Sol-gel chemistry and engineering background

Solid state reactions : precursors are thoroughly ground, mixed together and heated at high temperature. This procedure has to be repeated several times until an homogeneous product is obtained. Then, the materials have to be transformed into the desired shape : *single crystal, film, fiber, fine powder*…

Sol-gel synthesis : a new approach to the preparation of glasses and ceramics :

■ the **metal-organic route** with metal alkoxides in organic solvent

■ the **inorganic route** with metal salts in aqueous solution (chloride, oxychloride, nitrate..) : much cheaper and easier to handle than metal alkoxides, but their reactions are more difficult to control

1 – General mechanisms in the metal-organic route

Based on the growth of **metal oxo polymers** in a solvent

- inorganic step polymerization reactions through hydrolysis and condensation of metal alkoxides $M(OR)_Z$, where M = Si, Ti, Zr, Al, Sn, Ce…, OR is an alkoxy group and Z is the valence or the oxidation state of the metal
- first step : hydroxylation upon the **hydrolysis** of alkoxy groups :

$$\text{M-OR} + H_2O \rightarrow \text{M-OH} + \text{ROH}$$

- second step : polycondensation process leading to the formation of branched oligomers and polymers with a metal oxo based skeleton and reactive residual hydroxo and alkoxy groups ; 2 competitive mechanisms :

- **oxolation** : formation of oxygen bridges :

$$\text{M-OH} + \text{XO-M} \rightarrow \text{M-O-M} + \text{XOH}$$

where X = H, generally when **hydrolysis ratio h** = $H_2O/M >> 2$
or X = R, when h = $H_2O/M < 2$

- **olation** : formation of hydroxo bridges when the coordination of the metallic center is not fully satisfied (N - Z > 0) :

$$\text{M-OH} + \text{HO-M} \rightarrow \text{M-(OH)}_2\text{-M} \quad \text{where X = H or R}$$

The kinetics of olation are usually faster than those of oxolation

➢ formation of a metal oxo macromolecular network :

- a **sol** where the polymerized structures do not reach macroscopic sizes
- a **gel** when the recombination of the metal oxo polymers can produce bushy structures which invade the whole volume inside which the solvent, reaction by-products and free polymers are trapped
- a **precipitate** when the reactions produce dense rather than bushy structures

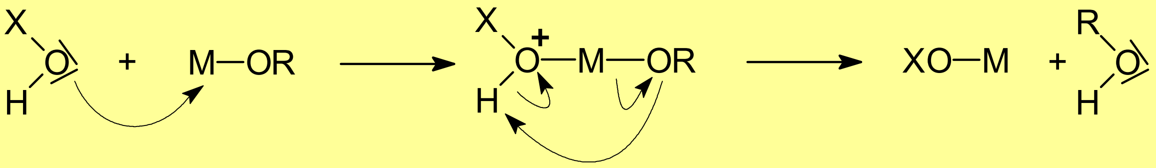
Depending on the control of the structures of these oxo polymers through

- the hydrolysis ratio h
- the use of catalysts, complexing ligands or nucleophilic reagents
- the steric hindrance of the alkoxy groups
- the nature of solvents
- the temperature

2 – Chemical reactivity of metal alkoxides

$$M(OR)_n \ + \ m\ XOH \ \rightarrow \ [M(OR)_{n-m}(OX)_m] \ + \ m\ ROH$$

where X stands for H (hydrolysis), M (condensation) or L (complexation by an organic ligand L)



oxidation state :	**Z**	**Z-1**	**Z**
coordination number :	**N**	**N+1**	**N**

Consequently, the chemical reactivity of metal alkoxides toward nucleophilic reactions mainly depends on :

- the strength of the nucleophile
- the electrophilic character of the metal atom (an electronegativity-related property characterized by the positive charge on the metal atom)
- its ability to increase its coordination number N : the degree of unsaturation of the metal coordination can be simply expressed by the difference N - Z, where N is the coordination number usually found in the oxide and Z is the oxidation state

alkoxides	χ	partial charge δ	ionic radius (Ă)	oxide	N	N - Z
$Si(OPr^i)_4$	1.74	+ 0.32	0.40	SiO_2	4	0
$Sn(OPr^i)_4$	1.89		0.60	SnO_2	6	2
$Ti(OPr^i)_4$	1.32	+ 0.60	0.64	TiO_2	6	2
$Zr(OPr^i)_4$	1.29	+ 0.64	0.87	ZrO_2	7	3
$Ce(OPr^i)_4$	1.17	+ 0.75	1.02	CeO_2	8	4

For similar alkoxy groups OR :

$$Si(OR)_4 \lll Sn(OR)_4$$

$$\text{and} \quad Ti(OR)_4 < Zr(OR)_4 < Ce(OR)_4$$

- **silicon** : relatively low electrophilicity and N - Z = 0 ; thus, silicon alkoxides are not very reactive : hydrolysis-condensation reaction rates must be increased by catalysts
- **tin** : higher electrophilic power and higher degree of unsaturation N – Z
- **titanium, zirconium and cerium** : lower electronegativity, but very high degree of unsaturation N – Z

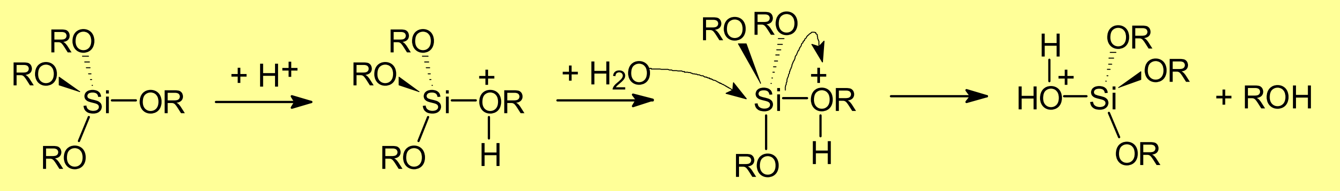
Hydrolysis and condensation reactions of non-silicate metal alkoxides must be controlled by using chemical additives

a) reactivity of silicon alkoxides (N = Z = 4)

SN_2 mechanism : involving a hypervalent silicon transition state (penta- or hexacoordinated metallic center)

- the rates of hydrolysis and condensation increase under pressure without affecting the distribution of hydrolyzed or condensed species
- the reactivity of silicon alkoxides decreases when the size of the alkoxy group increases because of steric hindrance factors

Under acidic conditions (e.g. with mineral acids), the hydrolysis reaction is speeded up more efficiently than the condensation reaction :

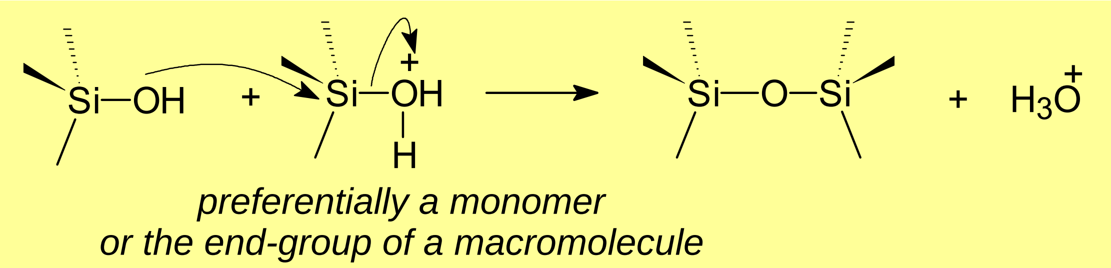


protonation of the alkoxo group, making alcohol a better leaving group

Condensation involves the attack of silicon atoms carrying protonated silanol species by neutral ≡Si-OH nucleophiles

- acidic conditions further the formation of protonated silanol species, but inhibit some nucleophiles

- the most basic silanol species (the most likely to be protonated) are those contained in monomers or weakly branched oligomers :



preferentially a monomer
or the end-group of a macromolecule

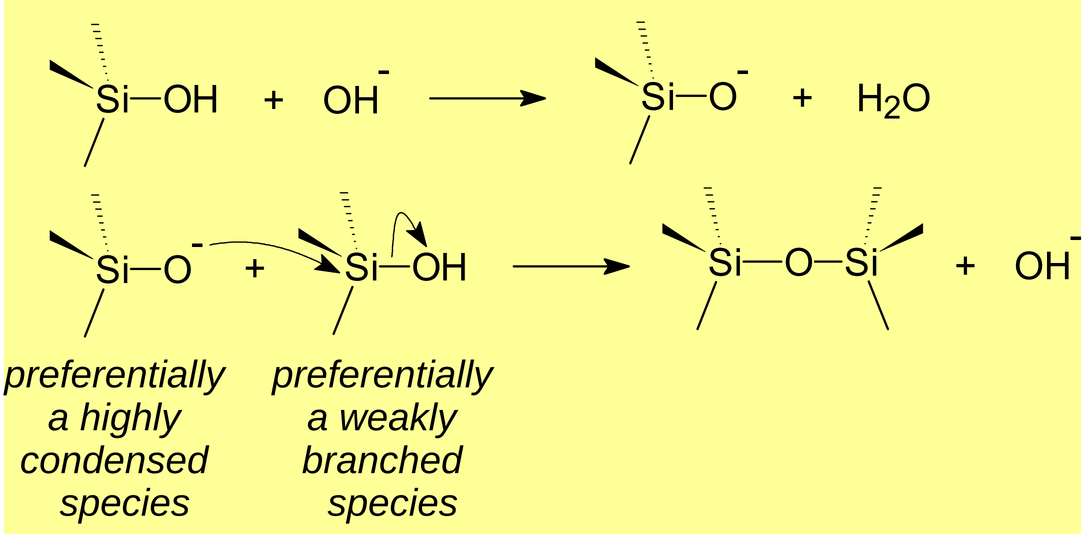
So a bushy network of weakly branched polymers is obtained

Under basic conditions (e.g. with ammonia), hydroxyl anions (OH^-) and deprotonated silanol ($\equiv Si\text{-}O^-$) are better nucleophiles than water and silanol species

- a fast attack at the silicon atom and both hydrolysis and condensation reactions occur simultaneously

The condensation involves the attack of a deprotonated silanol ($\equiv Si\text{-}O^-$) on a neutral siloxane species

- the acidity of silanol increases when -OH or -OR groups are replaced with -O-Si≡ groups because of the reduced electron density on Si atom



preferentially a highly condensed species

preferentially a weakly branched species

The result of basic catalysis is an **aggregation** (monomer-cluster) that leads to more compact highly branched silica networks, that are not interpenetrable before drying and thus behave as discrete species

The nucleophilic activation by Lewis bases (dimethylaminopyridine, *n*-Bu_4NF, NaF…) is also efficient for both hydrolysis and condensation reactions, which occur simultaneously as for basic catalysis

- reversible formation of a pentavalent intermediate with F^- that stretches and weakens the surrounding ≡Si-OR bonds
- the positive charge of the silicon atom increases, rendering the silicon atom more prone to nucleophilic attack

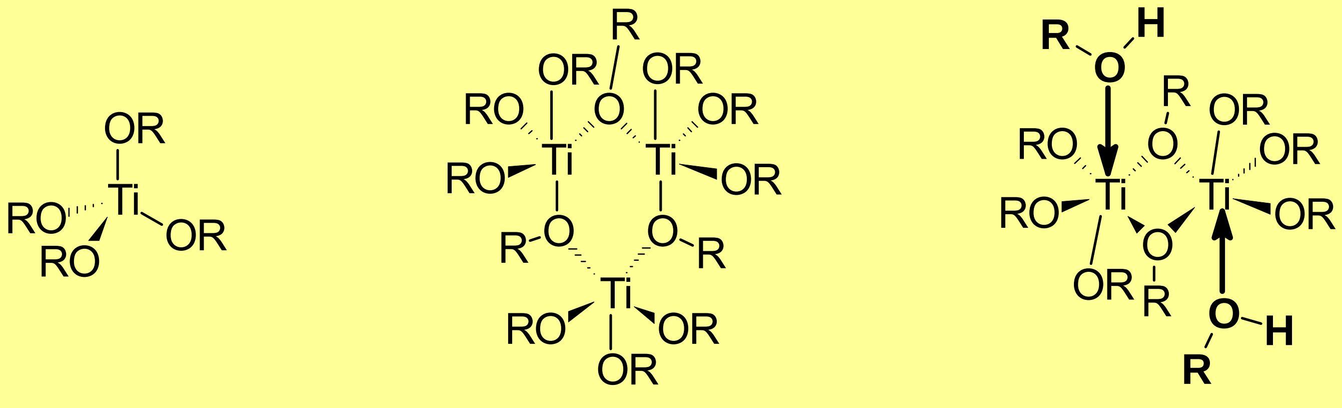
Highly branched silica networks are obtained.

b) reactivity of non-silicate tetravalent alkoxides (Z = 4)

Very sensitive to moisture, they must handled with care under a dry atmosphere otherwise precipitation occurs

Coordination expansion : self regulation of their reactivity by increasing the number of coordinating molecules using their vacant orbitals to accept electrons from nucleophilic ligands

- occurs by alkoxy bridging or solvation :



monomer

trimer
in pure benzene

dimer
in alcohol

- the molecular complexity depends on concentration, temperature, solvent, oxidation state of the metal, steric hindrance of the alkoxy groups

- it increases with the atomic size of the metal atom and decreases with increasing bulkiness of the OR groups
- in non-polar solvents, the molecular complexity of alkoxides is higher than in their parent alcohol, and therefore their hydrolysis reaction is slower and leads to the formation of clear gels

Control of the reactivity with inhibitors : **inorganic acids**, **β-diketones**, **carboxylic acids** or other complexing ligands which inhibit condensation reactions and therefore prevent precipitation, force the growth to a gel state or stop growth

ex : **acetylacetone** (AcacH) leads to less hydrolyzable M-Acac bonds : molecular clusters, chain polymers or colloidal particles depending on

- the hydrolysis ratio h = H_2O/M
- the complexation ratio x = Acac/M

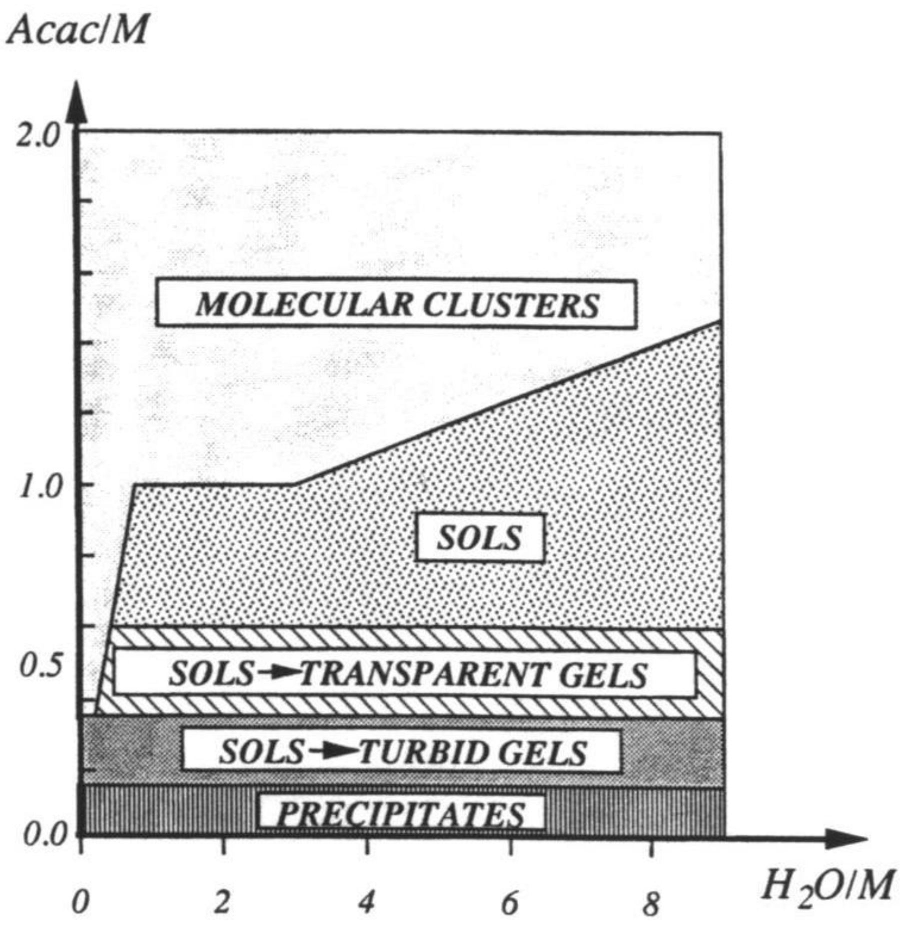


Figure 1 : State diagram describing the hydrolysis-condensation behavior of complexed tetravalent metal alkoxides

c) reactivity of different metal alkoxide combinations

Phase separation : ex : $Ti(OBu)_4$ generally reacts rapidly with water and precipitates out of the reaction mixture before it can react with $Si(OEt)_4$ network

- allowing $Si(OEt)_4$ species to prehydrolyse in the presence of water and an acid catalyst. Then, fast-reacting $Ti(OBu)_4$ is added ; it quickly hydrolyzes and at least partially condenses into the preexisting immature $Si(OEt)_4$-based network

3 – Gelation, aging, drying and firing

We focus on the mechanisms in silicate systems

a) gelation

Under acid catalyzed conditions : **« polymeric » gel**

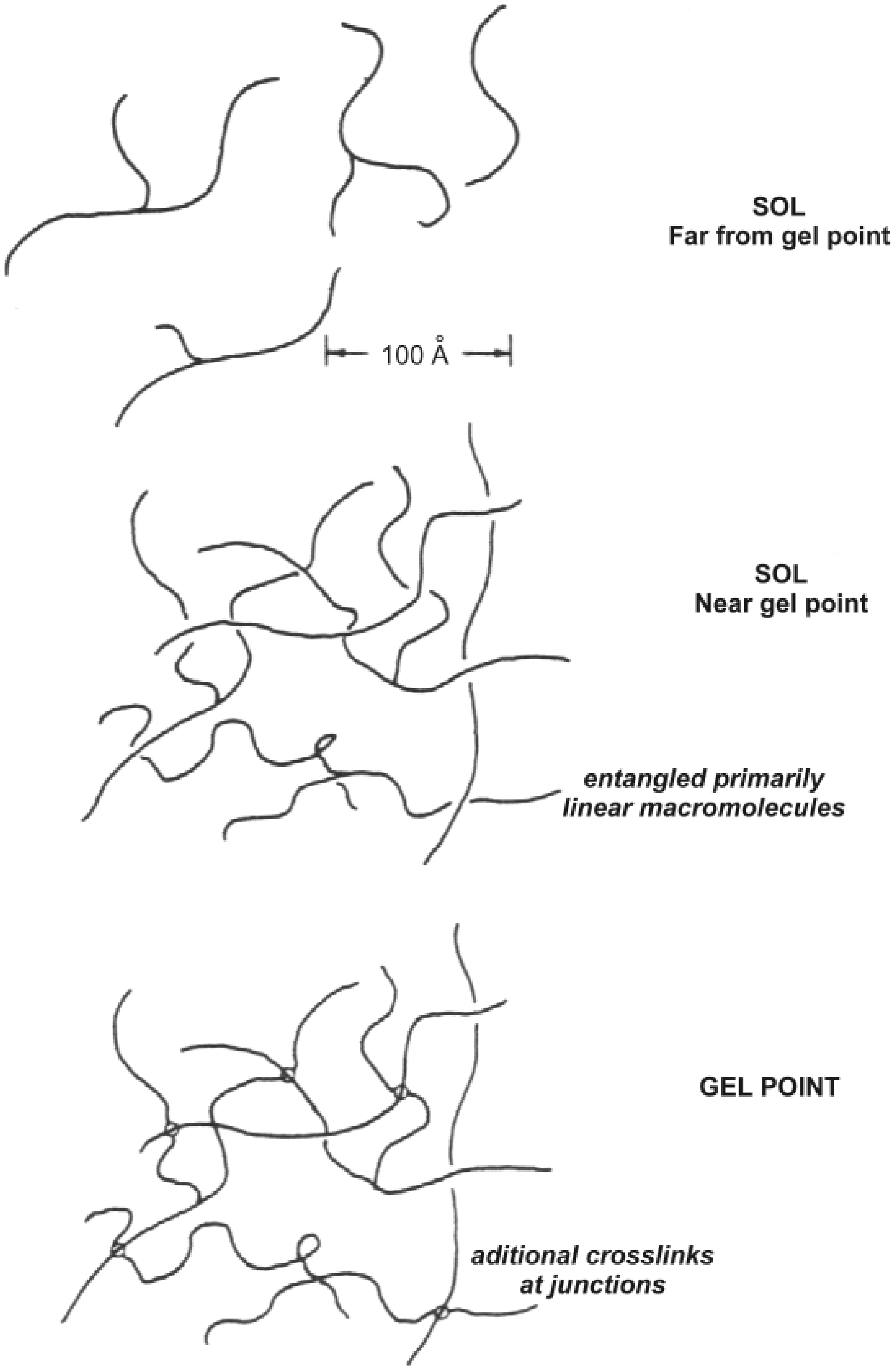


Figure 2 : Polymer growth and gel formation in acid-catalyzed systems (polymeric gel)

Under basic conditions and/or with higher additions of water (e.g. h ≥ 7) : more highly branched clusters which do not interpenetrate prior to gelation and thus behave as discrete species.

If the total concentration of alkoxysilane is low (< ~0.3 M) gelation leads to the formation of **colloidal silica** (Stöber process).

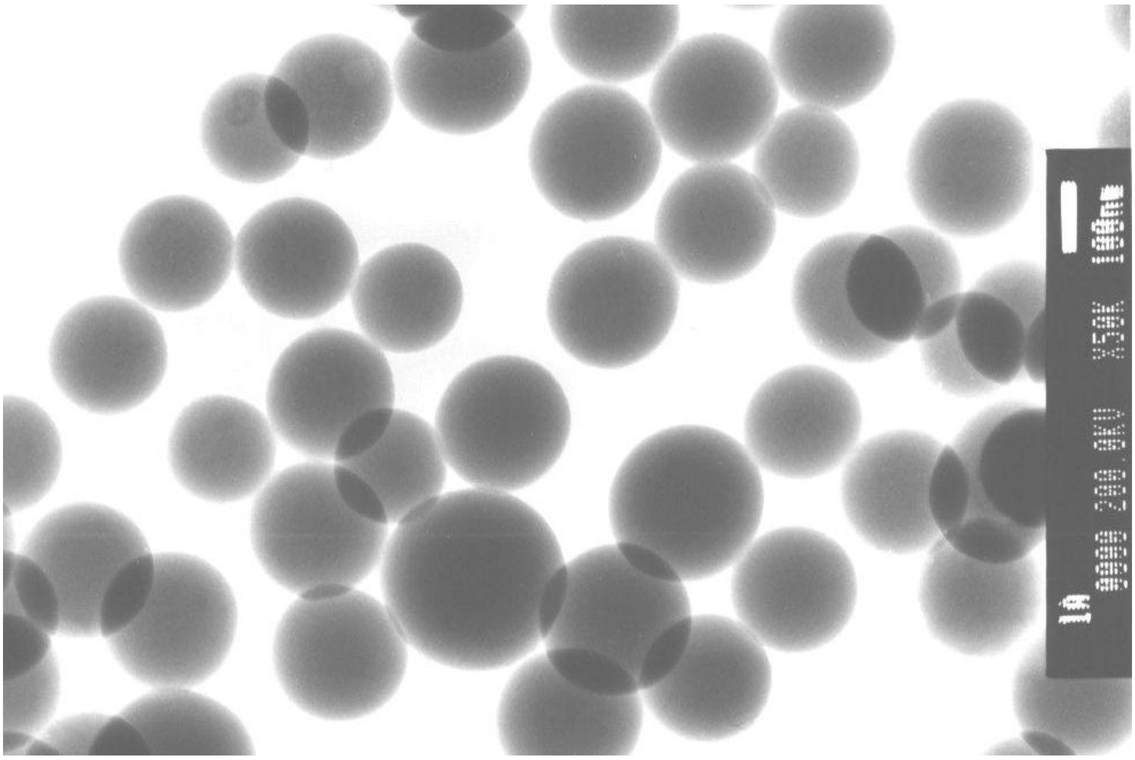


Figure 3 : TEM imaging of colloidal silica obtained through Stöber process

But for higher alkoxysilane concentrations : **« colloidal » gel**

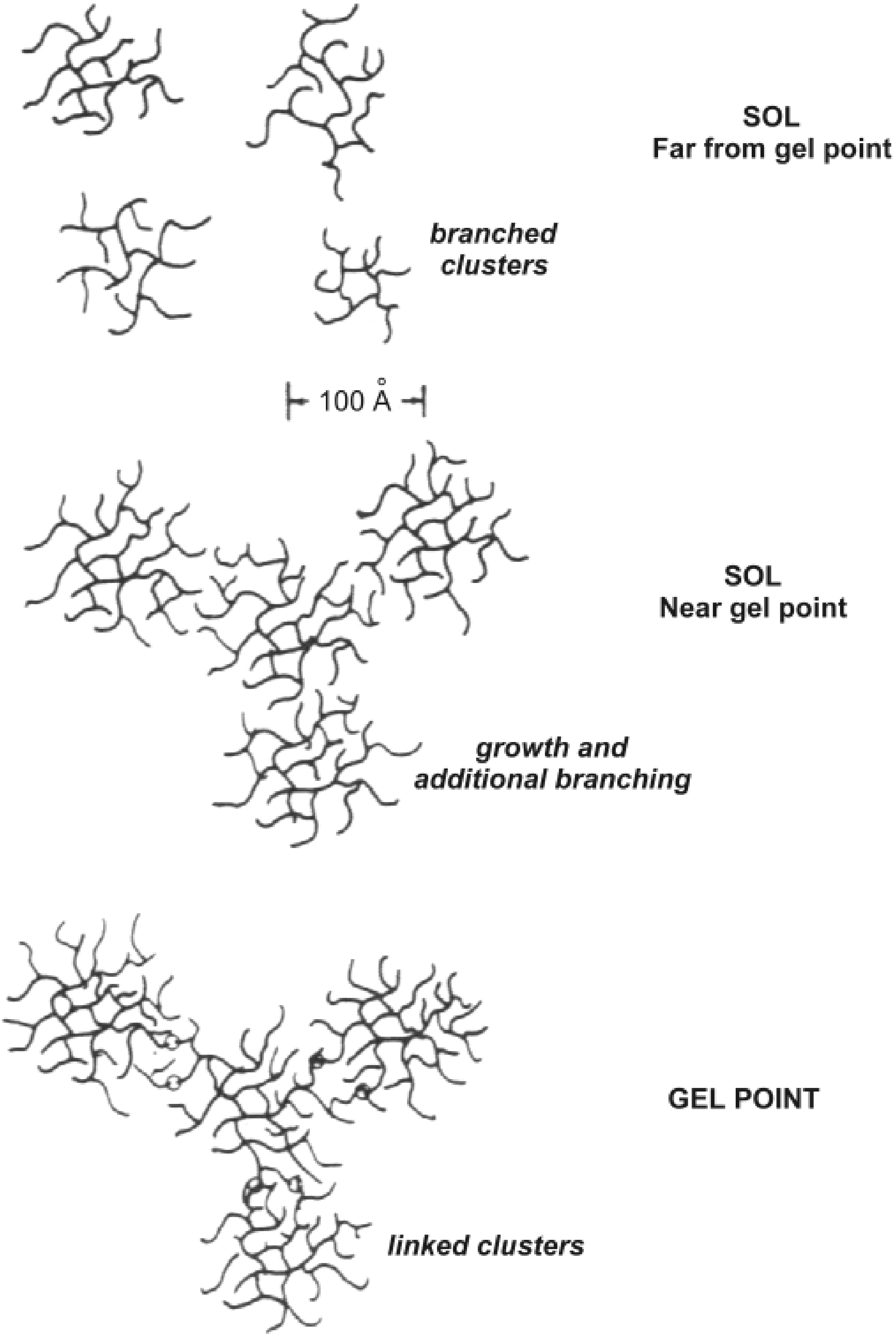


Figure 4 : Polymer growth and gel formation in base-catalyzed systems (colloidal gel)

b) aging

Gelation : freezing in a particular structure (i.e. may be considered as a rapid solidification process)

Aging : structure modifications with time depending on temperature, solvent and pH conditions

- ➢ gel separation into regions of high and low polymer density because it is expected that as the critical point is approached (e.g. during a change in concentration), fluctuations in polymer density grow larger in amplitude (than those resulting merely from thermal motions)
- ➢ promotion of additional crosslinking as unreacted terminal groups (OH and OR) come in contact in regions of higher polymer density
- ➢ acceleration of the **phase separation** process and creation of **liquid-solid interfaces**
- ➢ further structural changes attributed primarily to surface energy effects : it is well known that surfaces exhibiting positive radii of curvature dissolve more readily than surfaces exhibiting negative radii of curvature. Therefore as the dissolution rate is increased (e.g. by increased temperature or pH) dissolution-redeposition results in **neck formation** causing the gel structure to become **fibrillar** and the **pore formation**. Of course, when dissolution is extensive, the gel network would break down and ripen to form a colloidal sol.

c) drying (or desiccation)

Drying : removing of the solvent phase

Method influenced by the intended use of the dried material :

■ if **powdered ceramics** are desired, no special care need be exercised to prevent fragmentation

■ if **monoliths from colloidal gels** are desired, the drying procedures are largely determined by the need to minimize internal stresses associated with the volume changes on drying and the capillary forces in the gel pores :

- during the initial stages of drying, the volume change of the gel is equal to the volume of evaporated liquid. The gel network is still flexible and can rearrange to accommodate the decreasing volume. All pores are filled with solvent and liquid-air interfaces are not present
- as drying proceeds, the gel network becomes more restricted and the removal of liquid leads to the formation of such interfaces and the development of capillary stresses : the capillary pressure ΔP developed in a cylindrical capillary of radius r partially filled with a liquid of wetting angle θ, can be expressed by :

$$\Delta P = 2\gamma\cos\theta/r$$

where γ is the surface tension. The development of cracks in a drying gel is shown on figure 5 :

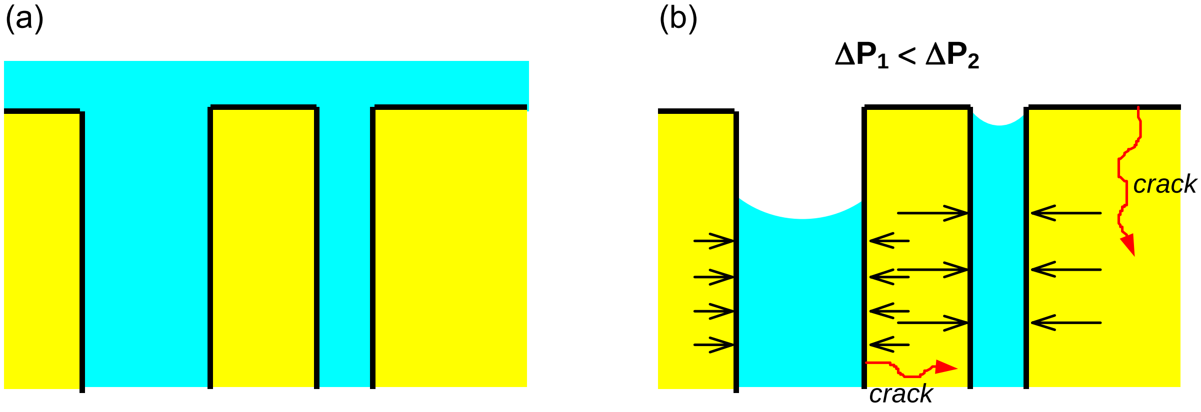


Figure 5 : Formation of differential strains at the pores during drying : (a) before and (b) after the onset of capillary forces.

When evaporation leads to the formation of menisci, the different radii of the pores cause unequal capillary pressures to generate differential stresses $\sigma_1 < \sigma_2$. If the stress difference $\sigma_2 - \sigma_1$ locally exceeds the strength of the gel network, a crack will result. The tendency toward fragmentation is thus determined by both the average pore size and the pore size distribution.

- ➢ generally, fractures associated with excessive capillary forces can be reduced or eliminated by :
  - ■ strengthening the gel by reinforcement
  - ■ enlarging the pores
  - ■ reducing the surface tension of the liquid with the use of surfactants
  - ■ making the interior surfaces hydrophobic
  - ■ evacuating the solvent by freeze-drying
  - ■ operating under **hypercritical conditions** : effected by heating the gel with methanol in an autoclave to temperatures and pressures exceeding the critical point of methanol (240°C/8.1MPa). A slow evacuation (3-4 hr) was followed by flushings with dry argon to eliminate the last traces of alcohol. This method produces dried gels with much larger pore volumes (**aerogels** : porosity of ~85 %, specific surface area of 250-600 $m^2.g^{-1}$ and pore size of 250-1250 Å) than conventional evaporative drying (**xerogels** : pore size $\leq$ 20 Å). Because of the absence of the liquid-vapor interfaces, no capillary forces arise to cause network collapse and shrinkage during drying

■ if **monoliths from polymeric gels** (such as those obtained by the acid catalysis of silicon alkoxide at low water contents) are desired : the polymeric species are weakly crosslinked and as solvent is removed, they can deform readily and form a dense gel structure while polymer itself shrinks and forms more crosslinks

- ➢ dense dried gel with no large voids

d) firing

Firing : heating to convert the dried gel to a dense ceramic. For silica gels, the following reactions occur :

- desorption of physically adsorbed solvent and water from the walls of micropores (100-200°C)
- decomposition of residual organic groups into CO_2 (300-500°C)
- collapse of small pores (400-500°C)
- collapse of larger pores (700-900°C)
- continued polycondensation (100-700°C)

■ if **powdered ceramics** are desired, no special care need be exercised to prevent fragmentation. Attention must, however, be directed to the removal of organics to avoid undesirable bloating, foaming or blackening

■ if **monolithic ceramics** are desired, special care must be taken to ensure complete removal of water, organic groups or decomposition products, prior to micropore collapse to avoid the development of stresses leading to fragmentation

- for the production of large monoliths of SiO_2, polycondensation has to be completed prior to pore collapse
- with non-optimized firing schedules, residual organic groups and H_2O can lead to blackening and fragmentation, as well as to the formation of bloated and foamed samples (in cases where **foams** are desired, specific agents such as urea can be used in forming the gel)

Sintering and densification phenomena also take place, via typical sintering mechanisms such as evaporation condensation, surface diffusion, grain boundary and bulk diffusion. The small particle size of the powders lead to high reactivities and enhanced sintering and/or coarsening rates (the principal process involved in densification is often viscous sintering)

4 – Applications and limitations of sol-gel techniques

a) advantages

Sol-gel processes allow the synthesis of ceramics of

- **high purity**, because organometallic alkoxy precursors can be purified by distillation or recrystallisation
- **high degree of homogeneity**, because reagents are mixed at the molecular level
- **low or high porosity**, by using appropriate heat treatment and firing times

The veritable explosion of interest in this area seems to result in large measure from the perceived technological opportunities :

- the ability to prepare glasses of materials which cannot be obtained as amorphous solids by cooling from the liquid state
- the capability of obtaining fully-dense amorphous solids at temperatures lower by hundreds of centigrade degrees than those required for conventional compaction/densification or for melting
- the possibility of obtaining fully-dense crystalline ceramics which cannot be prepared by conventional powder processing
- the ability to obtain materials with novel distributions of phases contained therein...

b) drawbacks

- **high cost** for the majority of alkoxide precursors
- **long processing times**
- **volatiles production**
- **shrinkage**
- development of stresses leading to **fragmentation**

c) applications

■ **novel glasses** produced from gel precursors in three ways :

- **melting gel-derived powders** : gel-derived powders are used as batch ingredients for glass melting primarily because of the high degree of chemical homogeneity which they offer. This leads to shorter melting times and lower melting temperature as well as compositional uniformity
- **sintering or hot pressing gel derived powders** : the key to glass formation is the development of an appropriate heat treatment schedule to remove the residual organic groups and achieve pore collapse without inducing crystallization in the sample
- **heat treating gels to produce monoliths** (already described)

The physical properties of gel-derived glasses are usually closely similar to those of glasses obtained from the melt. The most attractive feature is the development of novel glass compositions : $CaO-SiO_2$ or $Na_2O-ZrO_2-SiO_2$ with high ZrO_2 content, which simply cannot be obtained from the melt because the cooling rate must be very high to avoid detectable crystallization.

■ **fibers** : using appropriate hydrolysis conditions, continuous fibers may be drawn from solutions of metal alkoxides and converted to glass fibers by heating (ex : ZrO_2-SiO_2 or $Na_2O-ZrO_2-SiO_2$). Fibers can also be prepared by extruding gelled solutions (colloidal as well as polymeric gels) through dies of appropriate diameter (ex : polycrystalline alumina, microcrystalline $Al_2O_3-Cr_2O_3-SiO_2$, mullite $3Al_2O_3 \bullet 2SiO_2$, aluminum borosilicate $3Al_2O_3 \bullet B_2O_3 \bullet 3SiO_2$)

■ **abrasives** : after gelation and drying, the material is crushed (a simple process with frangible dried gel) and sized. The sized powders are then fired. In this way, Al_2O_3 abrasive particles with uniformly dispersed ZrO_2 particles and a very fine grain size (< 300 nm) can be obtained. Such abrasive particles have superior grinding performance compared with fused or sintered Al_2O_3-based abrasives in a number of applications

■ **thin films and coating** : the permissible drying rates, consistent with the avoidance of fracture, were evaluated and found to vary inversely with the thickness of the body being dried. This limitation leads naturally to the main use of gels in **coating applications**, where the thickness are small and the drying rates can be correspondingly high. Four techniques are mainly used for film deposition onto substrates :

- **dipping** (the most widely used), where the part to be coated is withdrawn from a solution. The faster the substrate is withdrawn, the thicker the deposited film

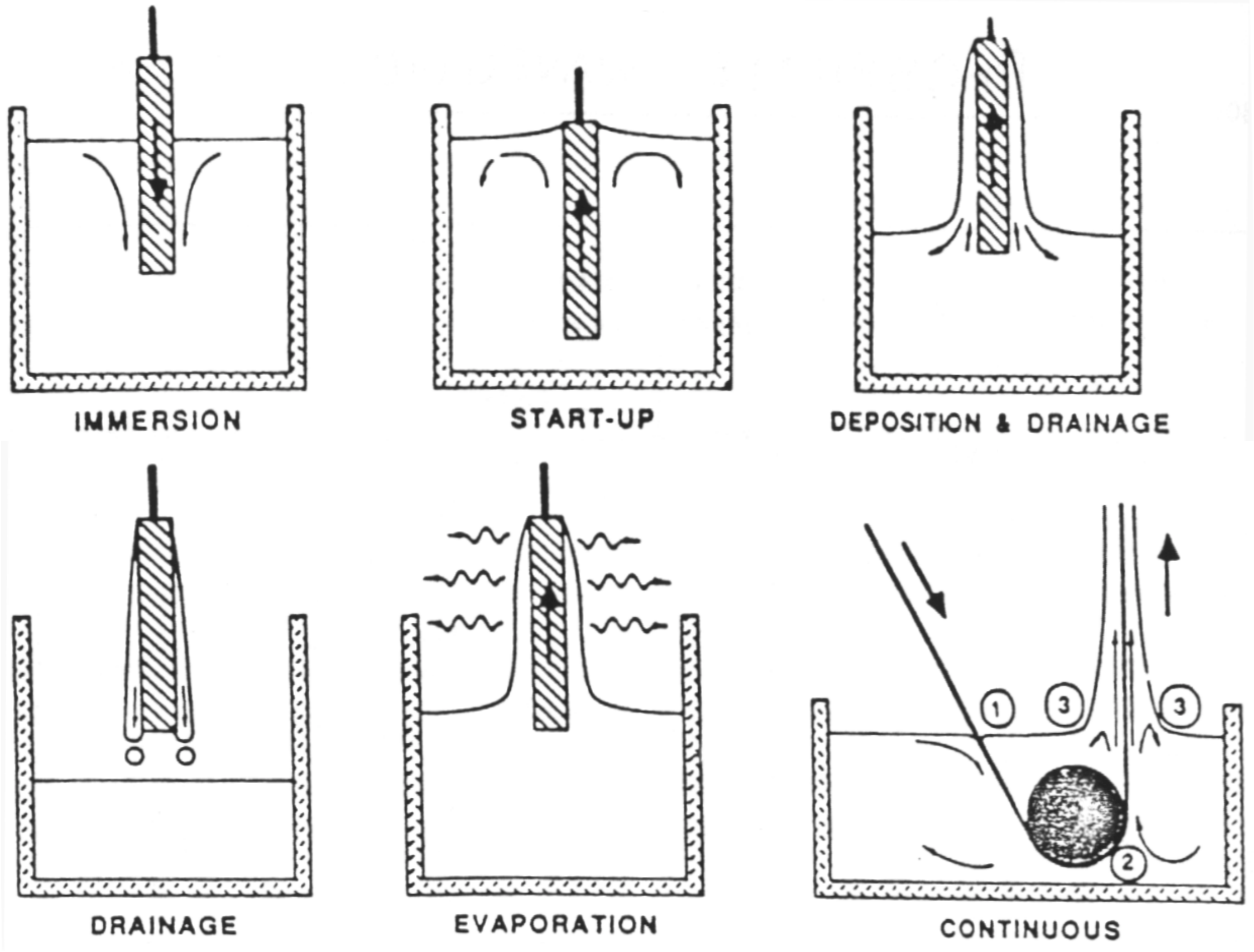
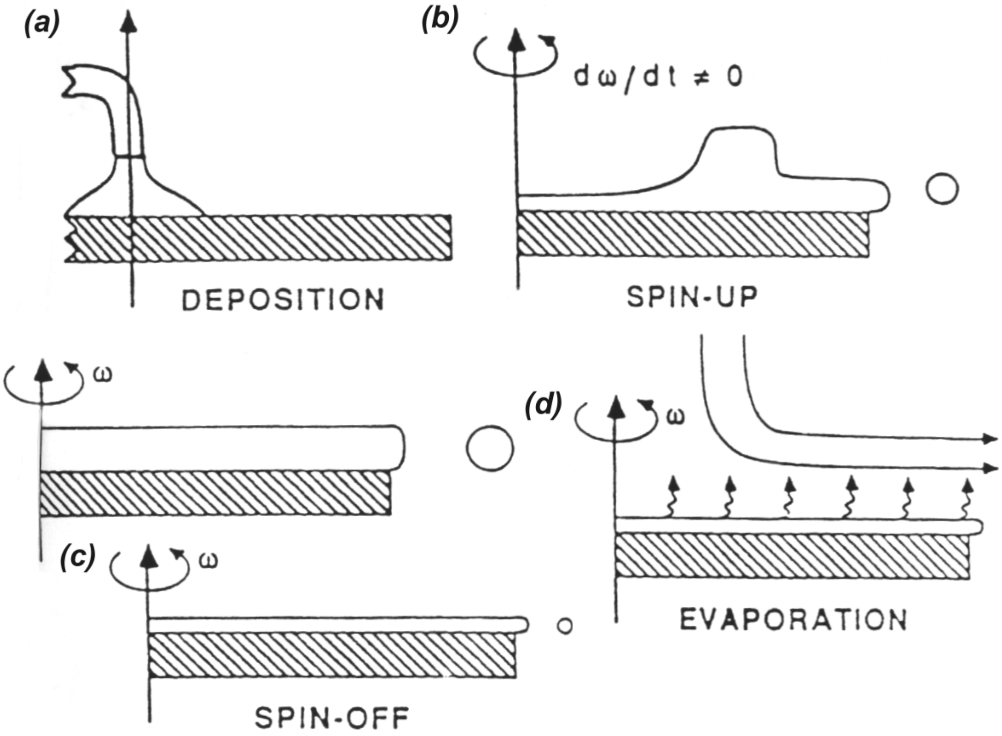


Figure 6 : Industrial dip-coating system

- **lowering**, where the object remains at rest and the liquid level is lowered
- **spinning**, where the liquid film is spread out by spinning the wetted surface. Advantages : the uniform thickness of the film due to the spin-off stage and the deposition onto small substrate from a small quantity of sol



● **spraying**, where the surfaces are sprayed with fine disperse solutions. This process has difficulty in maintaining strict tolerances and is thus used mostly for protective coatings.

Some of the coating-type applications which seem well-suited for sol-gel techniques include :

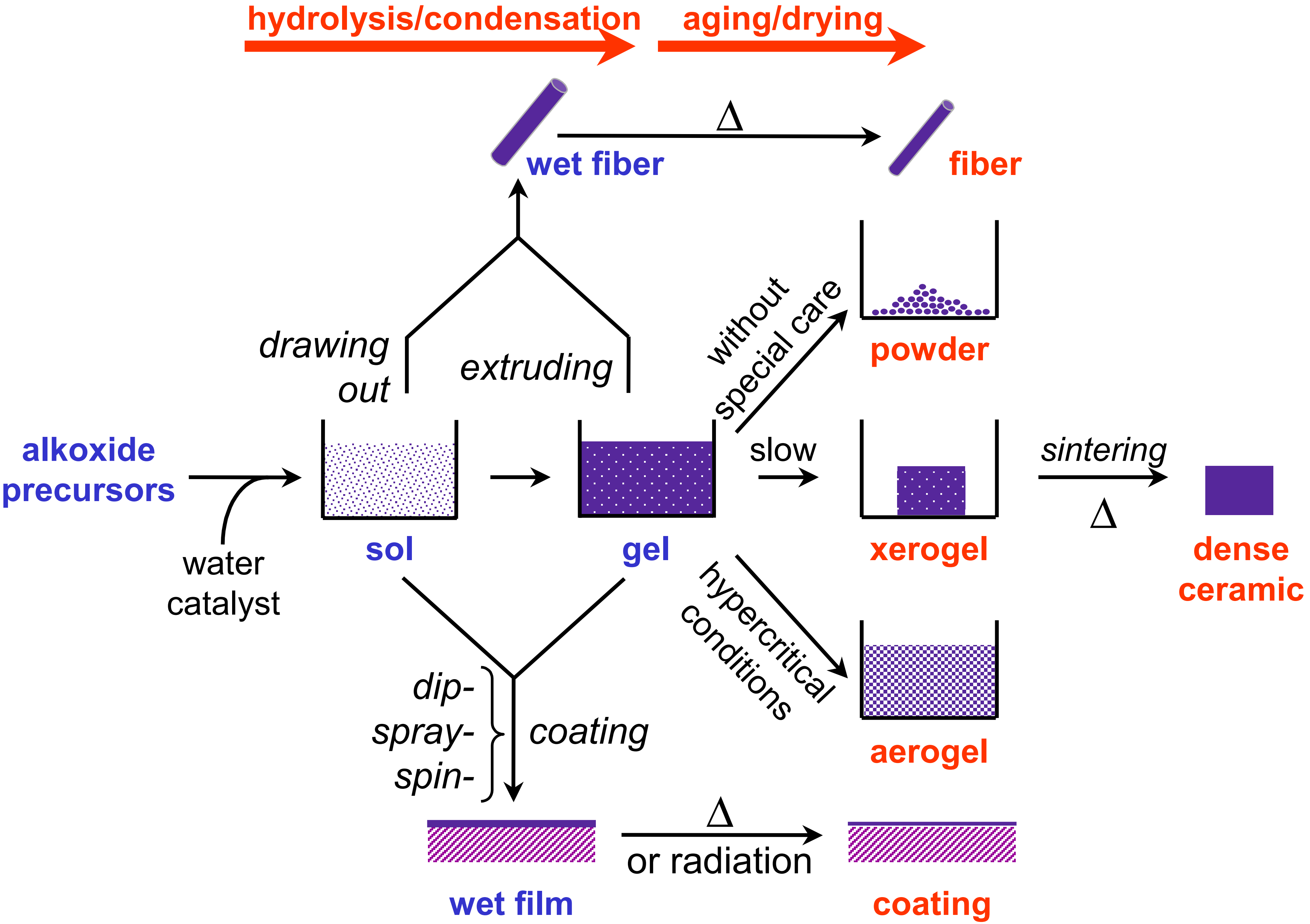
- ■ **antireflection coatings** (single layer or multilayer films)
- ■ **absorbing coatings**
- ■ **filters** for lighting and optical purposes
- ■ **semiconducting coatings**
- ■ **protective layers** (both chemical and thermal)
- ■ **independent films**, prepared by
  - ➢ pouring alkoxide solutions onto liquids which do not mix with the solution and allowing the film to hydrolyze
  - ➢ pouring the solution onto non-wetting surfaces such as Teflon
  - ➢ forming films using wire rings with solutions of appropriate viscosity

d) conclusion

Sol-gel chemistry is still in its infancy and a better understanding of the basic inorganic polymerization chemistry has still to be reached before a real mastery of the process can be obtained.

Nevertheless this low temperature processing may be exploited. **As a result, the incorporation of organic materials into sol-gel-derived oxides becomes possible**

summary of sol-gel process, techniques and products



hydrolysis/condensation → **aging/drying** →

wet fiber —Δ→ **fiber**

drawing out

extruding

alkoxide precursors

water
catalyst

sol → **gel**

without special care → **powder**

slow → **xerogel** —*sintering* Δ→ **dense ceramic**

hypercritical conditions → **aerogel**

dip-
spray-
spin-
coating

wet film —Δ or radiation→ **coating**

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