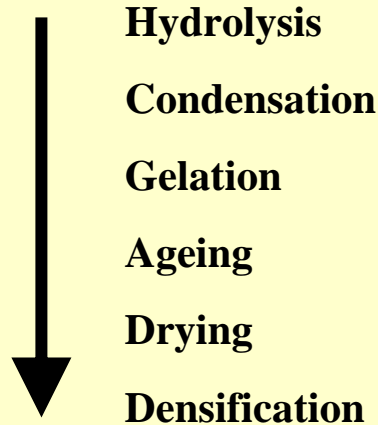


Sol-Gel Methods

Sol-gel process:



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

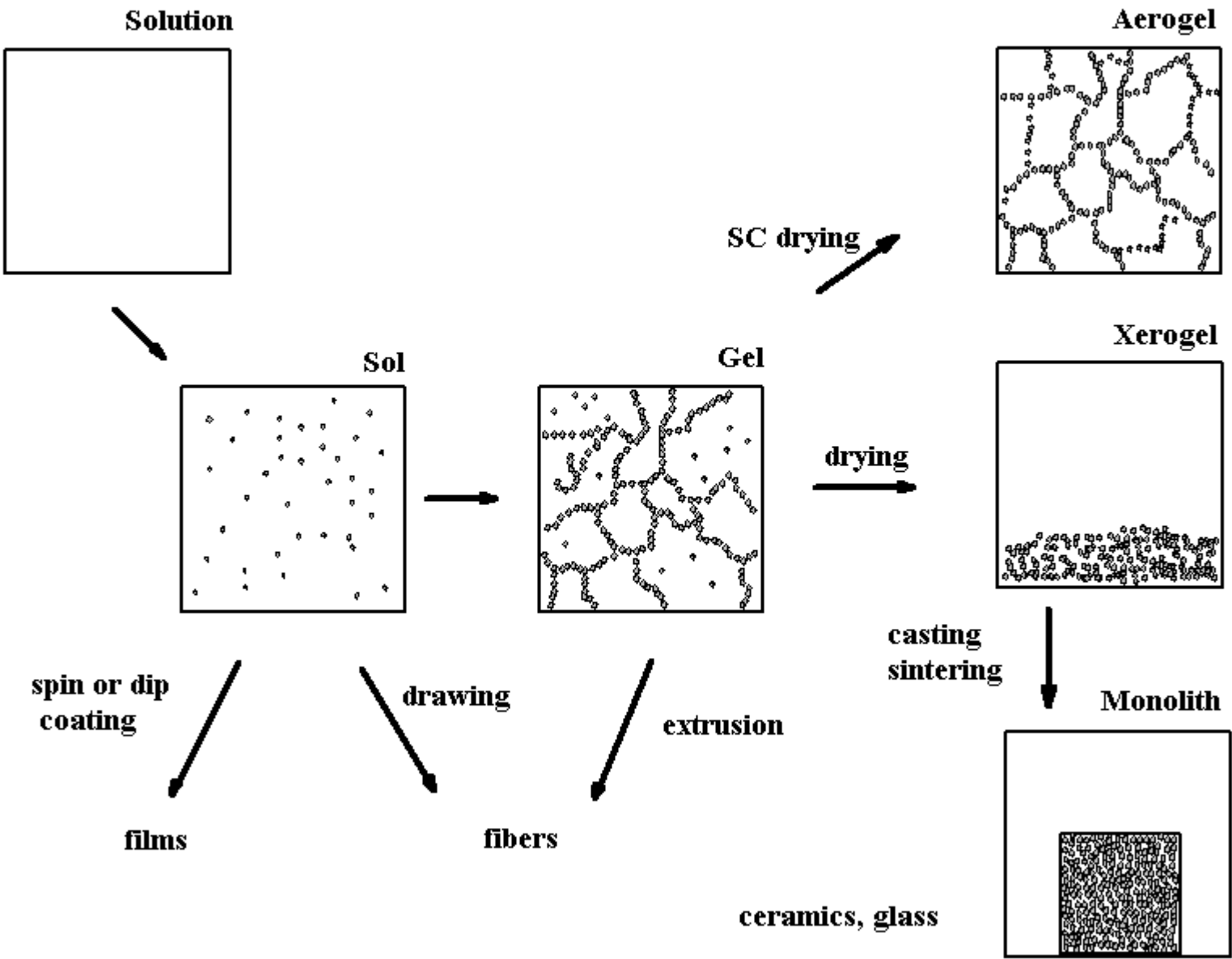
Gel = porous, three-dimensional, continuous solid network surrounding a continuous liquid phase

Colloidal (particulate) gels = agglomeration of dense colloidal particles

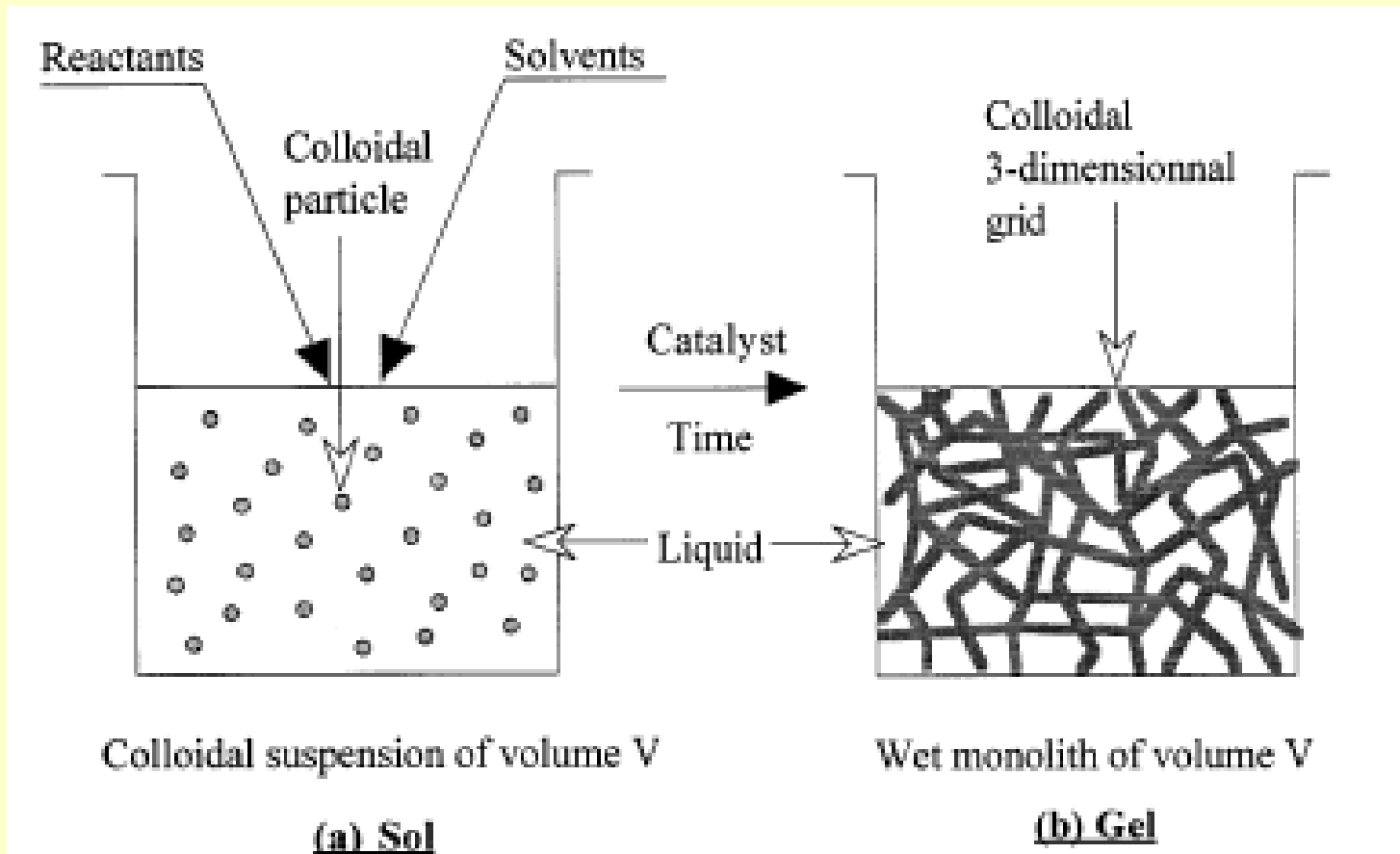
Polymeric gels = agglomeration of polymeric particles made from subcolloidal units

Agglomeration = covalent bonds, van der Waals, hydrogen bonds, polymeric chain entanglement

Sol-Gel Process



Sol and Gel

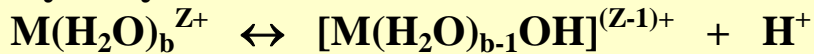


Colloid Route

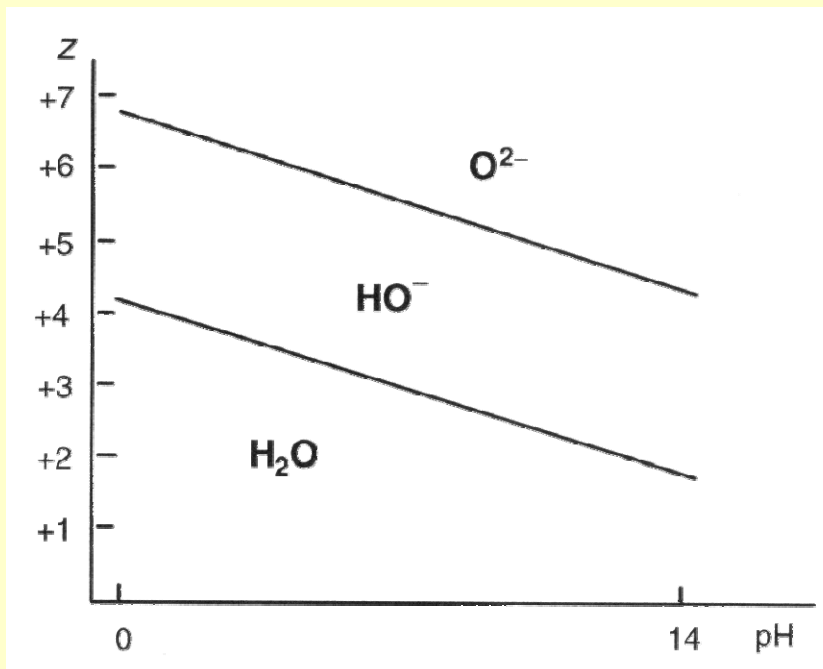
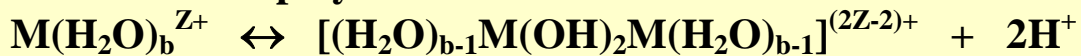
●* Colloid Route

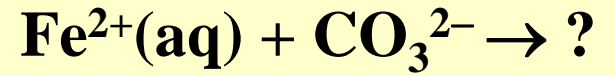
metal salts in aqueous solution, pH and temperature control

Hydrolysis

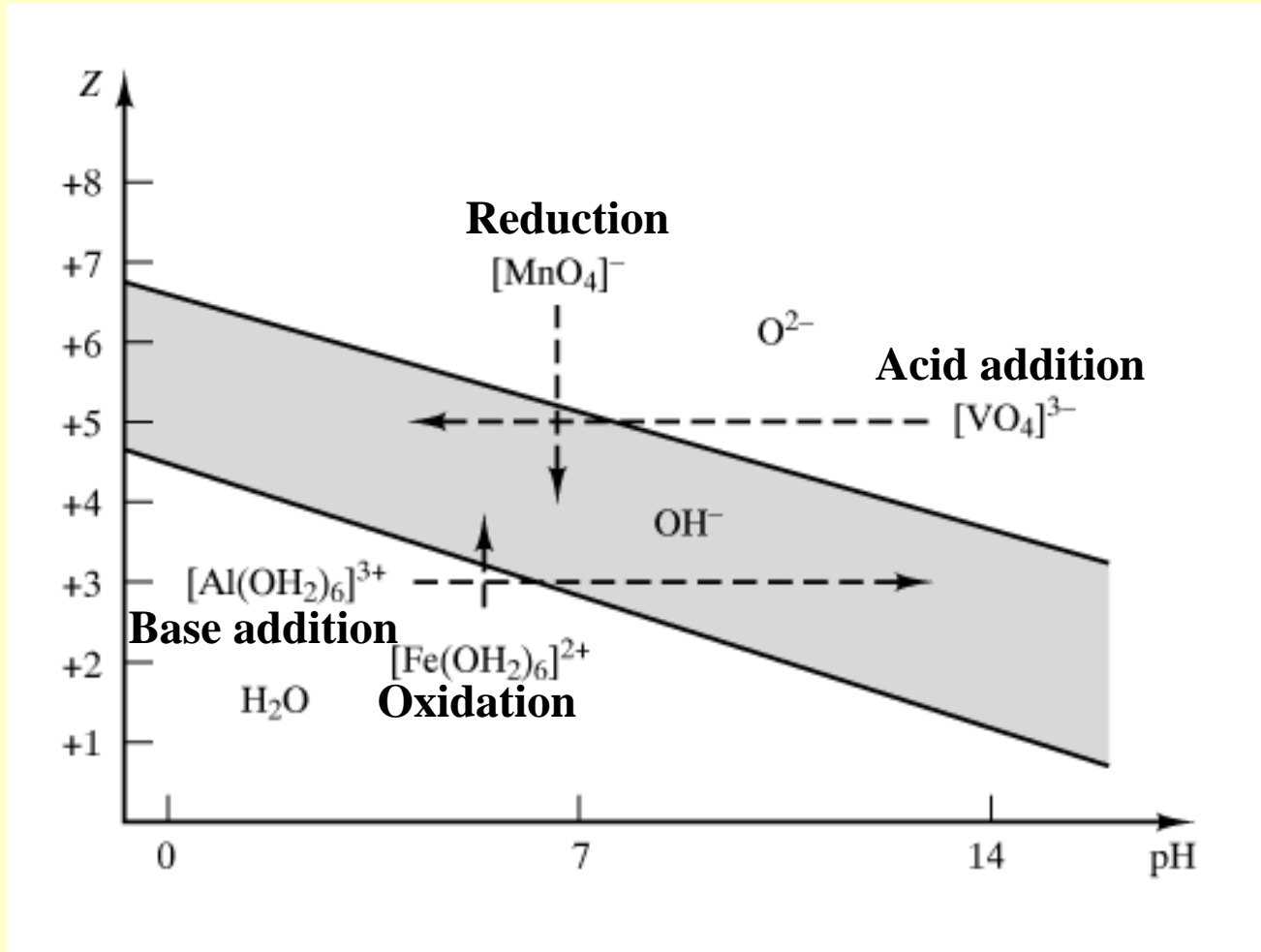
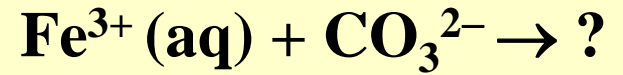


Condensation-polymerization

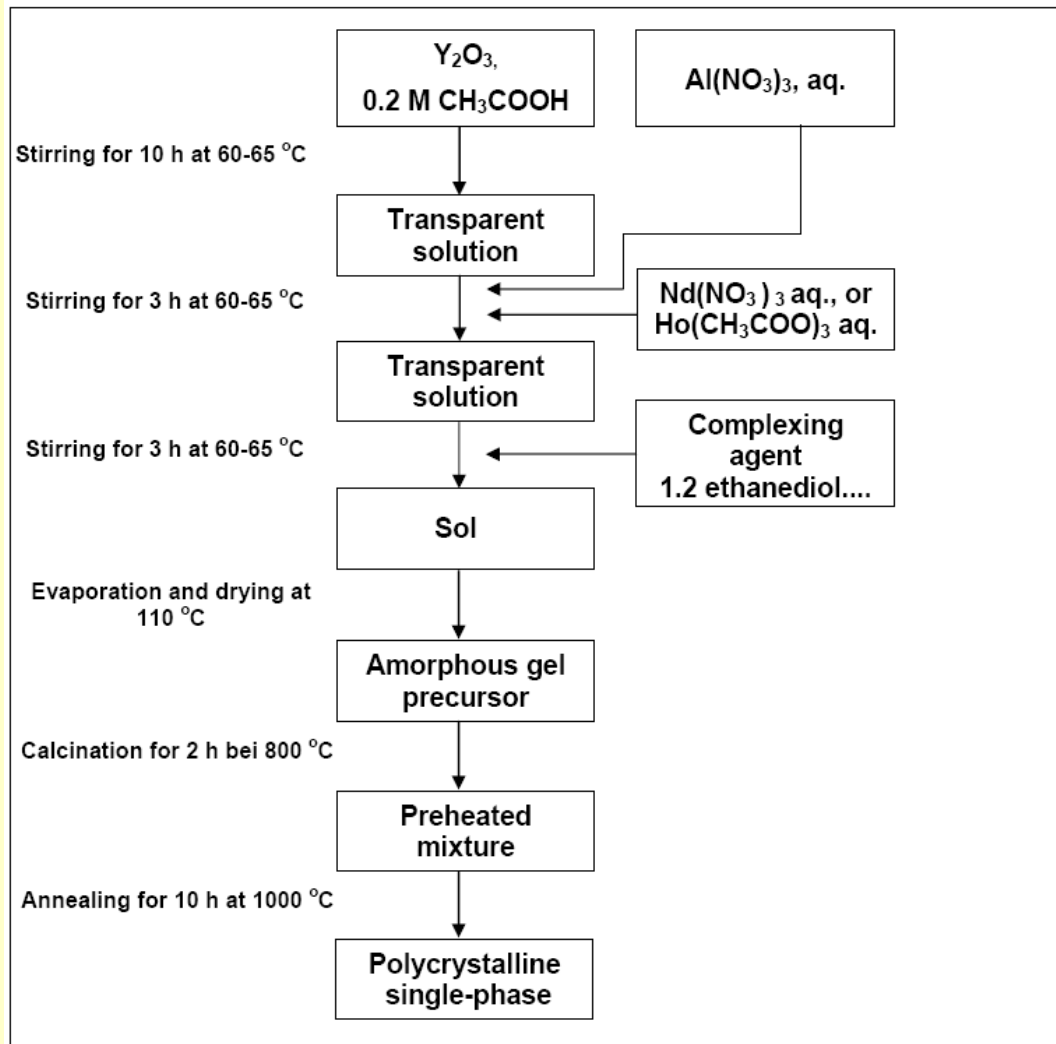




Colloid Route



Sol – Gel Procedure



Major components

Dopants

Gelling agent

Removal of solvents

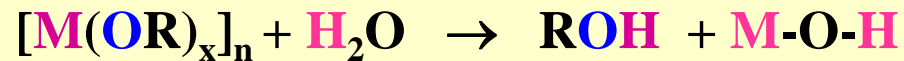
Removal of organics

Doped YAG product

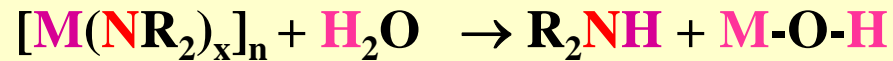
Metal-Organic (Alkoxide) Route

Hydrolysis

Metal Alkoxides



Metal Amides

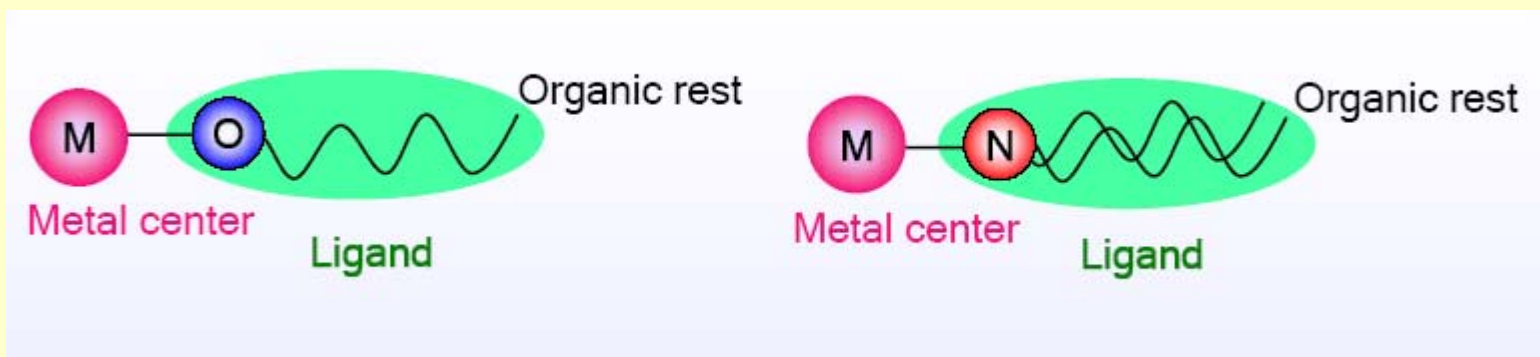


Condensation



OXIDE

Metal Alkoxides and Amides



Metal Alkoxides $[M(OR)_x]_n$

formed by the replacement of the hydroxylic hydrogen of an alcohol (ROH) through a metal atom

Metal Amides $[M(NR_2)_x]_n$

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: $[M(OR)_x]_n$

Heterometallic Alkoxides

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

Metal Amides

General Formula: $[M(NR_2)_x]_n$

M = Metal or metalloid of valency **x**

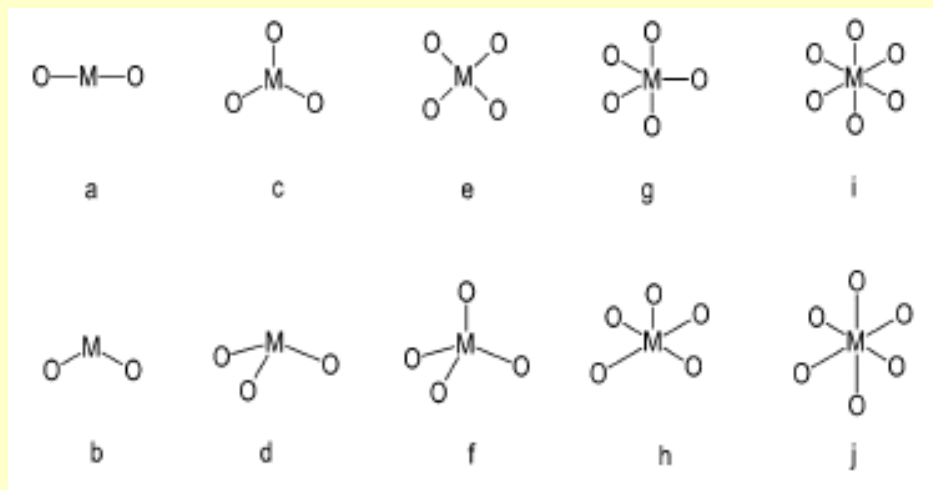
O = Oxygen Atom

N = Nitrogen atom

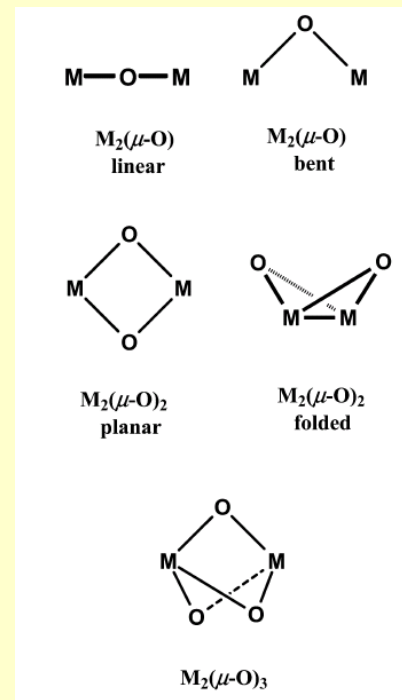
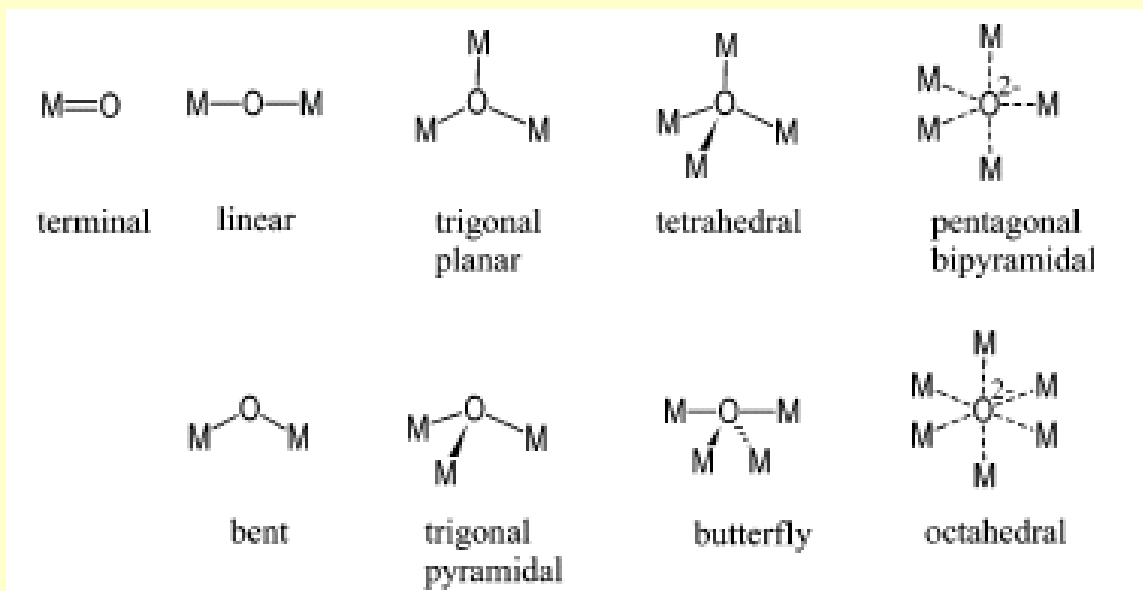
R = simple alkyl, substituted alkyl or aryl group

n = degree of molecular association

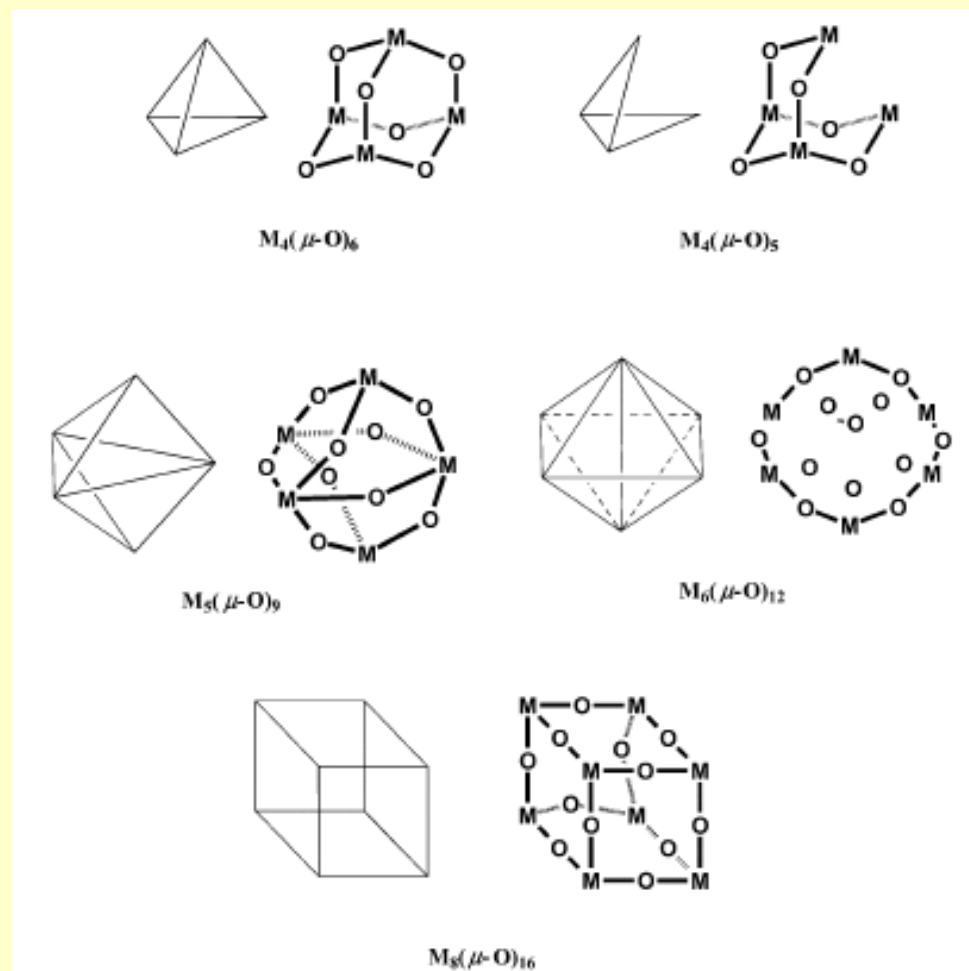
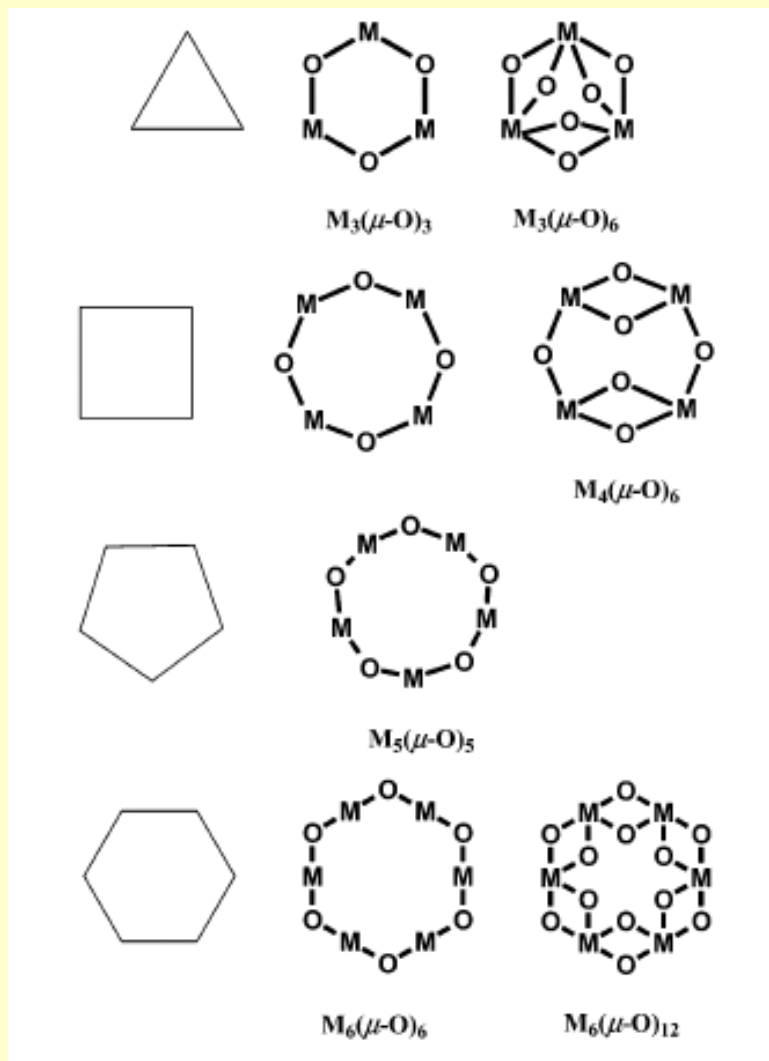
Metal Coordination



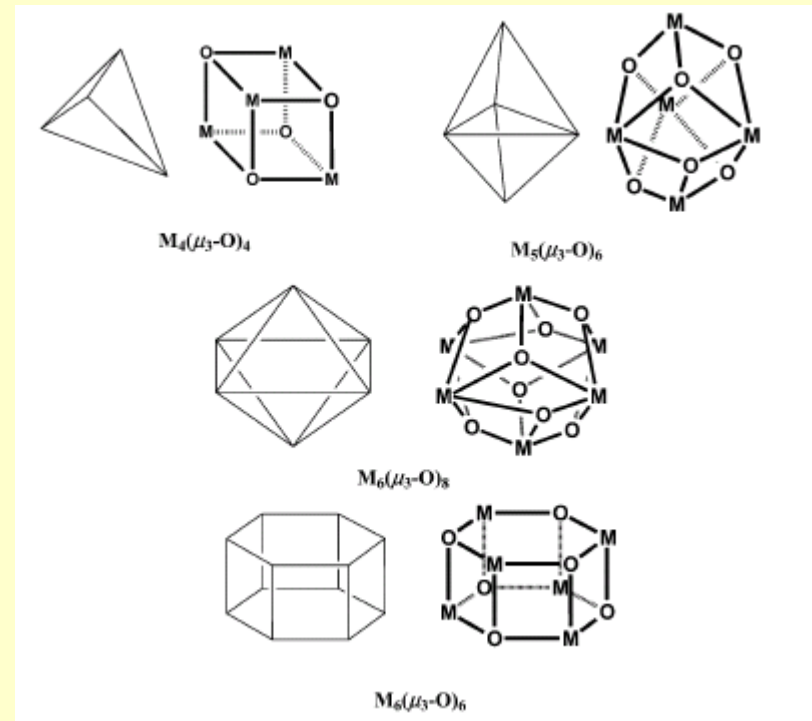
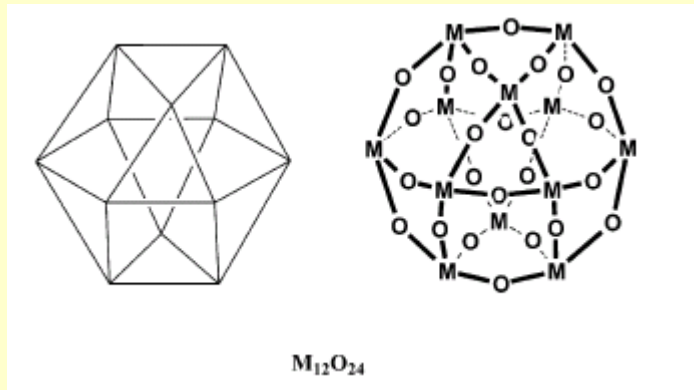
Oxygen Coordination



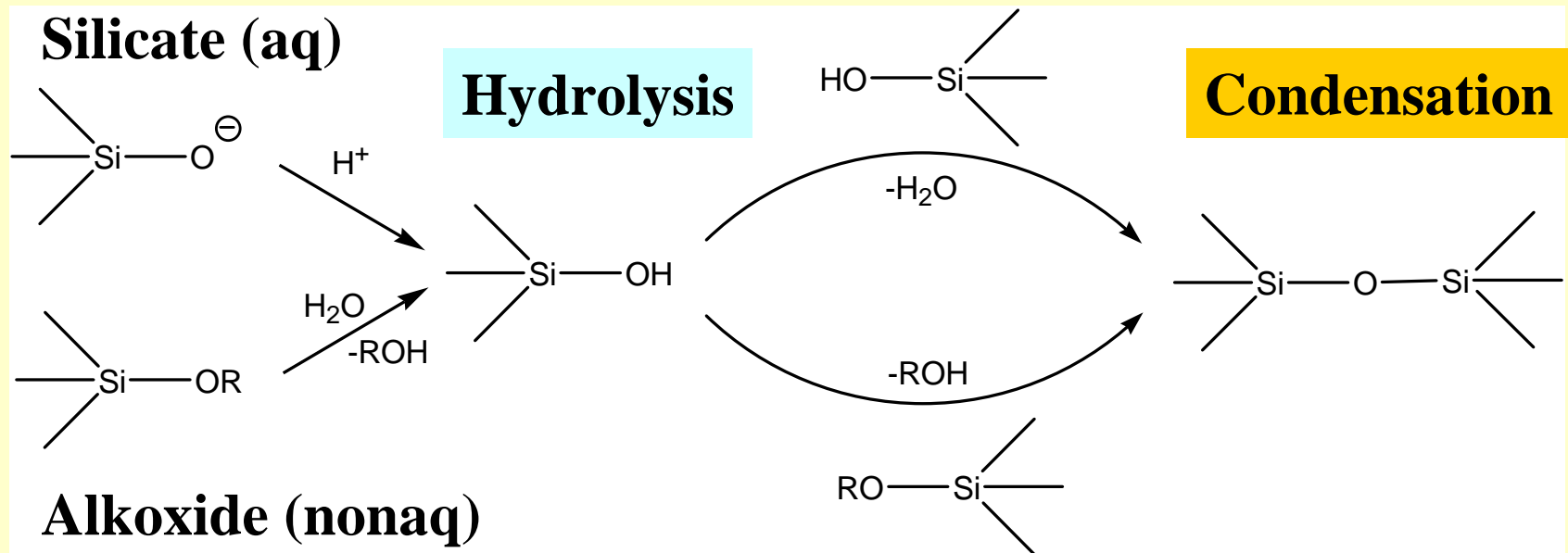
Metal-Oxide Clusters



Metal-Oxide Clusters



Sol-gel in Silica Systems

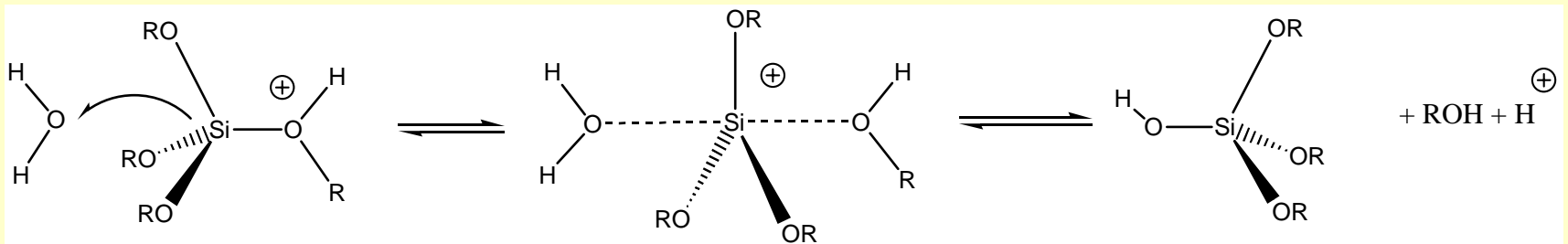


Metal-Organic Route

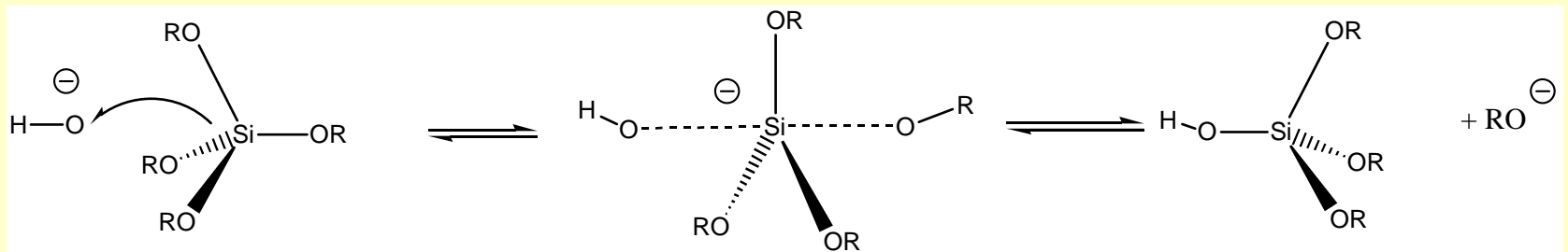
* Metal-organic Route

metal alkoxide in alcoholic solution, water addition

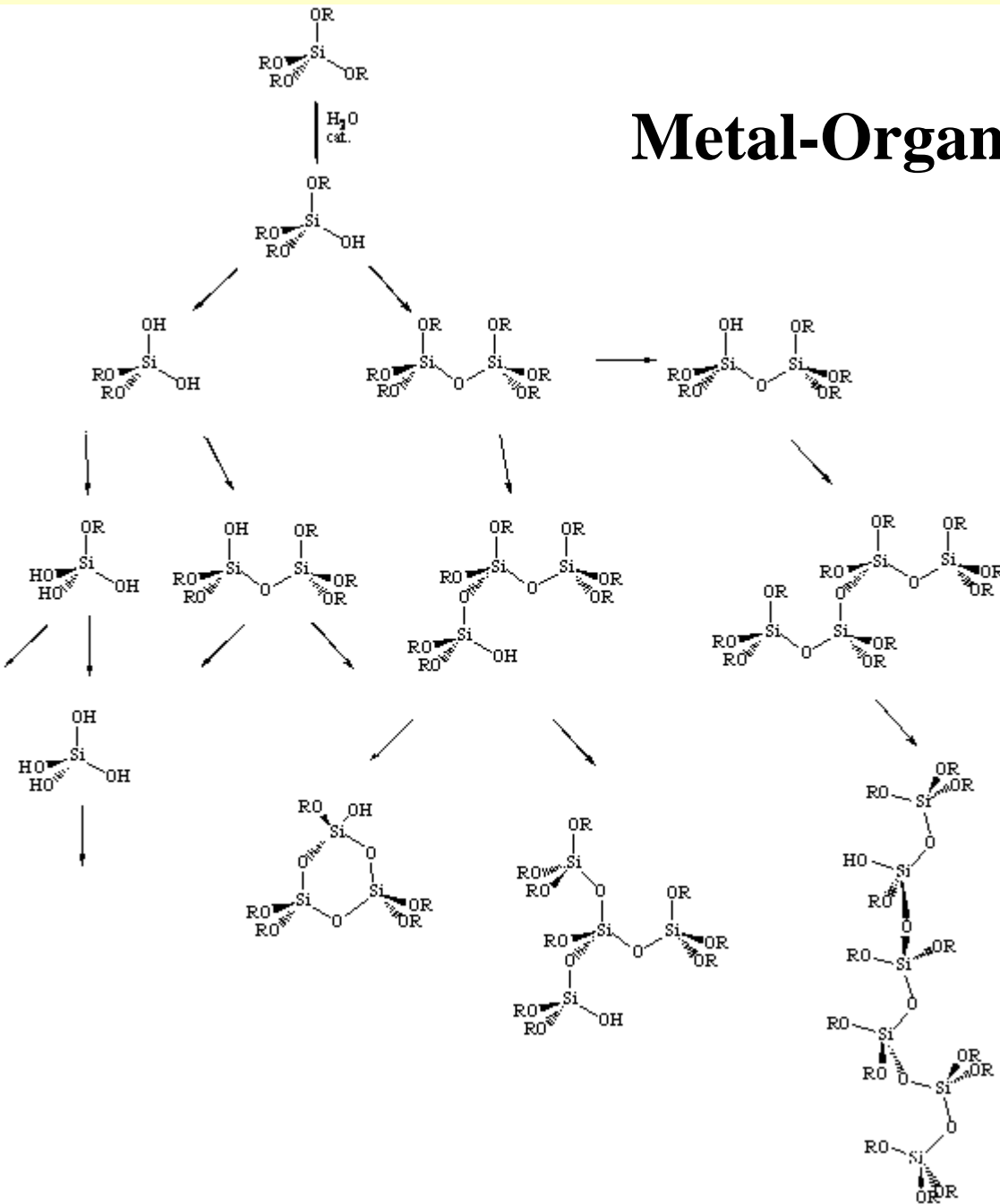
Acid catalysed hydrolysis



Base catalysed hydrolysis



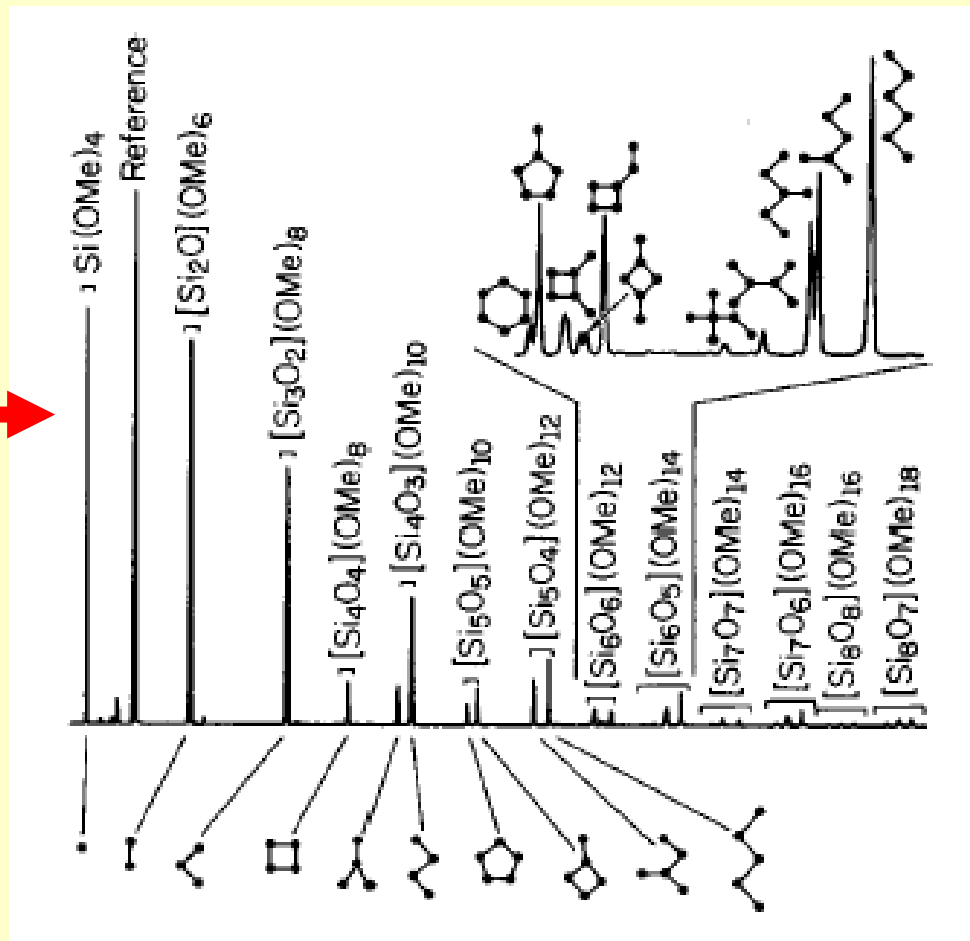
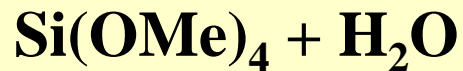
Metal-Organic Route

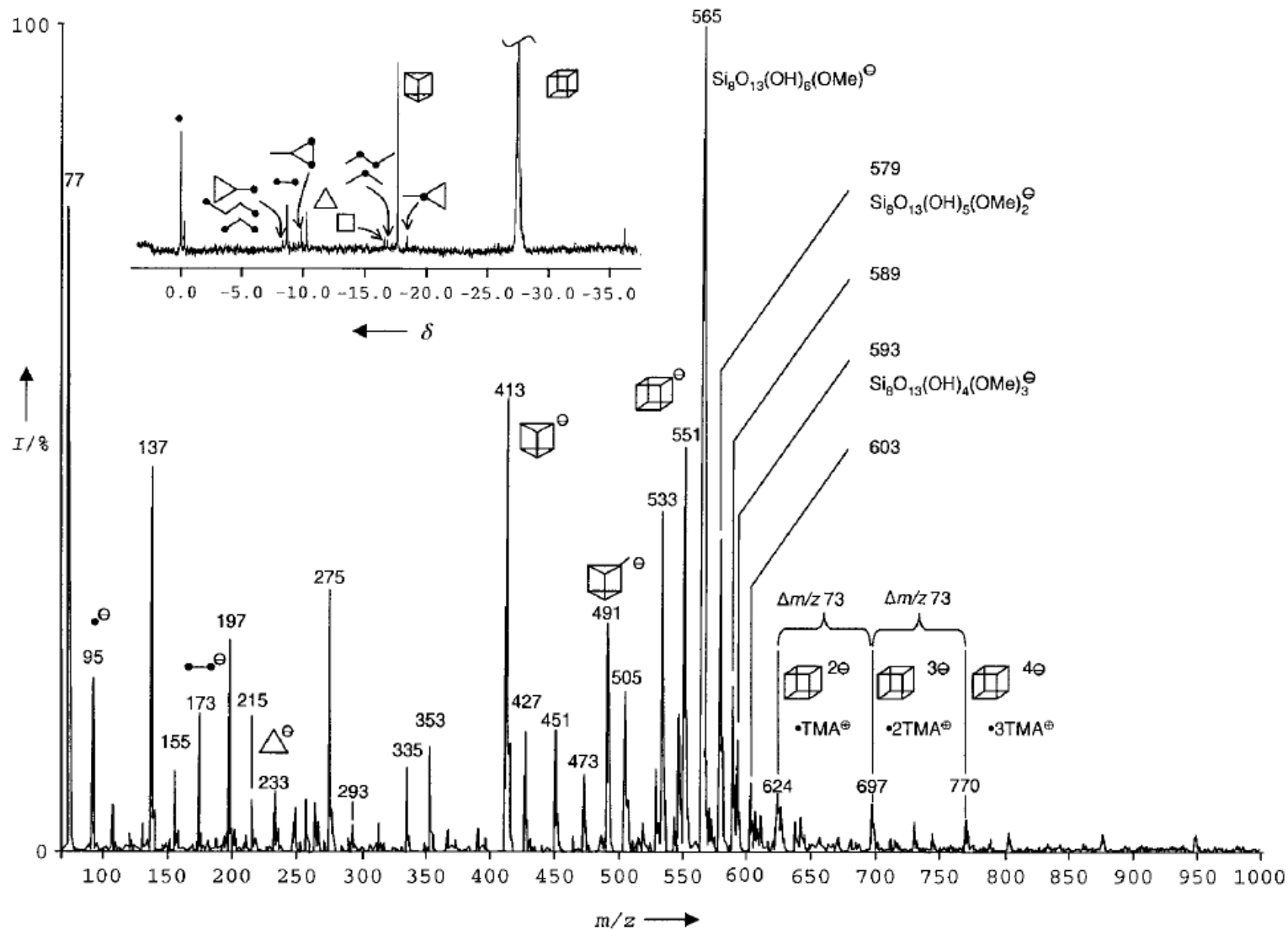


**Oligomers formed
by hydrolysis-condensation
process**

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

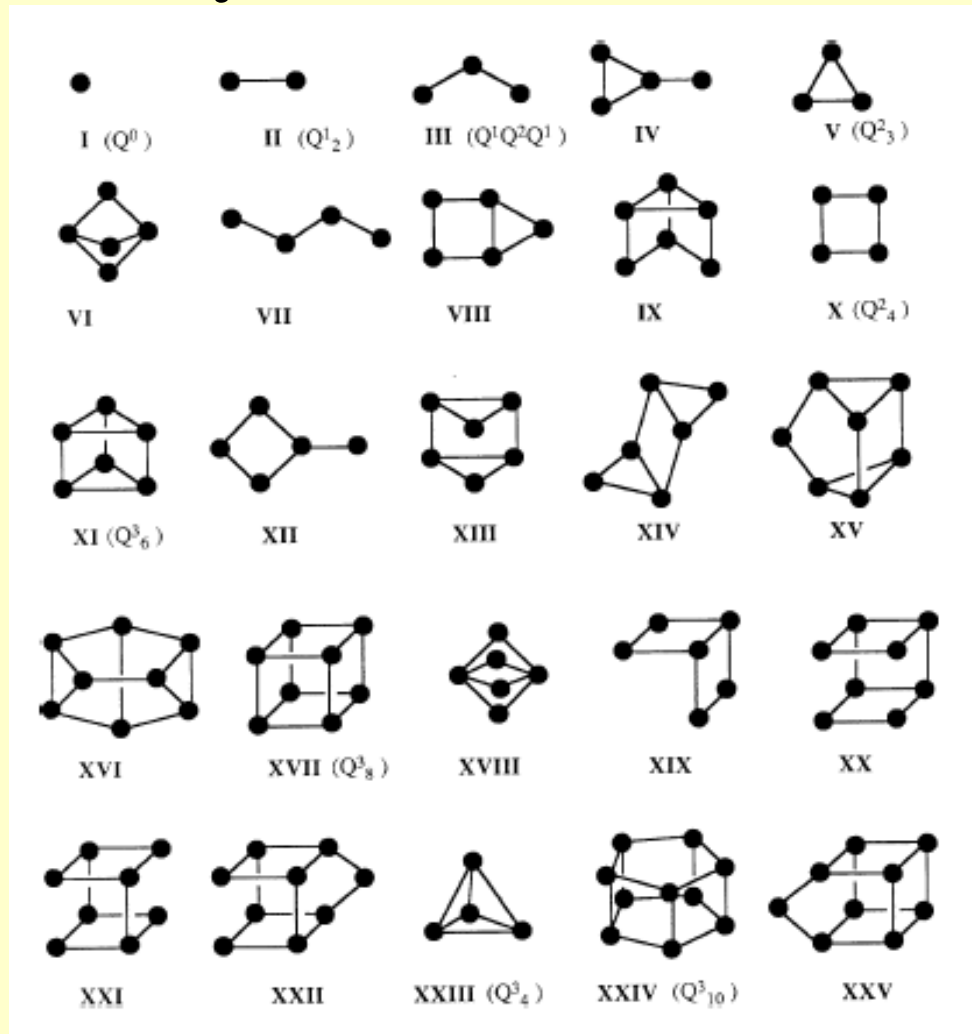
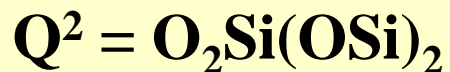
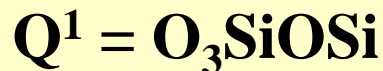
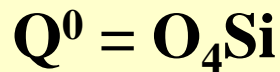
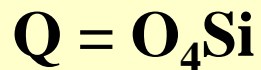
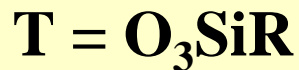
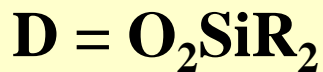
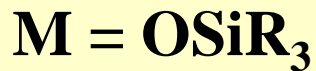
GC of TMOS hydrolysis products





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)



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

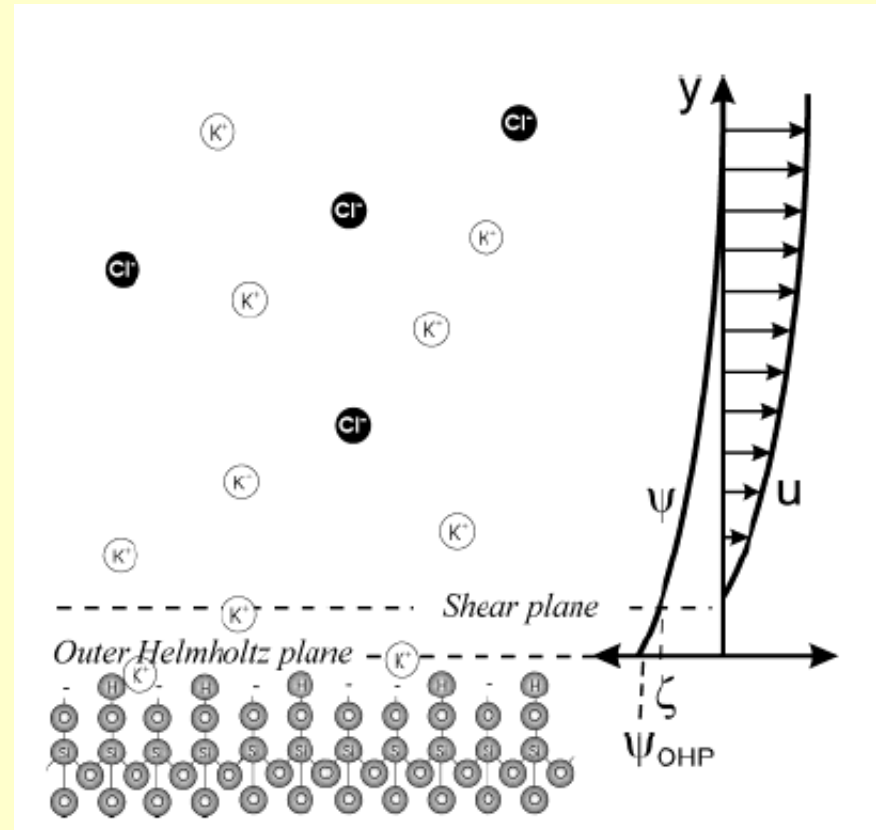
Shielding of this surface charge occurs

due to adsorbed ions inside the OHP

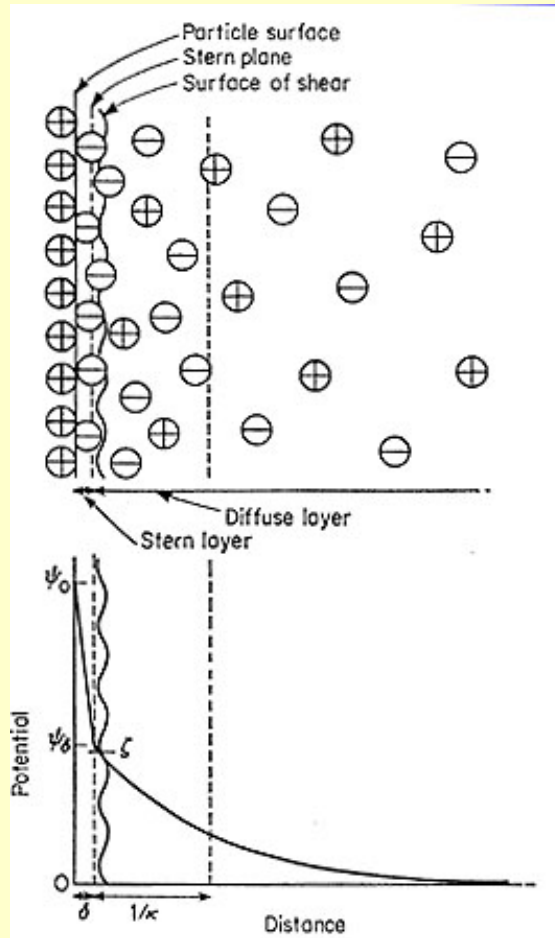
and by mobile ions in a diffuse layer
Potential and EOF velocity profiles are shown at right

The shear plane is where hydrodynamic motion becomes possible;

ζ is the potential at this plane



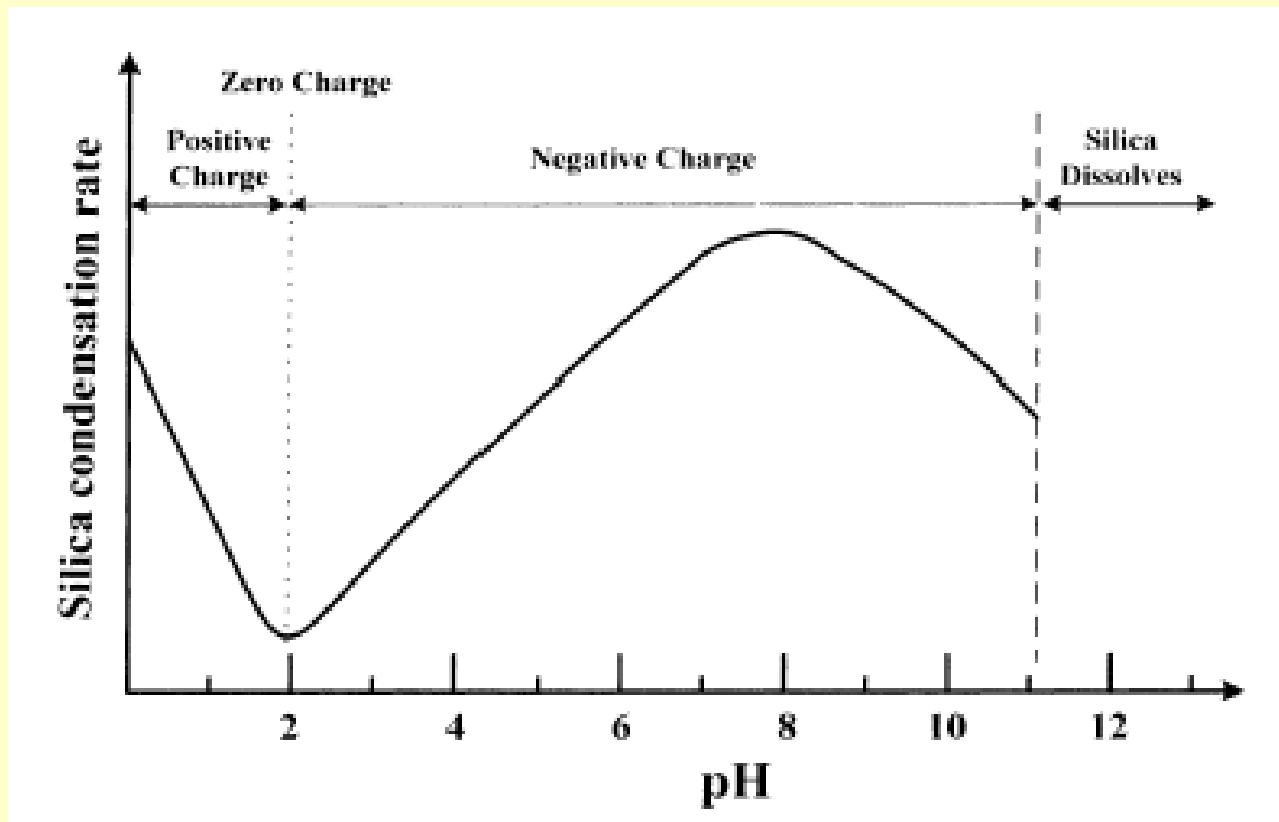
The Electrical Double Layer



Sol-Gel Methods

Isoelectric point: zero net charge

pH = 2.2 for silica



Sol-Gel Methods

Longest TEOS gel time
= the slowest reaction

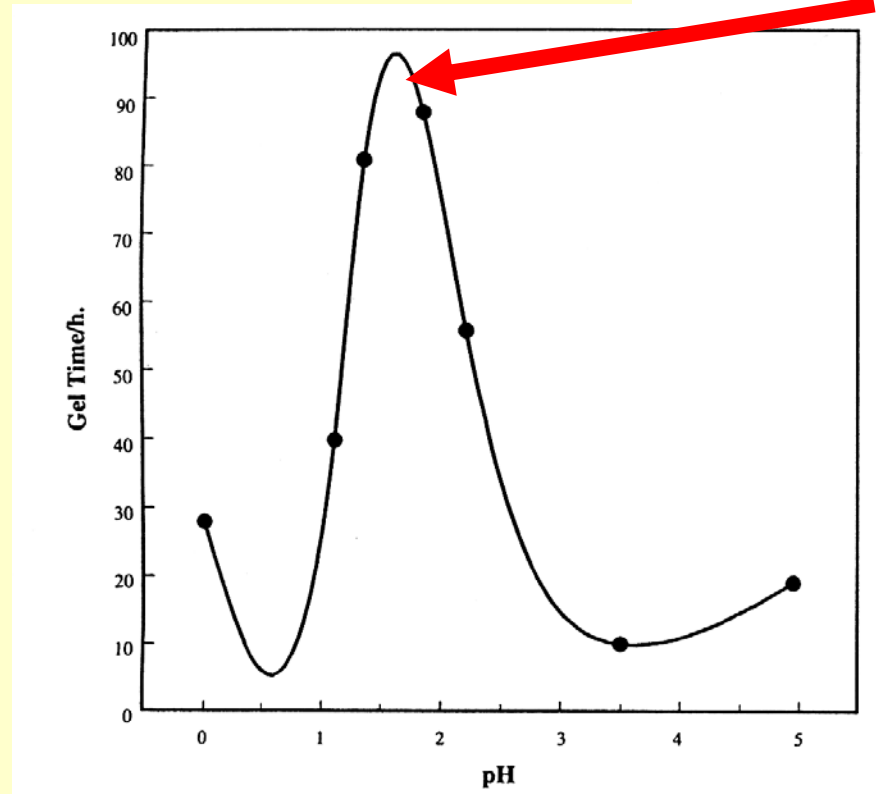
Effects on hydrolysis rate:

pH

substituents

solvent

water

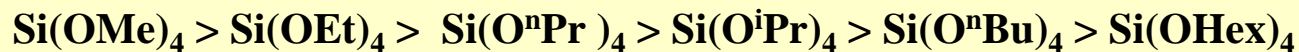


Rate of H^+ catalyzed TEOS hydrolysis (gel time) as a function of pH

Sol-Gel Methods

Precursor substituent effect

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



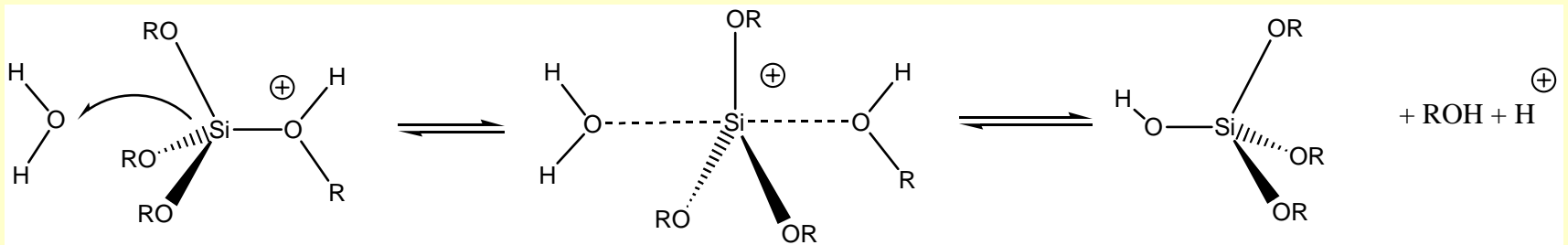
Inductive effects: electronic stabilization/destabilization of the transition state.

Electron density at Si decreases:

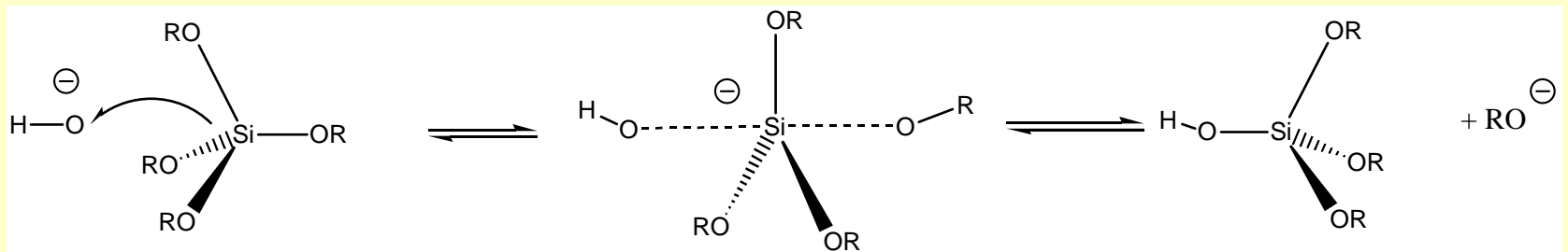


Hydrolysis

Acid catalysed hydrolysis



Base catalysed hydrolysis



Sol-Gel Methods

Acidic conditions:

reaction rate **decreases** as more alkoxy groups are hydrolyzed
reaction at terminal Si favored, linear polymer products, fibers
 RSi(OR)_3 more reactive than Si(OR)_4

Basic conditions:

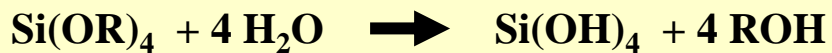
reaction rate **increases** as more alkoxy groups are hydrolyzed
reaction at central Si favored, branched polymer products,
spherical particles, powders
 RSi(OR)_3 less reactive than Si(OR)_4

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

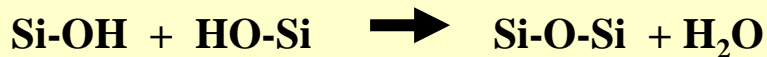
Sol-Gel Methods

Water:alkoxide ratio (R_w) effect

stoichiometric ratio for complete hydrolysis = 4

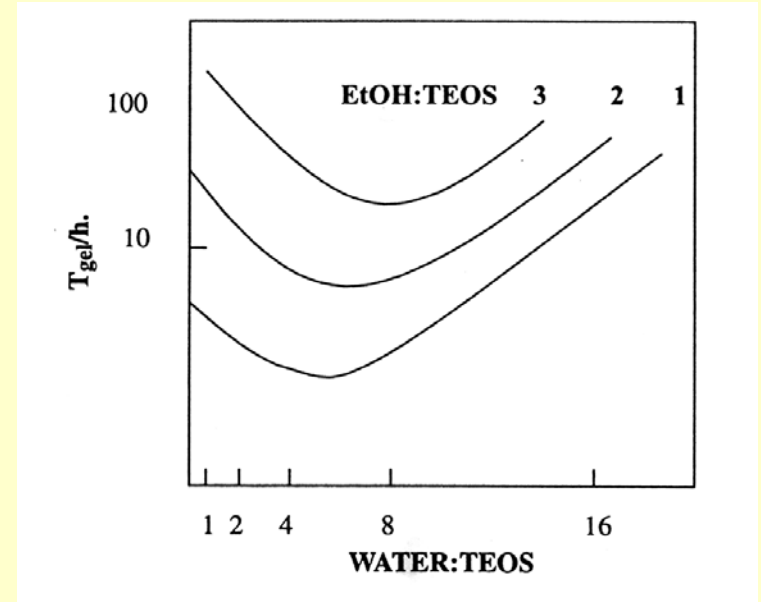


additional water from condensation



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

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



Sol-Gel Methods

Hydrophobic effect

$\text{Si}(\text{OR})_4$ are immiscible with water

cosolvent ROH to obtain a homogeneous reaction mixture

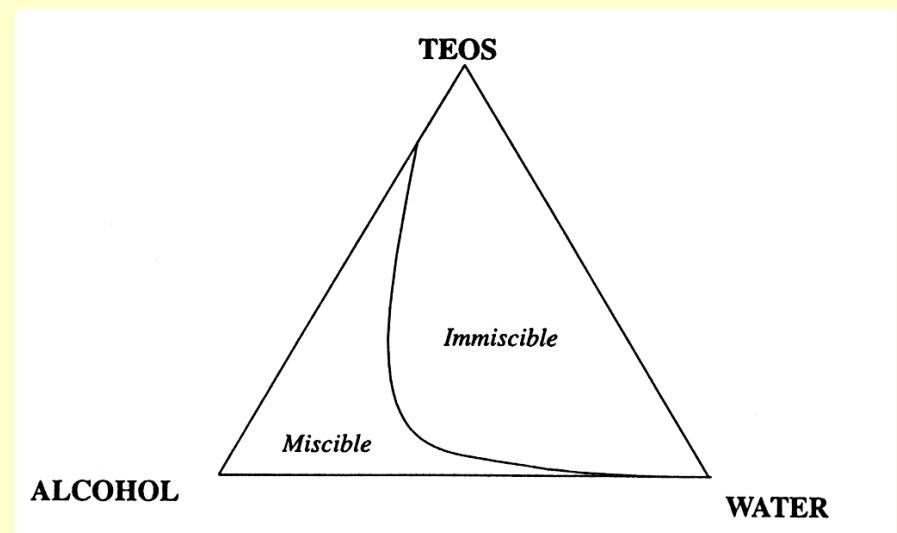
polarity, dipole moment, viscosity, protic behavior

alcohol produced during the reaction

alcohols - transesterification

sonication

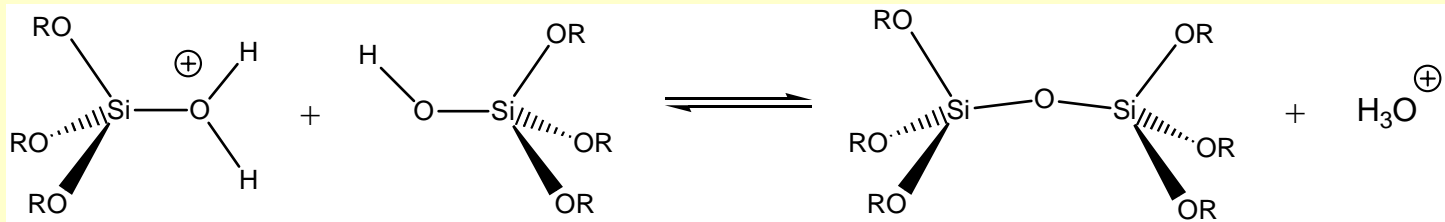
drying



Condensation

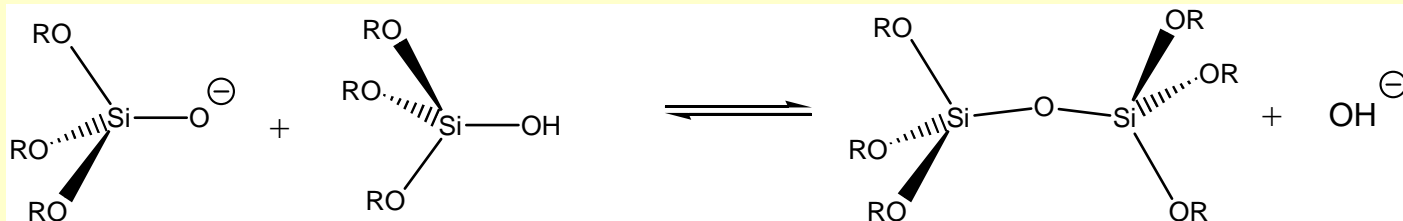
Acid catalysed condensation

fast protonation, slow condensation



Base catalysed condensation

fast deprotonation, slow condensation



Condensation

Acid catalysed condensation

positively charged transition state, fastest condensation for
 $(\text{RO})_3\text{SiOH} > (\text{RO})_2\text{Si}(\text{OH})_2 > \text{ROSi}(\text{OH})_3 > \text{Si}(\text{OH})_4$

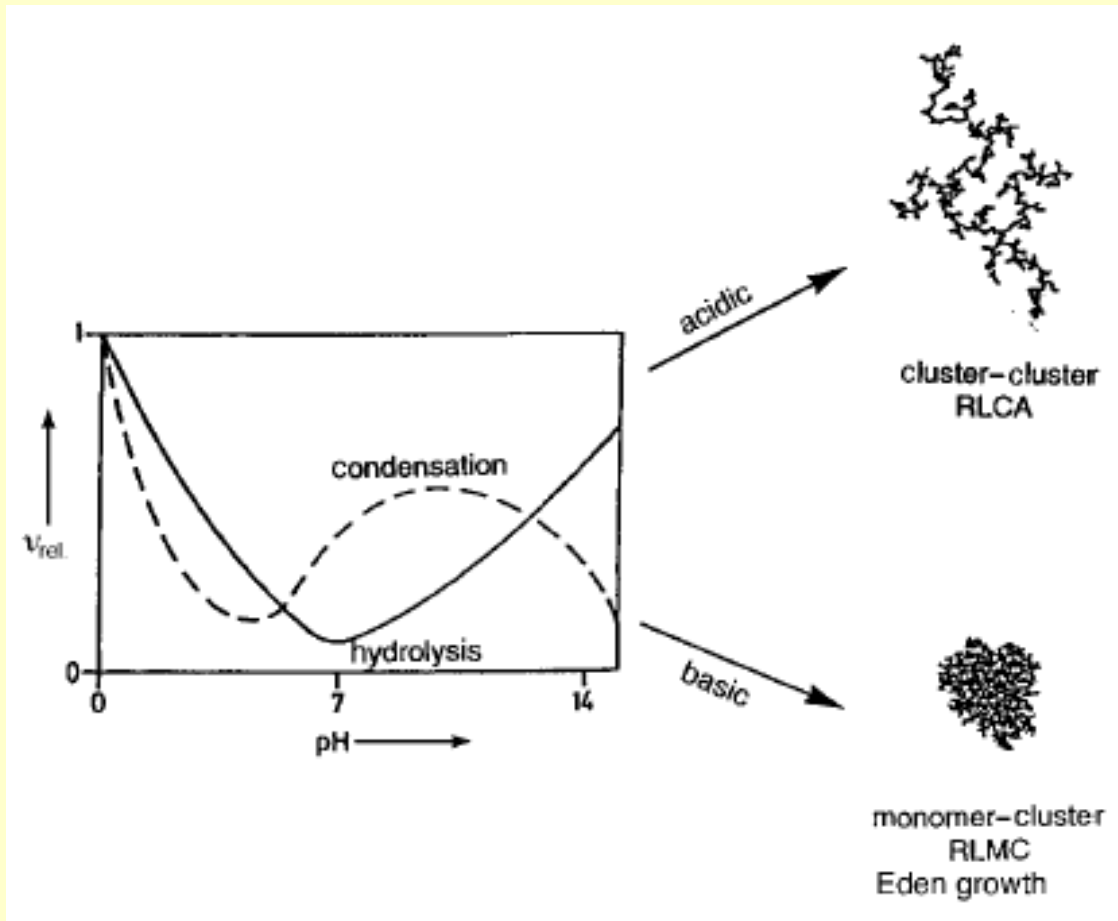
hydrolysis fastest in the first step, i.e. the formation of $(\text{RO})_3\text{SiOH}$
condensation for this species also fastest, the formation of linear chains

Base catalysed condensation

negatively charged transition state, fastest condensation for
 $(\text{RO})_3\text{SiOH} < (\text{RO})_2\text{Si}(\text{OH})_2 < \text{ROSi}(\text{OH})_3 < \text{Si}(\text{OH})_4$

hydrolysis speeds up with more OH, i.e. the formation of $\text{Si}(\text{OH})_4$
condensation for the fully hydrolysed species fastest, the formation
of highly crosslinked particles

Reaction limited cluster aggregation (RLCA)



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

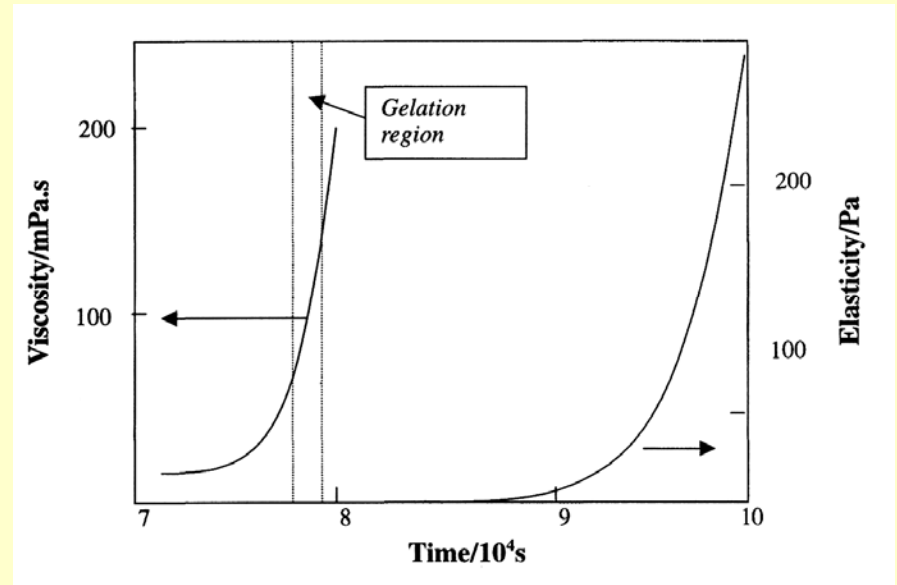
Gelation

Gelation

gel point - a spanning 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 than larger ones

Phase separation

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

Sol-Gel Methods

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 into the pores, surface tension creates large pressures, capillary stress, cracking

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

Sol-Gel Methods

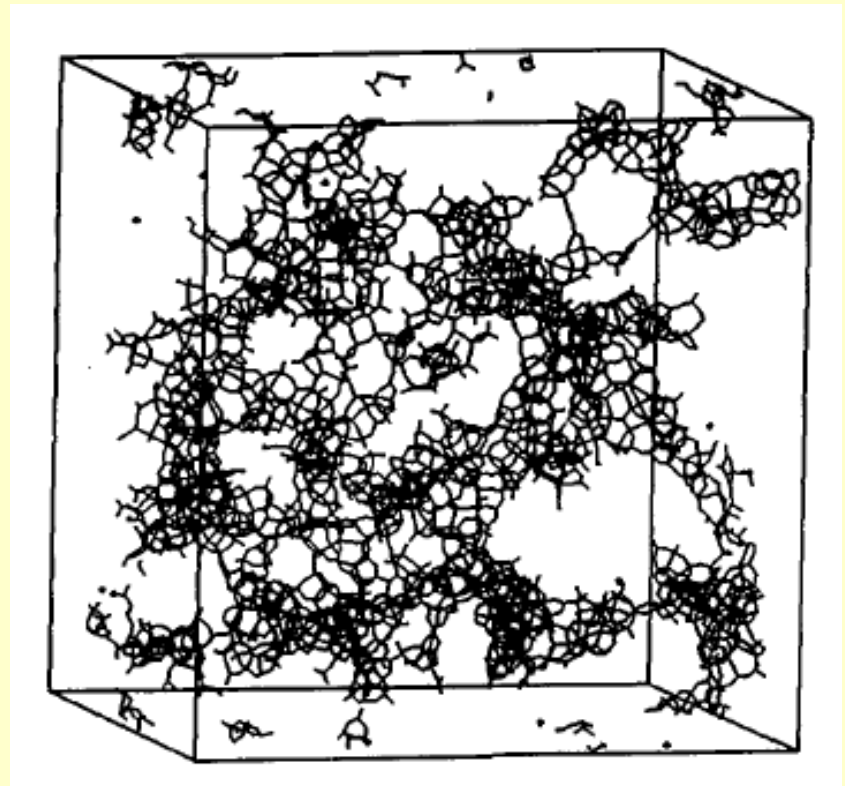
Drying methods

- 1. Supercritical drying**
- 2. Freeze-drying**
- 3. Drying control chemical additives**
- 4. Ageing**
- 5. Large pore gels**

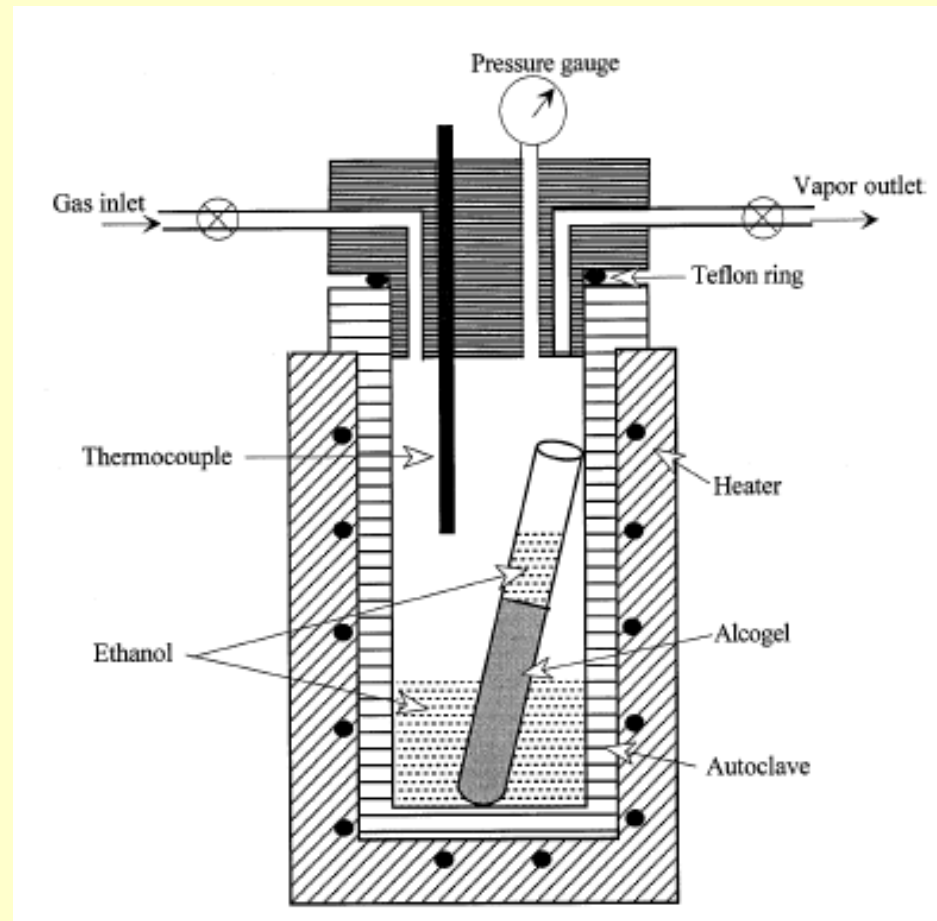
Aerogels

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

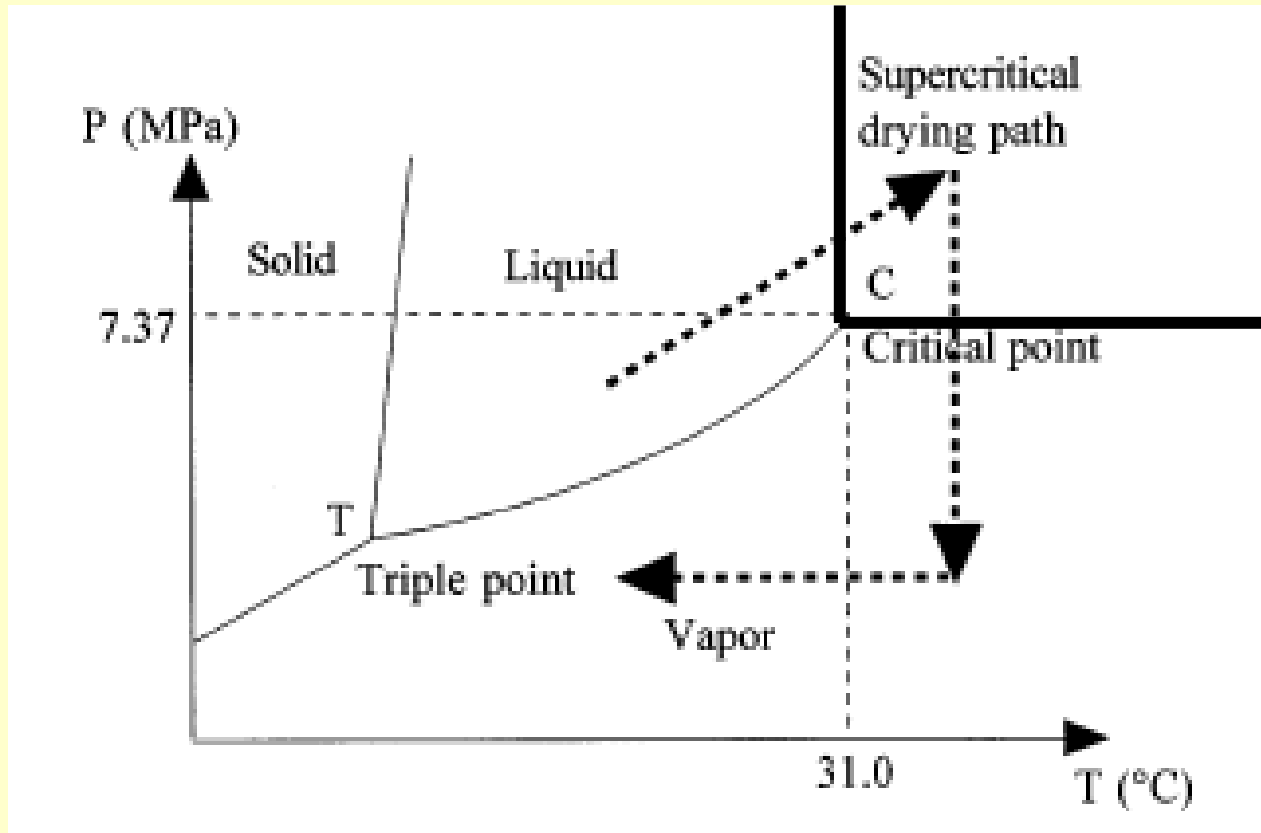
density is only three times that of air
200 kg/m³



Aerogels - Supercritical Drying



Supercritical Drying



Cold supercritical drying path in the Pressure (P) Temperature (T) phase diagram of CO₂

Supercritical Drying

fluid	formula	T_c (°C)	P_c (MPa)
water	H ₂ O	374.1	22.04
carbon dioxide	CO ₂	31.0	7.37
Freon 116	(CF ₃) ₂	19.7	2.97
acetone	(CH ₃) ₂ O	235.0	4.66
nitrous oxide	N ₂ O	36.4	7.24
methanol	CH ₃ OH	239.4	8.09
ethanol	C ₂ H ₅ OH	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 ₂ O	374	22.1	56
CO ₂	31	7.3	94
N ₂ O	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

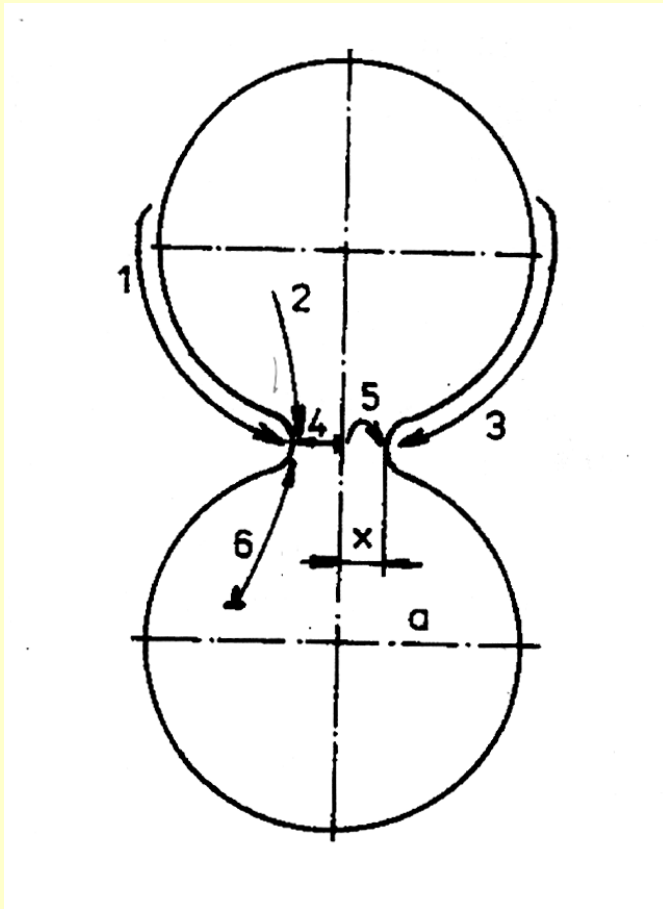
Stage III. Above 500 °C, no more weight loss, shrinkage only

close to glass transition temperature, viscous flow, rapid densification,

large reduction of surface area, reduction of interfacial energy,

thermodynamically favored

Sintering mechanisms



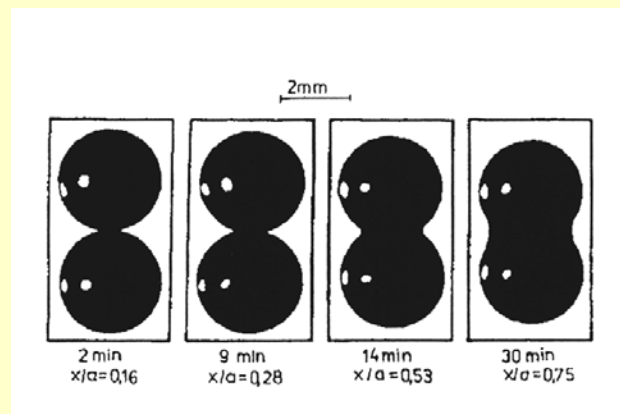
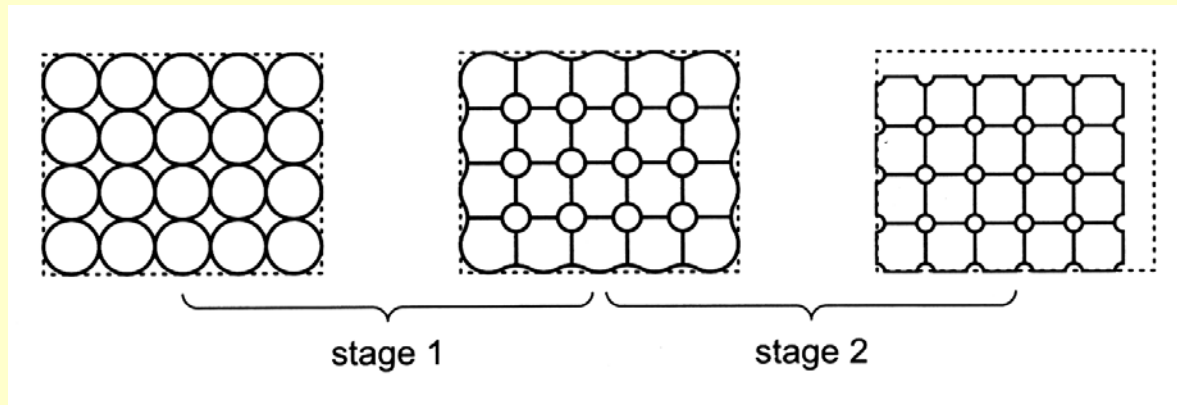
Sintering mechanisms

solid, liquid, gas phase

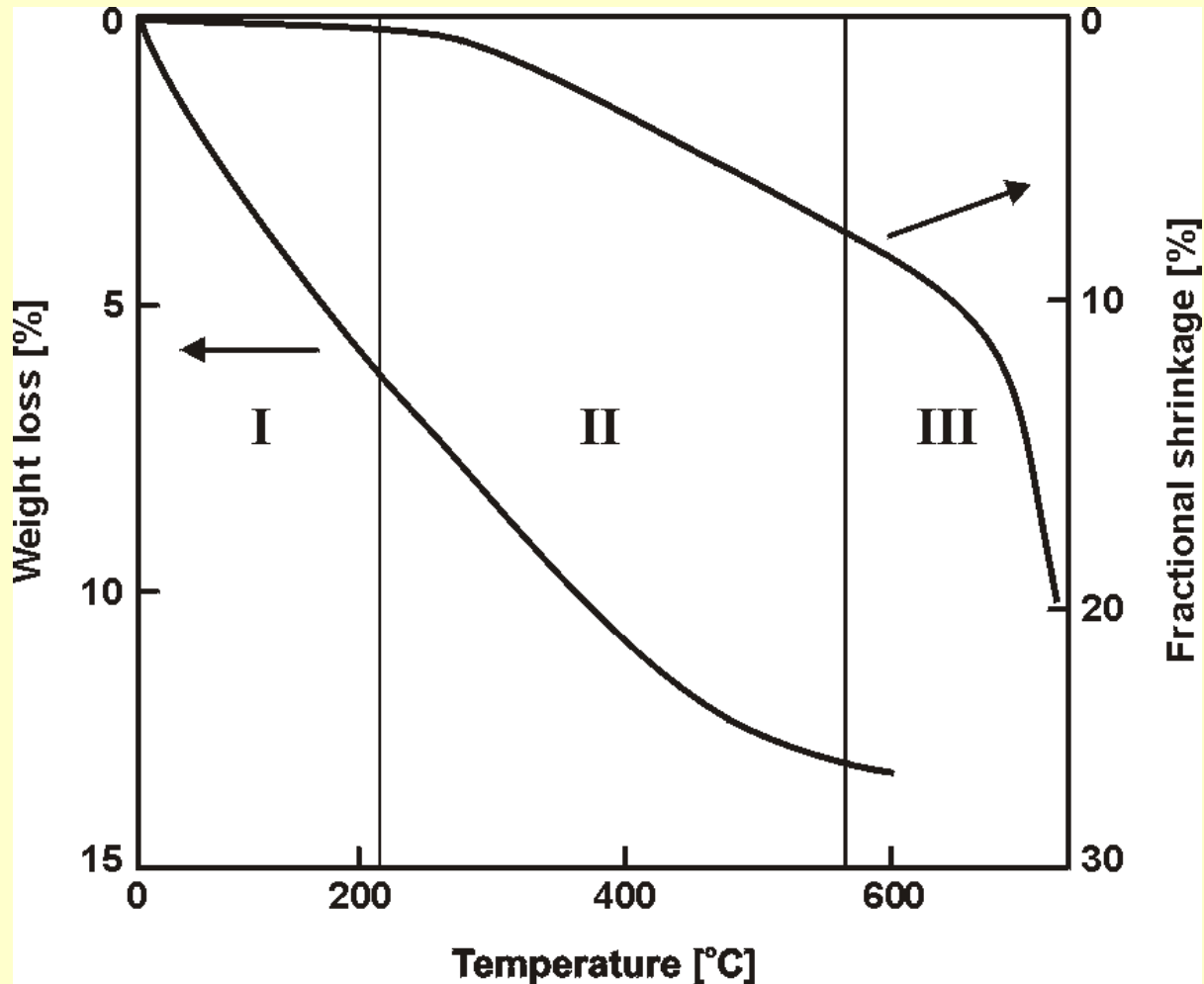
1. Evaporation-condensation and dissolution-precipitation
2. Volume diffusion
3. Surface diffusion
4. Grain boundary diffusion
5. Volume diffusion from grain boundaries
6. Volume diffusion from dislocations, vacancies

Densification

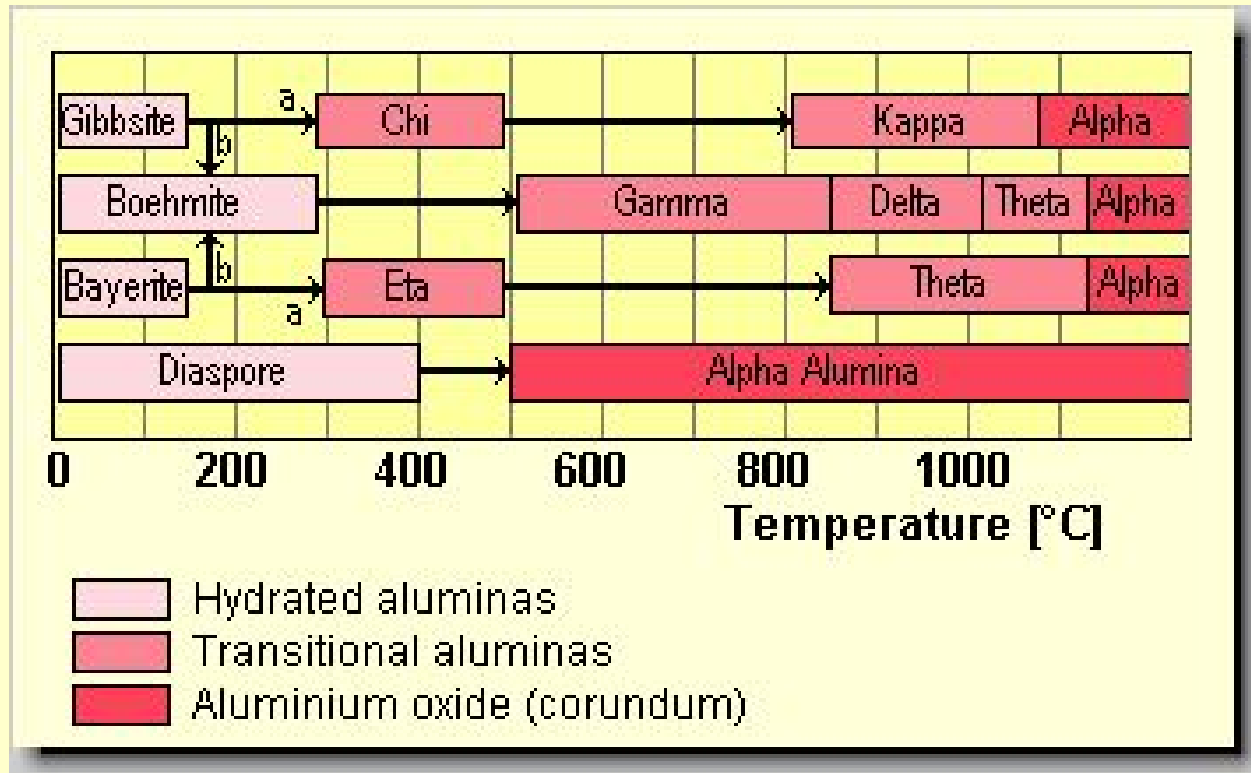
Densification



Densification



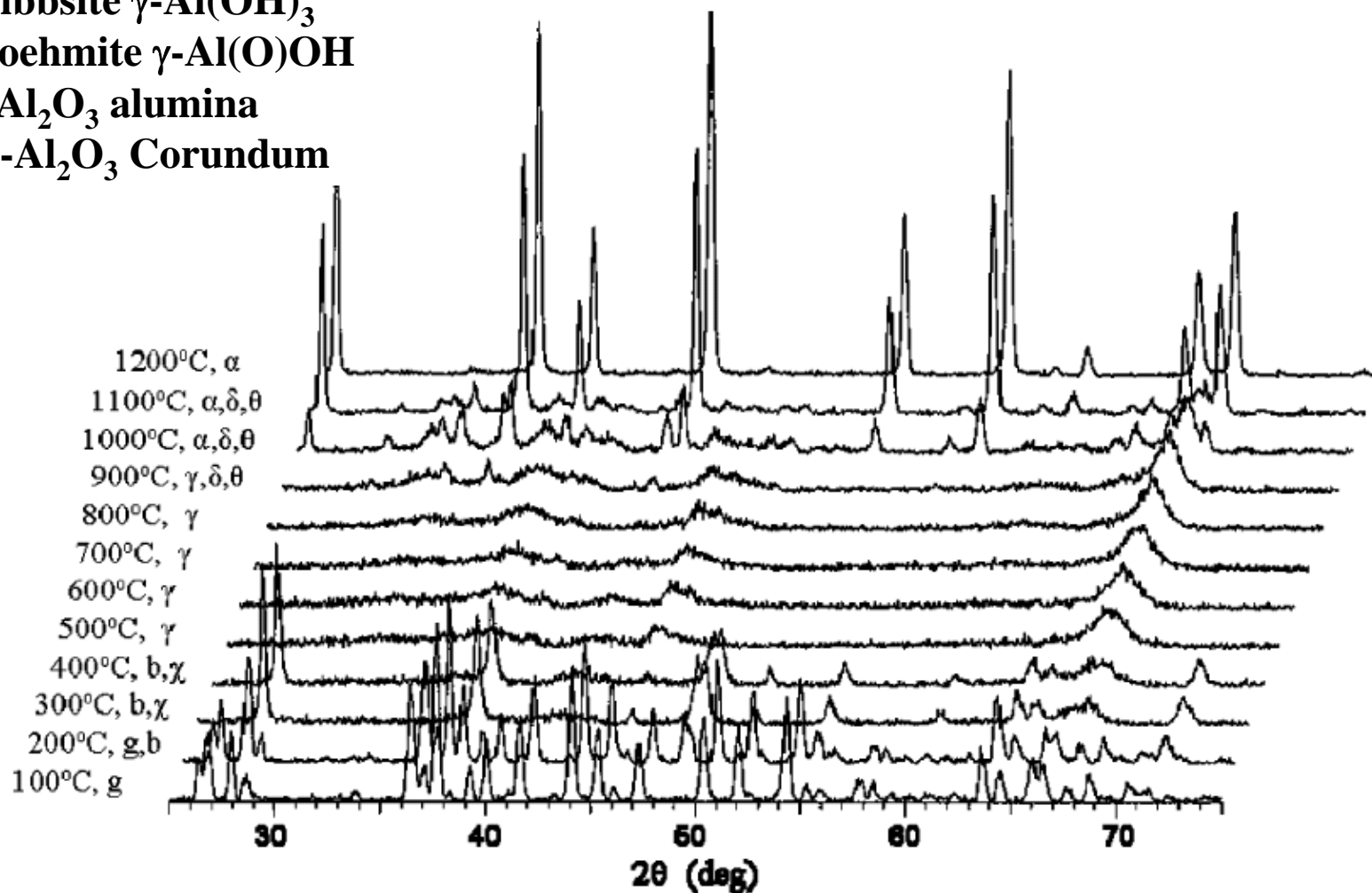
Dehydration sequence of hydrated alumina in air



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

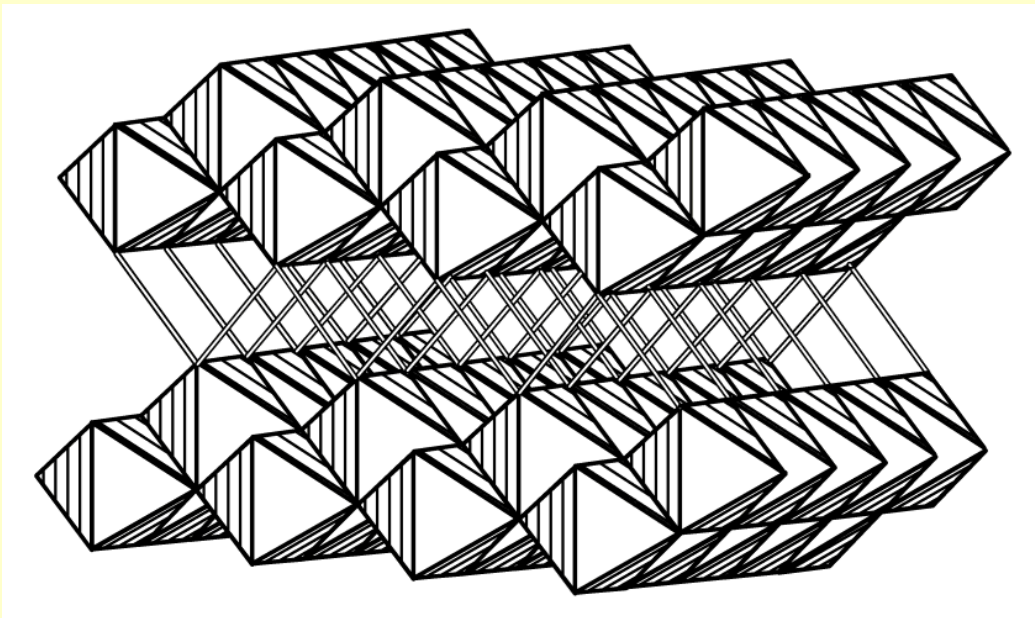
HT-XRD of the phase transitions

g = Gibbsite $\gamma\text{-Al}(\text{OH})_3$
b = Boehmite $\gamma\text{-Al}(\text{O})\text{OH}$
 γ = $\gamma\text{-Al}_2\text{O}_3$ alumina
 α = $\alpha\text{-Al}_2\text{O}_3$ Corundum

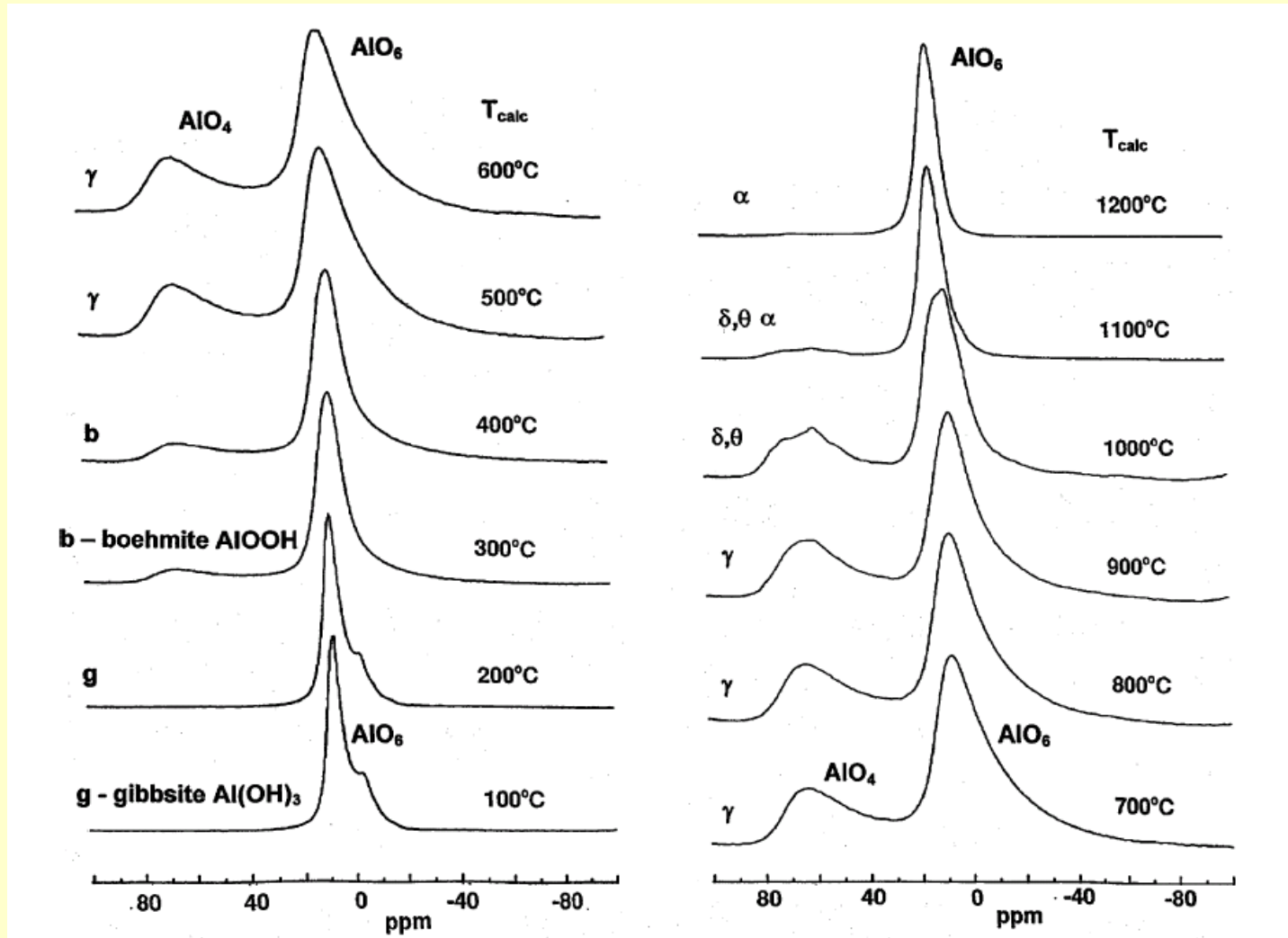


Gibbsite to Boehmite to Gamma

Gibbsite $\gamma\text{-Al(OH)}_3$ to Boehmite $\gamma\text{-Al(O)OH}$ to $\gamma\text{-Al}_2\text{O}_3$ alumina (defect spinel) CCP



^{27}Al Solid-State NMR spectra



Bayerite to Diaspore to Corundum

Bayerite $\alpha\text{-Al}(\text{OH})_3$ to Diaspore $\alpha\text{-Al}(\text{O})\text{OH}$ to $\alpha\text{-Al}_2\text{O}_3$ Corundum HCP

