# *Formation of mesoporous solids,structural evolution.*

Introduction

Recent advances

Hofmeister anion series

Hofmeister anion effects

Conclusion

# Introduction

Mesoporous inorganic solids with pore diameters in the range of 2-50nm have found great utility as catalysts and sorption media.

The discovery of M41S family of mesoporous molecular sieves by Mobil Oil Co., researchers marked the fundamental breakthrough in this field.

The main members of this family are called MCM-41 and MCM-48.

These materials have potential applications as acid catalysts for petro chemical processes, redox catalysis, adsorbents in separation processes and manymore.

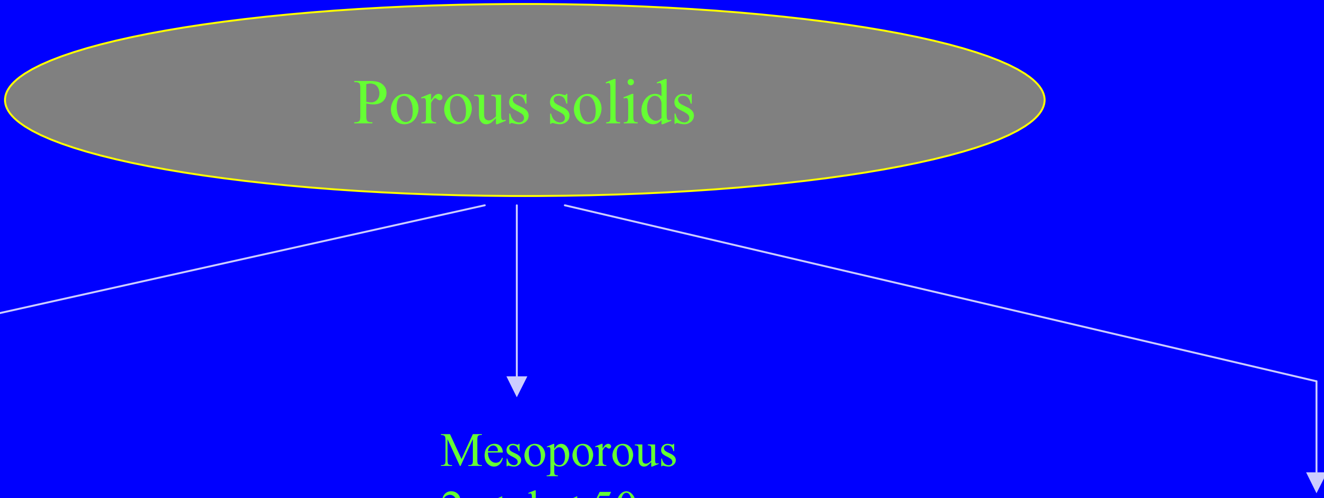
Recent work on mesoporous silica formation using cationic and non-ionic templates has unveiled a large number of anion effects.

Anions are seen to change the hydrolysis rates of the silicate precursors, affecting the surface properties and morphologies of the final products.

They often found to improve the hydrothermal stabilities of the final products.

The interaction between the organic template and the inorganic precursor plays a key factor in the control of formation of these materials.

# *Introduction*



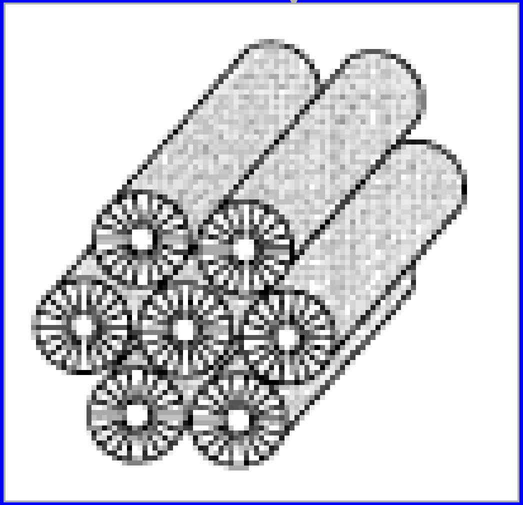
Porous solids

Microporous
$d < 2$ nm
Zeolites, $AlPO_4$

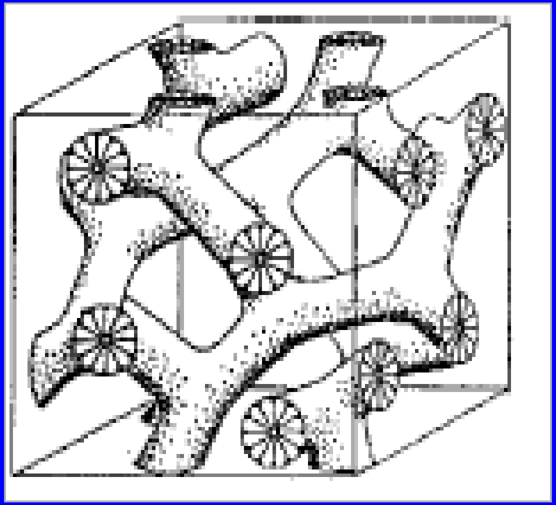
Mesoporous
$2 < d < 50$ nm
Mobil composition of materials (M41S)
Hexagonal mesoporous silica (HMS)
Mesoporous structural units (MSU)
Tech. Mesoporous silica (TMS)

Macroporous
$d > 50$ nm
Porous gels

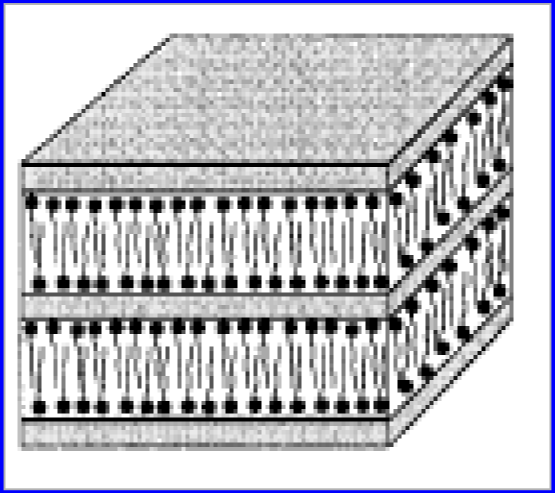
# Mesoporous M41S Materials



**Hexagonal MCM-41**

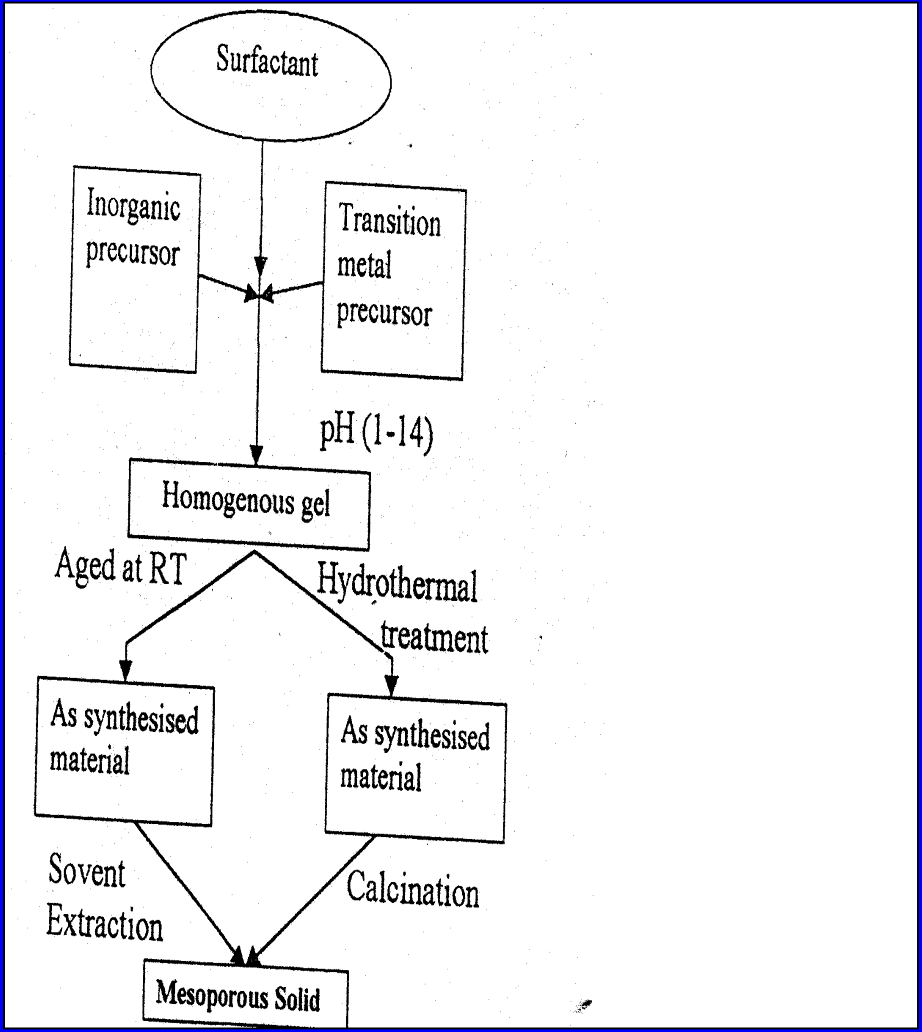


**Cubic MCM-48**



**Lamellar MCM-50**

# Schematic representation of the synthesis of mesoporous solids



# Recent advances in the formation mechanisms of these fascinating mesoporous solids.

Silica based materials prepared in presence of ionic or neutral surfactants.

Mesoporous non-siliceous oxides.

Mesoporous flims.

# Formation of silica based materials

In situ methods of investigation that use probe molecules which are able to give information on changes occurring in the micelle environment during the synthesis have been developed.

In situ EPR spectroscopy can be an effective technique to investigate the formation of these mesoporous materials.

The spin probe was incorporated into the CTAB micelles with its Nitroxide radical located near the silica surfactant interface.

The spin probe sensed the motional changes of the surfactant during the formation of of silica based MCM-41.

Two clear stages occur during the course of reaction.

In the first stage of the reaction, silicate oligomers formed in the aqueous solution interact with surfactant at the micelle surface and transform the micelles into an hexagonal array with a soft partially condensed silica matrix.

During the second slow stage of the reaction further condensation and dehydration occurs.

# Formation of aluminium containing micelle-templated silica.

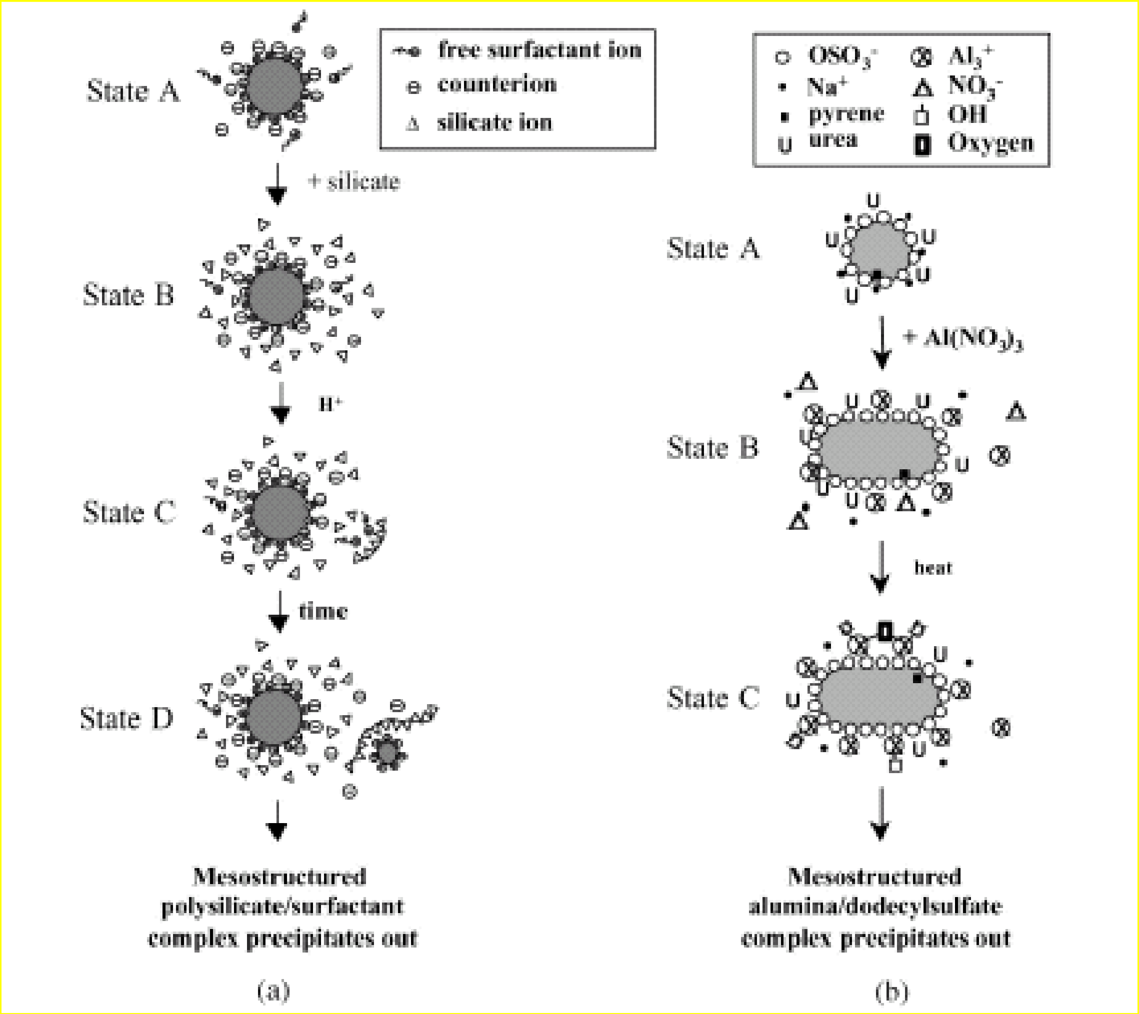
The formation mechanism of aluminium containing micelle-templated silica was investigated by in situ EPR combined with X-ray diffraction.

The analysis of the EPR spectra showed a decrease of the mobility of the probe and therefore of the surfactant micelles through out the reaction.

This decrease in the mobility is due to the formation of an inorganic lattice at the micelle surface.

The larger the micelles,the earlier the decrease of mobility.

According to XRD results, this mobility decrease corresponds to the transformation of an amorphous solid into an ordered hexagonal micelle-templated material.



Simplified and schematic representation of the formation of mesoporous hexagonal silica (a) and mesostructured hexagonal alumina(b)

# Formation of mesoporous non-siliceous oxides

A homogenous alkalinization method has been introduced by Yada et al. with the aim of a gentle and homogenous raise of $P^H$ to produce periodically mesostructured alumina .

The Dodecyl sulphate spherical micelles are initially surrounded by bound aluminium cations, some urea moloecules and a few nitrate anions.

Upon heating at 60°C, urea partially decomposes with the formation of hydroxyl ions.

The resulting PH increase initiates the formation of charged complex oxygenated aluminium species that can start polymerizing.

The growing polymeric species remain completely or partially bound to the negatively charged micelles .

Both light scattering and time-resolved fouorescence studies indicated that most of the growth of the inorganic polymer and of the polymer/surfactant micelle complexes takes place shortly before precipitation occurs.

The complex organization into a mesostructured hexagonal material occurs during or extremely shortly before precipitation.

# Formation of mesoporous flims

Formation of mesoporous or mesostructured inorganic materials in a thin film or membrane geometry is an active area of research.

They have high potential applications as selective electrodes, sensors and photocatalytic or electrochromic devices.

Mesostructure metal oxide – surfactant thinfilms are usually produced via solvent evaporation methods such as dip coating, spin coating, spontaneous growth of the nano composite as either a self-supporting film or on a substrate.

Recently, in situ luminescence of probe molecules was used to follow the chemical and structural changes occurring during the formation of lamellar silica films templated by SDS.

Preferential evaporation of alcohol gives a water-rich film near the end of the film development.

Pyrene fluorescence emission measurements provide evidence of micelle formation, breakup, and its transformation to the final lamellar structured films.

The mechanism inovlves cooperative nucleation of the inorganic silicate and its interaction with the organic SDS surfactant by the electrostatic forces followed by liquid-crystal formation of the lamellar hybrid phase structured by SDS.

# The Hofmeister Series of Anions

**The Hofmeister series orders ions with increasing salting-in potency from left to right,and is as follows.**

**$SO_4^{2-}$ ,$HPO_4^{2-}$,$OH^-$, $F^-$, $HCOO^-$, $CH_3COO^-$, $Cl^-$, $Br^-$, $NO_3^-$, $I^-$,**
**$SCN^-$, $ClO_4^-$**

**$Cl^-$ ion represents a border line case.**

**Ions on left of $Cl^-$ are called salting-out ions,water structure makers or cosmotropic ions.**

**Ions on the right of $Cl^-$ are called Salting-in,or water-structure breakers,or chaotropic ions.**

# Hofmeister anion effects

**Ion effects are ubiquitous in all branches of colloid science.**

**Recent works on mesoporous silica formation using cationic and non-ionic templates has unveiled a large number of anion effects.**

**Anions are seen to change the hydrolysis rates of the silica precursors,effecting the surface properties and morphologies of the final products after calcination.**

**They often improve the hydrothermal stability of the silica materials.**

The focus is exclusively on anions because – anions generally give stronger Hofmeister effects than cations and most mesoporous synthesis procedures use cationic or non-ionic surfactants as templates,and are strongly effected  by anions.

Recently,Ninham has argued that dispersion forces are involved in most reported Hofmeister effects.

Chaotropic ions are large and have large polarizabilities.

Cosmotroic ions are usually small,with relatively small polarizabilities.

Chaotropic ions easily lose their water and serve themselves as solvating species at an interface.

Cosmotropic ions will compete for water at various interfaces,leading to dehydration of the surface.

# Four distinct groups of anions with different interactions with cationic surfactants

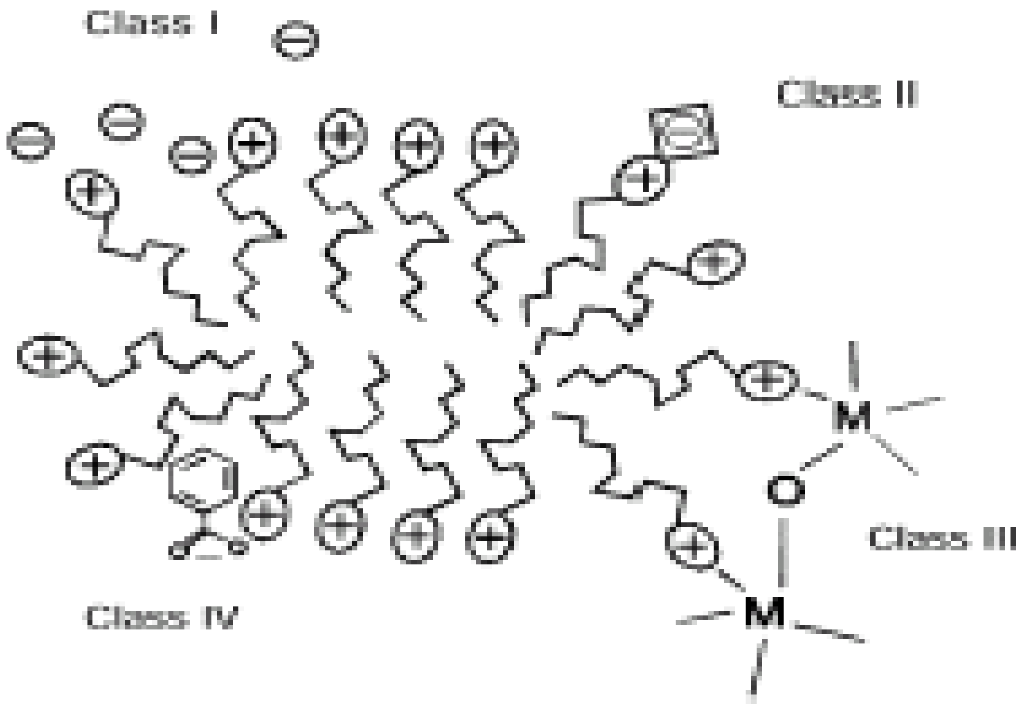


Fig. 1. A schematic of a cationic micelle with the four different classes of anions discussed in the text, which interact with the surfactant headgroups.

Class 1 : These ions do not bind strongly on the head groups and behave as typical counter ions.Most of the Hofmeister anions belong to this class.
Ex. $OH^-$ , $CH_3COO^-$ , $HCOO^-$

Class 2 : These ions are usually large complex ions with large polarizabilities which form water-insoluble ion pairs with the amine-based surfactants.
Ex. $AuCl_4^-$

Class 3 :This group consists of complex anions with transition metal ions, which form covalent bonds with the amine-head groups and also between themselves through oxygen bridges.

Class 4 : This group consists of a number of hydrophobic organic anions which partly dissolve in the palisade layer of the micelles.
Ex. Benzoate, salicilate, tosylate.

# Effect of Hofmeister anions on the size and shape of micelles of cationic surfactants.

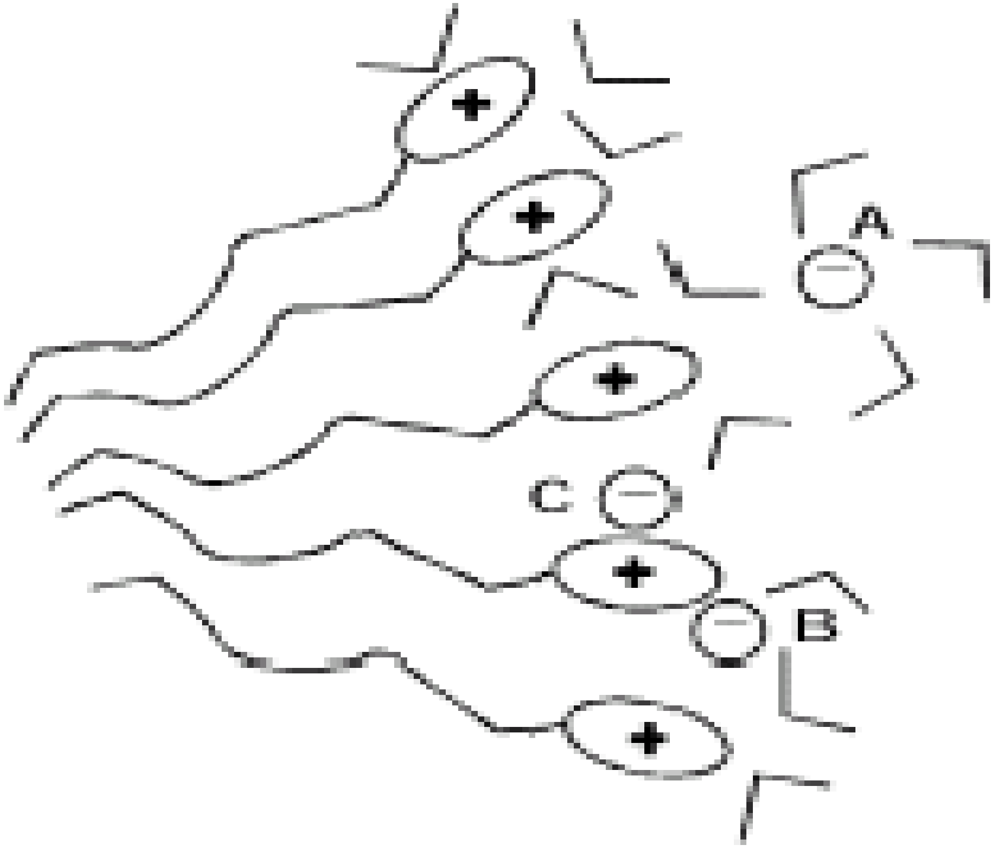


Fig. 2. A schematic of anion solvation in the palisade layer of cationic micelles.

Ions with larger hydrated sizes are not effective in neutralizing the surfactant charge thus leading to small spherical micelles.

As the hydrated size of the ion decreases and its polarizability increases the ions shield the electrostatic interactions better thus allowing the easier formation of rod like miceles.

Counter ion ability to induce the sphere-to-rod transition of alkyl trimethyl ammonium surfactants always follows the Hofmeister sequence.

$SCN^- > NO_3^- > Br^- > Cl^- > OH^- > F^-$

Quite high conc. of NaCl are required to obtain wormlike micelles with chloride-based cationic sufractants while $Br^-$ is a rod-inducing anion.

The affinity of anions towards cationic micelles is always found to follow the Hofmeister series.

# Conclusion:

The interaction between the inorganic precursor and the template is the key factor in the control of the material mesostructure.

However,the step where such interactions occur is still open to debate and appears to depend strongly on the synthesis conditions used.

It must be kept in mind that none of these mechanisms proposed provides an exclusive or definite answer.

Indeed,the characterization techniques are limited in terms of sampling, experiment time scale,and many more.
moreover, they specifically probe only one part of the system whereas the formation of these materials involves numerous steps.

This complexity probably explains the differences observed between the mechanisms proposed.

# References

M.E.Leonowicz,W.J.Roth,J.C.Vartuli,J.S.Beck
Nature,359(1992)710

Peter T.Tanev,Thomas J.Pinnavaia
Science,267(1995)865

Galen.D.Stucky,Qisheng Huo
Nature,368(1994)317

J.Patarin,B.Lebeau,R.Zana
Currnet opinion in colloid and interface science,7(2002)107-115

Epameinondas Leontidis
Current opinion in colloid and interface science,7(2002)81-91.