Chapter 3. Design of Nanomaterials based on Sol-gel Chemistry

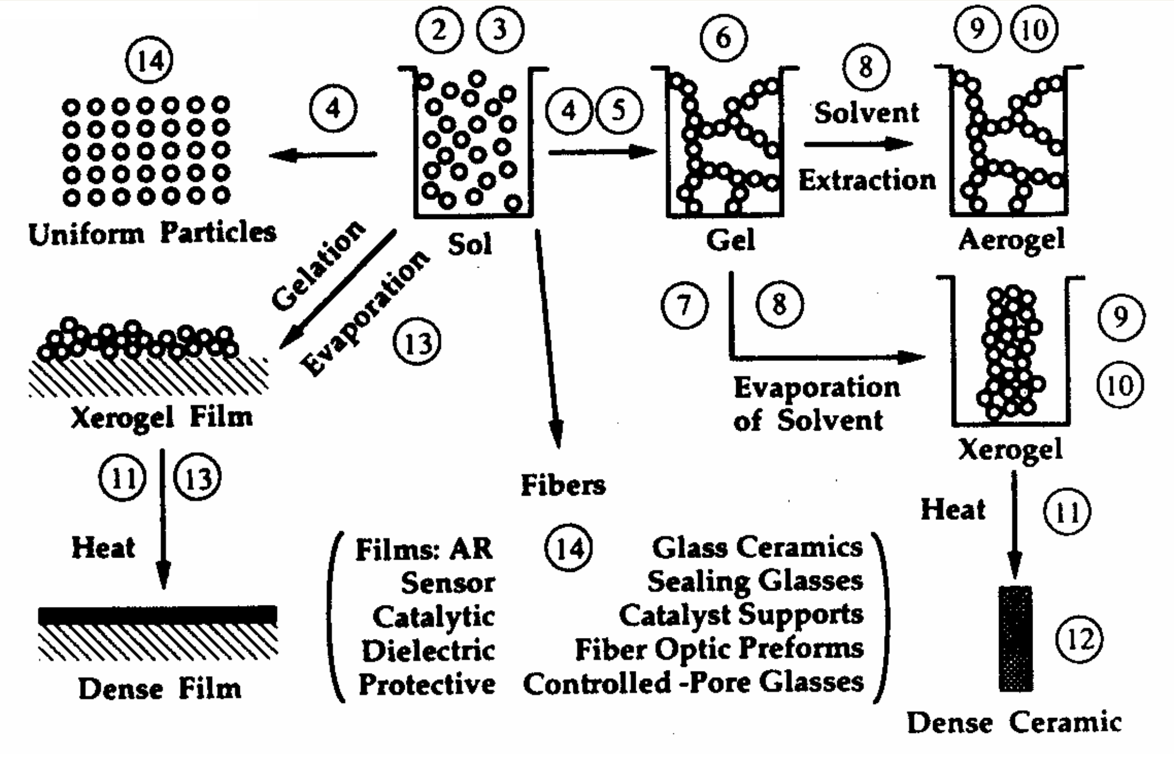
3.1. Introduction

- 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*

3.1. 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.

3.1. 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.

3.1. Introduction

- Basic concepts of sol-gel processing

-**Precursors**: starting materials on sol-gel process, inorganic salts (metal nitrates, halides, sulfates; $AlCl_3$, $Fe(NO_3)_2$) and metal-organic compounds (metal alkoxides, $Si(OEt)_4$)

-**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%.

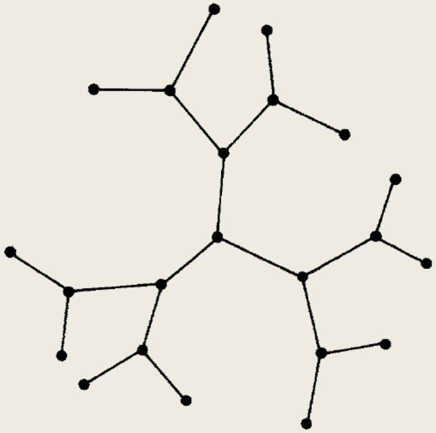
-**Cryogel**: powders obtained by freeze-drying

3.2. Theories of Sol-gel Chemistry

3.2.1. 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 Chmistry*, 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

3.2. Theories of 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

$$\boxed{p_c = 1/(z-1)}$$

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

$z=3$: $p_c=1/2$

$z=4$: $p_c=1/3$

3.2. Theories of 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 faction (w_g): the fraction of all monomers belonging to the gel
- $w_s+w_g=1$

- Below the gel point ($p \le p_c$)
: $w_s=1$, $w_g=0$ (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)

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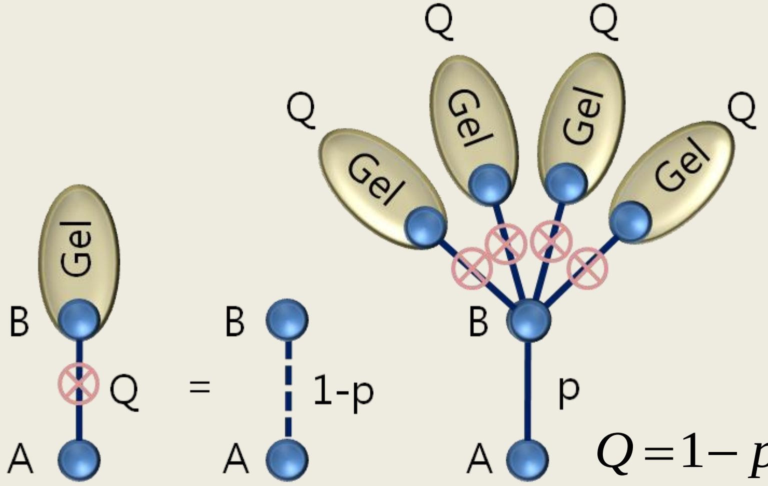
3.2. Theories of Sol-gel Chemistry



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

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

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

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

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

3.2. Theories of Sol-gel Chemistry

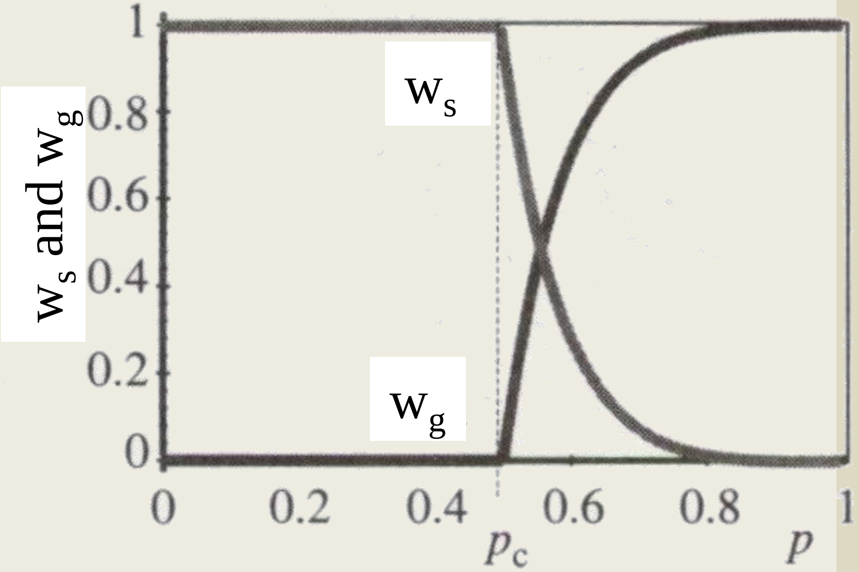
- MF prediction of sol and gel fraction for z=3

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

For z=3 ; p_c=1/2

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

$$\boxed{\begin{aligned} w_s &= \left(\frac{1-p}{p}\right)^3 \\ w_g &= 1 - w_s = 1 - \left(\frac{1-p}{p}\right)^3 \end{aligned}}$$



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

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3.2. Theories of Sol-gel Chemistry

- MF prediction of sol and gel fraction for z=4

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

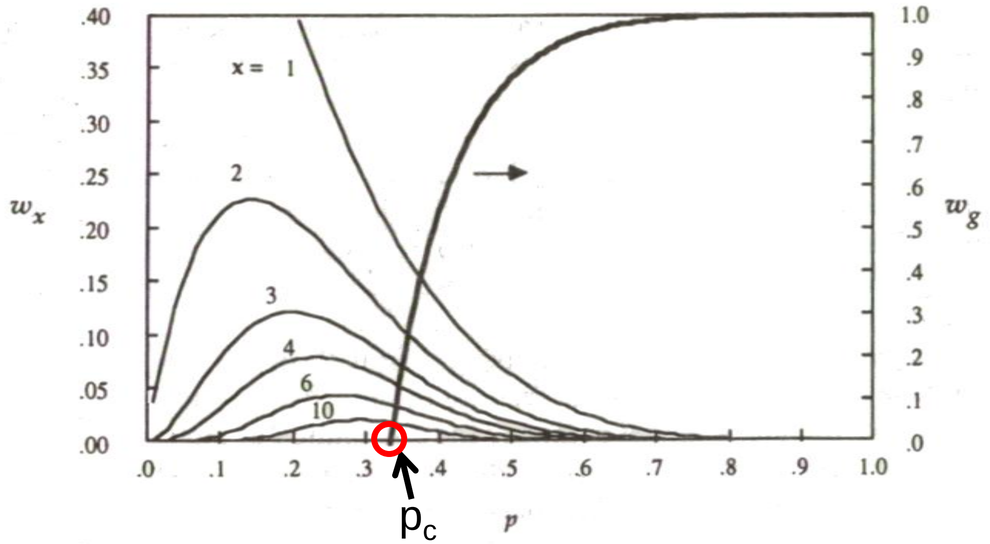
For z=4 ; p_c=1/3

$$w_s^{1/4} = 1 - p + p w_s^{3/4}$$

$$w_s = \frac{-p^2 + 2 + (p-2)\sqrt{-3p^2 + 4p}}{2p^2}$$

$$w_g = 1 - w_s = \frac{3p^2 - 2 - (p-2)\sqrt{-3p^2 + 4p}}{2p^2}$$

Fig. 10.



Weight fractions of various finite species (w_x, x = 1–10) and of gel (w_g) in tetrafunctional (z = 4) condensation as function of degree of reaction, p. Curves calculated from Eqs. 9 and 12.

3.2. Theories of 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^3 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^4 (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.

3.2. Theories of Sol-gel Chemistry

3.2.2. 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

3.2.2.1. Percolation threshold

3.2. Theories of Sol-gel Chemistry

3.2.2.1. 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

3.2. Theories of Sol-gel Chemistry

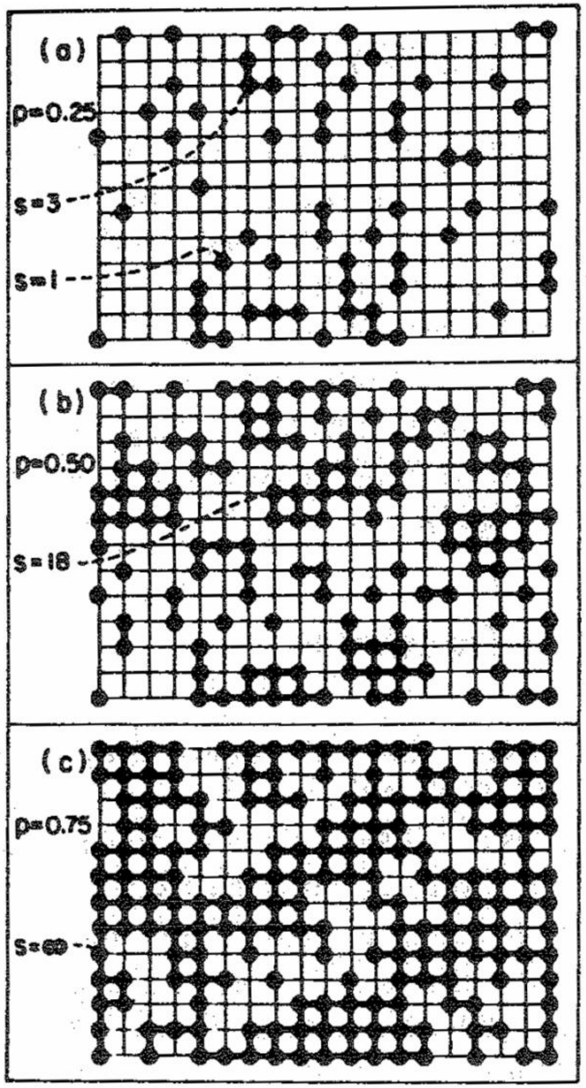
➢ Percolation threshold

- 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.

3.2. Theories of Sol-gel Chemistry

- Percolation theory can predict the behavior of the properties near the gel point (p_c)

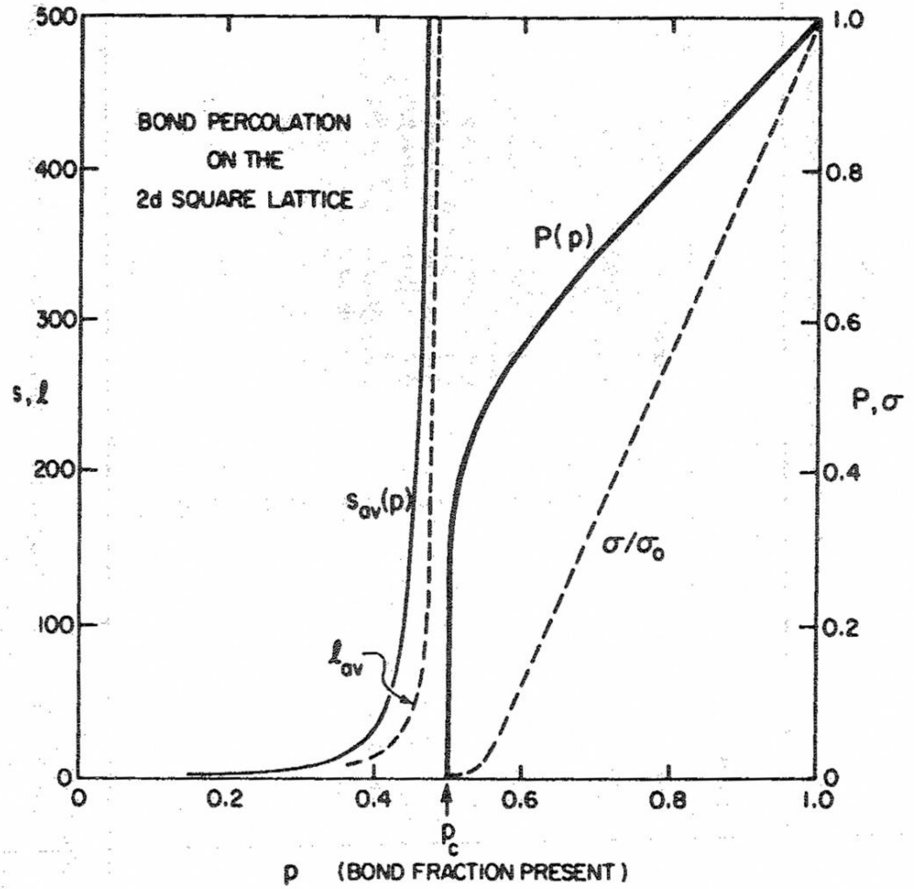
- Near p_c, the average cluster size (s_{av}) diverges, as does the spanning length, l_{av}

- P(p) : percolation probability that a given site (or bond) is attached to the spanning cluster, so it is equivalent to the gel fraction, w_g

$$\left(\begin{array}{l} p<p_c : P(p)=0 \\ p \geq p_c : P(p) \text{ rises rapidly} \end{array} \right)$$

- Electrical conductivity (σ) rises gradually beyond p_c : the current-carrying spine of the spanning cluster is sparse (most of the cluster is made up of “dead-ends” hanging off the spine)

Fig. 12.



The behavior, as a function of the fraction (p) of filled bonds, of key properties that characterize bond percolation on the square lattice in two dimensions. The percolation probability $P(p)$, the average cluster size $s_{av}(p)$, and conductivity σ are results of computer studies; the spanning length l_{av} is schematic. From Zallen, *The Physics of Amorphous Solids* (Wiley, New York, 1983), chapter 4.

3.2. Theories of Sol-gel Chemistry

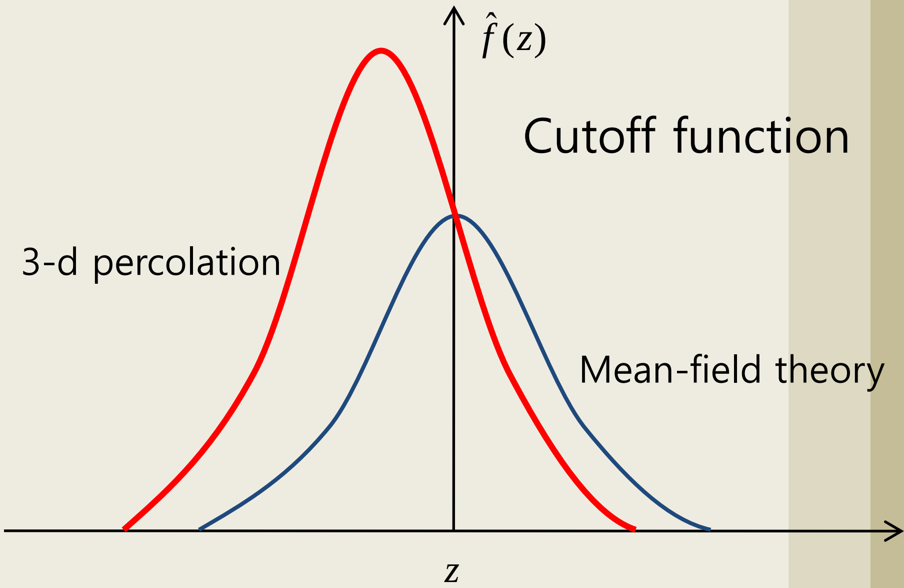
3.2.2.2. Scaling law

- General percolation problem : no simple analytical solution
  → computer simulations

- The number of polymers near the gel point has a power law dependence on the degree of polymerization

- The cutoff function for percolation is more complicated than the simple exponential of the mean-field theory; it is asymmetric and having different form below($f_+(N/N^*)$) and above($f_-(N/N^*)$) the gel point

- The values of the critical exponents and the cut off functions depend only on the dimension of space in which gelation takes place
  → **"Scaling laws of gelation"**



3.2. Theories of Sol-gel Chemistry

$$s_{av} = c(p_c - p)^{-\gamma} + c_1(p_c - p)^{-\gamma_1} + c_2(p_c - p)^{-\gamma_2} + \cdots \qquad (p \to p_c)$$

- γ : critical exponent (universal and independent of the lattice type)
  γ = 1.7 (3-d) and 2.4 (2-d) for percolation theory vs γ = 1 for MF theory

- d_f : the fractal dimension of the cluster
  d_f = 2.5 for percolation theory vs d_f = 4 for MF theory

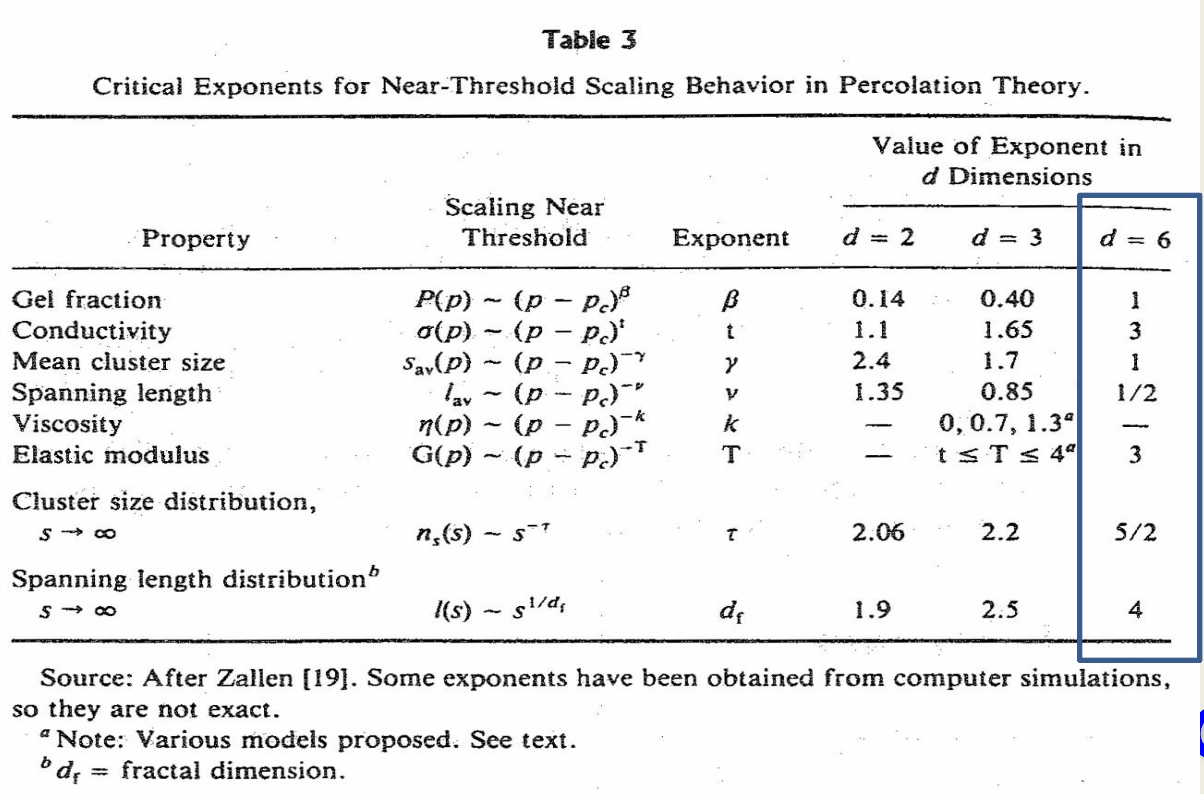


Table 3

Critical Exponents for Near-Threshold Scaling Behavior in Percolation Theory.

Property	Scaling Near Threshold	Exponent	Value of Exponent in *d* Dimensions $d = 2$	 $d = 3$	 $d = 6$
Gel fraction	$P(p) \sim (p - p_c)^{\beta}$	β	0.14	0.40	1
Conductivity	$\sigma(p) \sim (p - p_c)^{t}$	t	1.1	1.65	3
Mean cluster size	$s_{av}(p) \sim (p - p_c)^{-\gamma}$	γ	2.4	1.7	1
Spanning length	$l_{av} \sim (p - p_c)^{-\nu}$	ν	1.35	0.85	1/2
Viscosity	$\eta(p) \sim (p - p_c)^{-k}$	k	—	0, 0.7, 1.3[a]	—
Elastic modulus	$G(p) \sim (p - p_c)^{-T}$	T	—	$t \leq T \leq 4$[a]	3
Cluster size distribution, $s \to \infty$	$n_s(s) \sim s^{-\tau}$	τ	2.06	2.2	5/2
Spanning length distribution[b] $s \to \infty$	$l(s) \sim s^{1/d_f}$	d_f	1.9	2.5	4

Source: After Zallen [19]. Some exponents have been obtained from computer simulations, so they are not exact.

[a] Note: Various models proposed. See text.

[b] d_f = fractal dimension.

MF theory

3.2. Theories of Sol-gel Chemistry

3.2.2.3. Other percolation models

- There are obviously many differences in the percolation models.

- Bond percolation model

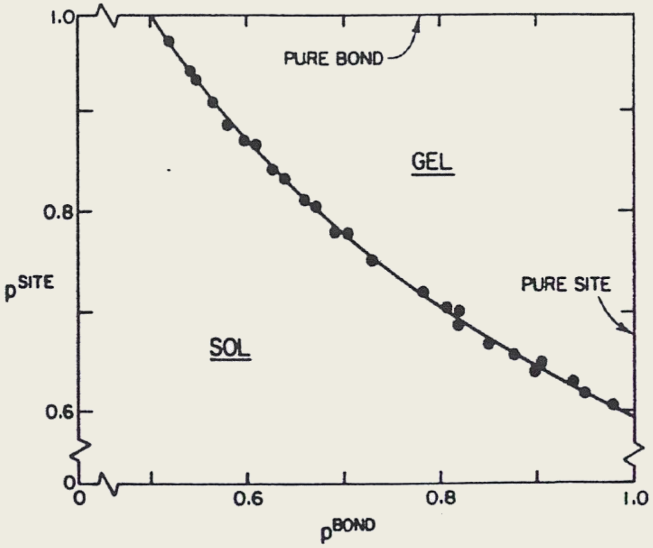
: The lattice is assumed to have a monomer on every site, whereas gelation generally occurs in dilute system.

- Site-bond percolation model

: The site are randomly populated with monomers and solvent molecules.

: As the concentration of solvent rises from zero, Pc increases continuously.

Phase diagram for site-bond percolation on the square lattice



- The distribution of solvent molecules and monomers on the lattice is influenced by an interaction energy.

→ At low temperature; separation into phases rich in monomer and solvent.

→ At high temperature; a single phase, and the random percolation exponents are found to apply along the entire sol-gel boundary.

3.2. Theories of Sol-gel Chemistry

- The percolation threshold corresponds to a certain volume fraction of occupied sites, whether on a lattice or in a continuum.

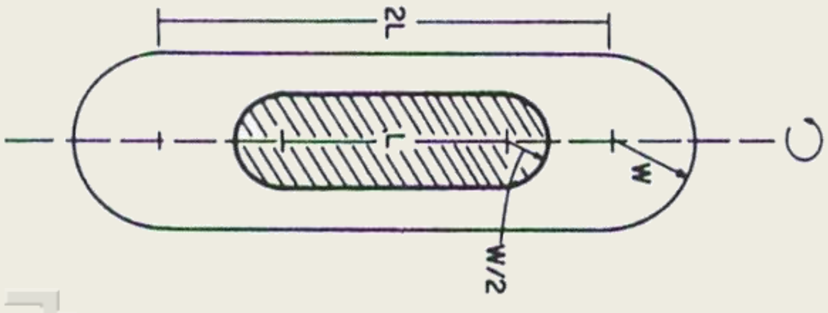
  - For isotropic objects (sphere), the threshold was found to be 16 vol%.
  - For anisotropic objects (plate & fiber), the volume fraction occupied at the percolation threshold depends on the aspect ratio of the object.

- For permeable objects, percolation occurs at a critical value of the excluded volume fraction, V_{ex}.

※ The excluded volume, <V>

: the volume around an object into which the center of another similar object cannot enter without overlapping of the objects.

1) Parallel objects

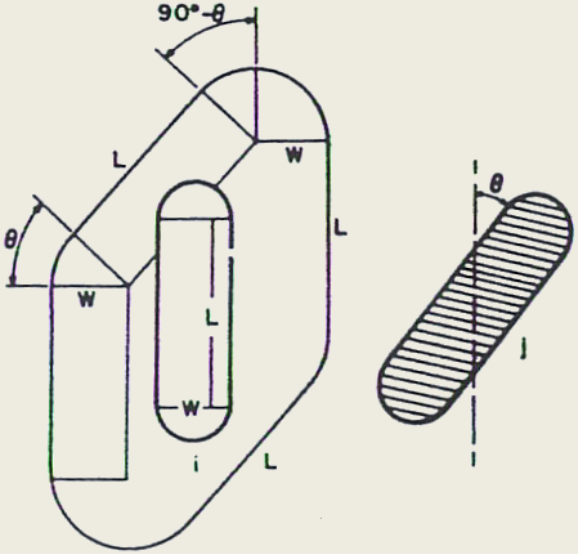


$\langle V \rangle = 2^3 \times V$

→ so a condition of constant excluded volume fraction is equivalent to a condition of constant volume fraction.

3.2. Theories of Sol-gel Chemistry

2) Randomly arranged objectes



<V> is no longer proportional to V.

For capped cylinder,

$$<V> = (4\pi/3)w^3 + 2\pi w^2 L + (\pi/2)wL^2 \quad \text{- (1)}$$

whereas

$$V = (\pi/6)w^3 + (\pi/4)w^2 L$$

- Percolation occurs at a particular value of the excluded volume fraction,

  $V_{ex} = N_c <V>$ - (2) where N_c is the number density of objects

- Eq 1 & 2 indicate that the critical density varies as

  $N_c \propto 1/<V> \propto (2/3 + a + a^2/4)^{-1}$ where a: aspect ratio= L/w

- The critical V_{ex} → different value for objects of different shapes
  → same value for objects of given shape differing in aspect ratio
  → The value remains constant when a distribution of sizes is present, but it increases when the objects are oriented. (given shape)

3.2. Theories of Sol-gel Chemistry

Advantage

- It is quite plausible that the reduced mobility of large clusters near the gel point would prevent equilibrium from being attained, so that the course of cluster growth would be altered.

Limitations

- Both percolation and the classical theory are equilibrium theories that give no information about the kinetics of gelation.→ 3.2.3. Kinetic Models

The difference between percolation and cluster growth (classical theory)

- percolation; bonds are randomly distributed on the lattice → bonds are uncorrelated.
- cluster growth; represent concentrations of bonds → bonds are correlated (grouped together)

3.2. Theories of Sol-gel Chemistry

3.2.3. 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

3.2.3.1. Smoluchowski's Equation

3.2.3.2. Computer simulation of cluster growth

3.2. Theories of Sol-gel Chemistry

3.2.3.1. Smoluchowski's Equation

- The Smoluchowski equation describes an aggregation process

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

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 apply, 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.

3.2. Theories of Sol-gel Chemistry

- For realistic collision model

$$K(ai,aj)=a^{\lambda}K(i,j)=a^{\lambda}K(j,i)$$ where λ is a constant

- For collisions of large clusters,

$$K(i,j)\approx i^{\mu}j^{v}(j\gg i,\lambda=\mu+v)$$

→ Ref.3-1

- Maximum value for the kernel K(j, j) ~ j^2; thus, $\lambda \le 2$ and $v \le 1$.
- Based on the value of μ, three different classes of behavior can be identified.

- Class I (μ > 0)	dominated by collisions between large clusters
- Class II (μ = 0)	has similar frequencies for collisions of large-with-large and large-with-small clusters
- Class III (μ < 0)	dominated by collisions of large-with-small clusters

3.2. Theories of Sol-gel Chemistry

❖ The rate of change of the total mass in clusters up to size s is

$$\frac{dM_s}{dt} = \sum_{j=1}^{s} j \frac{dn_j}{dt} = -\sum_{i=1}^{s} \sum_{j=s-i+1}^{\infty} iK(i, j) n_i n_j \qquad (33)$$

❖ For gelation to occur, $dM_\infty/dt>0$ while the total mass M ($M = \sum_{s=1}^{\infty} sn_s$) is constant,

and gelation will not occur if n_s decreases more rapidly than $n_s \sim s^{-\tau}$ as $s \to \infty$.

❖ The largest terms of Equation 33 are finite only if $\tau > (\lambda + 3)/2$, the total mass M remains finite only if $\tau > 2$.

→ Leading to the requirement that $\lambda > 1$ for gelling systems and $\lambda \le 1$ for nongelling systems.

Ex) Classical theory assumes that all sites are equally reactive

→ $K(I, j) \sim ij$; $\therefore$ $\mu = \nu = 1$ and $\lambda = 2$, so the system is expected to gel.

3.2. Theories of Sol-gel Chemistry

- For a nongelling system ($\lambda \leq 1$),

  the average cluster size grows as $s_{av} \sim t^{z},\ z = 1/(1-\lambda) \ \rightarrow\ e^{ct}$ as $\lambda \rightarrow 1$

∴ In order to $s_{av} \rightarrow \infty$, $t \rightarrow \infty$ (gelation cannot occur)

  and size distribution has the form $n_s = M s_{av}^{-2} f(s/s_{av})$

  where,

$$f(x) \sim x^{-\tau}\ (\mathrm{x} \rightarrow 0),\quad f(x) \sim x^{-\lambda} e^{-ax}\ (\mathrm{x} \rightarrow \infty),\quad \tau = 1+\lambda$$ Class I ($\mu > 0$)

$$f(x) \sim x^{-\tau}\ (\mathrm{x} \rightarrow 0),\quad f(x) \sim x^{-\lambda} e^{-ax}\ (\mathrm{x} \rightarrow \infty),\quad \tau < 1+\lambda$$ Class II ($\mu = 0$)

$$f(x) \sim \exp(-x^{-|\mu|}) \qquad (\mathrm{x} \rightarrow 0)$$ Class III ($\mu < 0$)

(bell shape distribution)

- For a gelling system ($1 < \lambda \leq 2$),

  the average cluster size diverges according to $s_{av} \sim (t - t_{gel})^{-\gamma}, \gamma = (\lambda - 1)/2$

  ∴ $t \rightarrow t_{gel}$, $s_{av} \rightarrow \infty$

  size distribution has the form $n_s = M s_{av}^{-\tau} f(s/s_{av})$ where $f(x) \sim x^{-\tau}, \tau = (\lambda + 3)/2$

3.2. Theories of Sol-gel Chemistry

Table. Properties of growing clusters according to Smoluchowski's theory compared with Flory-Stockmayer and percolation theories

$$K(i,j) \approx i^{u} j^{v} (j \rangle\rangle i, \lambda = u + v)$$

	λ	ν,	μ	Gelling	$n_s \sim s^{-\tau}$	$\sim M_w$
Class I	1<λ≤2	ν≤1	μ>0	Yes	τ=(λ+3)/2 < 2	$\lvert t_{gel}-t \rvert^{-\gamma}$, γ=1/(λ-1)
Class I	ν<λ≤1	ν<λ≤1	μ>0	No	τ=λ+1 < 2	t^{z}, z=1/(1-λ)
Class II	ν=λ≤1	ν=λ≤1	μ=0	No	τ<λ+1	t^{z}, z=1/(1-λ)
Class III	λ<ν	ν≤1	μ<0	No	bell-shaped dist.	t^{z}, z=1/(1-λ)

- One aspect of growth that is not explained by Smoluchowski's theory is the geometry of the clusters
  : it is not possible to predict the fractal dimension of a cluster, given knowledge of the form of the reaction kernel.

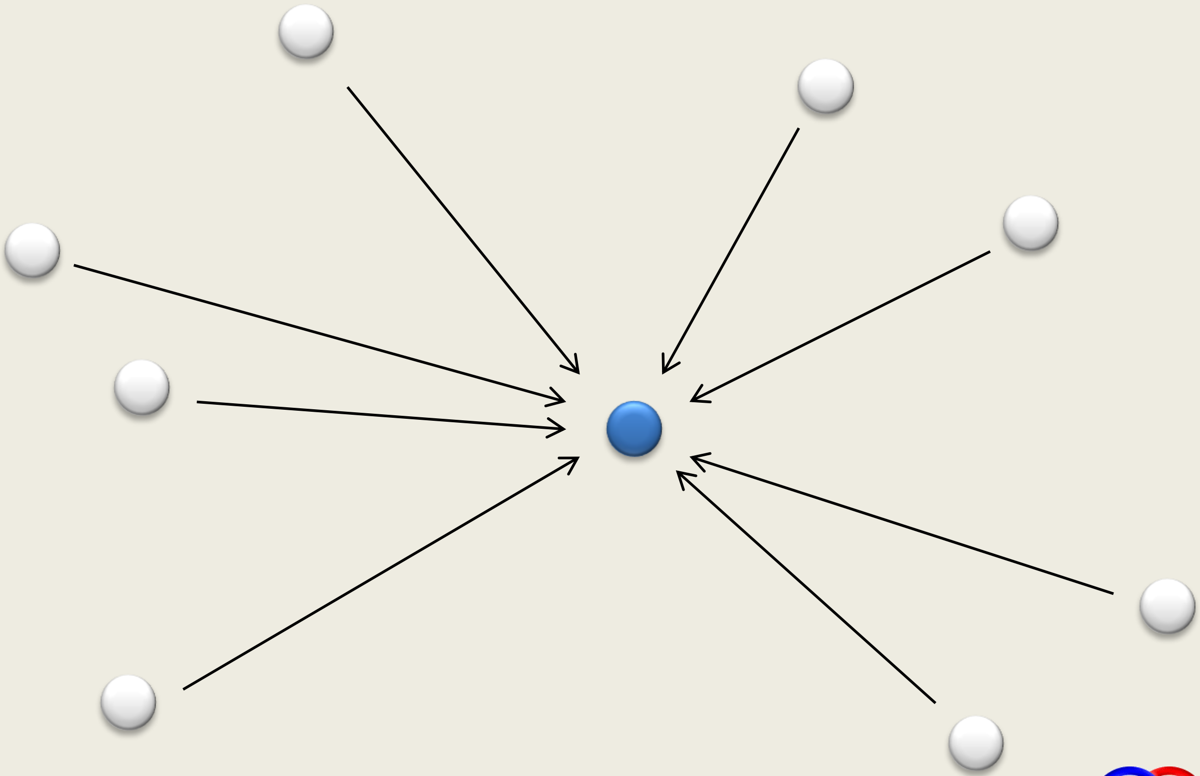
  → This information can only be obtained from the computer simulations

3.2. Theories of Sol-gel Chemistry

3.2.3.2. Computer simulation of cluster growth

0) Computer Models of Aggregation

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



3.2. Theories of Sol-gel Chemistry

1) Classification

- Ballistic Aggregation
  - Approaching polymers follow a <u>linear path</u>
  - A model of particle growth from the vapor phase

- Diffusion-limited Aggregation
  - sticking probability = 1 (colliding clusters <u>always stick together</u>)
  - Rate of aggregation is determined by transport kinetics
  - Erratic path of a diffusing cluster

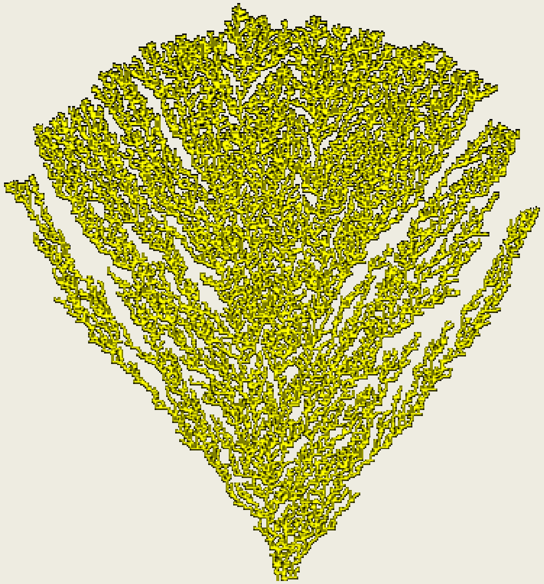
    → Make it difficult for one cluster to penetrate another without colliding and sticking

    → 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)
  - <u>More compact result</u>

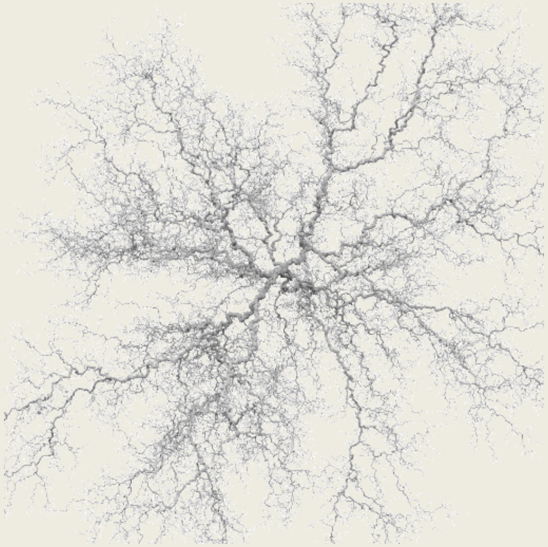
3.2. Theories of Sol-gel Chemistry

1) Classification

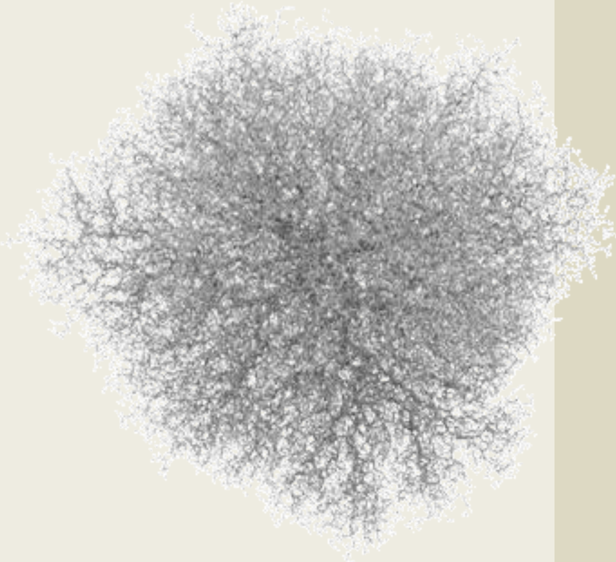


Ballistic Aggregation

Ref. ERCIM News No.29 - April 1997



Diffusion-limited Aggregation



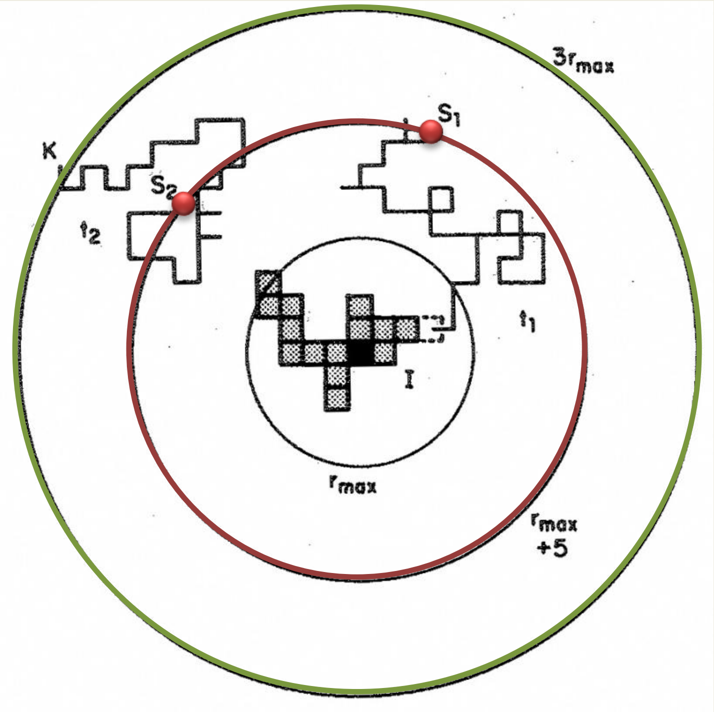
Reaction-limited Aggregation

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

3.2. Theories of Sol-gel Chemistry

2) Diffusion-limited Monomer-Cluster Aggregation

- Simple two-dimensional lattice model



○ launching circle
○ killing circle
r_{max} the maximum radius of the cluster

- Particles are created one at a time from randomly selected points (S_1 and S_2) on a “launching circle” that encloses the cluster.
- They are then moved to the nearest lattice site and undergo a random walk on the lattice.

- **t_1** eventually brings the particle into an unoccupied lattice site on the surface of the cluster (dashed border), where the trajectory is stopped and the surface site is filled;
- **t_2** moves the particle away from the cluster.

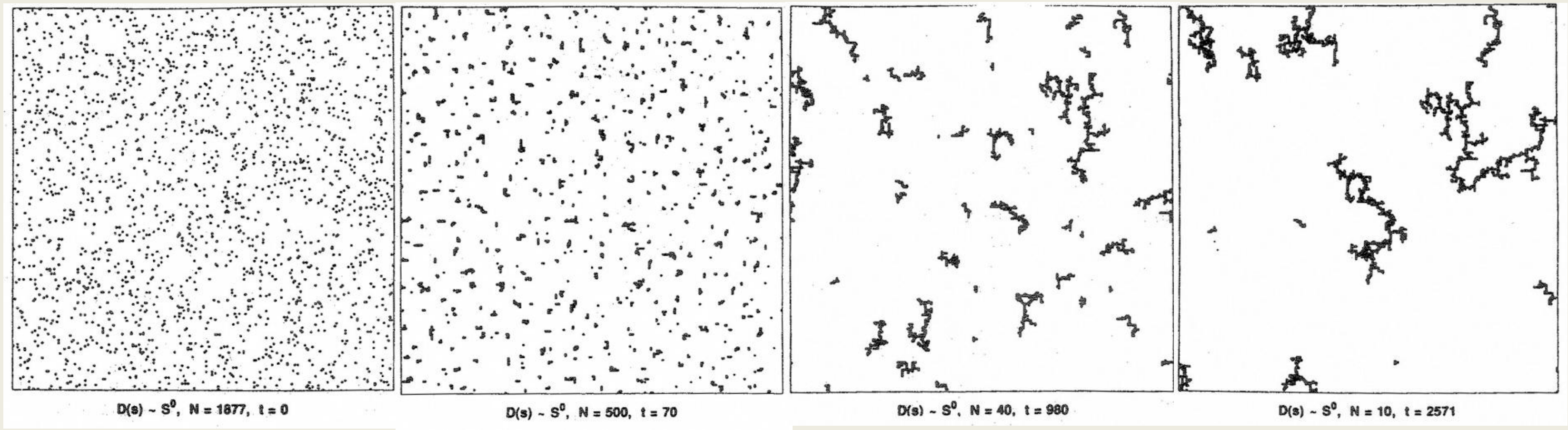
- When **t_2** crosses the “killing circle”, the trajectory is terminated and a new one is begun from a random point on the launching circle.

3.2. Theories of Sol-gel Chemistry

3) Cluster-Cluster Aggregation

Monomer-Cluster Aggregation	**Cluster-Cluster Aggregation**
Monomers are added to clusters	Whole clusters(as well as monomers) diffuse and collide

- Usually begins by distributing monomers at random on a lattice, then allowing them to diffuse, collide, and aggregate



$D(s) \sim S^0$, $N = 1877$, $t = 0$ $D(s) \sim S^0$, $N = 500$, $t = 70$ $D(s) \sim S^0$, $N = 40$, $t = 980$ $D(s) \sim S^0$, $N = 10$, $t = 2571$

- The cluster is moved by one lattice unit in a randomly selected direction
- After moving, the cluster's perimeter is examined for contact with other clusters

3.2. Theories of Sol-gel Chemistry

4) Fractal Dimensionality

Dimensionality d	**Path**	**Fractal Dimension**		
		Monomer-Cluster	Cluster-Cluster	
			Polydisperse	Hierarchical
2	Diffusion-limited	1.71	1.45	1.44
3		2.50	1.80	1.78
4		3.40	2.10	2.02
2	Ballistic	2.0	1.55	1.51
3		3.0	1.95	1.89
4		4.0	2.24	2.22
2	Reaction-limited	2.0	1.61	1.54
3		3.0	2.09	1.99
4		4.0	2.48	2.32

Polydisperse method
: illustrated in previous slide

Hierarchical method
: N monomers → N/2 dimers
→ N/4 tetramers → so on…
: clusters are monodisperse
→ not readily interpenetrate

- These procedures not only indicate the kinetics of aggregation, but also allow study of the size distribution and the fractal geometry of the clusters.
- Note that the monomer-cluster aggregation models produce dense nonfractal clusters, except for the diffusion-limited case, whereas cluster-cluster models yield fractal dimensions in good agreement with experiments on real colloids.

3.2. Theories of Sol-gel Chemistry

5) Effect of Restructuring on Fractal Dimension

Aggregation Path	**Fractal Dimension**			
	IR*=0	1	2	3
Diffusion-limited	1.80	2.09	2.17	2.18
Ballistic	1.95	2.13	2.18	2.19
Reaction-limited	2.09	2.18	2.24	2.25

*IR
Number of internal rotations
allowed after collision

- Clusters were allowed to rearrange by rotation around points of contact.
- Restructuring → Denser structures (i.e. higher fractal dimension)

- Fractal dimension of a single rotated DLCCA cluster (IR=1)
= Fractal dimension of an unmodified RLCCA cluster (IR=0)
- It is not possible to infer the aggregation mechanisms from the geometry of the clusters.

3.2. Theories of Sol-gel Chemistry

- These studies show that the kinetic aggregation models provide a good description of the growth kinetics and the structure of clusters in colloids.

- But neither RLCCA nor DLCCA produces gelation.
  → The reason is that the models are defined, and the supporting studies are performed in very dilute suspensions.

3.3. Experimental Approach

3.3.1 Silica sol-gel processing

- **Hydrolysis and condensation**

$$n\ \mathrm{Si(OR)_4} + 2n\ \mathrm{H_2O} \dashrightarrow n\ \mathrm{SiO_2} + 4n\ \mathrm{ROH}$$

$$\equiv \mathrm{Si} - \mathrm{OR} + \mathrm{H_2O} \longrightarrow \equiv \mathrm{Si} - \mathrm{OH} + \mathrm{ROH} \qquad \text{-(1)}$$

$$\equiv \mathrm{Si} - \mathrm{OR} + \mathrm{HO} - \mathrm{Si} \equiv \longrightarrow \equiv \mathrm{Si} - \mathrm{O} - \mathrm{Si} \equiv + \mathrm{ROH} \qquad \text{-(2)}$$

$$\equiv \mathrm{Si} - \mathrm{OH} + \mathrm{HO} - \mathrm{Si} \equiv \longrightarrow \equiv \mathrm{Si} - \mathrm{O} - \mathrm{Si} \equiv + \mathrm{HOH} \qquad \text{-(3)}$$

CNDL

3.3. Experimental Approach

Precursor molecules

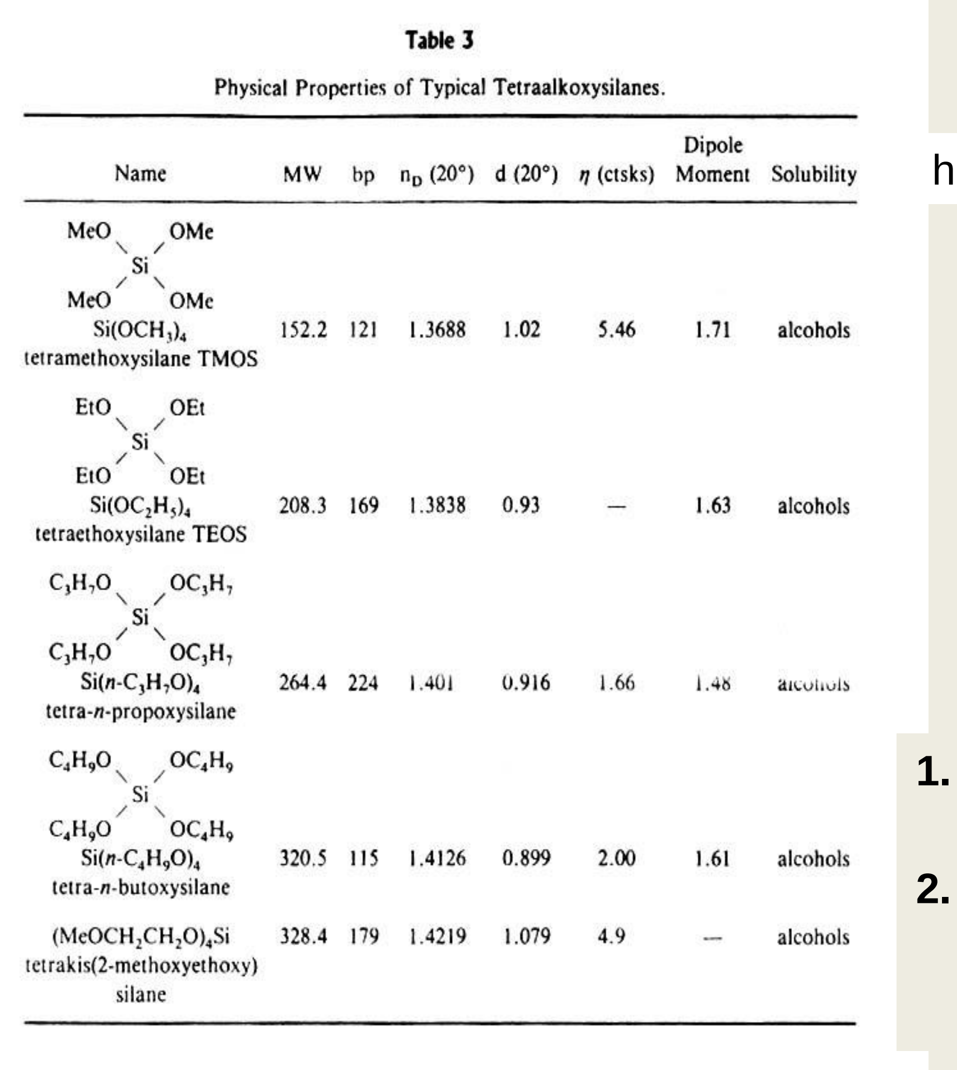
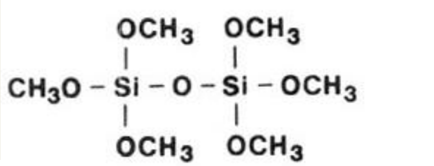


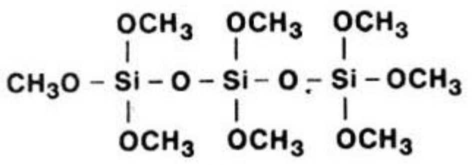
Table 3

Physical Properties of Typical Tetraalkoxysilanes.

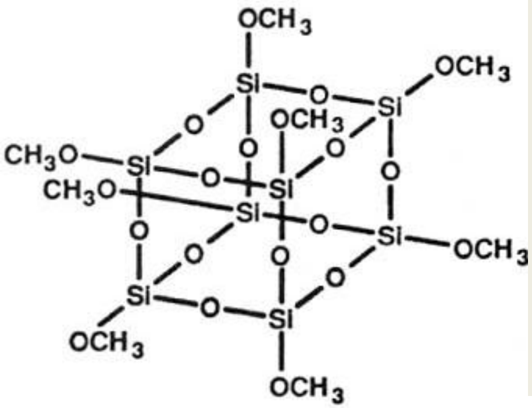
Name	MW	bp	n_D (20°)	d (20°)	η (ctsks)	Dipole Moment	Solubility
$Si(OCH_3)_4$ tetramethoxysilane TMOS	152.2	121	1.3688	1.02	5.46	1.71	alcohols
$Si(OC_2H_5)_4$ tetraethoxysilane TEOS	208.3	169	1.3838	0.93	—	1.63	alcohols
$Si(n\text{-}C_3H_7O)_4$ tetra-*n*-propoxysilane	264.4	224	1.401	0.916	1.66	1.48	alcohols
$Si(n\text{-}C_4H_9O)_4$ tetra-*n*-butoxysilane	320.5	115	1.4126	0.899	2.00	1.61	alcohols
$(MeOCH_2CH_2O)_4Si$ tetrakis(2-methoxyethoxy) silane	328.4	179	1.4219	1.079	4.9	—	alcohols



hexamethoxydisiloxane



octamethoxytrisiloxane



methoxylated cubic octamer

1. **$Si(OEt)_4$, $Si(OMe)_4$: the most commonly used precursors**
2. **Si-alkoxides : Ti-alkoxides**
   - **Hydrolysis rates ~ 5×10^{-9} (Si) vs. 10^{-3} (Ti).**
   - **Gelation time ~ days (Si) vs. ~minutes (Ti).**

3.3. Experimental Approach

- **Precursor molecules**

Table 1. Positive partial charge δ(M) for metals in various alkoxides

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**

Less susceptible to nucleophilic attack

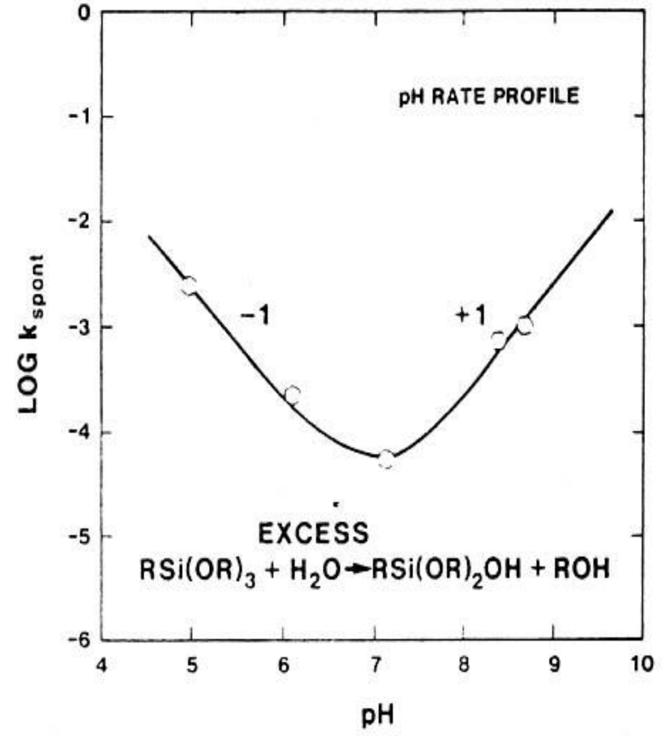
Si^{4+} (N = z)
(No coordination expansion)

$\longrightarrow$

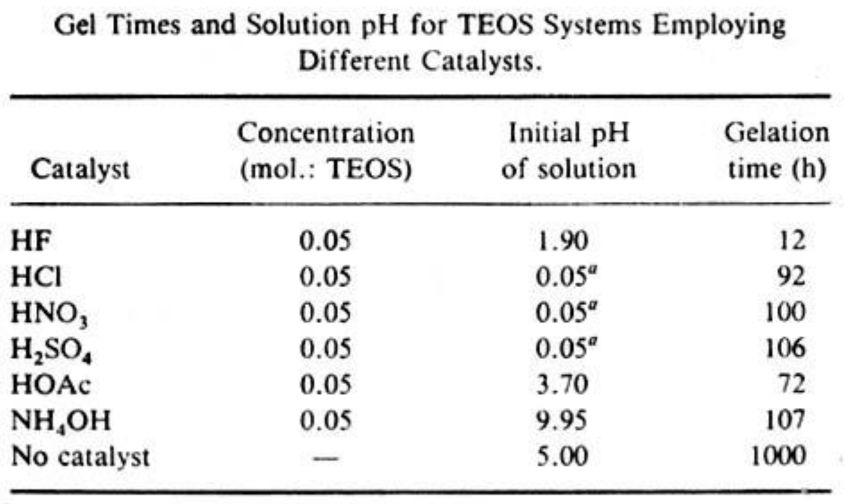
Slow hydrolysis & condensation reaction rate

3.3. Experimental Approach

3.3.1.1 Silicon alkoxides: Hydrolysis/Effect of catalysts



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



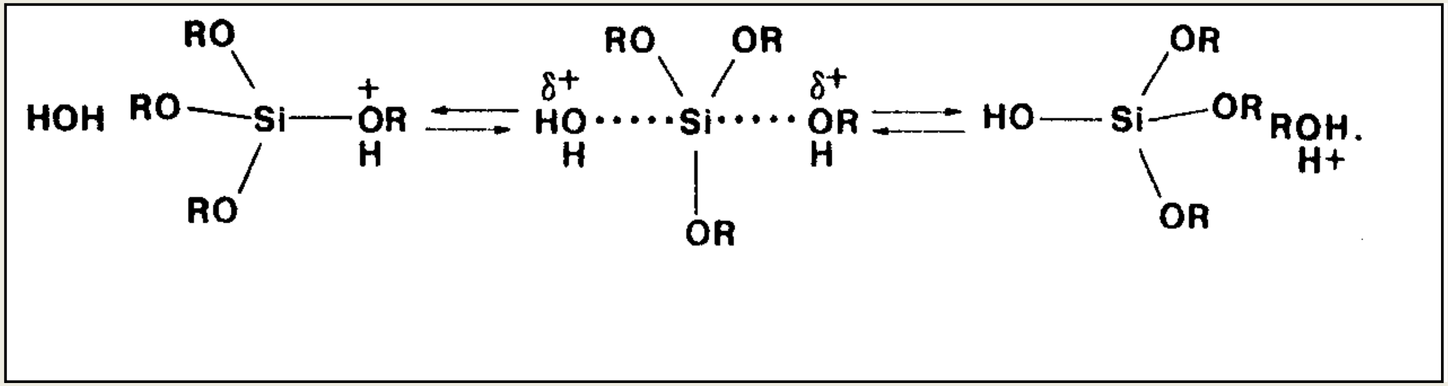
Gel Times and Solution pH for TEOS Systems Employing Different Catalysts.

Catalyst	Concentration (mol.: TEOS)	Initial pH of solution	Gelation time (h)
HF	0.05	1.90	12
HCl	0.05	0.05[a]	92
HNO_3	0.05	0.05[a]	100
H_2SO_4	0.05	0.05[a]	106
HOAc	0.05	3.70	72
NH_4OH	0.05	9.95	107
No catalyst	—	5.00	1000

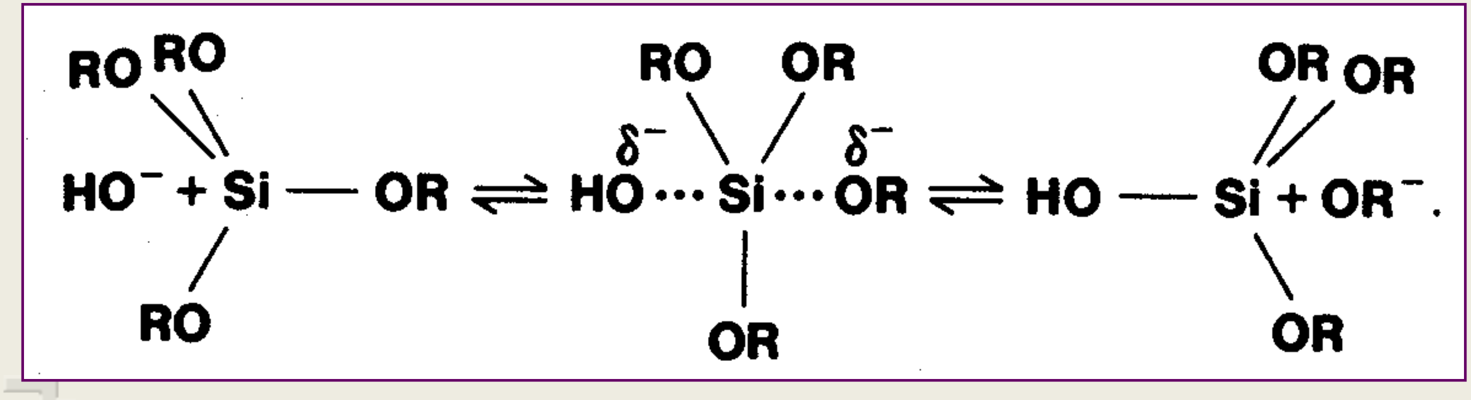
3.3. Experimental Approach

3.3.1.1 Silicon alkoxides: Hydrolysis/Effect of catalysts

Acid-catalyzed hydrolysis



Base-catalyzed hydrolysis



3.3. Experimental Approach

3.3.1.1 Silicon alkoxides: Hydrolysis/Steric effect

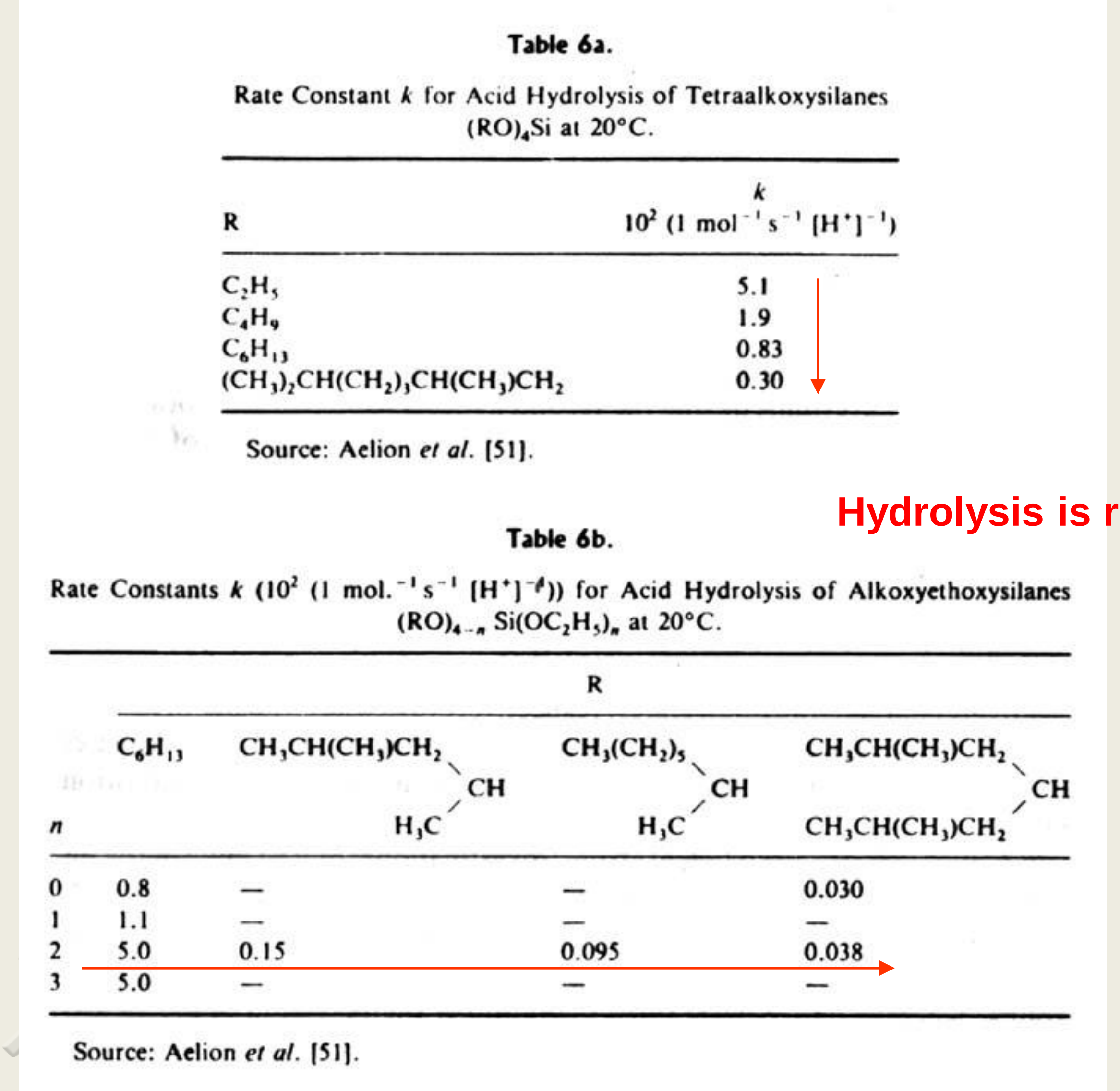


Table 6a.

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

R	k 10^2 (1 mol^{-1} s^{-1} [H$^+$]$^{-1}$)
C_2H_5	5.1
C_4H_9	1.9
C_6H_{13}	0.83
$(CH_3)_2CH(CH_2)_3CH(CH_3)CH_2$	0.30

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

Hydrolysis is retarded by bulky alkoxy groups

Table 6b.

Rate Constants *k* (10^2 (1 mol.$^{-1}$ s^{-1} [H$^+$]$^{-1}$)) for Acid Hydrolysis of Alkoxyethoxysilanes $(RO)_{4-n}Si(OC_2H_5)_n$ at 20°C.

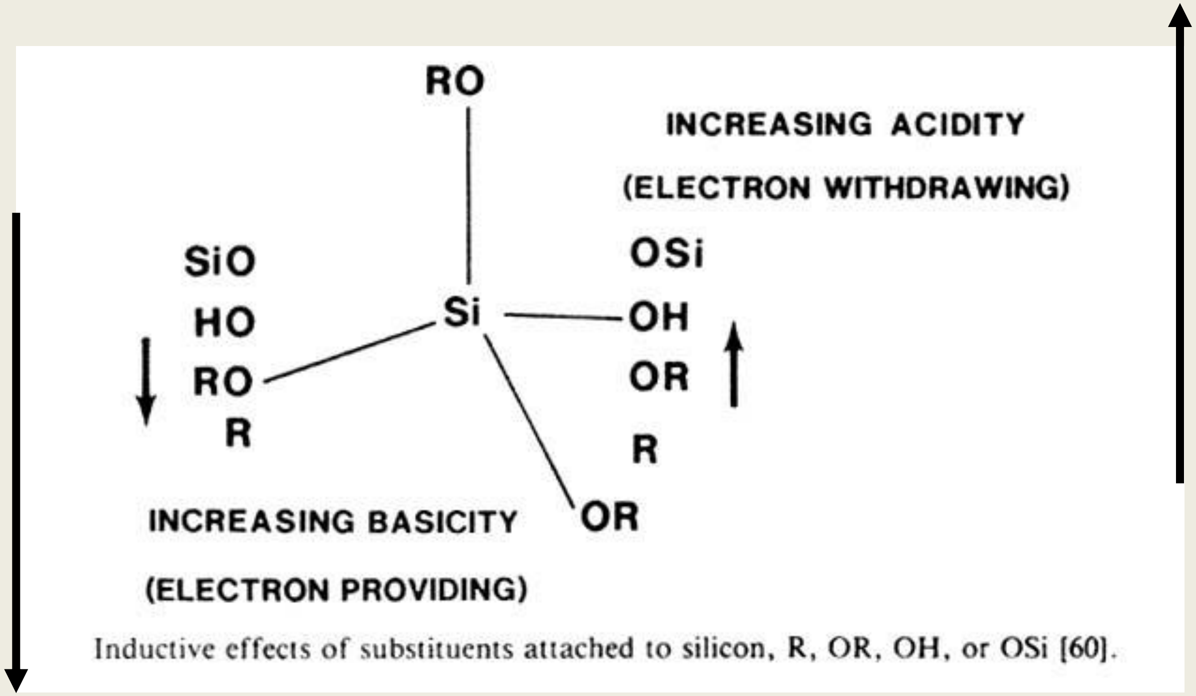
	R			
n	C_6H_{13}	$CH_3CH(CH_3)CH_2$ CH H_3C	$CH_3(CH_2)_5$ CH H_3C	$CH_3CH(CH_3)CH_2$ CH $CH_3CH(CH_3)CH_2$
0	0.8	—	—	0.030
1	1.1	—	—	—
2	5.0	0.15	0.095	0.038
3	5.0	—	—	—

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

3.3. Experimental Approach

3.3.1.1 Silicon alkoxides: Hydrolysis/Inductive effect

Increase the stability of negatively charged transition state

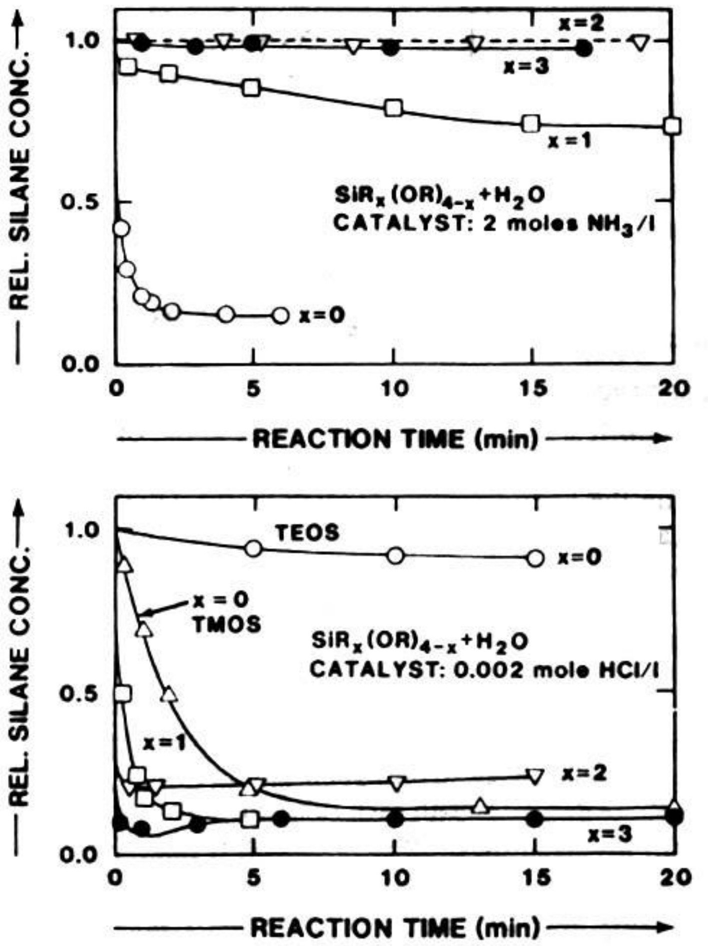


Inductive effects of substituents attached to silicon, R, OR, OH, or OSi [60].

Increase the stability of positively charged transition state

3.3. Experimental Approach

3.3.1.1 Silicon alkoxides: Hydrolysis/Inductive effect



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].

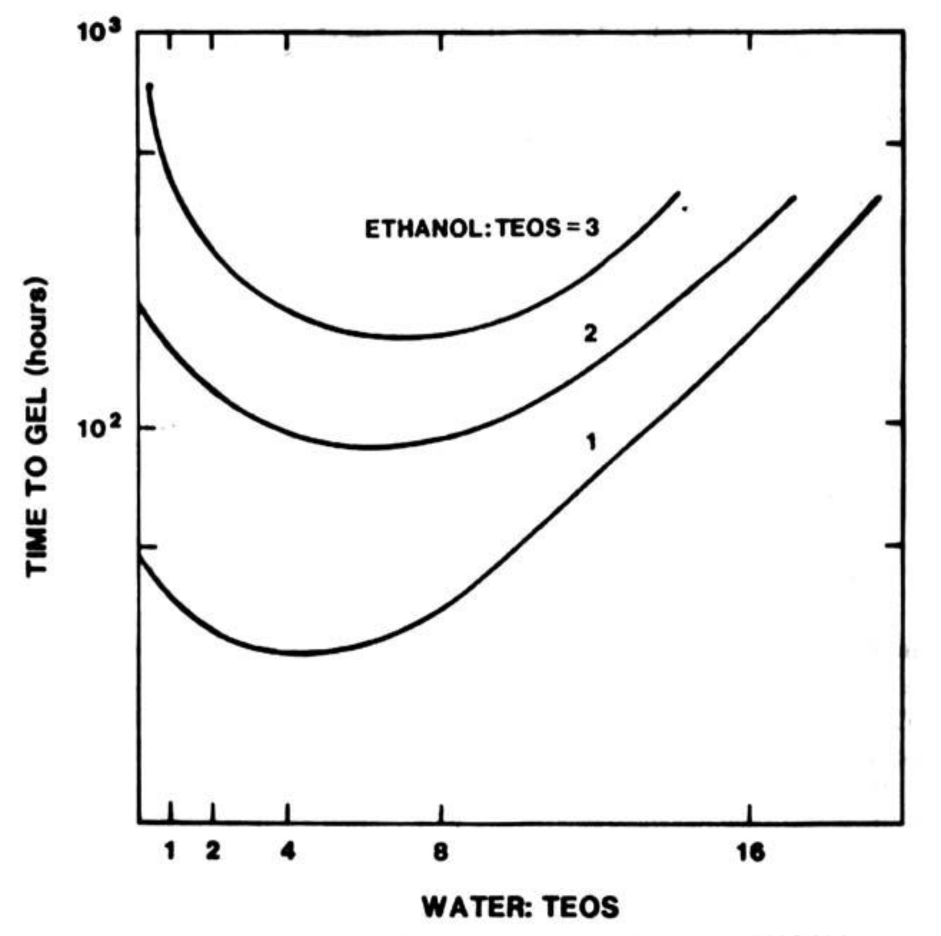
Hydrolysis rate decreases with increasing *x, under basic catalyst*

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

3.3. Experimental Approach

3.3.1.2 Silicon alkoxides: Condensation/H_2O:Si ratio effect

Silicate concentration is reduced

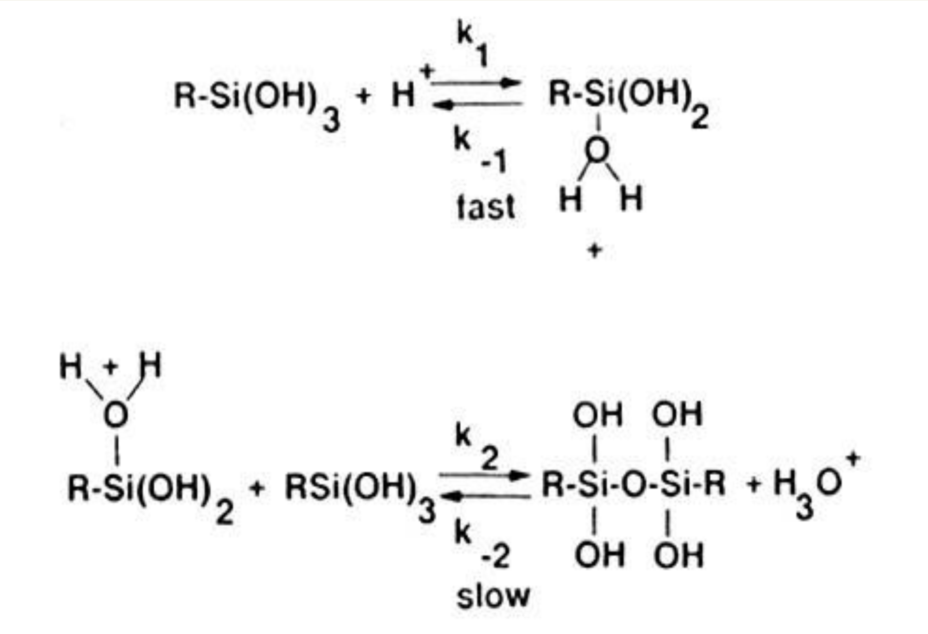


Gel times versus H_2O : TEOS ratio, *r*, for three ratios of EtOH to TEOS [64].

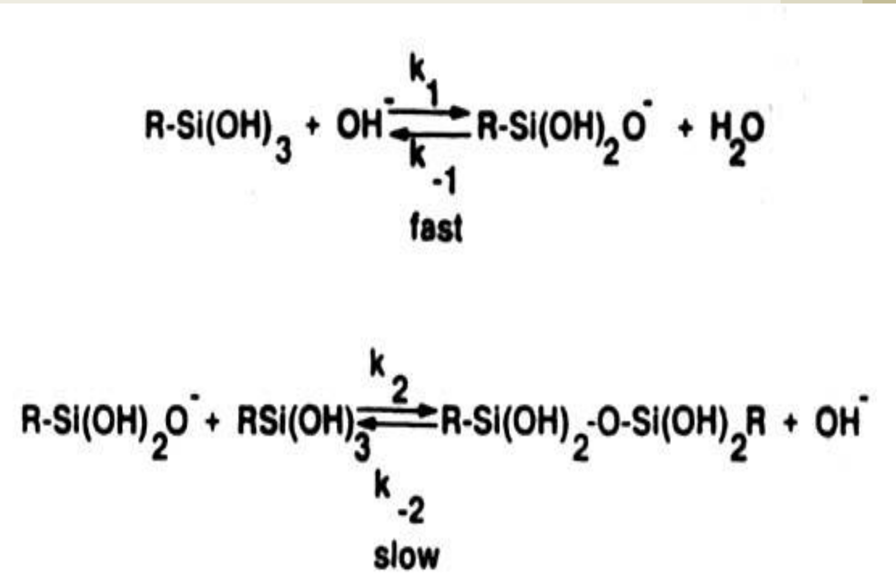
3.3. Experimental Approach

3.3.1.2 Silicon alkoxides: Condensation/Catalyst effect

Acid-catalyzed condensation

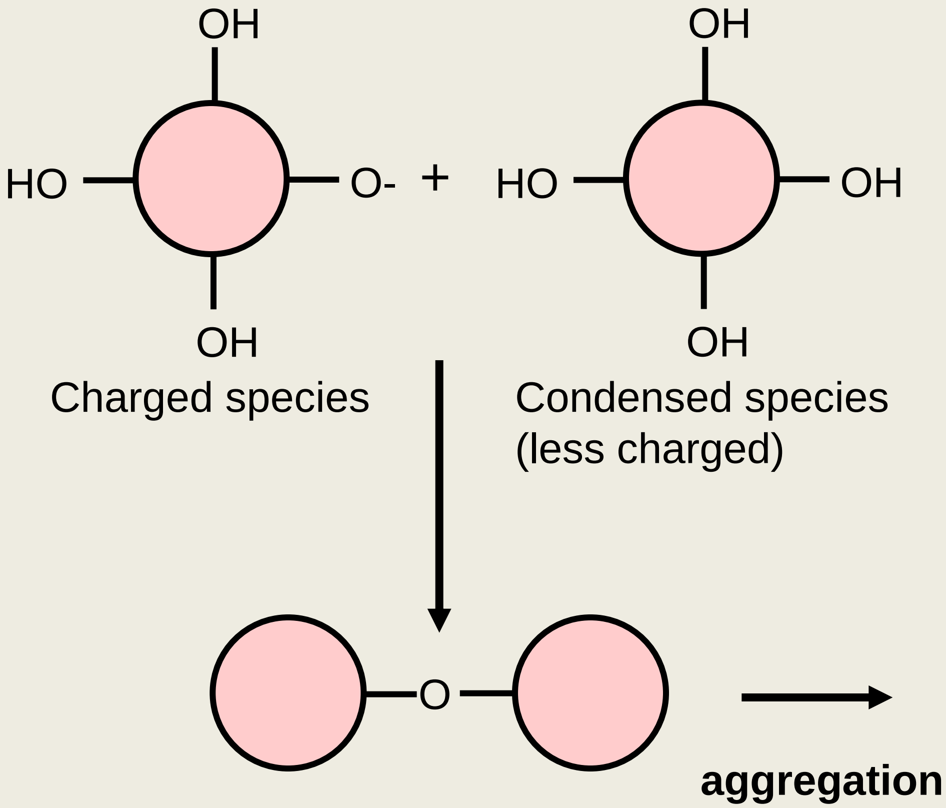


Base-catalyzed condensation



3.3. Experimental Approach

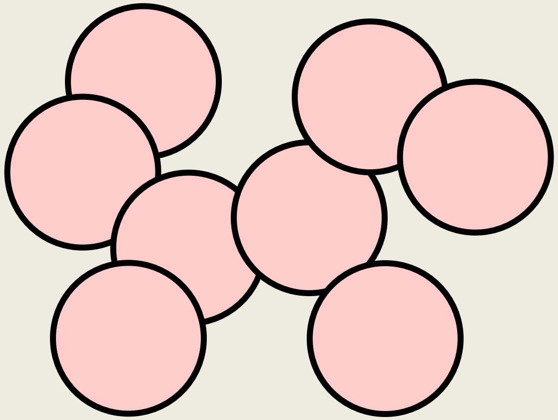
3.3.1.2 Silicon alkoxides: Condensation/Effect of catalysts-acid



Charged species

Condensed species (less charged)

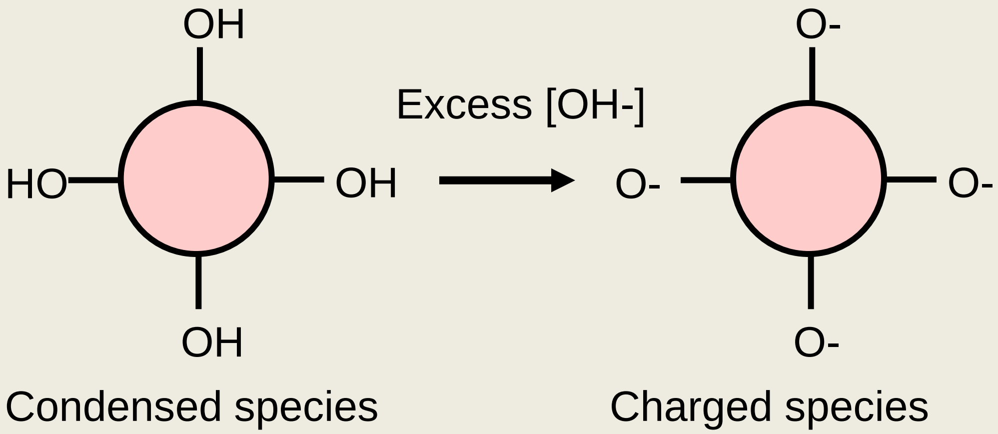
As the hydrolysis progresses:
# of OR groups decrease
→ Reactivity decreases
→ Hydrolysis rate decrease
→ Relative condensation rate increases
→ **Three-dimensional networks (polymeric gels)**



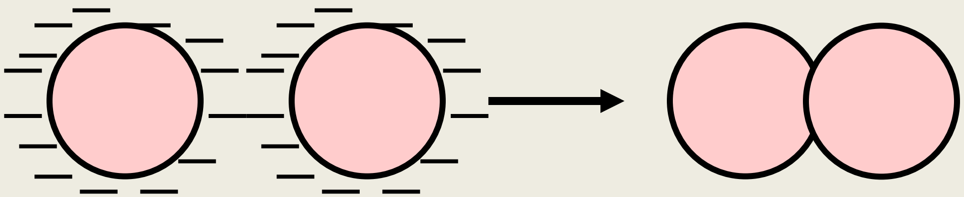
Reaction-limited cluster-cluster aggregation (RLCA)

3.3. Experimental Approach

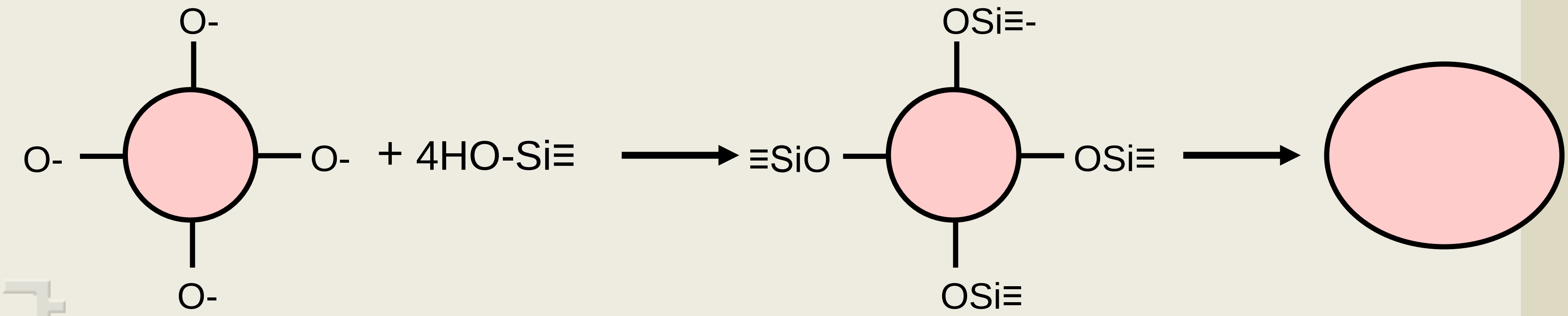
3.3.1.2 Silicon alkoxides: Condensation/Effect of catalysts-base



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)

3.3. Experimental Approach

3.3.1.2 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**

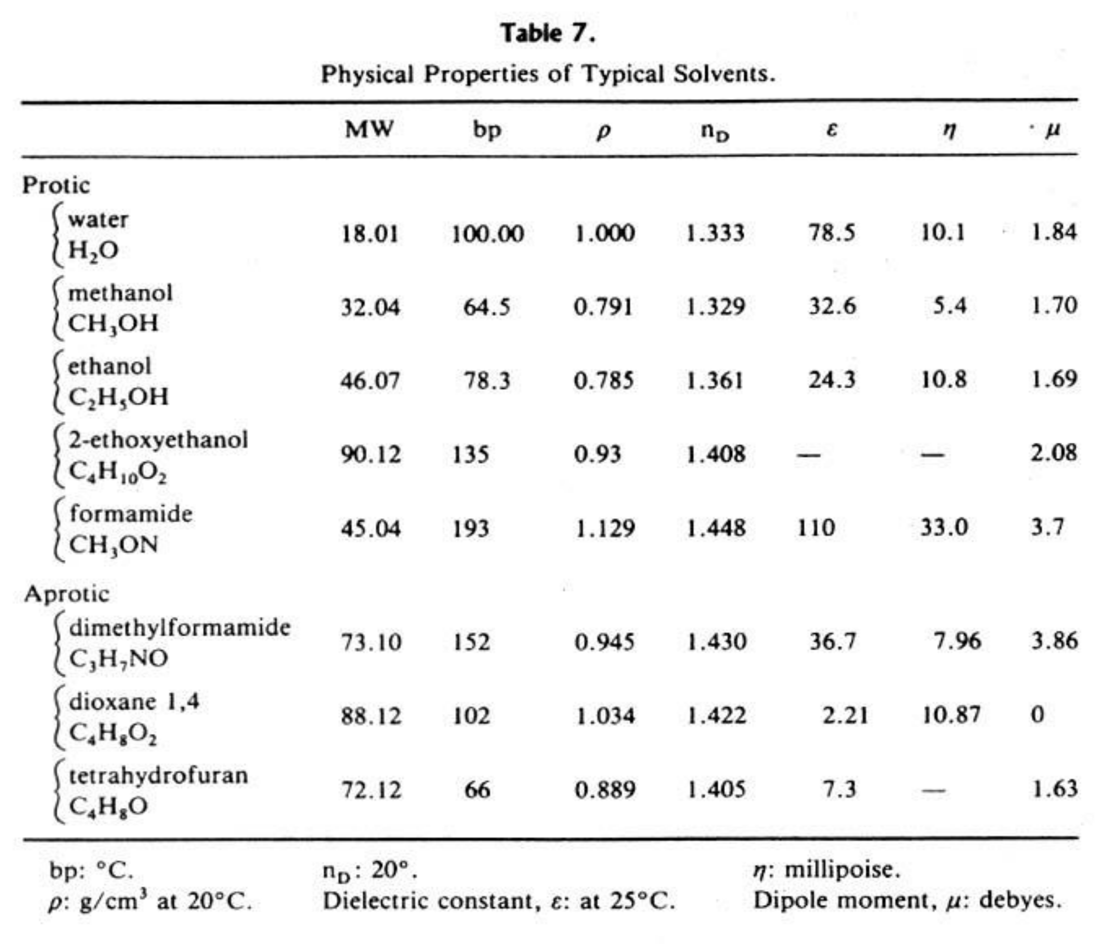


Table 7.

Physical Properties of Typical Solvents.

	MW	bp	ρ	n_D	ε	η	μ
Protic							
water H_2O	18.01	100.00	1.000	1.333	78.5	10.1	1.84
methanol CH_3OH	32.04	64.5	0.791	1.329	32.6	5.4	1.70
ethanol C_2H_5OH	46.07	78.3	0.785	1.361	24.3	10.8	1.69
2-ethoxyethanol $C_4H_{10}O_2$	90.12	135	0.93	1.408	—	—	2.08
formamide CH_3ON	45.04	193	1.129	1.448	110	33.0	3.7
Aprotic							
dimethylformamide C_3H_7NO	73.10	152	0.945	1.430	36.7	7.96	3.86
dioxane 1,4 $C_4H_8O_2$	88.12	102	1.034	1.422	2.21	10.87	0
tetrahydrofuran C_4H_8O	72.12	66	0.889	1.405	7.3	—	1.63

bp: °C. n_D: 20°. η: millipoise.

ρ: g/cm^3 at 20°C. Dielectric constant, ε: at 25°C. Dipole moment, μ: debyes.

- Protic solvent (H-bond to nucleophilic deprotonated silanols)

  :acid-catalyzed condensation

- Aprotic solvent (H-bond to electrophilic protonated silanols)

  :base-catalyzed condensation

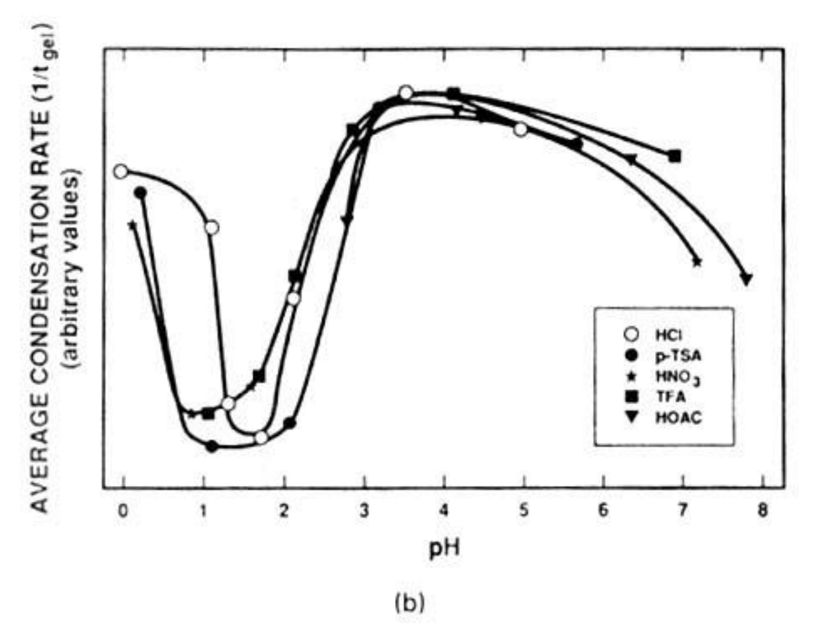
CNDL

3.3. Experimental Approach

3.3.1.2 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 [RxSi(OR)4-x], the value x determine the reaction mechanism and define what is meant by acid- or base-catalysed condensation.



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

PZC=pH where the surface charge is zero

3.3. Experimental Approach

3.3.1.3 Sol-gel kinetics

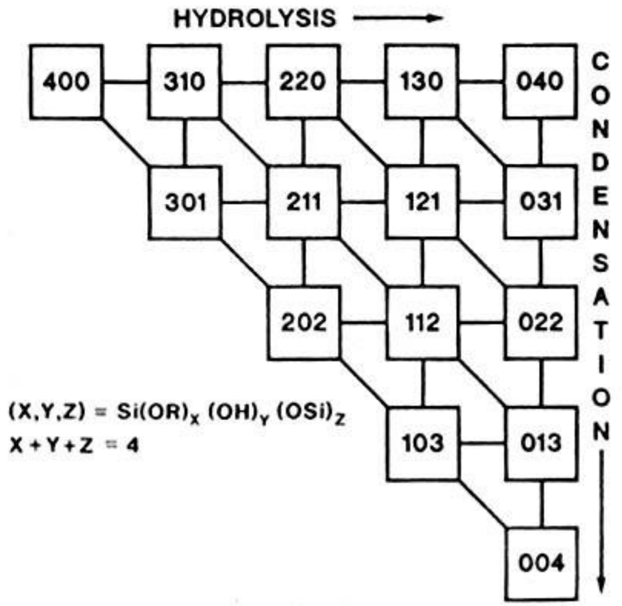
$$\mathrm{SiOR} + \mathrm{H_2O} \xrightarrow{k_h} \mathrm{SiOH} + \mathrm{ROH}$$

$$2\mathrm{SiOH} \xrightarrow{k_{cw}/2} 2(\mathrm{SiO})\mathrm{Si} + \mathrm{H_2O}$$

$$\mathrm{SiOH} + \mathrm{SiOR} \xrightarrow{k_{ca}/2} 2(\mathrm{SiO})\mathrm{Si} + \mathrm{ROH}$$

k_h : rate constant of hydrolysis
k_{cw} : condensation of water
k_{ca} : condensation of alcohol

$(X, Y, Z) = \mathrm{Si(OR)_X(OH)_Y(OSi)_Z}$
$X + Y + Z = 4$



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

3.3. Experimental Approach

3.3.1.3 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 [SiOH] equals the consumption of H_2O by hydrolysis.

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

$k_{cw} >> k_{ca}$: condensation rate proportional to $[SiOH]^2$
$k_{cw} << k_{ca}$: condensation rate proportional to [SiOH][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.

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

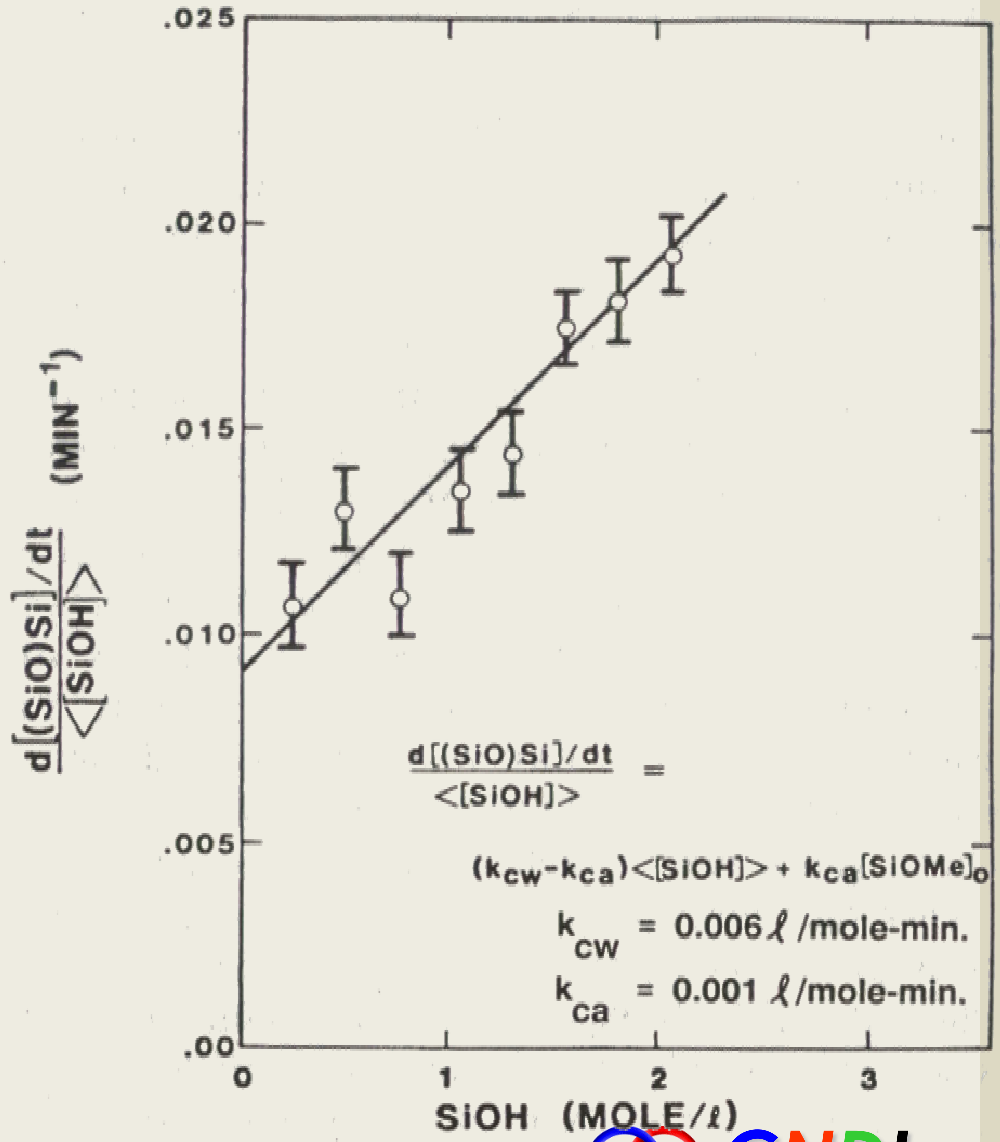
Valid at early times when the concentration of Si-O-Si is small compared to the initial methoxy functional group concentration.

3.3. Experimental Approach

3.3.1.3 Sol-gel kinetics

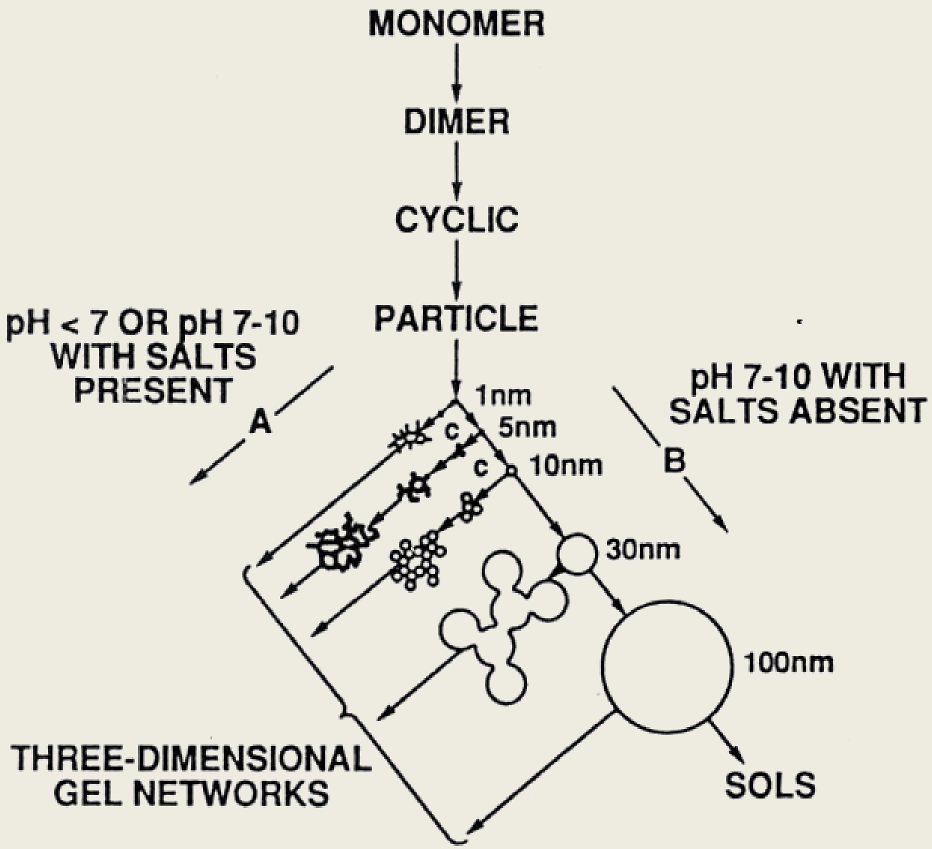
$$\frac{d[(\mathrm{SiO})\mathrm{Si}]/dt}{<[\mathrm{SiOH}]>} \quad \text{vs} \quad <[\mathrm{SiOH}]> \quad \text{plot}$$

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



3.3. Experimental Approach

3.3.1.4 Structural summary

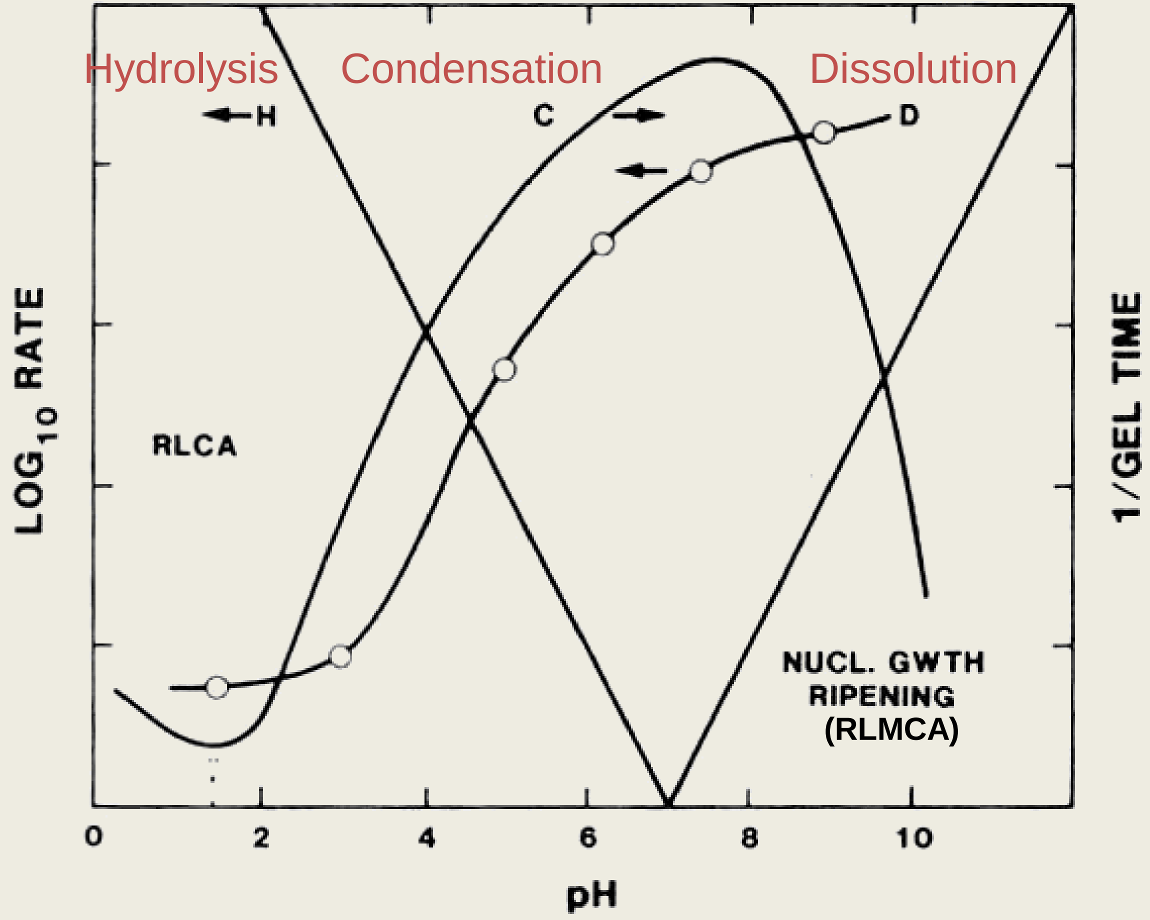


Polymerization behavior of aqueous silica. In basic solution (B) particles grow in size with decrease in number; in acid solution or in the presence of flocculating salts (A), particles aggregate into three-dimensional networks and form gels. From Iler [1].

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

3.3. Experimental Approach

3.3.1.4 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

3.3. Experimental Approach

3.3.1.4 Structural summary

1. Polymerization at pH 2-7
  - Condensation rate proportional to [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 [H^+]
  - Metastable
  - Gel network (composed of small primary particles(< 2 nm))

CNDL

3.3. Experimental Approach

3.3.2 Metal alkoxides

$M(OR)_x$

M : metal (typically Ti, Zr)
R : alkyl group (methyl, ethyl, isopropyl, butyl, etc.),
x: valence

- 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≥2)

3.3. Experimental Approach

3.3.2.1 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↑ → volatility↓

(3) Viscosity

- Affected by the chain length and branching of alkyl groups
- Affected by the degree of molecular association
- Degree of oligomerization↑ → viscosity↑

3.3. Experimental Approach

3.3.2.2 Sol-gel process of Metal alkoxides

Hydrolysis

$$M(OR)_x + mH_2O \rightarrow M(OR)_{x-m}(OH)_m + mROH$$

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

$$2M(OR)_{x-m}(OH)_m \rightarrow (OH)_{m-1}(OR)_{x-m}-M-O-M(OR)_{x-m}(OH)_{m-1} + H_2O$$

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

$$2M(OR)_{x-m}(OH)_m \rightarrow (OH)_{m-1}(OR)_{x-m}-M-O-M(OR)_{x-m-1} + ROH$$

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

3.3. Experimental Approach

3.3.2.3 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**

CNDL

3.3. Experimental Approach

3.3.2.3 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**

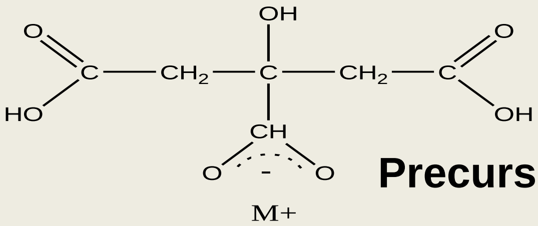
3.3. Experimental Approach

3.3.3 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

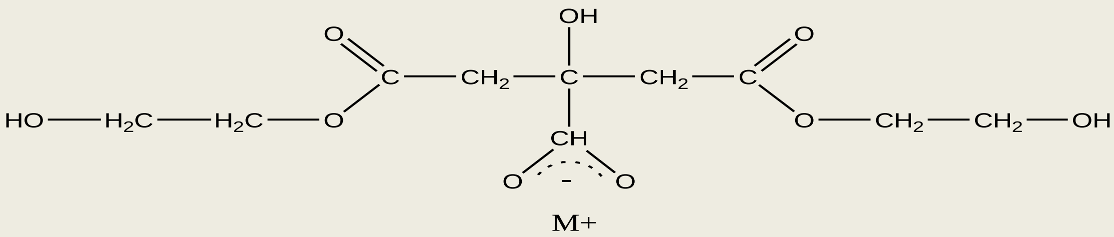


Precursors

nitric acid
100 °C

Ethylene glycol

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 um thick.