

## 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

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#### 3.2. 1-D Organic Materials

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# Chapter 2.2.1. Non-template Method

## 2.2.1. Sol-gel Method

### 1. Introduction

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### 3. The Sol-gel Chemistry of Nonsilicate

3.1. Solution chemistry of Inorganic Precursors

3.2. Solution chemistry of Metal alkoxide

3.3. Pechini processing



# 1. Introduction

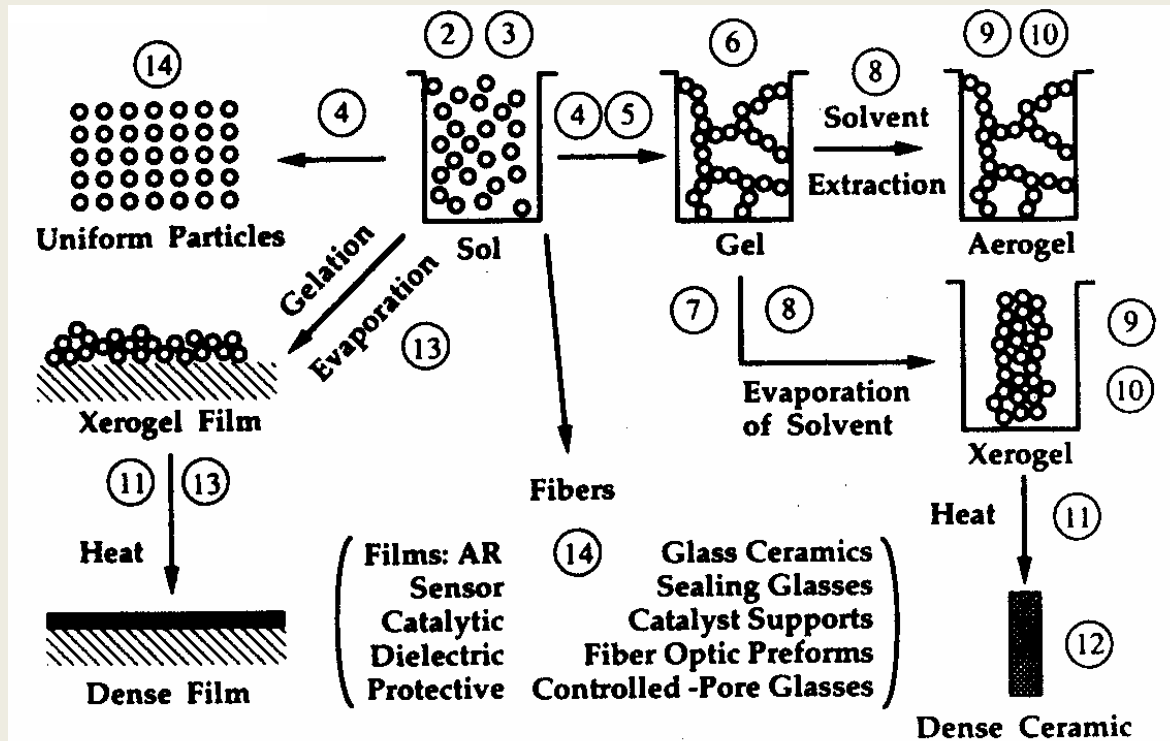
- Definition of sol-gel processing

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

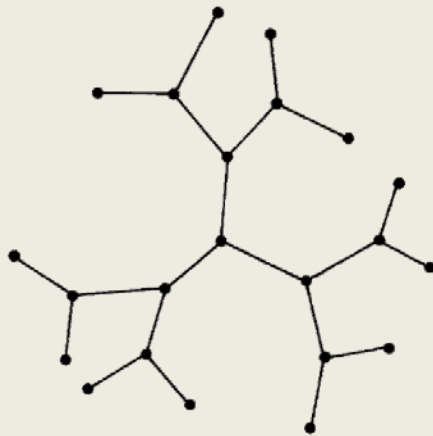
- The theory of gelation developed by Flory and Stockmayer is now generally known as the “classical” or “mean field” theory.

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

$z=3 : p_c=1/2$

$z=4 : p_c=1/3$



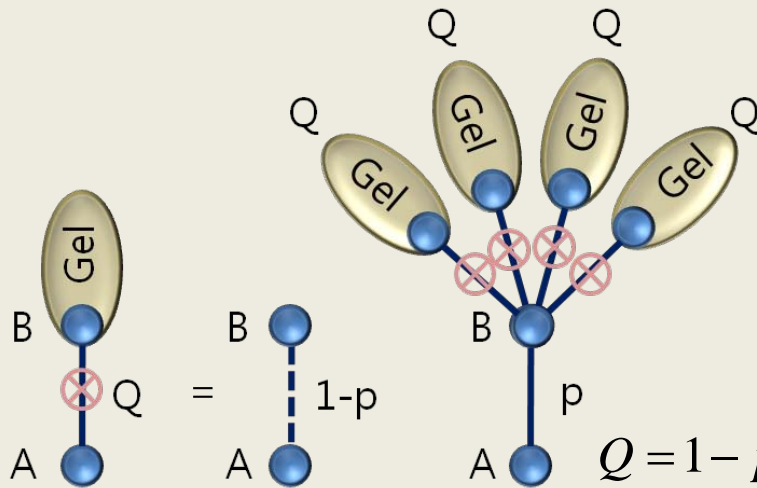


## 2. Some Theoretical Approaches to The Sol-gel Chemistry

- 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  $z=3$

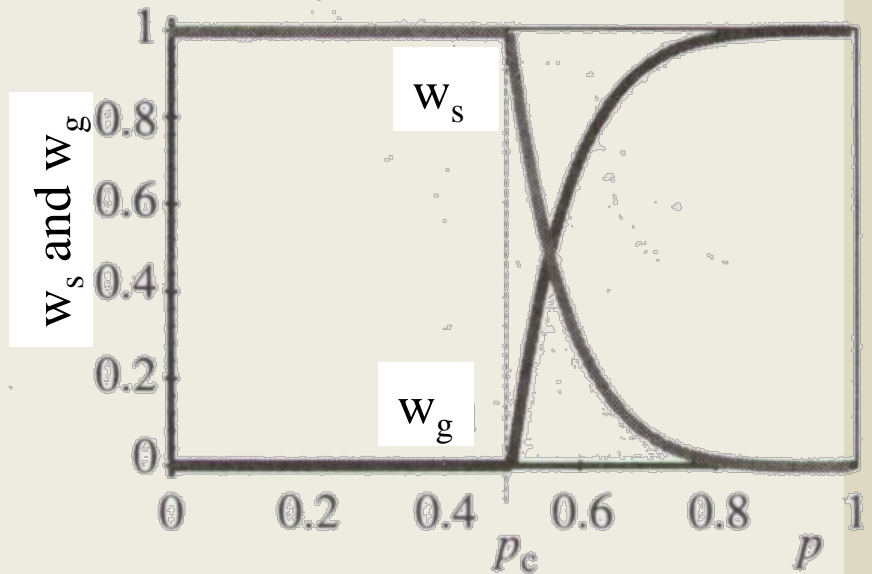
$$w_s^{1/z} = 1 - p + pw_s^{(z-1)/z}$$

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. 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

### 2.2.1. 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.

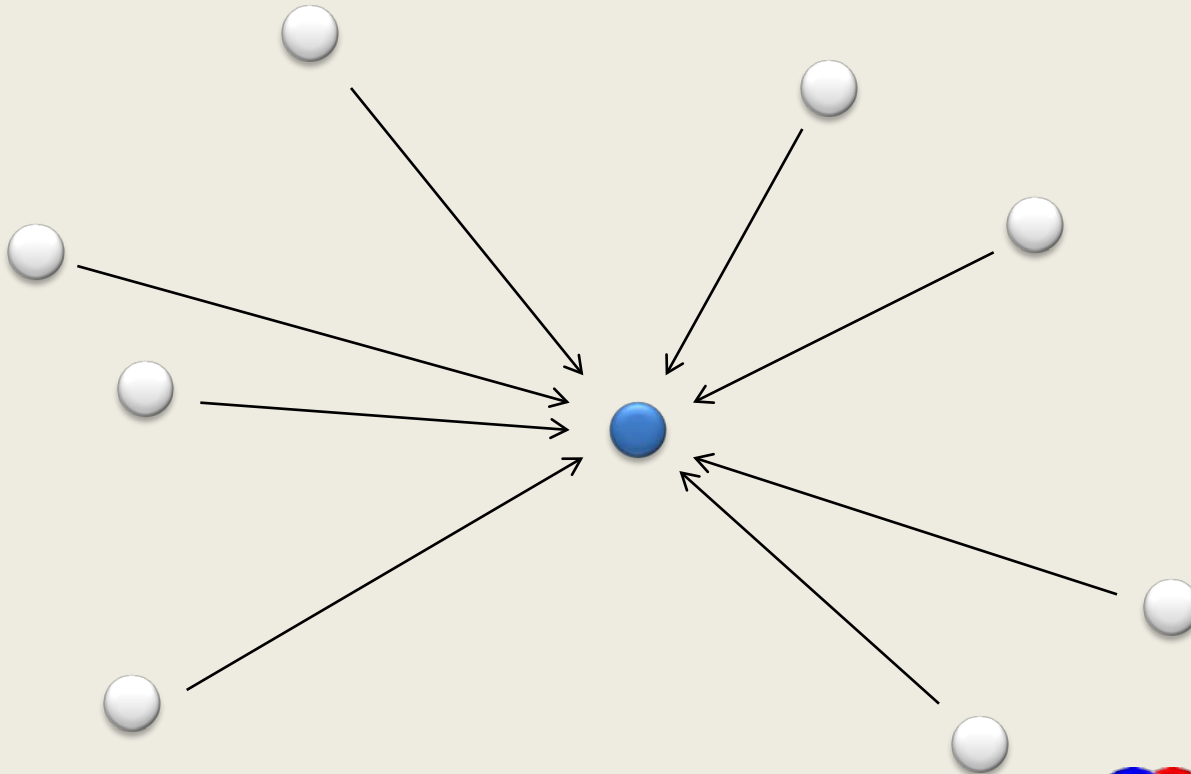


## 2. Some Theoretical Approaches to The Sol-gel Chemistry

### 2.2.2. 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

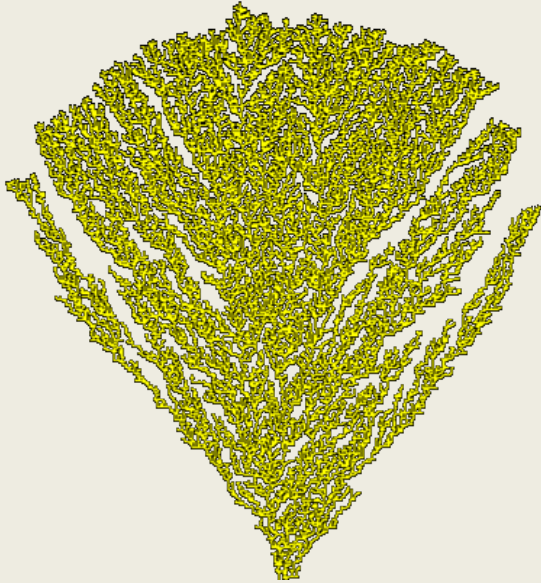
- **Ballistic Aggregation**
  - ▣ Approaching polymers follow a linear path
  - ▣ A model of particle growth from the vapor phase
  
- **Diffusion-limited Aggregation**
  - ▣ sticking probability = 1 (colliding clusters always stick together)
  - ▣ Rate of aggregation is determined by transport kinetics
  - ▣ 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





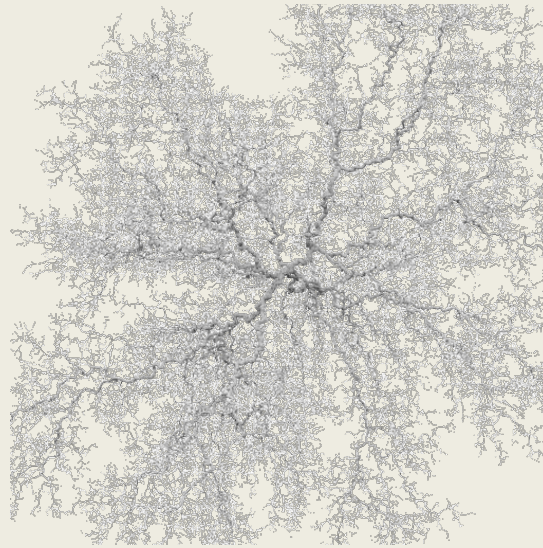
## 2. Some Theoretical Approaches to The Sol-gel Chemistry

### 3) Simulation model



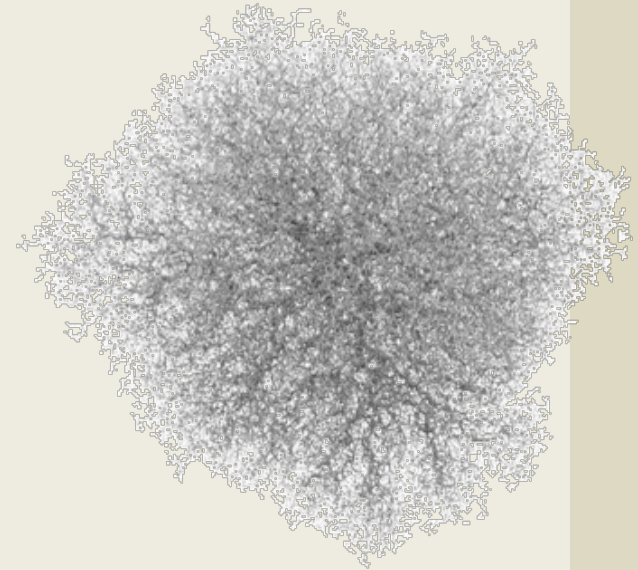
Ballistic Aggregation

Ref. ERCIM News No.29 - April 1997



Diffusion-limited Aggregation

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



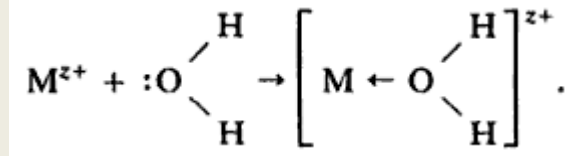
Reaction-limited Aggregation



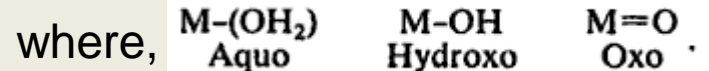
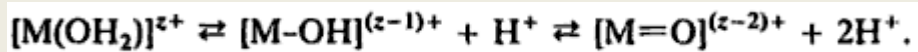
# 3. The Sol-gel Chemistry of Nonsilicate

## 3.1 Solution Chemistry of Inorganic precursors

### 3.1.1 Hydrolysis



- When dissolved in pure water, metal cations,  $M^{z+}$  often introduced as salts, are solvated by water molecules
- For  $M^{z+}$ , charge transfer occurs from the filled  $3a_1$  bonding orbital of  $H_2O$  to the empty  $d$  orbital of the  $M \rightarrow$  partial charge on the hydrogen to increase, making  $H_2O$  more acidic.
- Depending of the water acidity, the following equilibria are established, hydrolysis.



$N$  : coordination number of water molecules around  $M$

$h$  : molar ratio of hydrolysis

$h=0$ , aquo-ion,  $[MO_N H_{2N}]^{z+}$

$h=2N$ , oxy-ion,  $[MO_N]^{(2N-z)-}$

$0 < h < 2N$ ,

$h > N$ , oxo-hydroxo complex,  $[MO_x(OH)_{N-x}]^{(N+x-z)-}$

$h < N$ , hydroxo-aquo complex,  $[M(OH)_x(OH_2)_{N-x}]^{(z-x)+}$

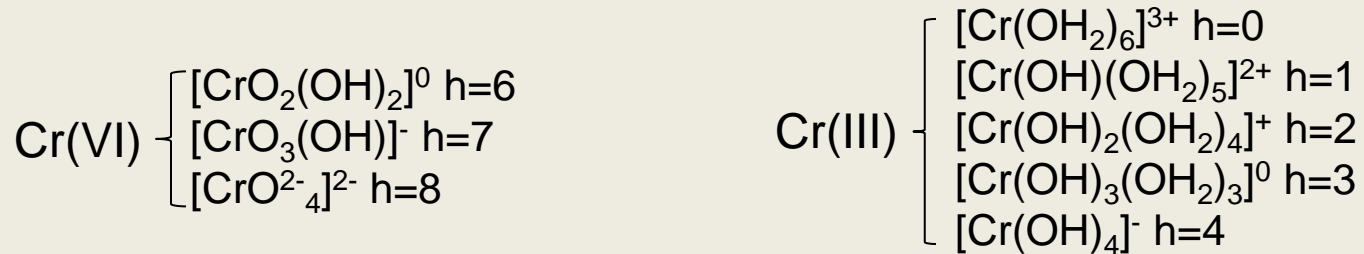
$h = N$ , hydroxo complex,  $[M(OH)_N]^{(N-z)-}$

- Hydrolysis is facilitated by increases in the charge density on the metal, the number of metal ions bridged by a hydroxo or oxo ligand, and the number of hydrogens contained in ligand.

- Hydrolysis is inhibited as the number of hydroxo ligands coordinating  $M$  increases

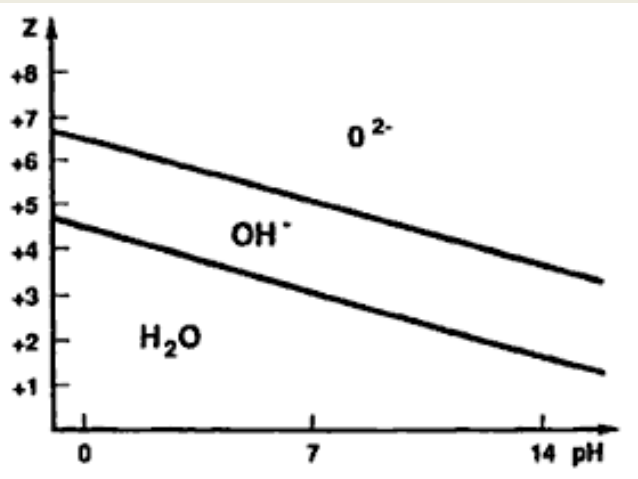
### 3. The Sol-gel Chemistry of Nonsilicate

- Only three Cr(VI) precursors have been experimentally characterized in aqueous solutions. Cr(VI) gives rise to only oxo-, hydroxo- or oxo complexes but never to aquo complexes.
- For Cr(III) however, five precursors have been reported. Cr(III) forms only aquo, aquo-hydroxo or hydroxo complexes in aqueous solutions but never oxo-complexes.



#### Effect of charge of the complex and pH of the aqueous solution

- The precise nature of the complex depends on the charge, z, coordination number, N, and electronegativity  $\chi^0_M$ , of the metal and the pH of the aqueous solution



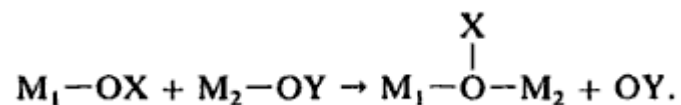
Charge vs pH diagram indicating the “aquo”, “hydroxo”, and “oxo” domains

- Hydrolysis of low-valent cations ( $z < 4$ ) yields aquo, hydroxo, or aquo-hydroxo complexes over the complete pH scale
- Hydrolysis of high-valent cations ( $z > 5$ ) yields oxo or hydroxo complexes over the same range of pH
- Tetravalent metals are on the borderline; depending on pH they can form any of the possible complexes.

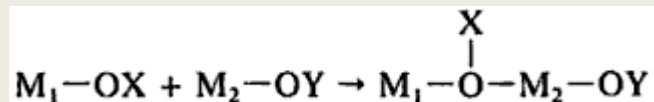
## 3. The Sol-gel Chemistry of Nonsilicate

### 3.1.2 Condensation

- Condensation can be produced by either of two nucleophilic mechanisms depending on the coordination of the metal. When the preferred coordination is satisfied, condensation occurs by nucleophilic substitution ( $S_N$ ):



- When the preferred coordination is not satisfied, condensation can occur by nucleophilic addition ( $A_N$ ):



- Oxo-ligands contained in oxy-ions ( $[MO_N]^{(2N-z)-}$ ) are good nucleophiles, but poor leaving group  $\rightarrow$  condensation occurs only by addition reactions when at least one of the reactant species is coordinatively unsaturated (maximum coordination number,  $N$ , is less than the oxidation state,  $z$ )
- Aquo-ligands in aquo-ions ( $[MO_NH_{2N}]^{z+}$ ) are good leaving group, but poor nucleophiles  $\rightarrow$  condensation does not occur, since no attacking group is present.
- Hydroxo-ions contains both good nucleophiles (O or OH) and good leaving groups ( $H_2O$  or OH). Condensation occurs as soon as one OH is present in the coordination sphere of  $M$ .
- Referring to the charge-pH diagram, it is generally necessary to be in the hydroxo domain to generate condensed species.

# 3. The Sol-gel Chemistry of Nonsilicate

## 3.1.2.1 Olation

- Olation is a condensation process in which a hydroxy bridge (“ol” bridge) is formed between two metal centers.
- For coordinatively saturated hydroxo-aquo precursors ( $h < N$ ,  $[M(OH)_x(OH_2)_{N-x}]^{(z-x)+}$ ), olation occurs by an  $S_N$  mechanism where the hydroxy group is the nucleophile and  $H_2O$  is the leaving group.

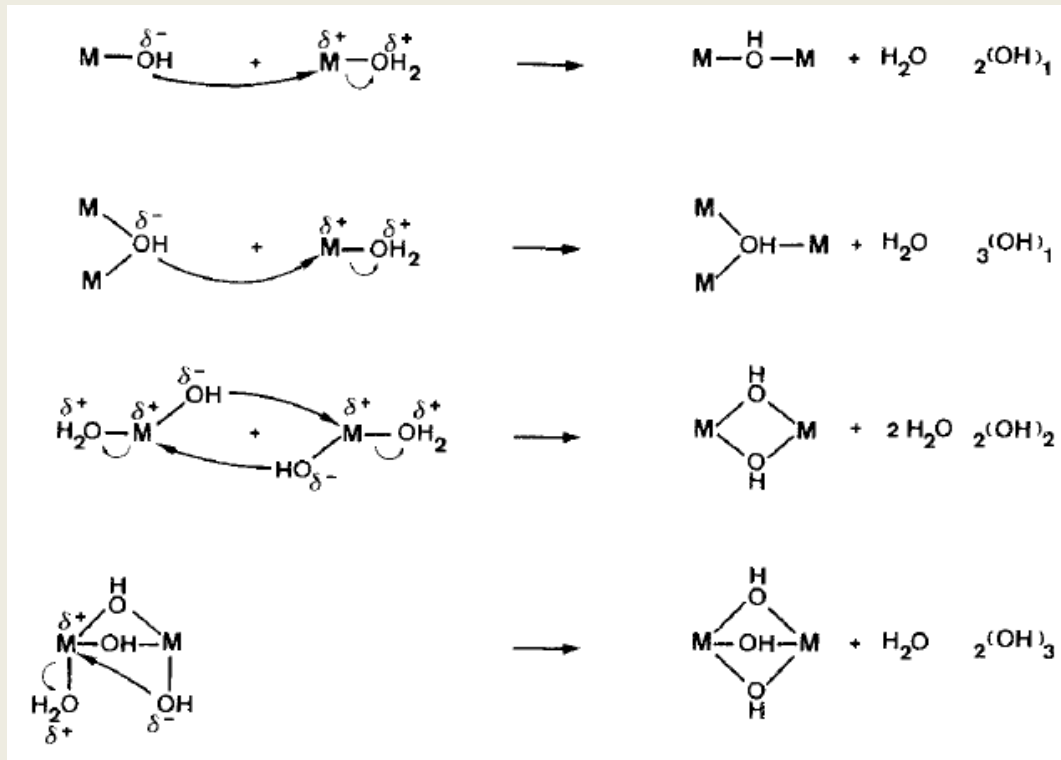


Fig. Olation mechanisms.

Several types of OH bridges can be formed as shown in Fig. where the terminology  $x(OH)_y$ , defines the number of M atoms bridged by a single OH (x) and the number of bridges formed between these x metal centers (y)

# 3. The Sol-gel Chemistry of Nonsilicate

## 3.1.2.1 Olation

- Since H<sub>2</sub>O is the leaving group, the kinetics of olation are related to the lability of the aquo ligand (ability to dissociate), which depends on size, electronegativity, and the electronic configuration of M.
- In general, the smaller the charge and the larger the size, the greater the rate of olation.

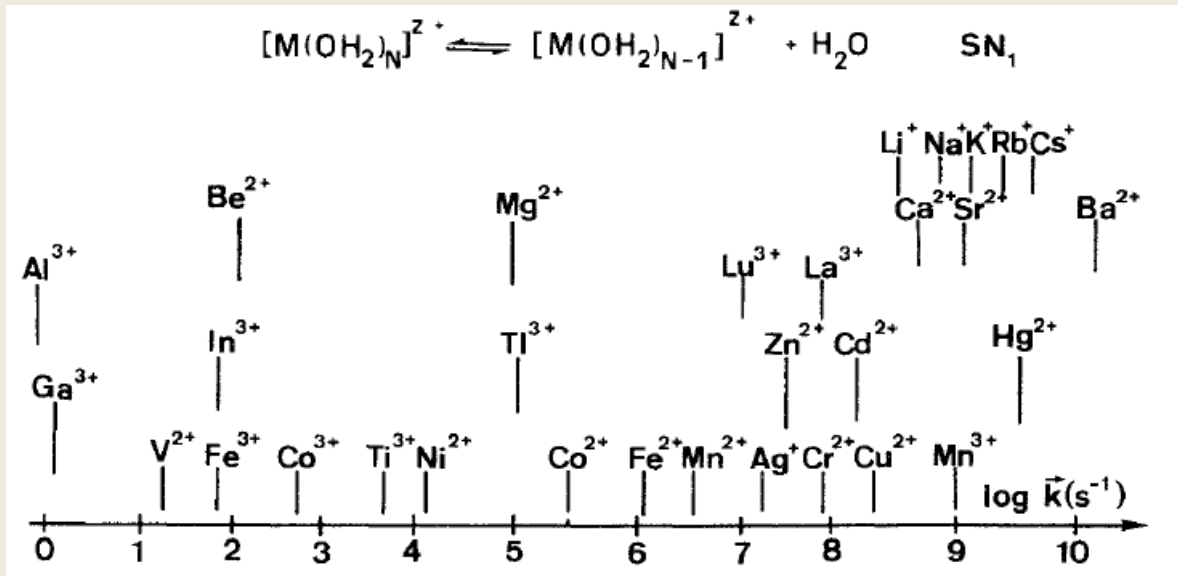


Fig. Lability of some aquo-ions ranked according to the dissociative rate constant

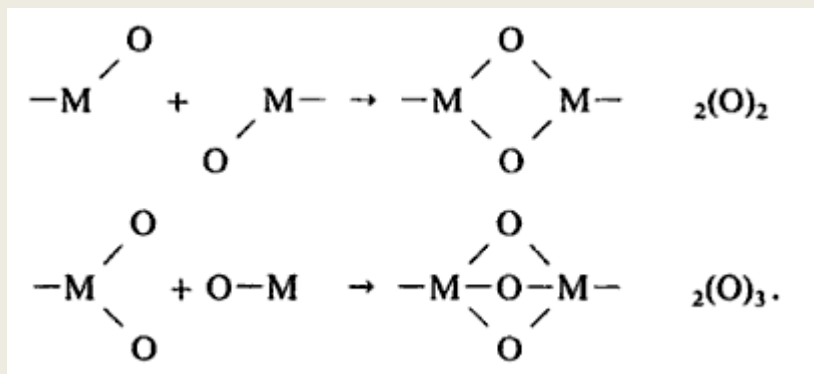
- Due to the S<sub>N</sub> mechanism, olation reactions between charged cationic precursors stop when  $\delta(OH) \geq 0$ .
- As electron-donating aquo ligands are removed during olation,  $\delta(OH)$  becomes progressively less negative, approaching zero.
- Depending on the nucleophilic power of the precursors, condensation in certain pH regimes is limited to dimers (Mn<sup>2+</sup>, VO<sup>2+</sup>, Fe<sup>3+</sup>, Ti<sup>3+</sup>, Cu<sup>2+</sup>) or tetramers (Zr<sup>4+</sup>, Hf<sup>4+</sup>, Co<sup>3+</sup>)



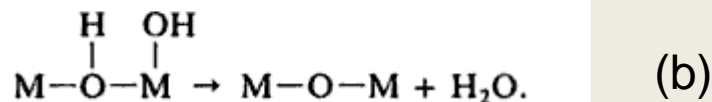
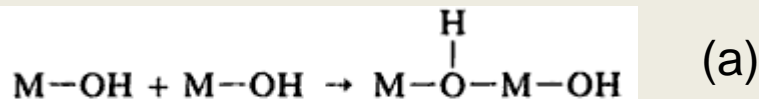
# 3. The Sol-gel Chemistry of Nonsilicate

## 3.1.2.2 Oxolation

- Oxolation is a condensation process in which an oxo- bridge is formed between two metal centers.
- When the metal is coordinatively unsaturated, oxolation occurs by nucleophilic addition ( $A_N$ ) with rapid kinetics ( $>10^5 M^{-1} s^{-1}$ ) leading to edge- or face-shared polyhedra



- For coordinatively saturated metals, oxolation proceeds by a two-step  $S_N$  reaction between oxyhydroxy precursors involving nucleophilic addition (a) followed by water elimination to form a M-O-M bond (b)



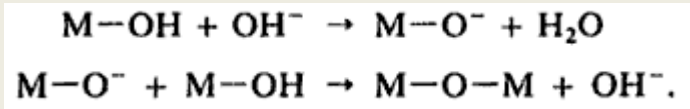
- Oxolation rather than oxolation would preferentially occur for aquohydroxy precursors containing good  $\text{H}_2\text{O}$  leaving groups.

# 3. The Sol-gel Chemistry of Nonsilicate

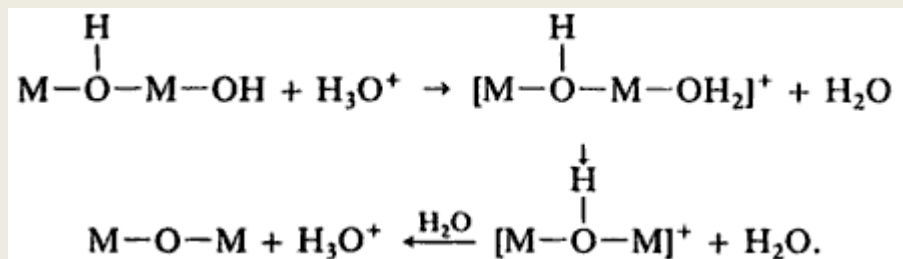


## 3.1.2.2 Oxolation

- (a) step is catalyzed by bases that deprotonate the hydroxo ligands creating stronger nucleophiles



- (b) step is catalyzed by acids that protonated hydroxo ligands creating better leaving groups.



- Thus compared to olation, oxolation occurs over a wider ranger of pH, but due to the two-step process, kinetics are slower and never diffusion-controlled.
- Generally oxolation kinetics are minimized at the isoelectic point(IEP) where  $[\text{MO}_{z-N}(\text{OH})_{2N-z}]^0$  species are predominant and hence neither step is catalyzed

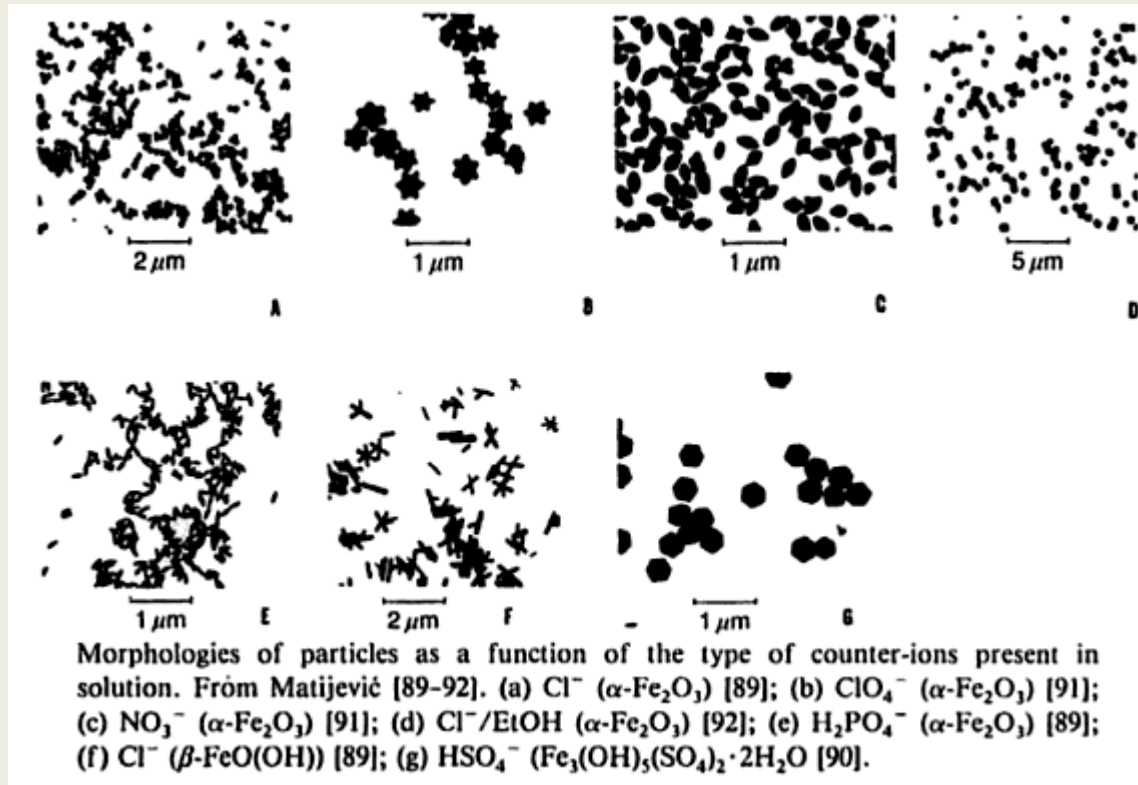




# 3. The Sol-gel Chemistry of Nonsilicate

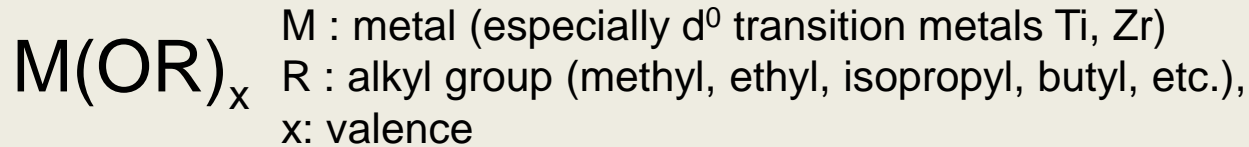
## 3.1.3 Role of the anion

- Most aqueous systems also contain counterions introduced by dissolution of inorganic salts in water. These anions compete with aquo ligands for coordination to the metal centers and strongly affect the evolving particle morphology and stability



# 3. The Sol-gel Chemistry of Nonsilicate

## 3.2 Solution Chemistry of Metal alkoxide



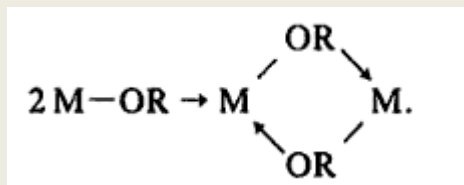
- Generally very reactive due to the presence of highly e-negative OR, stabilizing M in its highest oxidation state and rendering M very susceptible to nucleophilic attack
- # of alkyl groups depends on the valence of the metal
- Reaction rate varies throughout the process depending on the alkyl group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

## 3.2.1 Properties of Metal alkoxides

### (1) Molecular association between alkoxides

- Transition metal alkoxides dissolved in nonpolar solvents often form oligomers via alkoxy bridging, an  $A_N$  mechanism similar to olation



- In polar solvents such as alcohol, either alkoxy bridging or alcohol association can occur.
- 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  $\downarrow$

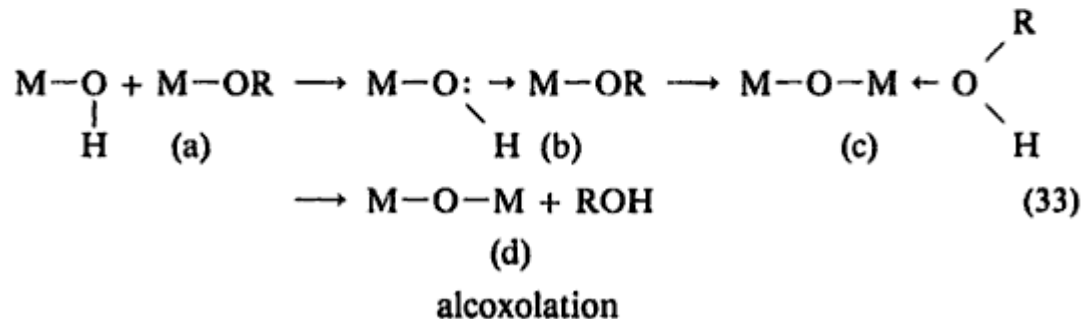
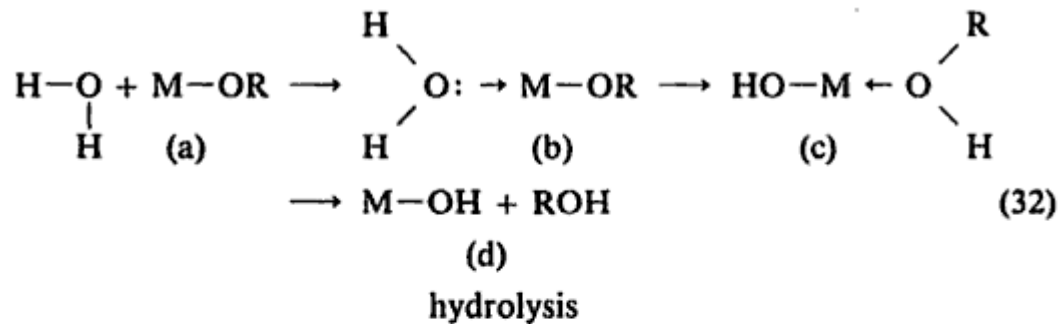
### (3) Viscosity

- 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. The Sol-gel Chemistry of Nonsilicate

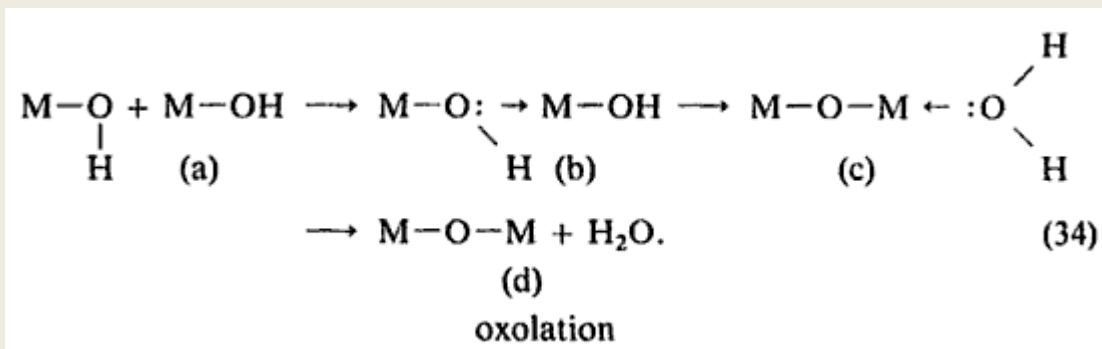
## 3.2.2 Mechanisms of Hydrolysis and Condensation

- For coordinatively saturated metals in the absence of catalyst, hydrolysis and condensation both occur by nucleophilic substitution ( $S_N$ ) mechanisms involving nucleophilic addition ( $A_N$ ) followed by proton transfer from the attacking molecule to an alkoxide or hydroxo-ligand within the transition state and removal of the protonated species as either alcohol (alcoxolation) or water (oxolation)



### 3. The Sol-gel Chemistry of Nonsilicate

#### 3.2.2 Mechanisms of Hydrolysis and Condensation



- The thermodynamics of hydrolysis, alcoxylation, and oxolation are governed by the strength of the entering nucleophile, the electrophilicity of the metal, and the partial charge and stability of the leaving group.
- These reactions are favored when  $\delta(\text{O}) \ll 0$ ,  $\delta(\text{M}) \gg 0$ , and  $\delta(\text{H}_2\text{O})$  or  $\delta(\text{ROH}) > 0$
- Alcoxylation should be the favored condensation reaction between partially hydrolyzed, coordinatively saturated metal alkoxide precursors

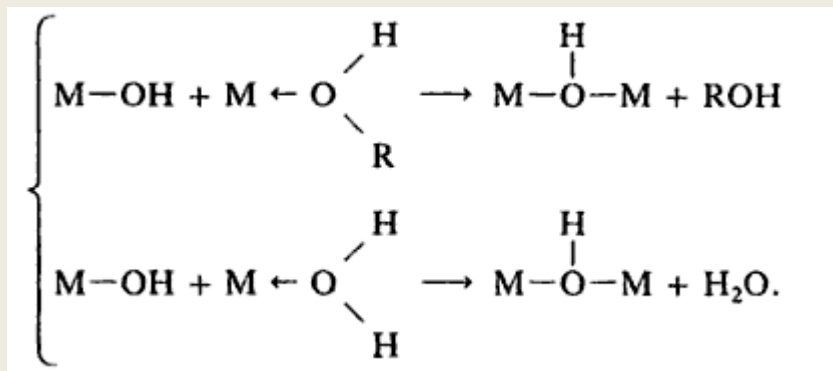


### 3. The Sol-gel Chemistry of Nonsilicate



#### 3.2.2 Mechanisms of Hydrolysis and Condensation

- When  $N - z > 0$ , condensation can occur by olation



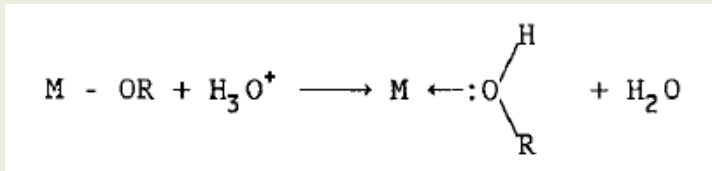
- Since the transition state involves an associative mechanism accompanied by a proton transfer, kinetics are governed by the extent of coordination under saturation of the metal,  $N - z$ , and the transfer ability of the proton.
- Larger values of  $(N - z)$  and greater acidities of the protons reduce the associated activation barriers and enhance the kinetics.
- The thermodynamics of olation depend on the strength of the entering nucleophile and the electrophilicity of the metal.
- The kinetics of olation are systematically fast because  $(N-z) > 0$  and because no proton transfer occurs in the transition state.

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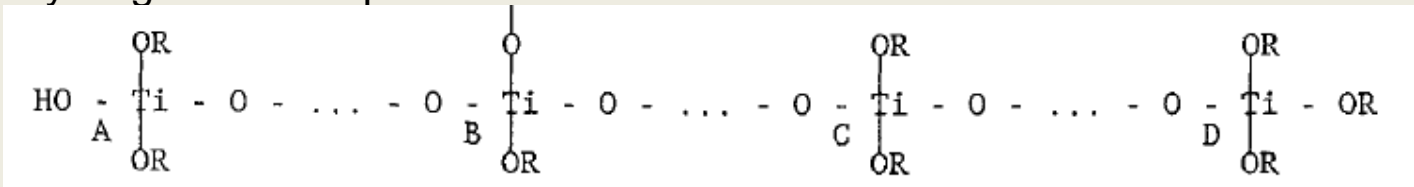
## 3.2.3 Parameters of Sol-gel process of Metal alkoxides

### 3.2.3.1 Effect of catalyst

- Acid or base catalysts can influence both the hydrolysis and condensation rates and the structure of the condensed product.
- Acids protonate negatively charged alkoxide groups, enhancing the reaction kinetics by producing good leaving groups and eliminating the requirement for H<sup>+</sup> transfer within the transition state.



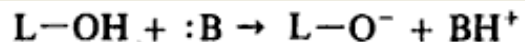
-Hydrolysis goes to completion when sufficient water is added



- The ease of protonation decreases as D >> A > C >> B, which decreases as alkoxy, hydroxo, oxo (reflects the electron providing power of ligands)
- Therefore acid-catalyzed condensation is directed preferentially toward the ends rather than the middles of chains, resulting in more extended, less highly branched polymers.
- Bases produce strong nucleophiles via deprotonation of hydroxo ligands

### 3. The Sol-gel Chemistry of Nonsilicate

-Bases produce strong nucleophiles via deprotonation of hydroxo ligands.



where L = M or H and B = OH<sup>-</sup> or NH<sub>3</sub>

-Hydrolysis rate is less in basic conditions than in acidic or neutral, because nucleophilic addition of OH<sup>-</sup> reduces δ(M)

-Condensation kinetics are systematically enhanced under basic conditions.

-The order of reactivity toward nucleophilic attack decreases as B >> C ~ A > D.

-Thus base-catalyzed condensation should be directed toward the middles rather than the ends of chains, leading to more compact, highly branched species.

#### 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. The Sol-gel Chemistry of Nonsilicate



## 3.2.3.2 Effects of the alkyl groups in the alkoxides

-The rate hydrolysis decreases with increasing size of the alkyl groups

R	$\delta(\text{Ti})$	$\delta(\text{OR})$	$\delta(\text{H})$
$\text{CH}_3$	+0.66	-0.16	+0.12
$\text{C}_2\text{H}_5$	+0.63	-0.16	+0.10
n- $\text{C}_4\text{H}_9$	+0.61	-0.15	+0.09
n- $\text{C}_6\text{H}_{13}$	+0.60	-0.15	+0.08
n- $\text{C}_9\text{H}_{19}$	+0.59	-0.15	+0.07
$\text{Ti}(\text{OR})_4$			

Charge distribution in  $\text{Ti}(\text{OR})_4$

-The positive partial charge of the metal atom M decreases with the length of the alkyl chain.  
→ The sensitivity of the alkoxide towards hydrolysis should then decrease

-The positive partial charge of the hydrogen atom decreases in the same way.  
→ Proton transfer should then become more difficult, which is an effect that could be related to the decrease of the kinetic constant

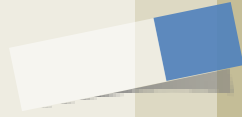
- The condensation time increases with the length of the alkyl chain

- Larger alkoxides tend to produce smaller polymeric condensations

- The use of the larger alkyl groups will be helpful for achieving nanostructured products.



## 3. The Sol-gel Chemistry of Nonsilicate



### 3.2.3.3 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

### 3.2.3.4 Effects of the hydrolysis temperature

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



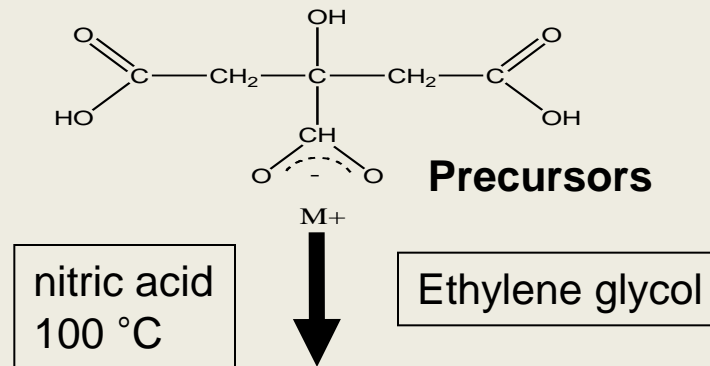
# 3. The Sol-gel Chemistry of Nonsilicate

## 3.3 Pechini processing

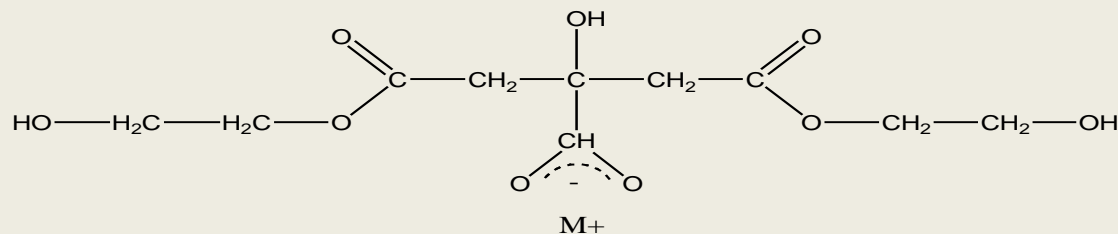
: For making multicomponent powders

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.