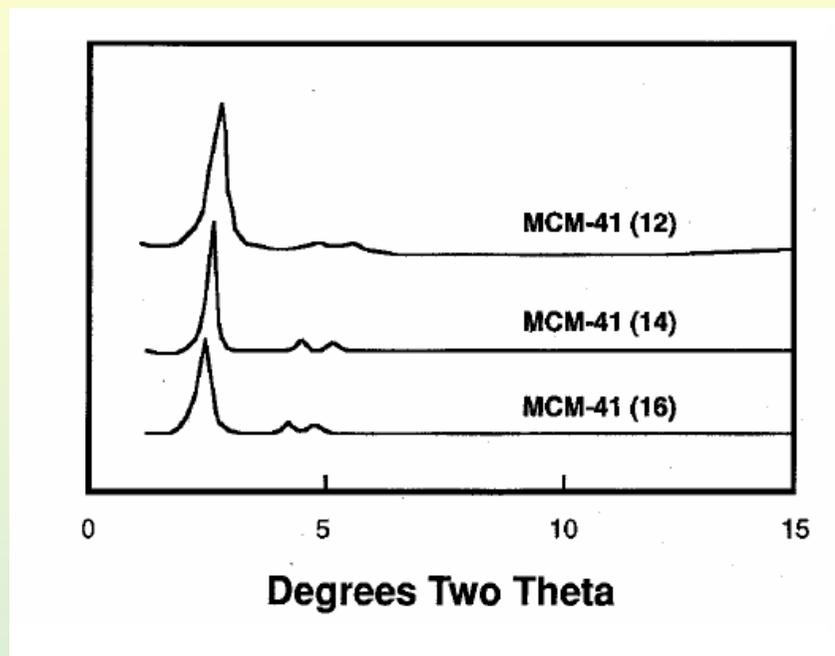
Control of Pore Size

Surfactant chain length - increasing the chain length = bigger pores

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

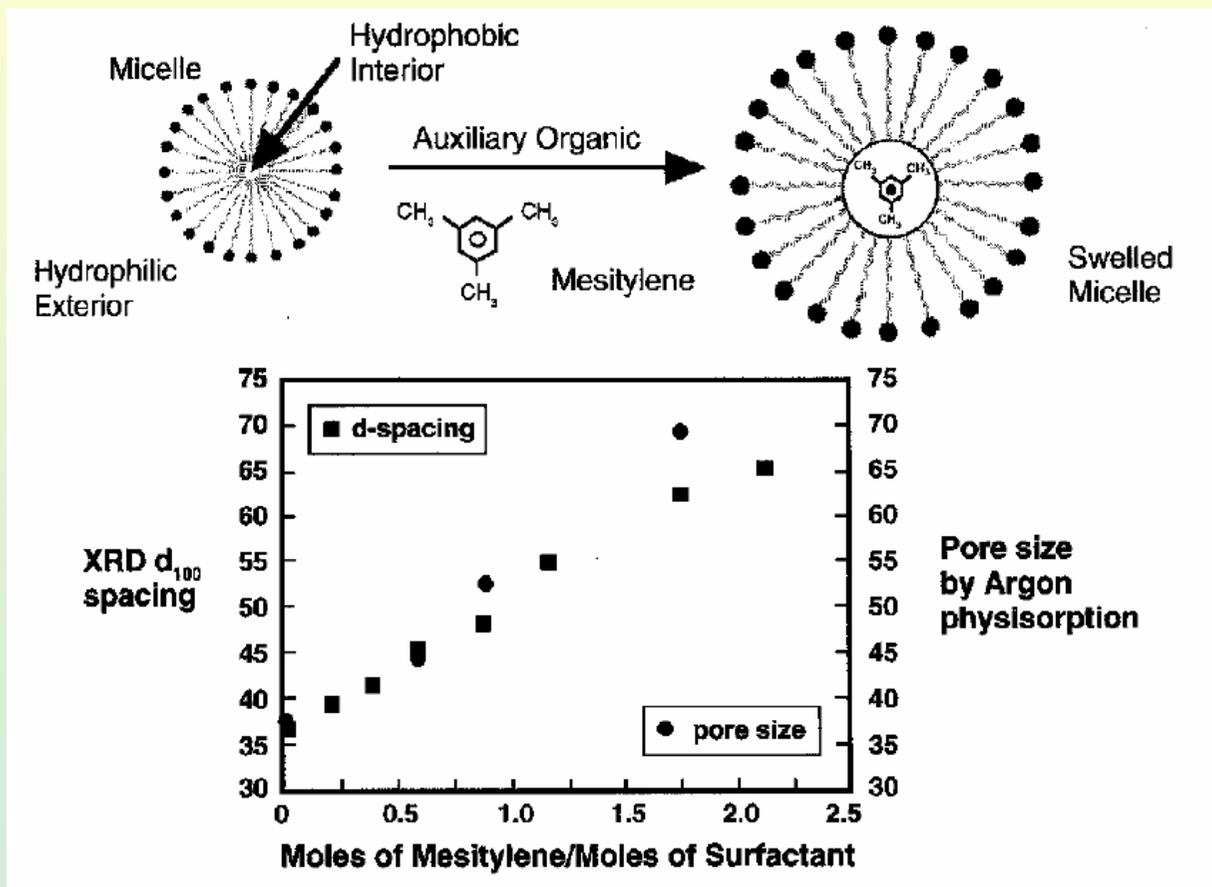
Post synthetic modification - after a material has been made the pore size can be reduced by modifying the interior surface = smaller pores

Control of Pore Size



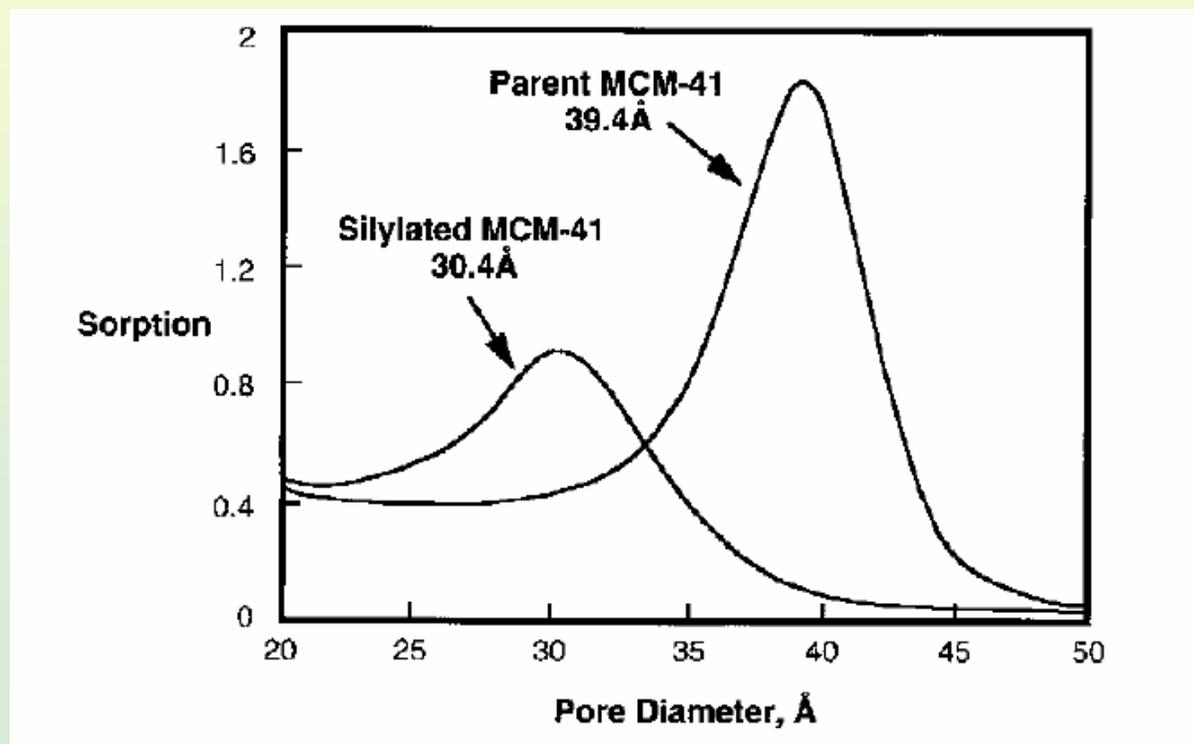
Surfactant chain length n $C_nH_{2n+1}NMe_3$	Lattice constant (Å)	Ar pore size (Å)	Maximum benzene uptake at 50 torr (wt%)
8	31	18	16
9	32	21	37
10	33	22	32
12	33	22	36
14	38	30	54
16	40	37	64

Control of Pore Size

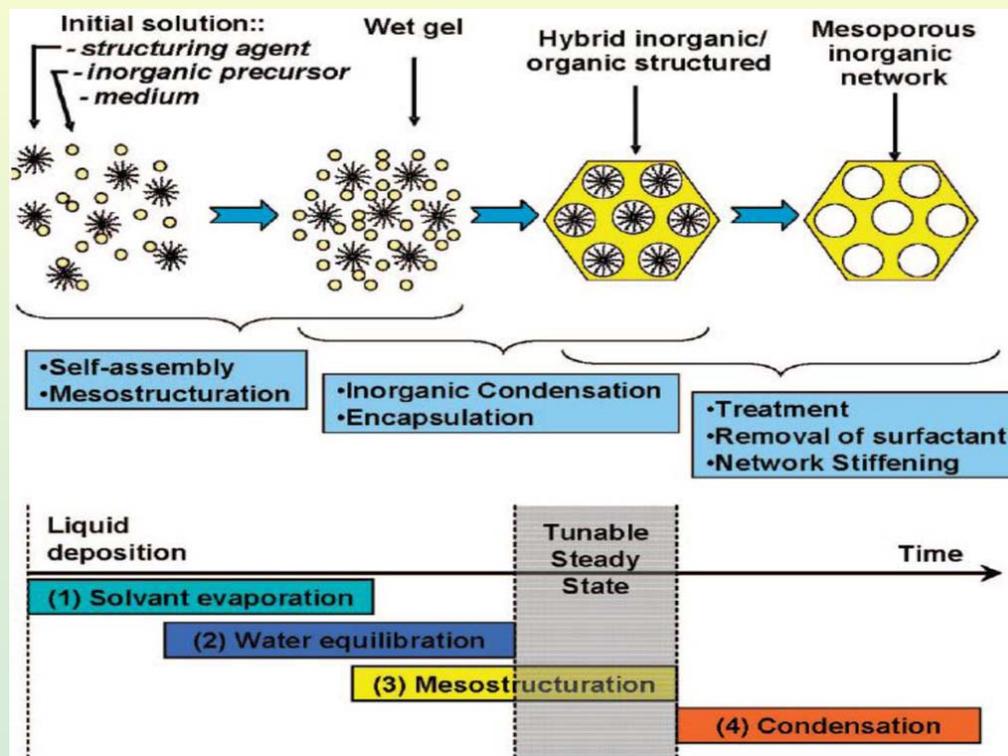
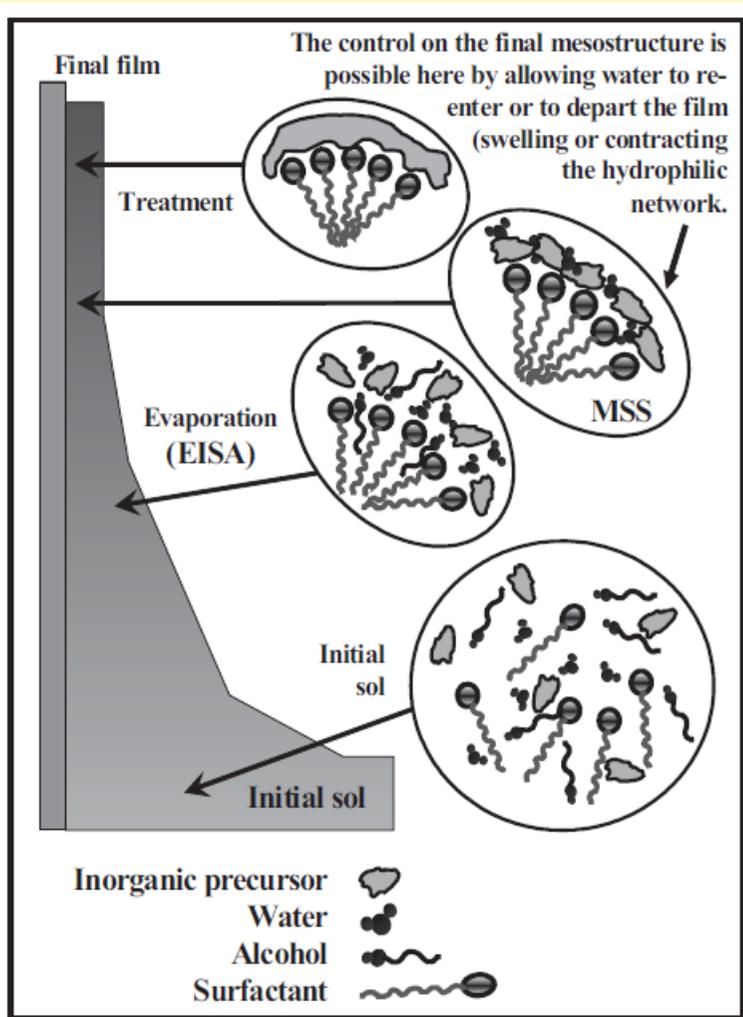


Control of Pore Size

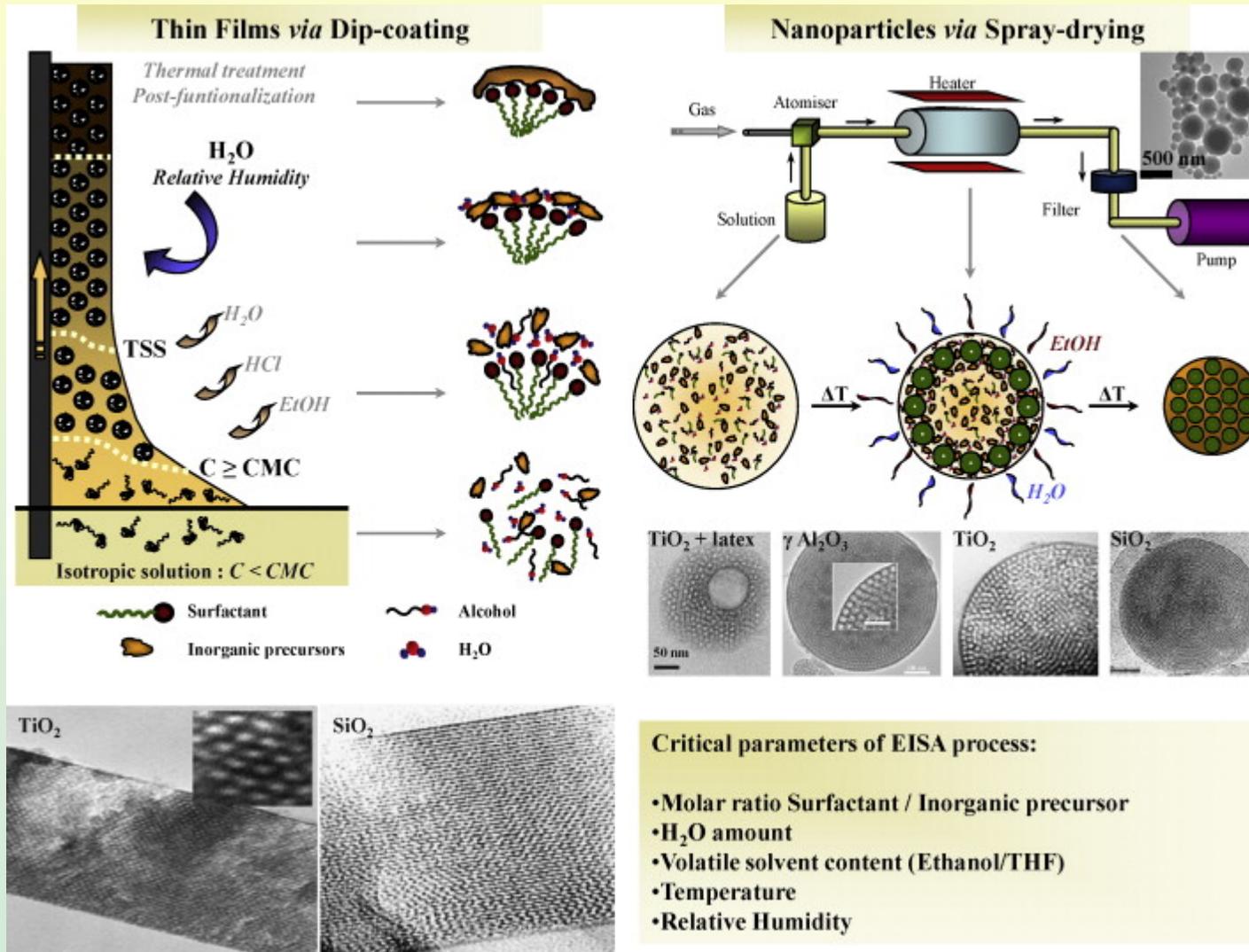
Silylation of hydroxyl groups in MCM-41 by Me_3SiCl reduces the effective pore size



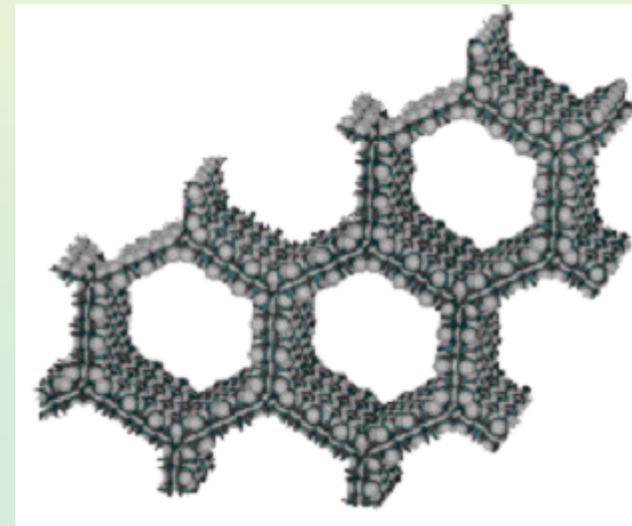
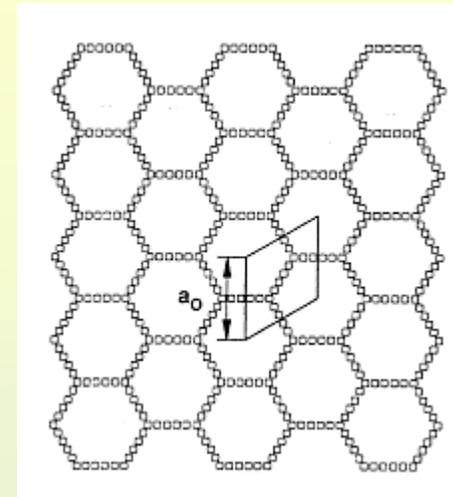
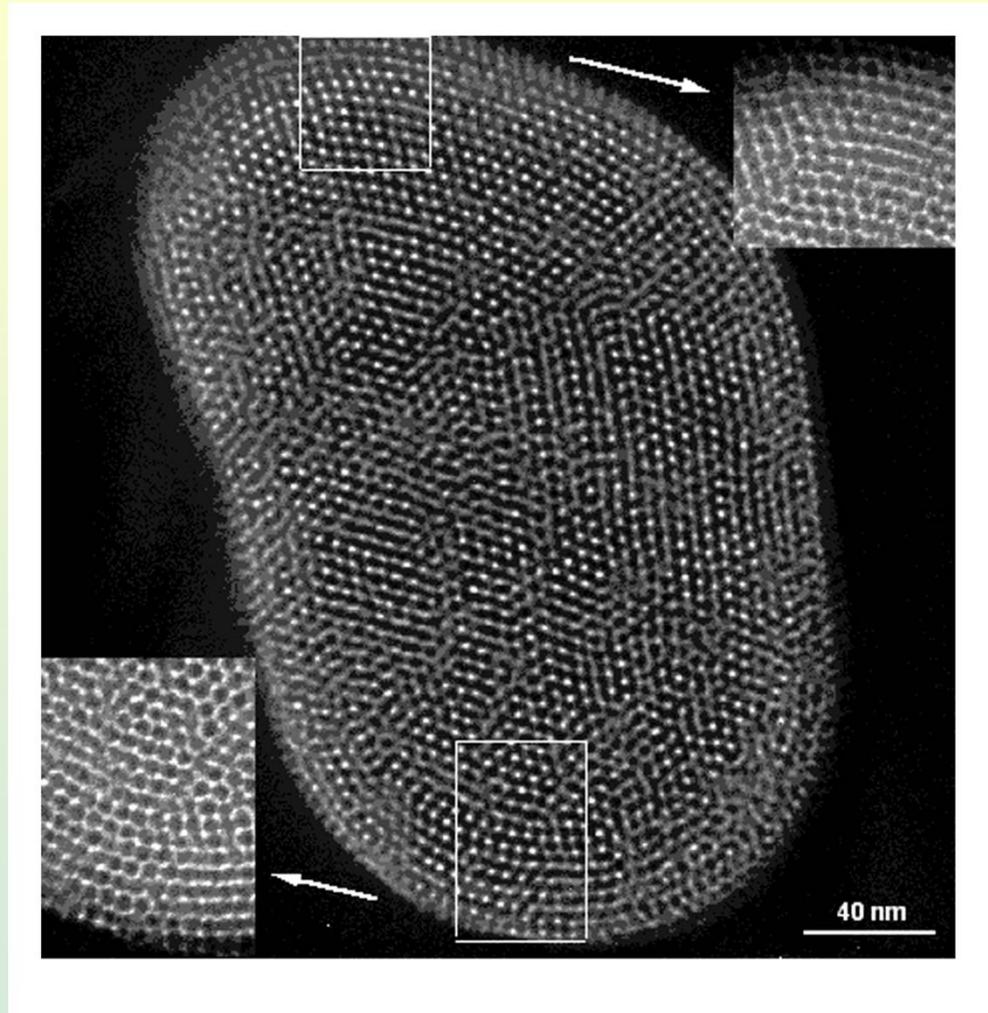
EISA = Evaporation-induced self-assembly



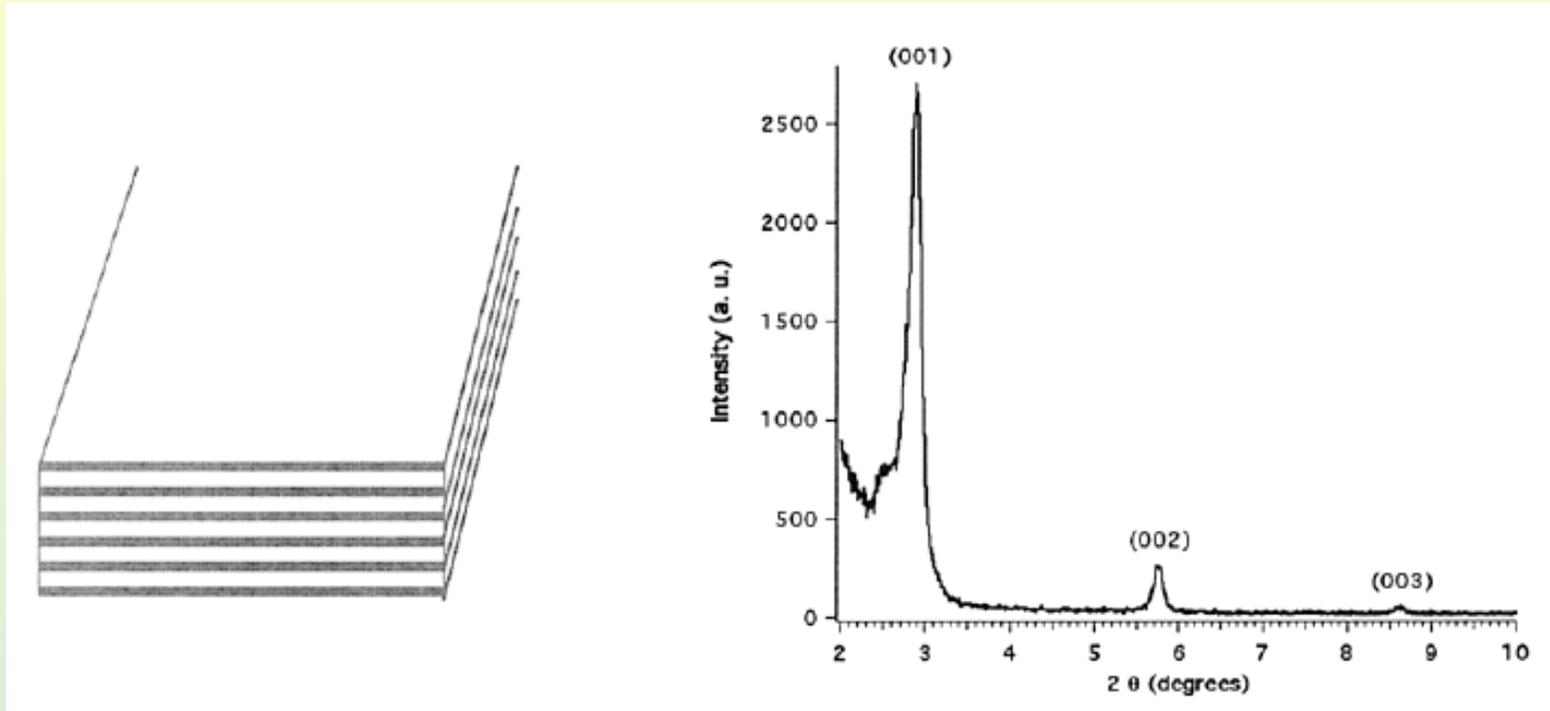
EISA



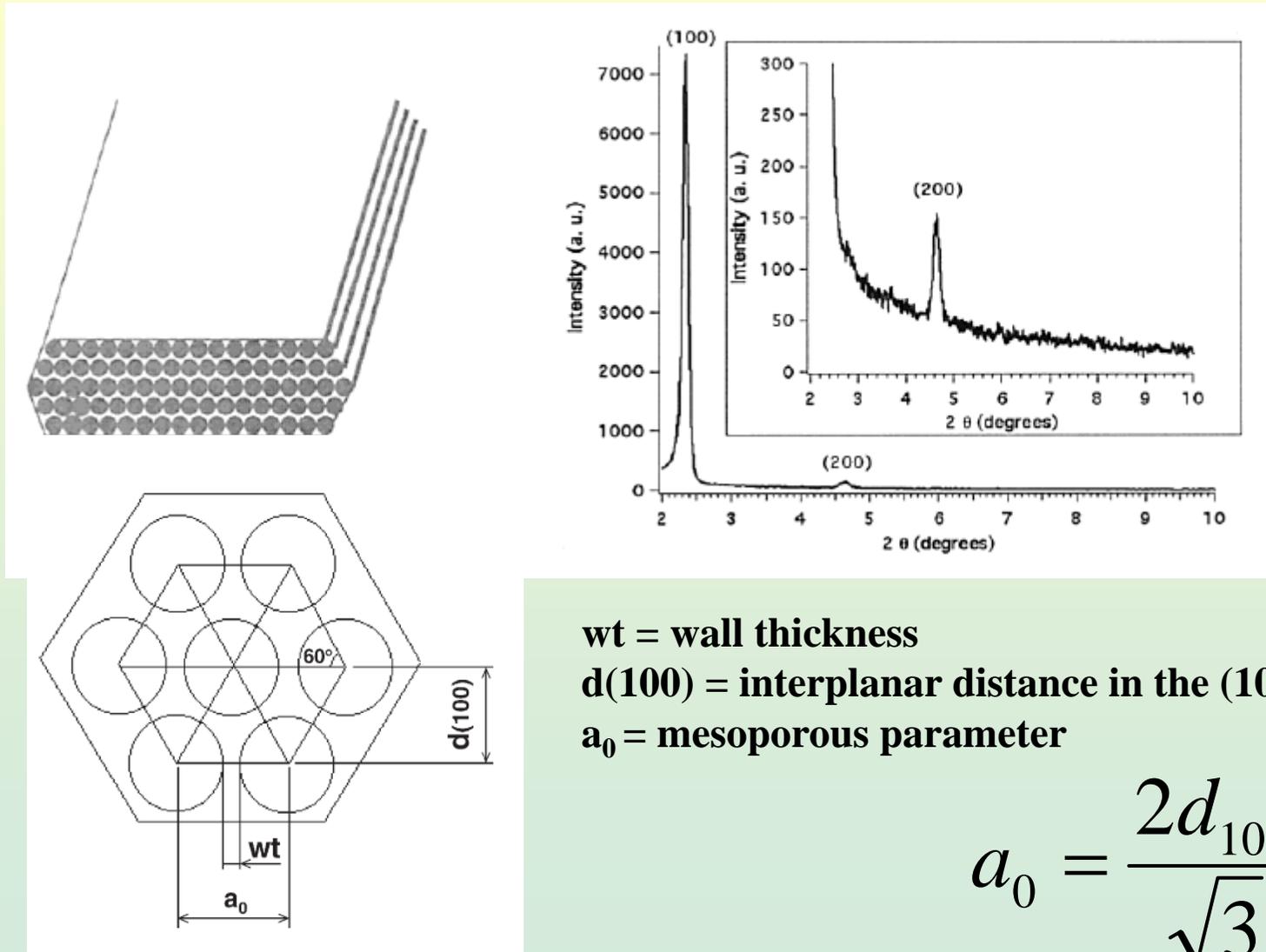
TEM micrograph of hexagonal molecular sieve



XRD of Lamellar MCM-50



XRD of Hexagonal MCM-41



wt = wall thickness

$d(100)$ = interplanar distance in the (100) plane

a_0 = mesoporous parameter

$$a_0 = \frac{2d_{100}}{\sqrt{3}} \quad 33$$

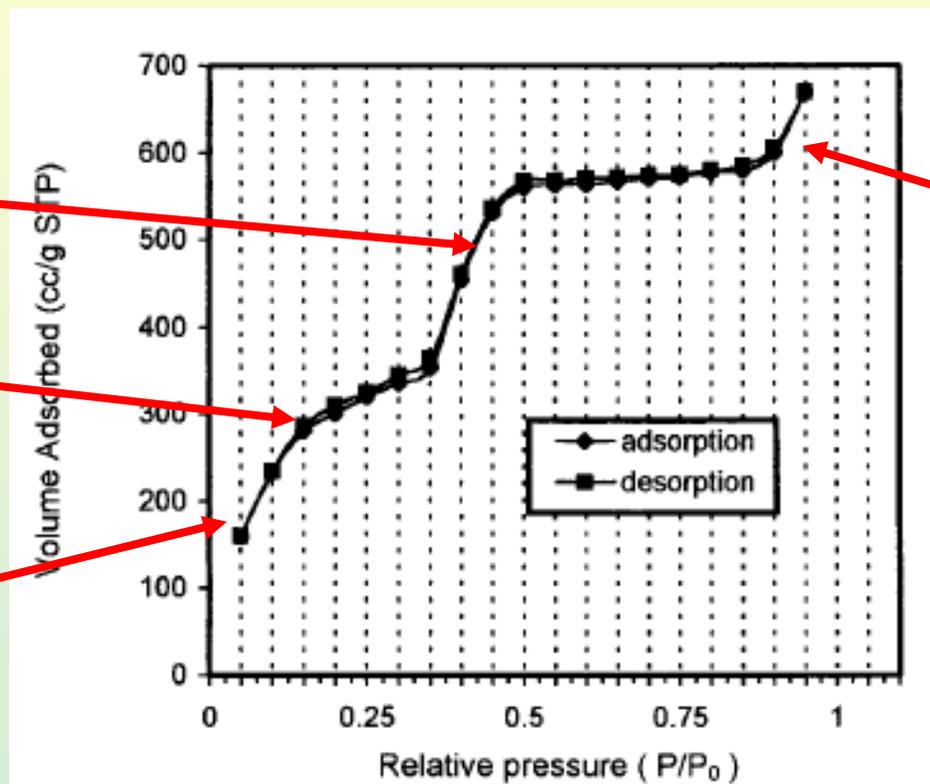
Gas Adsorption Isotherms

Mesopore filling

BET

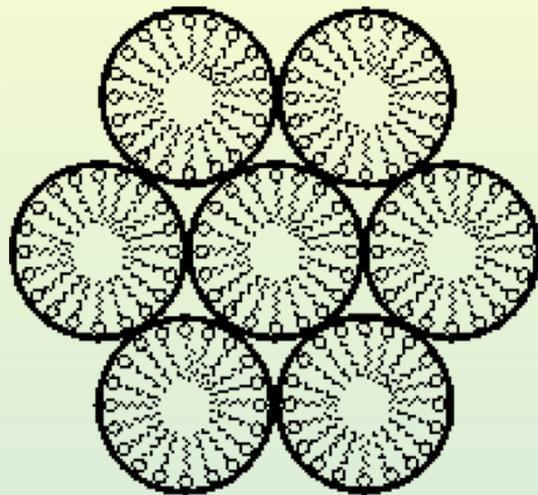
Surface area

Micropore filling



Pores filled
with LN2
Pore volume

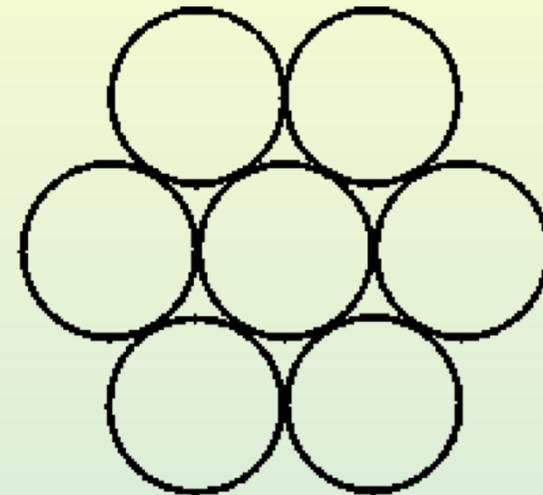
Template Removal



Calcination
→
-H₂O, -CO₂, -NO_x

Extraction
→
- template

O₃ treatment
→
-H₂O, -CO₂, -NO_x



Mesoporous Platinum Metal

$\text{H}_2[\text{PtCl}_6]$ or $(\text{NH}_4)_2[\text{PtCl}_6]$

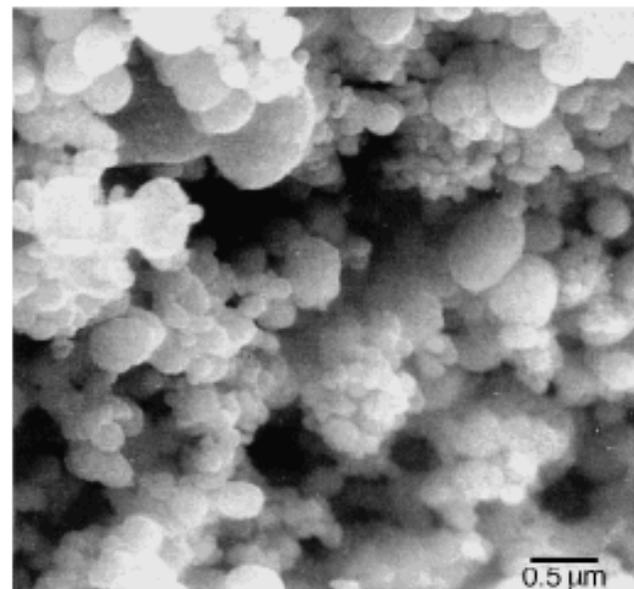
$\text{C}_{16}(\text{EO})_8$

Assembly of liquid crystalline phase

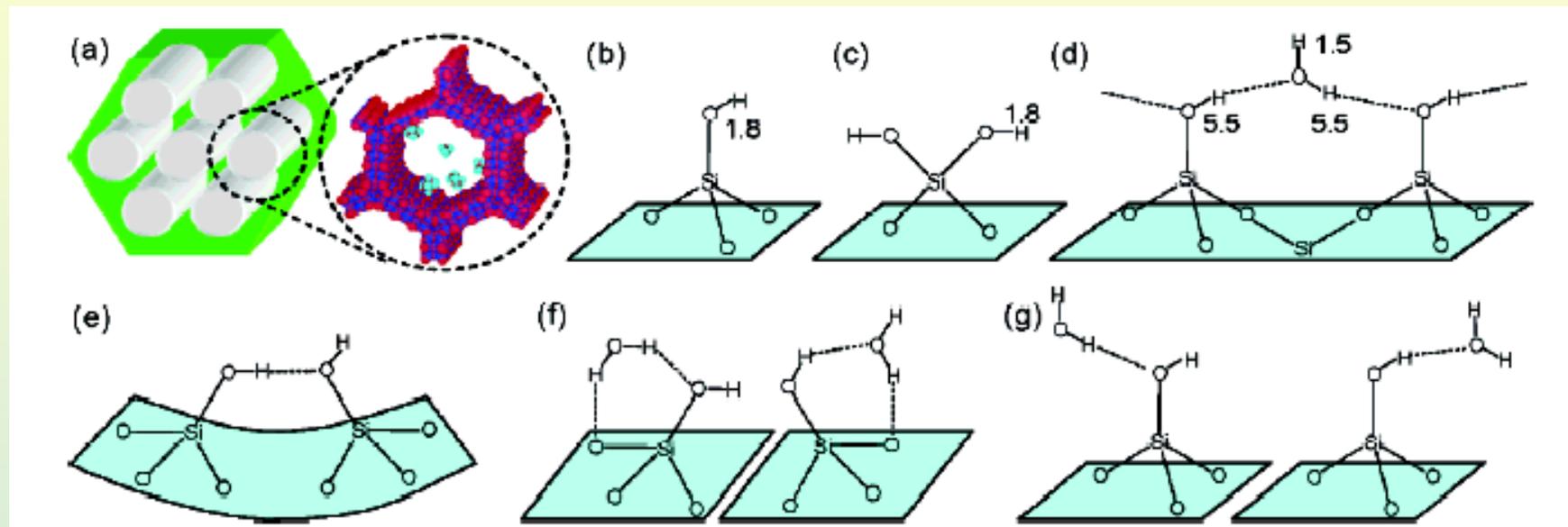
Reductants: Fe, Zn, Hg, NH_2NH_2

Washed with acetone, water, HCl

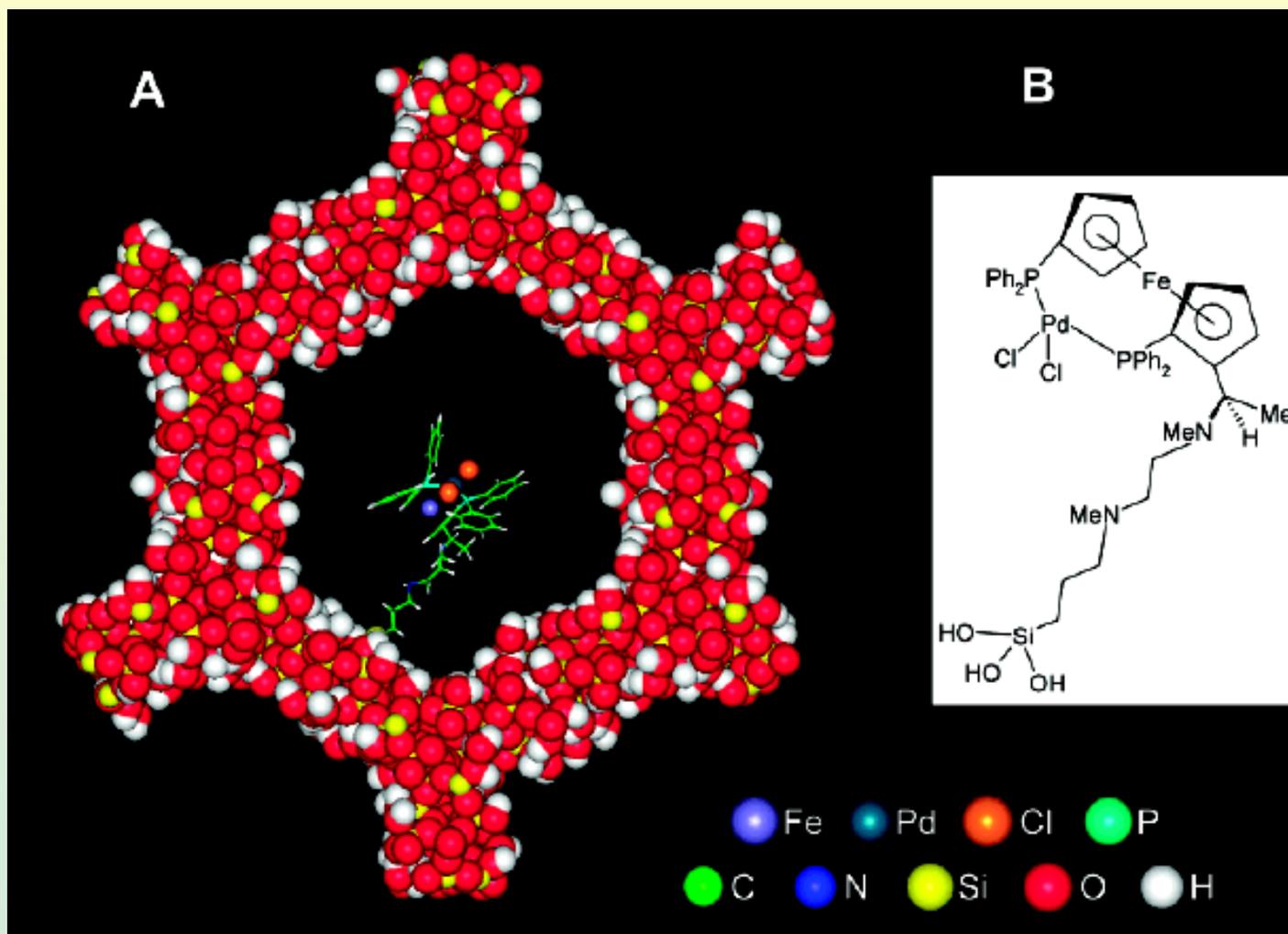
SEM (upper) and TEM (lower) images of mesoporous Pt metal show particles 90-500 nm in diameter and a pore diameter of 30 Å and a pore wall thickness of 30 Å.

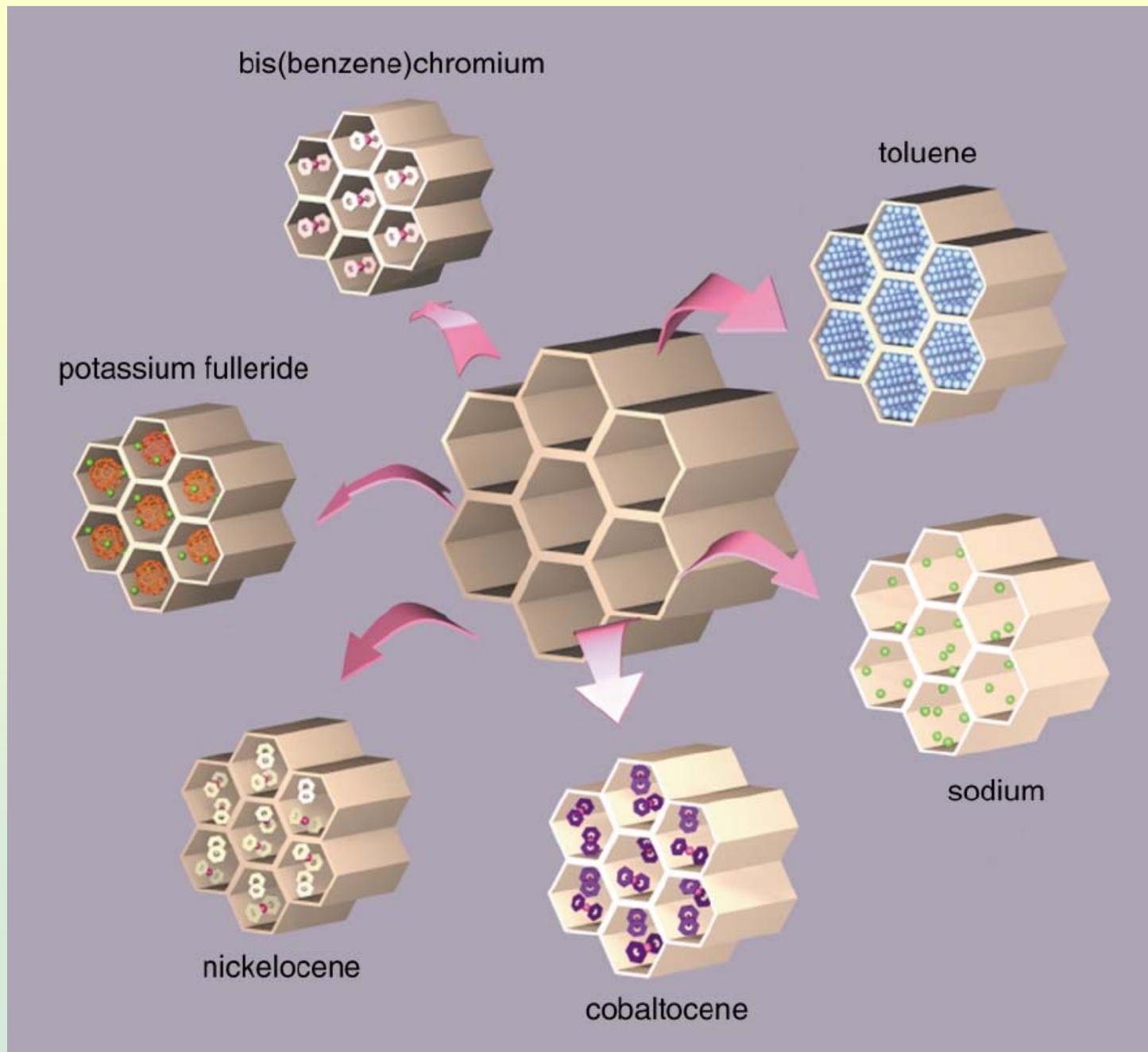


Surface Silanols in MCM-41 Pores

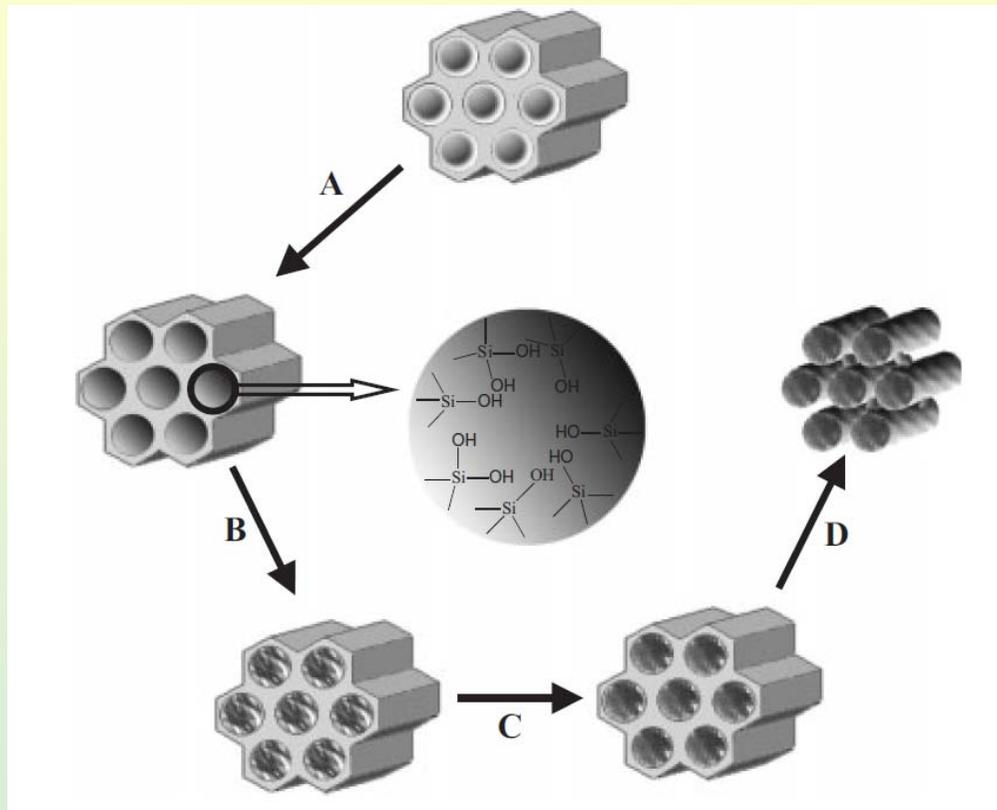


Chemistry inside the Pores

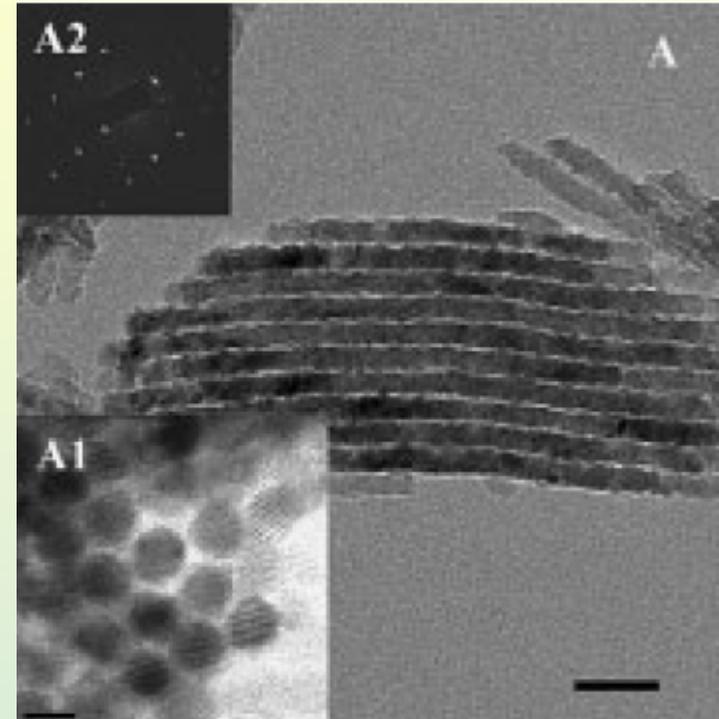




Hard Tempalting



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



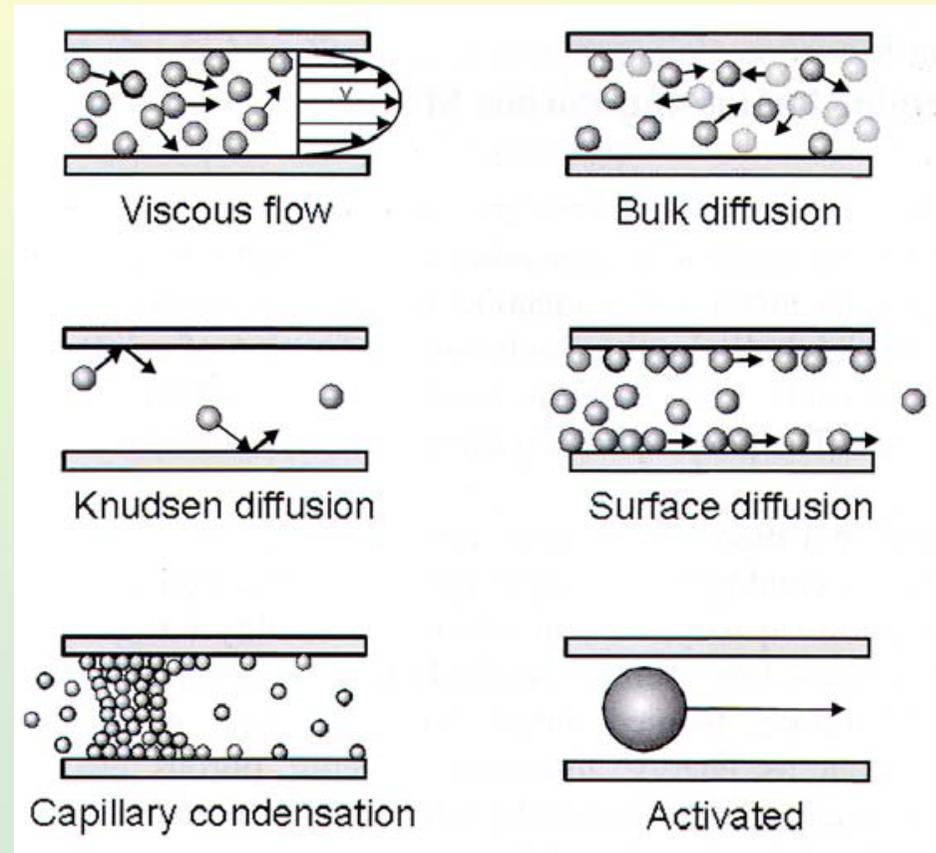
Cr_2O_3 crystalline nanowires
(bar = 25 nm for A, 10 nm for A1)

Pore Size Regimes and Transport Mechanisms

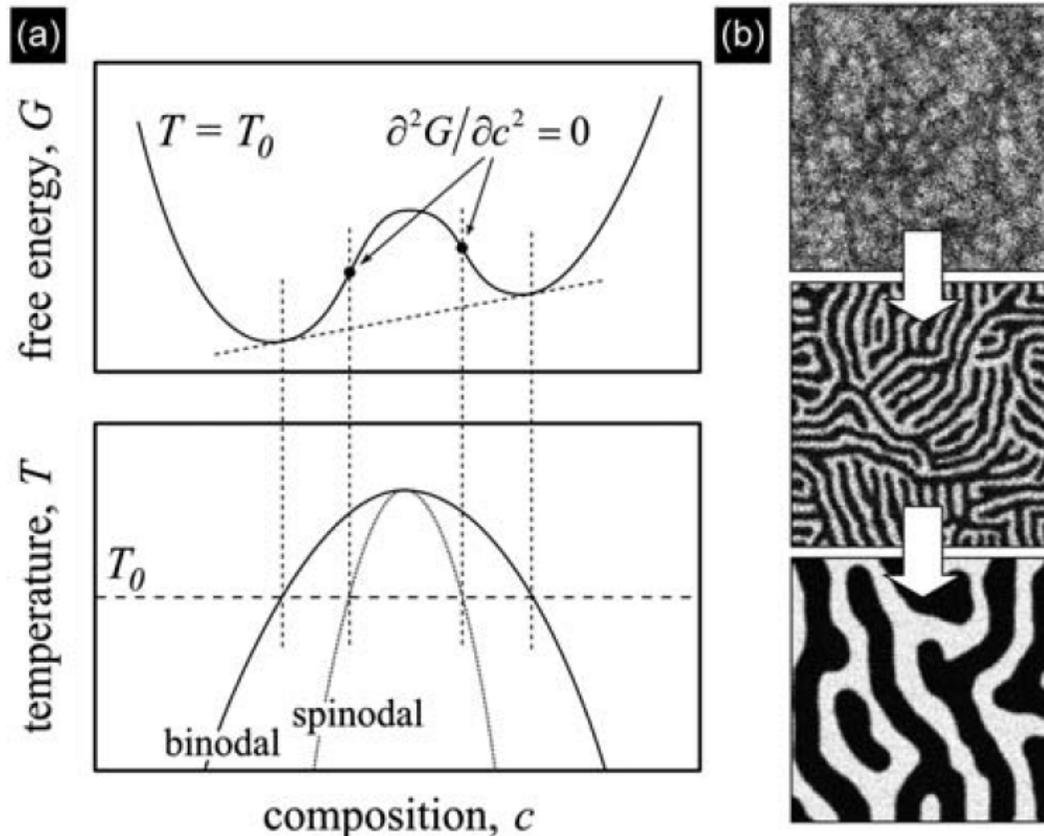
Macropores = larger than 50 nm
larger than typical mean free path length
of typical fluid. Bulk diffusion and
viscous flow.

Mesopores = between 2 and 50 nm
same order or smaller than the mean free
path length. Knudsen diffusion and
surface diffusion. Multilayer adsorption
and capillary condensation may
contribute.

Micropores = smaller than 2 nm
pore size comparable to the size of
molecules. Activated transport
dominates.



Spinodal Decomposition



(a) Free energy of a binary system as a function of composition and the miscibility region showing the origin of the binodal and spinodal lines

(b) Evolution of a blend microstructure phase separating by spinodal decomposition

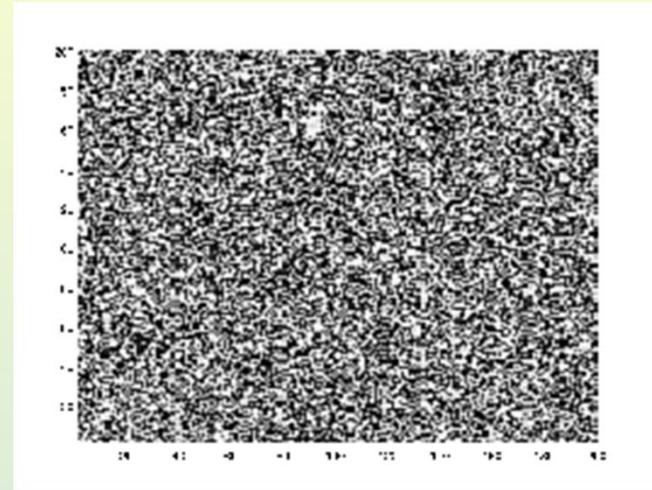
Spinodal Decomposition

A two component system with a composition, c , that is unstable to small fluctuations in concentration,

where

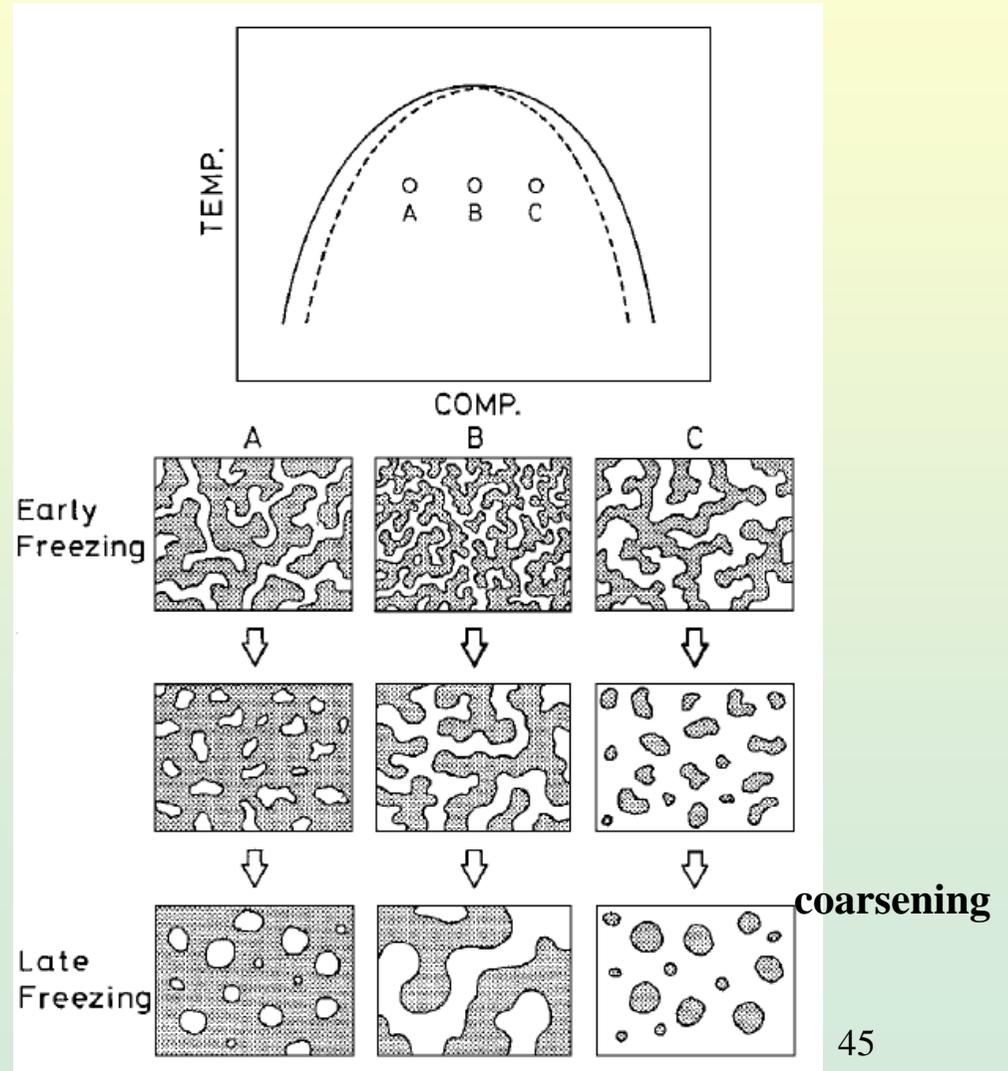
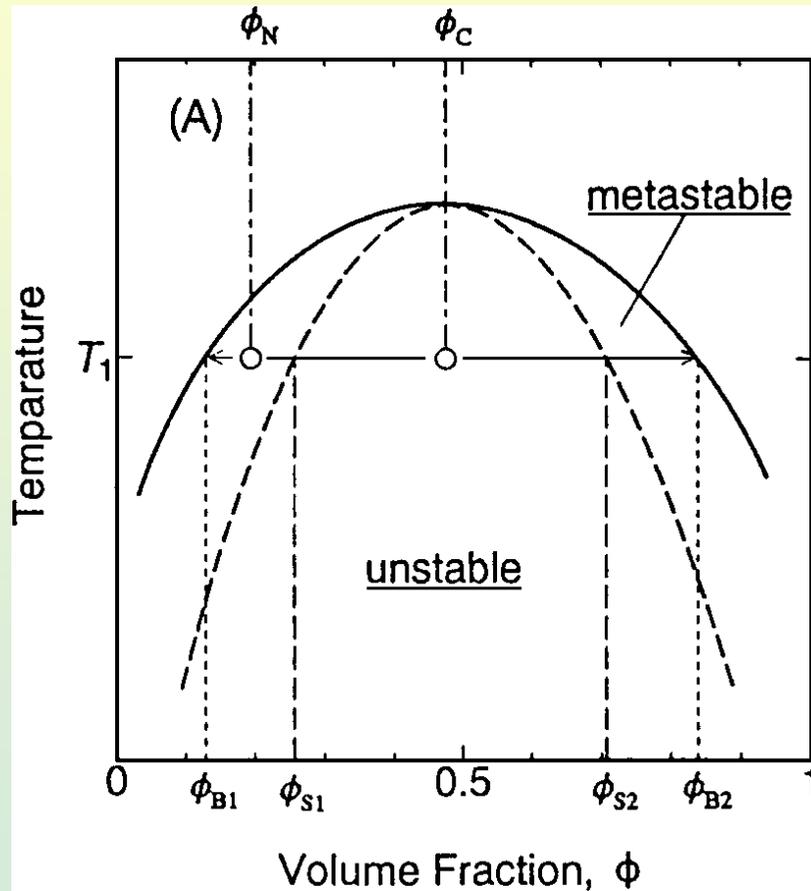
(G = the free energy),

$$\frac{\partial^2 G}{\partial c^2} < 0$$

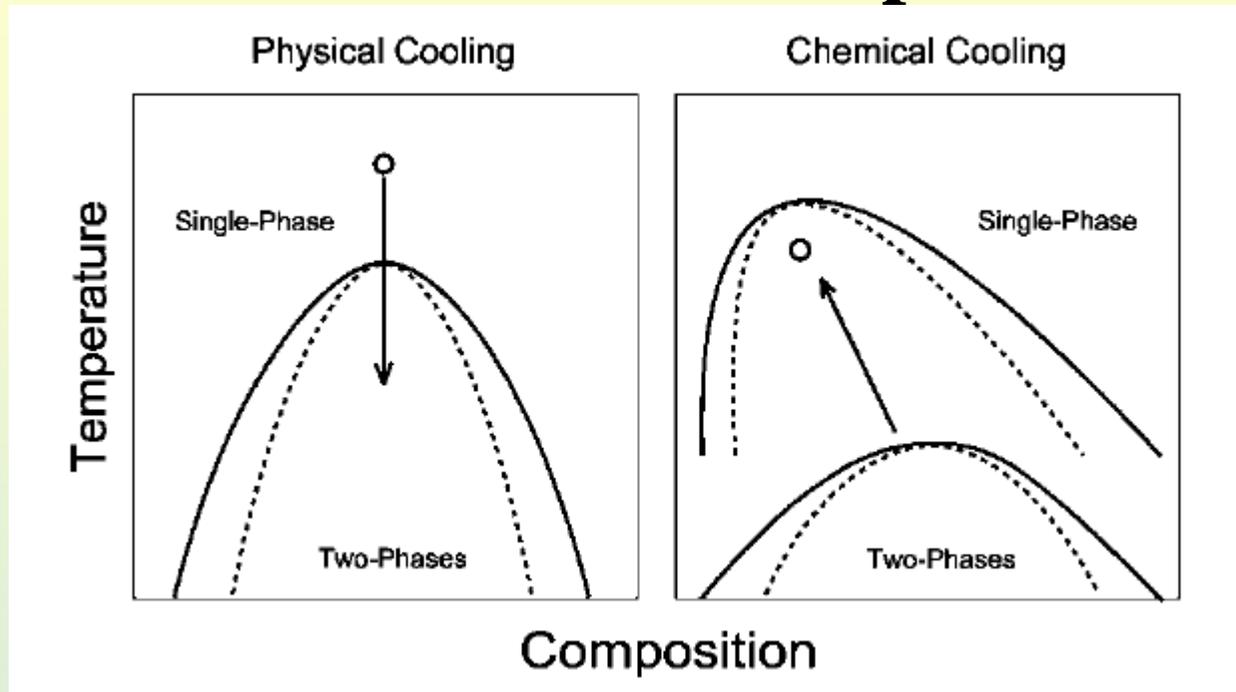


will spontaneously phase separate with the fluctuations increasing and coarsening over time.

Spinodal Decomposition



Sol–Gel with Phase Separation



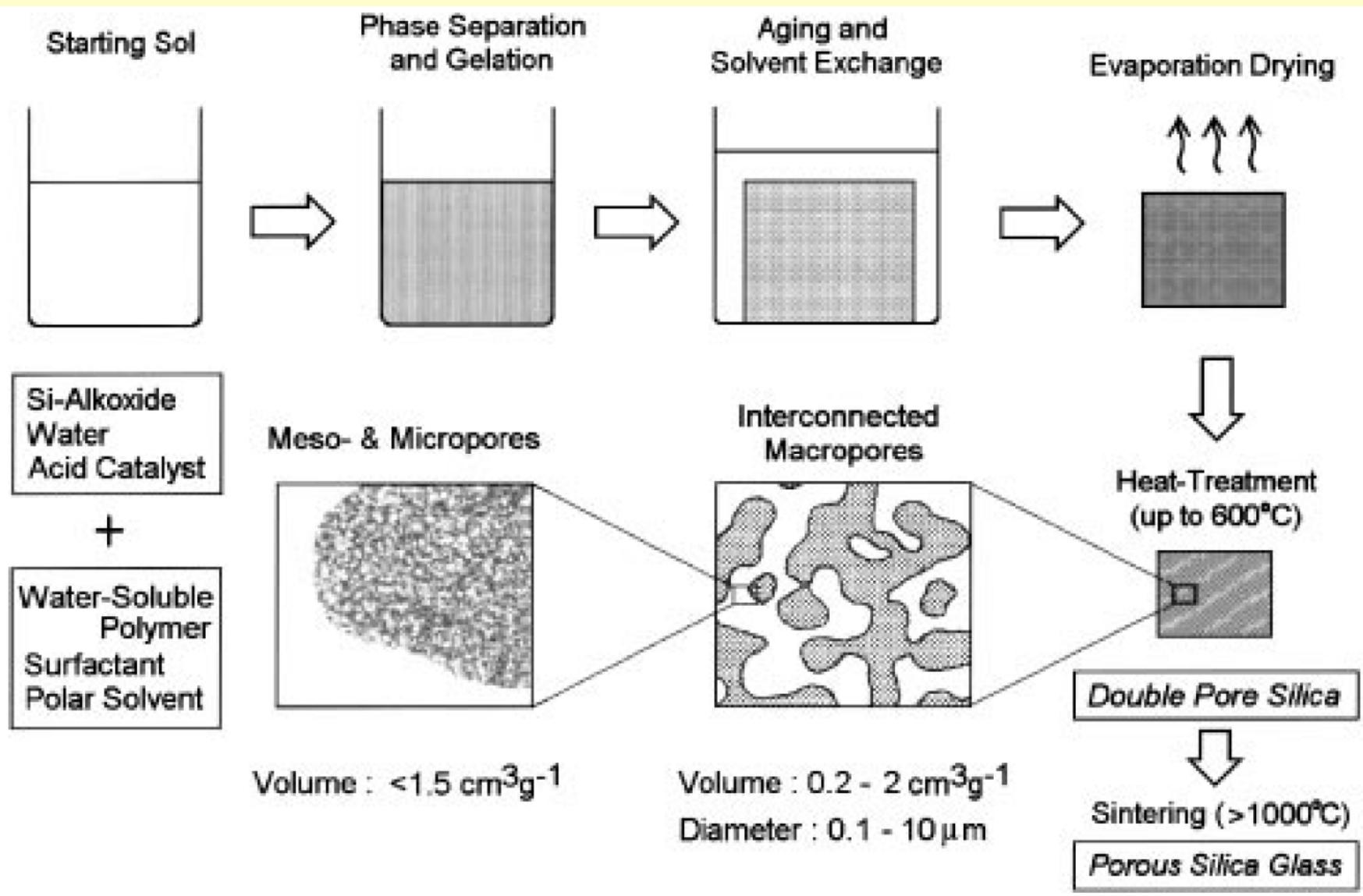
$$\Delta G \propto RT[(\phi_1/P_1) \ln \phi_1 + (\phi_2/P_2) \ln \phi_2 + \chi_{12}\phi_1\phi_2]$$

ϕ_i = the volume fraction

P_i ($i = 1, 2$) = the degree of polymerization of each component,

χ_{12} the interaction parameter

The former two terms in the bracket express the entropic contribution, and the last term the enthalpic contribution

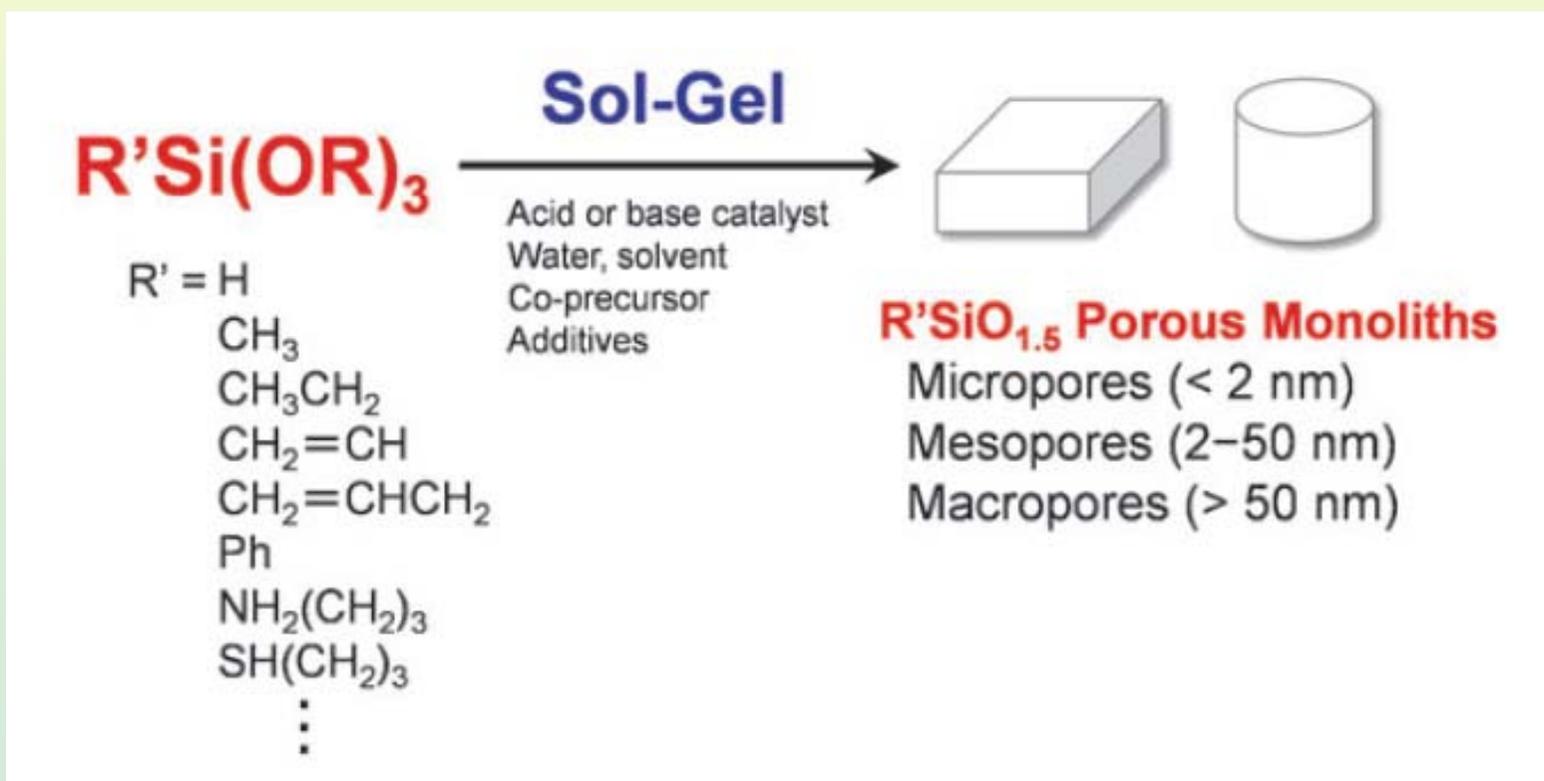


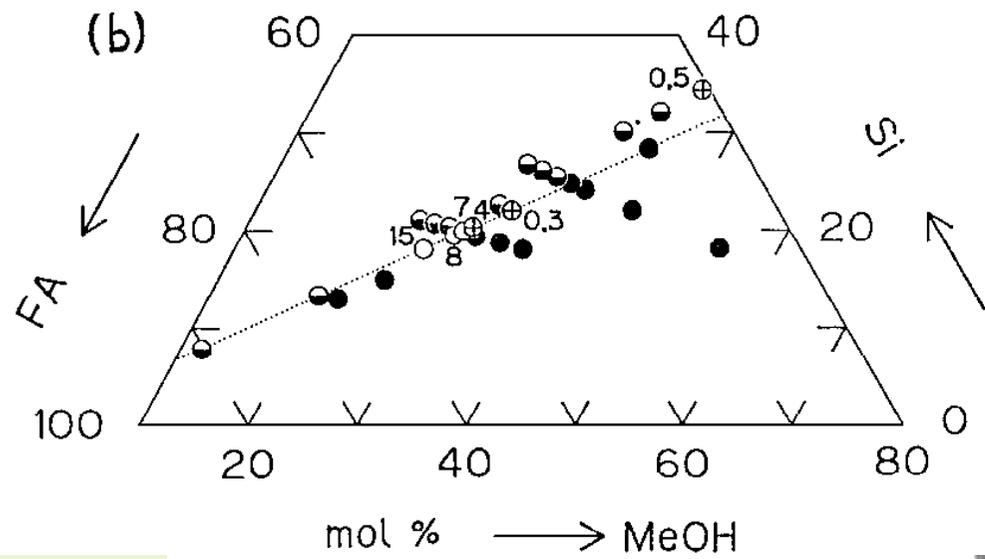
Hierarchically Porous Monoliths

Macroporous – good mass transport

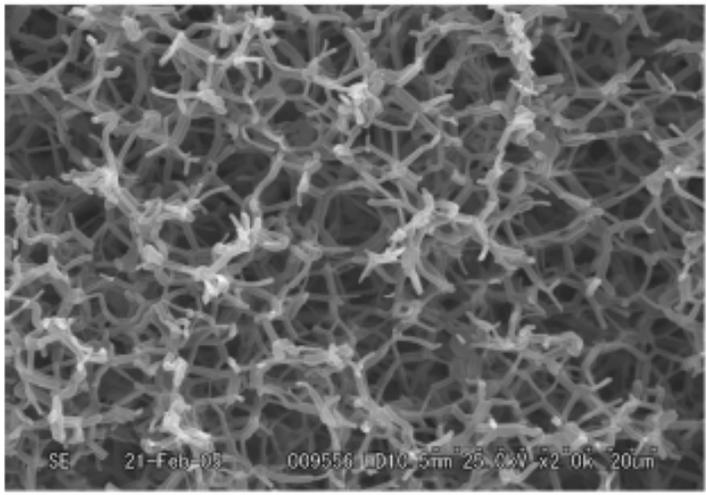
Mesoporous – large surface area available for active sites

Microporous – catalytic selectivity

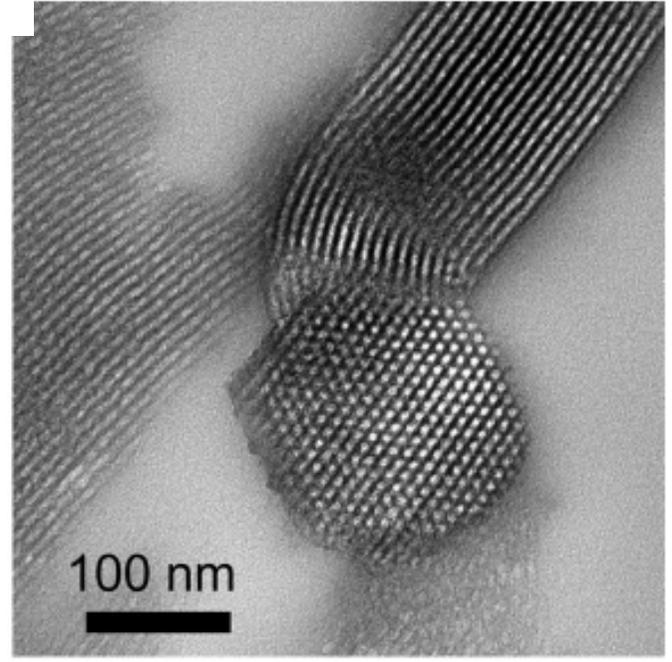




TMOS-Formamide-1M nitric acid (b) calculated composition.
Reaction temperature 40 °C; circles with cross and shaded areas denote the composition where the interconnected structure has been obtained. ●: nanoporous gel, ⊕: interconnected structure, ○: particle aggregates, ◡: macroscopic two-phase.

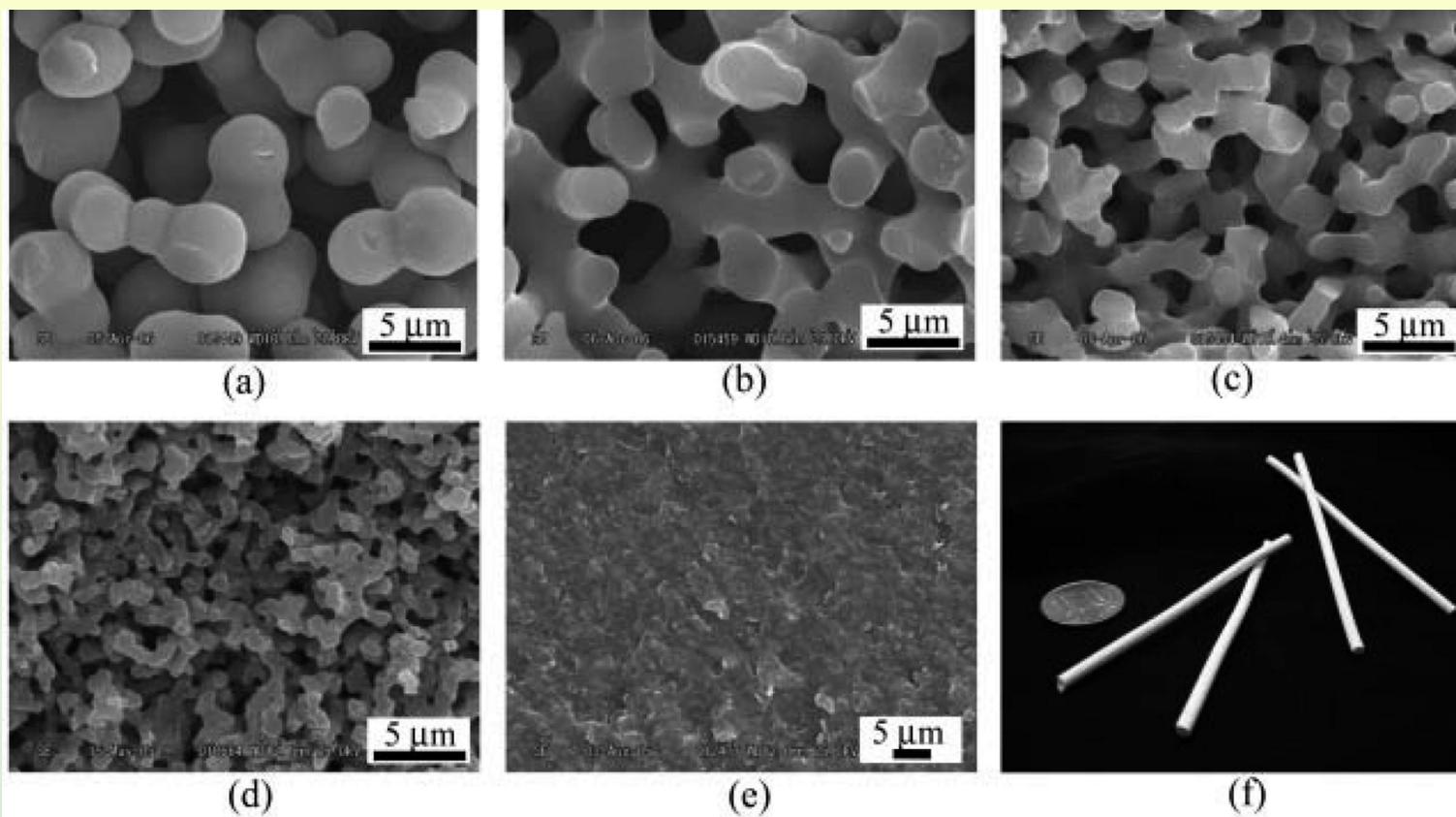


(a)



(b)

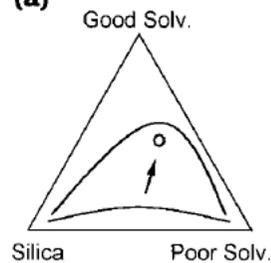
TiO₂



SEM images of dried TiO₂ gels prepared with varied water/TiO₂ molar ratios in the overall starting 1:0.5:0.5:*f* Ti(O_nC₃H₇)₄:HCl:formamide:water composition: (a) *f*) 20.50, (b) *f*) 20.75, (c) *f*) 21.00, (d) *f*) 21.25, and (e) *f*) 21.50. (f) Photo image of monolithic TiO₂ gels prepared in Teflon tubes and a coin.

Hierarchically Porous Monoliths

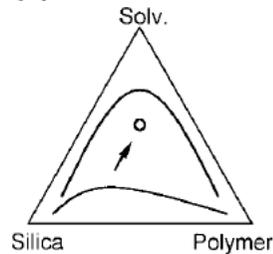
(a)



Alkoxide + Water ($r < 1.5$)
+ Formamide

Gel Phase : Silica + Good Solv.
Fluid Phase : Good & Poor Solvs.

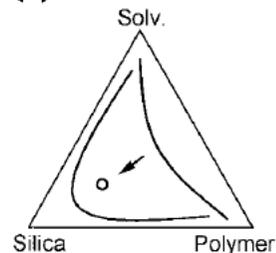
(b)



Alkoxide + Water ($r > 2$)
+ Weakly H.B. Polymer

Gel Phase : Silica + Solvent
Fluid Phase : Polymer + Solvent

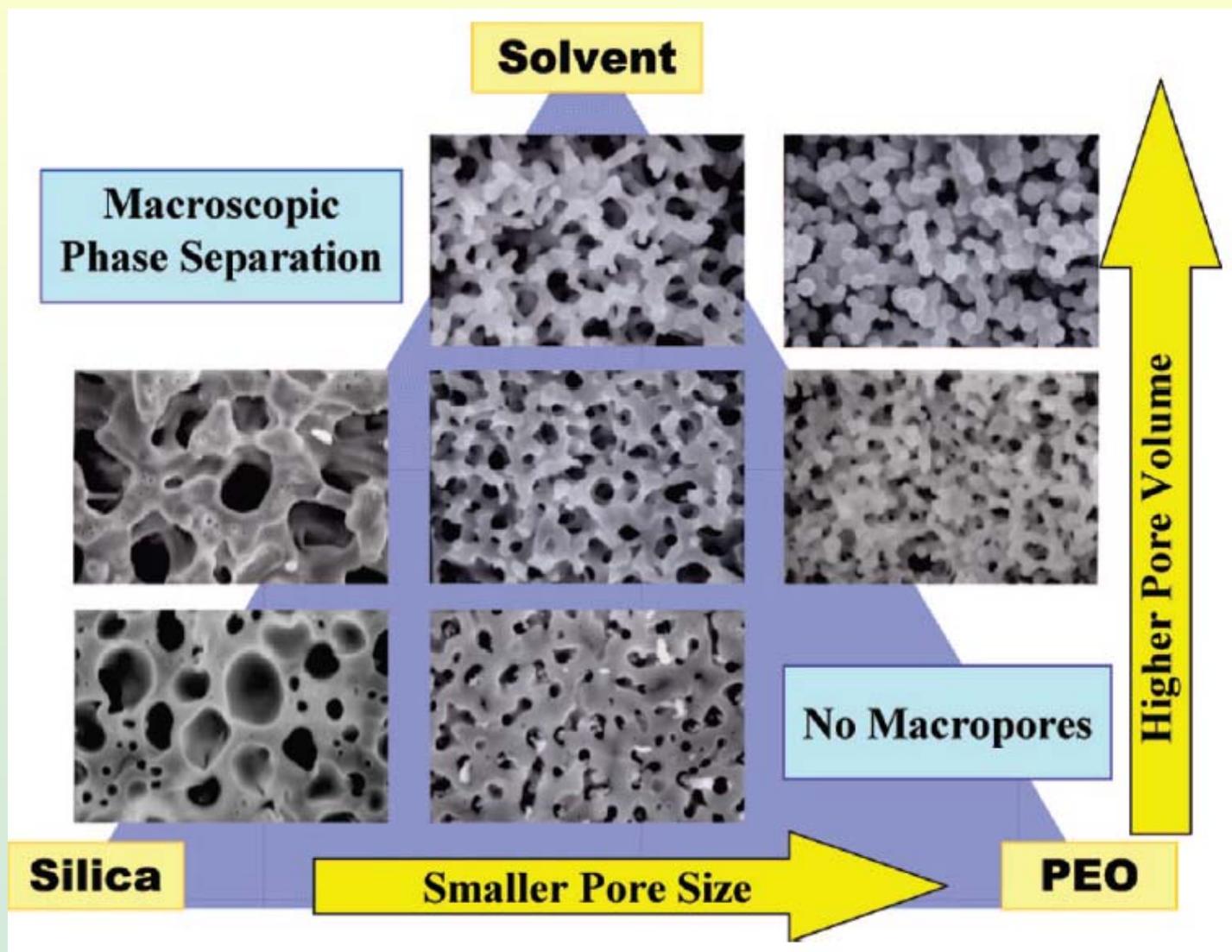
(c)



Alkoxide + Water ($r > 2$)
+ Strongly H.B. Polymer

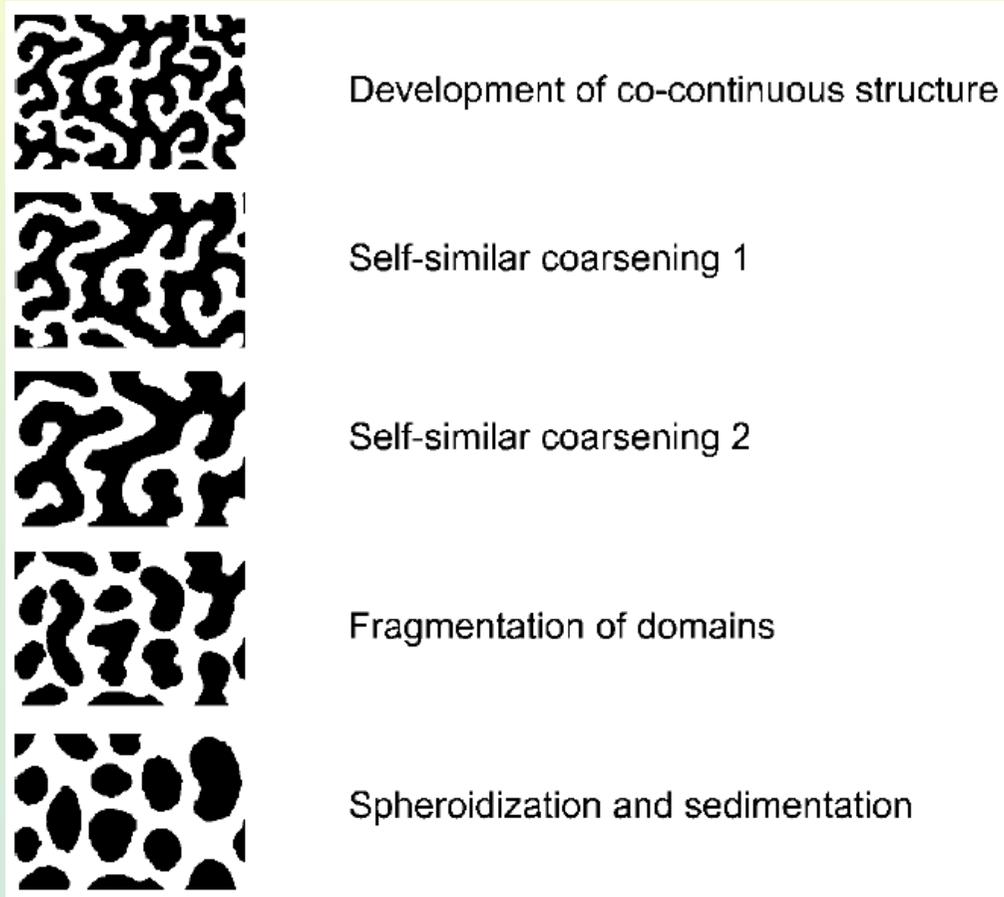
Gel Phase : Polymer + Silica
Fluid Phase : Solvent + Silica

Hierarchically Porous Monoliths

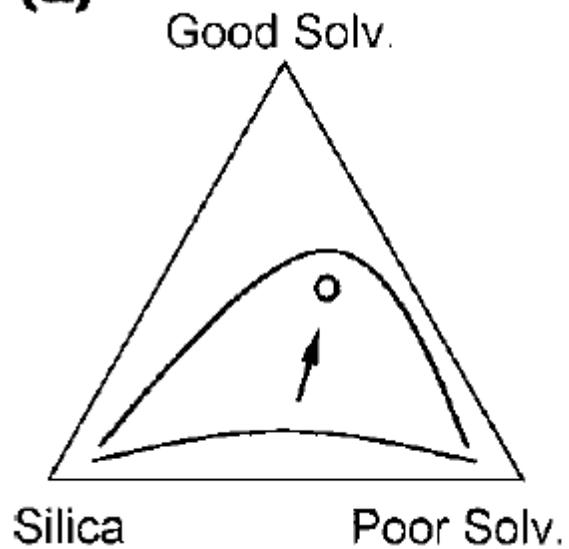


Hierarchically Porous Monoliths

Time evolution of a spinodally decomposing isotropic symmetrical system



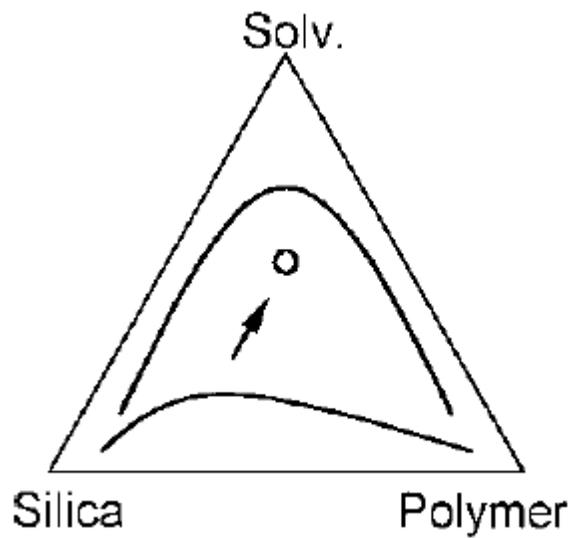
(a)



Alkoxide + Water ($r < 1.5$)
+ Formamide

Gel Phase : Silica + Good Solv.
Fluid Phase : Good & Poor Solvs.

(b)

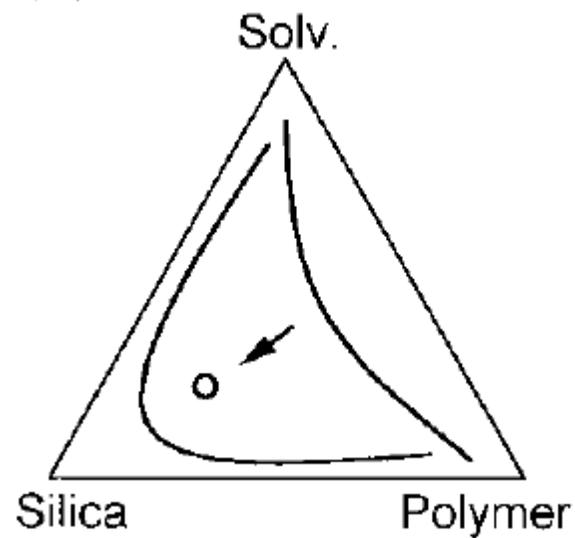


Alkoxide + Water ($r > 2$)
+ Weakly H.B. Polymer

Gel Phase : Silica + Solvent

Fluid Phase : Polymer + Solvent

(c)



Alkoxide + Water ($r > 2$)
+ Strongly H.B. Polymer

Gel Phase : Polymer + Silica

Fluid Phase : Solvent + Silica

