DICP Course - Dalian, 2012
Preparation of solid catalysts
Part 8

Supported by the Chinese Academy of Sciences

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IC2MP

Outline

Introduction and general aspects

Interfacial chemistry – Electrostatic adsorption

Impregnation, drying, calcination and/or reduction

Sol-gel chemistry processing

Deposition – Precipitation and Coprecipitation

Bimetallic catalysts

Outline

Shaping of solid catalysts – Monolith-based catalysts

Zeolite-based catalysts

Ordered mesoporous materials

Case studies:

- **Noble metal catalysts**
- **Methanol catalysts**
- **Hydrotreating catalysts**
- **……**

Outline

Zeolite-based catalysts

1) Introduction
   - hydrothermal synthesis

2) Acidity
   - zeolites
   - aluminophosphates

3) Synthesis
   - overall steps in zeolite crystallization
   - model for zeolite growth
   - aluminophosphates

Introduction

Zeolite = "boiling stone"

Definition: crystalline material with micropores and cation-exchange capacity, insoluble in water and with sufficient thermal stability
About 200 different framework types

Most important zeolites:
- **ultrastable Y (USY) (FAU = faujasite)**
- **ZSM-5 (MFI), ZSM-35 (FER = ferrierite) (ZSM = Zeolite Socony Mobil)**
- **mordenite (MOR)**
- **zeolite omega (MAZ = mazzite)**
- **SAPO-34 (CHA = chabazite)**

Applications:
FCC: fluid catalytic cracking (particles 70 – 100 µm)
Hydro-isomerization, hydrocracking…

Introduction: hydrothermal synthesis

Ex.: $M^{I}_{x}[Al_{x}Si_{y}O_{2(x+y)}]\cdot zH_2O$

$Na_2SiO_3 + NaOH + Al_2(SO_4)_3 + C_3H_7\text{-}NH_2 + (C_3H_7)_4N^+Br^- + H_2O$
160 °C, several days ➔ zeolites ZMS-5

Solvent: H_2O

Parameters:

- Temperature: T > boiling temperature (up to 300 °C)
- Pressure: increase with temperature

Ex.: water	T /°C	P /bar	
	120	1.9	(kitchen pressure cooker)
	150	4.5	
	200	14	
	250	33	

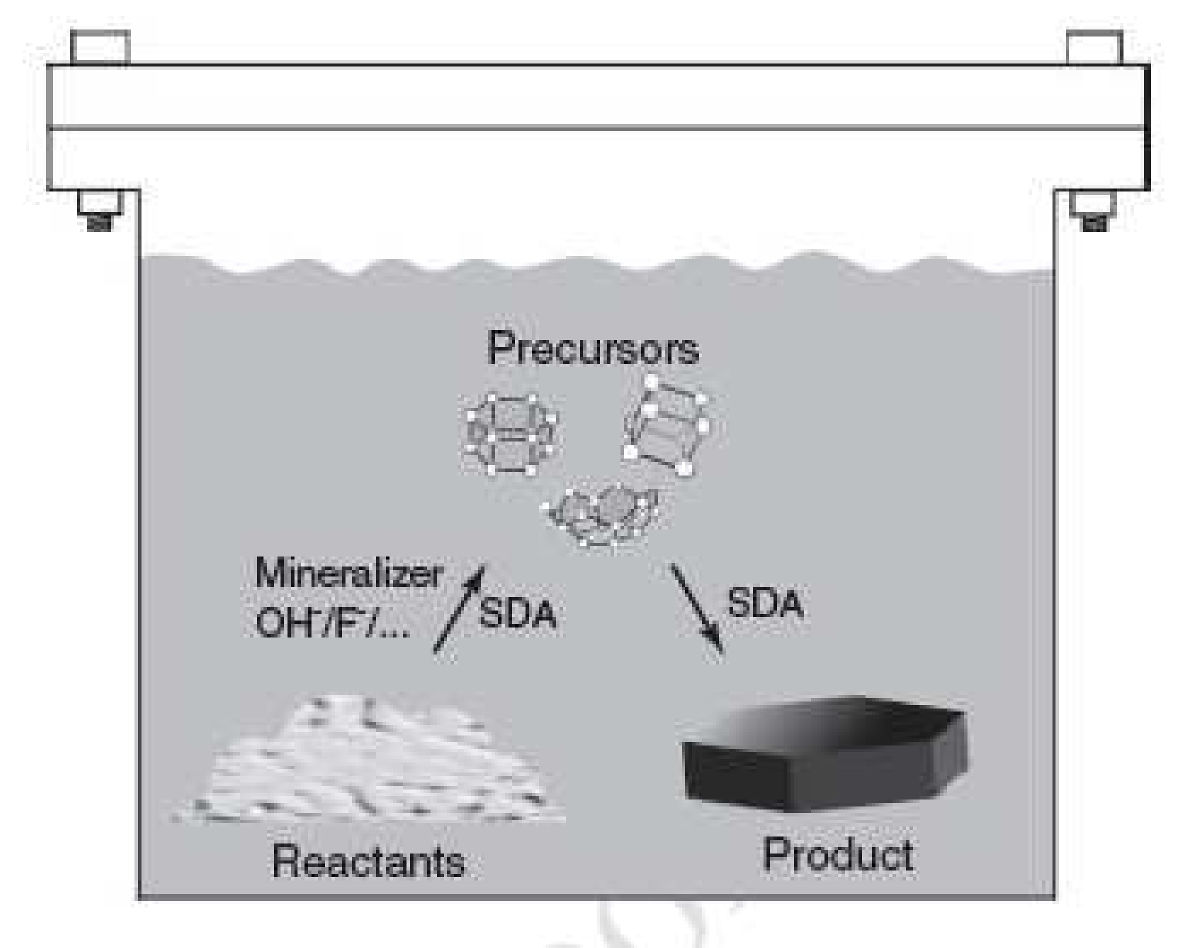
➔ use of autoclaves

First autoclave: 1645, Papin’s pot

Introduction: hydrothermal synthesis

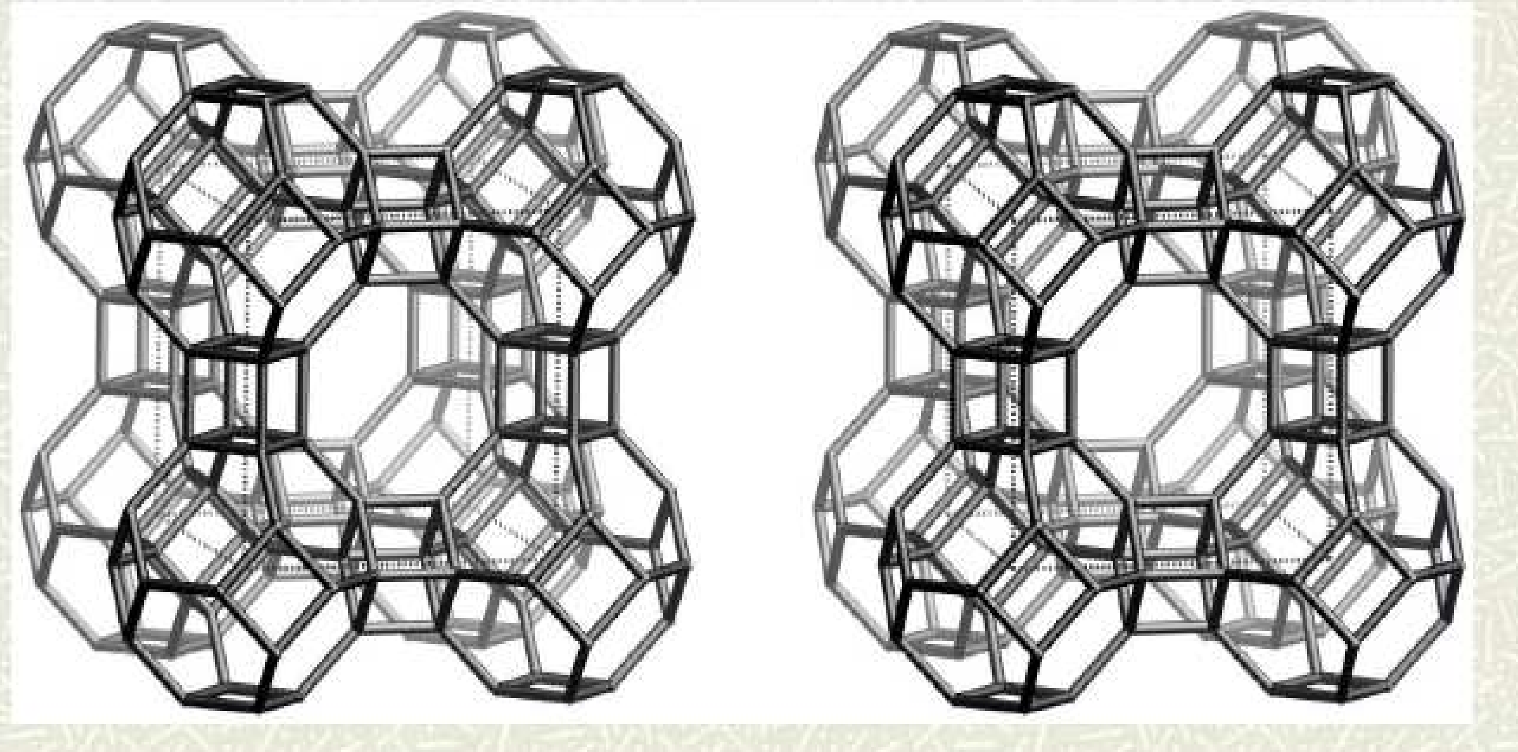
Schematic representation of zeolite formation process, from reactants to final crystalline product.

SDA = structure-directing agent (Handbook heterogeneous catalysis)



Introduction: exemple of structure

LTA framewotk



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Acidity: zeolites

Maximum number of protons (USY, ZSM-5…)
➔ 0.2 till 1.2 mmol g^{-1}
Depends on the Si/Al ratio

Formal charge of the bridging oxygen atoms:
Si-O-Si
Si-OH-Si
Si-O-Al
Si-OH-Al

Effect of structure on acid strength: Si-O-Al angle
➔ The higher the angle, the higher the acid strength of the proton
Angle between 130 ° (medium Brönsted acidity) and 180 ° (strong Brönsted acidity)

Acid strength is maximal at low Al concentration (high Si/Al ratio) ➔ isolated Al
Acis strength is minimal at the highest Al concentration

Acidity: aluminophosphates ($AlPO_4$-n)

P^{5+} and Al^{3+} cations alternate in T sites

O-P-O-Al-O-P-O-Al-O

→ no acidity

Si substitution to P → $SiAlPO_4$ (or SAPO)

→ variable acid properties → see figure

Ex.: SAPO-37 (FAU)

T-atom %	Si 12.5 %	Al 50 %	P 37.5 %

Environment:

Si: 4 Al

P: 4 Al

Al: 3 P + 1 Si

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Synthesis: overall steps in zeolite crystallization

Hydrothermal conversion in supersaturated conditions

Ex. sodium silicate Na_2SiO_3 + sodium aluminate $NaAl(OH)_4$ + organic bases $NR_4^+OH^-$

$M^n_{x/n}[Al_xSi_yO_{2(x+y)}]\cdot zH_2O$

Si/Al ratio adjustable

- **low (close to 1) ➔ 70 – 100 °C**
- **high ➔ hydrothermal synthesis ➔ gels, 100 – 350 °C, autoclave**

M: column 1 or 2

Parameter:

- **Si/Al ratio**
- **H_2O/Si ratio**
- **HO-/Si ratio**
- **inorganic cations/Si**
- **organic additives/Si ➔ templates**
  - **structure directing agent**
  - **structure determining effect**

Synthesis: overall steps in zeolite crystallization

Ex.: synthesis of ZSM-5

TPABr = $[(C_3H_7)_4N]^+ Br^-$
TPEABr = $[(CH_3\text{-}C_3H_7)_4N]^+ Br^-$
TPAOH = $[(C_3H_7)_4N]^+ HO^-$

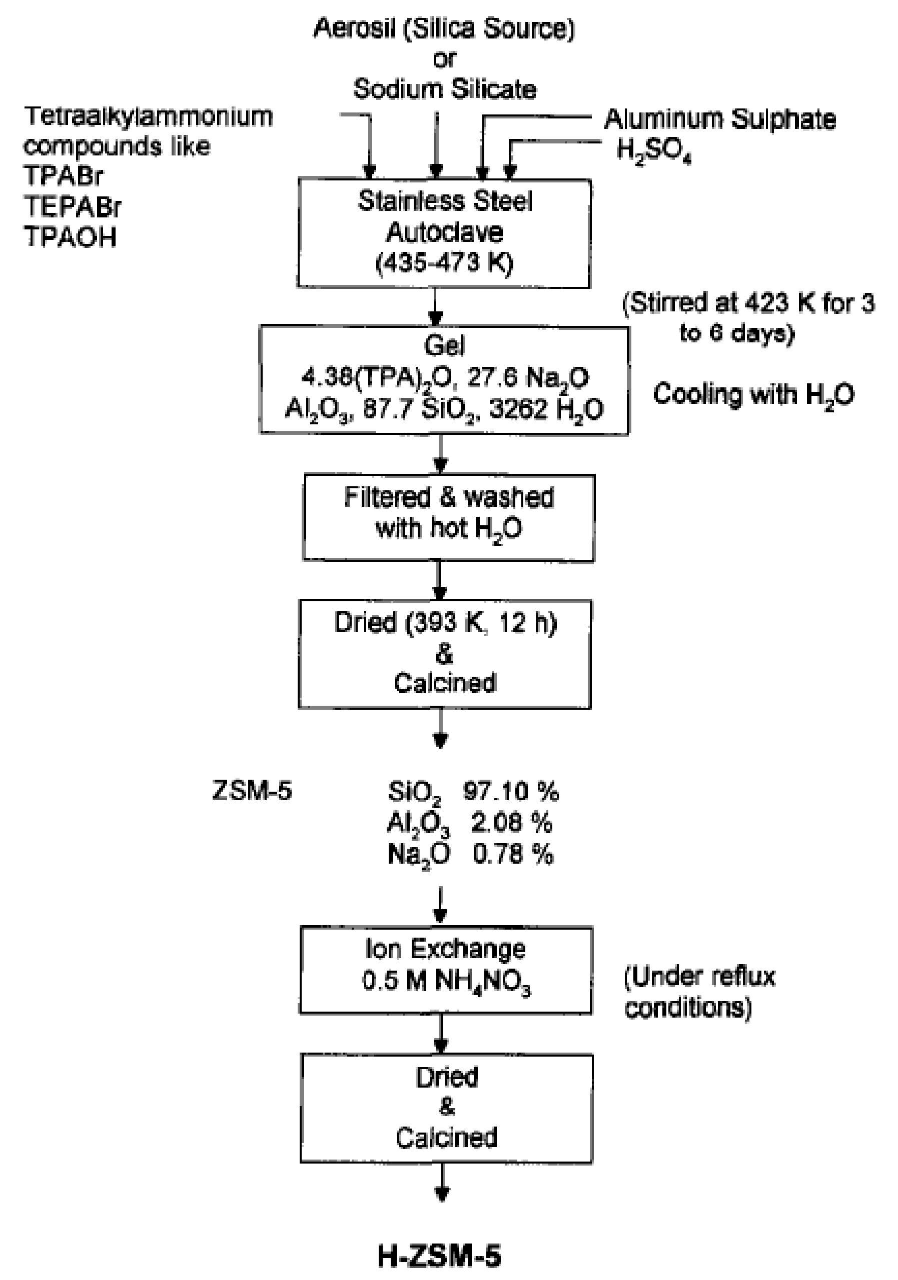
Composition of the gel
4.38 $(TPA)_2O$, 27.6 Na_2O
Al_2O_3, 87.7 SiO_2, 3262 H_2O

Ion exchange with NH_4NO_3

Drying, calcination 550 °C

Binding: binder alumina (50 wt.-%)
+ plasticizer (1 %) + peptizer (1 %)
Forming by extrusion ➔ pellets

C Perego, P. Villa, Catalysis Today 34 (1997) 281-305



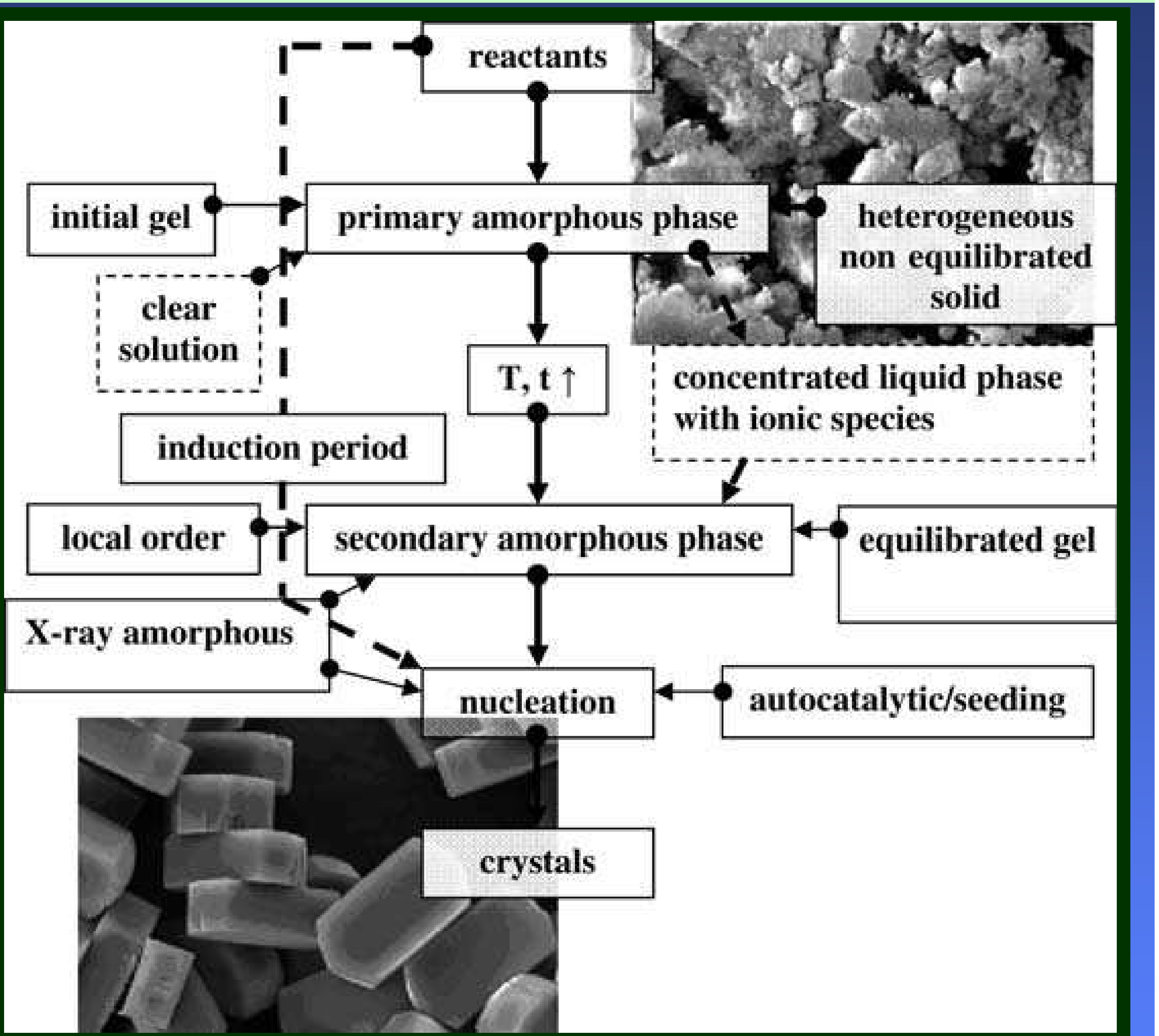
Synthesis: overall steps in zeolite crystallization

Induction period

Primary amorphous phase

Local order via successive depolymerization/polymerization

Secondary amorphous phase



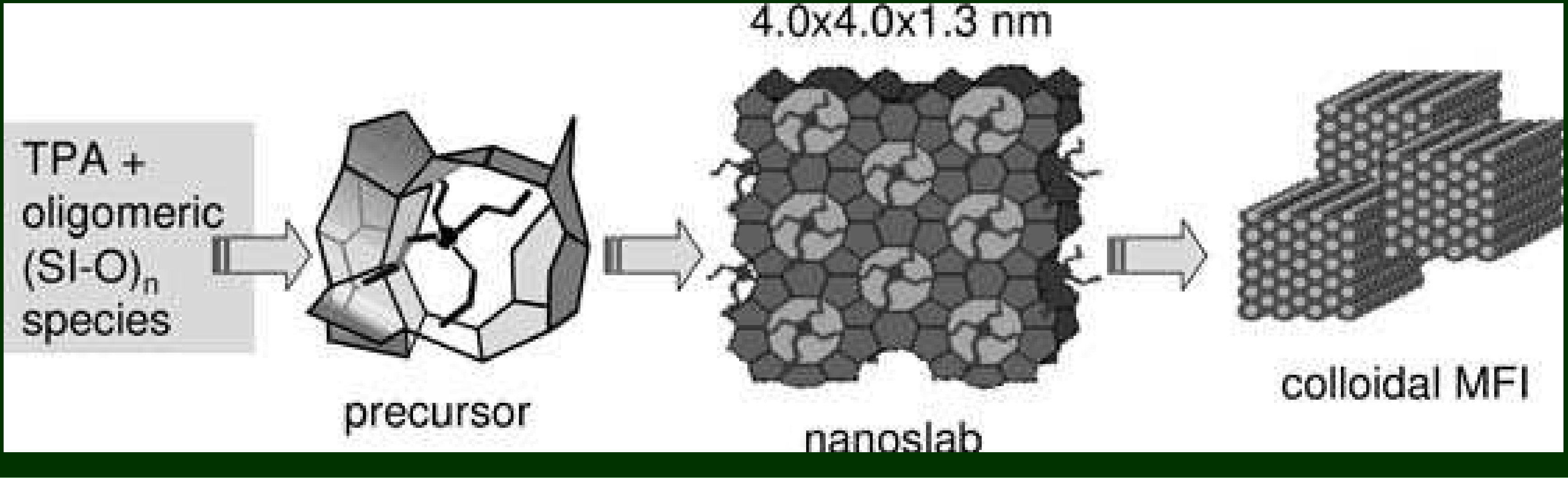
Scheme of equilibration and change of order during a zeolite synthesis

Synthesis: model for zeolite growth

Classical nucleation-crystallization theory
➔ Viable nucleus: between one and eigth unit cells

Role of structure directing agents (SDA)
Tetrapropylammonium ions (TPA, $N(C_3H_7)_4^+$) at interphase between aqueous and organosilicon (TEOS) phases. Silicate condenses around TPA ions
Zeolitization parameters: composition, basicity (pH 9 to 13), presence of mineralizing agents and template molecules
$x\ SiO_2 : y\ Al_2O_3 : z\ Na_2O : u\ R : v\ H_2O$ R = organic species

Schematic representation of successive agglomerations of Si–O intermediates synthesis of MFI structures, with nanoslabs as key intermediates



Synthesis: model for zeolite growth

Role of template (structure directing agent SDA) ➔ Influence zeolitization process

SDA species surrounded by alumino-silicates in a particular geometry

➔ building units

- Na$^+$(aq) templates four-rings (4Rs).
- TMA (tetramethyl ammonium)

➔ two 4Rs form D4R

➔ Si-rich of Al-rich zeolite A (LTA)

Low Al content

three 4R form D6R

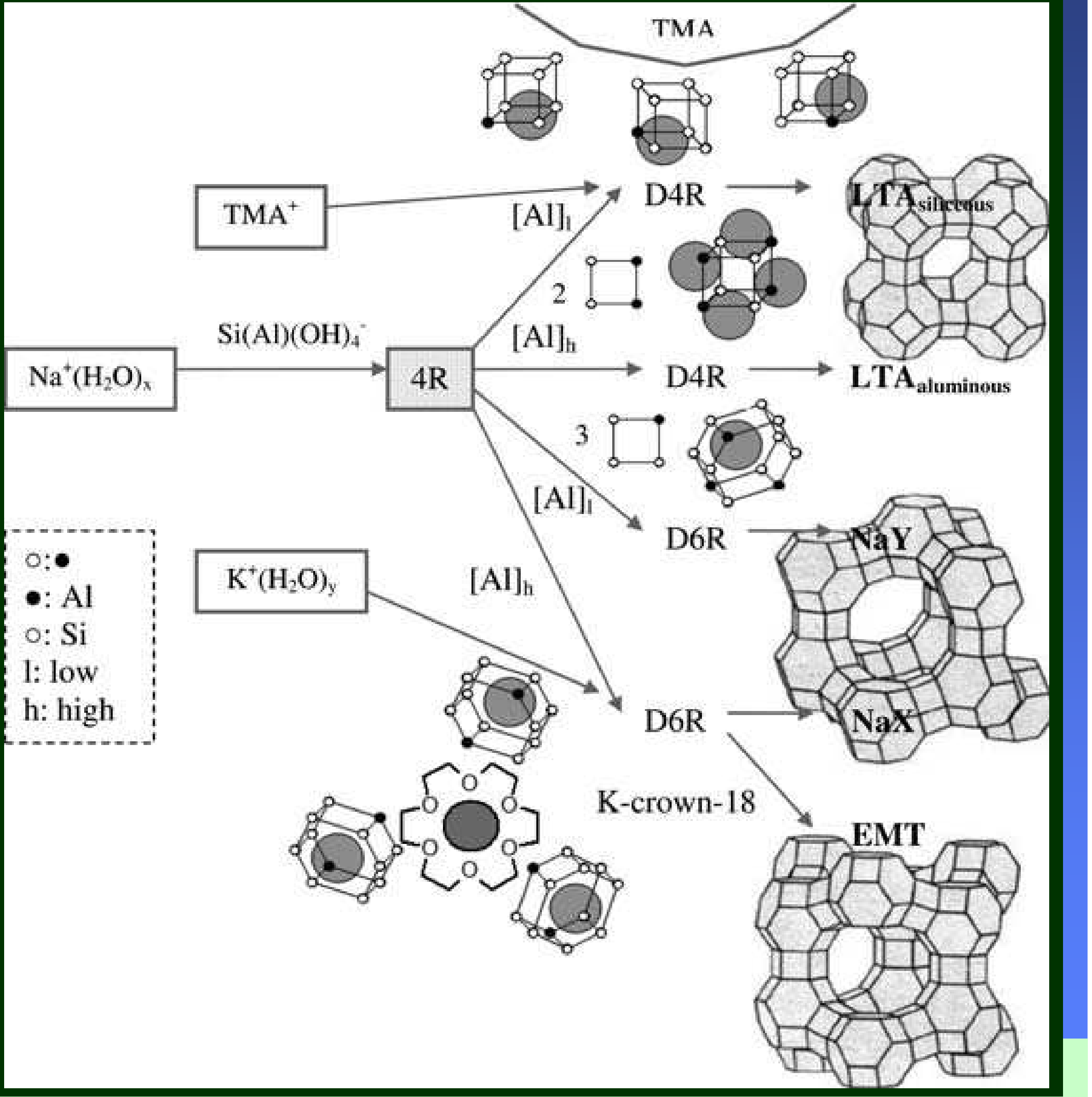
➔ NaY zeolite

high Al content and K$^+$(aq)

➔ NaX zeolite

- 18-crown-6

D6Rs ➔ EMT zeolite



(in de Jong, 2009)

Synthesis: AlPO4-n-based molecular sieve zeolites

Phosphate source: phophoric acid H_3PO_4 (pK_a 2, 7, 12)   pH 3 to 10
Al source: pseudoboehmite $AlO(OH)\cdot nH_2O$

Ex. $Pr_3N : Al_2O_3 : P_2O_5 : 40\ H_2O$

Acronyms and T atom composition of AlPO4-n-based molecular sieve zeolites.

Acronym	T atoms
AlPO4-n	Al, P
SAPO-n	Si, Al, P
MAPO-n	M (Co, Fe, Mg, Mn, Zn)
MAPSO-n	M, Al, P, Si
ElAPO	El (As, B, Be, Ga, Ge, Li, Ti)
ElAPSO	El, Al, P, Si

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Shaping of solid catalysts – Monolith-based catalysts

Zeolite-based catalysts

➡ **Ordered mesoporous materials**

Case studies:

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- **……**

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Ordered mesoporous materials

1) Introduction

2) mesoporous silica
    - synthesis strategy
    - pore models
    - exemples
    - pore size control
    - functionalization

3) mesoporous carbon

Introduction

New class of porous solids with uniform pore size 1.5 to 40 nm, large surface area (up to 2500 $m^2 g^{-1}$) and tunable structure
Driving force ➔ self-assembly of molecules
Weak bonds: van der Waals bonds, electrostatic bonds, hydrogen bonds, hydrophobic interactions, π-π stackings.

Pore wall remain amorphous (mesoporous silica)

1-D porosity ➔ cylindrical channels

2-D porosity ➔ lamellar silica sheets

3-D porosity ➔ cubic structure, channels extending in 3 directions

Synthesis - use of amphiphilic molecules (surfactants)

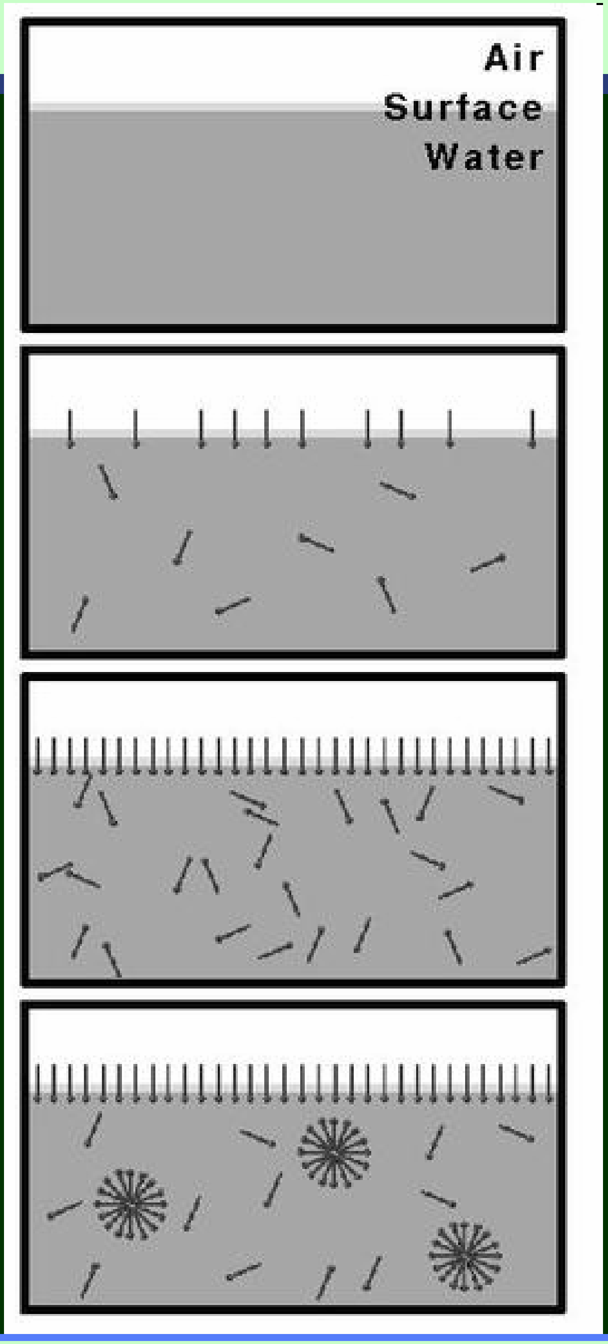
Evolution of structure versus the surfactant concentration
➔ Figure
Cmc = critical micelle concentration

Introduction

Evolution of structure versus surfactant concentration
Cmc = critical micelle concentration

Top to Bottom:
Increasing concentration of surfactant
→ forming a layer on the surface and
→ forming micelles above the CMC

The forming 1-D-tubes, 2-D bilayer and 3-D cubes

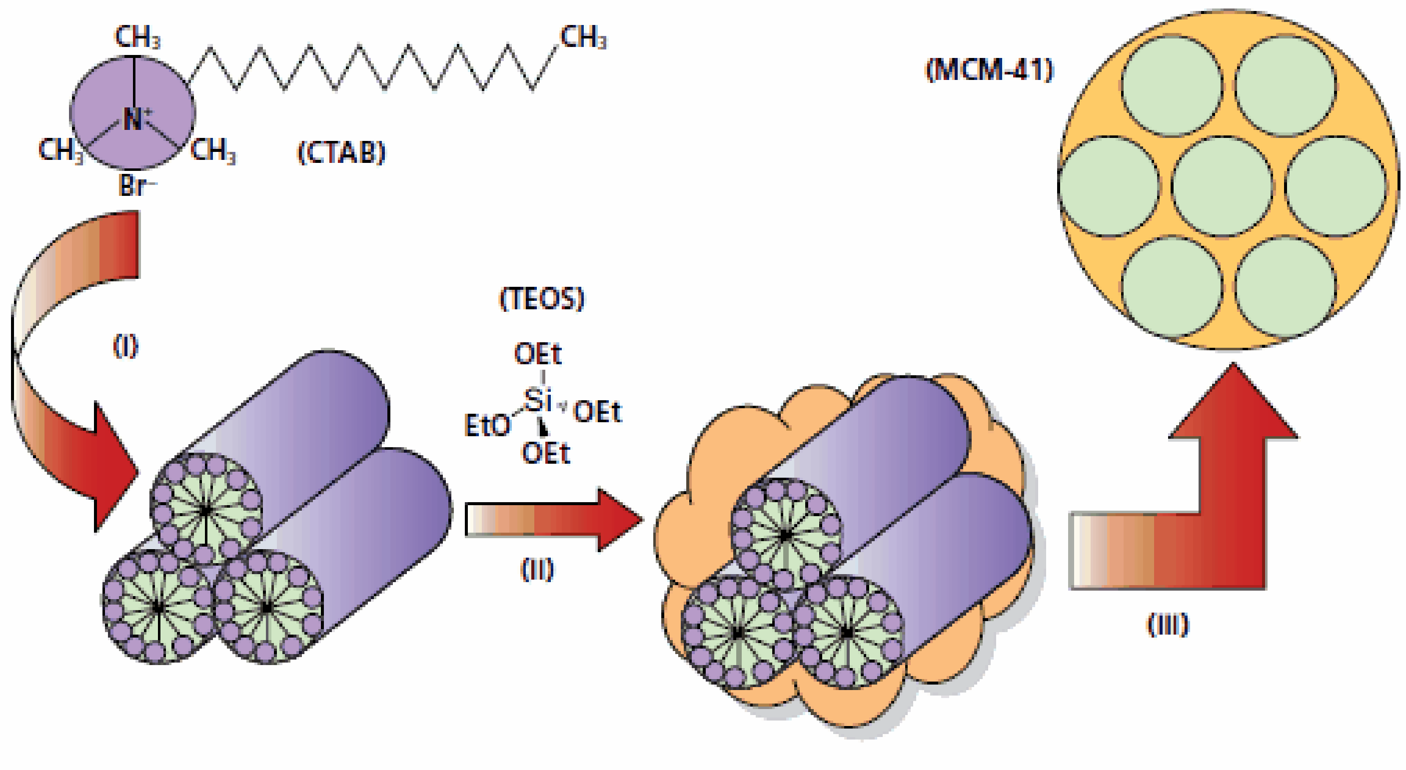


Introduction: exemple of preparation (MCM-41)

(i) Surfactant (cetyltrimethylammonium bromide, CTAB, $(CH_3)_3N(CH_2)_{15}CH_3Br$)
➔form liquid crystalline micelles in water

(ii) Ceramic sol-gel precursor (tetraethoxysilane, TEOS, $(C_2H_5O)_4Si$) is added
➔ silica network around the micelles upon hydrolyses and condensation

(iii) Removal of the organic template by calcination or solvent extraction
➔ mesoporous ceramic material



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→ **2) mesoporous silica**
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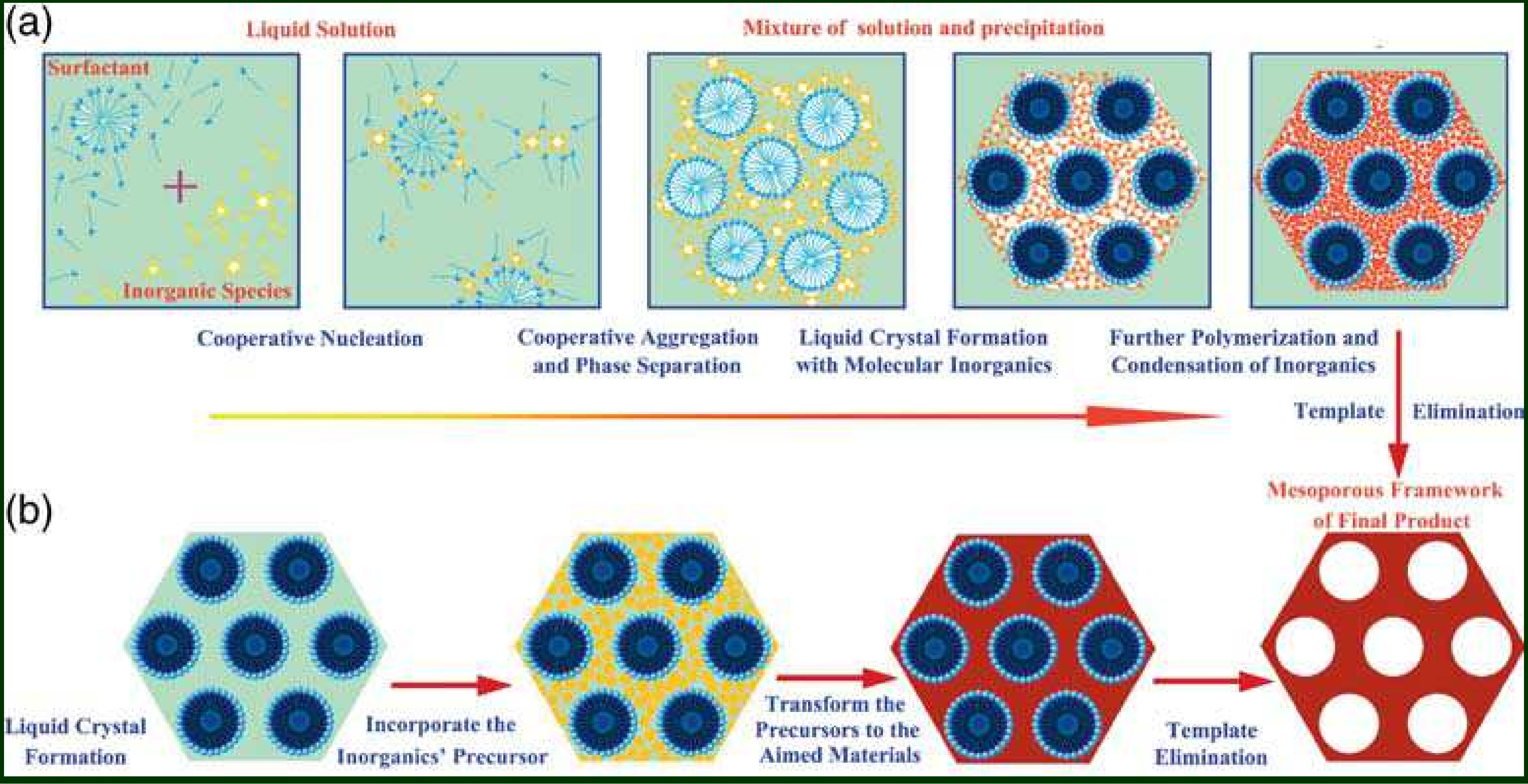
3) mesoporous carbon

Mesoporous silica: synthetic strategy

Route (a): cooperative self-assembly due to interaction between inorganic and organic species at the molecular scale → 3D ordered arrangements.

Route (b): true liquid-crystal template pathway → forms 3D ordered arrangements, and then incorporates the inorganic precursors.

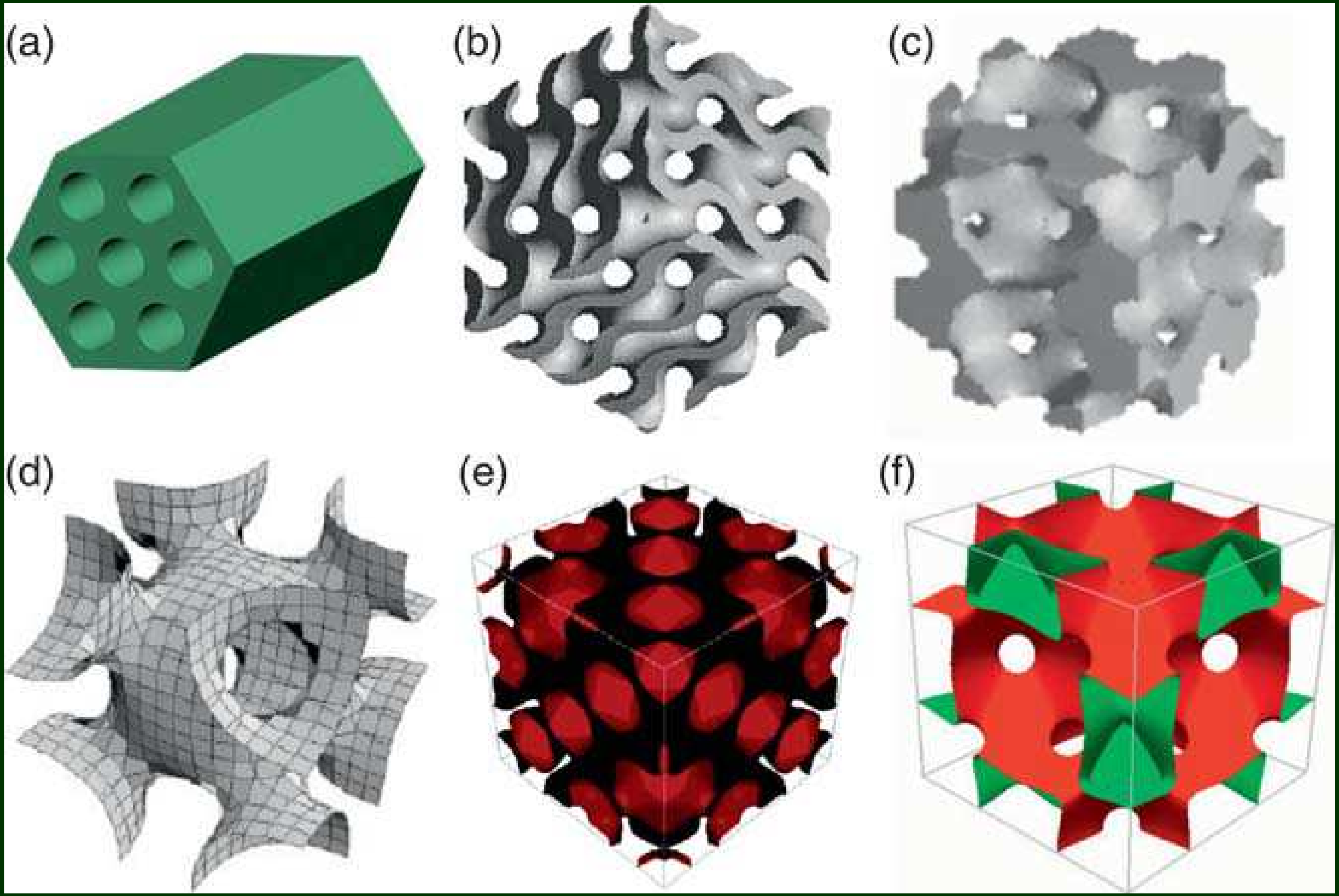
Most of the mesostructure belong to hexagonal or cubic phases



Mesoporous silica: pore models

Pore models of mesostructures with symmetries of

(a) p6mm,
(b) Ia3d,
(c) Pm3n,
(d) Im3m,
(e) Fd3m, and
(f) Fm3m.



Mesoporous silica: examples

MCM-41 = Mobil Catalytic Material #41

Quaternary cationic surfactants $[(CH_3)_3NC_nH_{2n+1}]^+ X^-$ (n even, 8 to 16; X = Cl, Br)

Cell parameters from XRD and TEM: about 4 nm

Symmetry: P6mm

Pore channel geometry: cylinders

Pore wall thickness about 1 nm

BET surface area > 1000 $m^2 g^{-1}$

SBA-15 = Santa Barbara Amorphous #15

Symmetry: P6mm

Prepared from P123 at 40 – 100 °C (triblock copolymer)

Pluronic123 = $HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{20}H$,

Uniform pore size 6.5 to 10 nm

Pore wall thickness 3.1 to 4.8 nm

➔ higher thermal stability

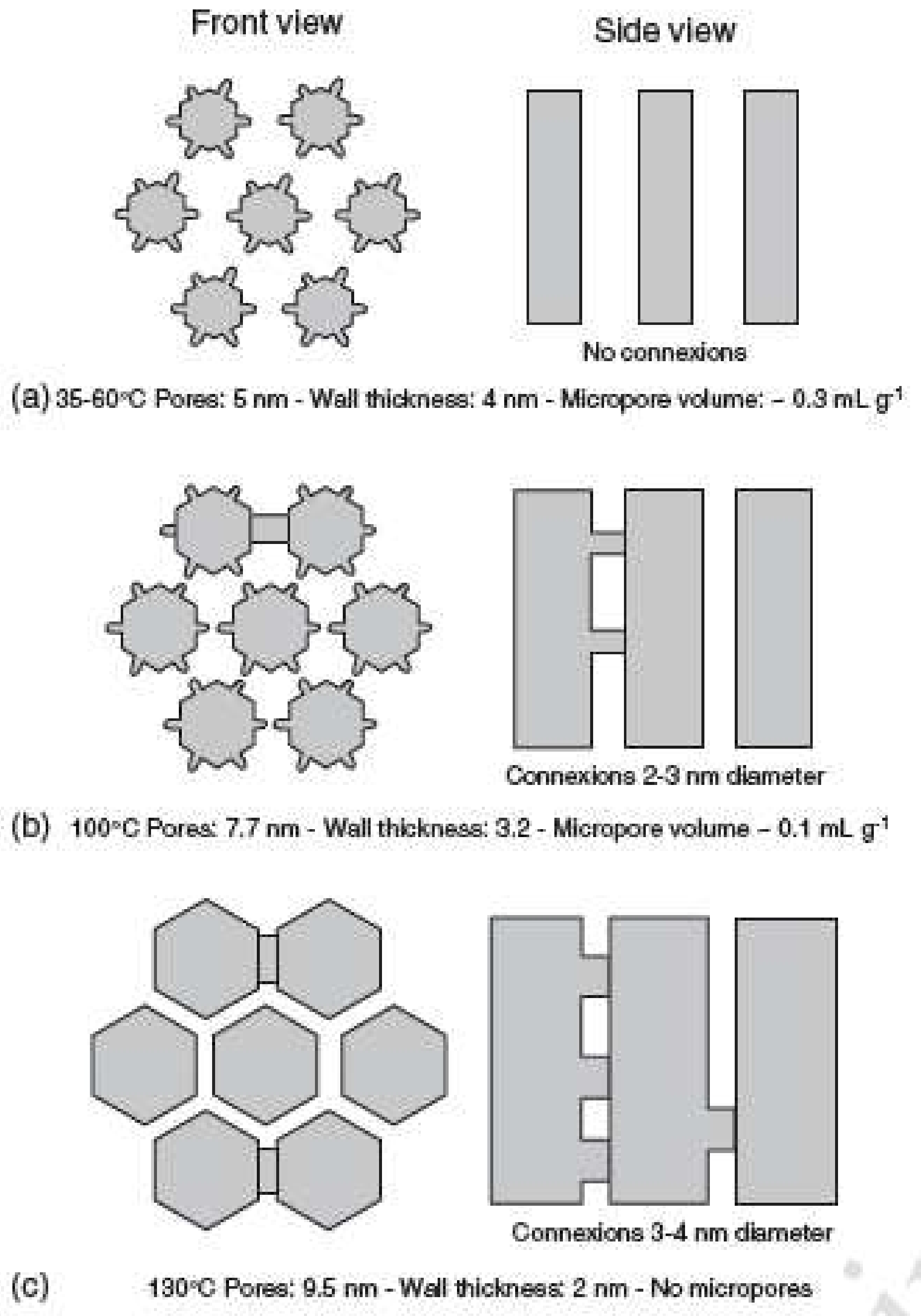
MCM-48

Symmetry: Ia-3d

Mesoporous silica: SBA-15

SBA-15 = Santa Barbara Amorphous #15
Left: representation of the pore topology, synthesis
(a) between 35 °C and 60 °C;
(b) at 100 °C;
and (c) at 130 °C.

➔ pore size increases
➔ channels progressively interconnected



(a) 35-60°C Pores: 5 nm - Wall thickness: 4 nm - Micropore volume: ~ 0.3 mL g^{-1}

(b) 100°C Pores: 7.7 nm - Wall thickness: 3.2 - Micropore volume ~ 0.1 mL g^{-1}

(c) 130°C Pores: 9.5 nm - Wall thickness: 2 nm - No micropores

Mesoporous silica: pore-size control

Pore sizes of ordered silica mesostructures obtained by various methods.

Pore size (nm)	Method
2–5	Surfactants with different chain lengths
4–7	Long-chain quaternary cationic salts as surfactants High-temperature hydrothermal treatment
5–8	Charged surfactants with addition of organic swelling agents such as TMB and midchain amines
2–8	Nonionic surfactants
4–20	Triblock copolymer surfactants

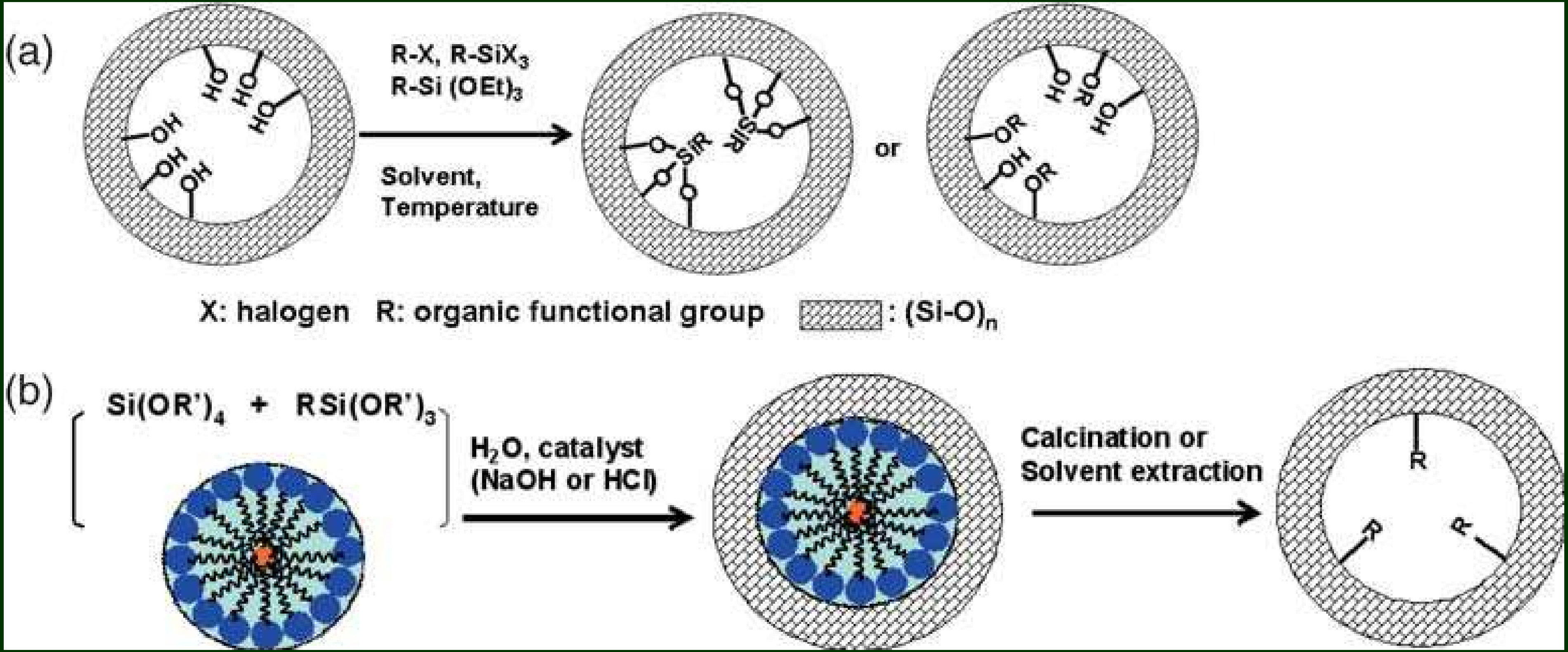
- Adding swelling agents expand pore sizes (ex.: dodecane, trimethyl benzene (TMB)

- Hydrothermal treatment: pore size of SBA-15 can be tuned from 4.6 to 10 nm by increasing the temperature from 70 to 130 °C

Mesoporous silica: functionalization

Schematic diagram for
(a) Grafting

(b) Co-condensation with surfactants



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➡ 3) mesoporous carbon

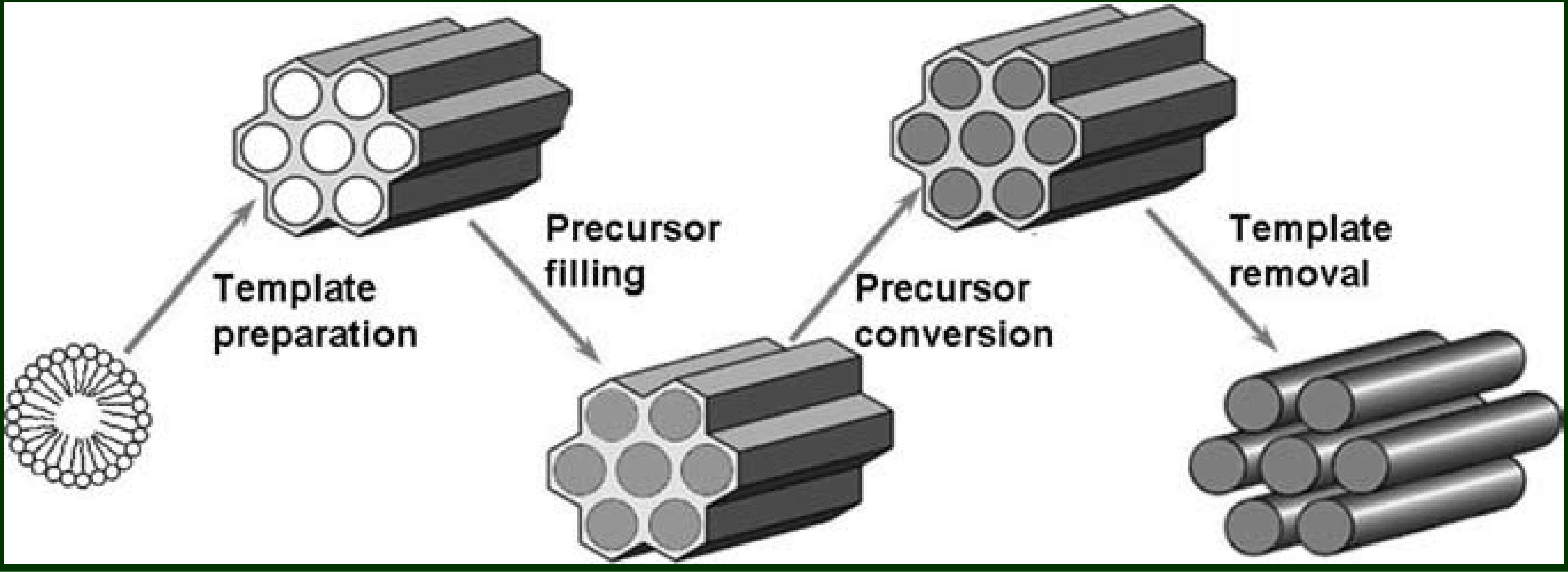
Carbon: hard templating approach by nanocasting

Ordered mesoporous silicates employed as templates for formation of other materials

Precursor incorporated in the channels (impregnation, ion-exchange, adsorption;;;)

Heat treatment ➔ precursors are decomposed, nanoparticles are formed and growth in the channels
Mesoporous silica templates are dissolved

➔ Pore size distribution wider than the silica template



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