Sol-Gel Methods

PRECURSOR

Sol-gel process (vertical arrow)
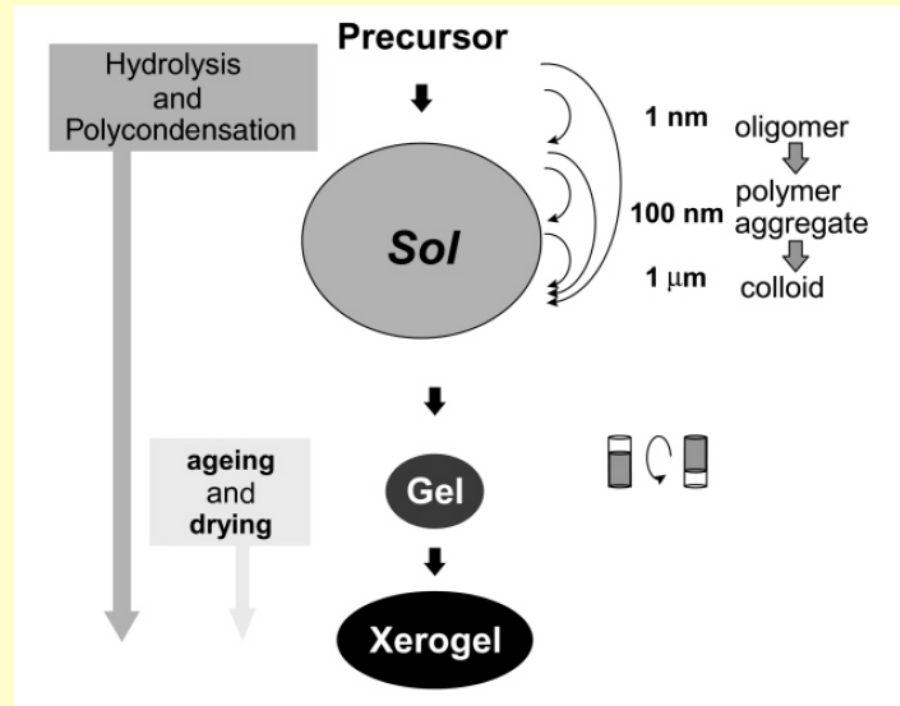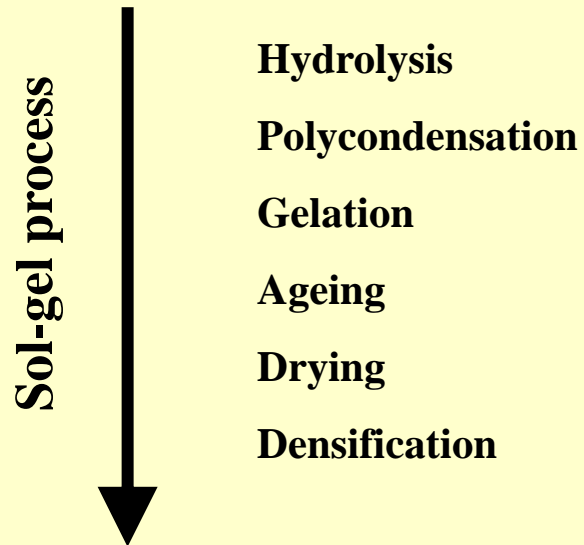
Hydrolysis

Polycondensation

Gelation

Ageing

Drying

Densification

Powders: microcrystalline, nanocrystalline, amorphous

Monoliths, Coatings, Films, Fibers

Aerogels

Glasses, Ceramics, Hybrid materials

Sol-Gel Methods

Sol = a fluid system of stable suspension of colloidal (1 nm – 1 μm) solid particles or polymeric molecules in a liquid

(Below 1 μm – Brownian motion, above – sedimentation)

Gel = nonfluid, porous, three-dimensional, continuous solid network (elastic or rigid) surrounded by a continuous liquid phase
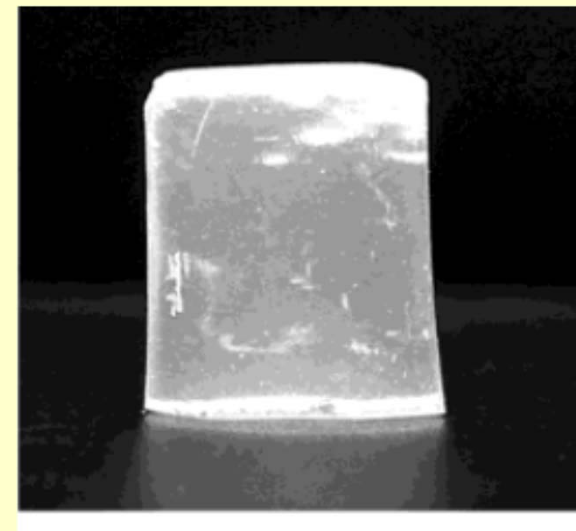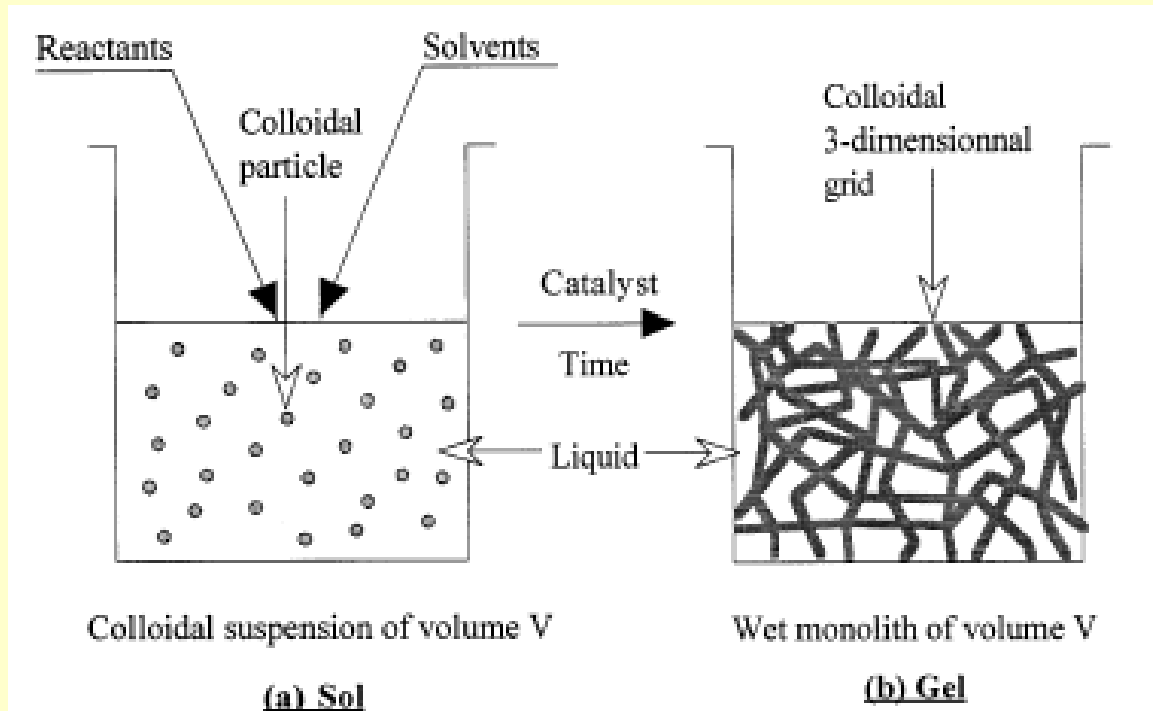
Colloidal (particulate) gels = agglomeration of dense colloidal particles

Polymeric gels = agglomeration of polymeric particles made from subcolloidal units

Agglomerate = assemblage of particles **rigidly** joined together, as by partial fusion (sintering) or by growing together, covalent bonds, hydrogen bonds, polymeric chain entanglement

Aggregate = assemblage of particles which are **loosely** coherent, van der Walls forces
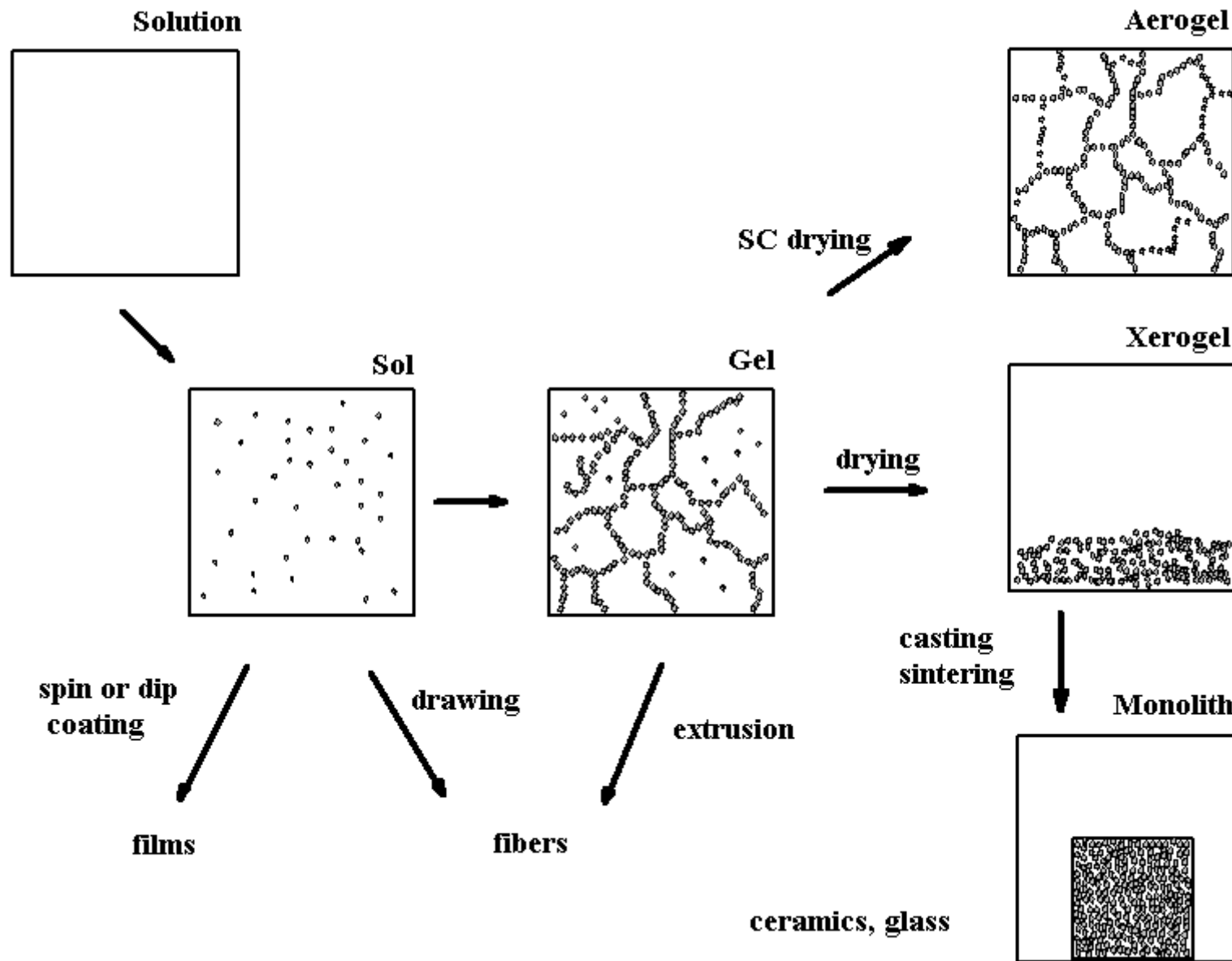
Sol and Gel

Reactants   Solvents

Colloidal
particle

Catalyst

Colloidal
3-dimensionnal
grid

Time

Liquid

Colloidal suspension of volume V

Wet monolith of volume V

(a) Sol

(b) Gel

Gel point = point of incipient network formation

Sol-to-Gel transition is difficult to define
Rheological methods = viscosity increases

Sol-Gel Methods

Sol-Gel Process

Solution

Aerogel

SC drying

Sol

Gel

Xerogel

drying

spin or dip coating

drawing

extrusion

casting sintering

films

fibers

Monolith

ceramics, glass
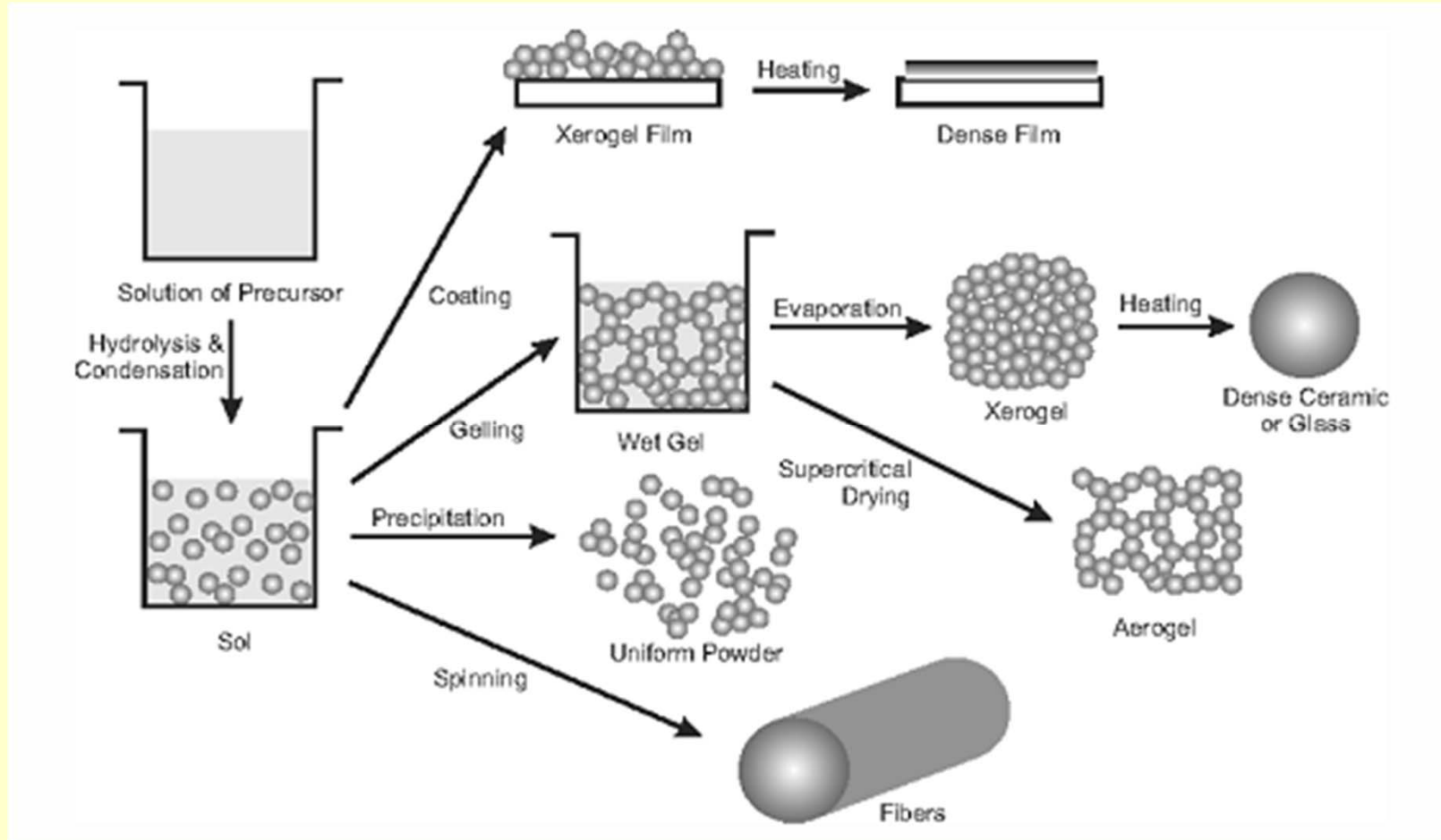
Sol-Gel Methods

Sol-Gel Chemistry

Aqueous

• **Colloid Route – inorganic salts, water glass, pH, hydrolysis, polycondensation**

• **Metal-Oragnic Route – metal alkoxides, amides, hydrolysis, polycondensation**

• **Pechini and Citrate Gel Method – inorganic metal salts, complexing agent, chelate formation, polyesterification with polyfunctional alcohol**
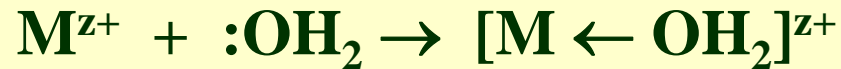
Nonaqueous

• **Hydroxylation**
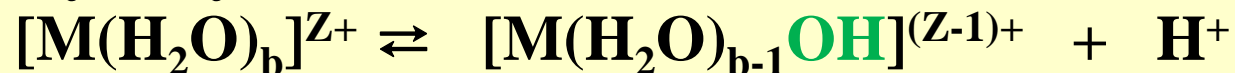
• **Heterofunctional Condensations**

Colloid Route

Metal salts in aqueous solution, pH and temperature control

Solvation – water molecule becomes more acidic

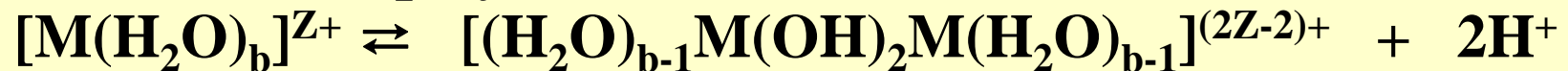$$M^{z+} + :OH_2 \rightarrow [M \leftarrow OH_2]^{z+}$$

For transition metal cations, charge transfer occurs from the filled bonding orbital of the water molecule to the empty d orbitals of the transition metal. Therefore, the partial positive charge on the H of water molecule increases, making the water molecule more acidic.
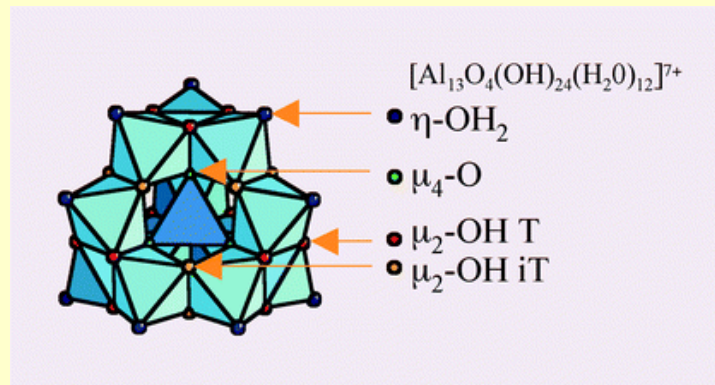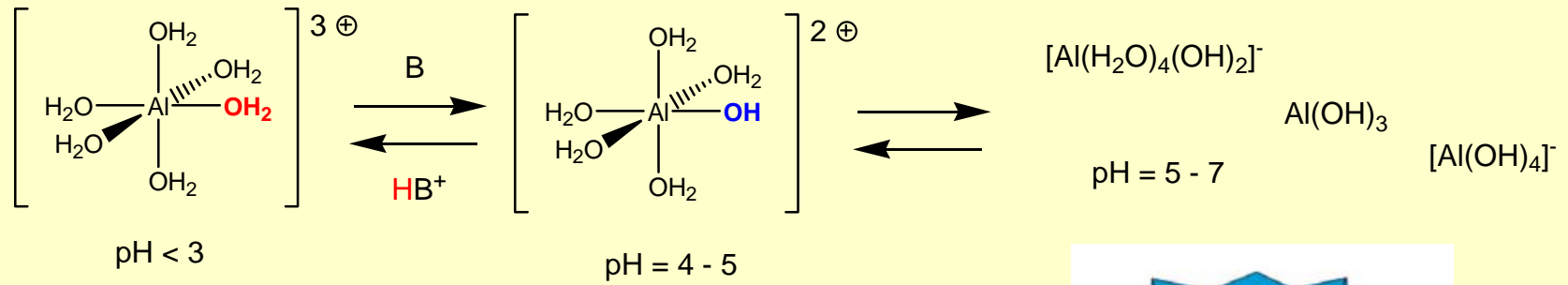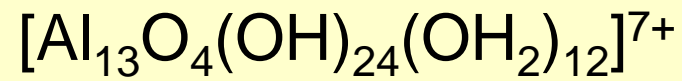
Hydrolysis

$$[M(H_2O)_b]^{Z+} \rightleftarrows [M(H_2O)_{b-1}OH]^{(Z-1)+} + H^+$$

Condensation-polymerization

$$[M(H_2O)_b]^{Z+} \rightleftarrows [(H_2O)_{b-1}M(OH)_2M(H_2O)_{b-1}]^{(2Z-2)+} + 2H^+$$

Colloid Route

$$\left[\begin{array}{c} \quad OH_2 \\ \qquad OH_2 \\ H_2O-Al''''OH_2 \\ H_2O \\ \quad OH_2 \end{array} \right]^{3\oplus} \xrightarrow[\;HB^+\;]{\;B\;} \left[\begin{array}{c} \quad OH_2 \\ \qquad OH_2 \\ H_2O-Al''''OH \\ H_2O \\ \quad OH_2 \end{array} \right]^{2\oplus}$$

pH < 3   pH = 4 - 5

$[Al(H_2O)_4(OH)_2]^-$

$Al(OH)_3$

pH = 5 - 7 $[Al(OH)_4]^-$

$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$

● η-OH_2
● μ_4-O
● μ_2-OH T
● μ_2-OH iT

the Keggin cation
$[Al_{13}O_4(OH)_{24}(OH_2)_{12}]^{7+}$

Sol-Gel Methods

8
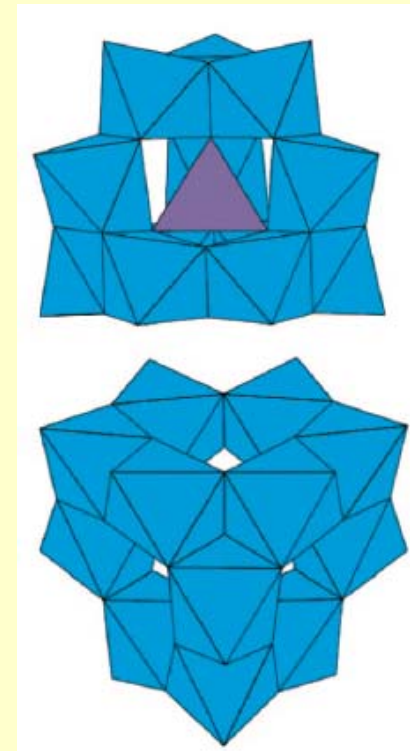
Colloid Route

Depending on the water acidity and the charge transfer, the following equilibria are established:

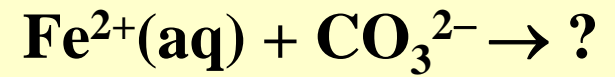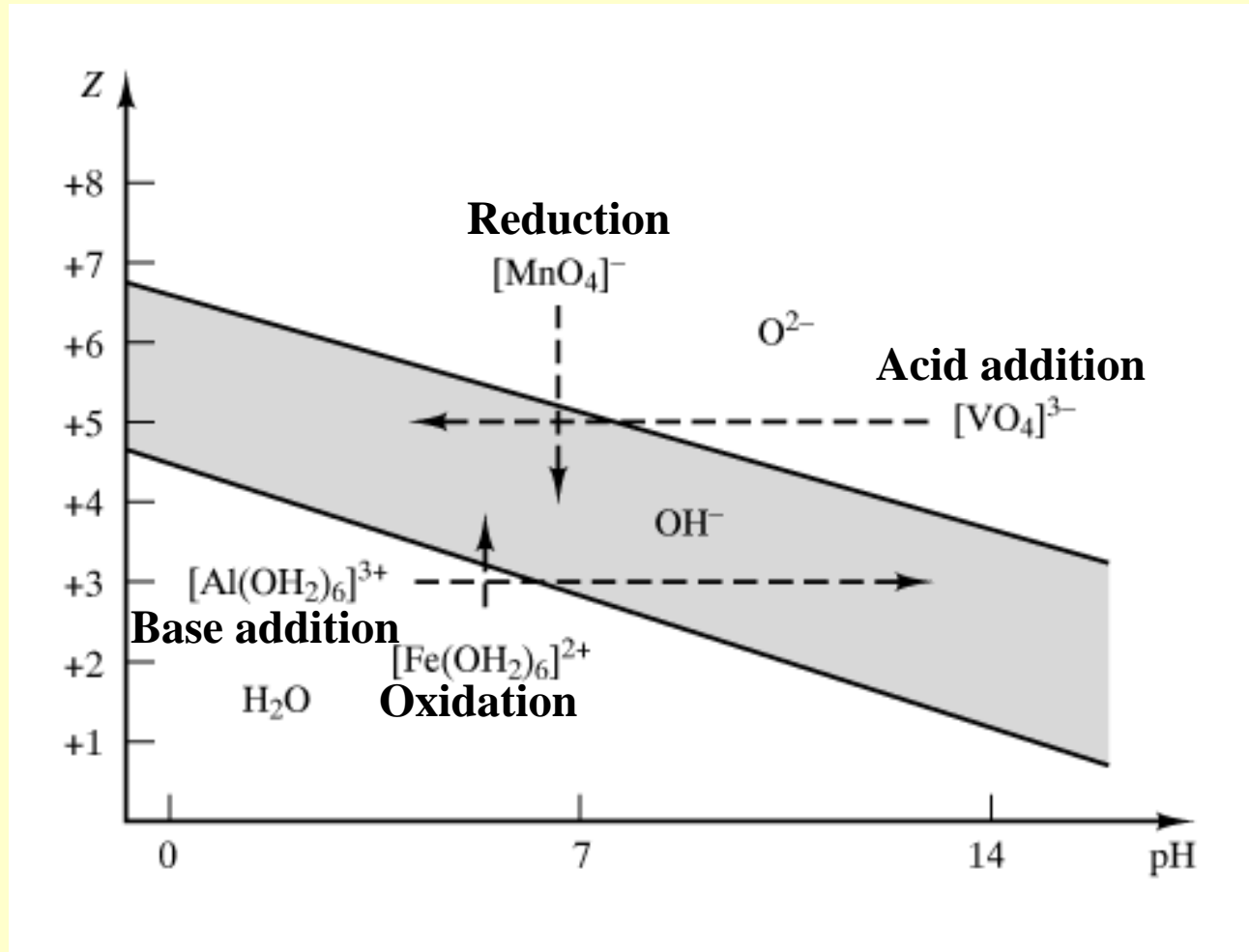$$[M(OH_2)]^{z+} \; \rightleftarrows \; [M-OH]^{(z-1)+} + H^+ \; \rightleftarrows \; [M=O]^{(z-2)+} + \; 2\,H^+$$
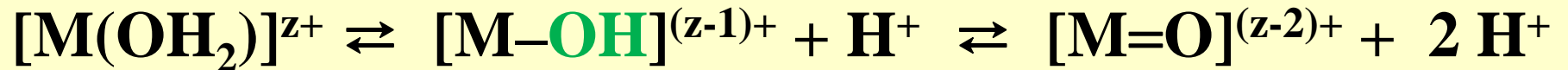
Aqua   **Hydroxo**   **Oxo**
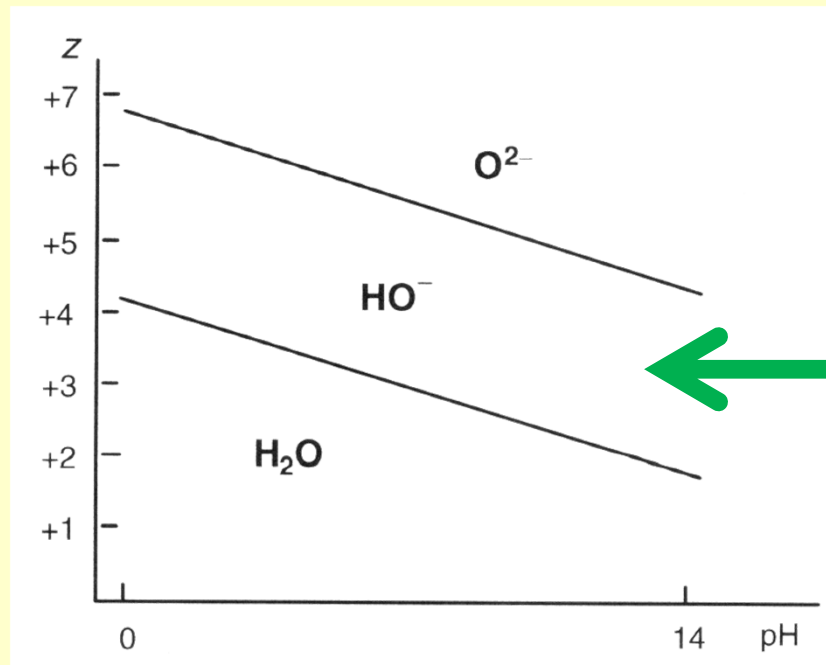
Only hydroxo can condense

$$\text{Fe}^{2+}(\text{aq}) + \text{CO}_3{}^{2-} \rightarrow ?$$

Colloid Route
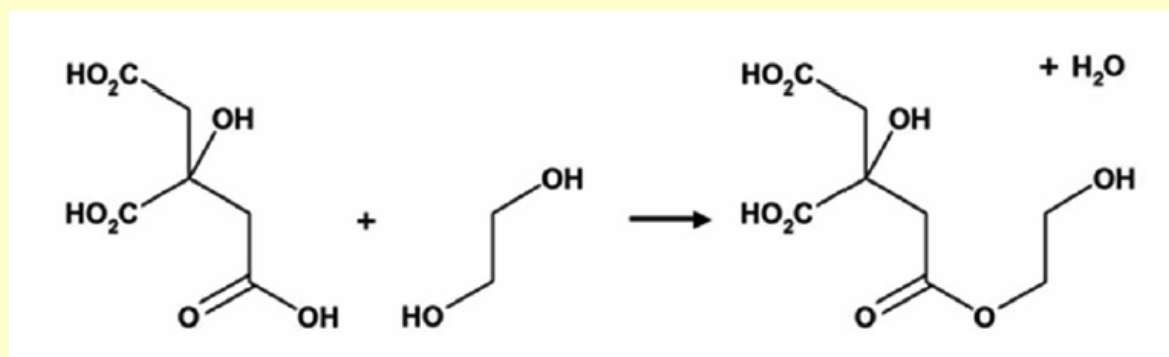
$$\text{Fe}^{3+}(\text{aq}) + \text{CO}_3{}^{2-} \rightarrow ?$$
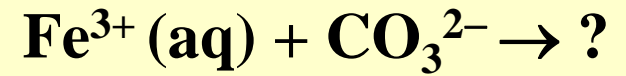
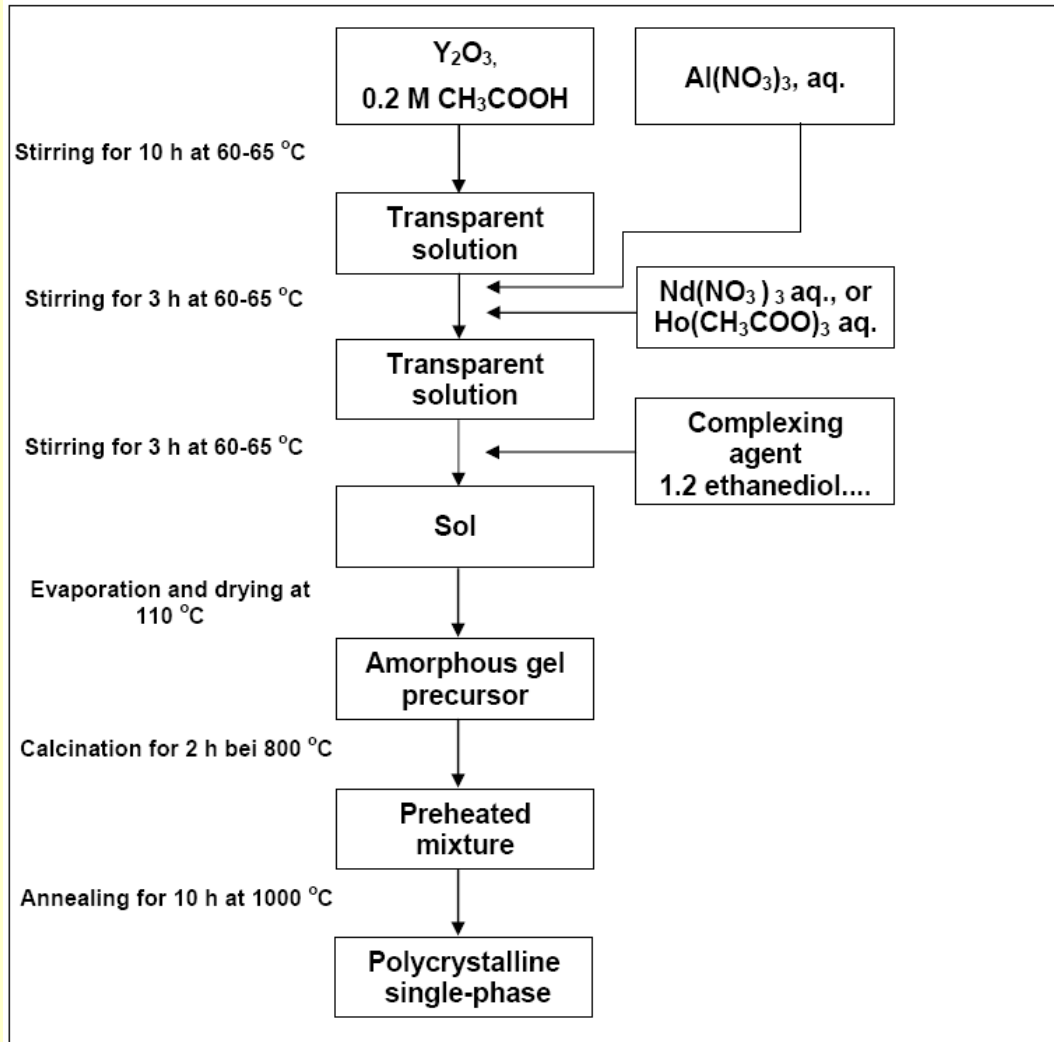# Pechini Sol-Gel Route

The transesterification reaction between citric acid and ethylene glycol
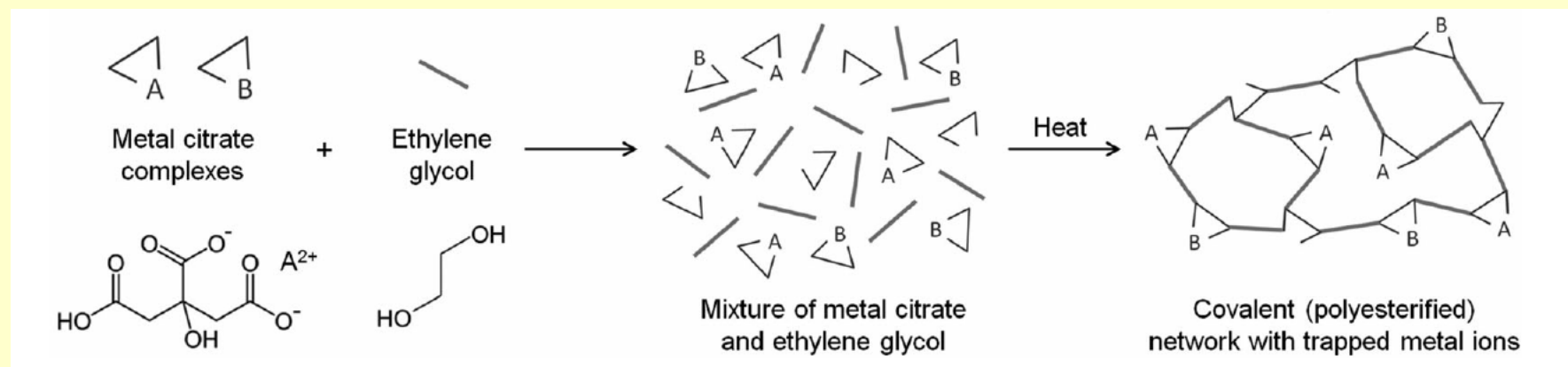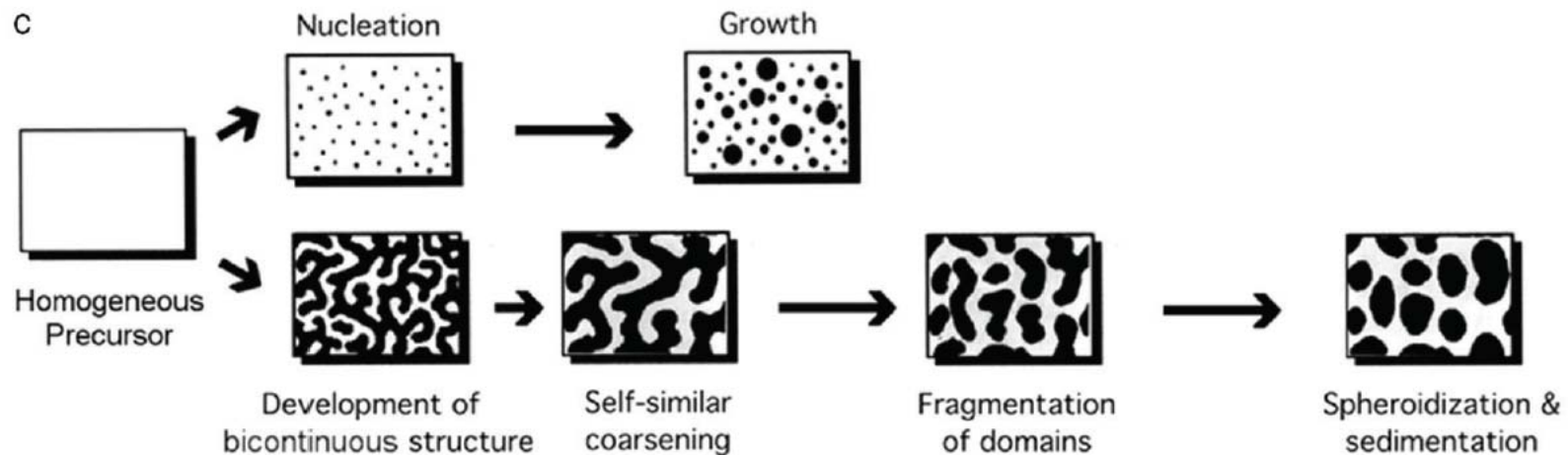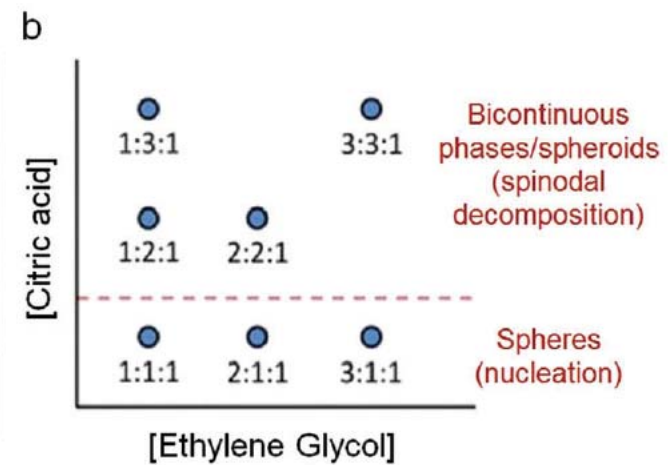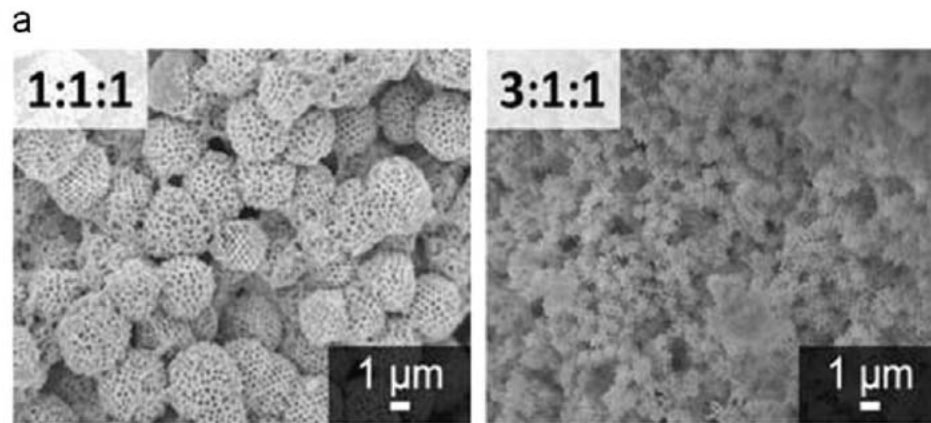
Pechini Sol-Gel Route

Flow diagram	Annotations
Y₂O₃, 0.2 M CH₃COOH → (Stirring for 10 h at 60-65 °C) → **Transparent solution**; **Al(NO₃)₃, aq.**	**Major components**
Nd(NO₃)₃ aq., or Ho(CH₃COO)₃ aq. → (Stirring for 3 h at 60-65 °C) → **Transparent solution**	**Dopants**
Complexing agent 1.2 ethanediol.... → (Stirring for 3 h at 60-65 °C) → **Sol**	**Gelling agent**
(Evaporation and drying at 110 °C) → **Amorphous gel precursor**	**Removal of solvents**
(Calcination for 2 h bei 800 °C) → **Preheated mixture**	**Removal of organics**
(Annealing for 10 h at 1000 °C) → **Polycrystalline single-phase**	**Doped YAG product**

12

Pechini Sol-Gel Route

EG : CA : M

Metal-Organic (Alkoxide) Route

Hydrolysis

Metal Alkoxides
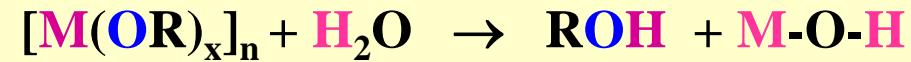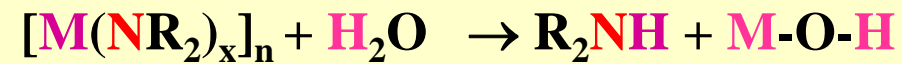
$$[M(OR)_x]_n + H_2O \rightarrow ROH + M\text{-}O\text{-}H$$

Metal Amides

$$[M(NR_2)_x]_n + H_2O \rightarrow R_2NH + M\text{-}O\text{-}H$$

Polycondensation
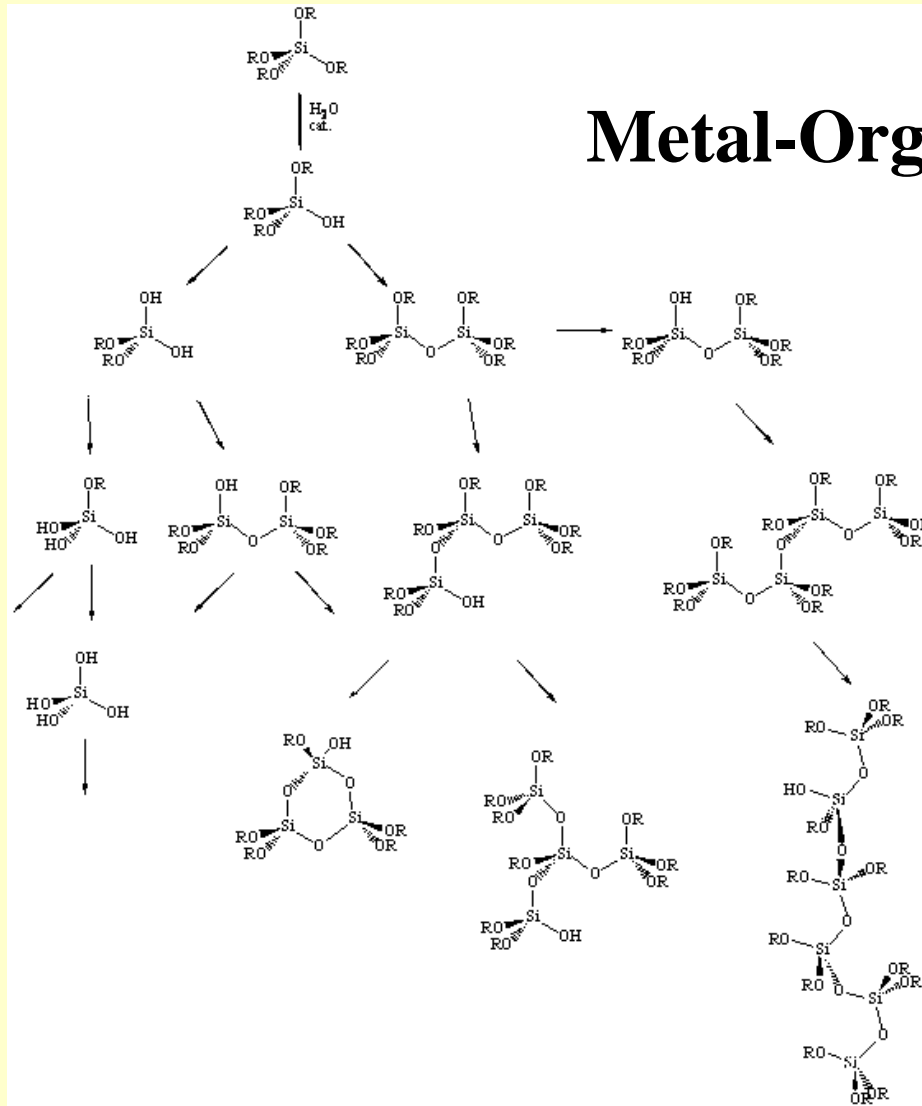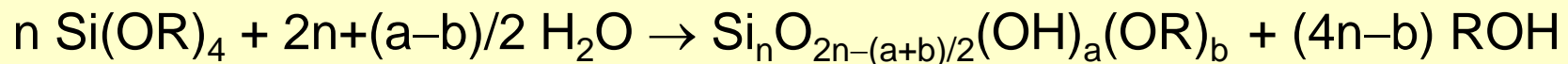
$$2\ M\text{-}O\text{-}H \rightarrow M\text{-}O\text{-}M + H_2O$$

OXIDE

Metal-Organic (Alkoxide) Route

**Oligomers formed
by hydrolysis-condensation
process**

**-linear
-branched
-cyclic
-polyhedral**

Never goes to pure SiO$_2$

$$n\ Si(OR)_4 + 2n+(a-b)/2\ H_2O \rightarrow Si_nO_{2n-(a+b)/2}(OH)_a(OR)_b + (4n-b)\ ROH$$

Metal Alkoxides and Amides as Precursors
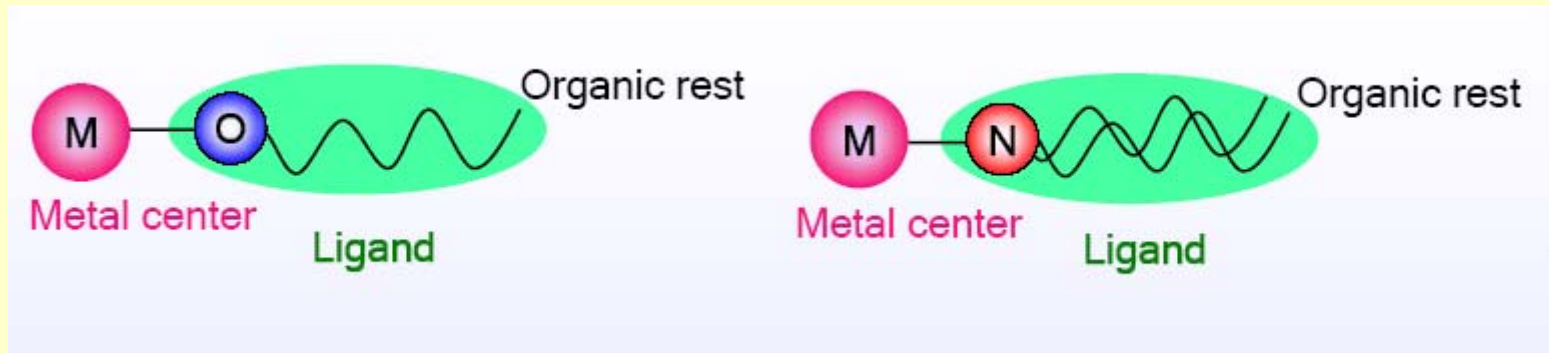
Metal Alkoxides [M(OR)$_x$]$_n$
formed by the replacement of the hydroxylic hydrogen of an alcohol
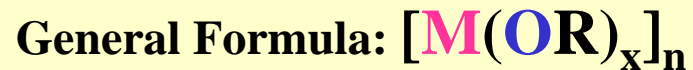(ROH) through a metal atom

Most frequently used precursor for sol-gel: TEOS = Si(OEt)$_4$

Metal Amides [M(NR$_2$)$_x$]$_n$
formed by the replacement of one of the hydrogen atoms of an amine
(R$_2$NH) through a metal atom

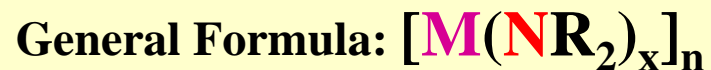# Metal Alkoxides and Amides as Precursors

Homometallic Alkoxides

    General Formula: $[M(OR)_x]_n$

Heterometallic Alkoxides

    General Formula: $M_aM'_b(OR)_x]_n$

Metal Amides

    General Formula: $[M(NR_2)_x]_n$
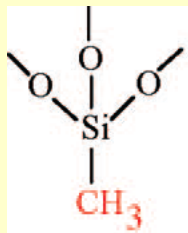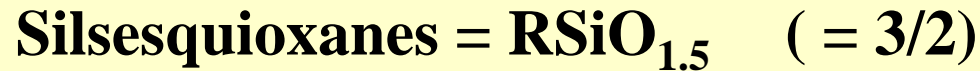
M = Metal or metalloid of valency x
O = Oxygen Atom
N = Nitrogen atom
R = simple alkyl, substituted alkyl or aryl group
n = degree of molecular association
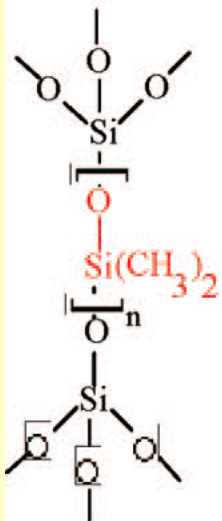
Modified Silicon Alkoxides as Precursors

Silsesquioxanes = RSiO$_{1.5}$ (= 3/2)

Methyl
Hydrophobicity

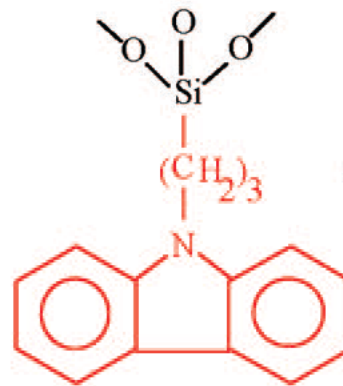**Terminal groups**
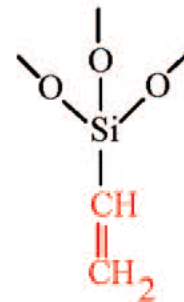
Vinyl
Crosslinking with acrylic

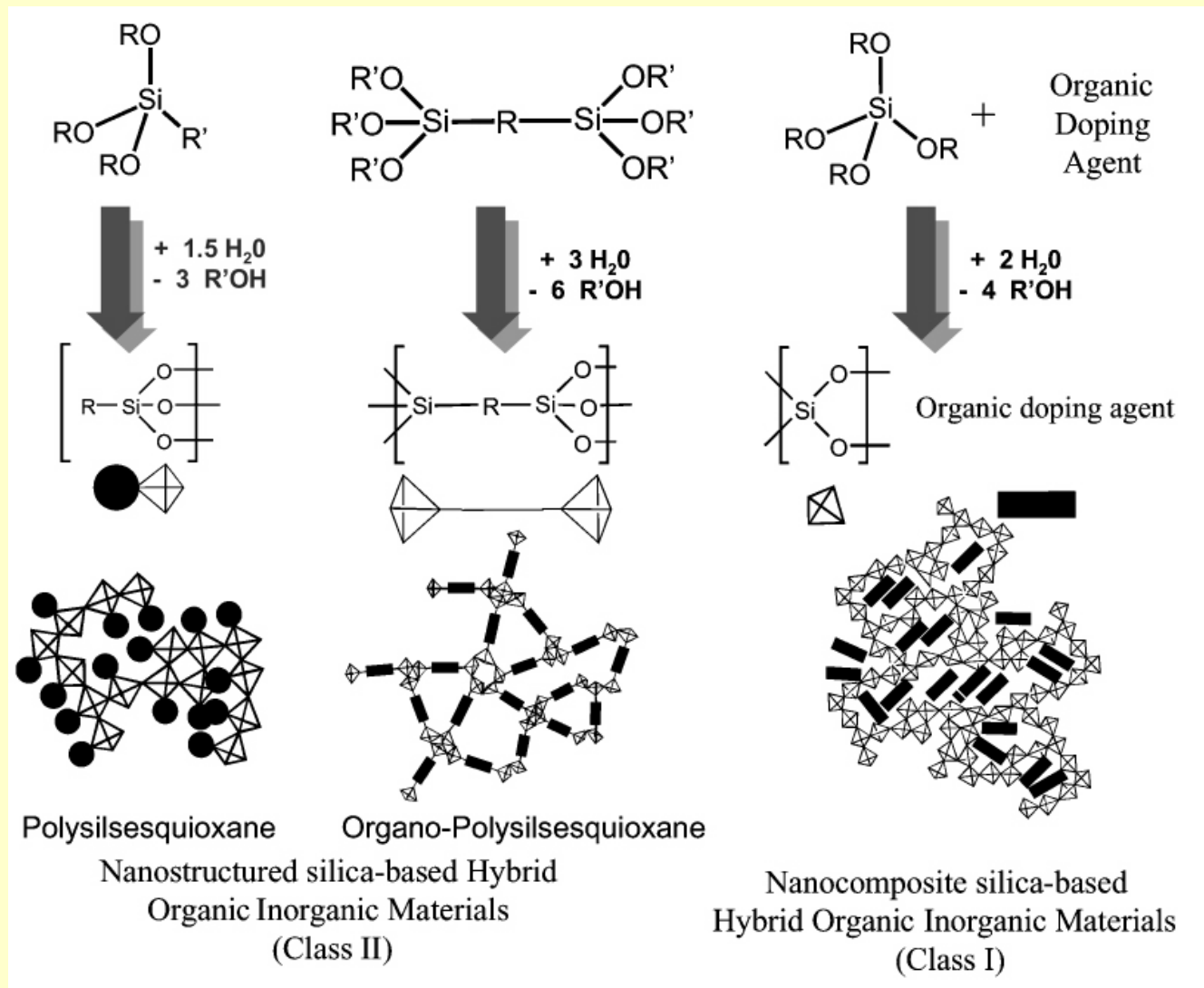**Polymerizable groups**

Polydimethylsiloxane
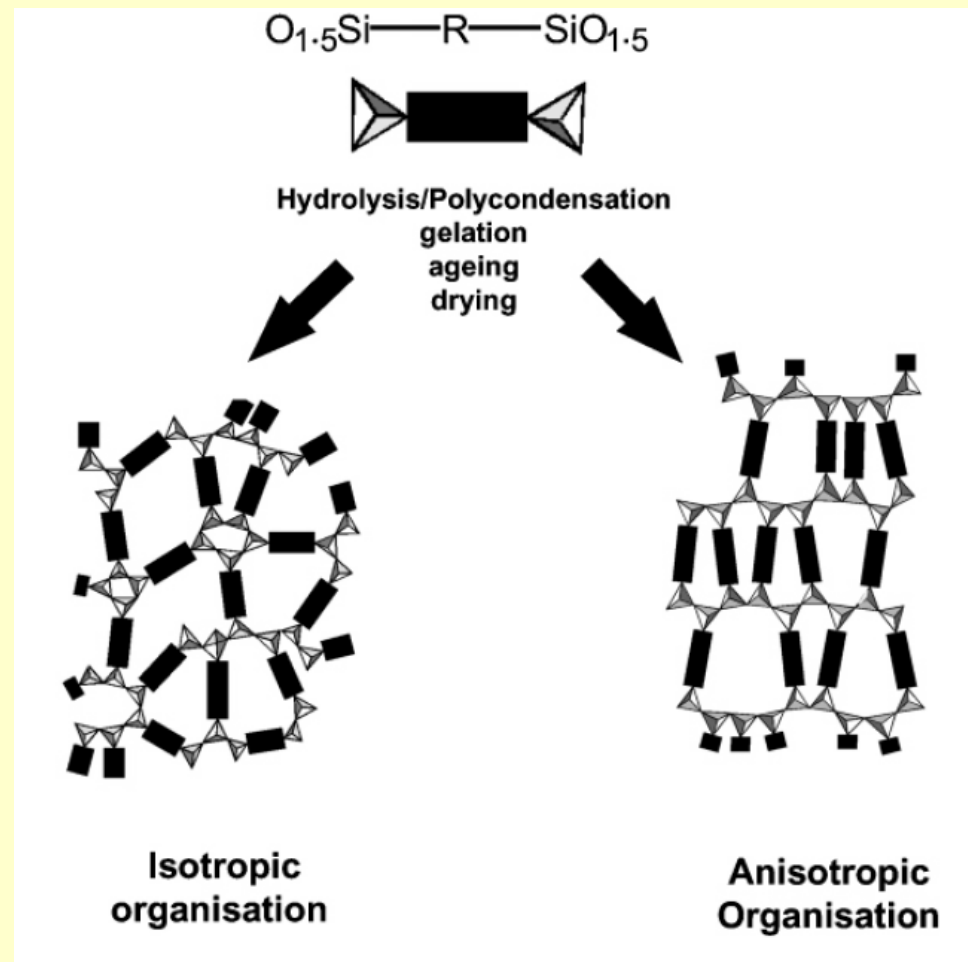**Rubbery behavior**

Bridging groups

Carbazole
Charge transport properties

Functional groups

Hybrid Inorganic-Organic Materials

Polysilsesquioxane   Organo-Polysilsesquioxane

Nanostructured silica-based Hybrid
Organic Inorganic Materials
(Class II)

Nanocomposite silica-based
Hybrid Organic Inorganic Materials
(Class I)

19

# Organization in Xerogels of Bridged Silicon Alkoxide Precursors

Self-Assembly of Bridged Silsesquioxanes

Nanostructuring of hybrid silicas through a Self-Recognition Process - the crystallization of the hydrolyzed species by H-bonding followed by their polycondensation in solid state
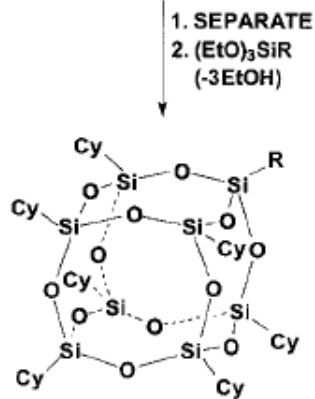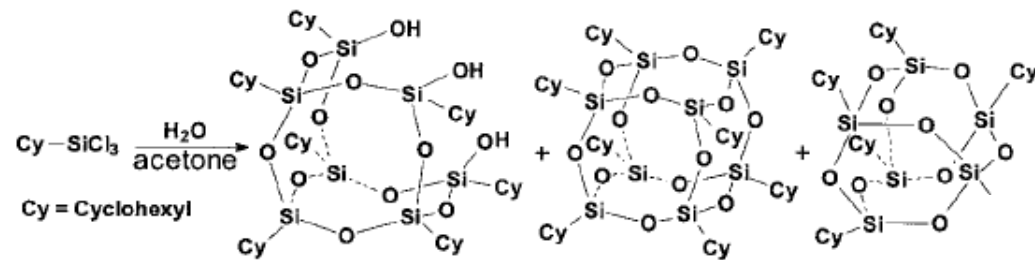
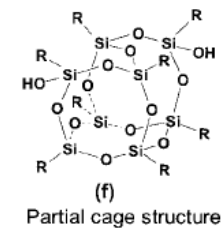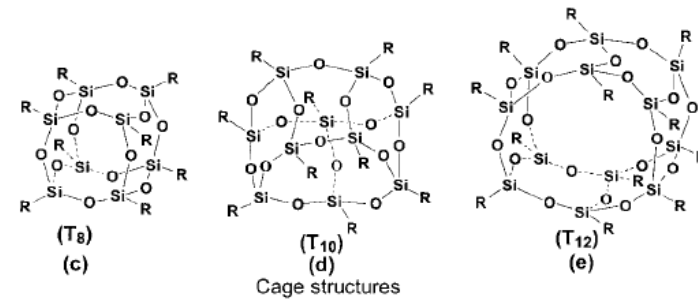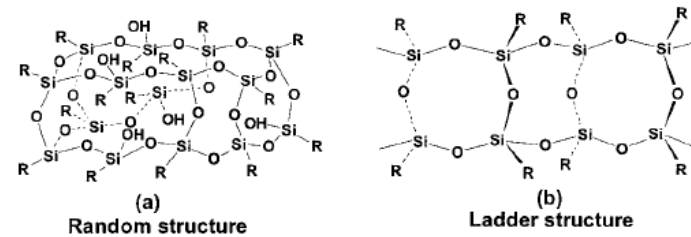1,4-Bis(triethoxysilyl)propylureidobenzene
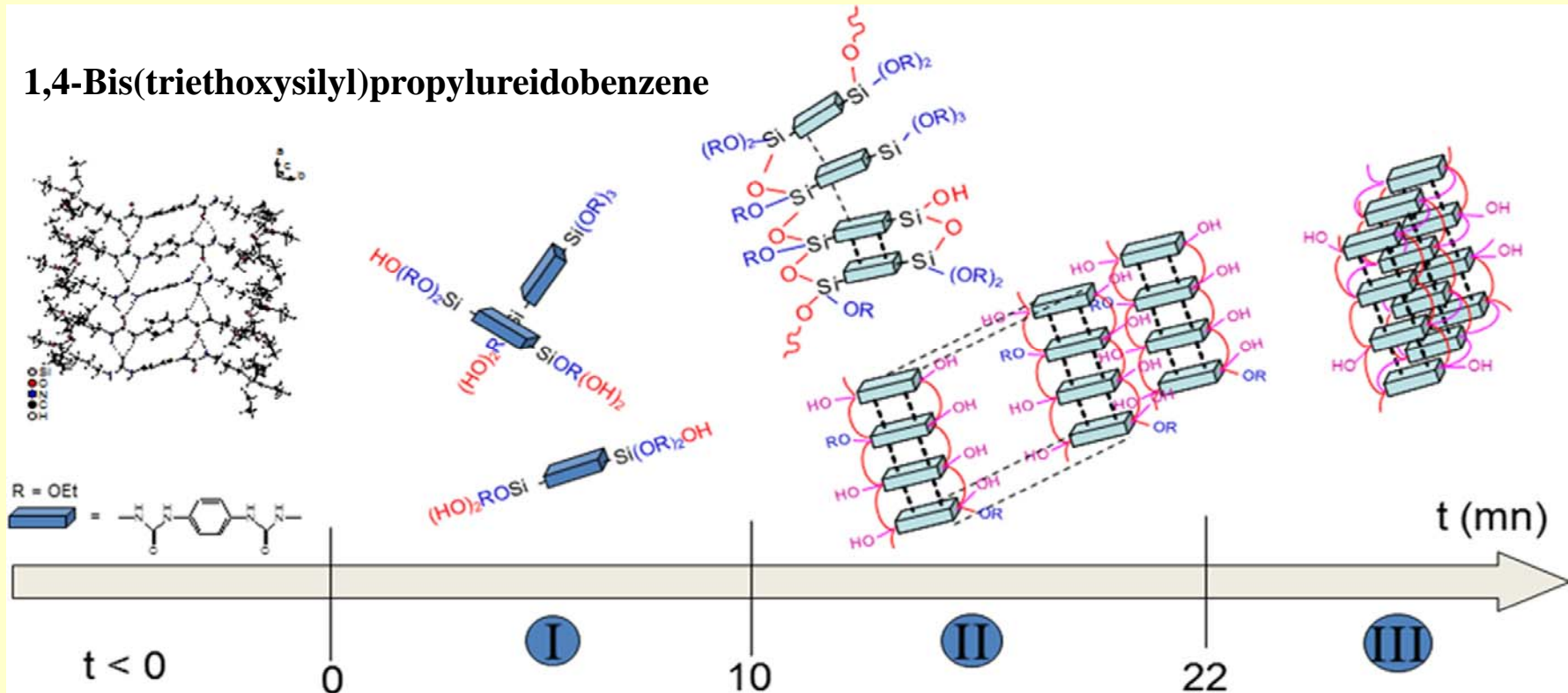
Templating Porosity in Bridged Polysilsesquioxanes

Cleavage of Bridging Groups
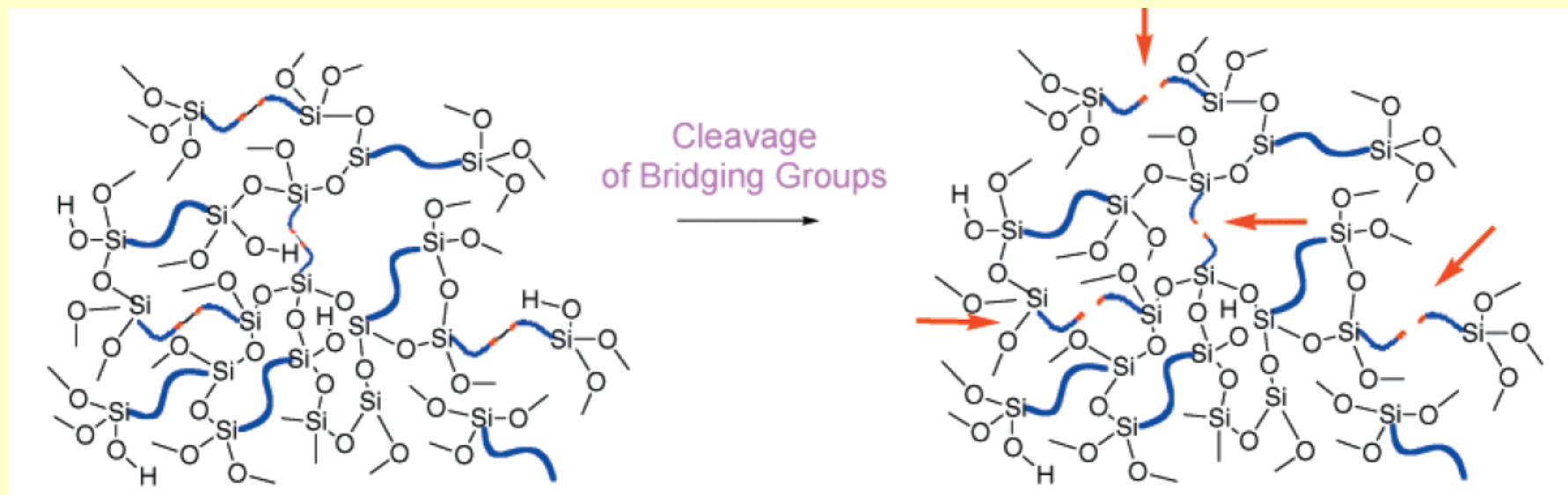
Polyhedral Oligomeric Silsesquioxanes (POSS)

Sol-Gel Meth

Polymers and Copolymers of POSS
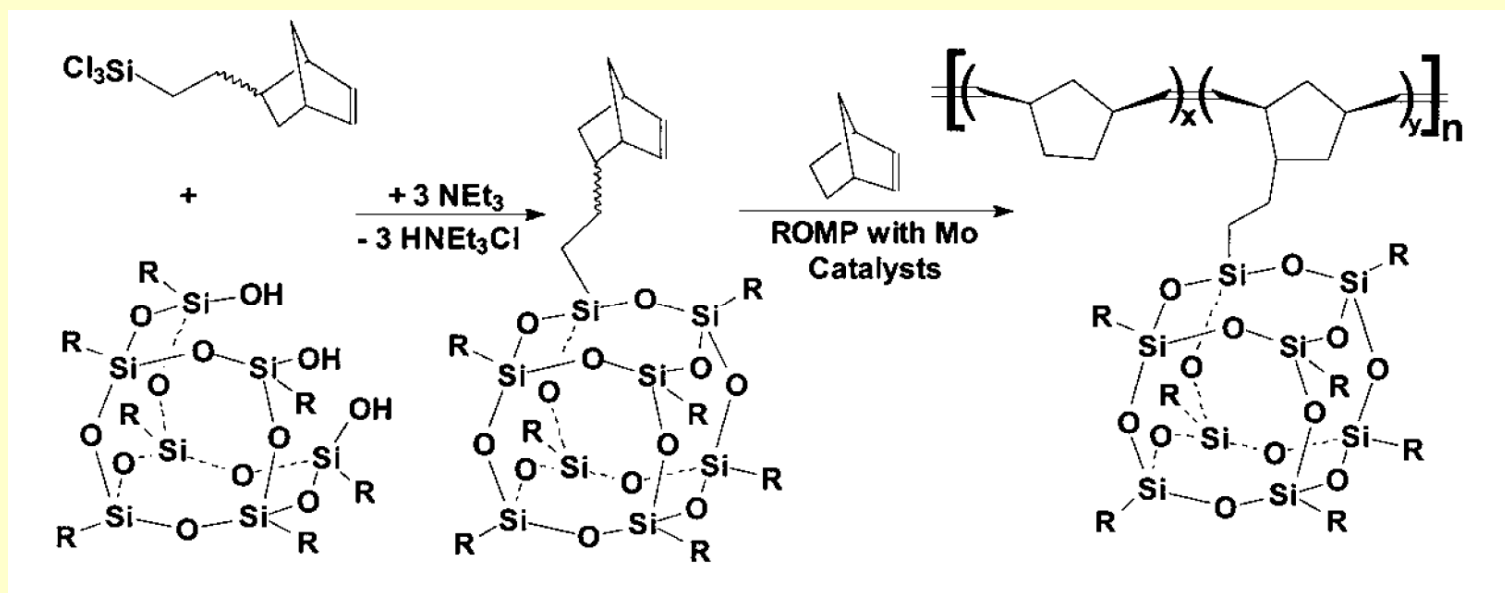
Polymers and Copolymers of POSS

a certain degree of crystallinity

Sol-Gel in Silica Systems

Silicate (aq) | **Hydrolysis** | **Polycondensation**

Alkoxide (nonaq)
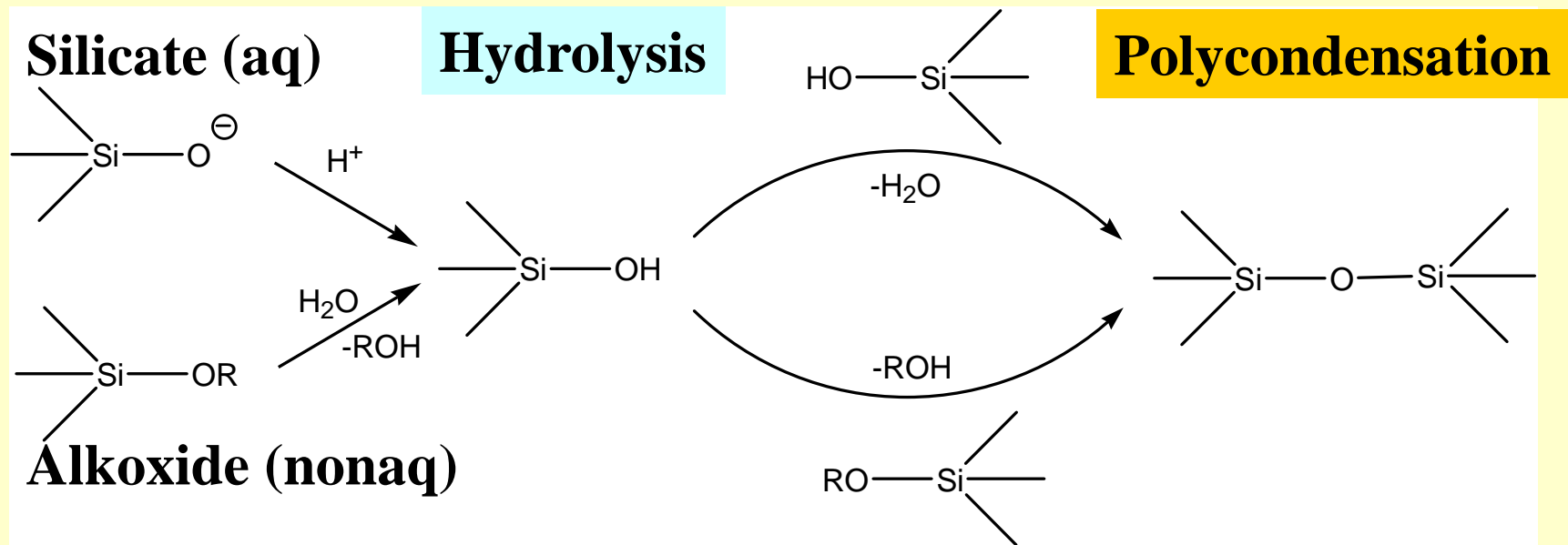
Metal-Oragnic (Alkoxide) Route
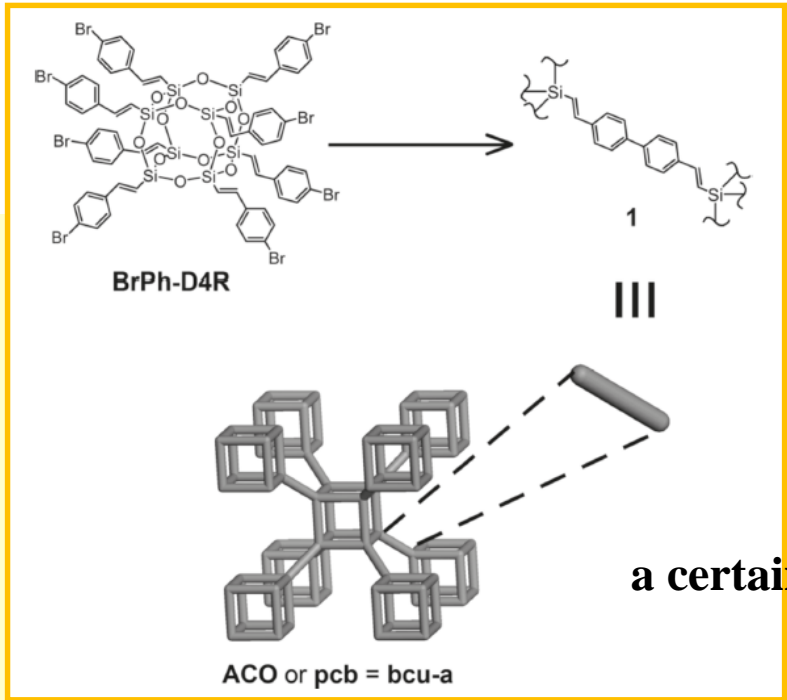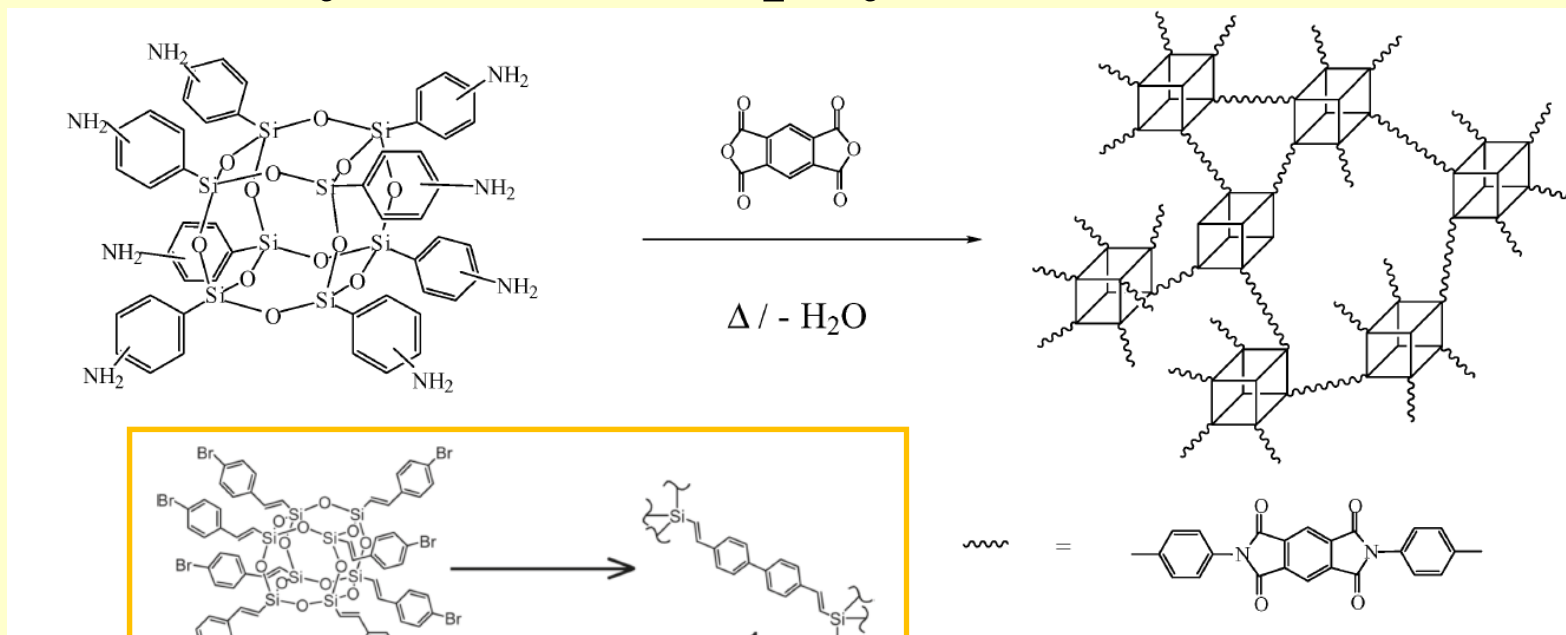
💣✳ **Metal-organic Route**
metal alkoxide in alcoholic solution, water addition

Acid catalysed hydrolysis
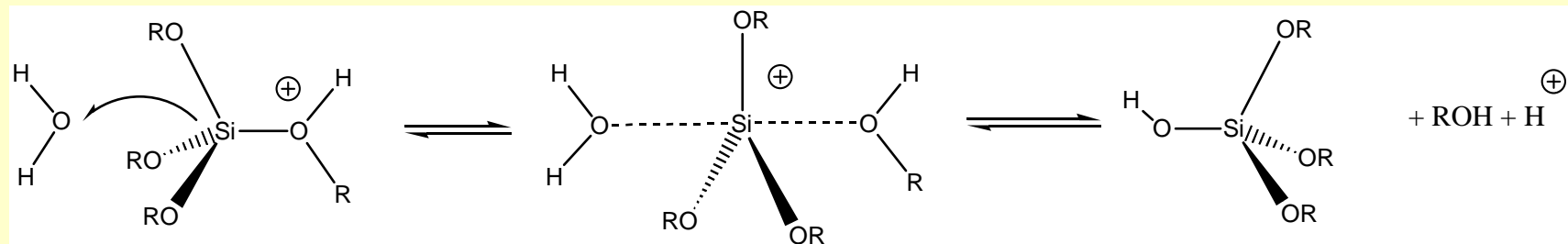
Base catalysed hydrolysis
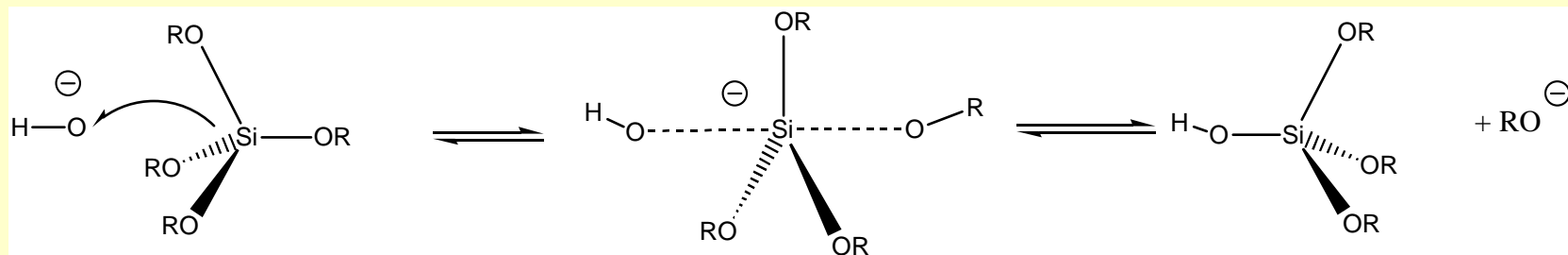
Metal-Oragnic (Alkoxide) Route

Isotope labelling experiments
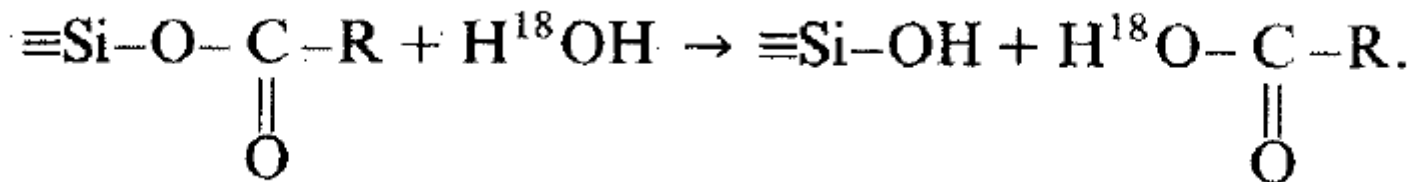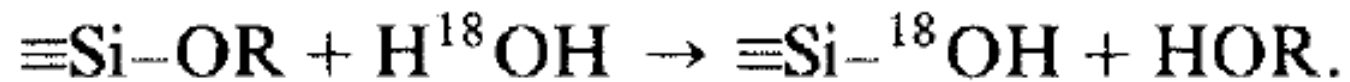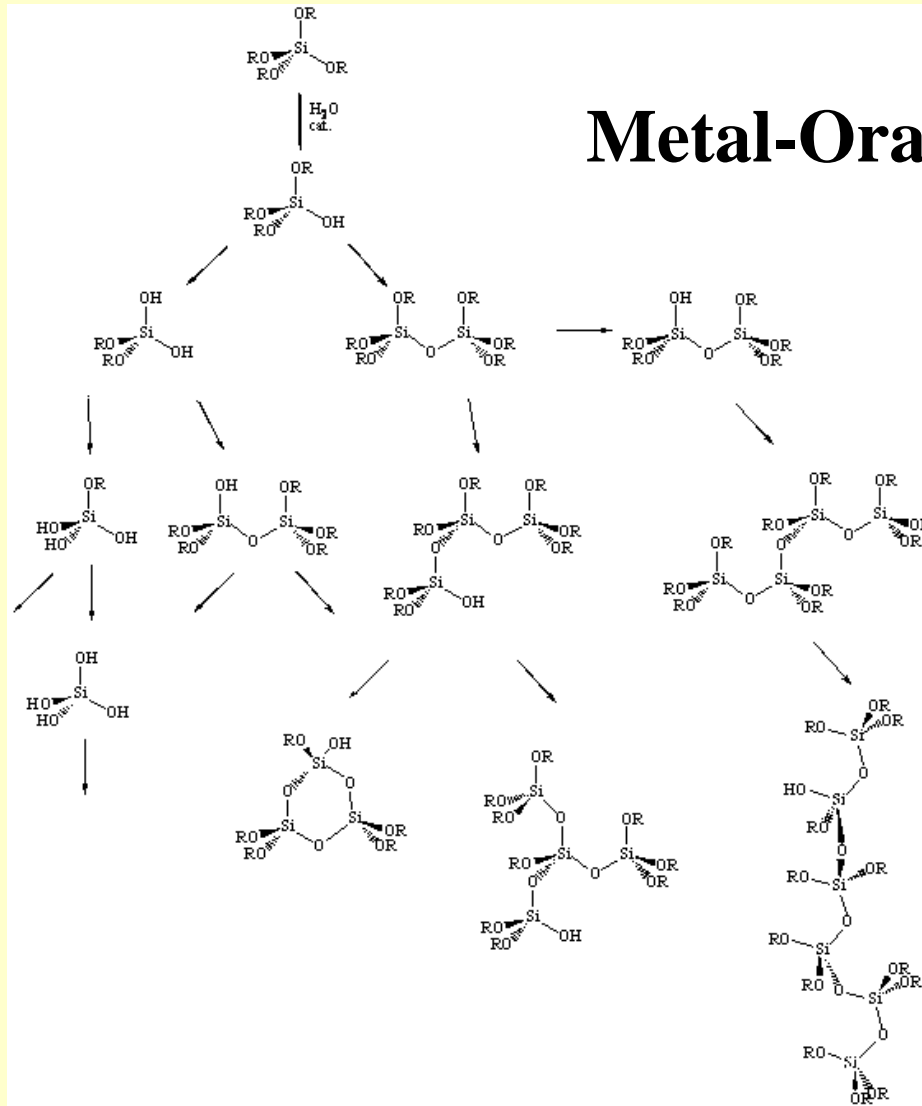
$$\equiv \text{Si--OR} + \text{H}^{18}\text{OH} \rightarrow \equiv \text{Si--}^{18}\text{OH} + \text{HOR}.$$

$$\equiv \text{Si--O--}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{--R} + \text{H}^{18}\text{OH} \rightarrow \equiv \text{Si--OH} + \text{H}^{18}\text{O--}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{--R}.$$

Metal-Oragnic (Alkoxide) Route

Oligomers formed by hydrolysis-condensation process

-linear
-branched
-cyclic
-polyhedral

Never goes to pure SiO_2

$$n\ Si(OR)_4 + 2n+(a{-}b)/2\ H_2O \rightarrow Si_nO_{2n-(a+b)/2}(OH)_a(OR)_b + (4n{-}b)\ ROH$$

GC of TMOS hydrolysis products

Si(OMe)$_4$ + H$_2$O
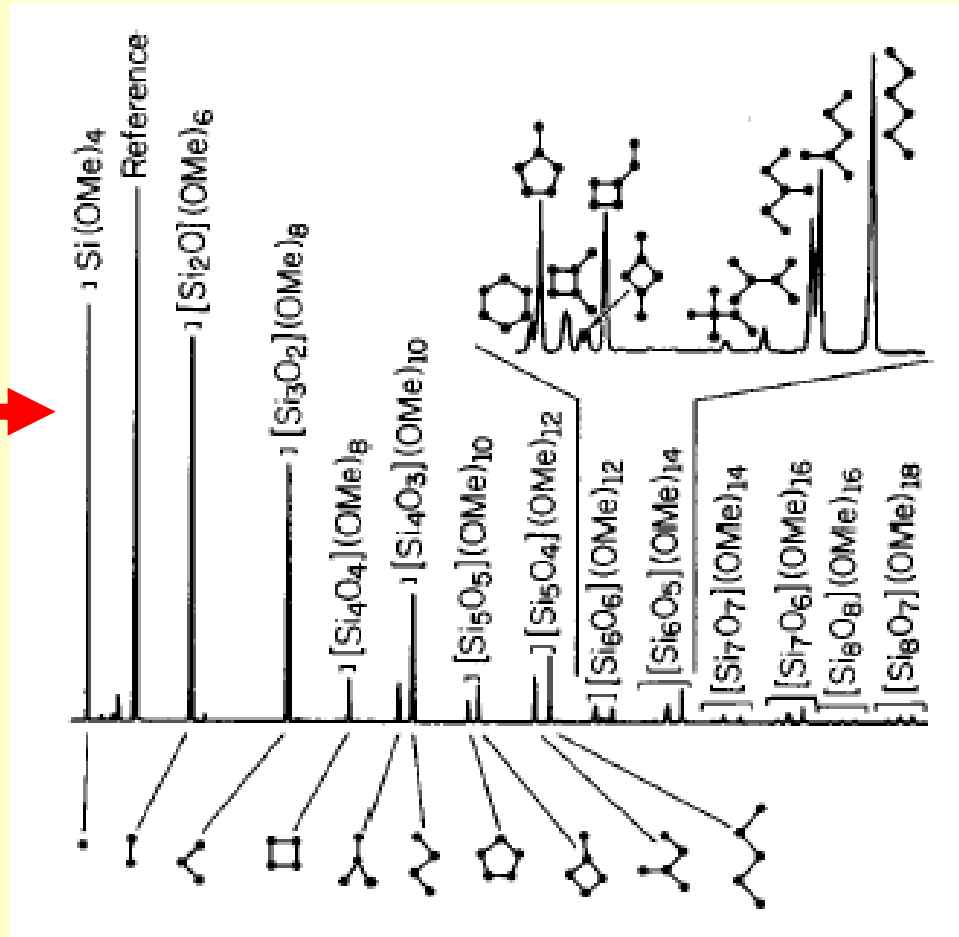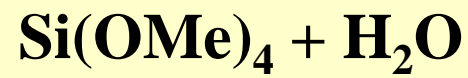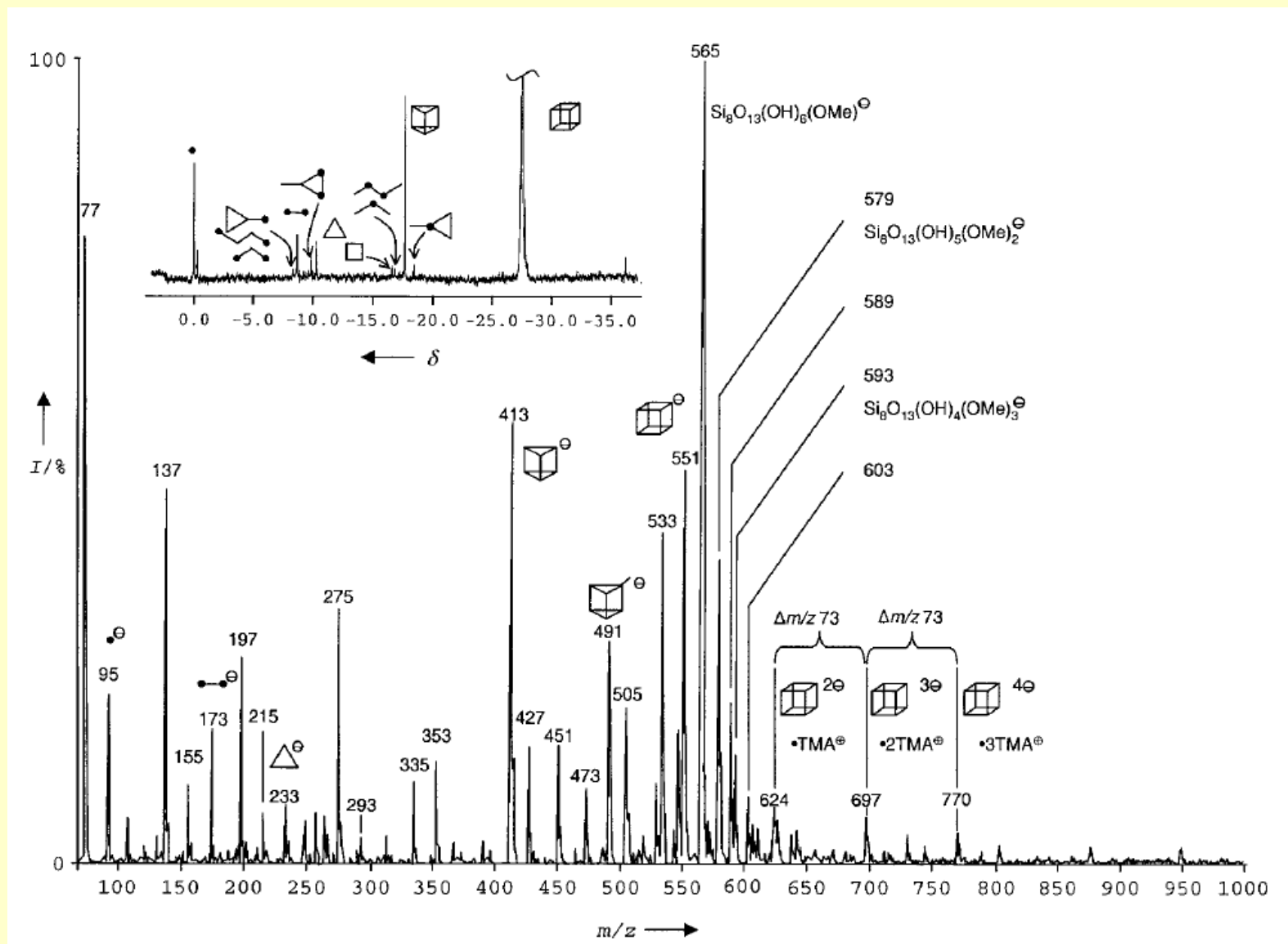
Neg. ion ESI-MS and ^{29}Si NMR of silicate aq with TMA ions

Q - notation

Q⁰   Q¹   Q²   Q³   Q⁴
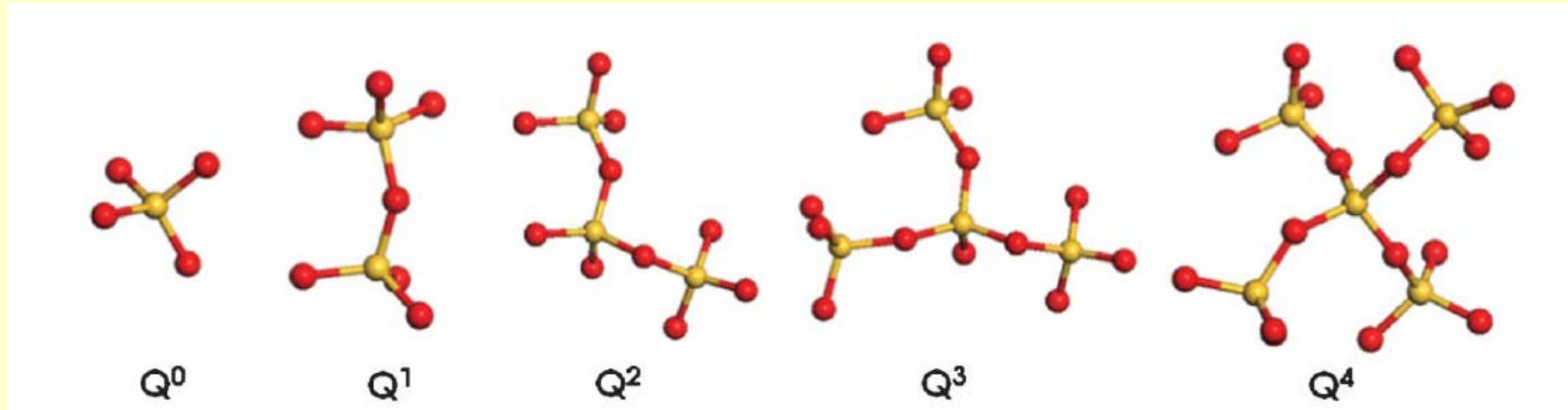
the notation of Q^a_b, "Q" stands for the maximum 4 siloxane bonds for each silicon, "a" is the actual number of siloxane bonds on each Si, and "b" is the number of Si in the unit
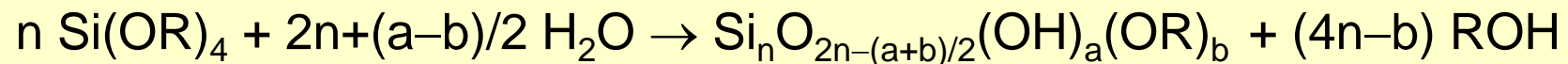
$$Q^0 = O_4Si$$

$$Q^1 = O_3SiOSi$$

$$Q^2 = O_2Si(OSi)_2$$

$$Q^3 = OSi(OSi)_3$$

$$Q^4 = Si(OSi)_4$$

Sol-Gel Methods
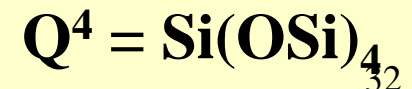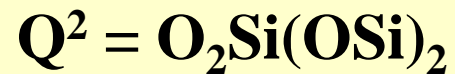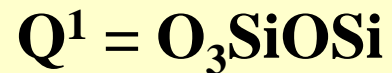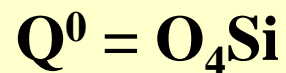
Silicate anions in aqueous alkaline media
(detected by ^{29}Si-NMR)

$M = OSiR_3$

$D = O_2SiR_2$

$T = O_3SiR$

$Q = O_4Si$

$Q^0 = O_4Si$

$Q^1 = O_3SiOSi$

$Q^2 = O_2Si(OSi)_2$

$Q^3 = OSi(OSi)_3$

$Q^4 = Si(OSi)_4$

I (Q^0)   II (Q^1_2)   III ($Q^1Q^2Q^1$)   IV   V (Q^2_3)

VI   VII   VIII   IX   X (Q^2_4)

XI (Q^3_6)   XII   XIII   XIV   XV

XVI   XVII (Q^3_8)   XVIII   XIX   XX

XXI   XXII   XXIII (Q^3_4)   XXIV (Q^3_{10})   XXV
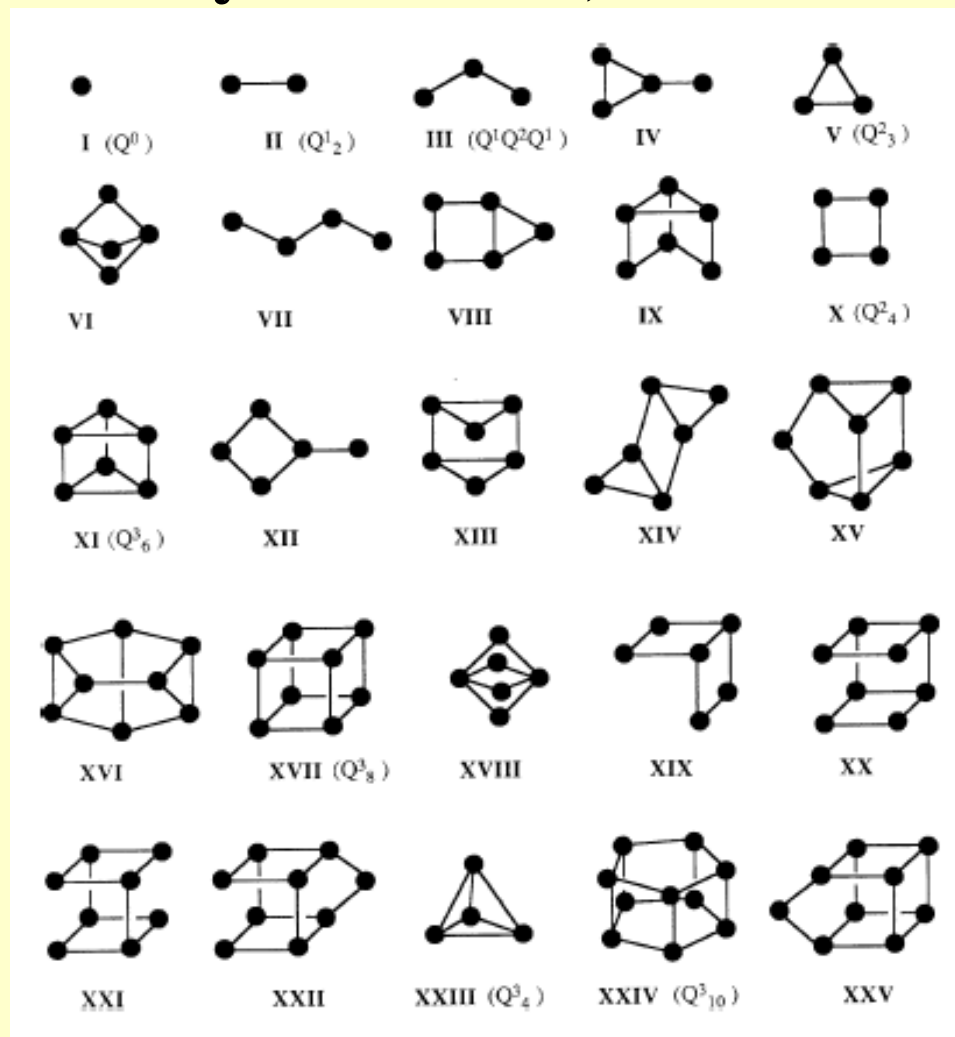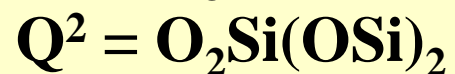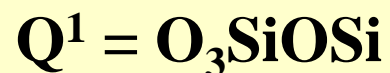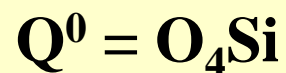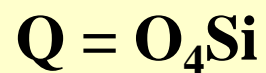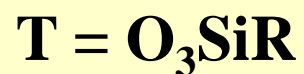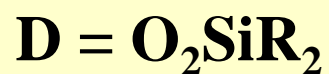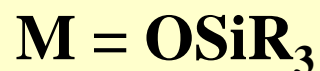
Oligomers formed by hydrolysis-condensation
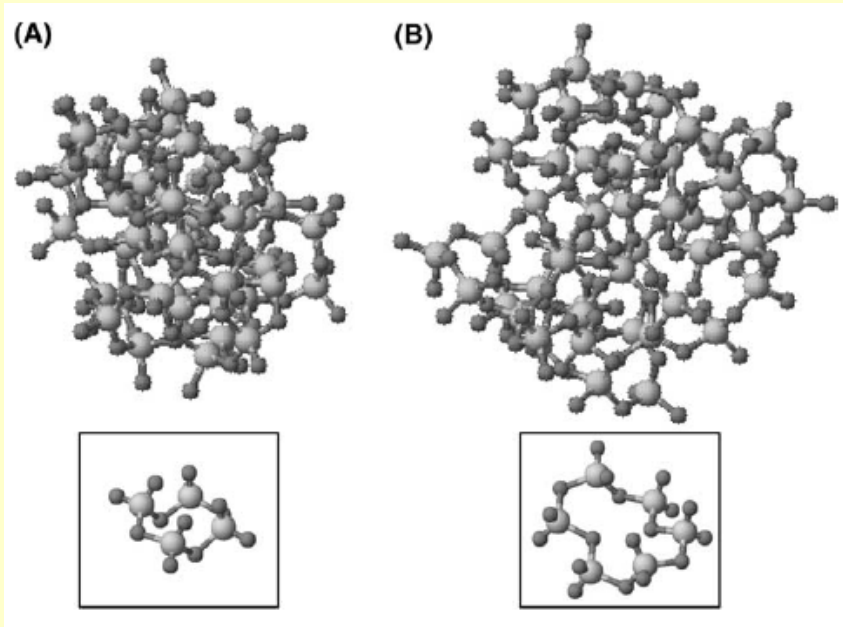
$Si_{50}O_{75}(OH)_{50}$ three-dimensional clusters formed by
(A) four-rings
(B) six-rings

IR spectrum of silica
ν, cm^{-1}

(a) (b) **800**

(c) (d) **1100**

(e) (f) **460**

νO-H

δH–O–H

ν_{as}Si-O-Si

νSi-O$_d$

ν_sSi-O-Si

HYD$_{0.5}$
HYD$_3$
HYD$_5$
HYD$_9$

Kubelka-Munk / a.u.
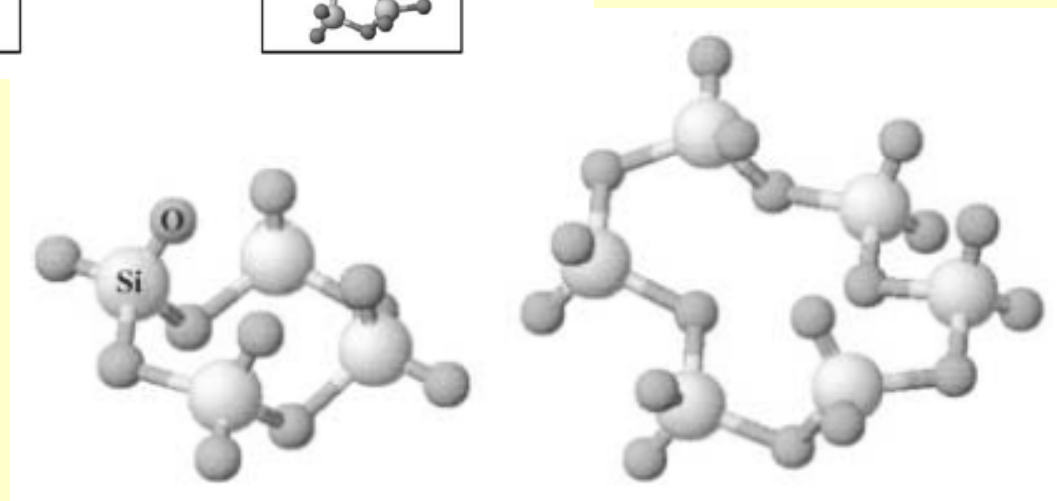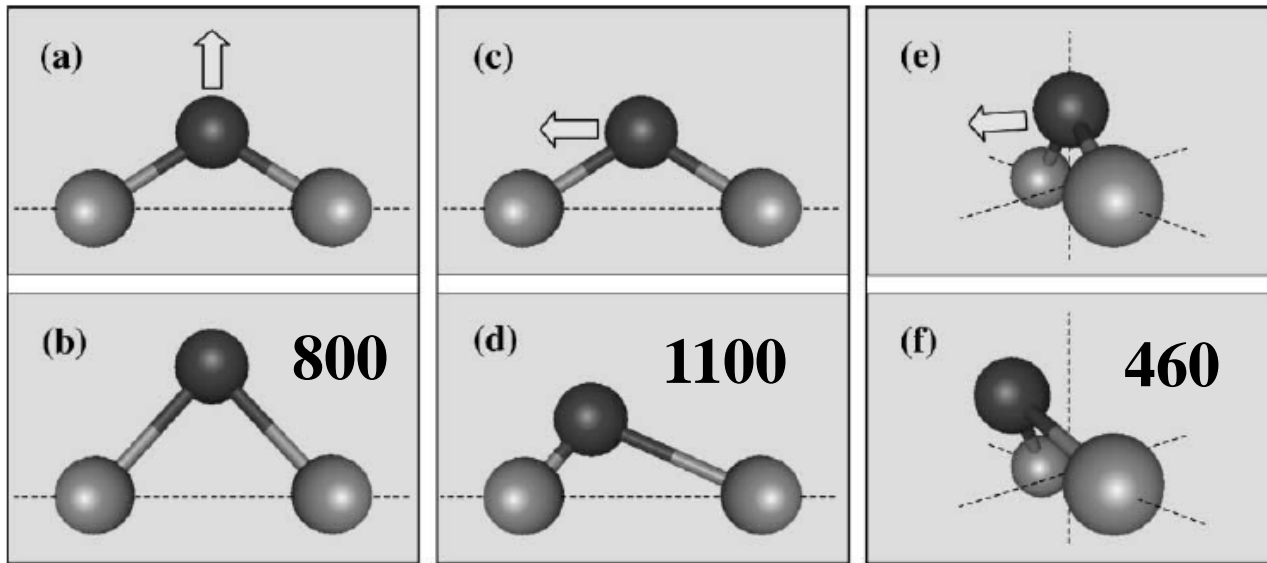
Wavenumber / cm^{-1}
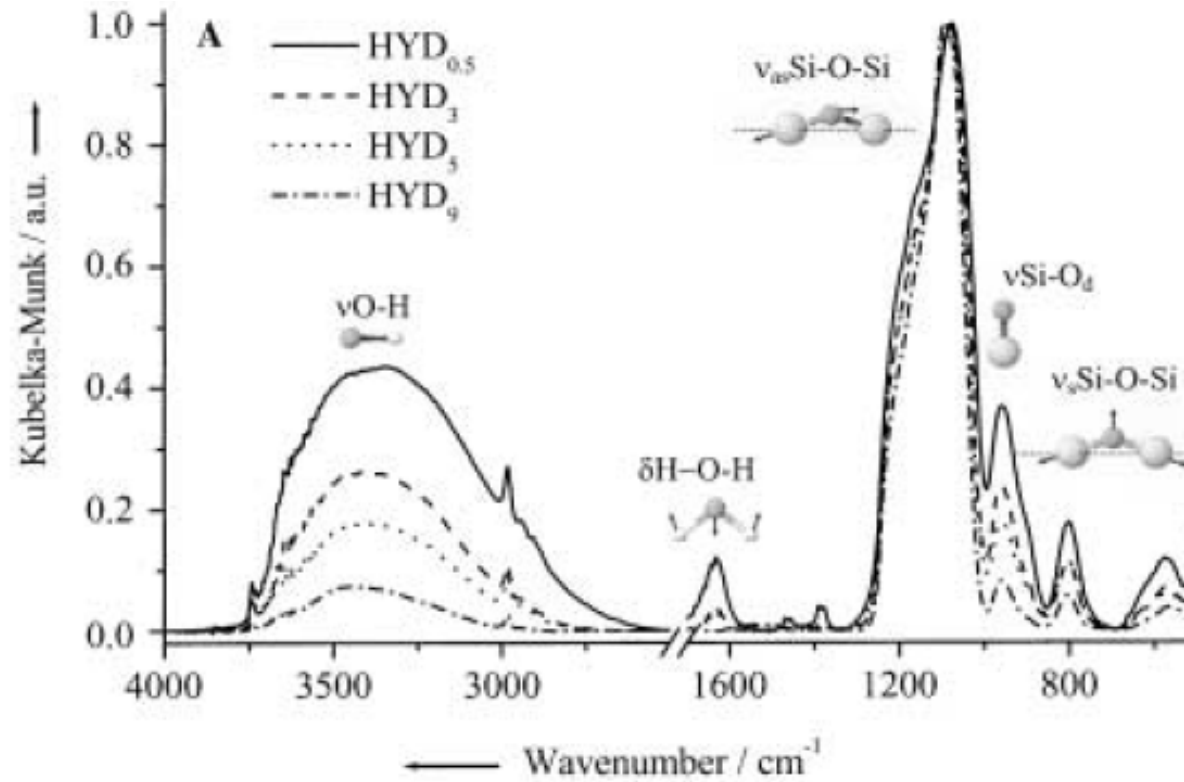
The Electrical Double Layer

The electrical double layer at the interface of silica and a diluted KCl solution

ψ = local potential
OHP = outer Helmholtz plane
u = local electroosmotic velocity

Negative surface charge
stems from deprotonated silanols
Shielding of this surface charge occurs
due to adsorbed ions inside the OHP
and by mobile ions in a diffuse layer

The shear plane = where hydrodynamic
motion becomes possible

Zeta = potential at the shear plane

Solution
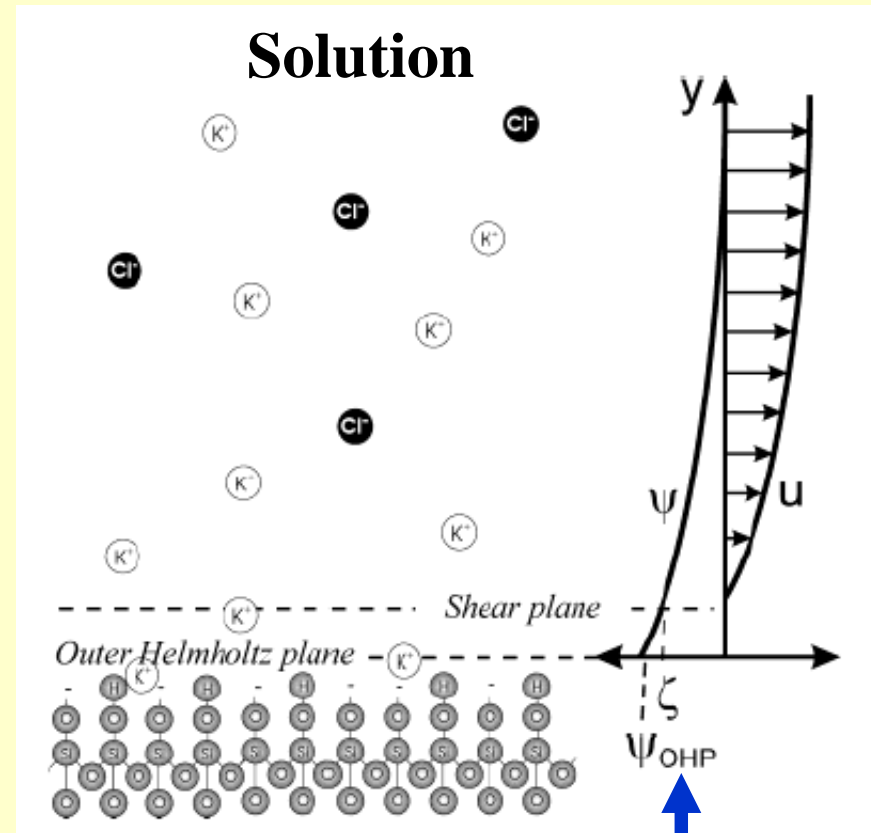
Silica surface

Zeta

Sol-Gel Methods

Isoelectric point: zero net charge

pH = 2.2 for silica

Si–O⁻

Si–OH

$Si–OH_2^+$
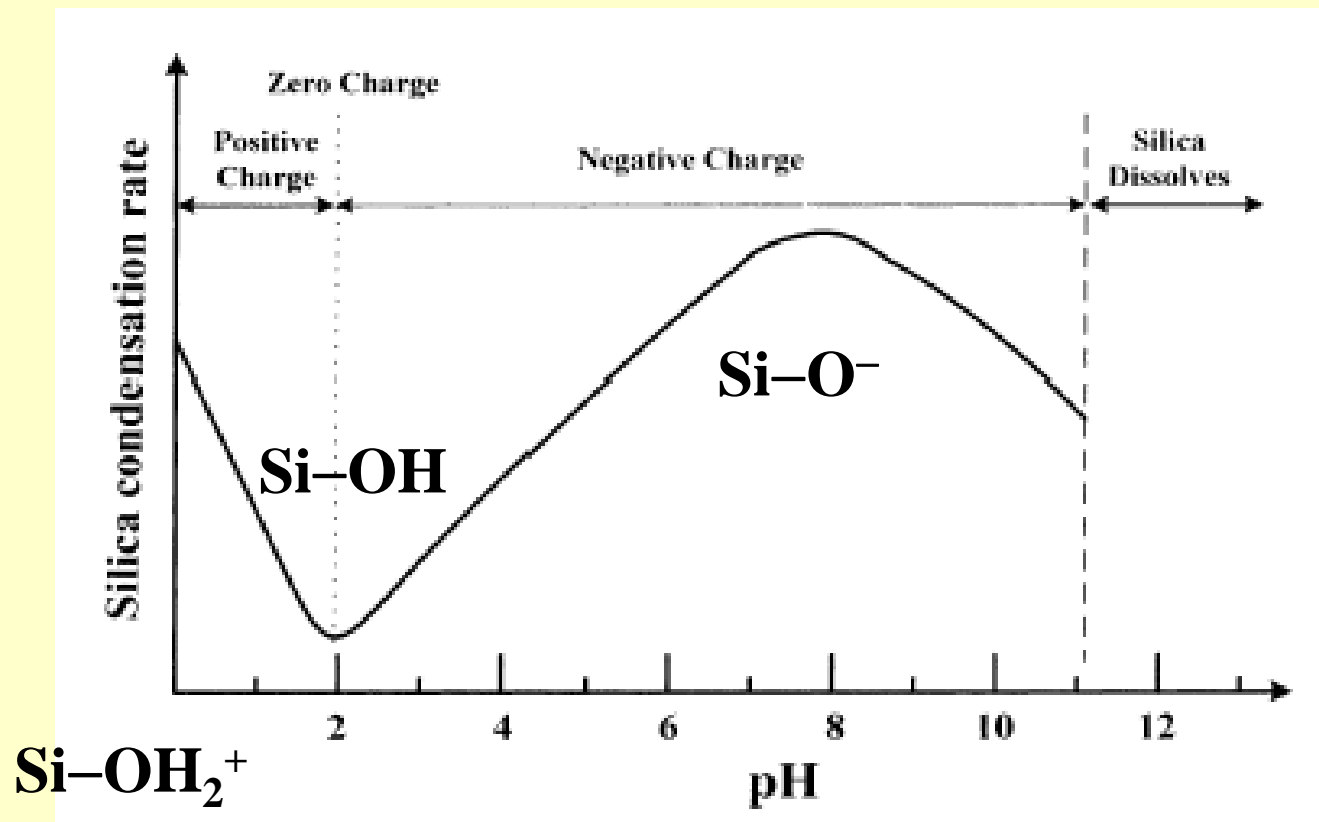
Sol-Gel Methods

Longest TEOS gel time = the slowest reaction

Effects on hydrolysis rate:

pH

substituents

solvent

water
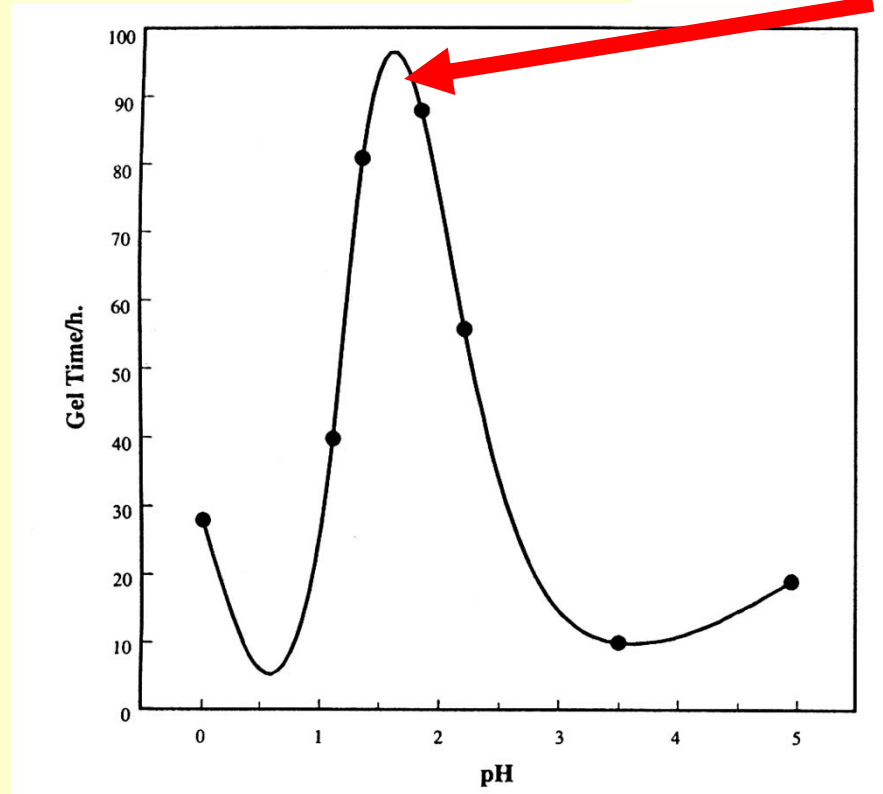
Rate of H$^+$ catalyzed TEOS hydrolysis (gel time) as a function of pH

Sol-Gel Methods

Precursor substituent effects:

Steric effects: branching and increasing of the chain

length LOWERS the hydrolysis rate

$Si(OMe)_4 > Si(OEt)_4 > Si(O^nPr)_4 > Si(O^iPr)_4 > Si(O^nBu)_4$

Inductive effects: electronic stabilization/destabilization

of the transition state (TS).

Electron density at Si decreases:

$R \rightarrow Si > RO \rightarrow Si > HO-Si > SiO \leftarrow Si$
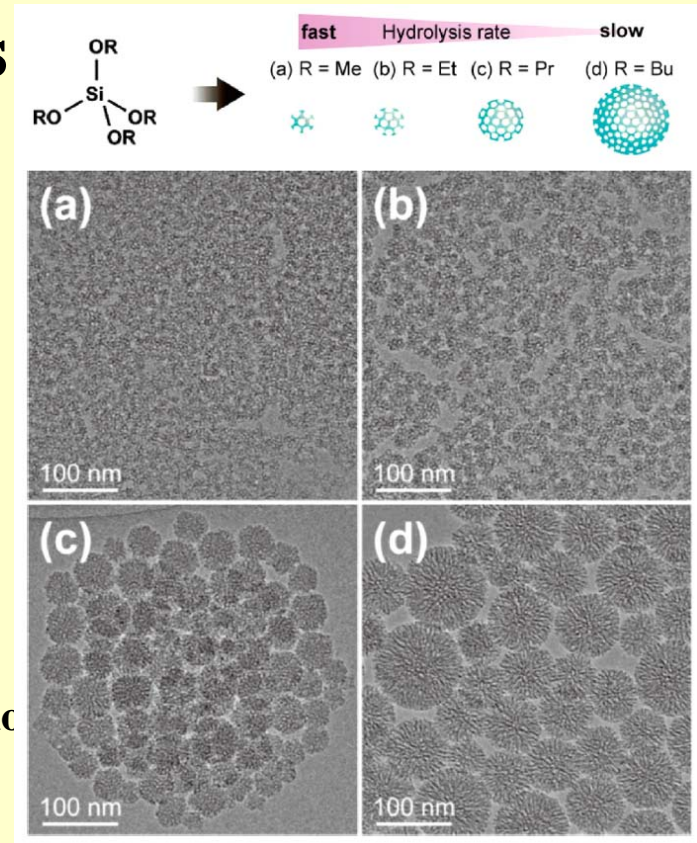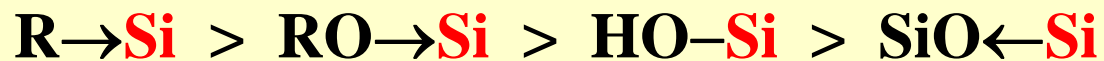
Partial Charge Model (Livage and Henry)

Electron transfer occurs when atoms combine to give a molecule.

Charge transfer causes each atom to acquire a partial positive or negative charge, δ_i.

This transfer mainly depends on the electronegativity difference between atoms.

The electronegativity χ_i of an atom varies linearly with its partial charge δ_i .
$$\chi_i = \chi^o_i + k\, \delta_i$$

Electron transfer must stop when all electronegativities have the same value called the mean electronegativity $\bar{\chi}$.

Partial Charge Model (Livage and Henry)

The mean electronegativity $\bar{\chi}$ of a molecule
z = the electric charge for ions
k = a constant that depends on the electronegativity scale (k = 1.36 in Pauling's units).

$$\bar{\chi} = \frac{\sum_i \sqrt{\chi_i} + 1.36z}{\sum_i (1/\chi_i)},$$

The partial charge δ_i on an element in the molecule

$$\delta_i = \frac{\bar{\chi} - \chi_i}{1.36\sqrt{\chi_i}}.$$

Table 1 Partial charge values δ_i of various silanes calculated by the partial charge model

	$Si(OR)_4$	$CH_3Si(OR)_3$	$C_2H_5Si(OR)_3$
δ_O values			
R = CH_3	−0.44	−0.46	−0.47
R = C_2H_5	−0.46	−0.47	−0.48
R = C_3H_7	−0.47	−0.48	−0.48
δ_{Si} values			
R = CH_3	+0.35	+0.33	+0.32
R = C_2H_5	+0.32	+0.31	+0.31
R = C_3H_7	+0.31	+0.30	+0.30

Partial Charge Model (Livage and Henry)

Alkoxide	$Zr(OEt)_4$	$Ti(OEt)_4$	$Nb(OEt)_5$	$Ta(OEt)_5$	$VO(OEt)_3$	$W(OEt)_6$	$Si(OEt)_4$
$\delta(M)$	+0.65	+0.63	+0.53	+0.49	+0.46	+0.43	+0.32

The hydrolysis rate depends on the $\delta(M)$:

$$k_h \approx 5 \cdot 10^{-9} \text{ mol}^{-1}\text{s}^{-1} \text{ for } Si(OEt)_4$$

$$k_h \approx 10^{-3} \text{ mol}^{-1}\text{s}^{-1} \text{ for } Ti(OEt)_4$$

Partial Charge Model

the number of valence electrons n* on the central atom of a radical ·AB

$$n^* = (N - p) + \frac{2m\chi_B}{\chi_A + \chi_B} - \frac{s\chi_A}{\chi_A + \chi_B}$$

N = the number of valence electrons on the free atom A
p = the number of valence electrons supplied by B when forming the A–B bond.
m = the number of bonds between A and B
s = the number of resonance contributions from A⁻ B+

Group electronegativity χ^g

$$\chi^g = 0.31 \left(\frac{n^* + 1}{r_A} \right) + 0.50$$

r_A = the covalent radius of atom A in the radical AB.

Partial Charge Model

Table 2 Group electronegativity χ^g values relevant to silanes-based sol–gel chemistry[a]

Group	χ^g	Group	χ^g
$-CH_3$	2.47	$-H$	2.62
$-C_2H_5$	2.48	$-OH$[b]	3.49
$-C_3H_7$	2.48	$-OCH_3$	3.54
$-C_6H_5$ ($-Ph$)	2.72	$-OC_2H_5$	3.54
$-CH=CH_2$	2.79	$-SiCl_3$	2.10
$-NH_2$	2.99	Si[c]	1.84

[a] Calculated using Gordy's electronegativity. [b] Hydroxide groups are believed to be more electronegative and withdraw more electrons than alkoxy groups presumably due to the solvation effects in polar solvent. [c] Gordy's electronegativity for neutral Si.
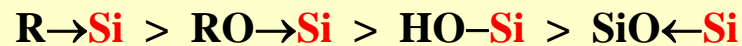
Hydrolysis

Acid catalysed hydrolysis

Transition State
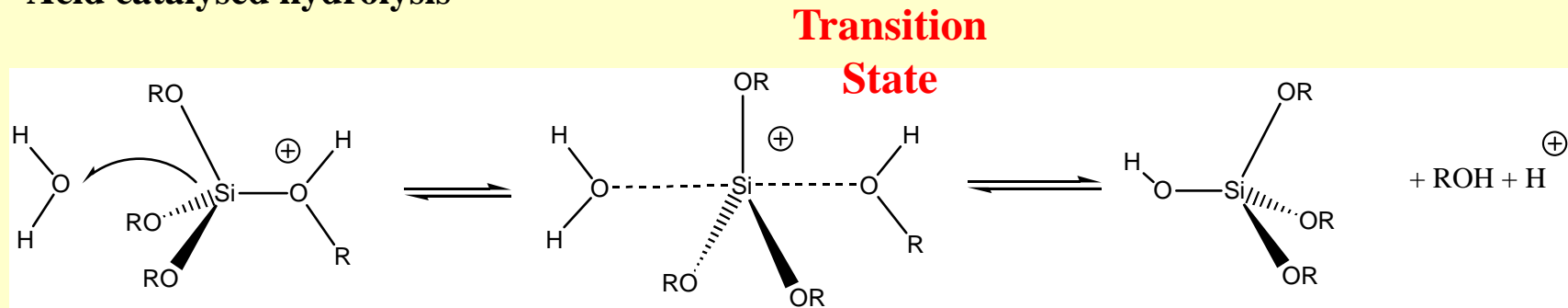
Acidic conditions:

Hydrolysis reaction rate decreases as more alkoxy groups are hydrolyzed

Electron density at Si decreases:

R→Si > RO→Si > HO−Si > SiO←Si

TS (+) is destabilized by increasing number of electron withdrawing OH groups (wrt OR)

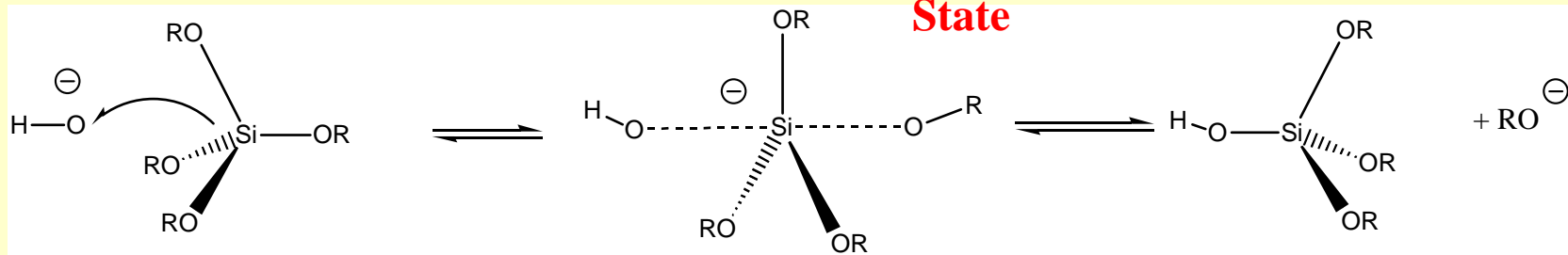**The reaction at terminal Si favored, as there is only one electron withdrawing SiO group**

Linear polymer products are favored, leading to fibers

$RSi(OR)_3$ is more reactive than $Si(OR)_4$

Hydrolysis

Base catalysed hydrolysis

Transition State

Basic conditions:

Hydrolysis reaction rate increases as more alkoxy groups are hydrolyzed

Electron density at Si decreases:

R→Si > RO→Si > HO−Si > SiO←Si

TS (−) is stabilized by increasing number of electron withdrawing OH groups (wrt OR)

The reaction at central Si favored, as there is more electron withdrawing SiO groups

Branched polymer products are favored, spherical particles, powders

$RSi(OR)_3$ less reactive than $Si(OR)_4$

Sol-Gel Methods

Si-OH becomes more acidic with increasing number of Si-O-Si bonds
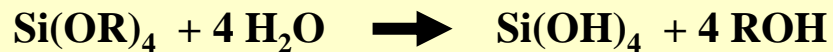
Nucleophilic catalysis:

F⁻   Si-F bonds
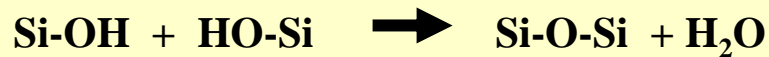
HMPA
N-methylimidazol
N,N-dimethylaminopyridin

Sol-Gel Methods

Water:alkoxide ratio (R_w) effect
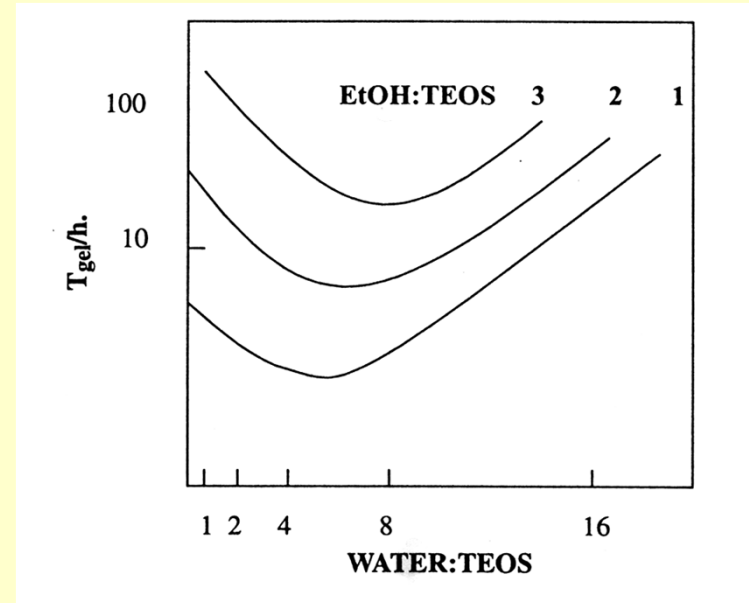
stoichiometric ratio for complete hydrolysis = 4

$$Si(OR)_4 + 4 H_2O \longrightarrow Si(OH)_4 + 4 ROH$$

additional water from condensation

$$Si\text{-}OH + HO\text{-}Si \longrightarrow Si\text{-}O\text{-}Si + H_2O$$

Small amount of water = slow hydrolysis due to the reduced reactant concentration

Large amount of water = slow hydrolysis due to the reactant dilution

Sol-Gel Methods

Hydrophobic effect

Si(OR)$_4$ are immiscible with water

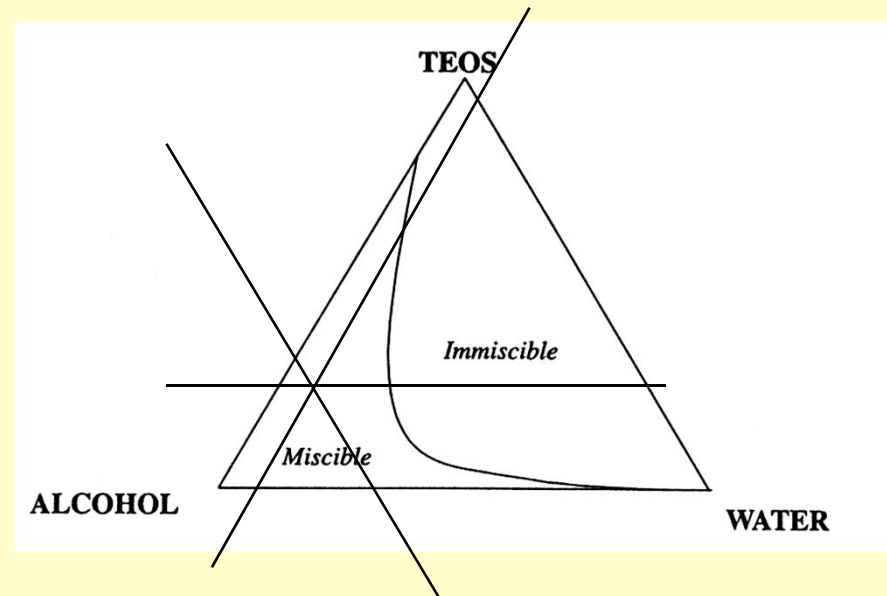cosolvent ROH is used to obtain a homogeneous reaction mixture

polarity, dipole moment, viscosity, protic behavior

alcohol produced during the reaction
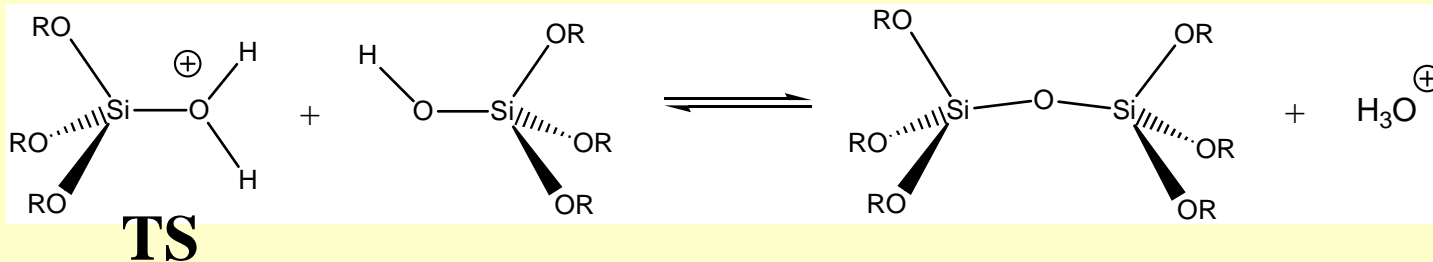
alcohols - transesterification

sonication

drying

Condensation

**Acid catalysed condensation
fast protonation, slow condensation**

TS

**Positively charged transition state, fastest condensation for
$(RO)_3SiOH > (RO)_2Si(OH)_2 > ROSi(OH)_3 > Si(OH)_4$**

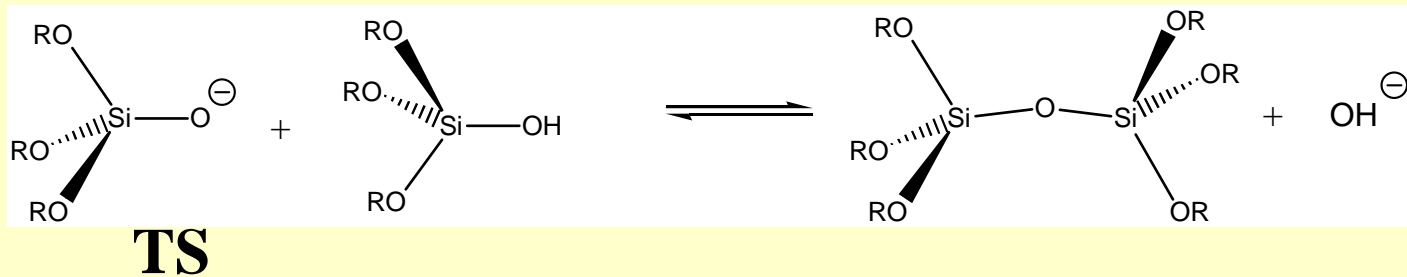**TS (+) is destabilized by increasing number of electron withdrawing OH groups**

Hydrolysis fastest in the first step, i.e. the formation of $(RO)_3SiOH$

Condensation for this species also fastest, the formation of linear chains

Condensation

Base catalysed condensation

fast deprotonation, slow condensation

TS

Negatively charged transition state, fastest condensation for
$(RO)_3SiOH < (RO)_2Si(OH)_2 < ROSi(OH)_3 < Si(OH)_4$

TS (−) is stabilized by increasing number of electron withdrawing OH groups

Hydrolysis speeds up with more OH, i.e. the formation of $Si(OH)_4$

Condensation for the fully hydrolysed species fastest, the formation of highly crosslinked particles

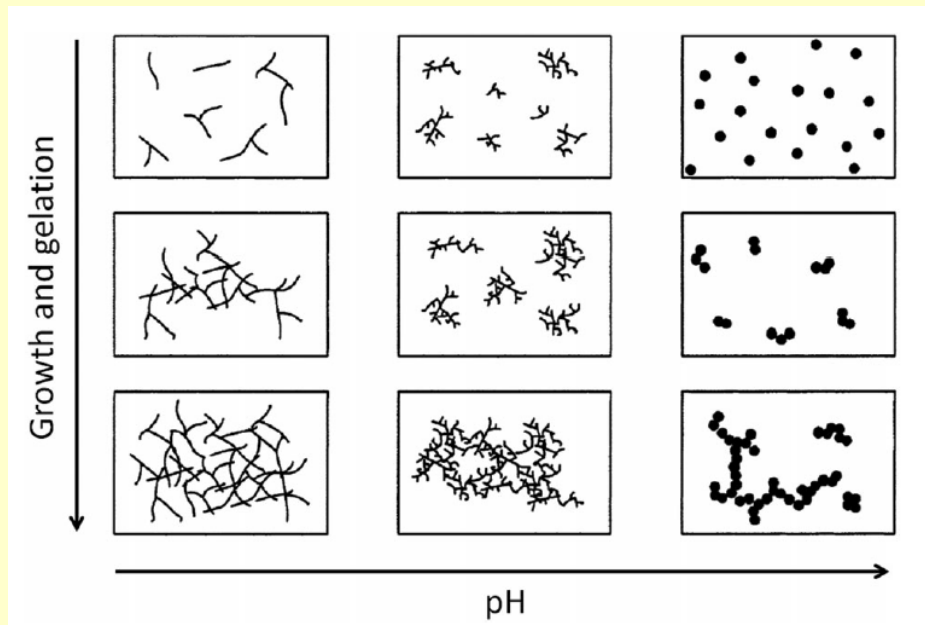**Reaction limited cluster aggregation (RLCA)**
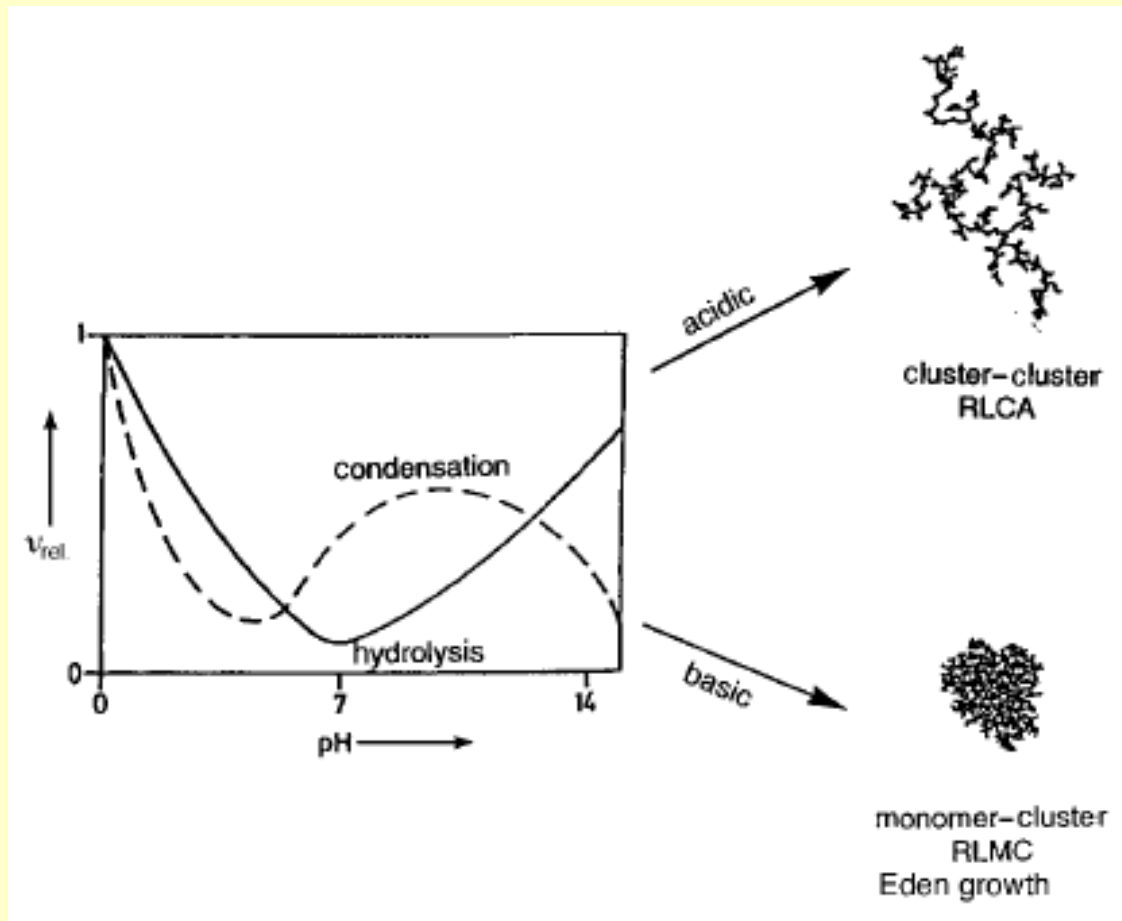
Acid catalysed

Base catalysed

**Reaction limited monomer cluster growth (RLMC)
or Eden growth**

Acid catalysed condensation

- **condensation to linear chains**
- **small primary particles**
- **microporosity, Type I isotherms**


Base catalysed condensation

- **condensation to highly crosslinked particles**
- **large primary particles**
- **mesoporosity, Type IV isotherms**

Gelation = Sol-to-Gel Transition

Gel point - a spannig cluster reaches across the container, sol particles, oligomers and monomer still present
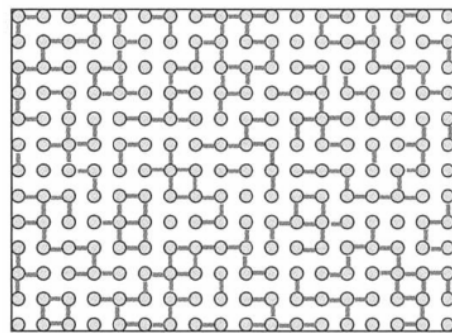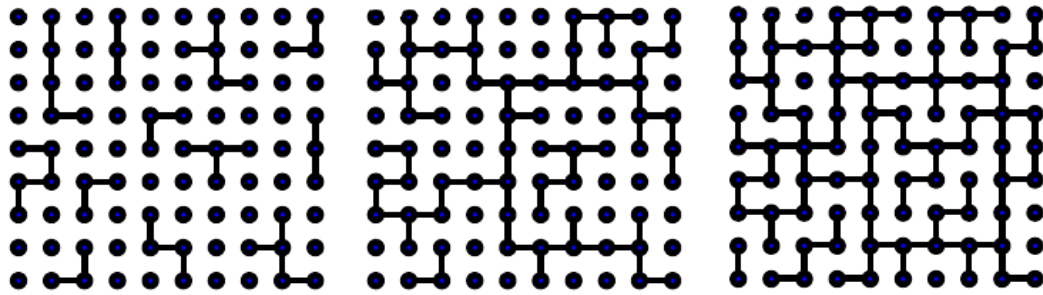
a sudden viscosity increase at the gel point

further crosslinking - increase in elasticity
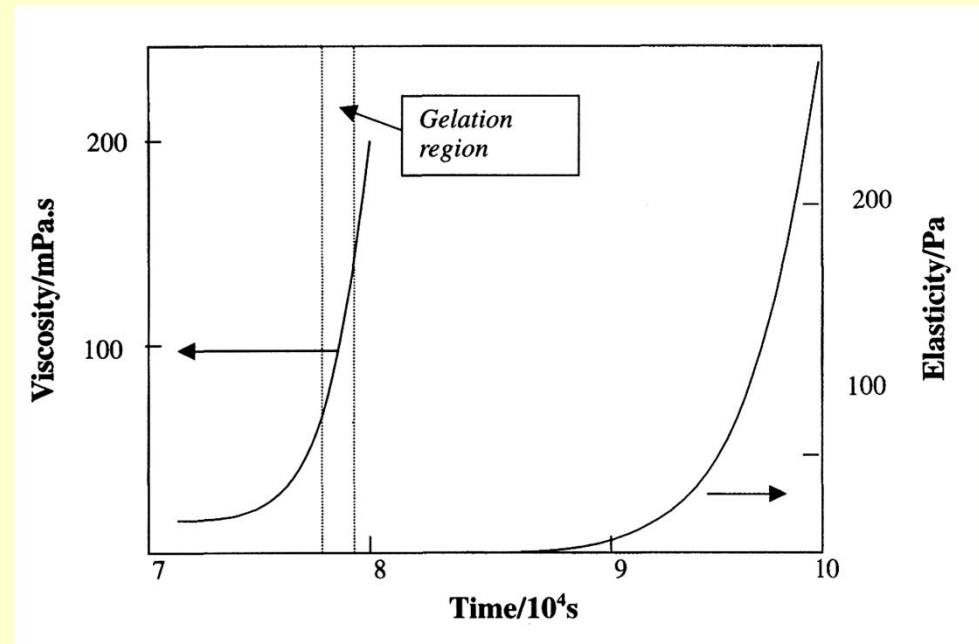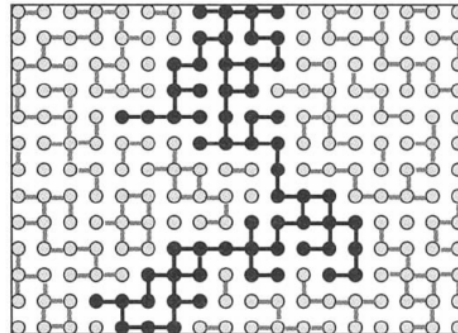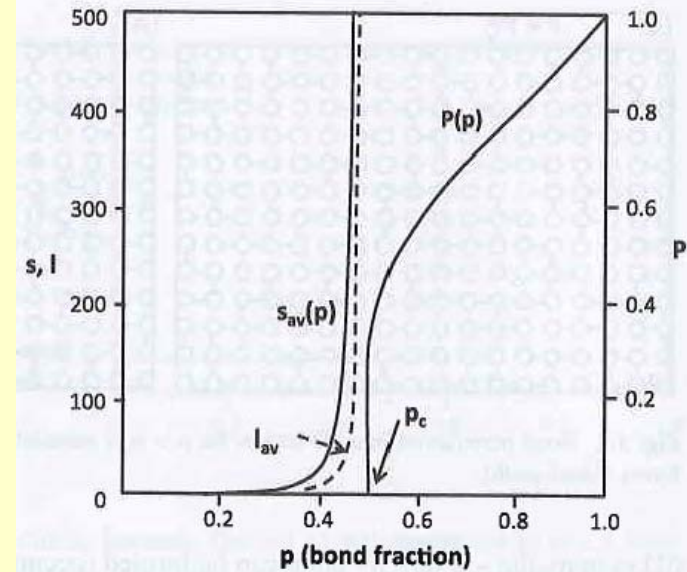
Bond Percolation

p = the fraction of created links
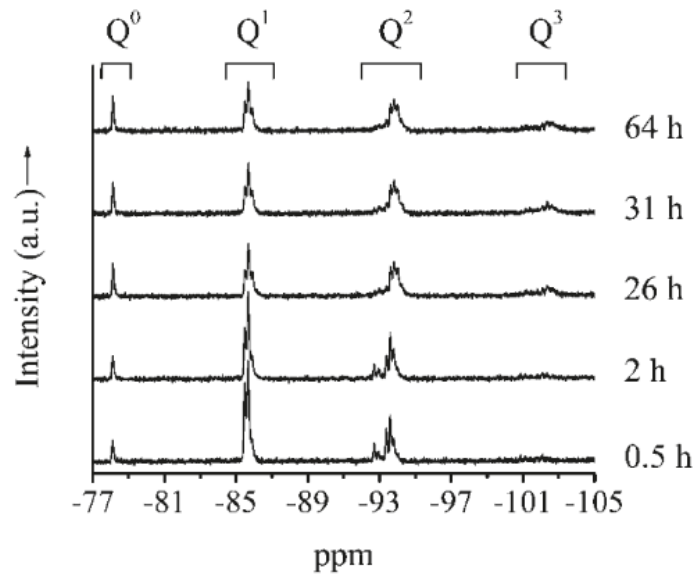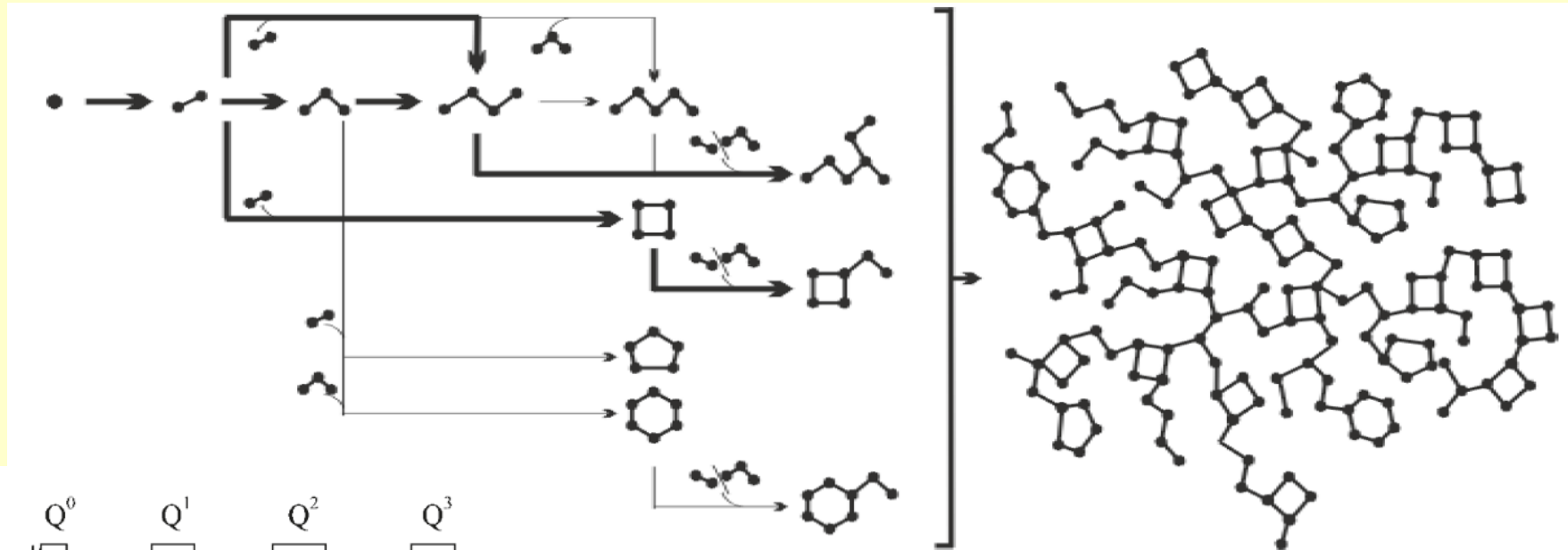

$p < p_c$

$p > p_c$
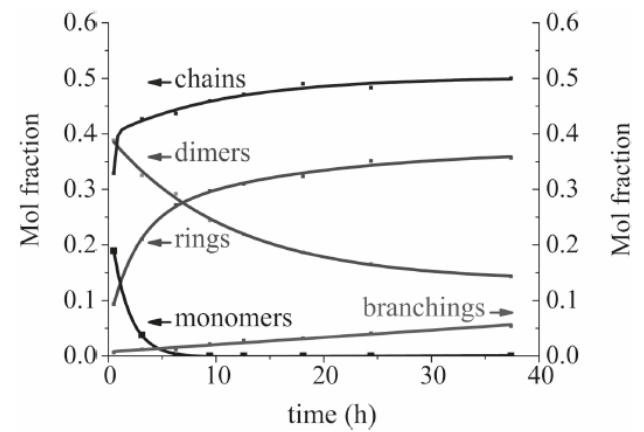
Sol-Gel Methods

$s_{av}(p)$ = average cluster size

$l_{av}(p)$ = average spanning length

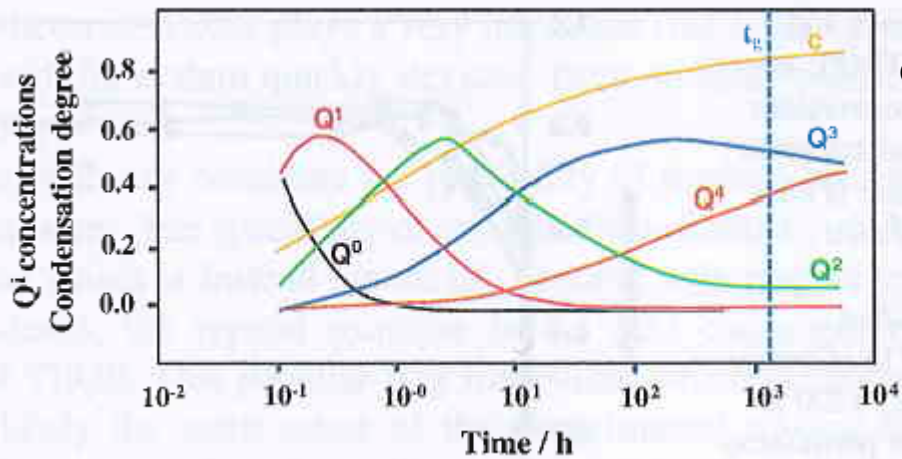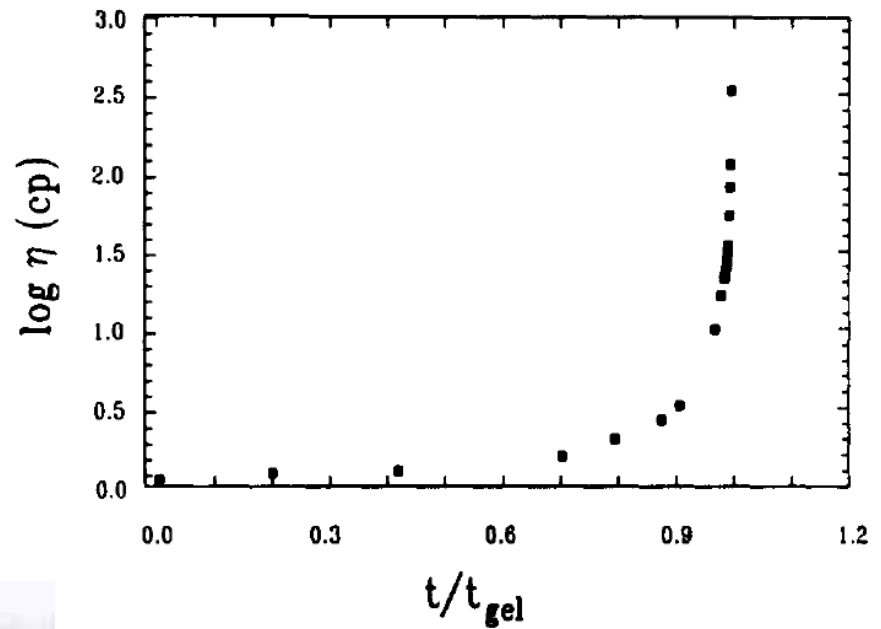P(p) = percolation probability = a bond is added to a spanning cluster

55

Sol-to-Gel Transition

Sol-Gel Methods

Sol-to-Gel Transition
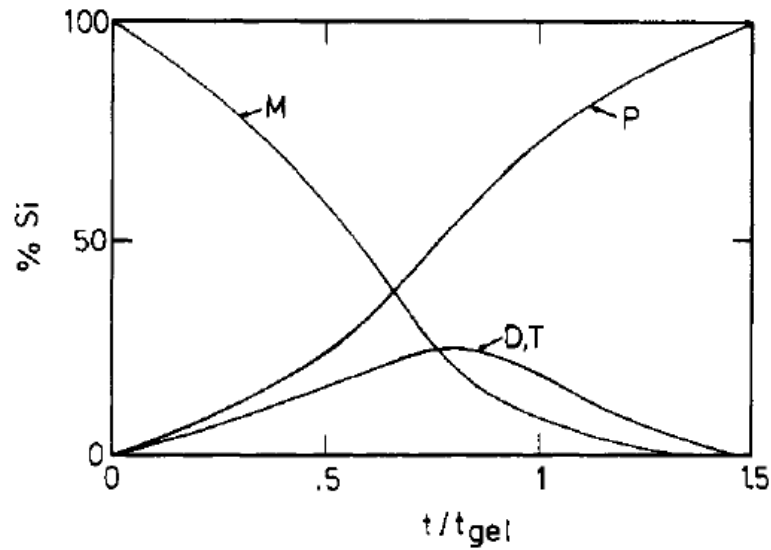
c = condensation degree, max 83 %

Ageing of Gel

Silica Alcogel → Evaporation → Silica Xerogel

Ageing

Crosslinking
condensation of the OH surface groups, stiffening and shrinkage

Syneresis
shrinkage causes expulsion of liquid from the pores

Coarsening
materials dissolve from the convex surfaces and deposits
at the concave surfaces: necks

Rippening
Smaller particles have higher solubility thean larger ones

Phase separation
Fast gelation, different miscibility, isolated regions of unreacted precursor,
inclusions of different structure, opaque, phase separation
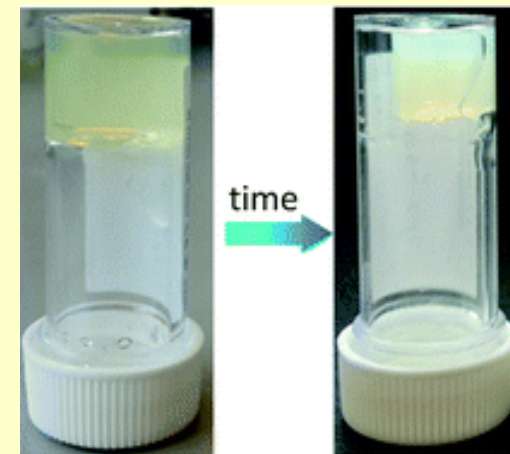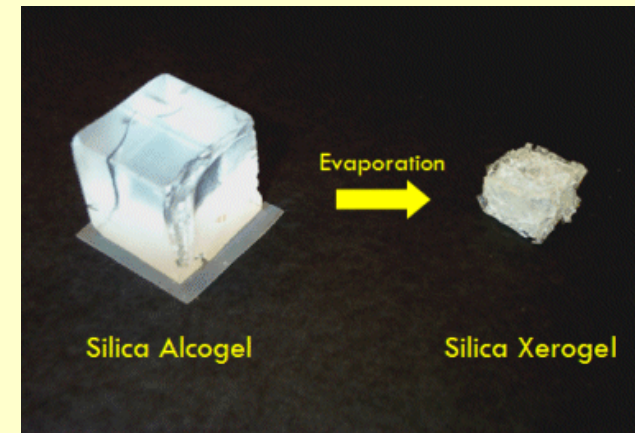
Drying

1. The constant rate period
the gel is still flexible and shrinks as liquid evaporates

2. The critical point
the gel becomes stiff and resists further shrinkage, the liquid begins to recede (contact angle θ) into the pores (radius r), surface tension γ creates large capillary pressures P_c, stress, cracking

$$P_c = \frac{2\gamma \cos\theta}{r}$$

3. The first falling-rate period
a thin liquid film remains on the pore walls, flows to the surface and evaporates, the menisci first recede into the largest pores only, as these empty, the vapor pressure drops and smaller pores begin to empty
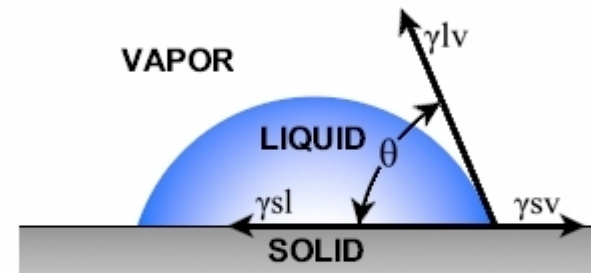
4. The second falling-rate period
liquid film on the walls is broken, further liquid transport by evaporation

Drying

$$P_c = \frac{-2\gamma_{LV} \cos\theta}{r}$$

Young's Equation

$$\gamma^{sv} = \gamma^{sl} + \gamma^{lv}\cos\theta$$

θ is the contact angle

γ^{sl} is the solid/liquid interfacial free energy

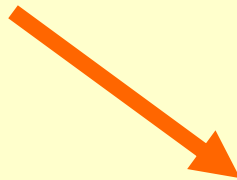γ^{sv} is the solid surface free energy

γ^{lv} is the liquid surface free energy

Drying Methods

To avoid cracking:

- No meniscus
- Decrease surface tension
- Increase wetting angle (isopropanol)
- Increase pore size
- Make a stiff gel

$$P_c = \frac{2\gamma \cos \theta}{r}$$

1. Supercritical drying

2. Freeze-drying

3. Drying control chemical additives

4. Ageing

5. Large pore gels

25 mmol (5.2 g) of tetraethoxysilane (TEOS)

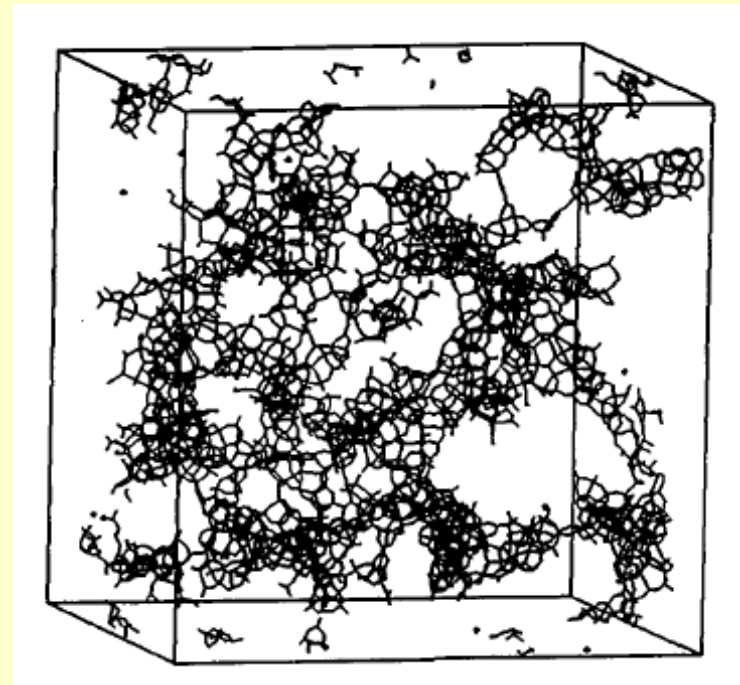TEOS:H_2O:HNO_3:ammonium acetate molar ratio of the solution is 1 : 10 : 0.002 : 0.02

Sol-Gel Methods

Aerogels

1931 Steven S. Kistler J. Phys. Chem. 34, 52, 1932

Aerogels = materials in which the typical structure of the pores and the network is largely maintained while the pore liquid of a gel is replaced by air

The record low density solid material - 0.001 g/cm^3
density of air 1.2 mg/cm^3
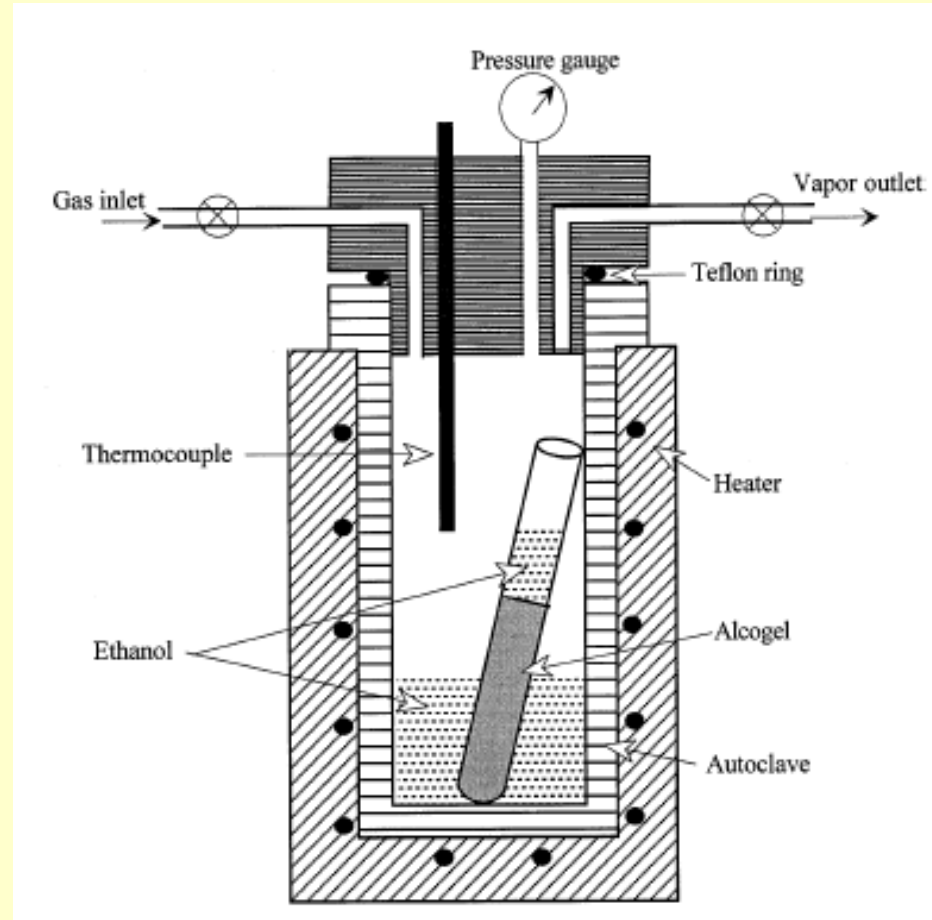
Aerogels - Supercritical Drying
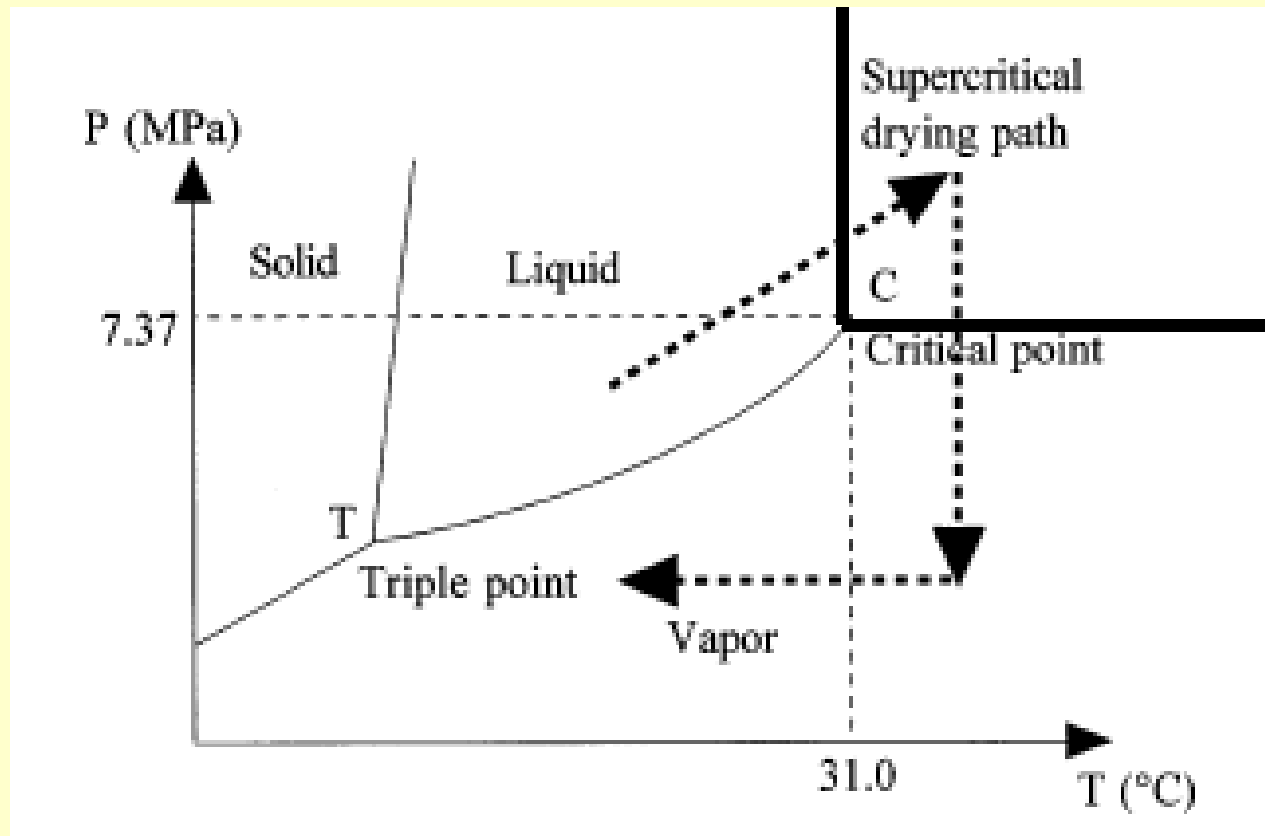
Silica aerogel

From sodium silicate – 3 steps
•**Salt washing**
•**Water replacement**
•**Supercritical drying**

From silicon alkoxides – 1 step
•**Supercritical drying**

Supercritical Drying

Cold supercritical drying path in the Pressure (P) Temperature (T) phase diagram of CO_2

Supercritical Drying

fluid	formula	T_c (°C)	P_c (MPa)
water	H_2O	374.1	22.04
carbon dioxide	CO_2	31.0	7.37
Freon 116	$(CF_3)_2$	19.7	2.97
acetone	$(CH_3)_2O$	235.0	4.66
nitrous oxide	N_2O	36.4	7.24
methanol	CH_3OH	239.4	8.09
ethanol	C_2H_5OH	243.0	6.3

Solvent	T_c [°C]	p_c [Mpa]	V_c [cm³mol⁻¹]
methanol	240	7.9	118
ethanol	243	6.3	167
acetone	235	4.7	209
2-propanol	235	4.7	
H_2O	374	22.1	56
CO_2	31	7.3	94
N_2O	37	7.3	97

Densification

Densification

Stage I. Below 200 °C, weight loss, no shrinkage

pore surface liquid desorption

Stage II. 150 - 700 °C, both weight loss and shrinkage

loss of organics - weight loss
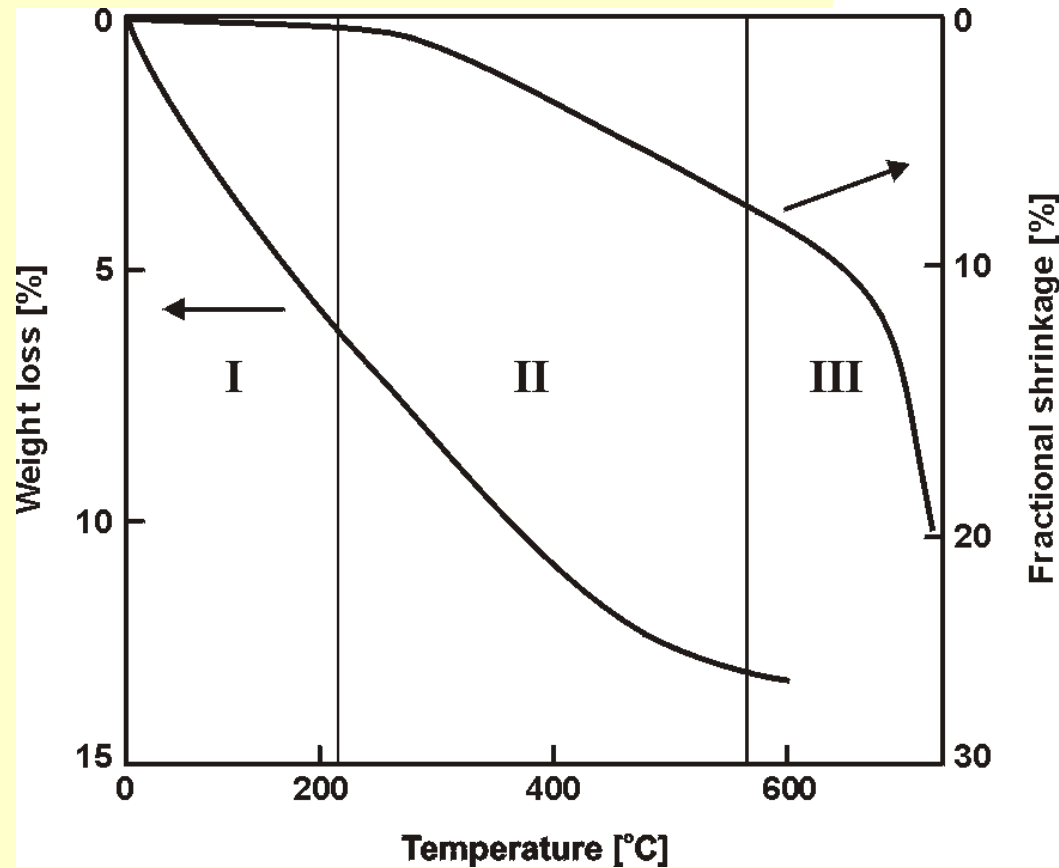**further condensation - weight loss and shrinkage**
structural relaxation - shrinkage

Stage III. Above 500 °C, no more weight loss, shrinkage only

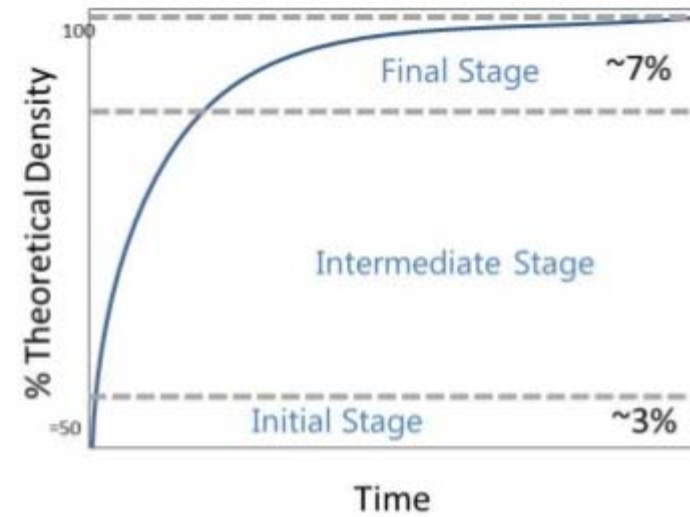**close to glass transition temperature, viscous flow, rapid densification,**
large reduction of surface area, reduction of interfacial energy,
termodynamically favored

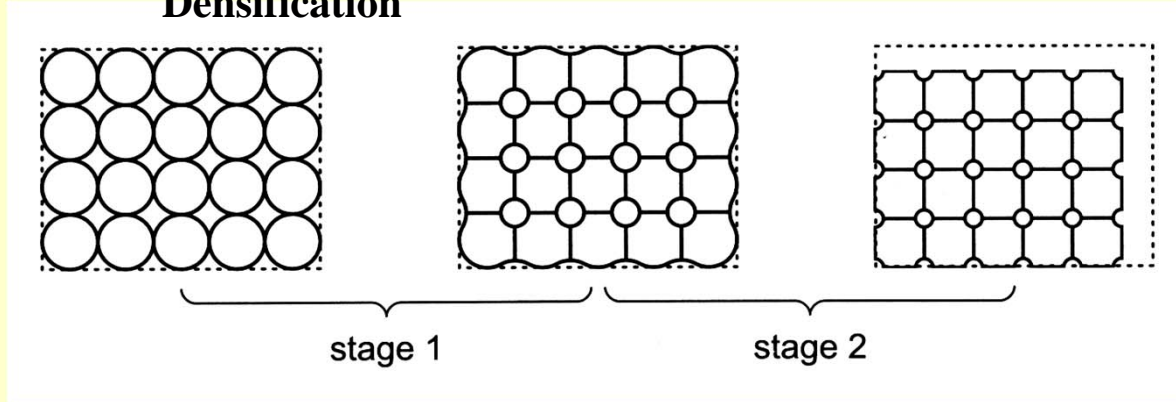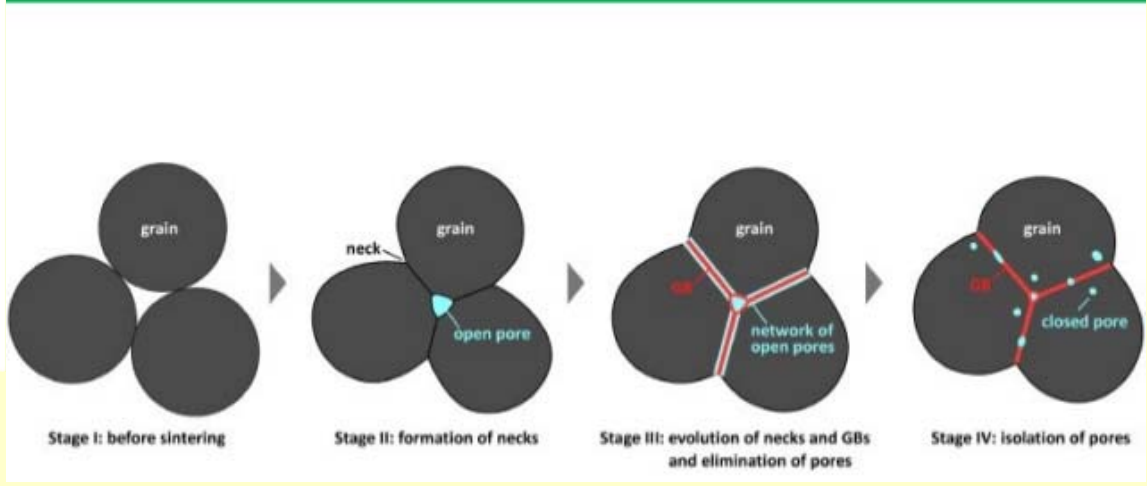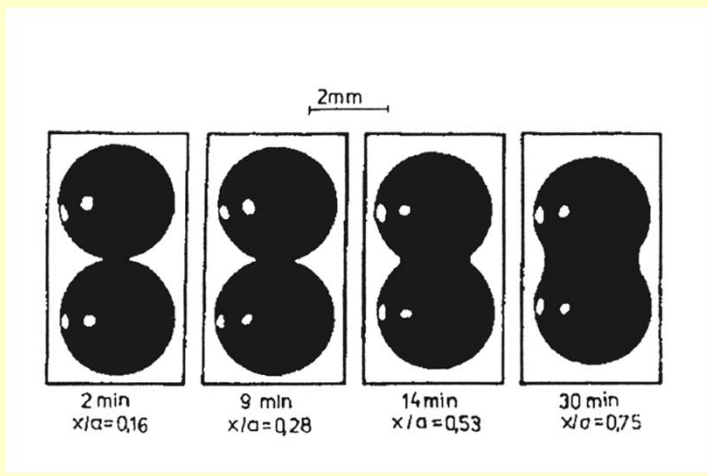# Densification - Sintering

Generalized Sintering Curve

Densification - Sintering

stage 1   stage 2

| 2 min | 9 min | 14 min | 30 min |
| x/a=0.16 | x/a=0.28 | x/a=0.53 | x/a=0.75 |

Stages of Sintering

Stage I: before sintering

Stage II: formation of necks

Stage III: evolution of necks and GBs and elimination of pores

Stage IV: isolation of pores

Sol-Gel Methods

69

Sintering mechanisms

Sintering mechanisms - solid, liquid, gas phase

1. Evaporation-condensation and dissolution-precipitation

2. Volume diffusion
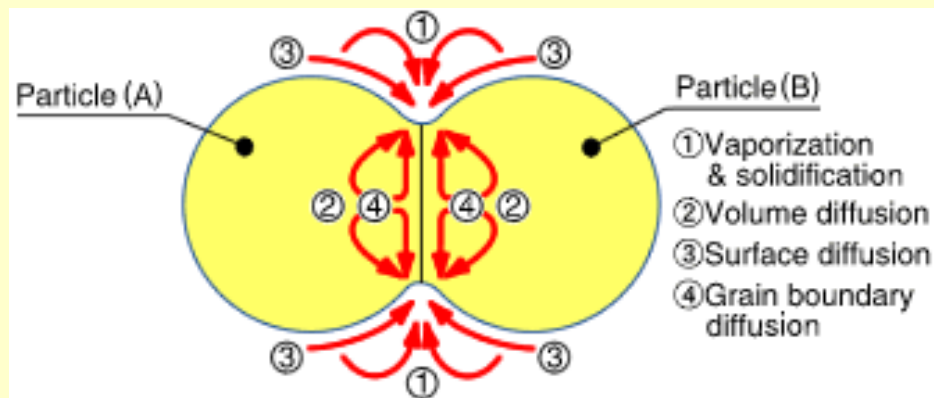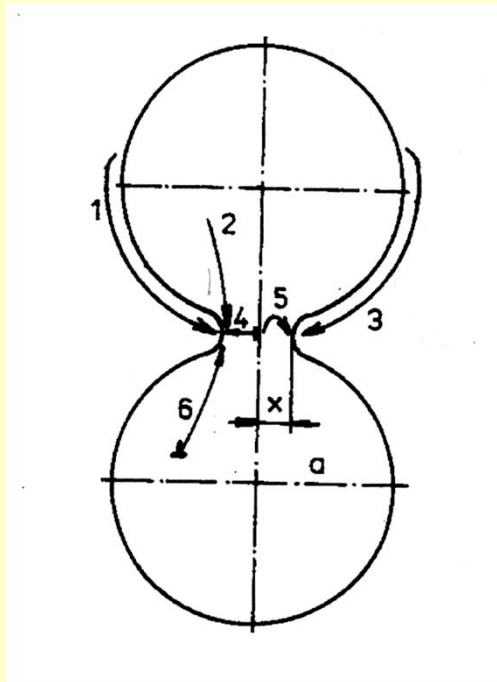
3. Surface diffusion

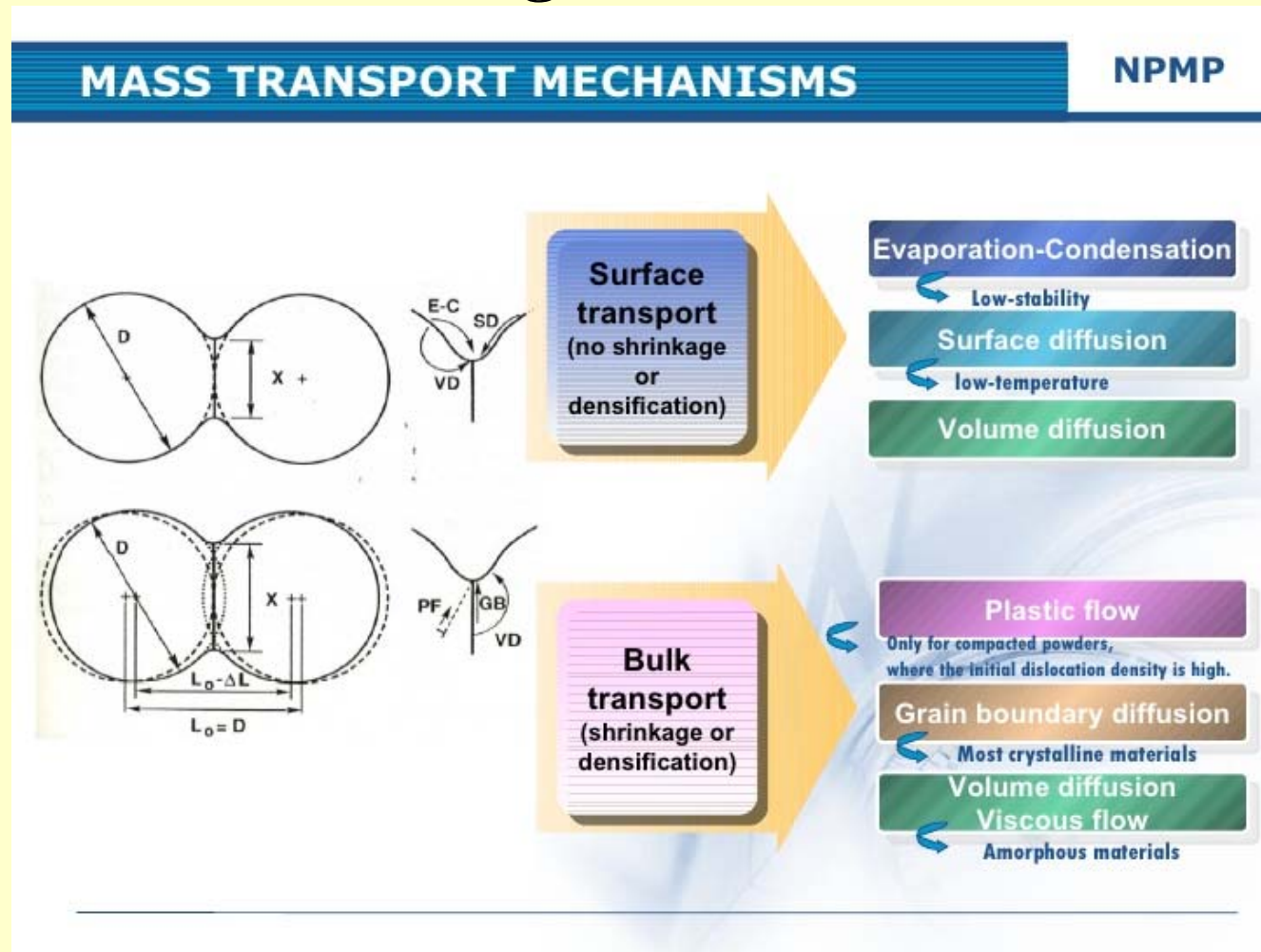**4. Grain boundary diffusion**

5. Volume diffusion from grain boundaries

6. Volume diffusion from dislocations – plastic flow

Volume diffusion from dislocations vacancies

Viscous flow

Particle (A)   Particle (B)

① Vaporization & solidification
② Volume diffusion
③ Surface diffusion
④ Grain boundary diffusion
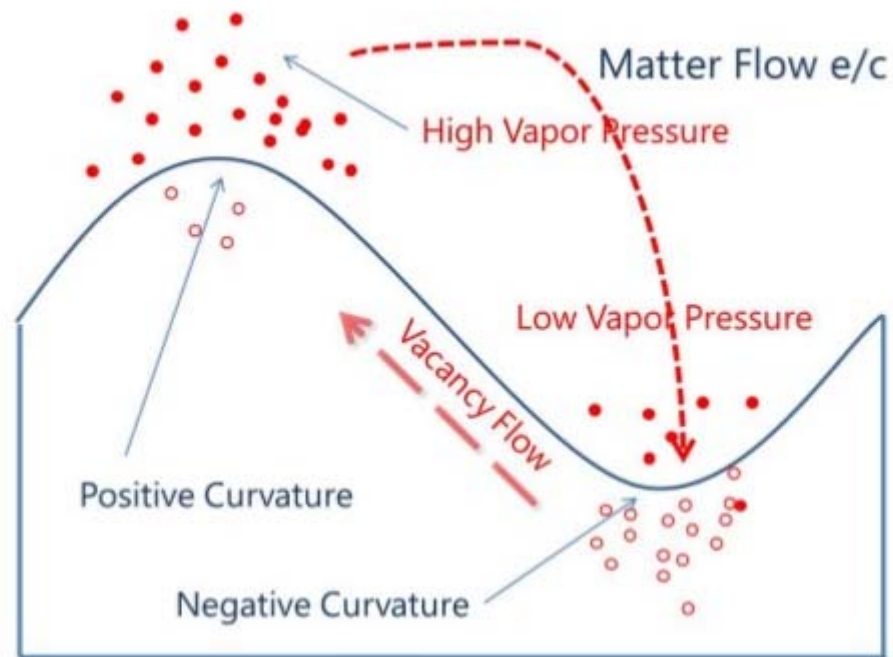
Sintering Mechanisms

Sintering Mechanisms

Figure : Curvature in solids, and their effect on vapor pressure
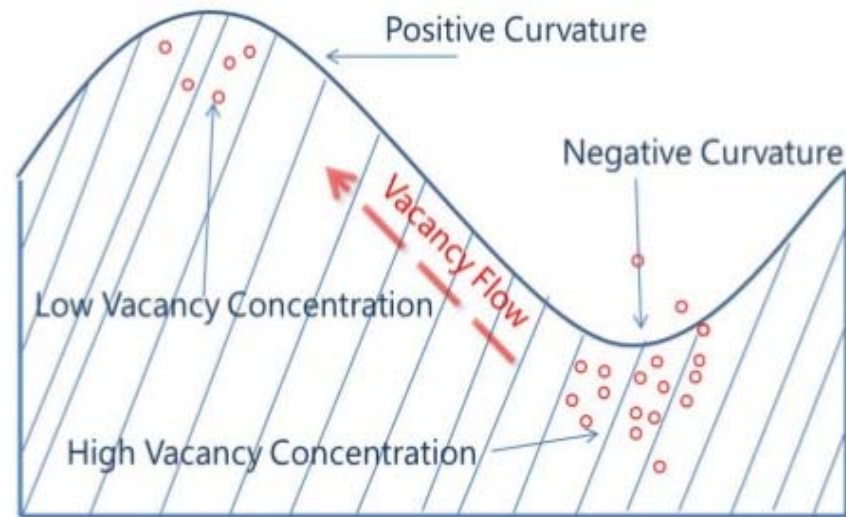
Sintering Mechanisms

Figure : Curvature in solids, and their effect of vacancy concentration

Sintering Mechanisms

Plastic Flow

Plastic flow is the motion of dislocations under stress.

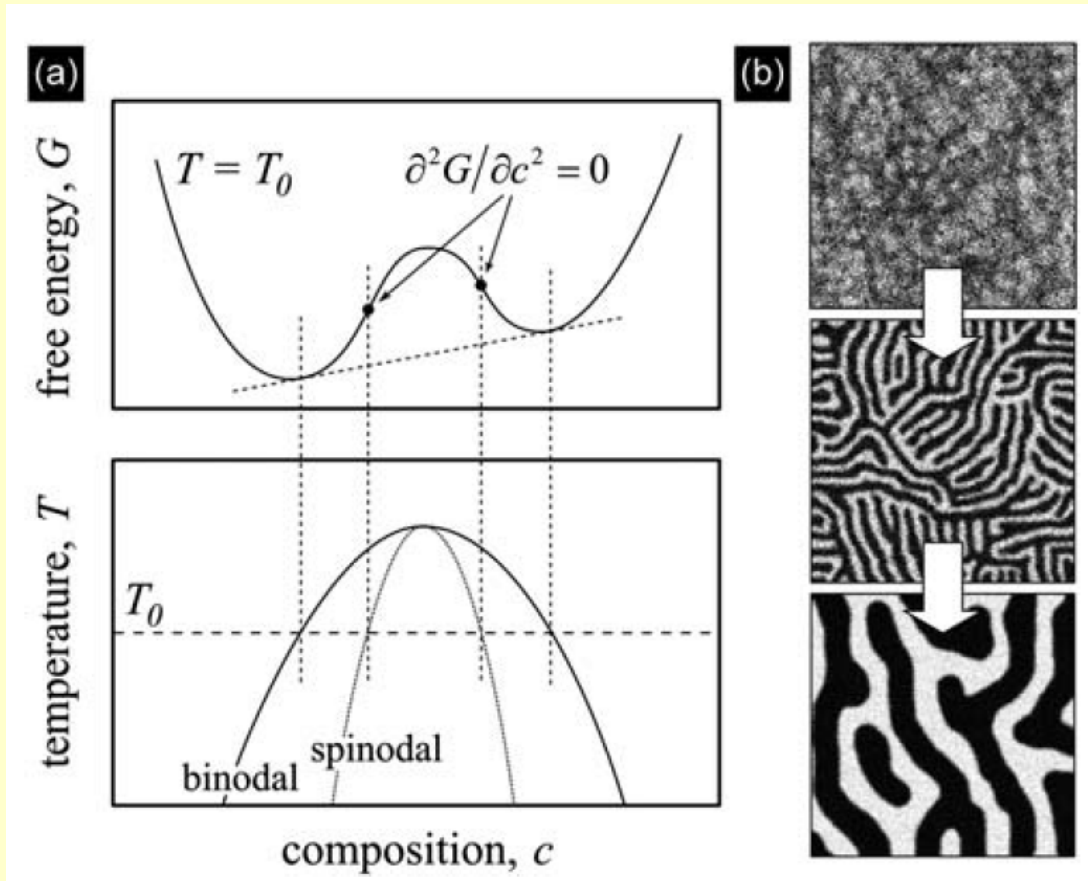| Siegel | Dislocation participate in sintering during heating, especially if the powders was subjected to plastic deformation during compaction. |

| Schatt and co-workers | Demonstrated densification rate improvements because of dislocation climb with the rate of pore elimination. |

The dislocation flow is restricted to the early stage of sintering.
: As the neck enlarges, the shear stress declines and falls below the flow stress for the material and the process becomes inactive.

74

Sintering Mechanisms

Spinodal Decomposition

(a) Free energy of a binary system as a function of composition and the miscibility region showing the origin of the binodal and spinodal lines, and (b) typical evolution of a blend microstructure phase separating by spinodal decomposition.
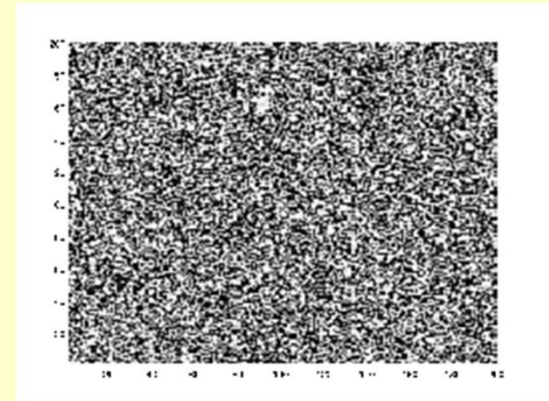
Spinodal Decomposition

A two component system with a composition, c, that is unstable to small fluctuations in concentration,
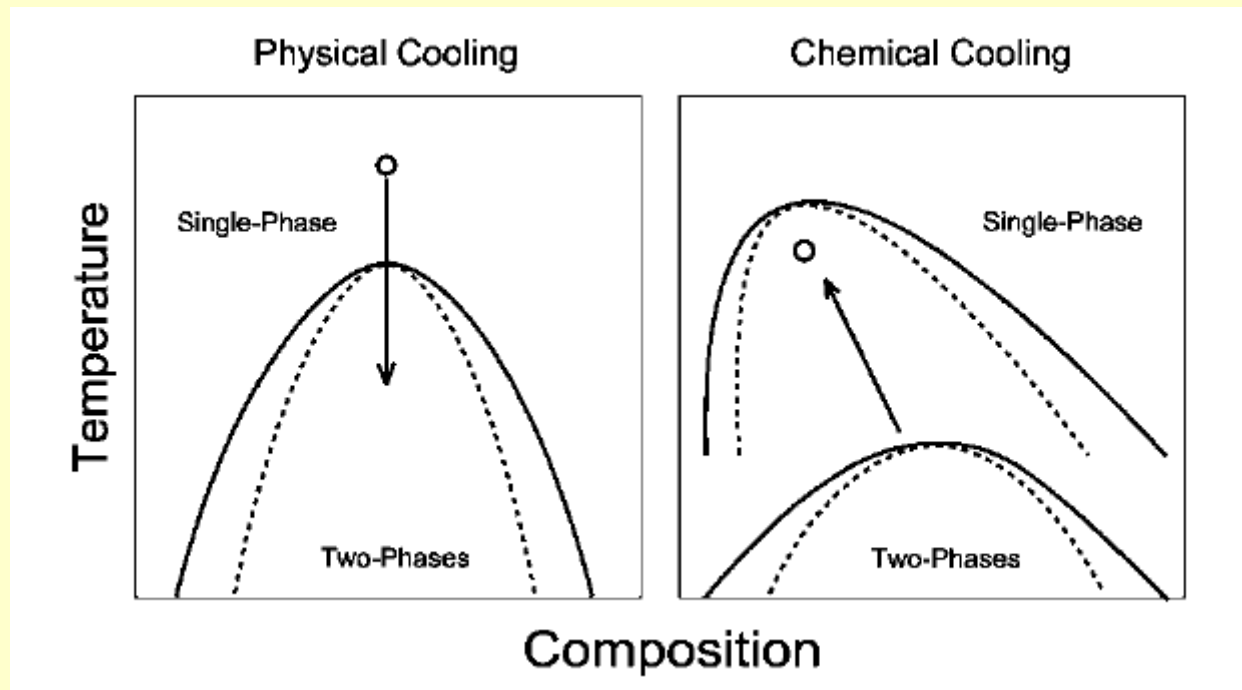
where
$$\frac{\partial^2 G}{\partial c^2} < 0$$

(G = the free energy),

will spontaneously phase separate with the fluctuations increasing and coarsening over time.
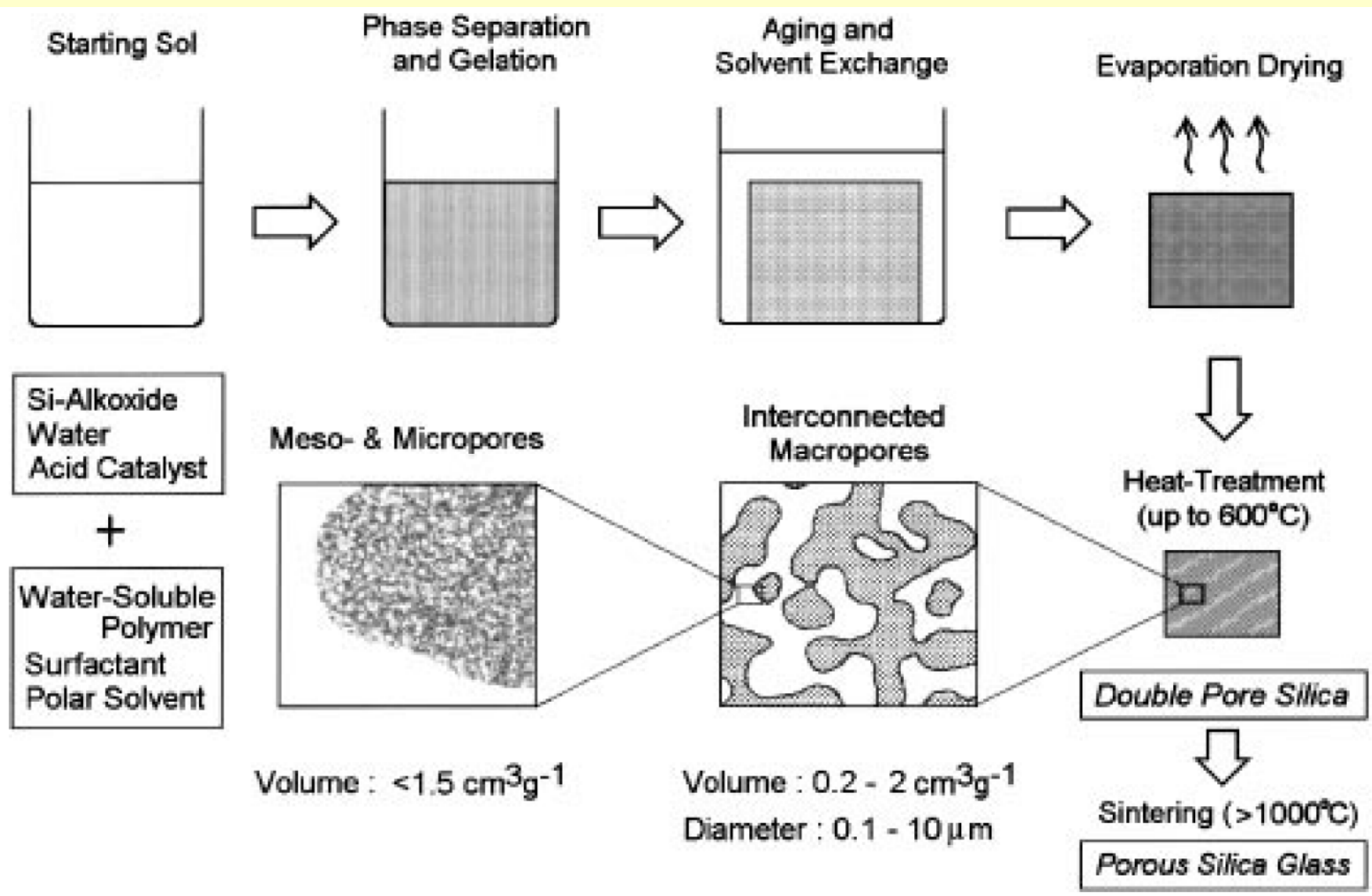
Sol–Gel with Phase Separation

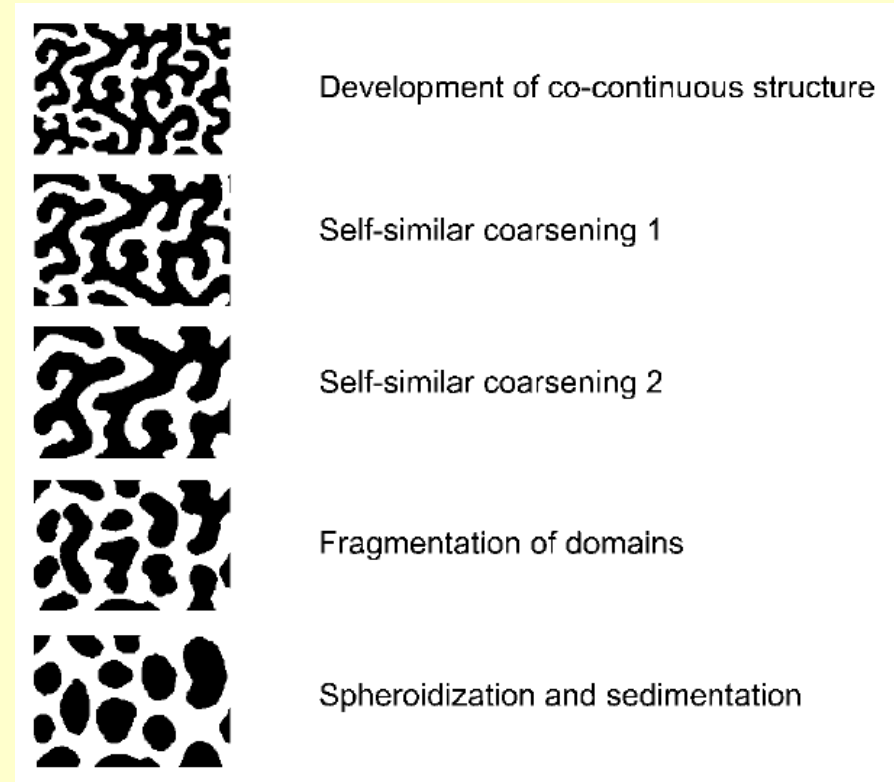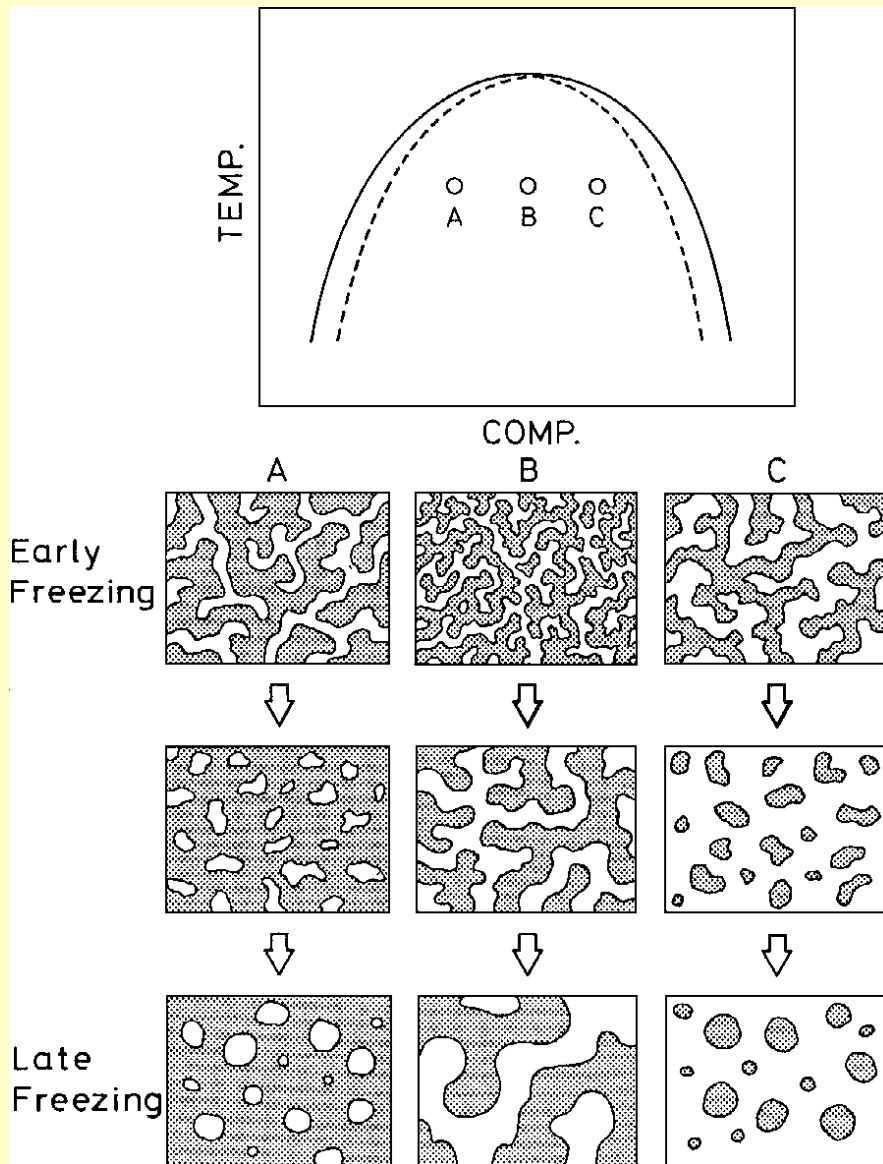$$\Delta G \propto RT[(\phi_1/P_1)\ln\phi_1 + (\phi_2/P_2)\ln\phi_2 + \chi_{12}\phi_1\phi_2]$$
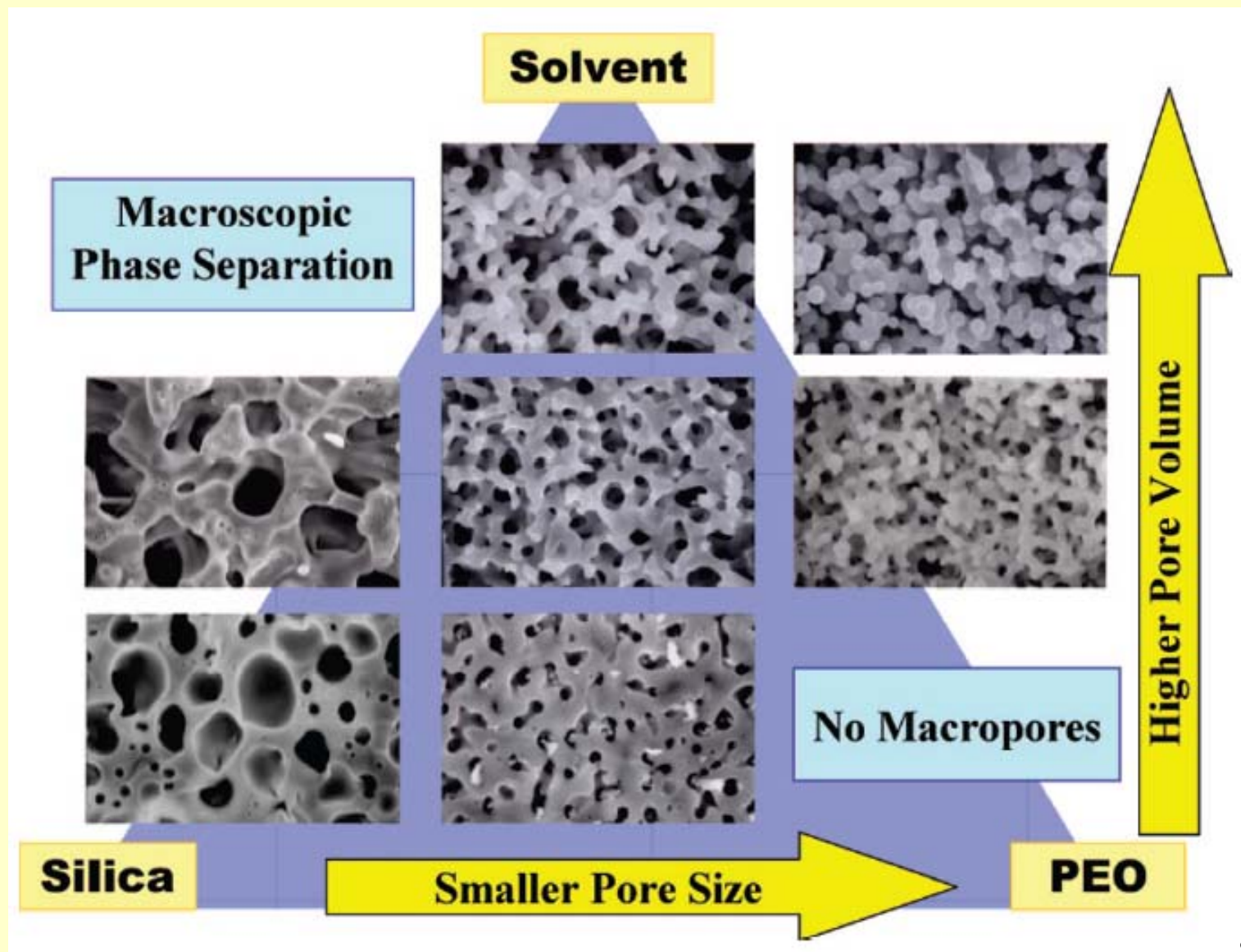
ϕi = the volume fraction

Pi (i = 1, 2) = the degree of polymerization of each component,
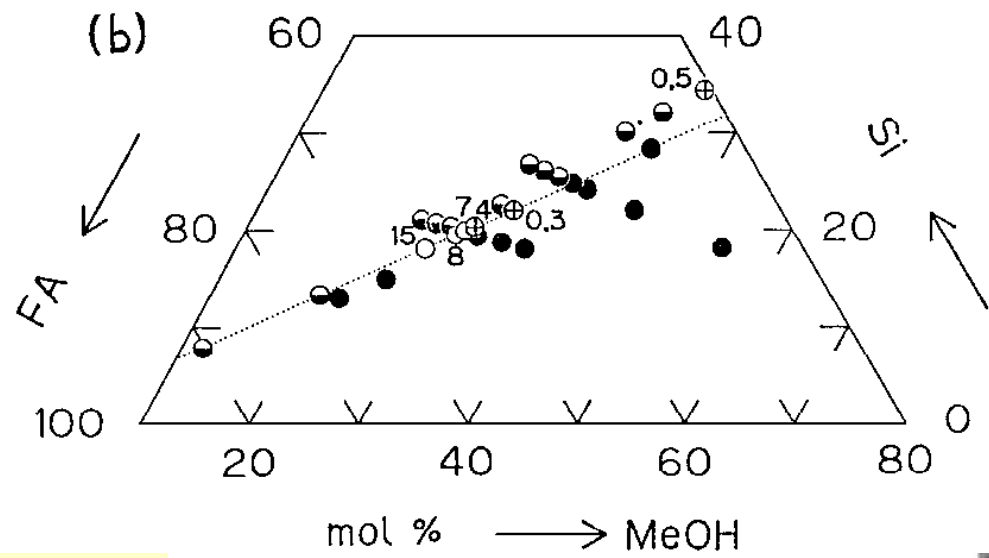
χ_{12} the interaction parameter

The former two terms in the bracket express the entropic contribution, and the last term the enthalpic contribution

Starting Sol

Phase Separation and Gelation

Aging and Solvent Exchange

Evaporation Drying

Si-Alkoxide
Water
Acid Catalyst

+

Water-Soluble Polymer
Surfactant
Polar Solvent

Meso- & Micropores

Interconnected Macropores

Heat-Treatment (up to 600°C)

Double Pore Silica

Volume : <1.5 cm^{3}g^{-1}

Volume : 0.2 - 2 cm^{3}g^{-1}
Diameter : 0.1 - 10 μm

Sintering (>1000°C)

Porous Silica Glass

79

TEMP.

COMP.

A   B   C

Early Freezing

Late Freezing

Development of co-continuous structure

Self-similar coarsening 1

Self-similar coarsening 2

Fragmentation of domains

Spheroidization and sedimentation

Solvent

Macroscopic Phase Separation

No Macropores

Silica

Smaller Pore Size

PEO

Higher Pore Volume

TMOS-Formamide-1M nitric acid (b) calculated composition. Reaction temperature 40 ºC; circles with cross and shaded areas denote the composition where the interconnceted structure has been obtained. •: nanoporous gel, ⊕: interconnected strucuture, ○: particle aggregates, ◗: macroscopic two-phase.
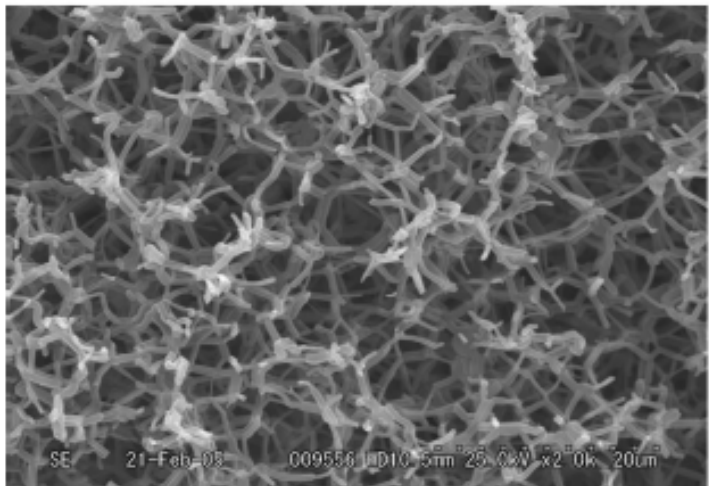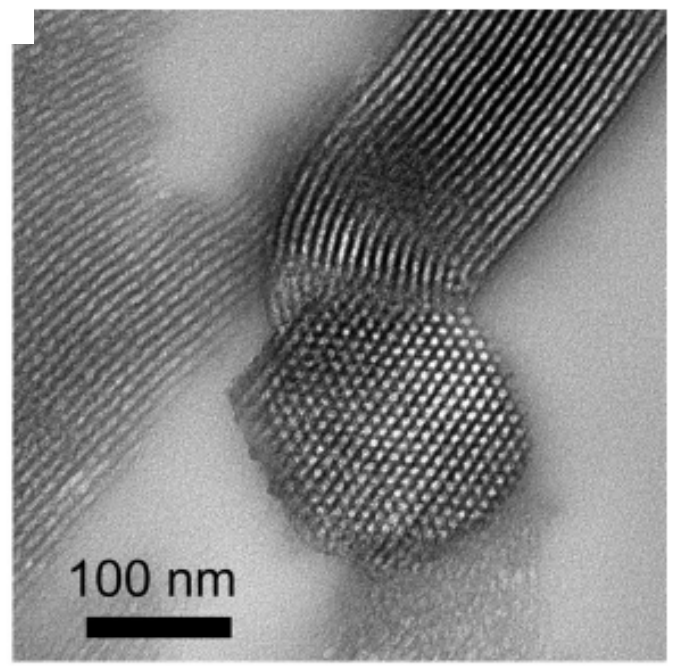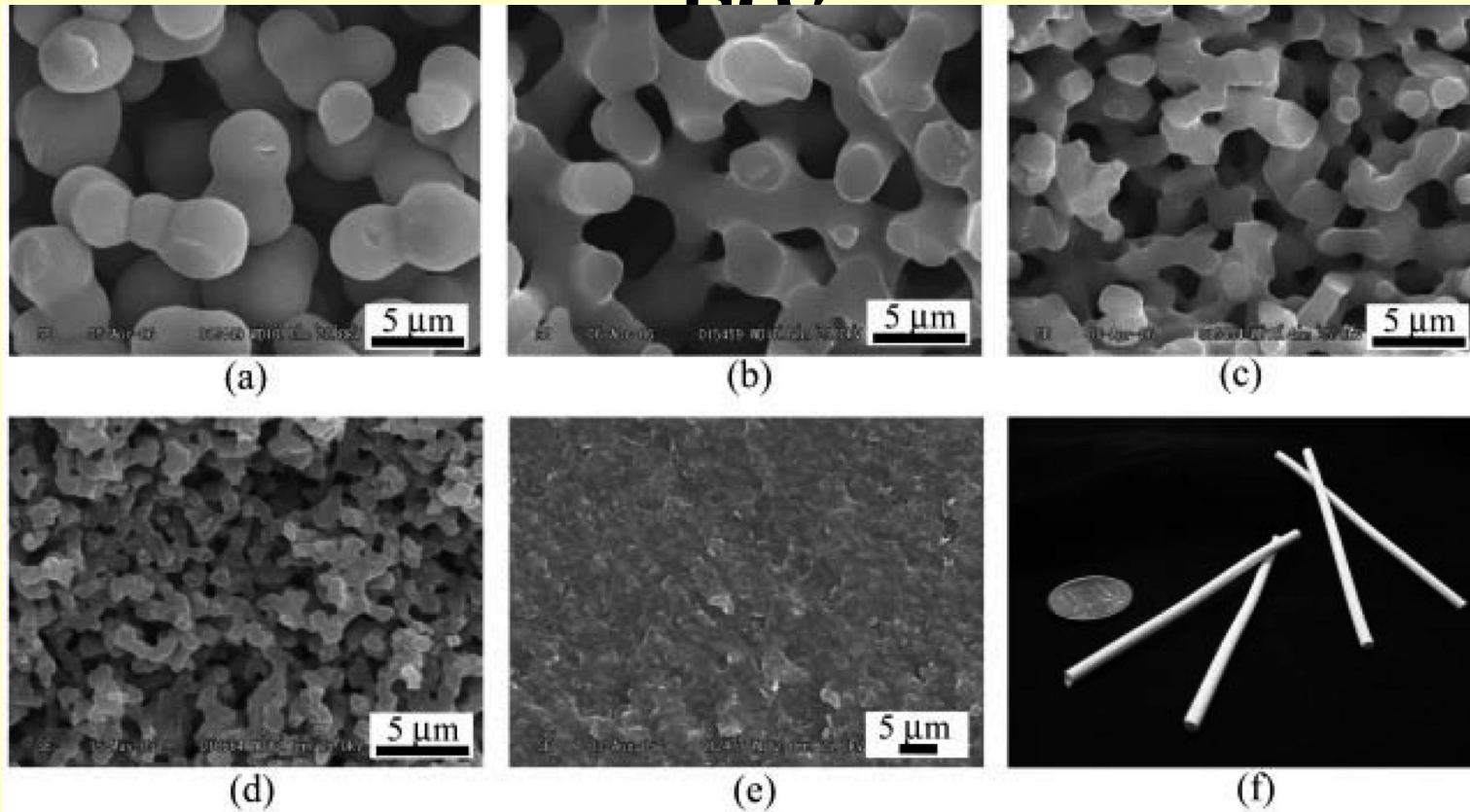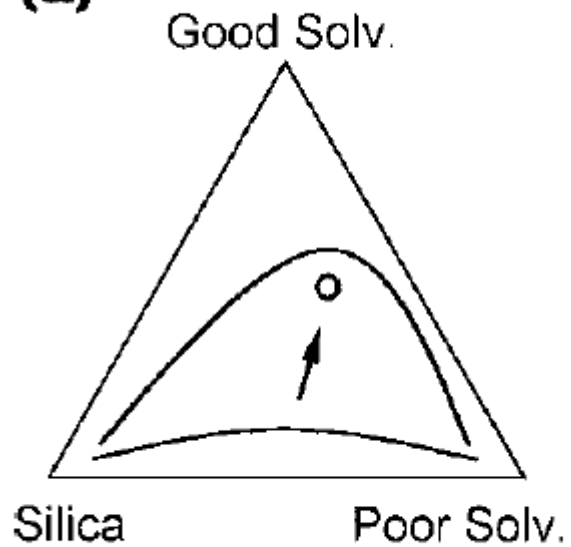
TiO2

SEM images of dried TiO_2 gels prepared with varied water/TiO_2 molar ratios in the overall starting 1:0.5:0.5:f Ti(O$_n$C$_3$H$_7$)$_4$:HCl:formamide:water composition: (a) f) 20.50, (b) f) 20.75, (c) f) 21.00, (d) f) 21.25, and (e) f) 21.50. (f) Photo image of monolithic TiO_2 gels prepared in Teflon tubes and a coin.
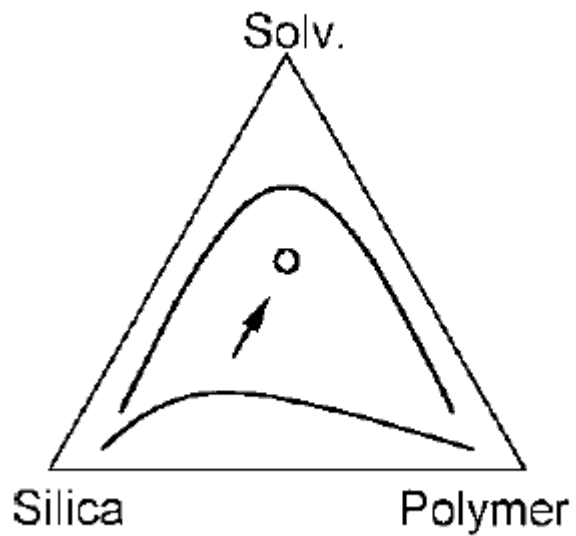
83

(a)

Alkoxide + Water (r < 1.5)
+ Formamide

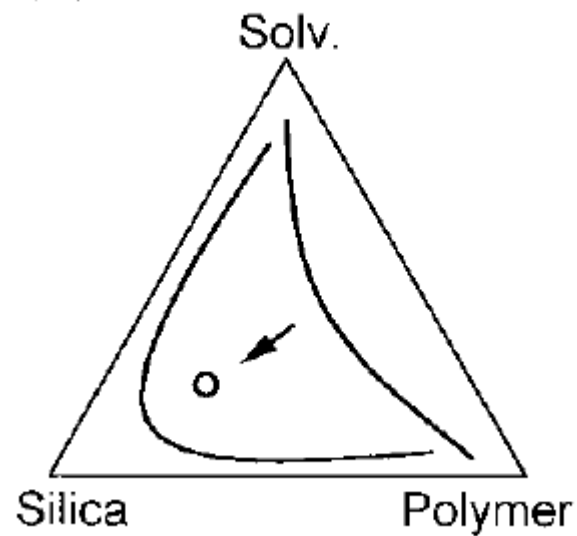**Gel   Phase : Silica + Good Solv.**
Fluid Phase : Good & Poor Solvs.

(b)

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

Gel Phase : Silica + Solvent
Fluid Phase : Polymer + Solvent
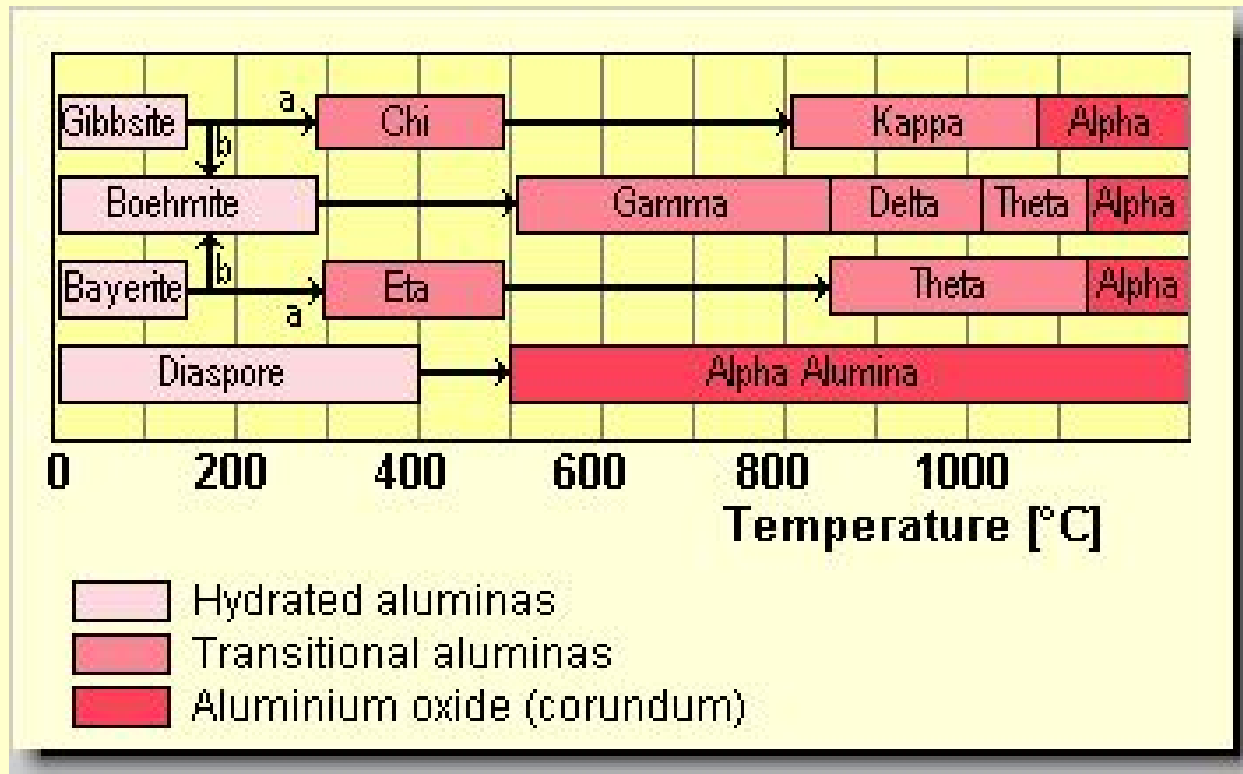
85

(c)

Solv.

Silica   Polymer

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

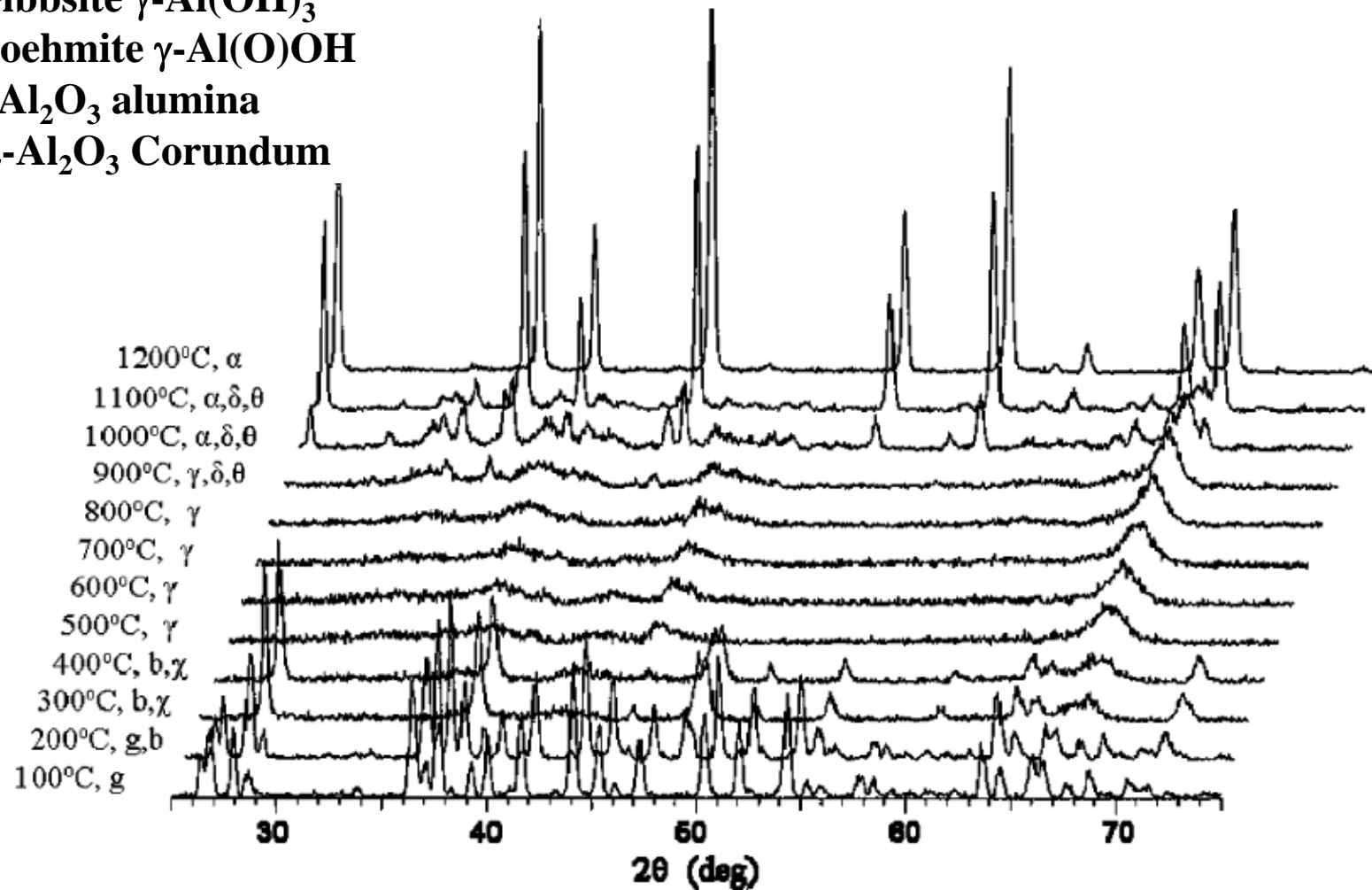**Gel   Phase : Polymer + Silica**
Fluid Phase : Solvent + Silica

Dehydration sequence of hydrated alumina in air

**Path (b) is favored by moisture, alkalinity, and coarse particle size (100μm)
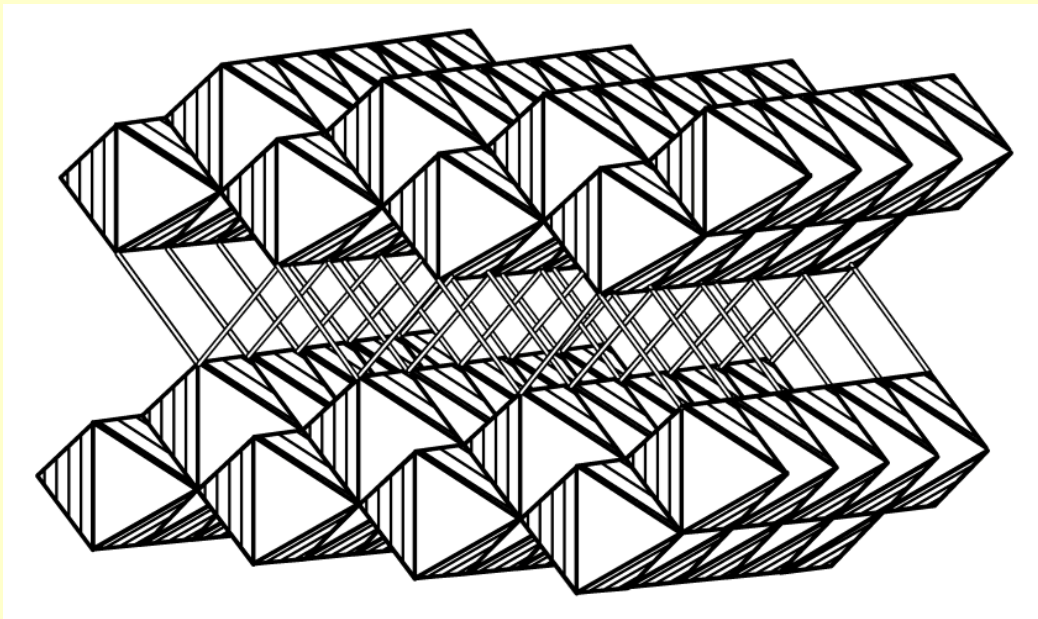path (a) by fine crystal size (<10μm)**

HT-XRD of the phase transitions

g = Gibbsite γ-Al(OH)$_3$
b = Boehmite γ-Al(O)OH
γ = γ-Al$_2$O$_3$ alumina
α = α-Al$_2$O$_3$ Corundum

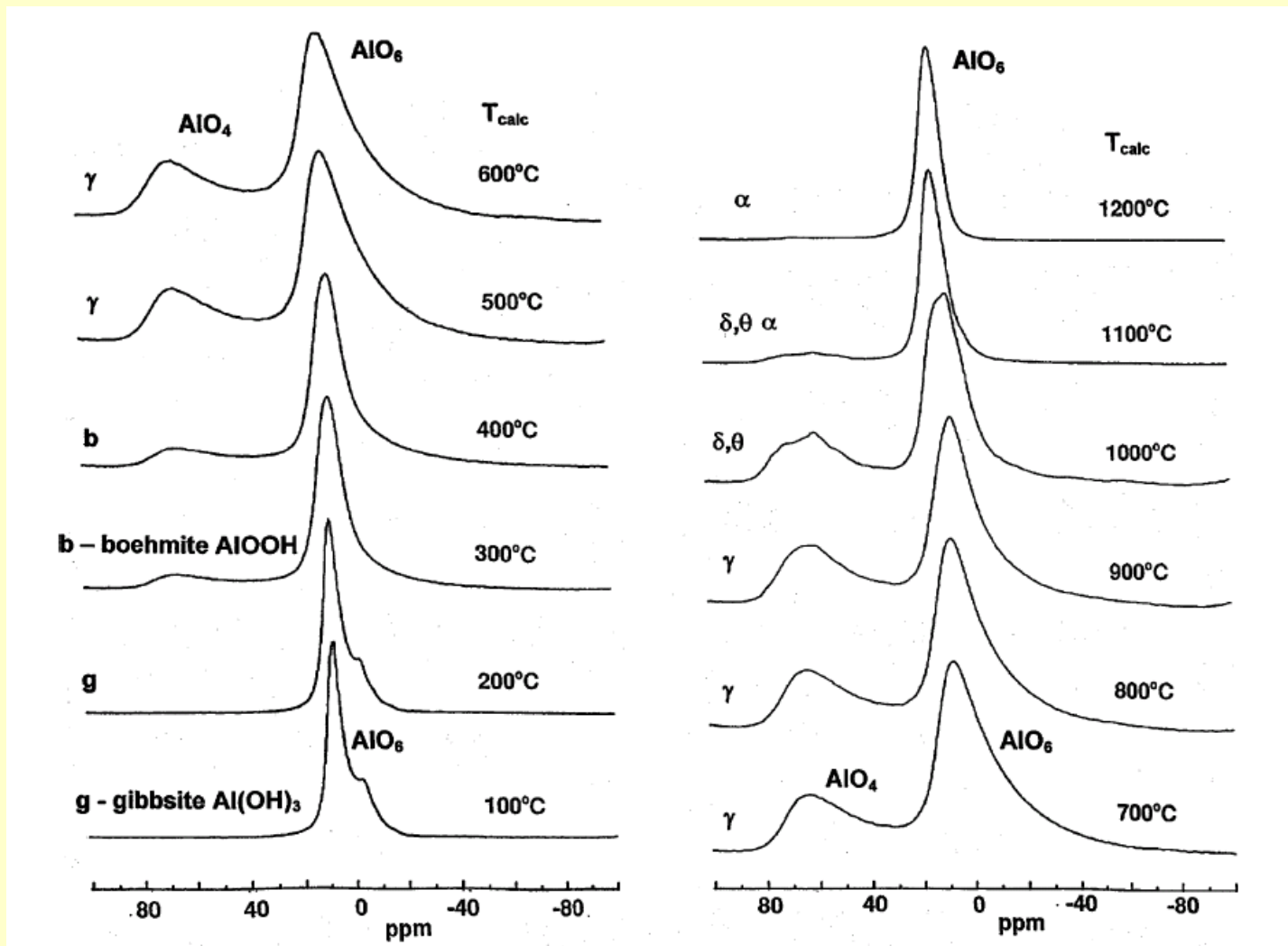# Gibbsite to Boehmite to Gamma

Gibbsite γ-Al(OH)$_3$ to Boehmite γ-Al(O)OH to γ-Al$_2$O$_3$ alumina (defect spinel) CCP
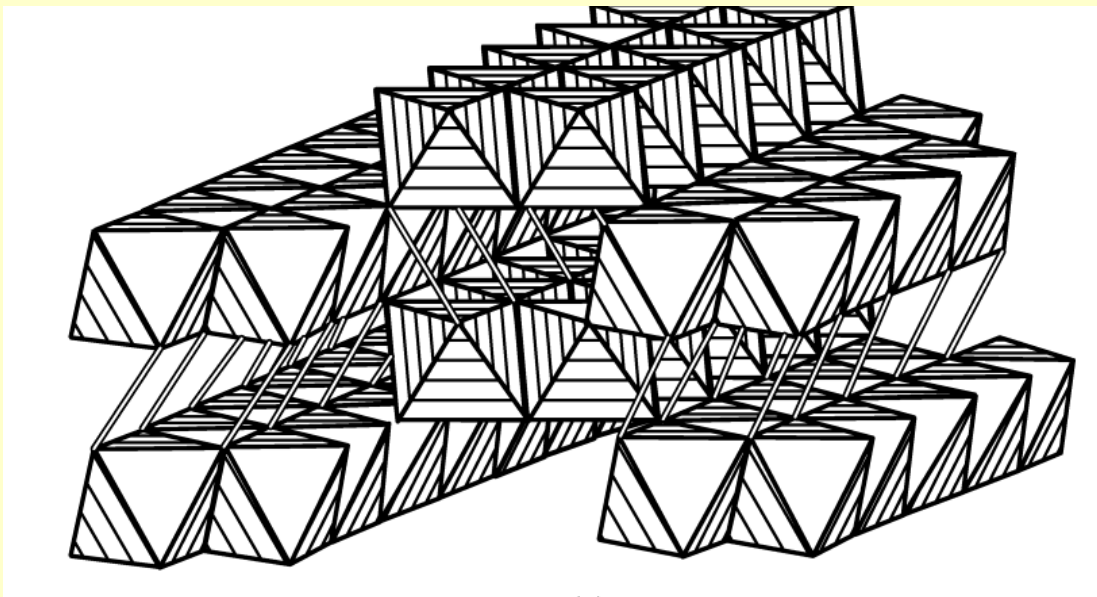
^{27}Al Solid-State NMR spectra

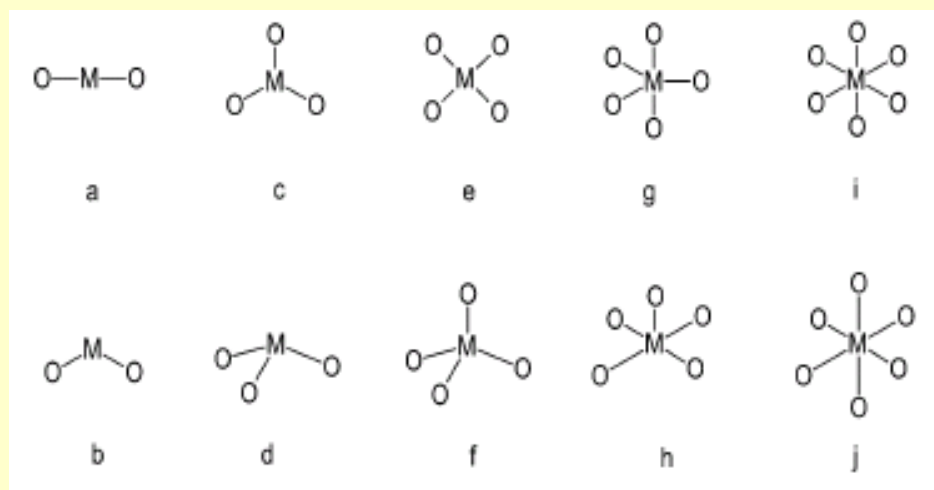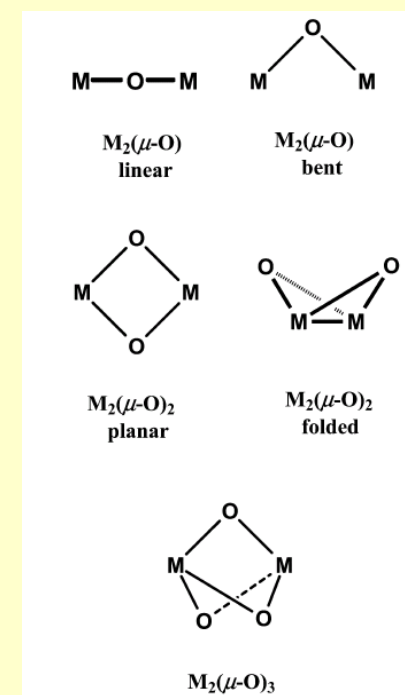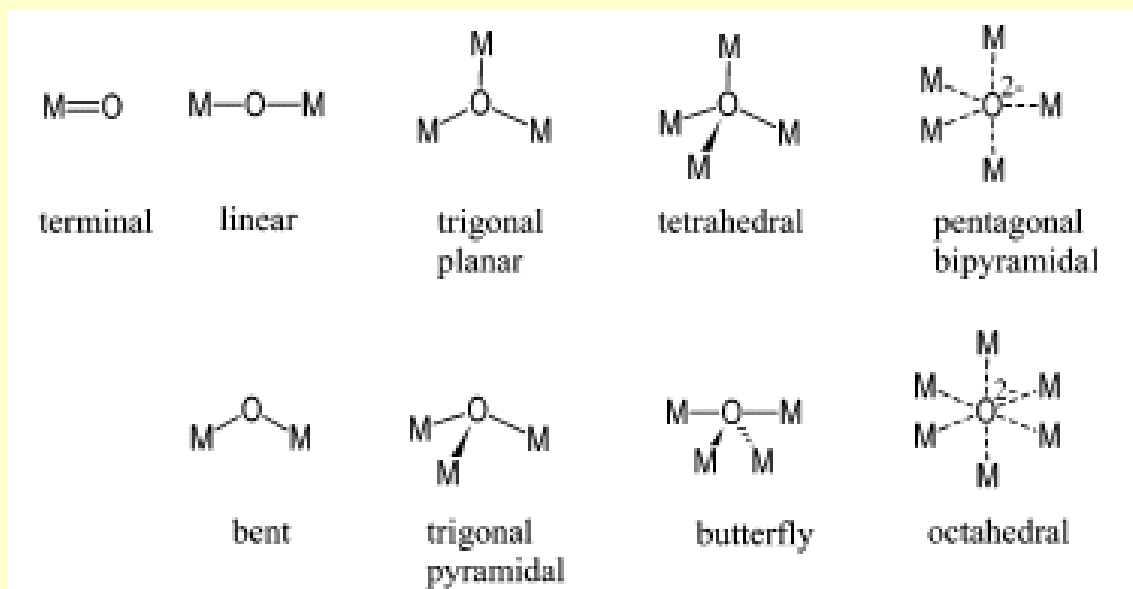# Bayerite to Diaspore to Corundum

Bayerite α-Al(OH)$_3$ to Diaspore α-Al(O)OH to α-Al$_2$O$_3$ Corundum HCP

Metal Coordination

Oxygen Coordination

Metal-Oxide Clusters

$M_3(\mu\text{-}O)_3$ $M_3(\mu\text{-}O)_6$ $M_4(\mu\text{-}O)_6$ $M_4(\mu\text{-}O)_5$

$M_4(\mu\text{-}O)_6$

$M_5(\mu\text{-}O)_5$ $M_5(\mu\text{-}O)_9$ $M_6(\mu\text{-}O)_{12}$

$M_6(\mu\text{-}O)_6$ $M_6(\mu\text{-}O)_{12}$ $M_8(\mu\text{-}O)_{16}$

Sol-Gel Methods

Metal-Oxide Clusters

$M_{12}O_{24}$

$M_4(\mu_3\text{-}O)_4$

$M_5(\mu_3\text{-}O)_6$

$M_6(\mu_3\text{-}O)_8$

$M_6(\mu_3\text{-}O)_6$