

## Basics for Designing Organic Nanomaterials

### Chapter 1. Characteristics of Nanomaterials

### Chapter 2. Methodology of Nanomaterials

#### 2.1 Template Method

##### 2.1.1. Microemulsion

##### 2.1.2. Nanostructured Polymer (Copolymer, Dendrimer, DNA)

##### 2.1.3. Nanostructured Ceramics (AAO, Porous Silica, Zeolite)

#### 2.2. Non-template Method

##### 2.2.1. Sol-gel Method

##### 2.2.2. Vapor Deposition (Physical, Chemical)

##### 2.2.3. Electrospinning

### Chapter 3. Structure, Property, and Applications of Organic Nanomaterials

#### 3.1. 0-D Organic Materials

#### 3.2. 1-D Organic Materials

#### 3.3. 2-D Organic Materials

#### 3.4. 3-D Organic Materials.

# Chapter 2.2.1. Non-template Method

## 2.2.1. Sol-gel Method

### 1. Introduction

### 2. Some Theoretical Approaches to The Sol-gel Chemistry

- 2.1. Classical theory
- 2.2. Percolation theory
- 2.3. Kinetic models

### 3. Experimental Approaches to The Sol-gel Chemistry

- 3.1. Silica sol-gel
- 3.2. Metal alkoxide
- 3.3. Pechini processing



# 1. Introduction

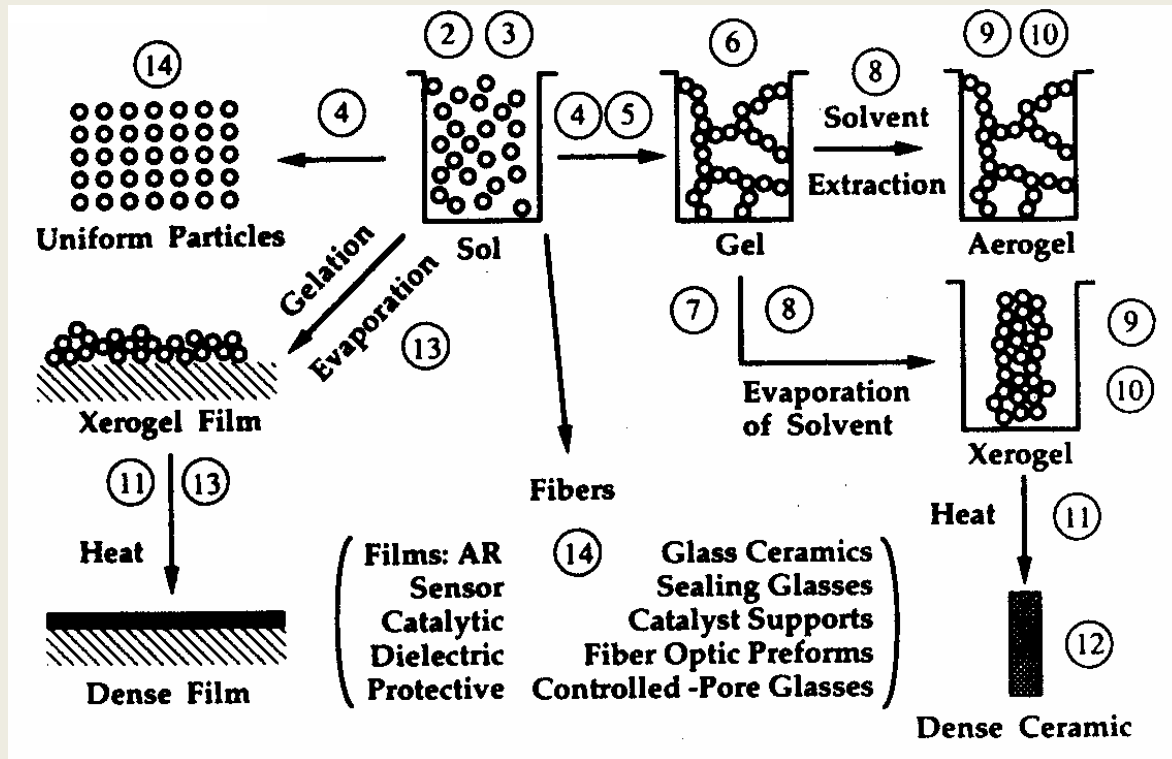
- Definition of sol-gel processing

The *sol-gel process* is a process for making glass/ceramic materials. The sol-gel process involves the transition of a system from a liquid (the colloidal "sol") into a solid (the "gel") phase. The sol-gel process allows the fabrication of materials with a large variety of properties: ultra-fine powders, monolithic ceramics and glasses, ceramic fibers, inorganic membranes, thin film coatings and aerogels. Sol-gel chemistry is a remarkably versatile approach for fabricating materials. Scientists have used it to produce the world's lightest materials and some of its toughest ceramics. - *From wikipedia*



# 1. Introduction

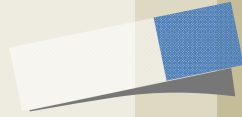
## Overview of sol-gel processing



- Sol-gel processing refer to r.T formation of solid inorganic materials from molecular precursors in liq. Solution
- Inorganic salts or metal-organic compounds are dissolved in aqueous or organic solvents to form polymeric particulates sols consisting of inorganic particles dispersed in the solvent. These sols are then condensed to various types of gels.



# 1. Introduction



- Advantages of sol-gel processing
  - Controlling composition and microstructure at molecular level
  - Room temperature synthesis: incorporation of heat sensitive materials (protein)
  - Conventional synthesis: high-temp ceramic method
  - Nano, organic-inorganic composites
  - Various forms: powder, film, fiber, monolith, etc.



# 1. Introduction

- Basic concepts of sol-gel processing

**-Precursors:** starting materials on sol-gel process, inorganic salts (metal nitrates, halides, sulfates;  $\text{AlCl}_3$ ,  $\text{Fe}(\text{NO}_3)_2$ ) and metal-organic compounds (metal alkoxides,  $\text{Si}(\text{OEt})_4$ )

**-Sol:** A stable dispersion of solid colloidal particles in a liquid (do not settle or agglomerate at a significant rate); aquasol, organosol

**-Gel:** system made of a continuous solid skeleton made of colloidal particles or polymers enclosing a continuous liquid phase

**-Xerogel:** a gel dried by evaporation under normal conditions; 5~10 factor shrinkage by capillary tension

**-Aerogel:** liquid removed to prevent any collapse or change in the structure as liquid is removed. Drying a wet gel in an autoclave above the critical point of liquid so that no capillary pressure is exerted. The product is mostly air, having volume fraction of solid as low as 0.1%.

**-Cryogel:** powders obtained by freeze-drying

## 2. Some Theoretical Approaches to The Sol-gel Chemistry

### 2.1. Classical Theory

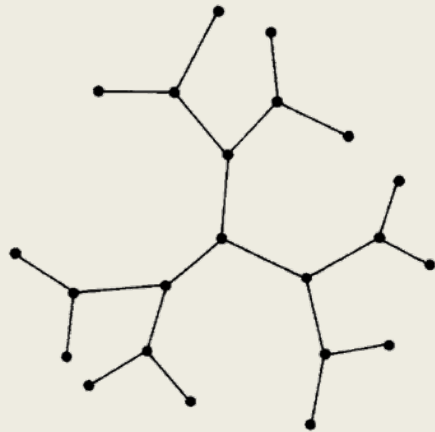
- The theory of gelation developed by Flory and Stockmayer is now generally known as the “classical” or “mean field” theory.

Ref.

[1] P.J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, New York, 1953

[2] R. Zallen, *The Physics of Amorphous Solids*, Wiley, New York, 1983

- The theory seeks to answer the following question:  
“Of all bonds that could form in a polymerizing system, what fraction ( $p_c$ ) must form before an infinitely large molecule appear?”



Cayley tree or Bethe lattice  
with functionality  $z=3$

The basic assumptions

- Consider the condensation polymerization of a  $z$ -functional monomer.
- The reactivity of all the functional groups on a monomer is equal to  $p$ .
- Bonds form only between polymers, not within them, so that the polymers contain no closed loops. (No intramolecular cross-linking is allowed)

※ Cayley tree or Bethe lattice

The growing polymer structure, which branches without ever forming rings

## 2. Some Theoretical Approaches to The Sol-gel Chemistry

- Travelling along a path of completed bonds, at each node we find  $z-1$  opportunities along a path of completed bonds  
: the probability that one of them is a completed bond is  $(z-1)p$ .
- For the polymer to form a gel, on average there must be at least one completed path from each node, so we require  $(z-1)p \geq 1$
- The critical condition for gel formation

$$p_c = 1 / (z - 1)$$

$z=2 : p_c=1 \rightarrow$  because such a system forms only linear chains that cannot cross-link into a network

$z=3 : p_c=1/2$

$z=4 : p_c=1/3$



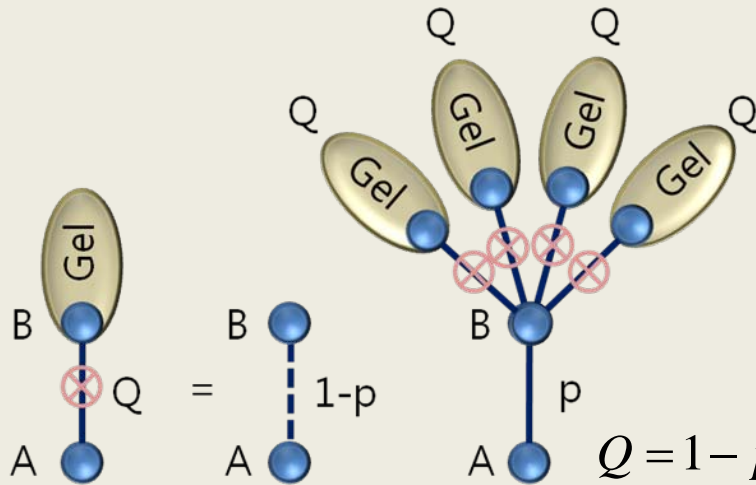


## 2. Some Theoretical Approaches to The Sol-gel Chemistry

- Sol and gel fractions
  - Sol fraction ( $w_s$ ): the fraction of all monomers that are either unreacted or being to finite-size polymers (sol)
  - Gel fraction ( $w_g$ ): the fraction of all monomers belonging to the gel
  - $w_s + w_g = 1$
  - Below the gel point ( $p \leq p_c$ )
    - :  $w_s = 1, w_g = 0$  (only finite-size branched polymers)
  - Above the gel point ( $p > p_c$ )
    - :  $w_s < 1, w_g > 0, w_s + w_g = 1$  (at least one infinite polymer(gel) and many finite-size branched polymers)



## 2. Some Theoretical Approaches to The Sol-gel Chemistry



$Q$  : the probability that a randomly selected site is not connected to the gel through a certain randomly selected path

the probability that the bond between A and B is reacted and does not lead to the gel

$$Q = 1 - p + pQ^{z-1}$$

the probability that the bond site A and B could be unreacted with probability  $1-p$

Sol fraction is the probability that a randomly selected site is not connected to the gel along any of its  $z$  paths

$$w_s = Q^z \quad Q = w_s^{1/z}$$

$$w_s^{1/z} = 1 - p + pw_s^{(z-1)/z}$$

## 2. Some Theoretical Approaches to The Sol-gel Chemistry

- MF prediction of sol and gel fraction for  $z=3$

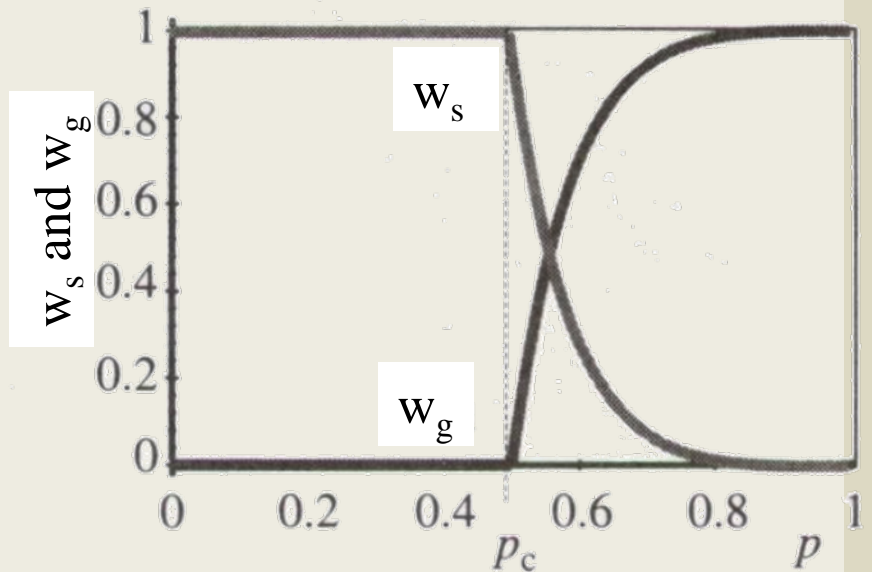
$$w_s^{1/z} = 1 - p + pw_s^{(z-1)/z}$$

For  $z=3$  ;  $p_c=1/2$

$$w_s^{1/3} = 1 - p + pw_s^{2/3}$$

$$w_s = \left( \frac{1-p}{p} \right)^3$$

$$w_g = 1 - w_s = 1 - \left( \frac{1-p}{p} \right)^3$$



*Mean-field prediction of sol and gel fractions for functionality  $z=3$*

## 2. Some Theoretical Approaches to The Sol-gel Chemistry

### Advantage

- The classical theory provides **formulas for important features of the gelling solution** : the critical degree of reaction at the gel point and distribution of molecular weights in the sol

### Limitations

- The reactivity of a functional group is independent of the degree of reaction.  
: Ex. a hydroxyl (OH) has the same reactivity on a silicic acid monomer and on a Q<sup>3</sup> group in the spanning cluster. → generally not true
- The growing polymers contain no closed loops (rings), which means that bonds form only between polymers, never within them.  
→ only probable at high concentrations of polymers
- The repeated branching results in crowding at the periphery of the polymer.  
: The mass, M, of such a polymer increases with R<sup>4</sup> (R: radius) ;  $M \propto R^4$   
: Since the volume  $V \propto R^3$  → the density increases in proportion to R ( $\rho \propto R$ )  
→ This result is physically unacceptable, because the density cannot increase indefinitely as the polymer grows.  
→ The classic model does not provide an entirely realistic picture of polymer growth.

## 2. Some Theoretical Approaches to The Sol-gel Chemistry

### 2.2. Percolation Theory

- Percolation theory offers a description of gelation that does not exclude the formation of closed loops and so does not predict a divergent density for large clusters.
- **Limitations**
  - : It generally does not lead to analytical solutions for such properties as the percolation threshold or the size distribution of polymers.
  - However, these can be determined with great accuracy from computer simulation, and the results are often quite different from the predictions of the classical theory.

Ref.  
[1] R. Zallen, *The Physics of Amorphous Solids*, Wiley, New York, 1983

[2] D. Stauffer, A. Coniglio, M. Adam, *Advances in Polymer Science*, **44** (1982) 103



## 2. Some Theoretical Approaches to The Sol-gel Chemistry

### 2.2.1. Percolation threshold

#### ➤ Gelation

: connectivity transition that can be described by a bond percolation

#### ➤ Bond percolation

- All sites of the lattice are assumed to be occupied by monomers
- The chemical reaction between monomers is modeled by randomly connecting monomers on neighboring sites by bonds

#### ➤ The extent of reaction, $p$

: the fraction of all possible bonds that are formed at any point in the rxn

#### ➤ The percolation threshold or gel point, $p_c$

- the point where the system undergoes a connectivity transition
- transition from a sol below  $p_c$  to a gel above  $p_c$

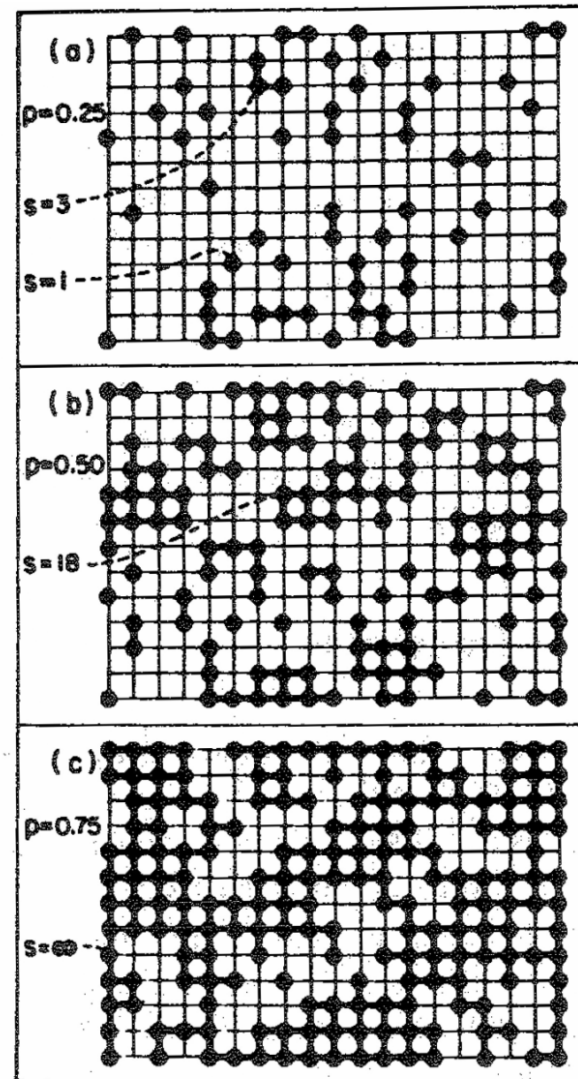


## 2. Some Theoretical Approaches to The Sol-gel Chemistry

### ➤ Percolation threshold

- Site percolation : Starting with an empty grid, circles are placed on sites at random
- Bond percolation : The sites are initially filled (with monomers) and the bonds are filled in at random
- Percolation threshold ( $p_c$ ): the critical value of  $p$  at which the spanning cluster first appears

$$p_c = 1 / (z - 1)$$



Site percolation on the square lattice, illustrating various cluster sizes ( $s$ ) for three values of  $p$ , the fraction of filled sites. For  $p = 0.75$ , an unbounded cluster is present. From Zallen, *The Physics of Amorphous Solids* (Wiley, New York, 1983), chapter 4.



## 2. Some Theoretical Approaches to The Sol-gel Chemistry

### 2.3. Kinetic Models

- An enormous amount of work has been done to model aggregation processes, leading to predictions of the kinetics of growth and the fractal structure of the resulting clusters.
- Ref.

[1] P. Meakin, Phase Transitions, 12 (1988) 335

[2] J.E. Martin, Time-Dependant Effects in Disordered Materials, Plenum, New York, 1986





## 2. Some Theoretical Approaches to The Sol-gel Chemistry

### 2.3.1. Smoluchowski's Equation

- The Smoluchowski equation describes an aggregation process

$$\frac{dn_s}{dt} = \frac{1}{2} \sum_{i+j=s} K(i, j)n_i n_j - n_s \sum_{j=1}^{\infty} K(s, j)n_j$$

where  $n_s$  = number of clusters of size  $s$   
 $s, i, j$  = size  
 $K(i, j)$  = rate coefficient

Rate of creation of clusters of size  $s$  by aggregation of two smaller clusters

Rate at which clusters of size  $s$  are eliminated by further aggregation

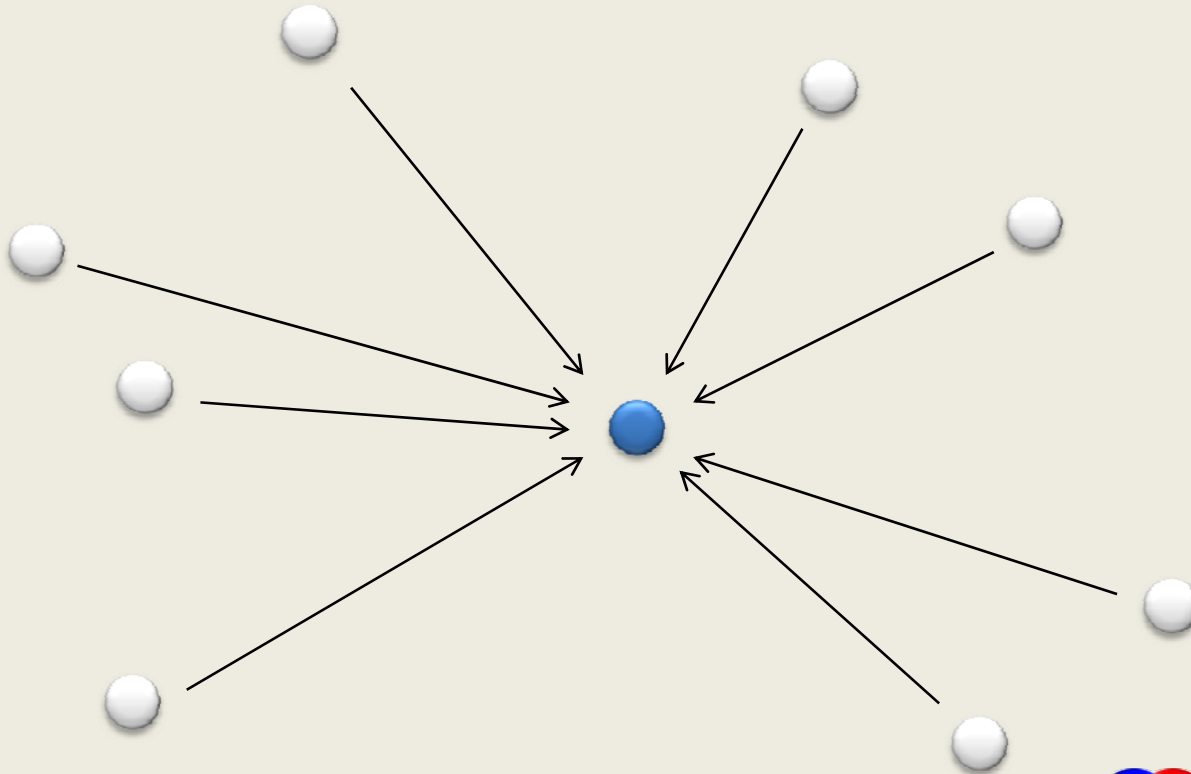
- For this equation applied, the sol must be so dilute that collisions between more than two clusters can be neglected, and the clusters must be free to diffuse so that the collisions occur at random.
- Since  $K$  depends only on  $i$  and  $j$ , ignoring the range of structures that could be present in a cluster of a given size, this is a mean-field analysis that replaces structural details with averages.

## 2. Some Theoretical Approaches to The Sol-gel Chemistry

### 2.3.2. Computer simulation of cluster growth

#### 1) Computer Models of Aggregation

- A monomer is placed at the center of a lattice
- Other monomers are launched toward it from some distance away



## 2. Some Theoretical Approaches to The Sol-gel Chemistry

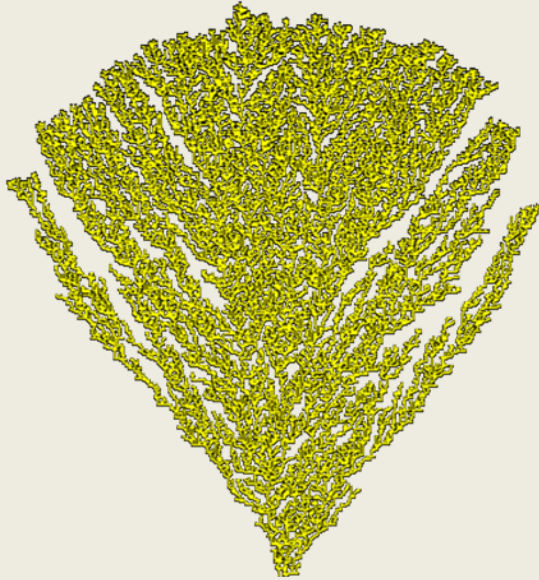
### 2) Classification

- **Ballistic Aggregation**
  - ▣ Approaching polymers follow a linear path
  - ▣ A model of particle growth from the vapor phase
  
- **Diffusion-limited Aggregation**
  - ▣ sticking probability = 1 (colliding clusters always stick together)
  - ▣ Rate of aggregation is determined by transport kinetics
  - ▣ Erratic path of a diffusing cluster
    - Make it difficult for one cluster to penetrate another without colliding and sticking
    - Attachment tends to occur at the periphery
  
- **Reaction-limited Aggregation**
  - ▣ In many cases, sticking probability  $< 1$
  - ▣ Many collisions will occur before two clusters link together
  - ▣ More opportunity for the clusters to interpenetrate (in the limiting case, all accessible attachment sites are equally probable)
  - ▣ More compact result



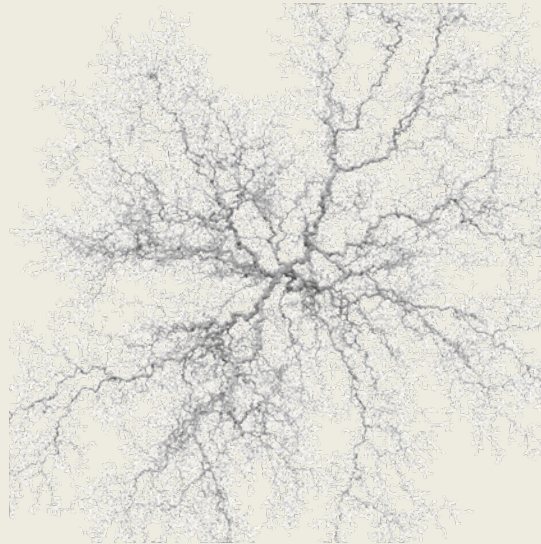
## 2. Some Theoretical Approaches to The Sol-gel Chemistry

### 3) Simulation model



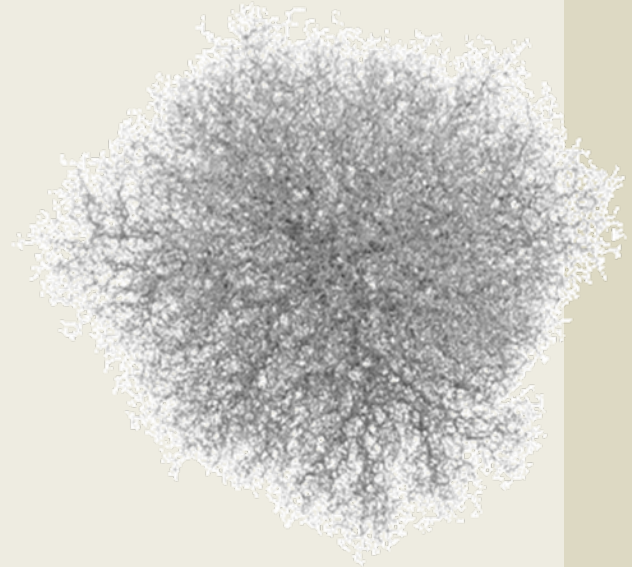
Ballistic Aggregation

Ref. ERCIM News No.29 - April 1997



Diffusion-limited Aggregation

Ref. <http://mark.technolope.org/dla3d/>



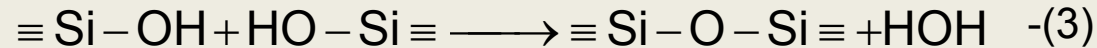
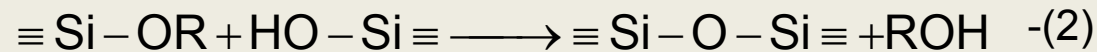
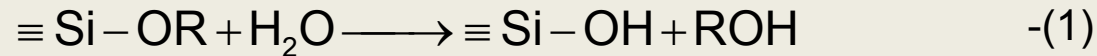
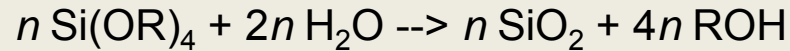
Reaction-limited Aggregation



# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.1 Silica sol-gel processing

- Hydrolysis and condensation



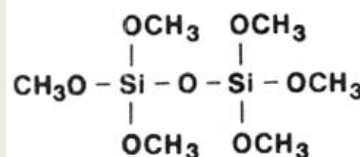
# 3. Experimental Approaches to The Sol-gel Chemistry

## ■ Precursor molecules

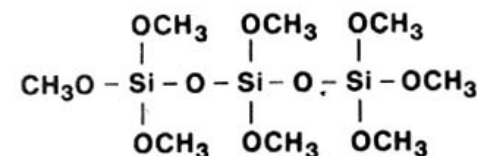
**Table 3**

Physical Properties of Typical Tetraalkoxysilanes.

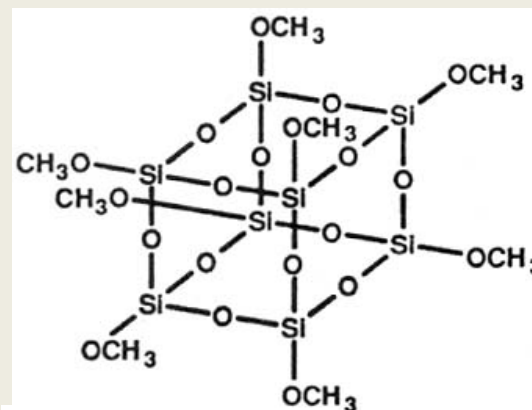
Name	MW	bp	$n_D$ (20°)	$d$ (20°)	$\eta$ (ctsks)	Dipole Moment	Solubility
$\begin{array}{c} \text{MeO} \quad \text{OMe} \\ \diagdown \quad / \\ \text{Si} \\ / \quad \diagdown \\ \text{MeO} \quad \text{OMe} \\ \text{Si}(\text{OCH}_3)_4 \\ \text{tetramethoxysilane TMOS} \end{array}$	152.2	121	1.3688	1.02	5.46	1.71	alcohols
$\begin{array}{c} \text{EtO} \quad \text{OEt} \\ \diagdown \quad / \\ \text{Si} \\ / \quad \diagdown \\ \text{EtO} \quad \text{OEt} \\ \text{Si}(\text{OC}_2\text{H}_5)_4 \\ \text{tetraethoxysilane TEOS} \end{array}$	208.3	169	1.3838	0.93	—	1.63	alcohols
$\begin{array}{c} \text{C}_3\text{H}_7\text{O} \quad \text{OC}_3\text{H}_7 \\ \diagdown \quad / \\ \text{Si} \\ / \quad \diagdown \\ \text{C}_3\text{H}_7\text{O} \quad \text{OC}_3\text{H}_7 \\ \text{Si}(n\text{-C}_3\text{H}_7\text{O})_4 \\ \text{tetra-}n\text{-propoxysilane} \end{array}$	264.4	224	1.401	0.916	1.66	1.48	alcohols
$\begin{array}{c} \text{C}_4\text{H}_9\text{O} \quad \text{OC}_4\text{H}_9 \\ \diagdown \quad / \\ \text{Si} \\ / \quad \diagdown \\ \text{C}_4\text{H}_9\text{O} \quad \text{OC}_4\text{H}_9 \\ \text{Si}(n\text{-C}_4\text{H}_9\text{O})_4 \\ \text{tetra-}n\text{-butoxysilane} \end{array}$	320.5	115	1.4126	0.899	2.00	1.61	alcohols
$\begin{array}{c} (\text{MeOCH}_2\text{CH}_2\text{O})_4\text{Si} \\ \text{tetrakis(2-methoxyethoxy)} \\ \text{silane} \end{array}$	328.4	179	1.4219	1.079	4.9	—	alcohols



hexamethoxydisiloxane



octamethoxytrisiloxane



methoxylated cubic octamer

1.  $\text{Si}(\text{OEt})_4$ ,  $\text{Si}(\text{OMe})_4$  : the most commonly used precursors

2. Si-alkoxides : Ti-alkoxides

- Hydrolysis rates  $\sim 5 \times 10^{-9}$  (Si) vs.  $10^{-3}$  (Ti).
- Gelation time  $\sim$  days (Si) vs.  $\sim$  minutes (Ti).

### 3. Experimental Approaches to The Sol-gel Chemistry

- Precursor molecules

Table 1. Positive partial charge  $\delta(M)$  for metals in various alkoxides

Alkoxide	Zr(OEt) <sub>4</sub>	Ti(OEt) <sub>4</sub>	Nb(OEt) <sub>5</sub>	Ta(OEt) <sub>5</sub>	VO(OEt) <sub>3</sub>	W(OEt) <sub>6</sub>	Si(OEt) <sub>4</sub>
$\delta(M)$	+0.65	+0.63	+0.53	+0.49	+0.46	+0.43	+0.32

Less susceptible to nucleophilic attack

Si<sup>4+</sup> (N = z)  
(No coordination expansion)

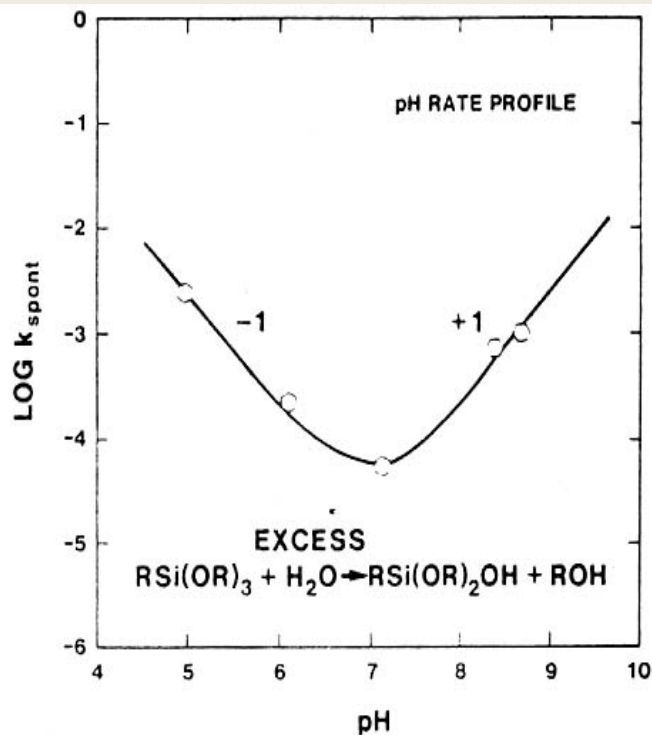


Slow hydrolysis & condensation  
reaction rate



# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.1.1 Silicon alkoxides: Hydrolysis/Effect of catalysts



pH rate profile for the hydrolysis of  $\gamma$ -glycidoxypropyltrialkoxysilane in aqueous solution [50].

Gel Times and Solution pH for TEOS Systems Employing Different Catalysts.

Catalyst	Concentration (mol.: TEOS)	Initial pH of solution	Gelation time (h)
HF	0.05	1.90	12
HCl	0.05	0.05 <sup>a</sup>	92
HNO <sub>3</sub>	0.05	0.05 <sup>a</sup>	100
H <sub>2</sub> SO <sub>4</sub>	0.05	0.05 <sup>a</sup>	106
HOAc	0.05	3.70	72
NH <sub>4</sub> OH	0.05	9.95	107
No catalyst	—	5.00	1000

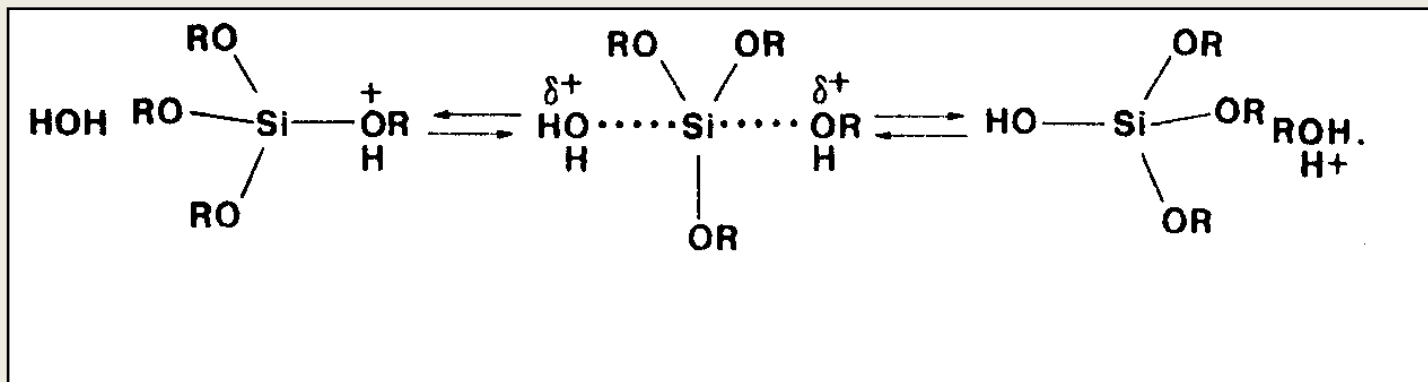




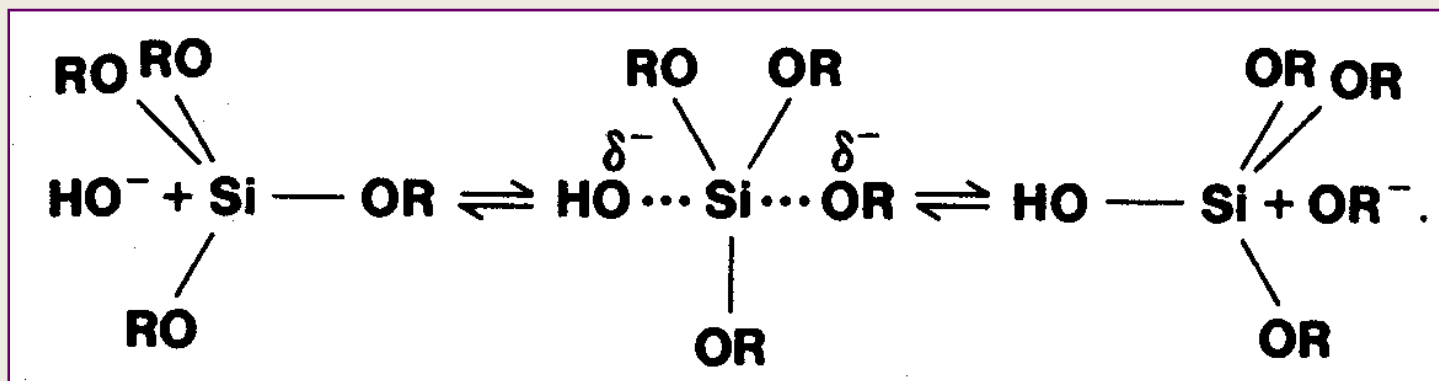
# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.1.1 Silicon alkoxides: Hydrolysis/Effect of catalysts

Acid-catalyzed hydrolysis



Base-catalyzed hydrolysis



# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.1.1 Silicon alkoxides: Hydrolysis/Steric effect

Table 6a.

Rate Constant  $k$  for Acid Hydrolysis of Tetraalkoxysilanes  $(RO)_4Si$  at 20°C.

R	$k$ $10^2 (1 \text{ mol}^{-1} \text{ s}^{-1} [\text{H}^+]^{-1})$
$\text{C}_2\text{H}_5$	5.1
$\text{C}_4\text{H}_9$	1.9
$\text{C}_6\text{H}_{13}$	0.83
$(\text{CH}_3)_2\text{CH}(\text{CH}_2)_3\text{CH}(\text{CH}_3)\text{CH}_2$	0.30

Source: Aelion *et al.* [51].

Hydrolysis is retarded by bulky alkoxy groups

Table 6b.

Rate Constants  $k$  ( $10^2 (1 \text{ mol}^{-1} \text{ s}^{-1} [\text{H}^+]^{-1})$ ) for Acid Hydrolysis of Alkoxyethoxysilanes  $(RO)_{4-n} \text{Si}(\text{OC}_2\text{H}_5)_n$  at 20°C.

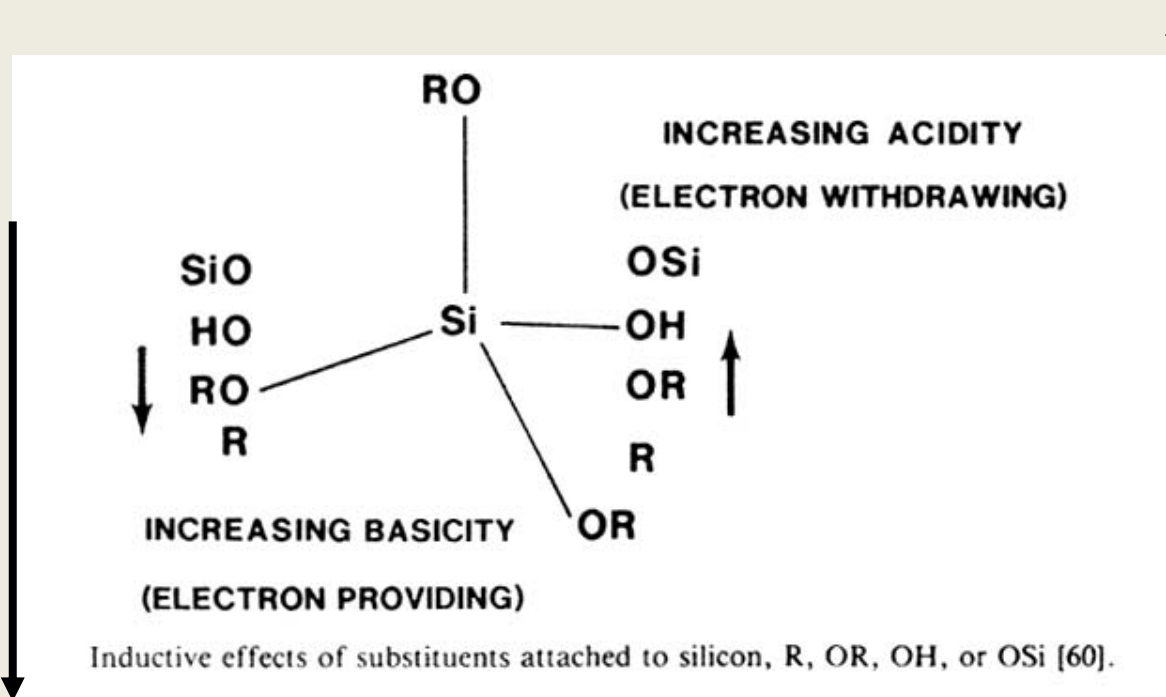
	R			
$n$	$\text{C}_6\text{H}_{13}$	$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2$ $\text{H}_3\text{C}-\text{CH}$	$\text{CH}_3(\text{CH}_2)_5$ $\text{H}_3\text{C}-\text{CH}$	$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2$ $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2-\text{CH}$
0	0.8	—	—	0.030
1	1.1	—	—	—
2	5.0	0.15	0.095	0.038
3	5.0	—	—	—

Source: Aelion *et al.* [51].

# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.1.1 Silicon alkoxides: Hydrolysis/Inductive effect

Increase the stability of negatively charged transition state

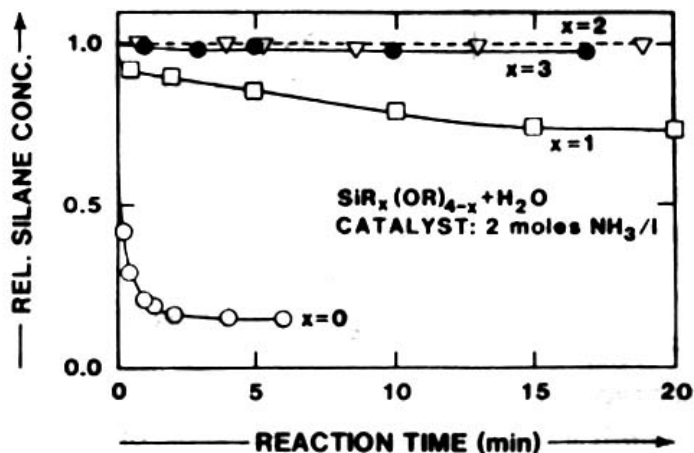


Increase the stability of positively charged transition state

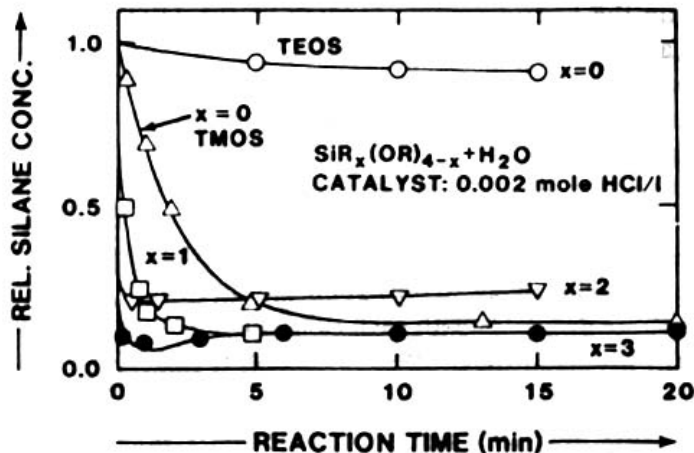


# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.1.1 Silicon alkoxides: Hydrolysis/Inductive effect



Hydrolysis rate decreases with increasing  $x$ , under basic catalyst



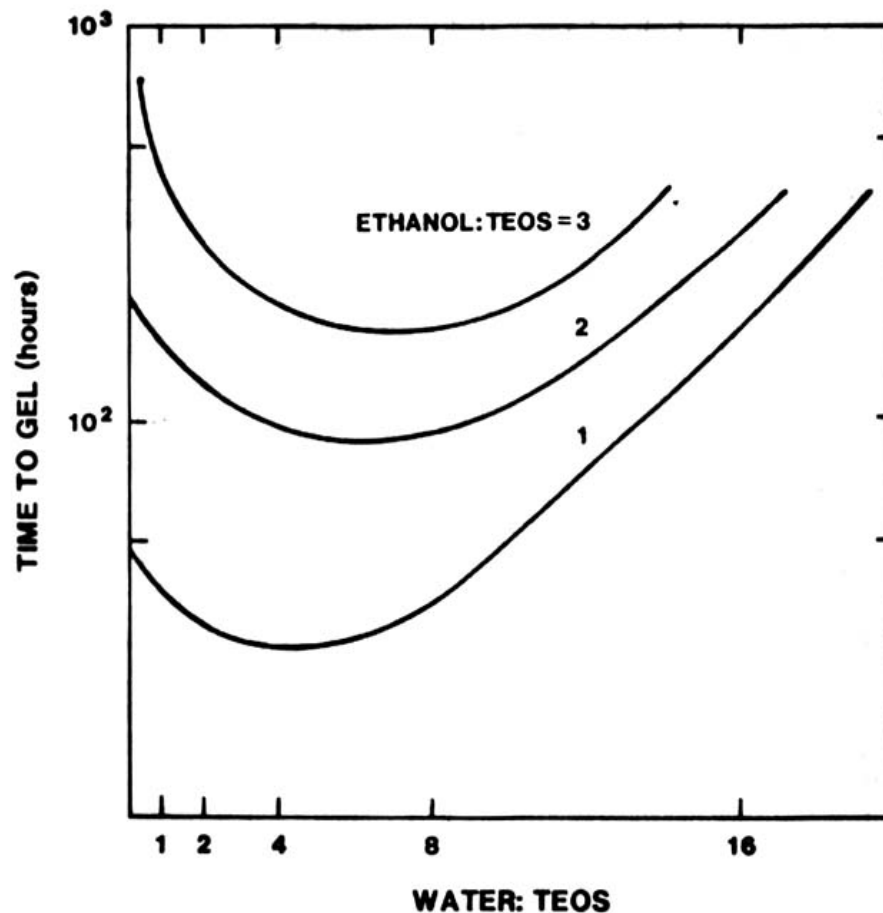
Hydrolysis rate increases with increasing  $x$ , under acidic catalyst

Relative silane concentration versus time during acid- and base-catalyzed hydrolysis of different silanes in ethanol (volume ratio silane to EtOH = 1 : 1). ●:  $(CH_3)_3SiOC_2H_5$ . ∇:  $(CH_3)_2Si(OC_2H_5)_2$ . □:  $CH_3Si(OC_2H_5)_3$ . ○:  $Si(OC_2H_5)_4$ . △:  $Si(OCH_3)_4$  [61].

# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.1.2 Silicon alkoxides: Condensation/ $H_2O:Si$ ratio effect

Silicate concentration is reduced

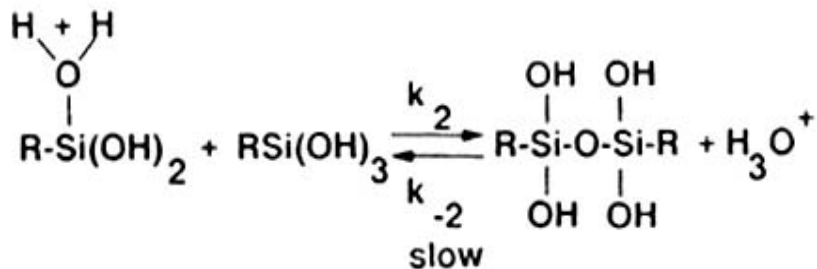
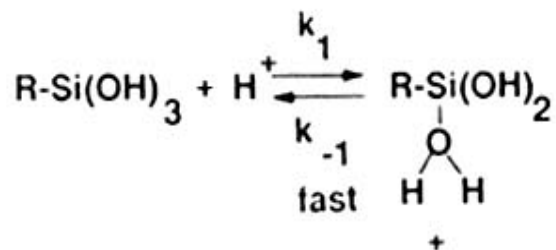


Gel times versus  $H_2O:TEOS$  ratio,  $r$ , for three ratios of EtOH to TEOS [64].

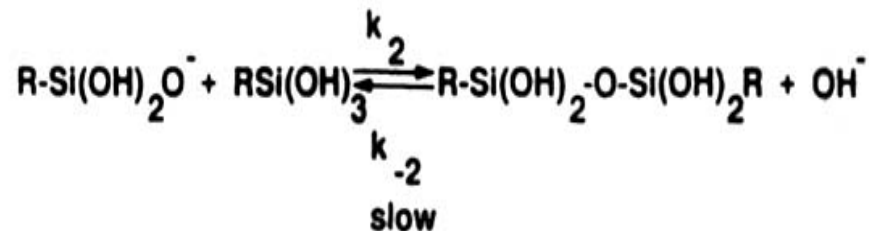
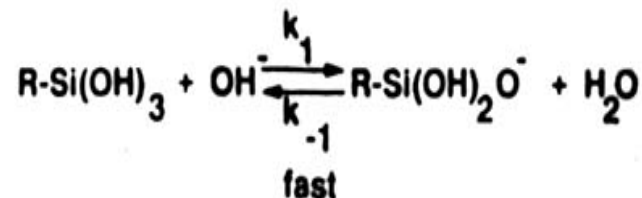
# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.1.2 Silicon alkoxides: Condensation/Catalyst effect

### Acid-catalyzed condensation

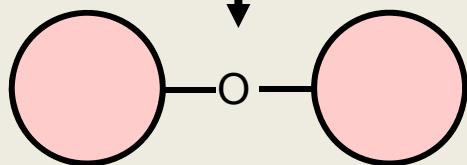
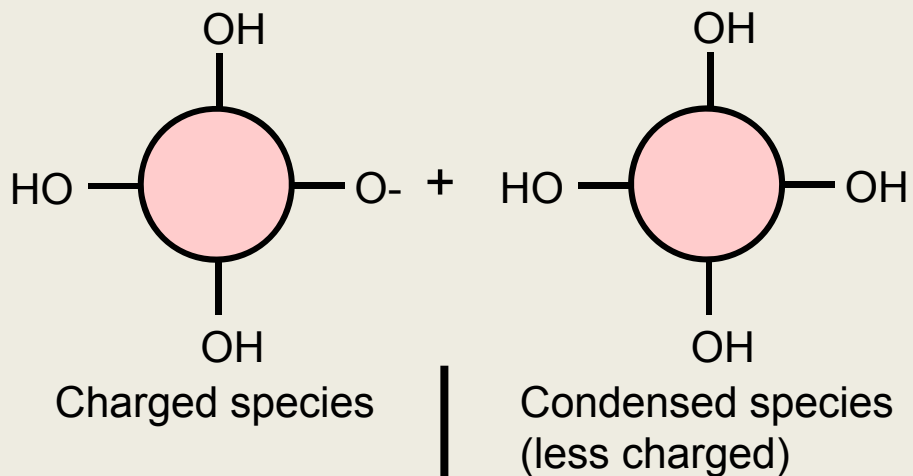


### Base-catalyzed condensation

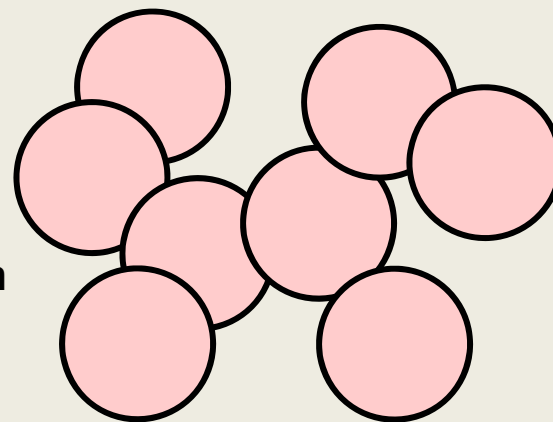


# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.1.2 Silicon alkoxides: Condensation/Effect of catalysts-acid



aggregation



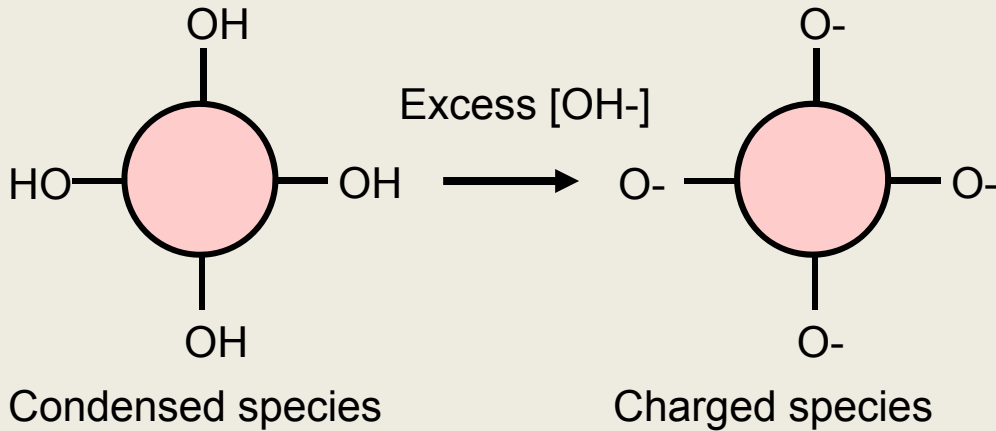
As the hydrolysis progresses:  
# of OR groups decrease  
→ Reactivity decreases  
→ Hydrolysis rate decrease  
→ Relative condensation rate increases  
→ **Three-dimensional networks (polymeric gels)**

Reaction-limited cluster-cluster aggregation (RLCA)



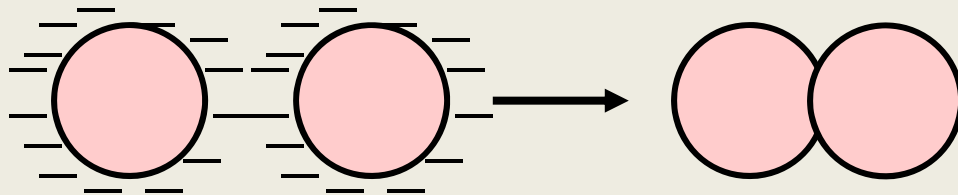
# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.1.2 Silicon alkoxides: Condensation/Effect of catalysts-base

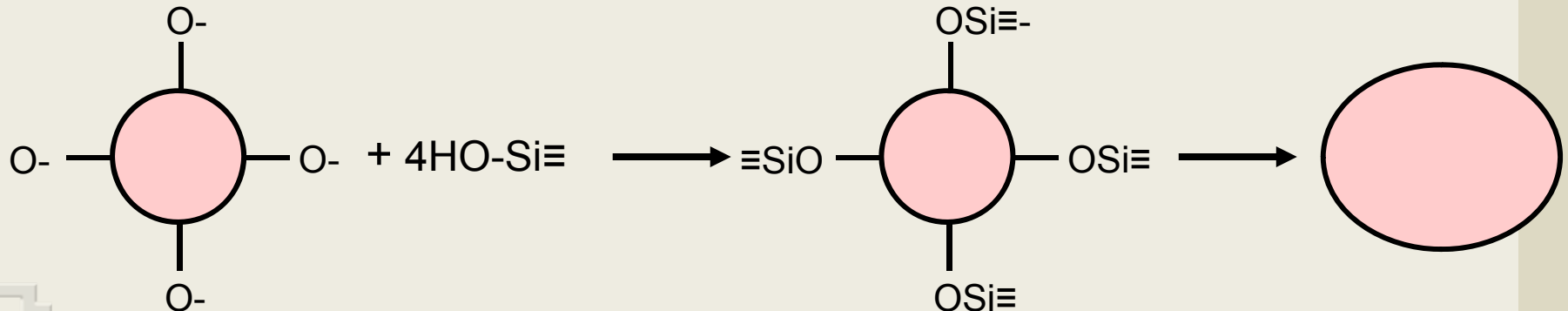


As the hydrolysis progresses:

- # of OR groups decrease
- Reactivity increases
- Hydrolysis rate increase
- Relative condensation rate decreases
- **Highly condensed large particles (particulate sols)**



Unlikely condensation (repulsion)



Reaction-limited monomer-cluster aggregation (MCA)





# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.1.2 Silicon alkoxides: Condensation/Solvent effect

### Role of solvent

- ✓ Prevent liquid-liquid phase separation during the initial stage
- ✓ Control of solubility of silicate and hence relative concentrations to water
- ✓ Drying process control

Table 7.

Physical Properties of Typical Solvents.

	MW	bp	$\rho$	$n_D$	$\epsilon$	$\eta$	$\mu$
Protic							
{ water H <sub>2</sub> O	18.01	100.00	1.000	1.333	78.5	10.1	1.84
{ methanol CH <sub>3</sub> OH	32.04	64.5	0.791	1.329	32.6	5.4	1.70
{ ethanol C <sub>2</sub> H <sub>5</sub> OH	46.07	78.3	0.785	1.361	24.3	10.8	1.69
{ 2-ethoxyethanol C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>	90.12	135	0.93	1.408	—	—	2.08
{ formamide CH <sub>3</sub> ON	45.04	193	1.129	1.448	110	33.0	3.7
Aprotic							
{ dimethylformamide C <sub>3</sub> H <sub>7</sub> NO	73.10	152	0.945	1.430	36.7	7.96	3.86
{ dioxane 1,4 C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88.12	102	1.034	1.422	2.21	10.87	0
{ tetrahydrofuran C <sub>4</sub> H <sub>8</sub> O	72.12	66	0.889	1.405	7.3	—	1.63

bp: °C.  
 $\rho$ : g/cm<sup>3</sup> at 20°C.

$n_D$ : 20°.  
Dielectric constant,  $\epsilon$ : at 25°C.

$\eta$ : millipoise.  
Dipole moment,  $\mu$ : debyes.

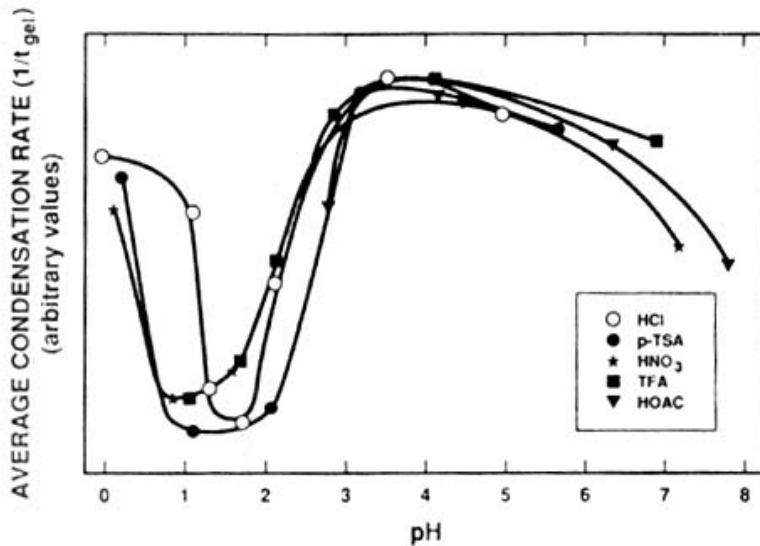
- **Protic solvent** (H-bond to nucleophilic deprotonated silanols)  
:acid-catalyzed condensation
- **Aprotic solvent** (H-bond to electrophilic protonated silanols)  
:base-catalyzed condensation

# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.1.2 Silicon alkoxides: Condensation/Steric and inductive effects

**Steric effect:** the longer length or branching of the alkyl group, the slower condensation rate

**Inductive effect:** e-donating alkyl groups (as in the state of the precursor) reduce the acidity of the corresponding silanol. This shifts IEP (Isoelectric point) towards higher pH, significantly influencing the pH-dependence of the condensation mechanism. That is, e-withdrawing groups (-OH or Osi, i.e. as the condensation reaction progresses) increase the silanol acidity, and the minimum condensation rate occurs at ab. pH 2. Thus the extent of both hydrolysis and condensation and, in organoalkoxysilanes  $[R_xSi(OR)_{4-x}]$ , the value x determine the reaction mechanism and define what is meant by acid- or base-catalysed condensation.



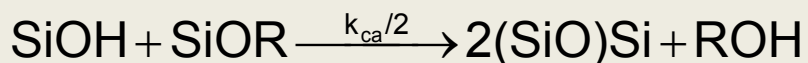
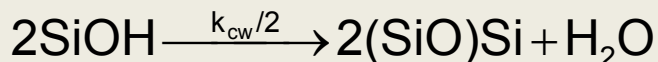
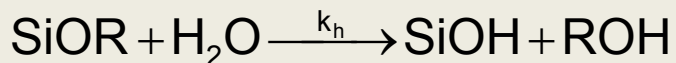
(b)

IEP=pH where the electrical mobility of the silica particles is zero

PZC=pH where the surface charge is zero

# 3. Experimental Approaches to The Sol-gel Chemistry

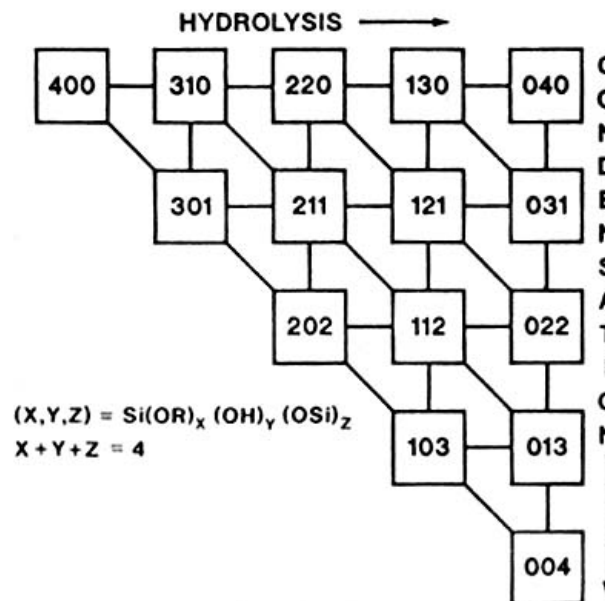
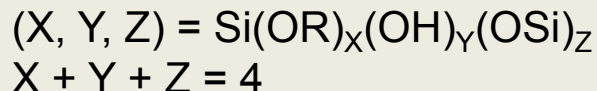
## 3.1.3 Sol-gel kinetics



$k_h$  : rate constant of hydrolysis

$k_{cw}$  : condensation of water

$k_{ca}$  : condensation of alcohol



Chemical speciation at next-to-nearest-neighbor level represented in matrix form.

# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.1.3 Sol-gel kinetics

The initial rate of the hydrolysis reaction is much larger than the sum of the rates of the condensation reactions so that  $[\text{SiOH}]$  equals the consumption of  $\text{H}_2\text{O}$  by hydrolysis.

$$d[(\text{SiO})\text{Si}]/dt = k_{\text{cw}} [\text{SiOH}]^2 + k_{\text{ca}} [\text{SiOH}][\text{SiOR}]$$

$k_{\text{cw}} \gg k_{\text{ca}}$  : condensation rate proportional to  $[\text{SiOH}]^2$

$k_{\text{cw}} \ll k_{\text{ca}}$  : condensation rate proportional to  $[\text{SiOH}][\text{SiOR}]$

In the case where the initial overall condensation reaction is negligible with respect to the initial hydrolysis rate and the initial hydrolysis reaction is complete.

$$\frac{d[(\text{SiO})\text{Si}]/dt}{< [\text{SiOH}] >} = (k_{\text{cw}} - k_{\text{ca}}) < [\text{SiOH}] > + k_{\text{ca}} [\text{SiOMe}]_0$$

Valid at early times when the concentration of Si-O-Si is small compared to the initial methoxy functional group concentration.

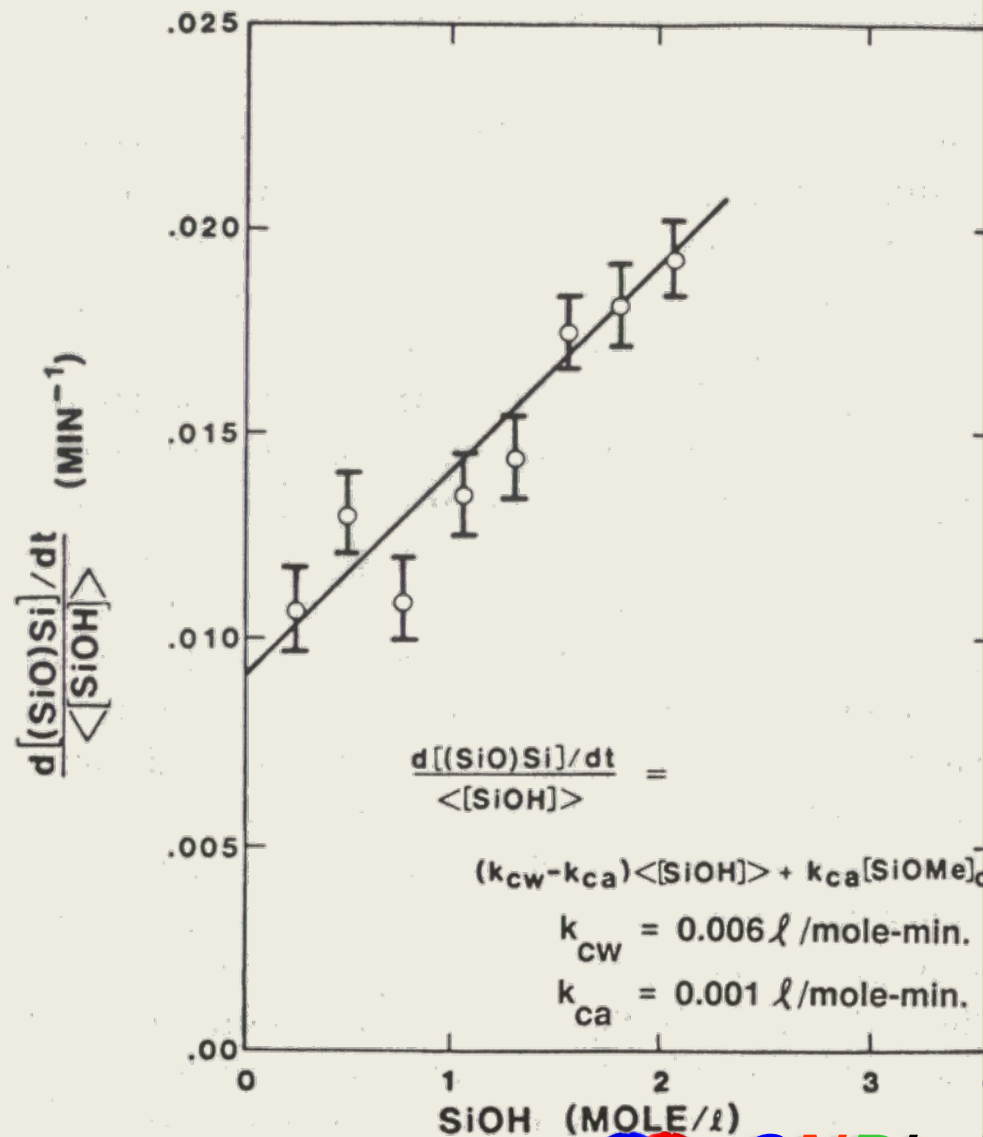


# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.1.3 Sol-gel kinetics

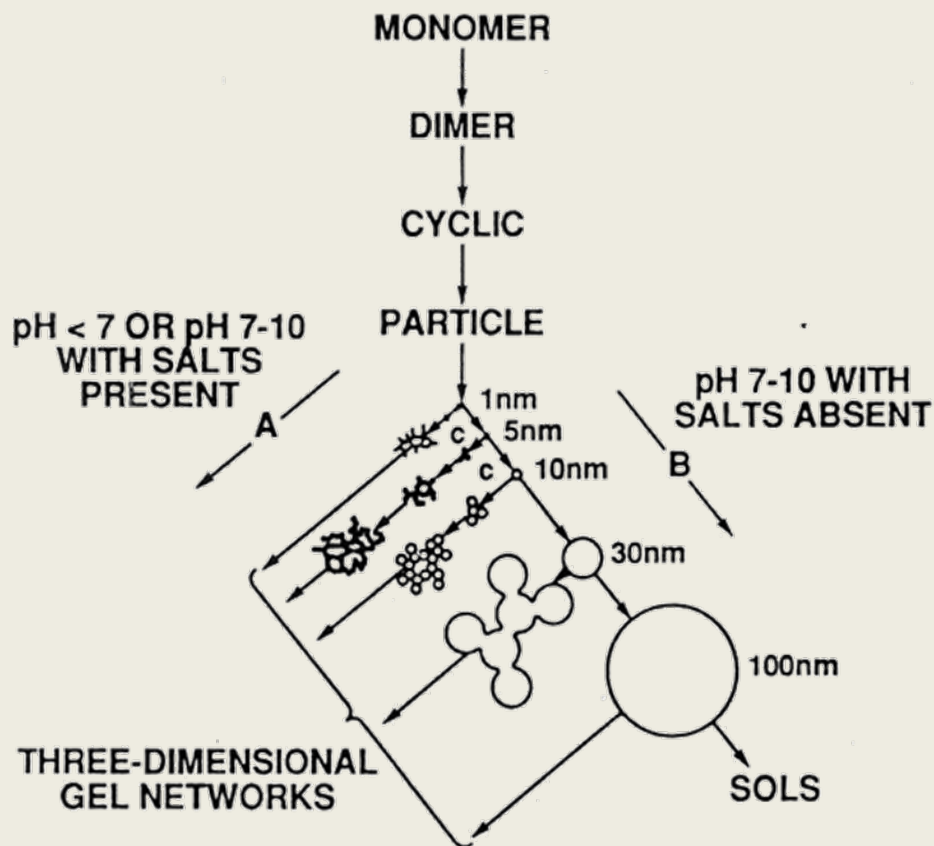
$\frac{d[(\text{SiO})\text{Si}]/dt}{\langle [\text{SiOH}] \rangle}$  vs  $\langle [\text{SiOH}] \rangle$  plot

- slope :  $k_{cw} - k_{ca}$
- intercept :  $k_{ca}[\text{SiOMe}]_o$



# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.1.4 Structural summary

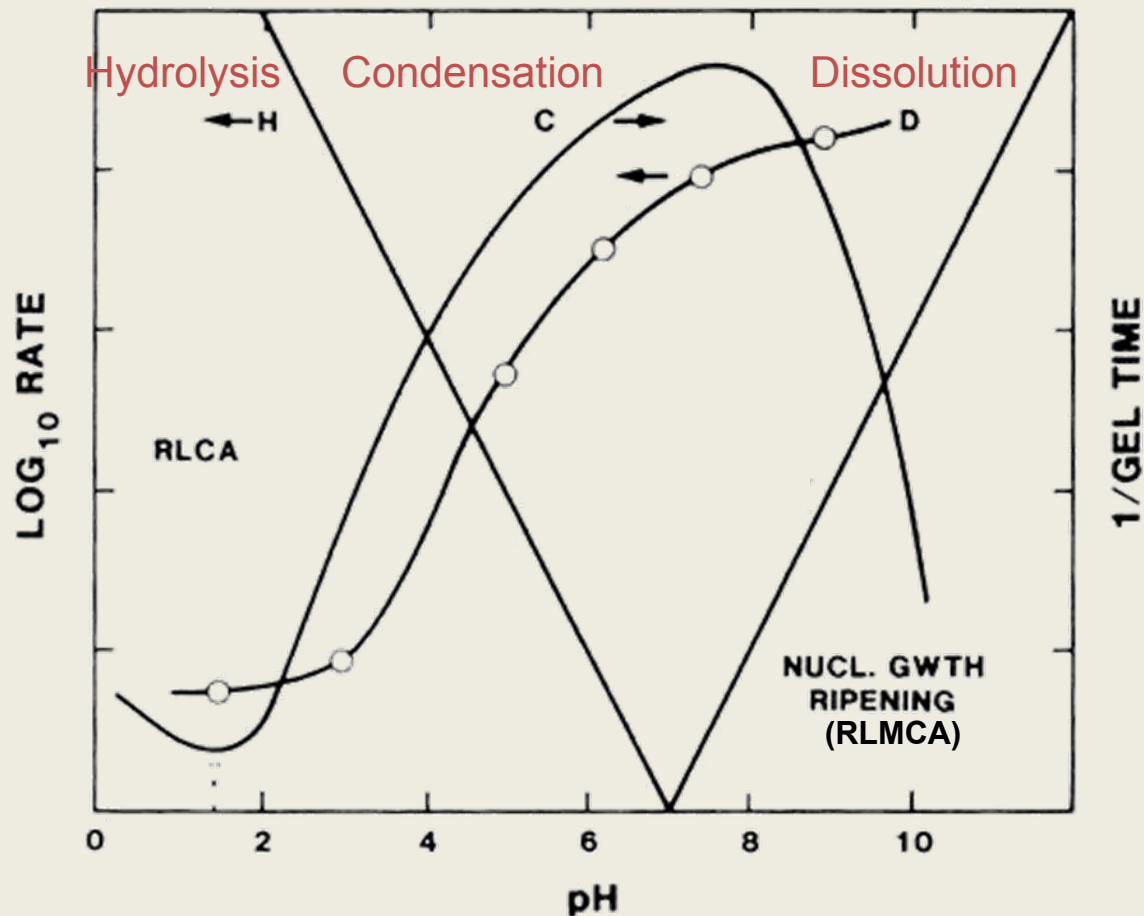


1. Polymerization of monomer to form particles
2. Growth of particles
3. Linking of particles into chain, then networks that extend throughout the liquid medium, thickening it to a gel

Polymerization behavior of aqueous silica. In basic solution (B) particles grow in size with decrease in number; in acid solution or in the presence of flocculating salts (A), particles aggregate into three-dimensional networks and form gels. From Iler [1].

# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.1.4 Structural summary



Schematic representation of the pH-dependences of hydrolysis (H), condensation (C), and dissolution (D) for an arbitrary value of  $r$  (1.5) [60].

RLCCA : Reaction-Limited Cluster-cluster Aggregation

RLMCA : reaction-limited Monomer-Cluster Aggregation



# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.1.4 Structural summary

### 1. Polymerization at pH 2-7

- Condensation rate proportional to  $[\text{OH}^-]$
- Aggregation of the condensed species : *three-dimensional networks (polymeric gel)*
- Solubility of silica is low in this range → particle growth stops when the size reaches 2-4 nm.

### 2. Polymerization above pH 7

- Growth of the primary particles continues by Oswald ripening (a process in which smaller, more soluble particles dissolve and reprecipitate on larger, less soluble particles).
- Highly condensed particles*

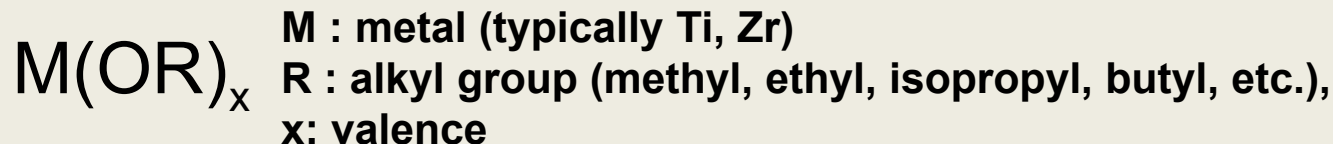
### 3. Polymerization below pH 2

- Polymerization rate proportional to  $[\text{H}^+]$
- Metastable
- Gel network (composed of small primary particles(< 2 nm))



# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.2 Metal alkoxides



- Generally very reactive due to the presence of highly e-negative OR groups, stabilizing M in its highest oxidation state and rendering M very susceptible to nucleophilic attack
- # of alkyl groups depends on the valence of the metal
- Reaction rate varies throughout the process depending on the alkyl group used

### - Synthesis of Metal alkoxides

- (1) Reactions of metals with alcohols:  $M + xROH \rightarrow M(OR)_x$
- (2) Reactions of halides with alcohols:  $MX + xROH \rightarrow M(OR)_x$
- (3) Reactions of metal hydroxides and oxides with alcohols
- (4) Alcohol interchange reactions
- (5) Transesterification reactions
- (6) Reactions of dialkylamides with alcohols
- (7) Heterobimetal alkoxides (Example :  $[MgAl_2(O^nBU)_8]_n, n \geq 2$ )

# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.2.1 Properties of Metal alkoxides

### (1) Molecular association between alkoxides

- Degree of oligomerization induces differences in the processing and the sol-gel transition
- Degree of association depends on the nature of the central metal atom and the alkoxy group and on the nature of solvent and the solute concentration

### (2) High volatility of some alkoxides

- Related with the degree of molecular association
- Degree of oligomerization $\uparrow$   $\rightarrow$  volatility $\downarrow$

### (3) Viscosity

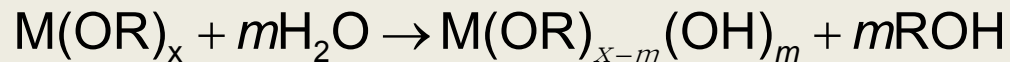
- Affected by the chain length and branching of alkyl groups
- Affected by the degree of molecular association
- Degree of oligomerization $\uparrow$   $\rightarrow$  viscosity $\uparrow$



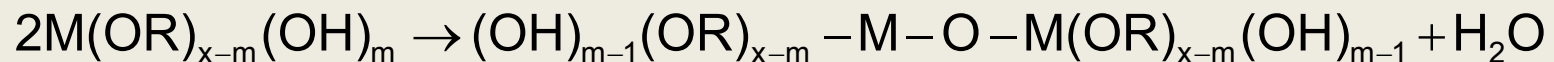
# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.2.2 Sol-gel process of Metal alkoxides

### Hydrolysis



### Water condensation (oxolation: water is condensation by-product)



### Alcohol condensation (alcoxolation: alcohol is condensation by-product)



- Acid or base can be used to hydrolyze as catalyst
- Catalysts will affect the pore structure of the gel.



# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.2.3 Parameters of Sol-gel process of Metal alkoxides

### 1) Effect of catalyst

Catalysts influence both the hydrolysis and condensation rates and the structure of the condensed products.

Acids protonate negatively charged alkoxide groups, enhancing the reaction kinetics by producing good leaving groups and eliminating the requirement for  $H^+$  transfer within the transition state.

Bases produce strong nucleophiles via deprotonation of hydroxo ligands

### Silica sol-gel processing

- In basic condition : production of both partially and totally hydrolyzed monomers which will then create more densely, highly branched, crosslinked polymers.
- In acidic condition : production of partially hydrolyzed monomers which condense into a more linear, lightly crosslinked network.

### Metal alkoxides

- In acidic condition : particulate granular morphology
- In basic condition : honeycomb morphology



# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.2.3 Parameters of Sol-gel process of Metal alkoxides

### 2) Effects of water/alkoxide ratio

- Water is a by-product of a condensation reaction
- An addition of excess water can inhibit condensation (Le Chatelier's principle)
- The higher the content of the hydrolysis water, the finer the texture of matrix
- When water/alkoxide ratio exceeds a critical con., localized condensation occurs

### 3) Effects of the alkyl groups in the alkoxides

- The alkoxides with large alkyl groups hydrolyze slowly and diffuse slowly
- Larger alkoxides tend to produce smaller polymeric condensations
- The use of the larger alkyl groups will be helpful for achieving nanostructured products.

### 4) Effects of the hydrolysis temperature

- The cold-water-hydrolyzed materials : coarse granular
- The hot-water-hydrolyzed materials : fine and fluffy structure

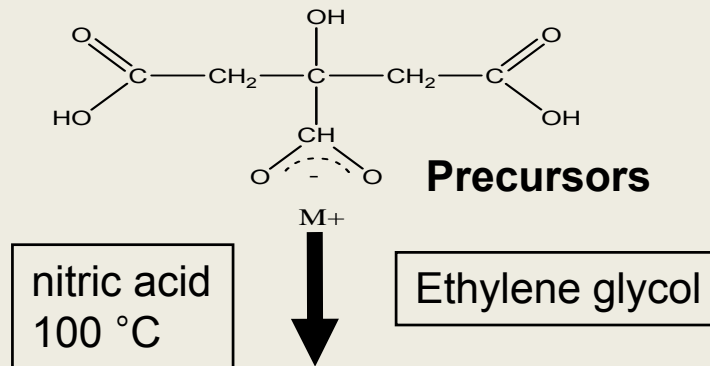
# 3. Experimental Approaches to The Sol-gel Chemistry

## 3.3 Pechini processing

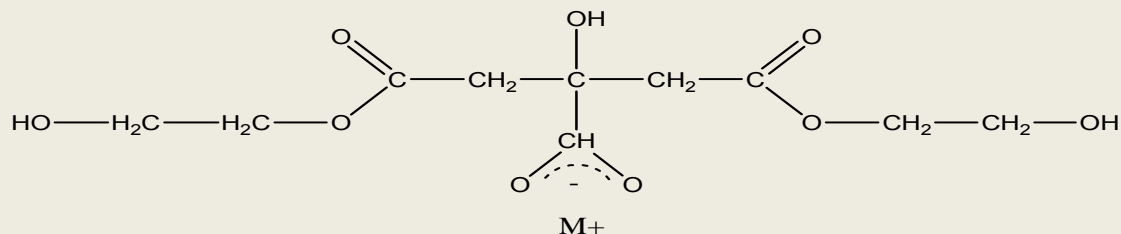
: For making multicomponent powders

The dissolution of metal salts in a mixture of a weak hydroxy carboxylic acid such as citric acid, and a polyhydroxy alcohol such as ethylene glycol.

Step 1: Chelation between complex cations and citric acid



Step 2: Polyesterification of the above chelate with glycol in a slightly acidified solution



Step 3: Heating to decompose the amorphous resin to obtain a homogeneous oxide powder. Resin can also be applied on a substrate as a film 0.3-0.5  $\mu\text{m}$  thick.