# TEM image of the Pd-grafted mesoporous silicate material


35 nm
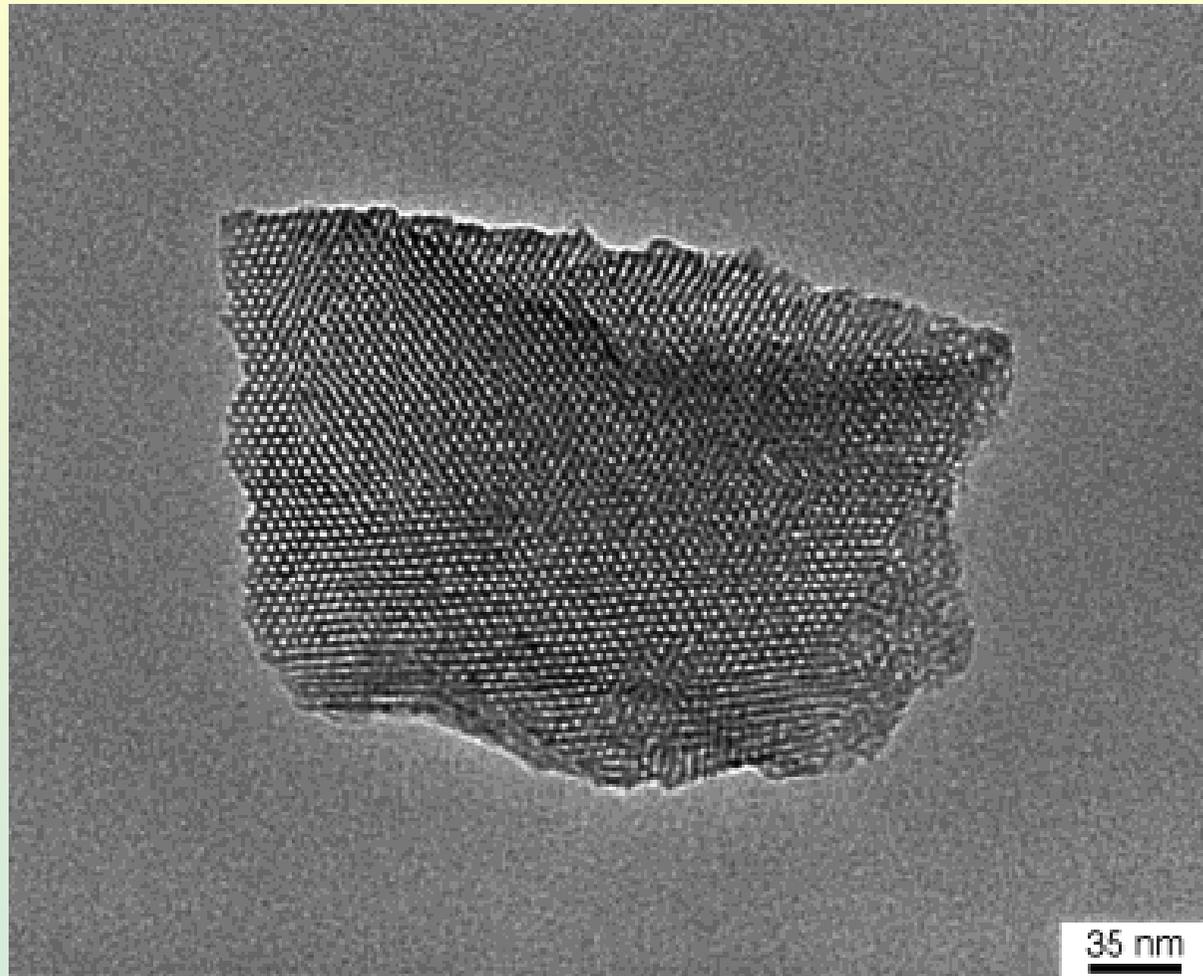
Mesoporous Materials

- **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
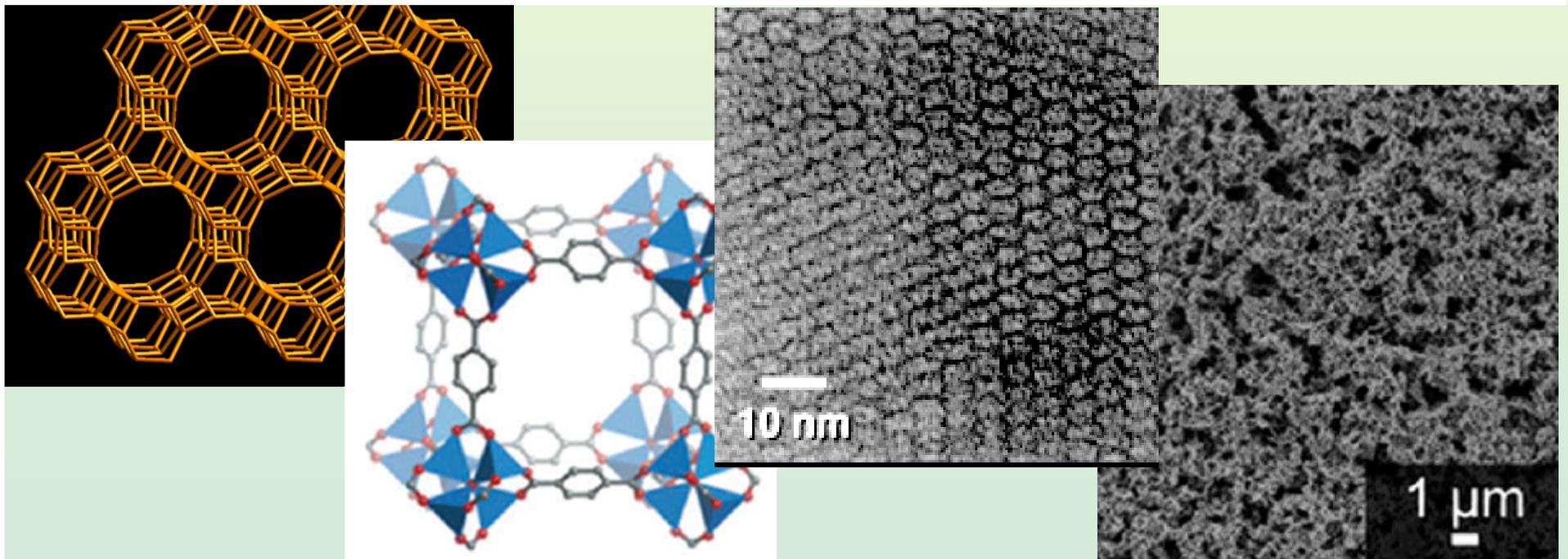
Mesoporous Materials

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

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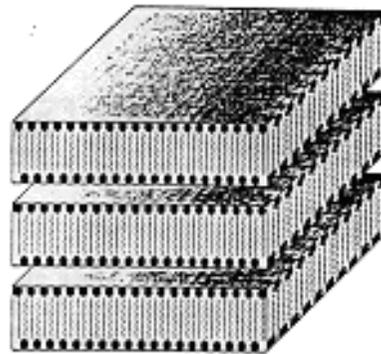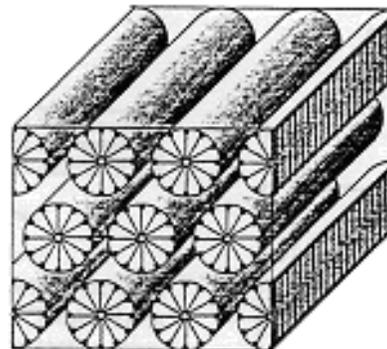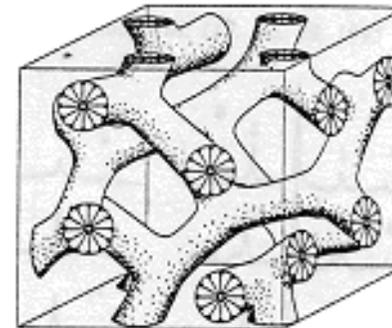
Pore size distribution
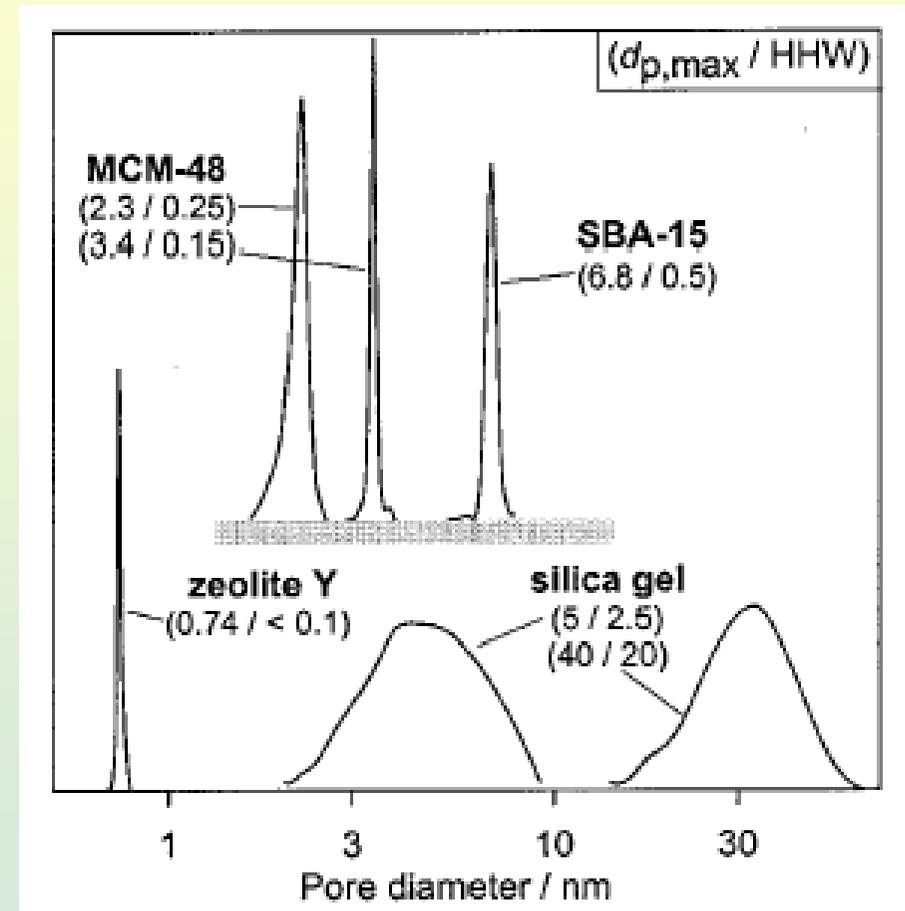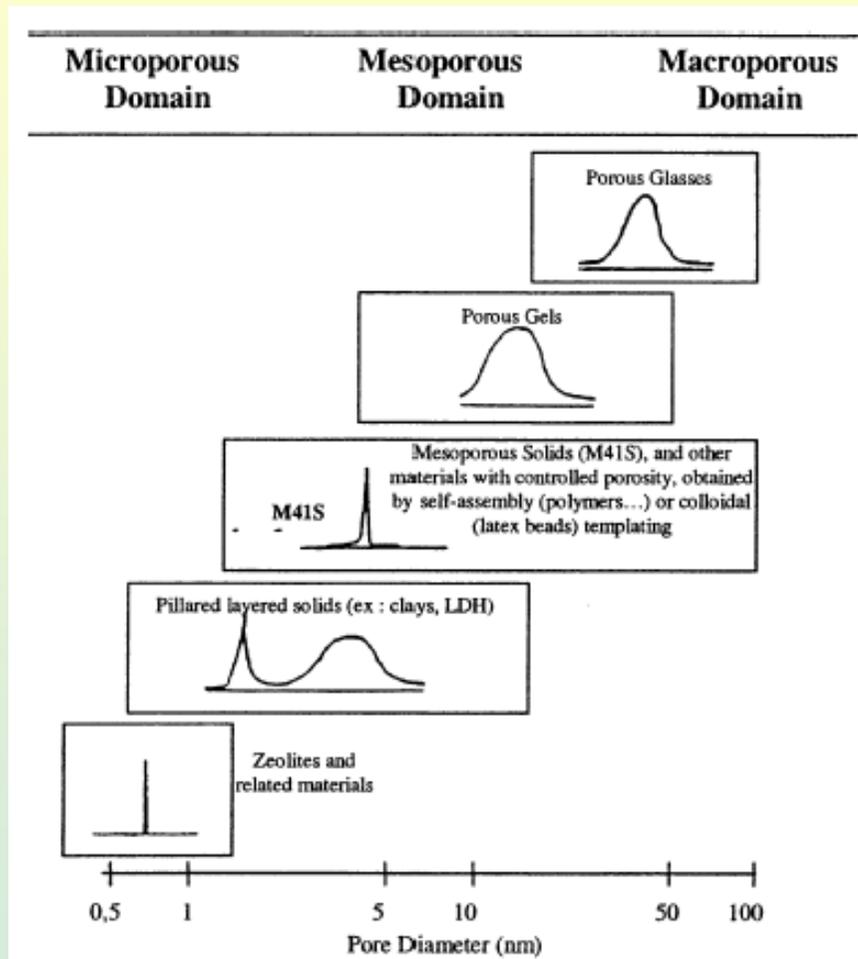
Micelles - Supramolecular Templates

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
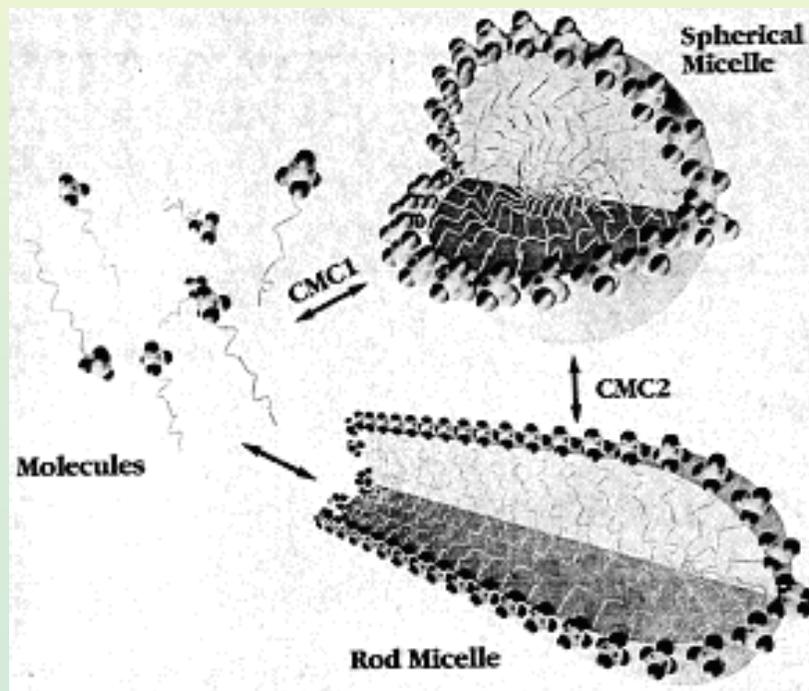
Mesostructure Assembly
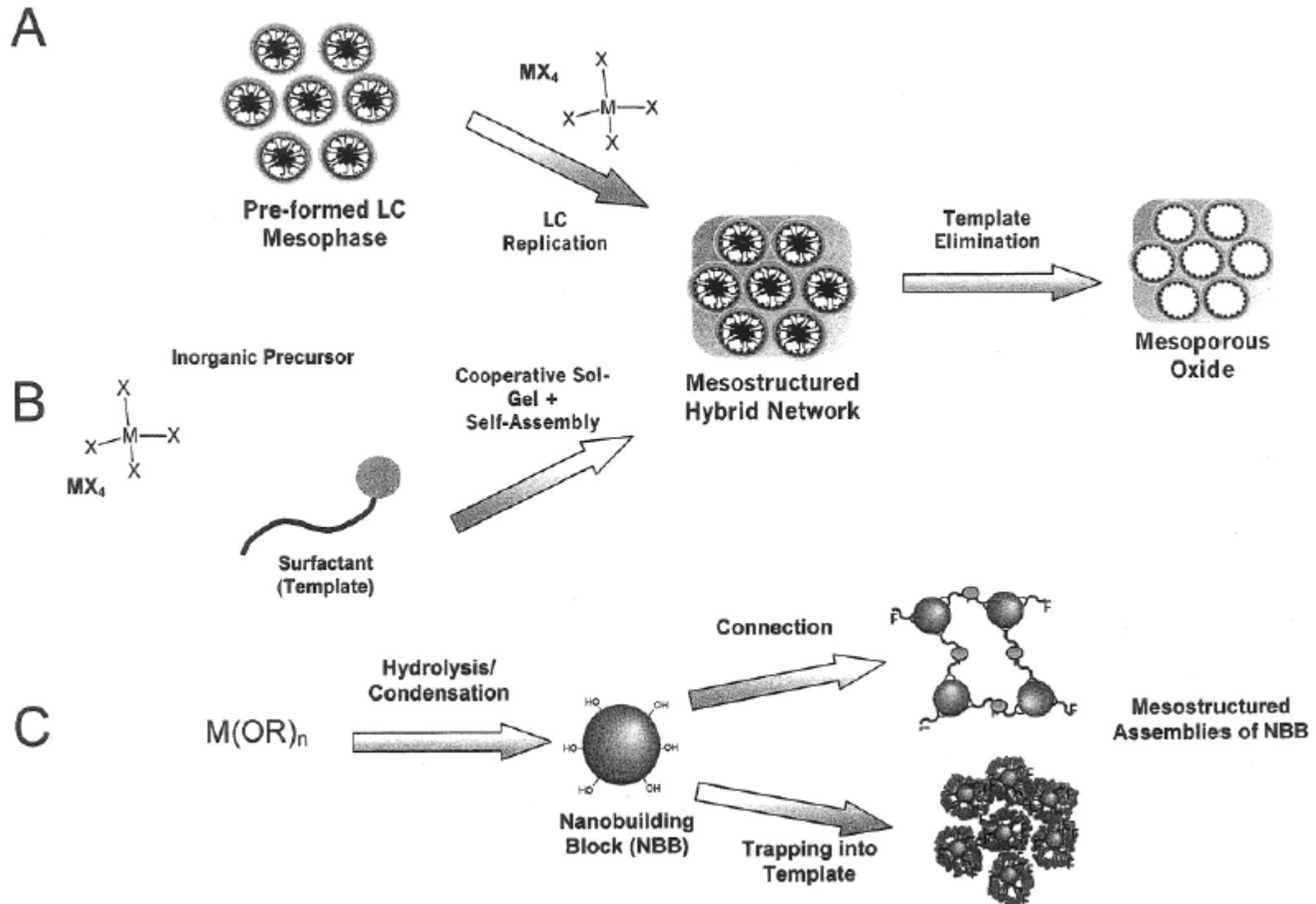
Supramolecular Templating

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
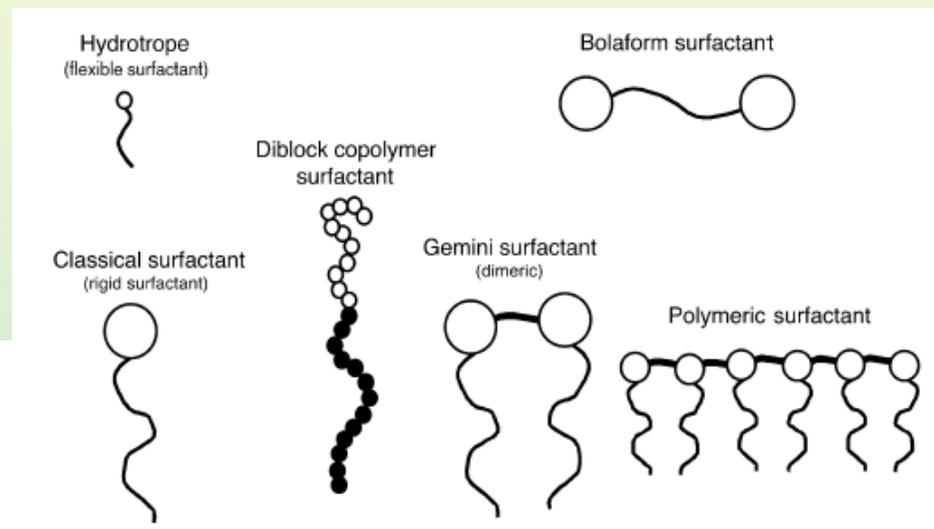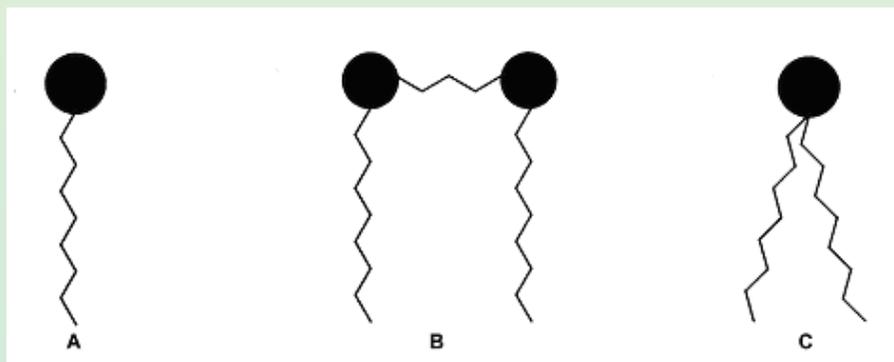
Surfactants

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, HSO_4

- *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
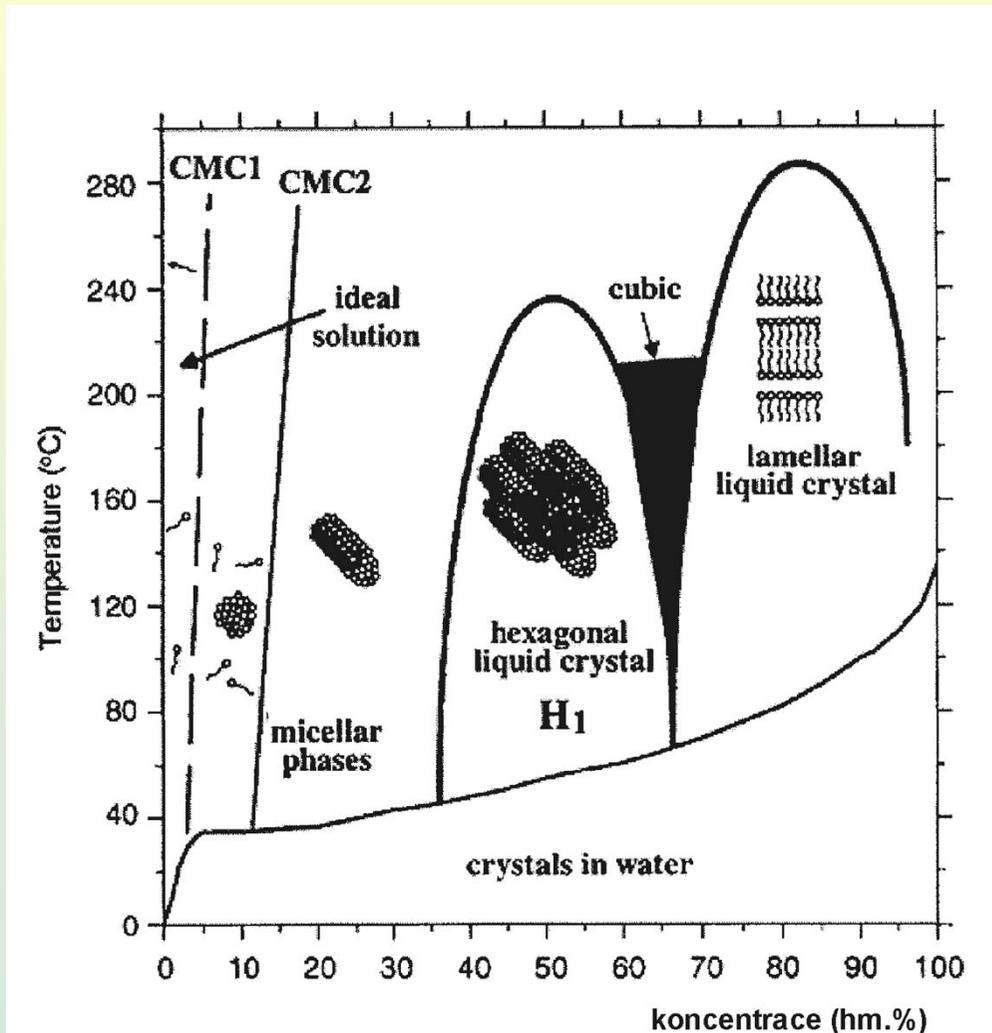
Phase diagram of $C_{16}TMABr$

CMC = critical micelle conc.

Micellar Shapes

Micellar shapes

A -spherical, B - rod-like, C - lamellar
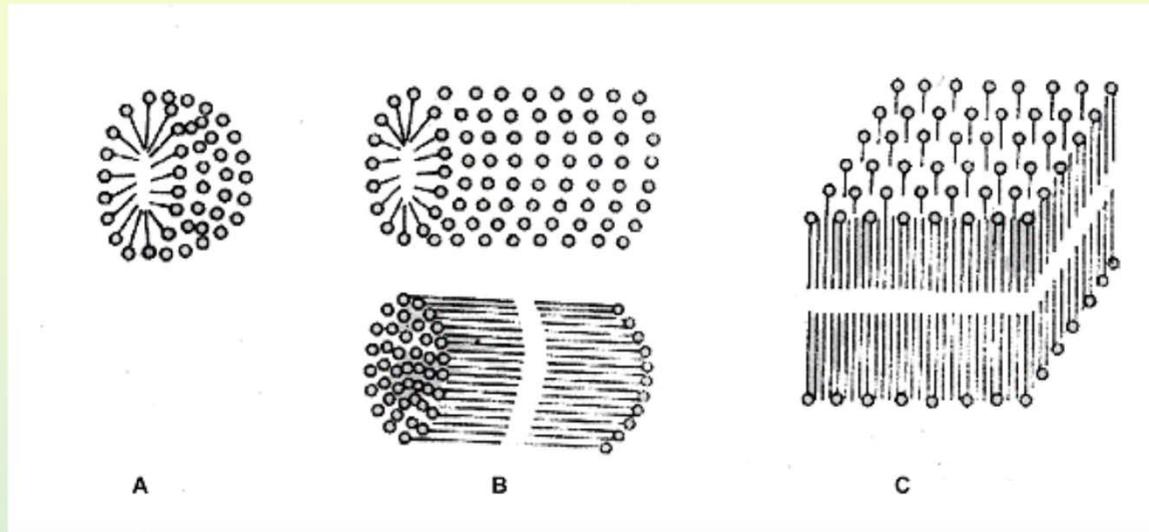
Micelles in media

A - normal, in polar solvent, H_2O

**B - inverse, in nonpolar solvent, organics**
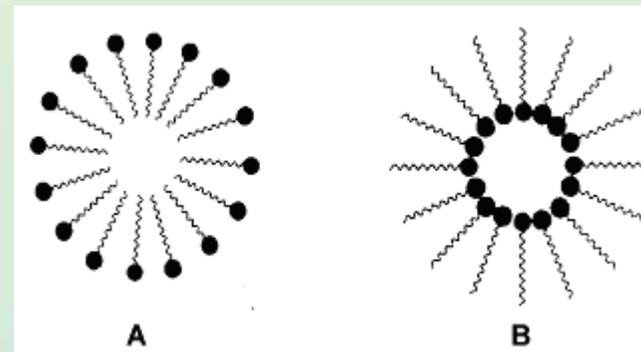
Surfactant Molecules

Critical packing parameter – CPP

$$CPP = V_H / a_0 l_c$$

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

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

n number of carbon atoms. l_c depends on the chain shape.
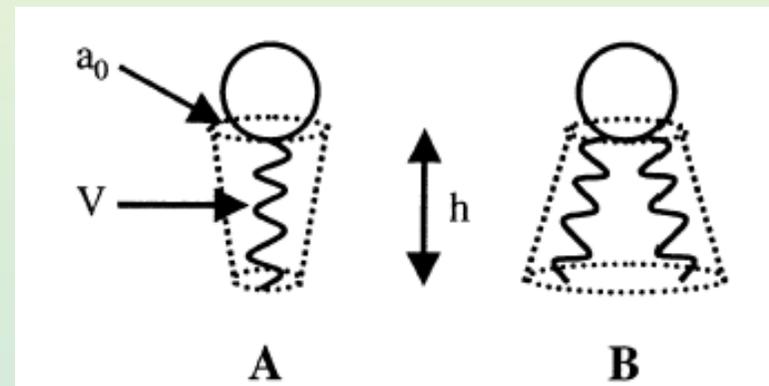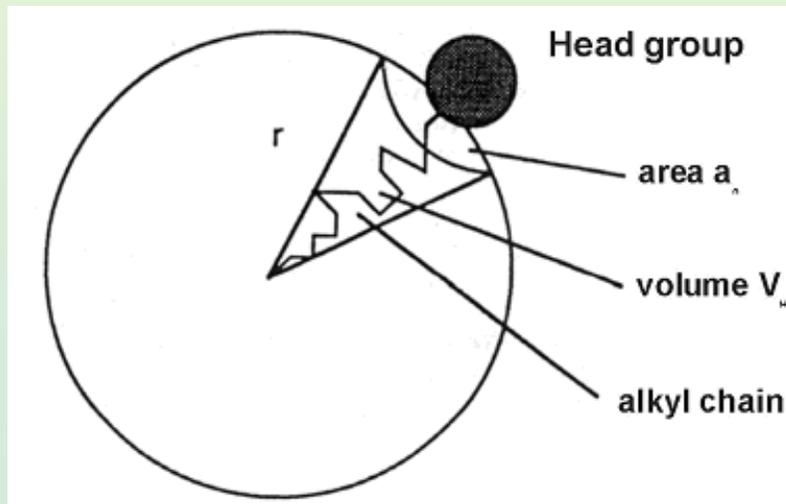
Conical (*icecream cone*, A)
Inverse conical (*champagne cork*, B)

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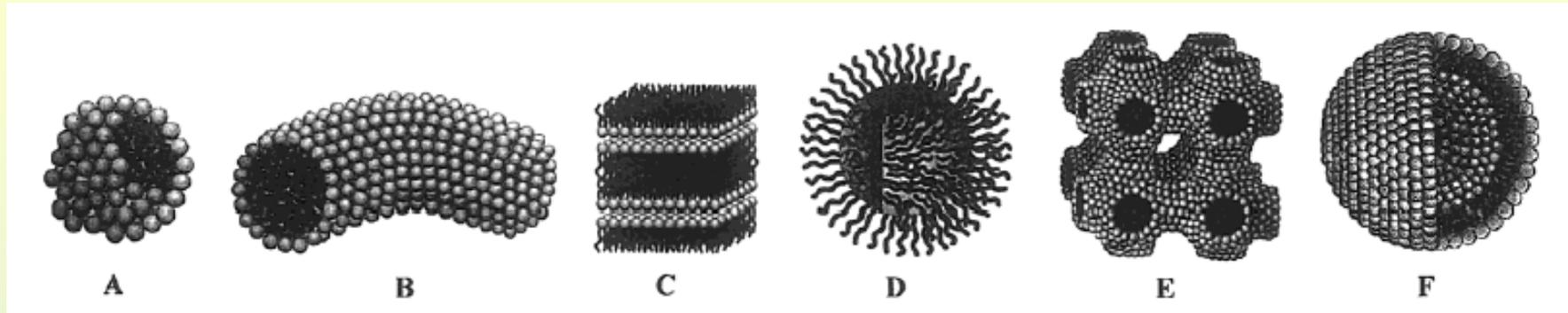
Micellar Shapes

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

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Surfactant Molecules
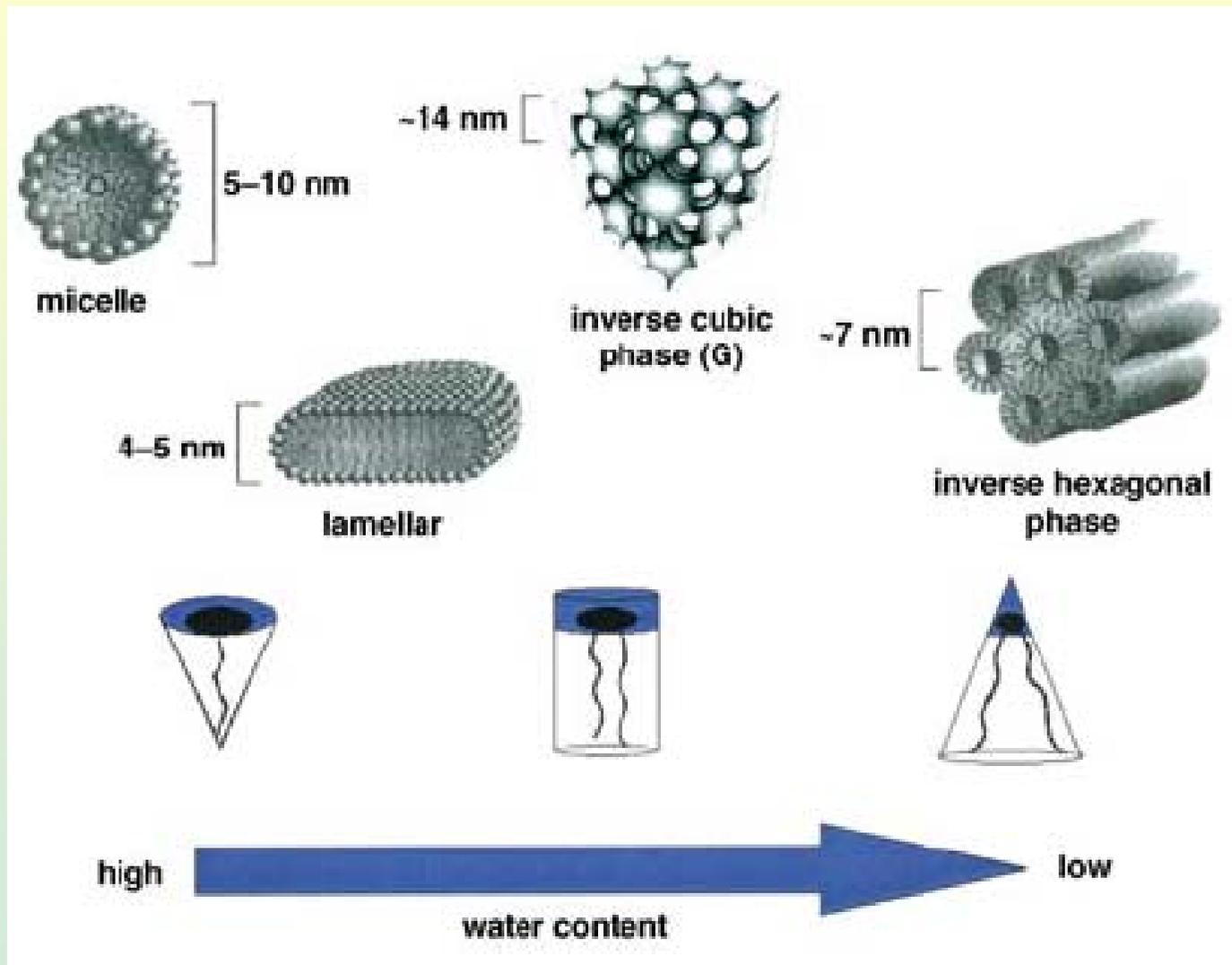
Mechanism of the Mesoporous Material Formation
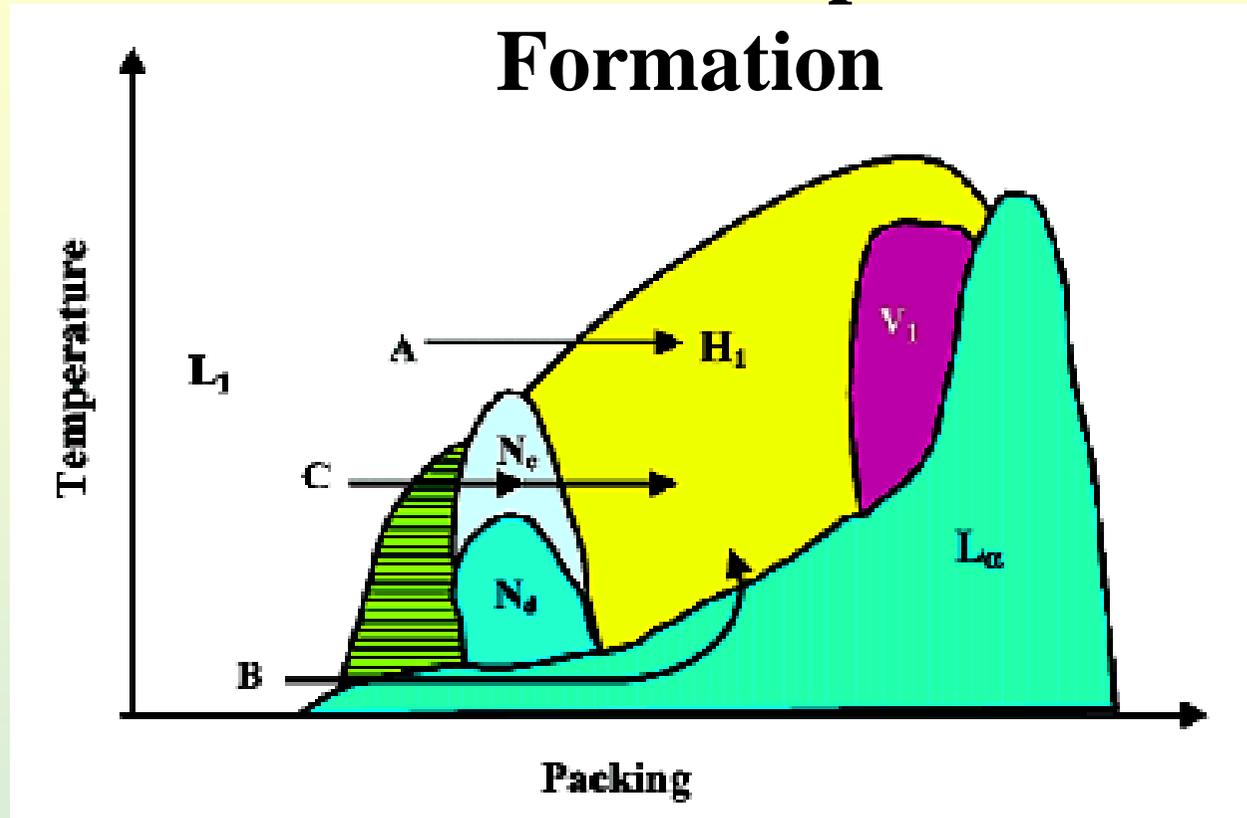
L_1= micellar solution; Nc = nematic phase; H_1 = normal hexagonal phase (MCM-41; SBA-15); V_1 = normal bicontinuous cubic phase (MCM-48); L_α = lamellar phase (MCM-50)

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

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# General Liquid Crystal Templating (LCT) Mechanism
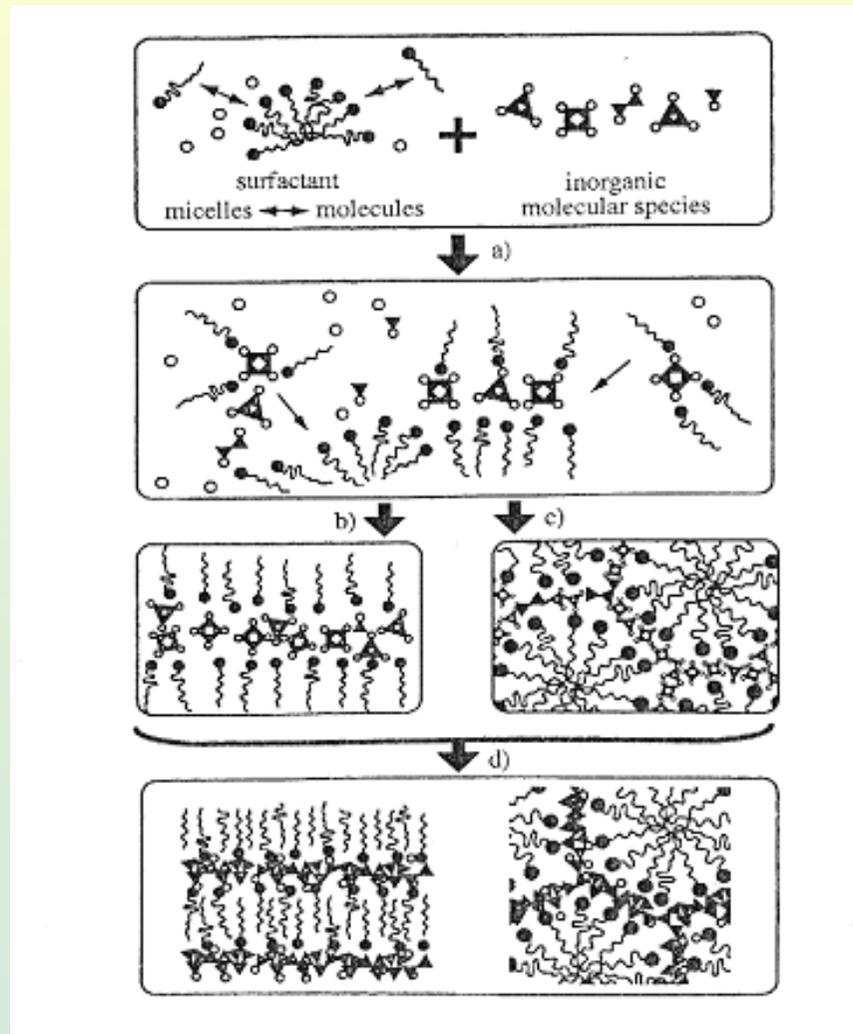
Mechanism of the Mesoporous Material Formation

Hexagonal, MCM-41

LCT Liquid Crystal Templating
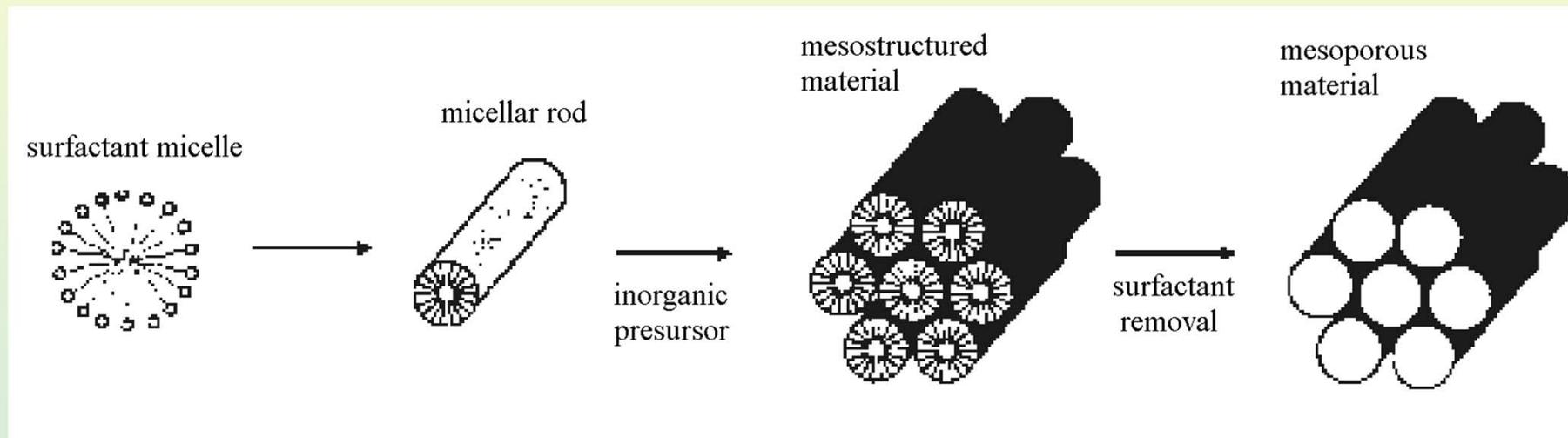
SLC Silicatropic Liquid Crystals Mechanism
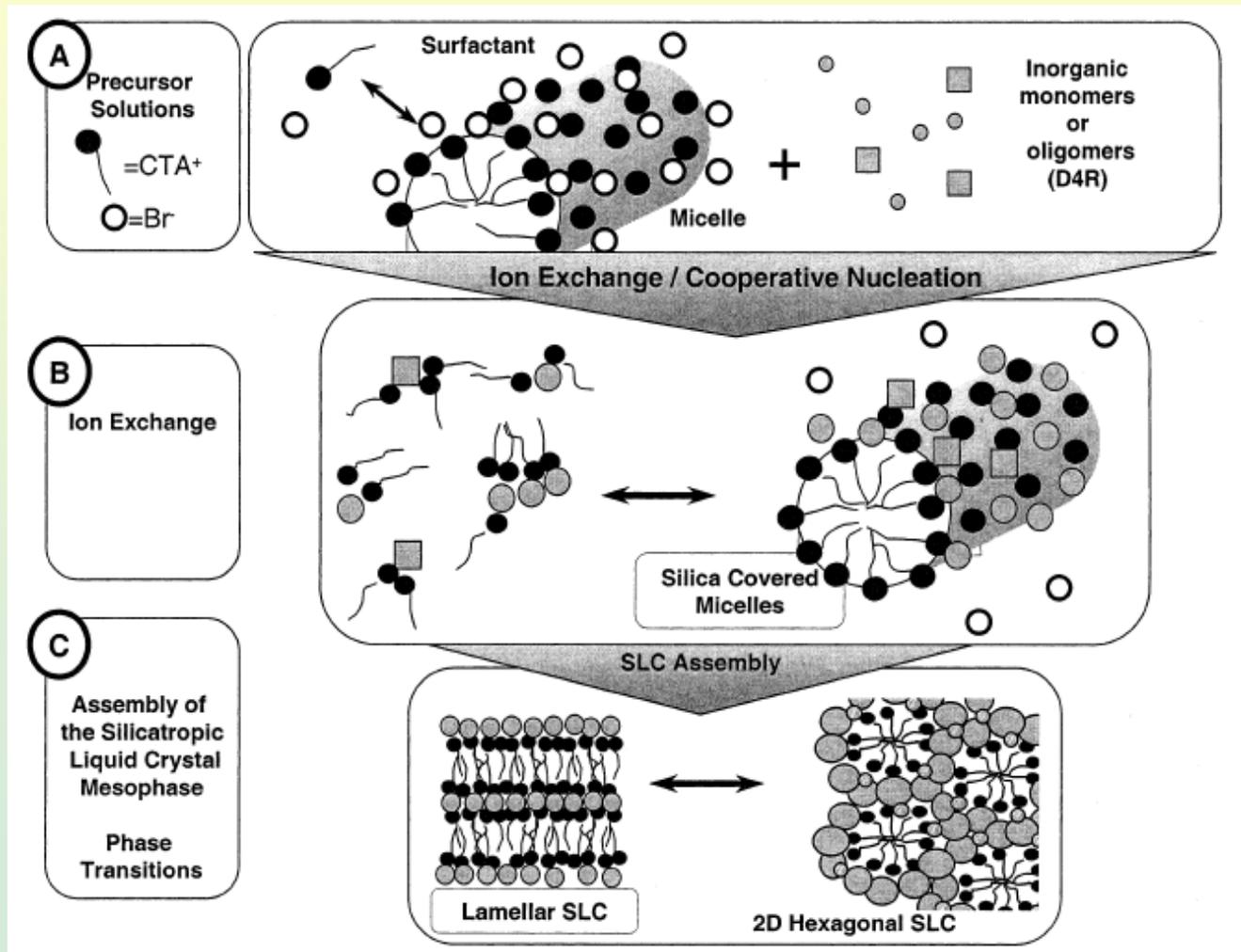
Lamellar to Hexagonal Transformation
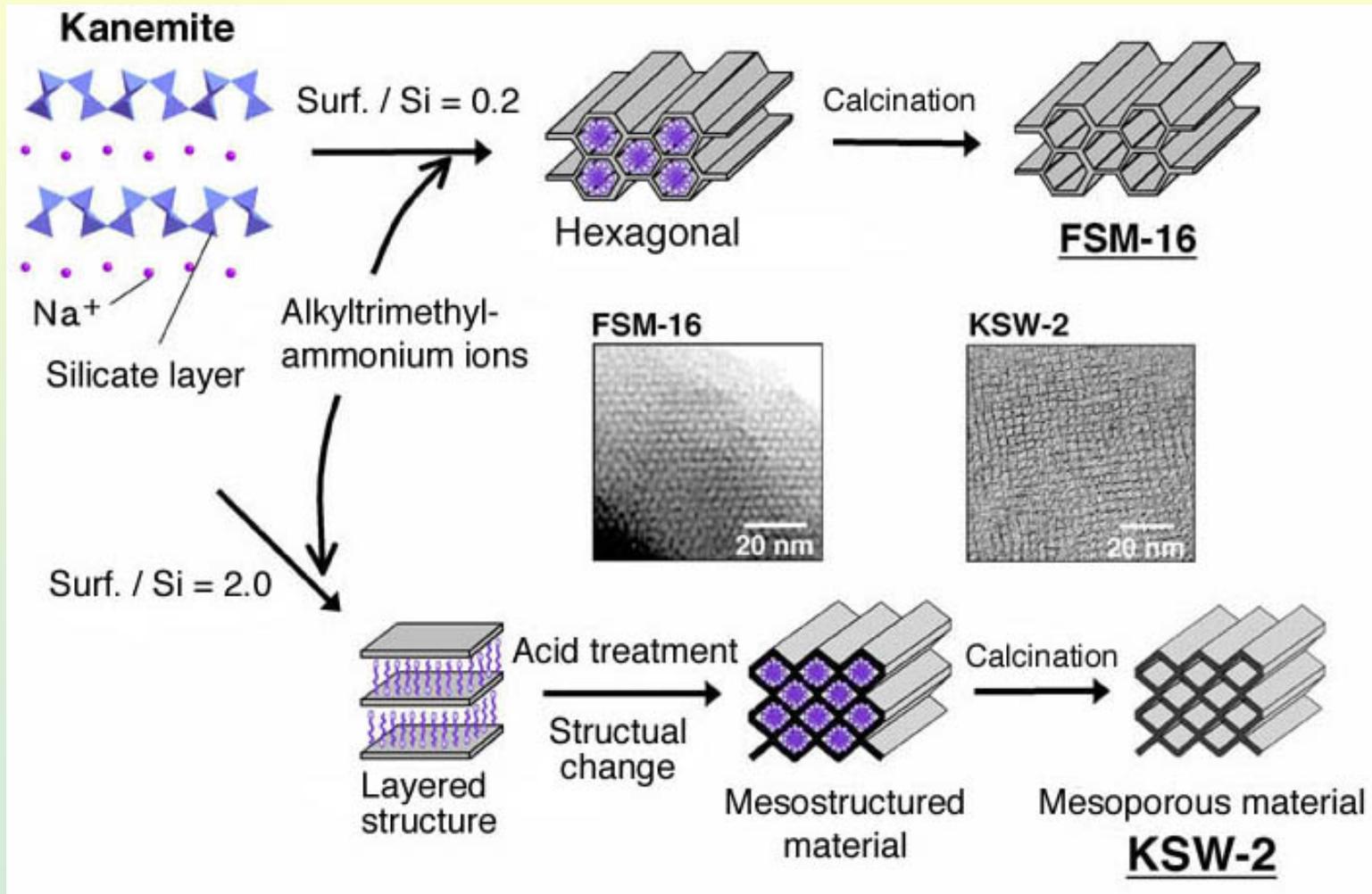
Charge Density Matching

SiO$_2$
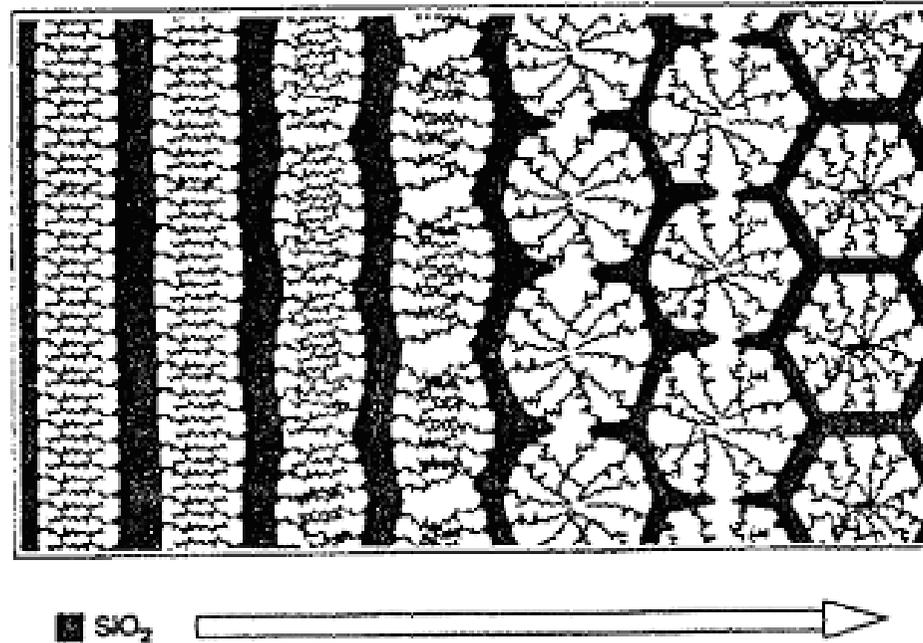
As condensation proceeds the charge on the silicate layer decreases

Si–O$^-$ → Si–O–Si

Zero Charge

Positive Charge

Negative Charge

Silica Dissolves

Silica condensation rate

pH

$X^-_{(aq)}$ +

Si-O$^-$ ⊕

Si-O$^-$ ⊕

Si-O$^-$ ⊕

pH < 2

pH >9

Si-OH··X^- ⊕

Si-OH··X^- ⊕

Si-OH··X^- ⊕

Strong electrostatic interaction

Weak hydrogen-bonding Interaction

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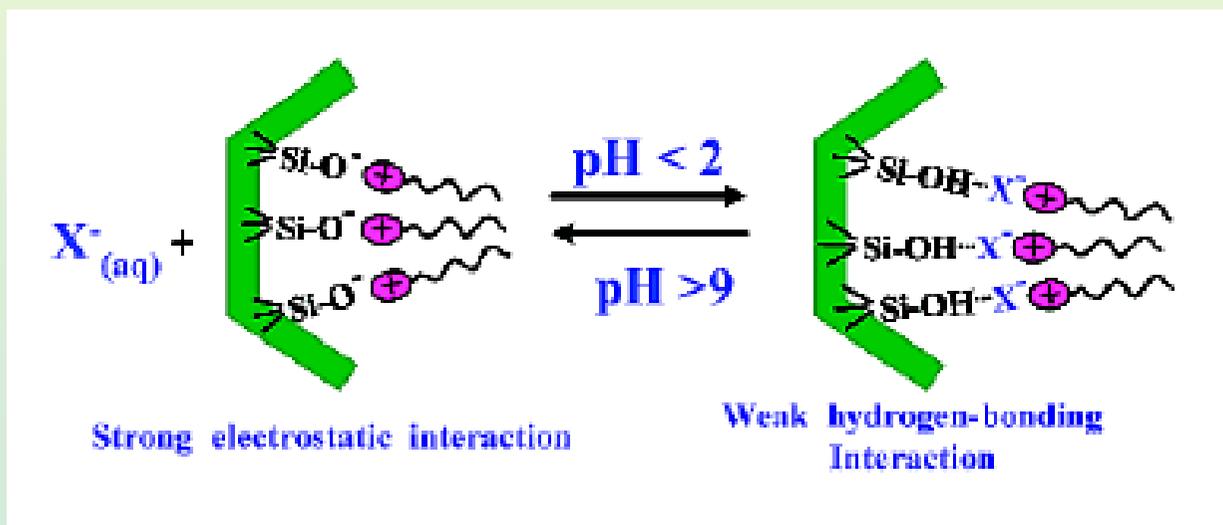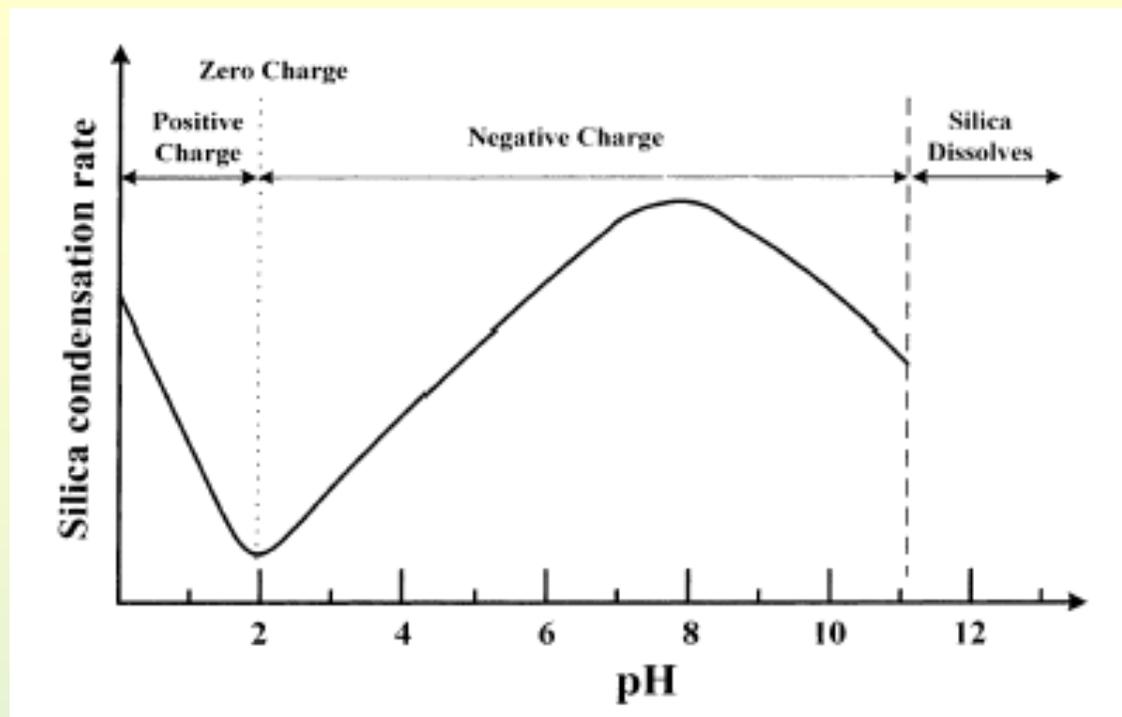
- **Electrostatic interactions**

a) S^+I^-

I = silicate

S = trimethylammonium

$I^{\ominus} S^{\oplus}$ ⌒⌒⌒⌒⌒⌒⌒

b) S^-I^+

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

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

S = sulfonane

$I^{\oplus} S^{\ominus}$ ⌒⌒⌒⌒⌒⌒

c) $S^+X^-I^+$

I = silicate – polyelectrolyte

positive charge

X = Cl

S = trimethylammonium

$I^{\oplus} X^{\ominus} S^{\oplus}$ ⌒⌒⌒⌒⌒⌒⌒

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

I = aluminate

M = Na

S = phophate

$I^{\ominus} M^{\oplus} S^{\ominus}$ ⌒⌒⌒⌒⌒⌒
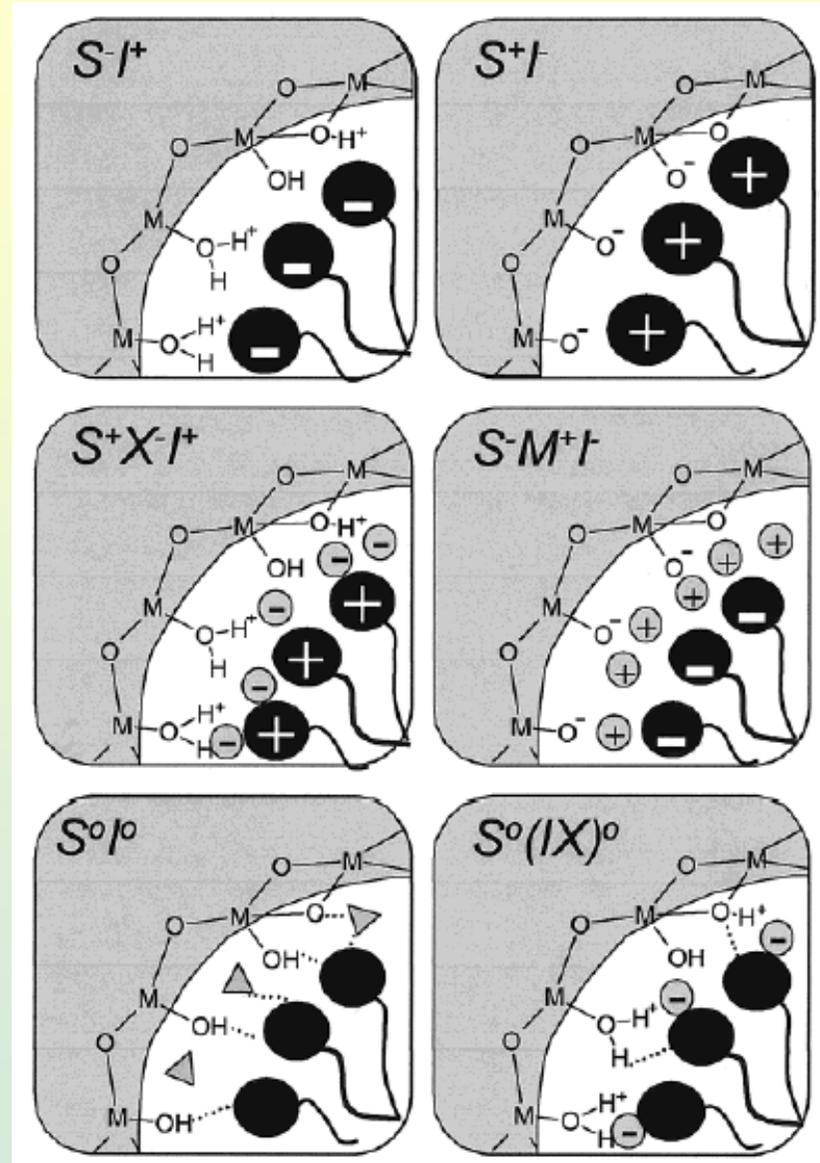
- **Hydrogen Bond**

  a) **S^0I^0**
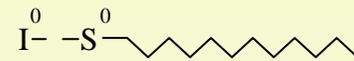
  $I = $ silicate

  $S = $ ammine

  $$I^0 - S^0 \sim\!\!\wedge\!\!\wedge\!\!\wedge\!\!\wedge\!\!\wedge\!\!\wedge$$

  b) **N^0I^0**

  $I = $ silicate

  $N = $ polyethylenoxide

  $$I^0 - N^0 \sim\!\!\wedge\!\!\wedge\!\!\wedge\!\!\wedge\!\!\wedge\!\!\wedge$$

- **Covalent Bond**

  a) **S-I**

  $I = $ niobate, tantalate

  $S = $ ammine

  $$I - S \sim\!\!\wedge\!\!\wedge\!\!\wedge\!\!\wedge\!\!\wedge$$

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Control of Pore Size

MCM-41

20Å 60Å
40Å 100Å

10nm
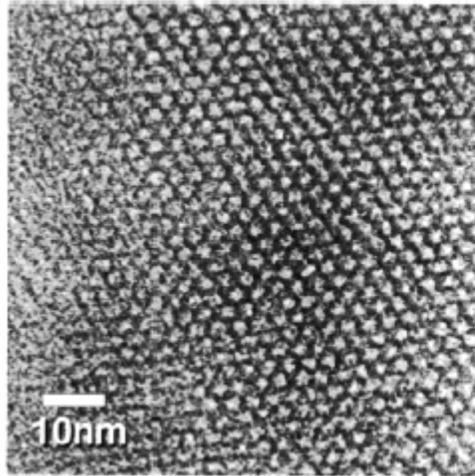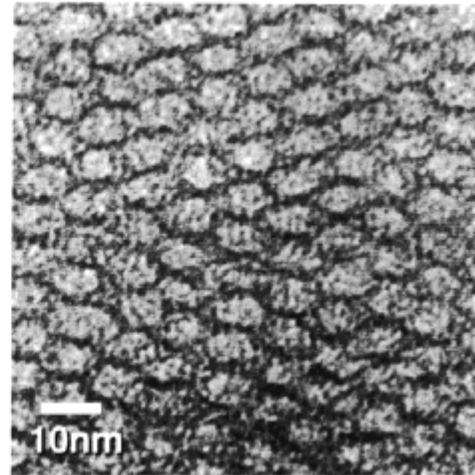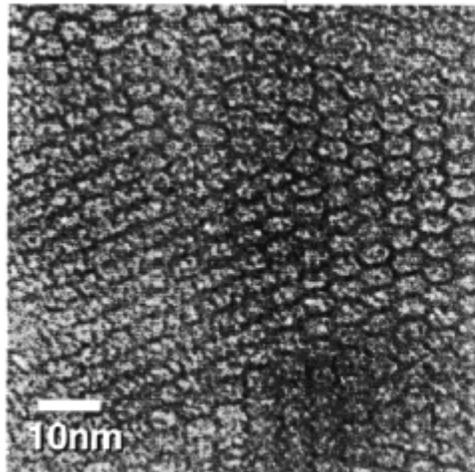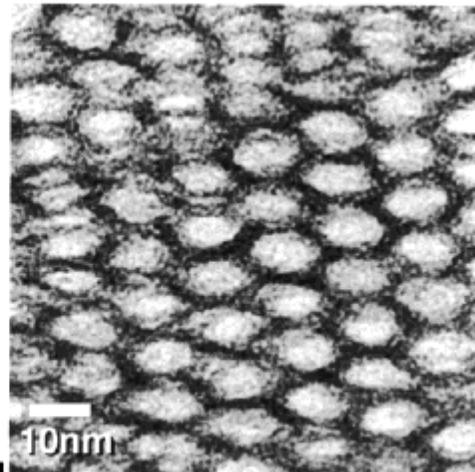
Prepared with Mesitylene Addition

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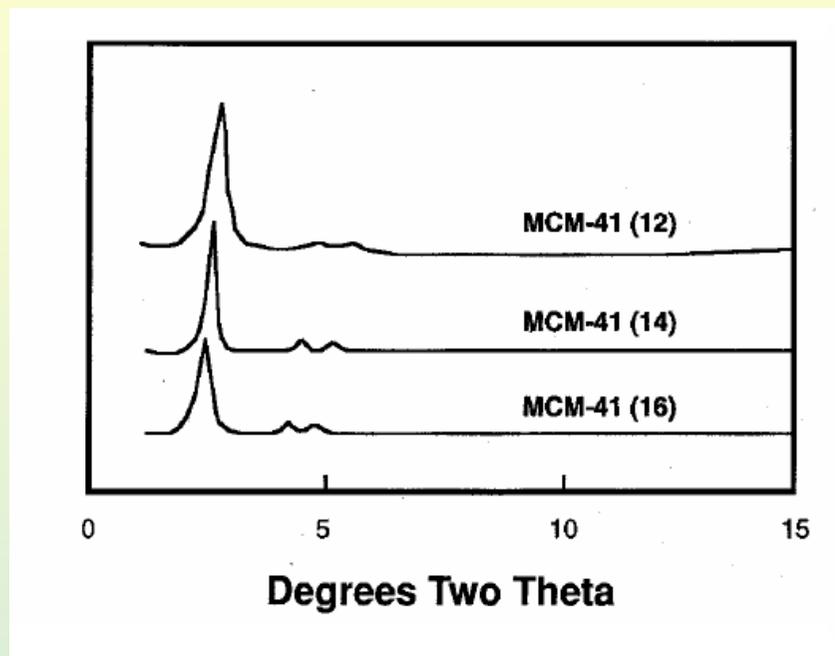
Surfactant chain length n $C_nH_{2n+1}NMe_3$	Lattice constant (Å)	Ar pore size (Å)	Maximum benzene uptake at 50 torr (wt%)
8	31	18	16
9	32	21	37
10	33	22	32
12	33	22	36
14	38	30	54
16	40	37	64

Control of Pore Size
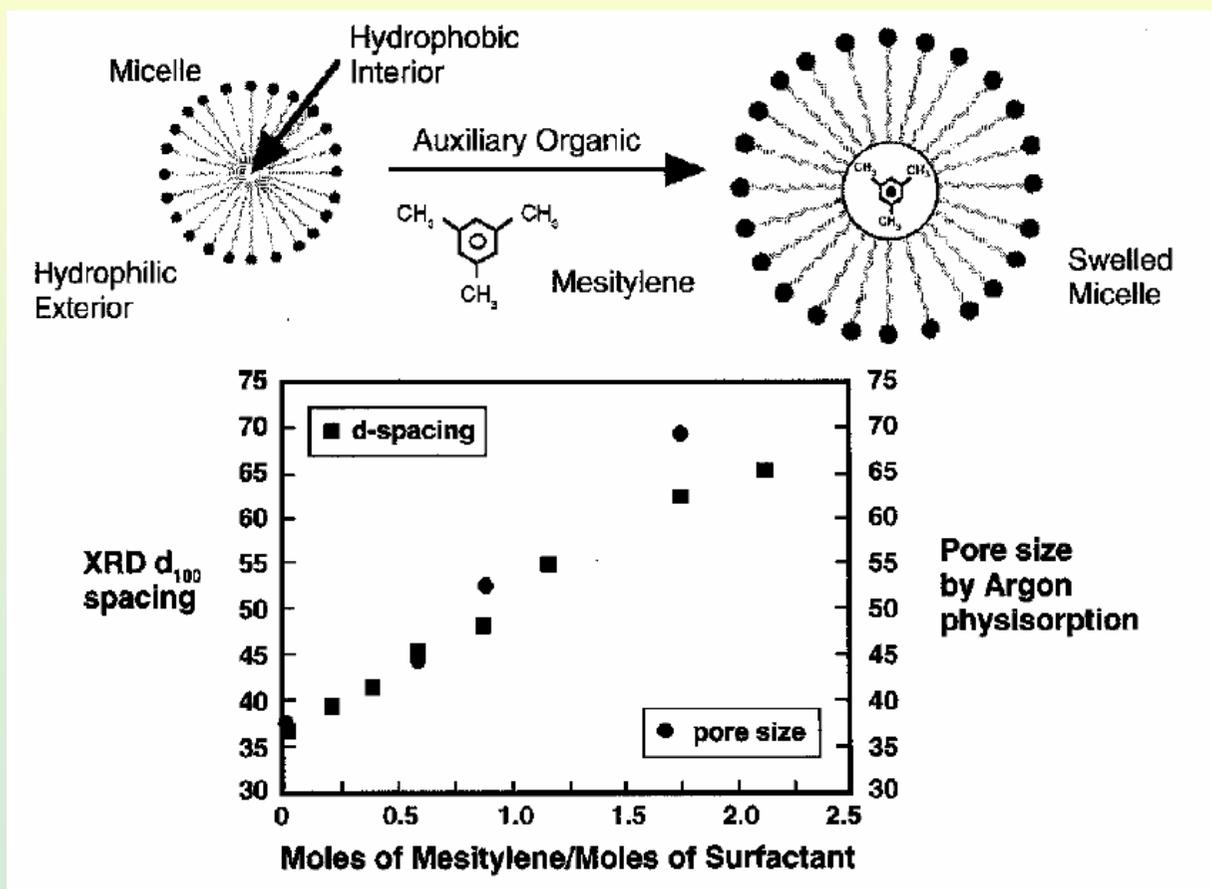
Control of Pore Size

Silylation of hydroxyl groups in MCM-41
by Me$_3$SiCl reduces the effective pore size

EISA

EISA

Thin Films *via* Dip-coating

Nanoparticles *via* Spray-drying

Critical parameters of EISA process:

- Molar ratio Surfactant / Inorganic precursor
- H_2O amount
- Volatile solvent content (Ethanol/THF)
- Temperature
- Relative Humidity

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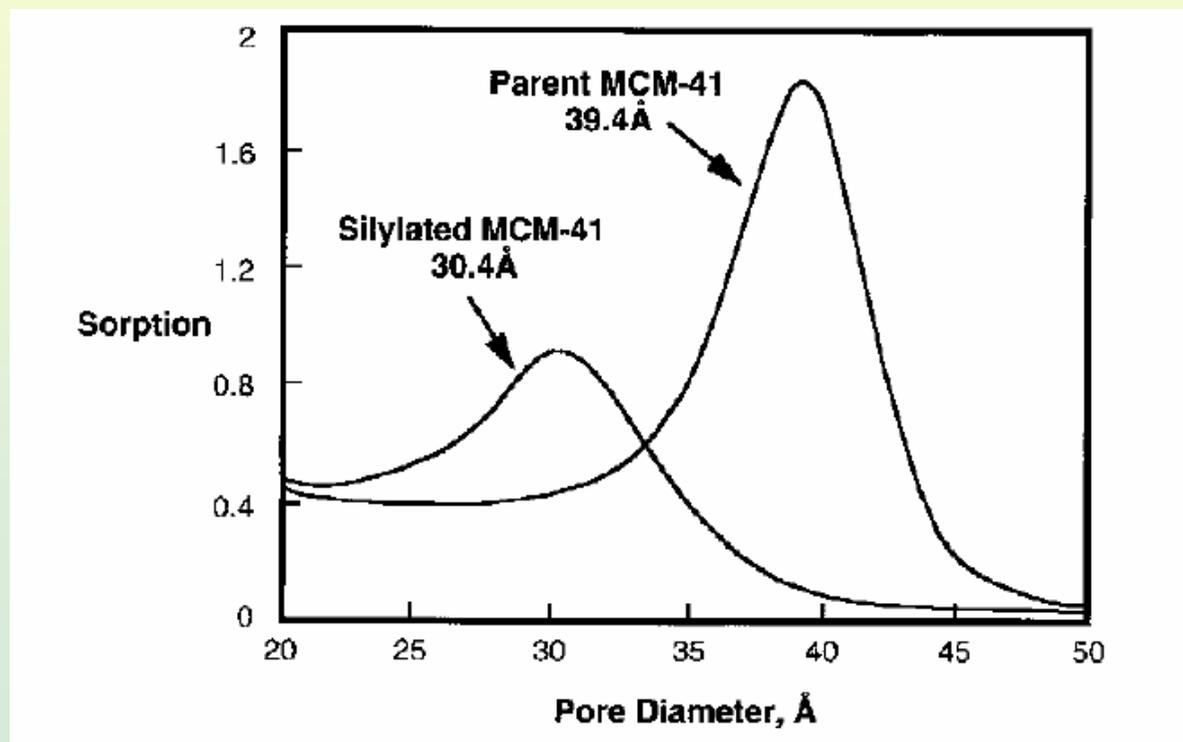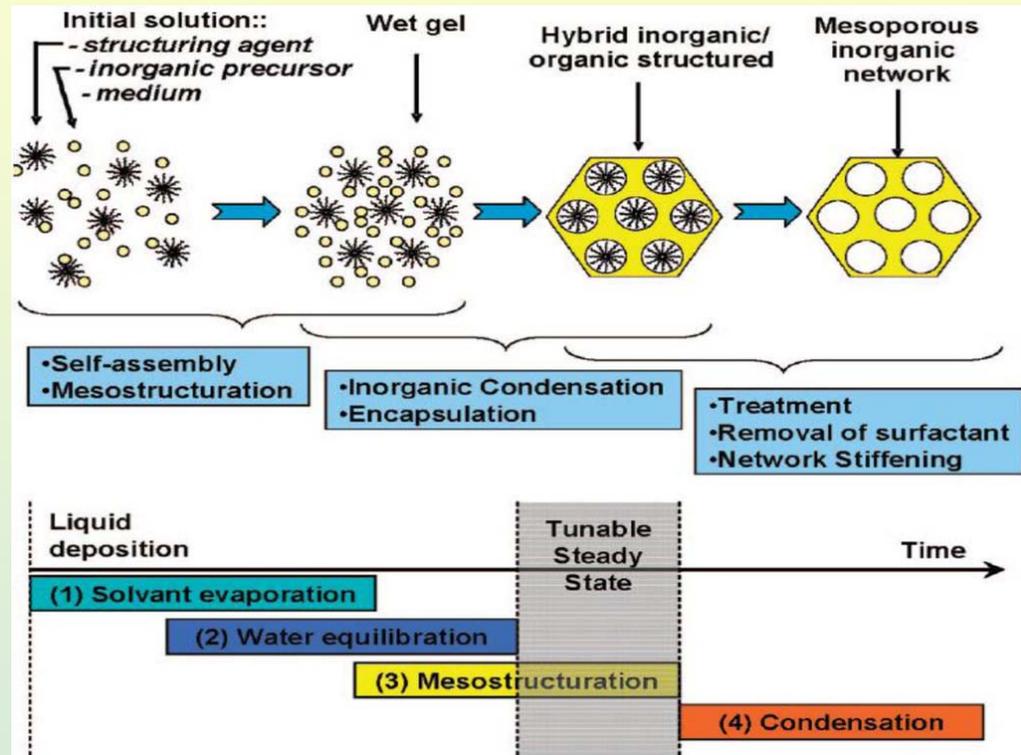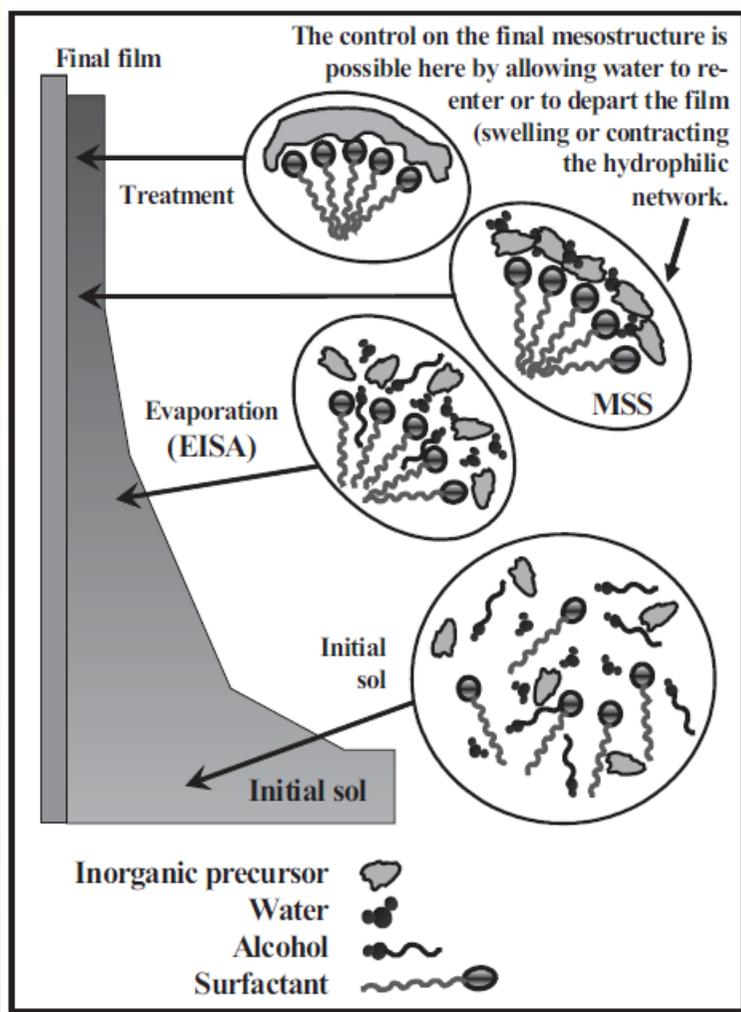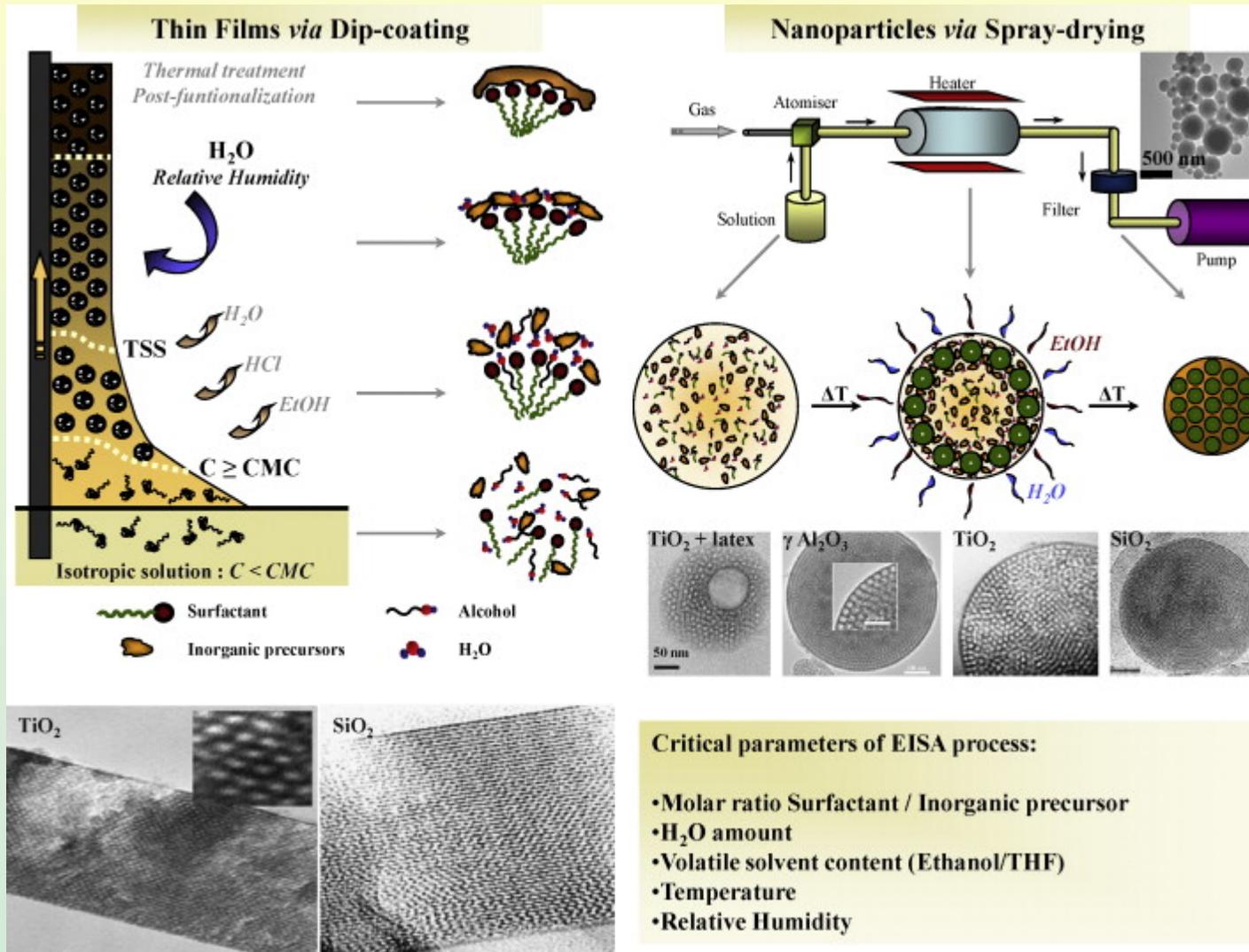
TEM micrograph of hexagonal molecular sieve
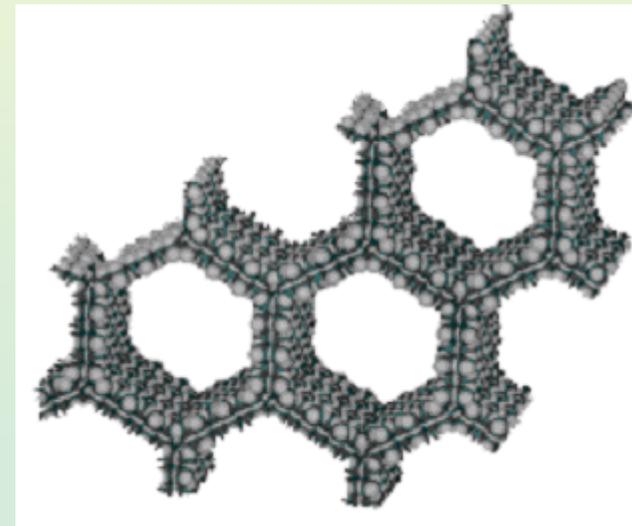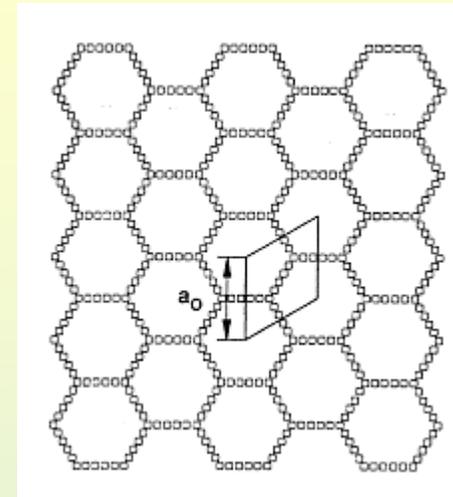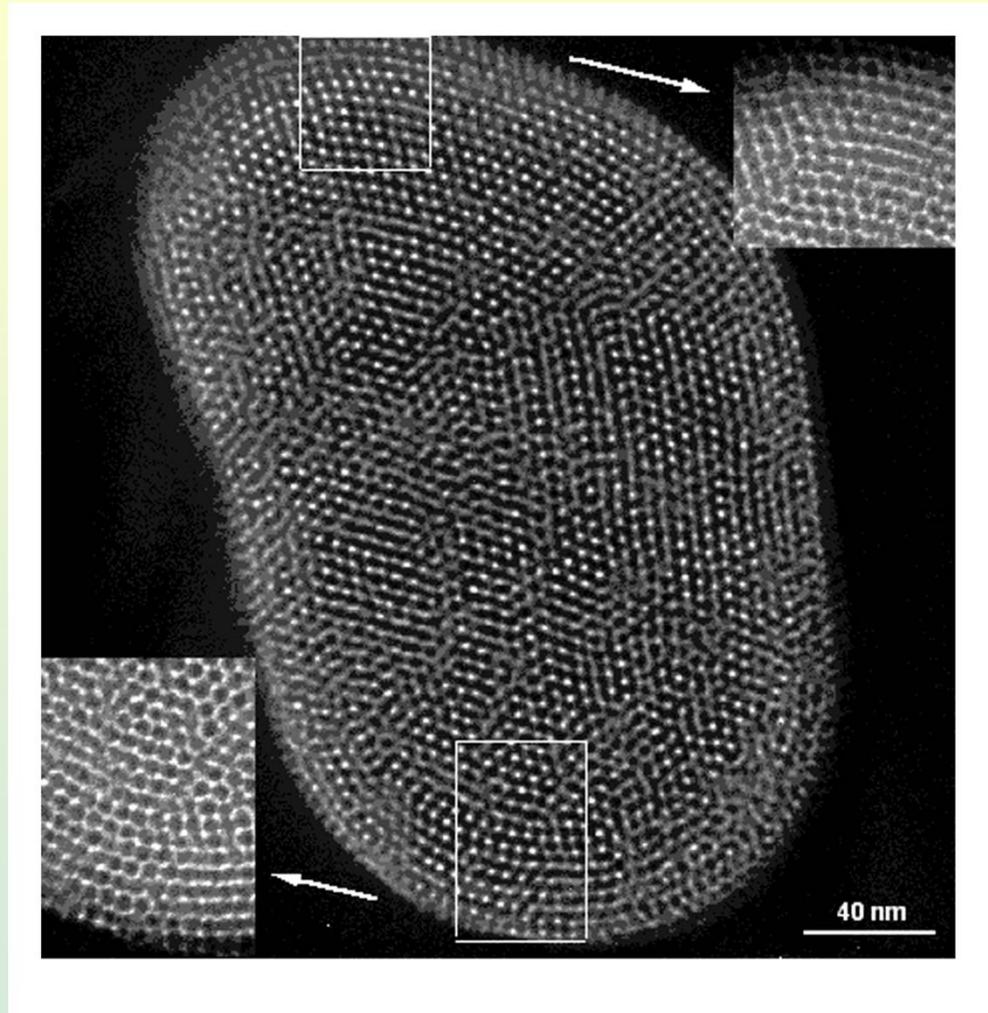
XRD of Lamellar MCM-50
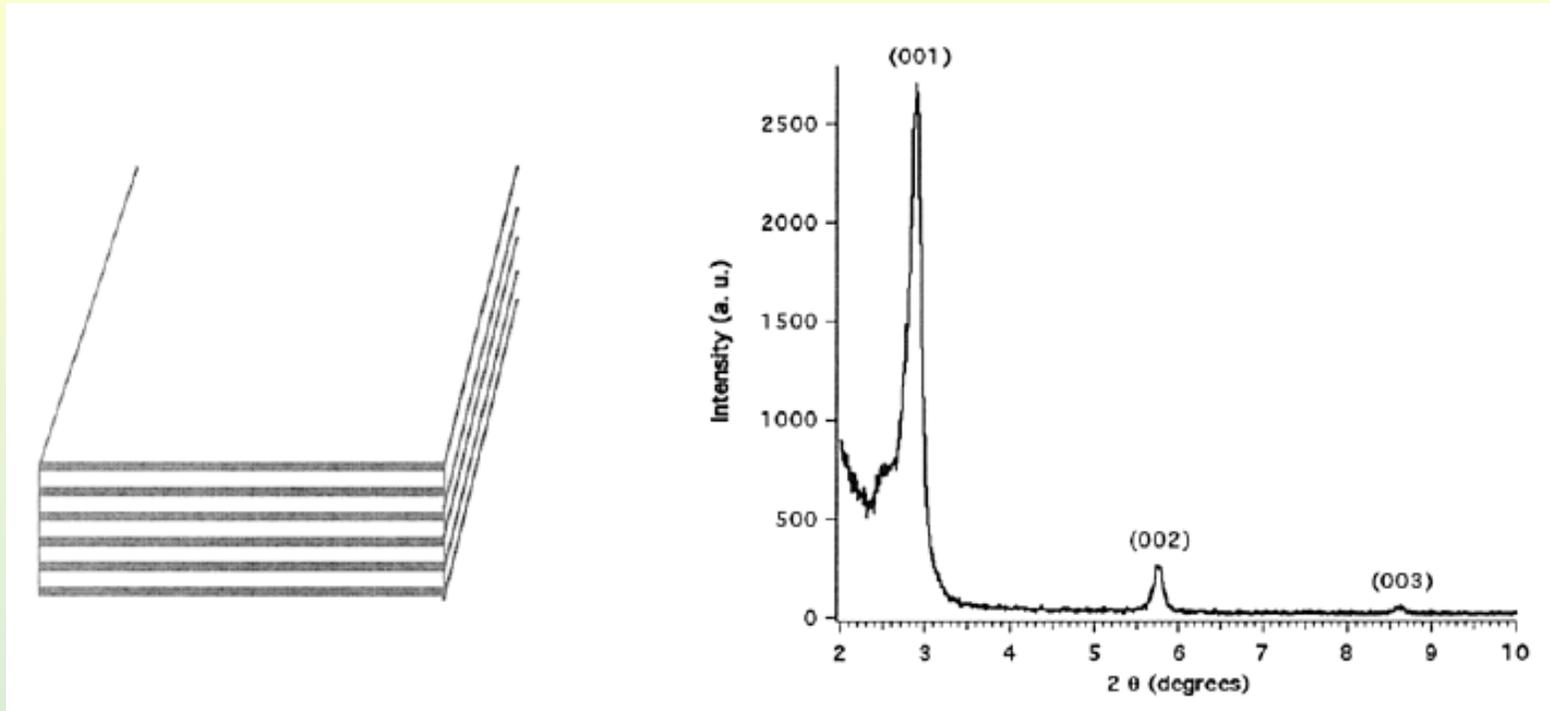
XRD of Hexagonal MCM-41
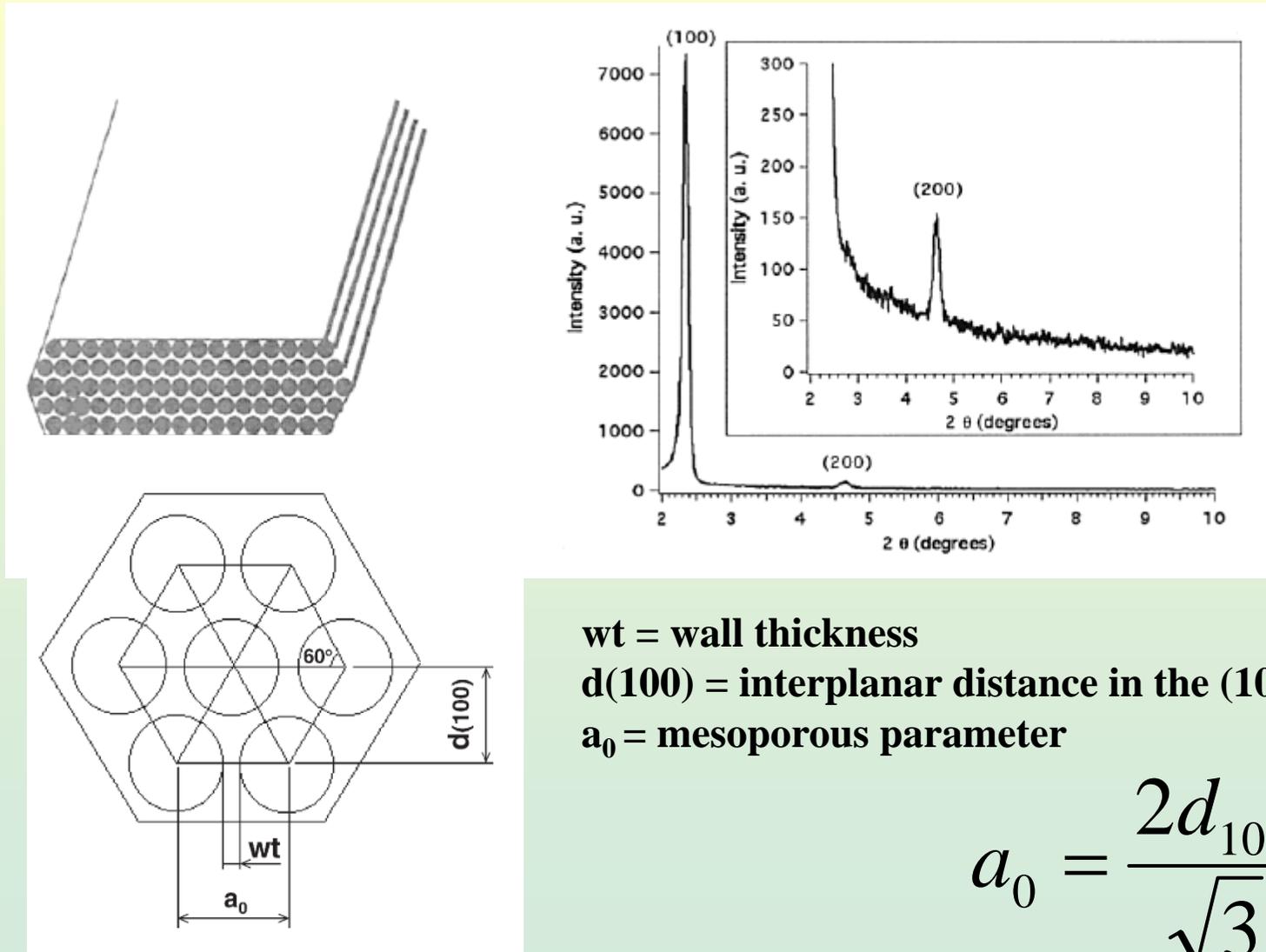
wt = wall thickness

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

a_0 = mesoporous parameter

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

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Gas Adsorption Isotherms

Mesopore filling

BET
Surface area

Micropore filling
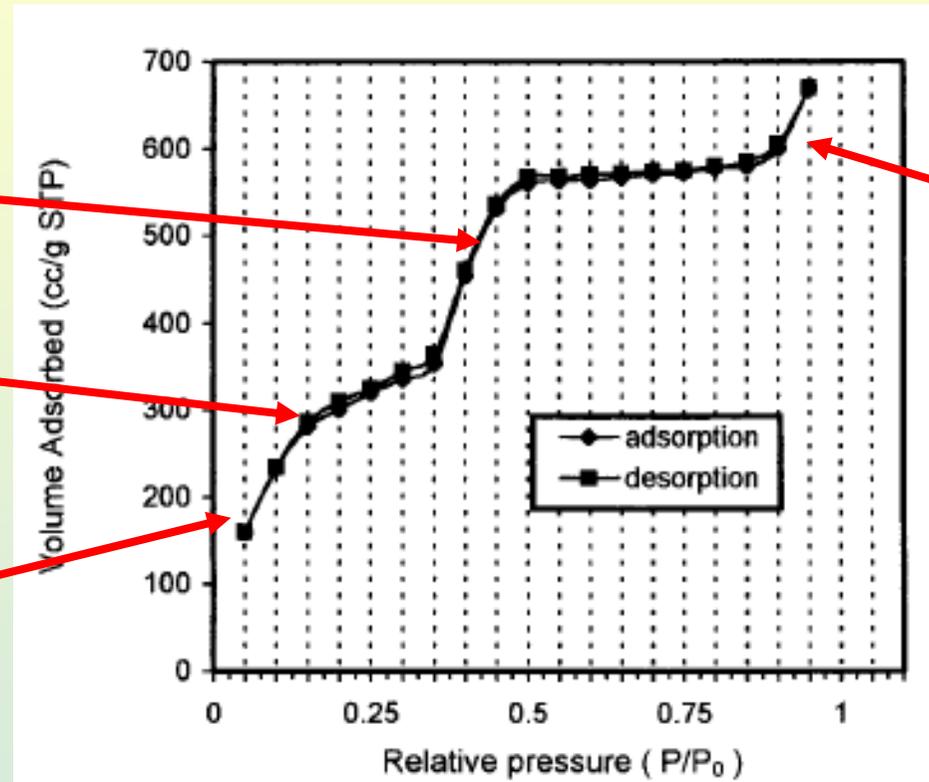
Pores filled
with LN2
Pore volume

34

Template Removal
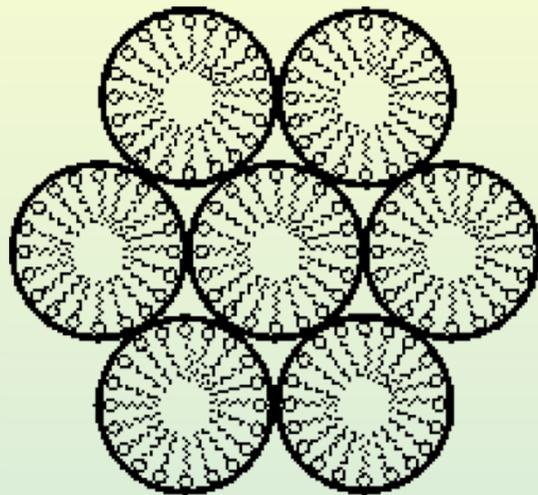
Calcination
$-H_2O$, $-CO_2$, $-NO_x$

Extraction
$-$ template

O_3 treatment
$-H_2O$, $-CO_2$, $-NO_x$
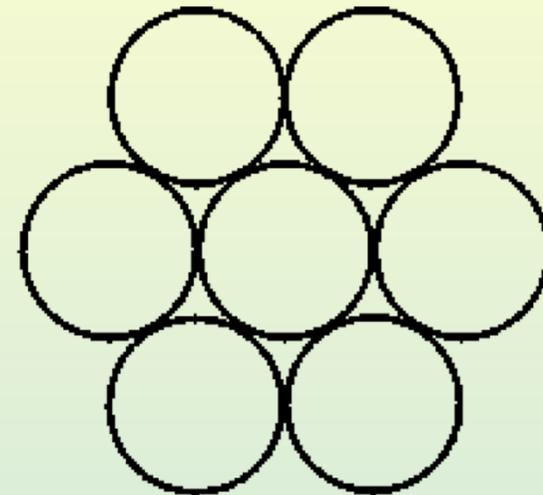
Mesoporous Platinum Metal

$H_2[PtCl_6]$ 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 A and a pore wall thickness of 30 A.
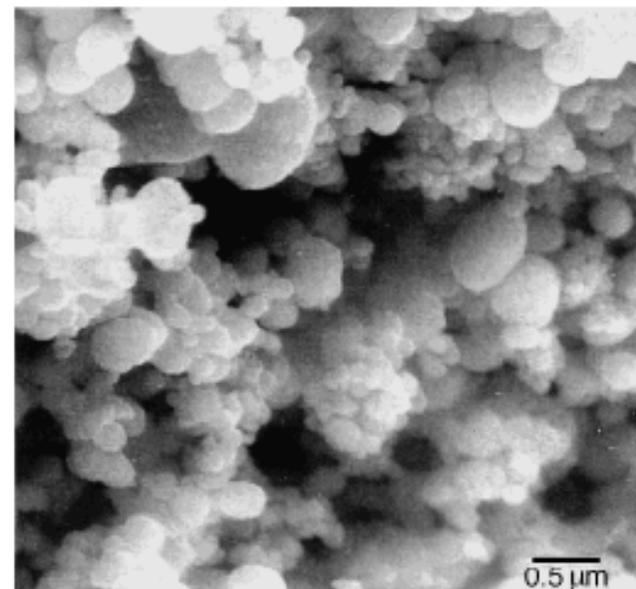
Surface Silanols in MCM-41 Pores
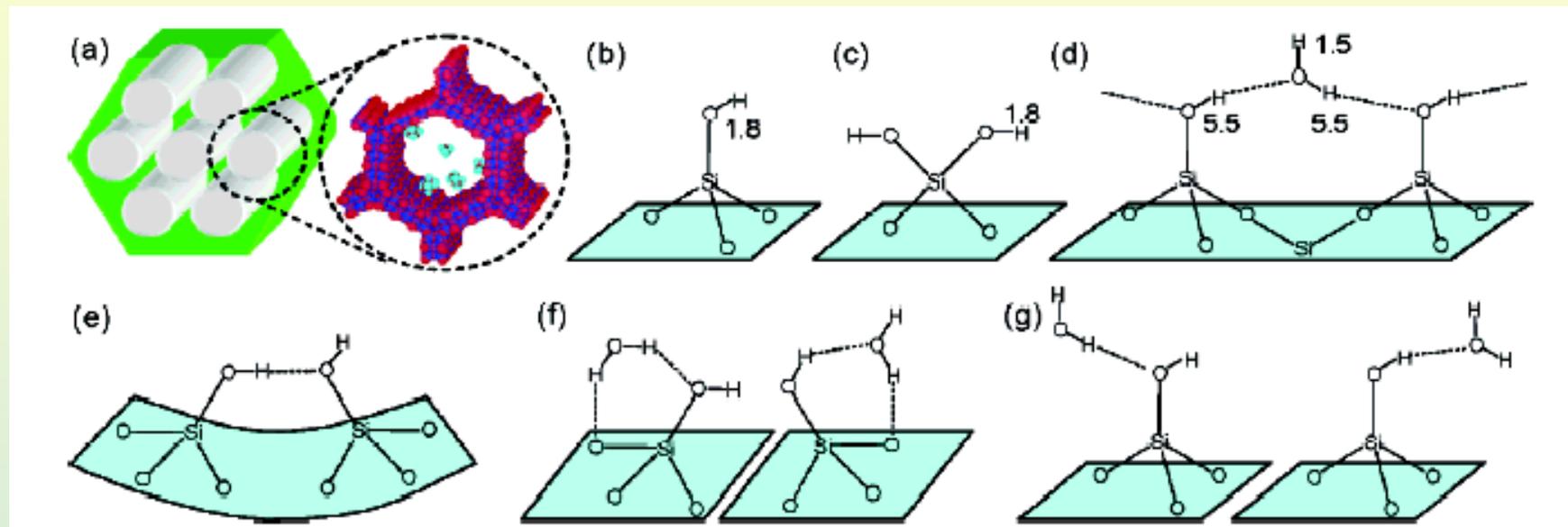
Chemistry inside the Pores

bis(benzene)chromium

toluene

potassium fulleride

sodium

nickelocene

cobaltocene

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Hard Tempalting

Cr$_2$O$_3$ crystalline nanowires
(bar = 25 nm for A, 10 nm for A1)
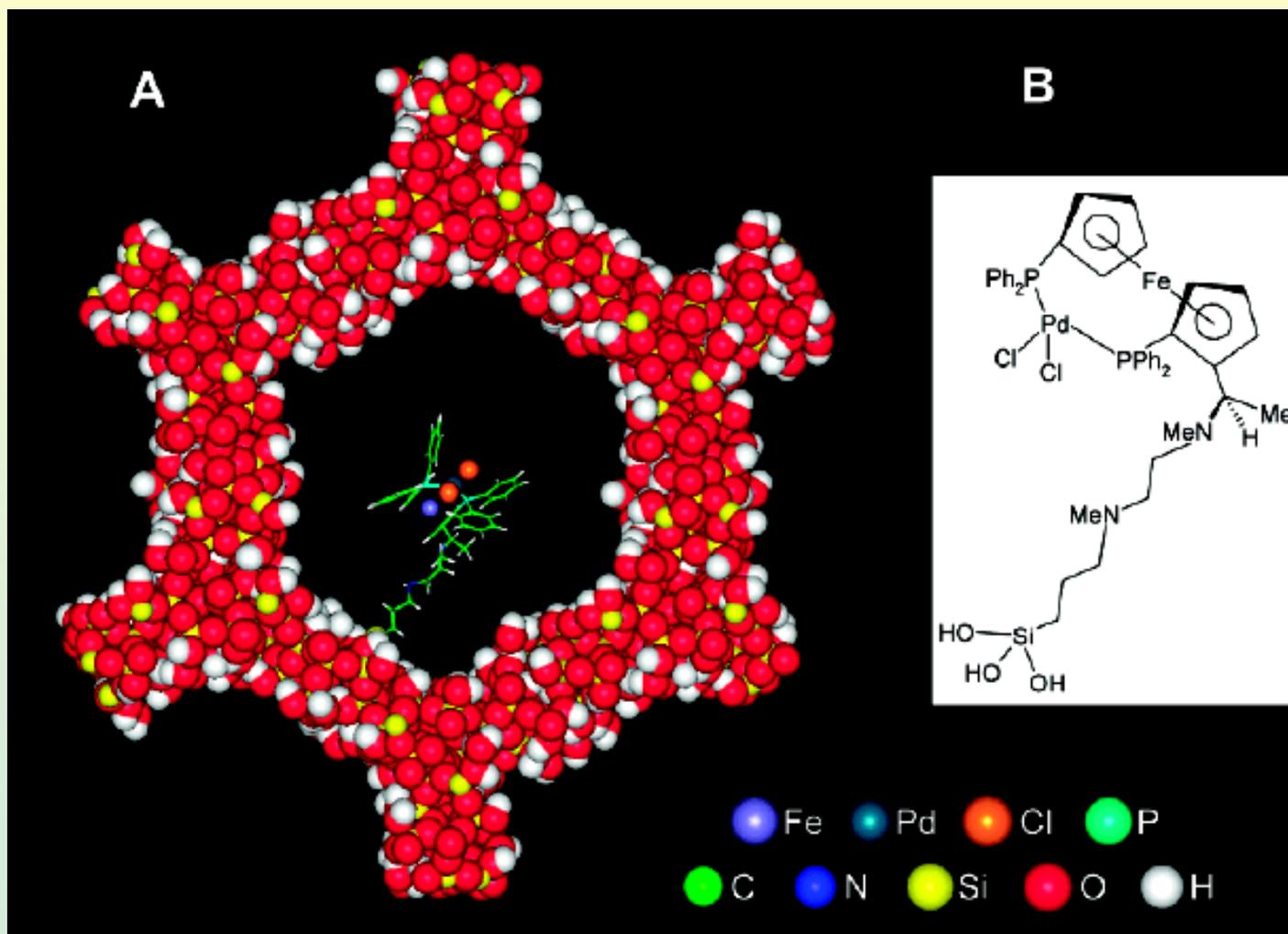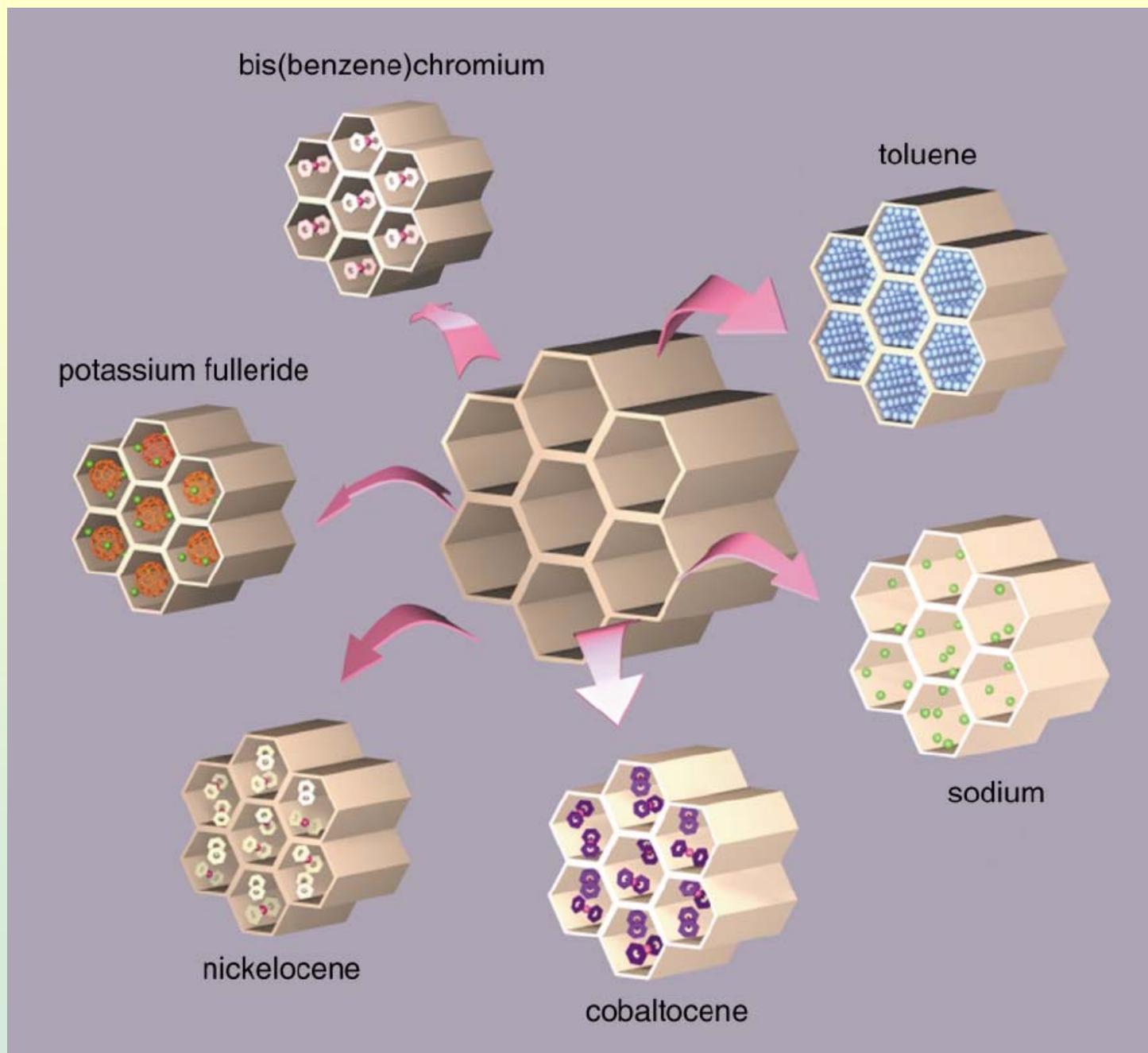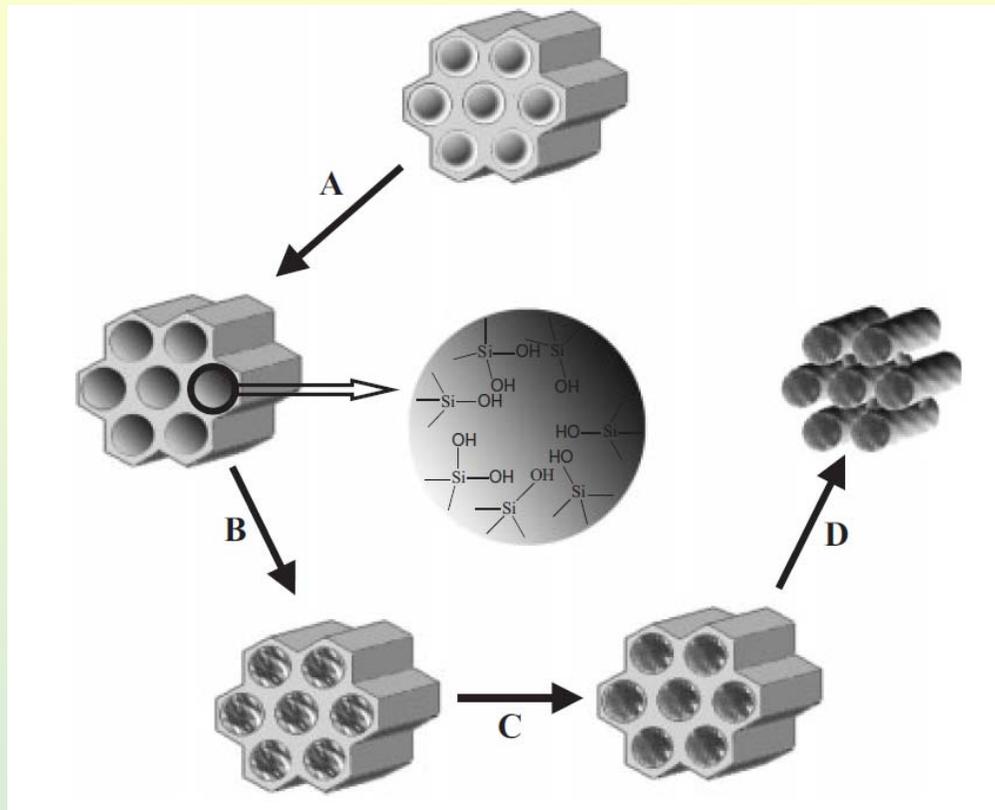
A = microwave digestion - template removal
B = introduction of metal salt solution
C = calcination
D = dissolution of SiO$_2$ in HF or NaOH

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.

Viscous flow

Bulk diffusion

Knudsen diffusion

Surface diffusion

Capillary condensation

Activated

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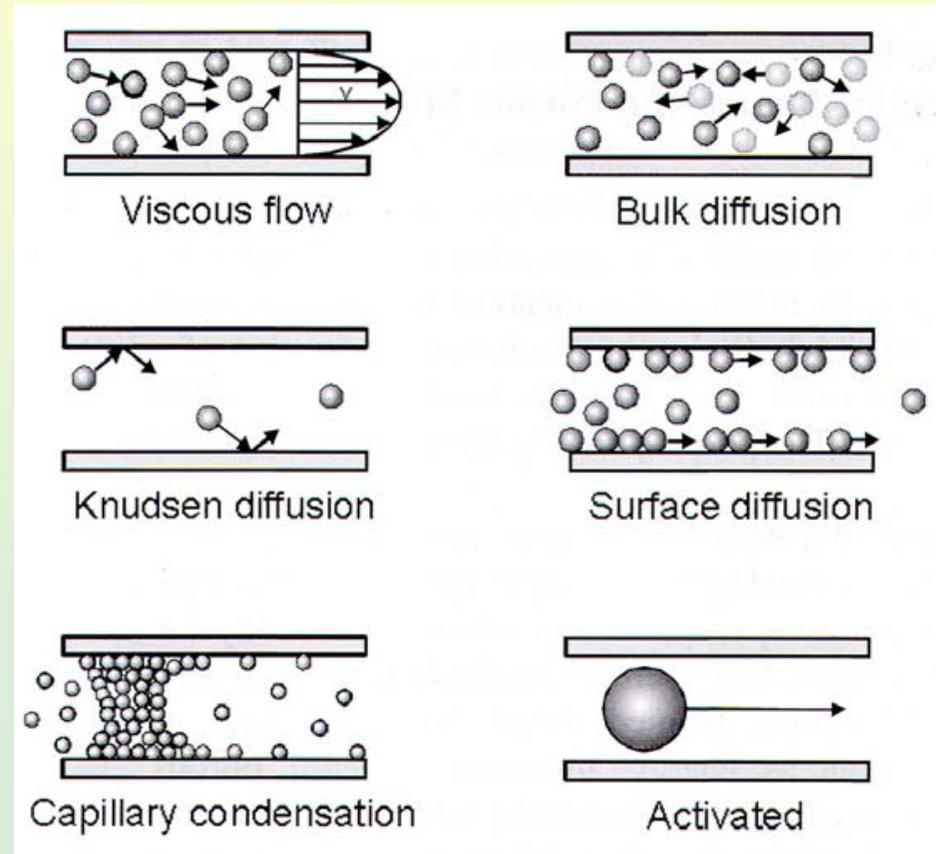
Hierarchically Porous Monoliths
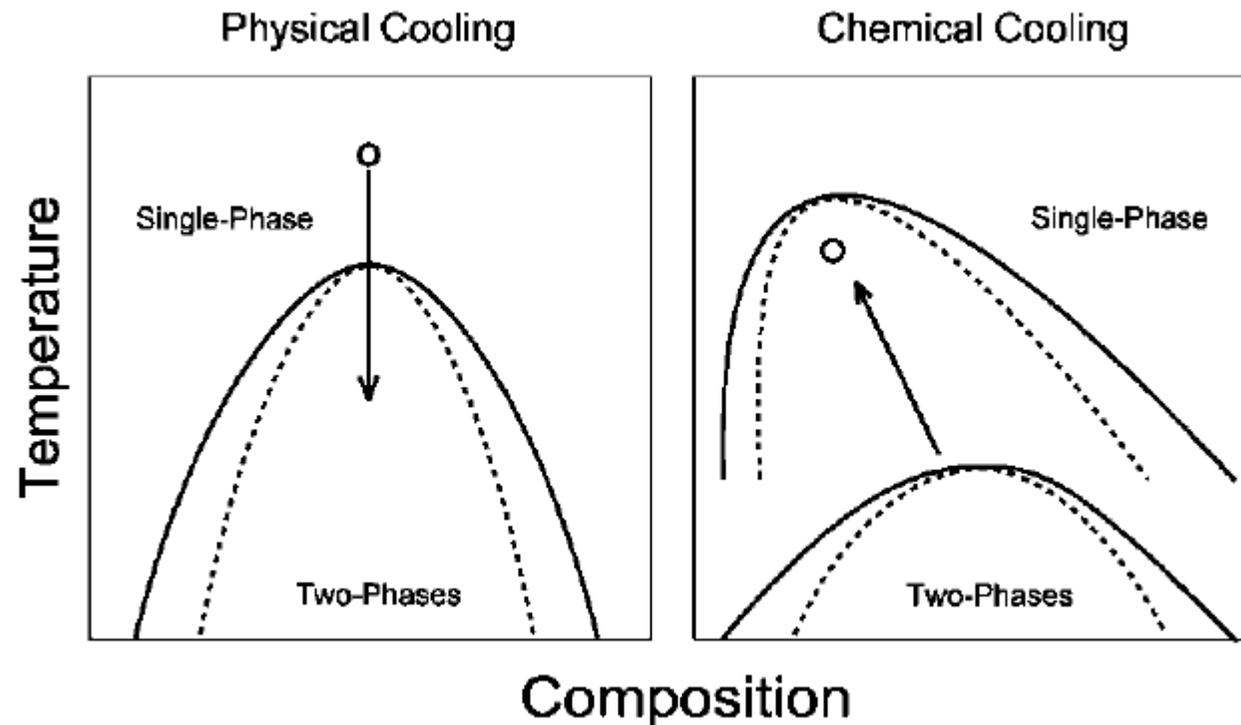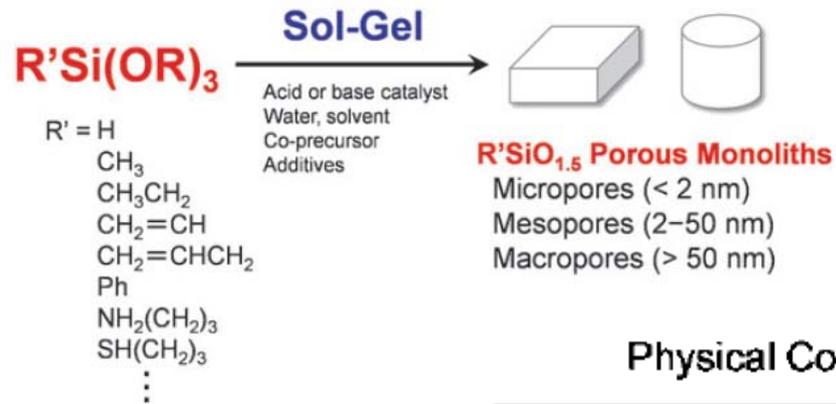
Spinodal Decomposition

Hierarchically Porous Monoliths


(a)
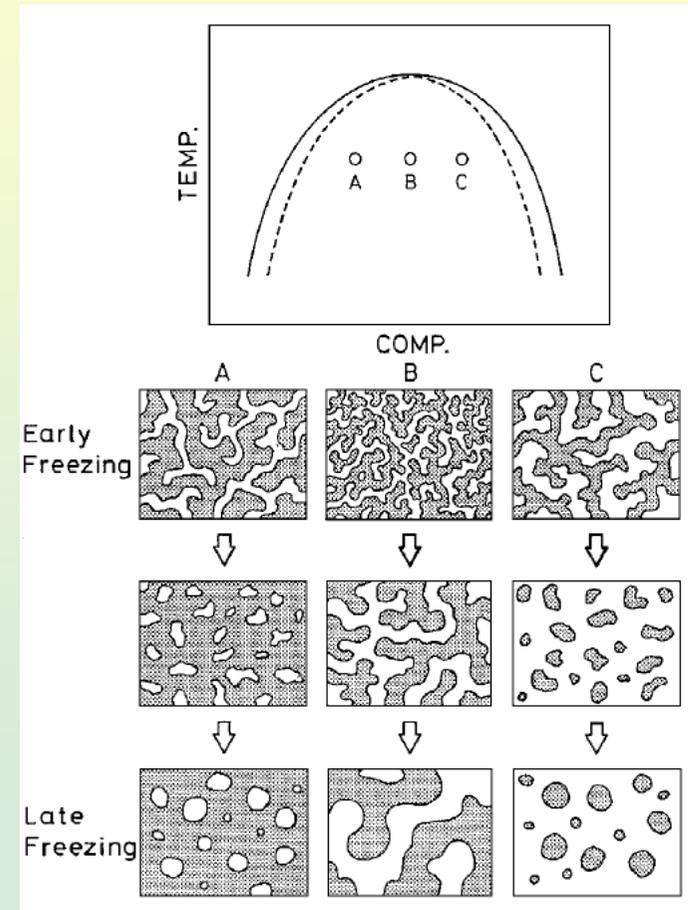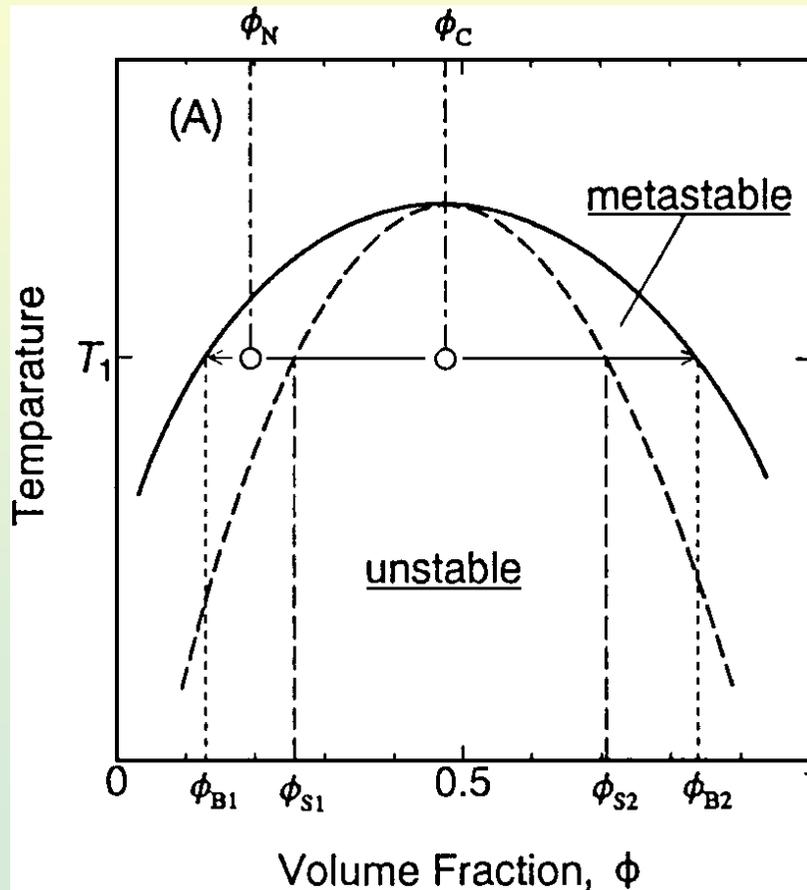
Good Solv.
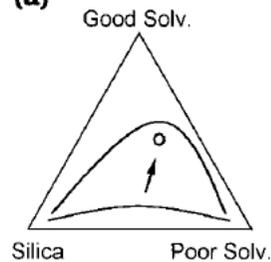
Silica   Poor Solv.

Alkoxide + Water (r < 1.5)
          + Formamide

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

(b)

Solv.
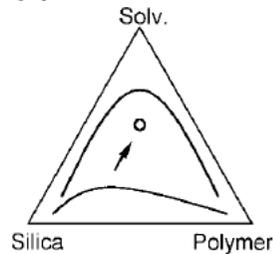
Silica   Polymer

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

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

(c)

Solv.
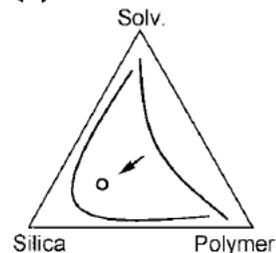
Silica   Polymer

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

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

# Hierarchically Porous Monoliths

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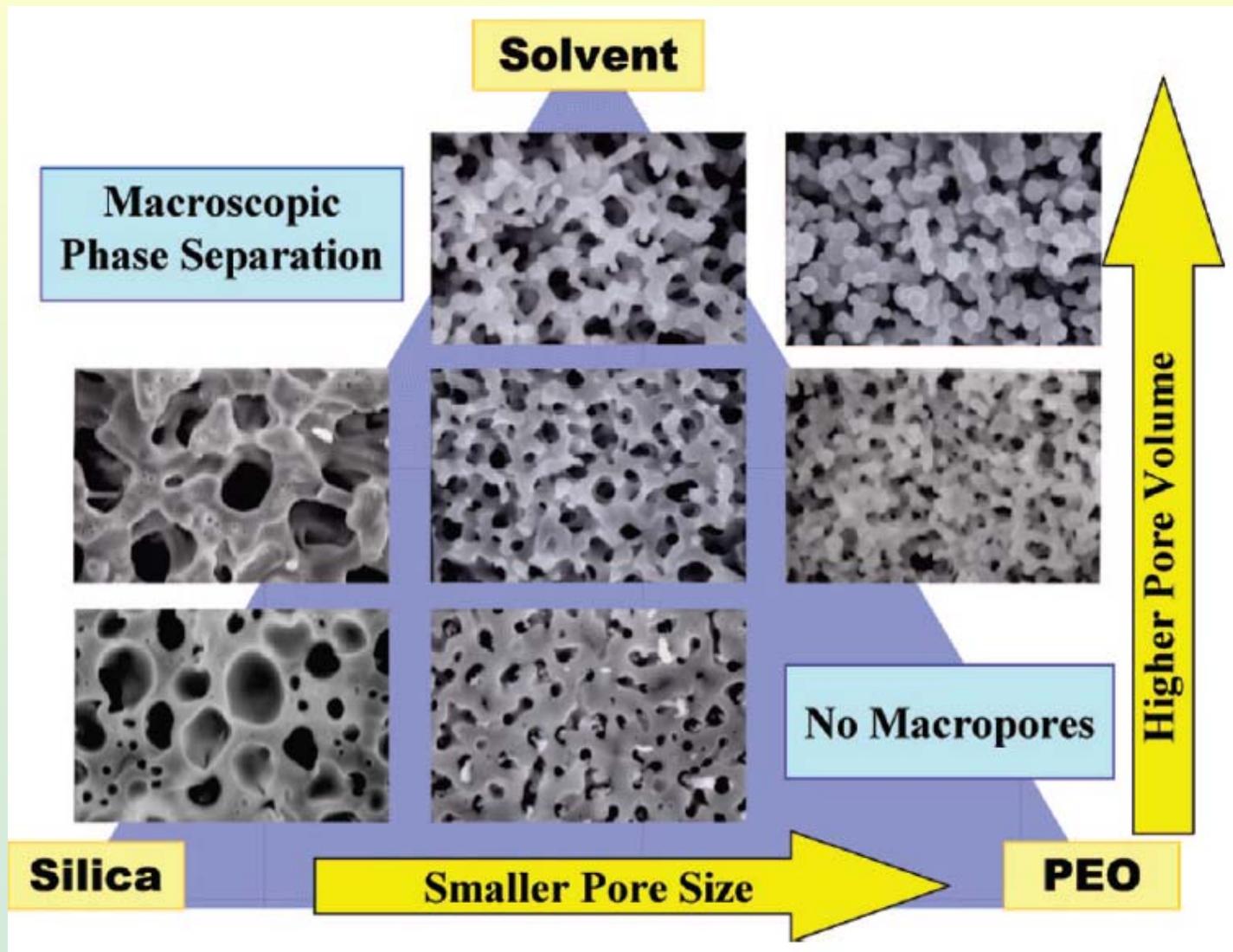
Hierarchically Porous Monoliths

Time evolution of a spinodally decomposing isotropic symmetrical system.

Development of co-continuous structure

Self-similar coarsening 1

Self-similar coarsening 2

Fragmentation of domains

Spheroidization and sedimentation