Sol-Gel Methods

Sol-gel process:

Hydrolysis

Condensation

Gelation

Ageing

Drying

Densification
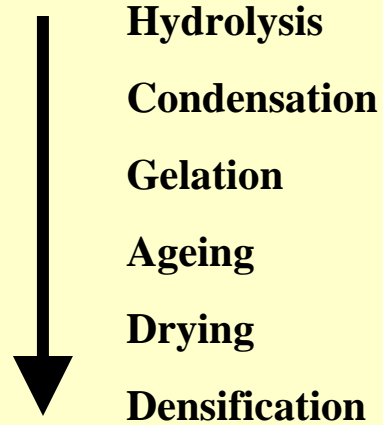
Powders: microcrystalline, nanocrystalline, amorphous

Monoliths, Coatings, Films, Fibers

Aerogels

Glasses, Ceramics, Hybrid materials

Sol-Gel Methods

Sol = a stable suspension of colloidal solid particles or polymers in a liquid

Gel = porous, three-dimensional, continuous solid network surrounding a continuous liquid phase
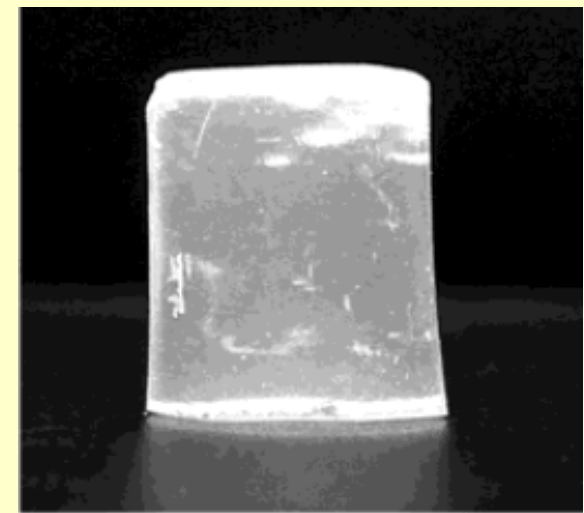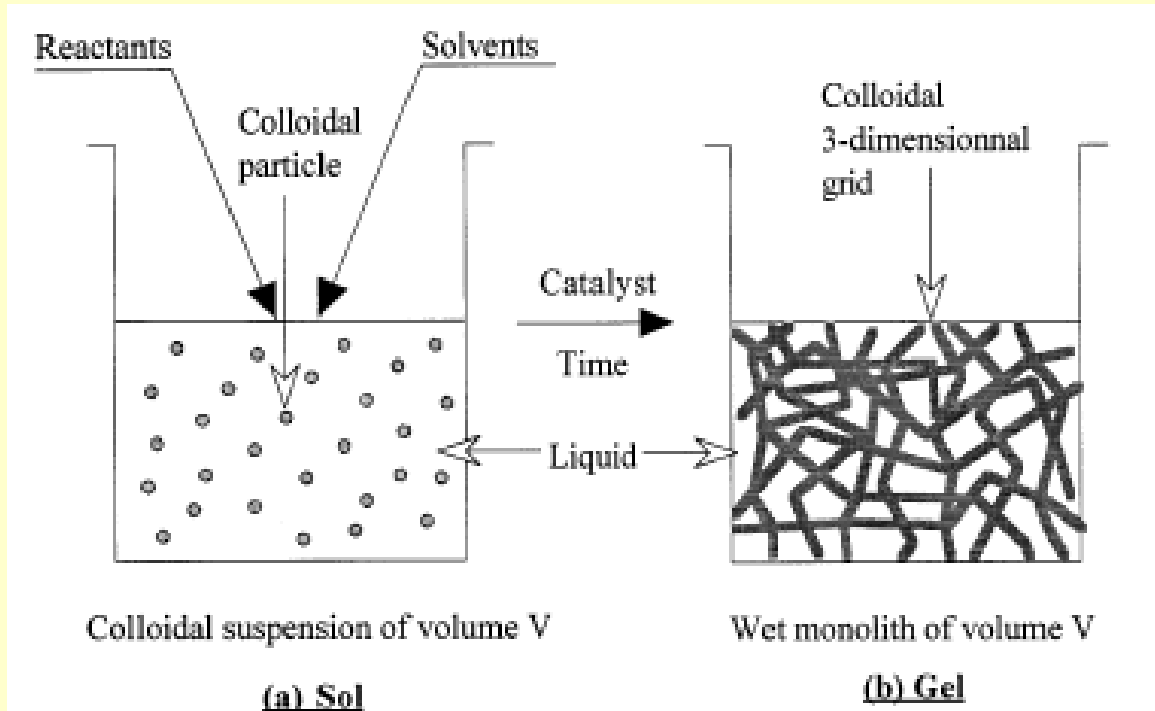
Colloidal (particulate) gels = agglomeration of dense colloidal particles

Polymeric gels = agglomeration of polymeric particles made from subcolloidal units

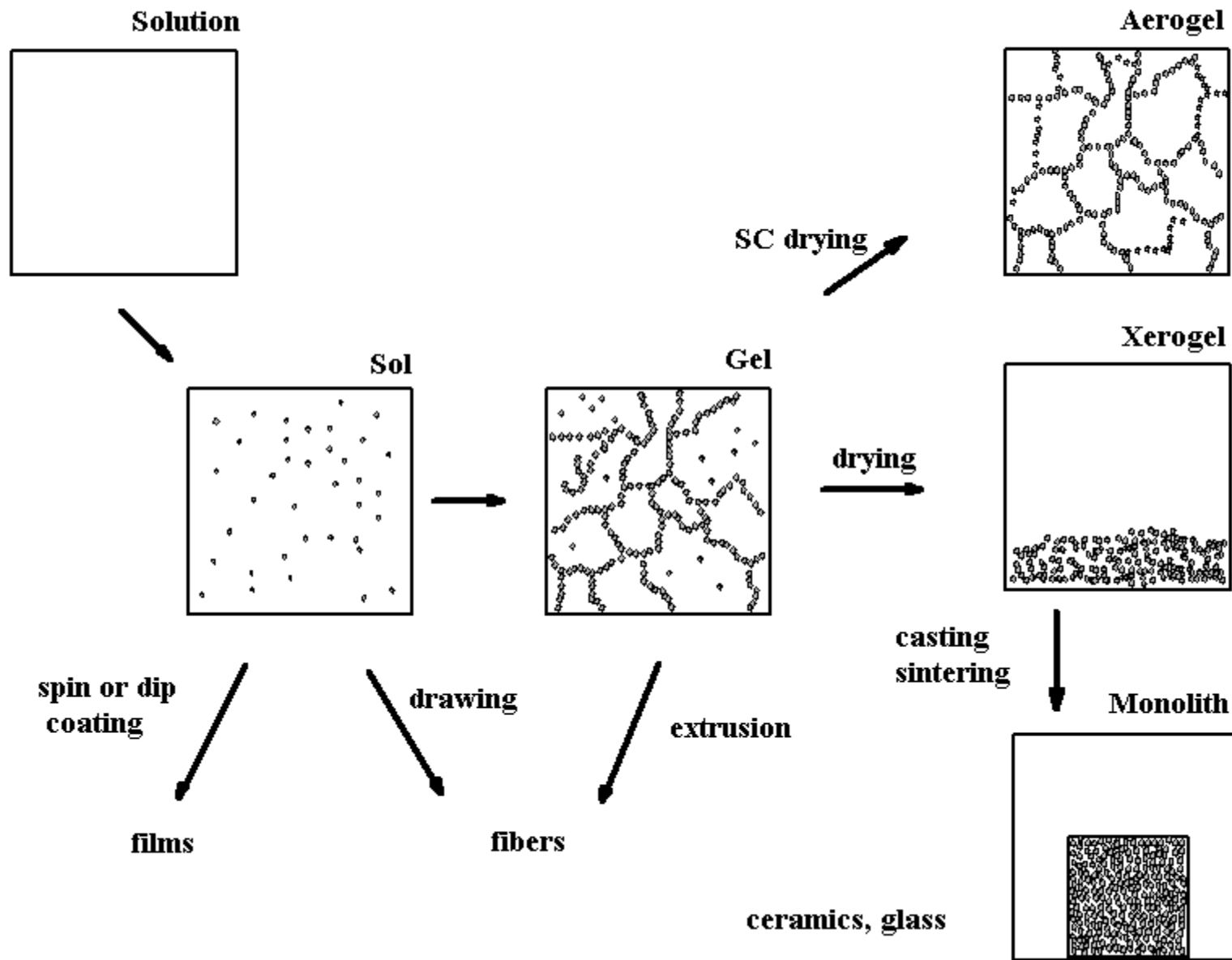Agglomeration = covalent bonds, hydrogen bonds, polymeric chain entanglement

Aggregation = van der Walls forces

Sol and Gel

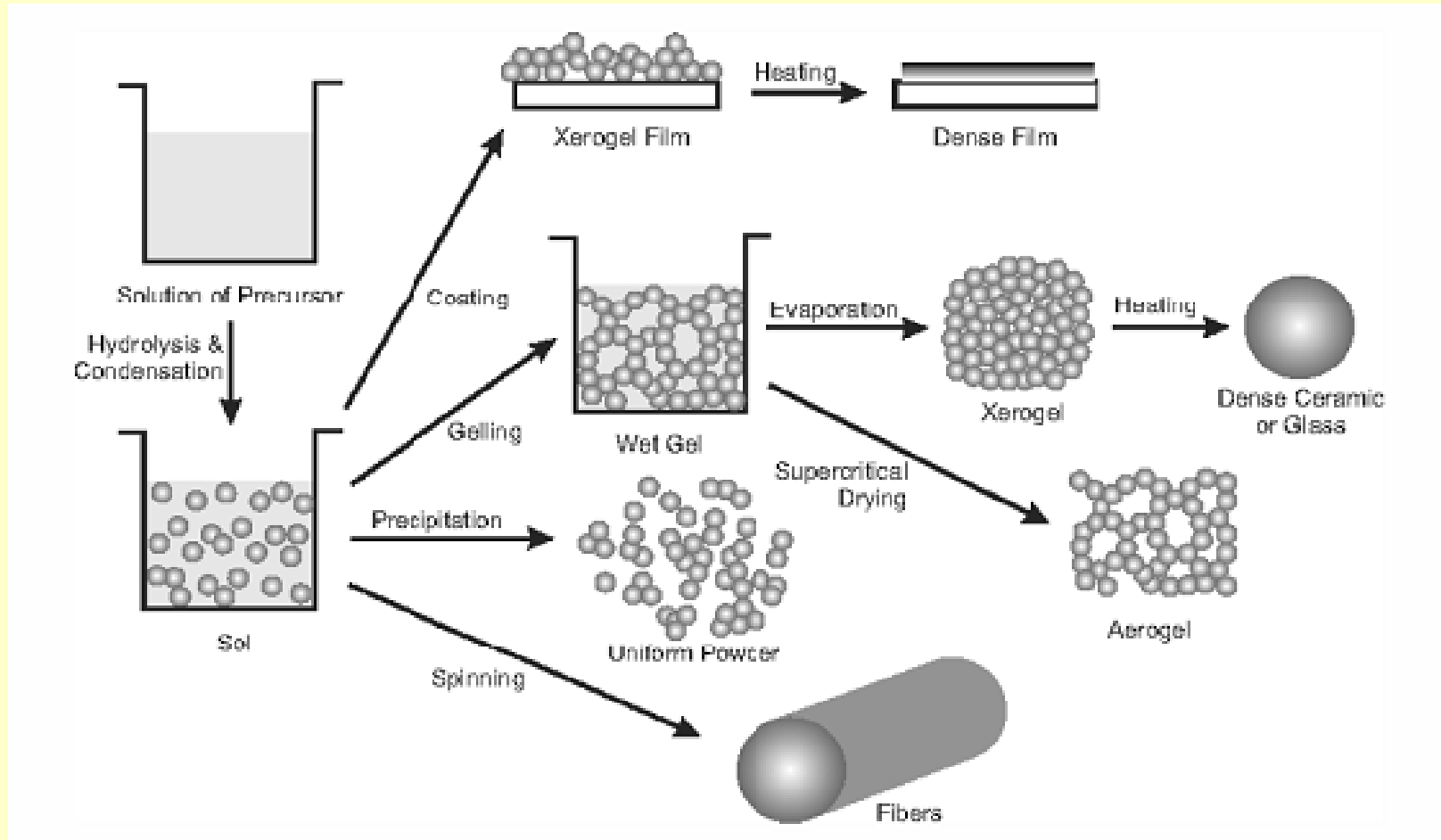Reactants   Solvents

Colloidal particle

Colloidal 3-dimensionnal grid

Catalyst
Time

Liquid

Colloidal suspension of volume V

Wet monolith of volume V

(a) Sol

(b) Gel

Sol-Gel Methods

Sol-Gel Process

Solution

Aerogel

SC drying

Sol

Gel

drying

Xerogel

spin or dip
coating

drawing

extrusion

casting
sintering

films

fibers

Monolith

ceramics, glass

Sol-Gel Methods

Sol-Gel Chemistry

Aqueous

•**Colloid Route – inorganic salts, 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**
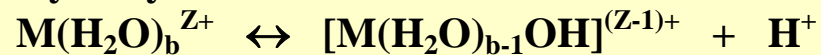
Nonaqueous

•**Hydroxylation**

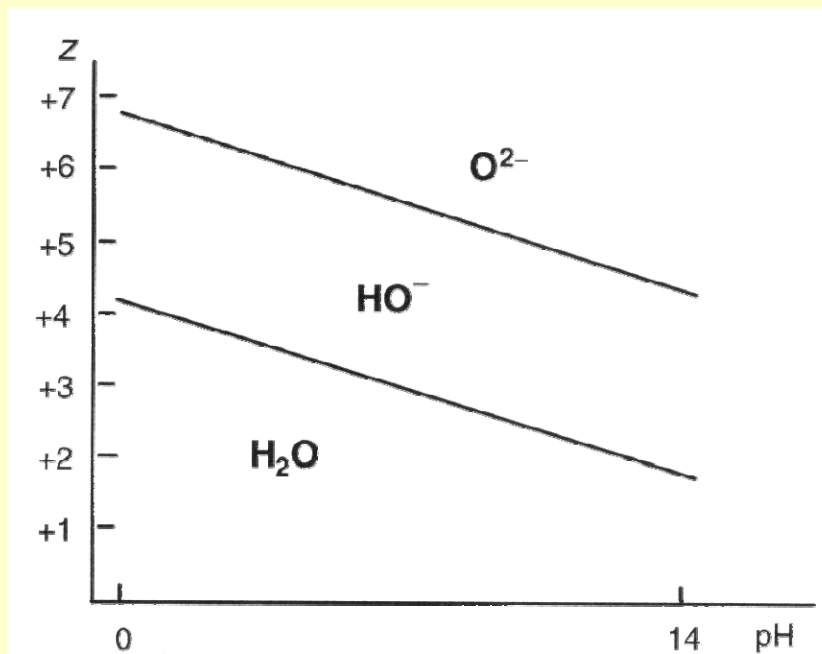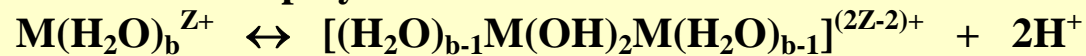•**Heterofunctional Condensations**

Colloid Route

🖤✳ **Colloid Route**
metal salts in aqueous solution, pH and temperature control
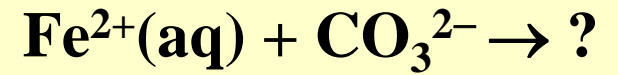
Hydrolysis
$$M(H_2O)_b^{Z+} \leftrightarrow [M(H_2O)_{b-1}OH]^{(Z-1)+} + H^+$$

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

Colloid Route

$$\left[\begin{array}{c} OH_2 \\ H_2O-\overset{|}{\underset{OH_2}{Al}}\overset{\cdots OH_2}{\underset{}{\overset{}{\longrightarrow}}} OH_2 \end{array}\right]^{3\oplus} \quad\overset{B}{\underset{HB^+}{\rightleftarrows}}\quad \left[\begin{array}{c} OH_2 \\ H_2O-\overset{|}{\underset{OH_2}{Al}}\overset{\cdots OH_2}{\underset{}{\overset{}{\longrightarrow}}} OH \end{array}\right]^{2\oplus}$$

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

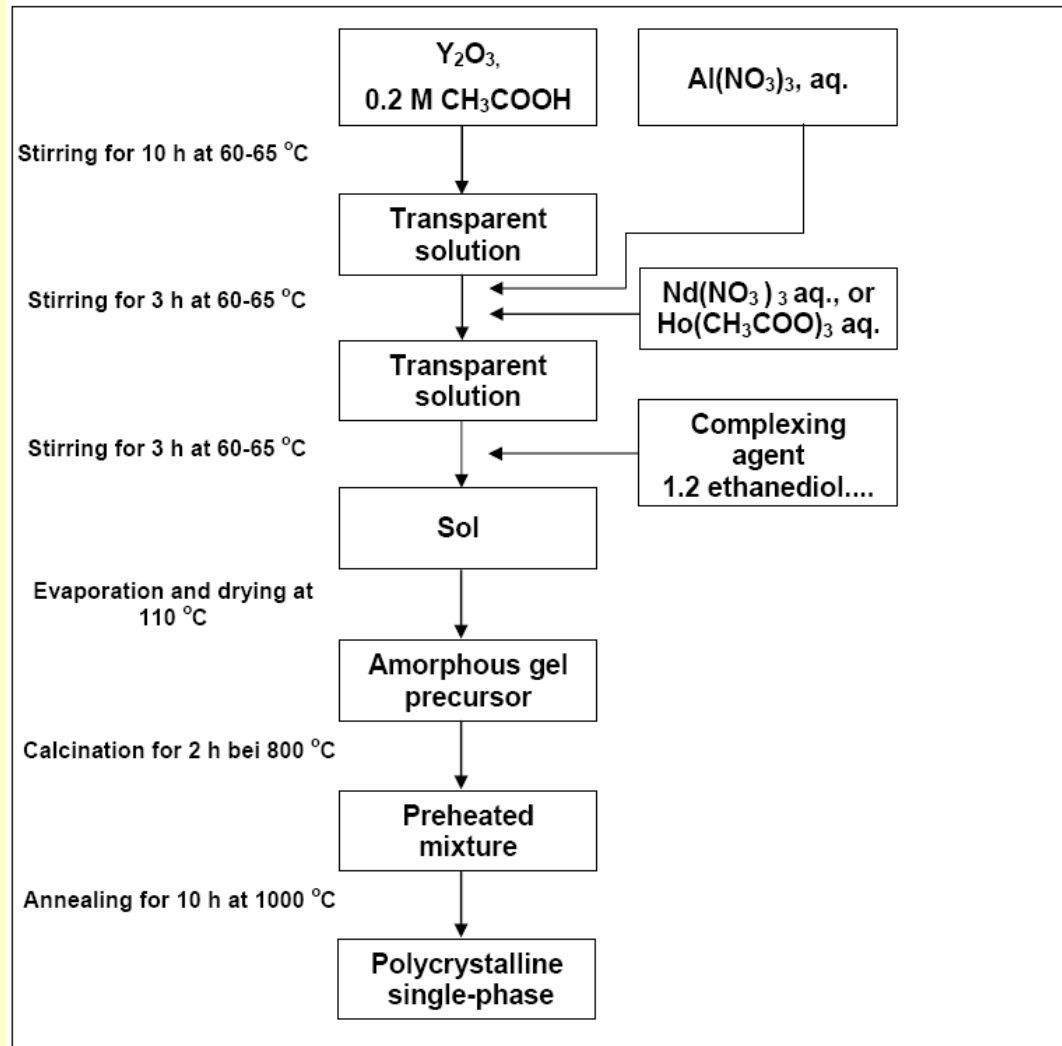$$Fe^{2+}(aq) + CO_3^{2-} \rightarrow \ ?$$

Colloid Route $Fe^{3+}(aq) + CO_3^{2-} \rightarrow \ ?$
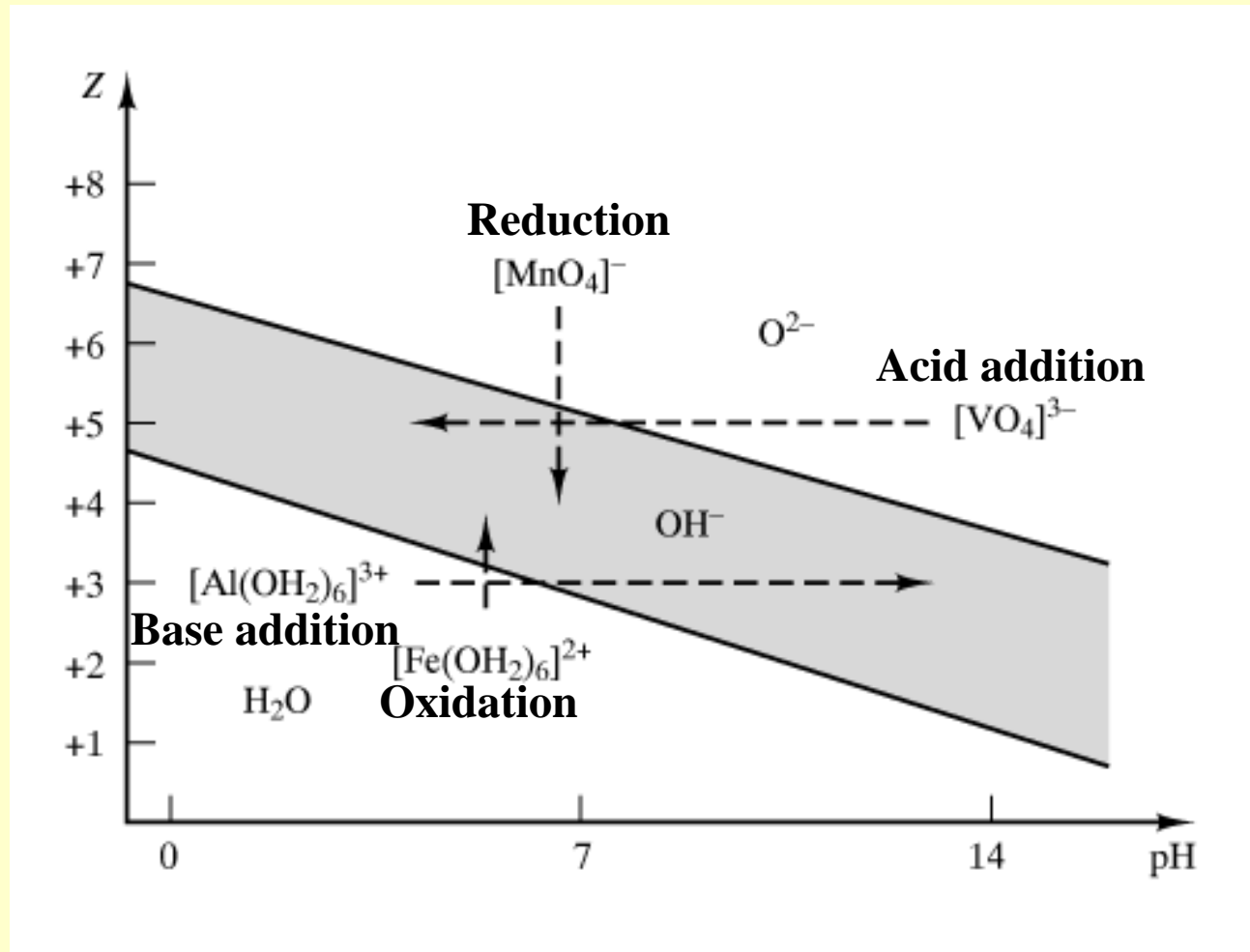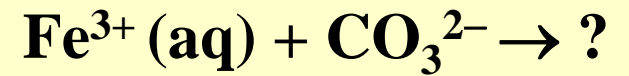
Pechini Sol-Gel Route

Major components

Dopants

Gelling agent

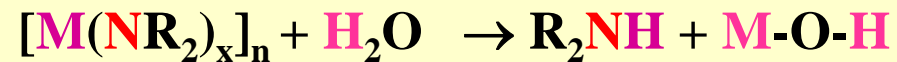Removal of solvents

Removal of organics

Doped YAG product

Metal-Oragnic (Alkoxide) Route

Hydrolysis

Metal Alkoxides

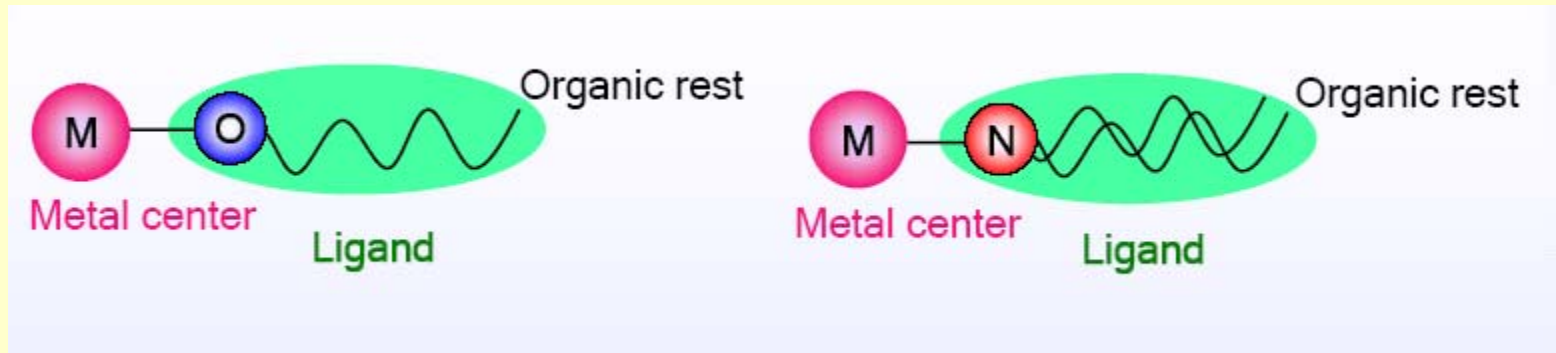$$[M(OR)_x]_n + H_2O \rightarrow ROH + M\text{-}O\text{-}H$$

Metal Amides

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

Condensation

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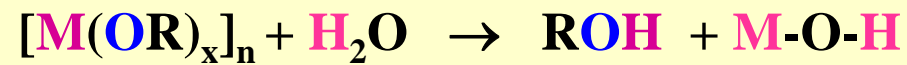
OXIDE

Metal Alkoxides and Amides

Metal Alkoxides $[\mathbf{M(OR)_x}]_n$
formed by the replacement of the hydroxylic hydrogen of an alcohol
(ROH) through a metal atom

Metal Amides $[\mathbf{M(NR_2)_x}]_n$
formed by the replacement of one of the hydrogen atoms of an amine
(R_2NH) through a metal atom

Metal Alkoxides and Amides

Homometallic Alkoxides

General Formula: $[\mathbf{M}(\mathbf{OR})_x]_n$

Heterometallic Alkoxides

General Formula: $\mathbf{M}_a\mathbf{M'}_b(\mathbf{OR})_x]_n$

Metal Amides

General Formula: $[\mathbf{M}(\mathbf{NR}_2)_x]_n$

M = Metal or metalloid of valency x
O = Oxygen Atom
N = Nitrogen atom
R = simple alkyl, substituted alkyl or aryl group
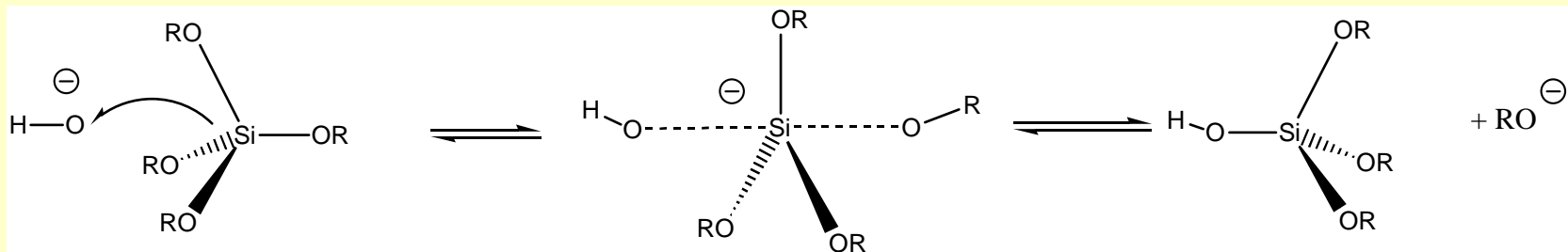**n** = degree of molecular association

Sol-gel in Silica Systems

Silicate (aq)

Hydrolysis

HO—Si

Condensation

Si—O$^{\ominus}$

H$^+$

—Si—OH

-H$_2$O

—Si—O—Si—

H$_2$O
-ROH

-ROH

Si—OR

RO—Si

Alkoxide (nonaq)

Metal-Oragnic Route
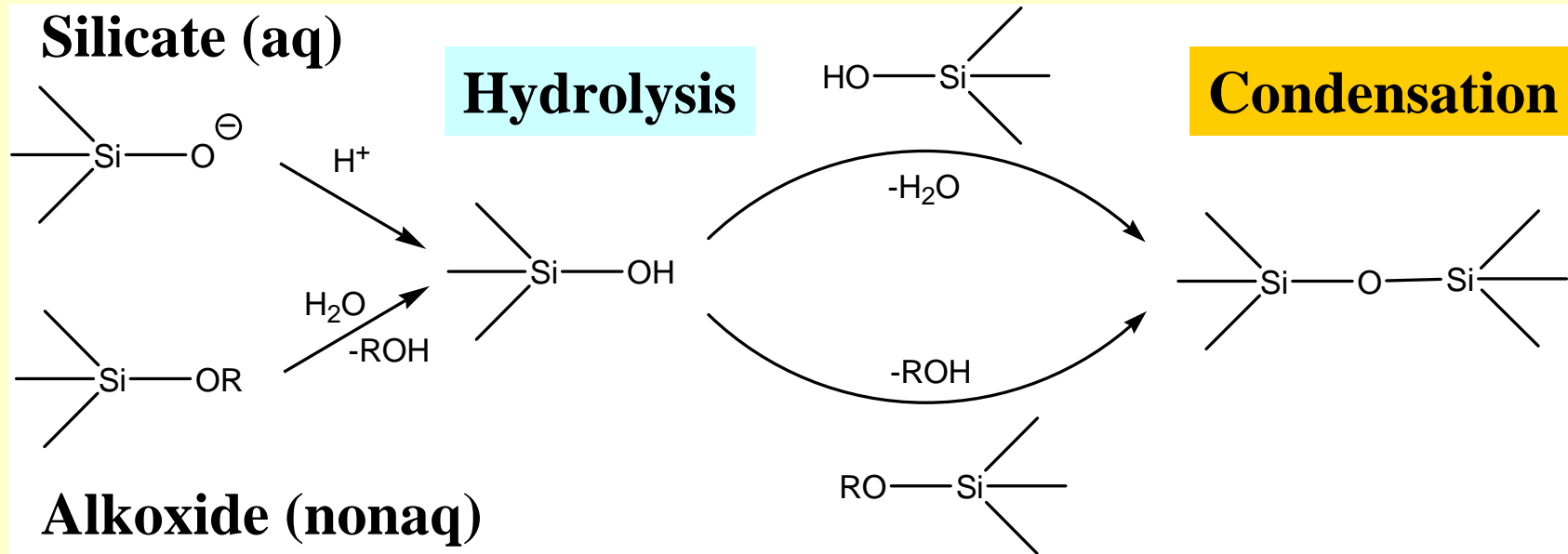
💣* **Metal-organic Route**
metal alkoxide in alcoholic solution, water addition

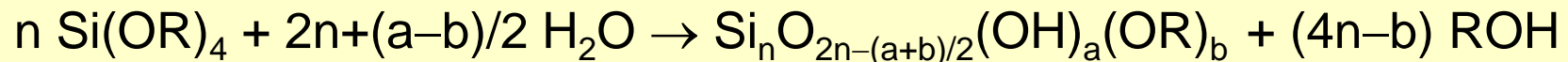### Acid catalysed hydrolysis
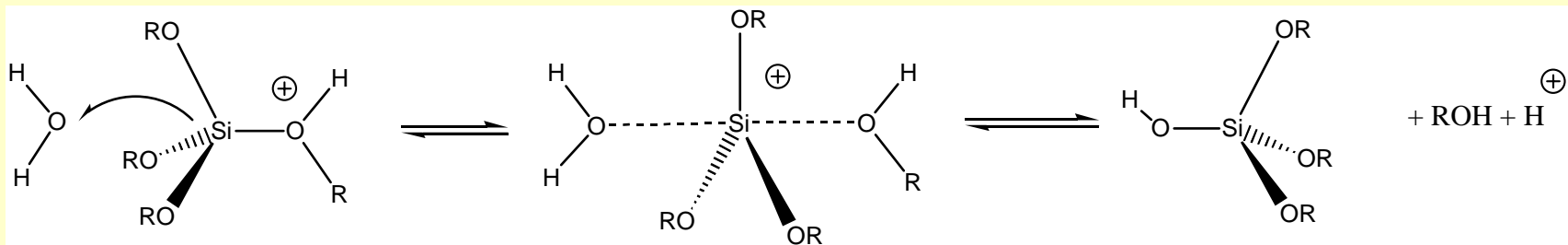
Base catalysed hydrolysis

Metal-Organic Route
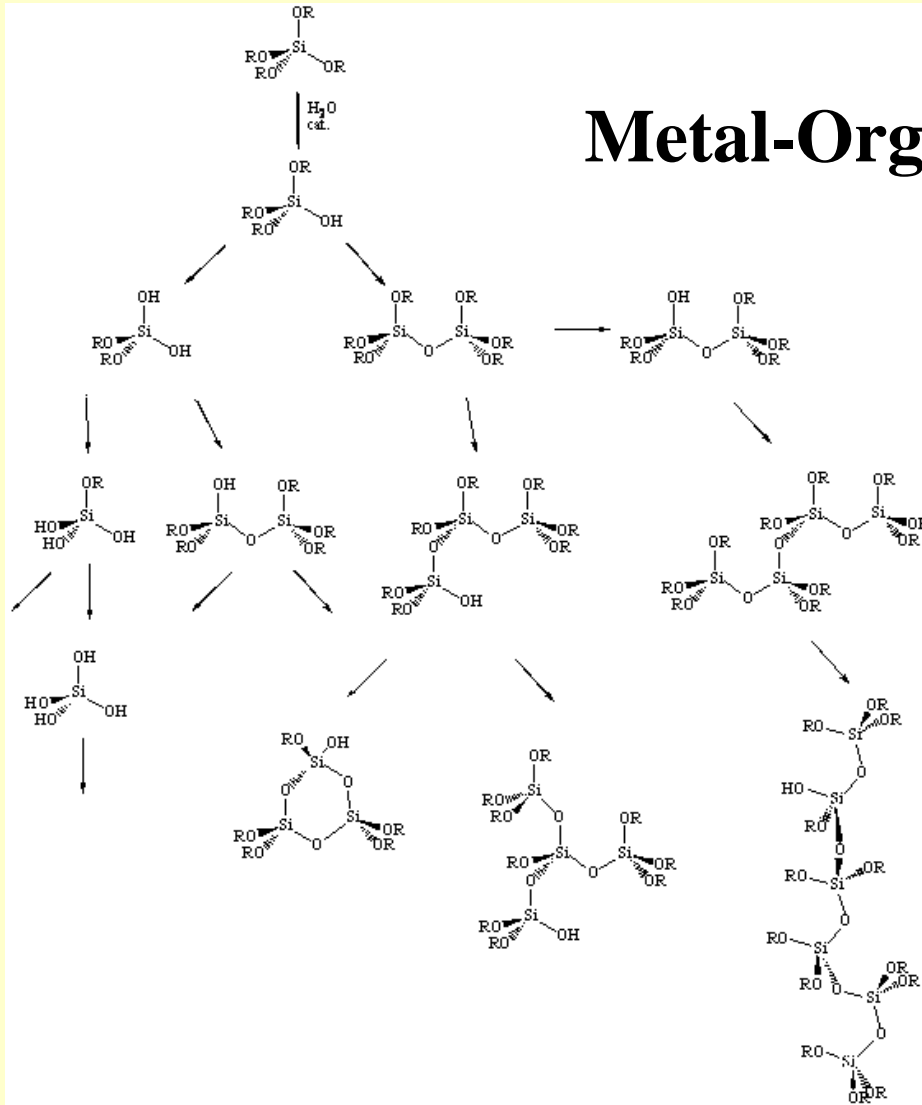
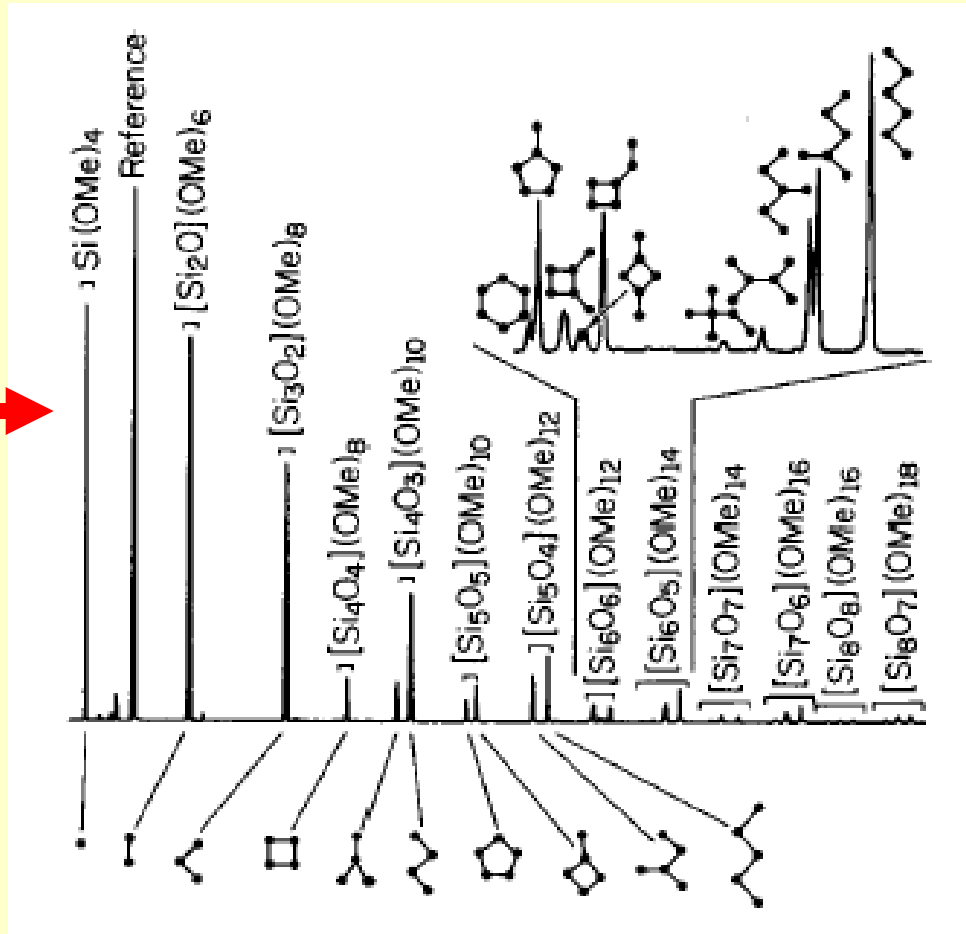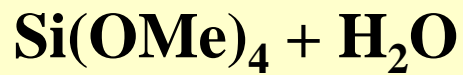**Oligomers formed
by hydrolysis-condensation
process**
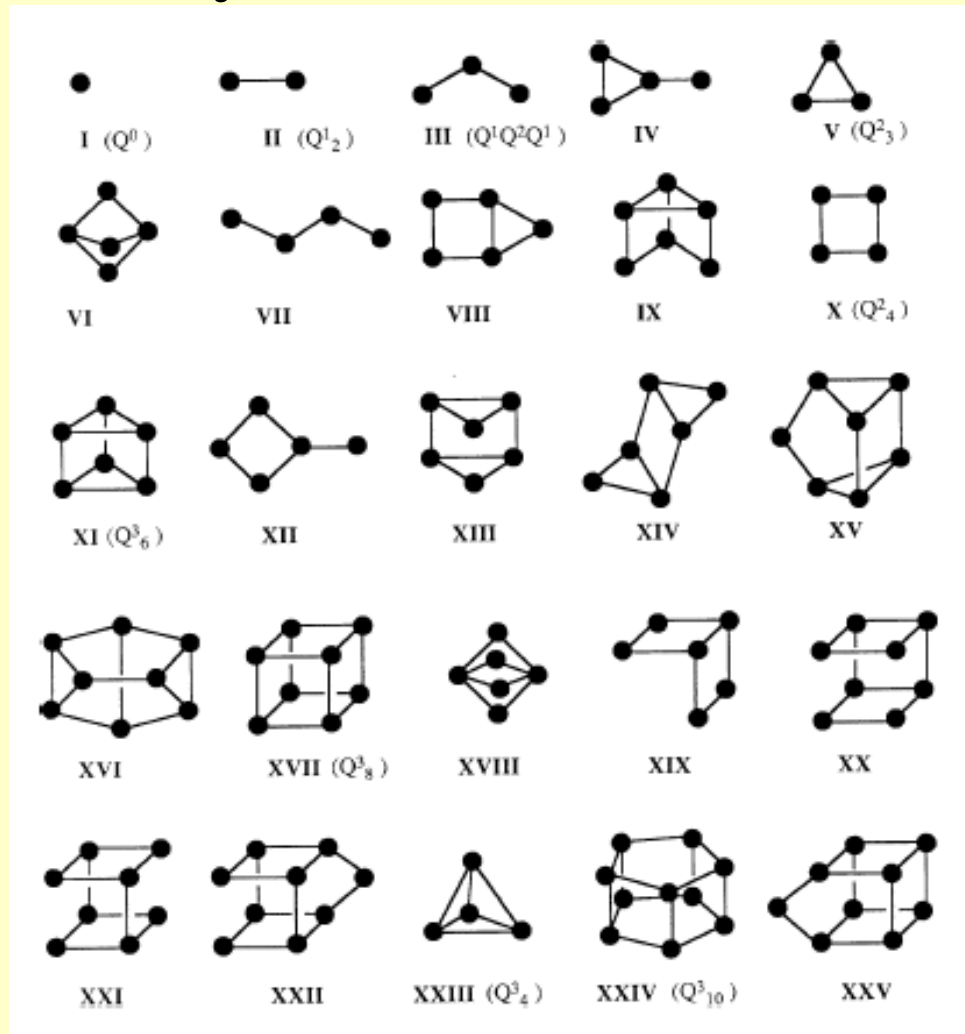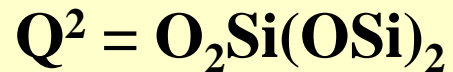
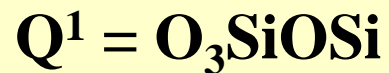**-linear
-branched
-cyclic
-polyhedral**

Never goes to pure SiO$_2$

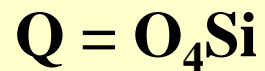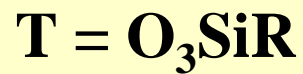$$n\ Si(OR)_4 + 2n+(a-b)/2\ H_2O \rightarrow Si_nO_{2n-(a+b)/2}(OH)_a(OR)_b + (4n-b)\ ROH$$

GC of TMOS hydrolysis products

$Si(OMe)_4 + H_2O$ →
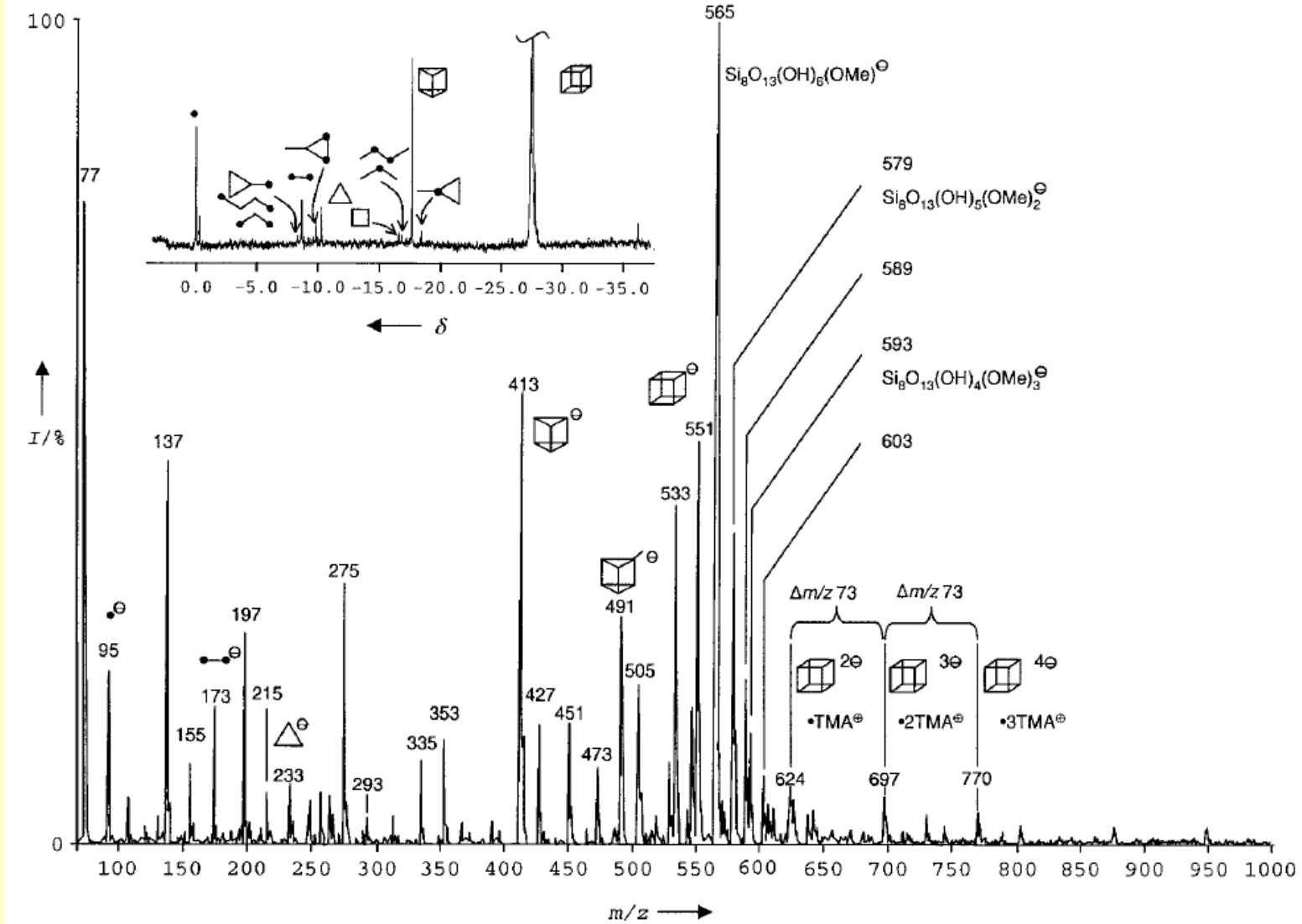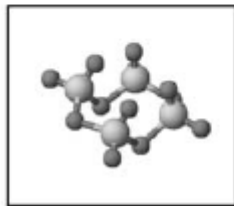
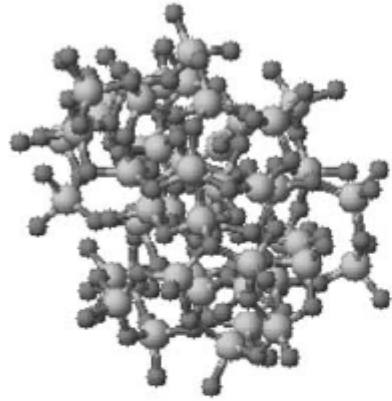**Neg. ion ESI-MS and ^{29}Si NMR of silicate aq with TMA ions**
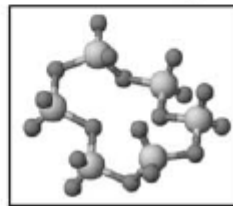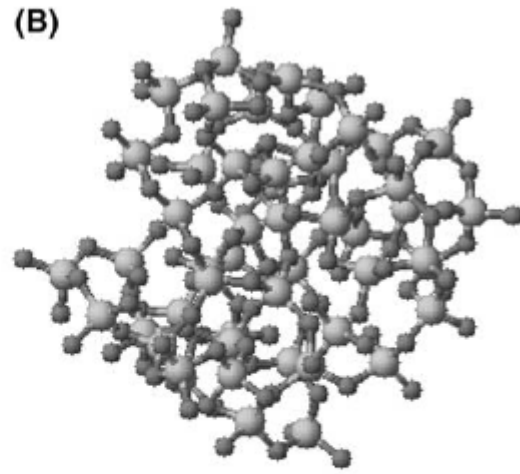
Silicate anions in aqueous alkaline media
(detected by ^{29}Si-NMR)

$M = OSiR_3$

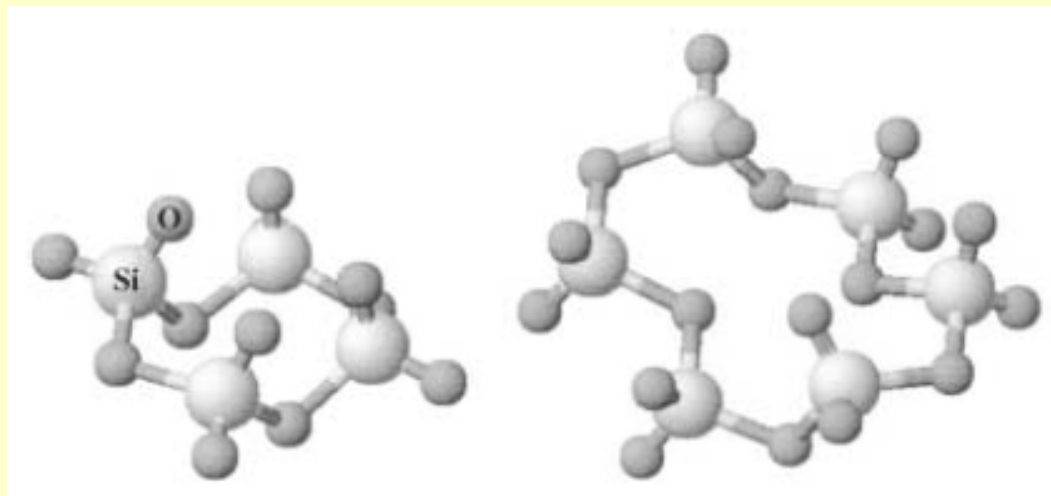$D = O_2SiR_2$

$T = O_3SiR$

$Q = O_4Si$

$Q^0 = O_4Si$
$Q^1 = O_3SiOSi$
$Q^2 = O_2Si(OSi)_2$
$Q^3 = OSi(OSi)_3$
$Q^4 = Si(OSi)_4$

Sol-Gel Methods

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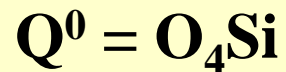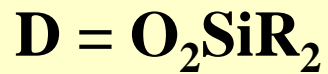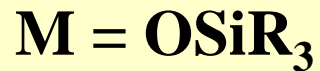
$Si_{50}O_{75}(OH)_{50}$ three-dimensional clusters formed by
(A) four-rings
(B) six-rings

20
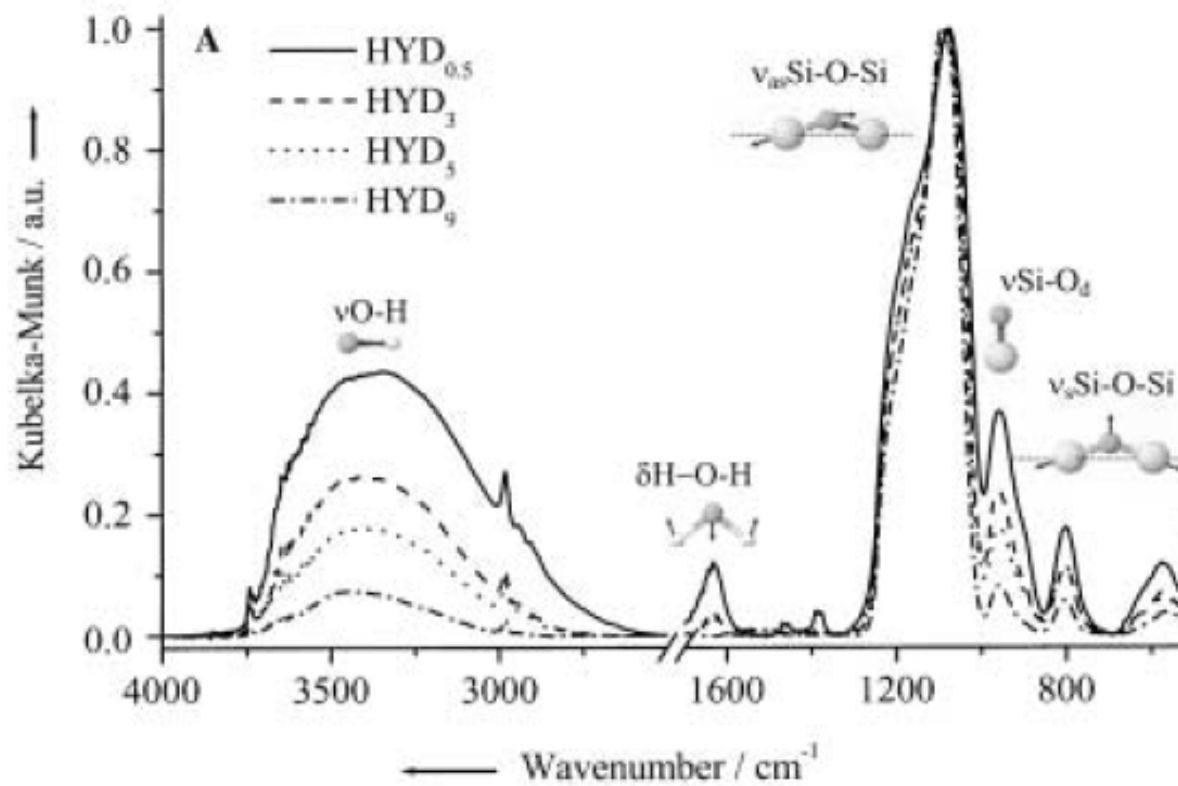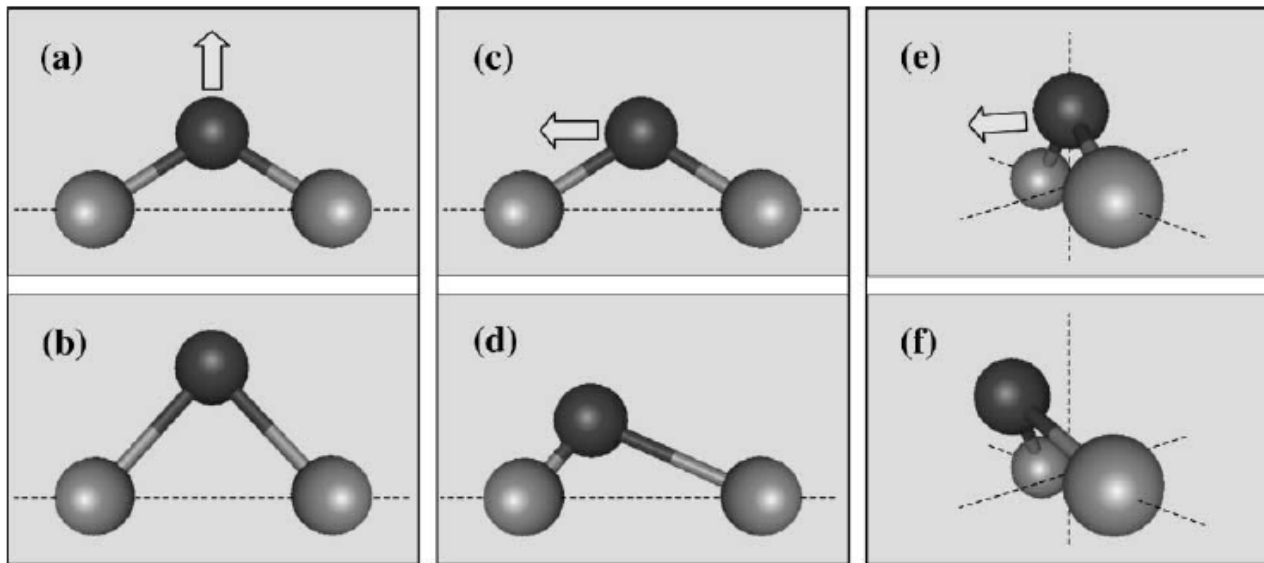
The Electrical Double Layer

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
Potential and EOF velocity profiles are
shown at right

The shear plane is where hydrodynamic
motion becomes possible;
z is the potential at this plane
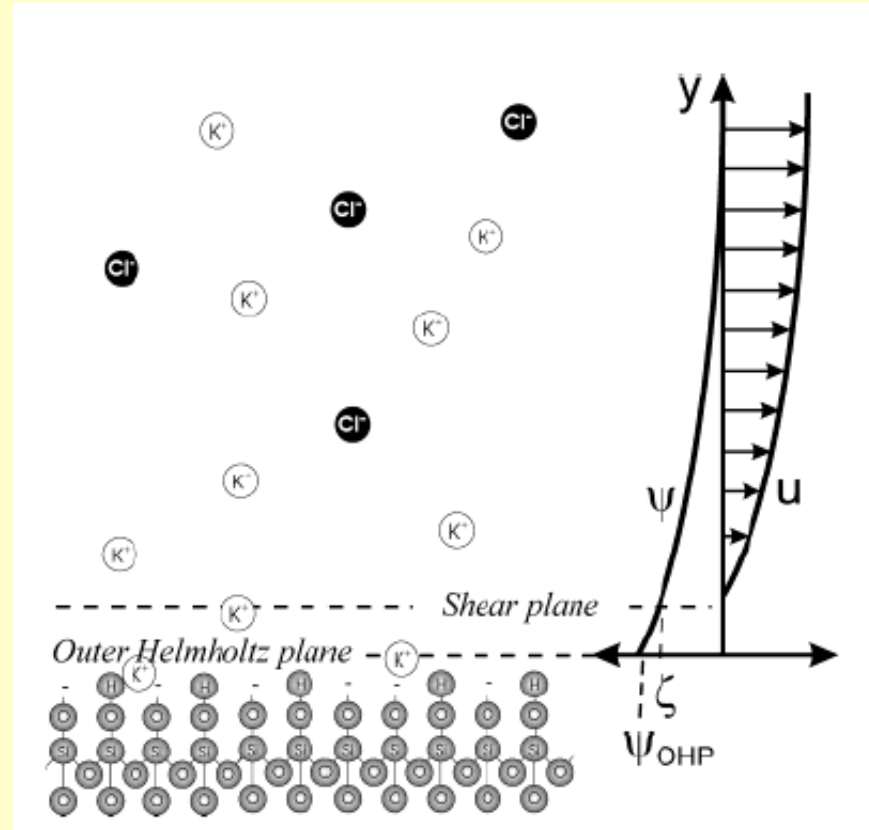
The Electrical Double Layer
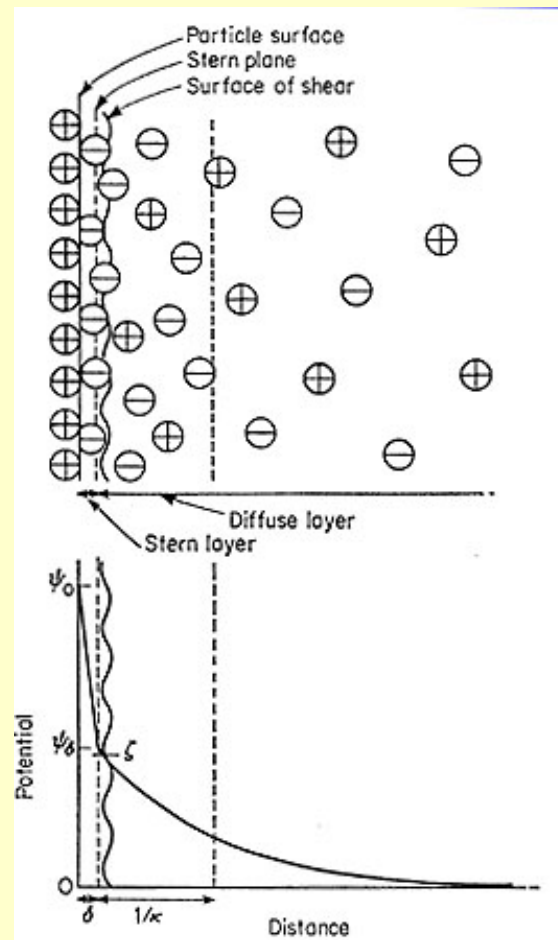
Sol-Gel Methods

Isoelectronic point: zero net charge

pH = 2.2 for silica
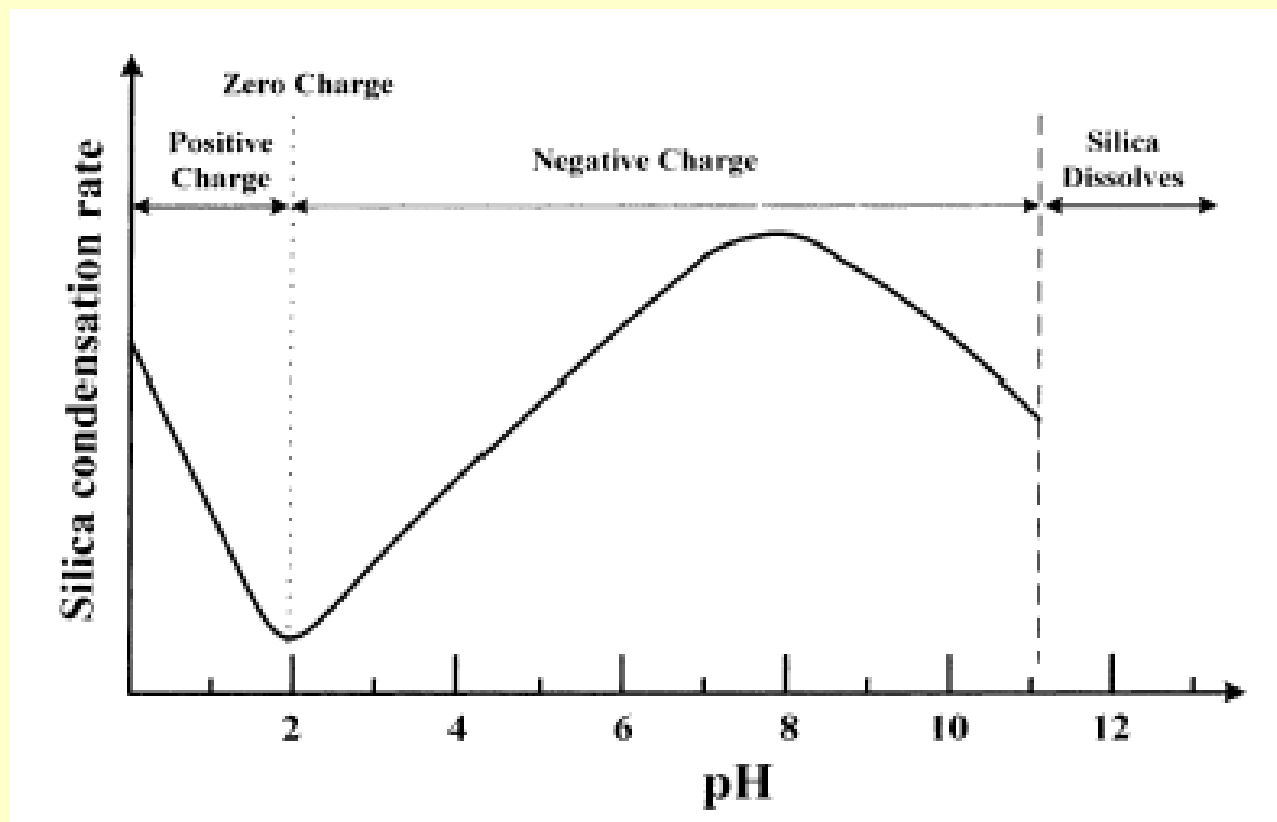
Sol-Gel Methods

Longest TEOS gel time = the slowest reaction

Effects on hydrolysis rate:

pH

substituents

solvent

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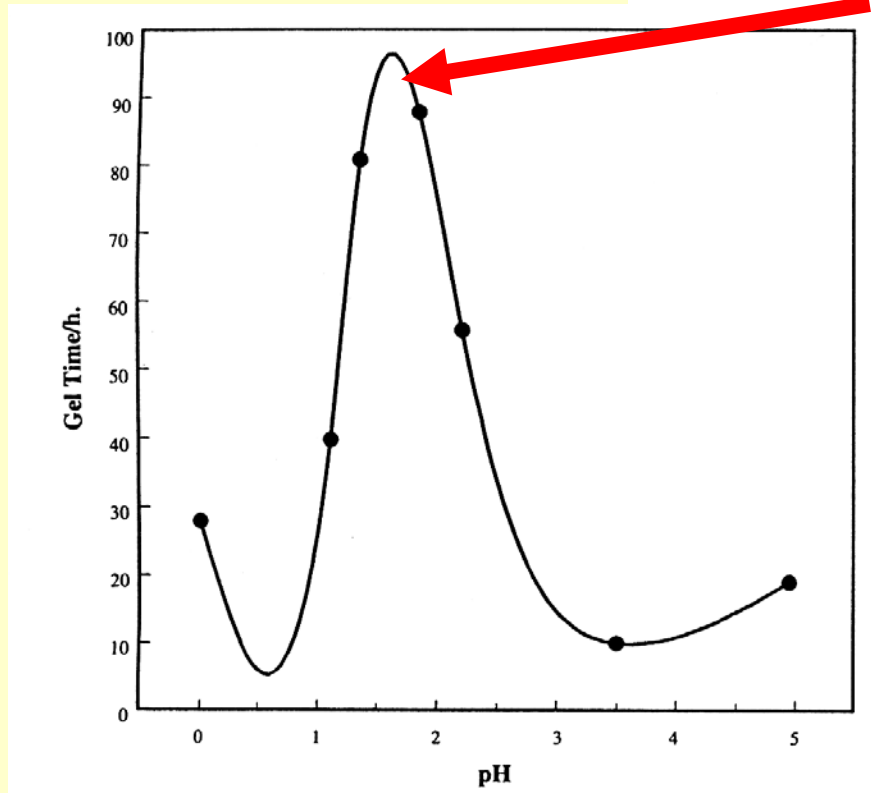
Rate of H$^+$ catalyzed TEOS hydrolysis (gel time) as a function of pH

Sol-Gel Methods

Precursor substituent effects

Steric effects**: branching and increasing of the chain length LOWERS the hydrolysis rate**

$Si(OMe)_4 > Si(OEt)_4 > Si(O^nPr)_4 > Si(O^iPr)_4 > Si(O^nBu)_4 > Si(OHex)_4$
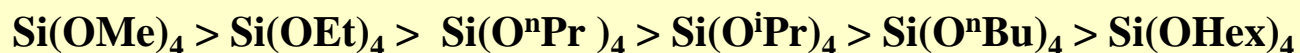
Inductive effects**: electronic stabilization/destabilization of the transition state (TS).**

Electron density at Si decreases:

$R \rightarrow Si > RO \rightarrow Si > HO-Si > SiO \leftarrow Si$
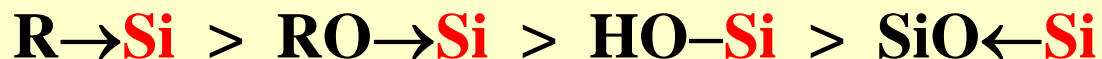
Hydrolysis

Acid catalysed hydrolysis

**Transition
State**
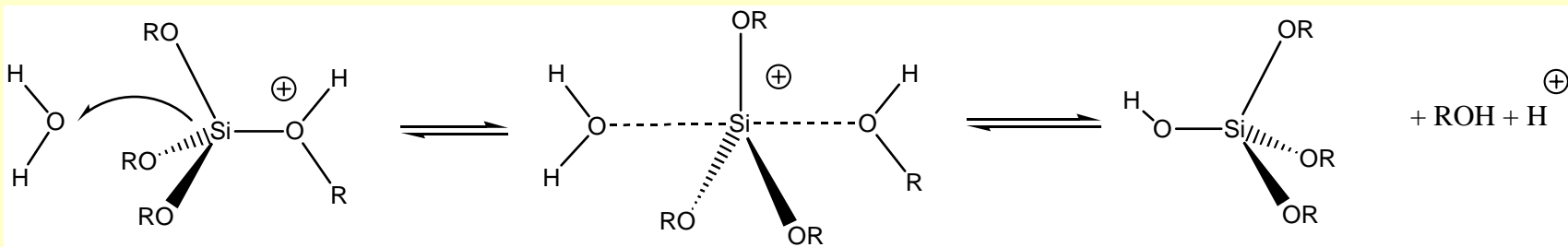
Acidic conditions:

Hydrolysis reaction rate decreases as more alkoxy groups are hydrolyzed

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

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

Linear polymer products are favored, fibers

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

Hydrolysis

Base catalysed hydrolysis

Transition State
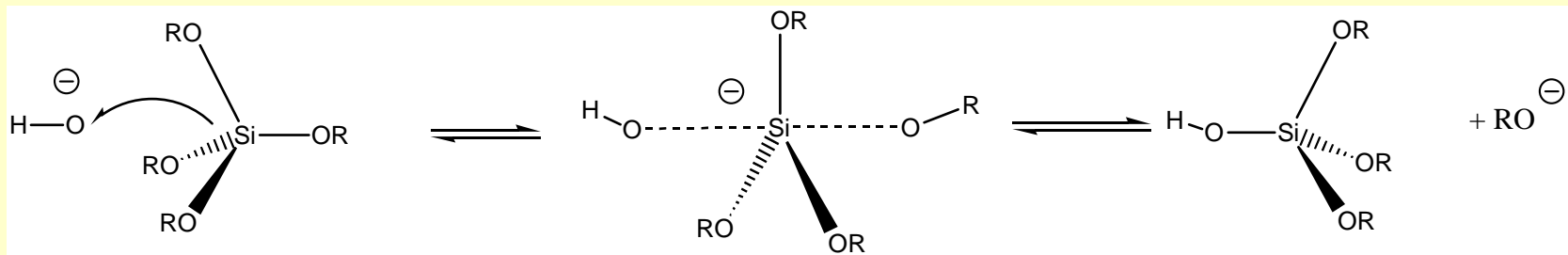
Basic conditions:

Hydrolysis reaction rate increases as more alkoxy groups are hydrolyzed

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

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^-

HMPA
N-methylimidazol
N,N-dimethylaminopyridin

Sol-Gel Methods

Water:alkoxide ratio (R_w) effect

stoichiometric ratio for complete hydrolysis = 4

$$Si(OR)_4 + 4\ H_2O \longrightarrow Si(OH)_4 + 4\ ROH$$
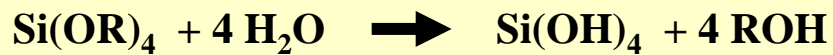
additional water from condensation

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

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

Large amount of water = slow hydrolysis due to the reactant dilution
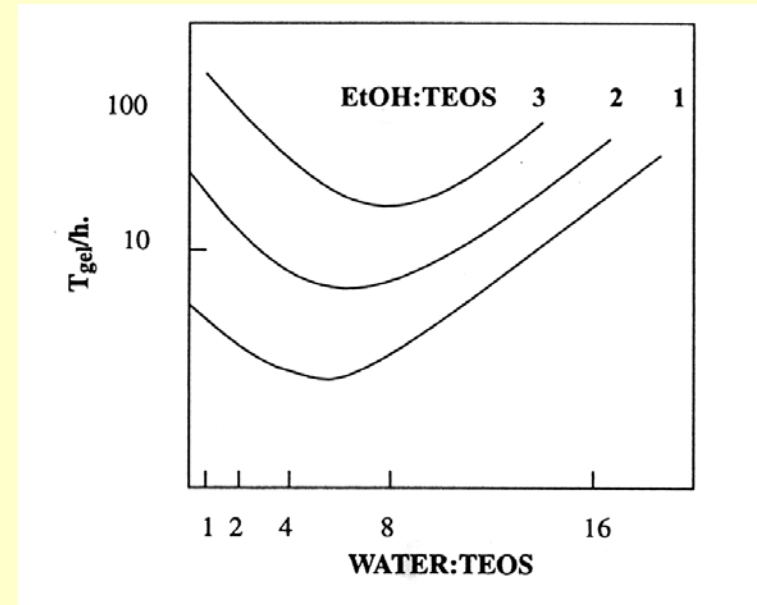
Sol-Gel Methods

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
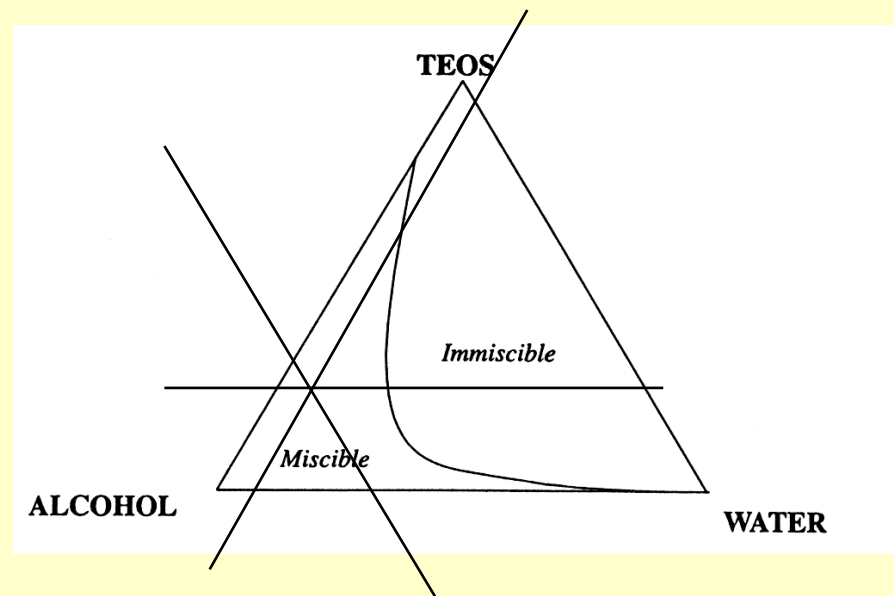**fast protonation, slow condensation**

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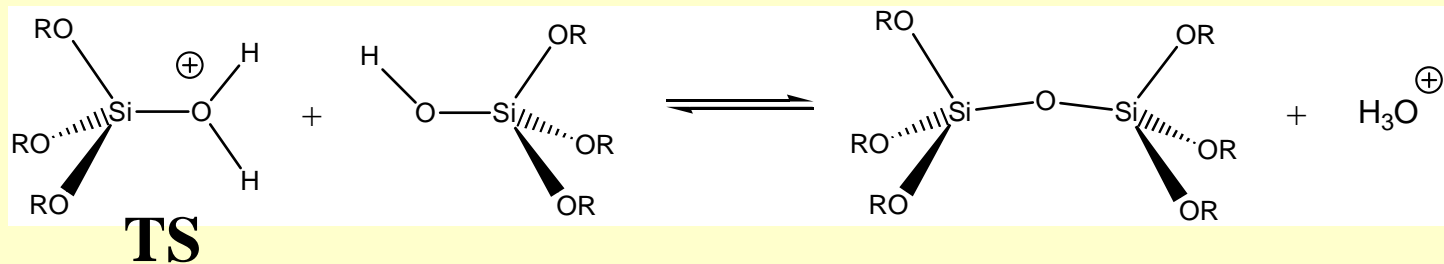
Positively charged transition state, fastest condensation for
$(RO)_3SiOH > (RO)_2Si(OH)_2 > ROSi(OH)_3 > Si(OH)_4$

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
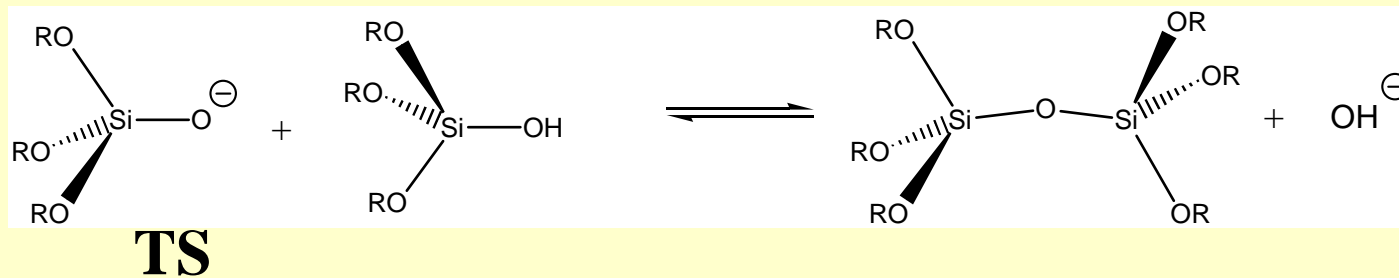
Condensation

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

cluster–cluster
RLCA

condensation

$v_{rel.}$

hydrolysis

basic

pH
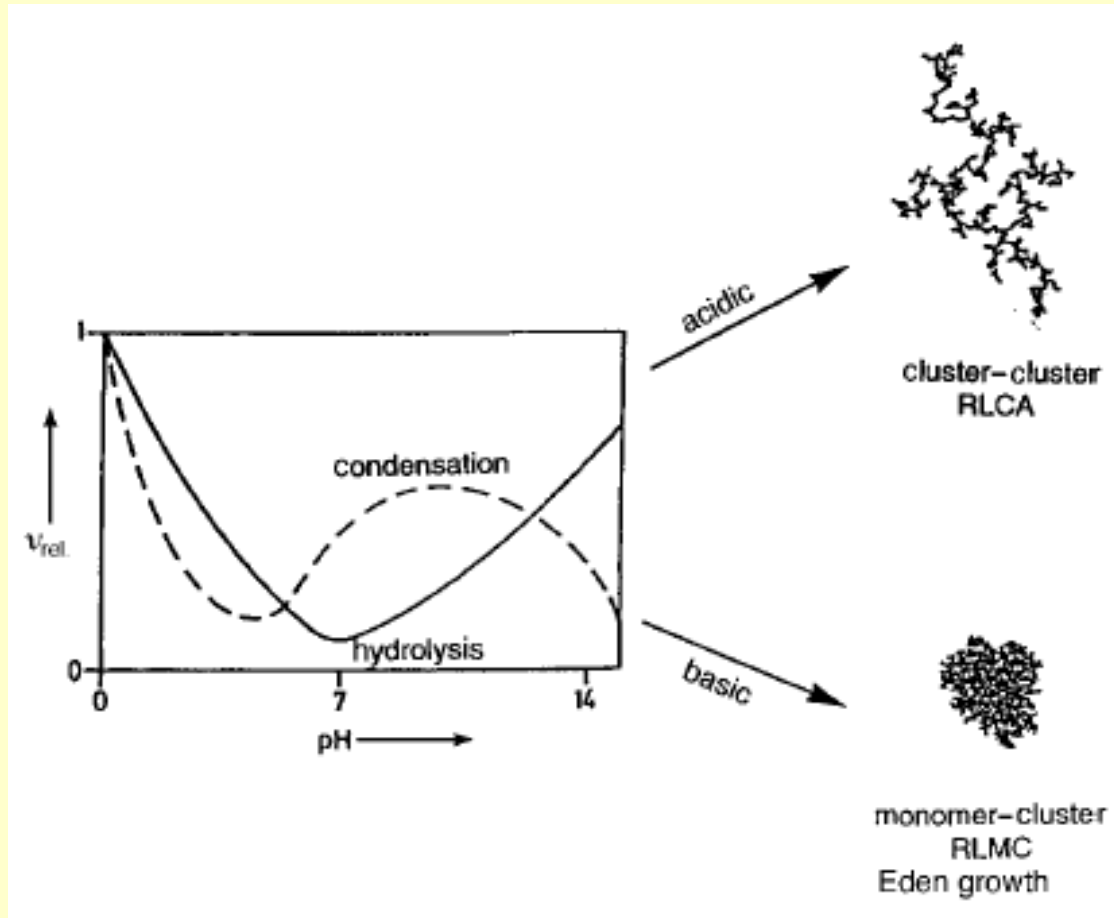
Base catalysed

monomer–cluster
RLMC
Eden growth

**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
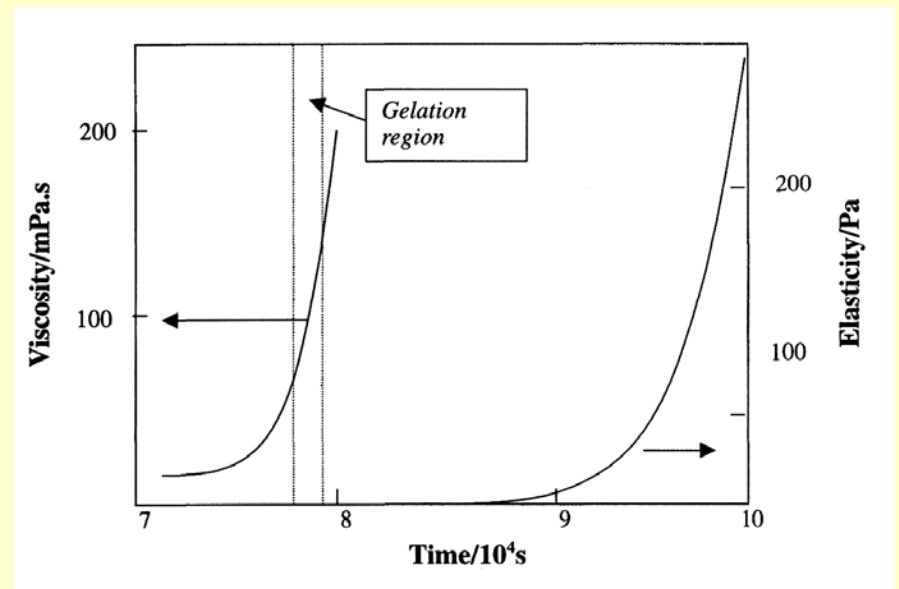
Gelation

Gelation

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

Sol-Gel Methods

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

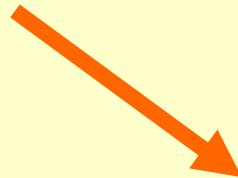**4. The second falling -rate period**
liquid film on the walls is broken, further liquid transport by evaporation

Drying 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

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
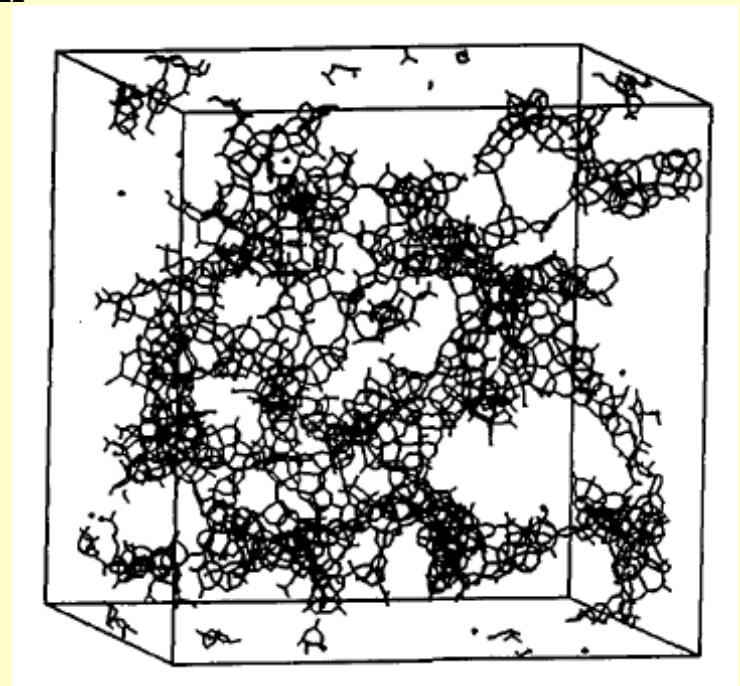
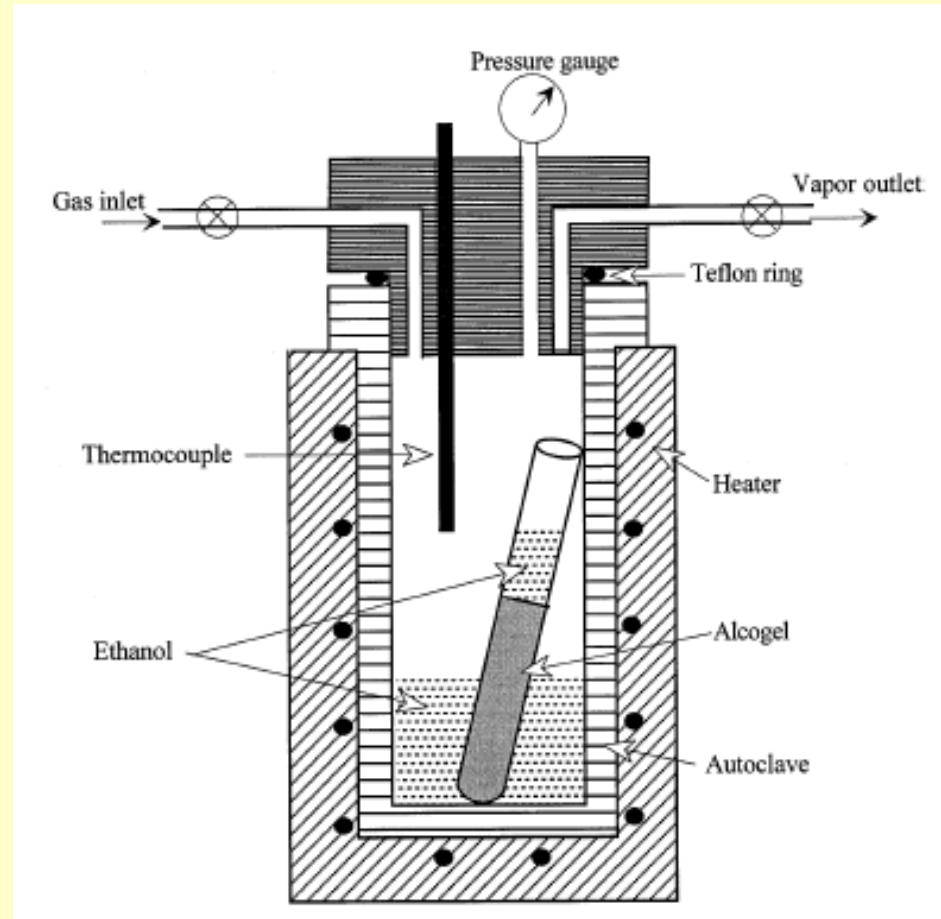# Aerogels - Supercritical Drying

Silica aerogel

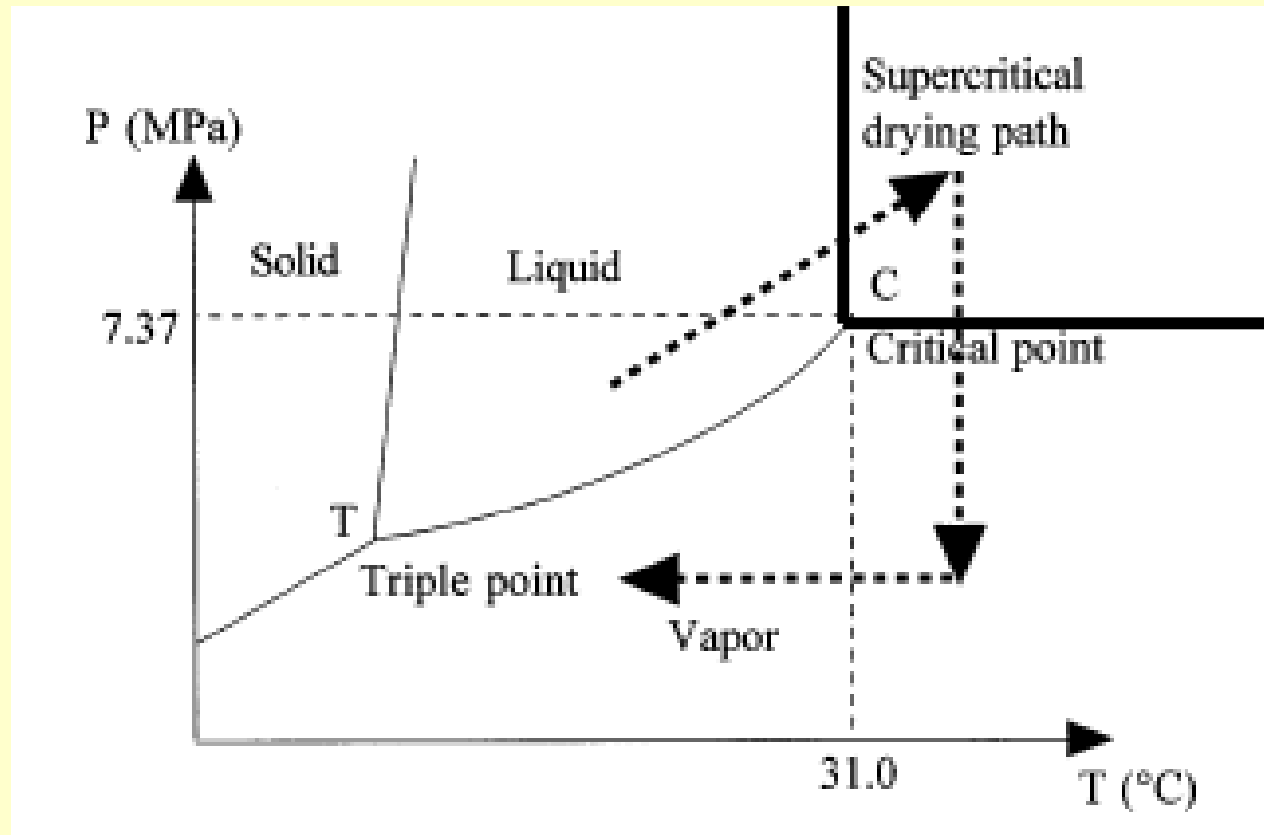**From sodium silicate – 3 steps**
•Salt washing
•Water replacement
•Supercritical drying

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 [cm^{3}mol^{-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
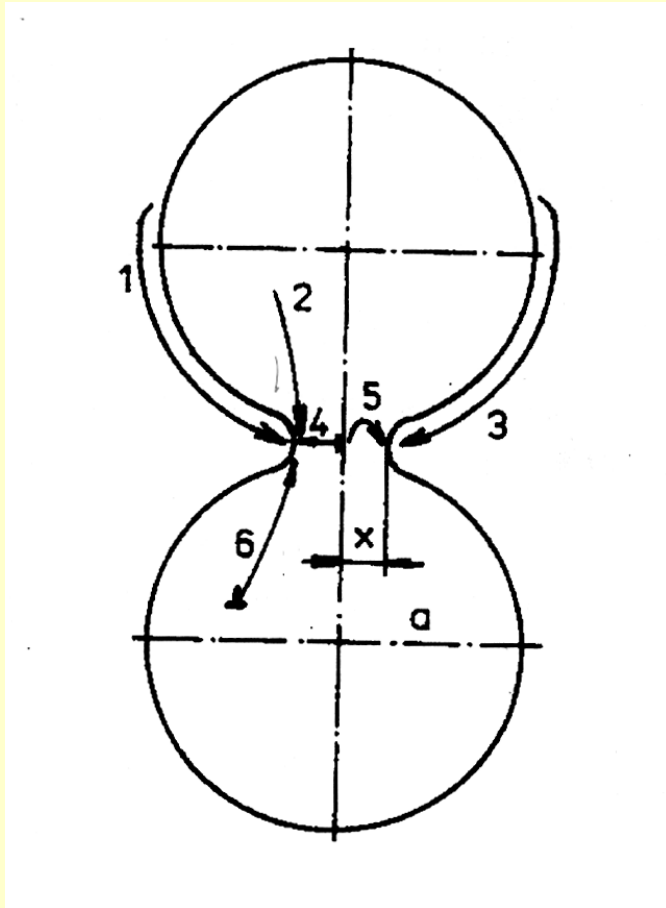**structural relaxation - shrinkage**

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

Sintering mechanisms

Sintering mechanisms

solid, liquid, gas phase

1. Evaporation-condensation and dissolution-precipitation

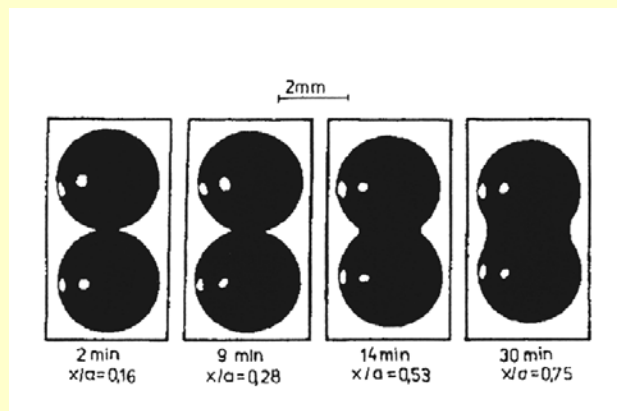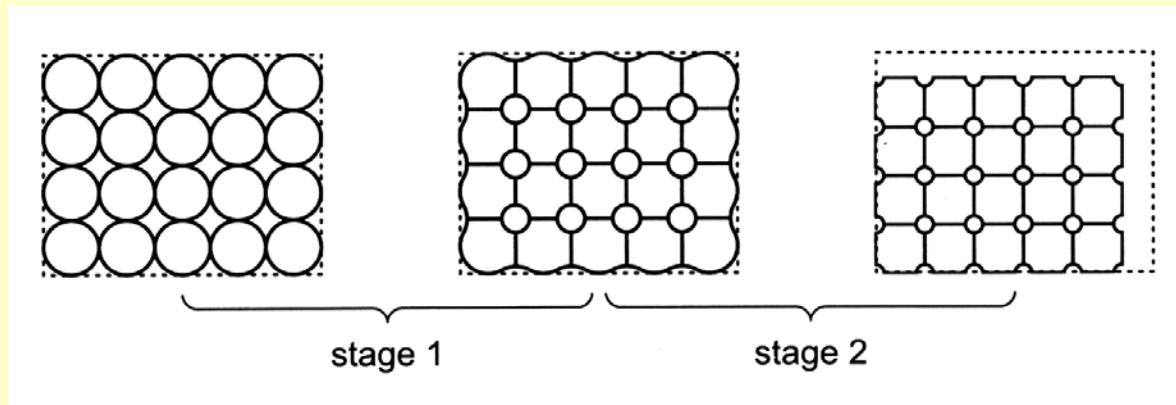**2. Volume diffusion**

3. Surface diffusion

4. Grain boundary diffusion
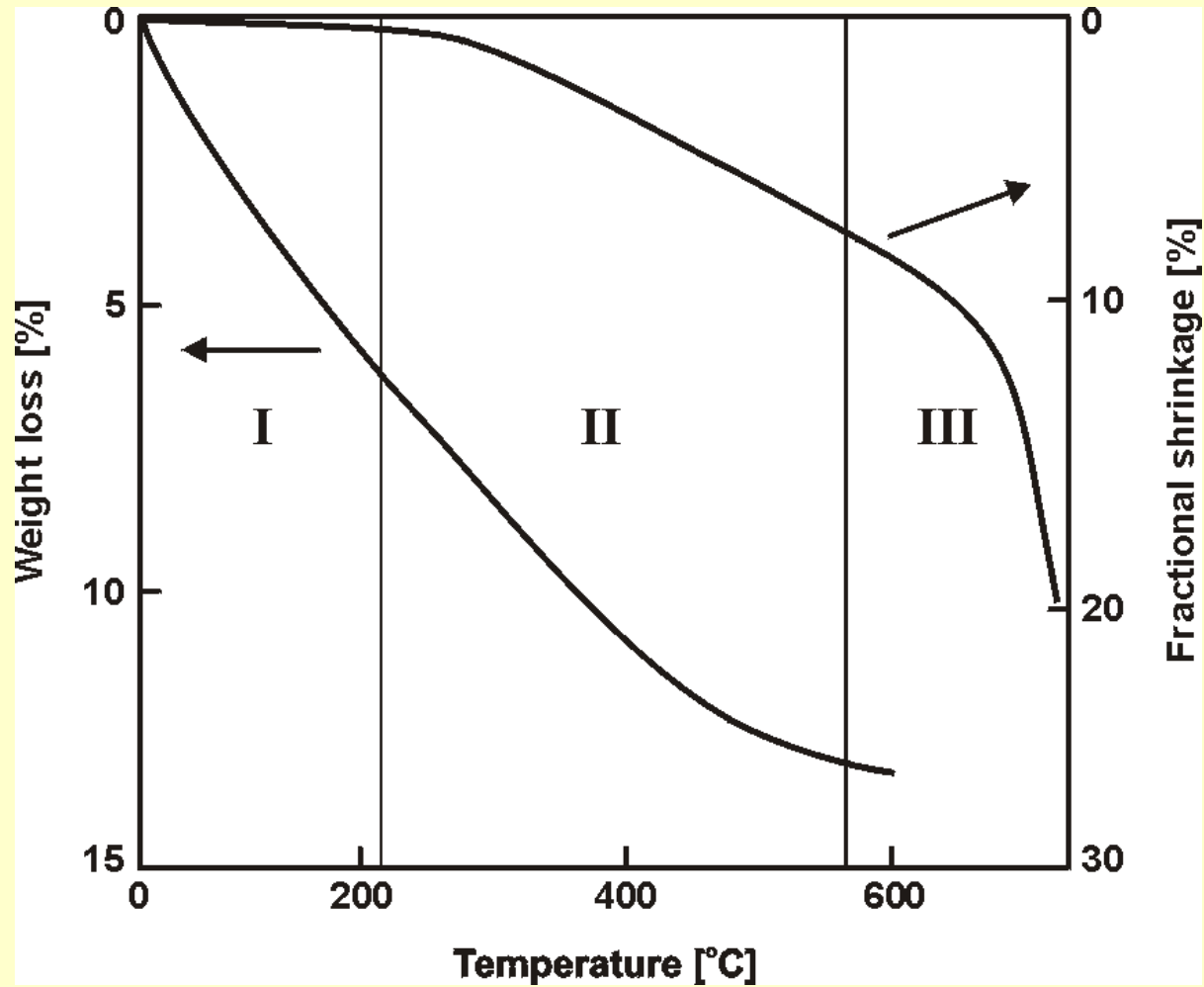
5. Volume diffusion from grain boundaries

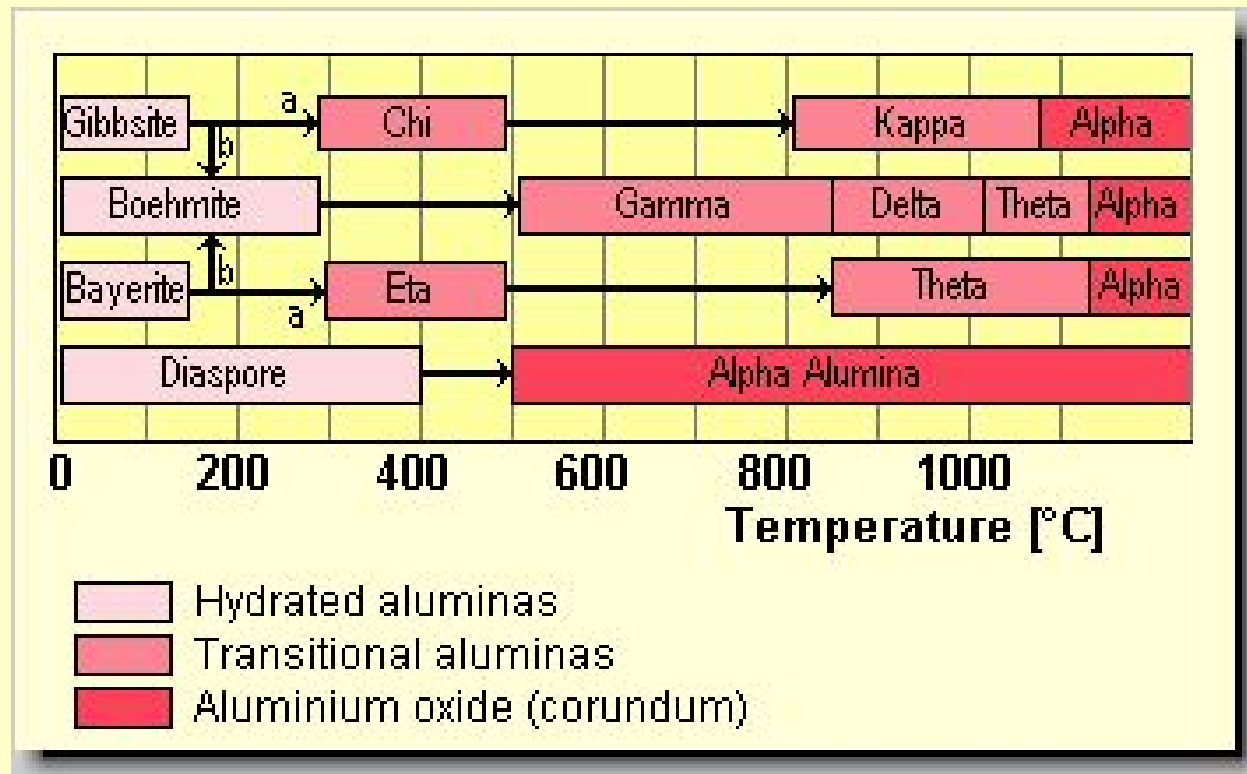**6. Volume diffusion from dislocations, vacancies**

Densification

Densification

stage 1   stage 2

2mm

2 min	9 min	14 min	30 min
x/a=0,16	x/a=0,28	x/a=0,53	x/a=0,75

Densification

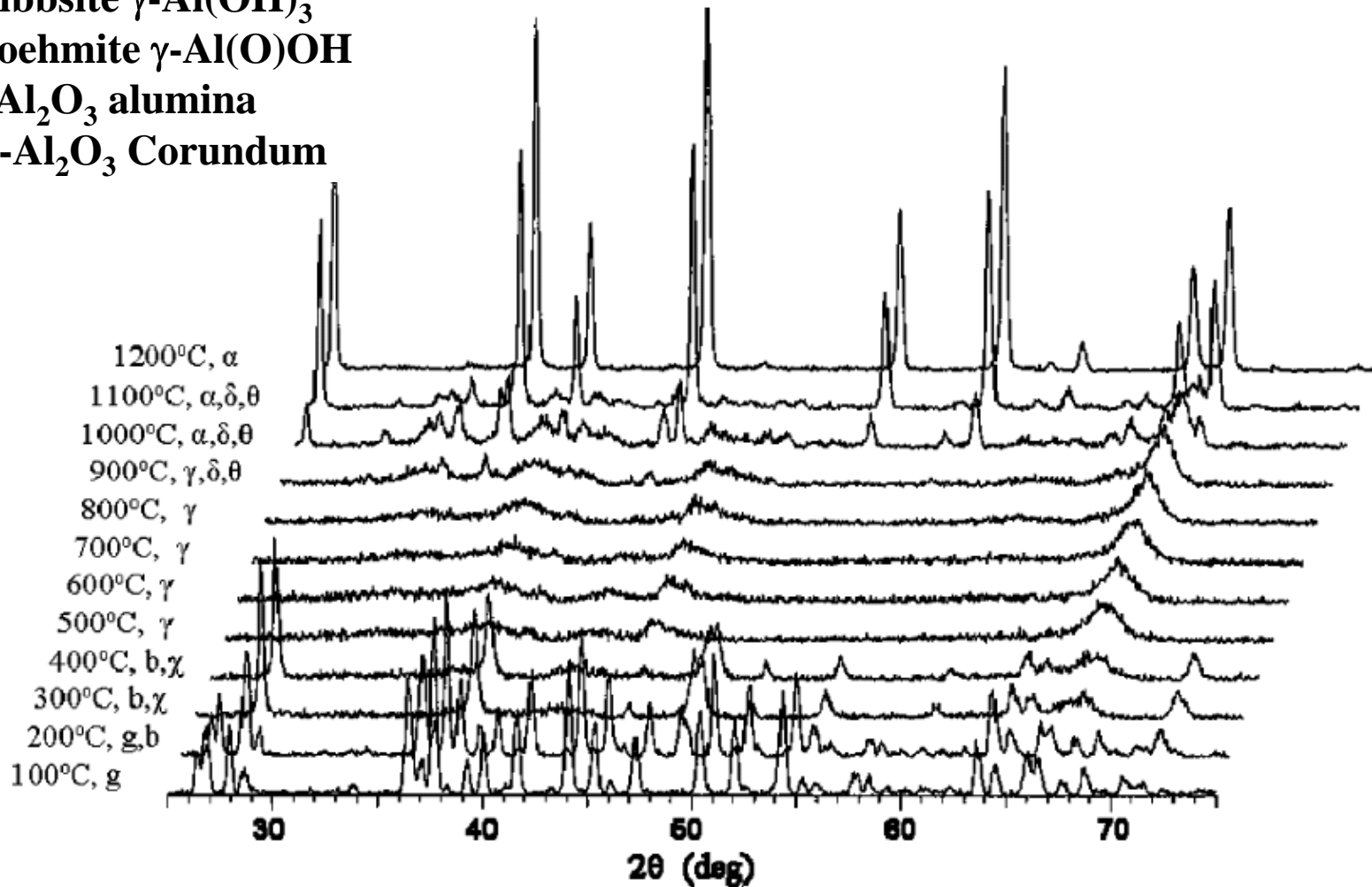# Dehydration sequence of hydrated alumina in air

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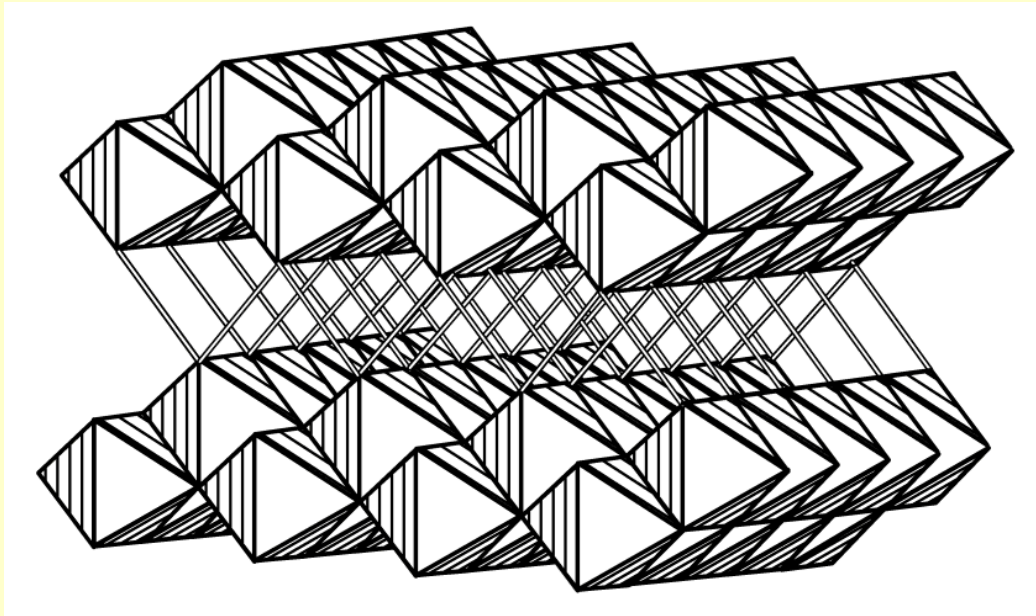**path (a) by fine crystal size (<10µm)**

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

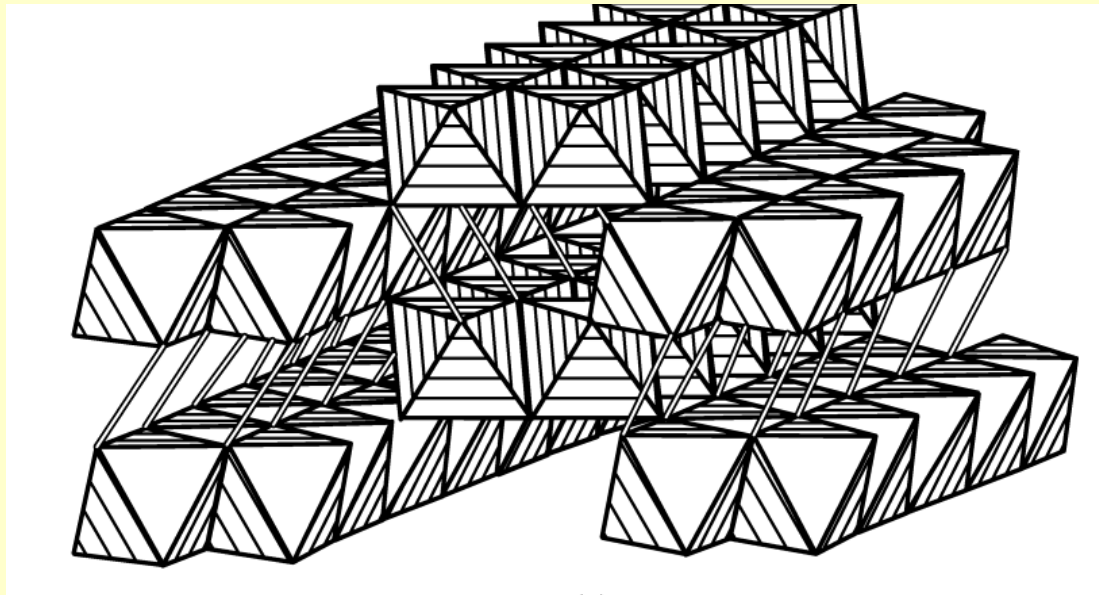**Gibbsite γ-Al(OH)$_3$ to Boehmite γ-Al(O)OH to γ-Al$_2$O$_3$ alumina (defect spinel) CCP**

^{27}Al Solid-State NMR spectra
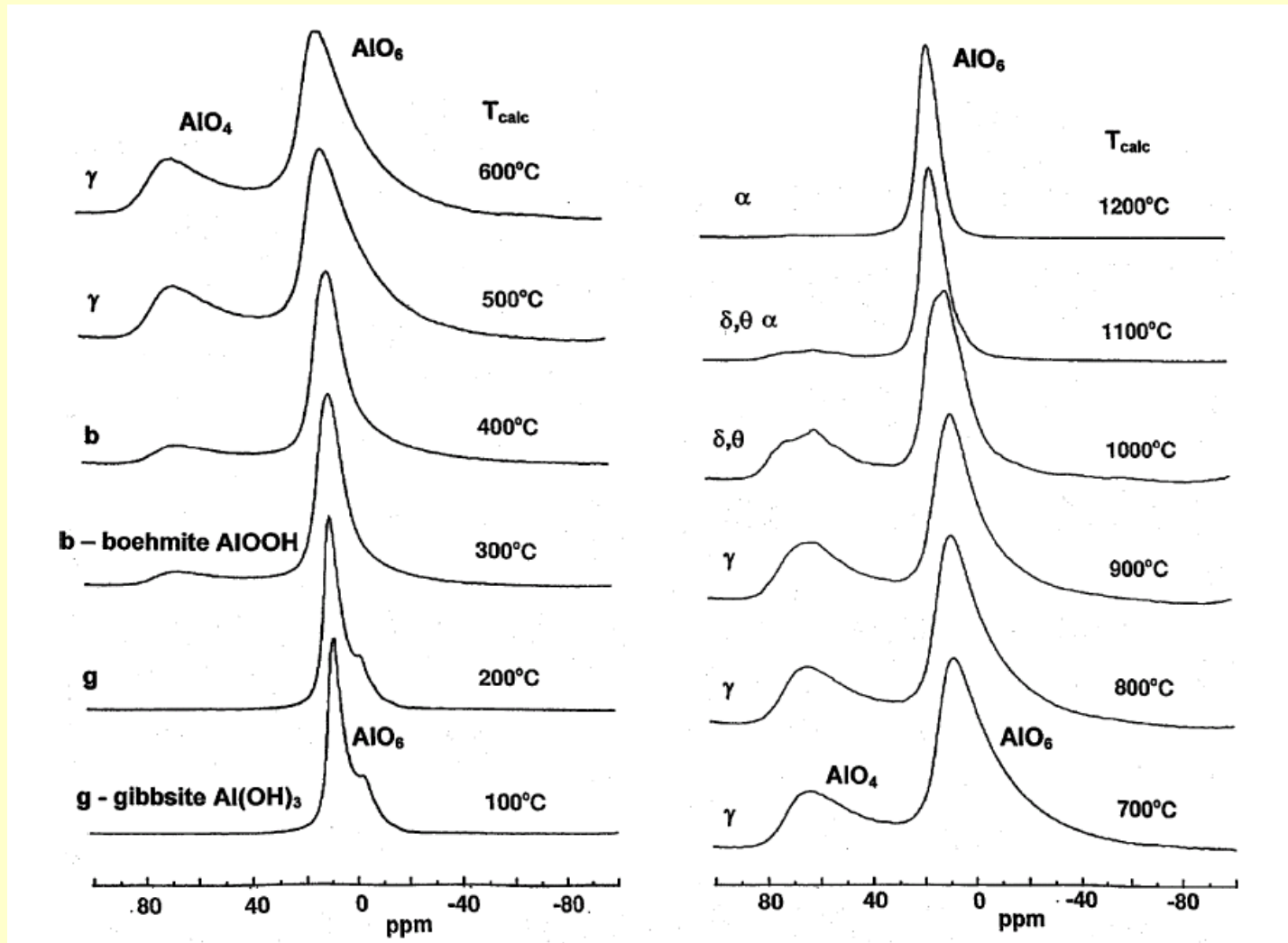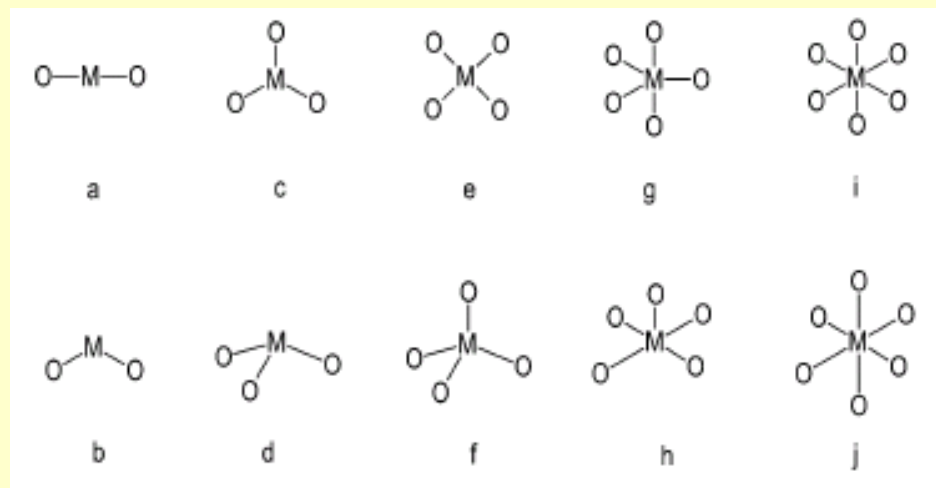
Bayerite to Diaspore to Corundum

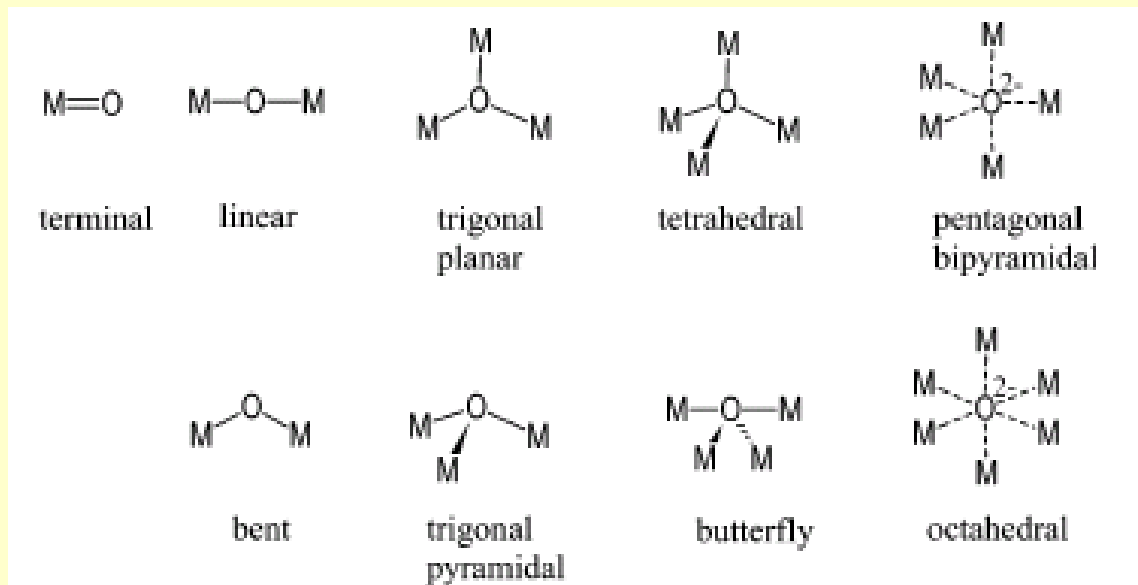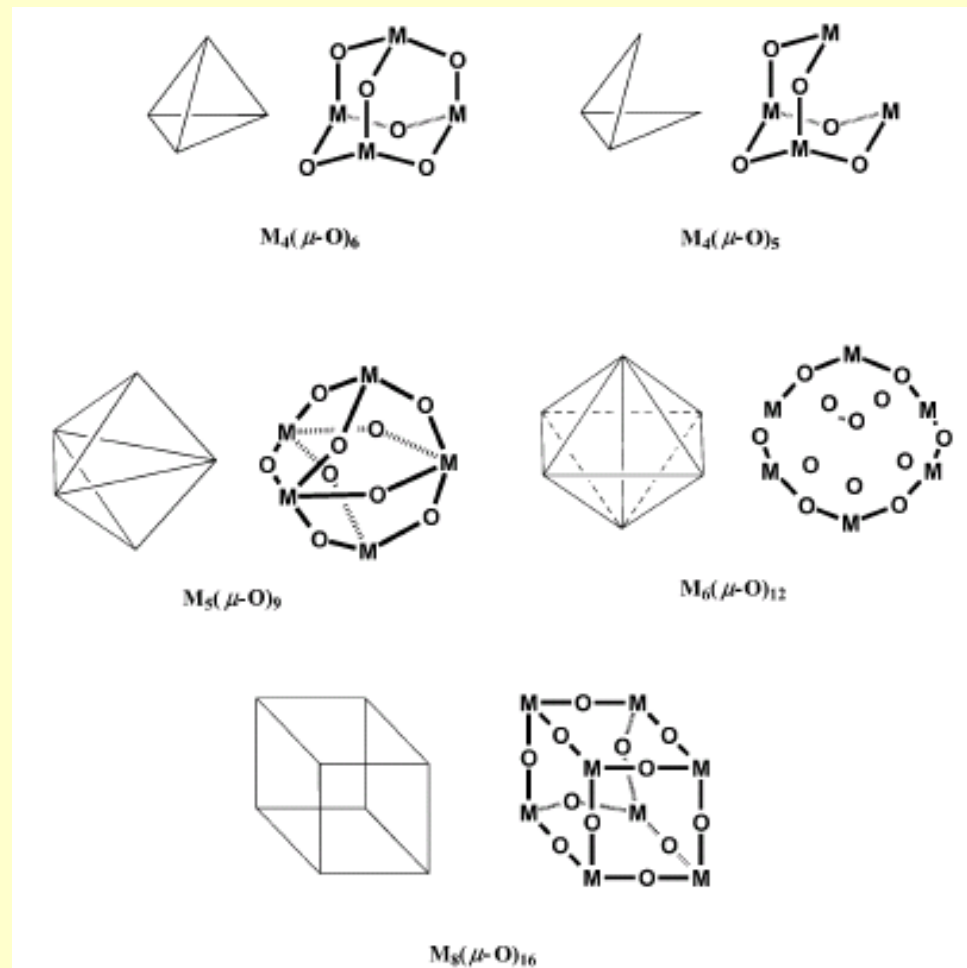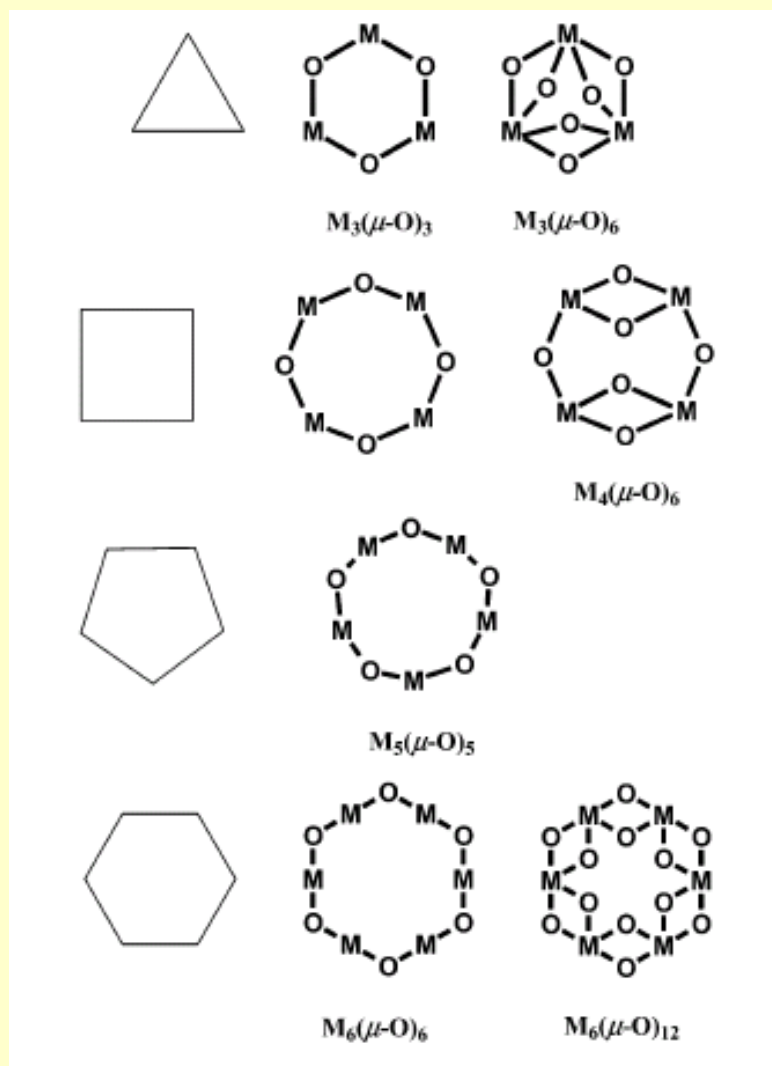**Bayerite α-Al(OH)$_3$ to Diaspore α-Al(O)OH to α-Al$_2$O$_3$ Corundum HCP**

Metal Coordination

Oxygen Coordination

Metal-Oxide Clusters

M$_3$(μ-O)$_3$ M$_3$(μ-O)$_6$

M$_4$(μ-O)$_6$

M$_4$(μ-O)$_6$ M$_4$(μ-O)$_5$

M$_5$(μ-O)$_5$

M$_5$(μ-O)$_9$ M$_6$(μ-O)$_{12}$

M$_6$(μ-O)$_6$ M$_6$(μ-O)$_{12}$

M$_8$(μ-O)$_{16}$

Sol-Gel Methods

Metal-Oxide Clusters

$M_{12}O_{24}$

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

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

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

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