

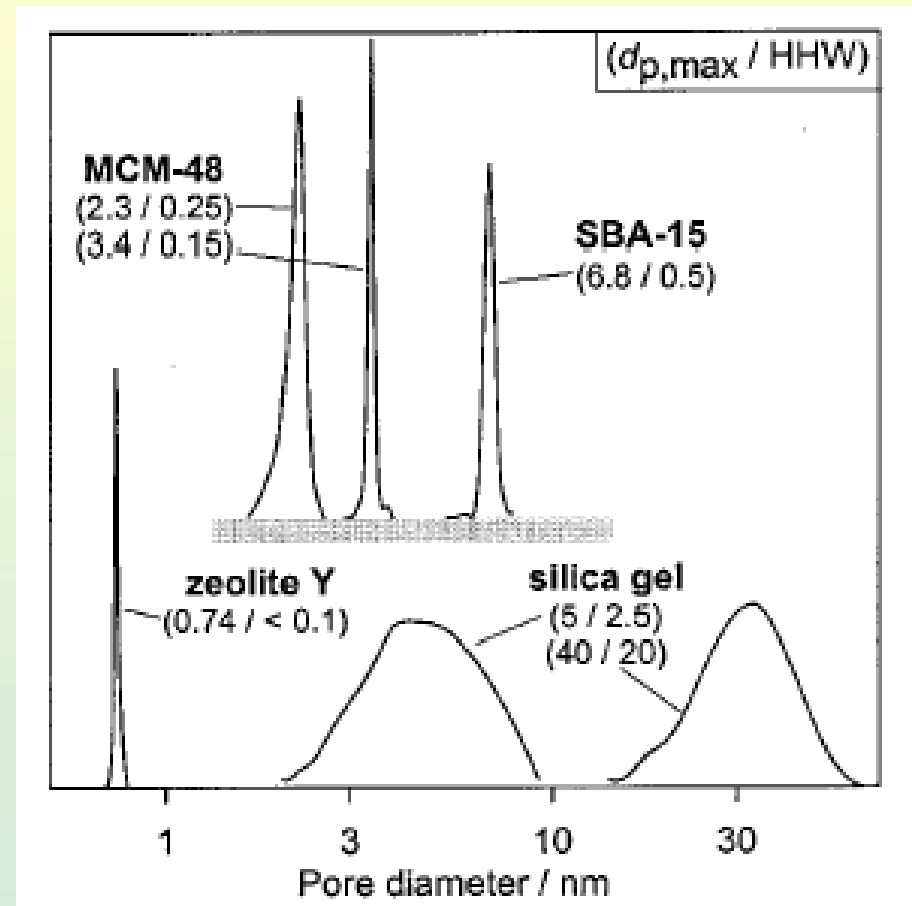
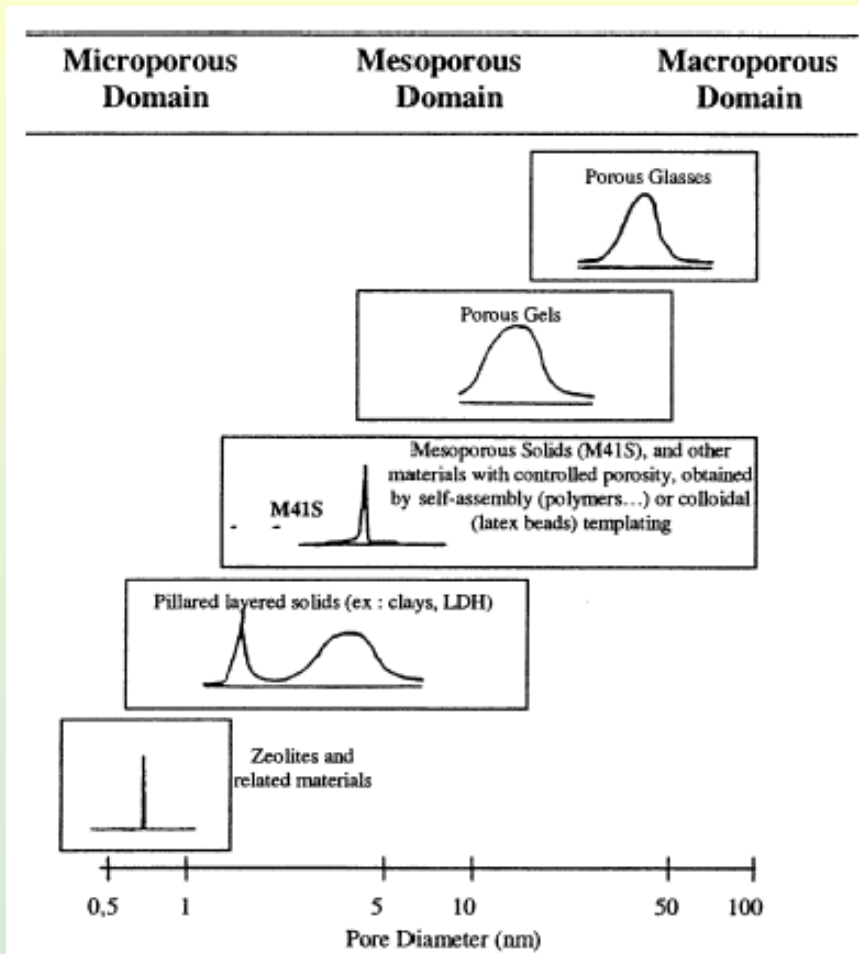
# Mesoporous Materials

Amorphous, disordered - silica xerogels

Ordered, amorphous walls

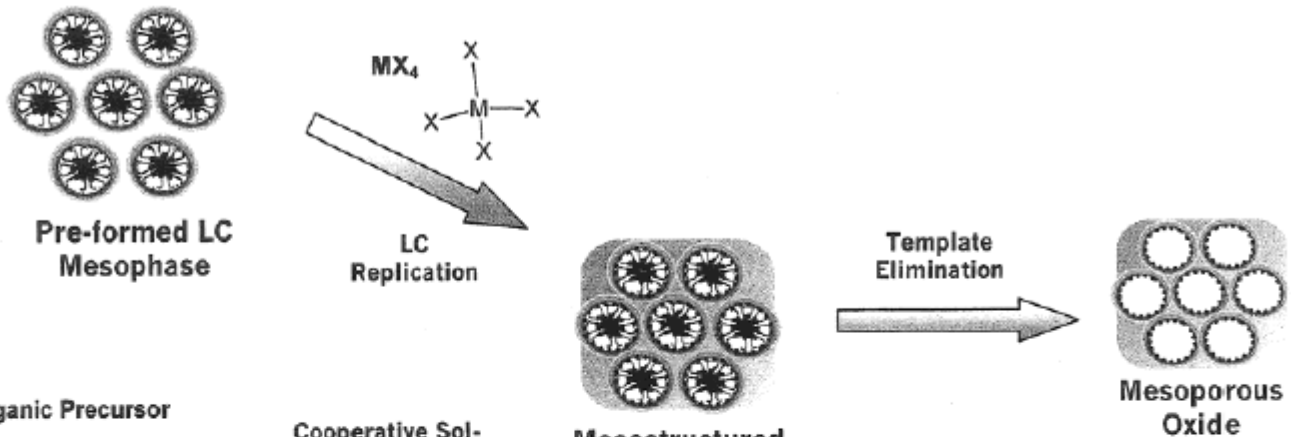
Pore diameter, $d$ [nm]	Material	Example
$d > 50$	Macroporous	Aerogels
$2 < d < 50$	Mesoporous	Xerogels
$d < 2$	Microporous	Zeolites

# Pore size distribution

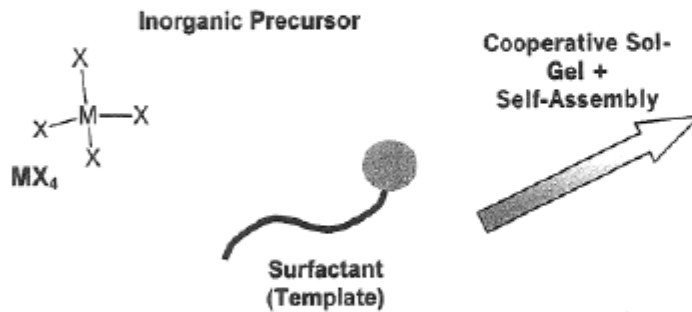


# Mesostructure Assembly

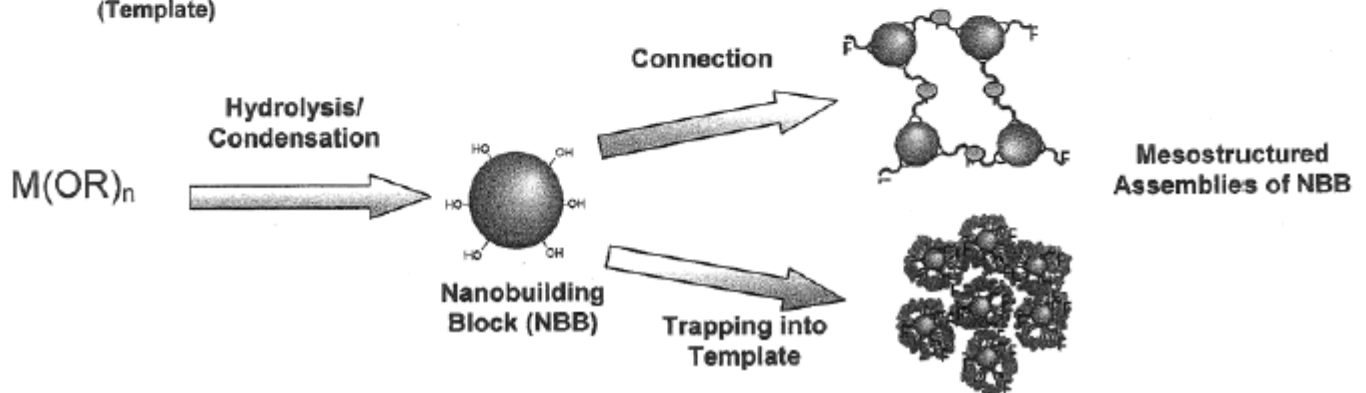
A



B



C



# Mesoporous Materials

**MMS** mesoporous molecular sieves

**MCM-n** Mobil Composition of Matter

**M41S**

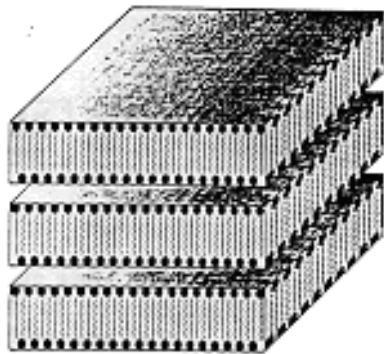
**Discovered 1992**

**A - lamellar MCM-50**

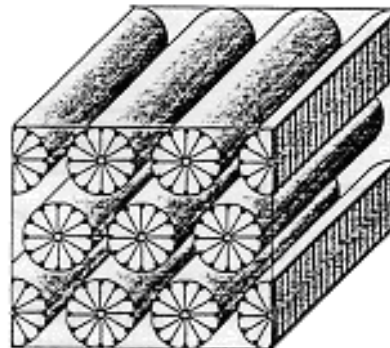
**B - hexagonal MCM-41**

**C - cubic MCM-48**

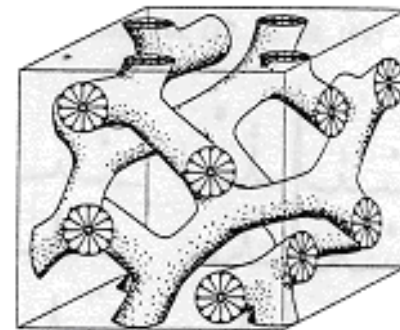
**Inverse hexagonal**



**A**



**B**

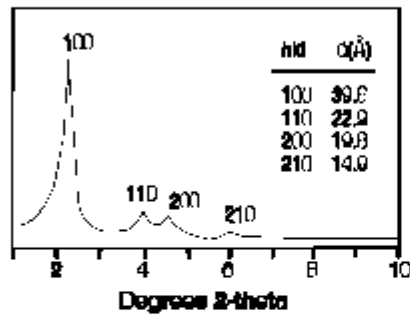


**C**

# Mesoporous Materials

**X-ray  
Diffraction  
Pattern**

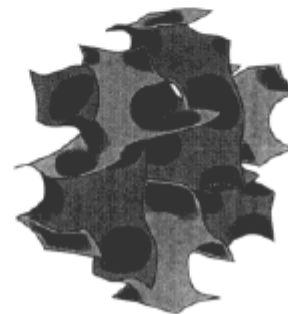
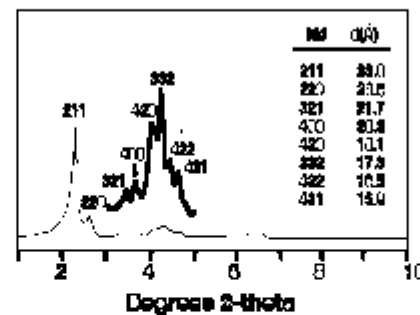
**MCM-41  
(Hexagonal)**



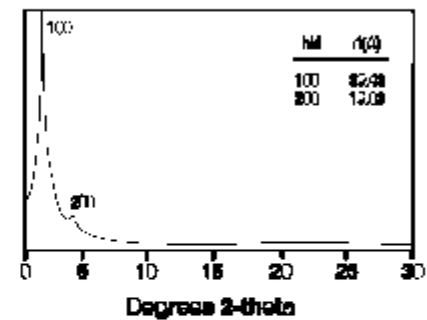
**Possible  
Structures**



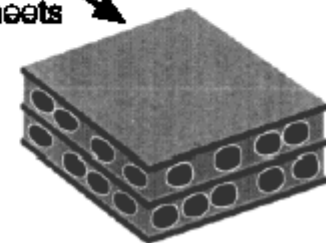
**MCM-48  
(Cubic)**



**MCM-50  
(Stabilized Lamellar)**



**Silica  
Sheets**



# Supramolecular Templating

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

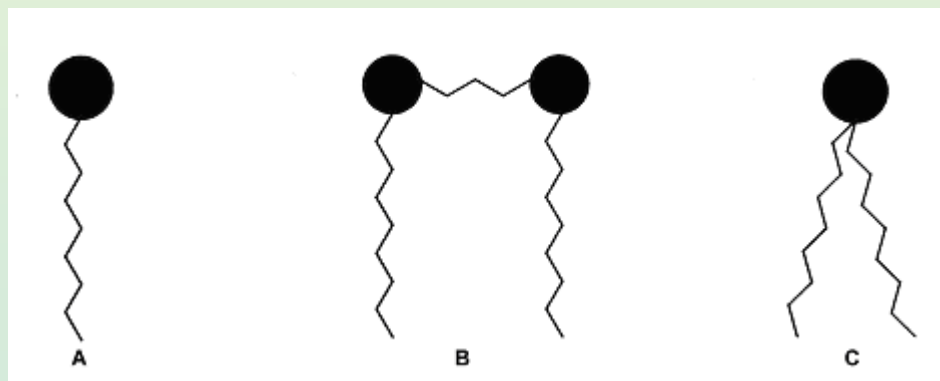
**Ionic surfactants, cationic, anionic, zwitterionic**

**Nonionic amines, polyethyleneoxides**

**A - normal surfactant molecule**

**B - gemini**

**C - swallow tail**



# Surfactants

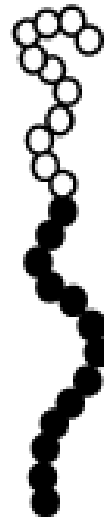
Hydrotrope  
(flexible surfactant)



Bolaform surfactant



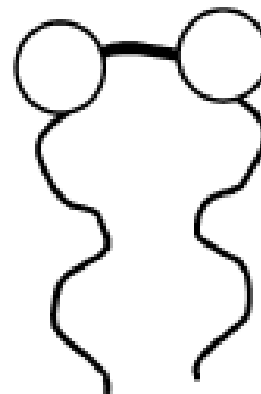
Diblock copolymer  
surfactant



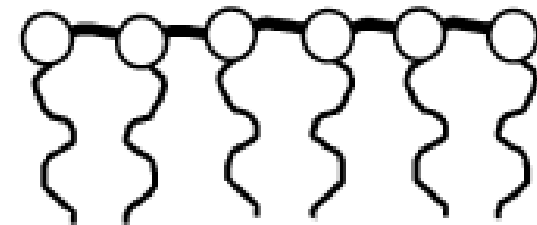
Classical surfactant  
(rigid surfactant)



Gemini surfactant  
(dimeric)



Polymeric surfactant



# 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<sub>4</sub>
- *dialkylammonium salts*:  $(C_{16}H_{33})_2(CH_3)_2N^+Br^-$

## Noionic

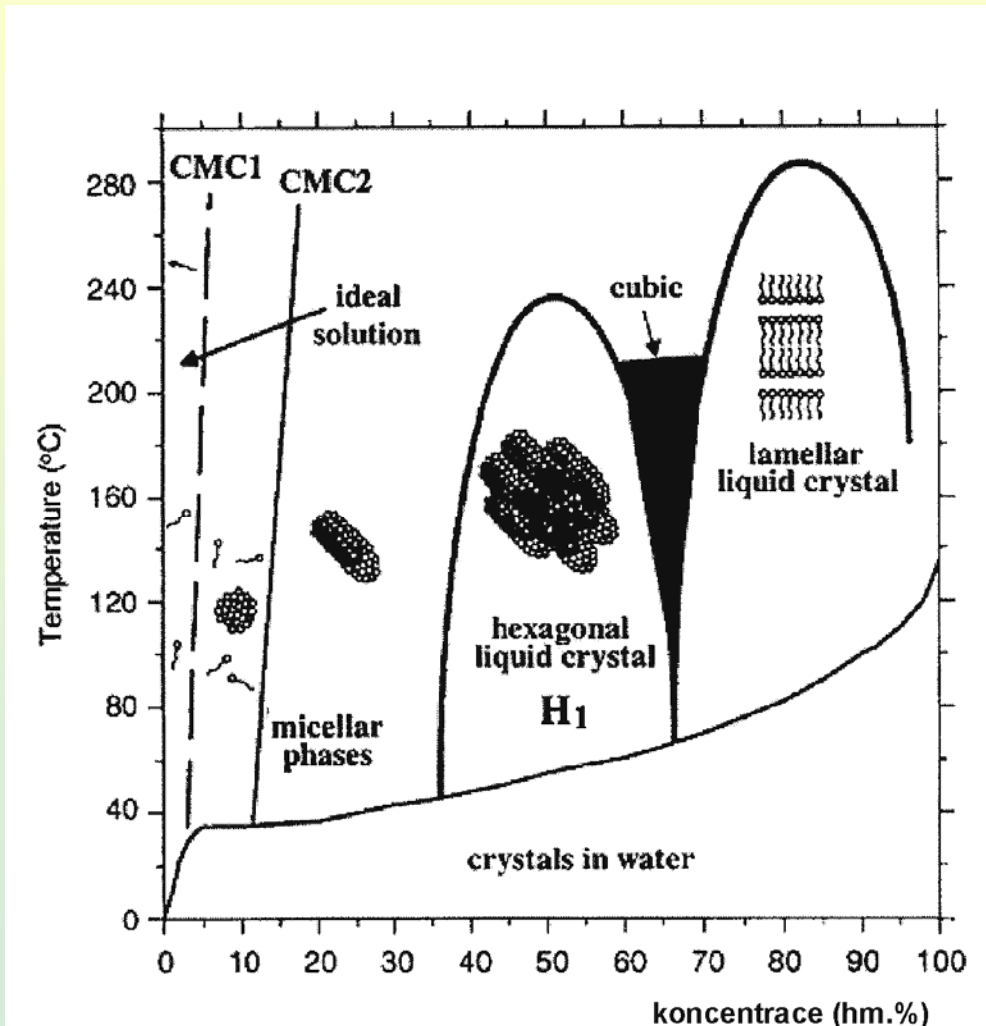
- *primary amines*:  $C_nH_{2n+1}NH_2$
- *polyethyleneoxides*:  $HO(CH_2CH_2O)_nH$



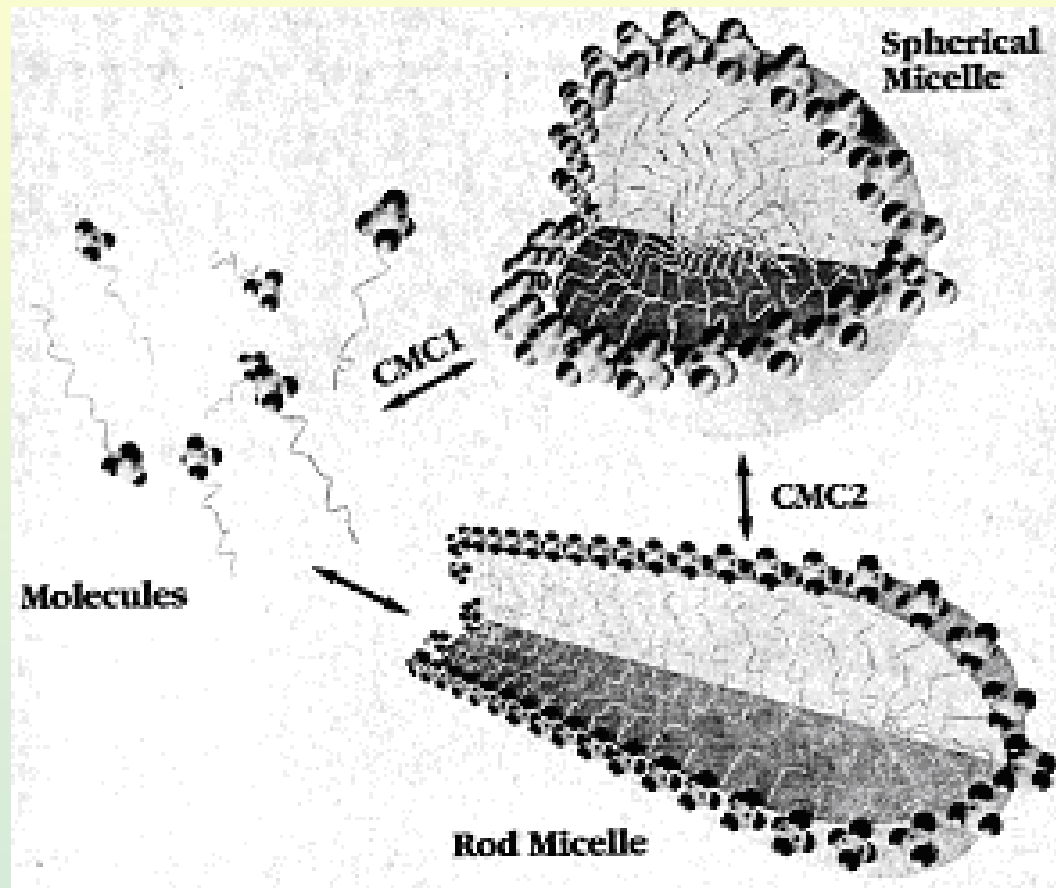
# Supramolecular templating

Phase diagram of  $C_{16}TMABr$

CMC = critical micelle conc.

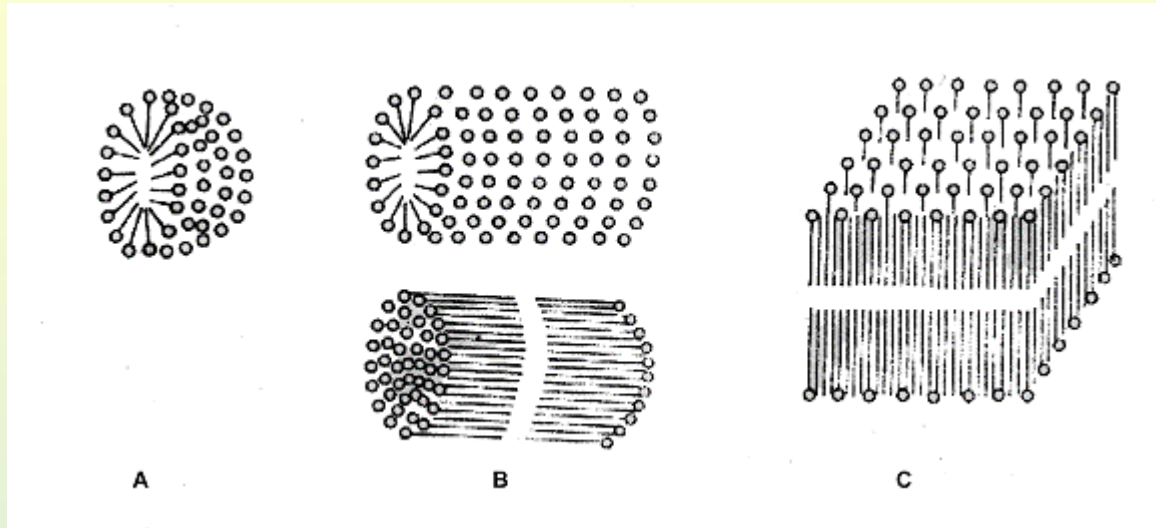


# Micelles - Supramolecular Templates



## Micellar shapes

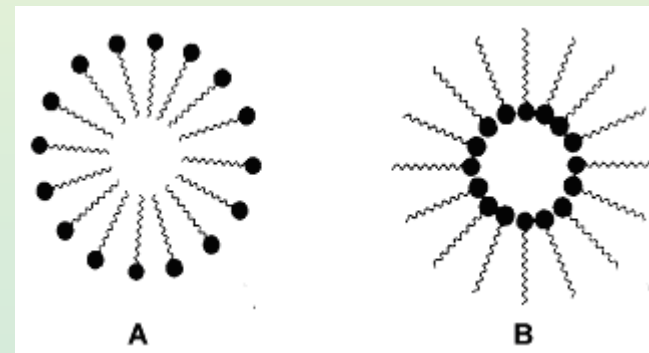
**A -spherical, B - rod-like, C - lamellar**



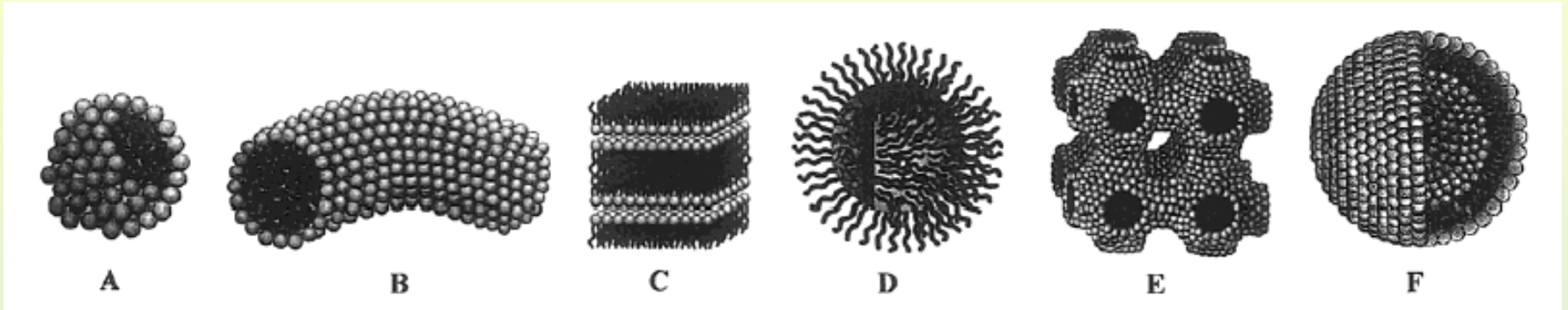
## Micelles in media

**A - normal, in polar solvent, H<sub>2</sub>O**

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



# Micellar shapes



## Micellar structures

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

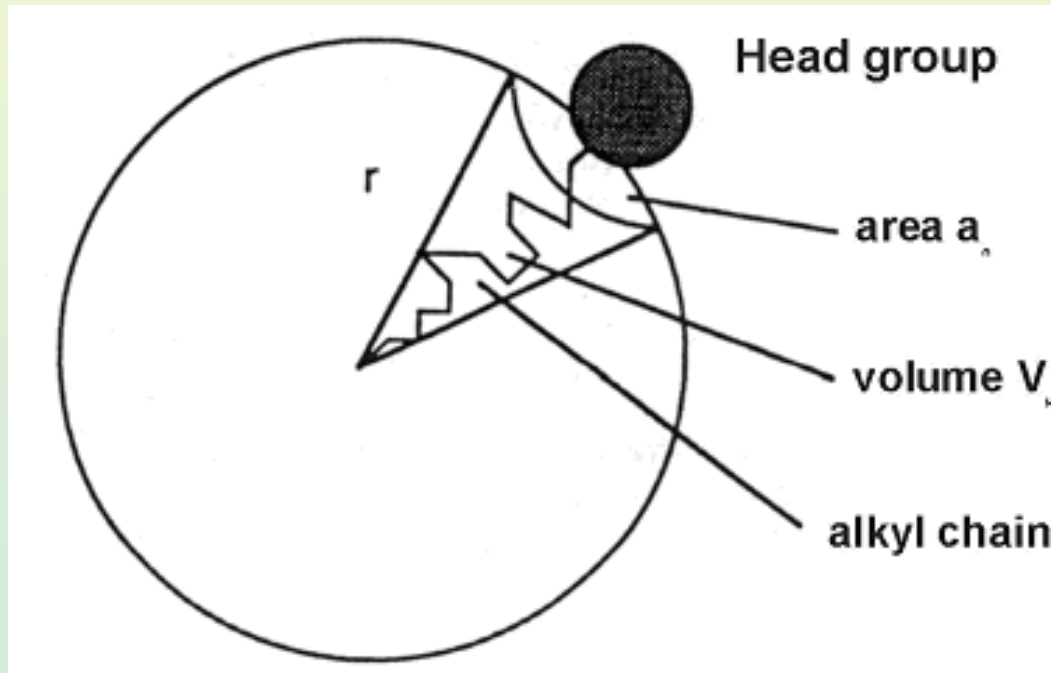
## Critical packing parameter – CPP

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

$V_H$  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.



**CPP**

**surfactant**

**micelle shape**

**< 0.33**

**linear chain, large head**

**spherical**

**0.33 - 0.5**

**linear chain, small head**

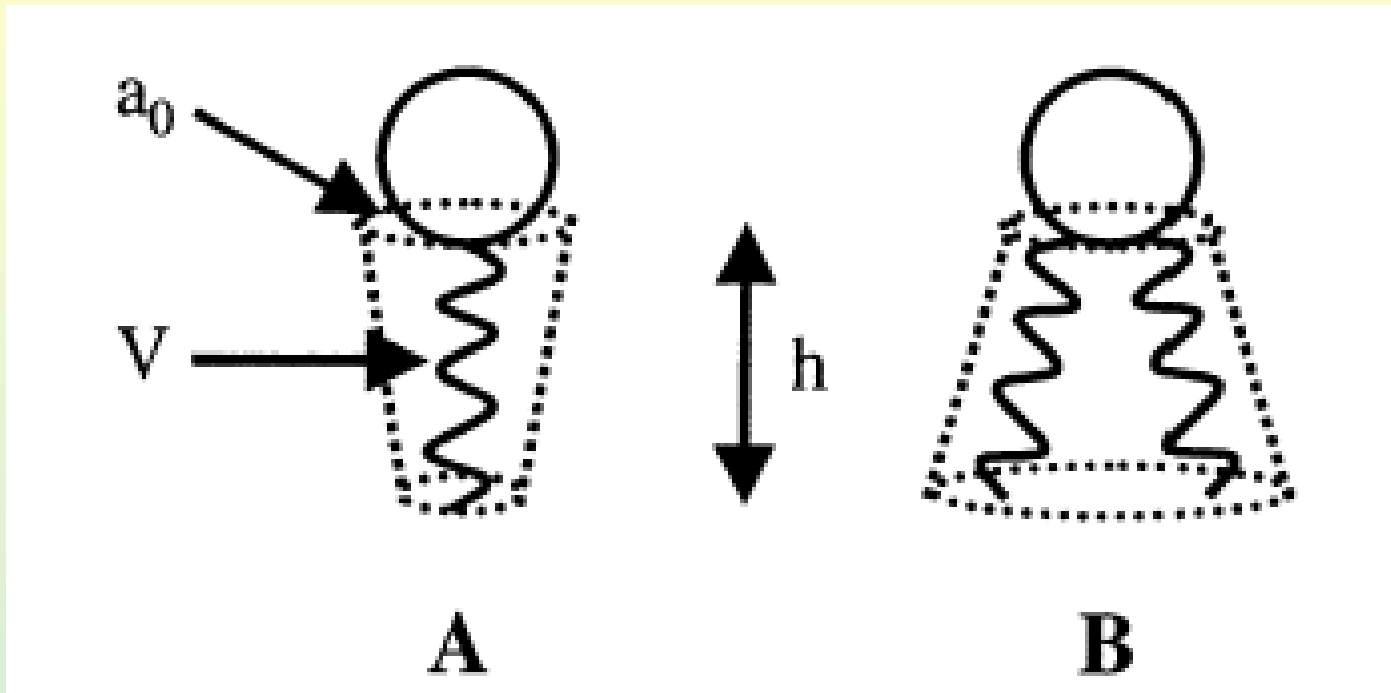
**cylindrical**

**0.5 - 1.0**

**two chains, large head**

**bilayers**

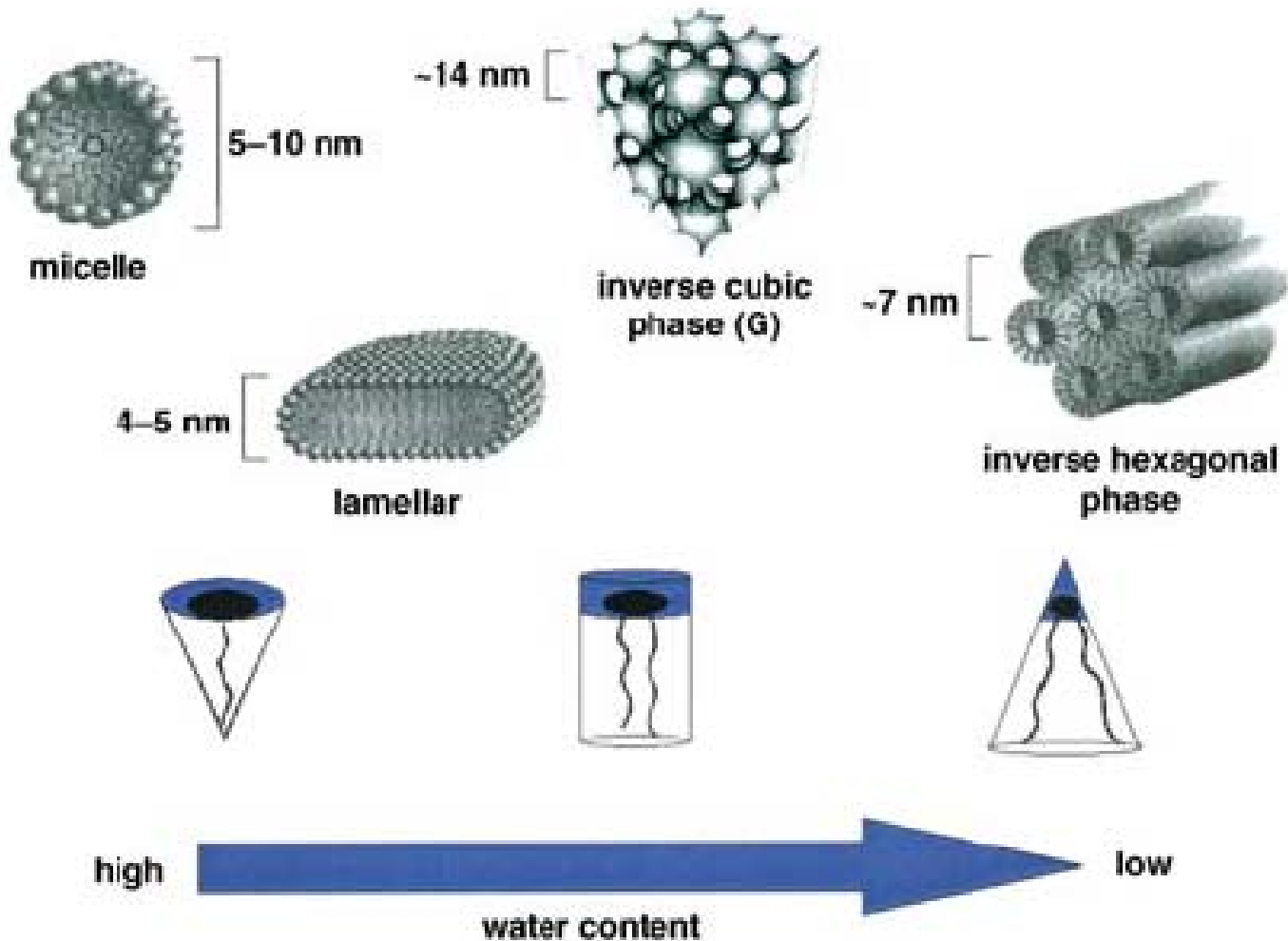
# Surfactant Molecules



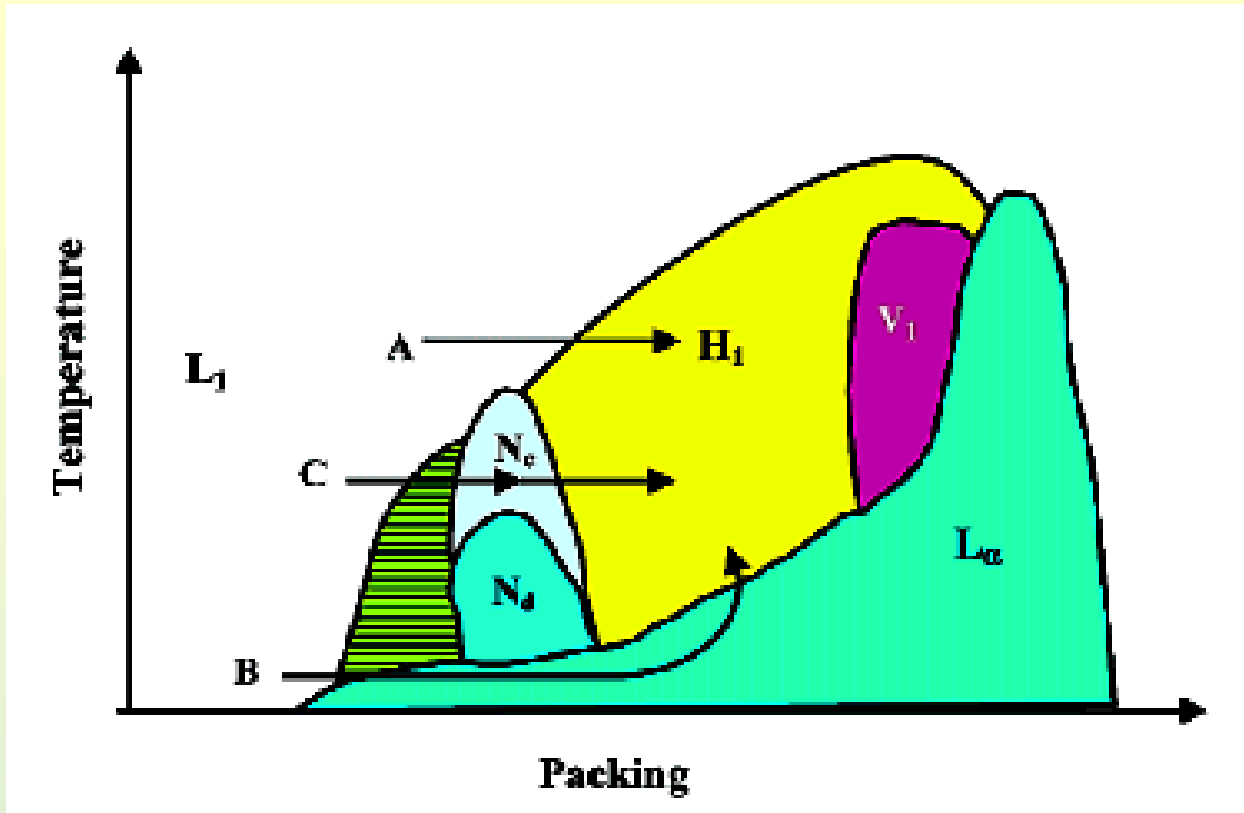
Conical (*icecream cone*, A)

Inverse conical (*champagne cork*, B)

# Surfactant Molecules





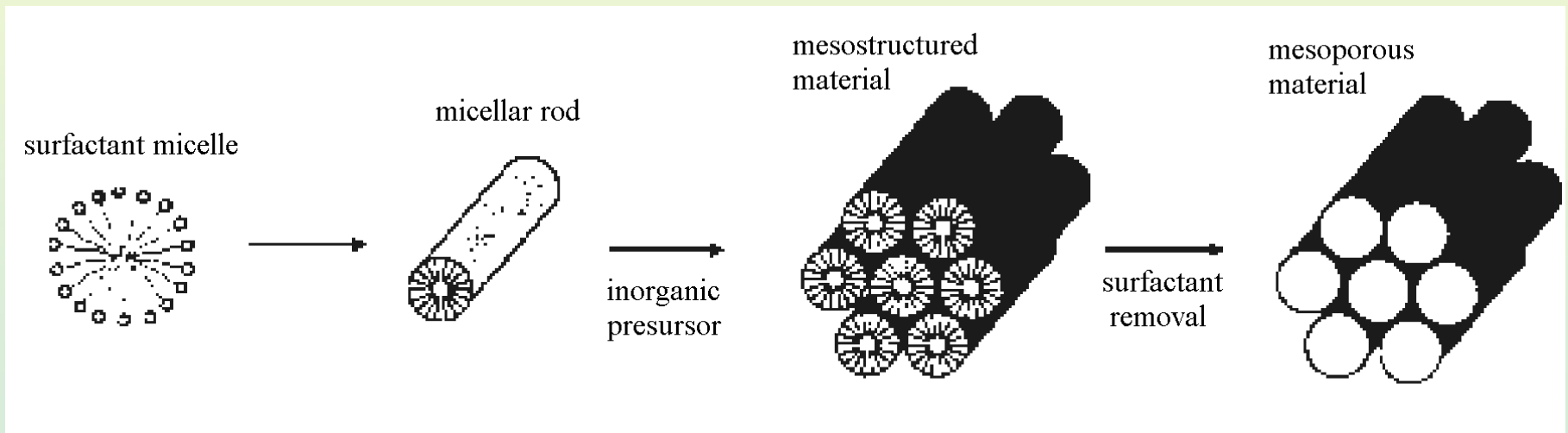


$L_1$  = micellar solution;  $N_c$  = nematic phase;  $H_1$  = normal hexagonal phase (MCM-41; SBA-15);  
 $V_1$  = normal bicontinuous cubic phase (MCM-48);  $L_\alpha$  = lamellar phase (MCM-50)

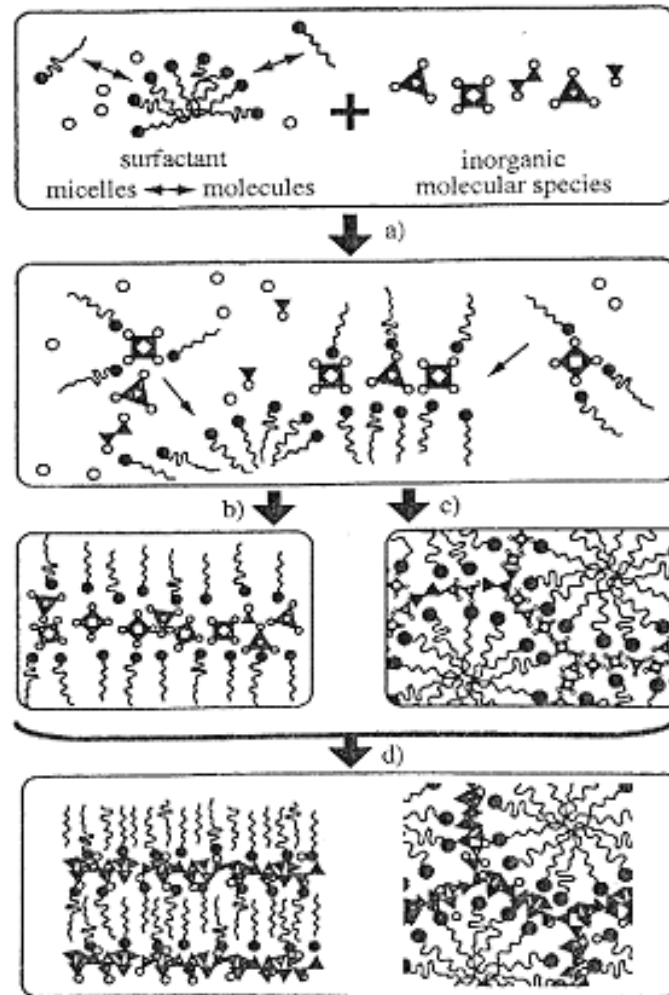
path A, the micellar solution route  
 path B, the lamellar phase route  
 path C, the nematic phase route

# Mechanism of the mesoporous material formation (hexagonal, MCM-41)

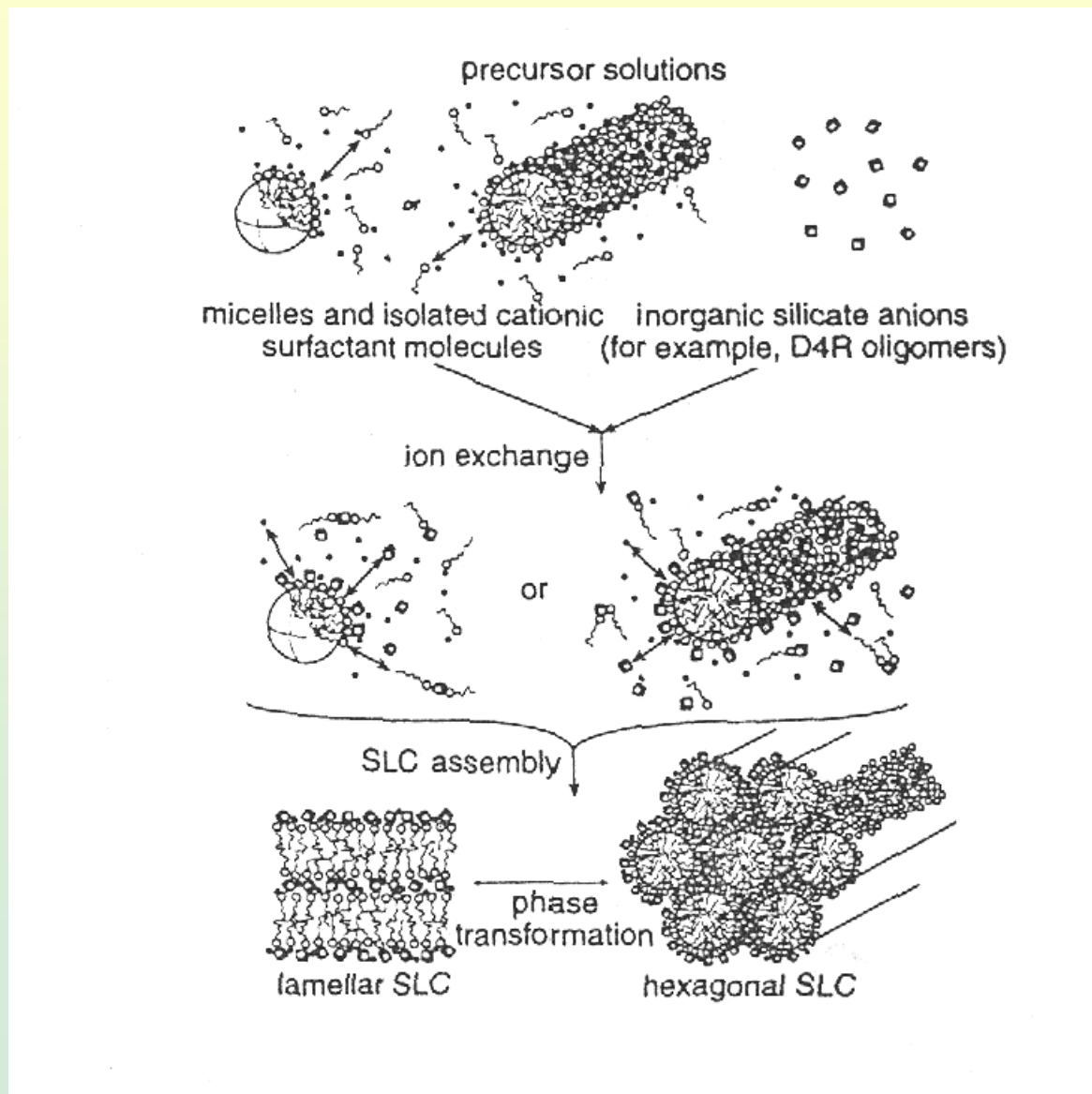
## LCT Liquid Crystal Templating

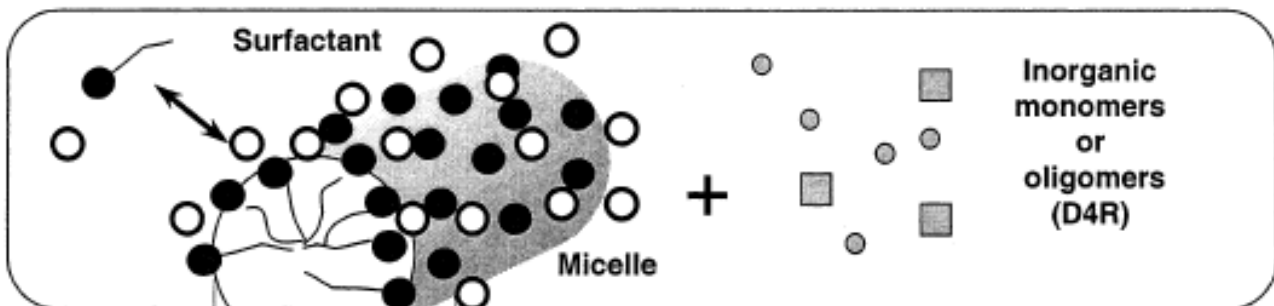
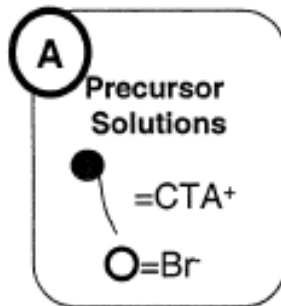


## General Liquid Crystal Templating (LCT) Mechanism

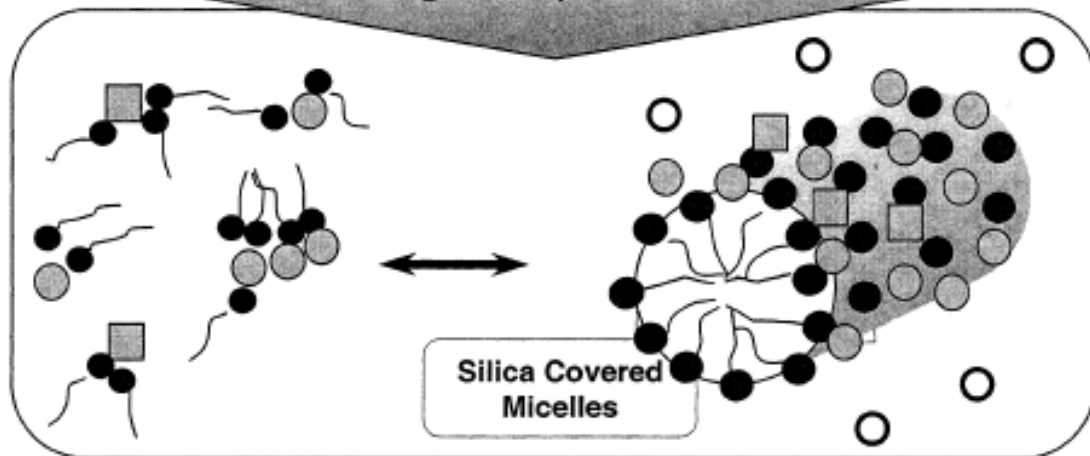
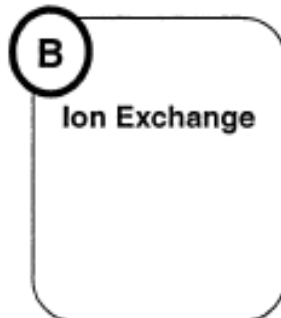


# SLC Silicatropic Liquid Crystals

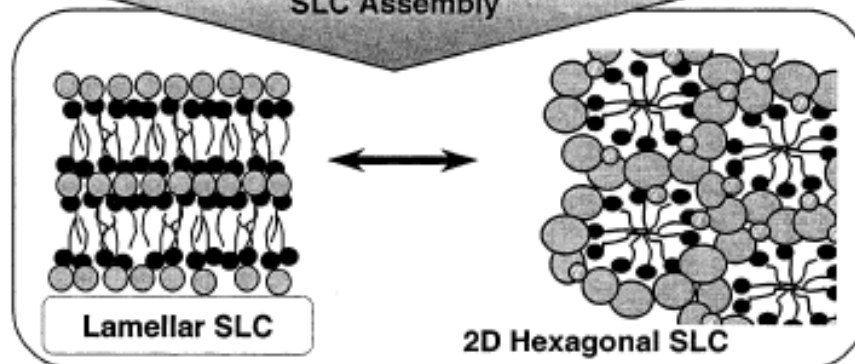
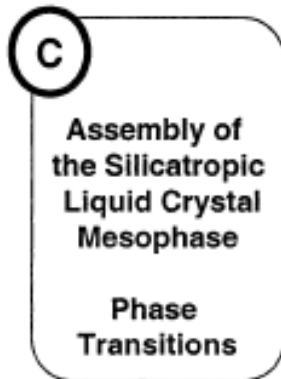




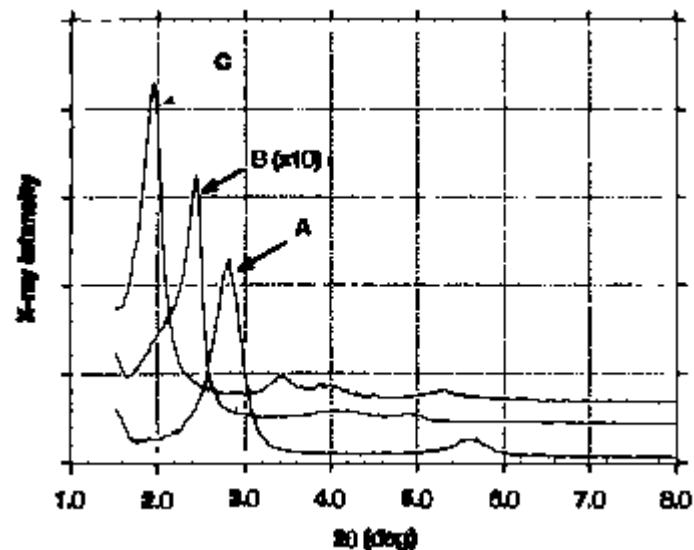
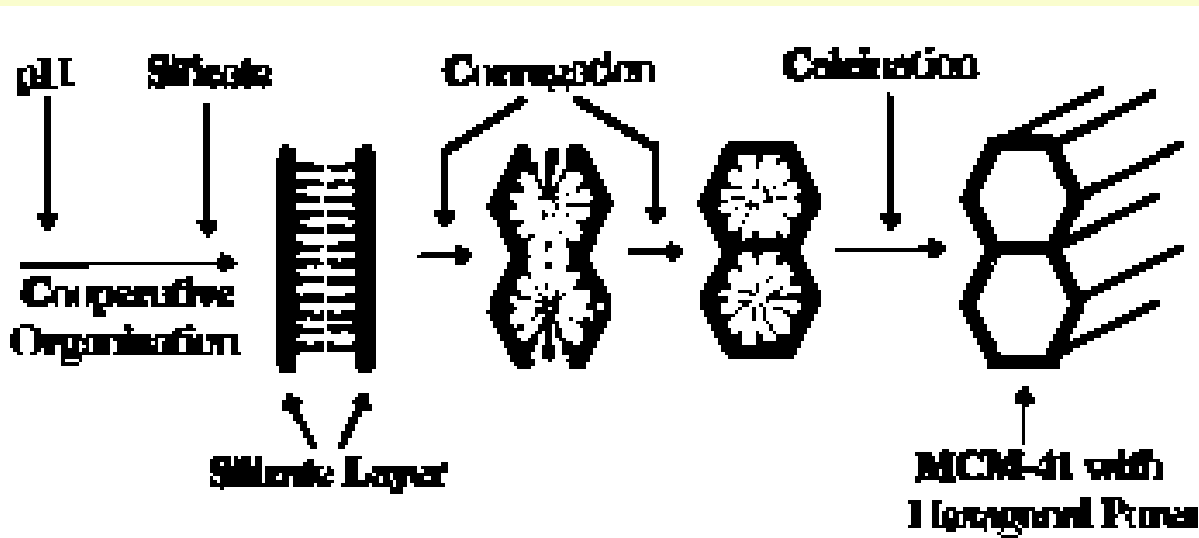
Ion Exchange / Cooperative Nucleation



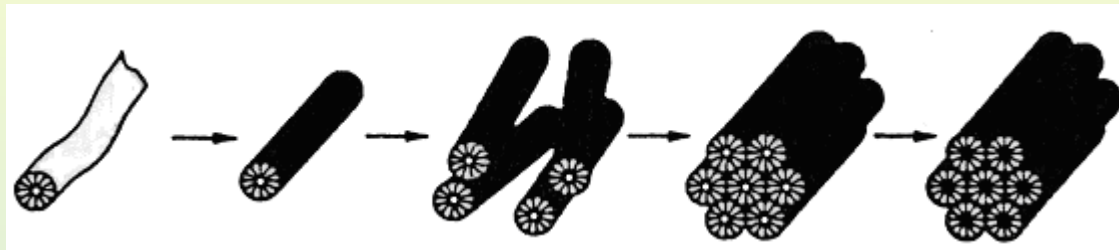
SLC Assembly



# Lamellar to Hexagonal Transformation



## Silicate Rod Assembly

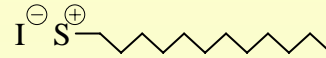


- **Electrostatic interactions**

a) **S<sup>+</sup>I<sup>-</sup>**

**I** = silicate

**S** = trimethylammonium

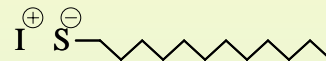


b) **ST<sup>+</sup>**

**I** = Fe<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>,

Mg<sup>2+</sup>, Mn<sup>2+</sup>, Pb<sup>2+</sup>, Al<sup>3+</sup>

**S** = sulfonane



c) **S<sup>+</sup>XI<sup>+</sup>**

**I** = silicate – polyelectrolyte  
positive charge

**X** = Cl

**S** = trimethylammonium



d) **S<sup>-</sup>M<sup>+</sup>I<sup>-</sup>**

**I** = aluminate

**M** = Na

**S** = phosphate



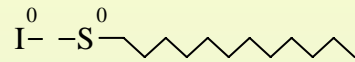


- **Hydrogen Bond**

a) **S<sup>0</sup>I<sup>0</sup>**

**I** = silicate

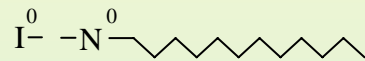
**S** = ammine



b) **N<sup>0</sup>I<sup>0</sup>**

**I** = silicate

**N** = polyethylenoxide

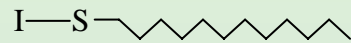


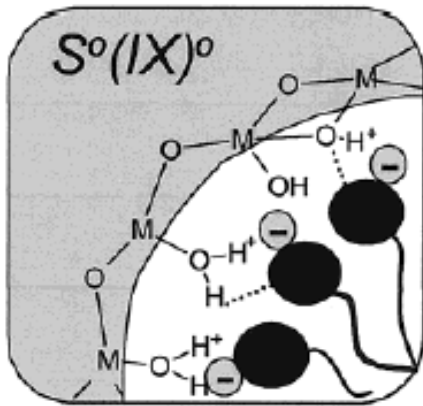
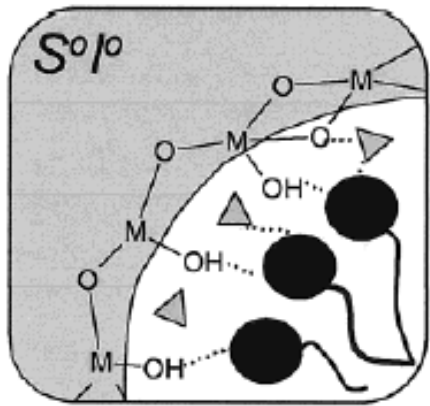
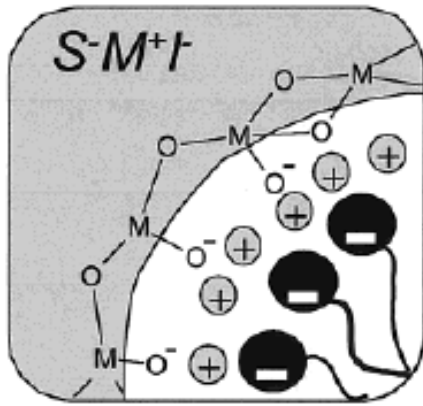
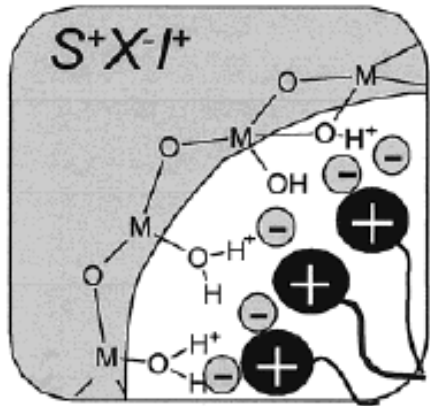
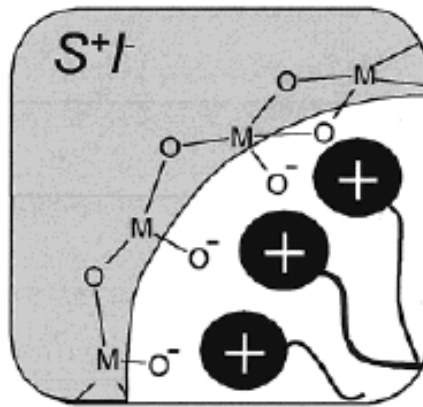
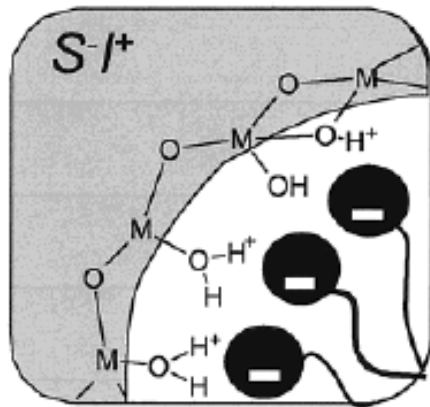
- **Covalent Bond**

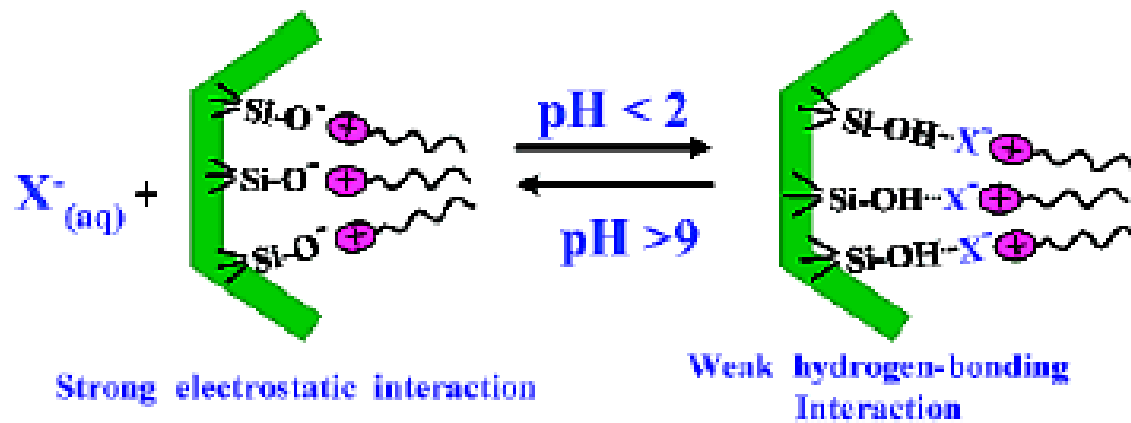
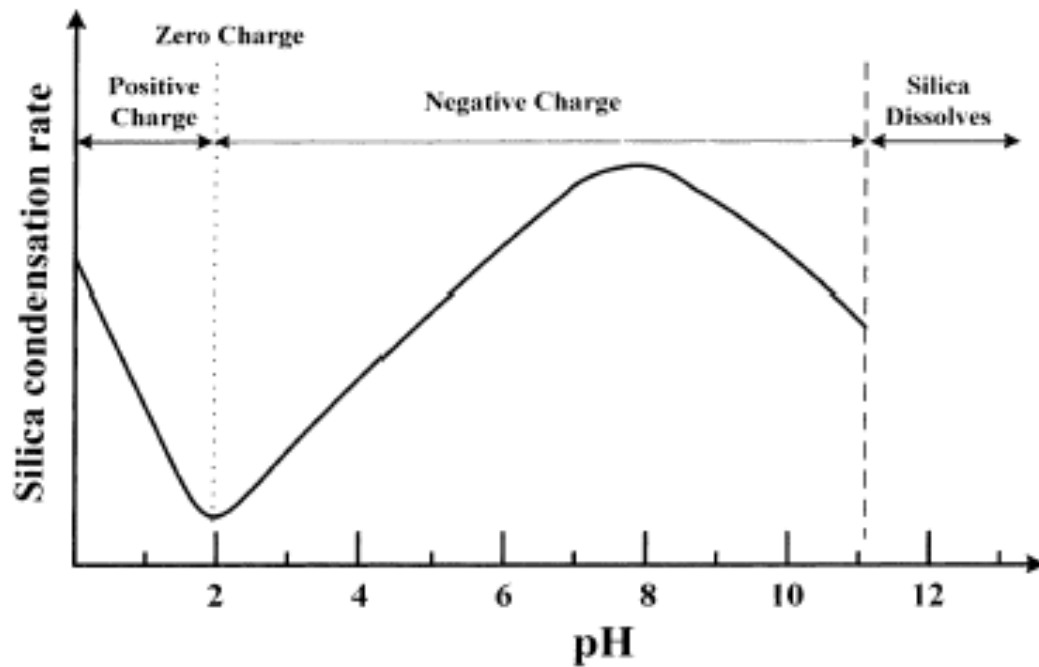
a) **S-I**

**I** = niobate, tantalate

**S** = ammine

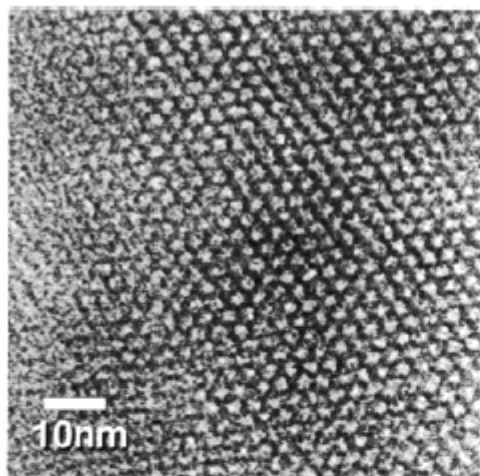




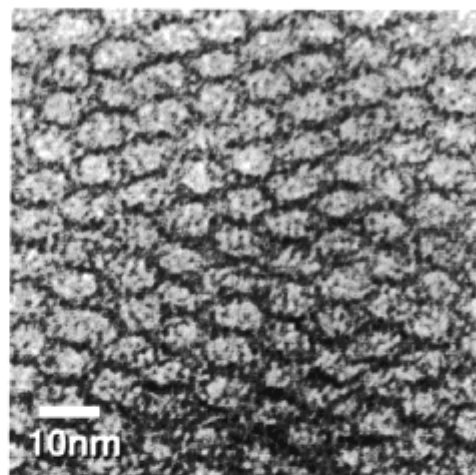


# MCM-41

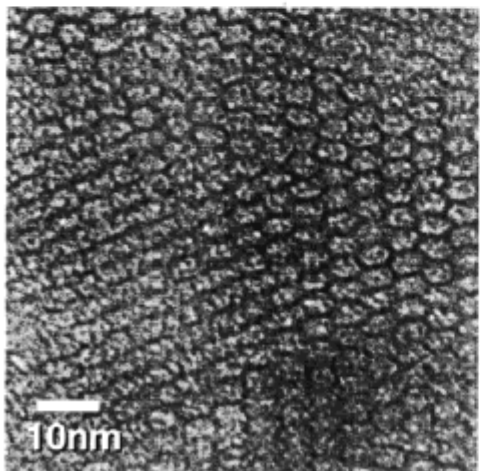
20Å



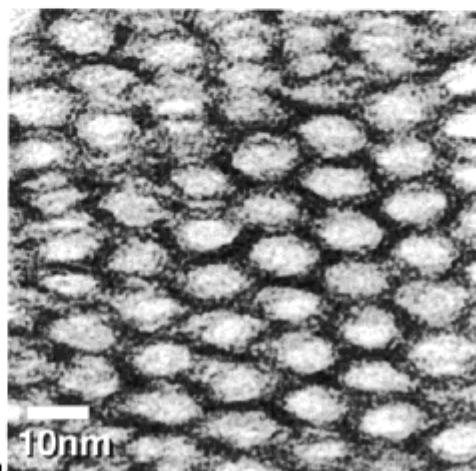
60Å



40Å

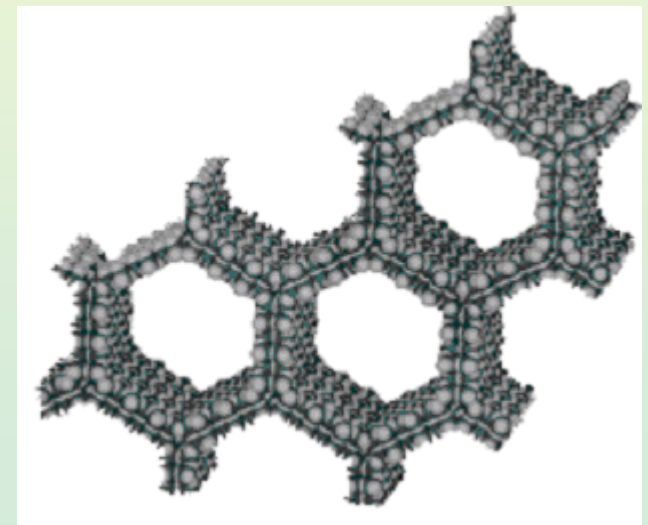
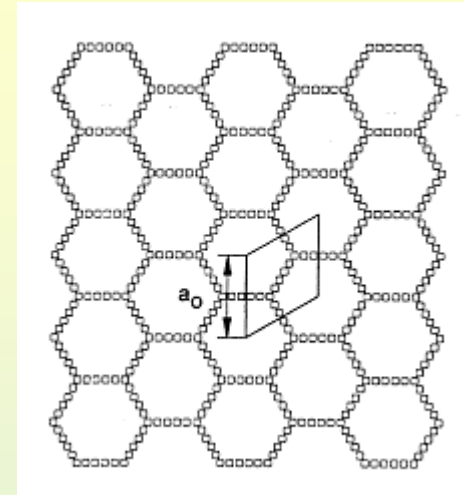
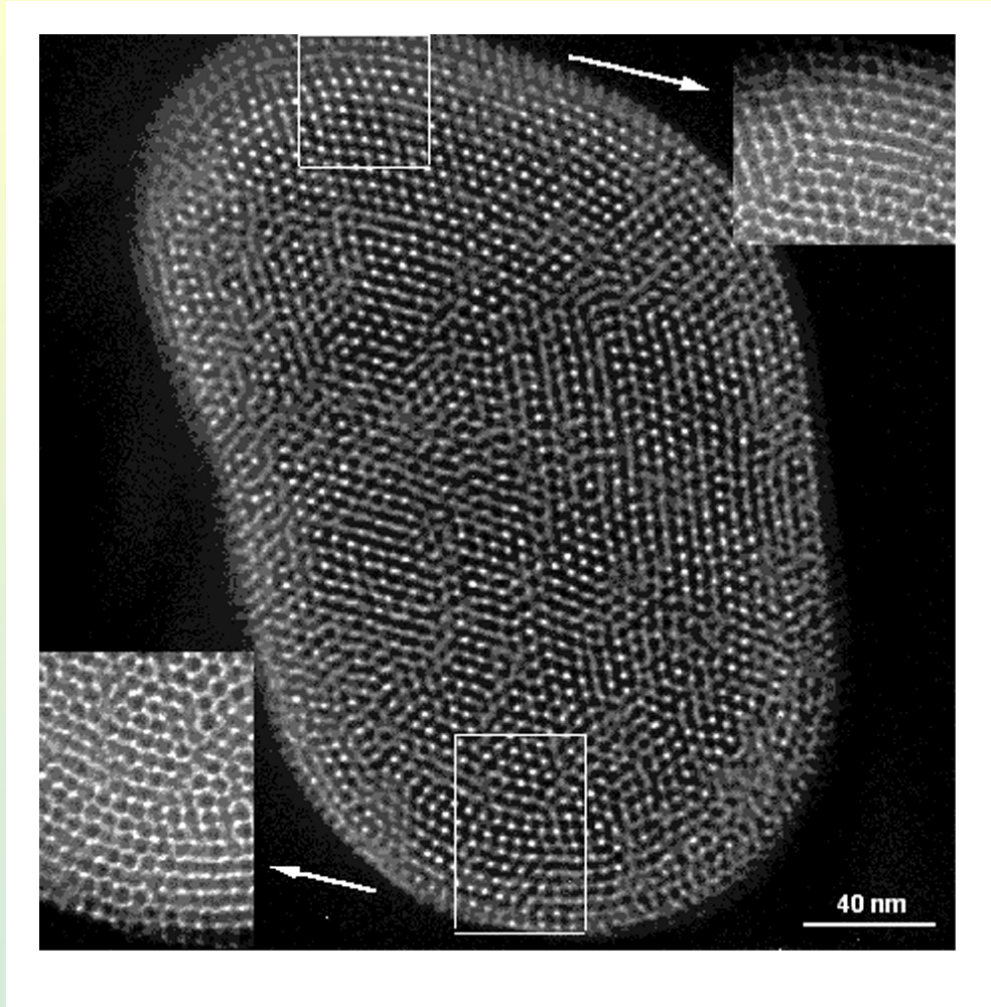


100Å

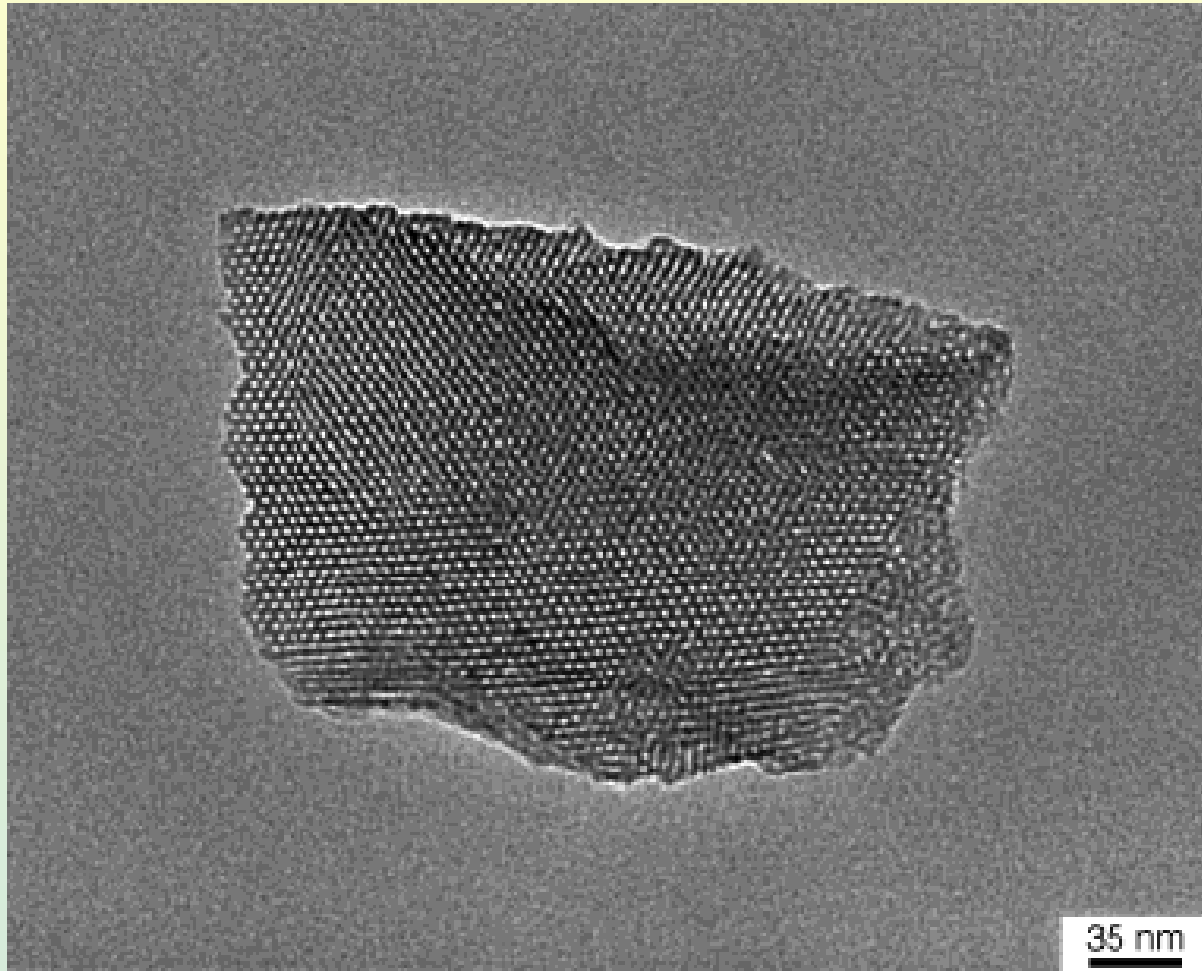


Prepared with Mesitylene Addition

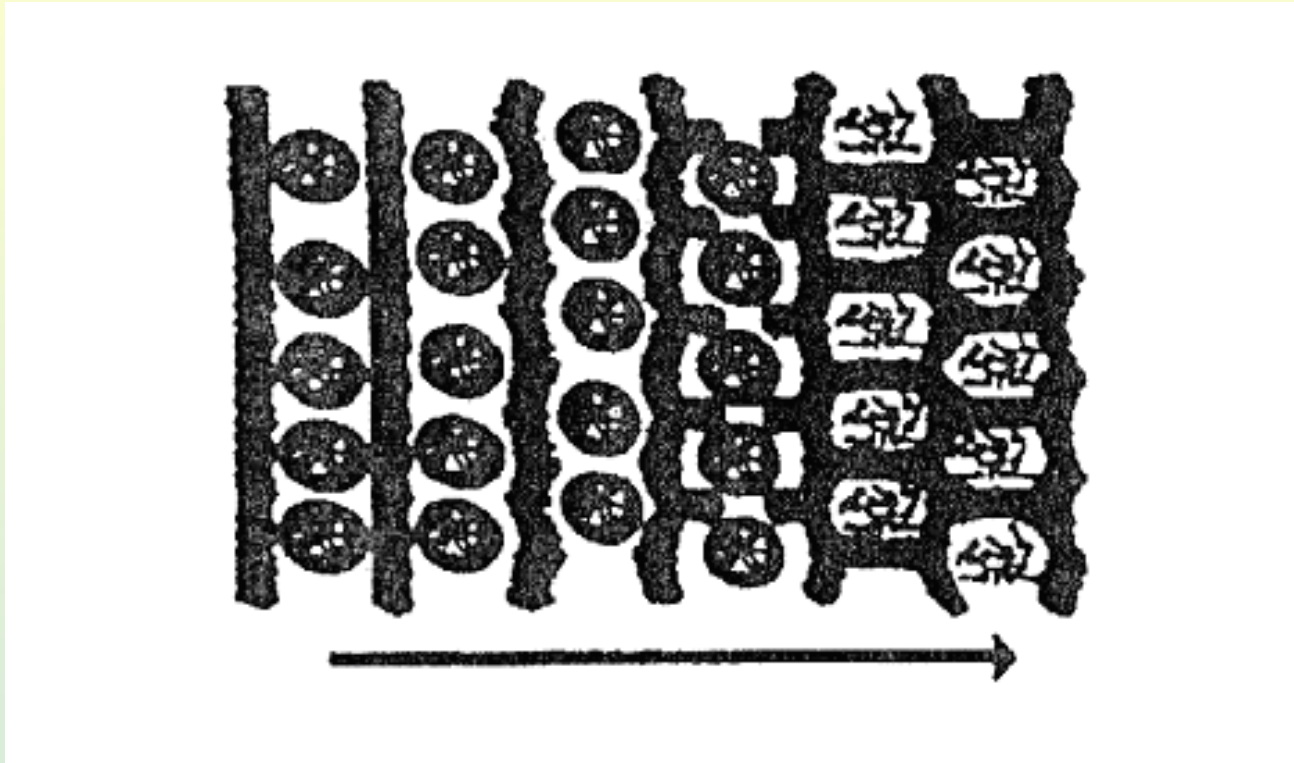
# TEM micrograph of hexagonal molecular sieve



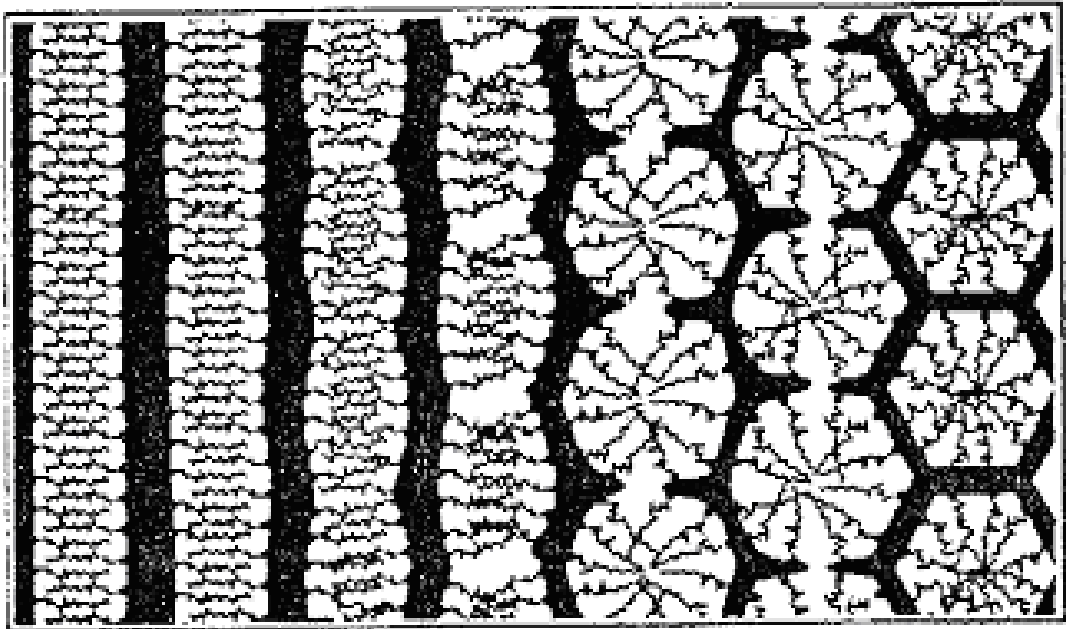
# TEM image of the Pd-grafted mesoporous silicate material



## Silicate Layer Puckering



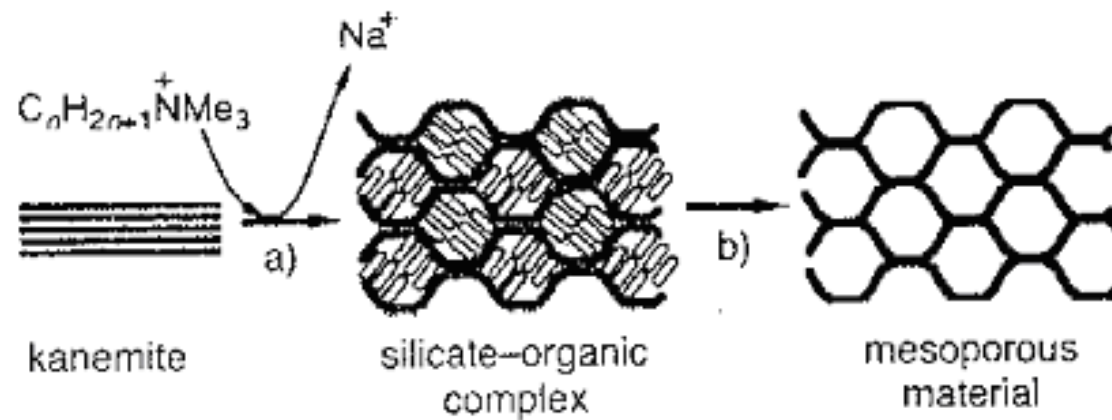
# Charge Density Matching



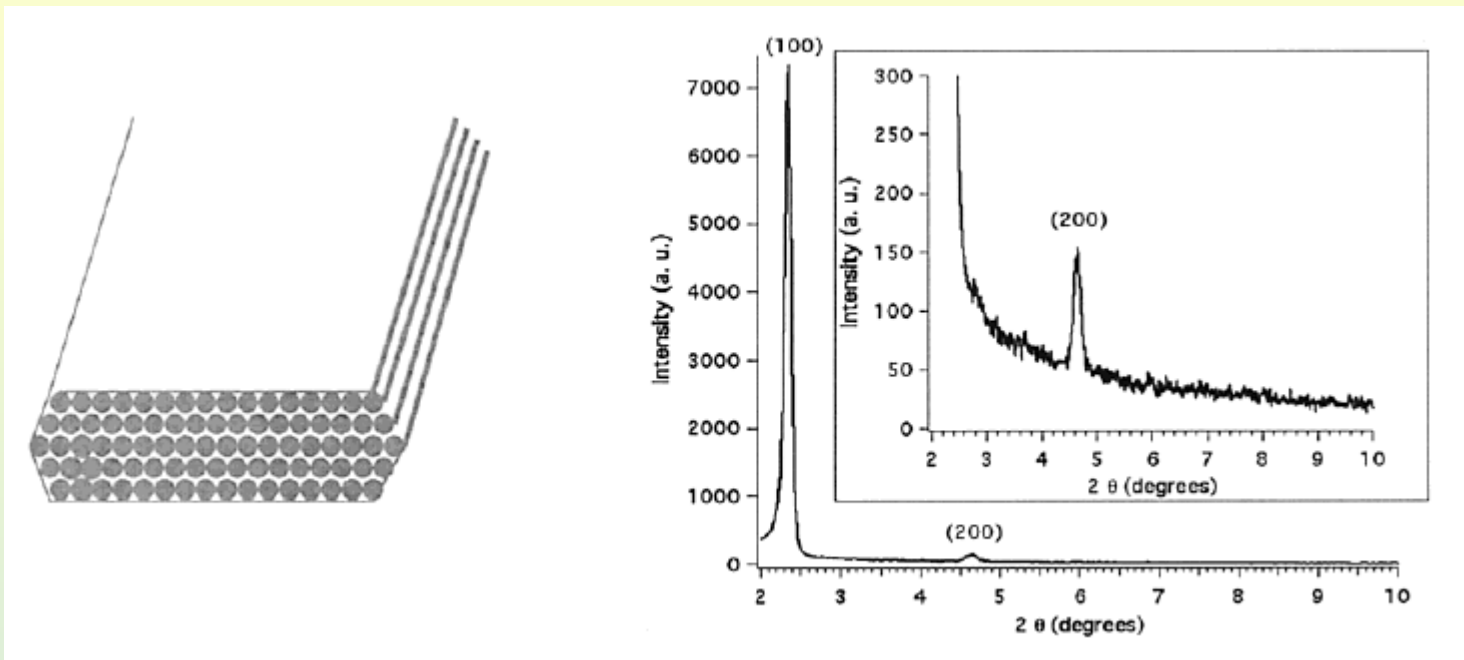
■  $\text{SO}_2$  



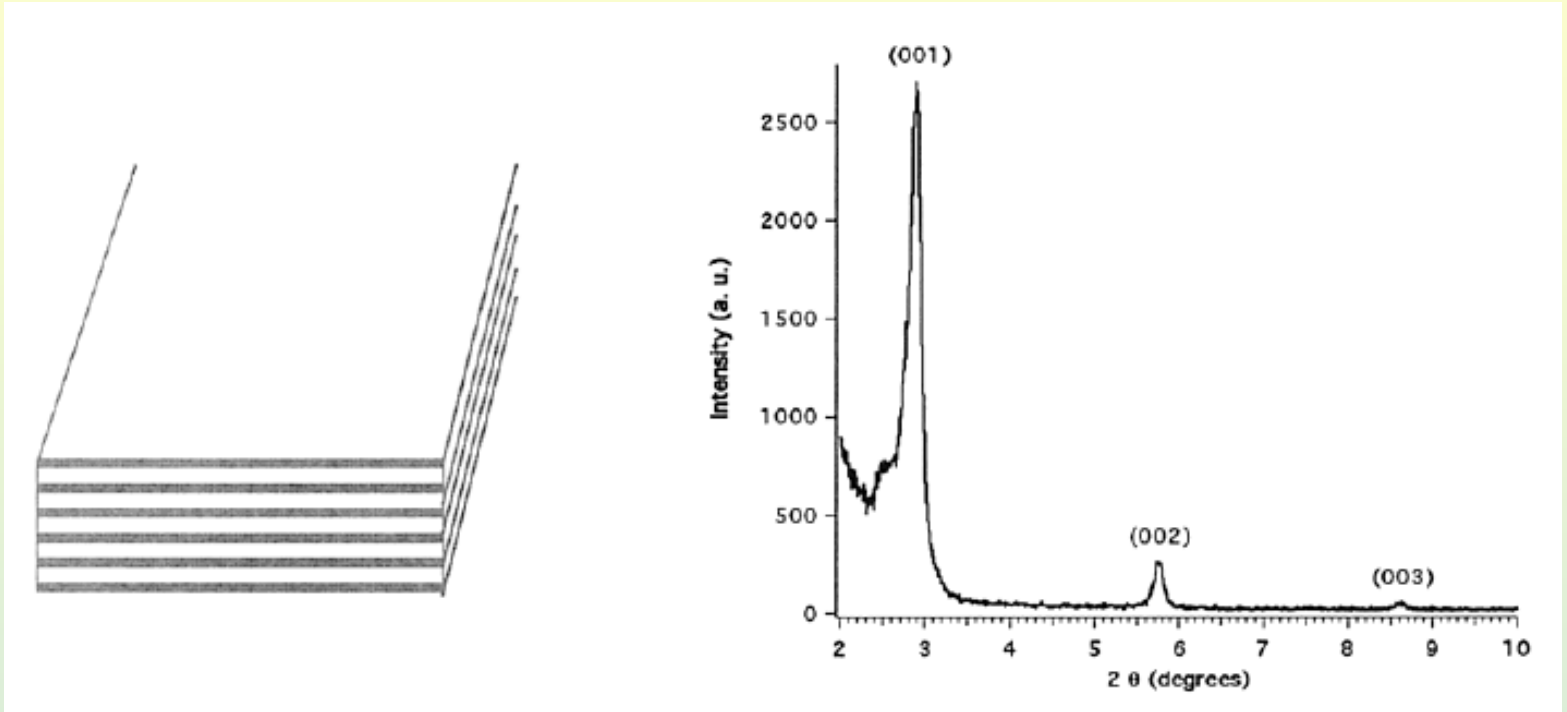
## Folding Sheets

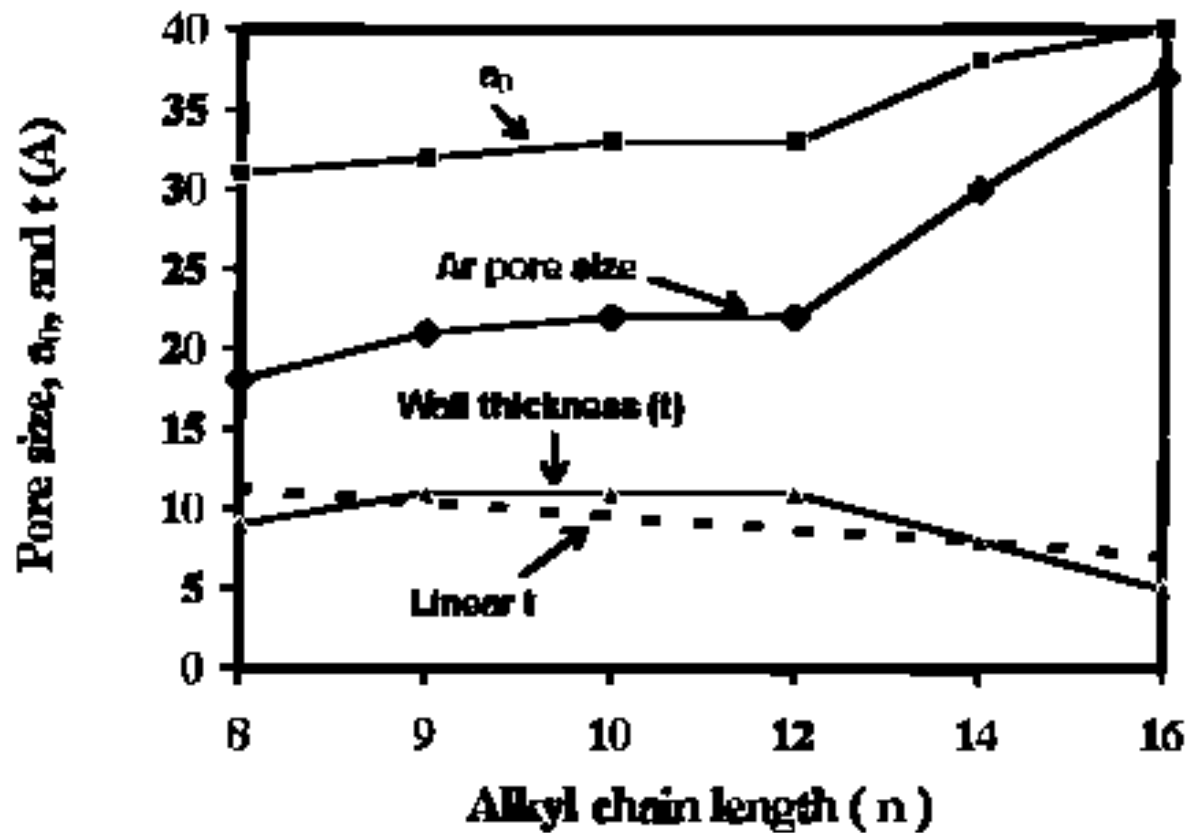


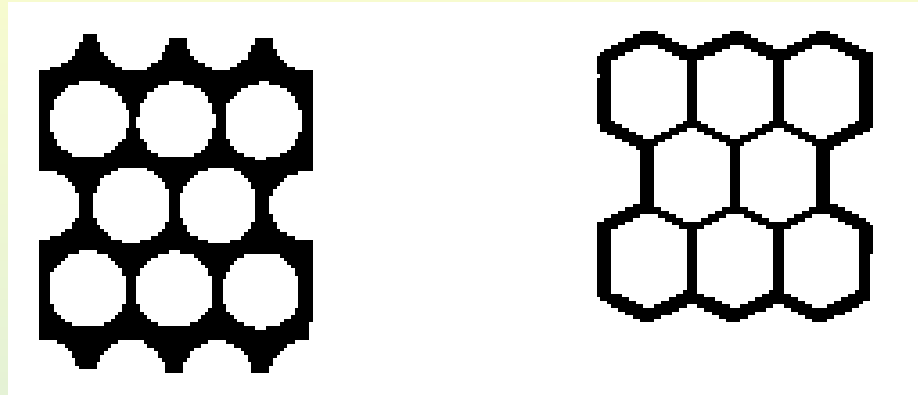
# XRD of hexagonal MCM-41



# XRD of lamellar MCM-50



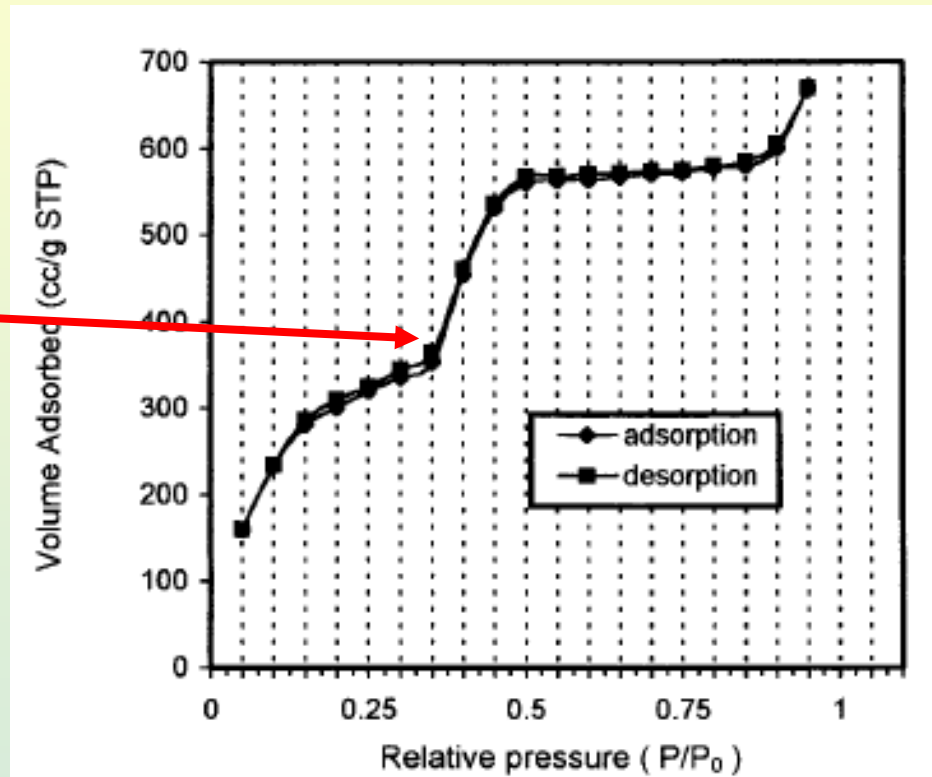




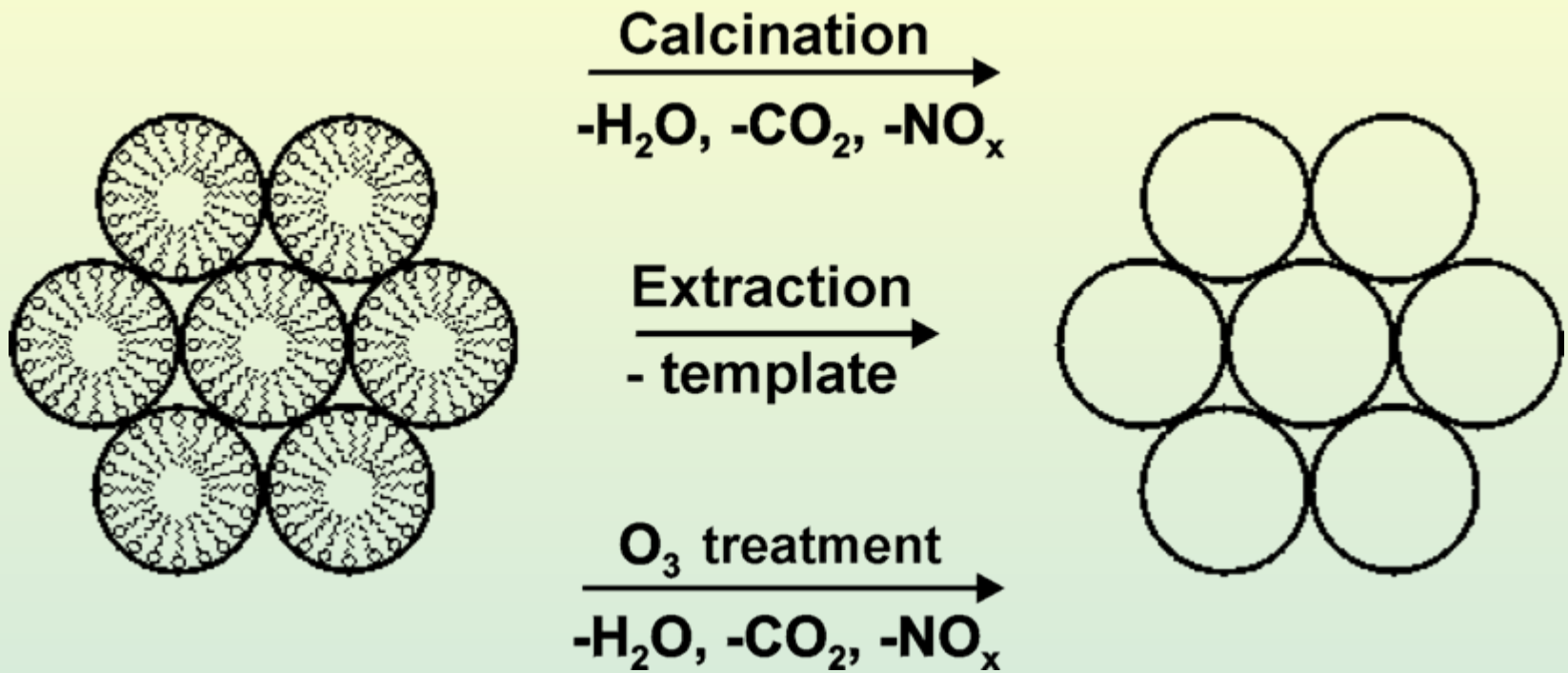
$$a_0 = \frac{2d_{100}}{\sqrt{3}}$$

# Gas Adsorption Isotherms

Pore filling



## Template Removal



## Mesoporous Platinum Metal

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

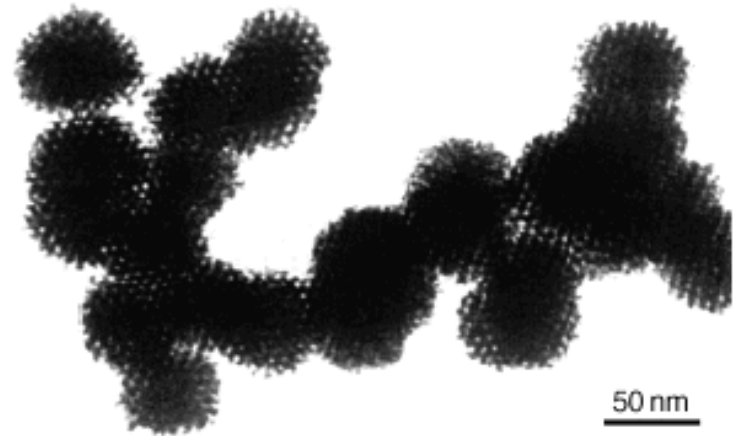
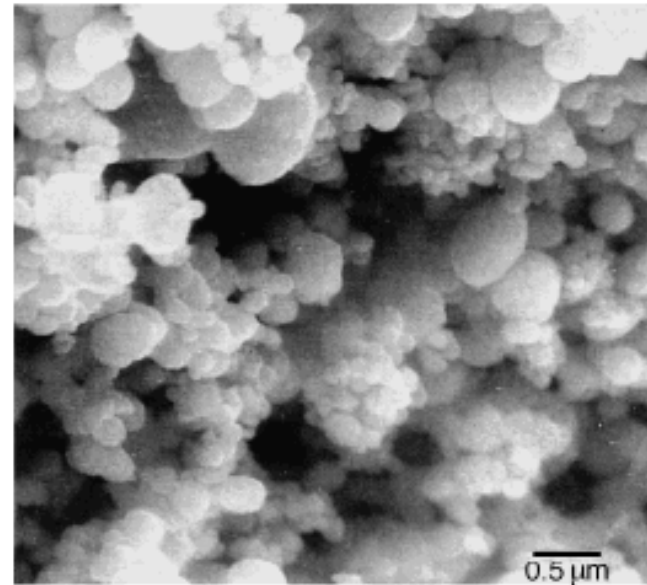
$\text{C}_{16}(\text{EO})_8$

Assembly of liquid crystalline phase

Reductants: Fe, Zn, Hg,  $\text{NH}_2\text{NH}_2$

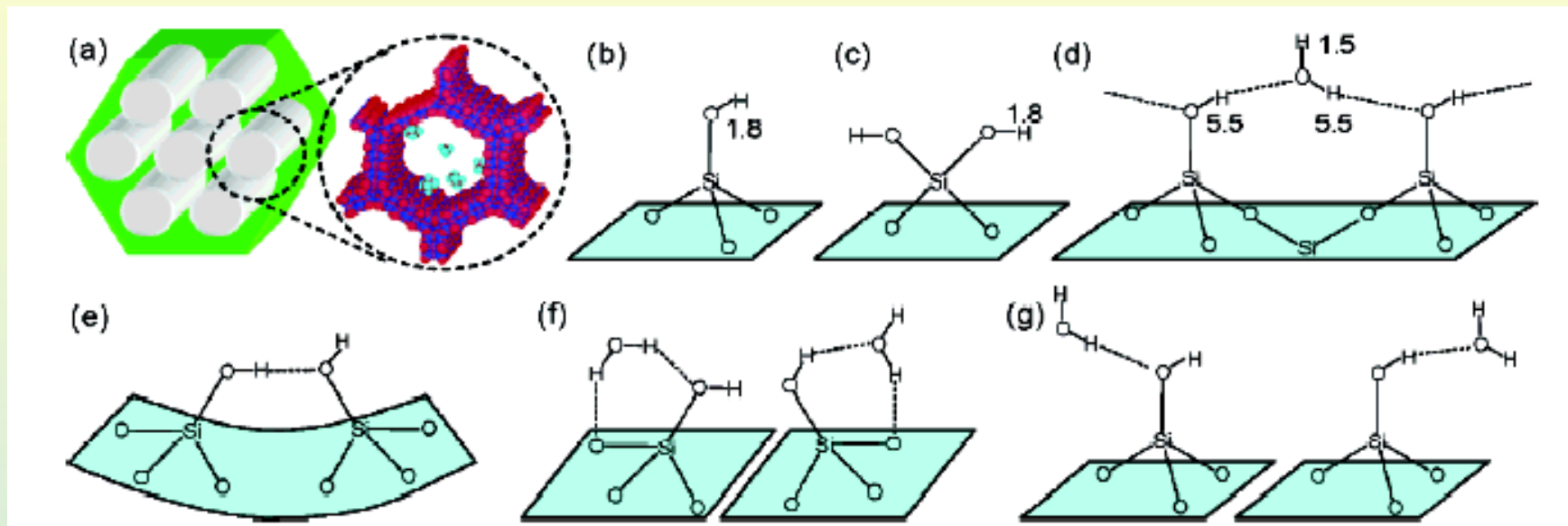
Washed with acetone, water, HCl

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.

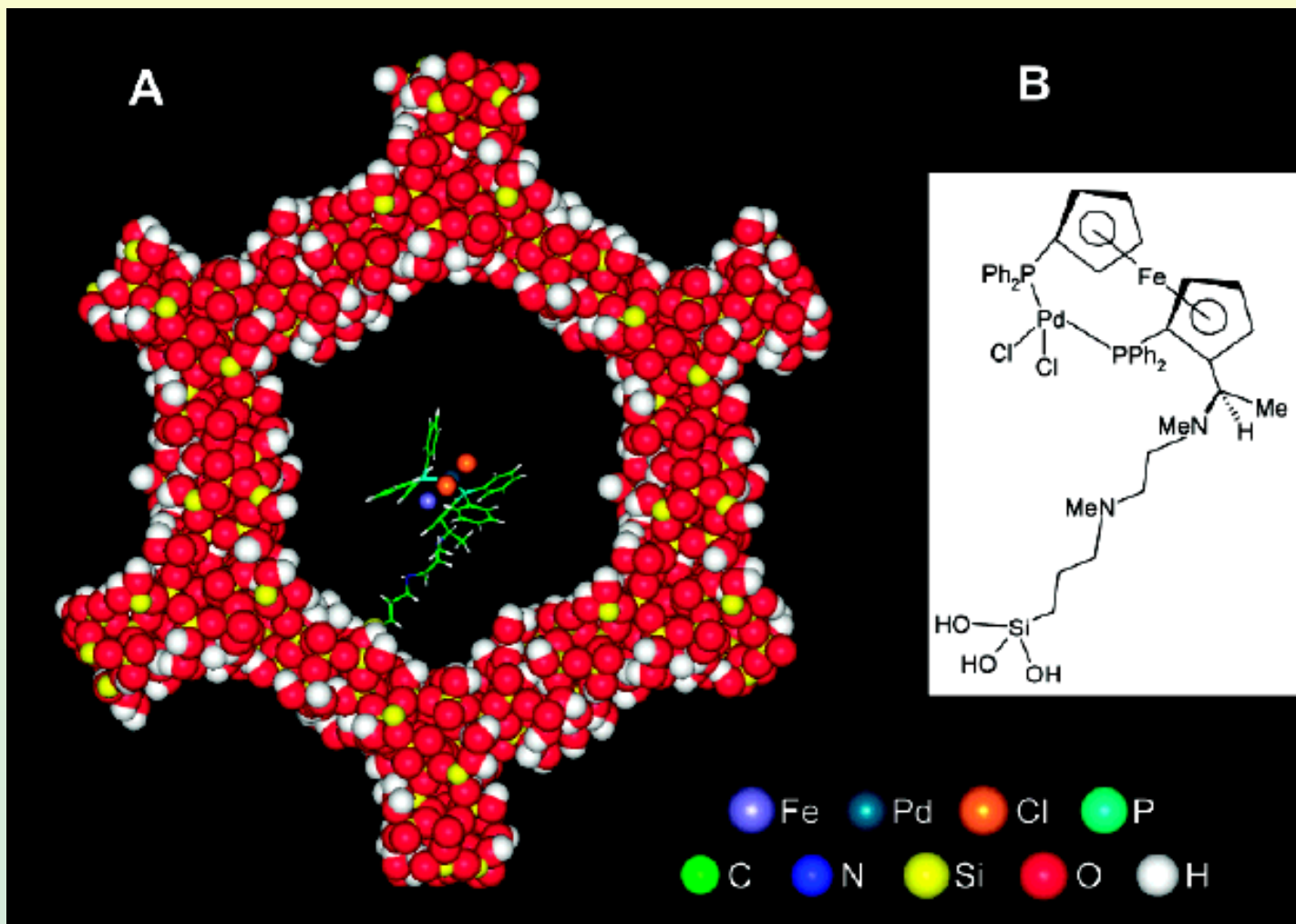




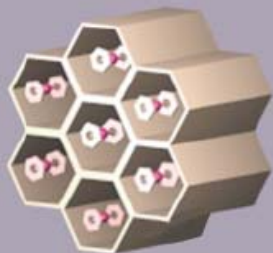
# Surface Silanols in MCM-41 Pores



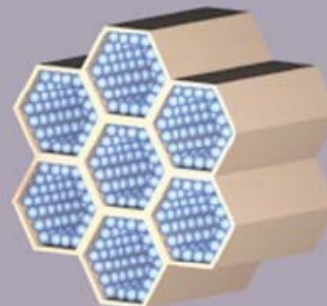
# Chemistry inside the Pores



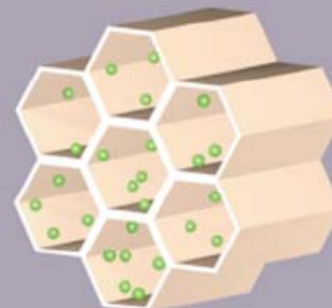
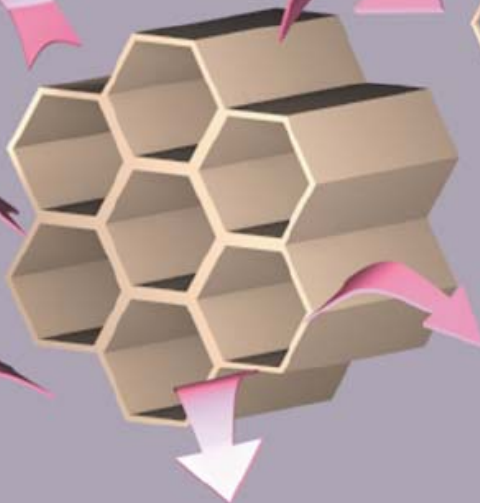
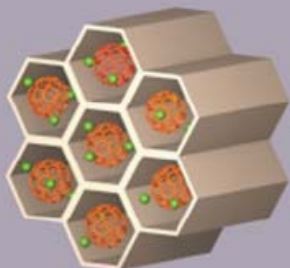
bis(benzene)chromium



toluene



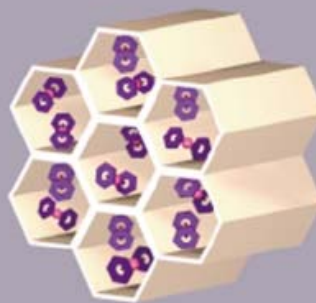
potassium fulleride



sodium



nickelocene



cobaltocene