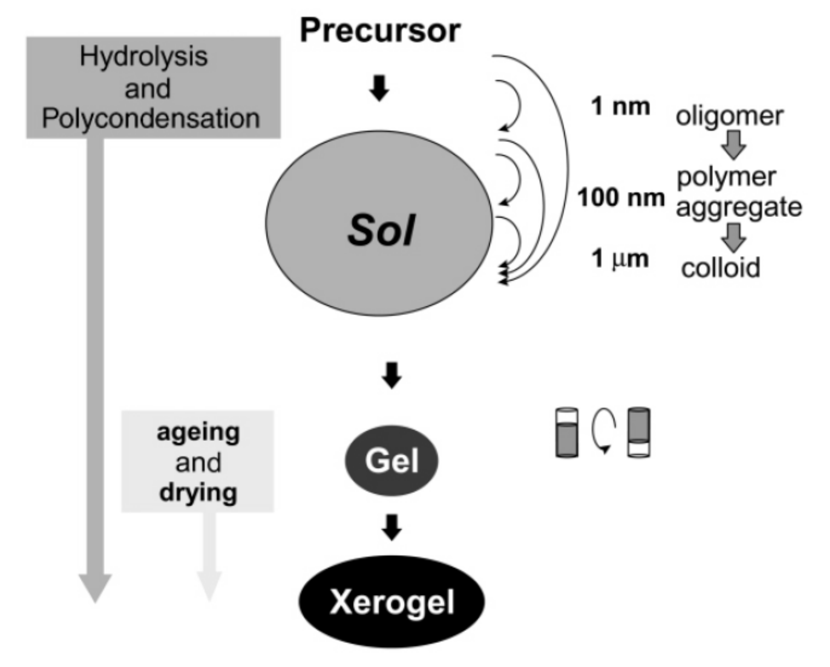
Sol-Gel Methods

PRECURSOR

Sol-gel process

- **Hydrolysis**
- **Polycondensation**
- **Gelation**
- **Ageing**
- **Drying**
- **Densification**



Crystallinity: Microcrystalline, Nanocrystalline, Amorphous, Glasses

Dimensionality: Monoliths, Coatings, Films, Fibers, Nanoparticles

Drying: Xerogels, Aerogels, Ionogels, Cryogels

Heat Treatment: Powders, Glasses, Ceramics

Composition: Oxides, Silicates, Phosphates, Nitrides, Carbon, Inorganic-Organic 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, larger than 1 μm – sedimentation)

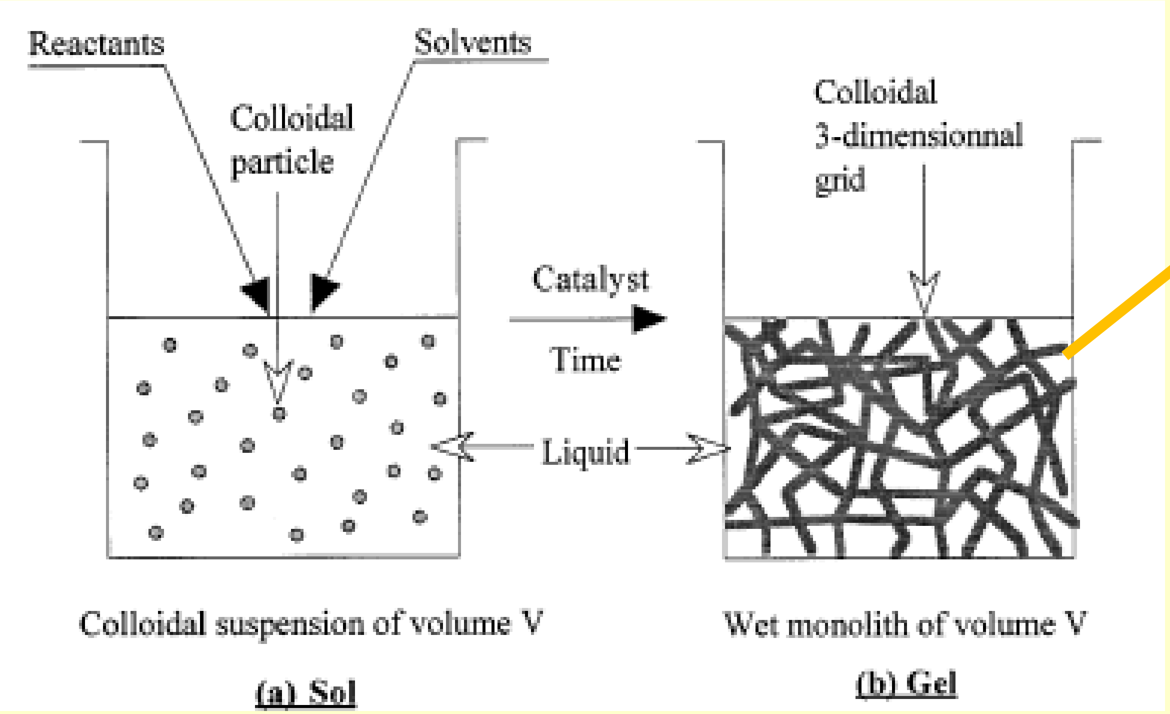
Gel = a nonfluid, porous, two-phase system of three-dimensional, continuous solid network (elastic or rigid) surrounded by a continuous liquid phase

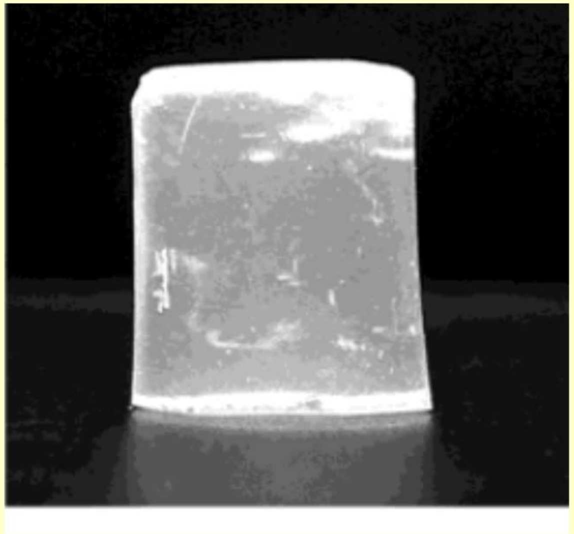
> **Colloidal (particulate) gels = agglomeration of dense colloidal particles**
>
> **Polymeric gels = agglomeration of polymeric particles made from subcolloidal units**

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



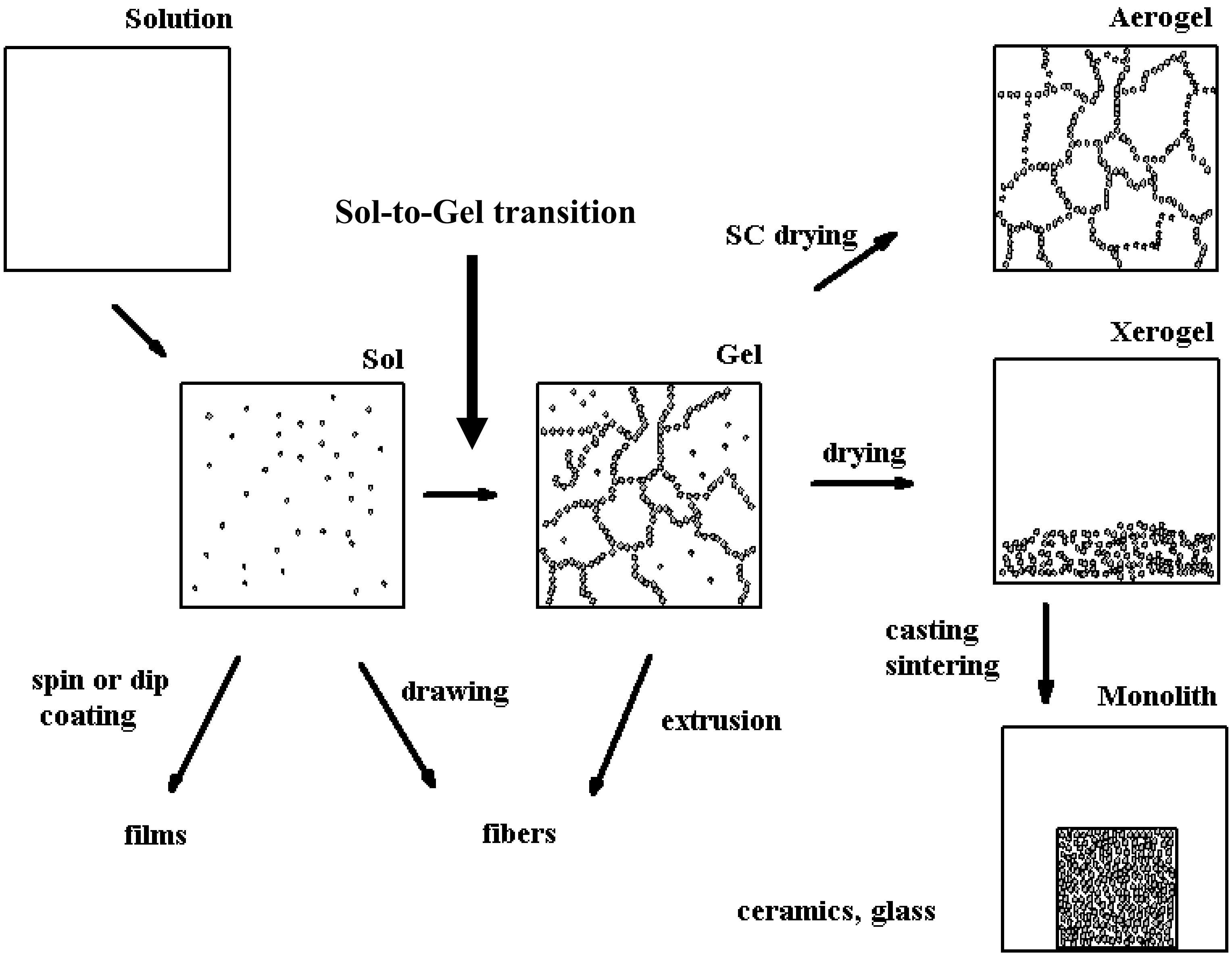


Gel point = point of incipient network formation

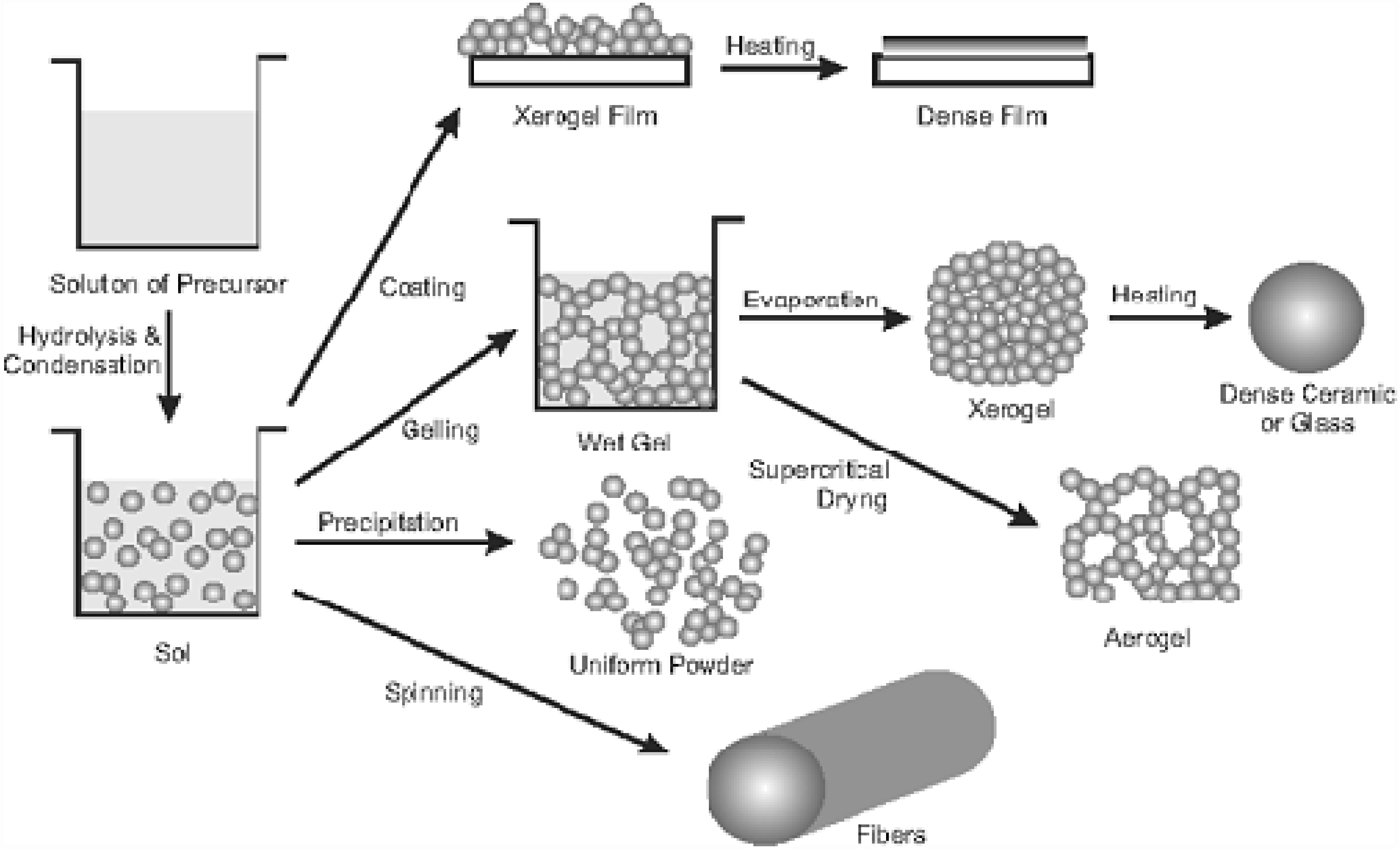
Sol-to-Gel transition is difficult to define

Rheological methods = viscosity increases

Sol-Gel Process



Sol-Gel Processes



Sol-Gel Chemistry

Aqueous

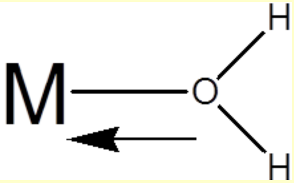
- Colloid Route – inorganic salts, water glass, change pH, hydrolysis, polycondensation
- Metal-Organic Route – metal alkoxides, amides, addition of water, hydrolysis, polycondensation
- Pechini and Citrate Gel Method – inorganic metal salts, complexing agent, chelate formation, polyesterification with polyfunctional alcohol

Nonaqueous

- Hydroxylation (= formation of M–OH)
- Heterofunctional Condensations ($M–X + Y–O–M \rightarrow XY + M–O–M$)

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

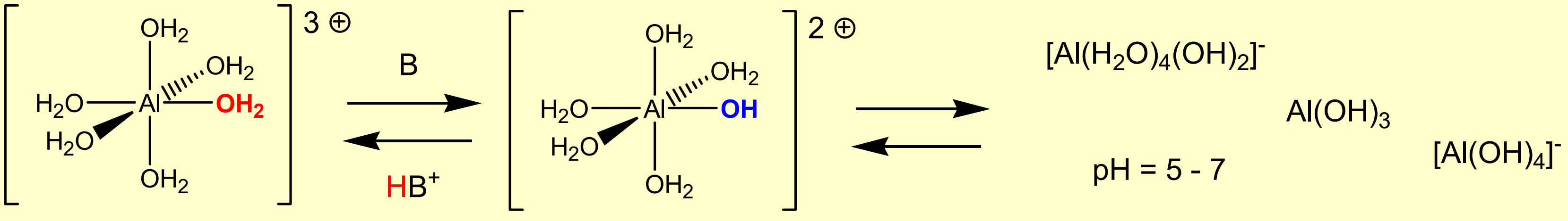
Hydrolysis

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

Condensation-polymerization

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

Colloid Route



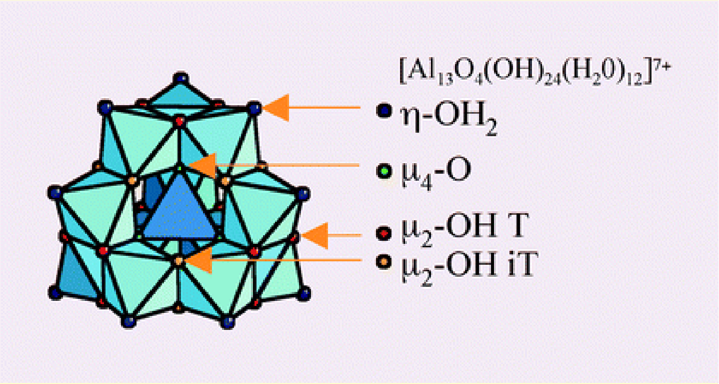
$[Al(H_2O)_4(OH)_2]^-$

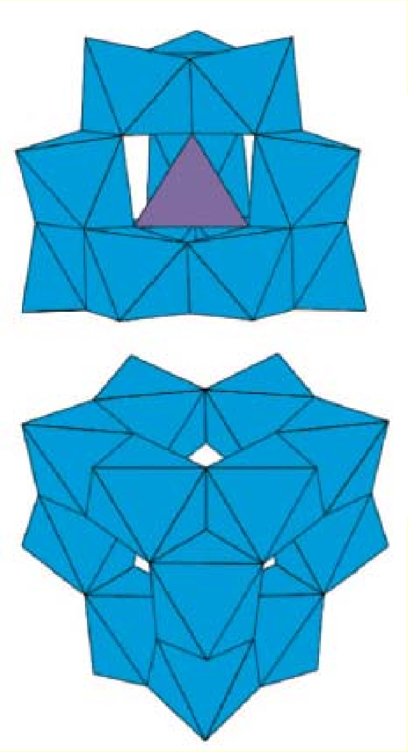
$Al(OH)_3$

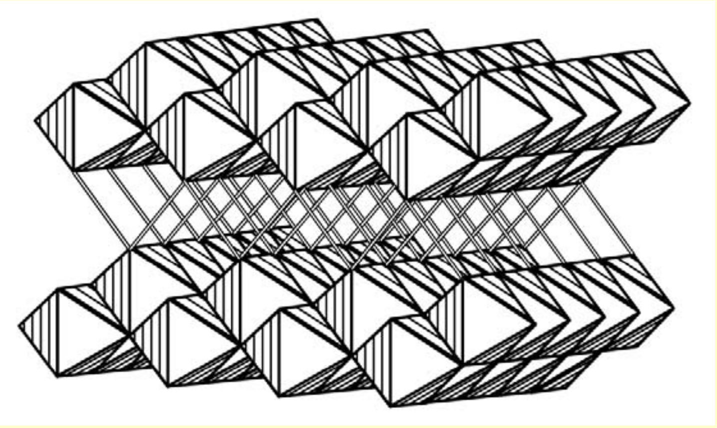
$[Al(OH)_4]^-$

pH = 5 - 7

pH < 3







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

Gibbsite
$Al(OH)_3$

Colloid Route

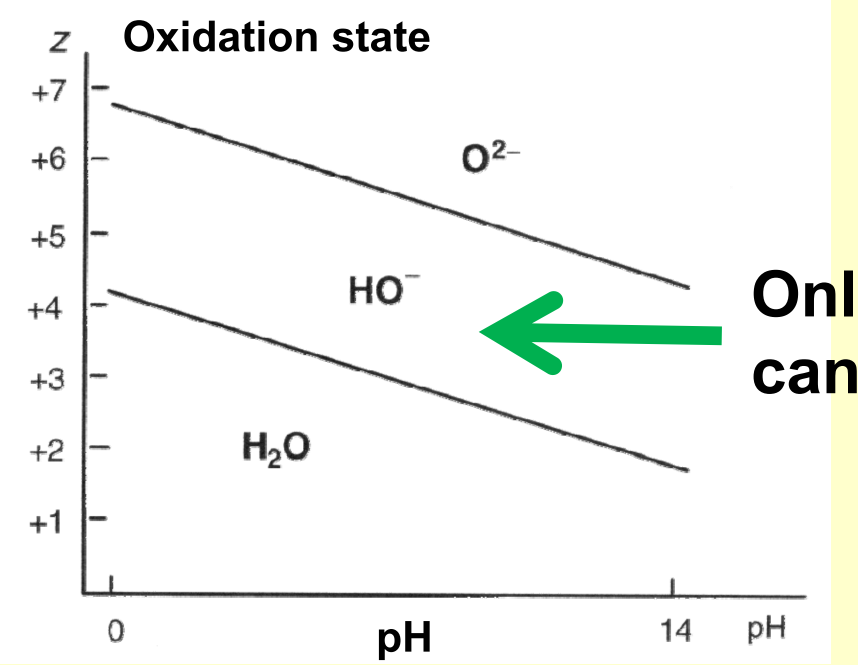
Depending on the water acidity and the charge transfer, the following equilibria are established:

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

Aqua **Hydroxo** **Oxo**

Composition of complexes depends on:

- nature of transition metal
- oxidation state
- charge
- ionic radius
- electronegativity
- nature of ligands
- coordination abilities
- pH of solution

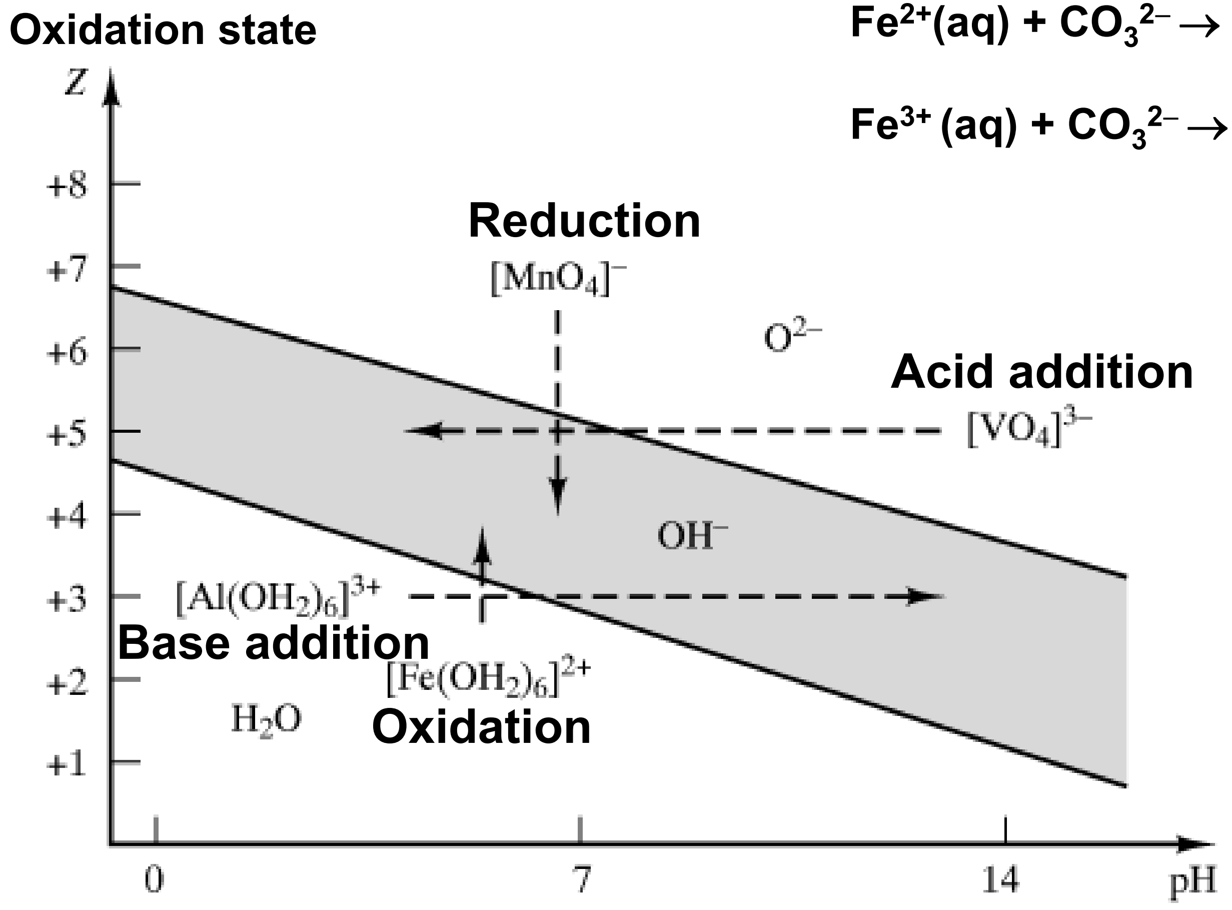


Only hydroxo can condense

Colloid Route

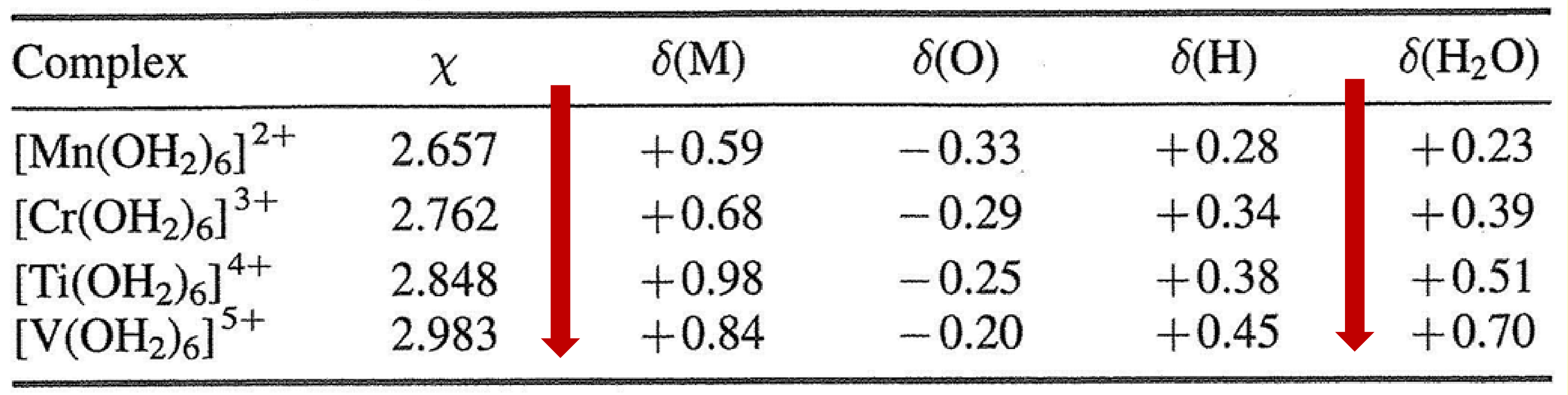
$Fe^{2+}(aq) + CO_3^{2-} \rightarrow$?

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



Colloid Route

χ **Electronegativity** δ **Partial charges on ions and H_2O molecule**



Complex	χ	$\delta(M)$	$\delta(O)$	$\delta(H)$	$\delta(H_2O)$
$[Mn(OH_2)_6]^{2+}$	2.657	+0.59	−0.33	+0.28	+0.23
$[Cr(OH_2)_6]^{3+}$	2.762	+0.68	−0.29	+0.34	+0.39
$[Ti(OH_2)_6]^{4+}$	2.848	+0.98	−0.25	+0.38	+0.51
$[V(OH_2)_6]^{5+}$	2.983	+0.84	−0.20	+0.45	+0.70

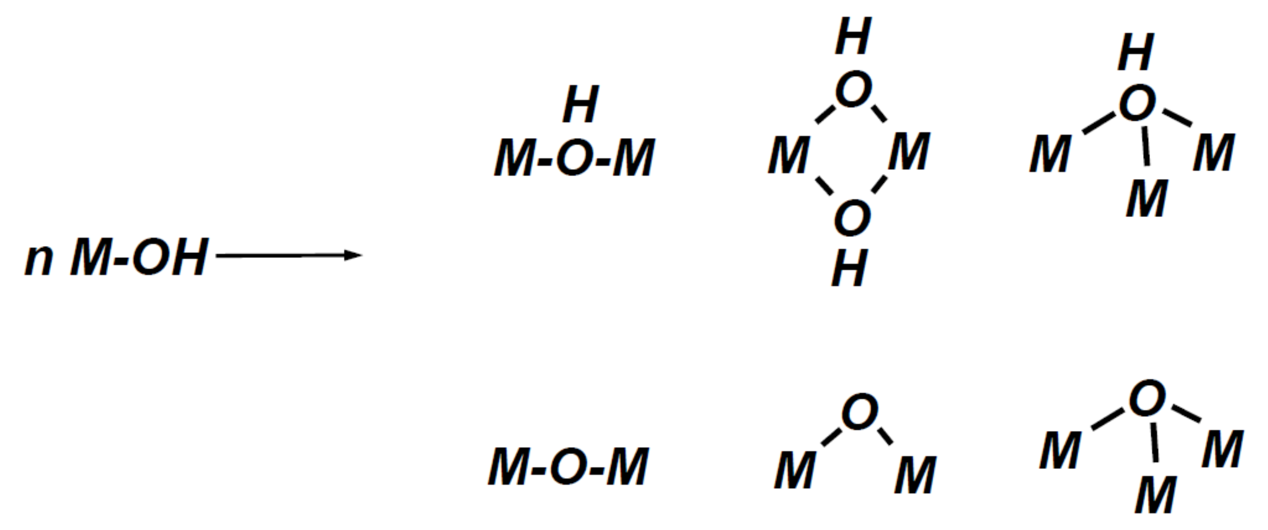
The higher a charge on ion, the more acidic coordinated waters are

Colloid Route

Only hydroxo groups can condense !!

Olation

= a hydroxo bridge (-OH- “ol” bridge) is formed between two metals centers

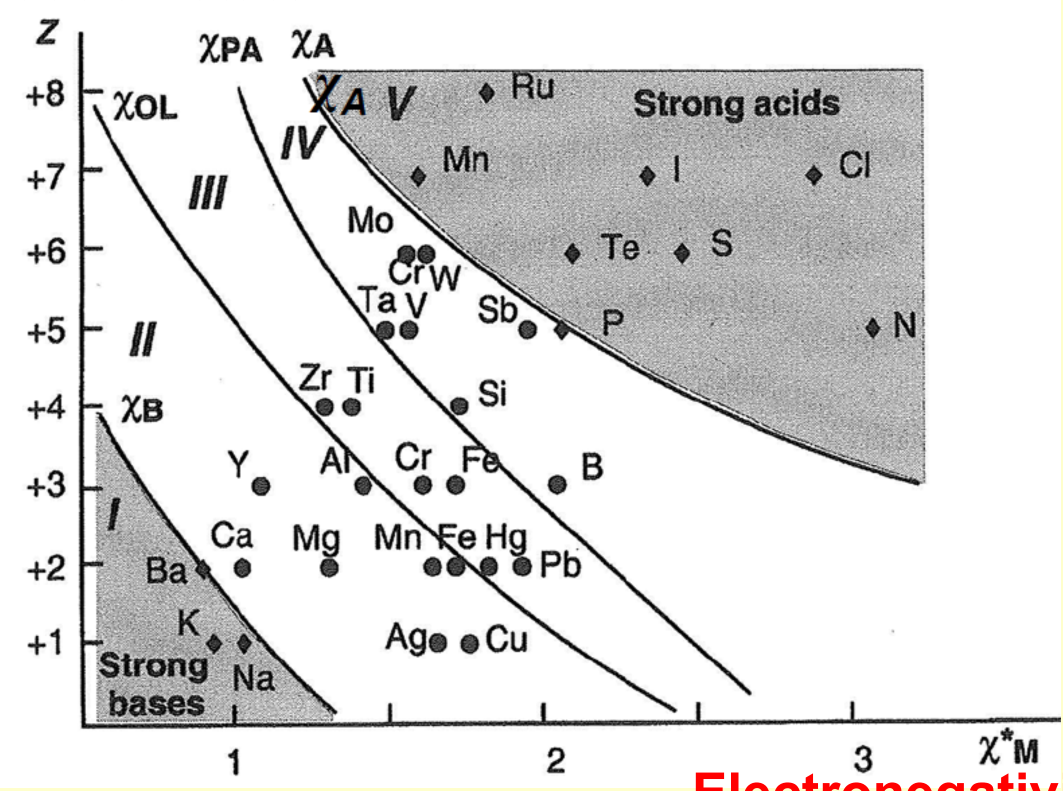


Oxolation

= an oxo bridge (–O–) is formed between two/three metals centers

Colloid Route

Oxidation state



Electronegativity

Electronegativity of a central atom

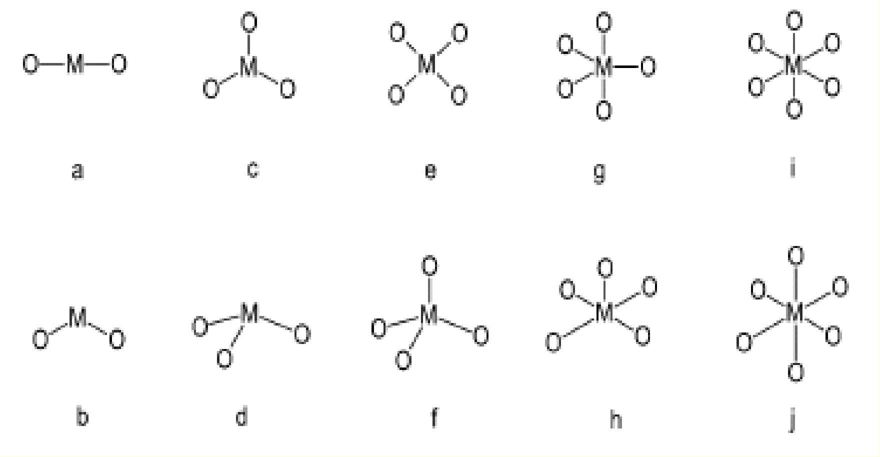
χ_M

determines degree and mechanism of condensation for neutral hydroxo containing species

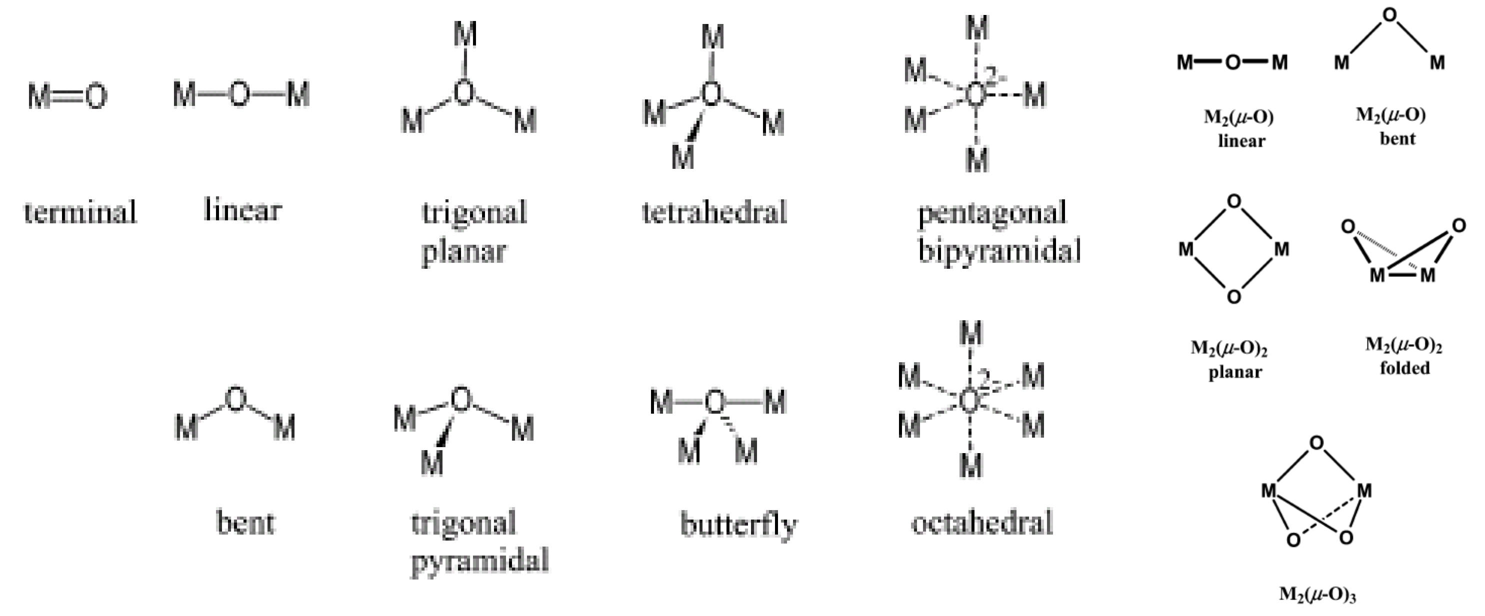
Area I : monomeric and soluble cations
Area II : condensation by olation (M–OH–M)
Area III : condensation by olation or oxolation
Area IV : condensation by oxolation (M–O–M)
Area V : monomeric and soluble anions

Colloid Route

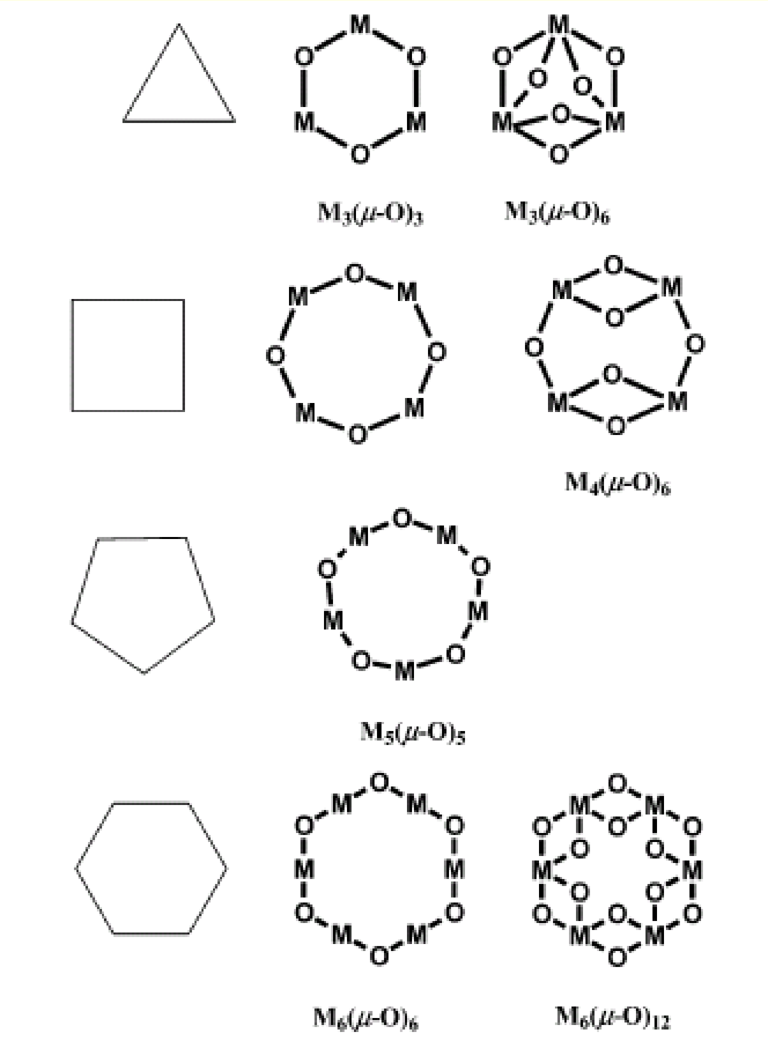
Metal Coordination

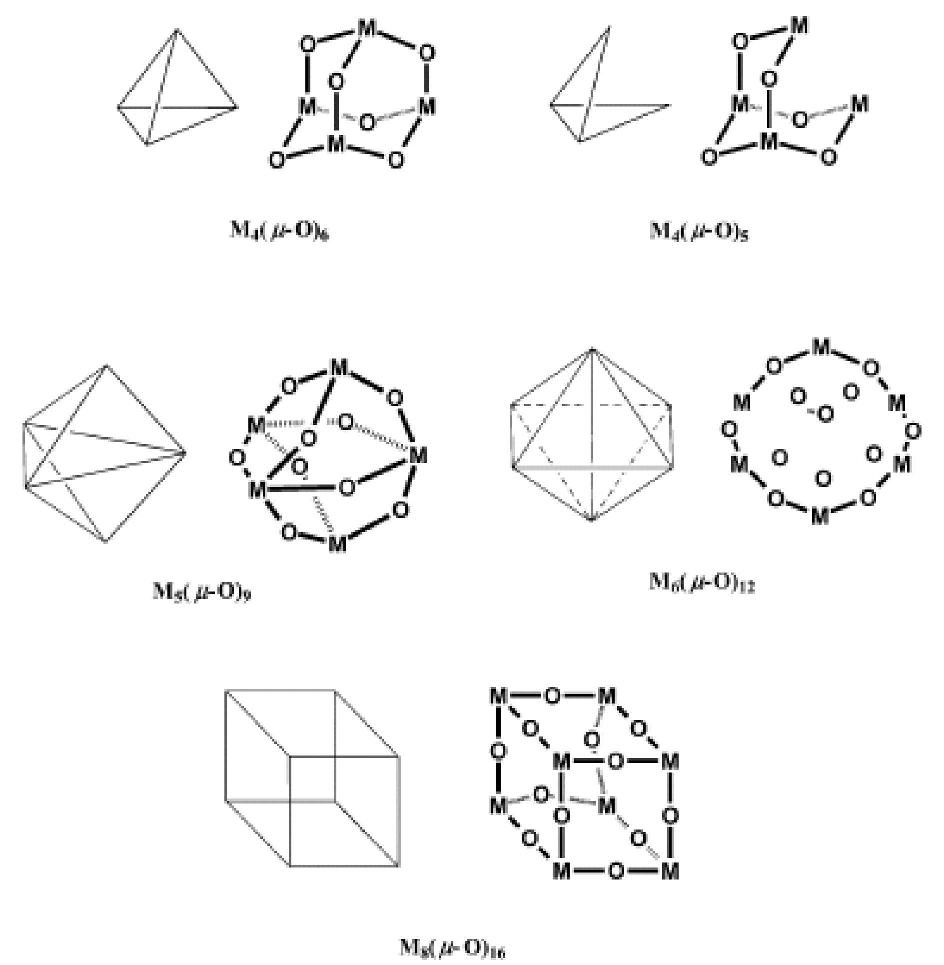


Oxygen Coordination

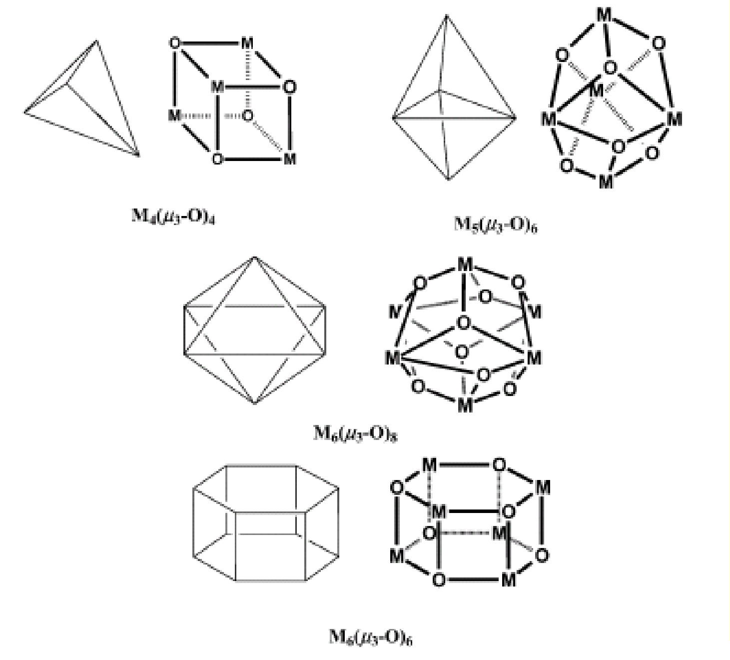


Metal-Oxide Clusters

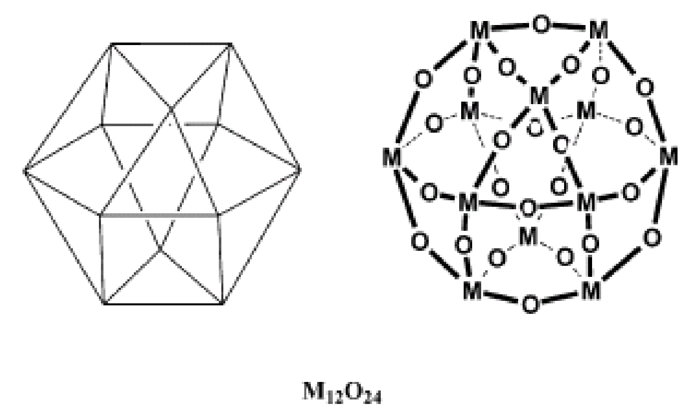


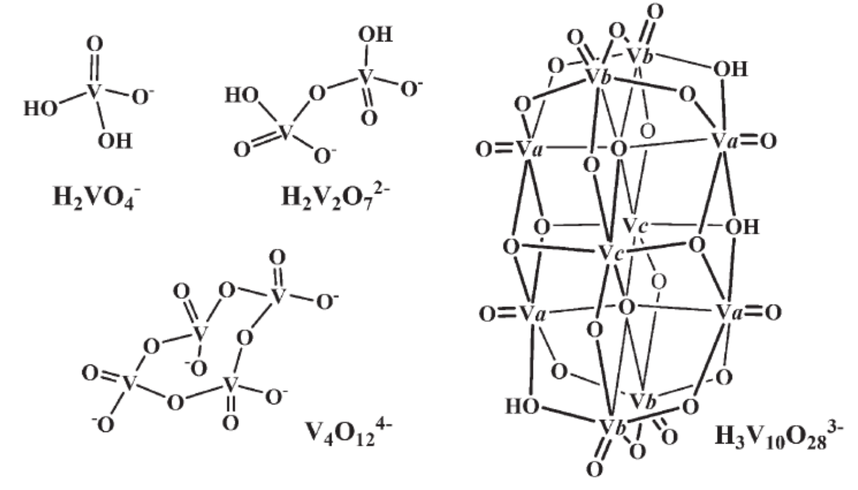


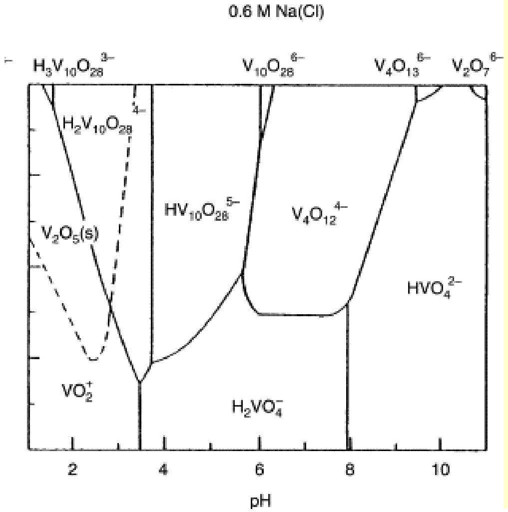
Metal-Oxide Clusters



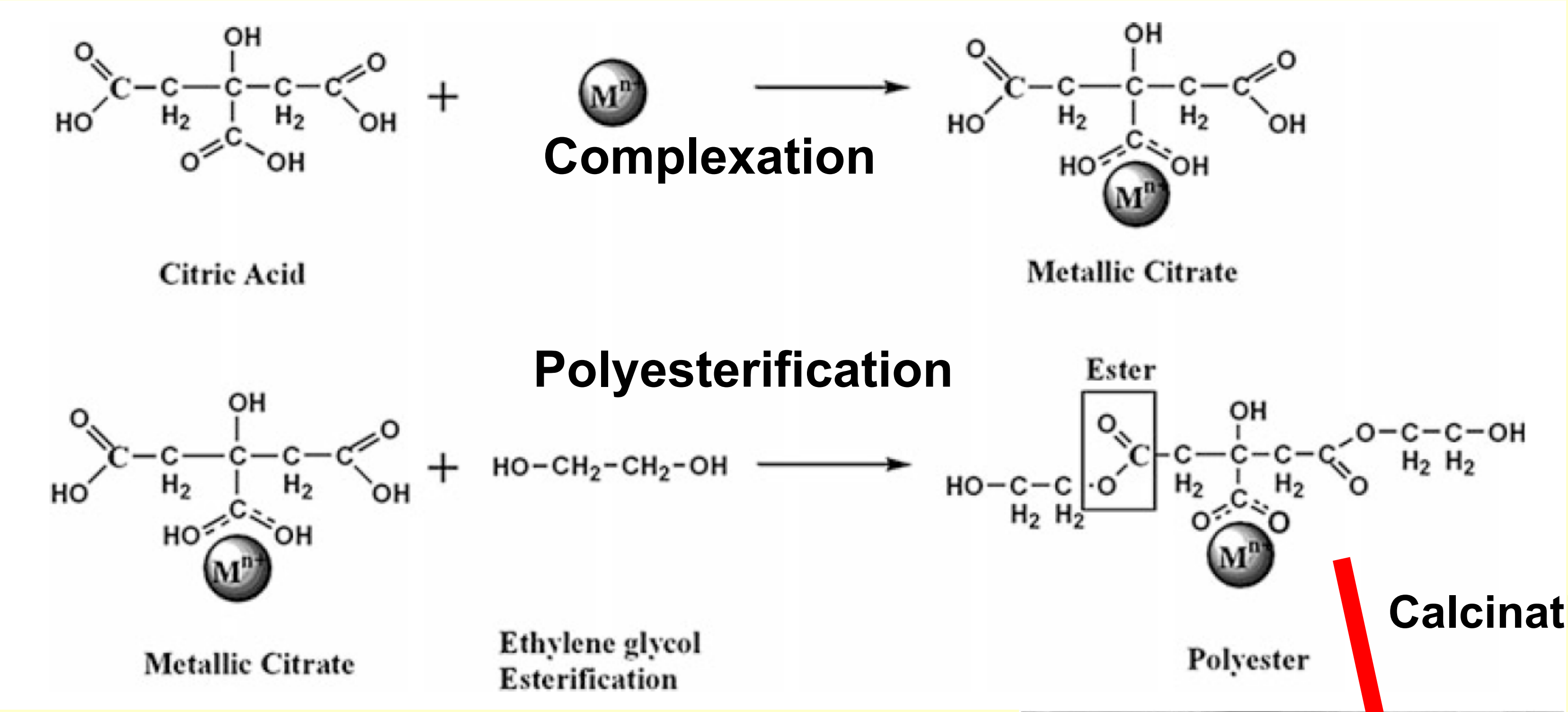
cuboctahedron







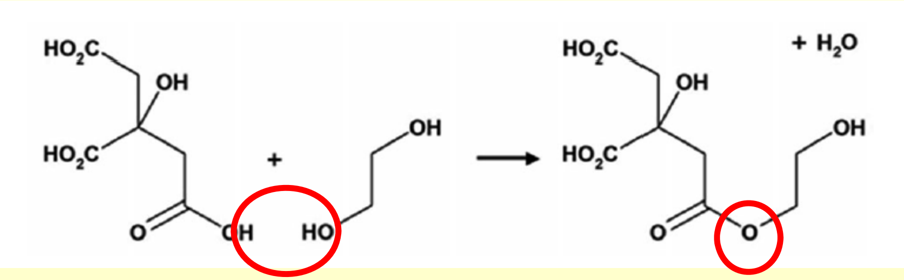
Pechini Sol-Gel Route

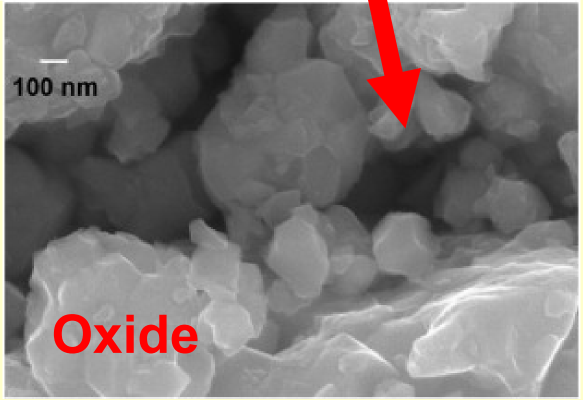


Complexation

Polyesterification

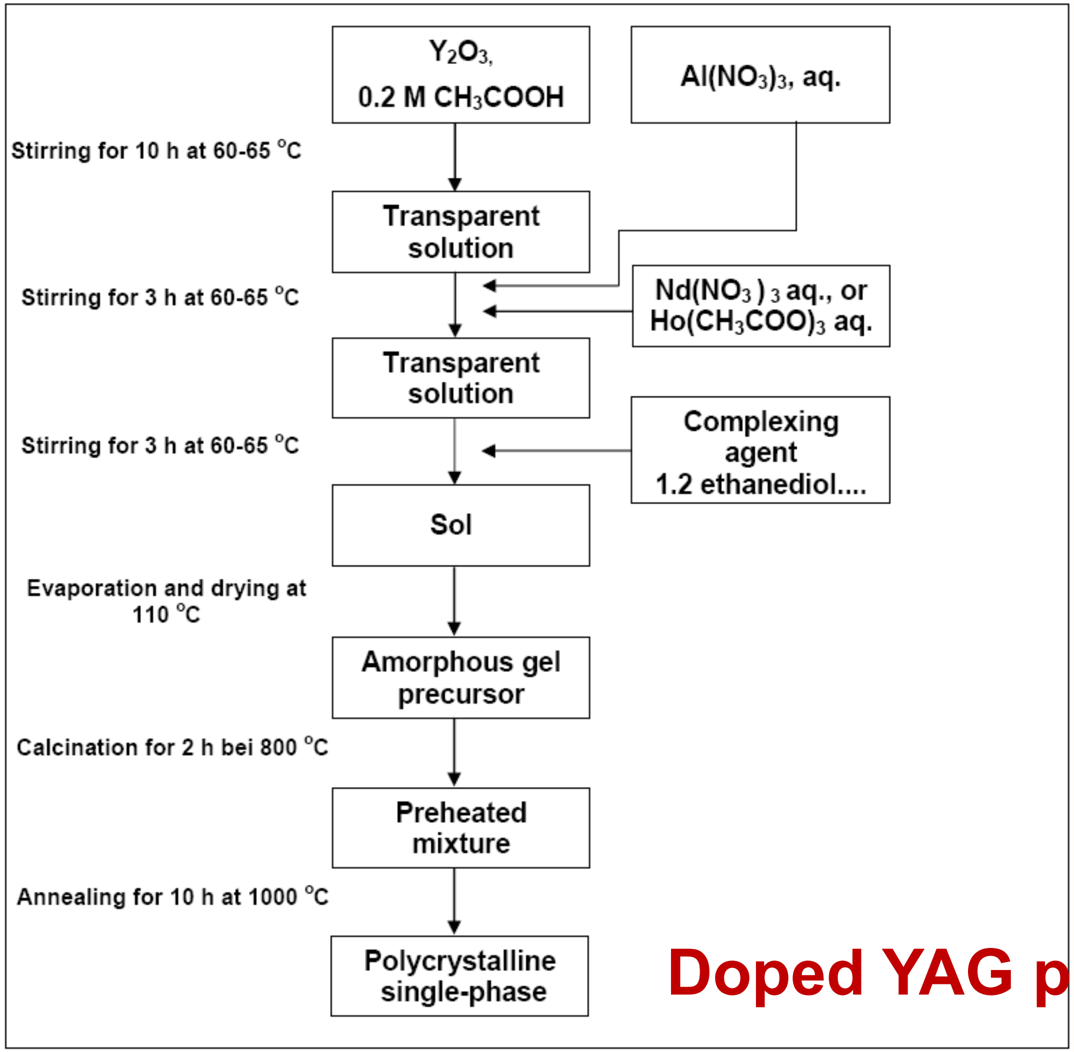
Calcination





Oxide

Pechini Sol-Gel Route



Y_2O_3, 0.2 M CH_3COOH

$Al(NO_3)_3$, aq.

Stirring for 10 h at 60-65 °C

Transparent solution

Stirring for 3 h at 60-65 °C

$Nd(NO_3)_3$ aq., or $Ho(CH_3COO)_3$ aq.

Transparent solution

Stirring for 3 h at 60-65 °C

Complexing agent 1.2 ethanediol....

Sol

Evaporation and drying at 110 °C

Amorphous gel precursor

Calcination for 2 h bei 800 °C

Preheated mixture

Annealing for 10 h at 1000 °C

Polycrystalline single-phase

Major components

Dopants

Gelling agents

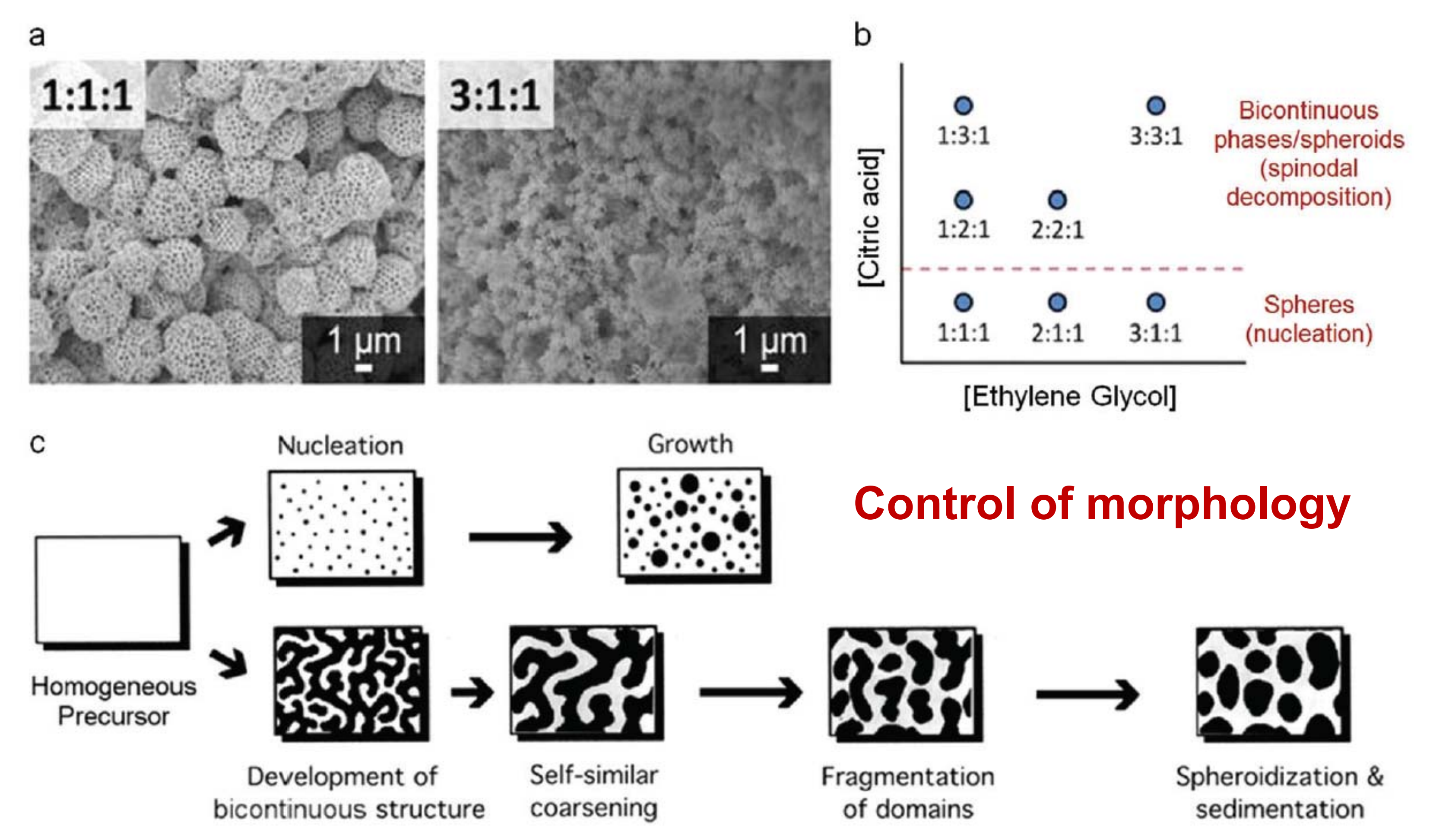
Removal of solvents

Removal of organics

Doped YAG product

Pechini Sol-Gel Route

EG : CA : M



Control of morphology

Metal-Organic (Alkoxide) Route

Hydrolysis

Metal / Metalloid Alkoxides

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

$Si(OEt)_4$ = TEOS

Metal Amides

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

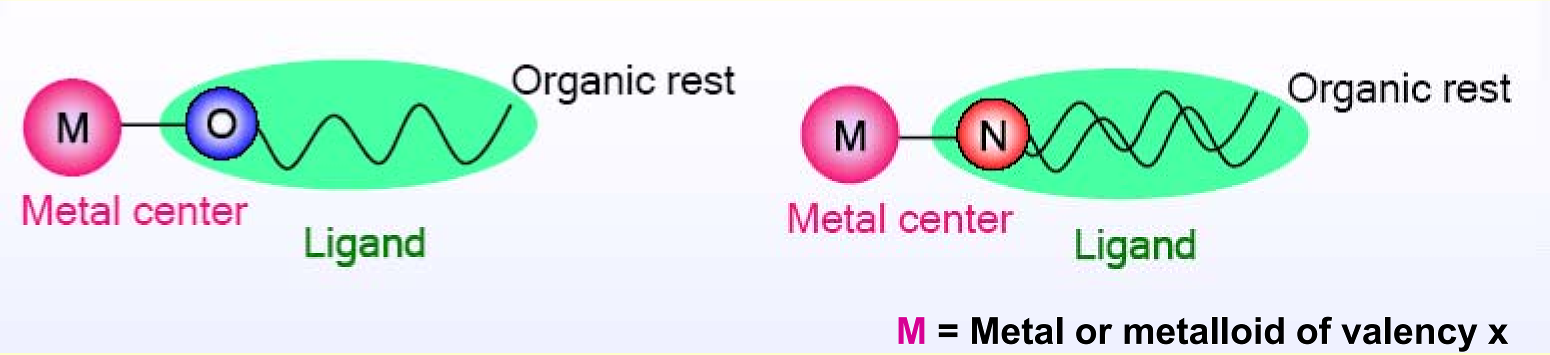
Polycondensation

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

⬇

Sol – Gel – Oxide xerogel

Metal-Organic Precursors



M = Metal or metalloid of valency x
n = degree of molecular association

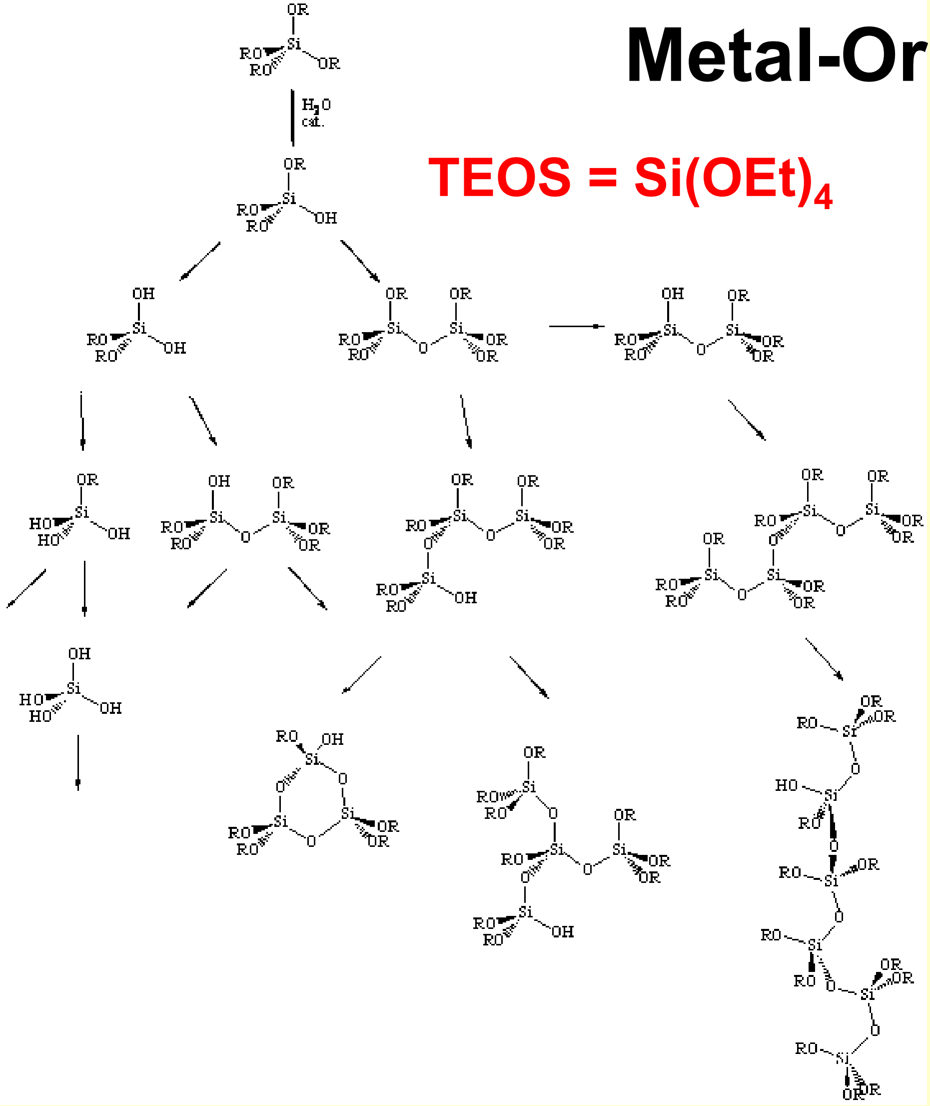
Metal Alkoxides $[M(OR)_x]_n$
formed by the replacement of the hydroxylic hydrogen of an alcohol (ROH) through a metal atom

Heterometallic Alkoxides $[M_aM'_b(OR)_x]_n$

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-Organic (Alkoxide) Route



TEOS = Si(OEt)$_4$

Oligomers formed by hydrolysis-condensation process

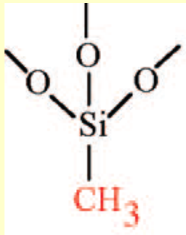
-linear
-branched
-cyclic
-polyhedral

Never goes to pure SiO$_2$

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

Modified Silicon Alkoxides as Precursors

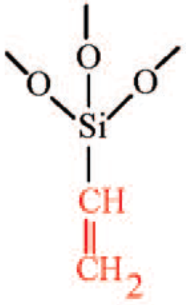
Silsesquioxanes = $RSiO_{1.5}$ (sesqui = 3/2)



Methyl

Hydrophobicity

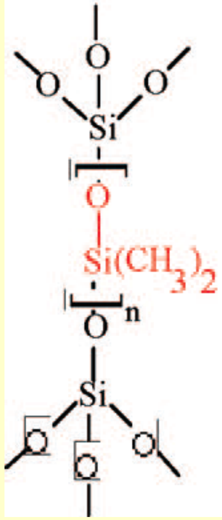
Terminal groups



Vinyl

Crosslinking with acrylic

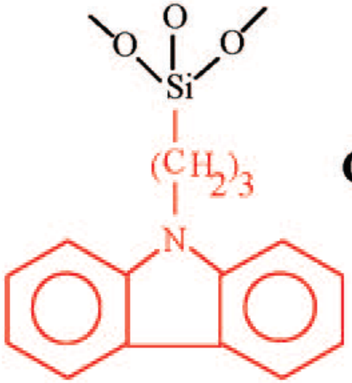
Polymerizable groups



Polydimethylsiloxane

Rubbery behavior

Bridging groups



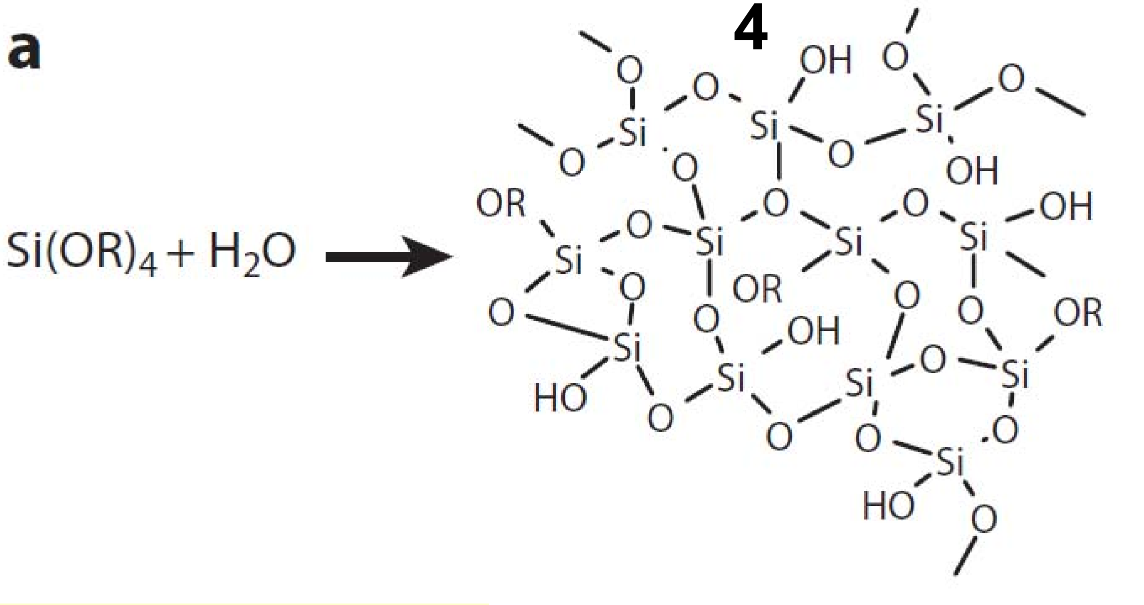
Carbazole

Charge transport properties

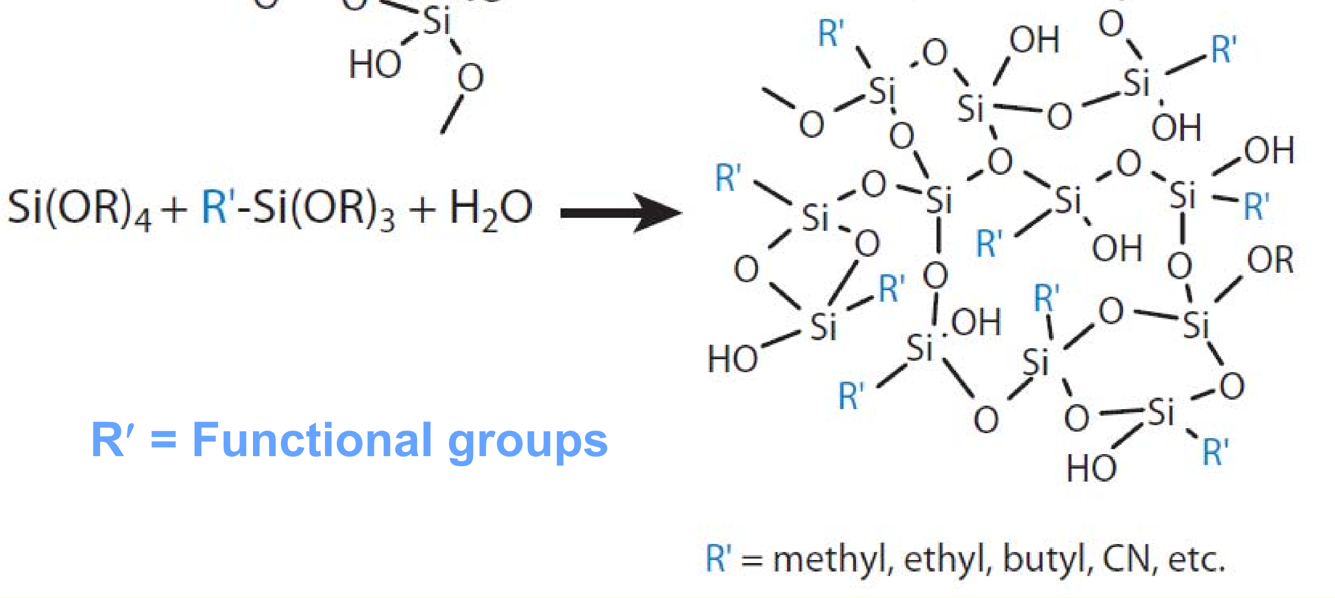
Functional groups

Modified Silicon Alkoxides as Precursors

Connectivity of Si
4



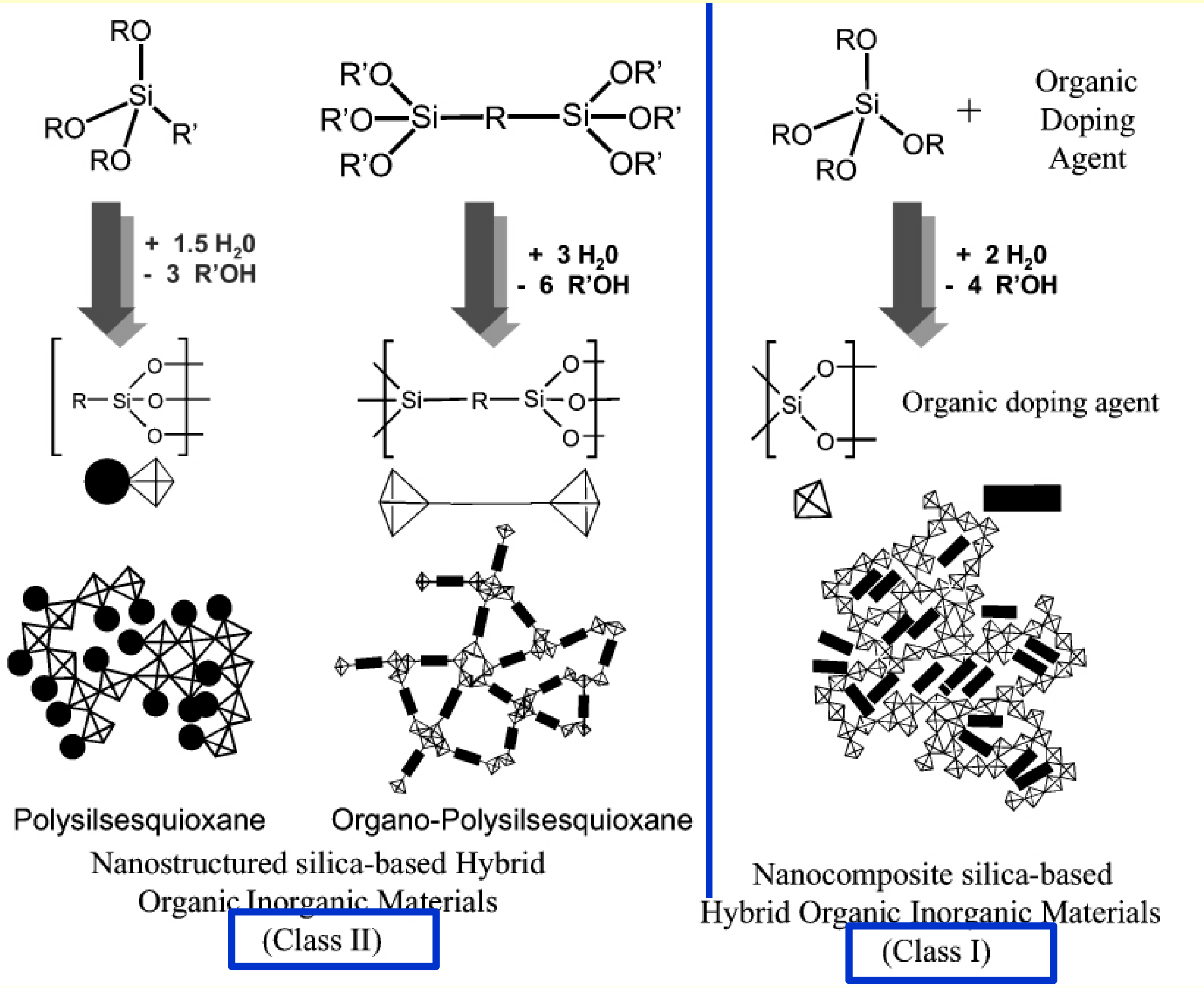
Connectivity of Si
3



R′ = methyl, ethyl, butyl, CN, etc.

R′ = Functional groups

Hybrid Inorganic-Organic Materials



Polysilsesquioxane

Organo-Polysilsesquioxane

Nanostructured silica-based Hybrid Organic Inorganic Materials

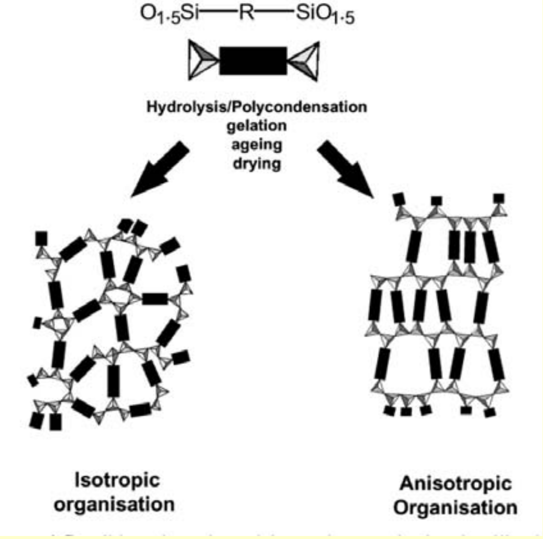
(Class II)

Nanocomposite silica-based Hybrid Organic Inorganic Materials

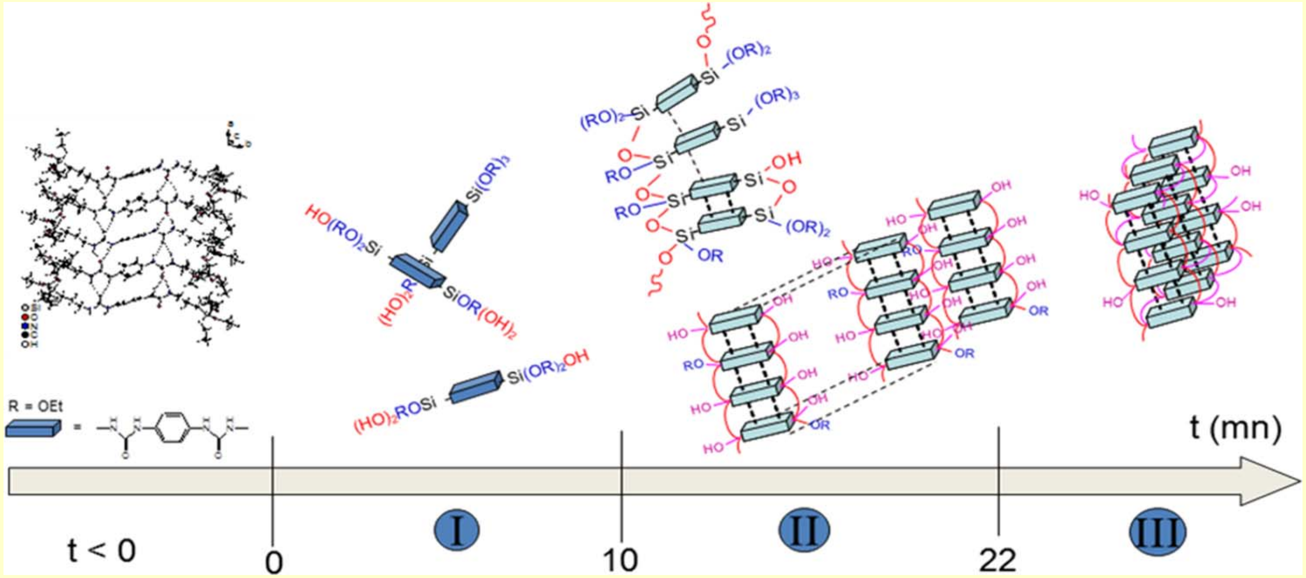
(Class I)

Self-Assembly of Bridged Silsesquioxanes

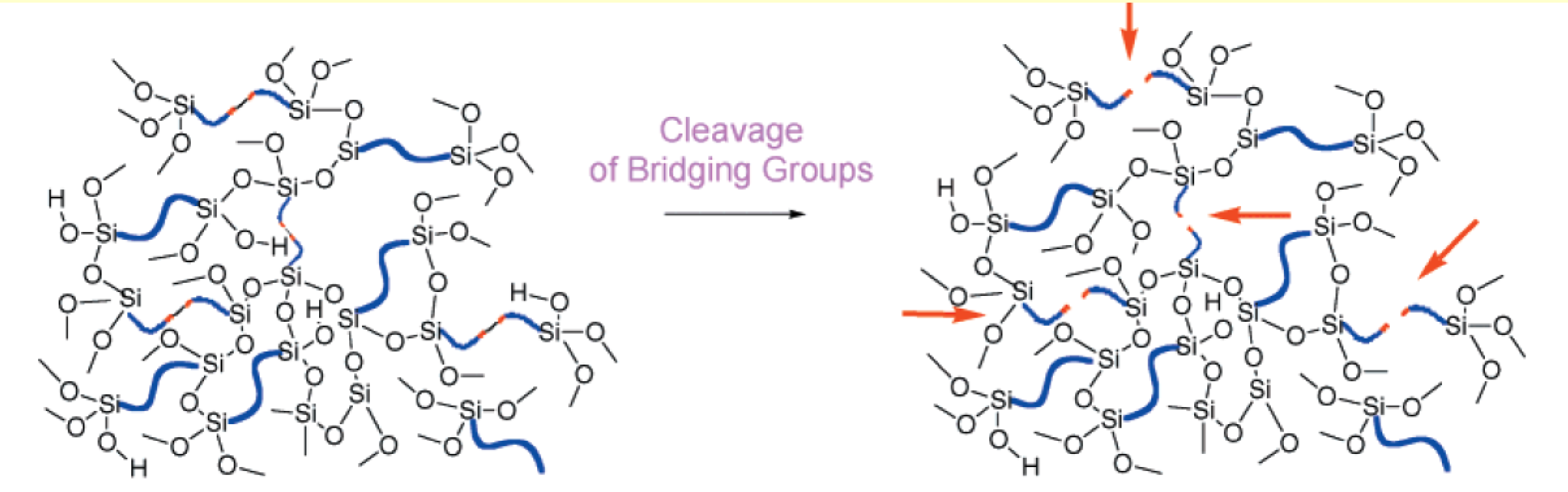
Nanostructuring of hybrid silicas through a Self-Recognition Process - the crystallization of the hydrolyzed species by H-bonding followed by their polycondensation in solid state



1,4-Bis(triethoxysilyl)propylureidobenzene

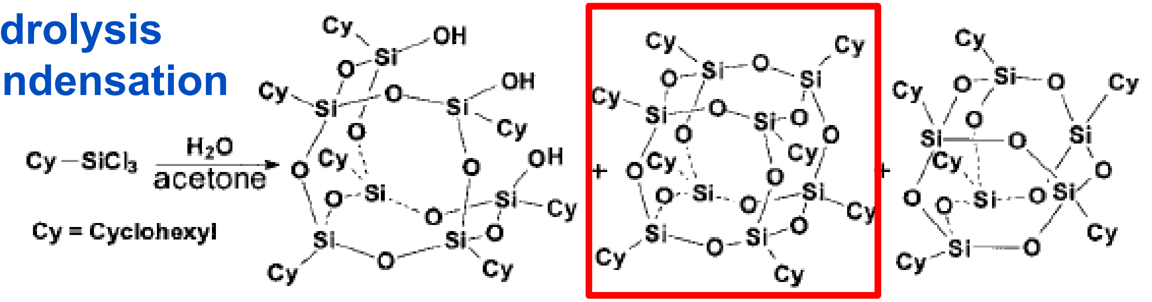


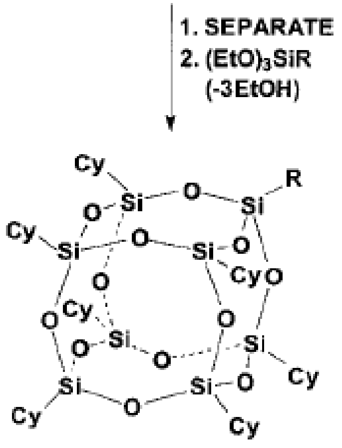
Templating Porosity in Bridged Polysilsesquioxanes



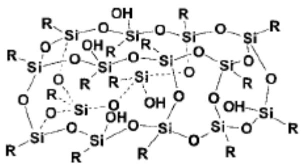
Polyhedral Oligomeric Silsesquioxanes (POSS)

Hydrolysis
Condensation

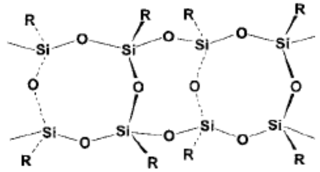




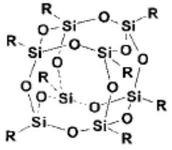
R = hydride
chloride
hydroxide
nitriles
amines
isocyanates
styryls
olefins
acrylics
epoxides
norbornyls
bisphenols
acid chlorides
alcohols
acids



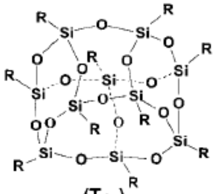
(a)
Random structure



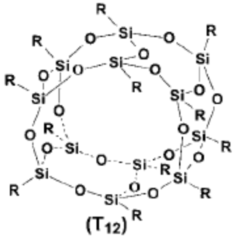
(b)
Ladder structure



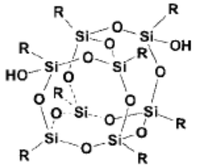
(T_8)
(c)



(T_{10})
(d)
Cage structures



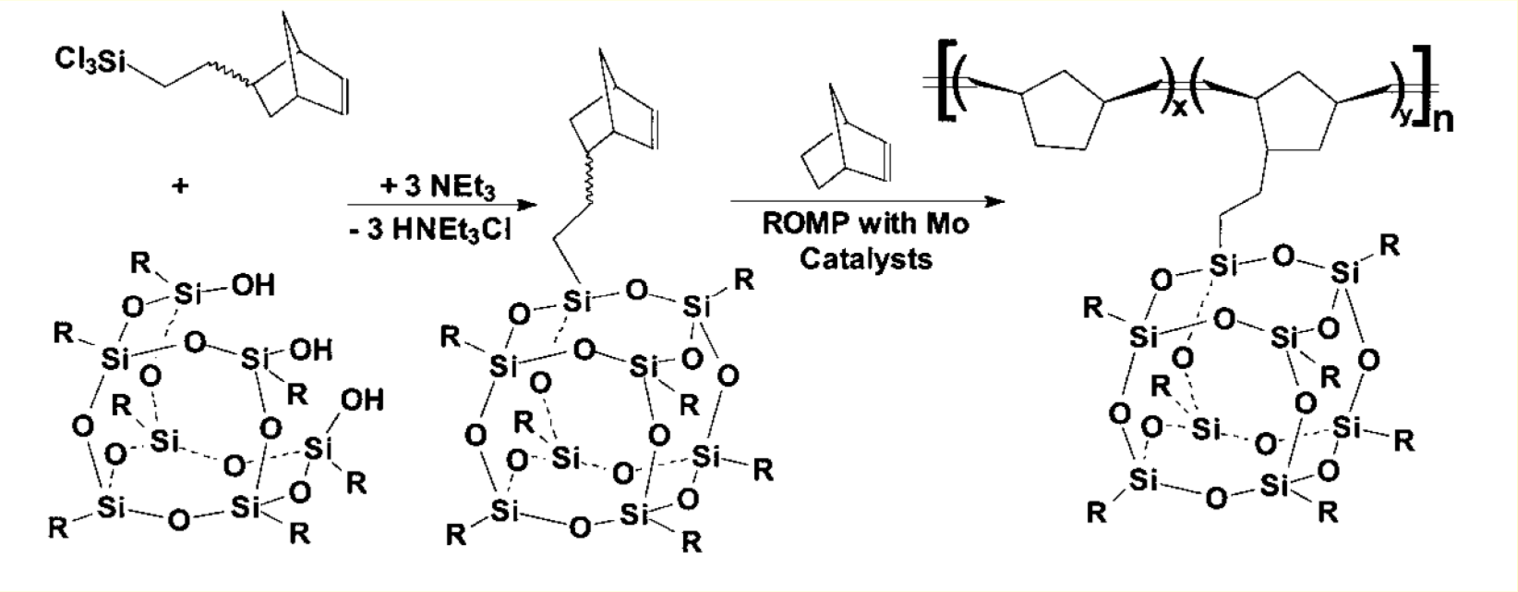
(T_{12})
(e)



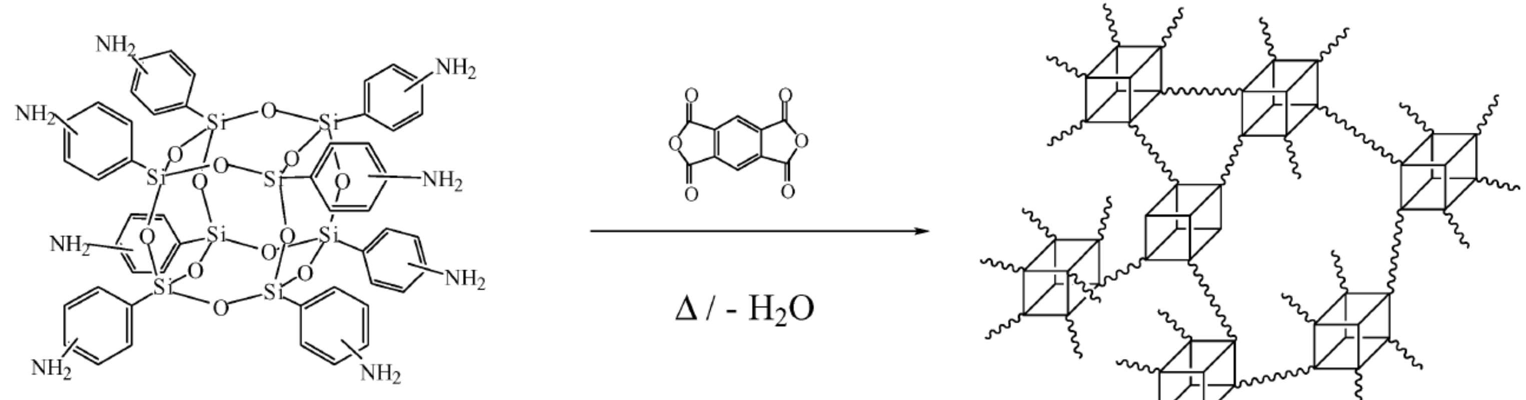
(f)
Partial cage structure

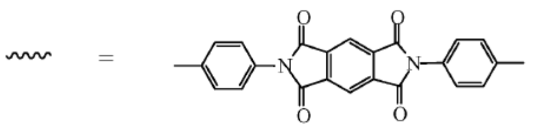
Polymers and Copolymers of POSS

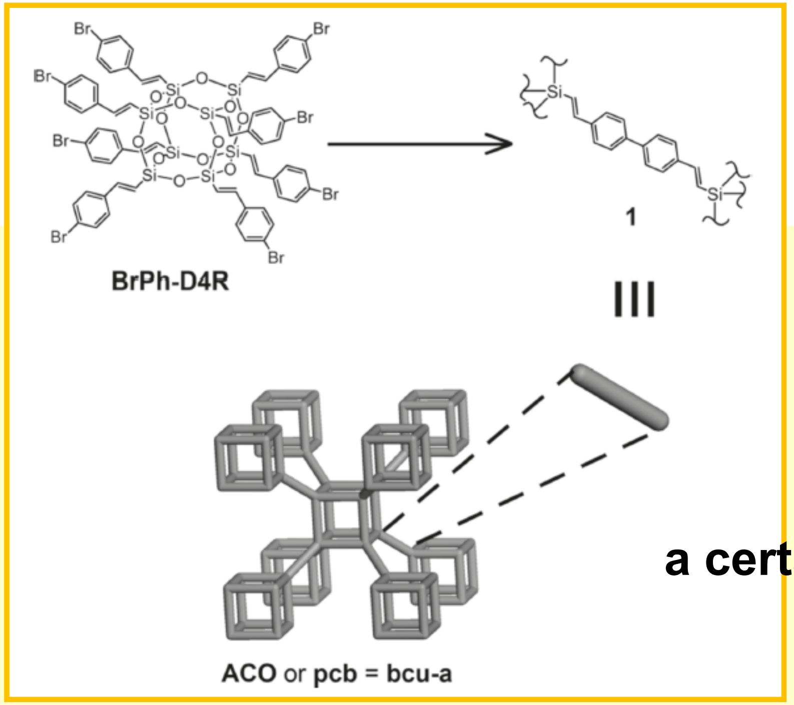
1D linear polymers



Polymers and Copolymers of POSS





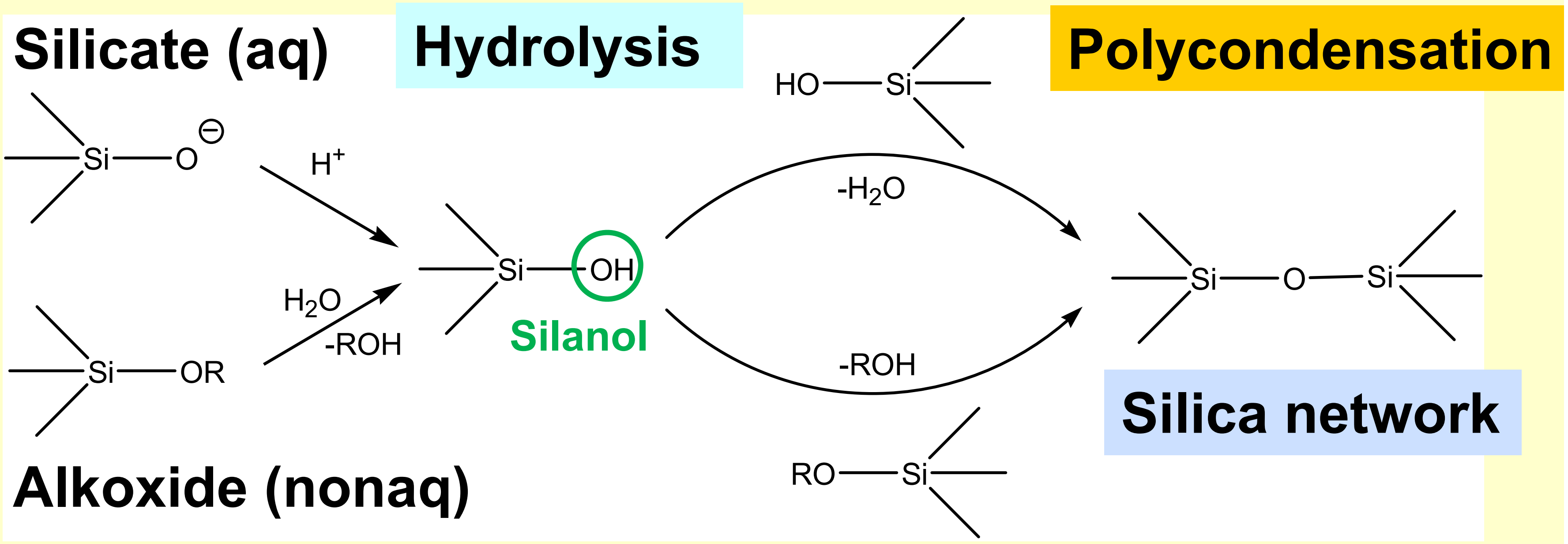


3D crosslinked polymers

a certain degree of crystallinity

Mechanism of Sol-Gel Reactions in Silica Systems

Colloid Route



Silicate (aq)

Hydrolysis

Polycondensation

Silanol

Silica network

Alkoxide (nonaq)

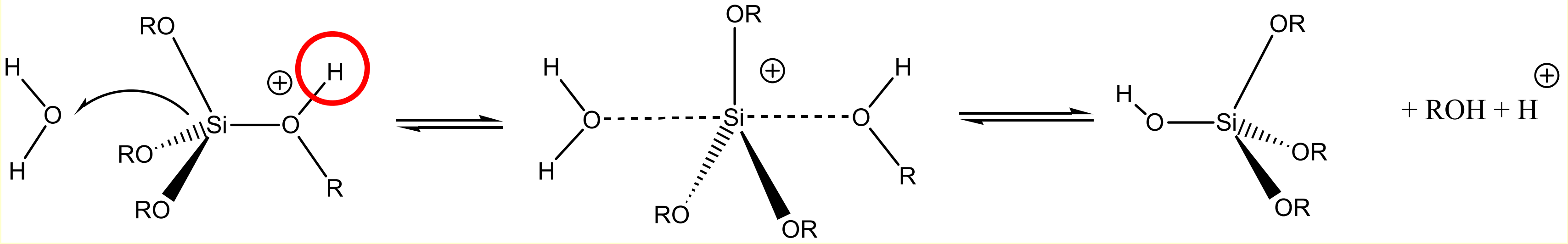
Metal-Organic Route

Metal alkoxide in alcoholic solution, water addition

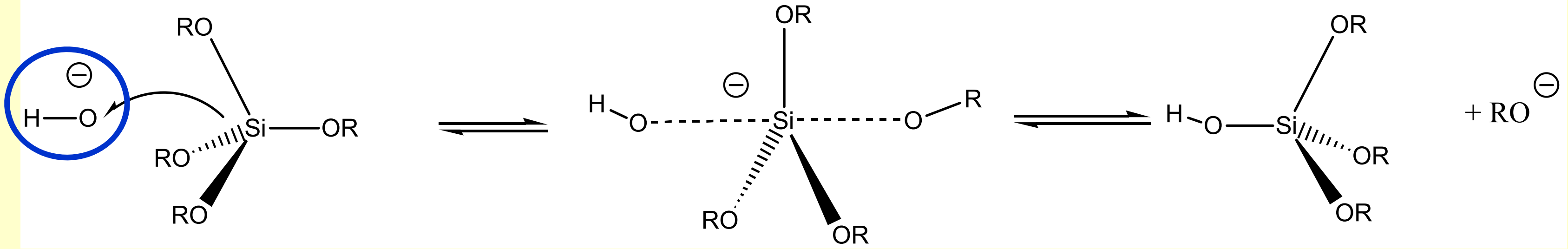
Mechanism of Silicon Alkoxide Route

Hydrolysis of silicon alkoxide in alcoholic solution by water addition is SLOW

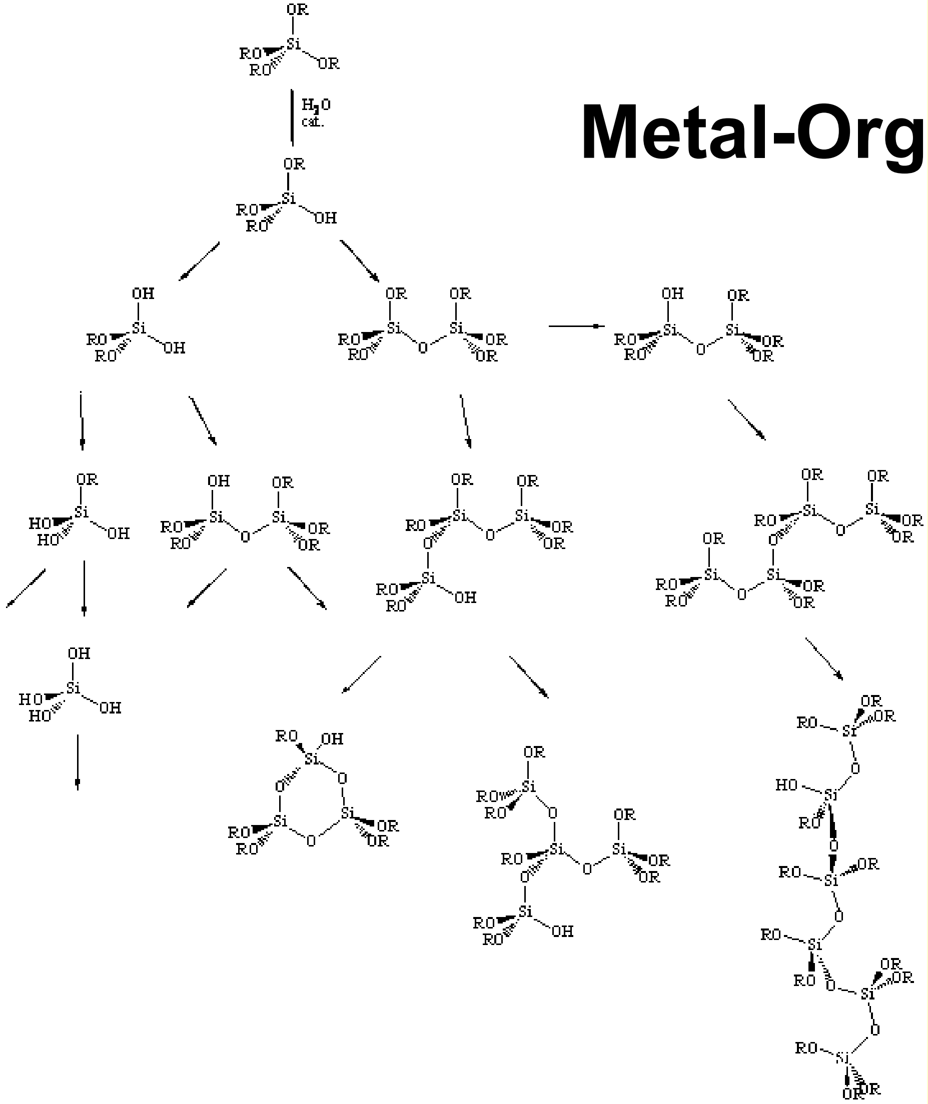
Acid catalysed hydrolysis



Base catalysed hydrolysis



Metal-Organic (Alkoxide) Route



Oligomers formed
by hydrolysis-condensation
process

-linear
-branched
-cyclic
-polyhedral

Never goes to pure SiO_2

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

Hydrolysis - Condensation Kinetics

$Si(OR)_x(OH)_y(OSi)_z$

Hydrolysis

$Si(OR)_4$ $\longrightarrow$ $Si(OH)_4$

400	310	220	130	040
	301	211	121	031
		202	112	022
			103	013
x y z				004

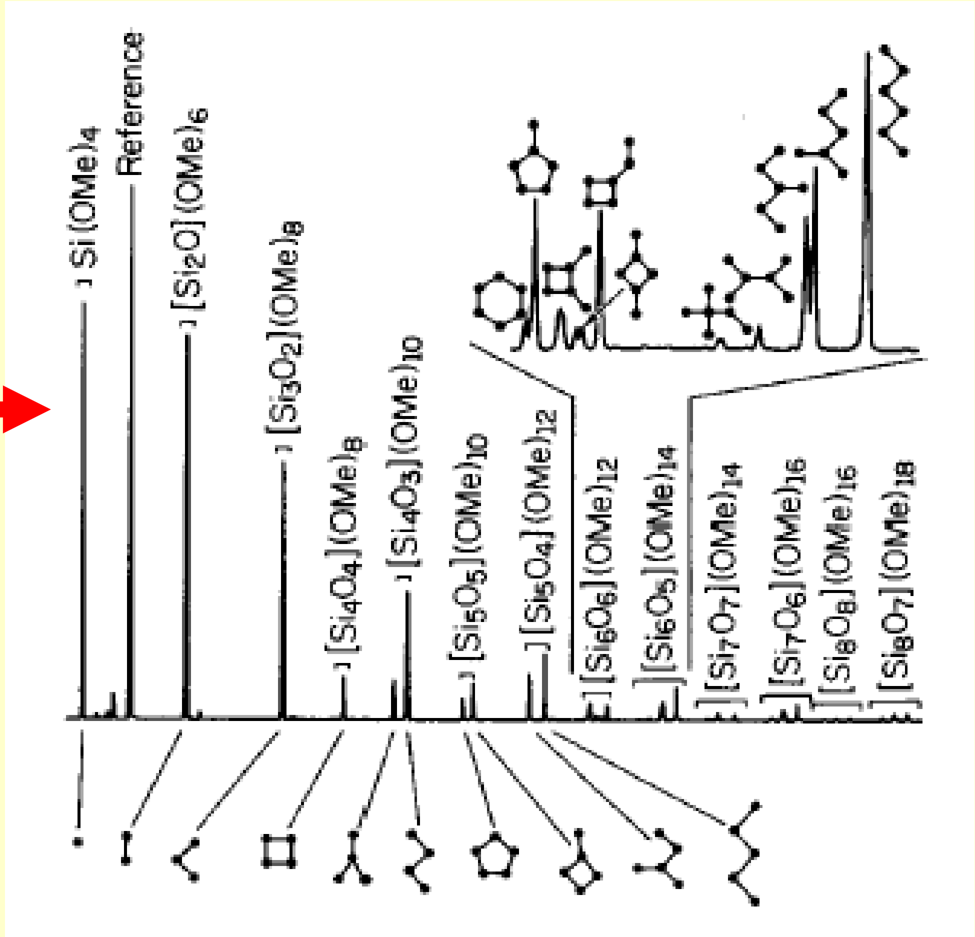
Condensation $\downarrow$

$Si(OSi)_4$

$x + y + z = 4$

Metal-Organic (Alkoxide) Route

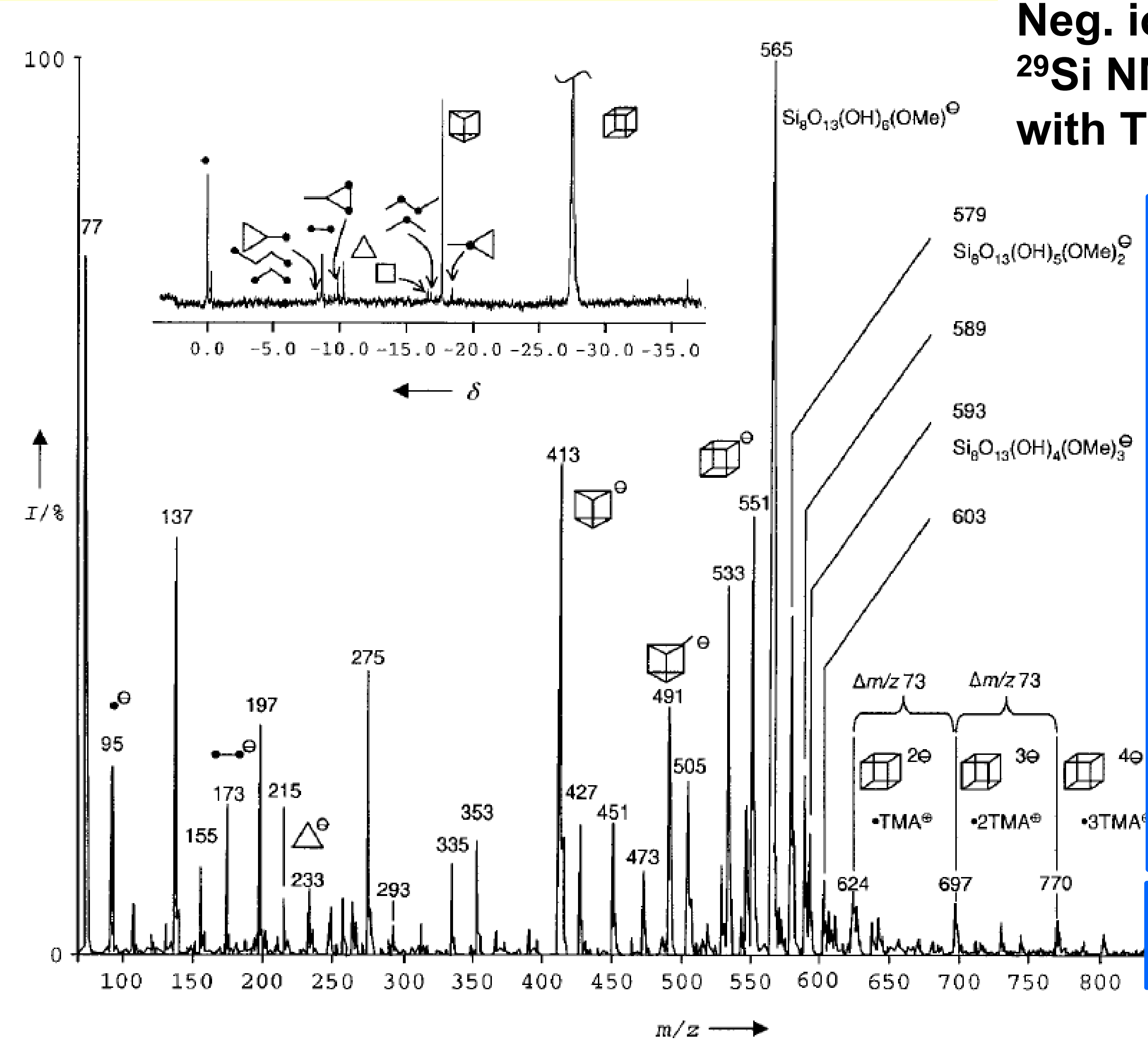
$Si(OMe)_4 + H_2O$

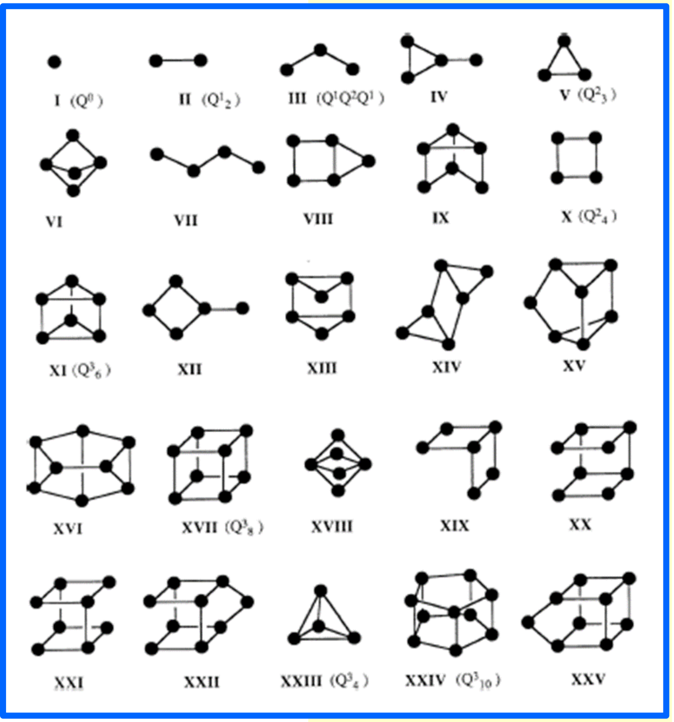


GC of TMOS hydrolysis products

Metal-Organic (Alkoxide) Route

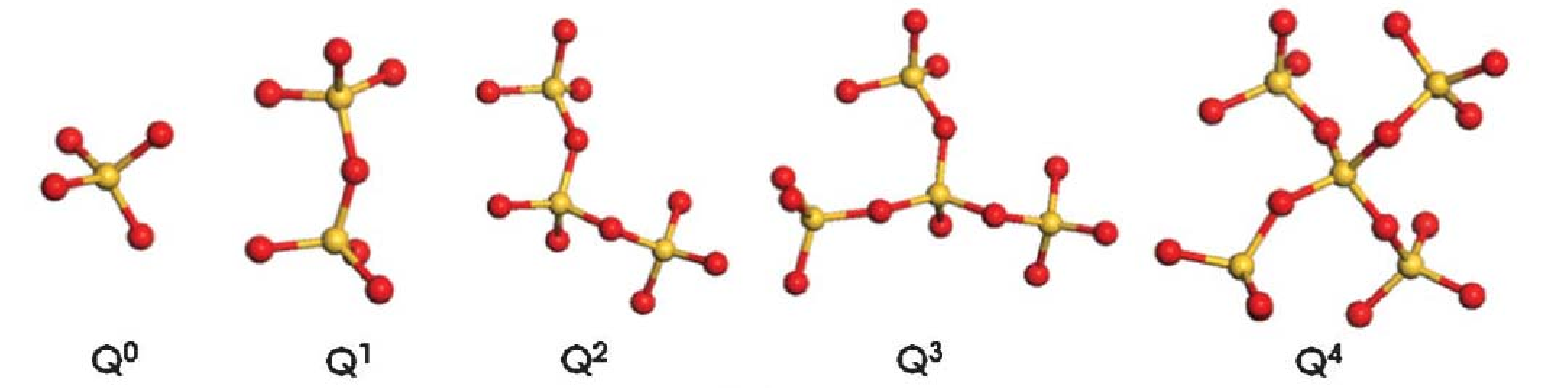
Neg. ion ESI-MS and ^{29}Si NMR of silicate aq with TMA ions





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

Q - Notation



M = $OSiR_3$
D = O_2SiR_2
T = O_3SiR
Q = O_4Si

The notation of Q^a_b

"Q" stands for the maximum 4 siloxane bonds for each Si
"a" is the actual number of siloxane bonds on each Si
"b" is the number of Si in the unit

$Q^0 = O_4Si$

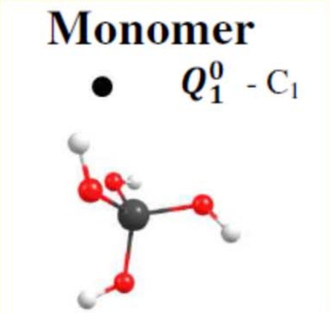
$Q^1 = O_3SiOSi$

$Q^2 = O_2Si(OSi)_2$

$Q^3 = OSi(OSi)_3$

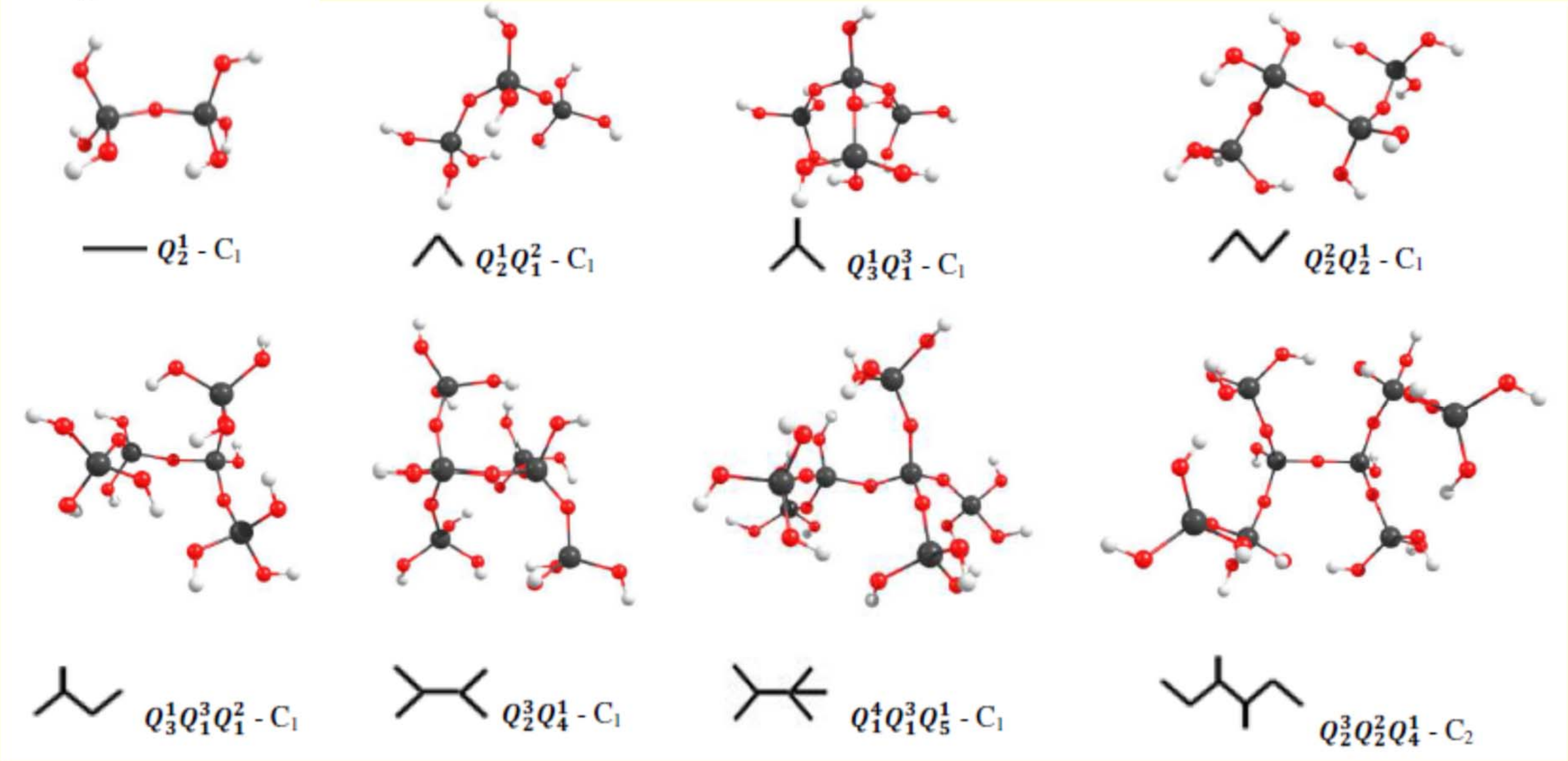
$Q^4 = Si(OSi)_4$

Linear and Branched Silicate Anions



The notation of Q^a_b

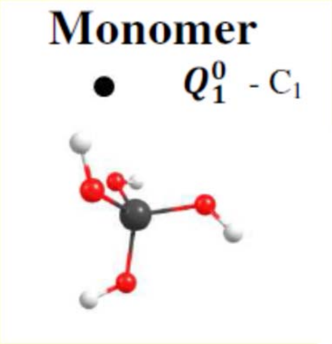
“Q” stands for the maximum 4 siloxane bonds for each Si
“a” is the actual number of siloxane bonds on each Si
“b” is the number of Si in the unit

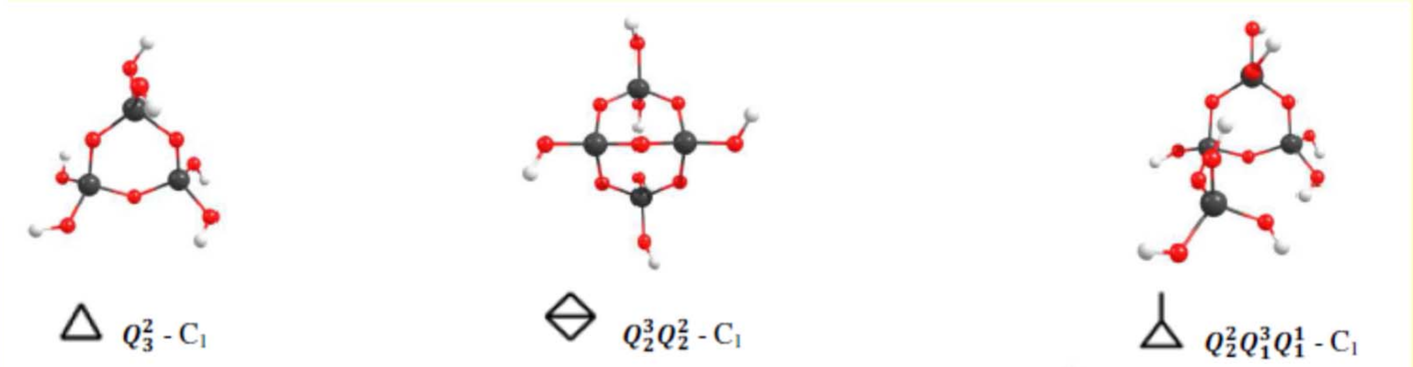


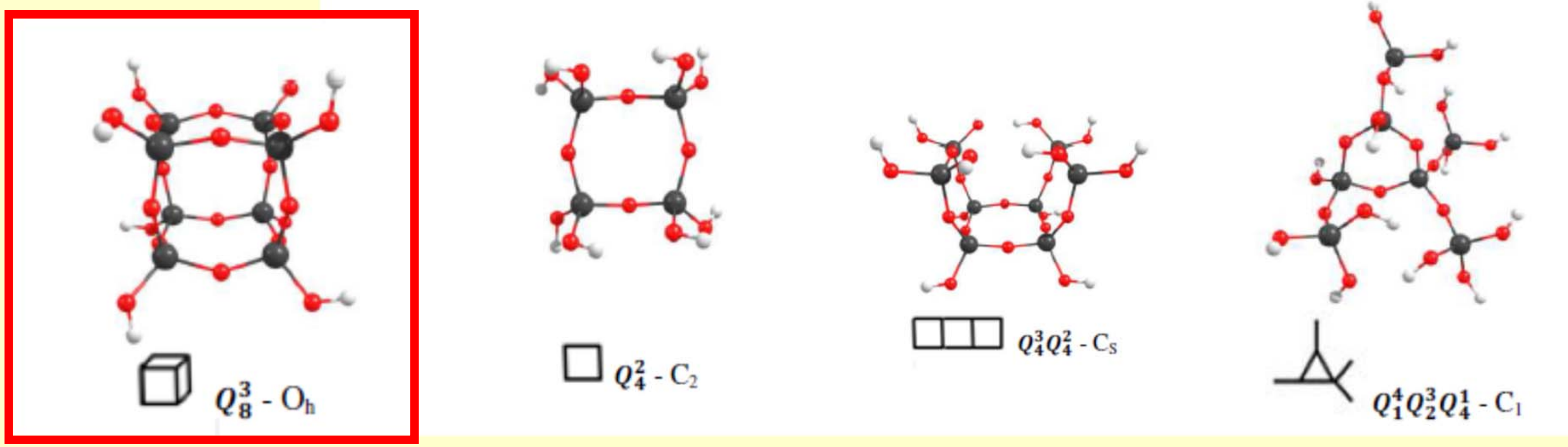
Cyclic and Polyhedral Silicate Anions

The notation of Q^a_b

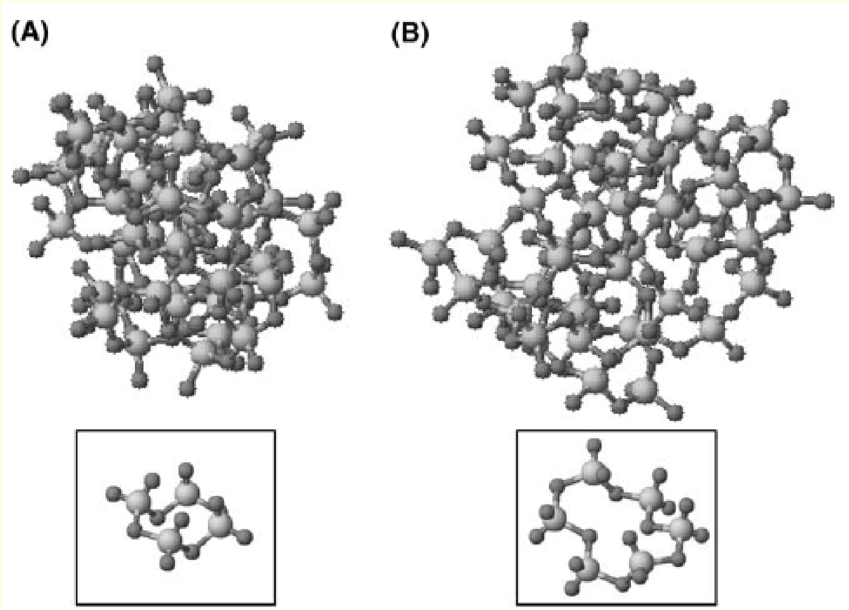
"Q" stands for the maximum 4 siloxane bonds for each Si
"a" is the actual number of siloxane bonds on each Si
"b" is the number of Si in the unit





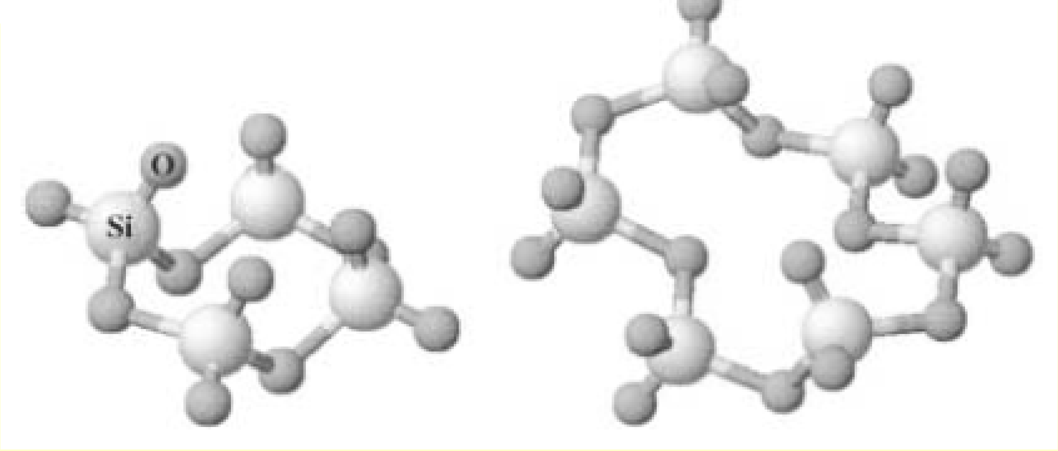


Oligomeric Silicate Anions

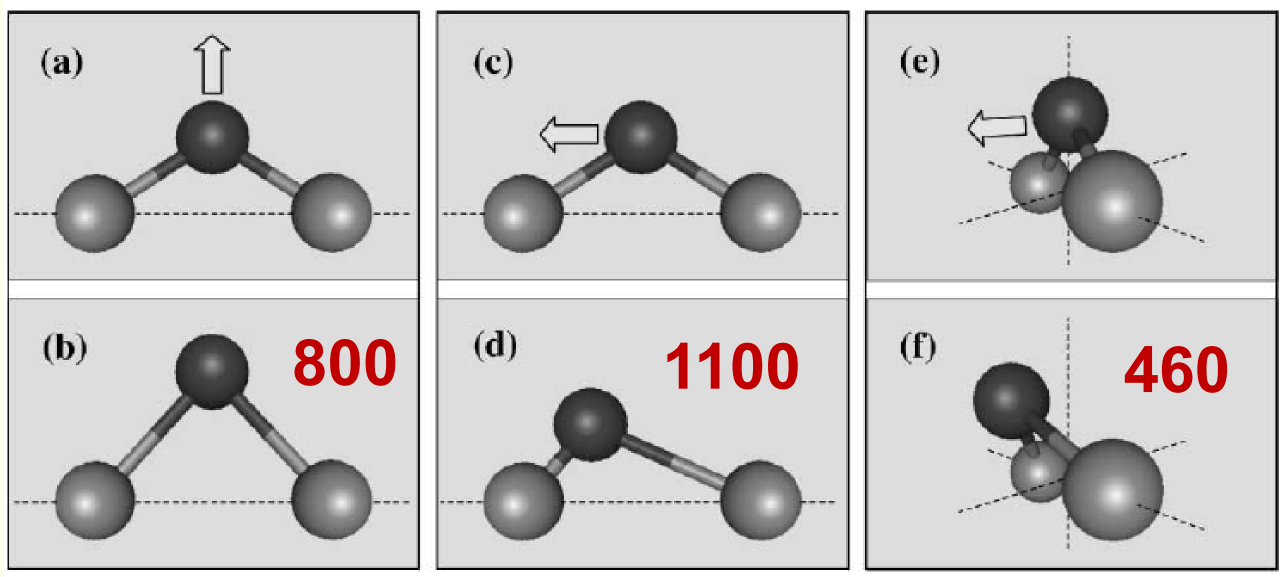


Oligomers formed by hydrolysis-condensation

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



IR spectrum of silica

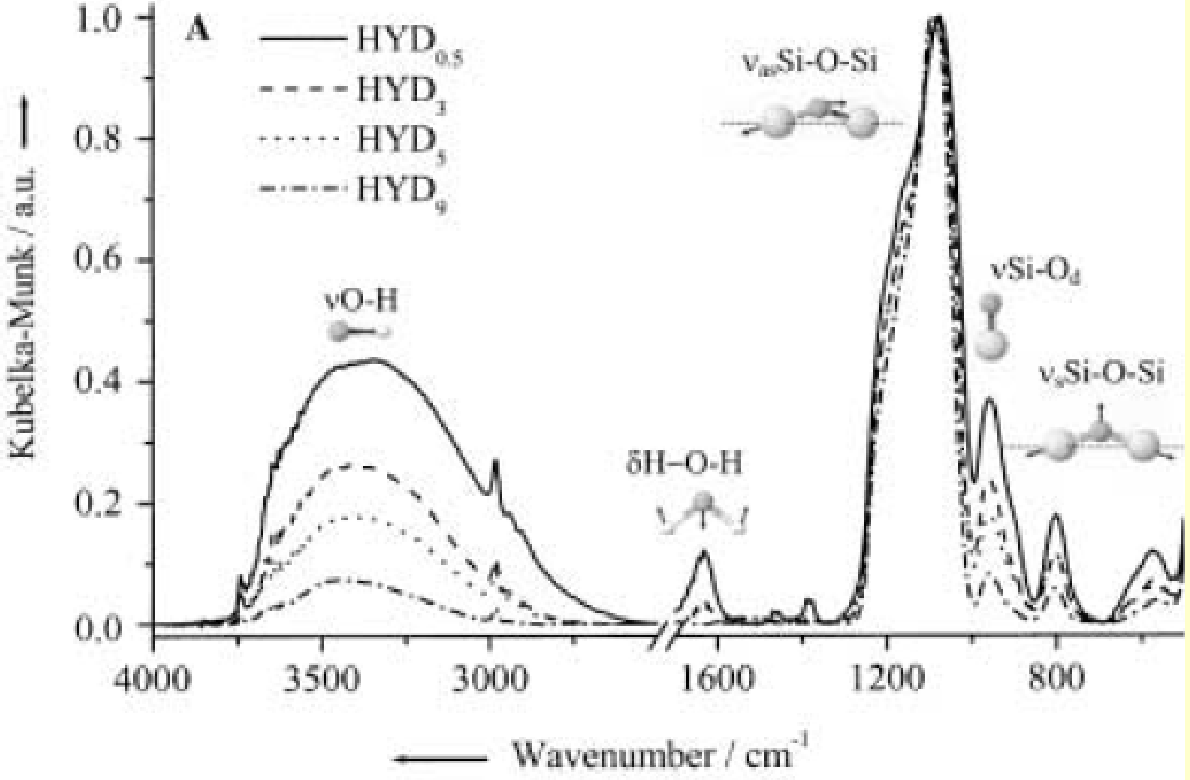


800

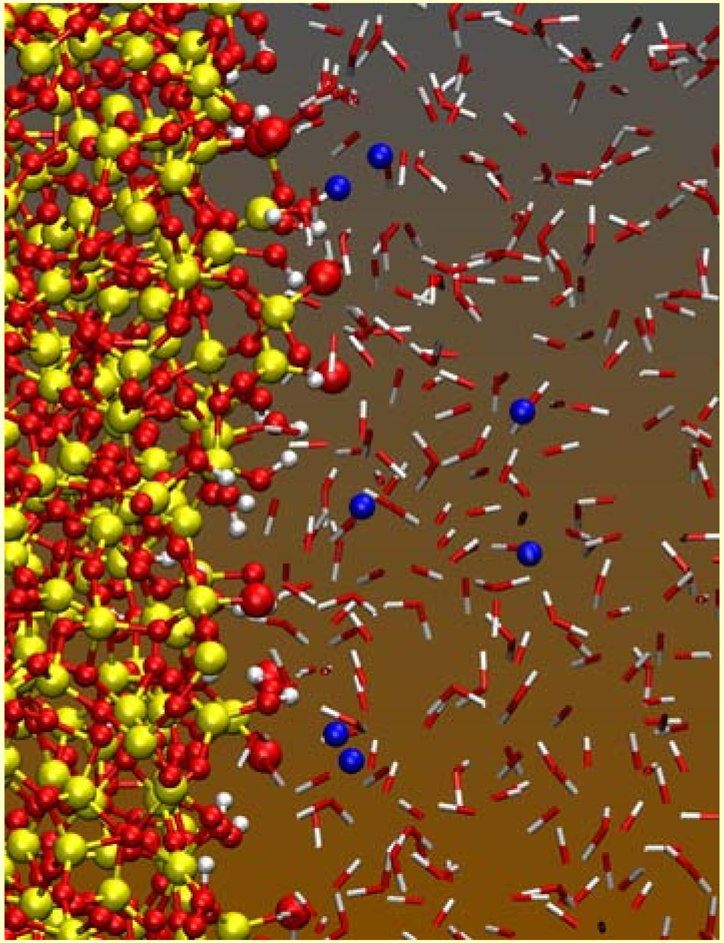
1100

460

ν, cm^{-1}



Amorphous Silica / Water Interface



H_2O
Cations
Anions
Protons
Si–O/H

The Electrical Double Layer

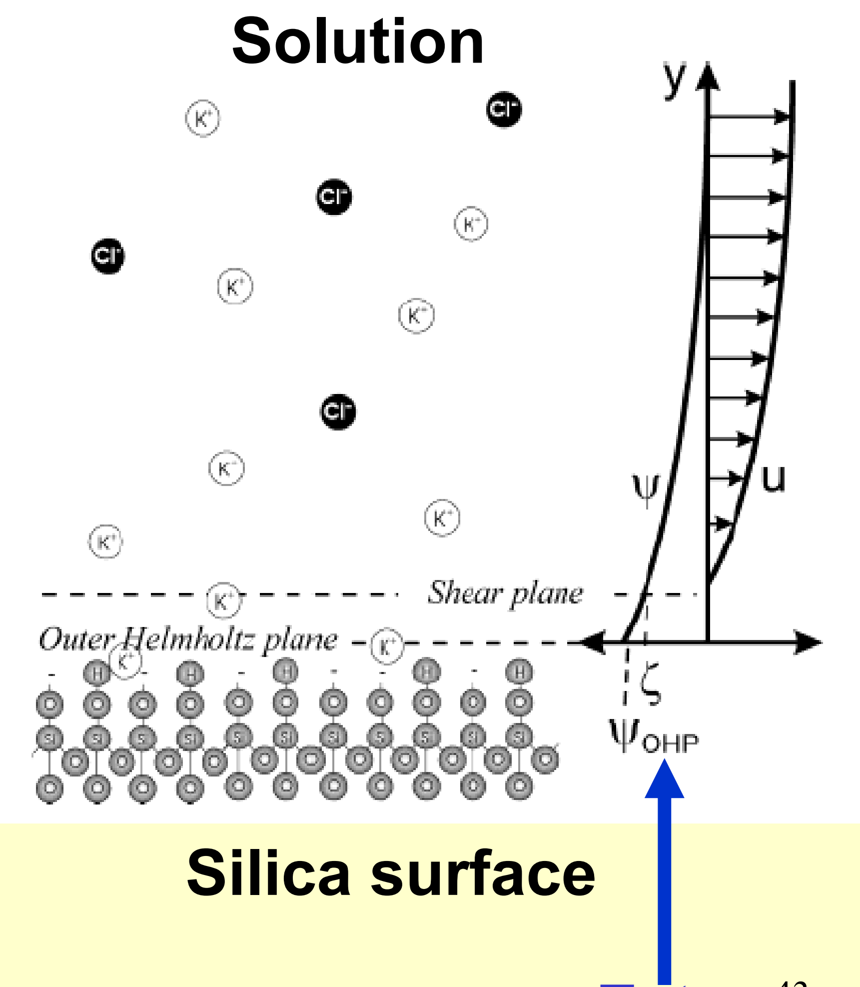
The electrical double layer at the interface of silica and a diluted KCl solution

ψ = local potential
OHP = Outer Helmholtz plane
***u* = local electroosmotic velocity**
y = distance from the surface

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

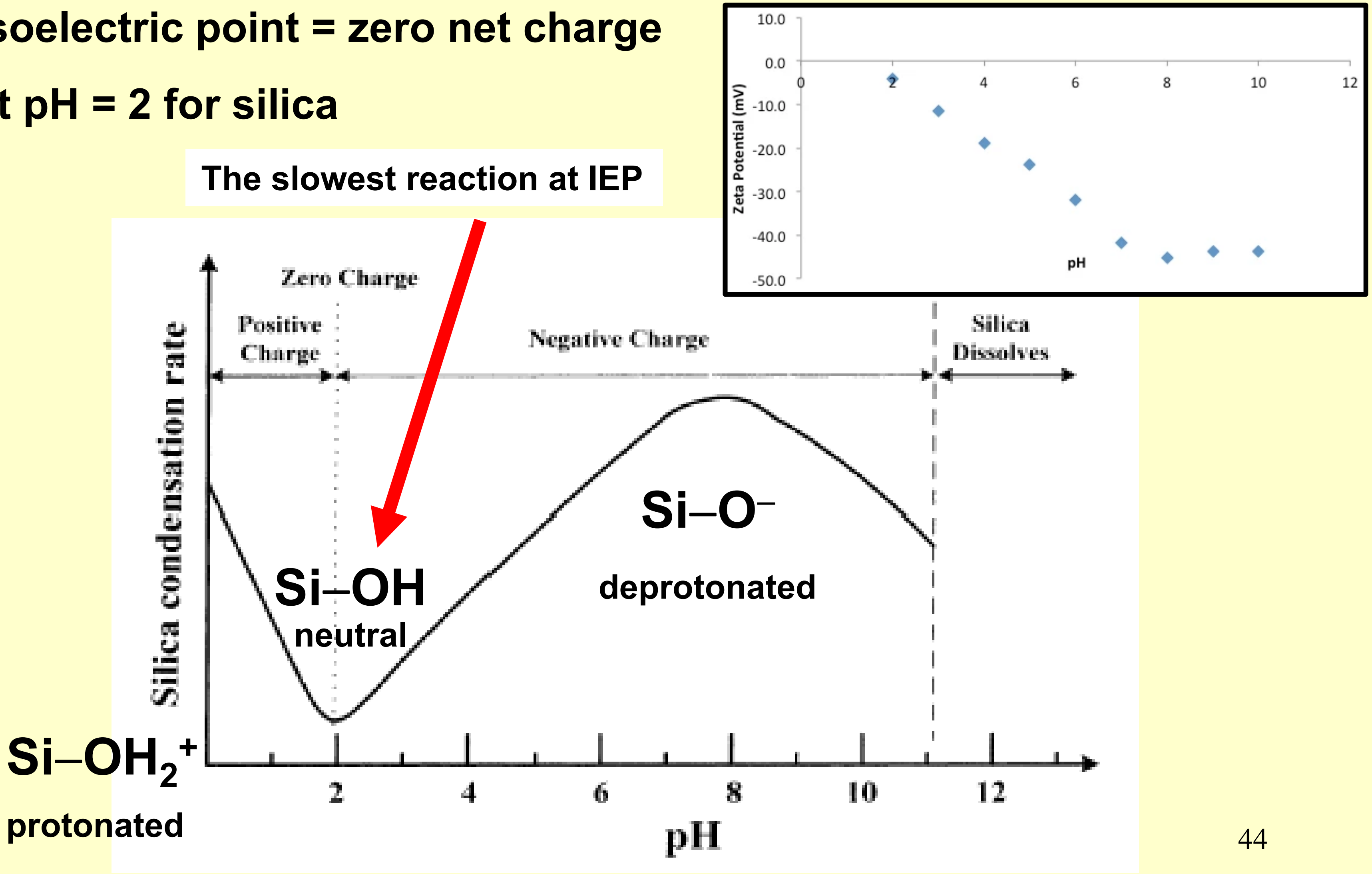
Zeta = potential at the shear plane



Sol-Gel Methods

Isoelectric point = zero net charge

at pH = 2 for silica



The slowest reaction at IEP

Si–OH
neutral

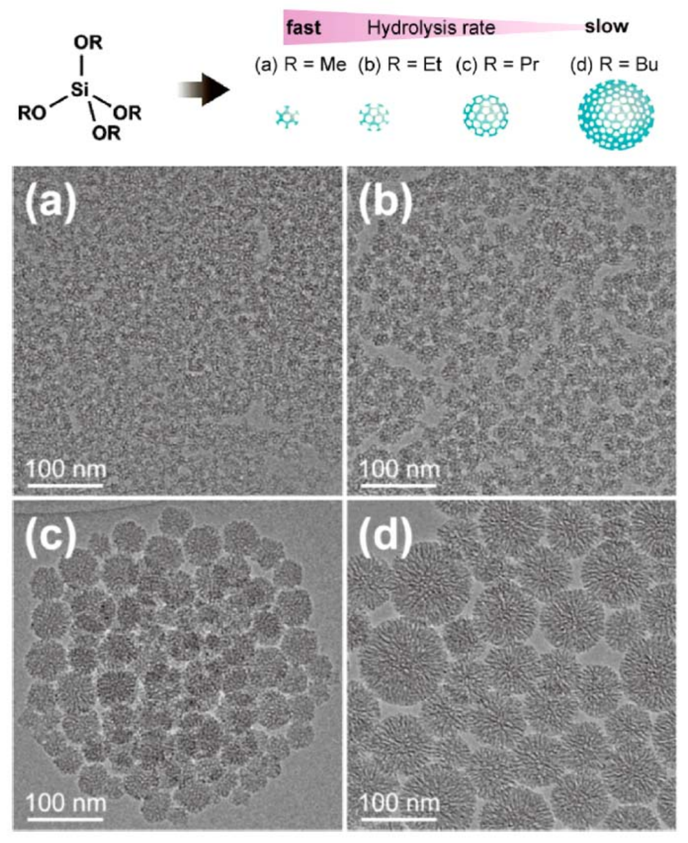
Si–O⁻

deprotonated

$Si–OH_2^+$

protonated

Precursor Substituent Effects



Steric effects:

branching and increasing of the chain length LOWERS the hydrolysis rate

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

Inductive effects:

electronic stabilization/destabilization of the transition state (TS)

Electron density at Si decreases:

$R \rightarrow Si > RO \rightarrow Si > HO{-}Si > SiO \leftarrow Si$

Partial Charge Model (Livage and Henry)

Electron transfer occurs when atoms combine to give a molecule

Charge transfer causes each atom to acquire

a partial positive or negative charge, δ_i

This transfer mainly depends on the electronegativity difference between atoms

The electronegativity χ_i of an atom varies linearly with its partial charge δ_i

$$\chi_i = \chi^o_i + k\,\delta_i$$

Electron transfer must stop when all electronegativities have the same value (Electronegativity equalization)

= the mean electronegativity $\bar{\chi}$

Partial Charge Model (Livage and Henry)

The mean electronegativity $\overline{\chi}$ 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 atom in the molecule

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

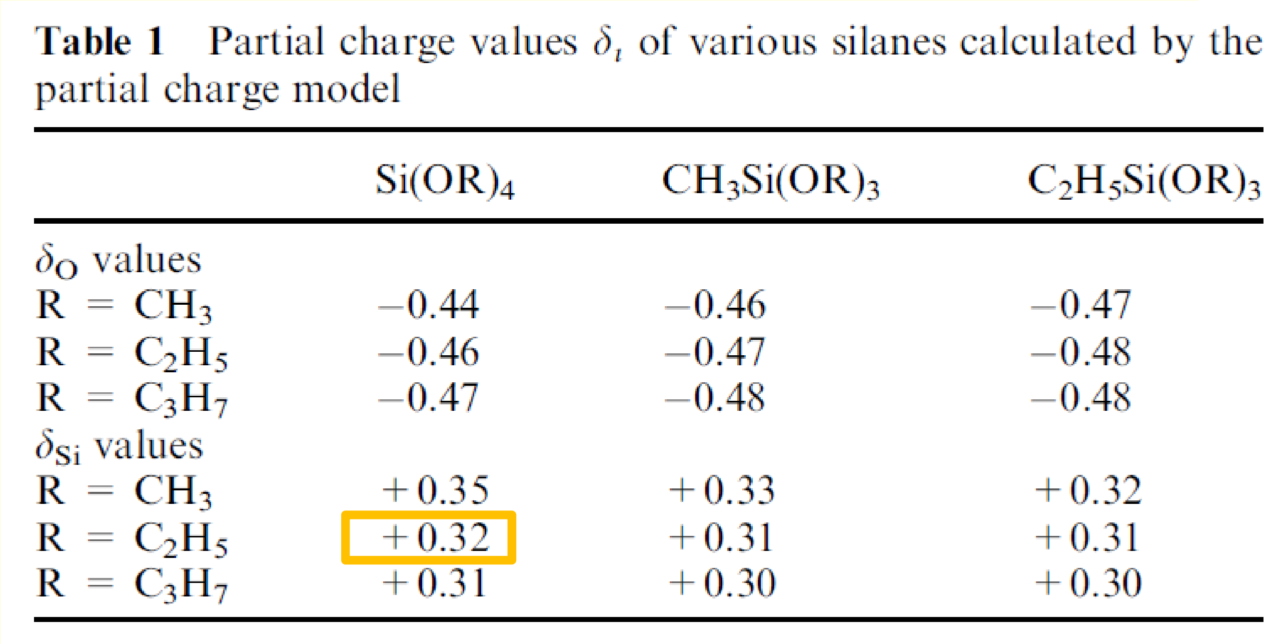


Table 1 Partial charge values δ_i of various silanes calculated by the partial charge model

	$Si(OR)_4$	$CH_3Si(OR)_3$	$C_2H_5Si(OR)_3$
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	$Zr(OEt)_4$	$Ti(OEt)_4$	$Nb(OEt)_5$	$Ta(OEt)_5$	$VO(OEt)_3$	$W(OEt)_6$	$Si(OEt)_4$
δ (M)	+0.65	+0.63	+0.53	+0.49	+0.46	+0.43	+0.32

The hydrolysis rate depends on the δ (M):

The more positive partial charge δ_i the faster hydrolysis reaction

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

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

There is a problem to prepare mixed-metal oxides Ti–O–Si
Hydrolysis/condensation leads to phase-separated mixture of TiO_2/SiO_2

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

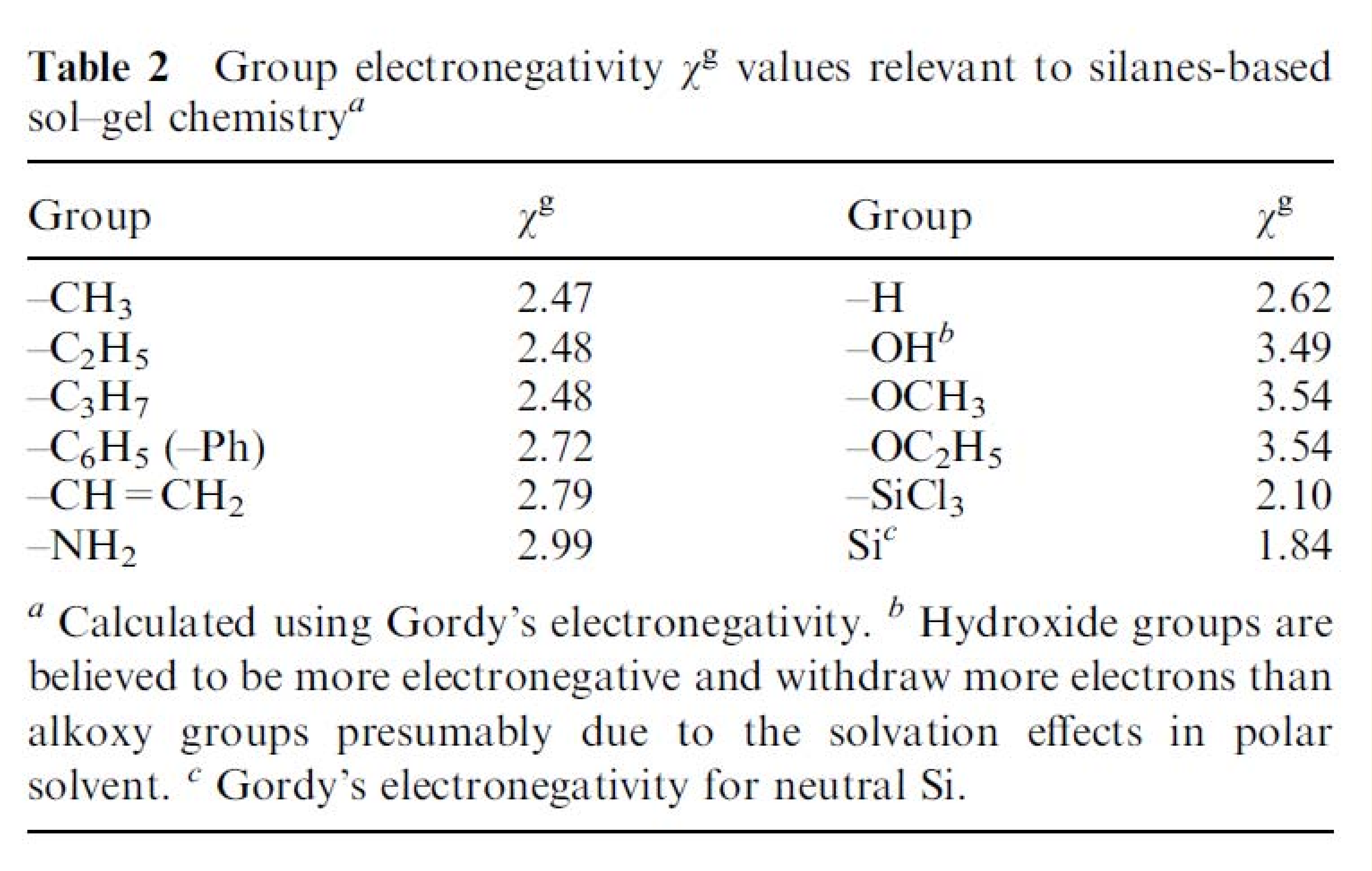


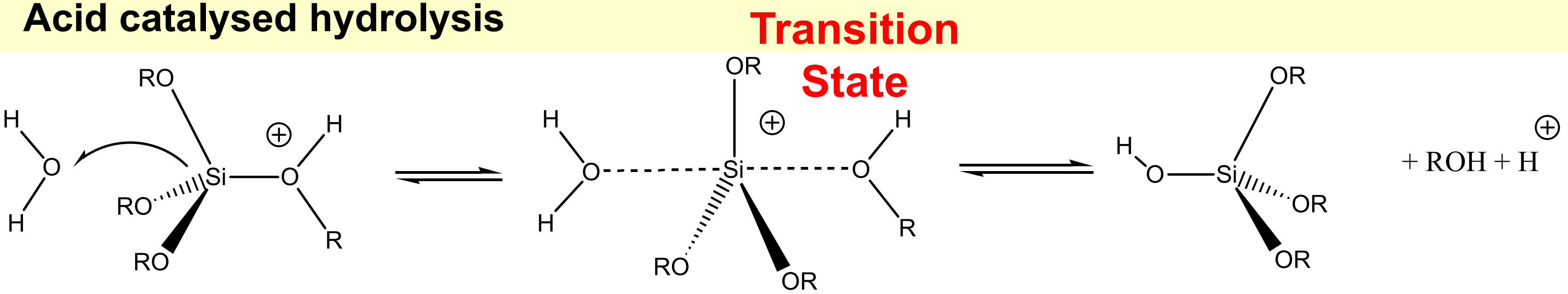
Table 2 Group electronegativity χ^g values relevant to silanes-based sol–gel chemistry[a]

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 Rate

Acid catalysed hydrolysis



Acidic conditions:

Hydrolysis reaction rate decreases as more alkoxy groups are hydrolyzed

Electron density at Si decreases:

$R \rightarrow Si > \boxed{RO \rightarrow Si > HO{-}Si} > SiO \leftarrow Si$

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

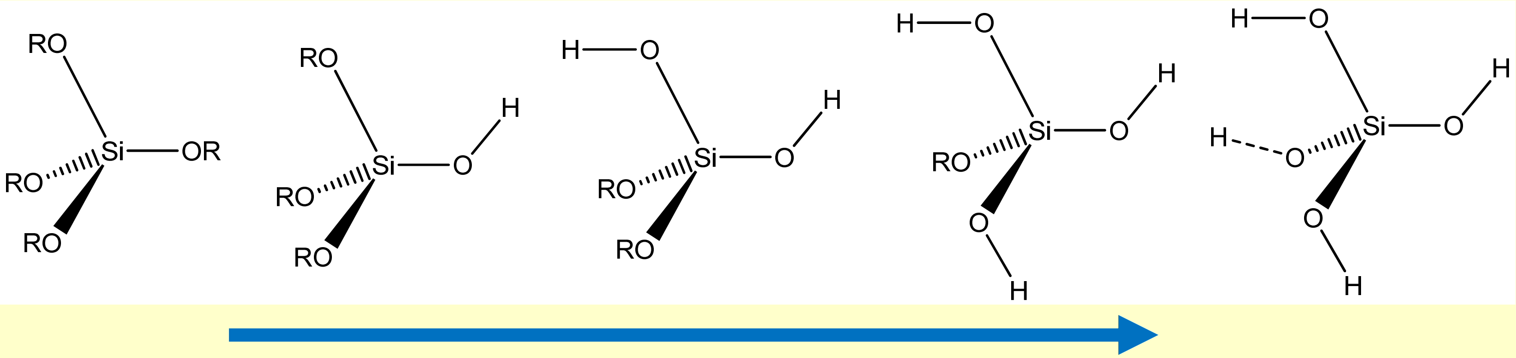
The reaction at terminal Si favored, as there is only one electron withdrawing SiO group

Linear polymer products are favored, leading to fibers

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

Hydrolysis Rate

Acid catalysed hydrolysis



Hydrolysis reaction rate decreases as more alkoxy RO groups are hydrolyzed and replaced with OH groups

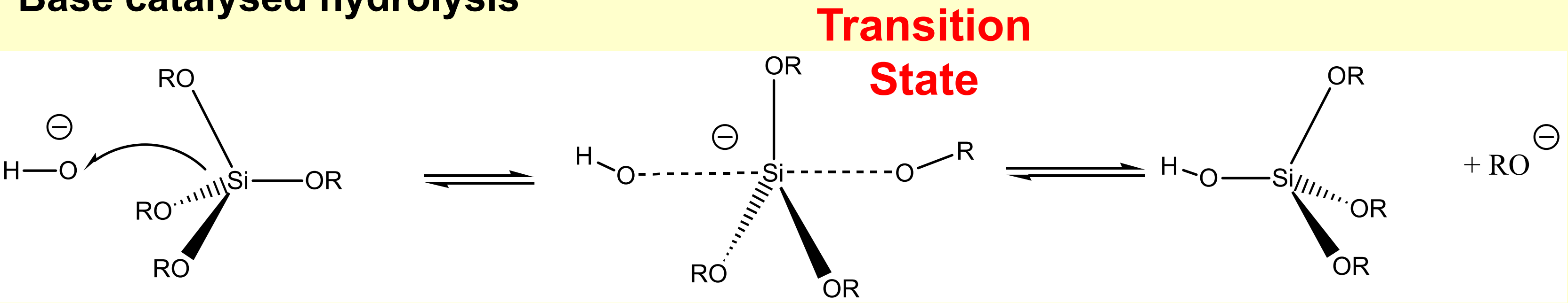
Electron density at Si decreases:

R→Si > RO→Si > HO–Si > SiO←Si

Electron-donating **Electron-withdrawing**

Hydrolysis Rate

Base catalysed hydrolysis



Basic conditions:

Hydrolysis reaction rate increases as more alkoxy groups are hydrolyzed

Electron density at Si decreases:

R→Si > $\boxed{\text{RO→Si > HO–Si}}$ > SiO←Si

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

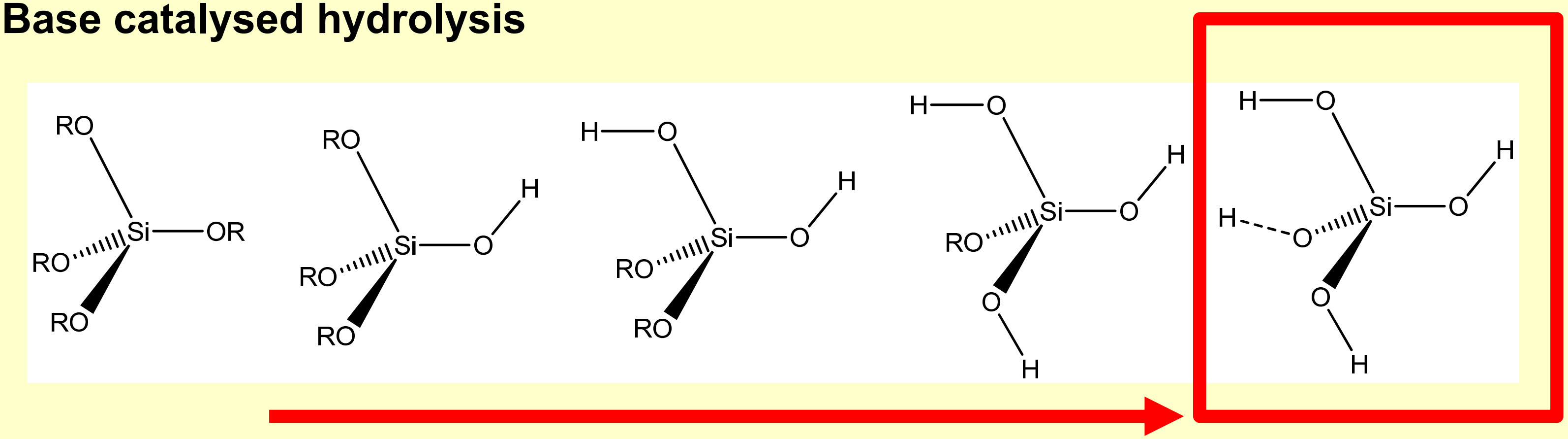
The reaction at central Si favored, as there is more electron withdrawing SiO groups

Branched polymer products are favored, spherical particles, powders

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

Hydrolysis Rate

Base catalysed hydrolysis



Hydrolysis reaction rate increases as more alkoxy RO groups are hydrolyzed and replaced with OH groups

Complete hydrolysis to $Si(OH)_4$

Electron density at Si decreases:

R→Si > RO→Si > HO–Si > SiO←Si

Electron-donating

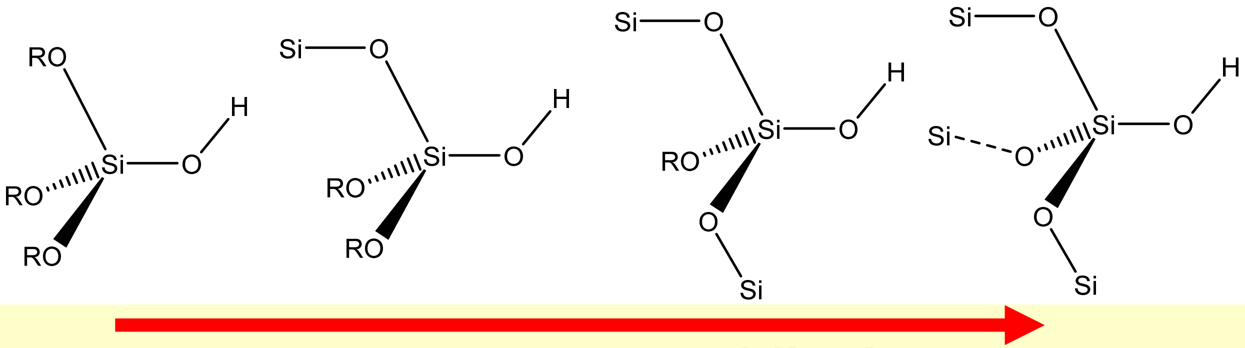
Electron-withdrawing

Hydrolysis Rate

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

Electron density at Si decreases:

R→Si > RO→Si > HO–Si > SiO←Si



acidity increases

Nucleophilic catalysis

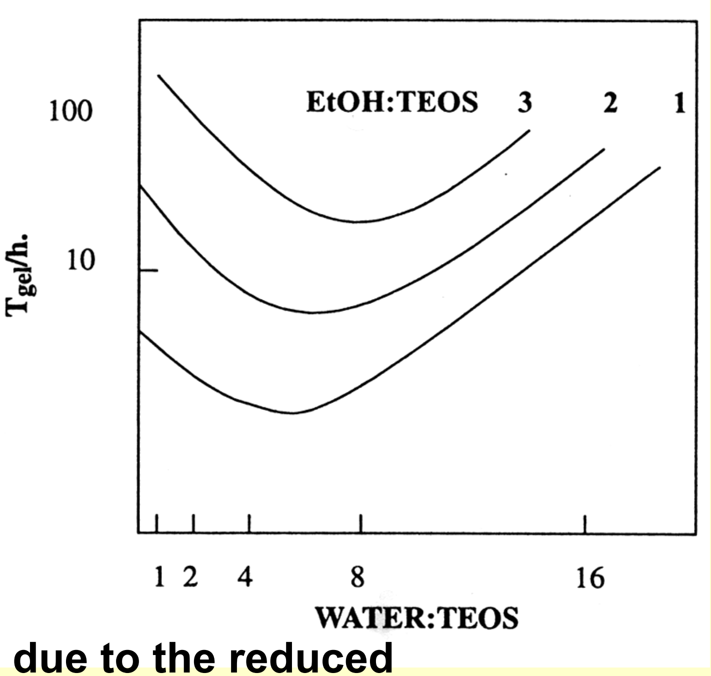
F$^-$ Si-F bonds

HMPA

N-methylimidazol

N,N-dimethylaminopyridin

Hydrolysis Rate



Water-to-Si ratio (k)

Stoichiometric ratio for complete hydrolysis
k = 4

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

additional water comes from condensation

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

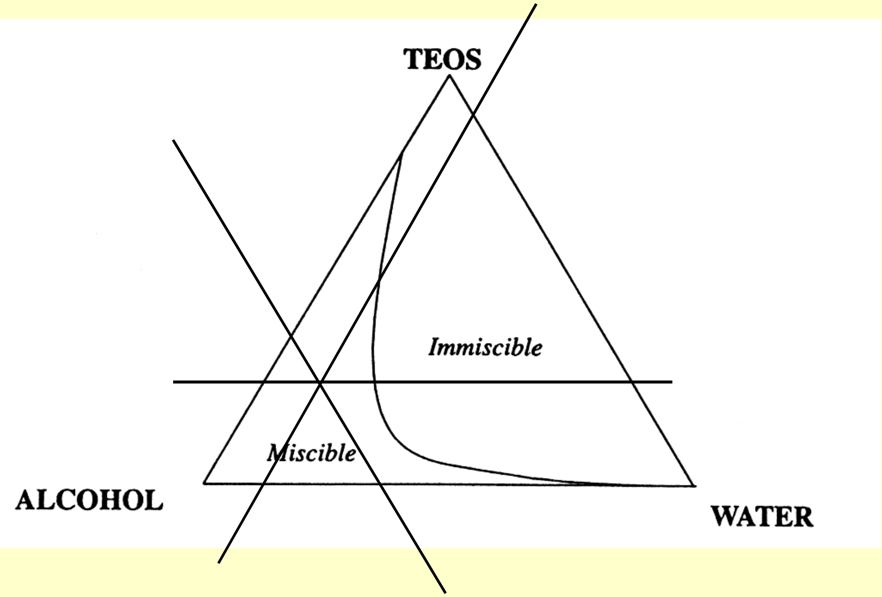
Small amount of water ($k < 4$) = slow hydrolysis due to the reduced reactant concentration
Condensation of incompletely hydrolyzed species

Large amount of water ($k > 4$) = slow hydrolysis due to the reactant dilution
Condensation of completely hydrolyzed species
Reverse reaction promoted - depolymerization of Si-O-Si

Hydrolysis Rate

Hydrophobic effect - $Si(OR)_4$ are immiscible with water

Cosolvent ROH is used to obtain a homogeneous reaction mixture and prevent phase separation



Cosolvent properties affect rates:

polarity, dipole moment, viscosity, protic behavior:

Protic (EtOH) - bind to $^{-}O–Si$

Aprotic (THF) - bind to HO–Si

Alcohol produced during the reaction

Alcohol/Alkoxide – transesterification

$Si(OR)_4 + R'OH \rightarrow Si(OR)_3(OR') + ROH$

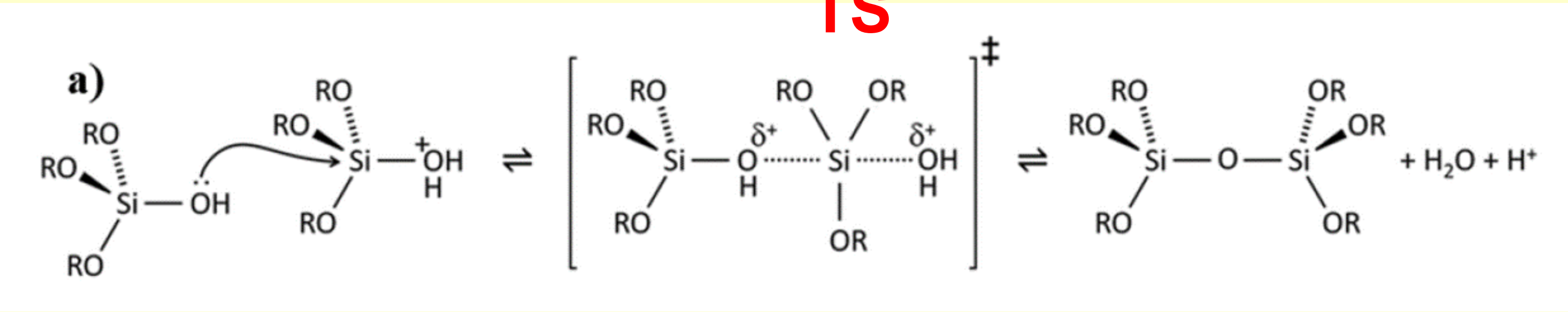
Sonication – homogenization, emulsion

Solvents affect drying

Condensation Rate

Acid catalysed condensation
fast protonation, slow condensation

TS



Electron density at Si decreases:

R→Si > RO→Si > HO–Si > SiO←Si

Positively charged transition state (TS), 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 $(RO)_3SiOH$

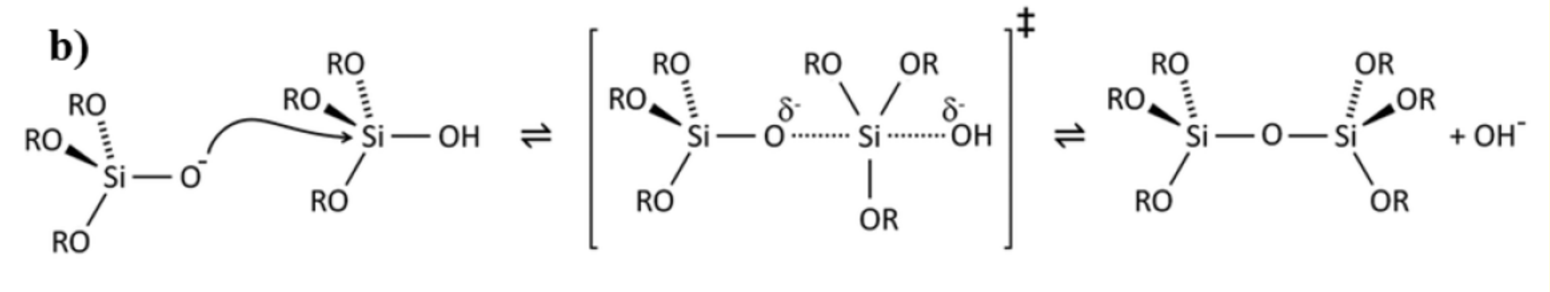
Condensation for this species also fastest, the formation of linear chains

Condensation Rate

Base catalysed condensation

fast deprotonation, slow condensation

TS



Electron density at Si decreases:

R→Si > RO→Si > HO–Si > SiO←Si

Negatively charged transition state (TS), 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 $Si(OH)_4$

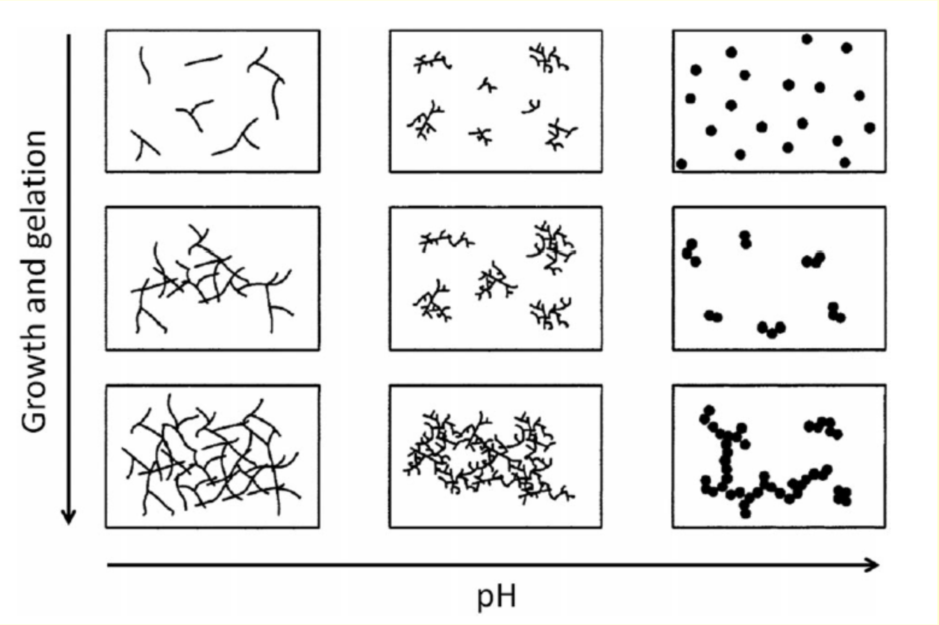
Condensation for the fully hydrolysed species fastest, the formation of highly crosslinked particles

Acid Catalysed Condensation

- For k > 4 : complete hydrolysis at early stage
- Reaction limited cluster aggregation (RLCA)
- Q^0 or terminal groups Q^1 on chains
- Irreversible reactions in acidic pH
- Condensation to linear chains or weakly branched

- For k < 4 : incomplete hydrolysis at early stage
- Unhydrolysed chains, highly concentrated solution without gelling
- Spinnable to fibers
- Small primary particles
- Microporosity, Type I isotherms

pH ~ 2

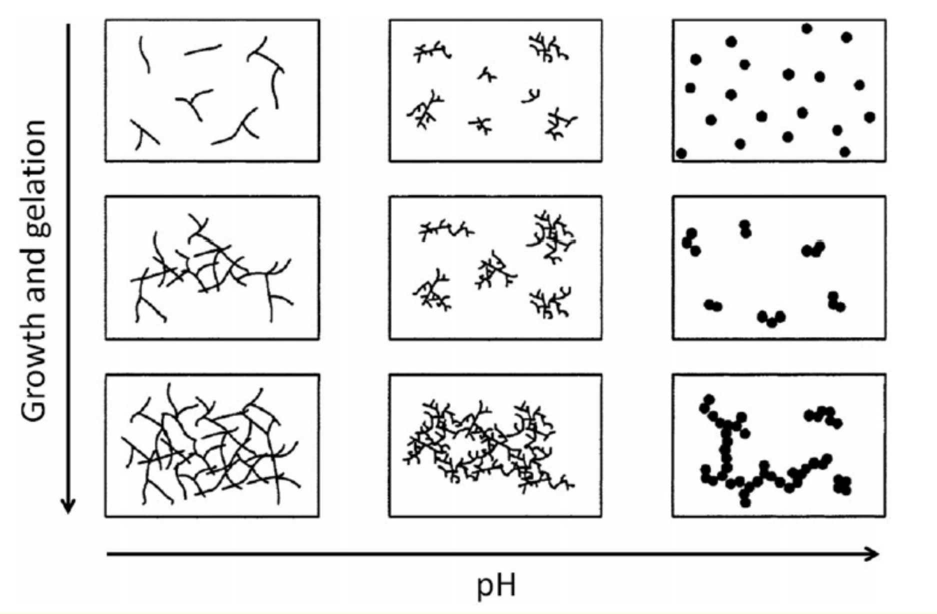


Base Catalysed Condensation

pH > 7

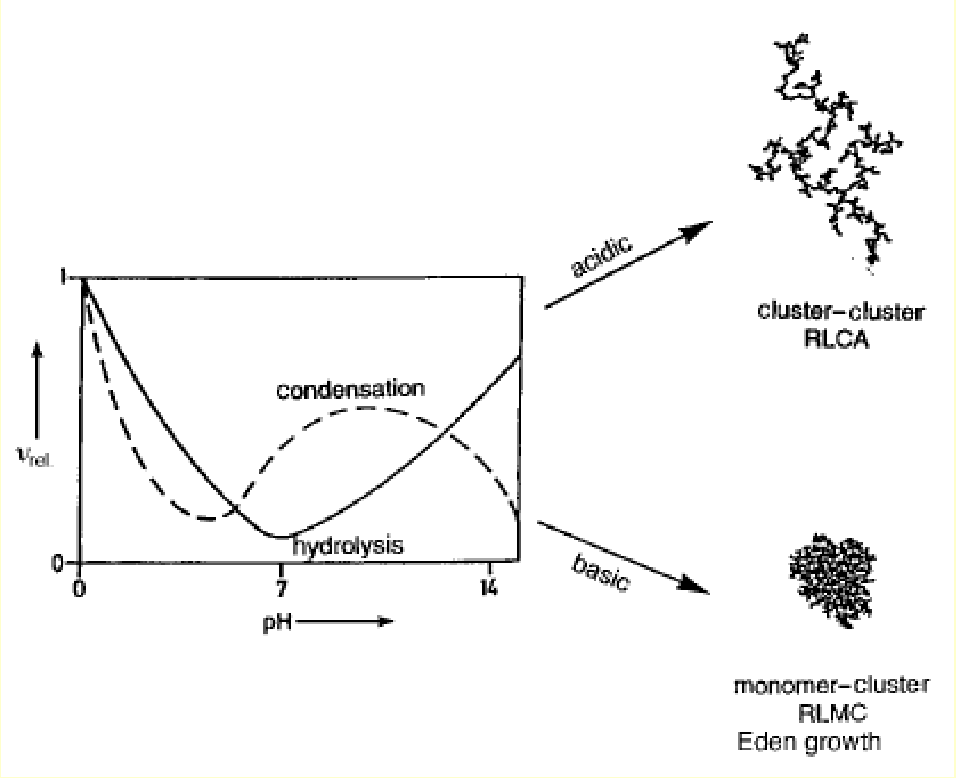
- For k > 4 : complete hydrolysis at early stage
- Reversible reactions in basic pH
- Chains cleaved at Q^1, source of Q^0
- Condensation to highly crosslinked particles
- Reaction limited monomer-cluster growth (RLMC)
- Compact nonfractal structure

- For k < 4 : incompletely hydrolysed species incorporated
- Fractal uniformly porous structure
- Large primary particles
- Mesoporosity, Type IV isotherms



Acid/Base Catalysed Condensation

Reaction limited cluster aggregation (RLCA)



Acid catalysed

Base catalysed

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

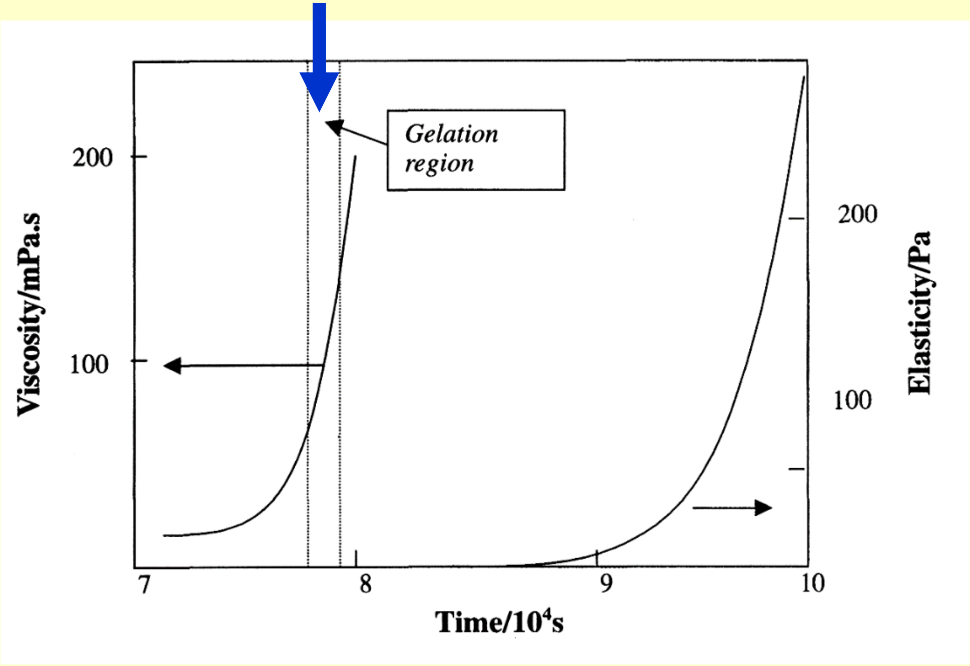
Gelation = Sol-to-Gel Transition

Gel point - a spannig cluster reaches across the container

Sol particles, oligomers and monomer still present

A sudden **viscosity** increase at the gel point

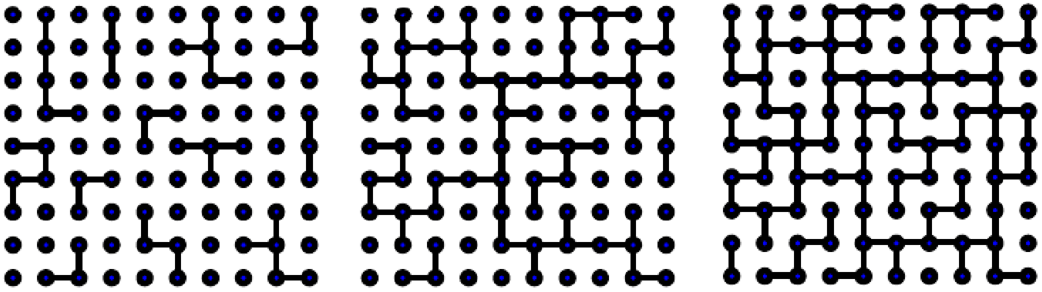
Further crosslinking - increase in elasticity

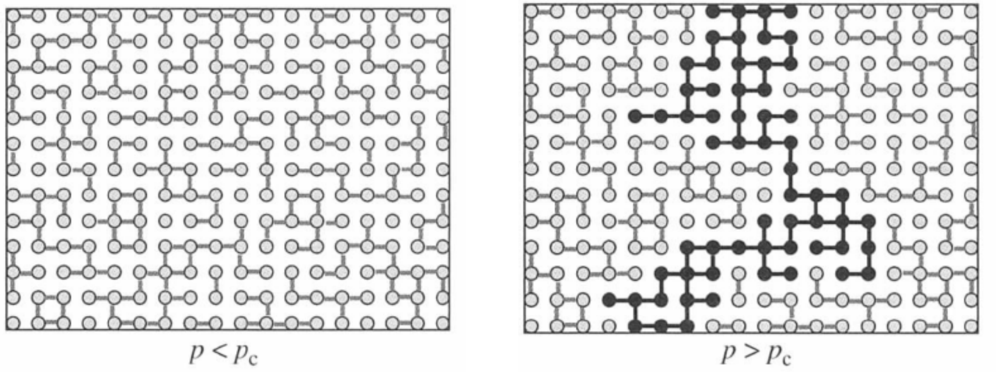


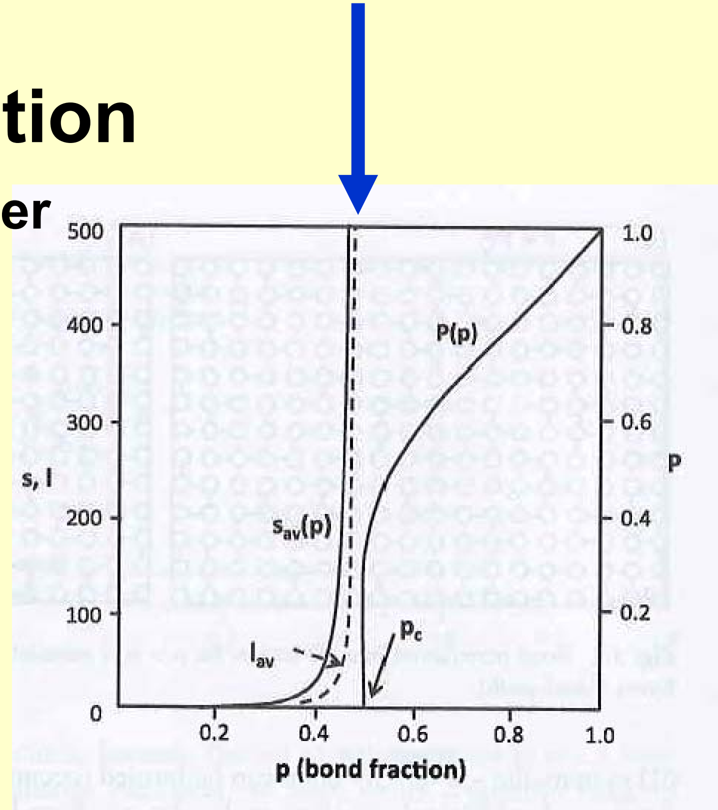
Bond Percolation

Gel point – modelling of a spannig cluster

p = the fraction of created links




$p < p_c$ $p > p_c$

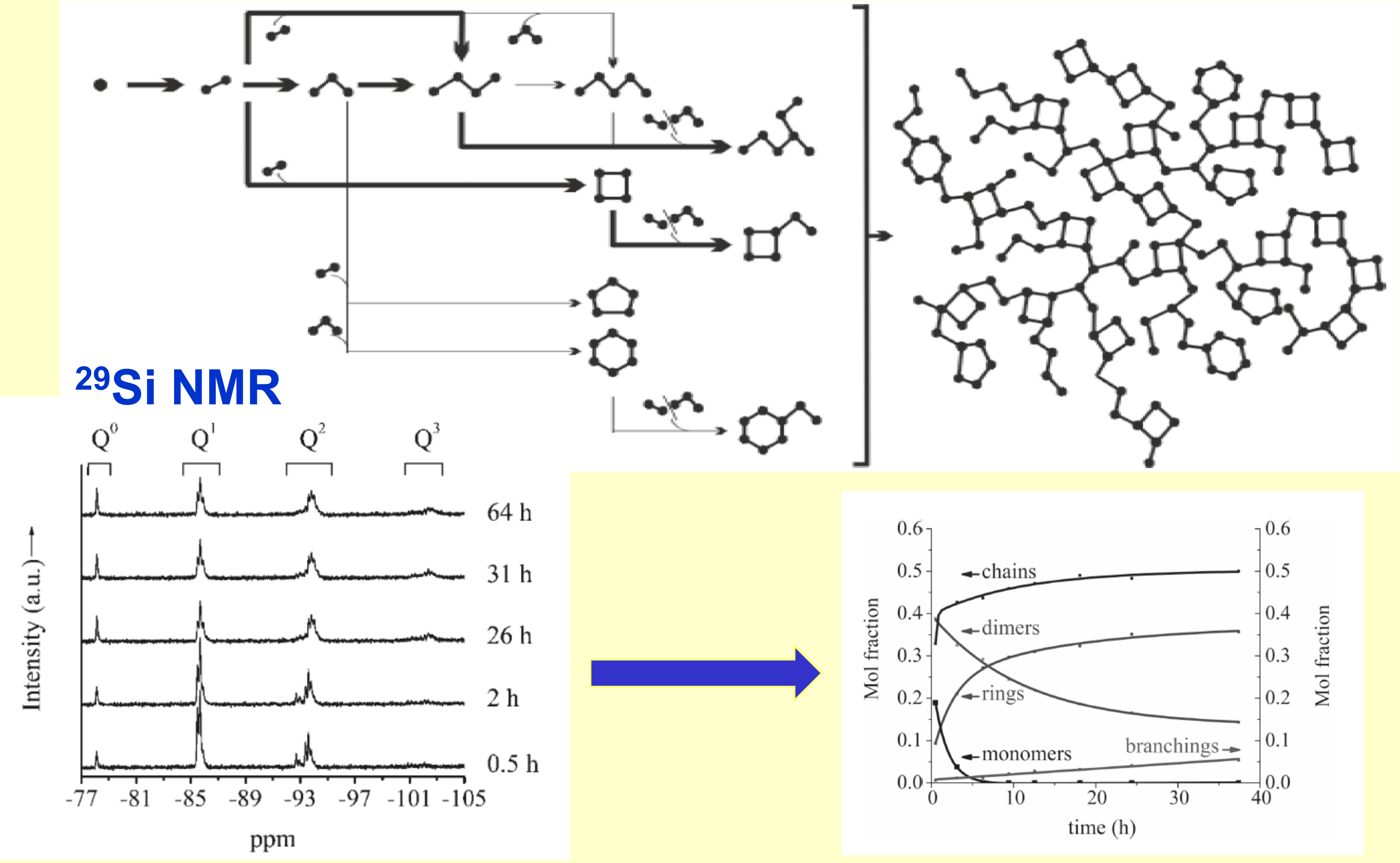


$s_{av}(p)$ = average cluster size

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

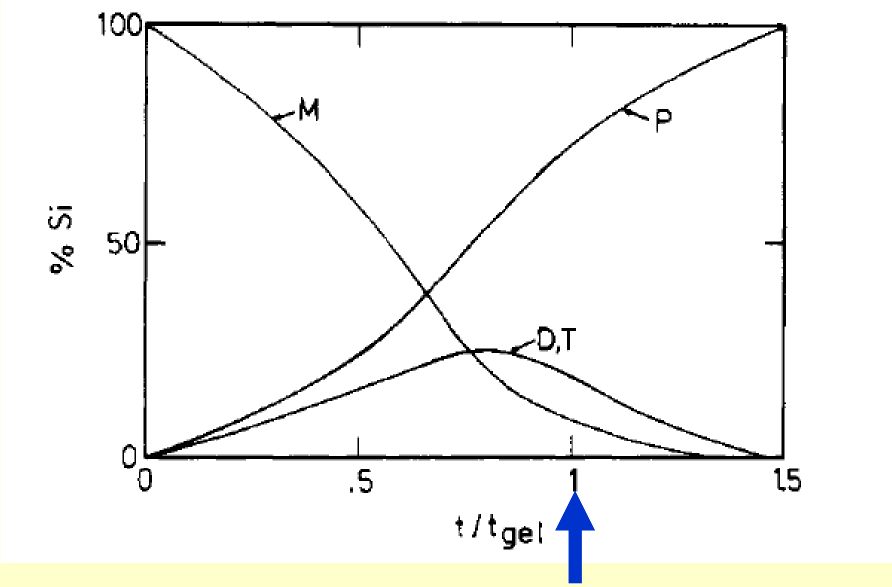
P(p) = percolation probability = a bond is added to a spanning cluster

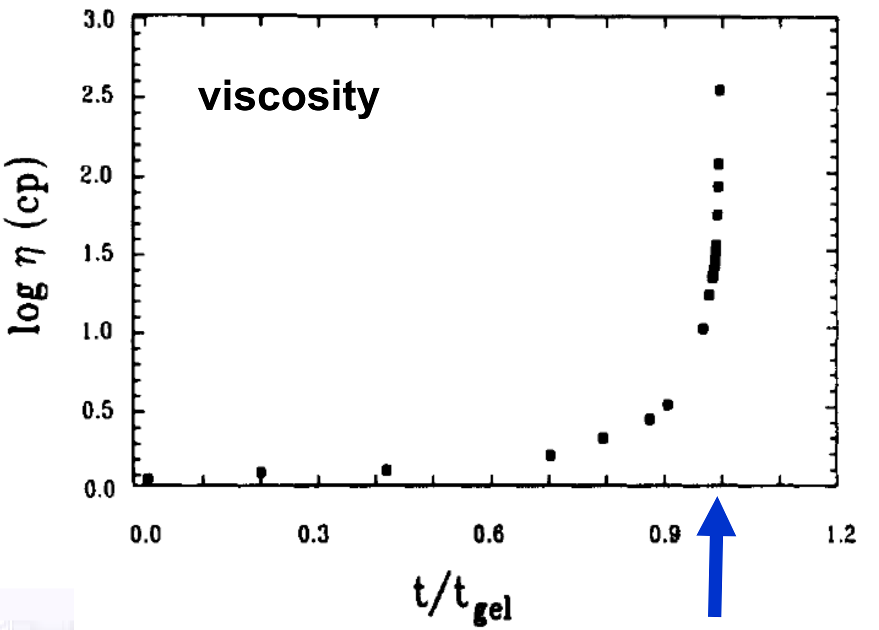
Kinetics of Sol-to-Gel Transition

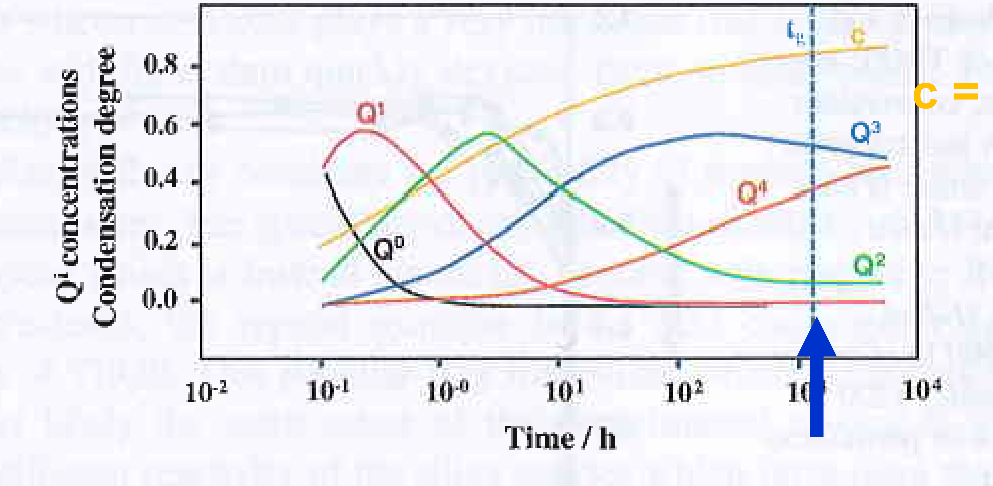


^{29}Si NMR

Kinetics of Sol-to-Gel Transition



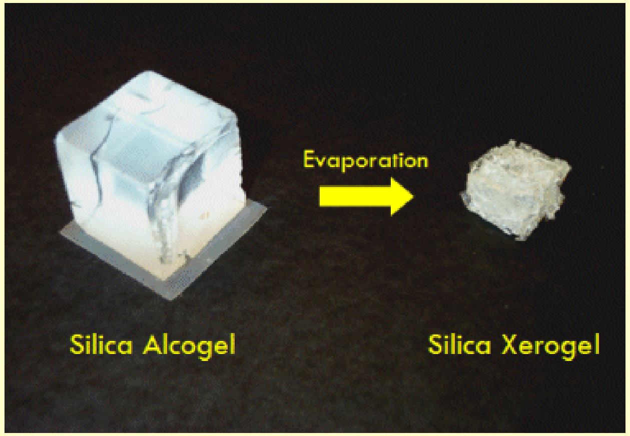




c = condensation degree, max 83 %

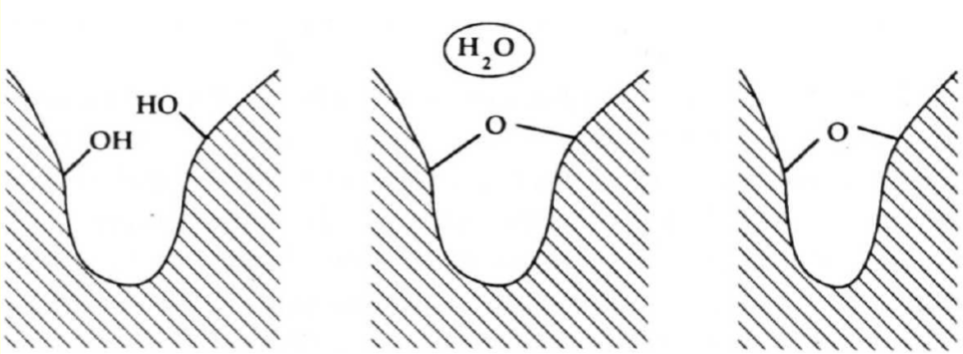
$Q^0 = O_4Si$
$Q^1 = O_3SiOSi$
$Q^2 = O_2Si(OSi)_2$
$Q^3 = OSi(OSi)_3$
$Q^4 = Si(OSi)_4$

Ageing of Gels

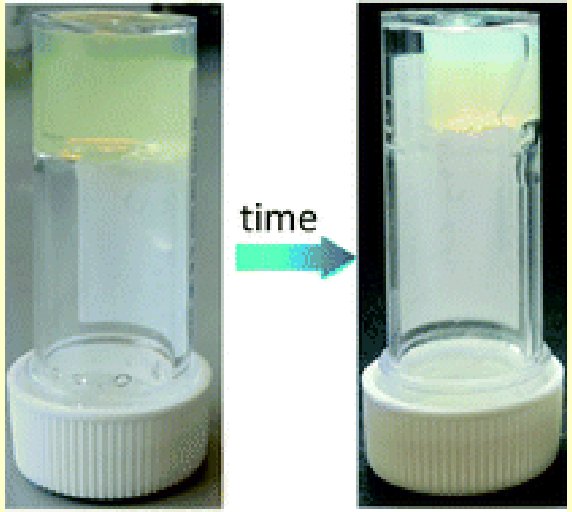


The sol-gel reactions continue
- unreacted species are retained in the porous structure
- reactive groups on the surface

Crosslinking
condensation of the OH surface groups, stiffening and shrinkage



Syneresis
shrinkage causes expulsion of liquid from the pores



Properties of the gel can be influenced by
ageing time, ageing temperature, solvent

Ageing of Gels

Coarsening

Dissolution and re-precipitation process
Materials dissolve from the convex surfaces and deposits at the concave surfaces: necks

Ostwald Rippening

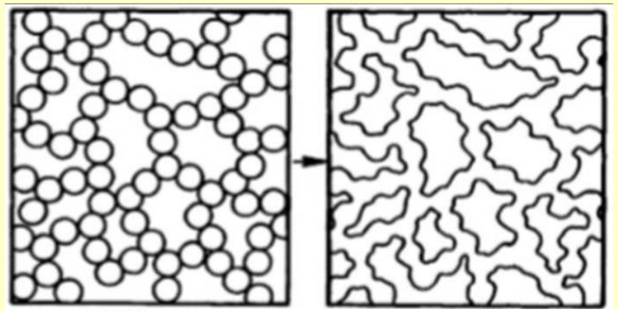
Smaller particles have higher solubility than larger ones

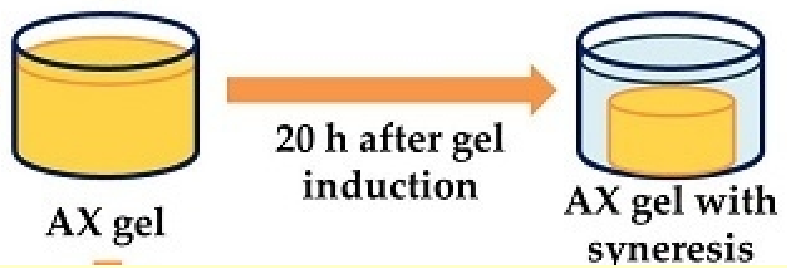
Phase Separation

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

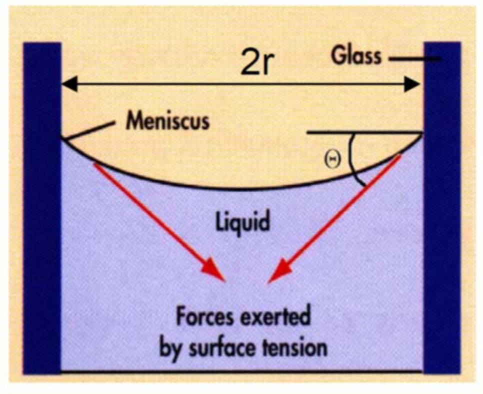
Strengthening

Ageing at high temperature
Soaking in a solvent with high solubilization power





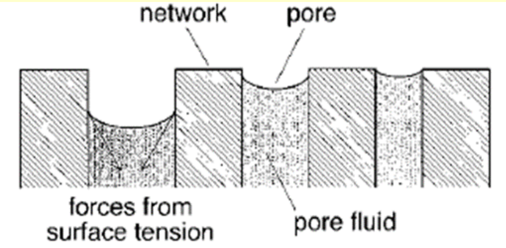
Drying of Gels



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 and deformation by surface tension, the liquid begins to recede (meniscus with a 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 of Gels

Coexistence of solid–vapor, liquid–vapor, and solid–liquid interfaces

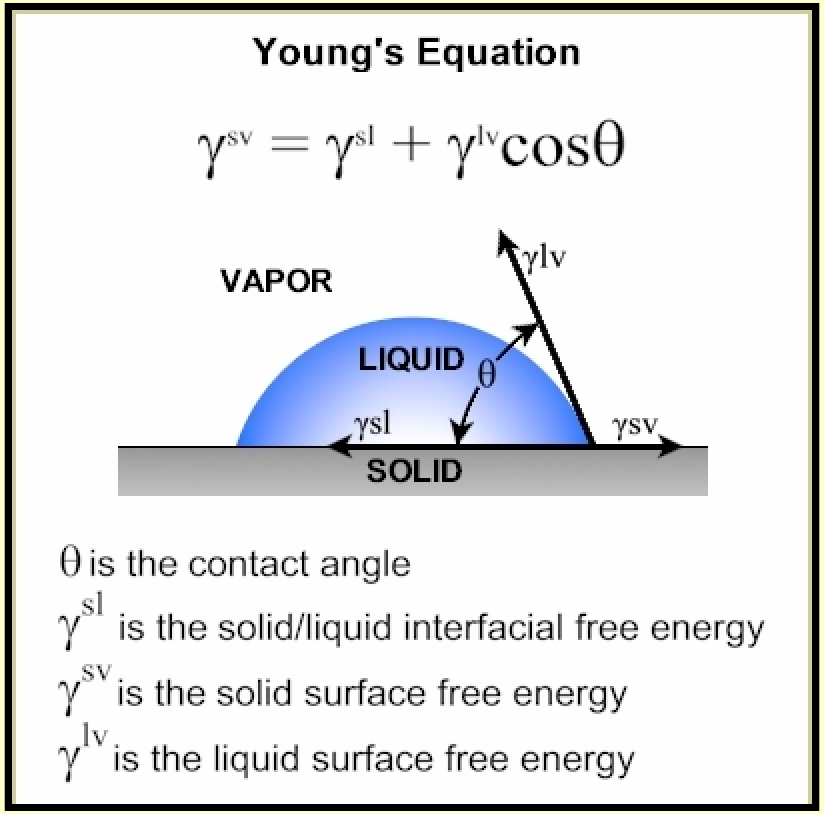
$$P_c = \frac{2\gamma_{LV}\cos\theta}{r}$$

Water is wetting the surface: cosθ = 1

Water: γ = 71.97 mN/m (25 °C)
Pore: r = 2.0 nm

P_c = 72 MPa

Solvent	**γ (mN/m, at 20 °C)**
Acetone	**23.7**
Isopropanol	**21.7**
n-Hexane	**18.4**



Young's Equation

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

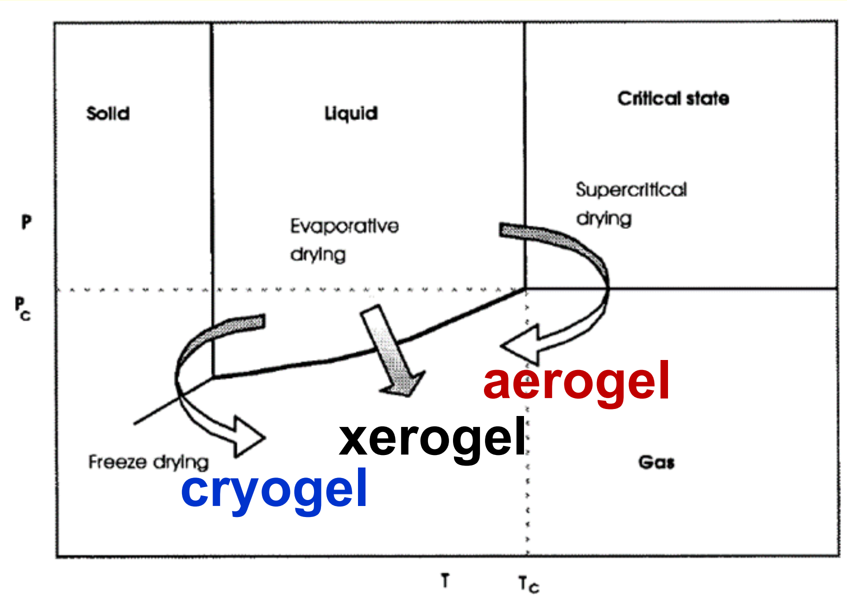
θ is the contact angle
γ^{sl} is the solid/liquid interfacial free energy
γ^{sv} is the solid surface free energy
γ^{lv} is the liquid surface free energy

Drying Methods

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

To avoid cracking:

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



1. **Supercritical drying – fluid state (= aerogel)**

2. Freeze-drying - solvent substitution in the pores by another with high sublimation pressure and low expansion coefficient (= cryogel)

3. Ambient drying
Surface modification by drying-control chemical additives - silylation by trimethylchlorosilane

4. Large pore gels

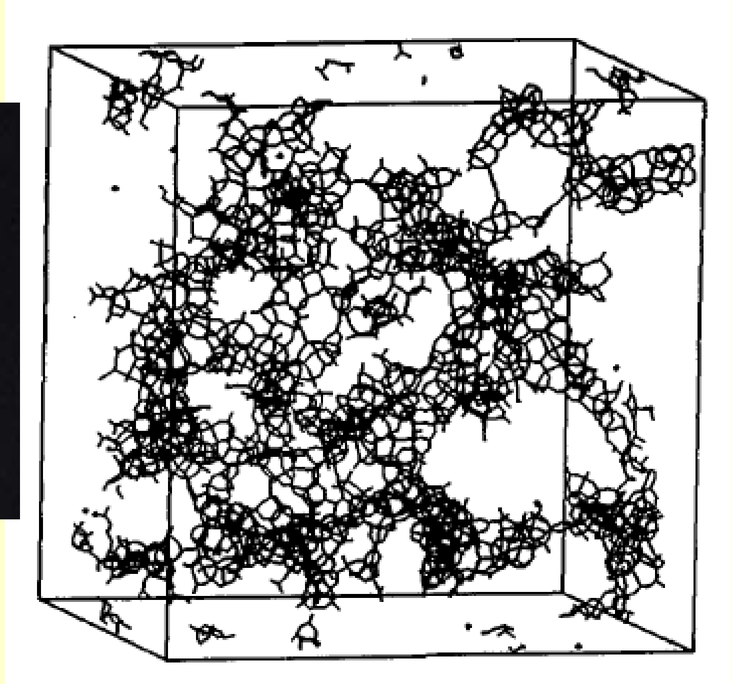
5. Ageing - stiffening

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

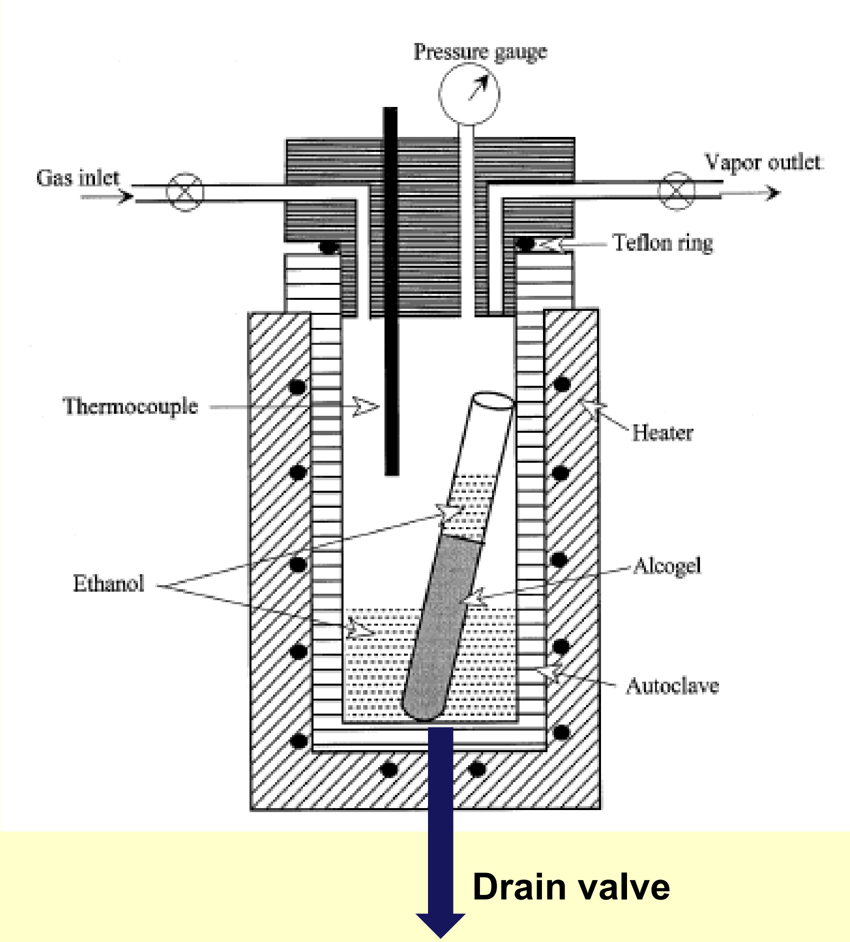
The record low density solid material - 10 mg/cm^3
Density of air - 1.2 mg/cm^3



Aerogels - Supercritical Drying

Silica aerogel

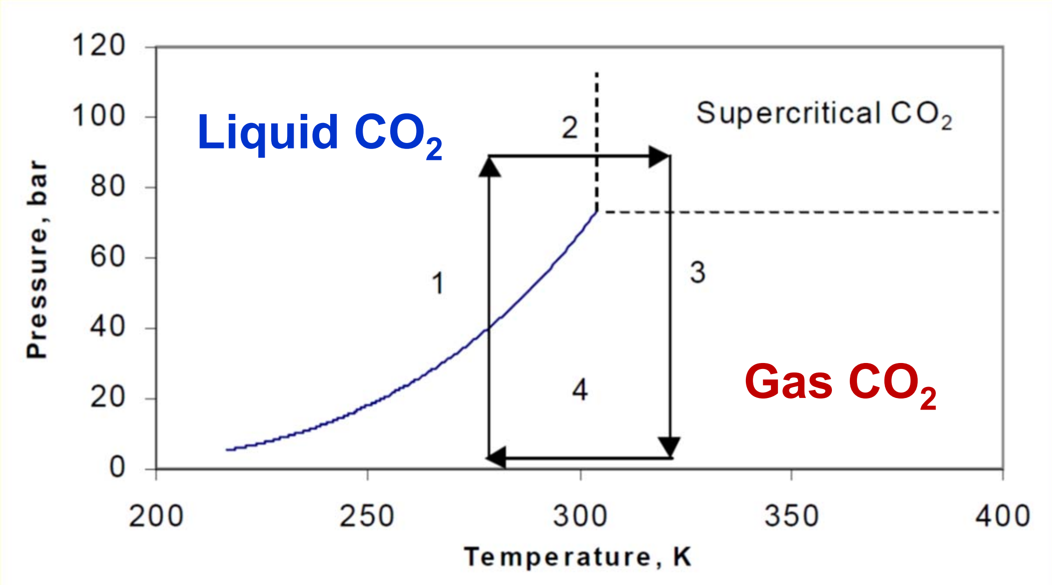
- **Wet gel is prepared**
- **Byproducts, salts, water washing**
- **Water replacement with acetone**
- **Loading to autoclave**
- **Supercritical drying**

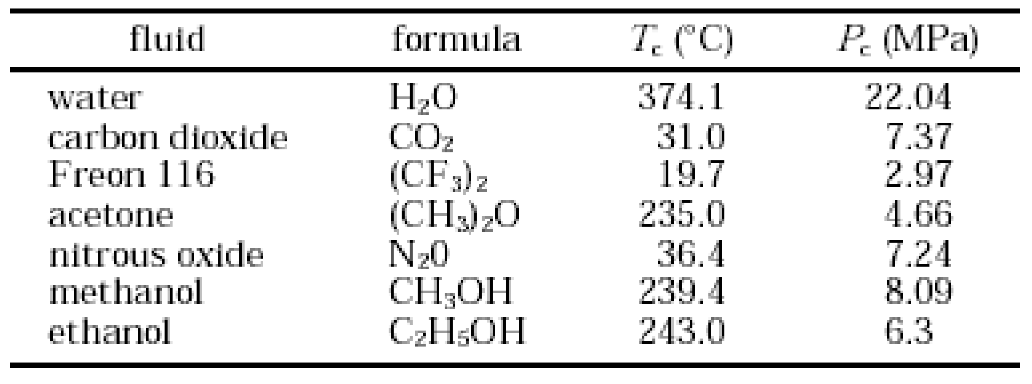


Supercritical Drying

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

- The gel containing excess amount of solvent (e.g., acetone) is placed in an autoclave
- Liquid CO_2 is pumped in at 4-10°C until the p = 100 bar (step 1)
- The solvent extracted by the liquid CO_2 is drained
- The temperature is raised to 40 °C aboveT_c of CO_2 (step 2)
- The fluid is slowly vented at constant T, resulting in a drop in p (step 3)
- At ambient pressure, the system is cooled down to the room temperature (step 4)



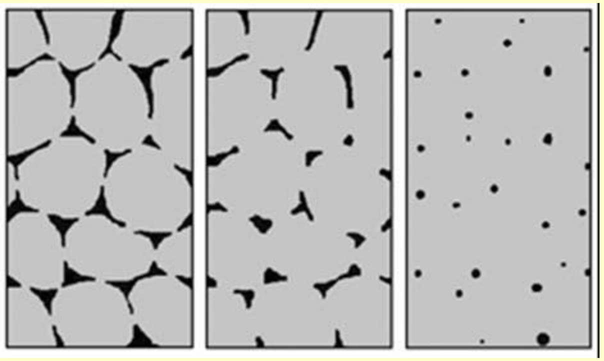


fluid	formula	T_c (°C)	P_c (MPa)
water	H_2O	374.1	22.04
carbon dioxide	CO_2	31.0	7.37
Freon 116	$(CF_3)_2$	19.7	2.97
acetone	$(CH_3)_2O$	235.0	4.66
nitrous oxide	N_20	36.4	7.24
methanol	CH_3OH	239.4	8.09
ethanol	C_2H_5OH	243.0	6.3

Sintering

Common ceramic and metallurgic manufacturing process
A process of bonding, densification and/or recrystallization of powder compacts
A treatment in which a green body is converted to a strong monolith

Thermal (solid-state) sintering
A powder pressed into a highly porous pellets
50-60 % of the maximum theoretical density = green pellets
Heating, the pellet densifies, reducing surface area and surface energy of individual particles without reaching melting point
Sintering time - several hours to several days



Other methods of sintering:

- Liquid-phase sintering
- Microwave sintering
- Spark-plasma sintering
- Oxidative sintering
- Pressure-assisted sintering

Control of sintering by sintering parameters: temperature, pressure, time, atmosphere

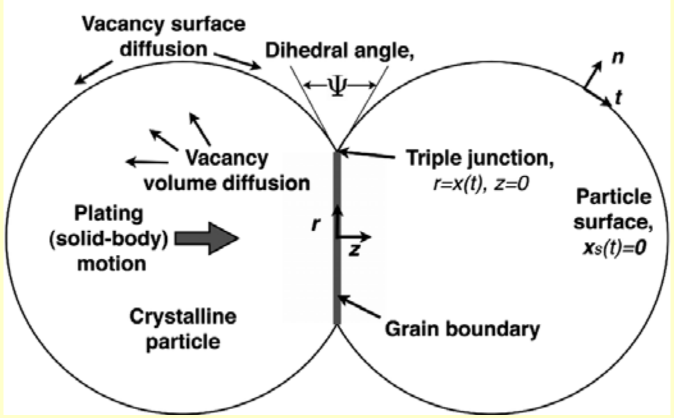
Sintering

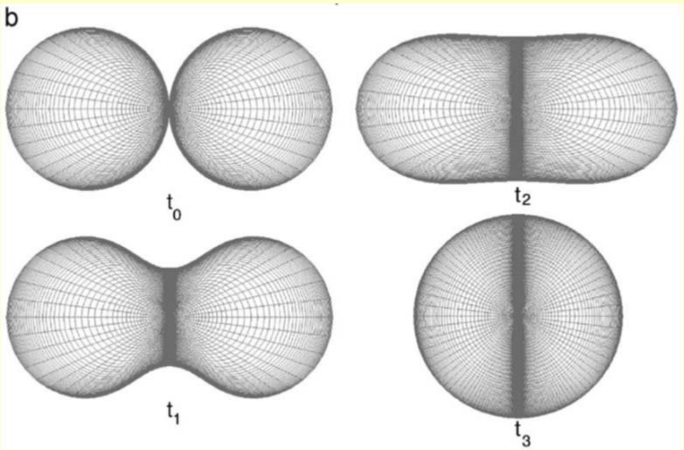
Sintering - self-diffusion of atoms in the crystal lattice

Atoms diffuse randomly through the lattice by moving into adjacent vacant lattice sites = vacancies
A vacant lattice site increases the energy of the lattice

Atoms on the surface of particles have higher energies than the atoms in the interior - energy is lower if the particle is in contact with another particle of the same material than if it is in contact with the atmosphere or a different material

The lattice sites that increase the contact area between particles are preferred = around the edges of the contact area





Sintering

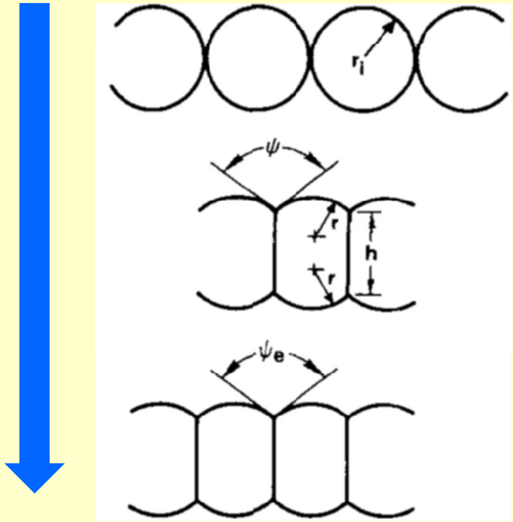
Atoms move out of the bulk and to the contact area = vacancies are created within the bulk

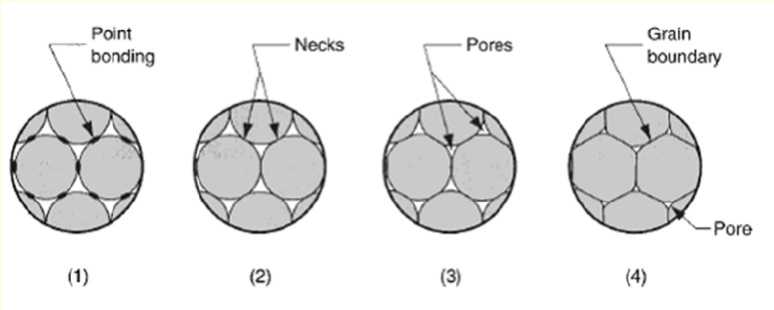
The overall energy change - the difference of the energy reduced by increasing the surface area and the energy increased by creating a vacancy = the sintering stress

The magnitude of the sintering stress depends on the contact angle between the particles = the dihedral angle ψ

As the contact area increases the dihedral angle widens

Eventually it reaches a wide enough angle that the sintering stress is zero and sintering stops = the equilibrium dihedral angle ψ_e





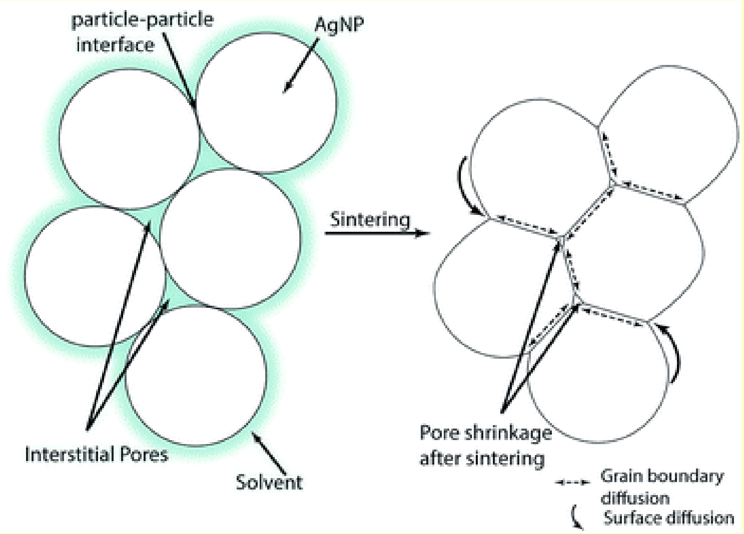
Sintering

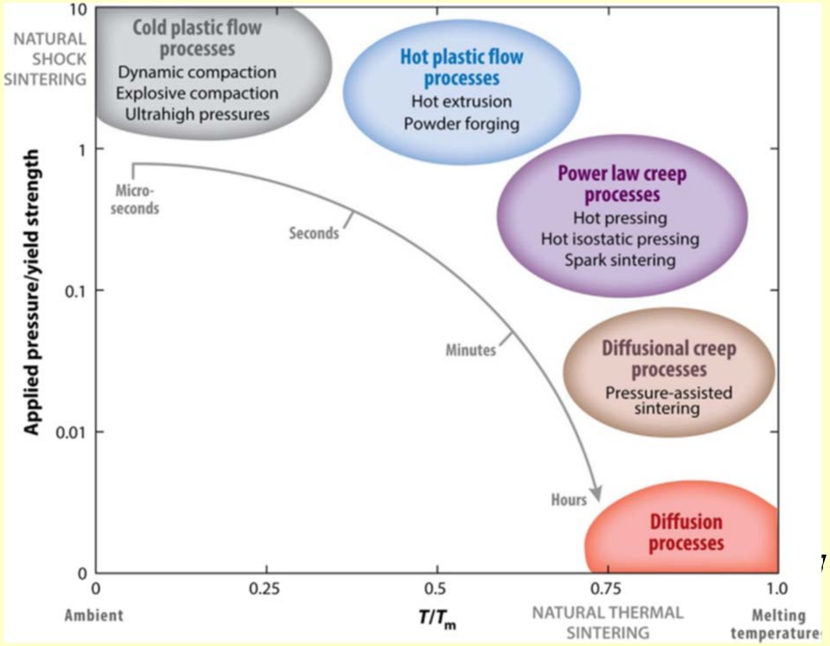
Because of the limit on the dihedral angle, it is possible for sintering to reach equilibrium with pores still present in the material

The rate of sintering is controlled by the diffusion rate and sintering stress

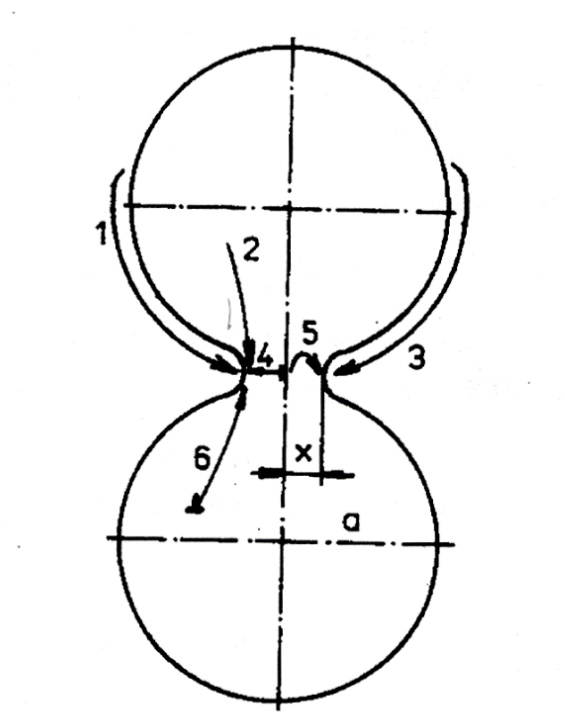
The diffusion rate is affected by the defect concentration and temperature

More defects = more atoms can diffuse simultaneously
High temperatures = atoms to diffuse faster = sintering is done at high temperature





Sintering Mechanisms



Sintering mechanisms - solid, liquid, gas phase

1. Evaporation-condensation and dissolution-precipitation

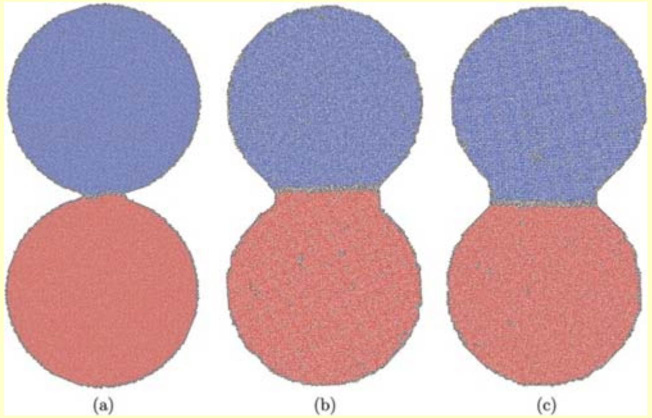
2. Volume diffusion – viscous flow (amorphous)

3. Surface diffusion

4. Grain boundary diffusion

5. Volume diffusion from grain boundaries

6. Volume diffusion of dislocations – plastic flow



Sintering Mechanisms

Vapor Pressure over a Curved Surface

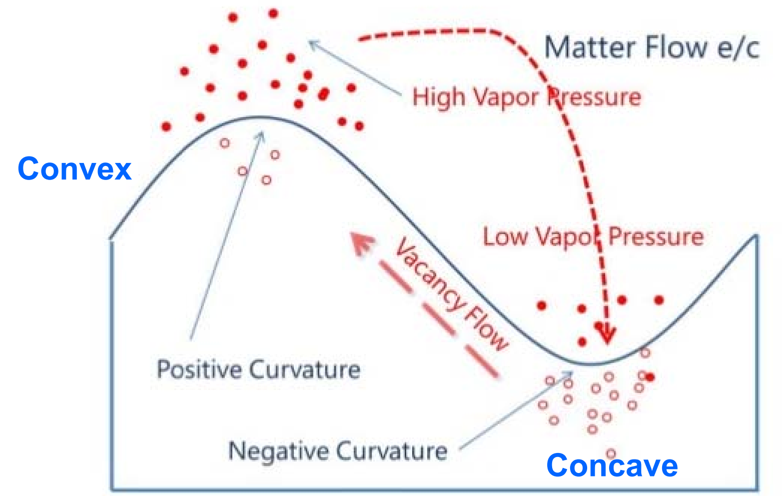


Figure : Curvature in solids, and their effect on vapor pressure

Curvature

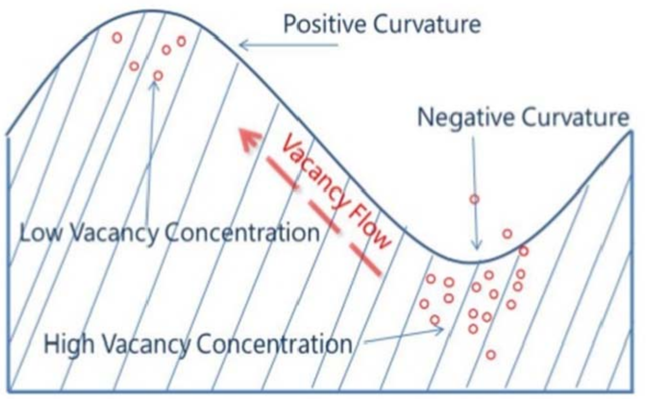
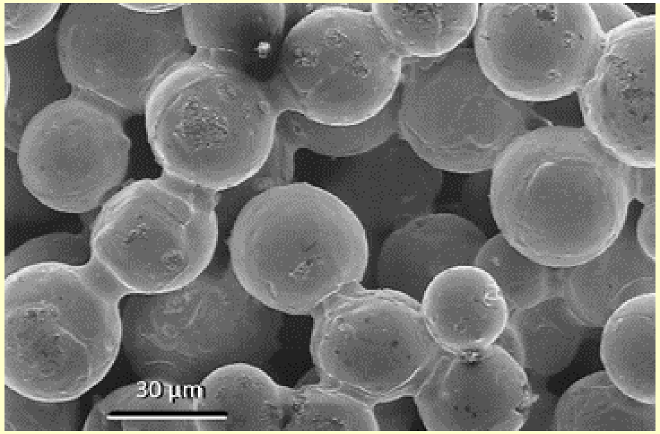


Figure : Curvature in solids, and their effect of vacancy concentration

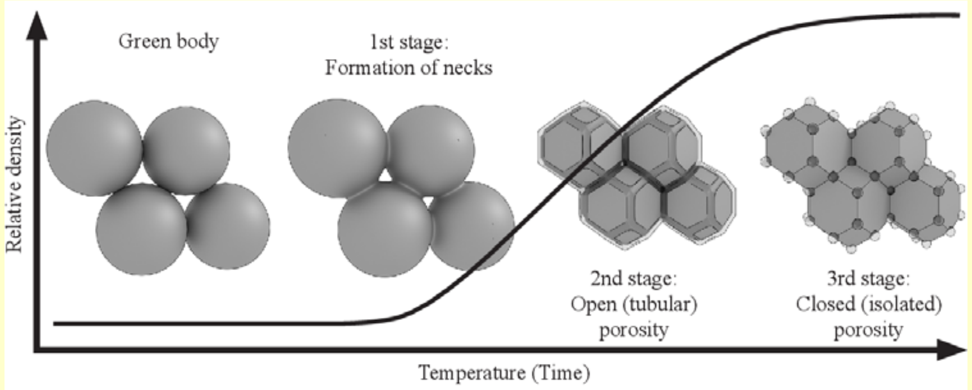


Sintering

Stage 1
The particles increase their contact areas through the formation of necks, it ends once neck growth ceases to be the major mechanism

Stage 2
The overall density increases as the pores decrease in size
The contact areas grow into planes = grain boundaries
The pores become columnar in shape as they shrink into tunnel systems on grain boundaries and triple junctions

Stage 3
The pores become closed off to the surface
Grain boundary motion begins as the lattice continues to decrease its overall energy by decreasing the surface area between grains
Large grains grow at the expense of smaller grains



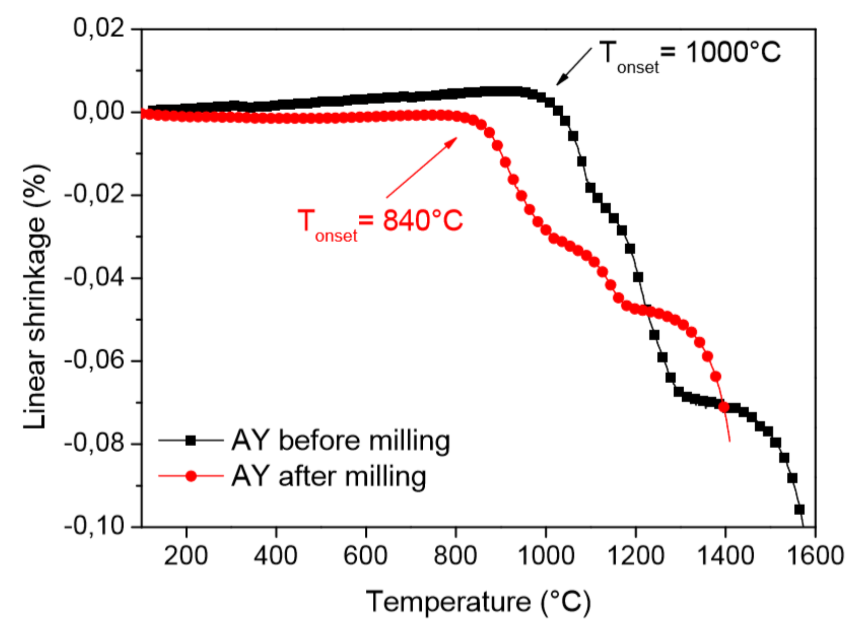
Sintering

Larger agglomerates/grains

= higher sintering temperature

Agglomerates 3 μm

Agglomerates 0.5 μm



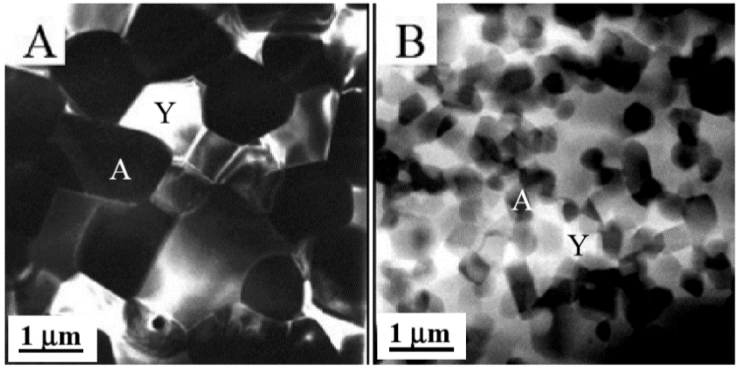


Figure 5. Transmission Electron Microscopy (TEM) images of AY materials. (**a**) Un-milled powder, sintered ad 1600 °C/3 h; (**b**) Milled powder sintered at 1420 °C/3 h. Characters A and Y refer to α-Al_2O_3 (black grains) and YAG (white grains), respectively.

Densification

Densification process

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

Desorption of liquid from pore surface

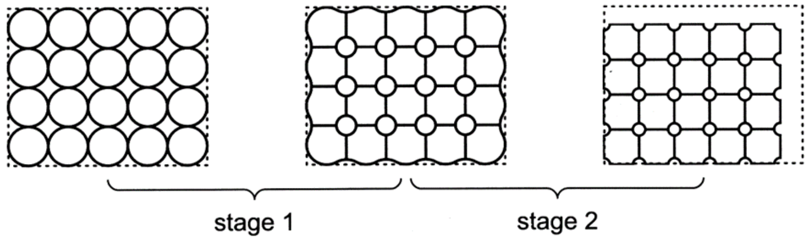
Stage II. 150 - 700 °C, both weight loss and shrinkage

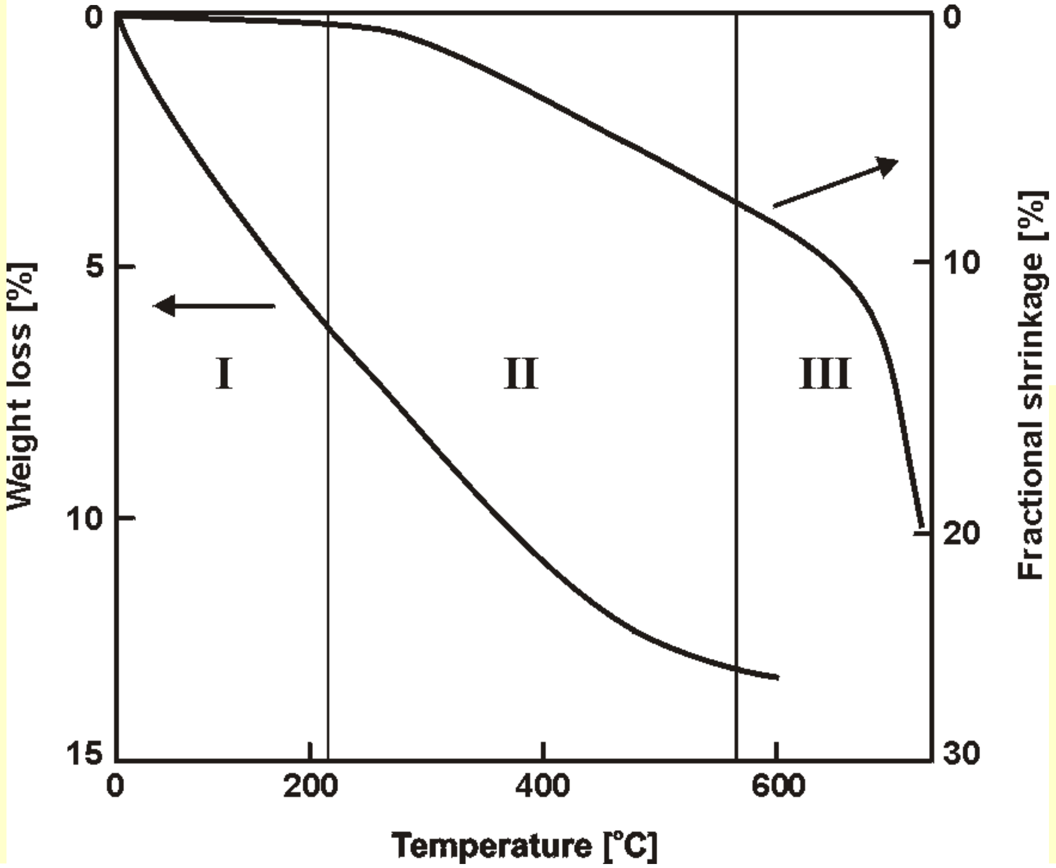
Loss of organics - weight loss
Further condensation - weight loss and shrinkage
Structural relaxation - shrinkage

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

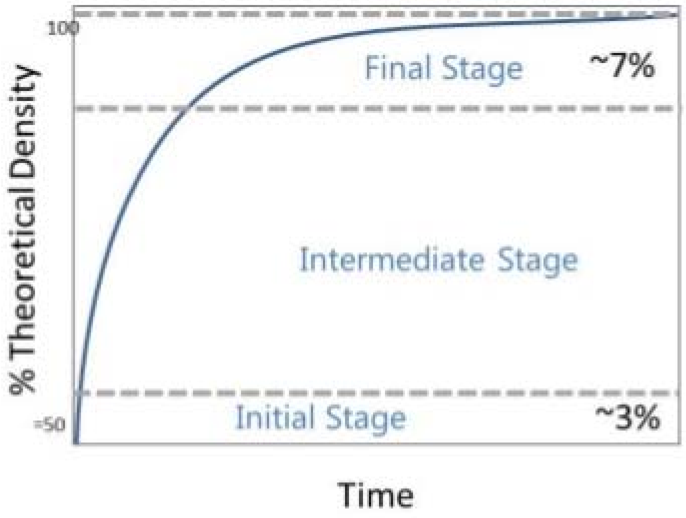
Close to glass transition temperature, viscous flow, rapid densification, large reduction of surface area, reduction of interfacial energy, termodynamically favored

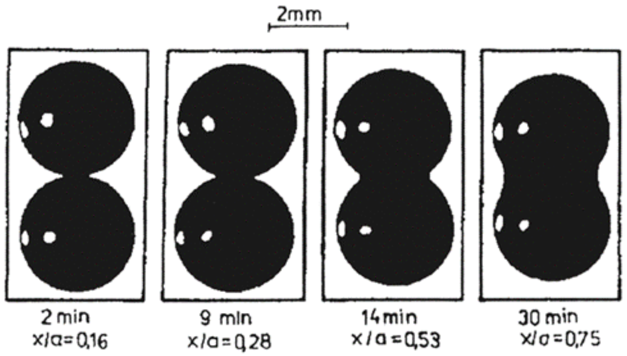
Densification - Sintering



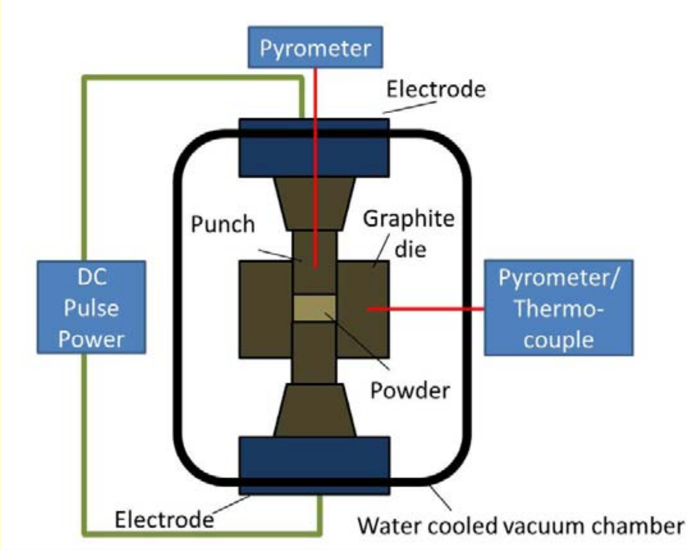


Generalized Sintering Curve





SPS/FAST – Spark Plasma Sintering



- **Field assisted sintering technique**
- **No spark, No plasma**
- **Pulsed electric current sintering**
- **High pressure – limitation by high temperature fracture strength**
- **Graphite 100-150 MPa, WC or SiC – 1GPa**
- **High temperature – up to 2400 °C**
- **Joule heating – resistence - at contact points**
- **Up to 10 V, current 10 kA**
- **Extreme heating rates: 1000 K/min**
- **Near theoretical density at lower sintering temperature compared to conventional sintering techniques**