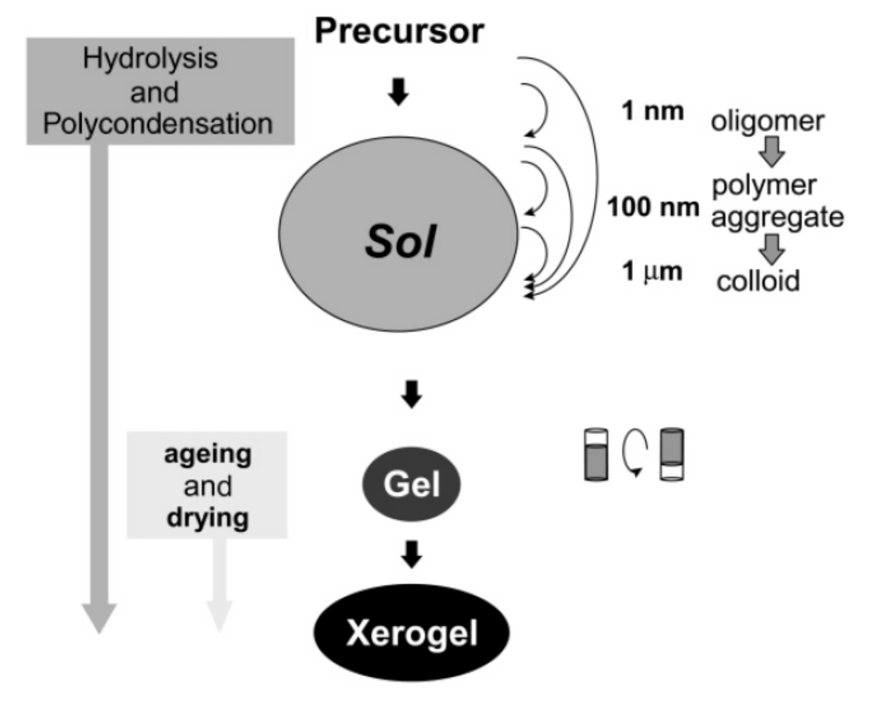
Sol-Gel Methods

PRECURSOR

Sol-gel process

- **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

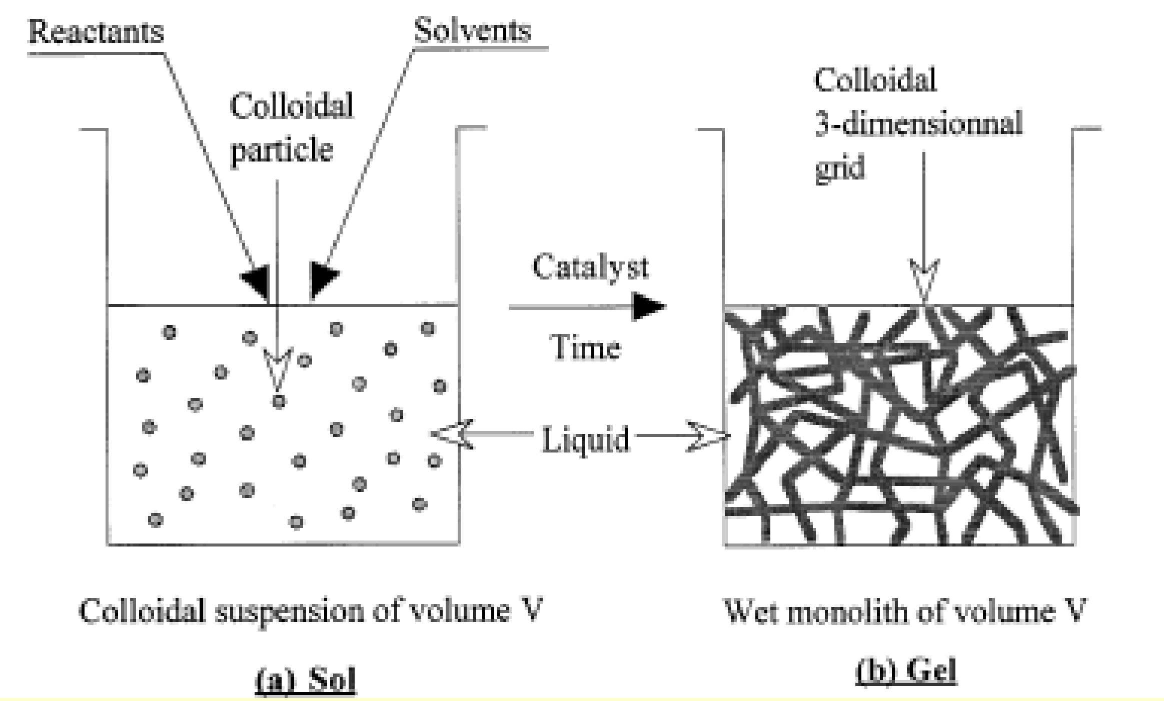
Colloidal (particulate) gels = agglomeration of dense colloidal particles

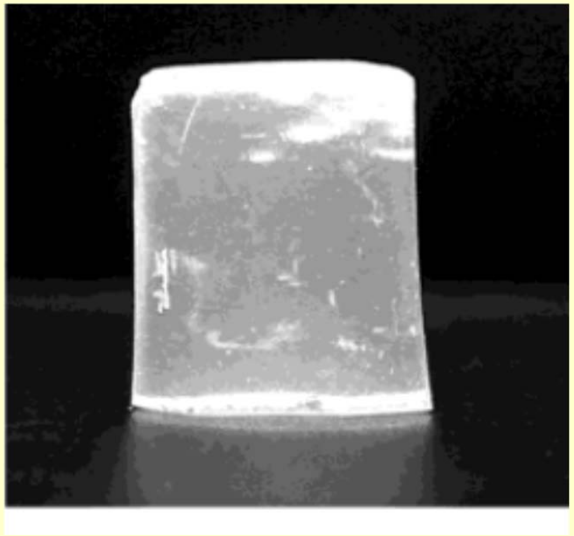
Polymeric gels = agglomeration of polymeric particles made from subcolloidal units

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



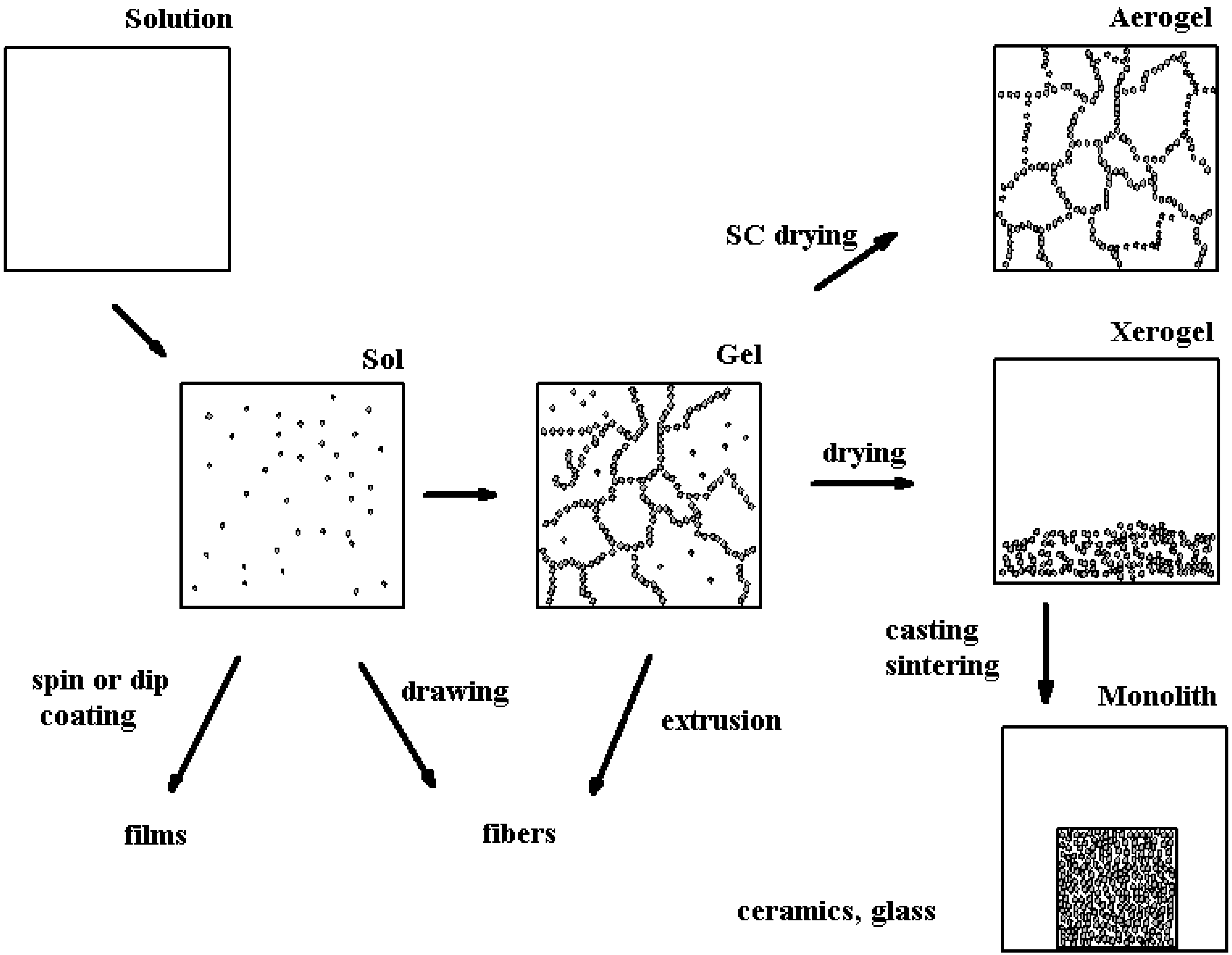


Gel point = point of incipient network formation

Sol-to-Gel transition is difficult to define

Rheological methods = viscosity increases

Sol-Gel Process



Solution

Sol

Gel

SC drying

Aerogel

drying

Xerogel

casting
sintering

Monolith

spin or dip
coating

drawing

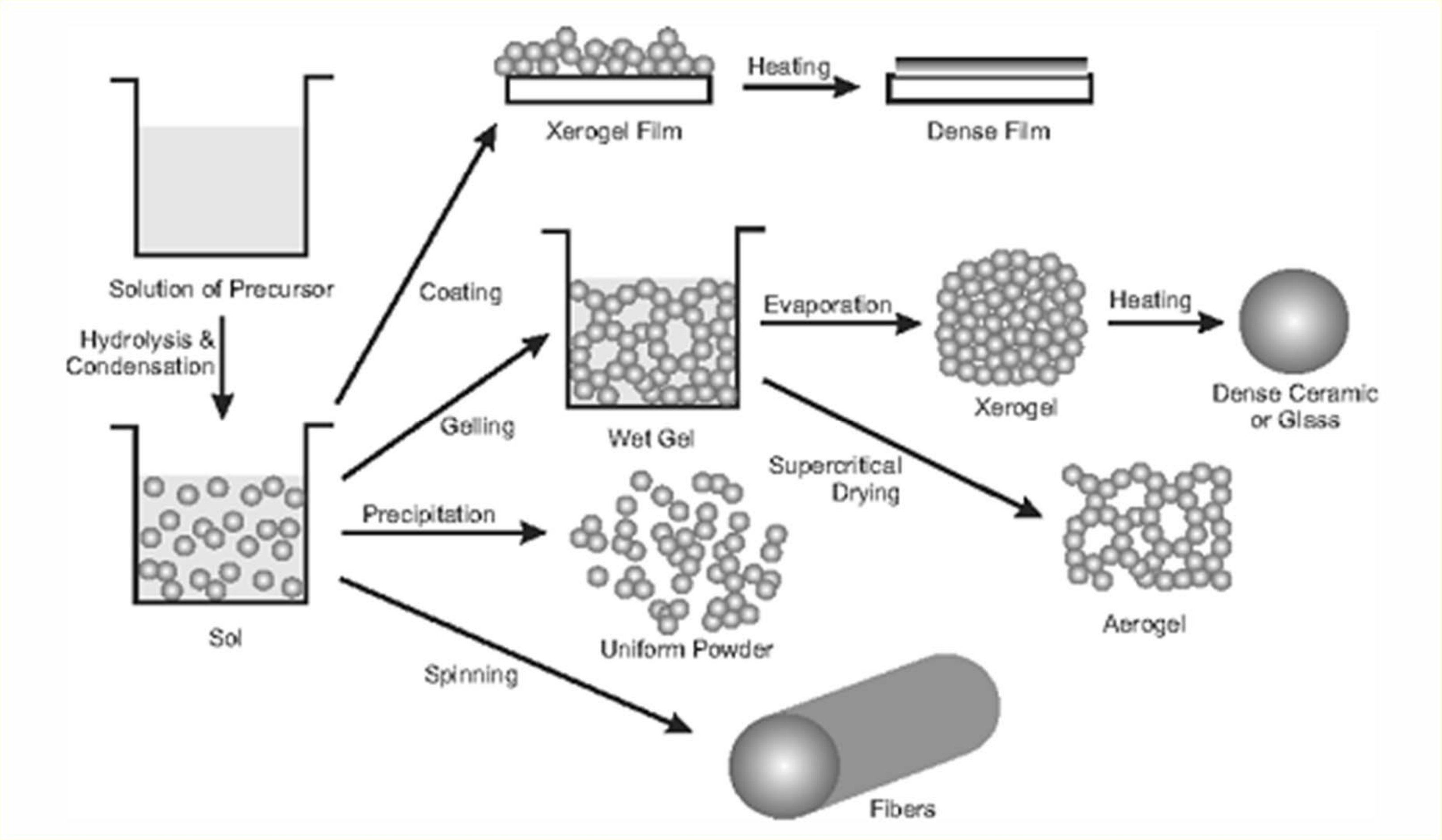
extrusion

films

fibers

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.

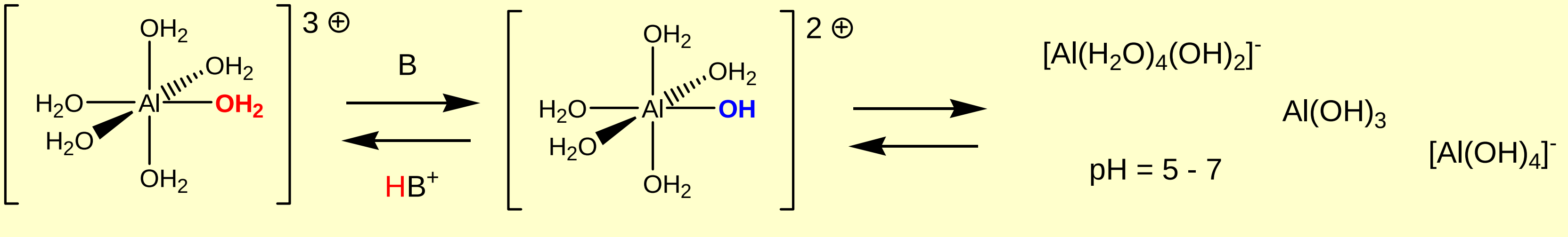
Hydrolysis

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

Condensation-polymerization

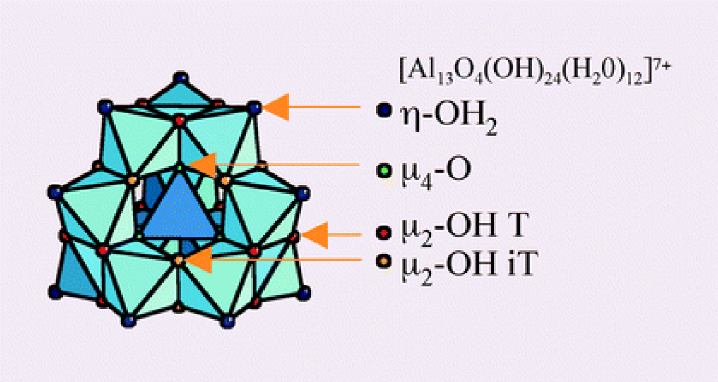
$$[M(H_2O)_b]^{Z+} \rightleftarrows [(H_2O)_{b-1}M(OH)_2M(H_2O)_{b-1}]^{(2Z-2)+} + 2H^+$$

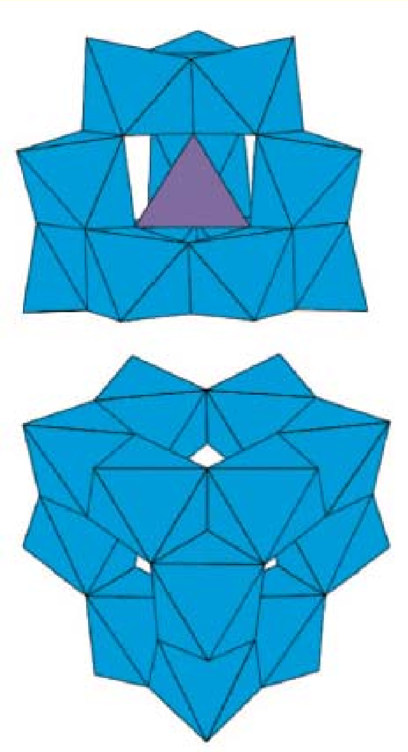
Colloid Route



pH < 3

pH = 4 - 5





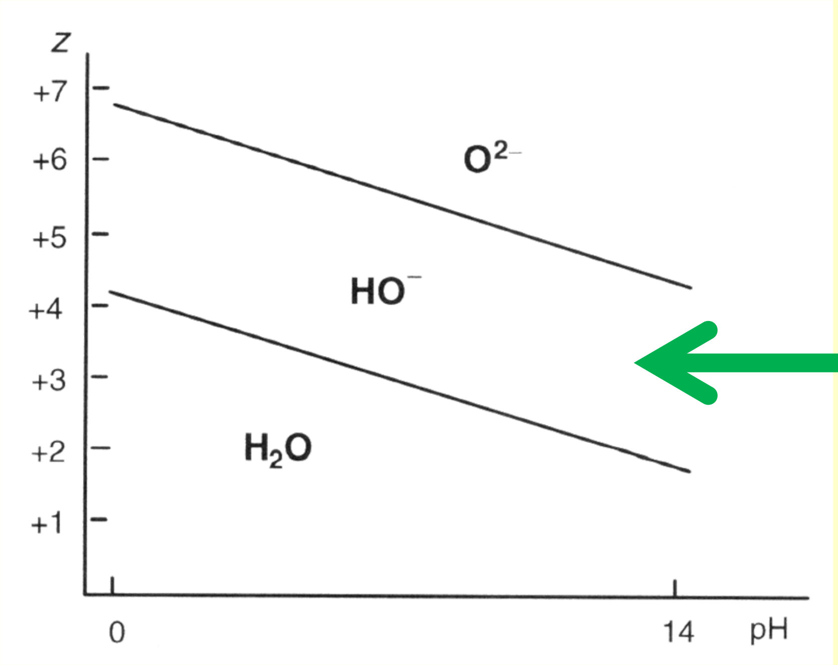
the Keggin cation $[Al_{13}O_4(OH)_{24}(OH_2)_{12}]^{7+}$

Colloid Route

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

$$[M(OH_2)]^{z+} \rightleftarrows [M\text{–}OH]^{(z-1)+} + H^+ \rightleftarrows [M{=}O]^{(z-2)+} + 2\,H^+$$

Aqua **Hydroxo** **Oxo**

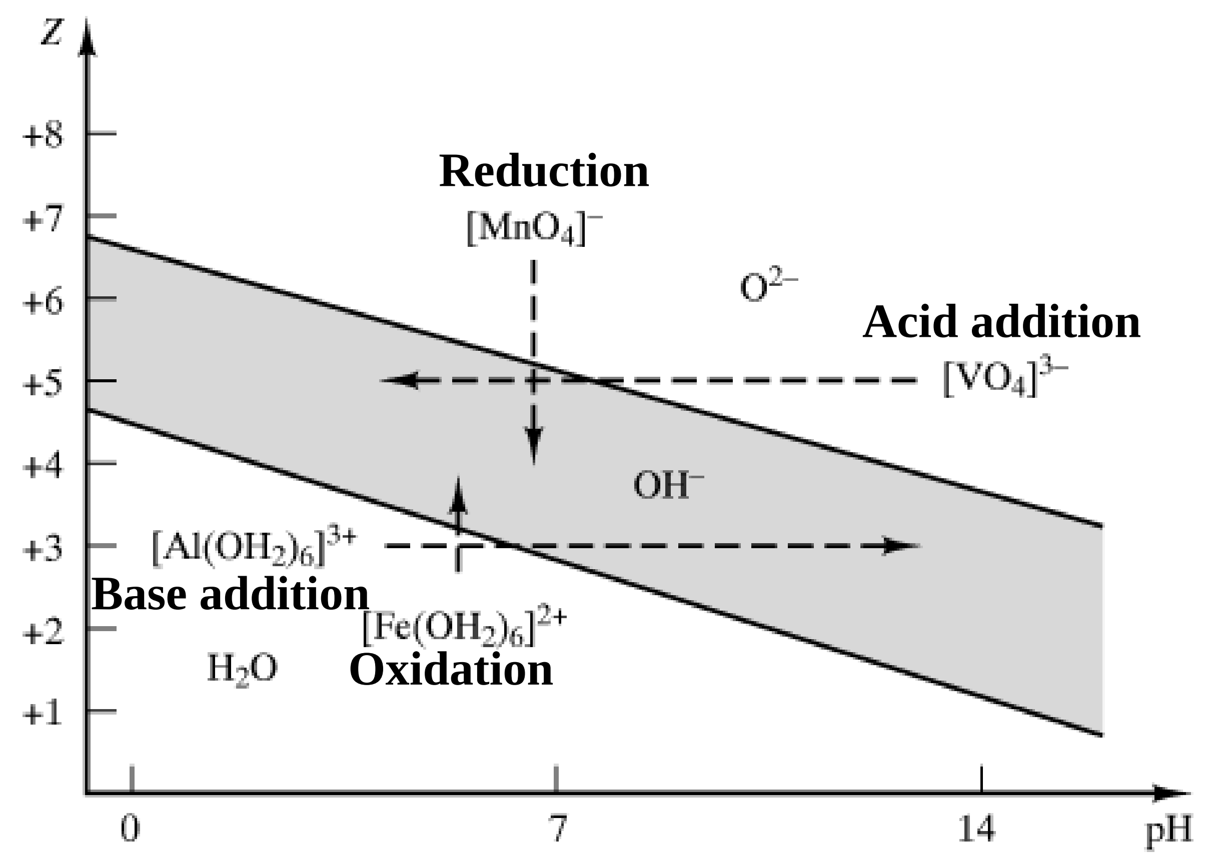


Only hydroxo can condense

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

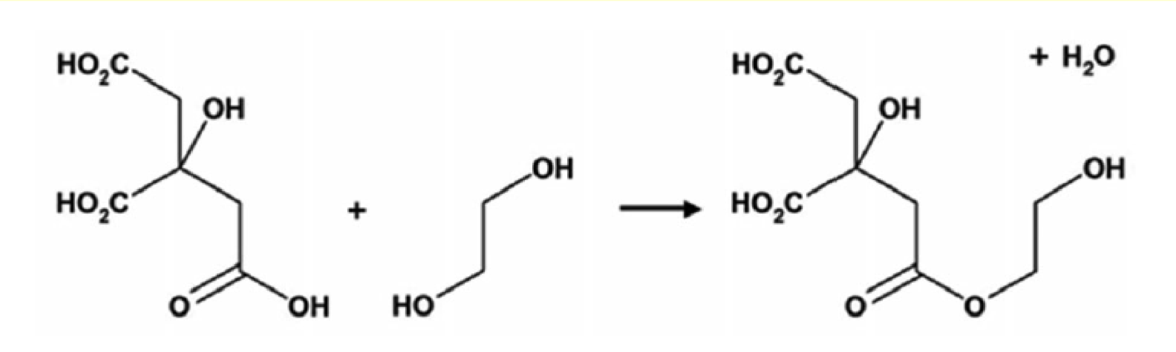
Colloid Route

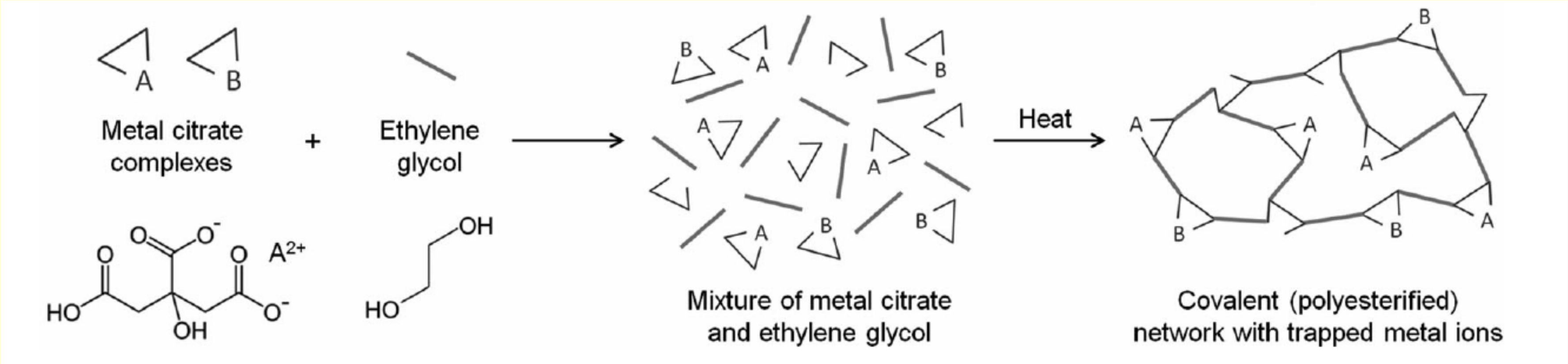
$Fe^{3+}(aq) + CO_3^{2-} \rightarrow ?$



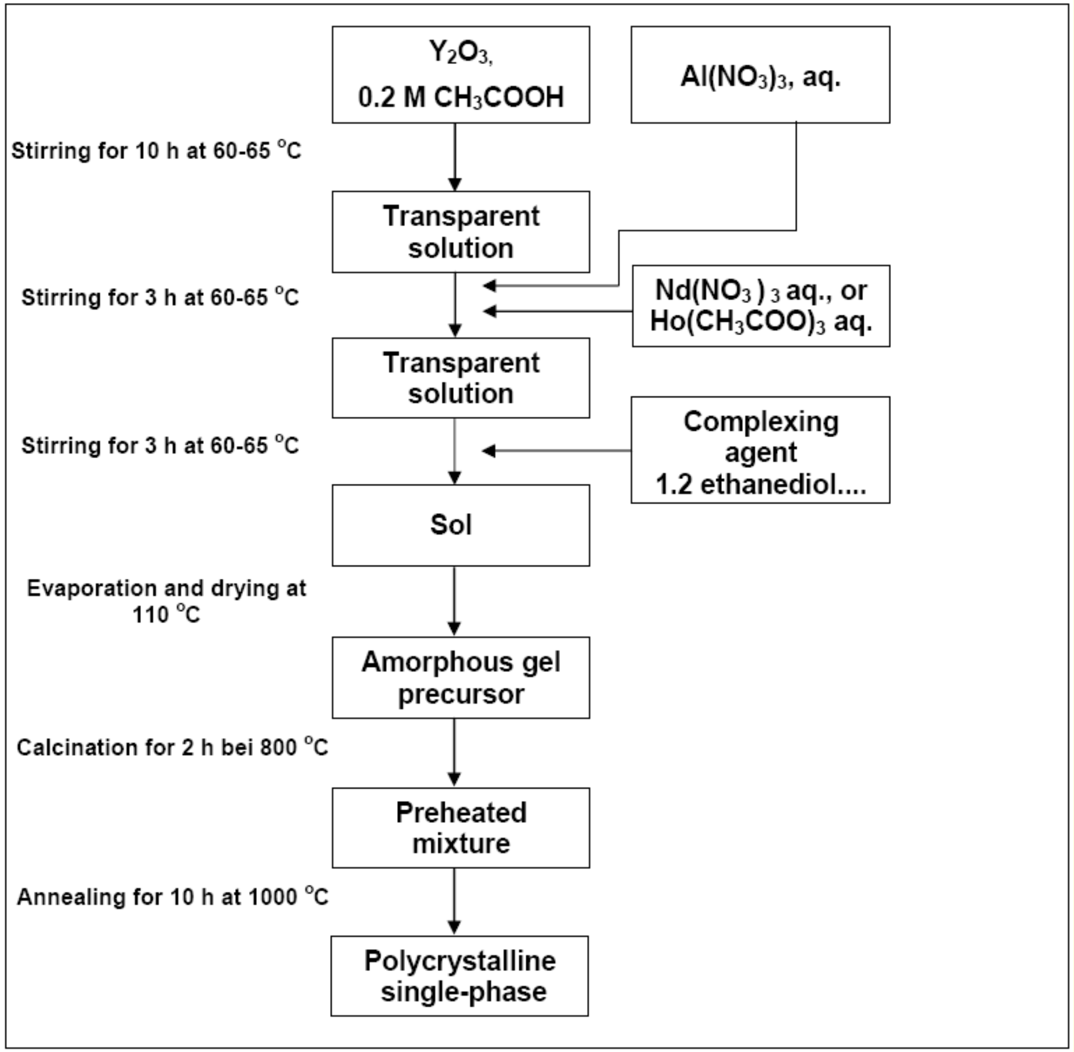
Pechini Sol-Gel Route

The transesterification reaction between citric acid and ethylene glycol





Pechini Sol-Gel Route



Major components

Dopants

Gelling agent

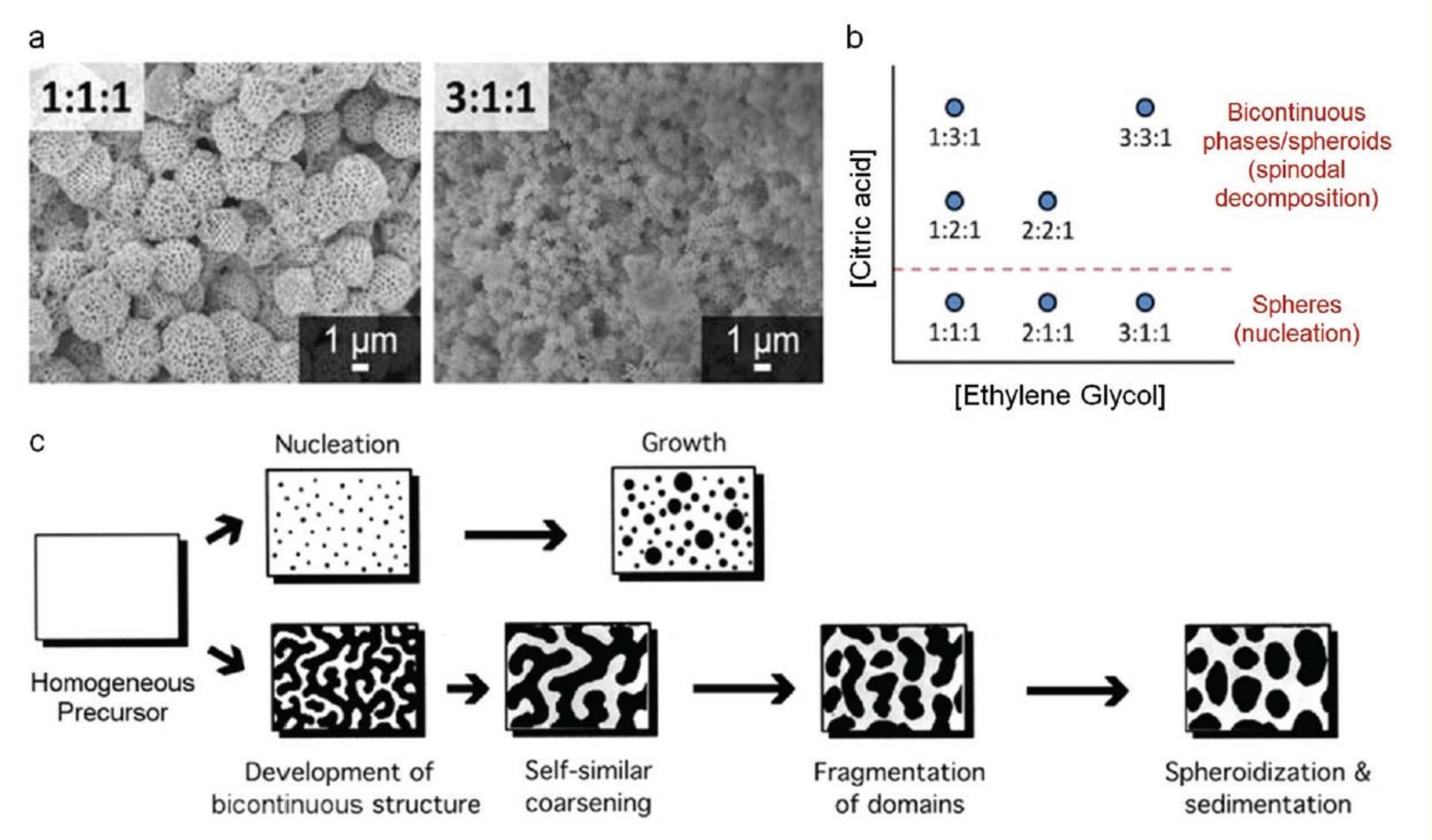
Removal of solvents

Removal of organics

Doped YAG product

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

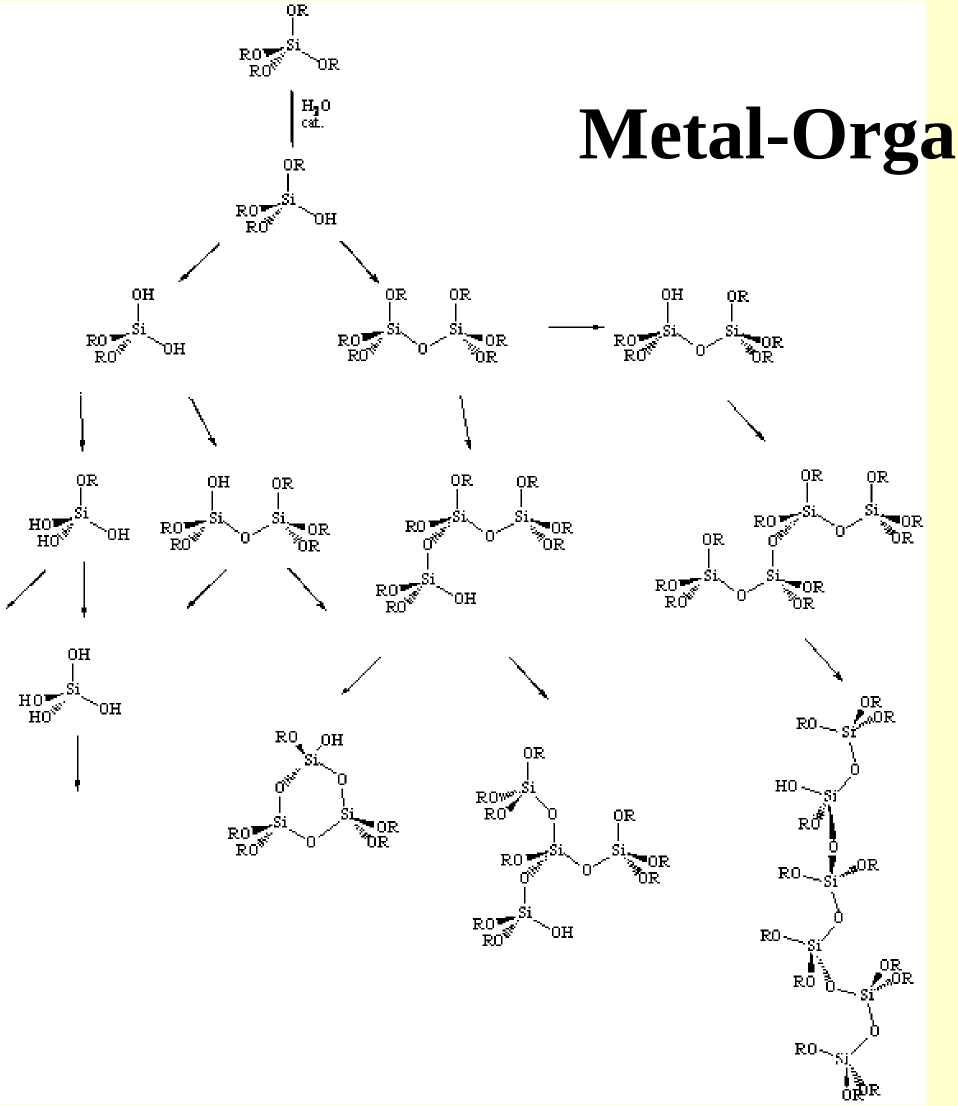
$[M(NR_2)_x]_n + H_2O \rightarrow R_2NH + M\text{-}O\text{-}H$

Polycondensation

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

OXIDE

Metal-Organic (Alkoxide) Route



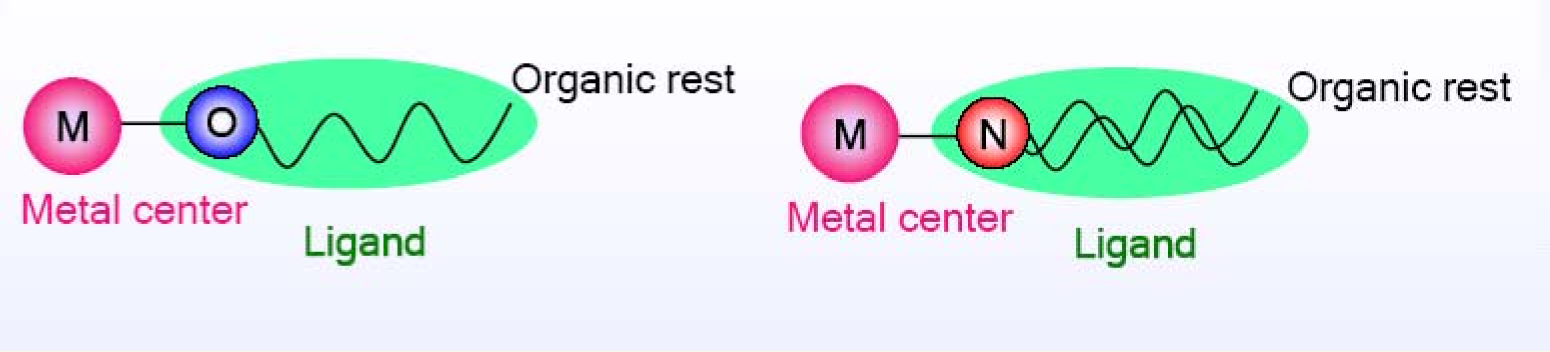
Oligomers formed by hydrolysis-condensation process

-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_2NH) through a metal atom

Metal Alkoxides and Amides as Precursors

Homometallic Alkoxides

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

Heterometallic Alkoxides

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

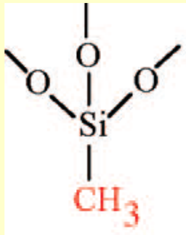
Metal Amides

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

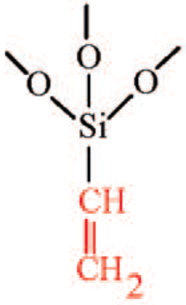
Silsesquioxanes = $RSiO_{1.5}$ (= 3/2)



Methyl

Hydrophobicity

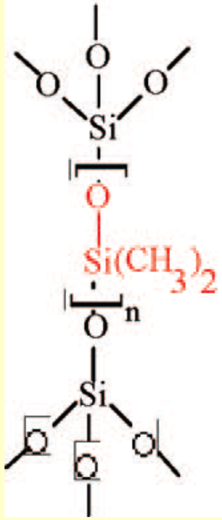
Terminal groups



Vinyl

Crosslinking with acrylic

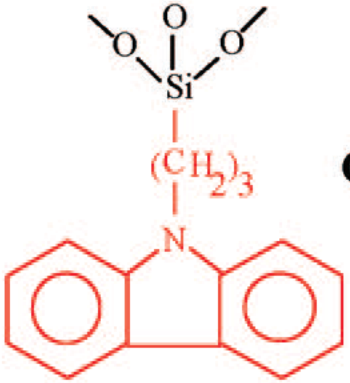
Polymerizable groups



Polydimethylsiloxane

Rubbery behavior

Bridging groups

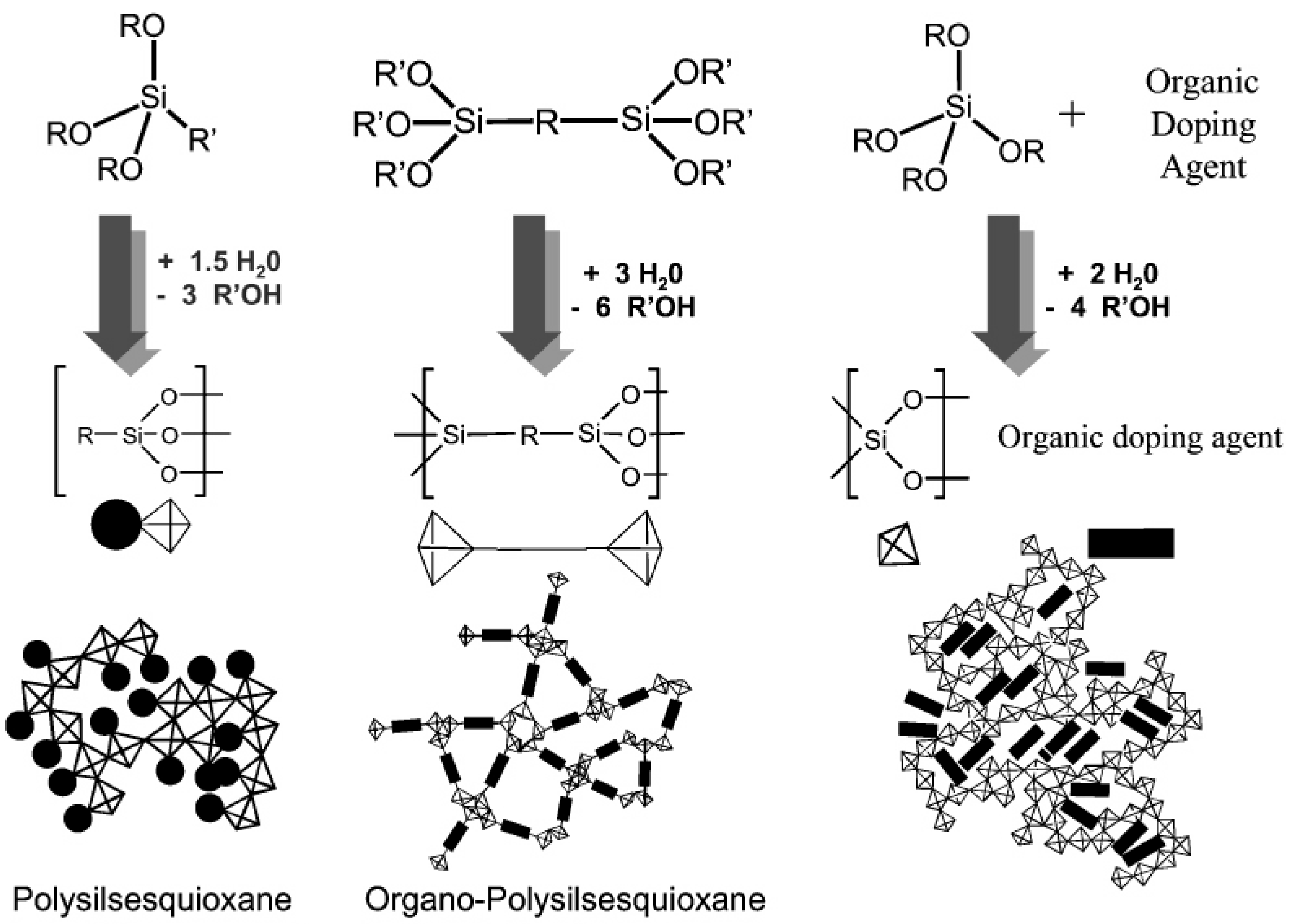


Carbazole

Charge transport properties

Functional groups

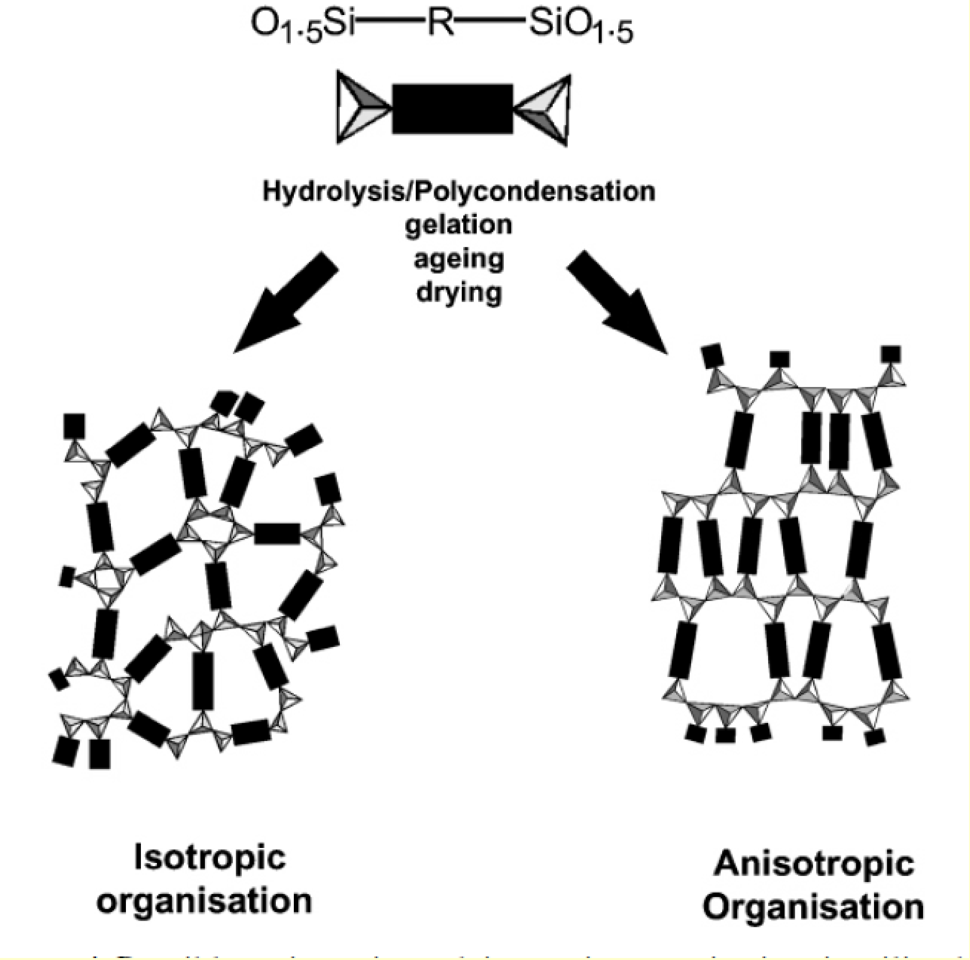
Hybrid Inorganic-Organic Materials



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

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

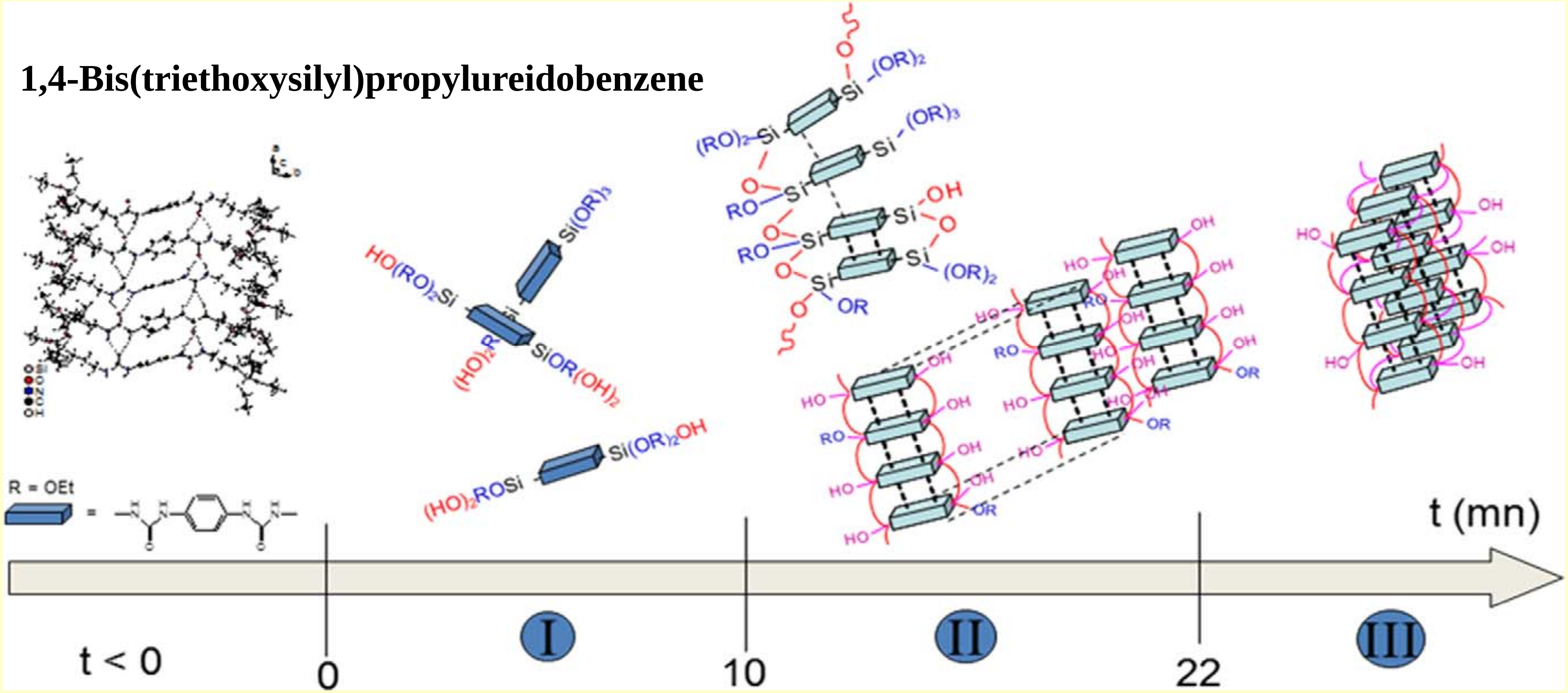
Organization in Xerogels of Bridged Silicon Alkoxide Precursors



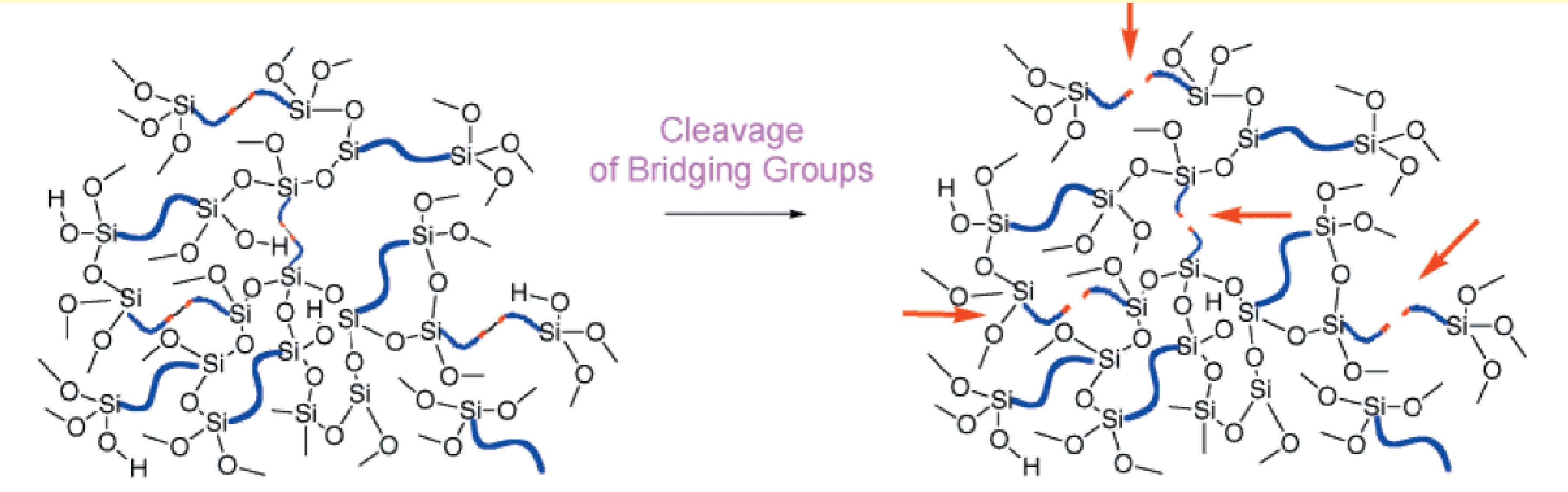
Self-Assembly of Bridged Silsesquioxanes

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

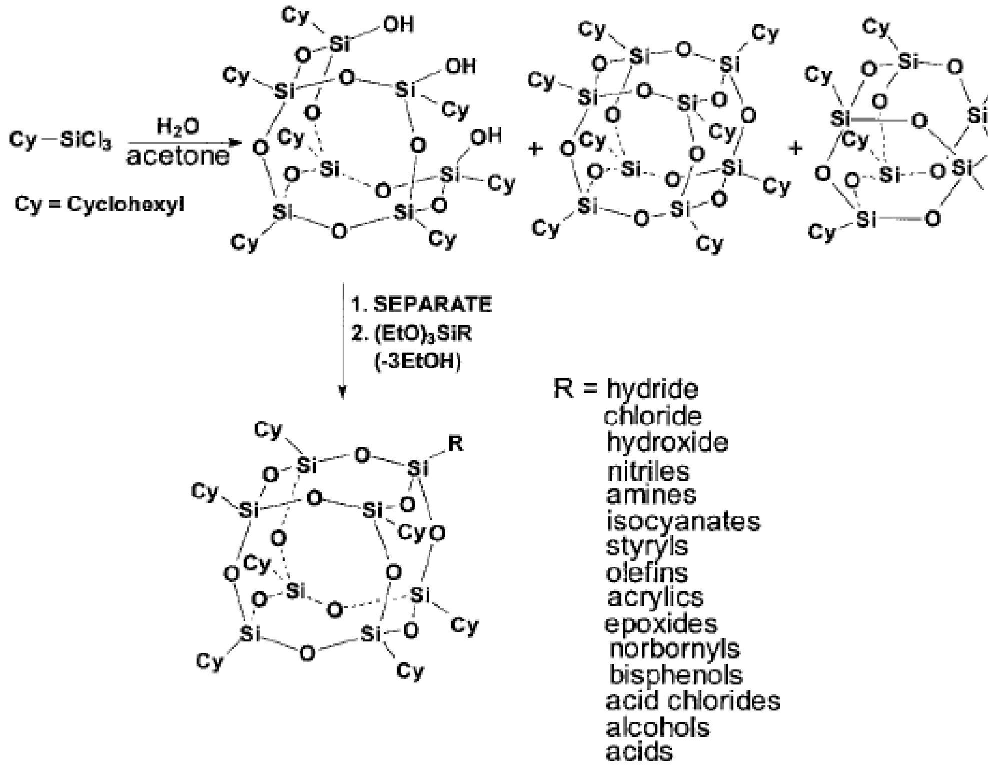
1,4-Bis(triethoxysilyl)propylureidobenzene

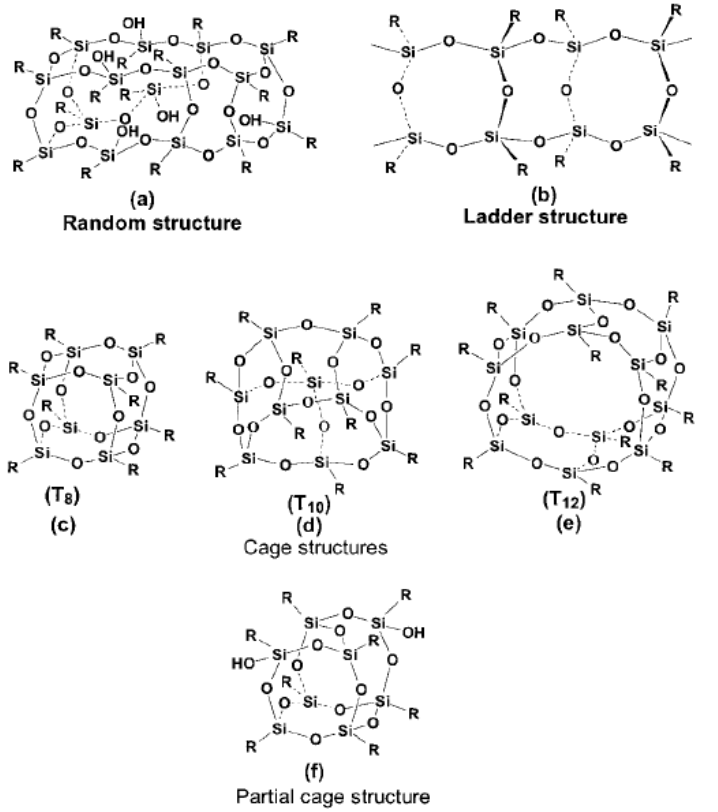


Templating Porosity in Bridged Polysilsesquioxanes

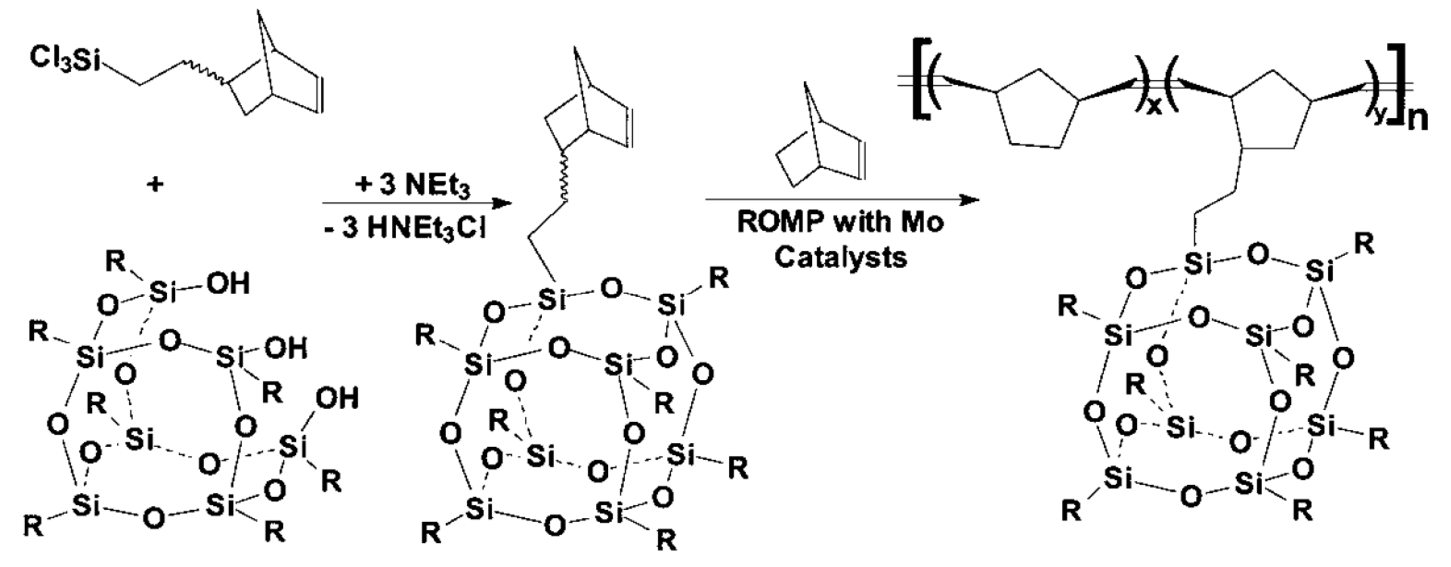


Polyhedral Oligomeric Silsesquioxanes (POSS)

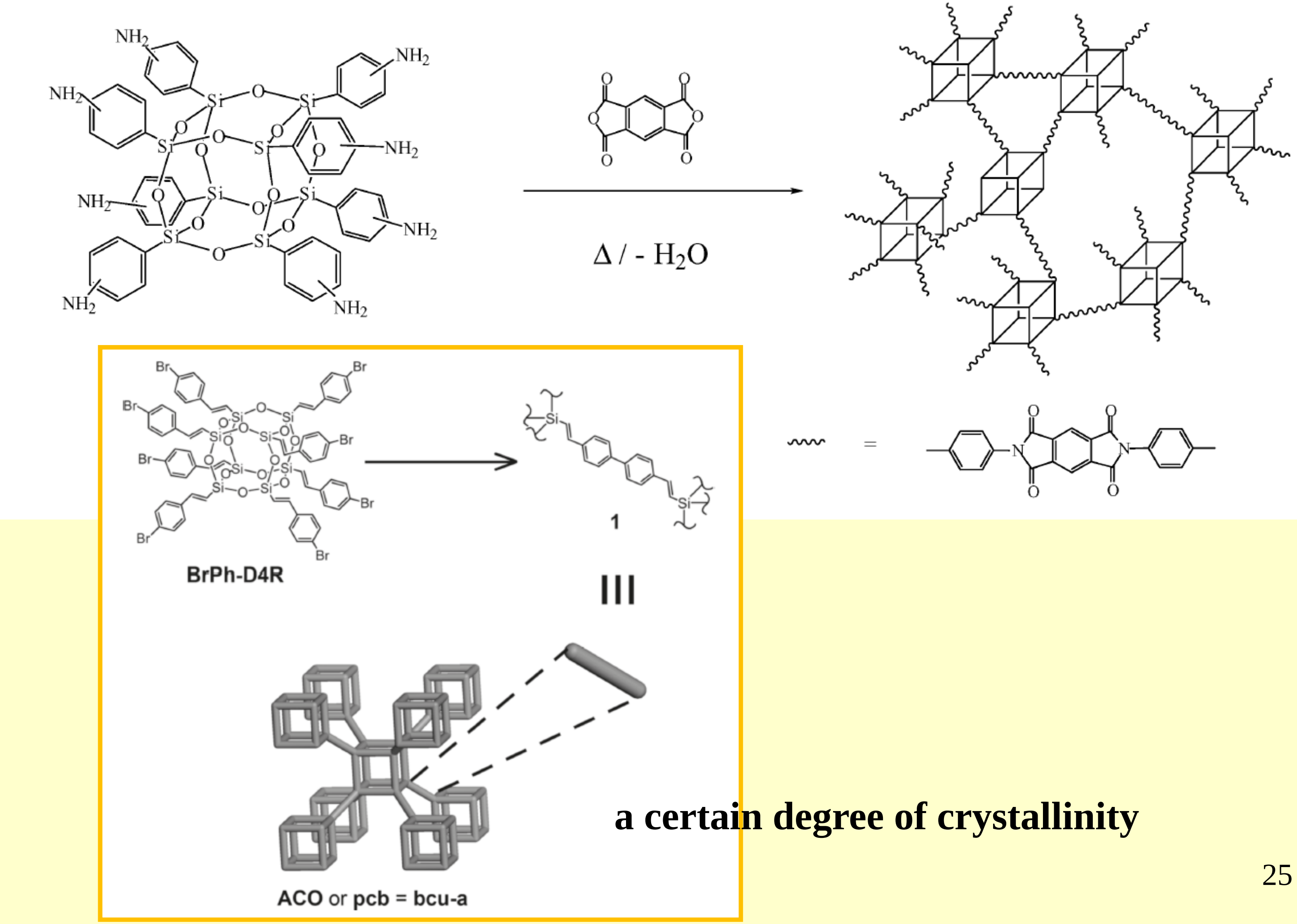




Polymers and Copolymers of POSS

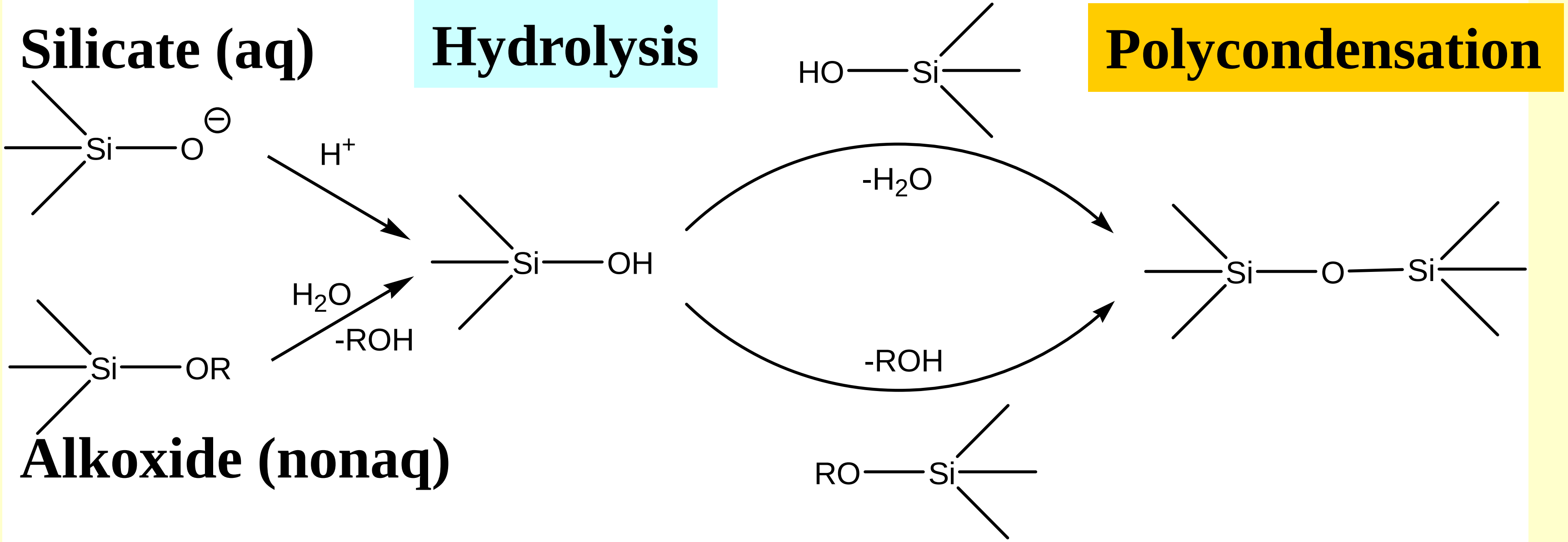


Polymers and Copolymers of POSS



a certain degree of crystallinity

Sol-Gel in Silica Systems


Silicate (aq)

Hydrolysis

Polycondensation

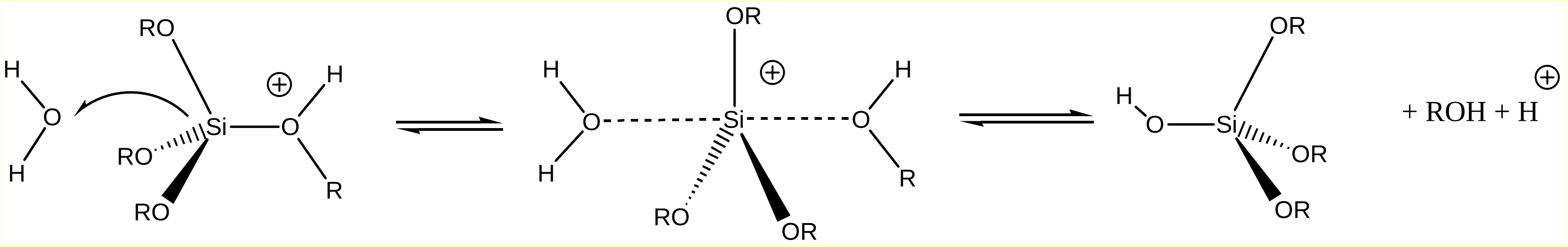
Alkoxide (nonaq)

Metal-Oragnic (Alkoxide) Route

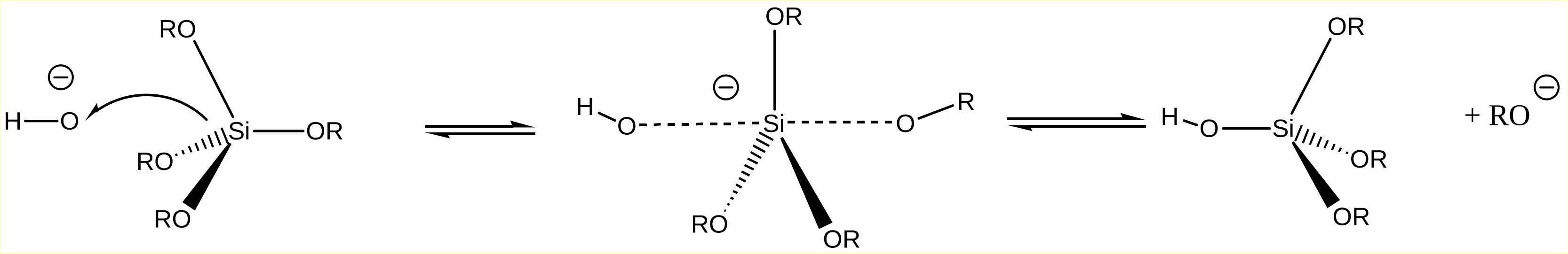
- **Metal-organic Route**

metal alkoxide in alcoholic solution, water addition

Acid catalysed hydrolysis



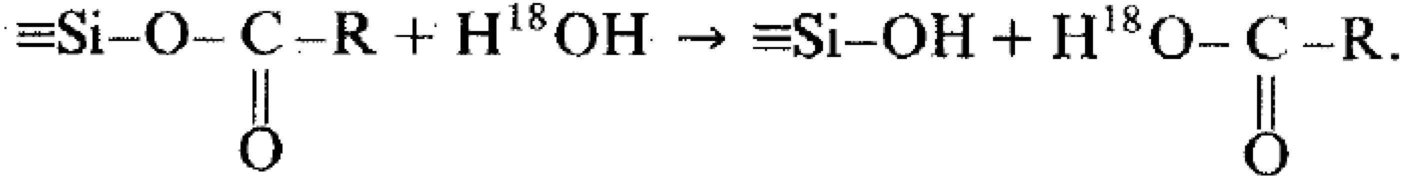
Base catalysed hydrolysis



Metal-Oragnic (Alkoxide) Route

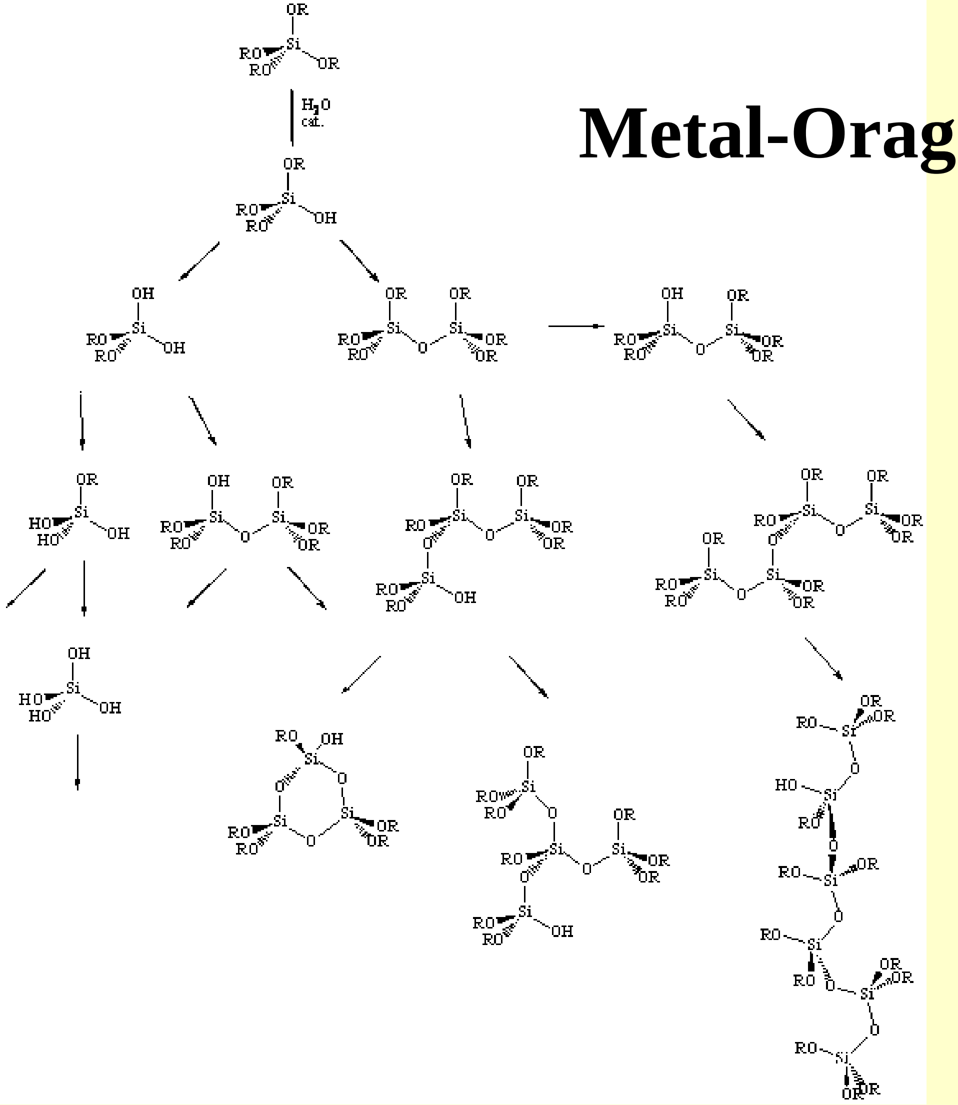
Isotope labelling experiments

$$\equiv\mathrm{Si{-}OR} + \mathrm{H^{18}OH} \rightarrow \equiv\mathrm{Si{-}^{18}OH} + \mathrm{HOR}.$$



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

Metal-Oragnic (Alkoxide) Route



Oligomers formed by hydrolysis-condensation process

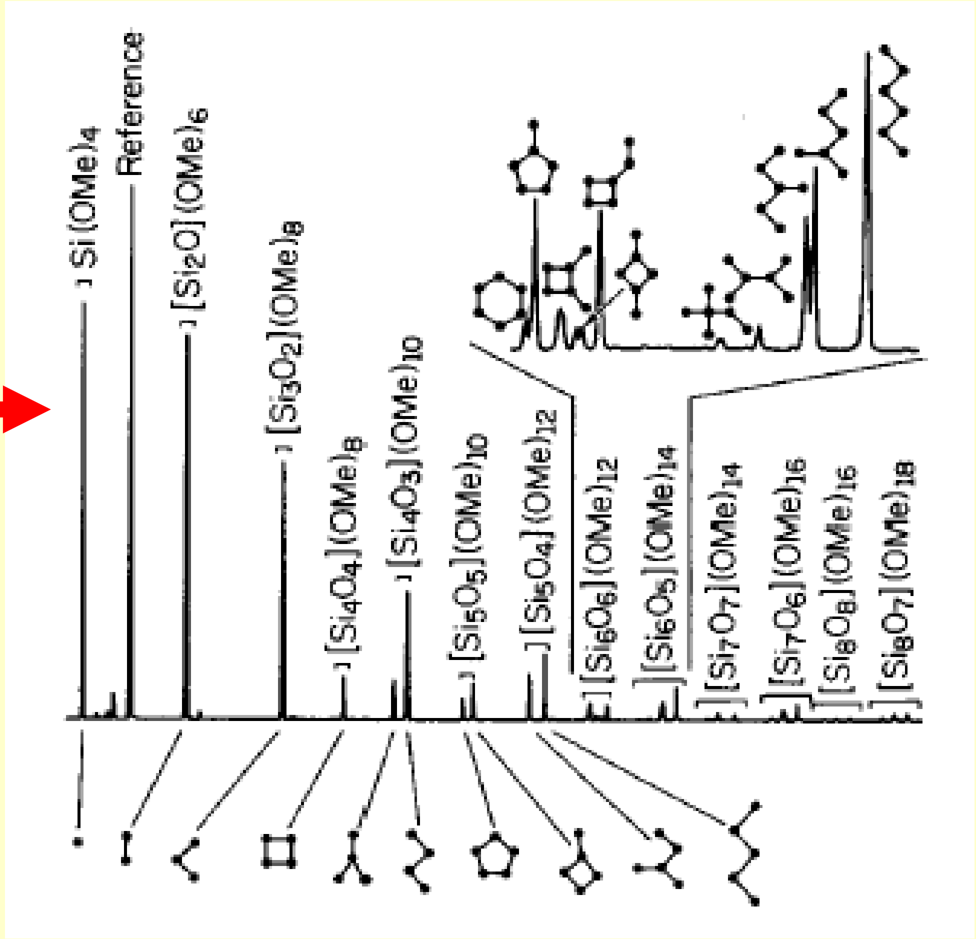
-linear
-branched
-cyclic
-polyhedral

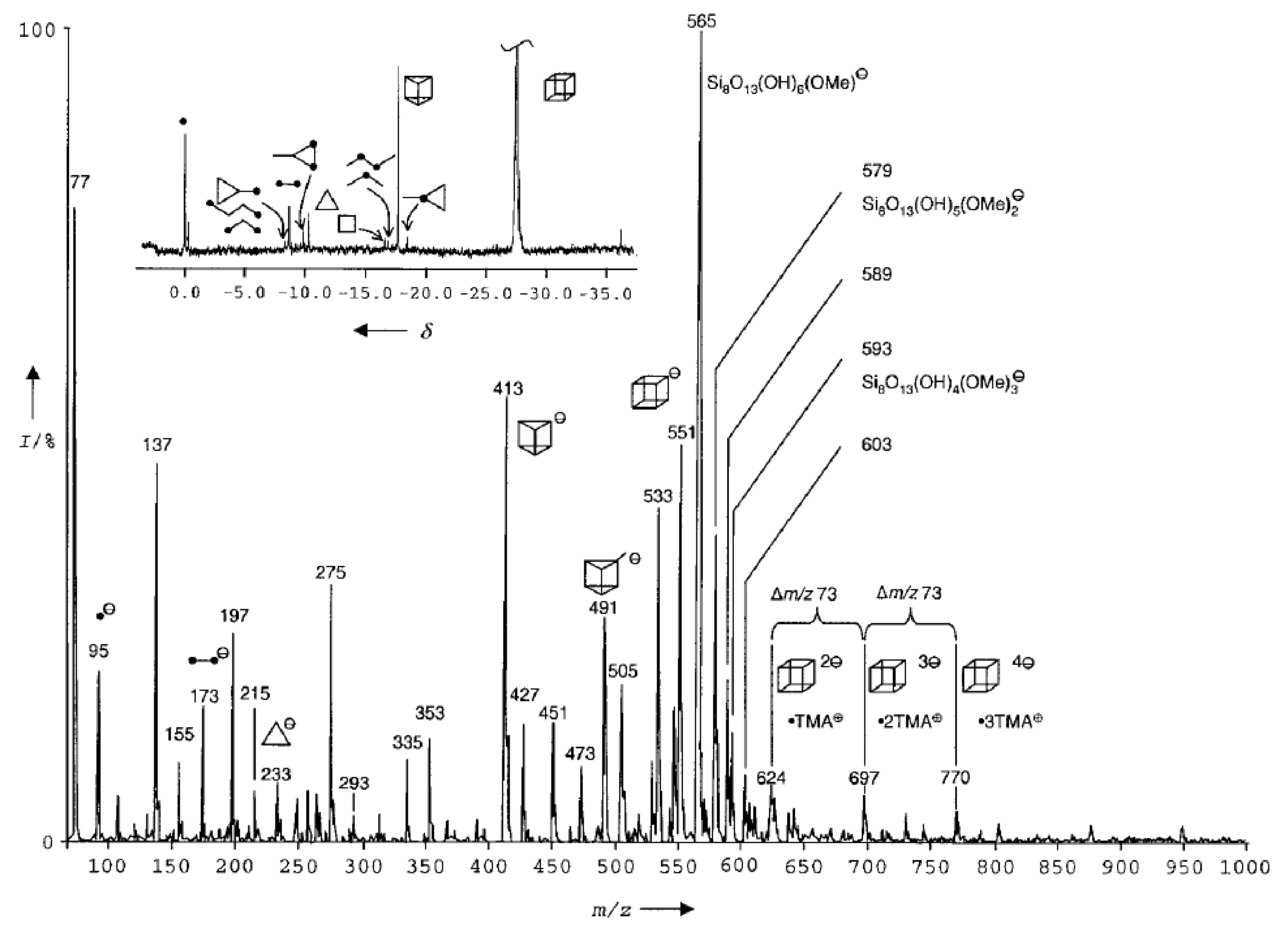
Never goes to pure SiO_2

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

GC of TMOS hydrolysis products

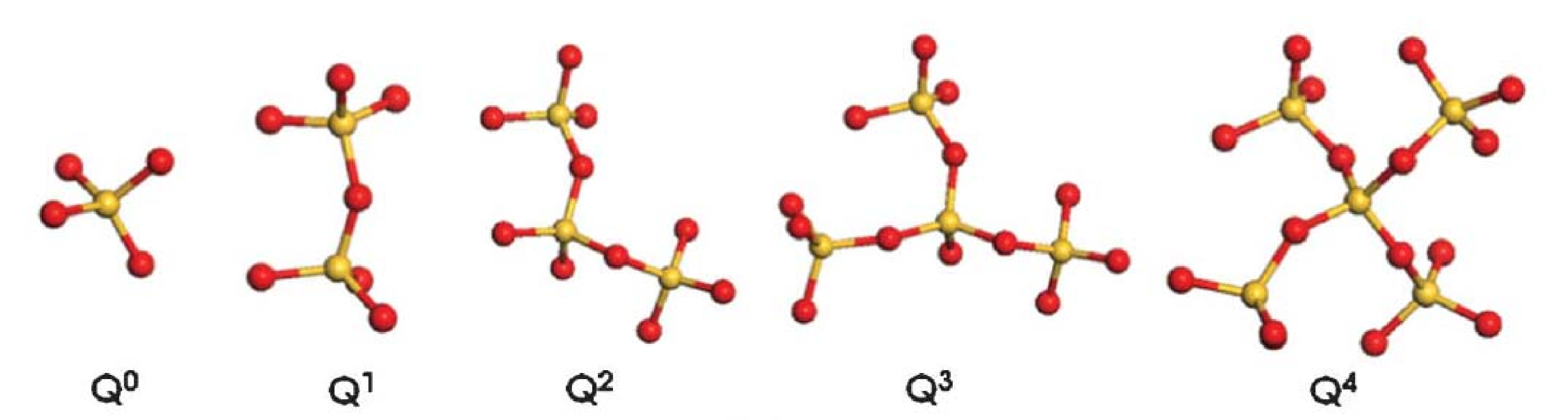
$Si(OMe)_4 + H_2O$





Neg. ion ESI-MS and ^{29}Si NMR of silicate aq with TMA ions

Q - notation



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

$Q^0 = O_4Si$

$Q^1 = O_3SiOSi$

$Q^2 = O_2Si(OSi)_2$

$Q^3 = OSi(OSi)_3$

$Q^4 = Si(OSi)_4$

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

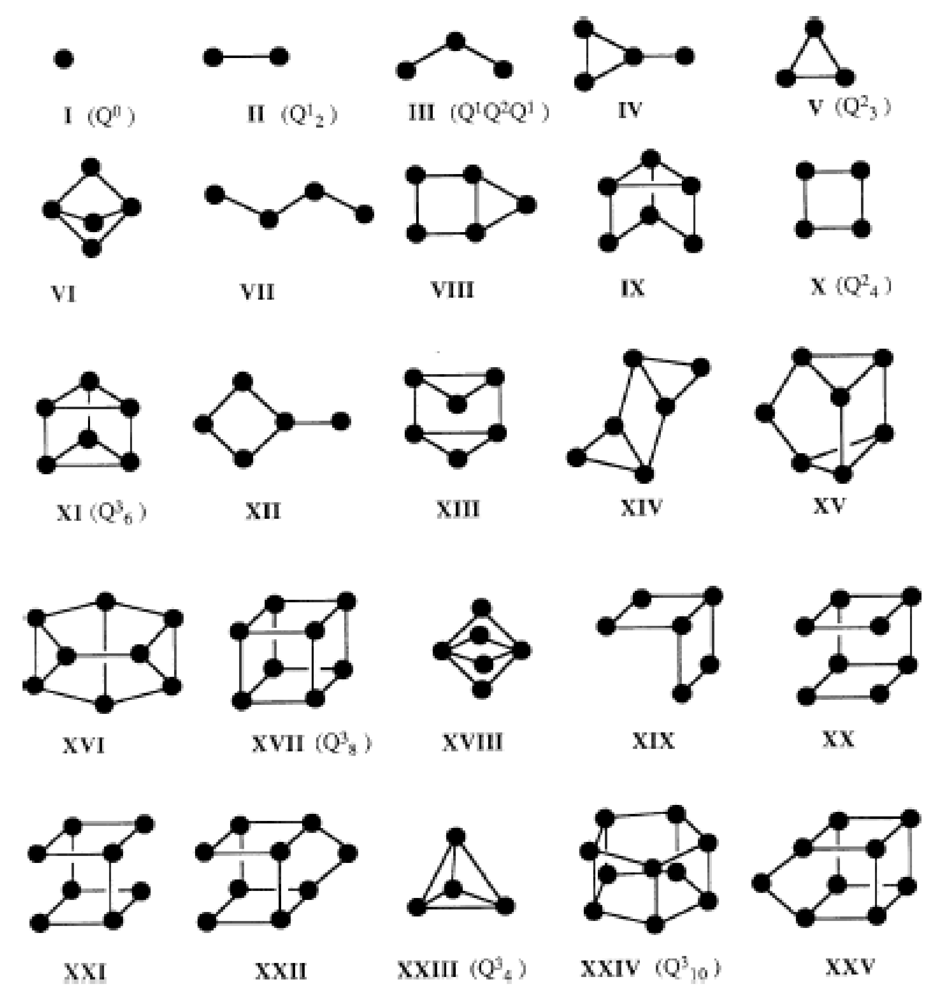
M = $OSiR_3$

D = O_2SiR_2

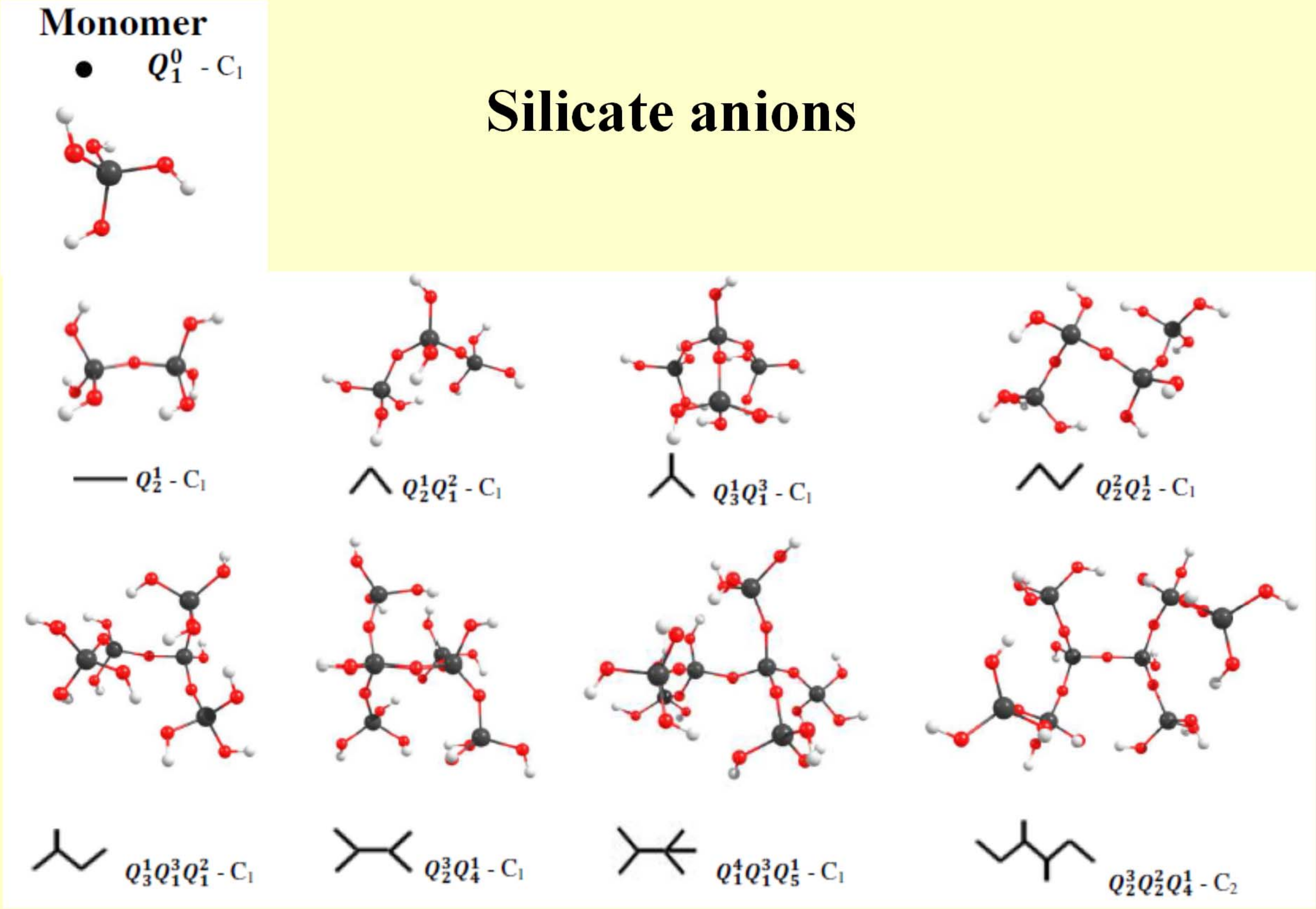
T = O_3SiR

Q = O_4Si

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



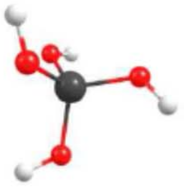
Silicate anions

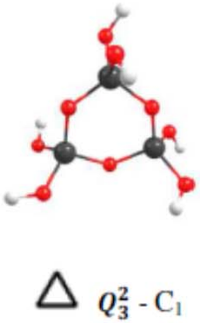


Silicate anions

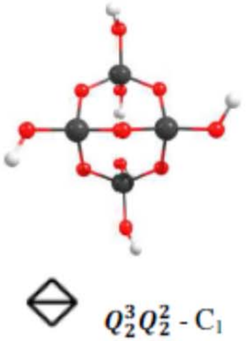
Monomer

● Q_1^0 - C_1

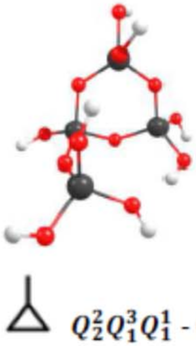




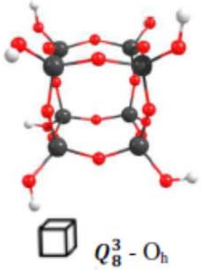
Q_3^2 - C_1



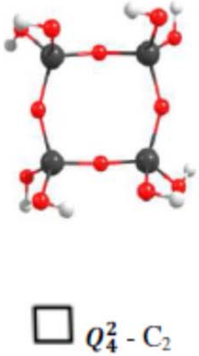
$Q_2^3Q_2^2$ - C_1



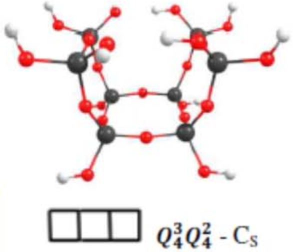
$Q_2^2Q_1^3Q_1^1$ - C_1



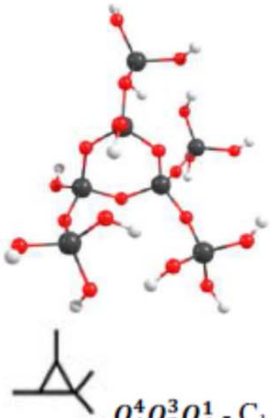
Q_8^3 - O_h



Q_4^2 - C_2

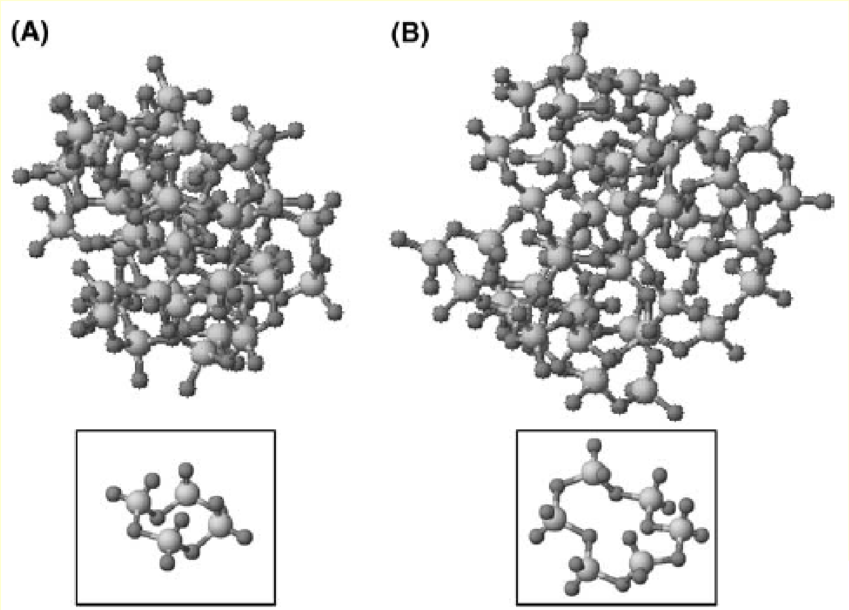


$Q_4^3Q_4^2$ - C_S



$Q_1^4Q_2^3Q_4^1$ - C_1

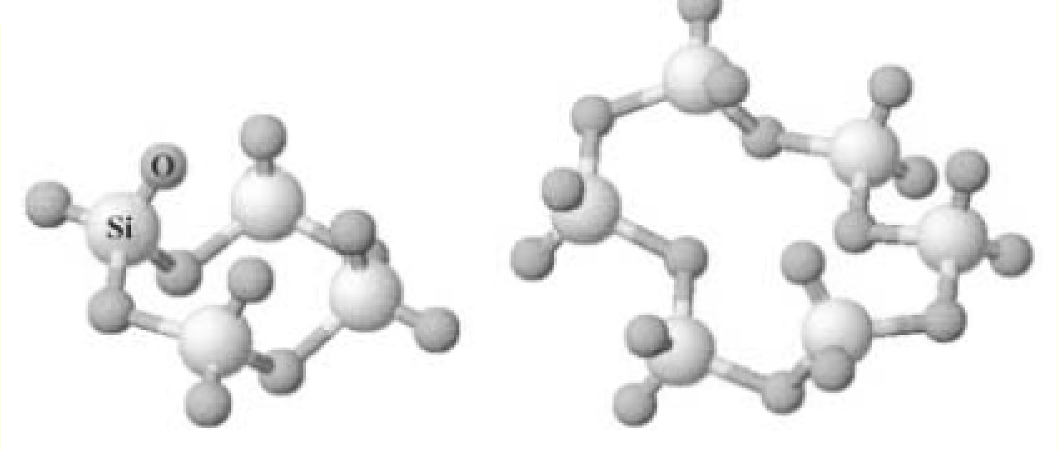
Oligomers formed by hydrolysis-condensation



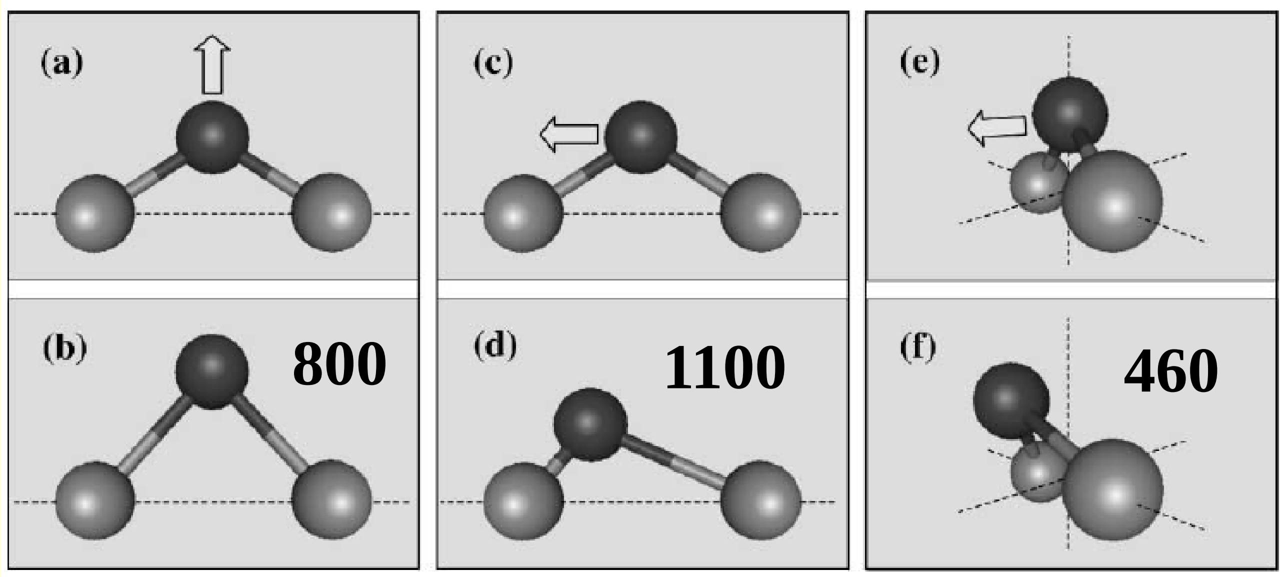
$Si_{50}O_{75}(OH)_{50}$ **three-dimensional clusters formed by**

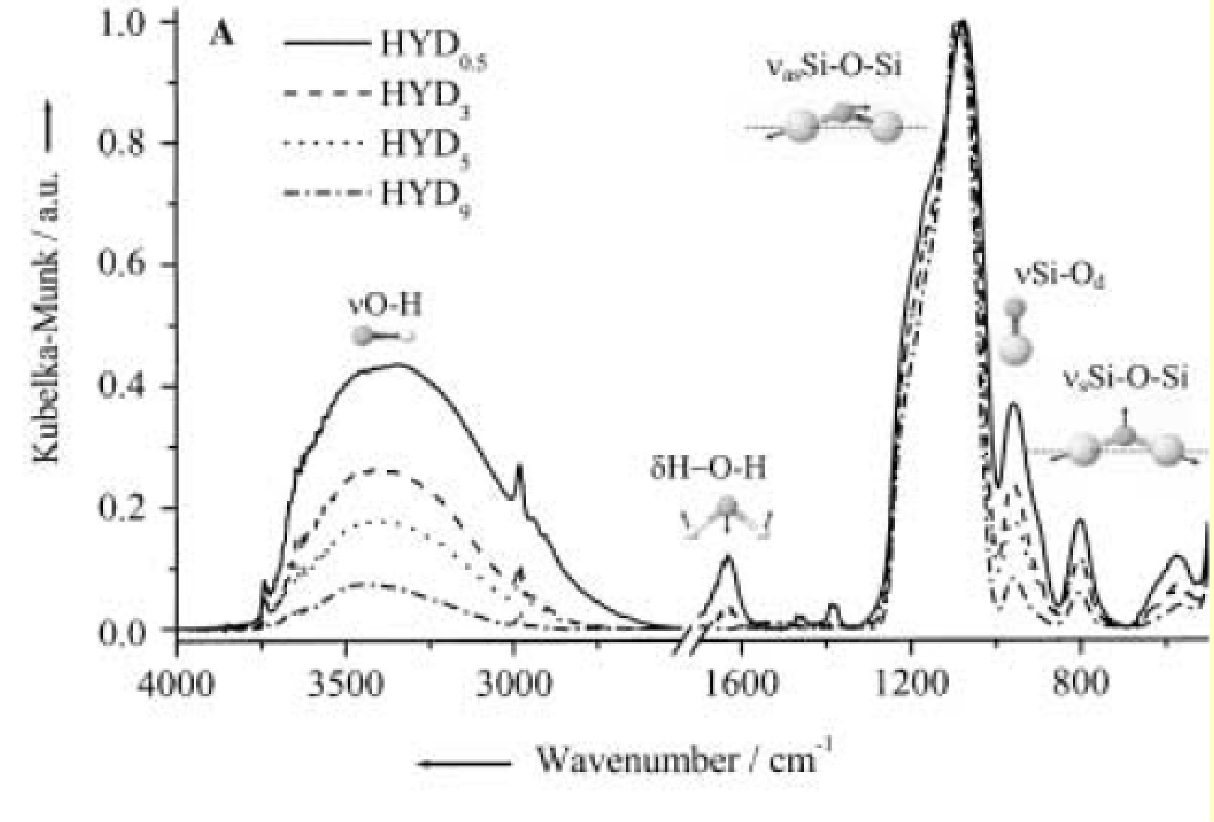
(A) four-rings

(B) six-rings



IR spectrum of silica
ν, cm^{-1}





The Electrical Double Layer

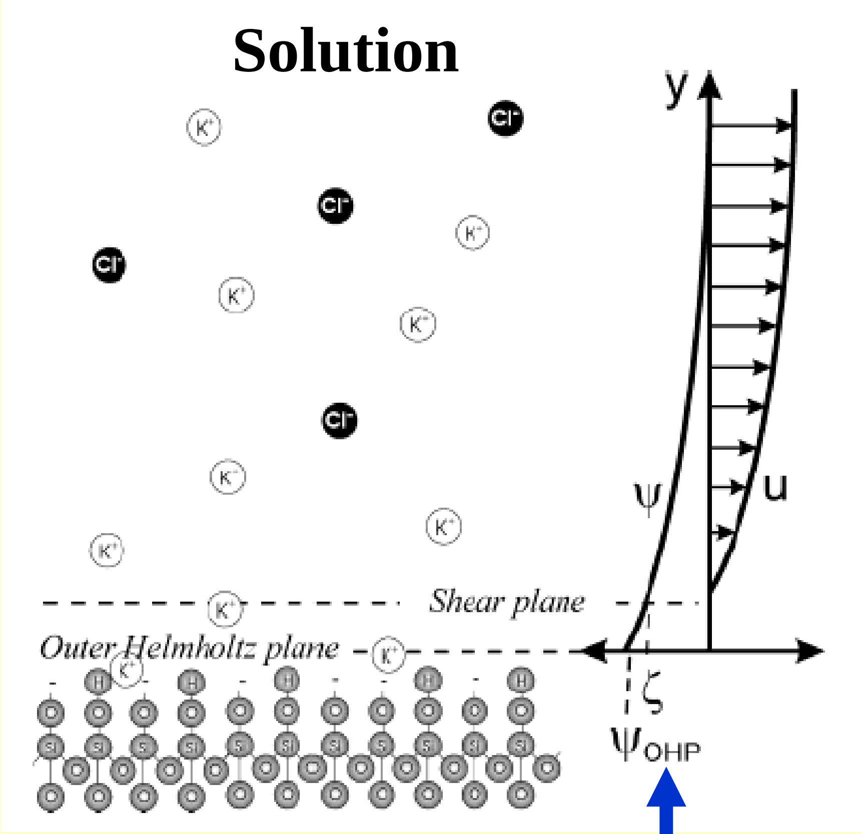
The electrical double layer at the interface of silica and a diluted KCl solution

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



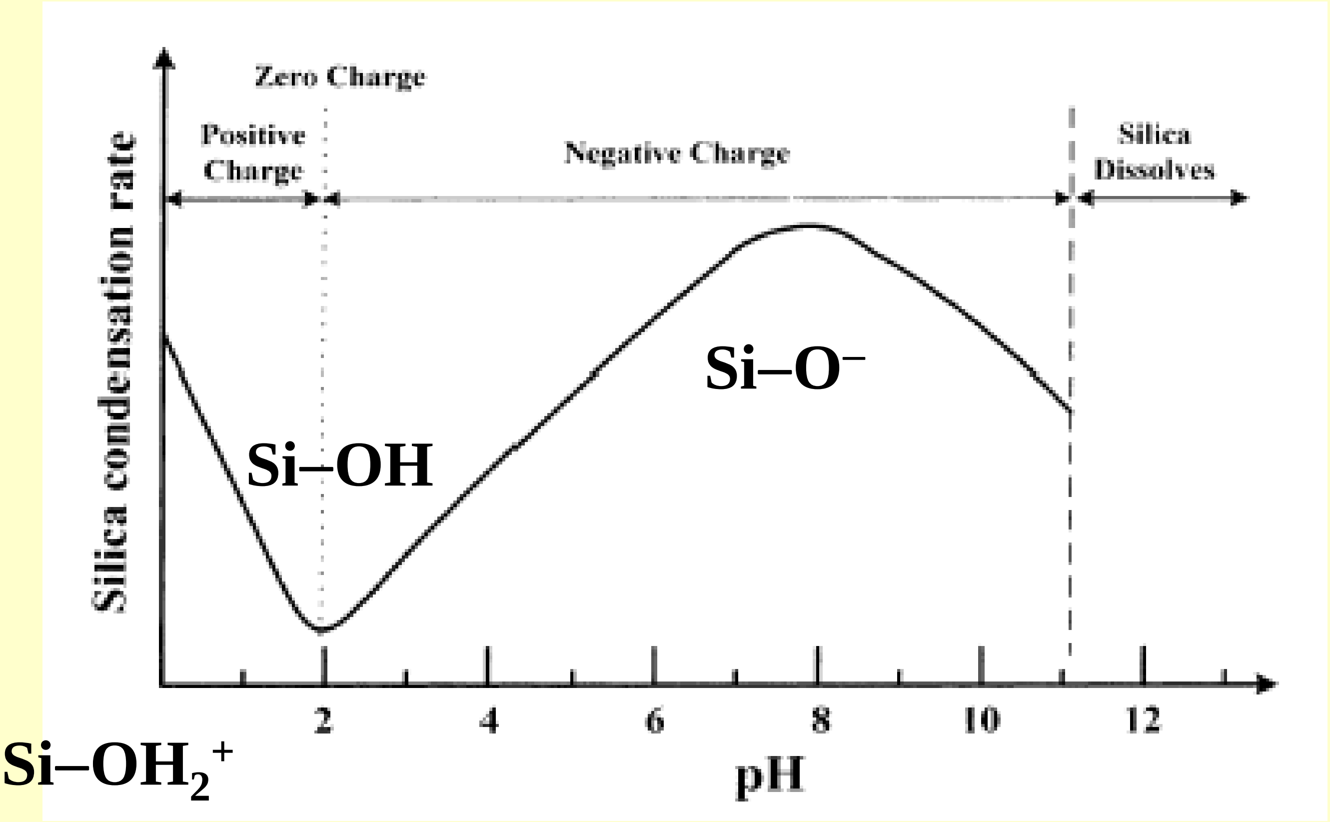
Silica surface

Zeta

Sol-Gel Methods

Isoelectronic point: zero net charge

pH = 2.2 for silica



Sol-Gel Methods

Longest TEOS gel time = the slowest reaction

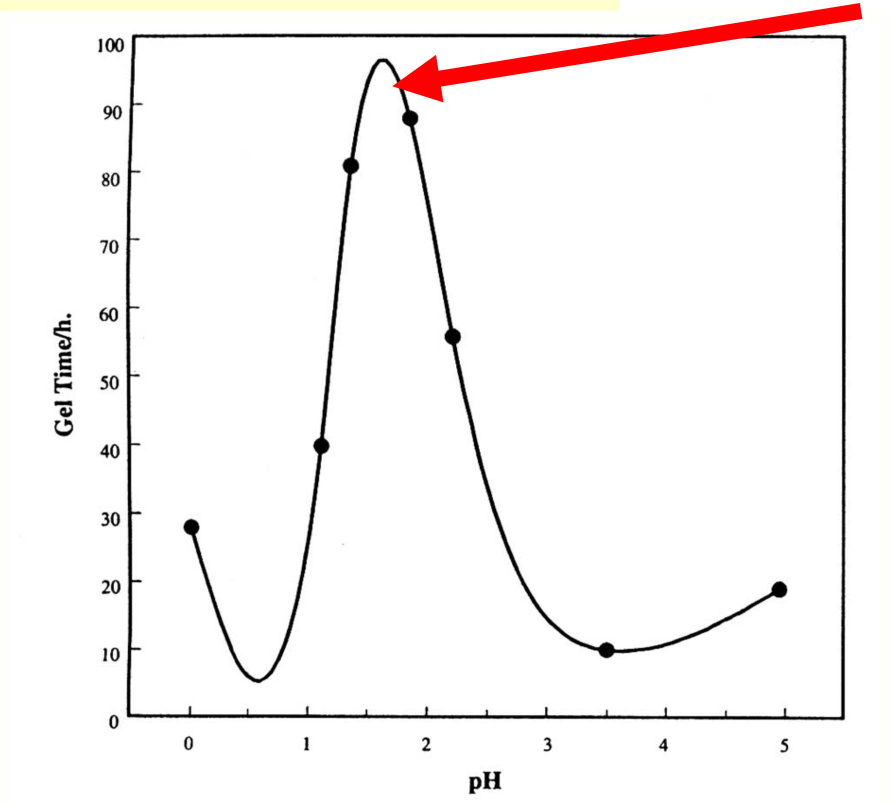
Effects on hydrolysis rate:

pH

substituents

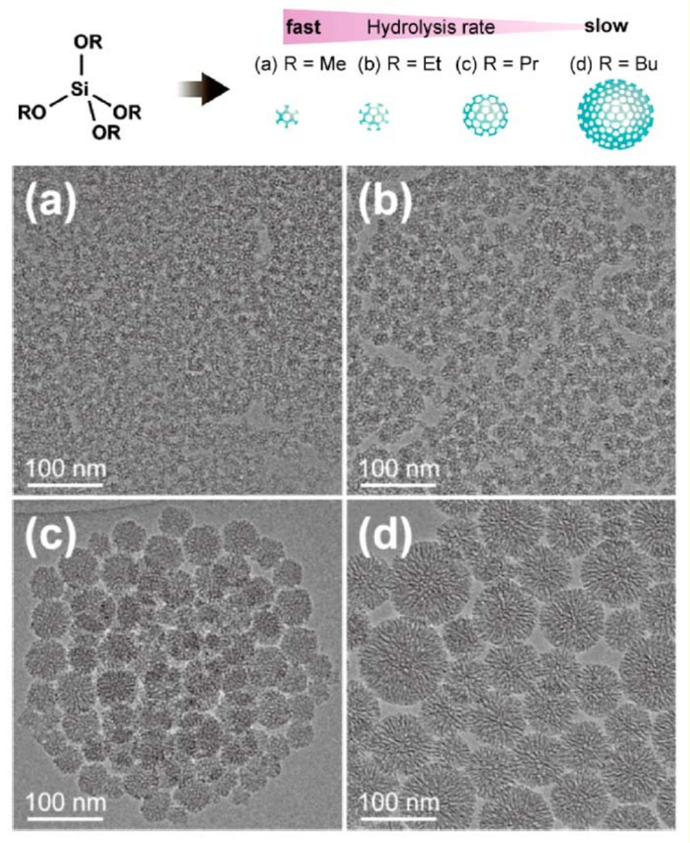
solvent

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

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

Inductive effects: electronic stabilization/destabilizati of the transition state (TS).

Electron density at Si decreases:

R→Si > RO→Si > HO–Si > SiO←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

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

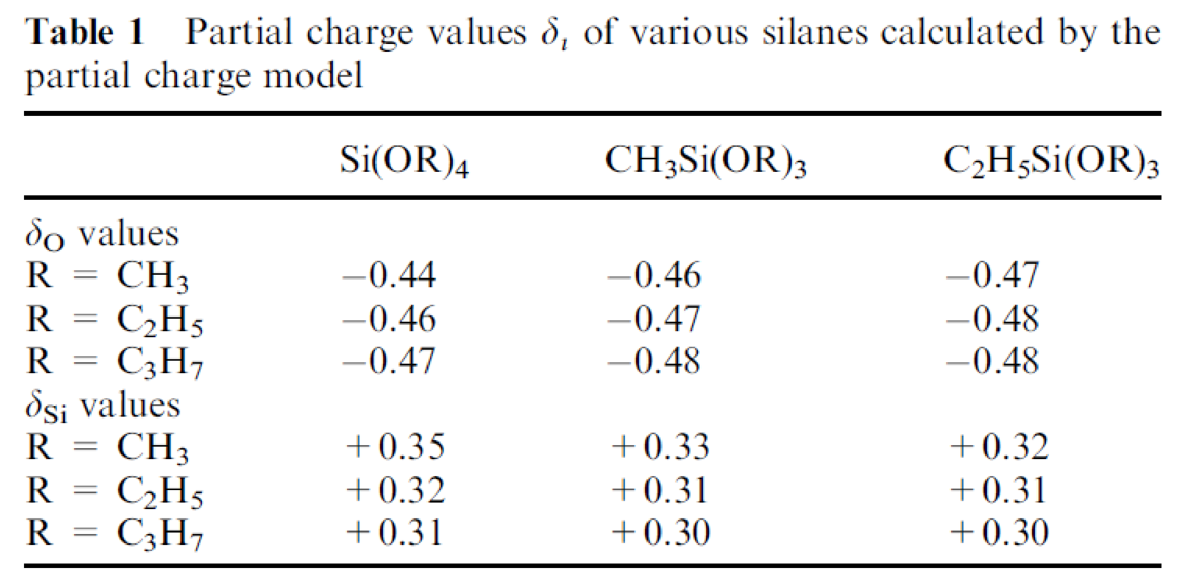


Table 1 Partial charge values δ_i of various silanes calculated by the partial charge model

	$Si(OR)_4$	$CH_3Si(OR)_3$	$C_2H_5Si(OR)_3$
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 $\delta(M)$:

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

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

Partial Charge Model

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

$$n^* = (N - p) + \frac{2m\chi_{\mathrm{B}}}{\chi_{\mathrm{A}} + \chi_{\mathrm{B}}} - \frac{s\chi_{\mathrm{A}}}{\chi_{\mathrm{A}} + \chi_{\mathrm{B}}}$$

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

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

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

Partial Charge Model

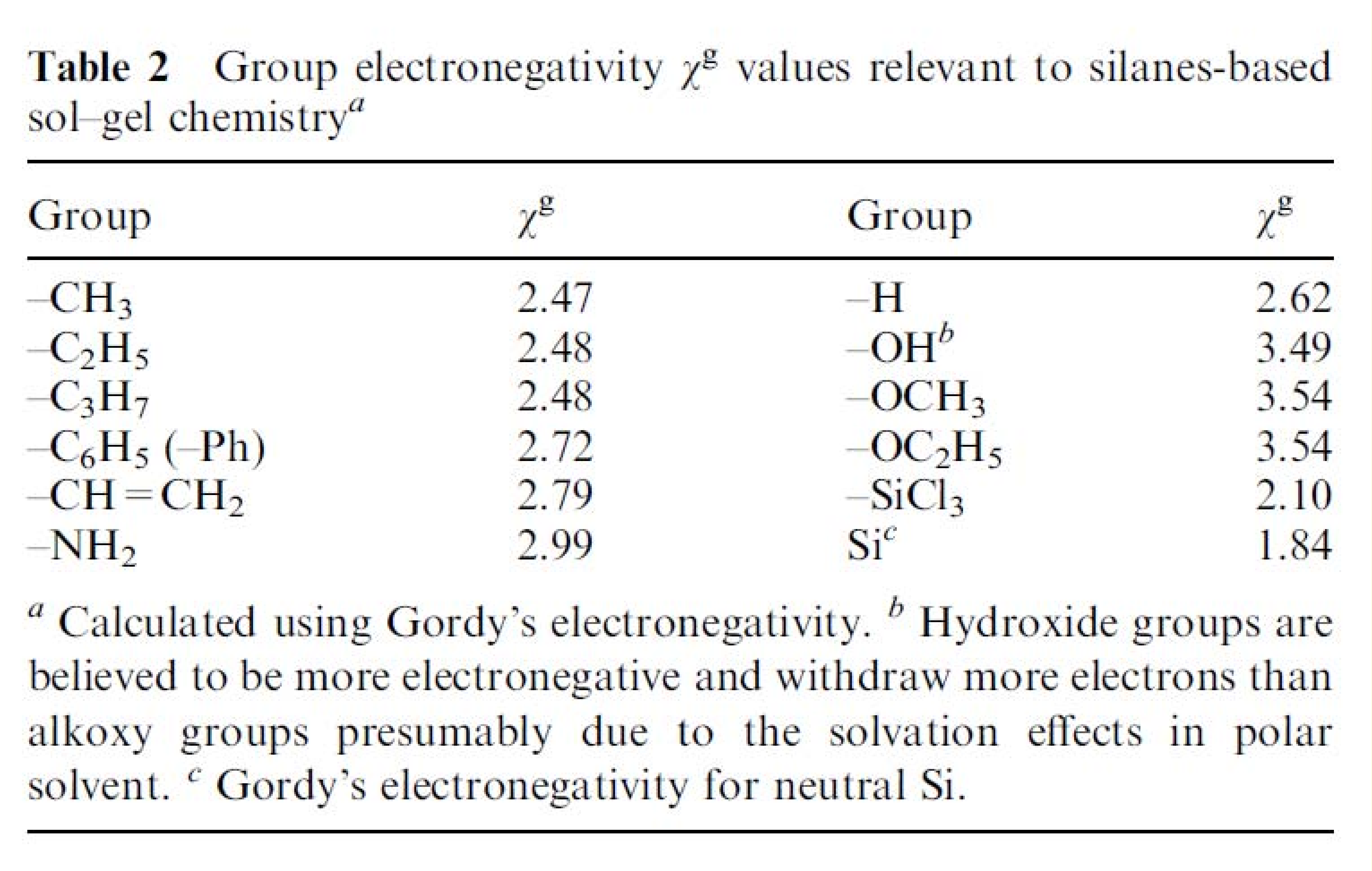


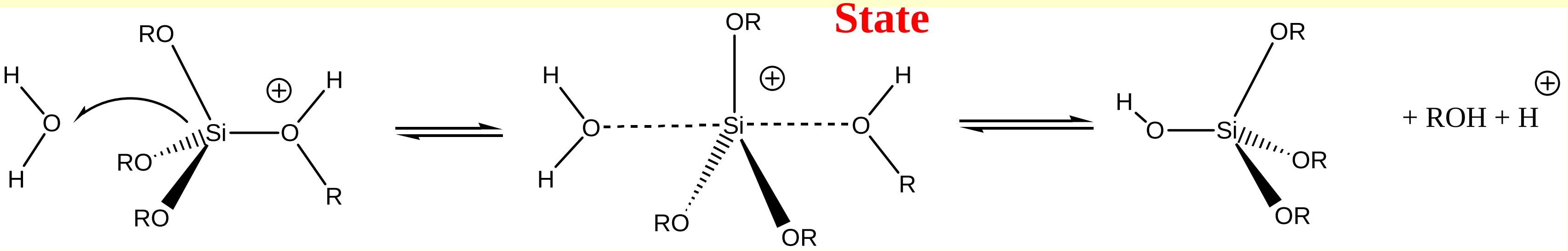
Table 2 Group electronegativity χ^g values relevant to silanes-based sol–gel chemistry[a]

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:

$R \rightarrow Si$ > $RO \rightarrow Si$ > $HO–Si$ > $SiO \leftarrow Si$

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

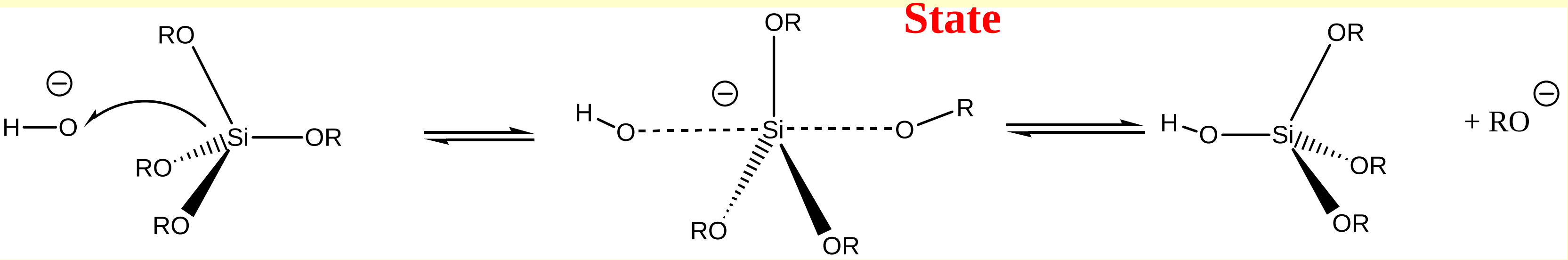
The reaction at terminal Si favored, as there is only one electron withdrawing SiO group

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:

$R \rightarrow Si > RO \rightarrow Si > HO–Si > SiO \leftarrow Si$

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

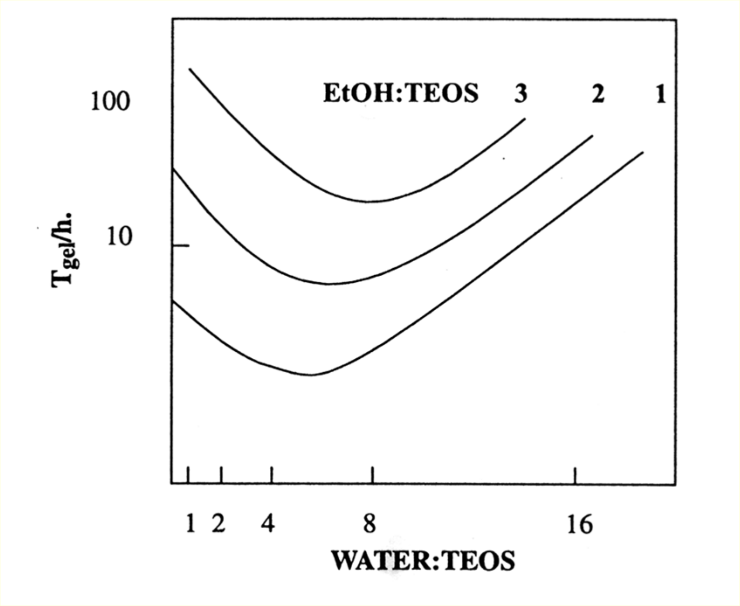
Si-OH becomes more acidic with increasing number of Si-O-Si bonds

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

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

additional water from condensation

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

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

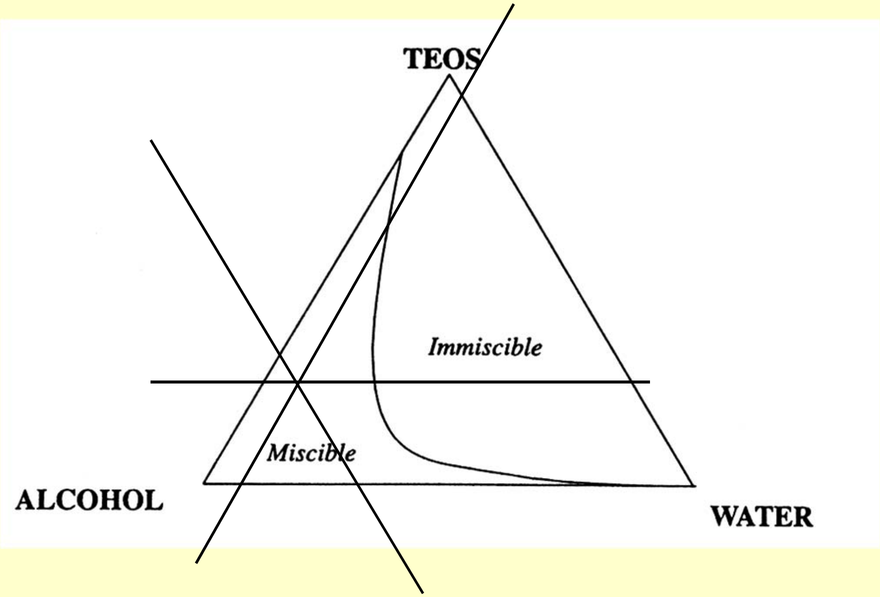
polarity, dipole moment, viscosity, protic behavior

alcohol produced during the reaction

alcohols - transesterification

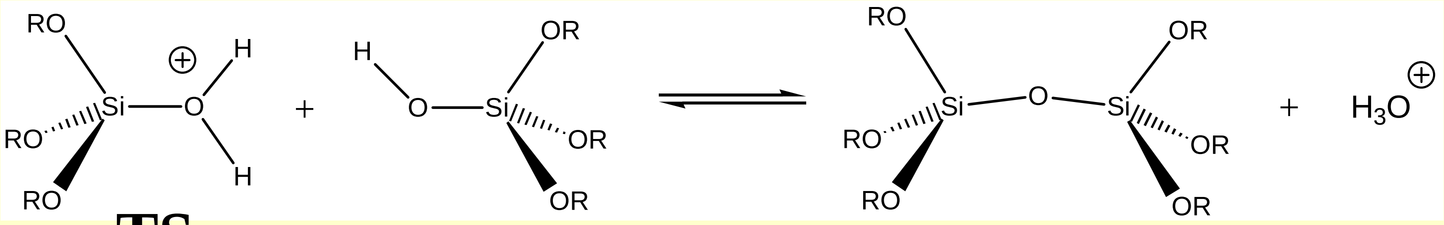
sonication

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

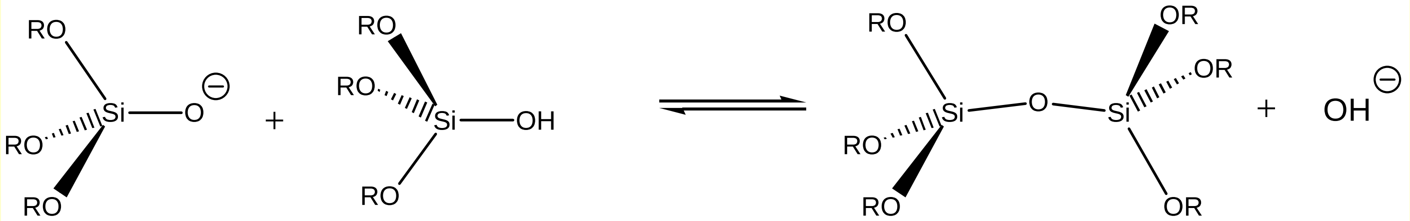
Hydrolysis fastest in the first step, i.e. the formation of $(RO)_3SiOH$

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

Condensation

Base catalysed condensation

fast deprotonation, slow condensation



TS

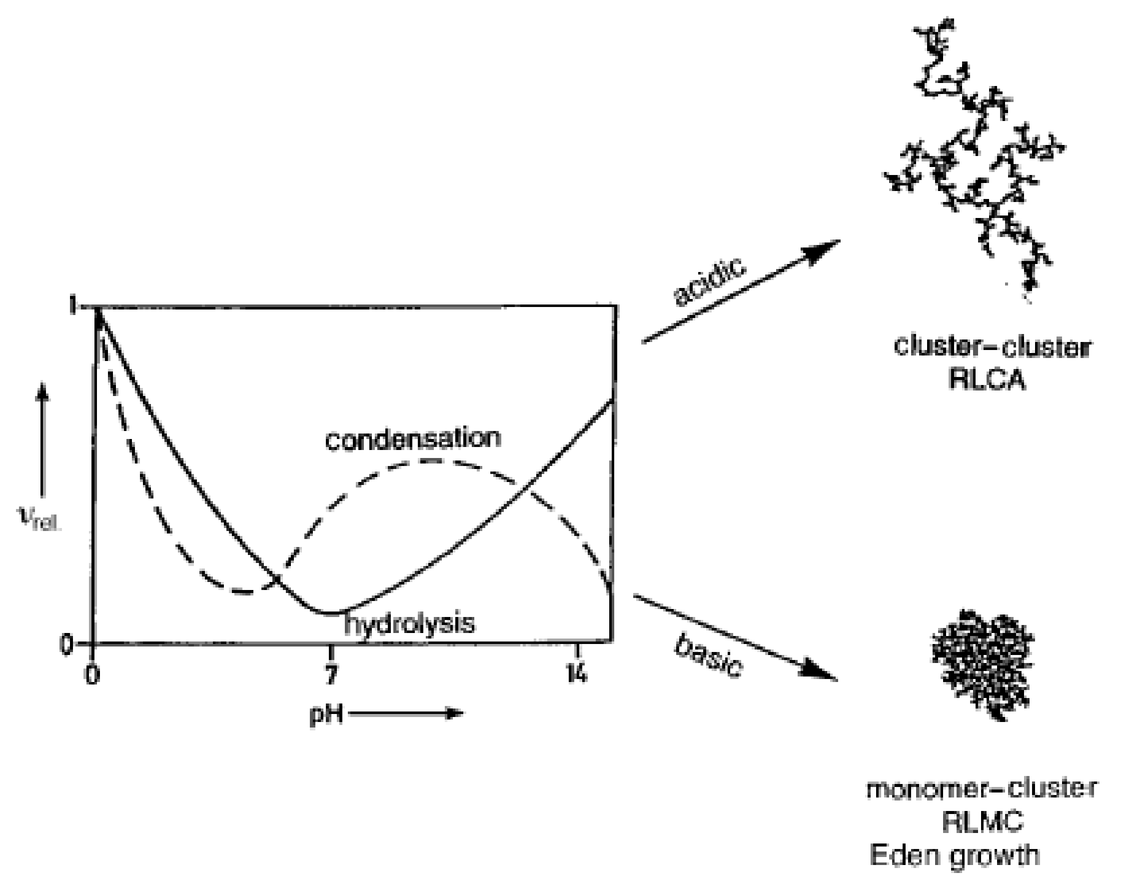
Negatively charged transition state, fastest condensation for $(RO)_3SiOH < (RO)_2Si(OH)_2 < ROSi(OH)_3 < Si(OH)_4$

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)



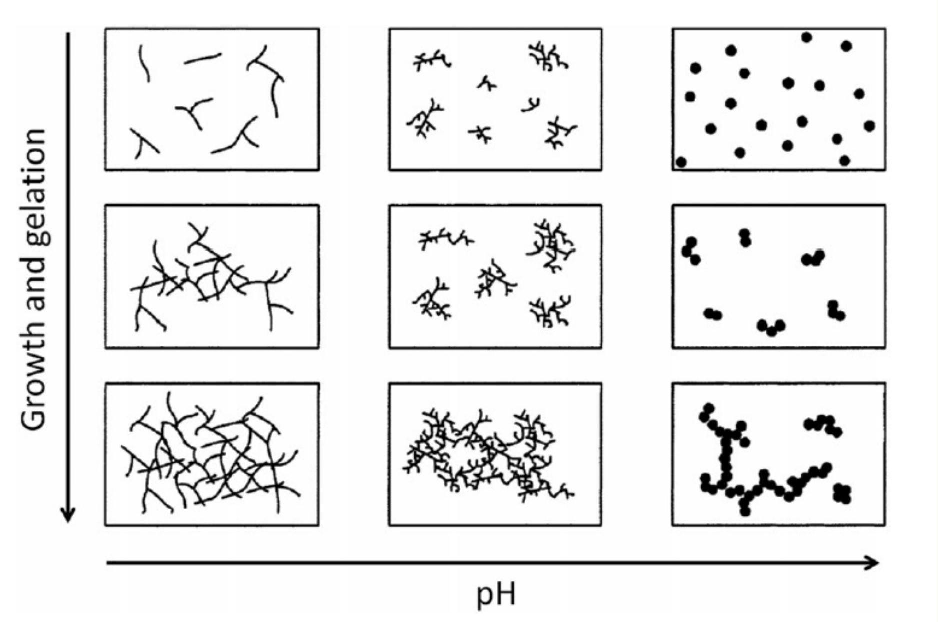
Acid catalysed

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

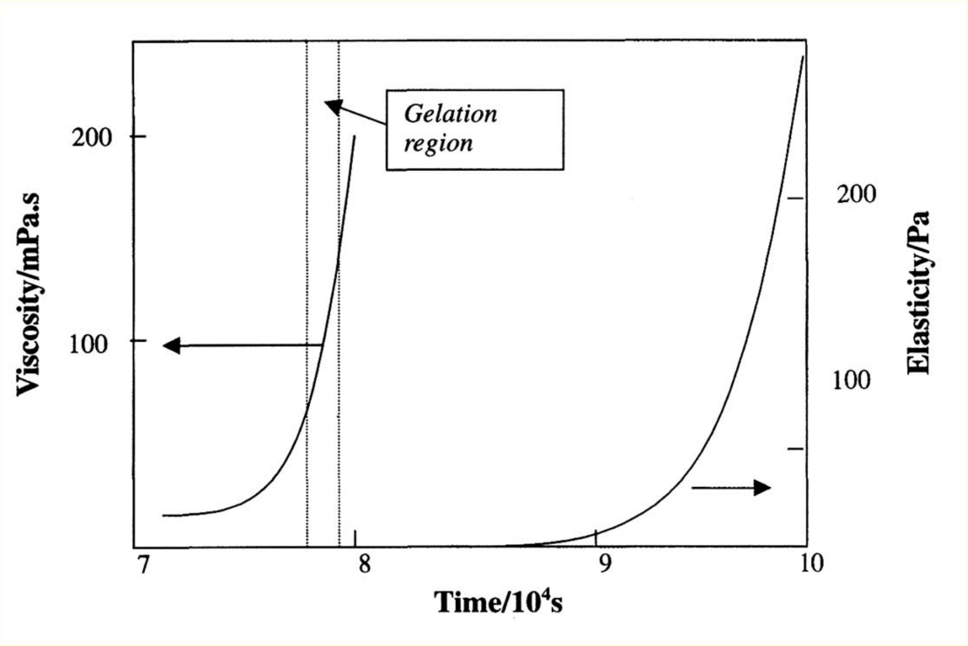
- condensation to highly crosslinked particles
- large primary particles
- mesoporosity, Type IV isotherms

Gelation = Sol-to-Gel Transition

Gel point - a spannig cluster reaches across the container, sol particles, oligomers and monomer still present

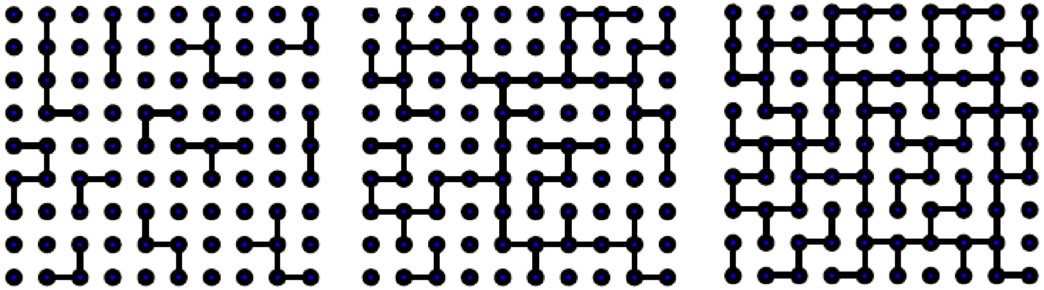
a sudden viscosity increase at the gel point

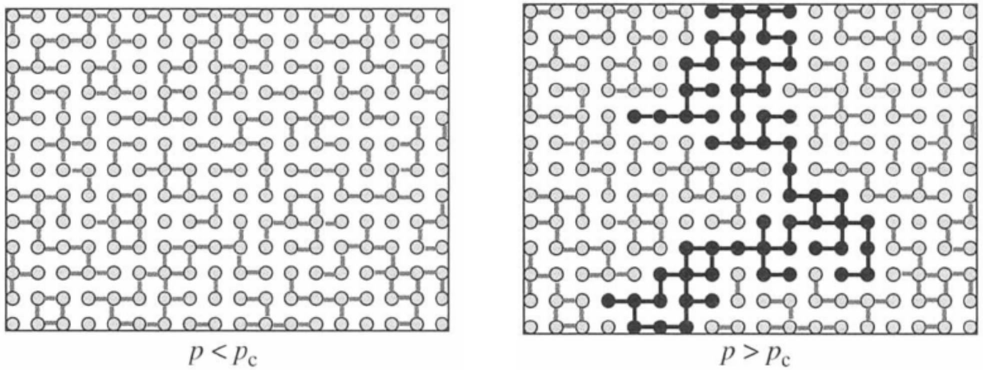
further crosslinking - increase in elasticity

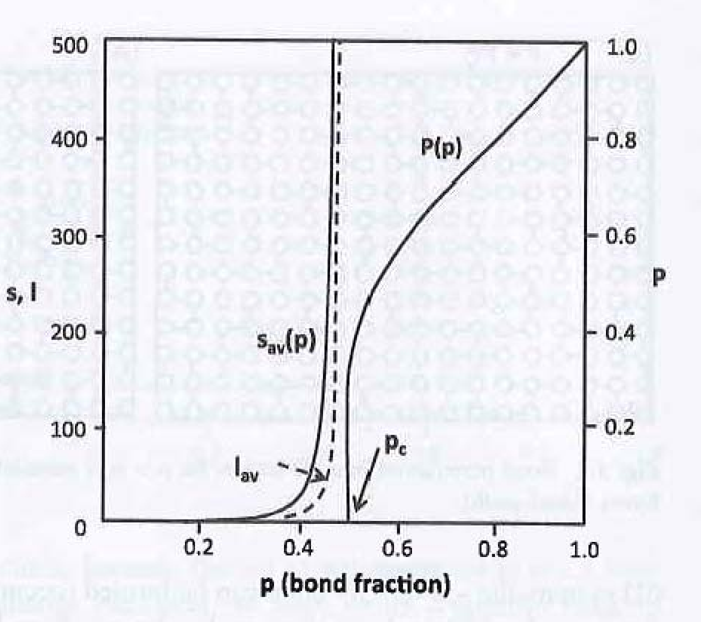


Bond Percolation

p = the fraction of created links




$p < p_c$ $p > p_c$

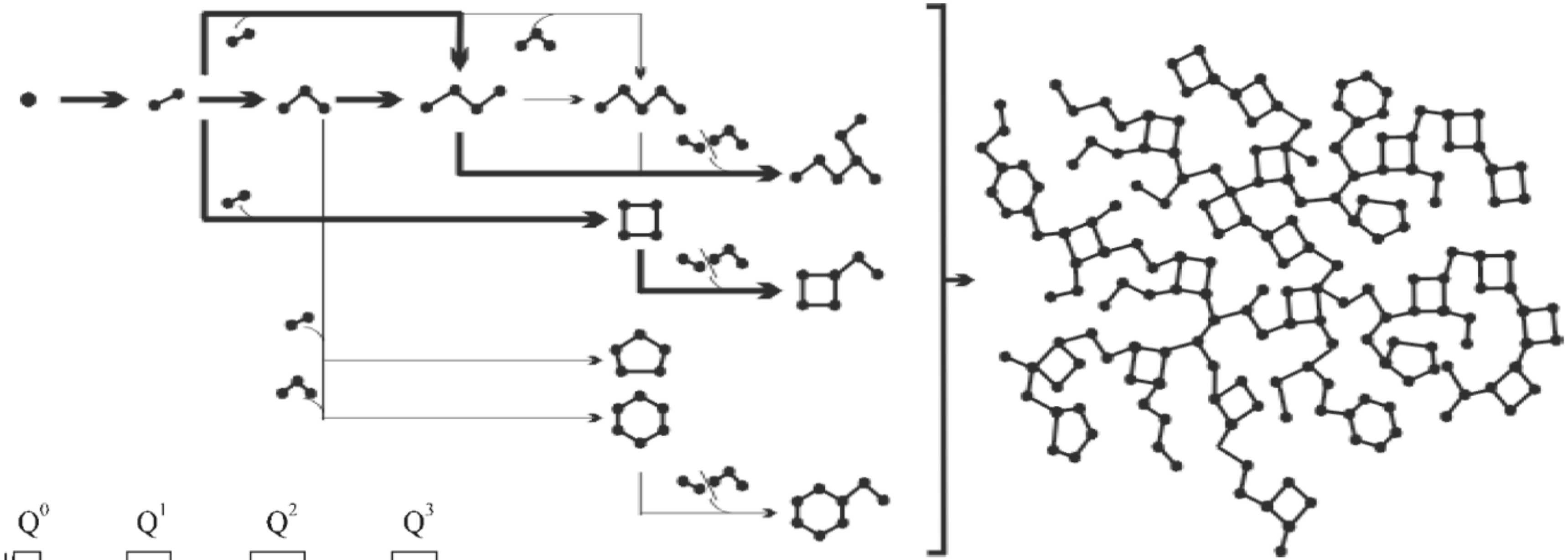


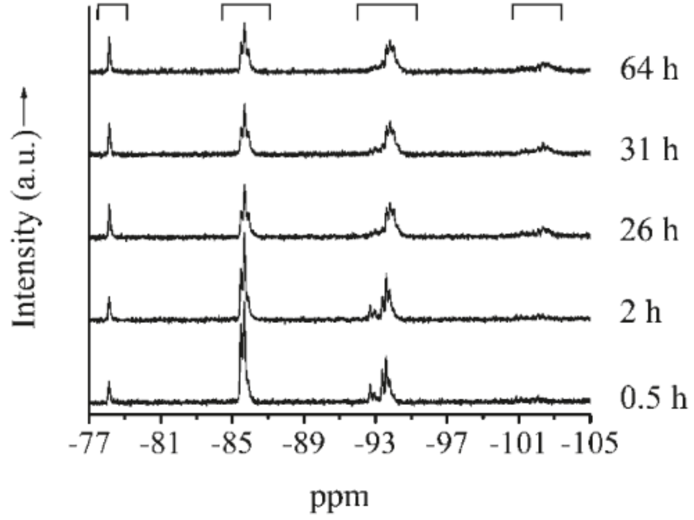
$s_{av}(p)$ = average cluster size

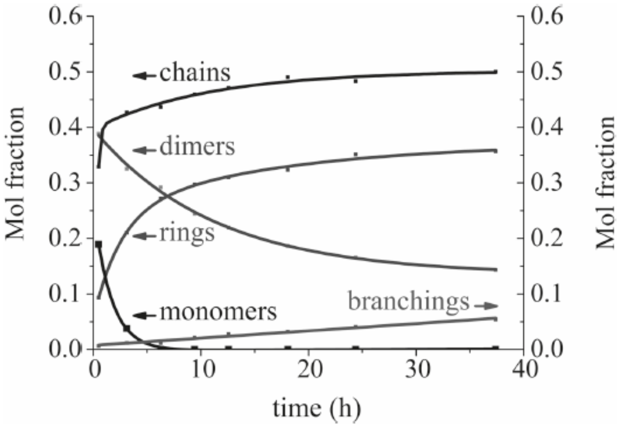
$l_{av}(p)$ = average spanning length

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

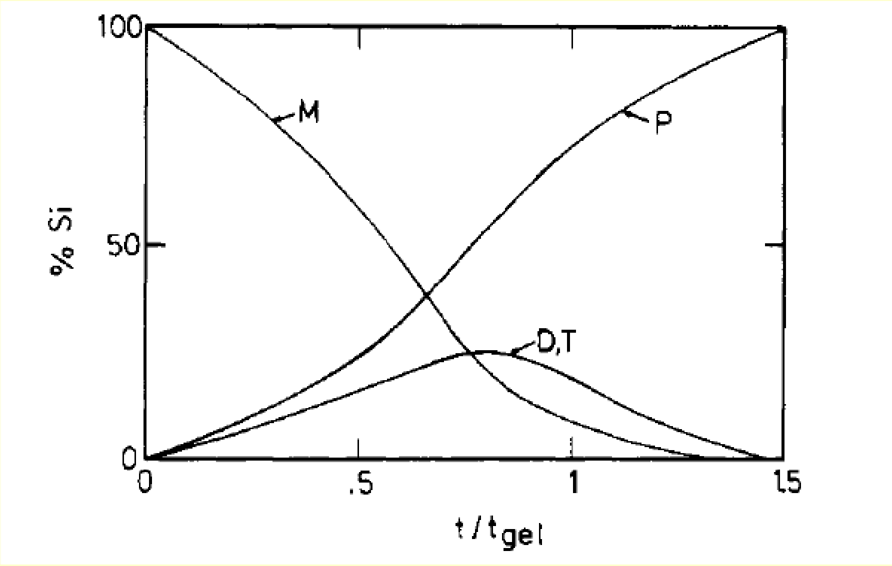
Sol-to-Gel Transition

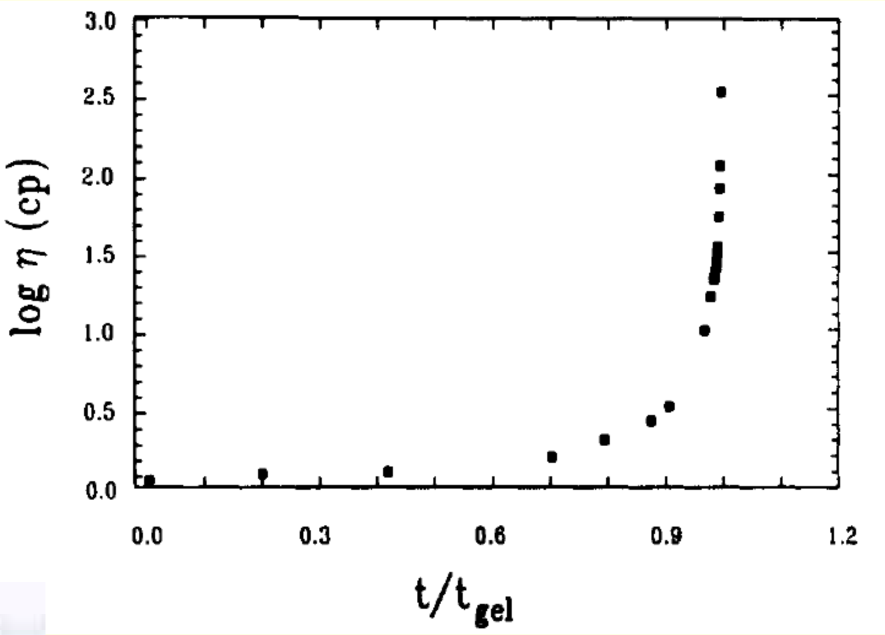


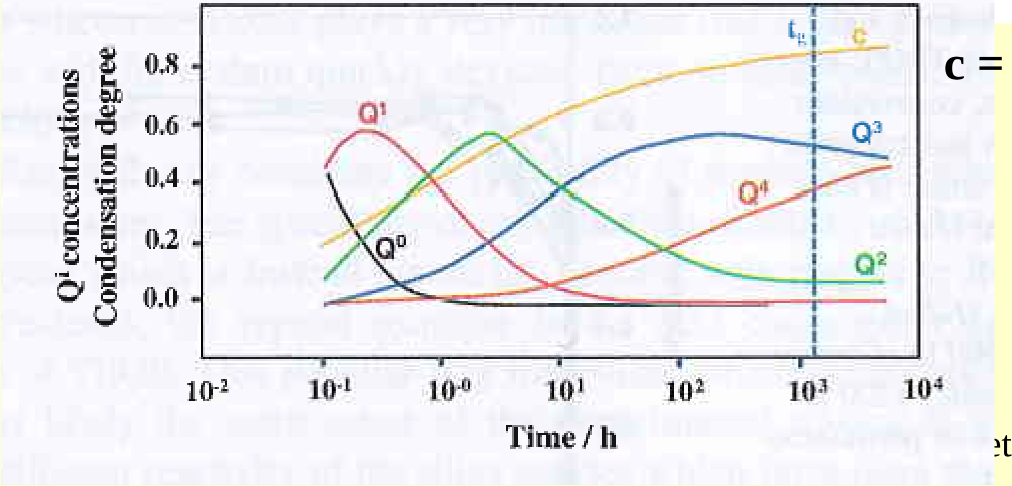




Sol-to-Gel Transition

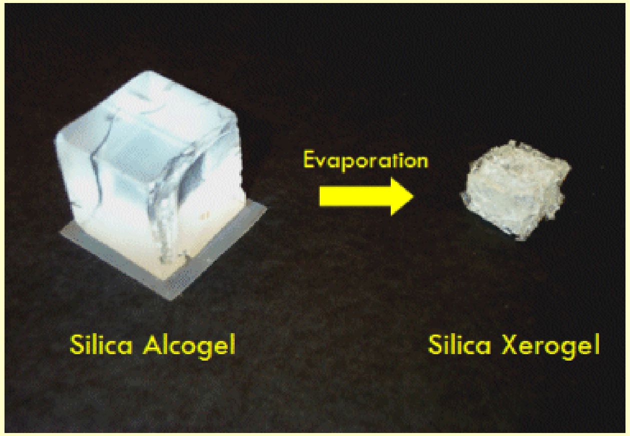






c = condensation degree, max 83 %

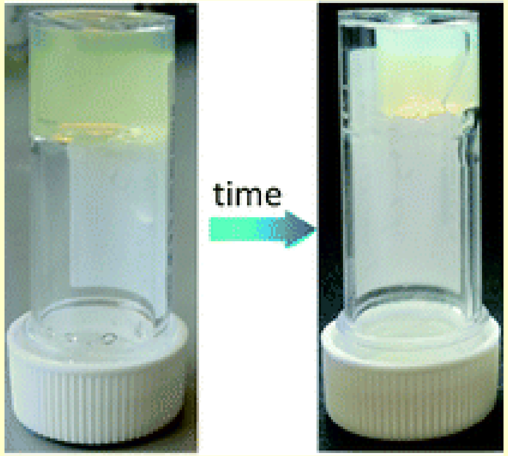
Ageing of Gel



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

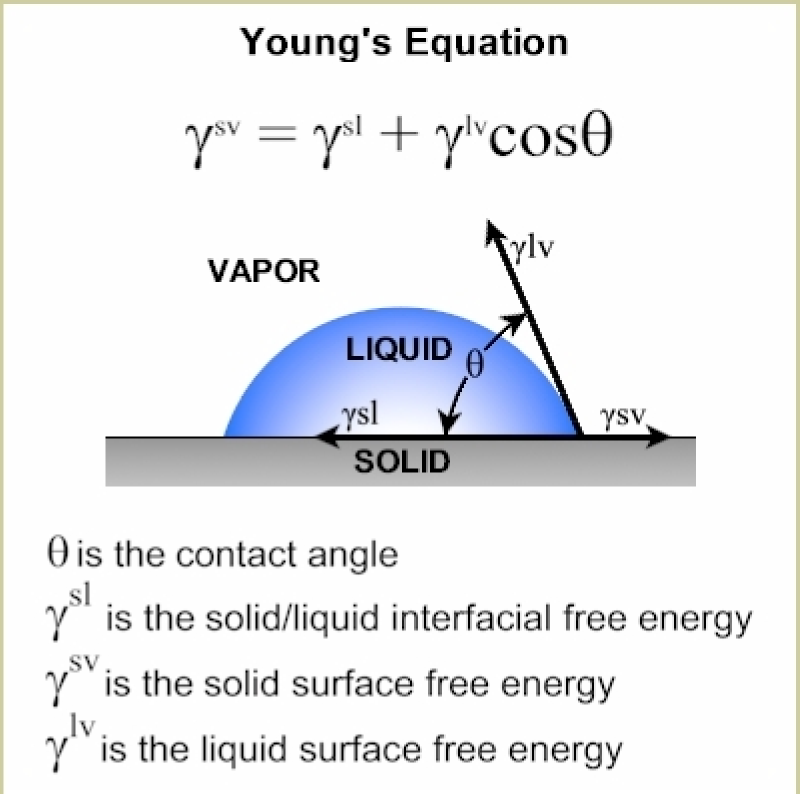
$$P_c = \frac{2\gamma\cos\theta}{r}$$

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:

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

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

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)

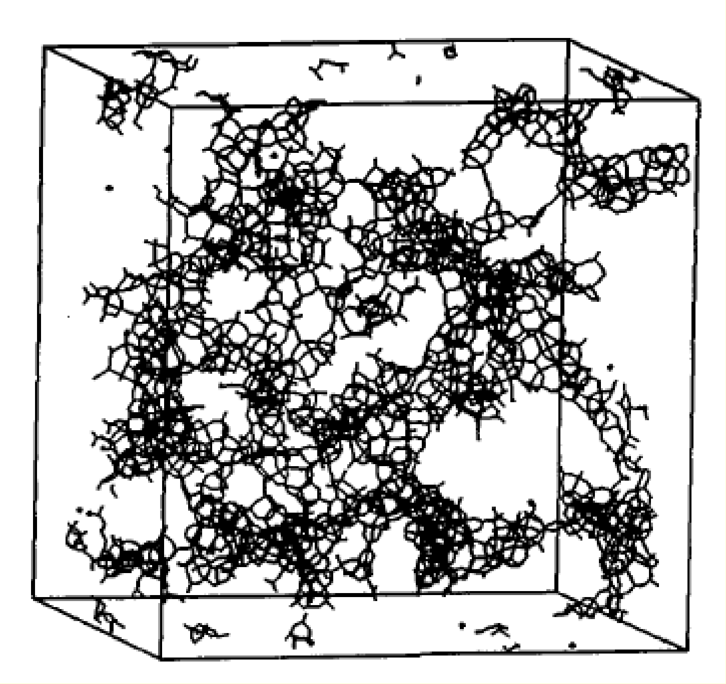
TEOS:H_2O:HNO_3:ammonium acetate molar ratio of the solution is 1 : 10 : 0.002 : 0.02

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

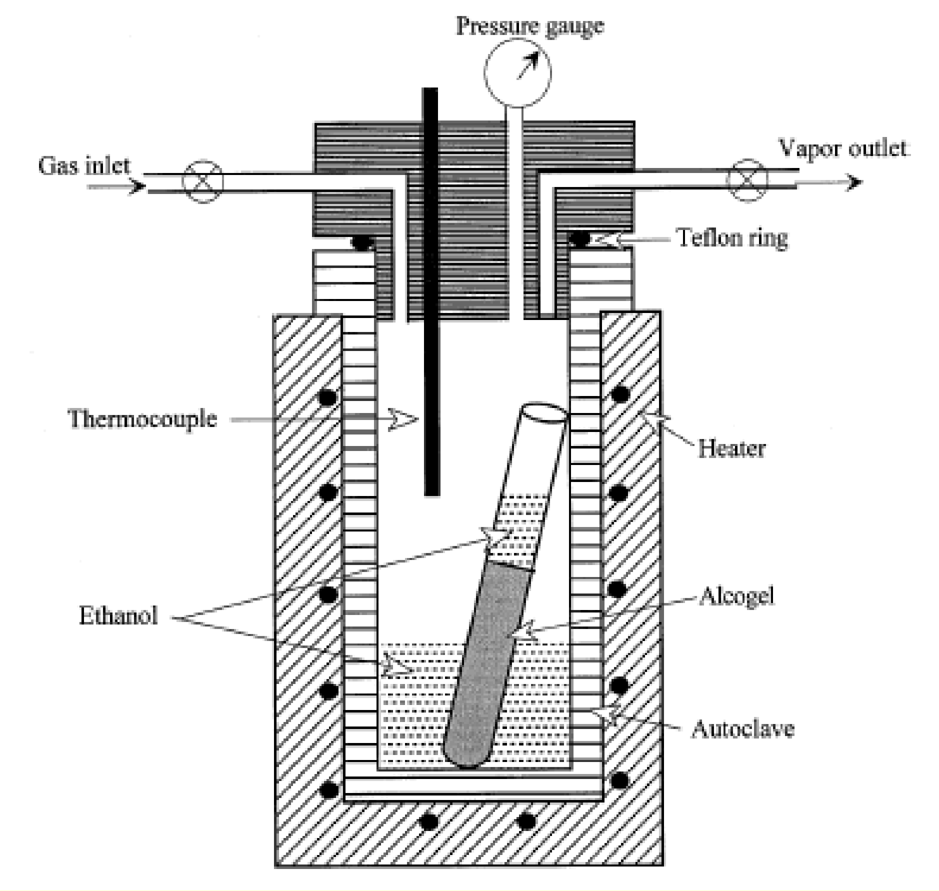


Aerogels - Supercritical Drying

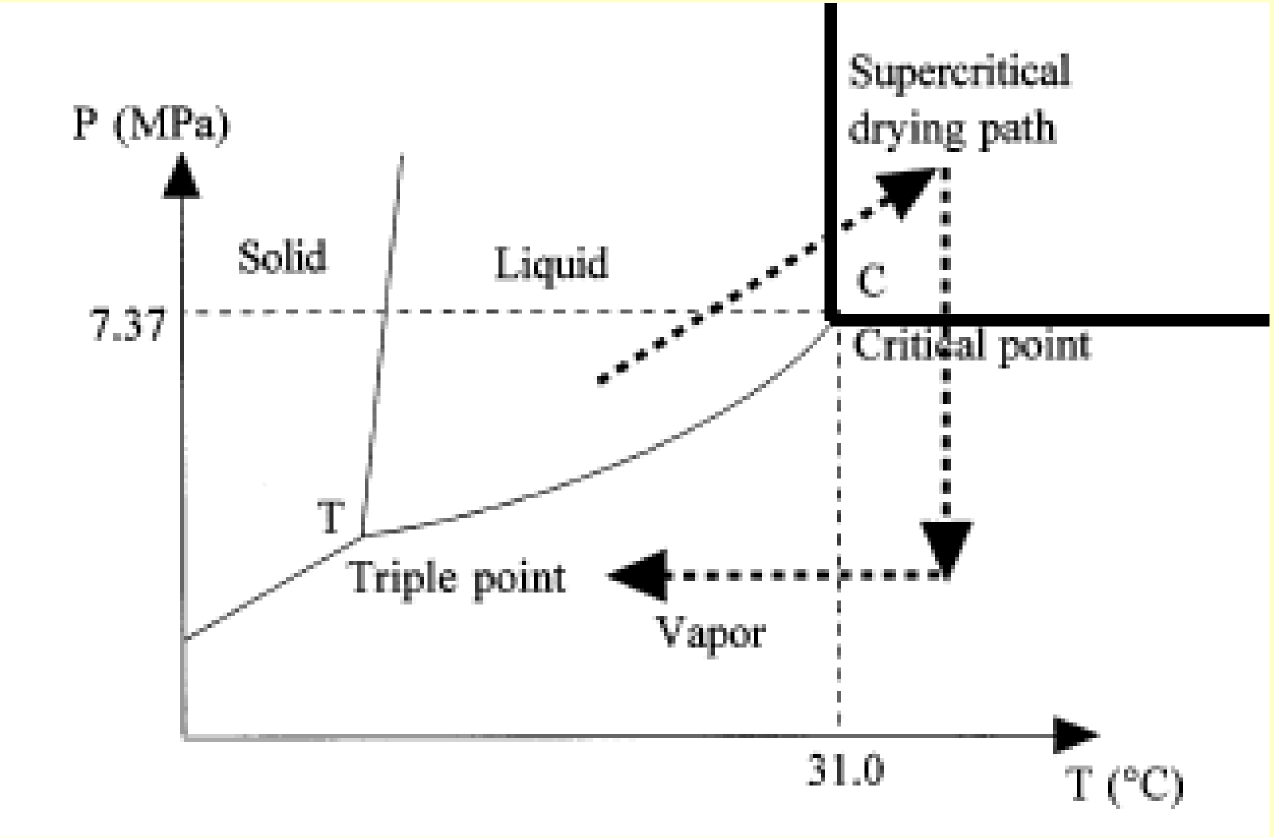
Silica aerogel

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

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

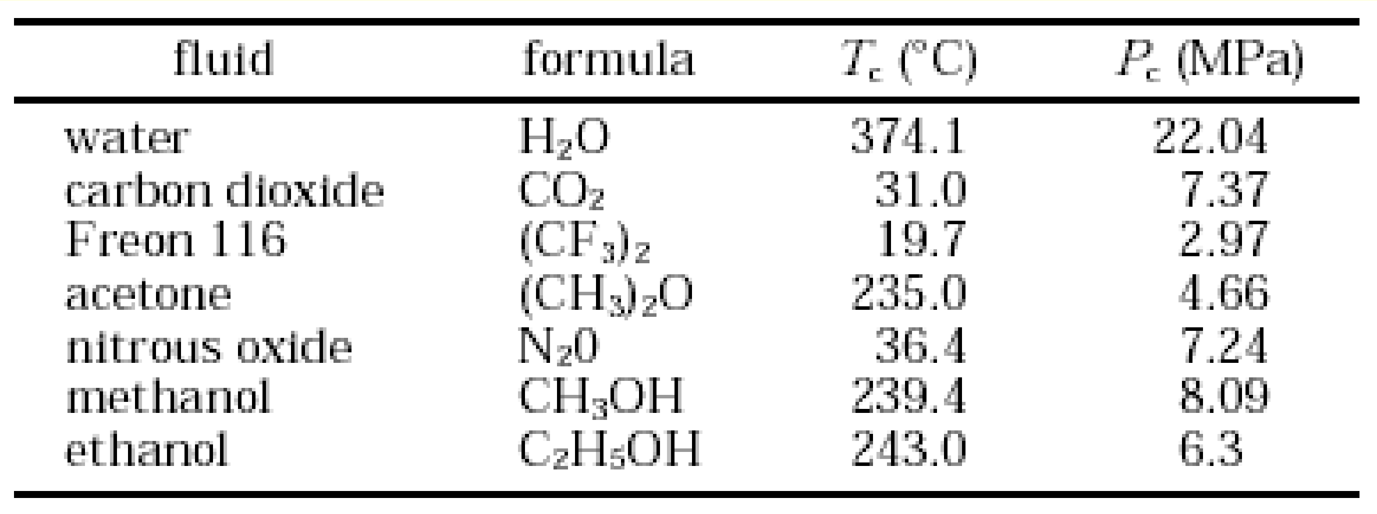


Supercritical Drying

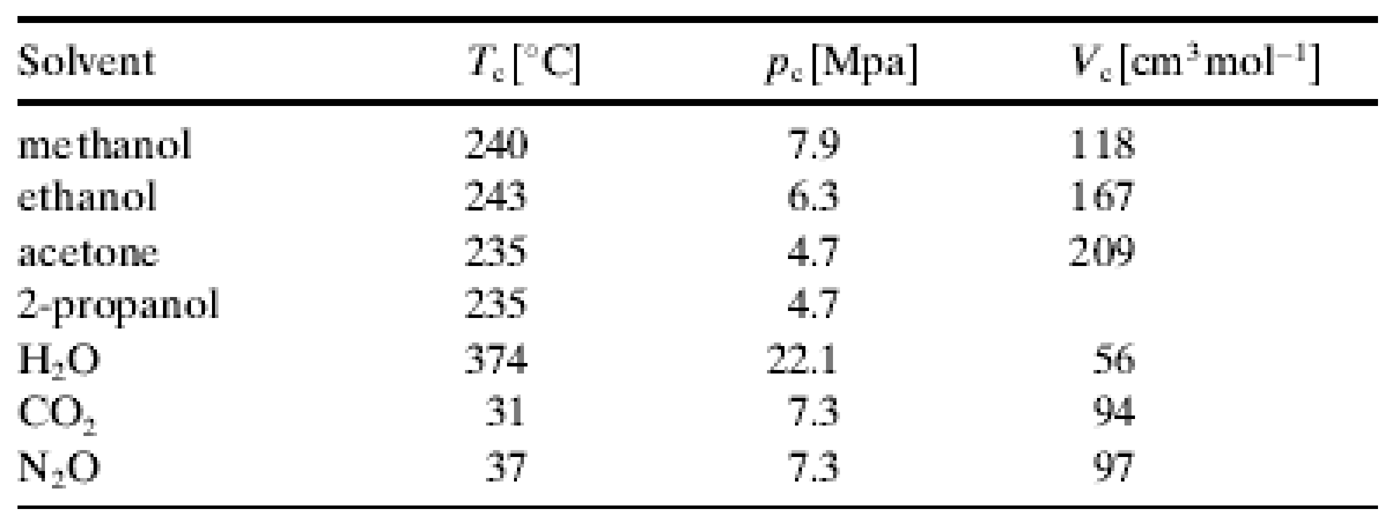


Cold supercritical drying path in the Pressure (P) Temperature (T) phase diagram of CO_2

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_20	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

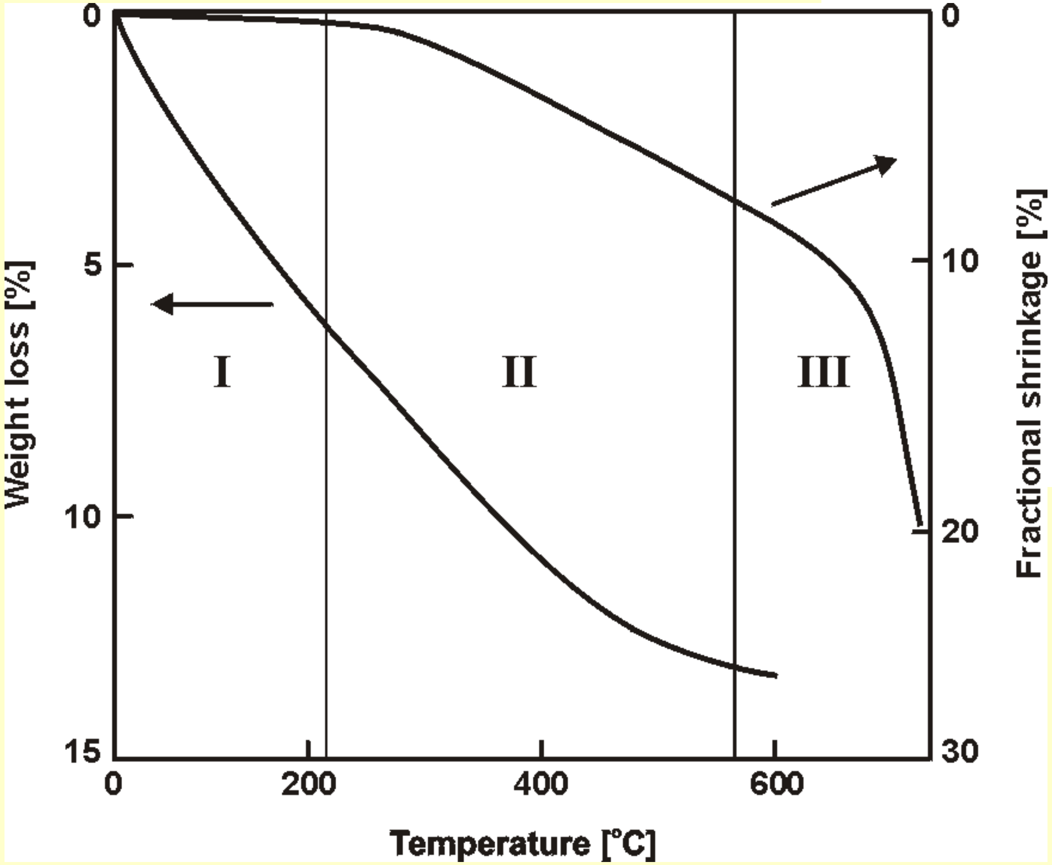
Stage II. 150 - 700 °C, both weight loss and shrinkage

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

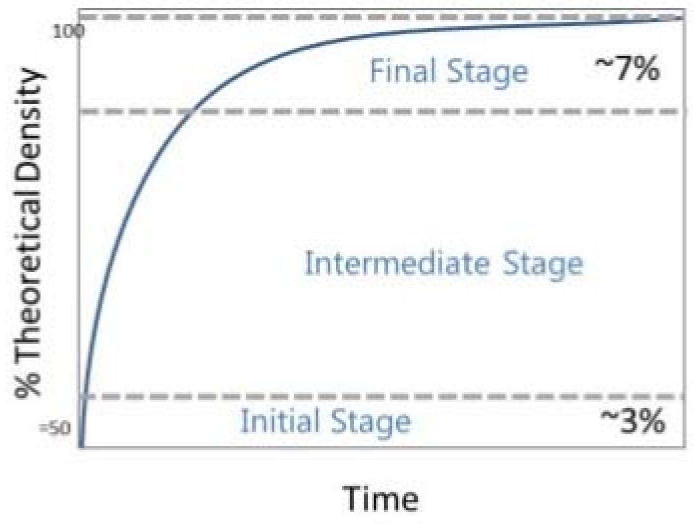
Stage III. Above 500 °C, no more weight loss, shrinkage only

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

Densification - Sintering

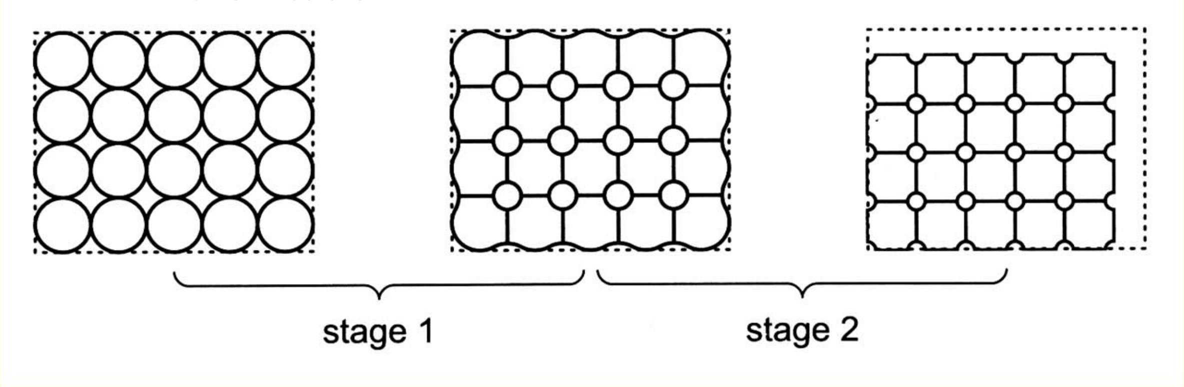


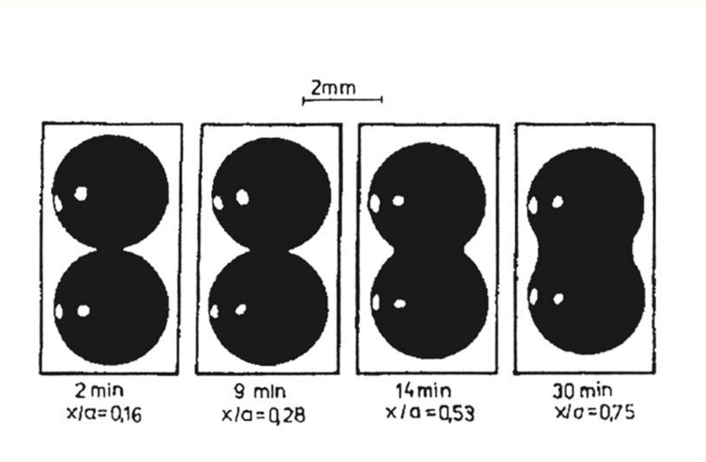
Generalized Sintering Curve

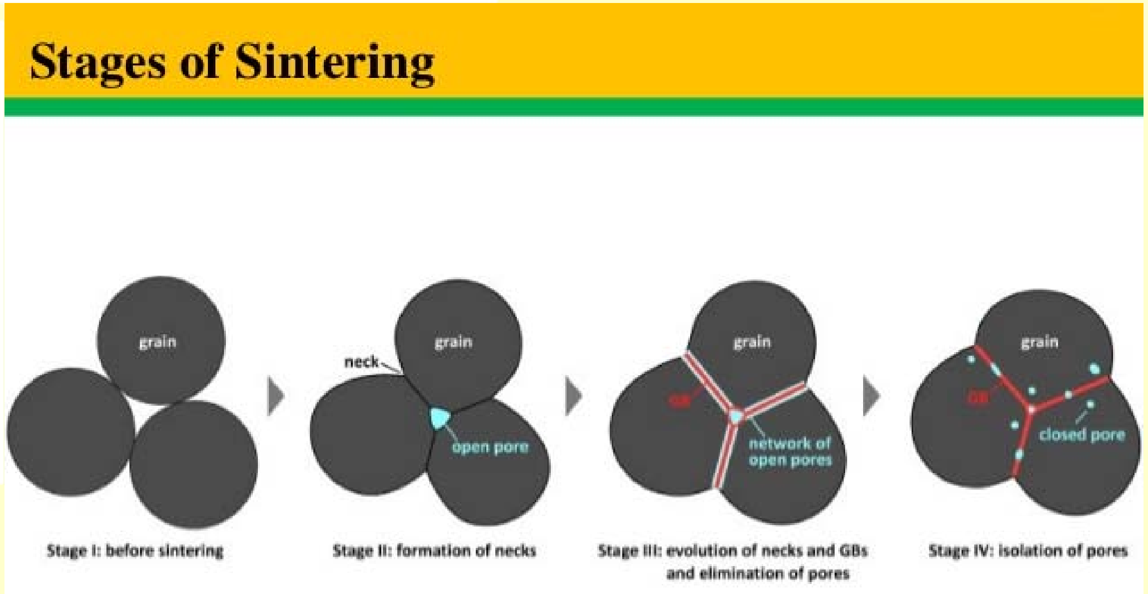


Densification - Sintering

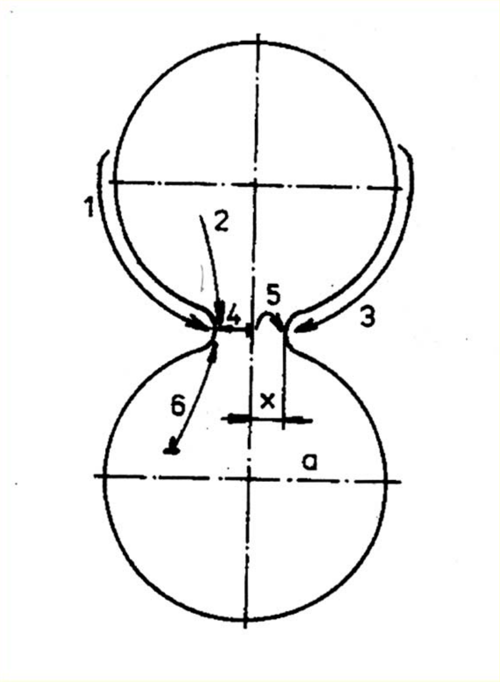
Densification







Sintering mechanisms



Sintering mechanisms - solid, liquid, gas phase

1. Evaporation-condensation and dissolution-precipitation

2. Volume diffusion

3. Surface diffusion

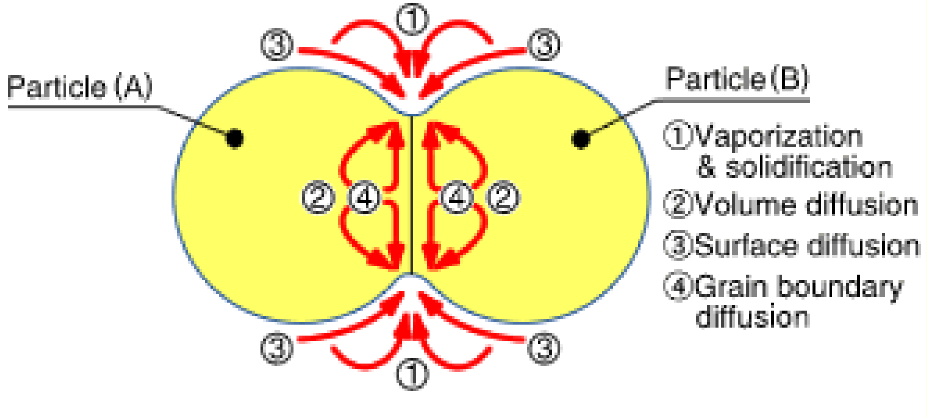
4. Grain boundary diffusion

5. Volume diffusion from grain boundaries

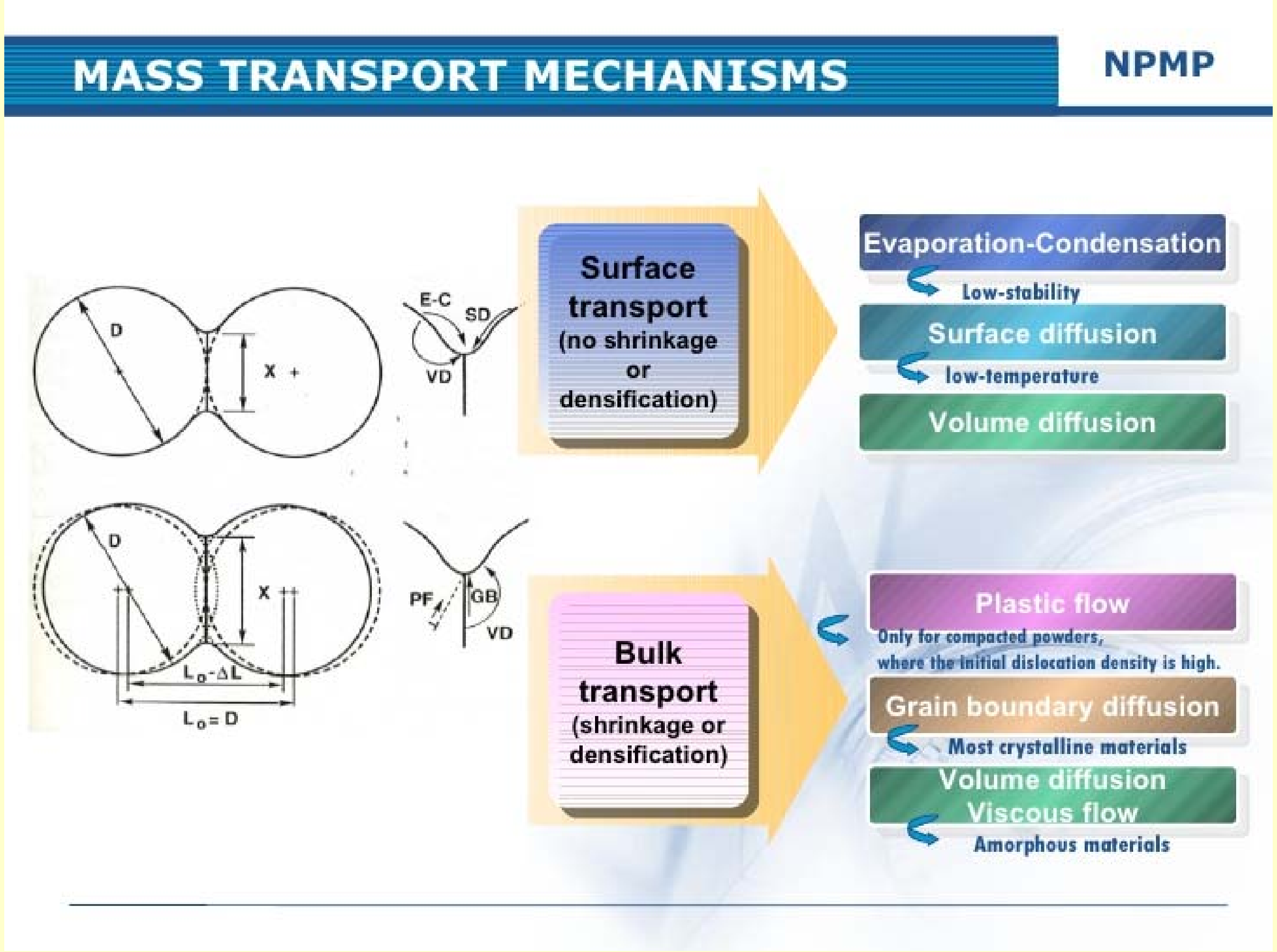
6. Volume diffusion from dislocations – plastic flow

Volume diffusion from dislocations vacancies

Viscous flow



Sintering Mechanisms



MASS TRANSPORT MECHANISMS

NPMP

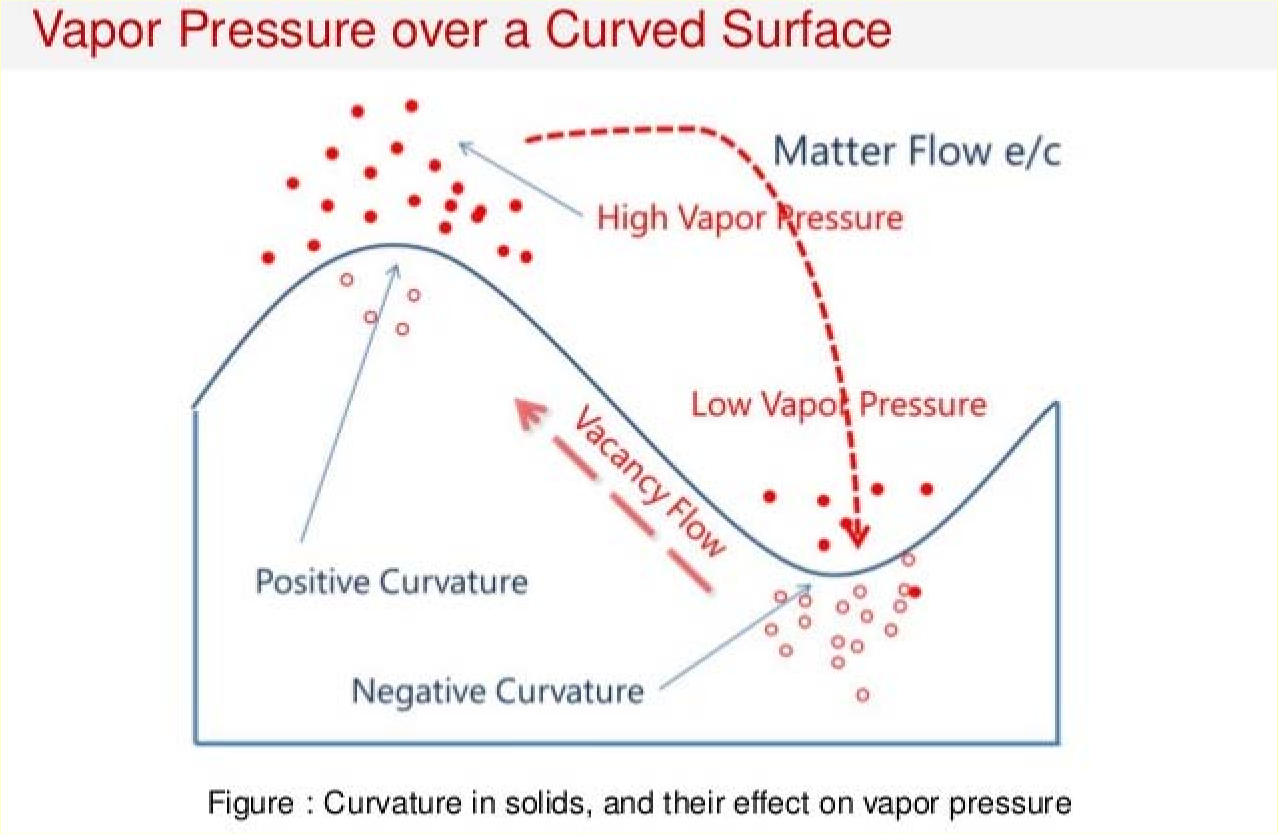
Surface transport (no shrinkage or densification)

- Evaporation-Condensation
  - Low-stability
- Surface diffusion
  - low-temperature
- Volume diffusion

Bulk transport (shrinkage or densification)

- Plastic flow
  - Only for compacted powders, where the initial dislocation density is high.
- Grain boundary diffusion
  - Most crystalline materials
- Volume diffusion
  Viscous flow
  - Amorphous materials

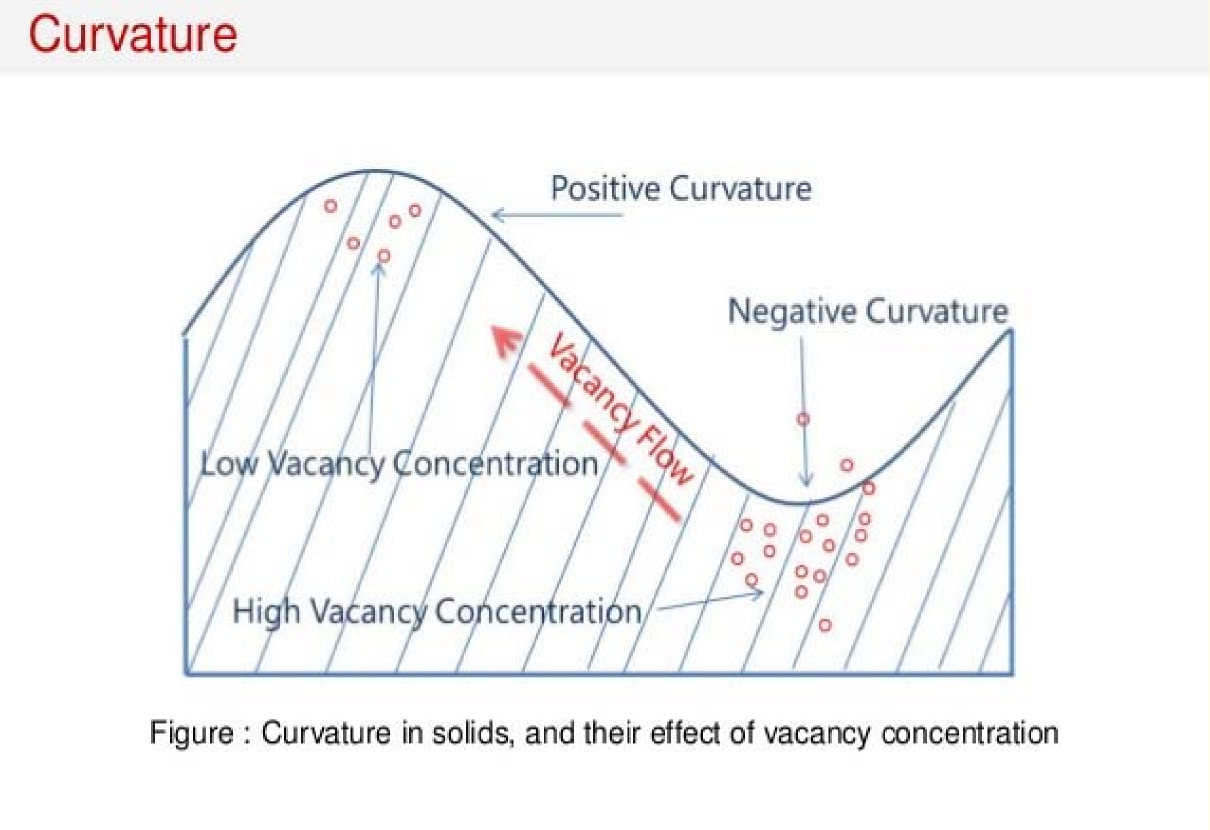
Sintering Mechanisms



Vapor Pressure over a Curved Surface

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

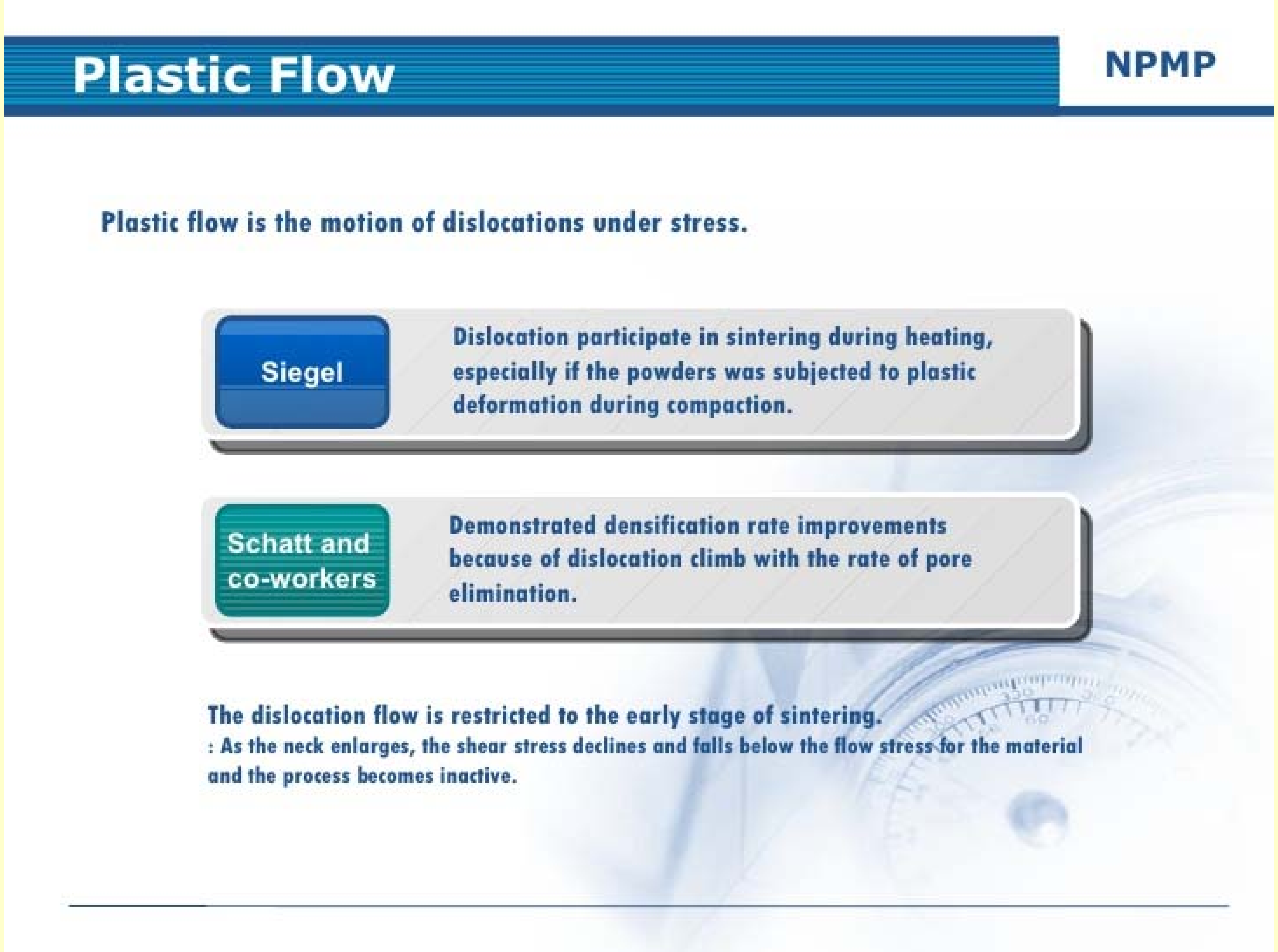
Sintering Mechanisms



Curvature

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

Sintering Mechanisms



Plastic Flow

NPMP

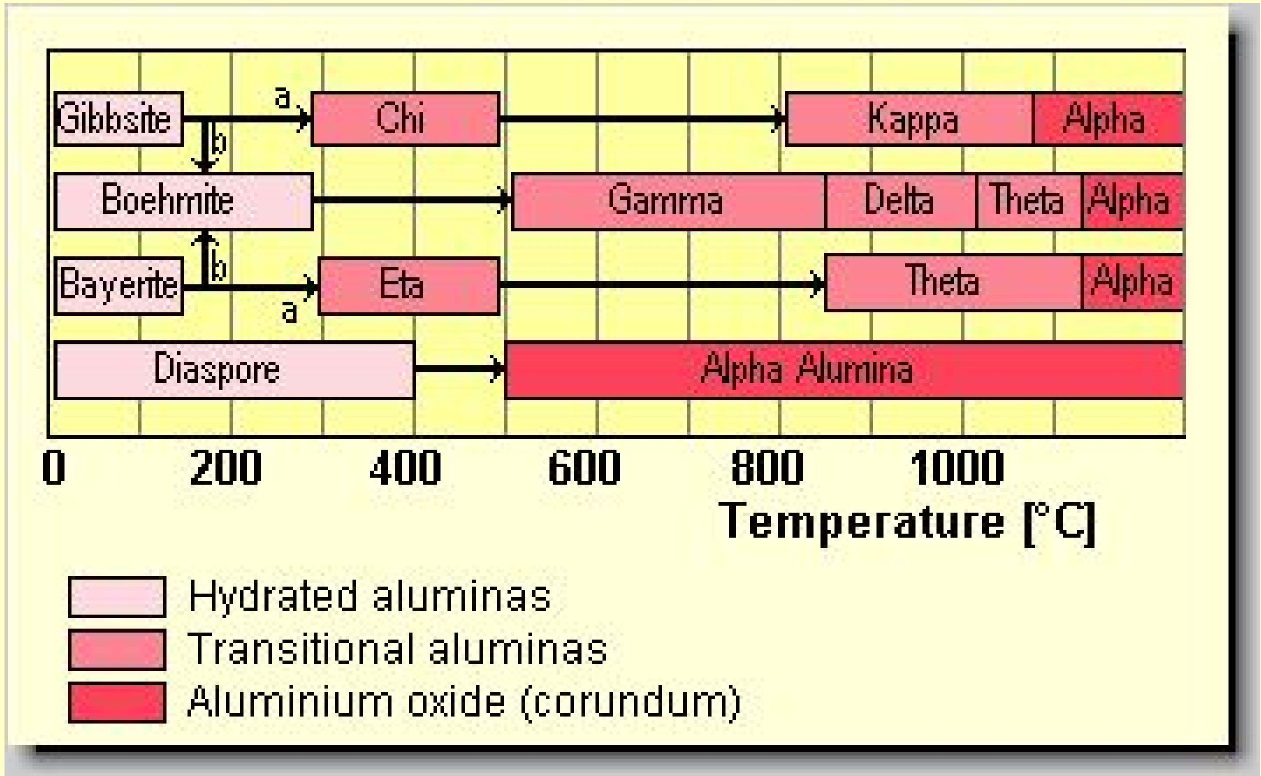
Plastic flow is the motion of dislocations under stress.

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.

Sintering Mechanisms

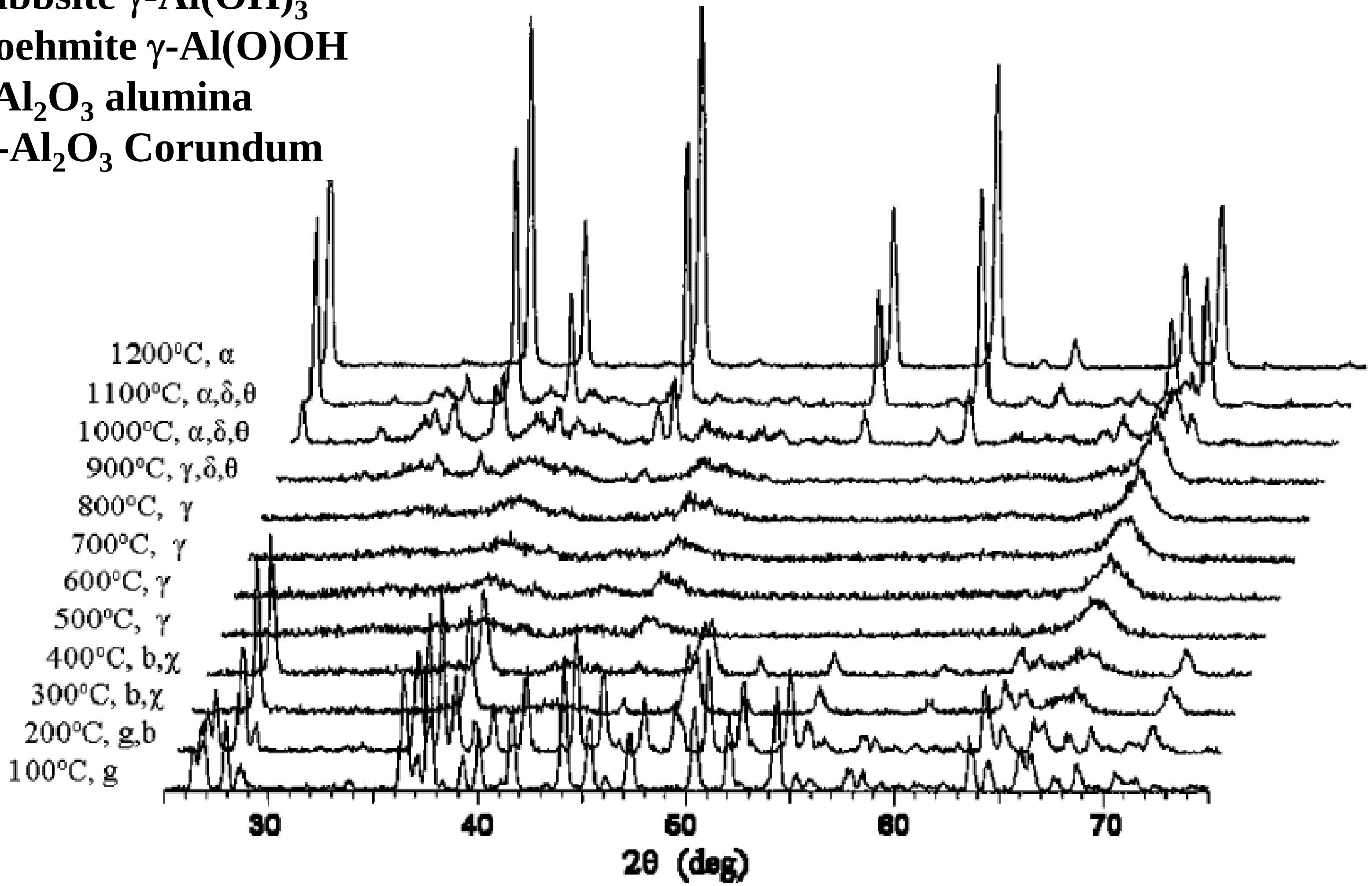
Dehydration sequence of hydrated alumina in air



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

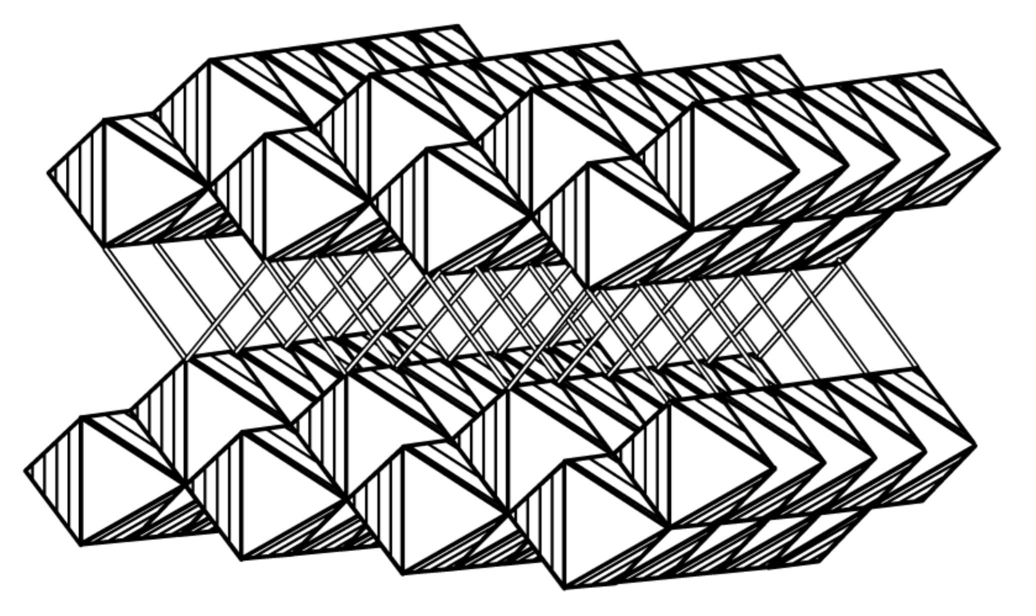
HT-XRD of the phase transitions

g = Gibbsite γ-$Al(OH)_3$
b = Boehmite γ-Al(O)OH
γ = γ-Al_2O_3 alumina
α = α-Al_2O_3 Corundum

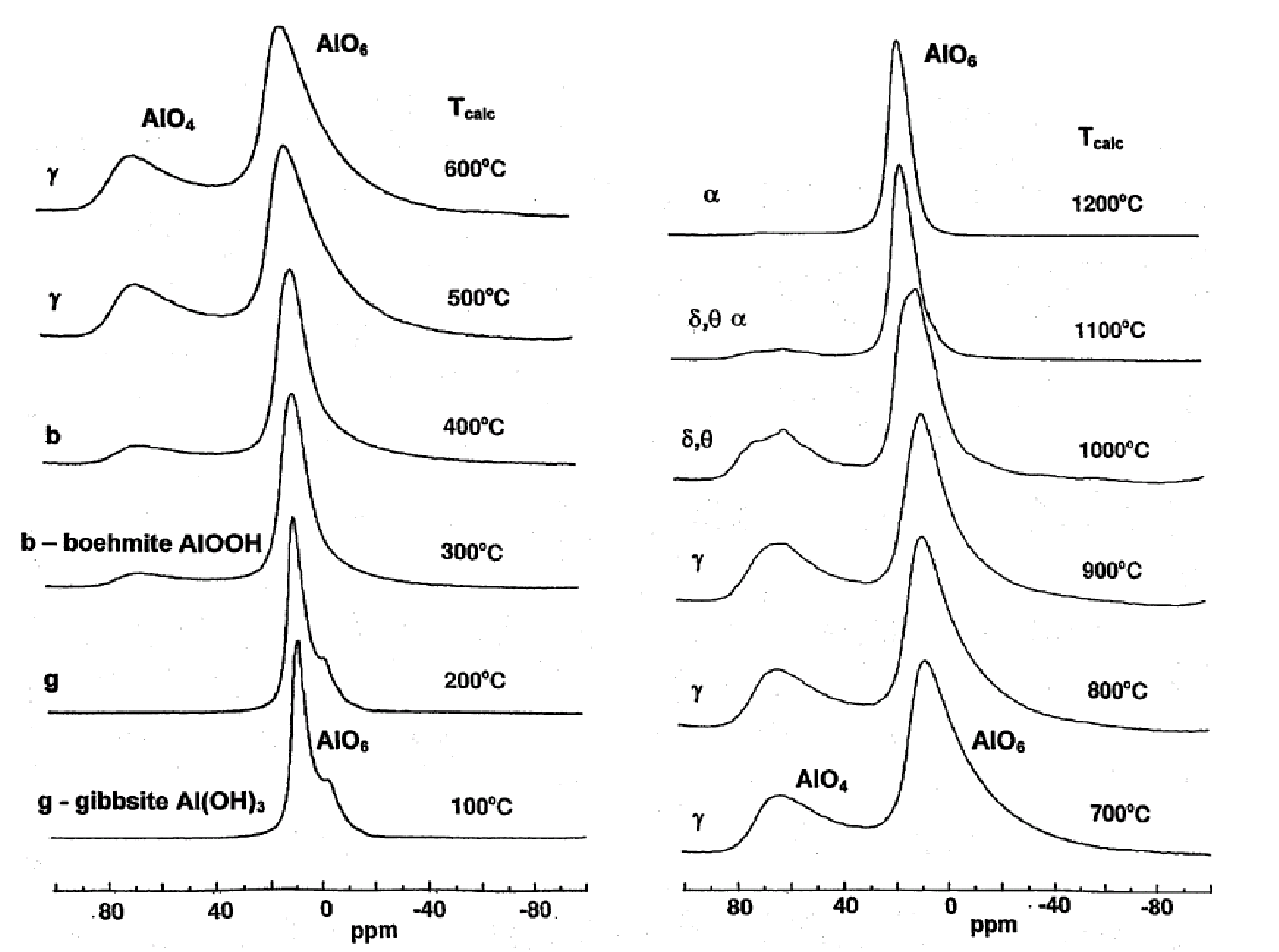


Gibbsite to Boehmite to Gamma

Gibbsite γ-$Al(OH)_3$ to Boehmite γ-$Al(O)OH$ to γ-Al_2O_3 alumina (defect spinel) CCP

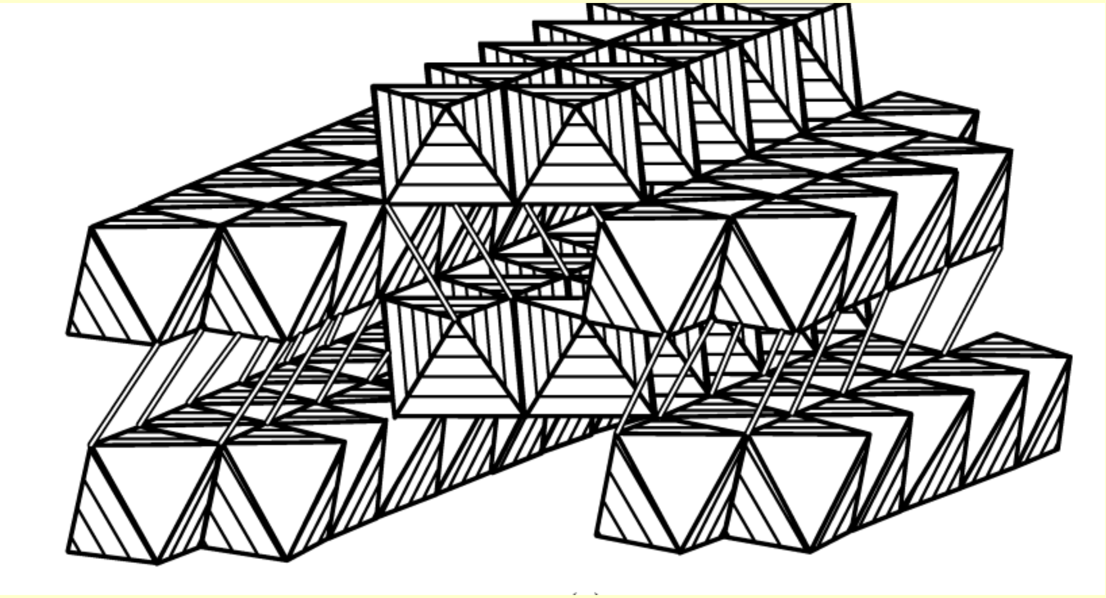


^{27}Al Solid-State NMR spectra

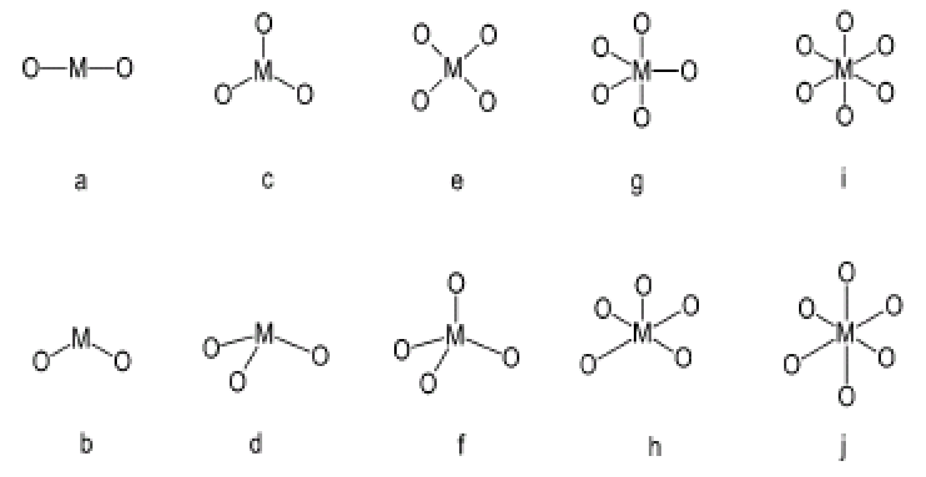


Bayerite to Diaspore to Corundum

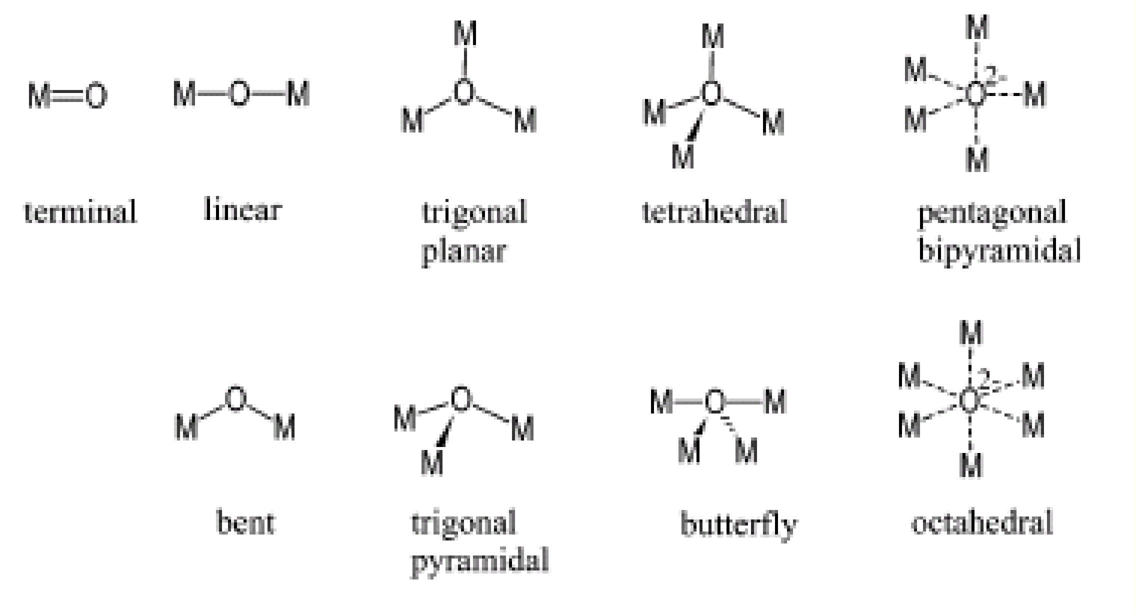
Bayerite α-Al(OH)$_3$ to Diaspore α-Al(O)OH to α-Al$_2$O$_3$ Corundum HCP

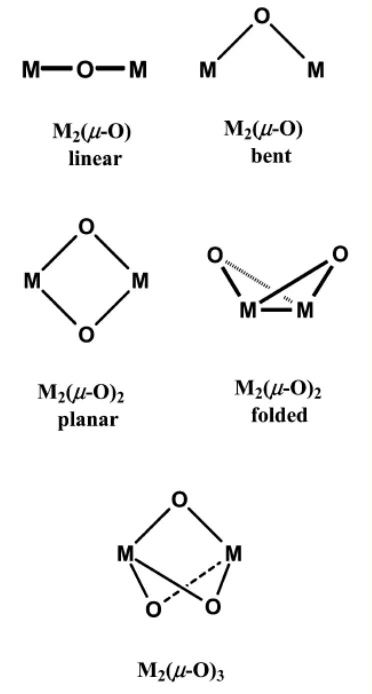


Metal Coordination

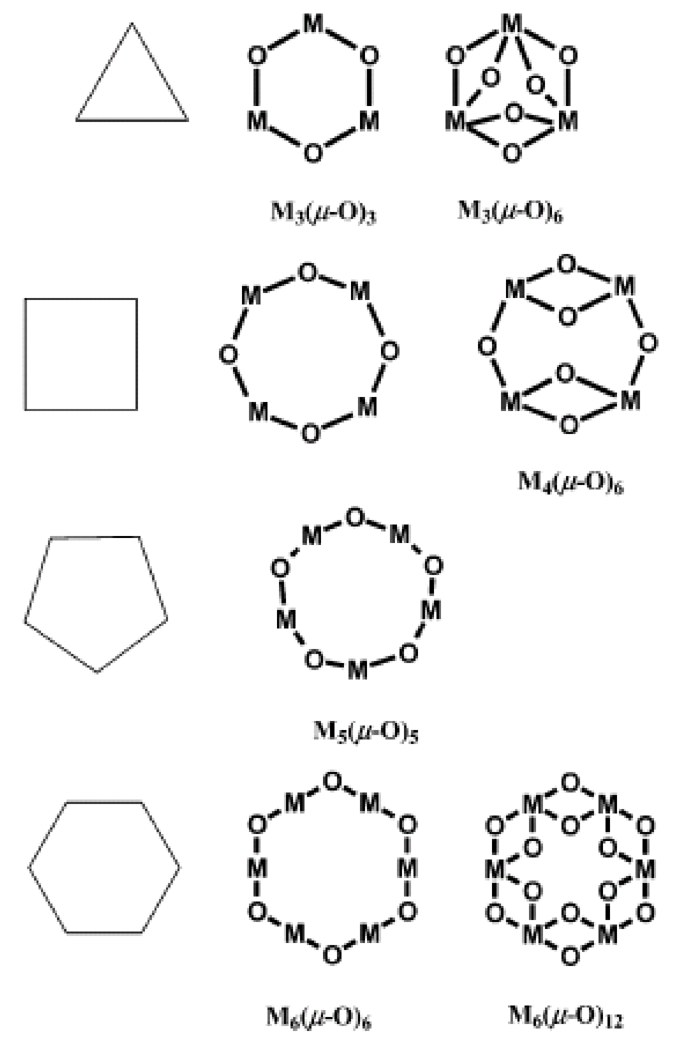


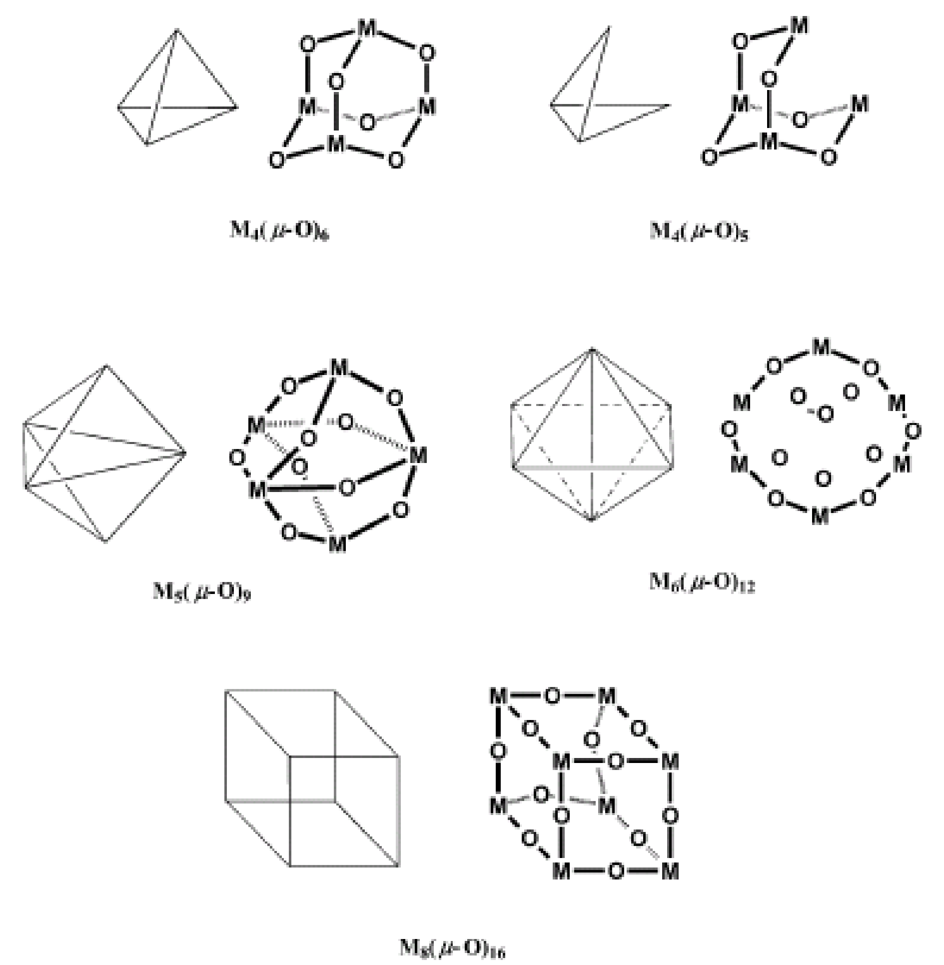
Oxygen Coordination



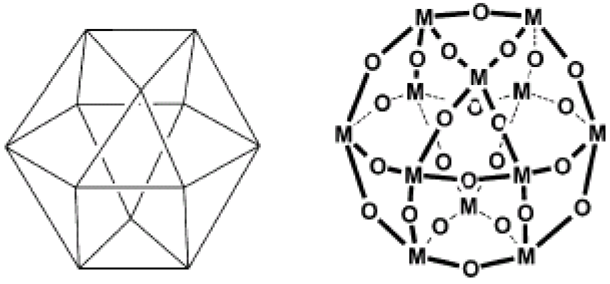


Metal-Oxide Clusters

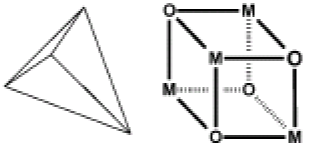




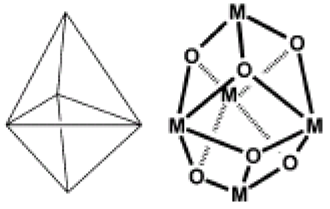
Metal-Oxide Clusters



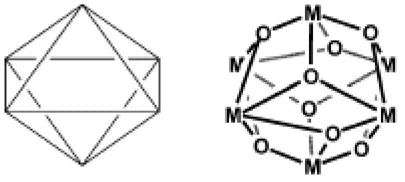
$M_{12}O_{24}$



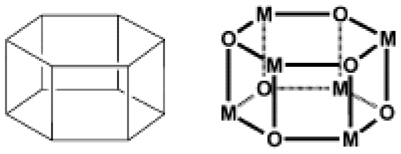
$M_4(\mu_3\text{-O})_4$



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



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



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