Chapter 2.1. Template Method

2.1.3 Nanostructured Ceramics (AAO, Porous Silica, Zeolite)

2.1.3.1 AAO

1. Introduction of AAO
2. Fabrication method
3. Theoretical analysis
4. Application of AAO

2.1.3.2 Mesoporous Silica

1. Introduction of porous silica
2. Synthetic mechanism of porous silica
3. Structure of porous silica
4. Application of porous silica

2.1.3.3 Zeolite

1. Introduction of Zeolite
2. Properties and Applications of Zeolite
3. Synthesis of Zeolite
4. Zeolite Template for Organic Nanomaterial Synthesis

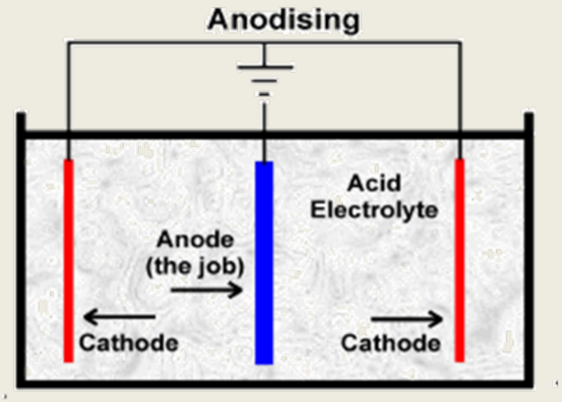
1.1. Introduction of AAO

- **Anodzing**

Anodizing is an electrochemical process in which the part is made the anodic electrode in a suitable electrolyte. Sufficiently high voltage is deliberately applied to establish the desired polarization to deposit oxygen at the surface (O_2 overvoltage). The metal surfaces or ions react with the oxygen to produce adherent , oxide coatings, distinguishing the process from electro-brightening or electropolishing processes.

- **Aluminum Anodzing**

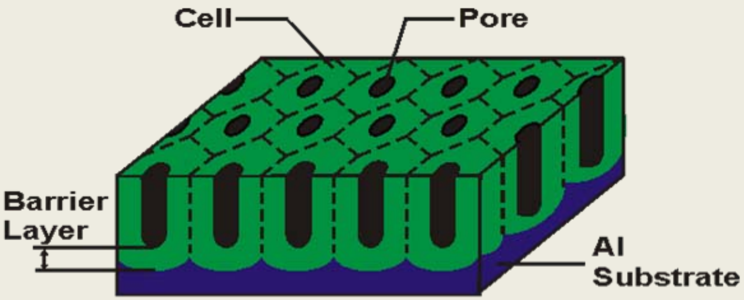
- Electrolyte: acid/water solution
- Power: DC electric current
- Cathode: Lead, Pt



1.1. Introduction of AAO

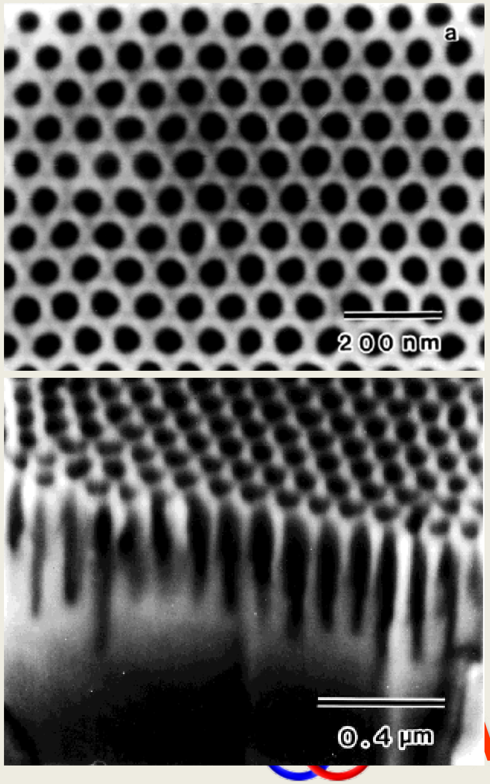
- **What is AAO (Anodic aluminum oxide)?**

Aluminum oxide grown on an Al substrate in an electrolytic cell. The resulting structure consists of an array of tunable nanometer-sized pores surrounded by an alumina backbone.



- **The Advantages of AAO**

- Ease of fabrication
- Low cost process
- High aspect ratio (~1000)
- High pore density (~10^{11} pores/cm^2)
- High uniformity
- Simple control of diameter, length, density
- Large area fabrication



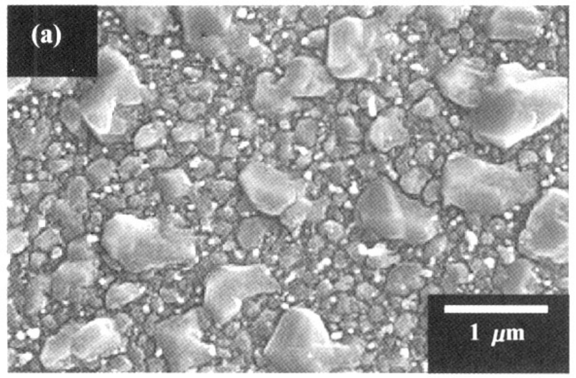
Adv. Mater., **2000**, *12*, 444.

1.2. Fabrication Method

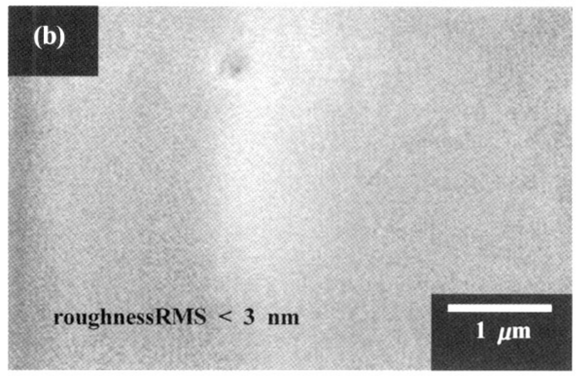
- **Conventional process**

Annealing → Electropolishing → Anodizing → Pore widening

1. Annealing aluminum plate
   - Enhancing the grain size, Reducing the internal stress
2. Electropolishing
   - Remove surface irregularity (Surface roughness: 5㎛→2~3nm)
   - Electrolyte: $HClO_4$, H_2SO_4



Before electropolishing



After electropolishing

1.2. Fabrication Method

- **Conventional process (continue)**

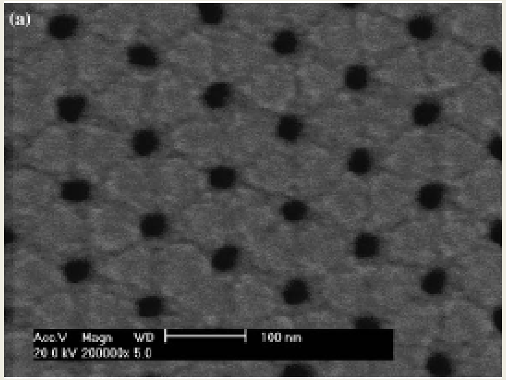
3. Anodizing
   - Electrolyte : Oxalic acid, Phosphoric acid
   - Voltage range : 25~40V
   - Thickness of wall is proportional to the voltage.
   - Pores initiate **at random positions** through field-assisted dissolution of the oxide at the oxide/electrolyte interface.
   - Irregular arrangement of aluminum oxide pores : Shortcoming of AAO

4. Pore widening
   - Surfuric, oxalic, phosphoric acid dissolves aluminum oxide
   - Controlling the pore size up to 500nm

1.2. Fabrication Method

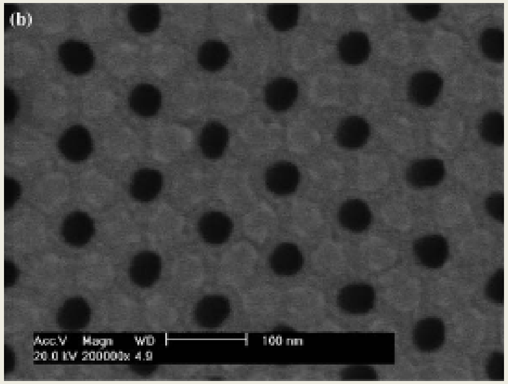
4. Pore widening (continue)

Time dependence



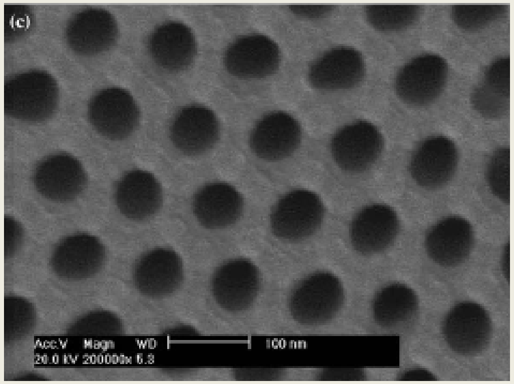
Before widening

<



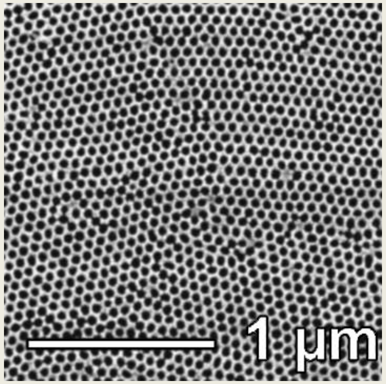
30min widening

<



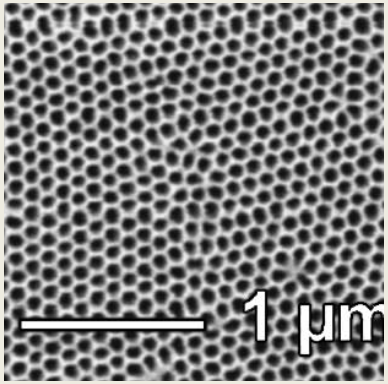
50min widening

Acid dependence



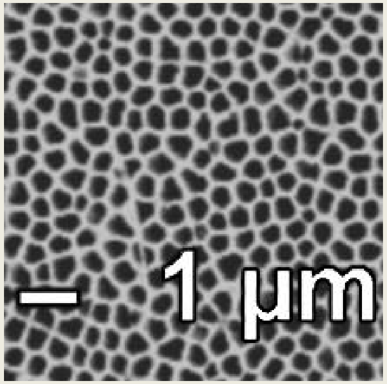
Sulfuric acid

<



Oxalic acid

<<



Phosphoric acid

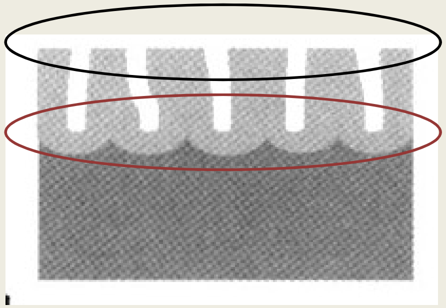
Cur. Appl. Phys., **2006**, *6S1*, e125.

1.2. Fabrication Method

- **Two-step anodizing process**

Masuda found that pores were self-organized in specific condition(proper voltage, long anodization times).

Volume of alumina is bigger than that of aluminum, thus there are forces between neighboring pores due to the mechanical stress which is associated with the expansion during oxide formation at the metal/oxide interface.



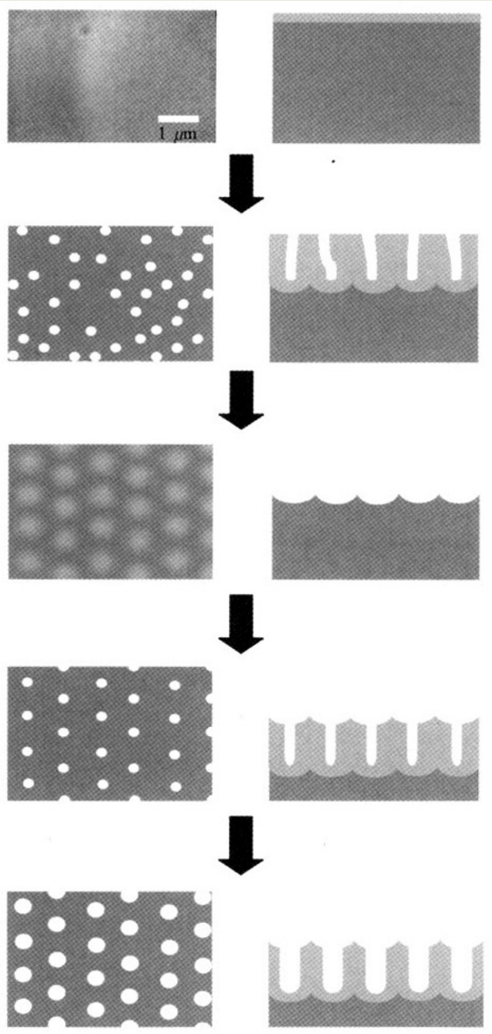
Pores are randomly generated on the surface

As pores grow, they are self-organized

That film is then removed with acid, leaving a regularly arranged array of indentations in the underlying aluminum. These indentations are seeds for the generation of an ordered pore array during a second anodization step.

1.2. Fabrication Method

- **Two-step anodizing process (continue)**



Annealing, Electropolishing

1st anodizing

Removal oxide layer
(Regular pore generated)

2nd anodizing

Pore widening

CNDL

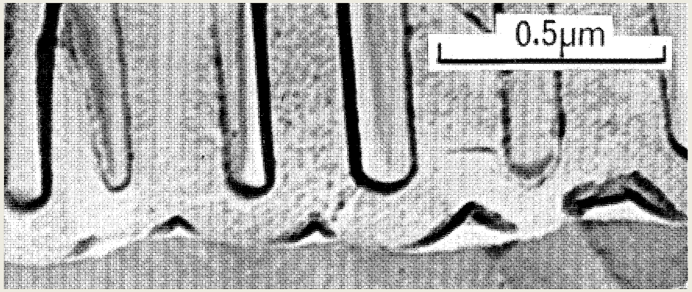
1.2. Fabrication Method

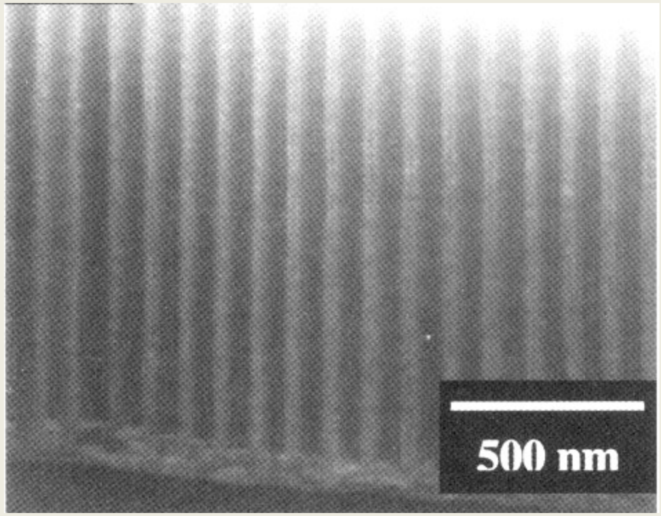
- **Comparing two processes**

Conventional press

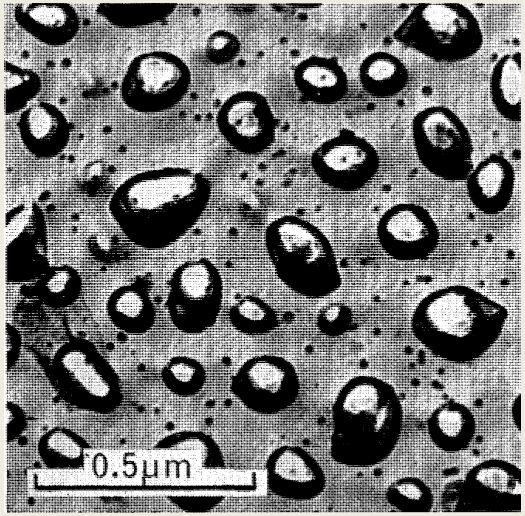
Two-step anodizing process

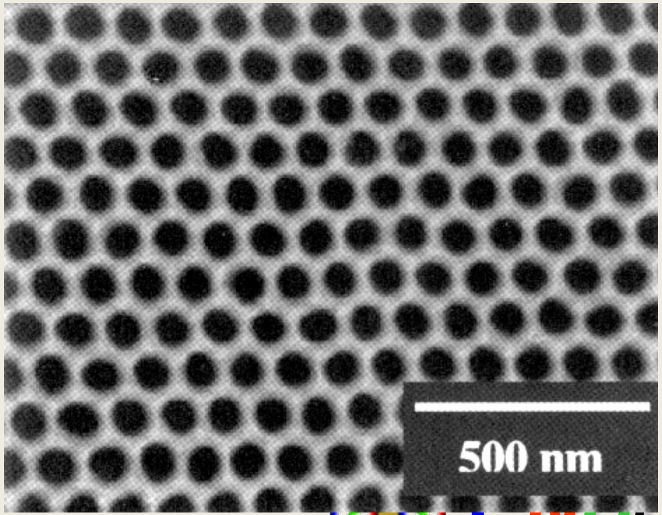
Side view





Top view



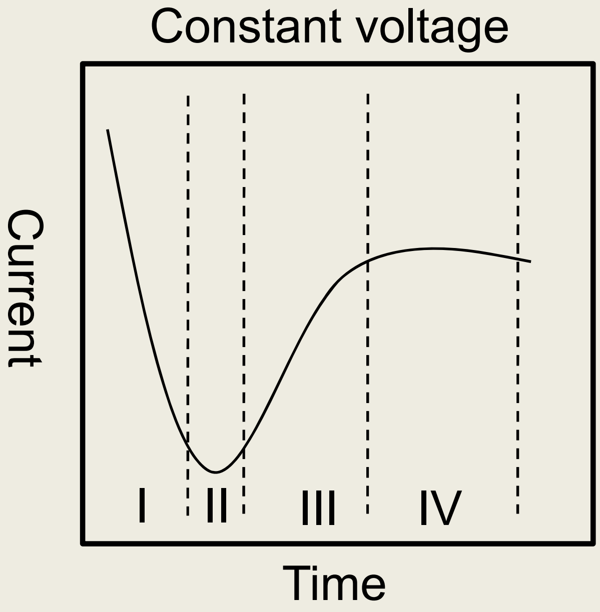


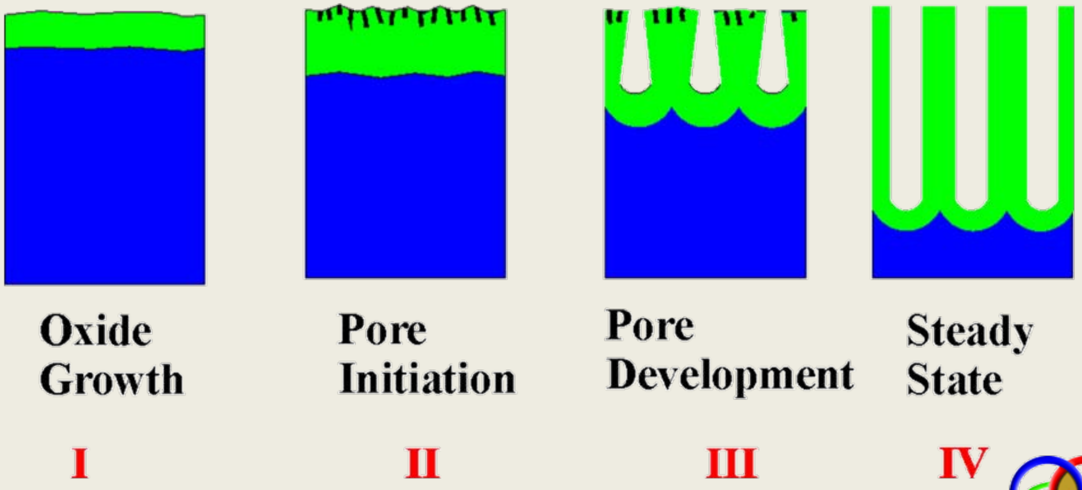
Science, **1995**, *268*, 1466., *Proc. Roy. Soc. Lond. A.*, **1970**, *317*, 511.

1.3. Theoretical analysis

- **Overview of film anodization**

  - Initially oxide growth dominates. (I)
  - Dissolution becomes competitive, barrier layer thins, and pores initiate. (II)
  - Approaches steady state where both mechanisms occur at roughly the same rate. (III and IV)





J. Phys. D:Appl. Phys., **1992**, *25*, 1258.

1.3. Theoretical analysis

- **Stage I**

  - Immediately after switching on the anodic bias a barrier oxide layer starts to grow
  - Current decreases due to the resistance of aluminum oxide

(1) Al^{3+} ions form at the metal/oxide interface

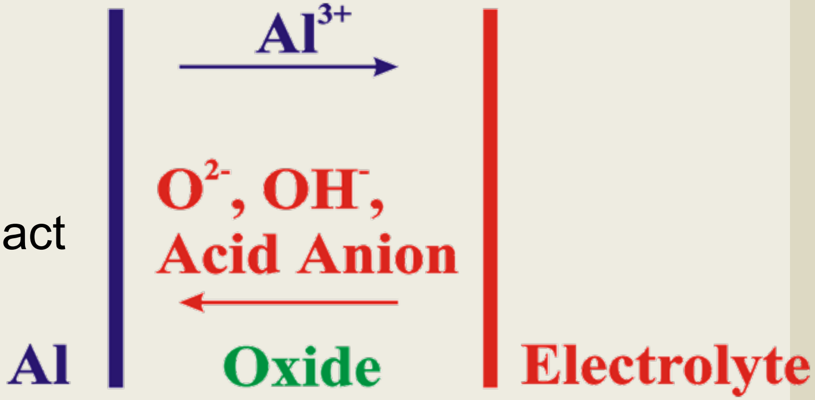
$$2Al \rightarrow 2Al^{3+} + 6e^-$$

(2) The electrolysis of water occurs at the oxide/electrolyte interface

$$3H_2O \rightarrow 3O^{2-} + 6H^+$$

(3) Due to the electric field, the O^{2-} ions migrate within the barrier layer, and react with the Al^{3+} ions

$$2Al^{3+} + 3O^{2-} \rightarrow Al_2O_3$$



Al^{3+}

O^{2-}, OH^-, Acid Anion

Al

Oxide

Electrolyte

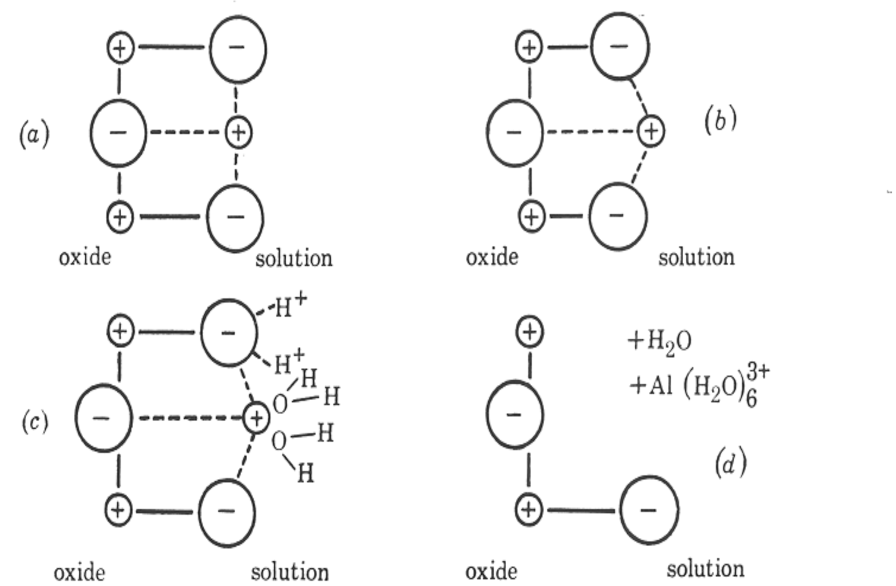
1.3. Theoretical analysis

- **Stage II**

  - Relatively fine-featured pathways are then revealed in the outer regions of the barrier oxide prior to any true pore formation.

  - There is an electric-field-enhanced oxide dissolution at the electrolyte/oxide interface.

$$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+}(aq) + 3H_2O$$



Schematic representation of the field-assisted dissolution of Al_2O_3 (*a*) before polarization, (*b*) after polarization, (*c*) removal of Al^{3+} and O^{2-} ions, and (*d*) the remaining oxide.

1.3. Theoretical analysis

- **Stage II (continue)**

  - This polarization effectively lowers the activation energy for dissolution of the oxide.

  - This promotes solvation of Al^{3+} ions by water molecules and the removal of O^{2-} ions by H^+ ions.

  - This processes is strongly dependent on the E-field strength.

- **Stage III**

  - Further anodizing results in propagation of individual paths through the barrier oxide with their heads becoming enlarged.

  - Aluminum oxide barrier become thinner → Resistance decreases → Current increases.

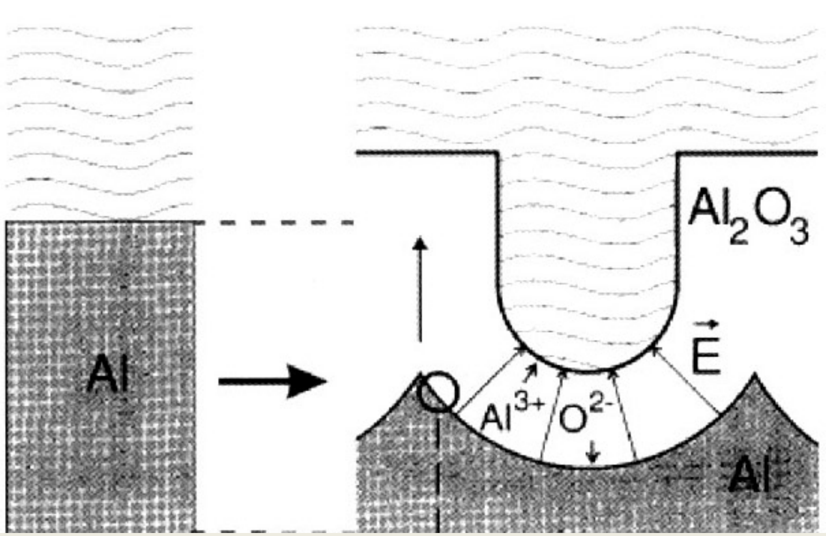
  - Etching rate is still higher than oxidation rate.

1.3. Theoretical analysis

- **Stage IV**

  - Reaction of etching and oxidation reaches steady-state.

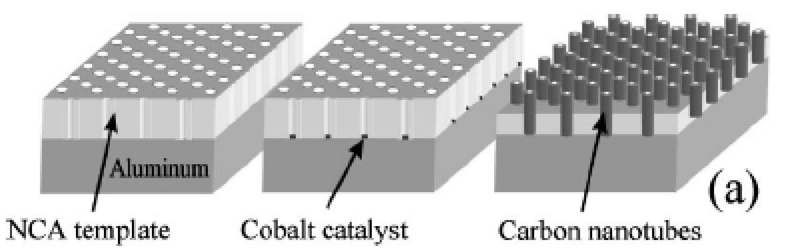
  - A steady-state pore structure is formed by closely packed cylindrical cells. Each containing a pore at the center and separated from the aluminum metal by a layer of scalloped hemispherical barrier oxide.



CNDL

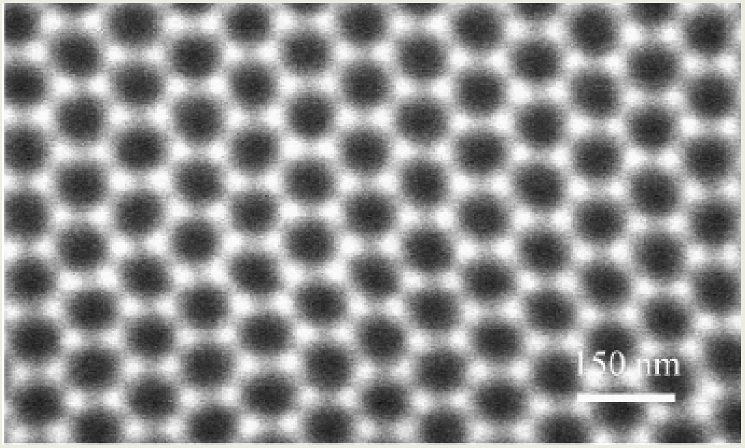
1.4. Application of AAO

- **Ordered carbon nanotubes**

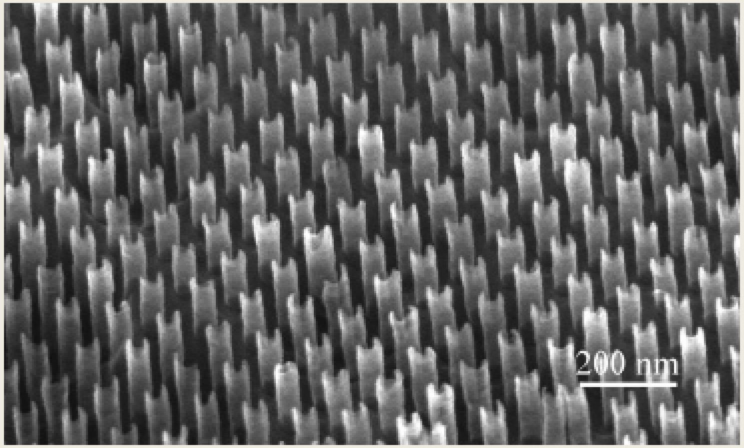


Al anodization → Co deposition → Acetylene pyrolysis

✓ Anodizing an aluminum sheet in a 0.3 M oxalic acid solution at 15 °C under a constant voltage of 40 V.



Hexagonal close-packed alumina template

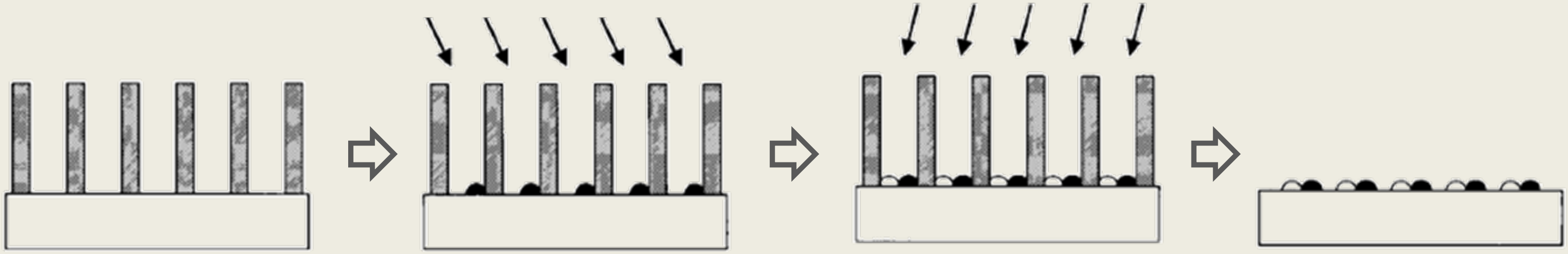


Highly ordered CNT

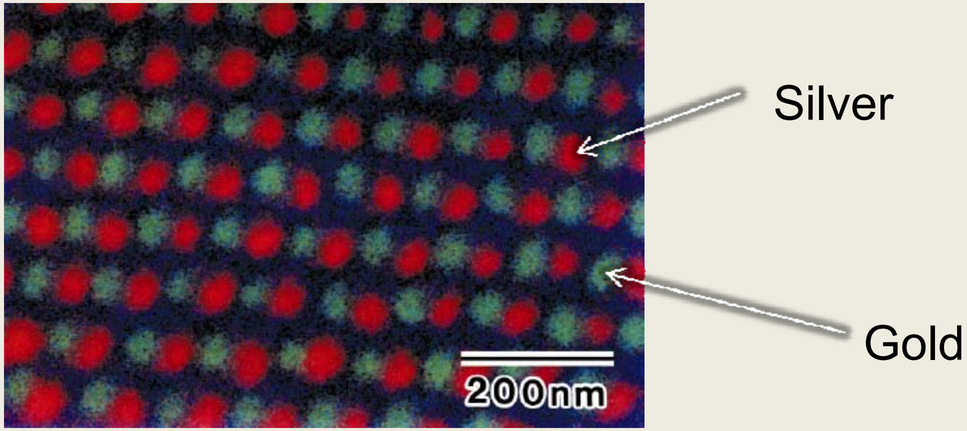
Appl. Phys. Lett., **1999**, *75*, 367.

1.4. Application of AAO

- **Quantum dots generation**



✓ The appropriate angle for the spatially resolved deposition, in which half of the incident beam was shadowed by the wall of the holes, is calculated to be approximately 5 from the ratio of the diameter to the depth of the apertures.



High controllability of the site of the components in each dot via the adjustment of the incident angle of the beam

Fig. Images of the array of bimetallic dots of Au and Ag.

Adv. Mater. ***2000***, *12*, 1031

2.1. Introduction of Porous silica

- **Silica**

Formula

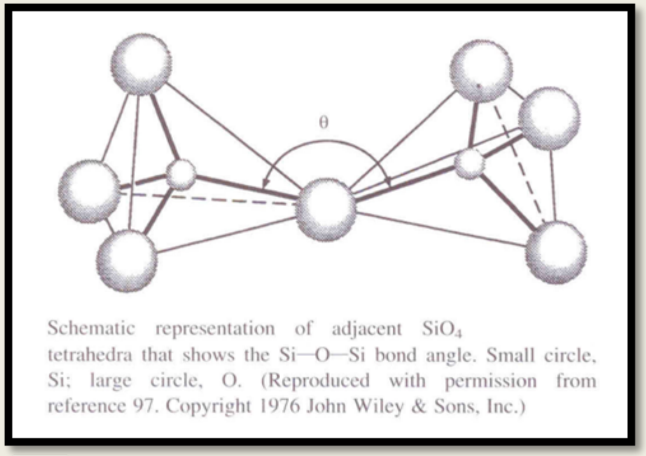
- Silicon dioxide (**SiO_2**)

Structure of silica

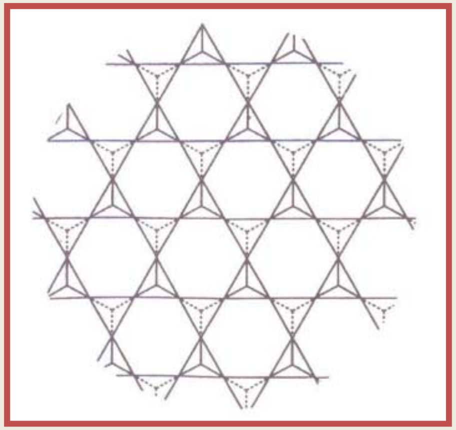
- crystal & amorphous structure
- consist of SiO_4 tetrahedral groups

Silica	Density (g/ml at 273K)
Coesite	3.01
α-Quartz	2.65
β-Quartz	2.53
β-Tridymite	2.26
β-Cristobalite	2.21
Amorphous silica	2.2

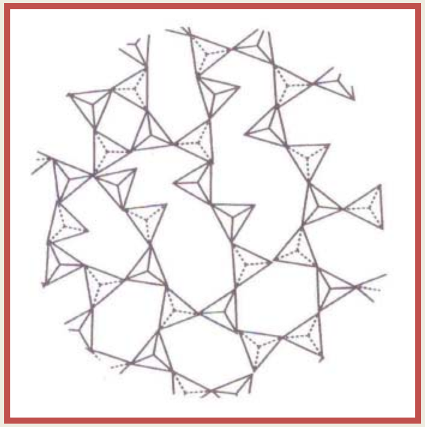
< Various silica & density >



Schematic representation of adjacent SiO_4 tetrahedra that shows the Si—O—Si bond angle. Small circle, Si; large circle, O. (Reproduced with permission from reference 97. Copyright 1976 John Wiley & Sons, Inc.)



< Crystal structure >



< Amorphous structure >

H. E. Bergna, et al., ‘Colloidal Silica : Fundamentals and Applications ‘ 2006, New York

2.1. Introduction of Porous silica

Porous silica

Definition

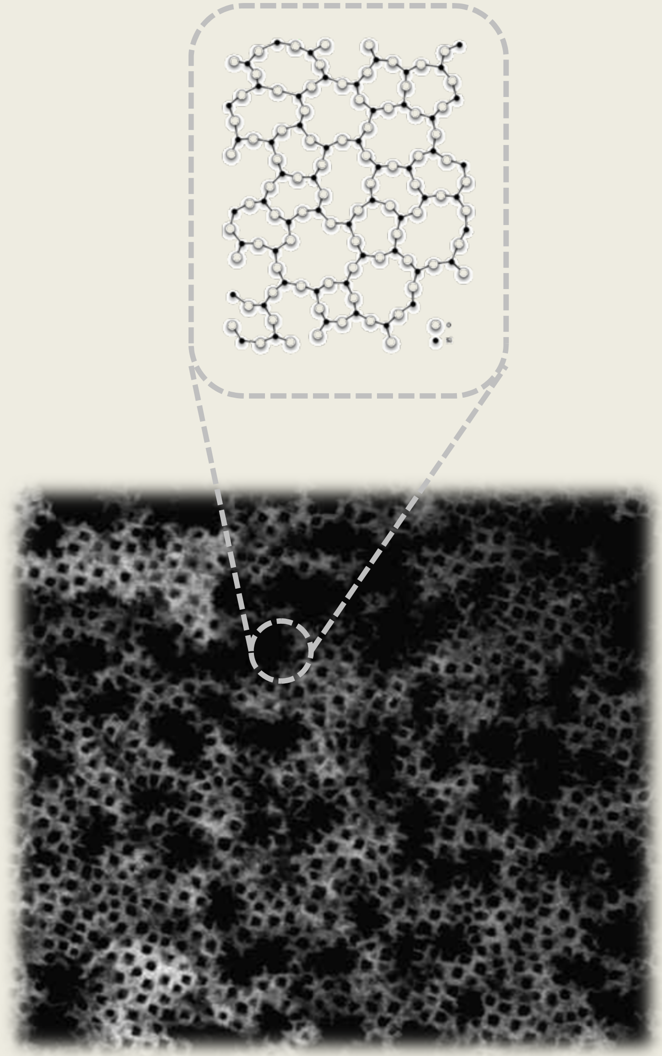
- Nanosized-Silicon dioxide (**SiO_2**) having **porous structure**

Representative nanoplatelets

- Multifunctional ceramic material that is being used in various industries
- Used as
  - .. Filler
  - .. Performance additive
  - .. Processing aids
  - .. Rheological modifier

Advantages of porous silica

- Available in wide range of hydrophilic and hydrophobic forms
- Easy to control the extremely fine size of the material



http://chem.ch.huji.ac.il/surface-asscher/Image12.jpg

2.1. Introduction of Porous silica

Porous silica

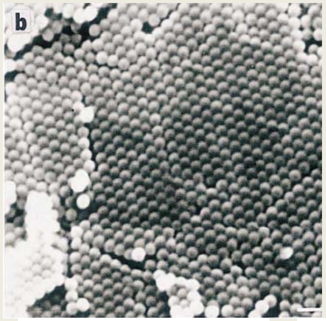
Hydrolysis

Ex) $Si(OR)_4 + H_2O \rightarrow HO\text{-}Si(OR)_3 + R\text{-}OH$

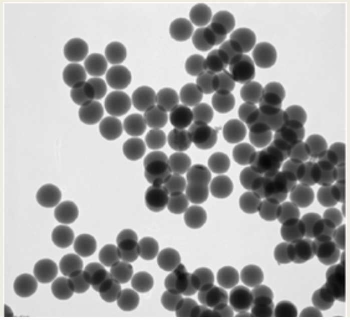
Condensation

Ex) $(OR)_3\text{–}Si\text{-}OH + HO\text{–}Si\text{-}(OR)_3$

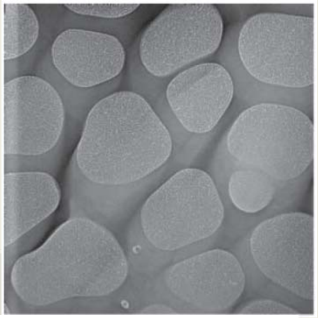
$\rightarrow [(OR)_3Si\text{–}O\text{–}Si(OR)_3] + H\text{-}O\text{-}H$



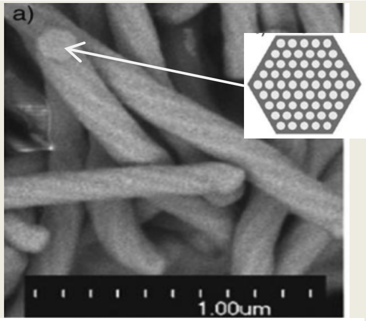
Nature, 389 (1997) 447-448



http://www.rsc.org/ej/CC/2008/b804593c/b804593c-f1.gif



Nature materials, 3, (2004) 337-341



Angew. Chem. Int. Ed., 45 (2006) 3216 – 3251

Synthesis of the porous silica

- Using sol-gel reaction
- Using surfactant for mesoporous structure

Various morphologies

- Available various morphologies using surfactant
  - .. Nanoparticle, Nanosphere
  - .. Nanorod
  - .. Hexagonal structure, lamella structure

Applications

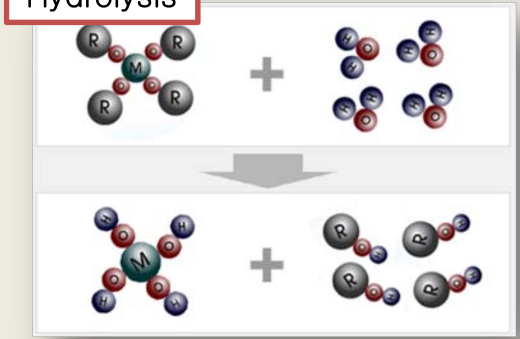
- Drug delivery system
- Catalyst
- Biosensor

2.2. Synthesis mechanism of porous silica

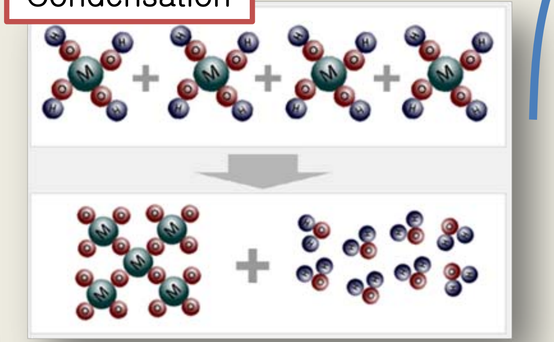
Sol-gel reaction

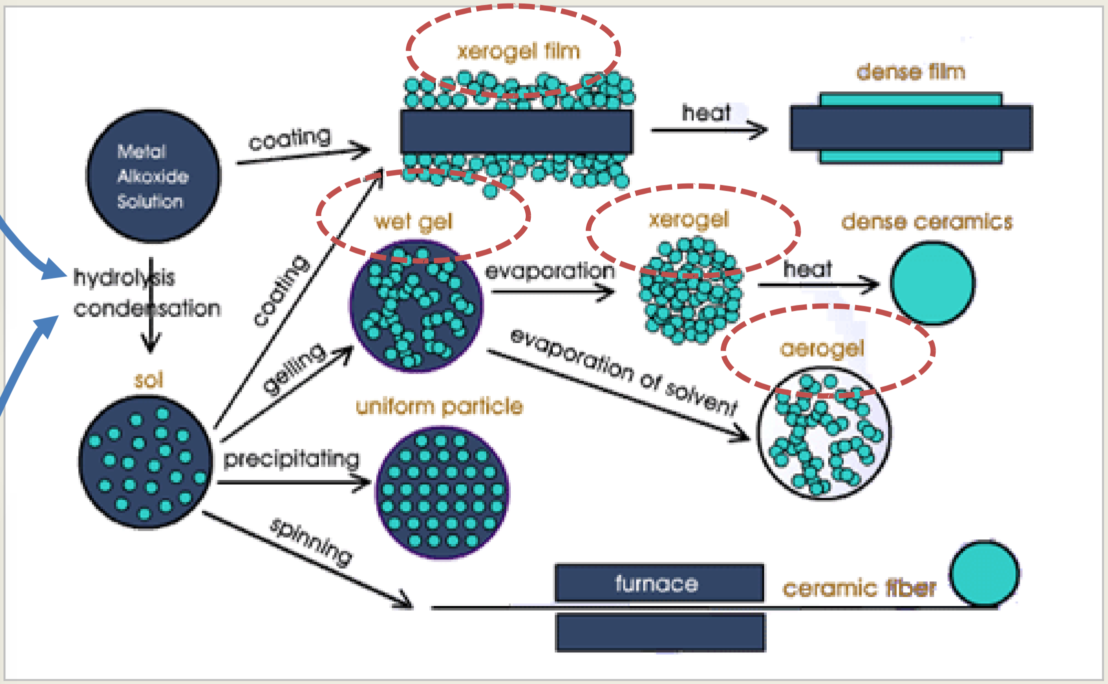
- **What is sol-gel reaction?**

Hydrolysis



Condensation





http://www.gaematech.co.kr/sub2/sub2_main_02.html

2.2. Synthesis mechanism of porous silica

Sol-gel reaction

- **Sol-gel reaction for porous silica**

  Sol-gel reaction : from silicon alkoxide sol-gel

$$\equiv\text{Si}-\text{OR} + H_2O \xrightleftharpoons[\text{estrification}]{\text{hydrolysis}} \equiv\text{Si}-\text{OH} + \text{ROH}$$

$$\equiv\text{Si}-\text{OR} + \text{HO-Si}\equiv \xrightleftharpoons[\text{alcoholysis}]{\text{alcohol condensation}} \equiv\text{Si}-\text{O}-\text{Si}\equiv + \text{ROH}$$

$$\equiv\text{Si}-\text{OR} + \text{HO-Si}\equiv \xrightleftharpoons[\text{hydrolysis}]{\text{water condensation}} \equiv\text{Si}-\text{O}-\text{Si}\equiv + H_2O$$

Morphology of porous silica from sol-gel reaction

- wet gel / aerogel / xerogel

Precursor solution

- silicon alkoxide + water + alcohol + catalyst
- H_2O:Si molar ratio : 1~over 50
- Concentration of acids or bases : 0.01~7M

2.2. Synthesis mechanism of porous silica

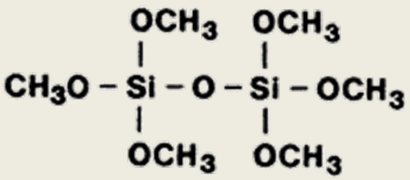
Sol-gel reaction

- **Precursor molecules**

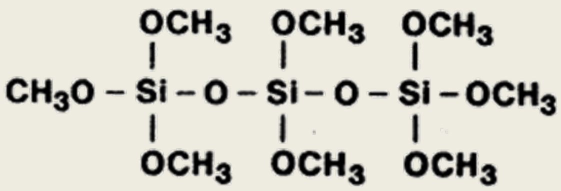
< Tetraalkoxysilane >
- $Si(OR)_4$

< Organoalkoxysilane >
- $R_nSi(OR)_3$

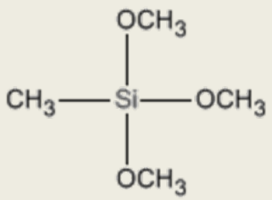
< Molecular building block >



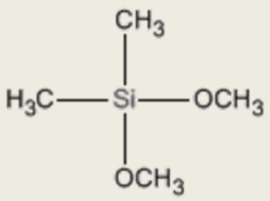
TEOS
(tetraethoxysilane)



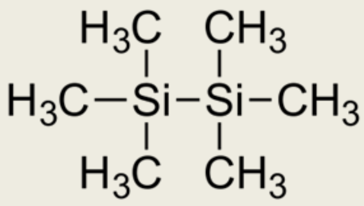
TMOS
(tetramethoxysilane)



MTMS
(methyltrimethoxysilane)



DMDMS
(dimethyldimethoxysilane)



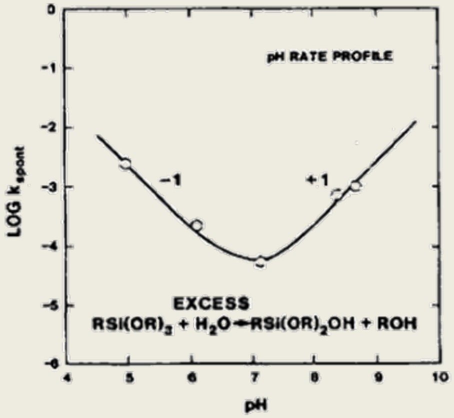
hexamethoxydisilane

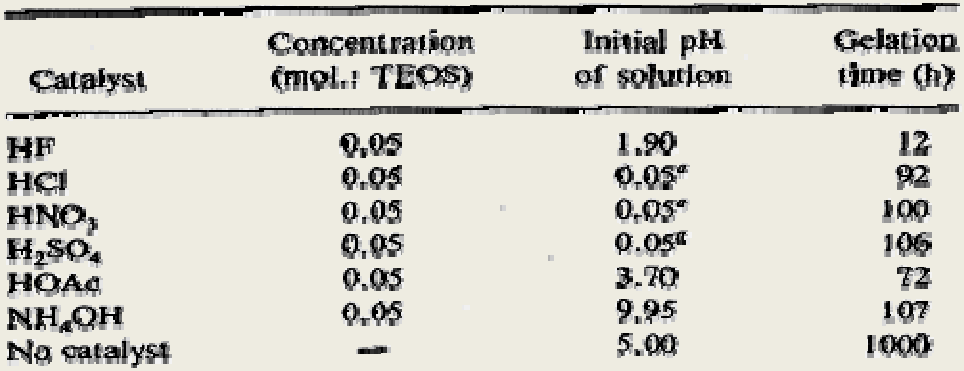
2.2. Synthesis mechanism of porous silica

Sol-gel reaction

Hydrolysis process

- **Effect of catalyst**

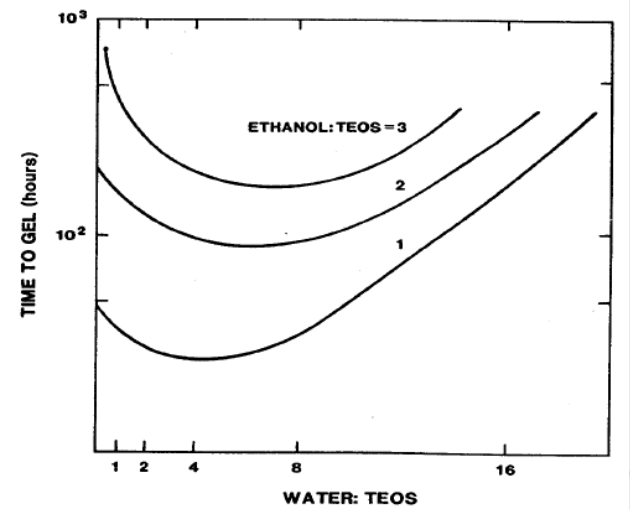




Catalyst	Concentration (mol.: TEOS)	Initial pH of solution	Gelation time (h)
HF	0.05	1.90	12
HCl	0.05	0.05[a]	92
HNO_3	0.05	0.05[a]	100
H_2SO_4	0.05	0.05[a]	106
HOAc	0.05	3.70	72
NH_4OH	0.05	9.95	107
No catalyst	—	5.00	1000

- **H_2O/Si ratio (r)**

Increase of r → increase of gel time

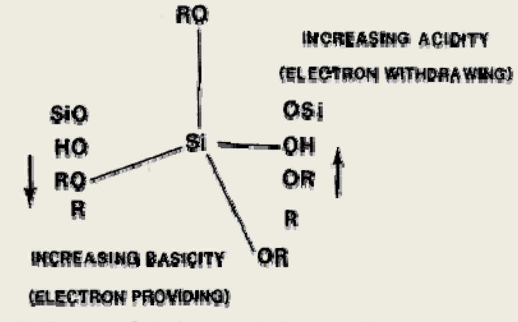


2.2. Synthesis mechanism of porous silica

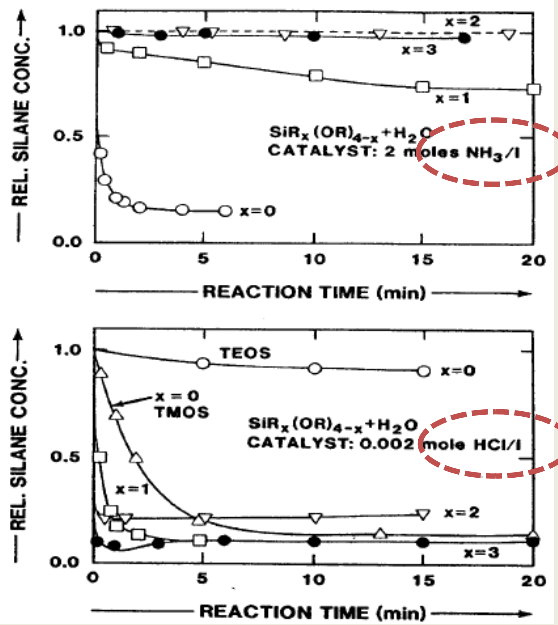
Sol-gel reaction

Hydrolysis process

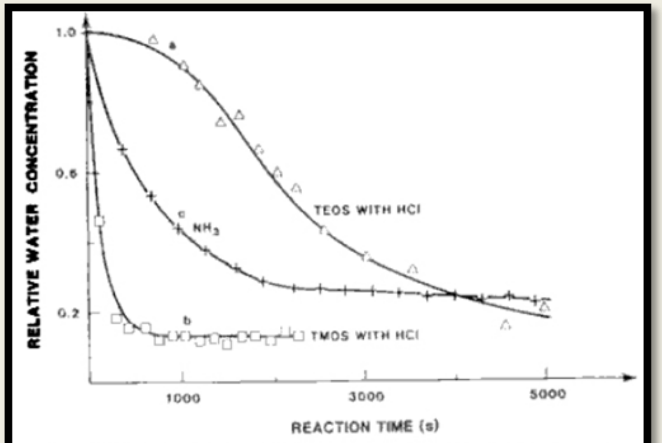
- **Steric & inductive effects**



Inductive effects of substituents attached to silicon, R, OR, OH, or OSi



- **Effects of solvent**



Relative water concentration versus time during acid-or base-catalyzed hydrolysis of TEOS or TMOS [58].

Protic solvent
→ enhancement of hydrolysis

2.2. Synthesis mechanism of porous silica

Sol-gel reaction

Condensation process

- **Effects of catalyst**

  Min : about pH=1.5

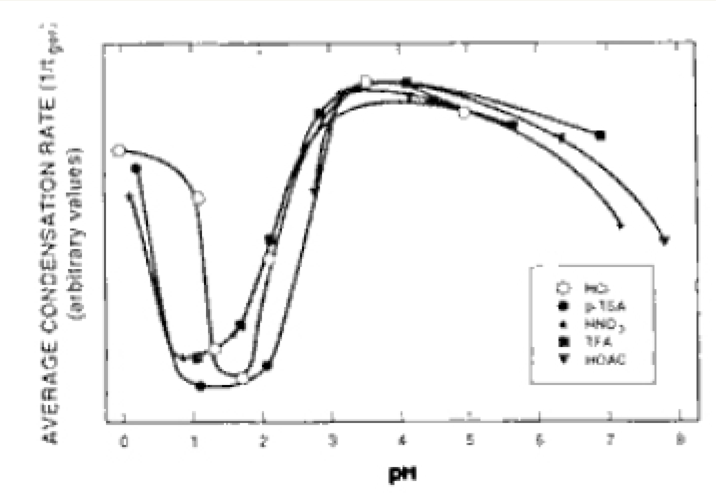
  Max : intermediate pH

  Acid catalyzed condensation (pH<2)

  - protonated silanol

  Base catalyzed condensation (pH>2)

  - deprotonated silanol



- **Steric & inductive effects**

Acidity of silanol – higher pH IEP(isoelectric point)

Basicity of silanol – lower pH IEP

* Total electric charge = 0

In acid-catalyzed, steric effects > inductive effects

- **Effects of solvent**

Protic solvents → acid-catalyzed condensation

Aprotic solvents → base-catalyzed condensation

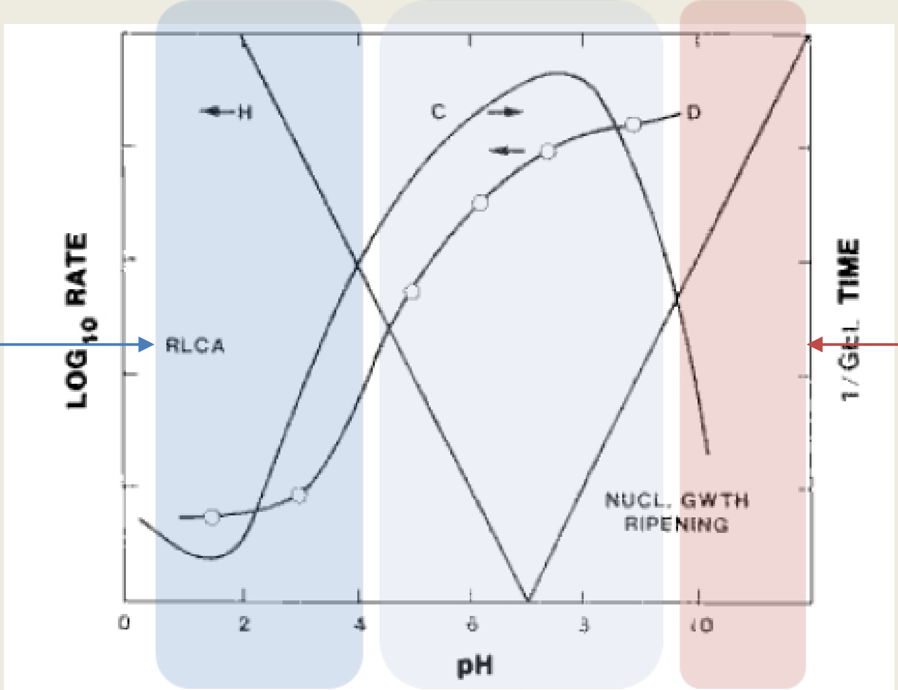
2.2. Synthesis mechanism of porous silica

Sol-gel reaction

Structural summary

Hydrolysis rate > condensation rate
cluster-cluster growth → network structure

Unhydrolyzed monomer
monomer-monomer growth → particles



Schematic representation of the pH-dependences of hydrolysis (H), condensation (C), and dissolution (D) for an arbitrary value of *r* (1.5) [60].

Minimum of hydrolysis rate
Rate limiting

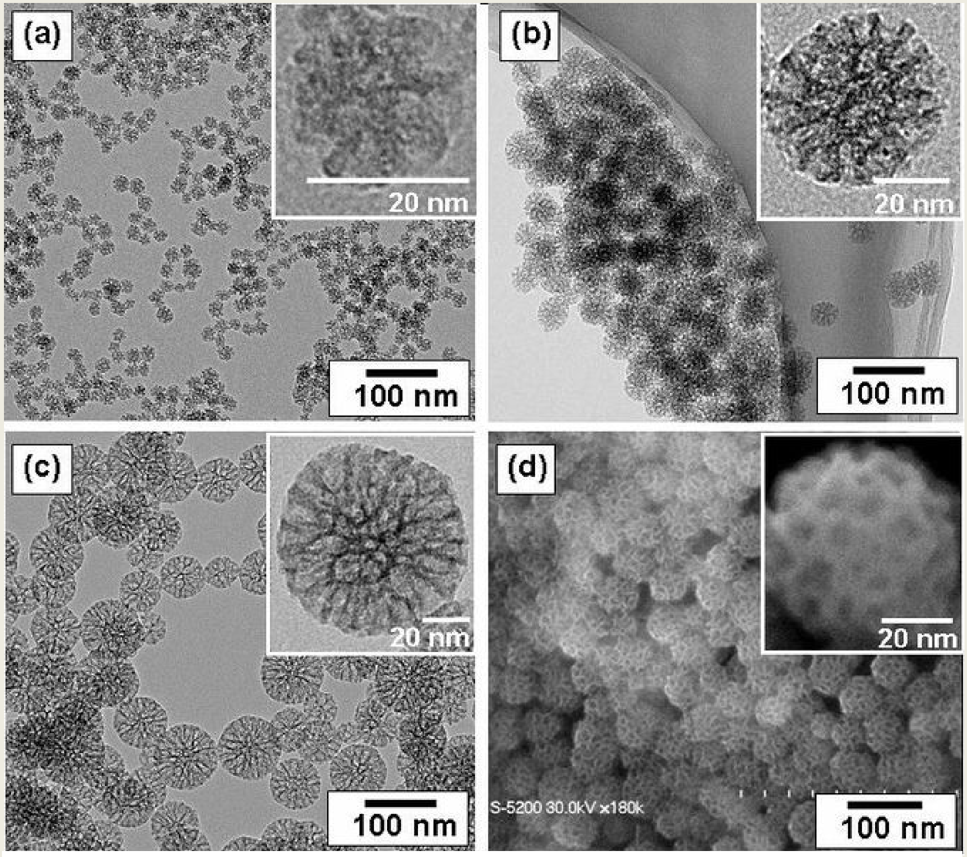
CNDL

2.2. Synthesis mechanism of porous silica

Mesoporous silica using surfactant

- **What is mesoporous silica?**

  Porous silica which has 2~50nm size of mesoporous structure
  Various structure & possibility of application



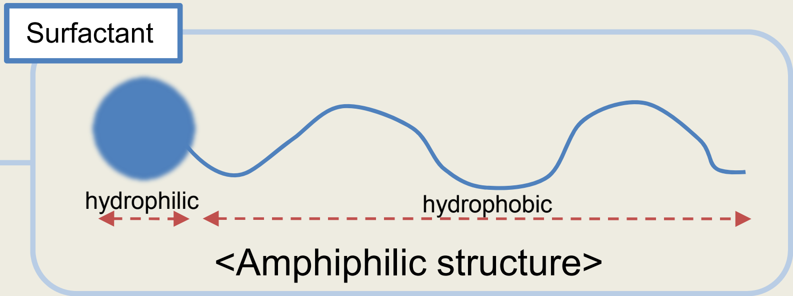
http://en.wikipedia.org/wiki/Mesoporous_silica

2.2. Synthesis mechanism of porous silica

Mesoporous silica using surfactant

- **Mesoporous structure from the using of Surfactant**

  Sol-gel reaction of the precursors on the surface of the template



Surfactant

hydrophilic

hydrophobic

<Amphiphilic structure>

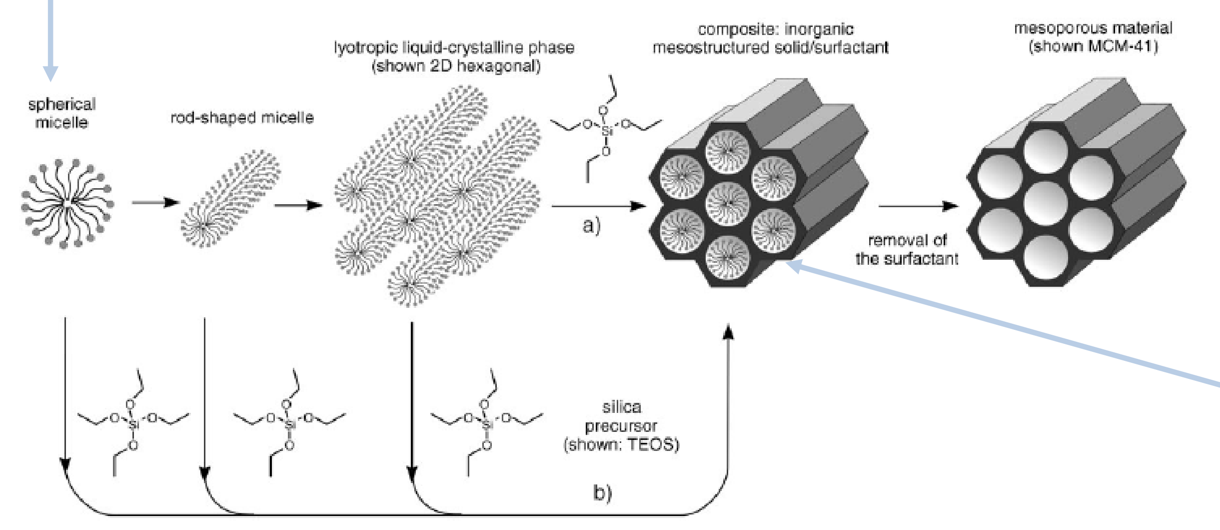


Figure 2. Formation of mesoporous materials by structure-directing agents: a) true liquid-crystal template mechanism, b) cooperative liquid-crystal template mechanism.

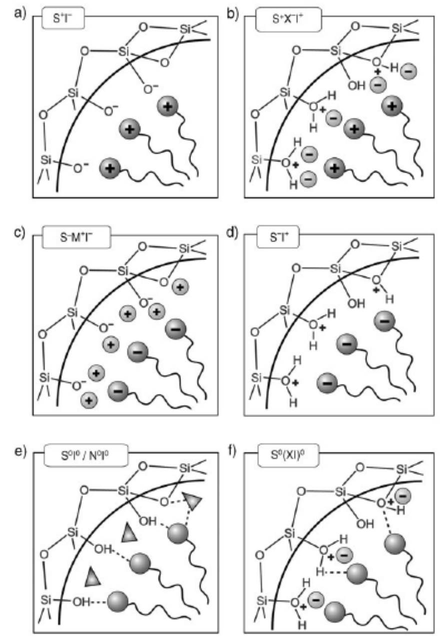


Figure 3. Interactions between the inorganic species and the head group of the surfactant with consideration of the possible synthetic pathway in acidic, basic, or neutral media. Electrostatic: S^+I^-, $S^+X^-I^+$, $S^-M^+I^-$, S^-I^+; through hydrogen bonds: S^0I^0/N^0I^0, $S^0(XI)^0$.

Angew. Chem. Int. Ed. **2006**, *45*, 3216 – 3251

2.2. Synthesis mechanism of porous silica

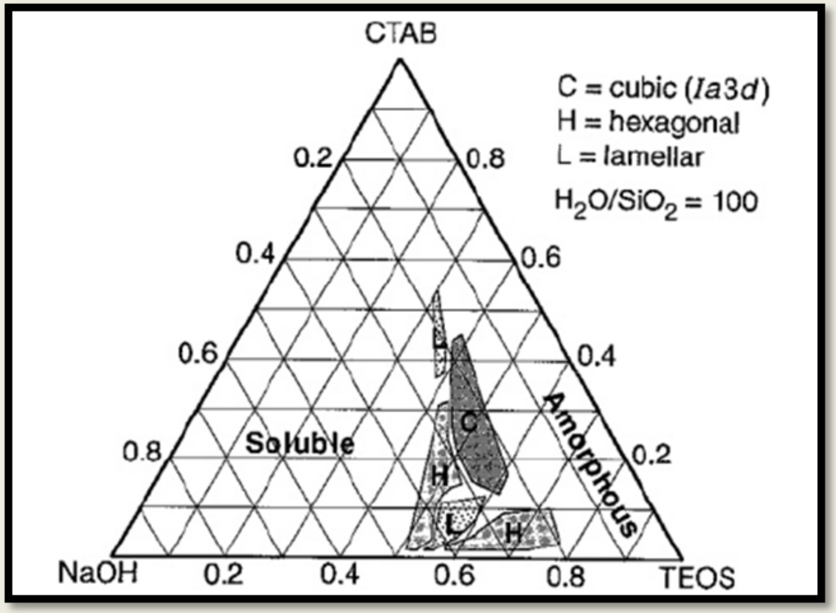
Mesoporous silica using surfactant

- **Mesoporous structure from the using of Surfactant**

  Morphology controllable by component ratio change

$$\Delta G_{\mathrm{ms}} = \Delta G_{\mathrm{inter}} + \Delta G_{\mathrm{inorg}} + \Delta G_{\mathrm{org}} + \Delta G_{\mathrm{sol}}$$

ΔG_{inter} : the inorganic-organic interface
ΔG_{inorg} : the inorganic framework
ΔG_{org} : the self-assembly of the organic molecules
ΔG_{sol} : the contribution of the solution



< Fig. Synthesis-space diagram of mesostructures established by XRD measurements >

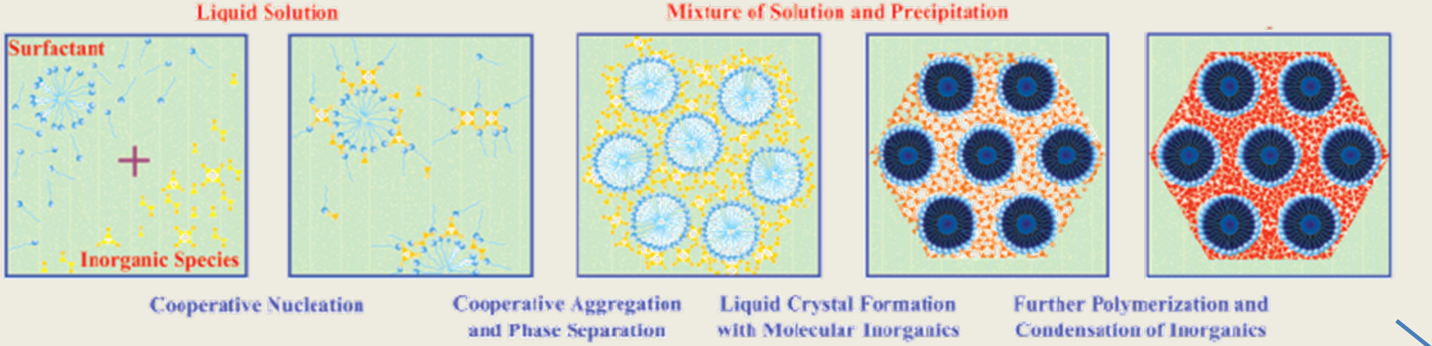
Chemical Reviews, **2007**, *107*, 2823

2.2. Synthesis mechanism of porous silica

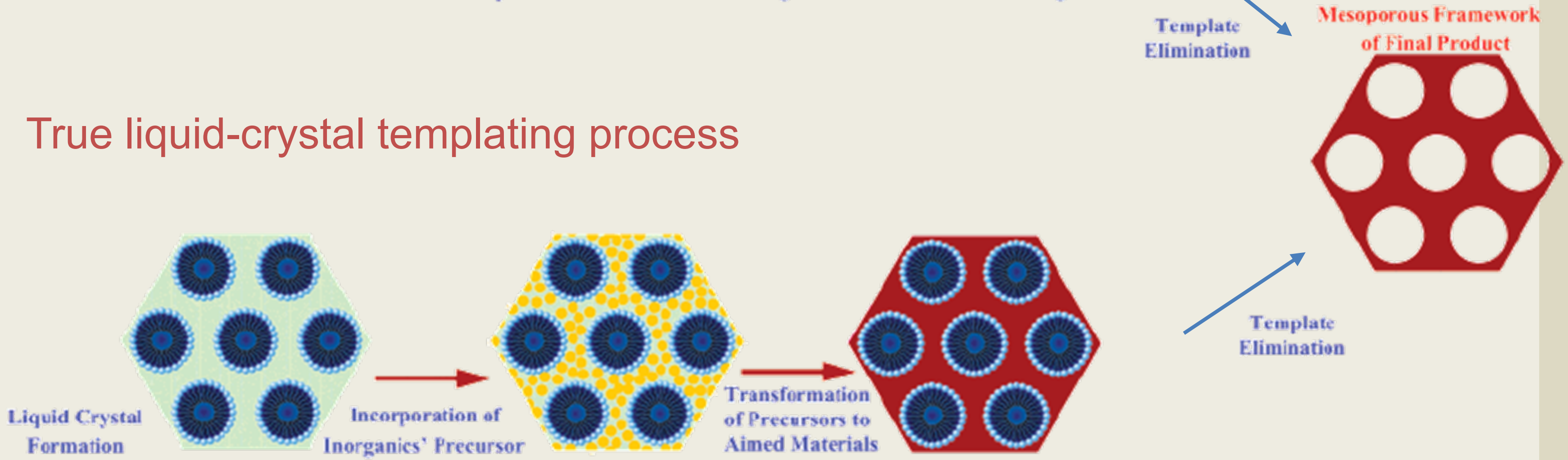
Mesoporous silica using surfactant

- **Synthesis strategies of mesoporous silica**

Cooperative self-assembly



True liquid-crystal templating process

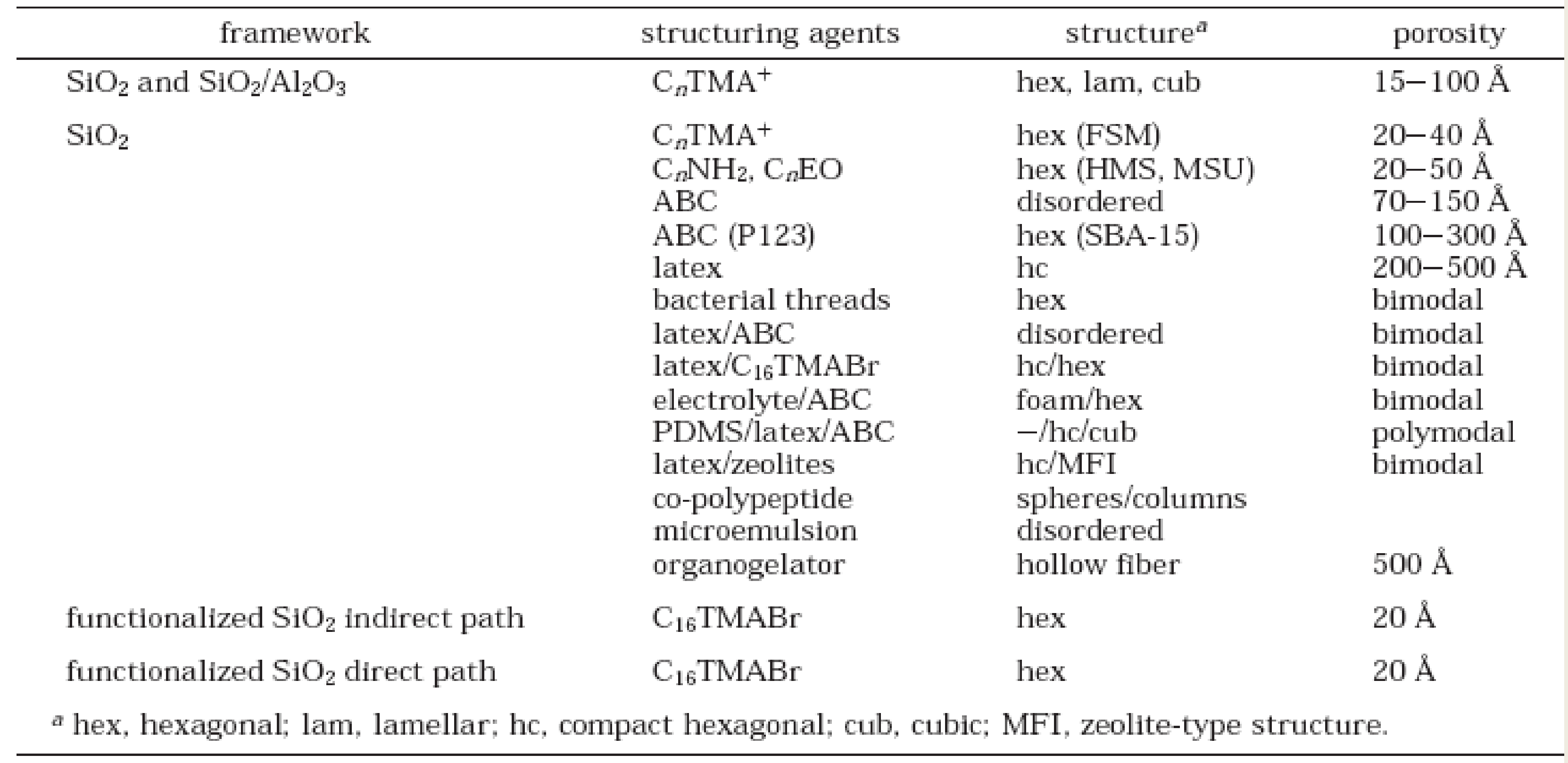


Chemical Reviews, **2007**, *107*, 2823

2.2. Synthesis mechanism of porous silica

Mesoporous silica using surfactant

- **Main Research Concerning the Synthesis of Micro-, Meso-, and Macrostructured Silica in the Presence of Organic Templates**



framework	structuring agents	structure[a]	porosity
SiO_2 and SiO_2/Al_2O_3	C_nTMA^+	hex, lam, cub	15–100 Å
SiO_2	C_nTMA^+	hex (FSM)	20–40 Å
	C_nNH_2, C_nEO	hex (HMS, MSU)	20–50 Å
	ABC	disordered	70–150 Å
	ABC (P123)	hex (SBA-15)	100–300 Å
	latex	hc	200–500 Å
	bacterial threads	hex	bimodal
	latex/ABC	disordered	bimodal
	latex/$C_{16}TMABr$	hc/hex	bimodal
	electrolyte/ABC	foam/hex	bimodal
	PDMS/latex/ABC	–/hc/cub	polymodal
	latex/zeolites	hc/MFI	bimodal
	co-polypeptide	spheres/columns	
	microemulsion	disordered	
	organogelator	hollow fiber	500 Å
functionalized SiO_2 indirect path	$C_{16}TMABr$	hex	20 Å
functionalized SiO_2 direct path	$C_{16}TMABr$	hex	20 Å

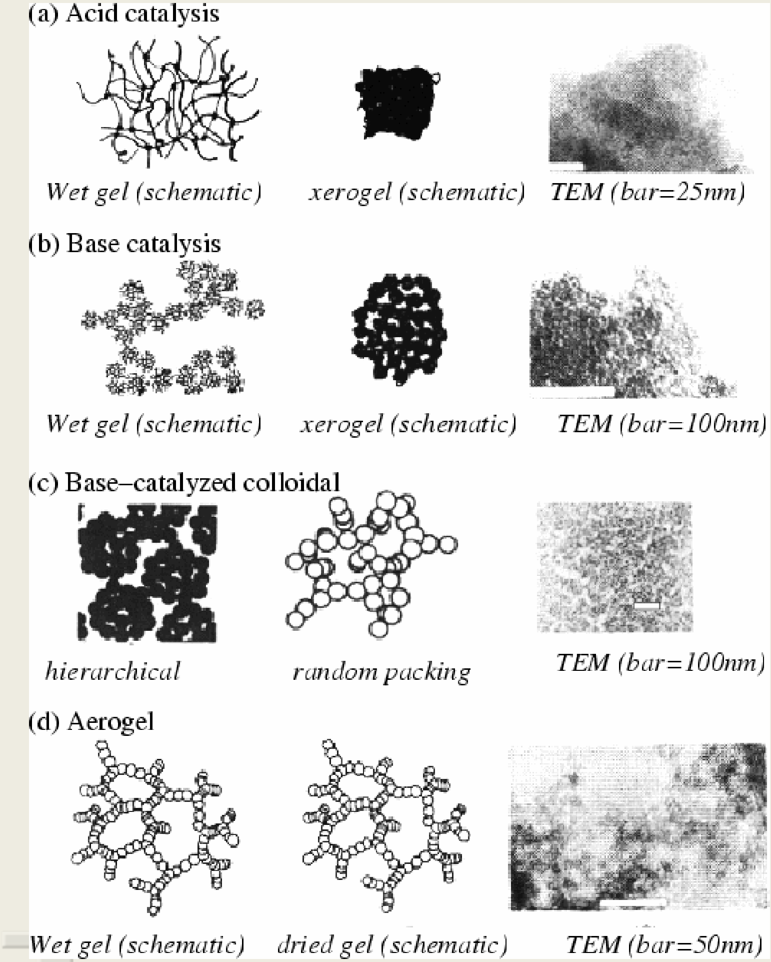
[a] hex, hexagonal; lam, lamellar; hc, compact hexagonal; cub, cubic; MFI, zeolite-type structure.

Chemical Reviews, **2002**, *102*

2.3. Structure of porous silica

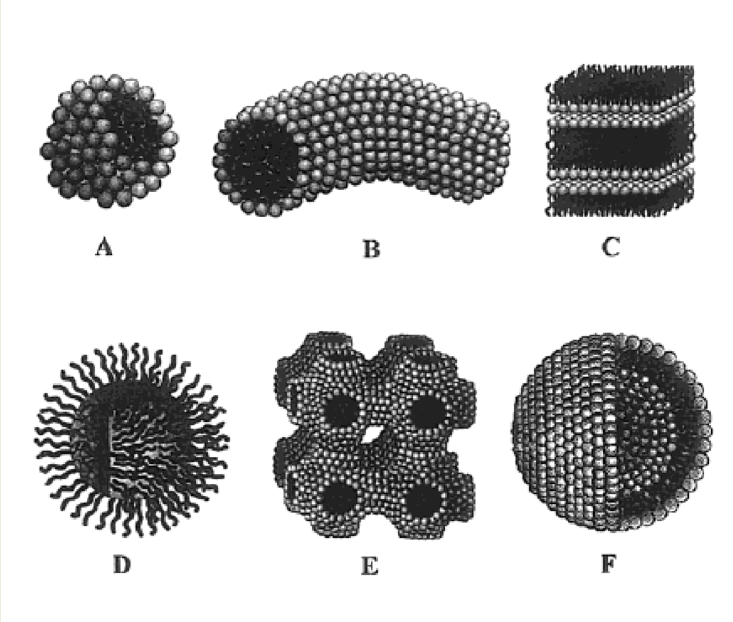
Structures of porous silica

- **Schemes of porous silica structure from using sol-gel process & surfactant**



< Schematic wet and dry gel morphologies and representative transmission electron micrographs >

www.chemistry.wustl.edu/%7Egelb/solgel.html

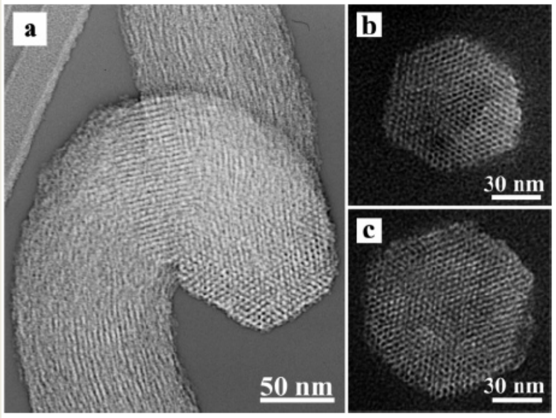


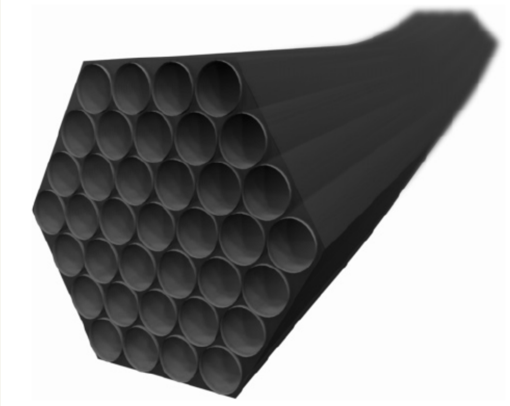
< Fig. Micellar structures (A) sphere, B) cylinder, C) planar bilayer, D) reverse micelles, E) bicontinuous phase, F) liposomes) >

Chemical Reviews, **2007**, *107*, 2823

2.3. Structure of porous silica

Structure control by heat treatment condition change





< Fig. TEM image of a nanofiber synthesized with C_{16}TMAC surfactant at 50°C >

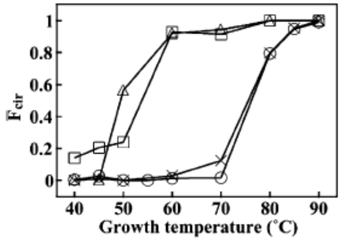
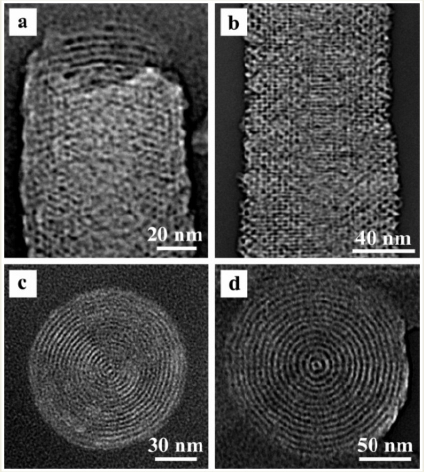
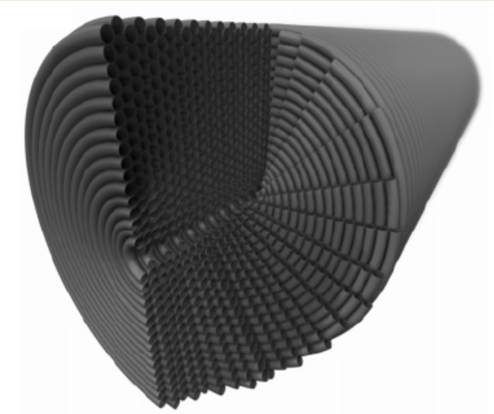


Figure 12. Fraction of the nanofibers with circular pore architectures (F_{cir}) as a function of the growth temperature. Circles, crosses, triangles, and squares represent that the nanofibers were synthesized with C_{16}TMAC, C_{16}TMAB, C_{16}-PC, and C_{16}PB surfactants, respectively. The lines are guides to eye.



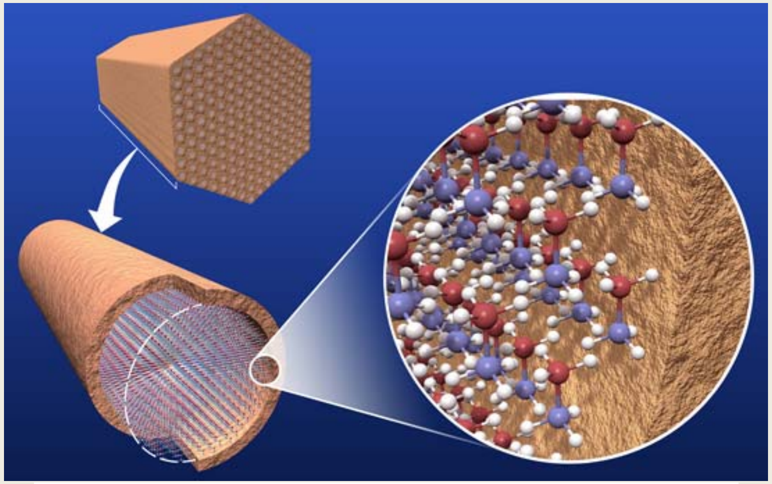


<Fig. TEM image of a nanofiber synthesized with C_{16}TMAC surfactant at 85°C >

Chem. Mater., **2004**, *16*

2.4. Application of porous silica

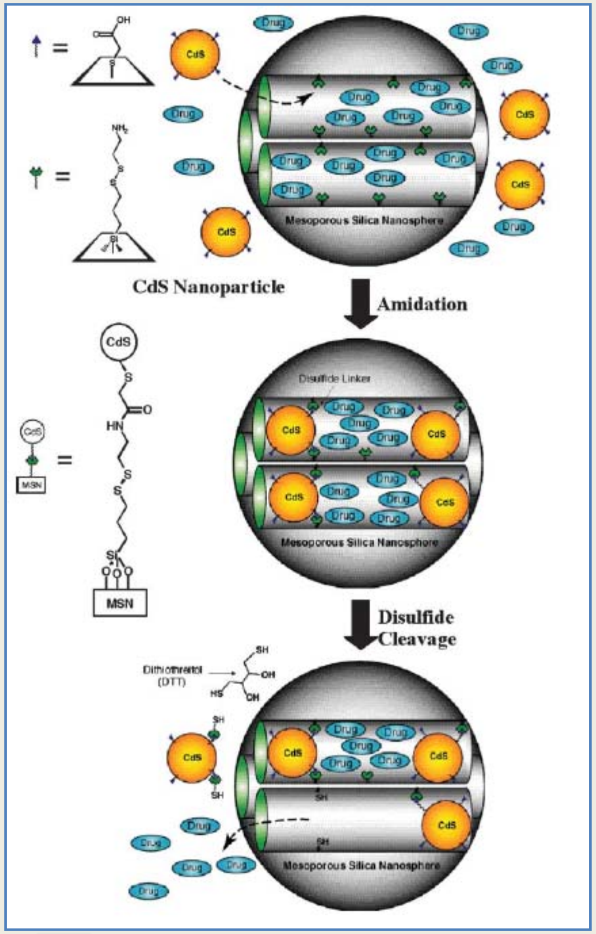
- **Drug delivery system**
  - High surface area
  - available to functionalize
- **Biosensor or chemical sensors**
  - Water-soluble
    → possible to use in human body system
- **Catalyst**
  - High surface area
  - Thermal stability
- **Optical Applications**
  - Dye inclusion
  - Nanocrystals (Quantum Dots)
  - Organometallic complexes
  - Photochromic materials
- **Insulator materials**
- **Low k materials**
- **Hydrogen Stroage and electrode materials**



http://availabletechnologies.pnl.gov/images/fullsize/87_1.jpg

2.4. Application of porous silica

Drug delivery system



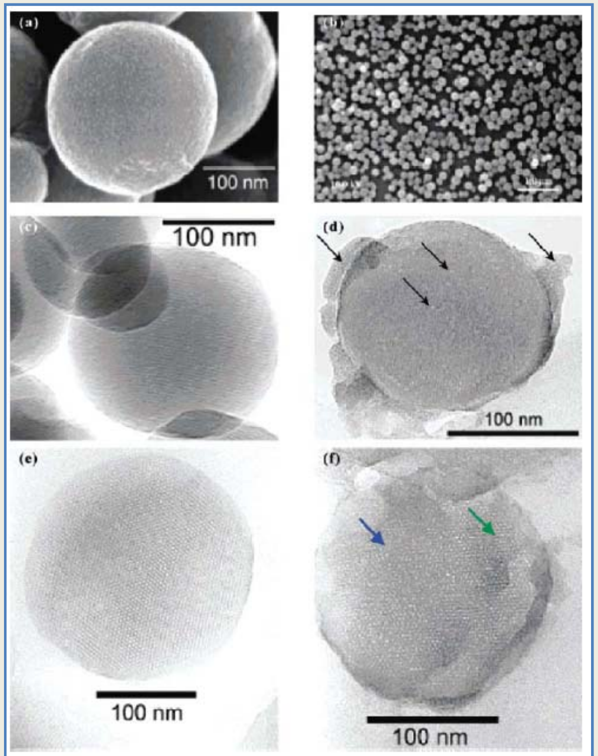


Fig. 4 SEM (a, b) and TEM (300 kV) micrographs of the Linker-MSN (c, e). The TEM micrographs (d, f) of the CdS-capped MSN clearly exhibit aggregations of CdS nanoparticles on the exterior surface of MSN material represented by dots in the areas indicated by black arrows in (d). The TEM micrographs (d–f) were measured on ultramicrotomed samples with section thickness of 60–80 nm.

Porous silica used as the **Linker** for CdS nanoparticles by functionalization of the surface with amide bond

CdS nanoparticles

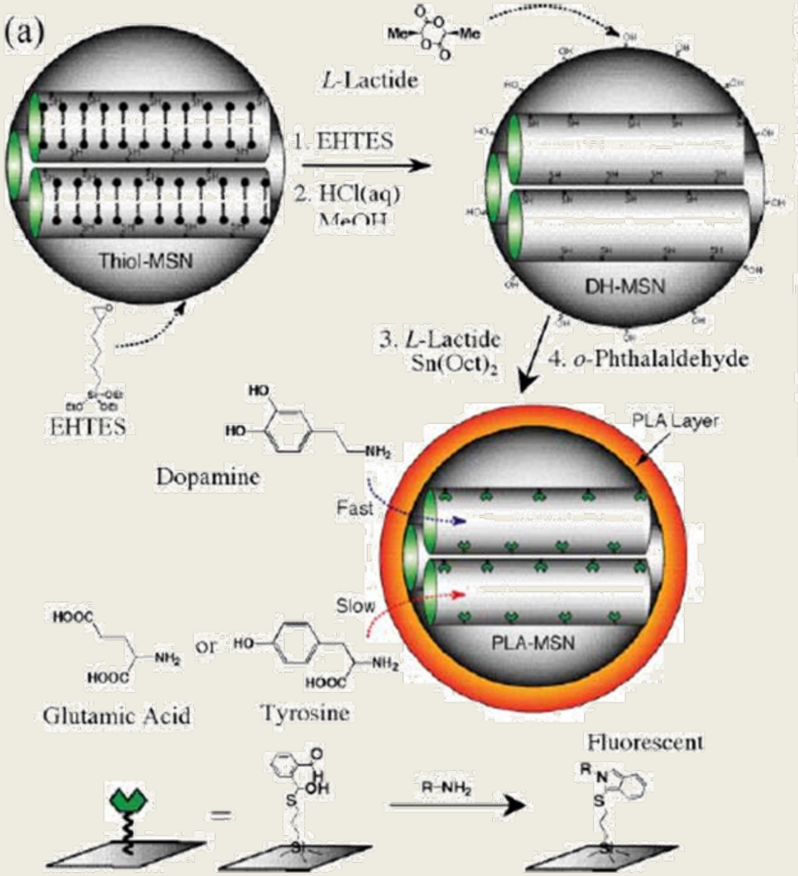
- Magnetized material
- useful for sensor
- Water-soluble

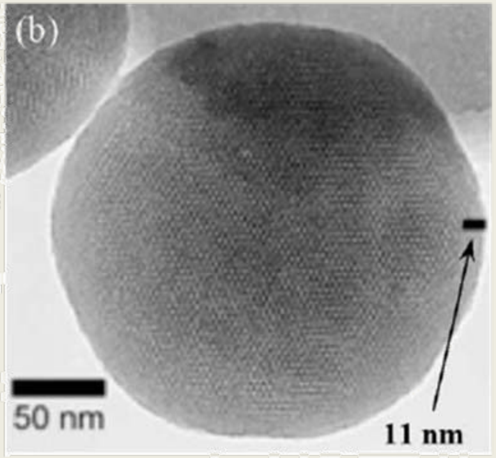
The loading efficiency of vancomycin and ATP : 83.9 and 30.3 mol%

Chem. Commun., **2007**, 3236

2.4. Application of porous silica

Biosensor





< Schematic representation of the synthesis of PLA-coated MSN-based fluorescence sensor system for detection of amine-containing neurotransmitters >

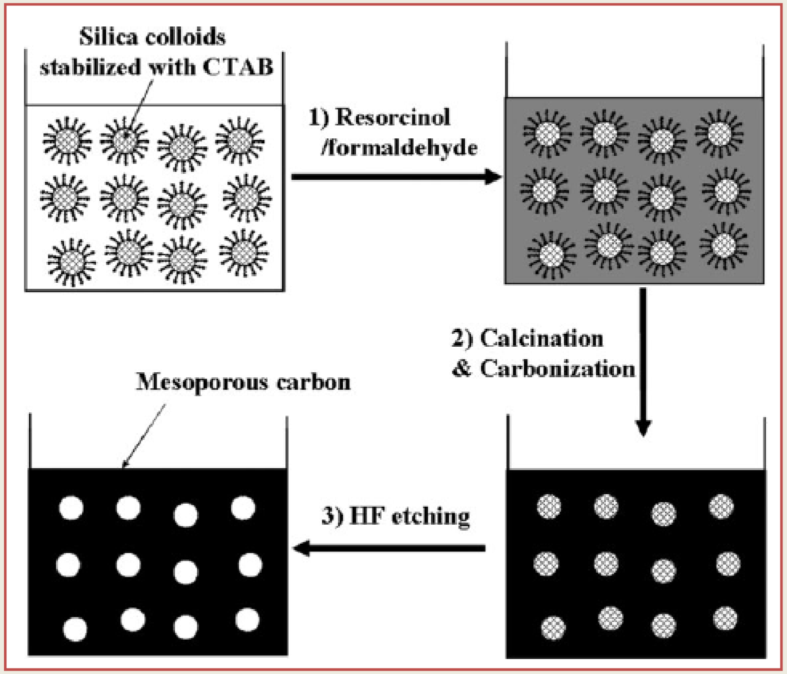
Biosensor for detecting dopamine, glutamic acid, tyrosine, and etc.

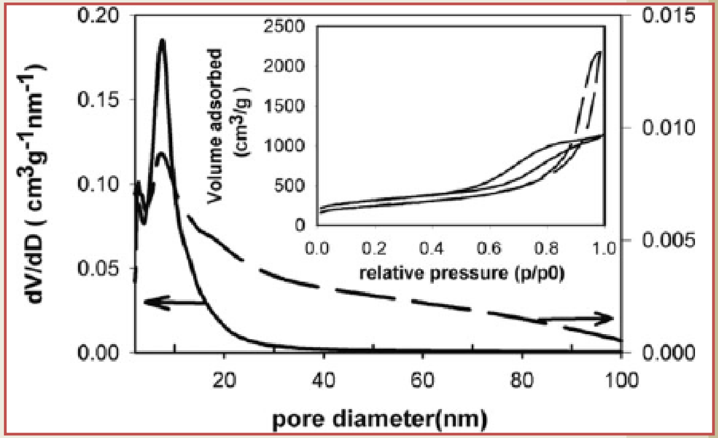
Available to distinguish between several structurally similar neurotransmitter by fluorescence

PLA : negative charged in pH 7.4 buffer
→ faster kinetics for Dopamine (positive charged)

2.4. Application of porous silica (Template for organic nano material)

- Silica colloid nanoparticles as template for porous carbon materials





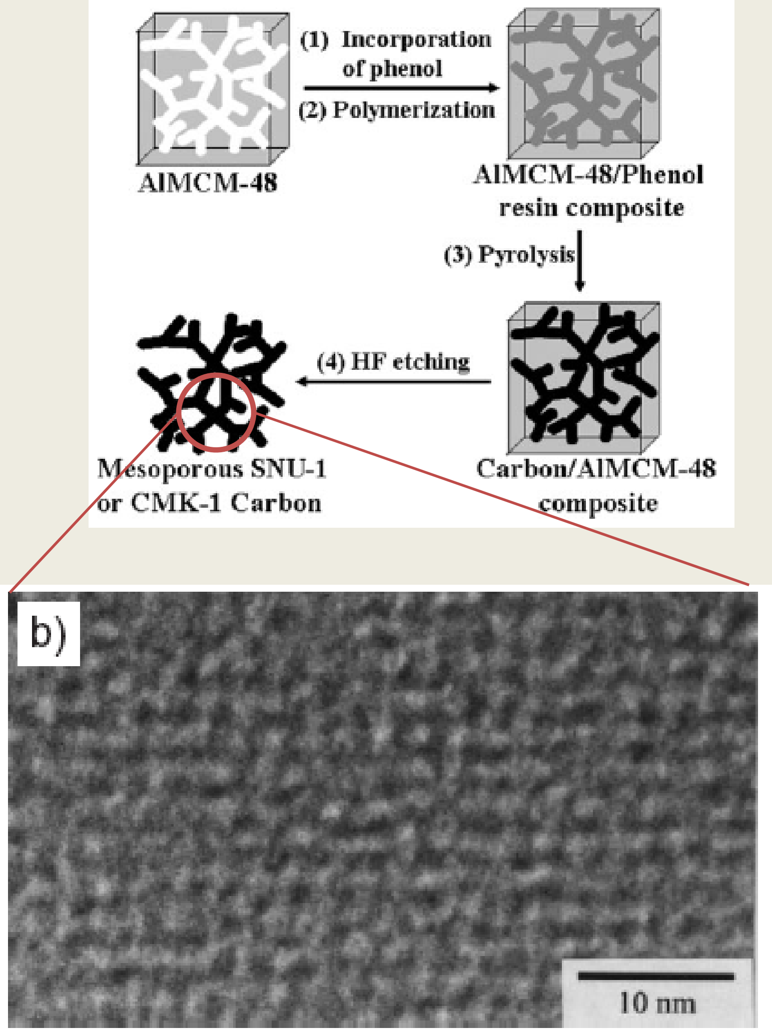
< Synthetic strategy for uniform mesoporous carbons using RF >

. Using silica template with CTAB as surfactant & RF as carbon source
. Carbonization at 850℃
. **Controlled pore-size & surface area**
. used as the stationary phase for reverse-phase liquid chromatography
in the separation of alkylbenzenes, such as benzene, ethylbenzene, and
propylbenzene

* S. Han, T. Hyeon, *Chem. Commun.* **(1999) 1955**

2.4. Application of porous silica (Template for organic nano material)

- Ordered mesoporous carbon materials using mesoporous silica templates



< synthesis scheme & TEM image of ordered mesoporous carbon SNU-1 >

. Mesoporous silica (MCM-48) as template
. Phenol & formaldehyde as carbon precursor
. **in situ polymerization** of phenol and formaldehyde in the pores of the MCM-48 aluminosilicate template
. regular array of 2 nm sized pores separated by 2 nm thick carbon walls

* J. Lee, S. Yoon, T. Hyeon, S. M. Oh, K. B. Kim, *Chem. Commun.* **(1999) 2177.**

3.1. Introduction of Zeolite

What is zeolite?

✓ Greek derivation (zein,“to boil”; lithos,“a stone”) means “stones that boil”.

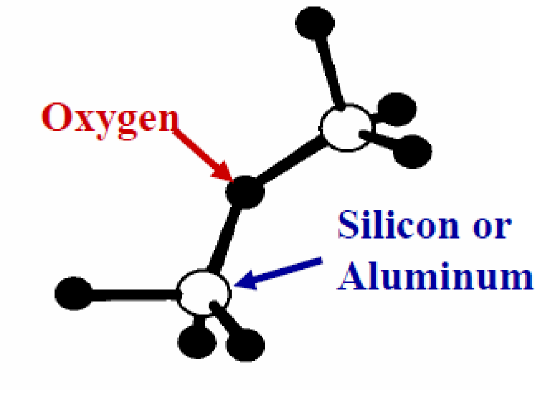
✓ Crystalline Aluminosilicate

✓ Consist of Corner-sharing Tetrahedra, TO4 (T=Al or Si)

✓ Uniform molecular size pores (10 – 20 Å diameter) running throughout the solid.

✓ 40 natural and 130 synthetic zeolites known

✓ Aluminosilicates based on rigid anionic framework with well-defined channels and cavities.

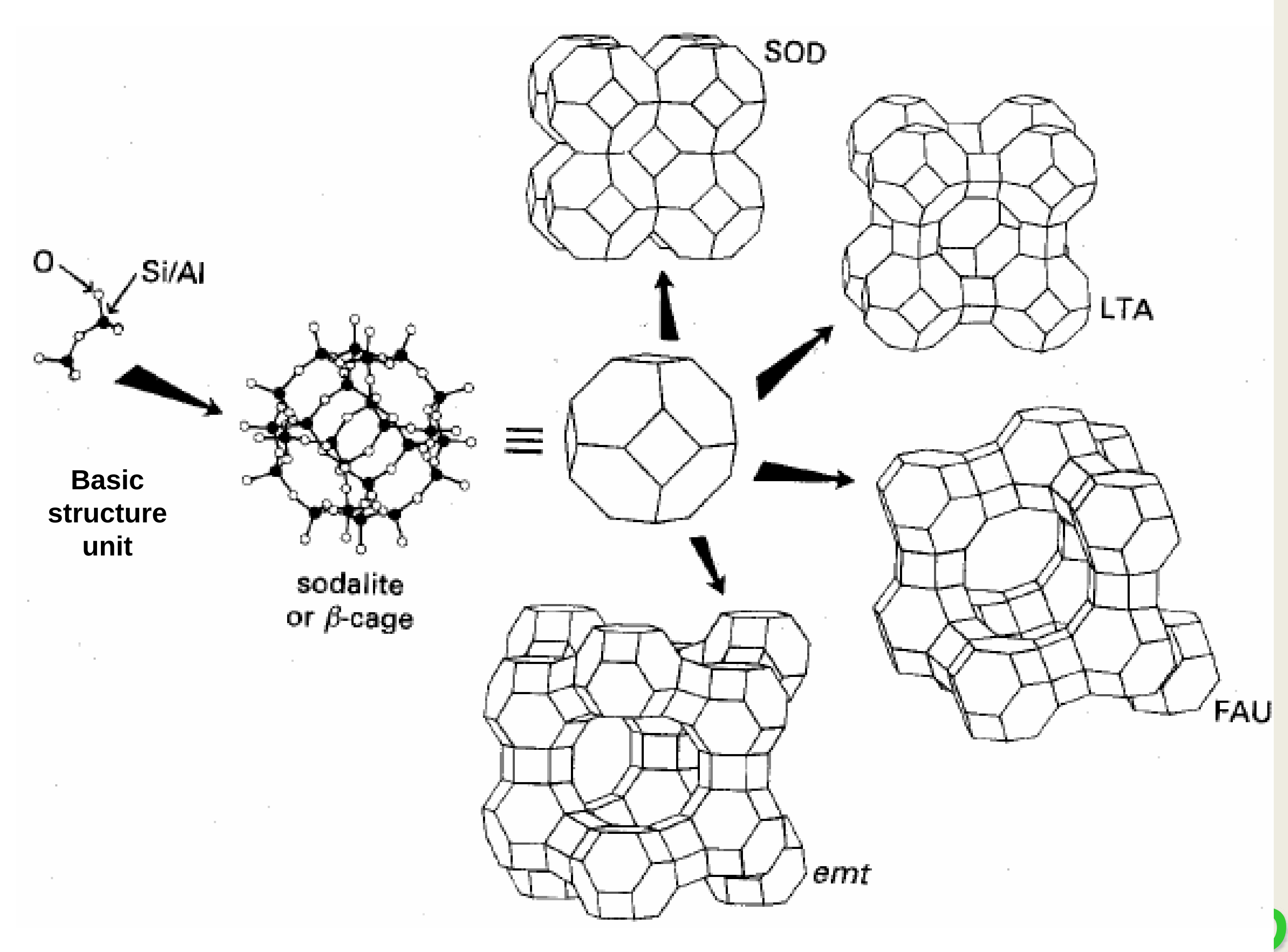


Corner-sharing TO_4
(T=Si or Al)

Introduction to Zeolite Science and Practice; Van Bekkum, H. et al. Eds; Elsevier: 1991.

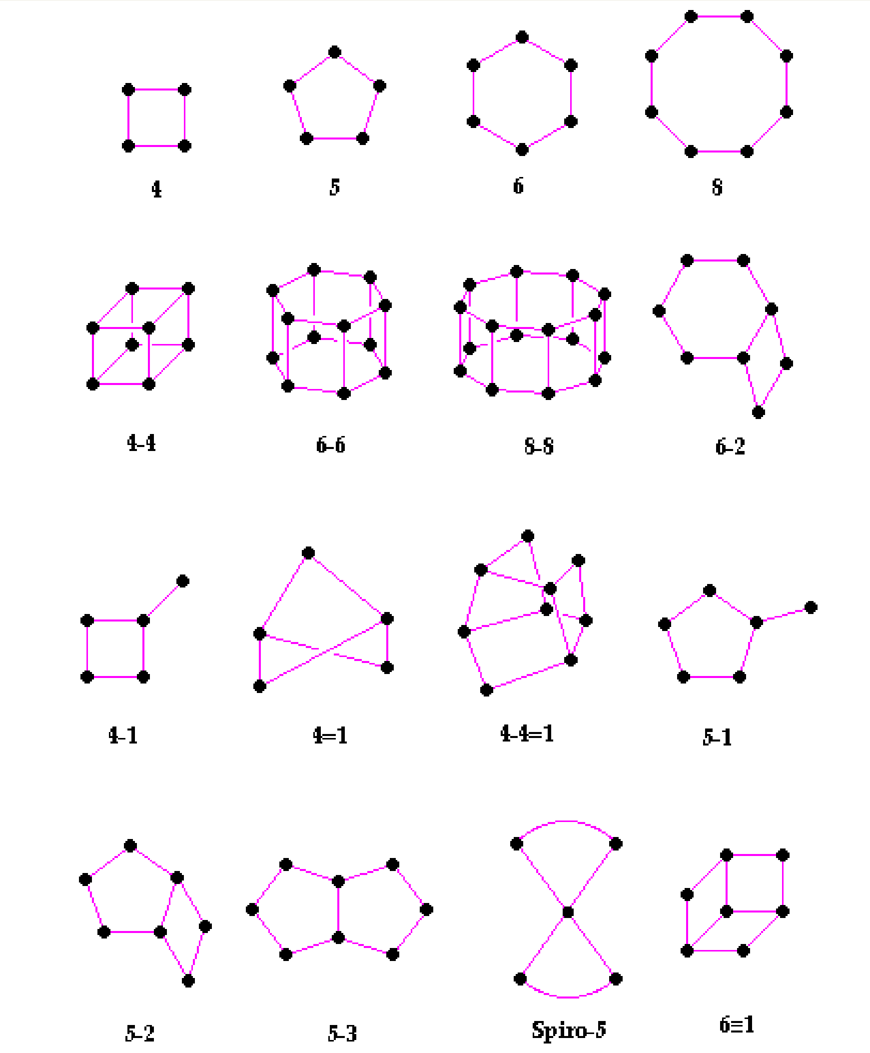
3.1. Introduction of Zeolite

Principle in zeolite construction (Self-assembly behavior)



3.1. Introduction of Zeolite

Secondary building units (SBU)



-The various zeolite structures can be classified according to their secondary building units (SBU) building units (SBU)

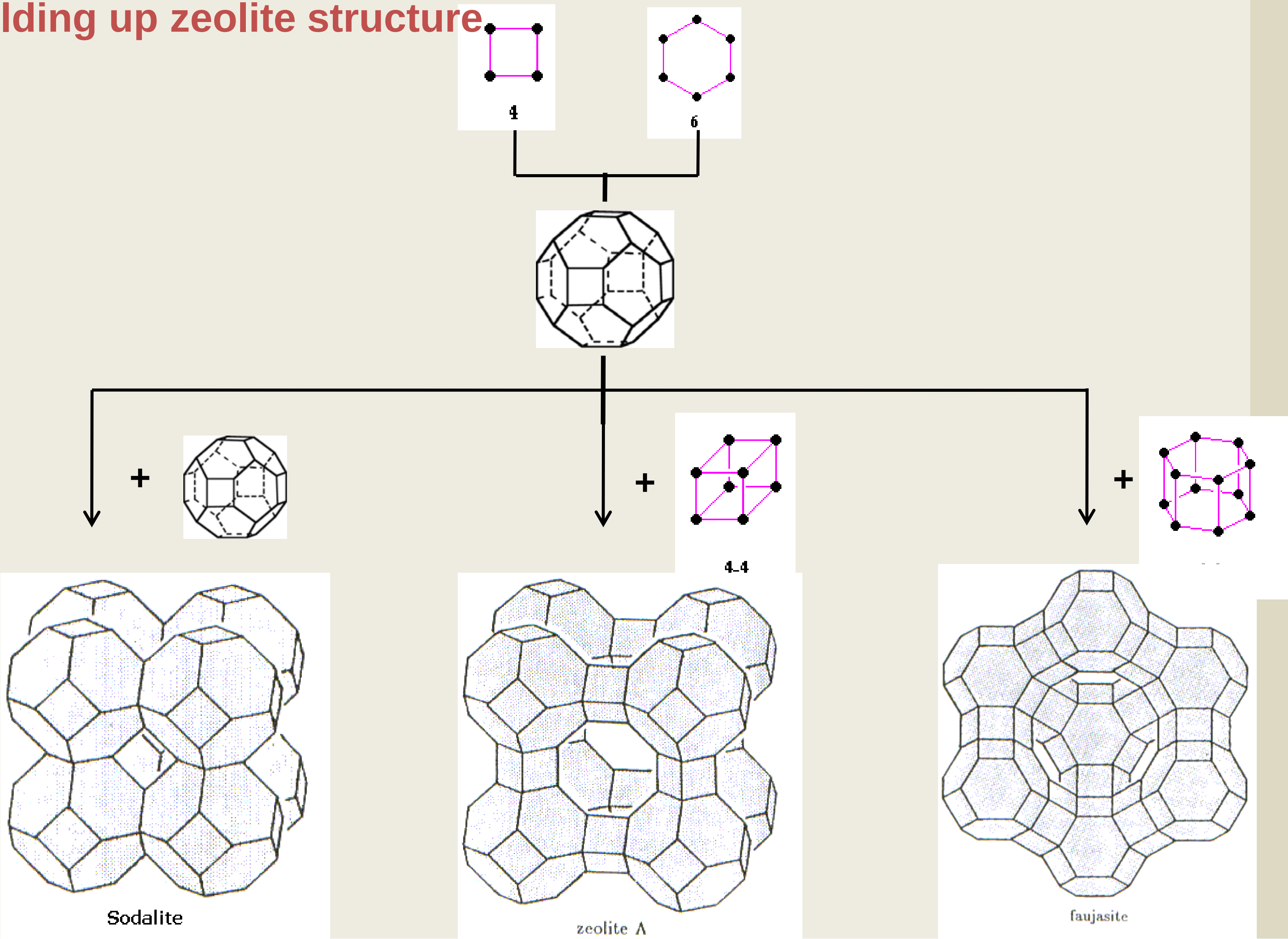
- In the figure- the T atom of the TO_4 tetrahedron is located at each of the corners, and the oxygens are located towards the mid-points of the lines joining each T atom (*the oxygens are not shown to aid clarity*).

- These SBU can contain up to 16 T atoms. It can be noted that SBU's are non-chiral.

CNDL

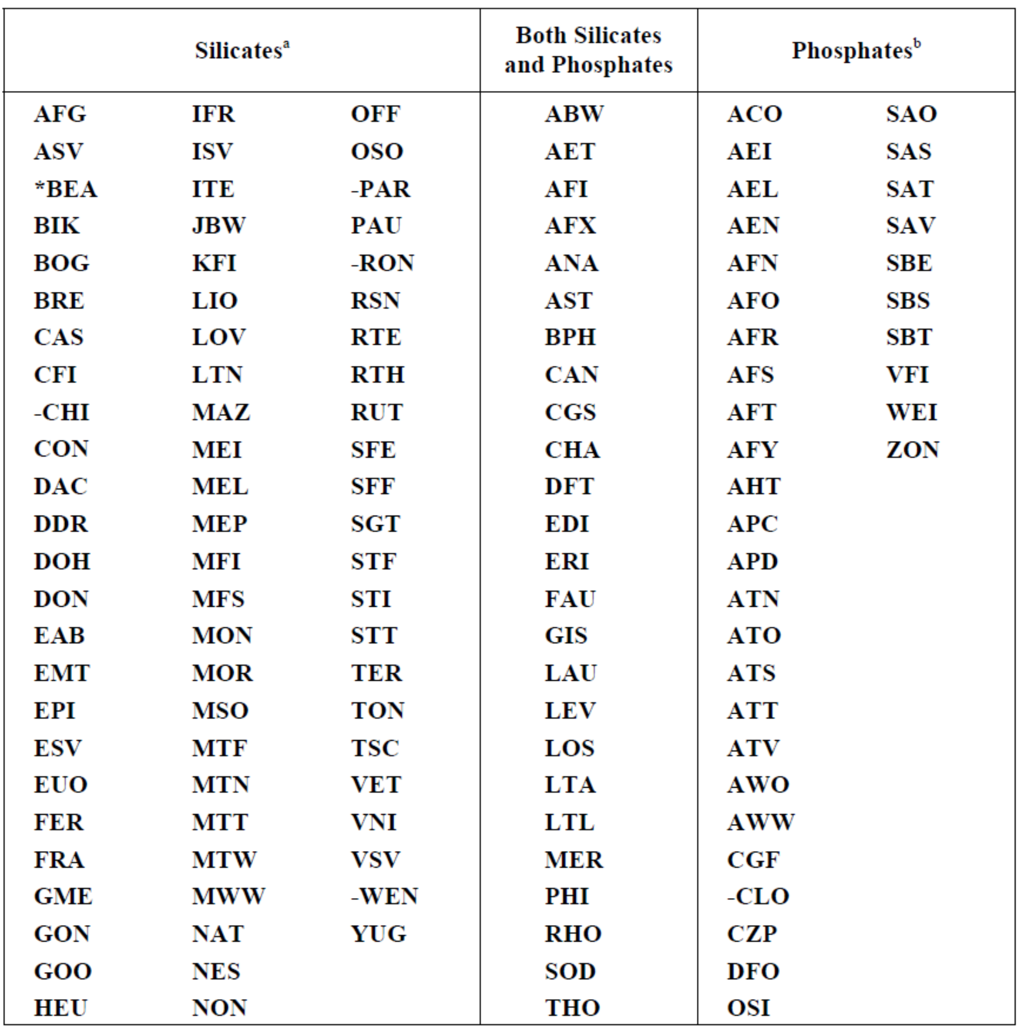
3.1. Introduction of Zeolite

Building up zeolite structure



3.1. Introduction of Zeolite

Structure Code



Silicates[a]			Both Silicates and Phosphates	Phosphates[b]	
AFG	IFR	OFF	ABW	ACO	SAO
ASV	ISV	OSO	AET	AEI	SAS
*BEA	ITE	-PAR	AFI	AEL	SAT
BIK	JBW	PAU	AFX	AEN	SAV
BOG	KFI	-RON	ANA	AFN	SBE
BRE	LIO	RSN	AST	AFO	SBS
CAS	LOV	RTE	BPH	AFR	SBT
CFI	LTN	RTH	CAN	AFS	VFI
-CHI	MAZ	RUT	CGS	AFT	WEI
CON	MEI	SFE	CHA	AFY	ZON
DAC	MEL	SFF	DFT	AHT	
DDR	MEP	SGT	EDI	APC	
DOH	MFI	STF	ERI	APD	
DON	MFS	STI	FAU	ATN	
EAB	MON	STT	GIS	ATO	
EMT	MOR	TER	LAU	ATS	
EPI	MSO	TON	LEV	ATT	
ESV	MTF	TSC	LOS	ATV	
EUO	MTN	VET	LTA	AWO	
FER	MTT	VNI	LTL	AWW	
FRA	MTW	VSV	MER	CGF	
GME	MWW	-WEN	PHI	-CLO	
GON	NAT	YUG	RHO	CZP	
GOO	NES		SOD	DFO	
HEU	NON		THO	OSI	

[a] including germanates
[b] including arsenates

Composition based classification

Origin of some code

✓ A- : the first synthesized

✓ ZSM : synthesized by Socony Mobil.

✓ LT- : synthesieze by Linde. (Linde Type-)

Atlas of zeolite structure types; Walter M. Meier. et al. Eds; Elsevier: 2001.

3.2. Properties and Applications of Zeolite

Representative properties

✓ The microporous character with uniform pore dimensions – allowing certain hydrocarbon molecules to enter the crystals while rejecting others based on too large a molecular size.

✓ The ion-exchange properties – allowing to perform all sorts of ion exchange reaction.

✓ The ability to develop internal acidity – making the zeolites interesting materials for catalyzing organic reactions

✓ Framework robustness and high thermal stability

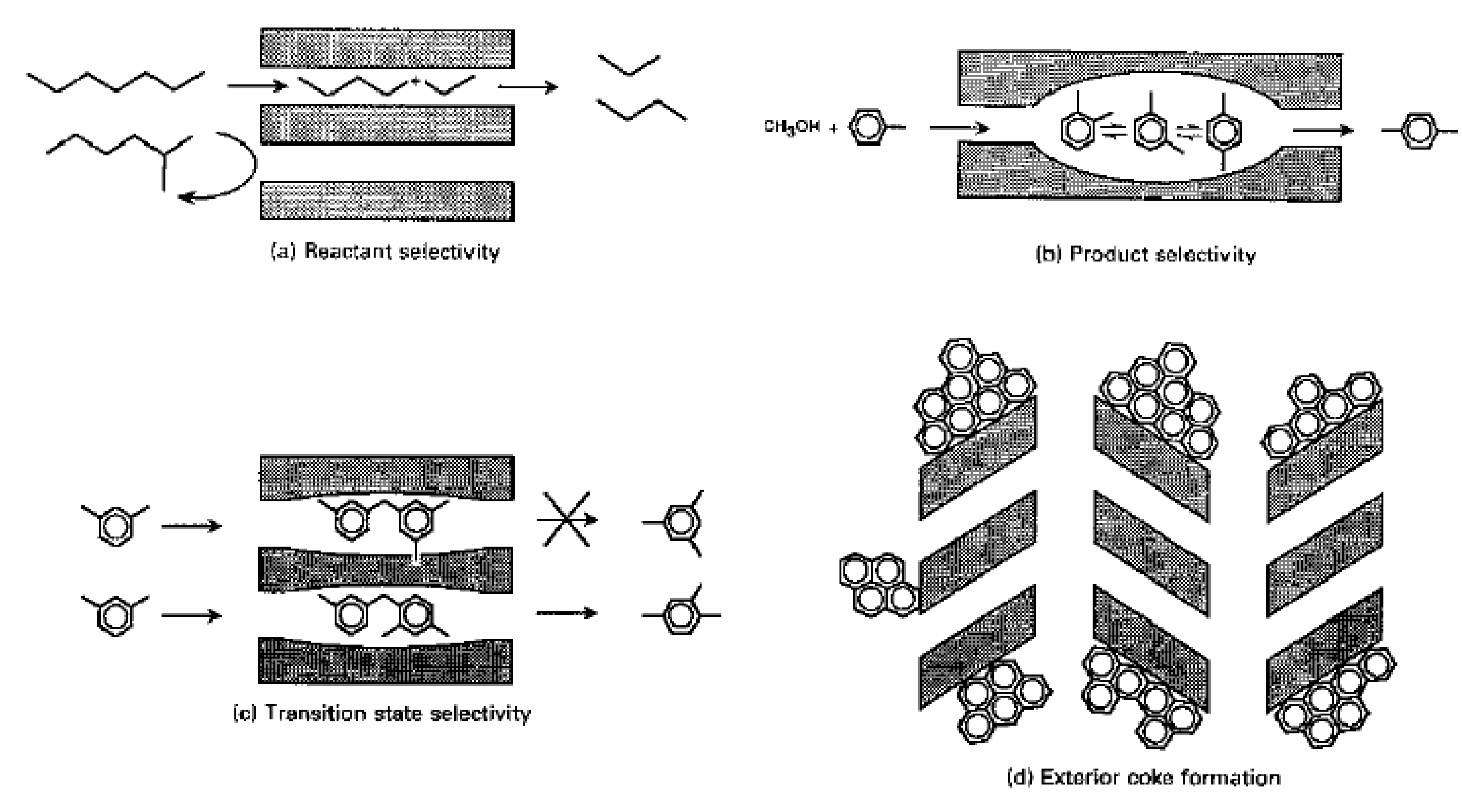
Introduction to Zeolite Science and Practice; Van Bekkum, H. et al. Eds; Elsevier: 1991.

3.2. Properties and Applications of Zeolite

Applications (Shape, Size selectivity)

✓ Molecular sieves : Separation of straight & branched chain hydrocarbons, Separation of CO2 from natural gas

✓ Shape-selective catalysis: Reaction of methanol & toluene to form p-xylene selectively



(a) Reactant selectivity

(b) Product selectivity

(c) Transition state selectivity

(d) Exterior coke formation

3.2. Properties and Applications of Zeolite

Applications (Ion exchange)

✓ Zeolite usually contain cations (e.g., Na^+, K^+, or NH_4^+) after the synthesis.

✓ Cation exchange : radioactive decontamination, e.g. removal of Sr2+ and Cs+ from “dump waters” of nuclear power stations; industrial “water softeners”, to prevent lime-scale blocking up cooling pipes in manufacturing facilities; removal of heavy metals from the environment, e.g. lead, zinc, copper, mercury, cadmium

✓ Anion absorption. Environmental contamination by toxic anions may also be removed, by reaction with heavy metal cations previously exchanged into the zeolite

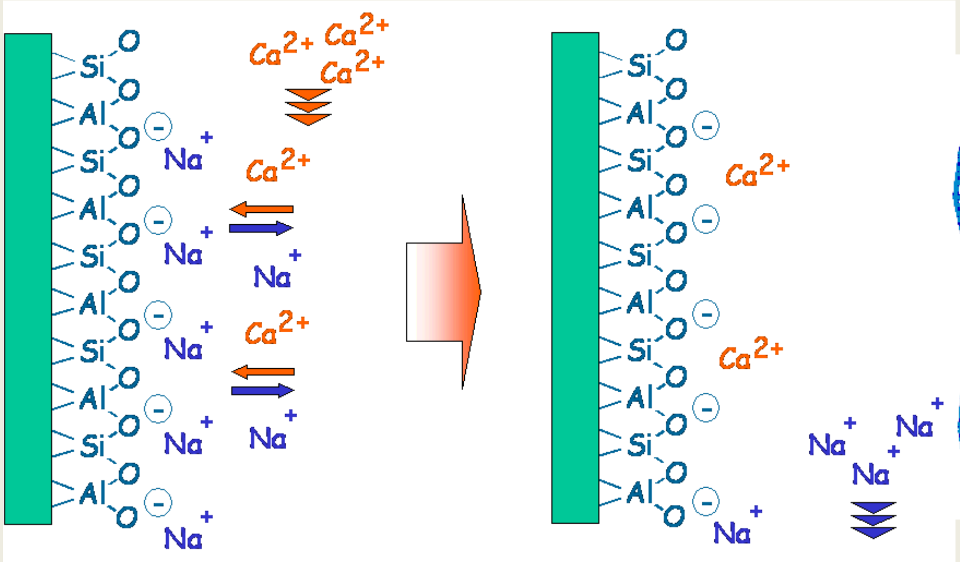


Fig. Ion-exchangers to remove cationic species from aqueous solutions by replacing them by sodium cations.

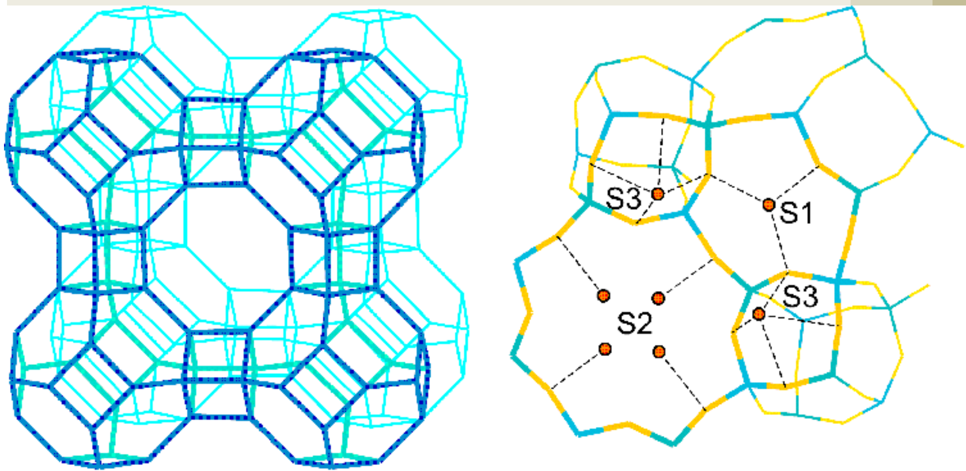
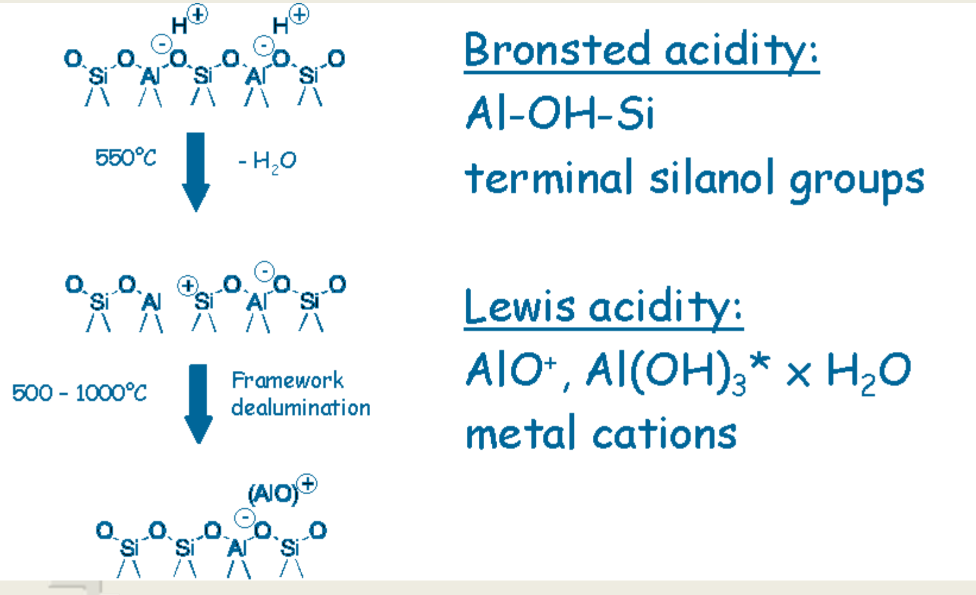


Fig. the most common cation sites in Zeolite A as an example

3.2. Properties and Applications of Zeolite

Applications (Acidity)

✓ Protonated zeolites have acidic properties.
✓ Reduction in NOx emissions from vehicles, using zeolite-loaded “catalytic converter”.
✓ Catalysts : petroleum refining, synfuel production, petrochemical production.
✓ p-xylene is needed for the production of polyesters - Xylenes can be rearranged over ZSM-5



Bronsted acidity:

Al-OH-Si

terminal silanol groups

Lewis acidity:

AlO^+, $Al(OH)_3^* \times H_2O$

metal cations

Fig. Acidity in zeolite

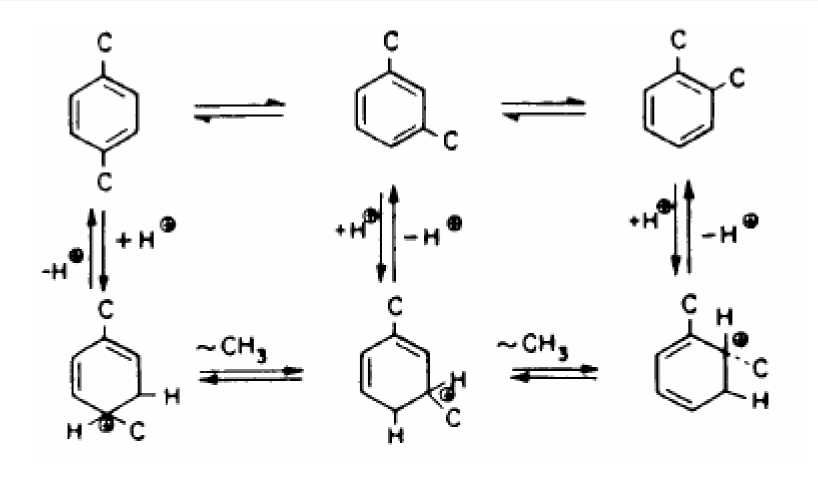


Fig. selectively obtained p-xylene

3.2. Properties and Applications of Zeolite

Applications (The others)

✓ Medical applications: Hemosorb and QuikClot are commercial products based on zeolites which when applied to wounds (in accidents or surgery) are said to cause an "instant" cessation of bleeding. Zeolites are also used in kidney dialysis machines, to absorb ammonia from blood and prevent it from building up in the body (a job that healthy kidneys normally do).

✓ Agriculture: for supplying K+ and NH4+ to plants from soils that have been enriched with zeolites exchanged specifically with these cations. It is suggested that such "zeoponics", as the strategy is called, might be used to grow food on long space missions.

✓ Separation of gases: there are commercial units that can provide oxygen of 95% purity for use in hospitals or for patients e.g. suffering from emphysema and other forms of Obstructive Pulmonary Disease (OPD), by separating it from air. Nitrogen (80% of air) is preferentially absorbed over oxygen because of its much larger molecular electric quadrupole moment, and so enables oxygen to separate from air almost in a state of purity.

Annu. Rep. Prog. Chem., Sect. C, **2007**, 103, 287

3.3. Synthesis of Zeolites

Hydrothermal synthesis

✓ Most zeolites have been synthesized under hydrothermal conditions.

✓ 'hydros' in the Greek meaning water and 'thermos' meaning heat

✓ After Si and Al sources and mineralizers such as NaOH or KOH are mixed in water, the hydrogels obtained are heated at prescribed temperature and crystallized into zeolites

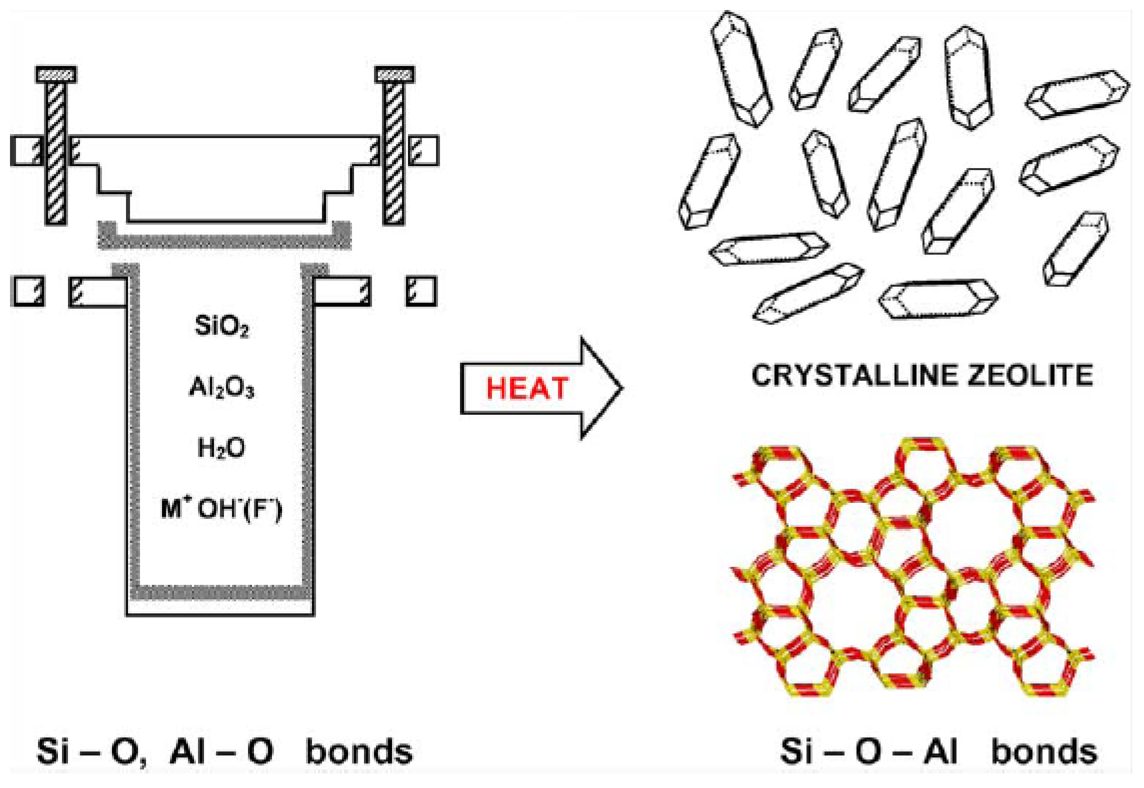
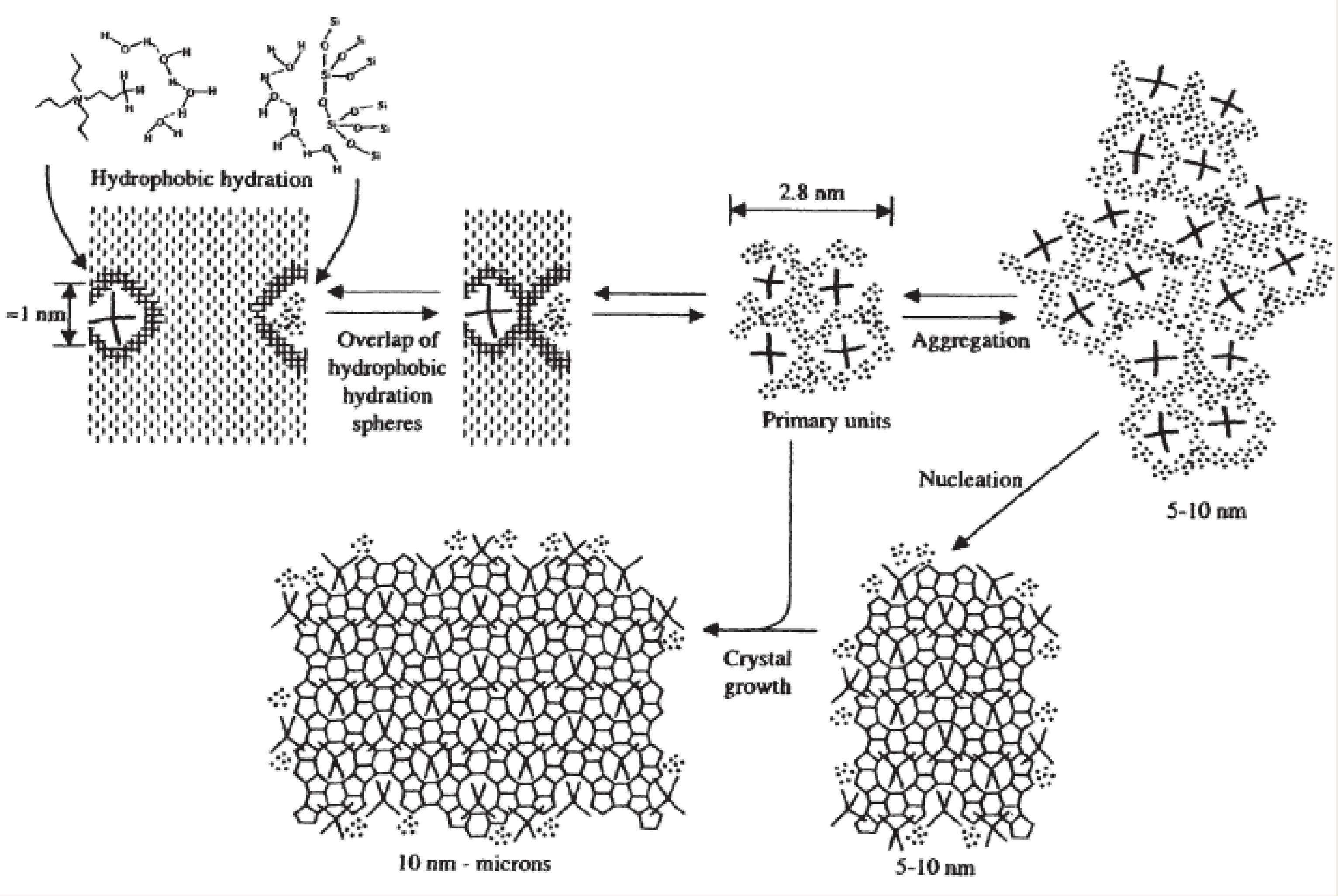


Fig. Hydrothermal reaction for synthesis of zeollite

Micropor. Mesopor. Mater. **2005**, 82, 1.

3.3. Synthesis of Zeolites

Overview of crystallization mechanism of zeolite



Chem. Lett. **2005**, 34, 276

3.3. Synthesis of Zeolites

The evolution of order

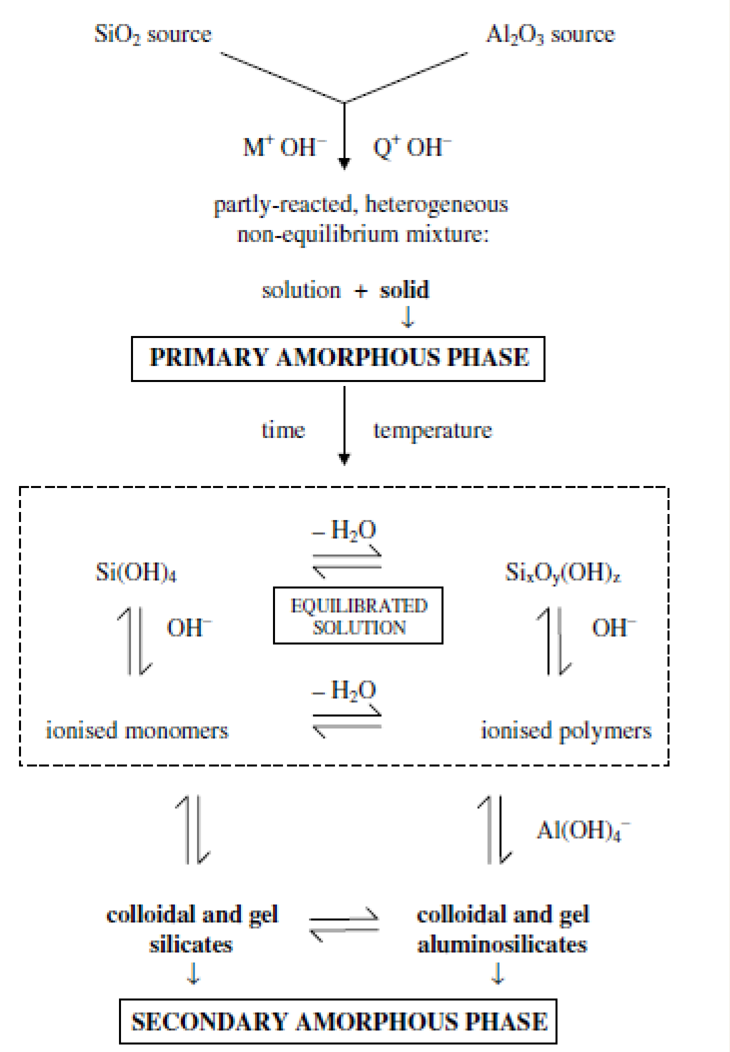


Fig. Equilibration of the starting mixture to establish a partly ordered intermediate (secondary amorphous phase) and a characteristic distribution of solution species.

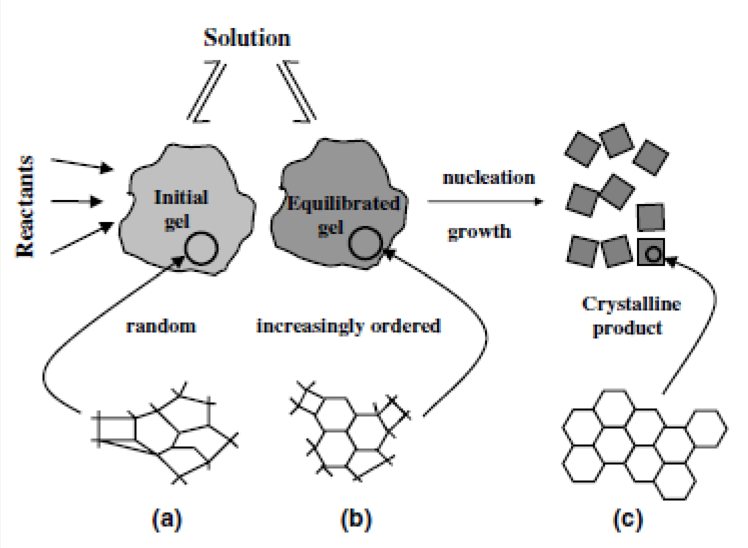


Fig. The evolution of order, from the primary amorphous phase (a) through the secondary amorphous phase (b) to the crystalline product (c)

Micropor. Mesopor. Mater. **2005**, 82, 1.

3.3. Synthesis of Zeolites

Nucleation

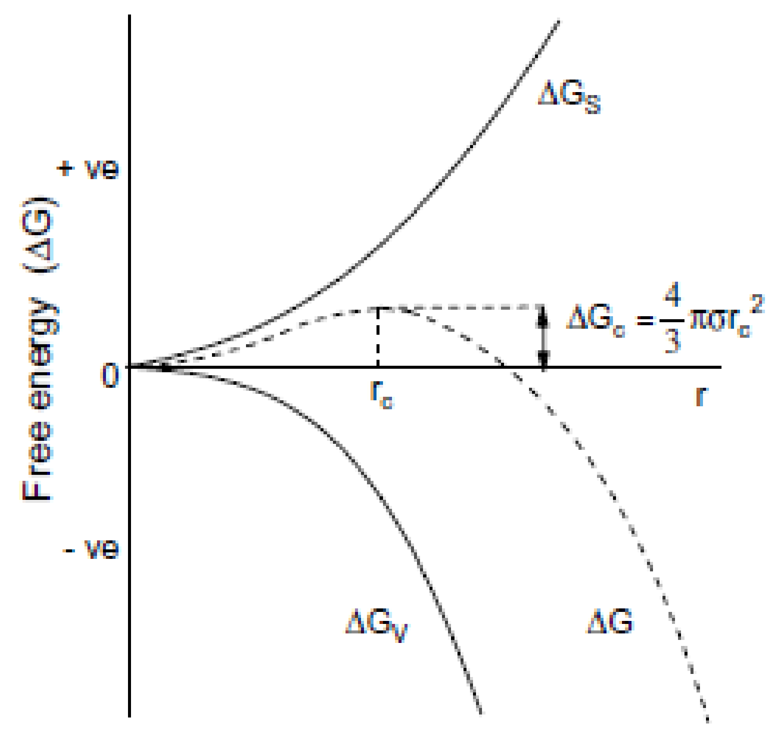


Fig. The energetics of nucleation, illustrating the concept of a critical nucleus of radius r_c; beyond this size, the net energy gain from the resultant (ΔG) of cohesive (ΔG$_v$) and surface (ΔG$_s$) terms is favourable to growth

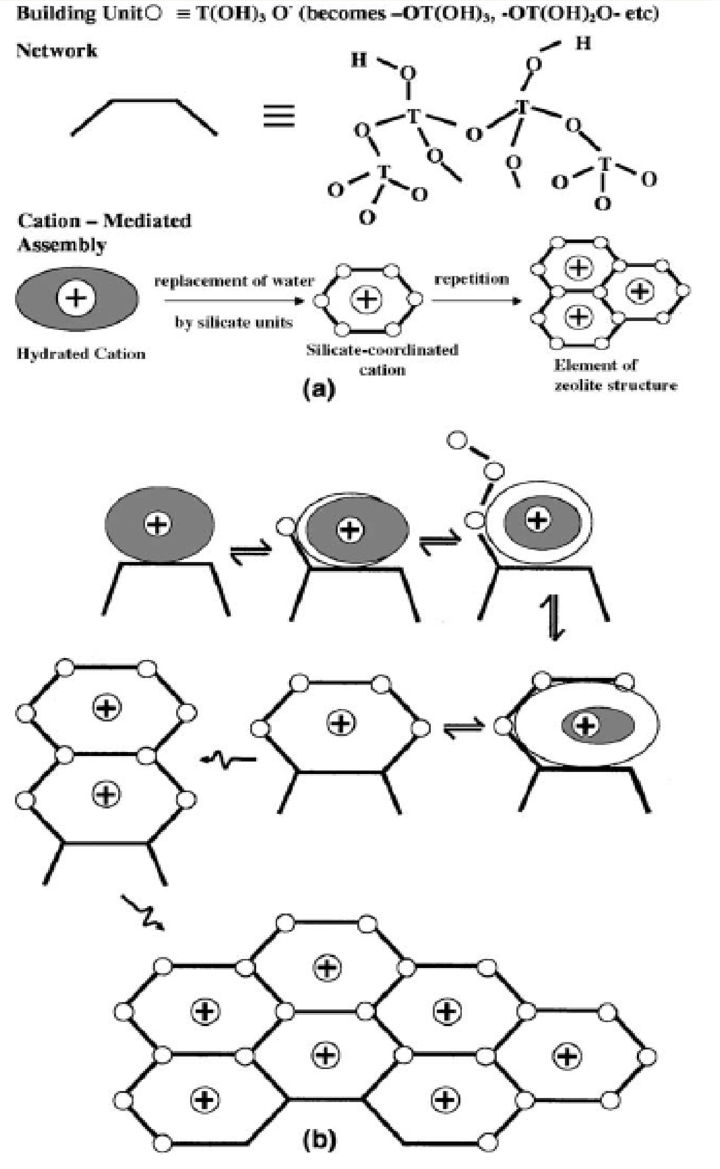


Fig. The basic mechanism for the cation-mediated assembly of ordered regions: (a) nomenclature and symbolism; (b) details of in-situ construction process by addition of solution units to a surface site

Micropor. Mesopor. Mater. **2005**, 82, 1.

Ref : Phase transformation Textbook

3.3. Synthesis of Zeolites

Crystal growth

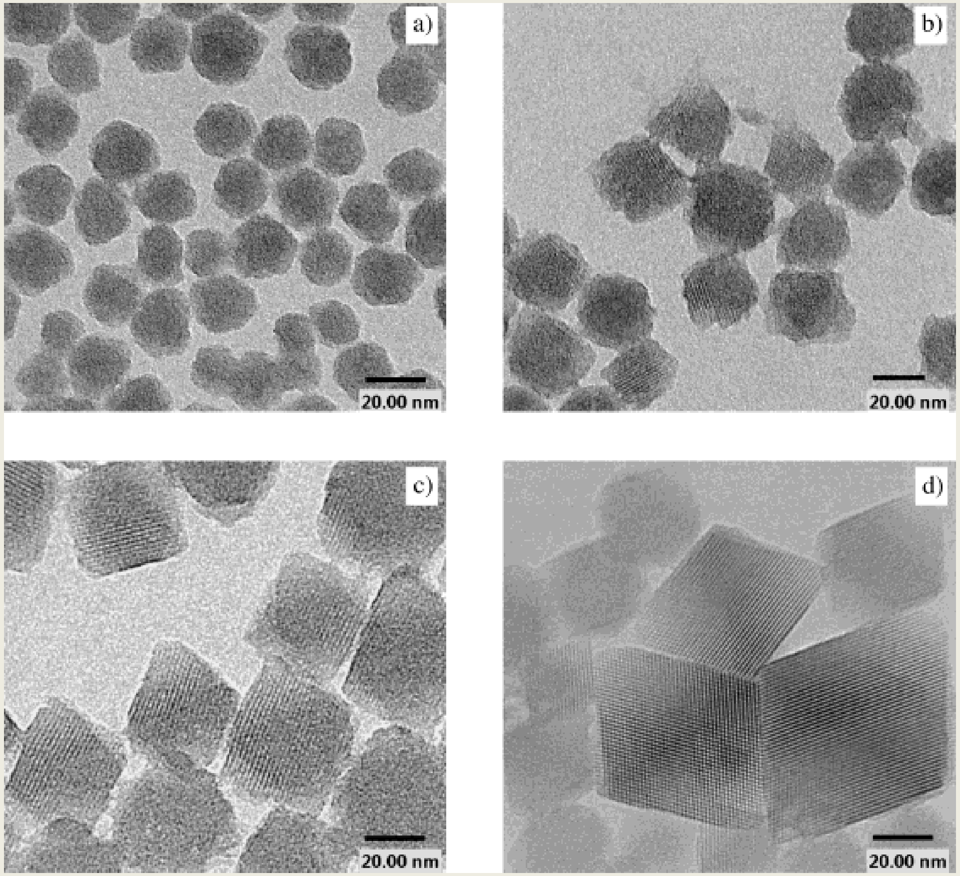


Fig. Particles in a) freshly prepared aluminosilicate solution for the synthesis of zeolite Y and after hydrothermal treatment at 100°C for b) 28, c) 48, and d) 75 h

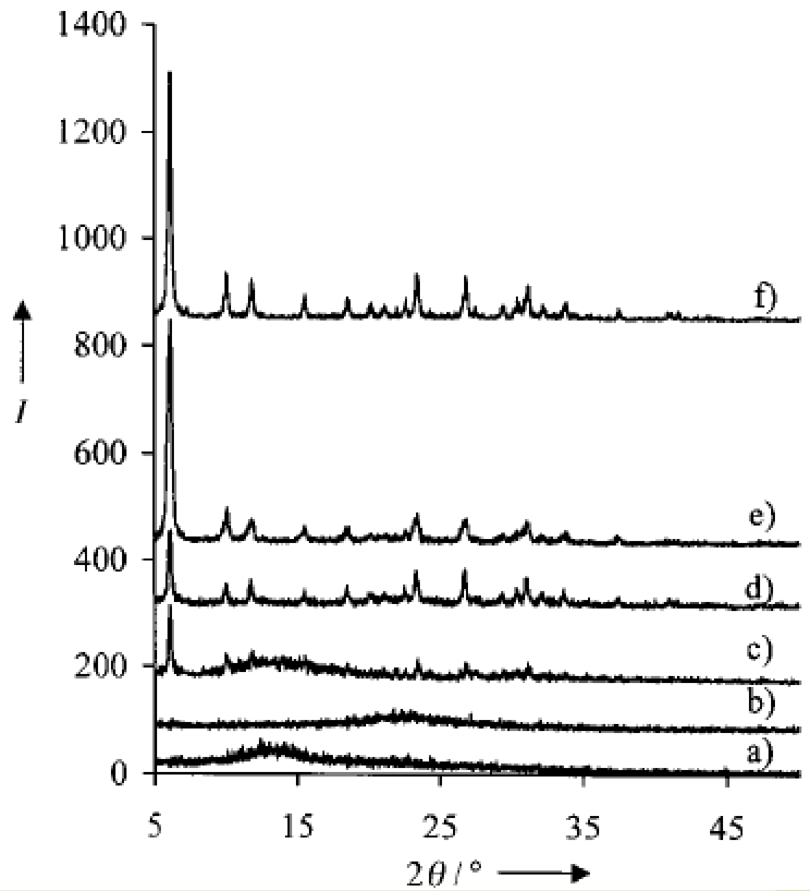


Fig. Powder diffraction patterns of a) the freshly prepared solution for the synthesis of zeolite Y (containing all reagents) and after hydrothermal treatment for b) 24, c) 28, d) 38, e) 55, and f) 75 h.

Angew. Chem. Int. Ed., **1999**, 38, 3201.

3.3. Synthesis of Zeolites

Crystal growth

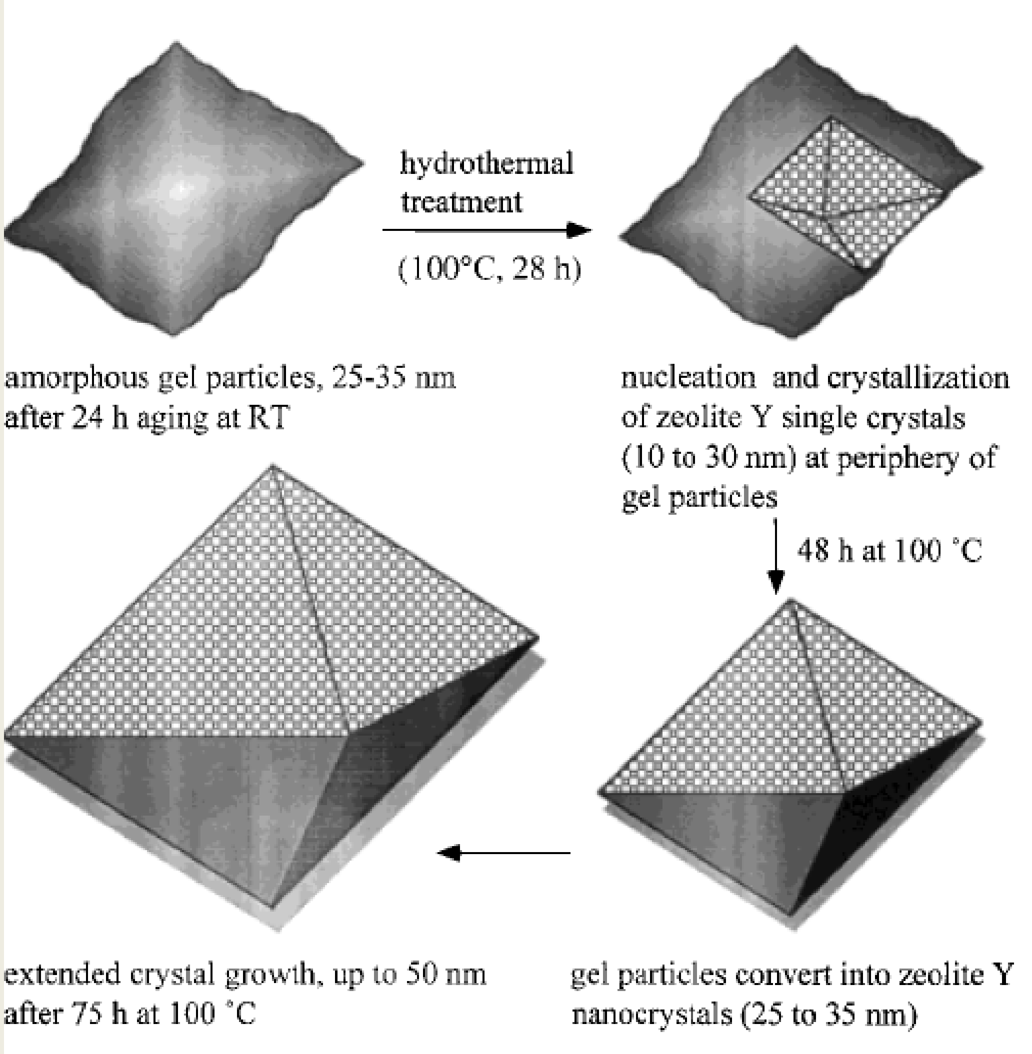


Fig. Proposed reaction scheme for the zeolite growth mechanism in colloidal solution.

Angew. Chem. Int. Ed., **1999**, 38, 3201.

3.3. Synthesis of Zeolites

Crystal growth (Detail)

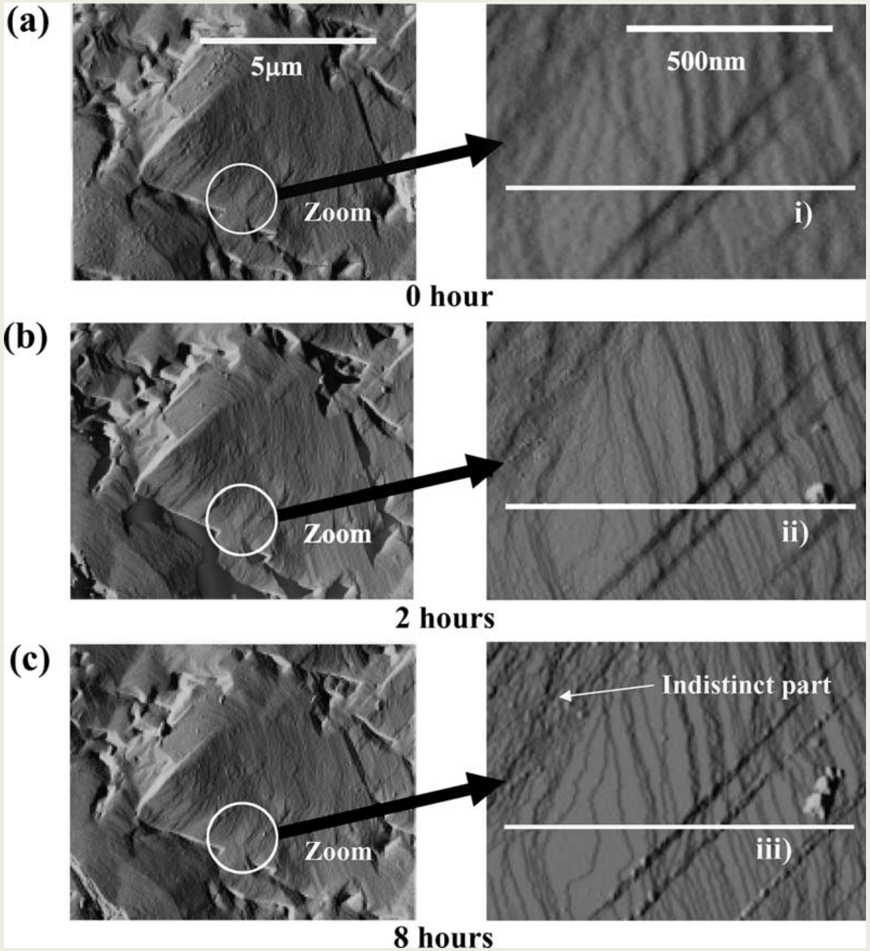


Fig. Changes in the faujasite surface at the same position on a (1 1 1) face during seeded growth observed by AFM. The images were taken at (a) 0 h, (b) 2 h, and (c) 8 h of the growth period

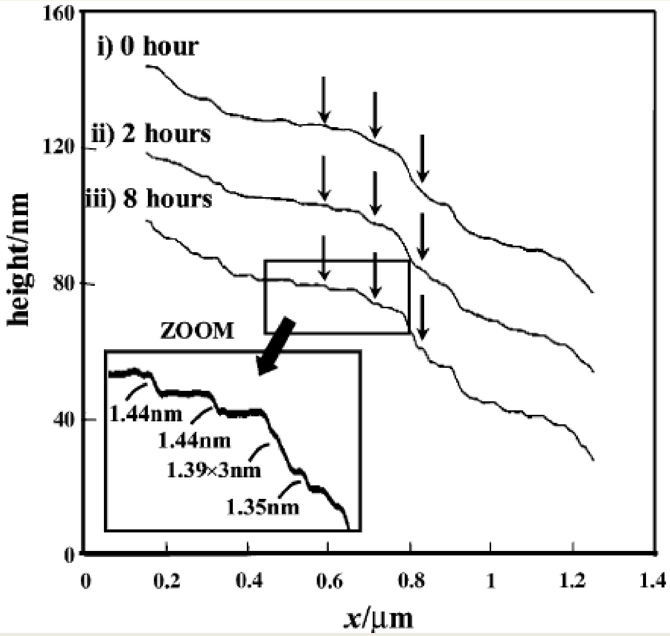


Fig. Cross-sectional profiles of (i), (ii) and (iii) along with the lines as labeled in (a), (b), and (c), respectively.

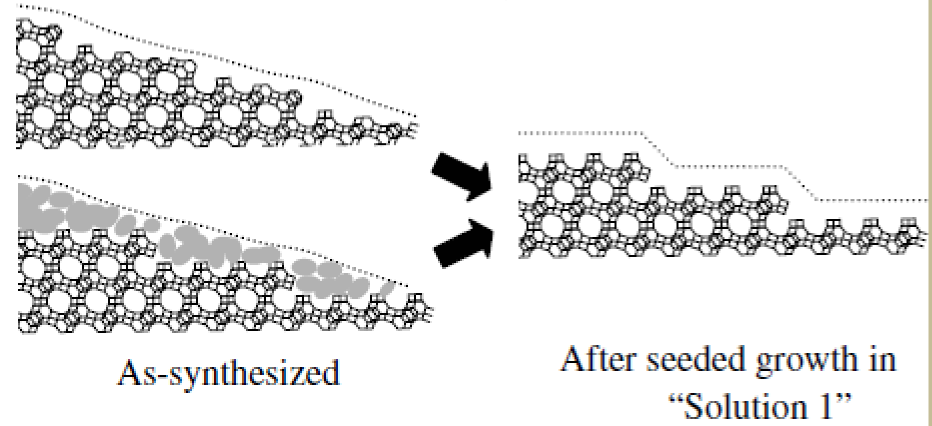
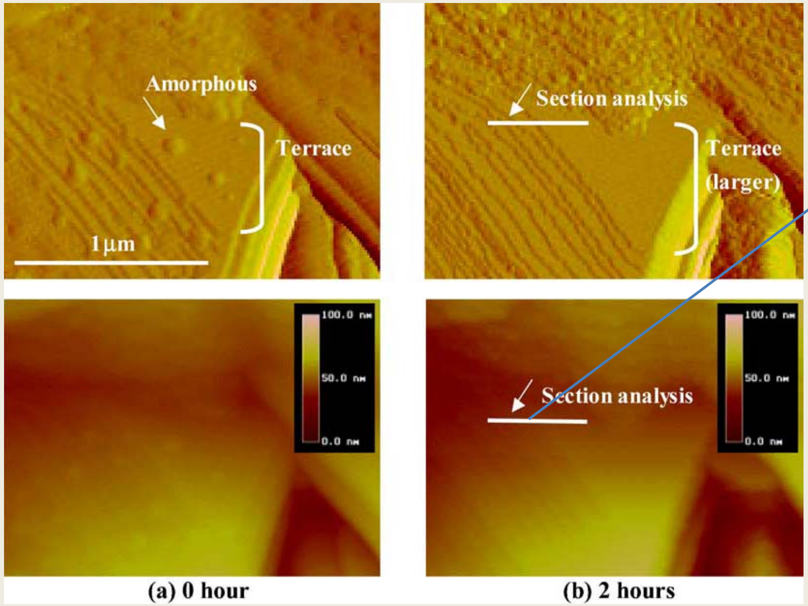


Fig. A model of the changes in the top-surface structure. The left part is a model of as-synthesized faujasite. The top surface is terminated with various structures (upper left) and/or is covered with amorphous matter (lower left). The right part is after the seeded growth in solution 1, where it is assumed that the top surface is terminated with D6Rs as shown in Fig. 5(c)

Micropor. Mesopor. Mater. **2004**, 70, 7.

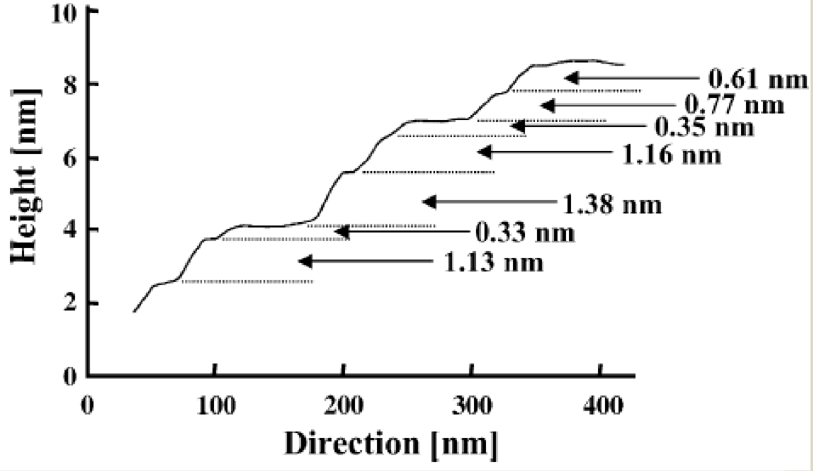
3.3. Synthesis of Zeolites

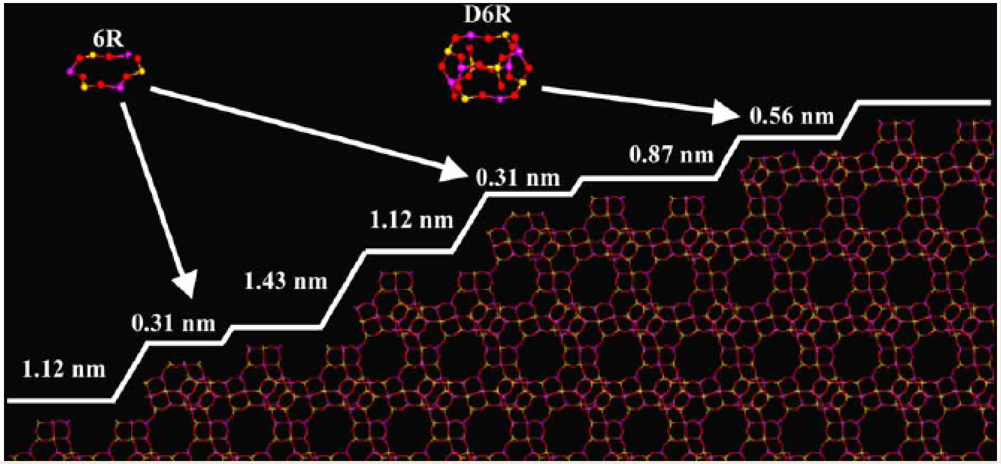
Crystal growth (Detail)



(a) 0 hour (b) 2 hours

Fig. Magnified images of the lower part of Fig. 8, as labeled (a) 0 h and (b) 2 h





✓ The rough surface of the seed changed into a well-ordered (1 1 1) face during the seeded growth near equilibrium.

✓ This surface ordering proceeded by thermodynamic stabilization of the top-surface structure via the mutual transfer of aluminosilicate species between the solution and solid phases, and/or by dissolution of the amorphous matter on the seed.

Micropor. Mesopor. Mater. **2004**, 70, 7.

3.4. Zeolite Template for Organic Nanomaterial Synthesis

Zeolite Templated Carbons (ZTC)

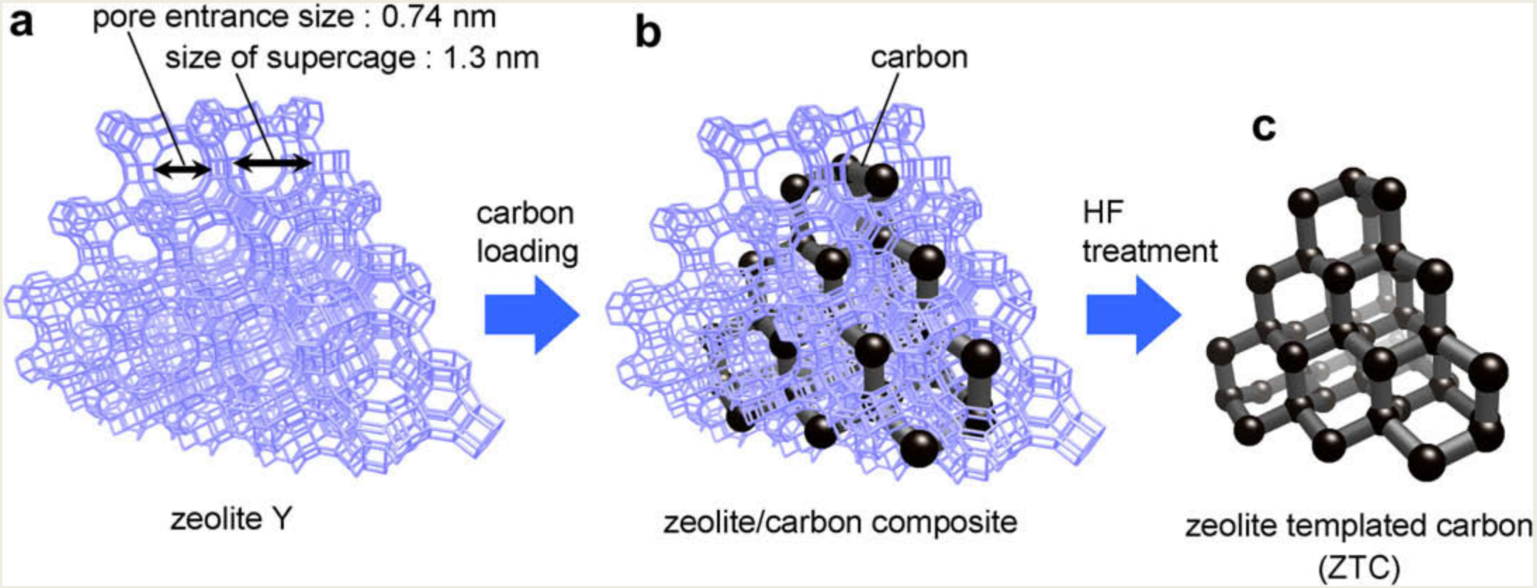


Fig. Synthesis procedure of the ZTC. (a) Crystal structure of the zeolite Y template, (b) illustration of zeolite/carbon composite. Impregnated carbon is shown by a black framework and (c) framework structure of the liberated ZTC after HF washing.

Carbon, **2009**, 47, 1220.

3.4. Zeolite Template for Organic Nanomaterial Synthesis

Zeolite Templated Carbons (ZTC)

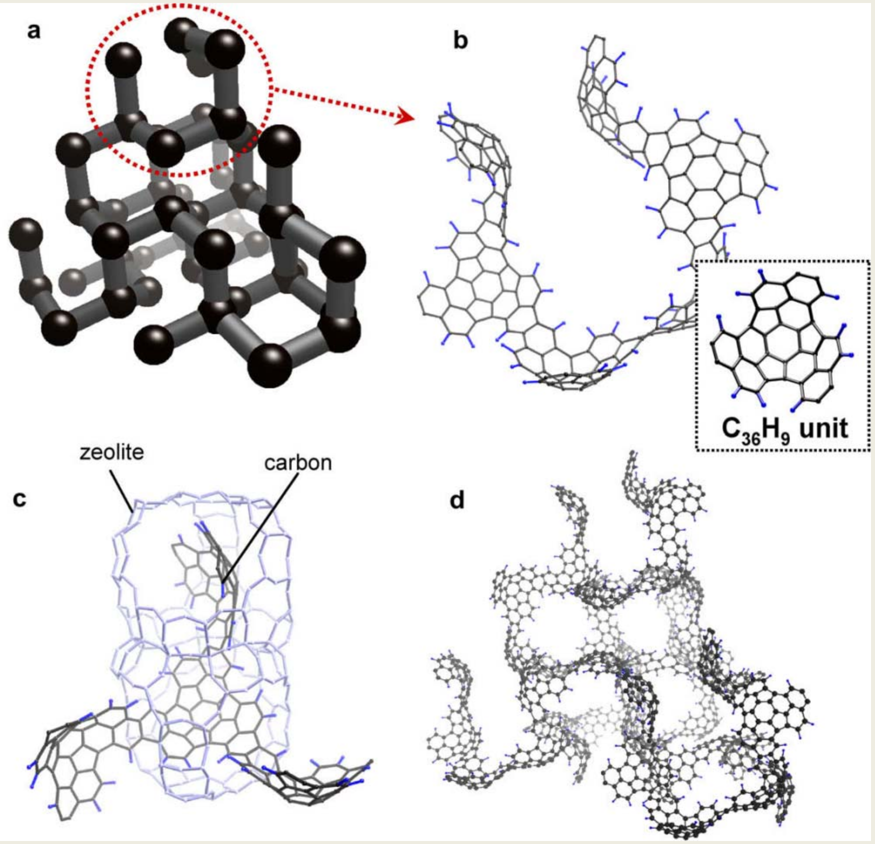


Fig. Idealized molecular model containing only carbon and hydrogen atoms. (a) A ball and stick model for the structure of the ZTC framework. Black sphere and gray stick correspond to a basic buckybowl unit and the connection between two units, respectively, (b) an idealized molecular model constructed with six buckybowl units of C36H9 (inset). All the graphene edges are passivated with hydrogen atoms. The structure in (b) corresponds to the part indicated by a dotted circle in the network structure in (a), (c) the molecular model constructed with four buckybowl units with zeolite framework and (d) a large-sized molecular model that is constructed with the buckybowl units following the regularity of the zeolite Y template. The model (d) has the same network structure as the model (a)

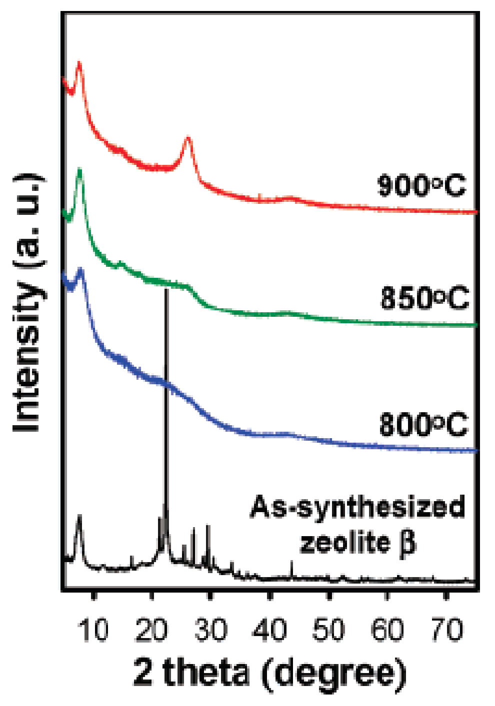
Carbon, **2009**, 47, 1220.

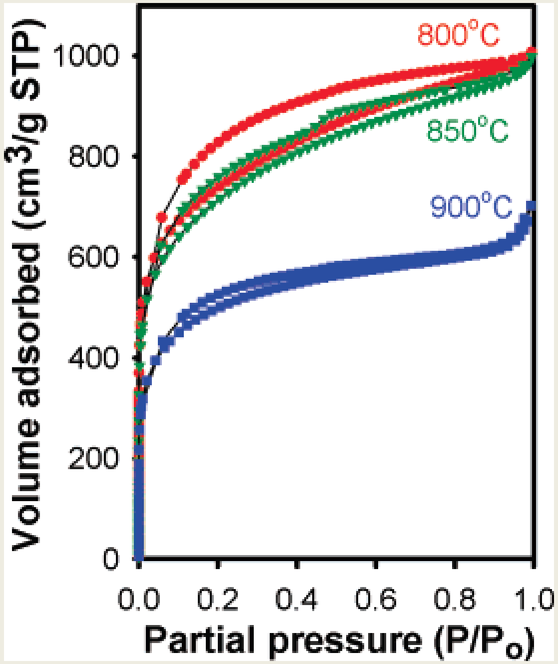
3.4. Zeolite Template for Organic Nanomaterial Synthesis

Zeolite-Like Carbons Nanocast Using As-Synthesized Zeolite Templates

Synthesis procedures:

1. An alumina boat with 0.5 g of dry as-synthesized zeolite β was placed in tube furnace
2. Heated to the required temperature (800-900 °C) under a flow of nitrogen saturated with acetonitrile for 3 h and cooling under a flow of nitrogen only.
3. Resulting zeolite/carbon composites were recovered and washed with 25% hydrofluoric (HF) acid for 3 days to remove the zeolite framework





CVD temp (°C)	N content (wt %)	surface area (m^2/g)[a]	pore volume (cm^3/g)[b]
800	3.3	2535 (1631)	1.56 (0.77)
850	3.5	2470 (1611)	1.54 (0.76)
900	4.6	1721 (1310)	1.09 (0.61)

J. Phys. Chem. C., **2008**, 112, 2764.

3.4. Zeolite Template for Organic Nanomaterial Synthesis

Zeolite-Like Carbons Nanocast Using As-Synthesized Zeolite Templates

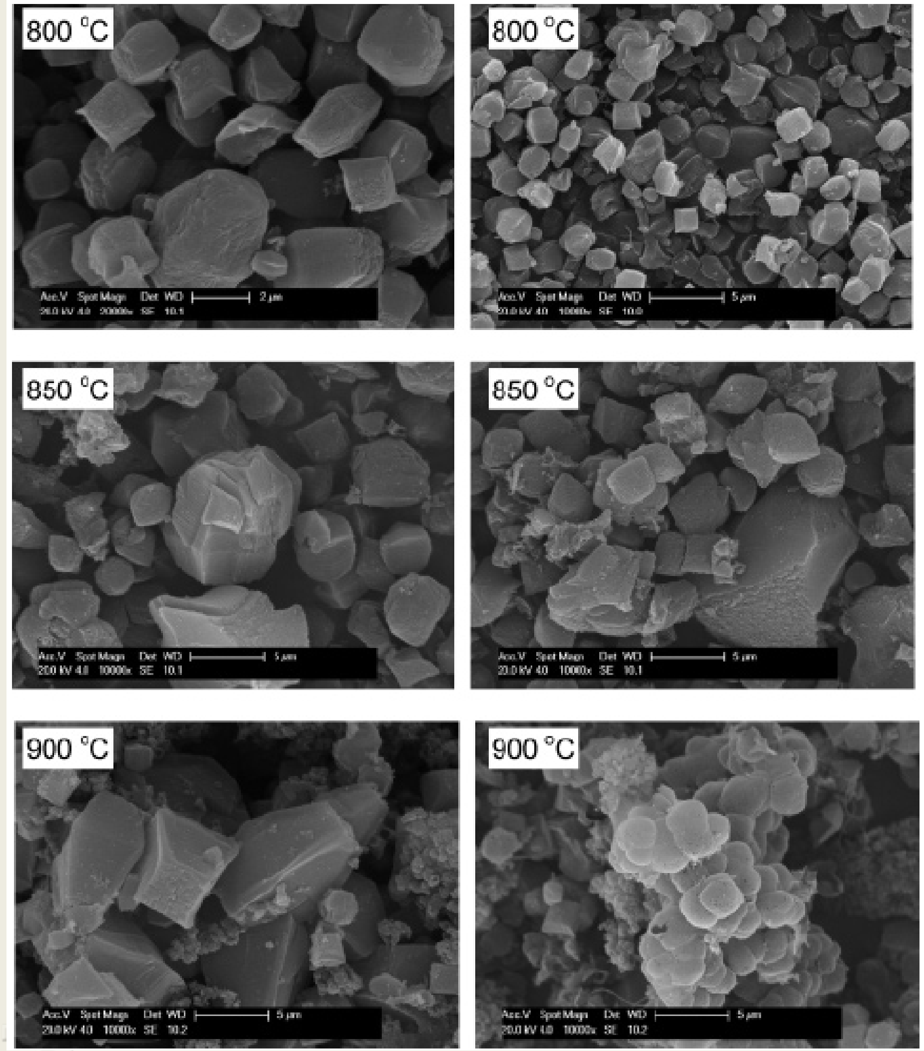


Fig. SEM micrographs of carbon materials prepared using zeolite template via CVD at various temperature

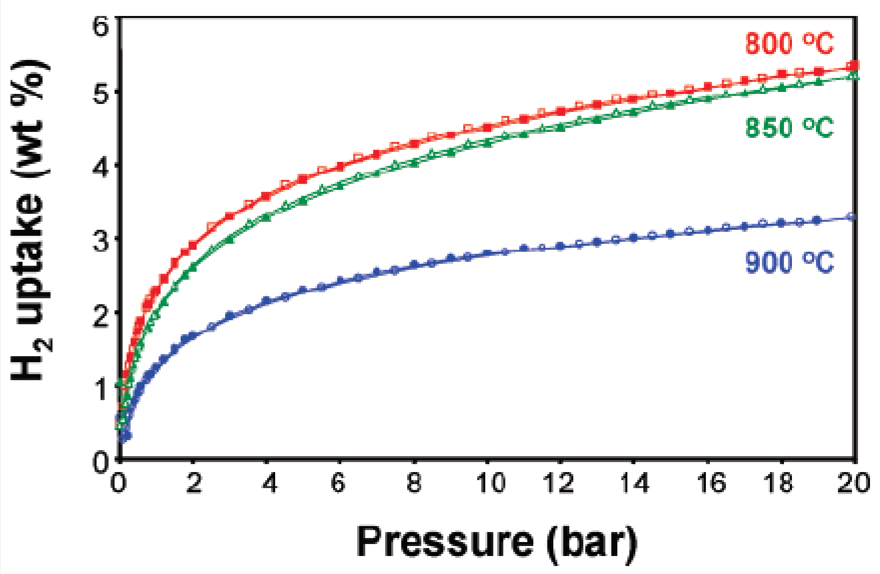


Fig. Hydrogen sorption isotherms at -196 °C of carbons obtained via CVD at various temperatures using as-synthesized zeolite as template.

J. Phys. Chem. C., **2008**, 112, 2764.