

Sol-Gel methods

The sol-gel process may be described as:

”Formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid.”

A **sol** is a **stable dispersion of colloidal particles or polymers in a solvent**. The particles may be amorphous or crystalline. An aerosol is particles in a gas phase, while a sol is particles in a liquid,

A **gel** consists of a **three dimensional continuous network**, which encloses a liquid phase, In a colloidal gel, the network is built from agglomeration of colloidal particles. In a polymer gel the particles have a polymeric sub-structure made by aggregates of sub-colloidal particles. Generally, the sol particles may interact by van der Waals forces or hydrogen bonds. A gel may also be formed from linking polymer chains. In most gel systems used for materials synthesis, the interactions are of a covalent nature and the gel process is irreversible. The gelation process may be reversible if other interactions are involved.

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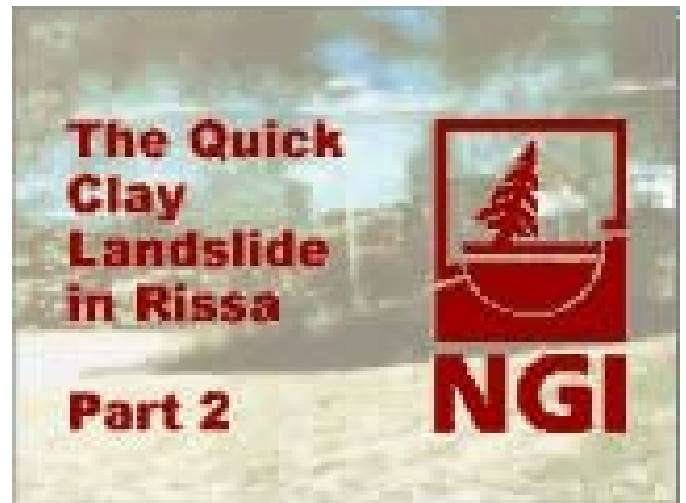
- The idea behind sol-gel synthesis is to “dissolve” the compound in a liquid in order to bring it back as a solid in a controlled manner.
- Multi component compounds may be prepared with a controlled stoichiometry by mixing sols of different compounds.
- The sol-gel method prevents the problems with co-precipitation, which may be inhomogeneous, be a gelation reaction.
- Enables mixing at an atomic level.
- Results in small particles, which are easily sinterable.

The sol-gel method was developed in the 1960s mainly due to the need of new synthesis methods in the nuclear industry. A method was needed where dust was reduced (compared to the ceramic method) and which needed a lower sintering temperature. In addition, it should be possible to do the synthesis by remote control.

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One of the well known examples of a sol-gel system often cited is quick clay. Clay may form a sol (quick clay) if it is washed sufficiently to remove the counter ions. Quick clay may be gelled if enough counter ions are added, so that the colloidal particles aggregate. (exfoliation/restacking may be involved)

Landslide in Rissa, 1978



Sol-gel synthesis may be used to prepare materials with a variety of shapes, such as porous structures, thin fibers, dense powders and thin films.

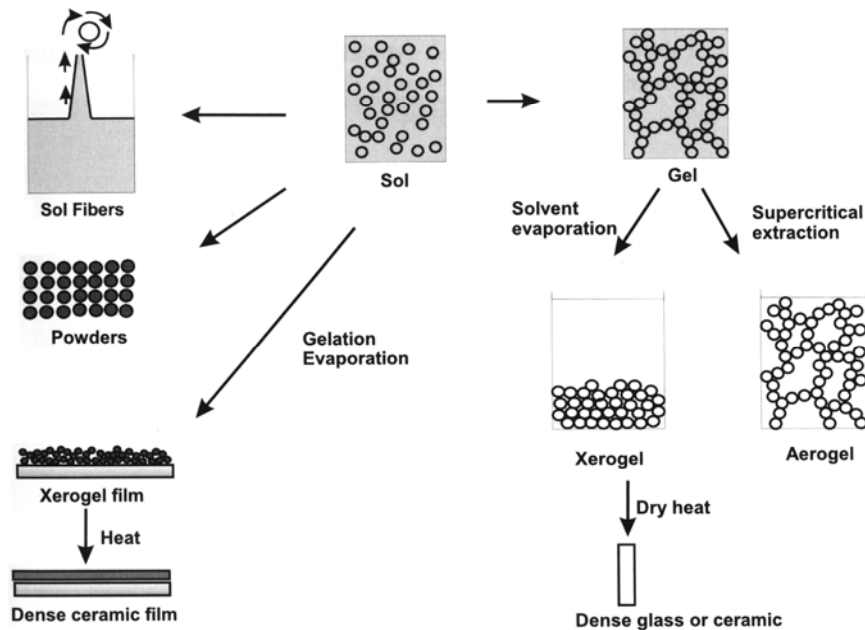


Figure 4-42. Sol-gel processing options.

If the gel is dried by evaporation, then the capillary forces will result in shrinkage, the gel network will collapse, and a xerogel is formed.

If drying is performed under supercritical conditions, the network structure may be retained and a gel with large pores may be formed. This is called an aerogel, and the density will be very low. A record is $< 0.005 \text{ g/cm}^3$.

Physical properties of silica aerogels

Property	Value	Comments
Apparent Density	0.003-0.35 g/cm ³	Most common density is ~0.1g/cm ³
Internal Surface Area	600-1000 m ² /g	As determined by nitrogen adsorption/desorption
% Solids	0.13-15%	Typically 5% (95% free space)
Mean Pore Diameter	~20 nm	As determined by nitrogen adsorption/desorption (varies with density)
Primary Particle Diameter	2-5 nm	Determined by electron microscopy
Index of Refraction	1.0-1.05	Very low for a solid material
Thermal Tolerance	to 500 C	Shrinkage begins slowly at 500 C, increases with inc. temperature. Melting point is >1200 C
Coefficient of Thermal Expansion	2.0-4.0 x 10 ⁻⁶	Determined using ultrasonic methods
Poisson's Ratio	0.2	Independent of density. Similar to dense silica.
Young's Modulus	10 ⁶ -10 ⁷ N/m ²	Very small (<10 ⁴ x) compared to dense silica
Tensile Strength	16 kPa	For density = 0.1 g/cm ³ .
Fracture Toughness	~0.8 kPa*m ^{1/2}	For density = 0.1 g/cm ³ . Determined by 3-point bending
Dielectric Constant	~1.1	For density = 0.1 g/cm ³ . Very low for a solid material
Sound Velocity Through the Medium	100 m/sec	For density = 0.07 g/cm ³ . One of the lowest velocities for a solid material

Applications and properties of aerogels



Example of a ceramics fiber (PZT) made from sol-gel methods

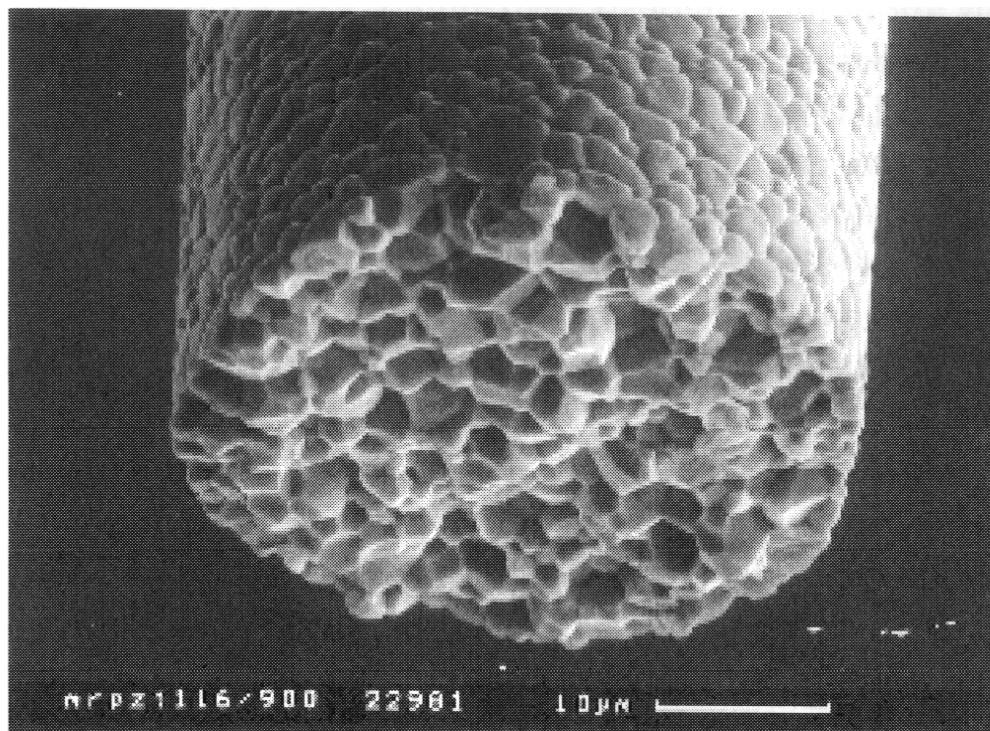
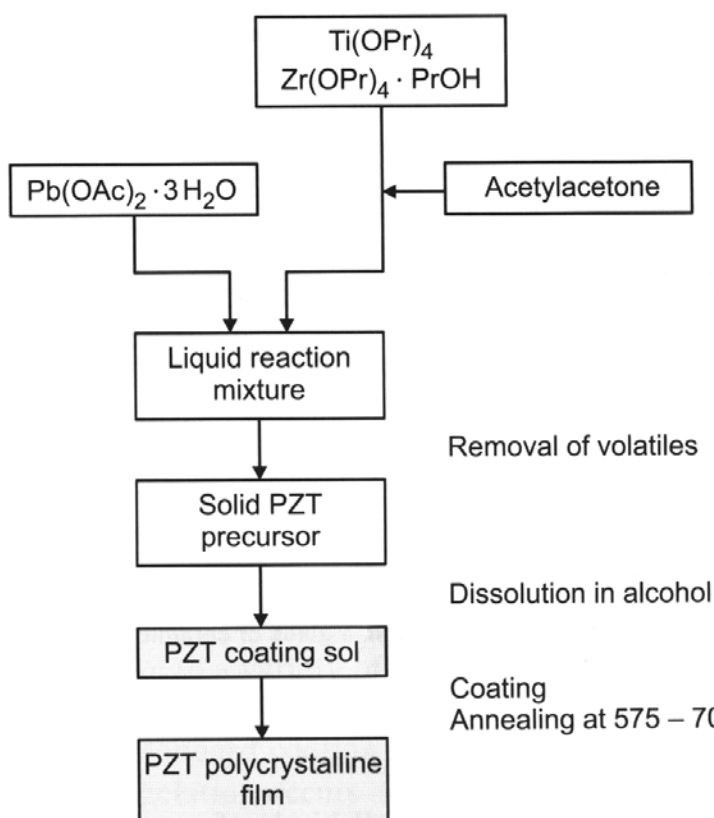


Figure 4-45. Cross-section of a dense, polycrystalline PZT fiber with the composition $\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$. The grain size (▶ glossary) is 2–4 μm .

PZT, $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$



There are many application of sol-gel synthesis

The method may provide good control over stoichiometry and reduced sintering temperature. This is especially important if one of the components are volatile. May also enable production of low temperature phases.

PZT ($\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$) is a very important material. The largest piezoelectric response is obtained for $x = 0.47$. The stoichiometry is difficult to control be the ceramic method, where heating at $575 - 700 \text{ }^\circ\text{C}$ for several hours is needed.

Figure 4-43. Processing steps for the preparation of polycrystalline PZT films.

Sol

A sol consists of a liquid with colloidal particles which are not dissolved, but do not agglomerate or sediment.

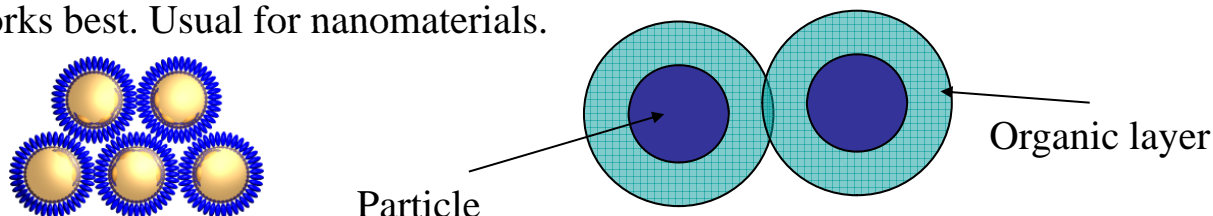
Agglomeration of small particles are due to van der Waals forces and a tendency to decrease the total surface energy. Van der Waals forces are weak, and extend only for a few nanometers.

In order to counter the van der Waals interactions, repulsive forces must be established.

May be accomplished by:

Electrostatic repulsion. By adsorption of charged species onto the surface of the particles, repulsion between the particles will increase and agglomeration will be prevented. Most important for colloidal systems.

Steric hindrance. By adsorbing a thick layer of organic molecules, the particles are prevented from approaching each other reducing the role of the van der Waals forces. Works best in concentrated dispersions. Branched adsorbates works best. Usual for nanomaterials.



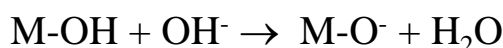
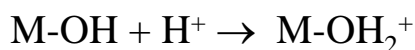
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PZC, Point of zero charge

Stabilization due to electrostatic repulsion are due to formation of a double layer at the particle.

The surface of a particle is covered by ionic groups, which determines the surface potential. Counter ions in the solution will cover this layer, shielding the rest of the solution from the surface charges.

For hydroxides the surface potential will be determined by reactions with the ions H^+ and OH^- . Thus, the surface potential is pH dependent.



The pH where the particle is neutral is called PZC, point of zero charge.

For $pH > PZC$ the surface is **negatively** charged

For $pH < PZC$ the surface is **positively** charged.

Typical values: **MgO 12, Al₂O₃ 9.0, TiO₂ 6.0, SnO₂ 4.5, SiO₂ 2.5**

Depends somewhat on the size of the particle and the degree of condensation

The size of the surface potential ϕ_0 depends on the difference between pH and PZC.

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Double layer

Double layer for a positively charged surface

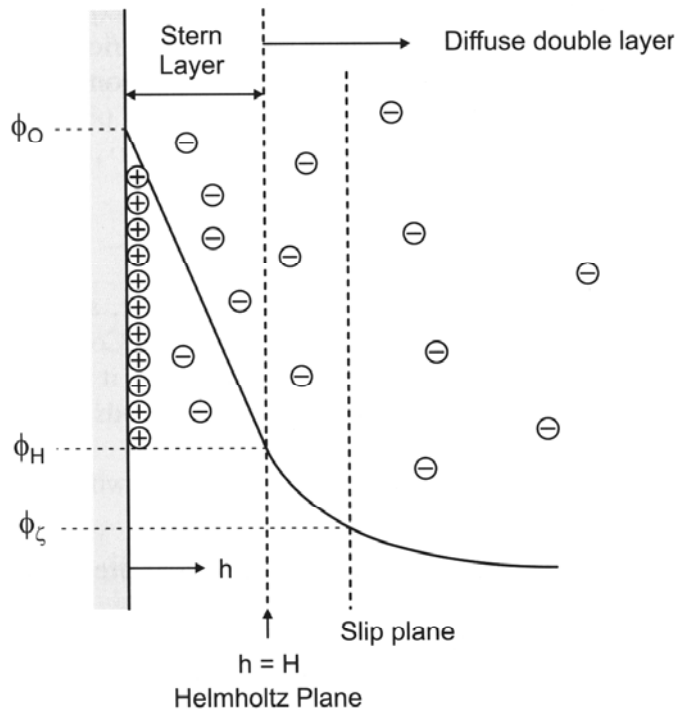


Figure 4-47. Electric double layer over a positively charged surface. h is the distance to the particle surface and V_R the repulsive potential.

In an electric field the particle will move toward the electrode with the opposite charge. It will carry the adsorbed layer and part of the counter ions.

The “slip plane” divides the part that moves with the particle and the solution. The potential at the slip plane is called the zeta (ζ) potential ϕ_ζ .

The pH for which $\phi_\zeta=0$ is called the isoelectrical point (IEP)

The stability of a colloid depends on ϕ_ζ ; the larger the ϕ_ζ the more stable the colloid. Should be $> 30\text{-}50\text{ mV}$.

Given the same surface potential, the repulsive forces will increase with the particle size.

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Coagulation/flocculation

Coagulation of a sol may occur if:

The surface potential (ϕ_0) is lowered (by changing pH)

By increasing the number of counter ions. An increase in the concentration of counter ions result in a decrease of the thickness of the double layer.

In some cases a coagulated colloid may be re-dispersed. This is called “**peptizing**” This is done e.g. by removing the surplus counter ions by washing, or by adding charged ions, so that the double layer is restored.

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Silicates

Silicates form gels easily because it is not very electropositive and not susceptible to nucleophilic reactions.

A sol-gel process occur in several steps:

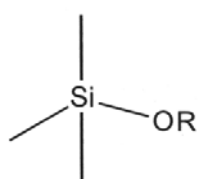
- Hydrolysis and condensation of molecules. Formation of a sol.
- Gelation (sol-gel transformation)
- Ageing.
- Drying.



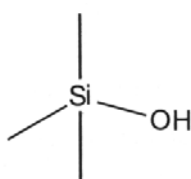
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Hydrolysis and condensation

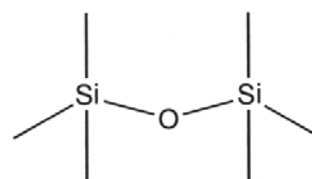
The starting point for formation of a silica gel may be alkoxides or silanols. These are reacted to siloxane groups.



Alkoxide

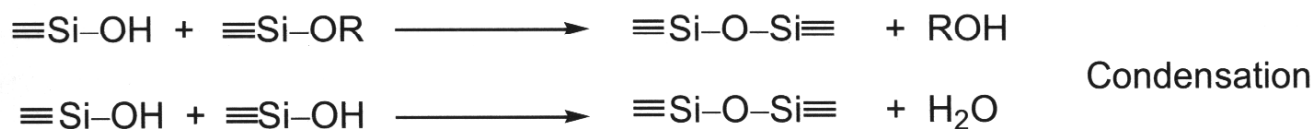


Silanol



Siloxane

Figure 4-48. Silicon–oxygen groups relevant to sol–gel processing.



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Silica gel

The starting materials for formation of silica gels are usually “water glass”, Na_2SiO_3 , or silicon alkoxides (e.g. $\text{Si}(\text{OMe})_4$). The differences are:

- Water glass is dissolved in water while the alkoxide is dissolved in an organic solvent, usually alcohol.
- The reactive groups in water glass are silanol. In the alkoxide system, a hydrolysis reaction occur, converting Si-OR to Si-OH . Gelation therefore starts with a change in pH (in water based systems) or by addition of water (in alcohol based systems).
- The alkoxide systems are more complex with more parameters. This may result in better control of the reactions.

Two reaction paths; acidic and basic environments:

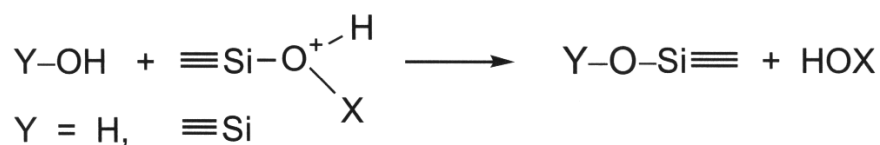
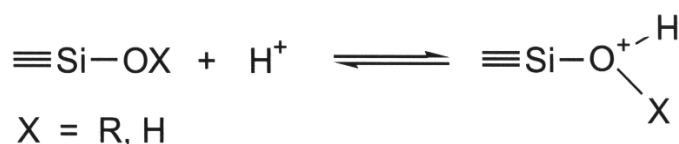
At $\text{pH} < \text{PZC}$ the species are positively charged

At $\text{pH} > \text{PZC}$ the species are negatively charged

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Reactions in acidic environments

The oxygen atom in Si-OH or Si-OR is protonated and H-OH or H-OR are good leaving groups. The electron density are shifted from the Si atom, making it more accessible for reaction with water (hydrolysis)) or silanol (condensation)



hydrolysis reaction: $\text{X} = \text{R, Y} = \text{H}$

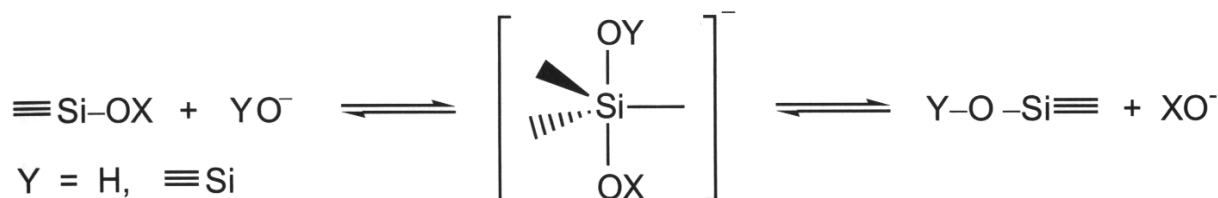
condensation reaction: $\text{X} = \text{R or H, Y} = \text{Si}\equiv$

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Reactions in basic environments

Nucleophilic attack by OH^- or Si-O^- on the central Si atom. These species are formed by dissociation of water or Si-OH.

The reactions are of $\text{S}_{\text{N}}2$ type where OH^- replaces OR^- (hydrolysis) or silanolate replaces OH^- or OR^- (condensation).



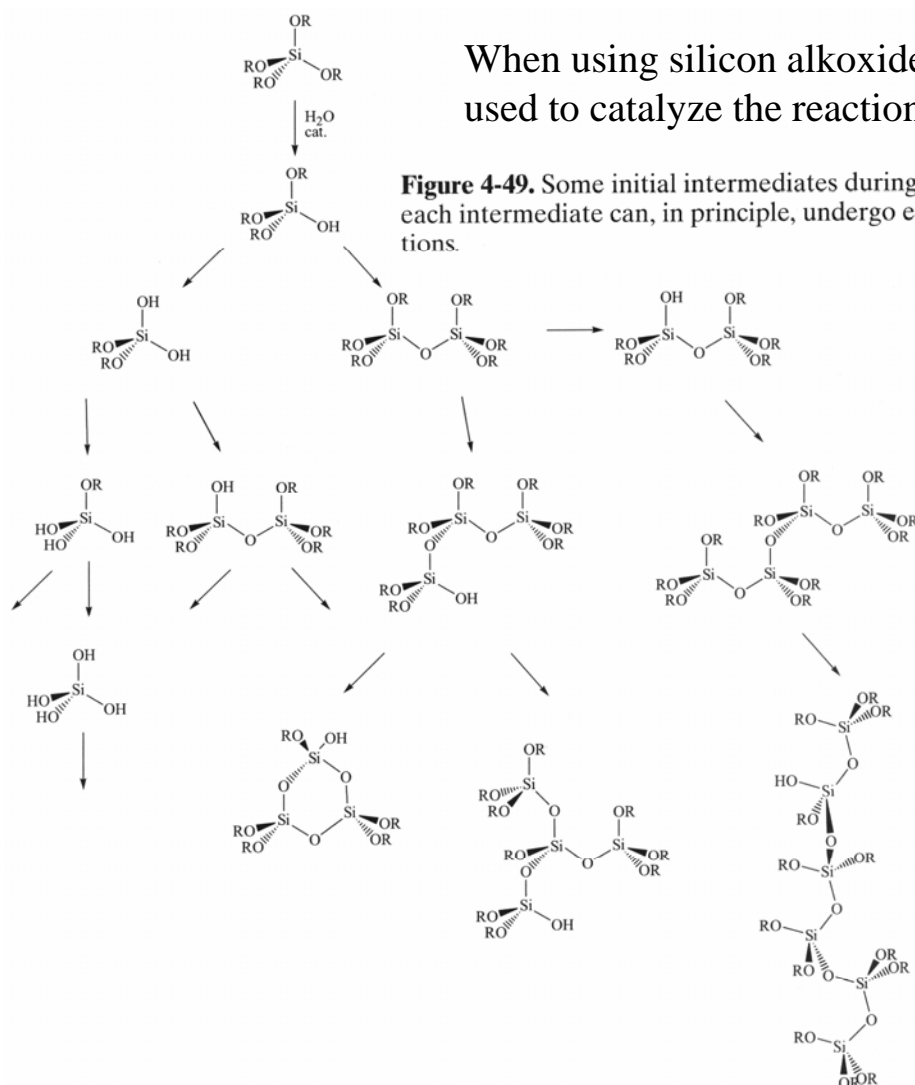
hydrolysis reaction: $\text{X} = \text{R}, \text{Y} = \text{H}$

condensation reaction: $\text{X} = \text{R or H}, \text{Y} = \text{Si}\equiv$

Reactions are reversible

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When using silicon alkoxides, acid or base must be used to catalyze the reactions



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Condensation

The condensation process is dynamic, and may be steered in the desired direction by adjusting the proper parameters.

Parameters which influences the condensation process:

- Type of precursor
- The ratio between alkoxide and water (R_w)
- Type of catalyst used
- Type of solvent
- Temperature
- pH
- Relative and absolute concentrations of the reactants.

The stability and reactivity of the silicon alkoxides are influenced by a steric factor.

Bulky ligands slow down the hydrolysis:



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Condensation, parameters

The electron density on Si will influence the reaction rate.



Acid catalyzed reaction demands high electron density

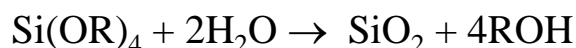
Base catalyzed reaction demands low electron density

This results in:

Acid catalyzed: more straight chains

Base catalyzed: more branched network

The water ratio, R_w . (OR/H₂O)



The reaction states that a water ratio of $R_w = 2$ (OR/H₂O) is needed to convert everything to SiO₂. A water ratio of $R_w=1$ leads to complete hydrolysis but no condensation.

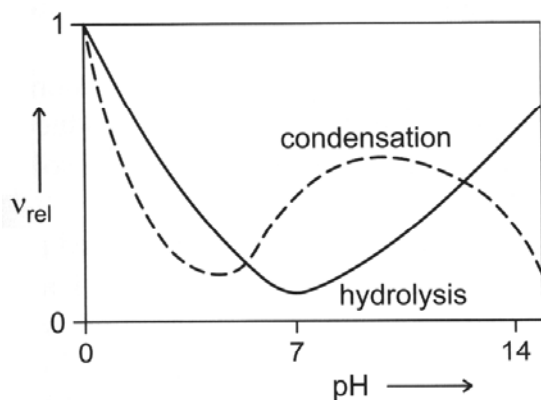
Increasing the water content (i.e. lower R_w) will reduce condensation

Reducing the water content increases the condensation

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Condensation, parameters

pH: The dependence of the reaction rate with pH is different for acid and base catalyzed systems.



A minimum for hydrolysis is observed at pH = 7 and for condensation at pH = 4.5 (IEP for silica). The sol particles may be reached without an electrostatic barrier.

Figure 4-50. Dependence of the relative rates of hydrolysis and condensation reactions of $\text{Si}(\text{OR})_4$ on the pH.

Solvent: The polarity, dipolar moment, viscosity, protolytic/non protolytic properties are important for the reactions taking place.

Polar solvents stabilize polar gels by hydrogen bonding.

Non-polar solvents are better for systems which are not completely hydrolyzed.

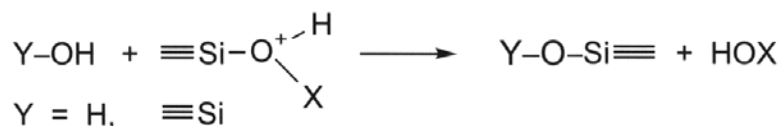
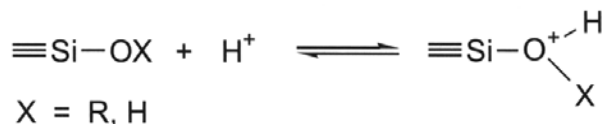
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The water glass system

Three pH intervals:

pH < 2:

The species are positively charged and the reaction rate is proportional to $[\text{H}^+]$

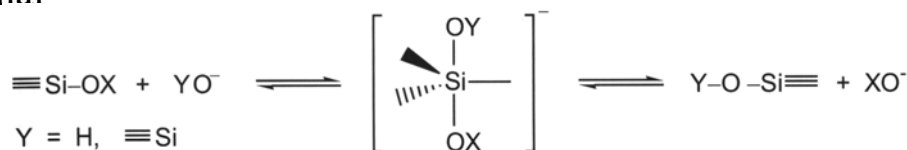


hydrolysis reaction: X = R, Y = H

condensation reaction: X = R or H, Y = $\text{Si}\equiv$

pH 2-7:

The reaction rate is proportional to $[\text{OH}^-]$



pH > 7:

The re-dispersion rate is at maximum, and the solution consists of anionic species, which repels each other.

hydrolysis reaction: X = R, Y = H

condensation reaction: X = R or H, Y = $\text{Si}\equiv$

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Network formation

During reaction, objects will grow.
However, a gel may not form

As the sol aggregates the viscosity will increase until a gel is formed. The sol-gel transition (gel-point) is reached when a continuous network is formed.

The gel-time is determined as the time when it is possible to turn the container upside-down. All fluid is kept in the gel, and the volume is maintained.

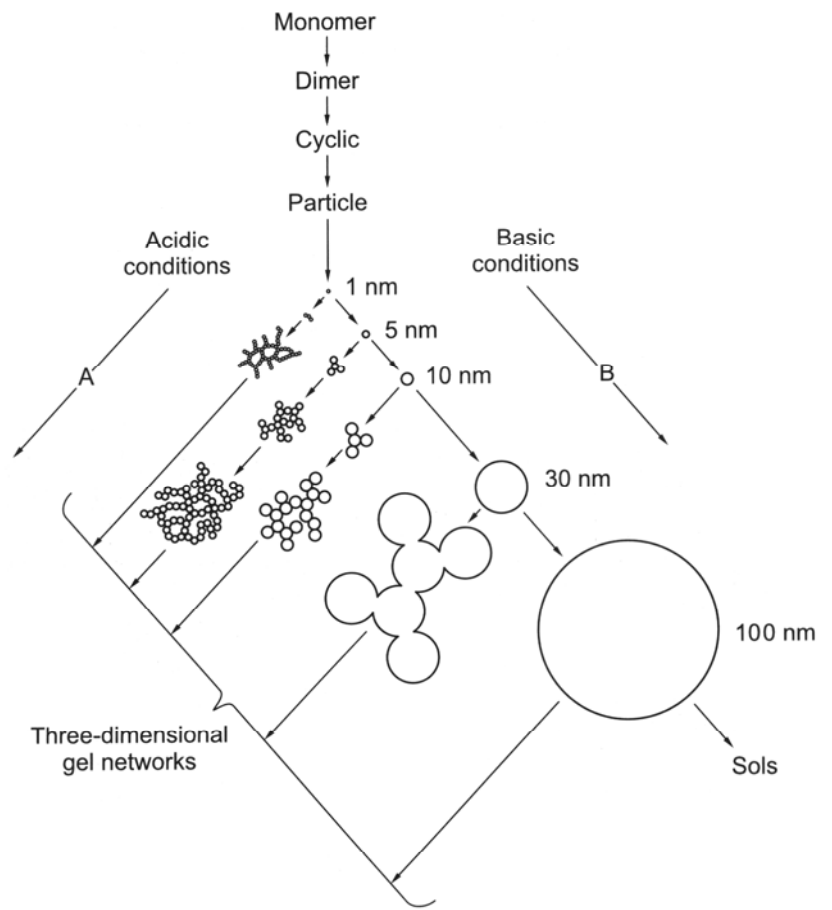


Figure 4-51. Structural development of silica gels.

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Gel time with 0.05 mole catalyst:

HCl	92 h
H ₂ SO ₄	106 h
NH ₄ OH	107 h
HI	400 h
uten	1000 h

A gel grows by forming a network, which extends across the entire container.

Gel point

When the gel is formed, a large number of sol particles and clusters will still not have reacted. Ageing of the gel is therefore a very important stage in the process.

The gel point is not a thermodynamic event

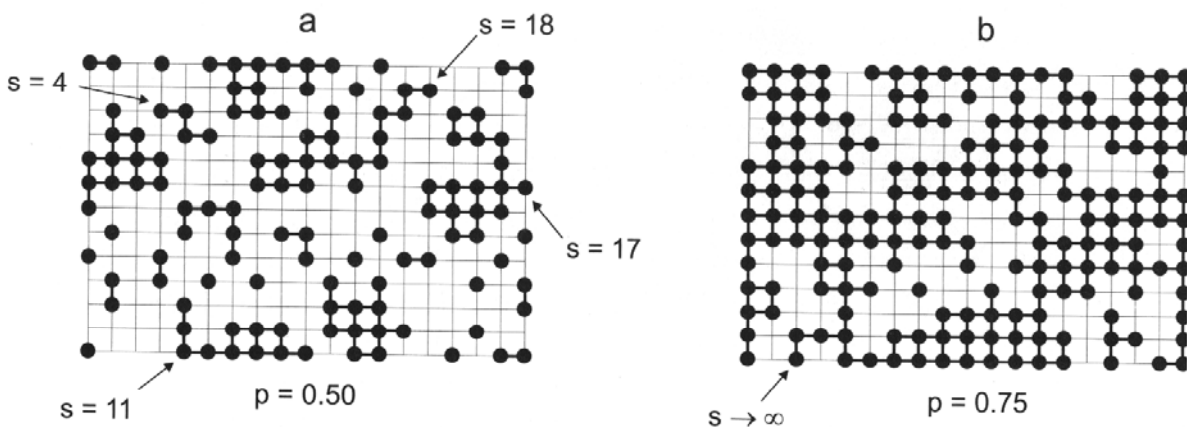


Figure 4-52. Site percolation on a square lattice: (a) for $p = 0.50$, and (b) for $p = 0.75$ (p is the fraction of filled spheres).

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Ostwald ripening

Small particles dissolve faster than larger particles. As the process is dynamic and reversible, smaller particles may be dissolved to feed growth of the larger particles.

The growth stops when the difference in solubility between the largest and smallest particle is a few ppm.

It is therefore possible to prepare monodisperse silica particles from a gel

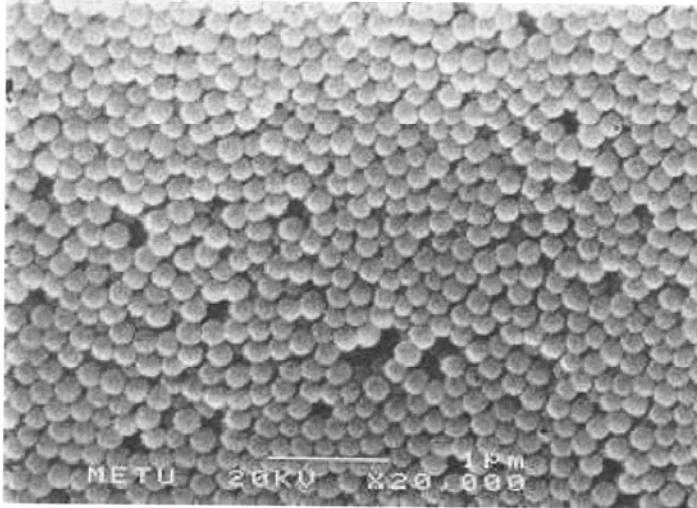


Figure 4-53. Monodisperse silica spheres with a diameter of about 0.2 μm made by the Stöber process.

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Ageing

As the viscosity rapidly increase, the solvent is “trapped” inside the gel.

The structure may change considerably with time, depending on pH, temperature and solvent. The gel is still “alive”.

- The liquid phase still contains sol particles and agglomerates, which will continue to react, and will condense as the gel dries.
- The gel is originally flexible. Groups on neighbouring branches will condense, making the gel even more viscous. This will squeeze out the liquid from the interior of the gel, and shrinkage occur. This process will continue as long as there is flexibility in the gel.
- Hydrolysis and condensation are reversible processes, and material from thermodynamically unfavourable points will dissolve and precipitate at more favourable points.

(Note the similarity to the sintering process)

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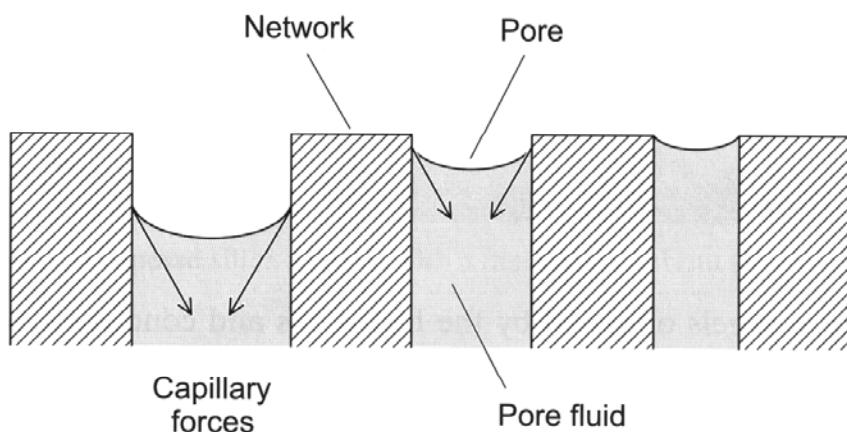
Drying

When the liquid is removed from the gel several things may happen. When the liquid in the gel is replaced by air, major changes to the network structure may occur.

If the structure is maintained, an aerogel is formed

If the structure collapses, a xerogel is formed.

- Normal drying of the gel leads to structural collapse due capillary forces drawing the walls of the pores together, and reducing the pore size.
- OH groups on opposite sides may react and form new bonds by condensation.
- Cracking may occur when the tension in the gel is so large that it cannot shrink anymore.
- Gas will enter the pores with a thin film of liquid on the walls. This will evaporate and only isolated spaces with liquid are left.

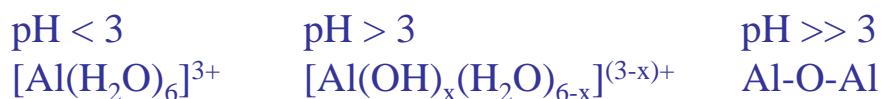


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Figure 4-54. Contracting surface forces in pores of different size during drying.

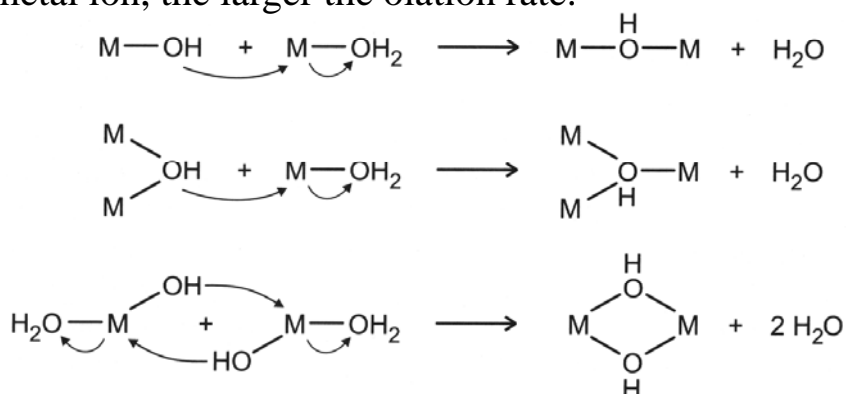
Metal oxides

Metals may be used for formation of gels, almost as silicon. However, many metals will form oxides when increasing pH. The water molecules of the hydrated metal ions are more acidic than for Si, and hydrolyses will occur. The reactions are moved toward lower pH.



A network may be formed via two routes:

Olation: Hydroxy bridges are formed by nucleophilic substitution, where an OH group attacks and water leaves. It is important that water is not coordinated too hard to the metal in order for this reaction to occur. The smaller the charge and the larger the metal ion, the larger the olation rate.



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Oxolation

Oxolation is a condensation reaction where an oxo-bridge is formed. If the metal is under-coordinated, the oxolation happens by fast nucleophilic addition reactions:

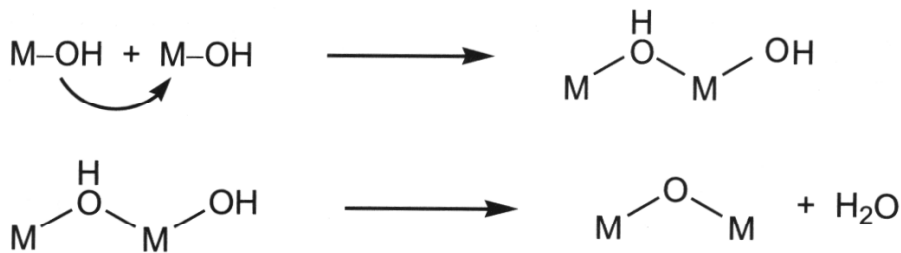


Otherwise, oxolation is a two-step addition/elimination process

At basic conditions step one is catalyzed

At acidic conditions, step two is catalyzed

The reaction is slow at the isoelectrical point



Whether gel formation or precipitation occur depends on the reaction conditions and the kinetics. Gel formation occur when reactions are slow. 29



Metal oxide systems



There is a big difference between metal oxides and the silica system. Silicon are tetrahedrally coordinated to oxygen, while metals are usually octahedrally coordinated. Tetrahedra give more flexibility than octahedra.

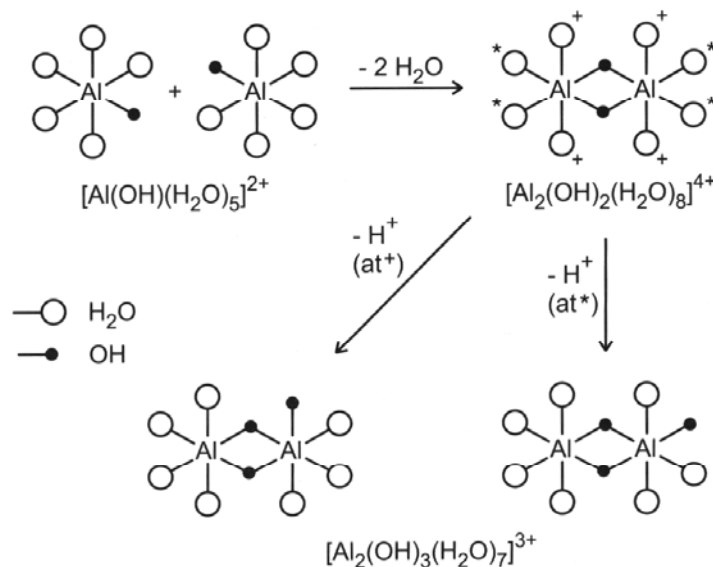


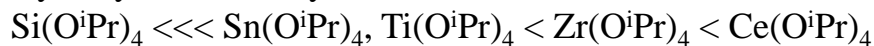
Figure 4-55. Stereochemical possibilities for the condensation of $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ by an oxolation mechanism.

Alkoxide precursors

Differences between $\text{Si}(\text{OR})_4$ and $\text{M}(\text{OR})_x$

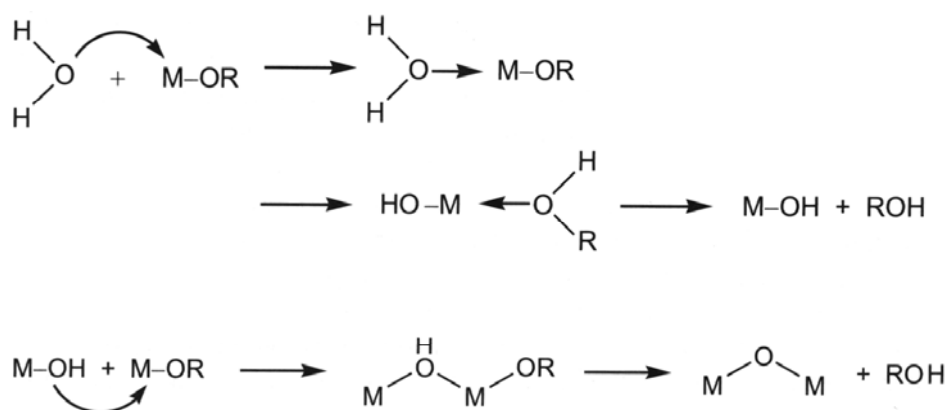
- Metal alkoxides are stronger Lewis acids and will promote nucleophilic attack. Hydrolysis of $\text{Ti}(\text{OR})_4$ is up to 10^5 times faster than for the corresponding silicon alkoxide.
- Most metals have several stable coordination numbers or may easier expand the coordination sphere.

Hydrolysis, reactivity:



When reacting with water many metal alkoxides form precipitates. While the alkoxy silanes needs catalysts, the reaction rates must be decreased for metal alkoxides.

Hydrolysis occur through an addition/elimination mechanism:



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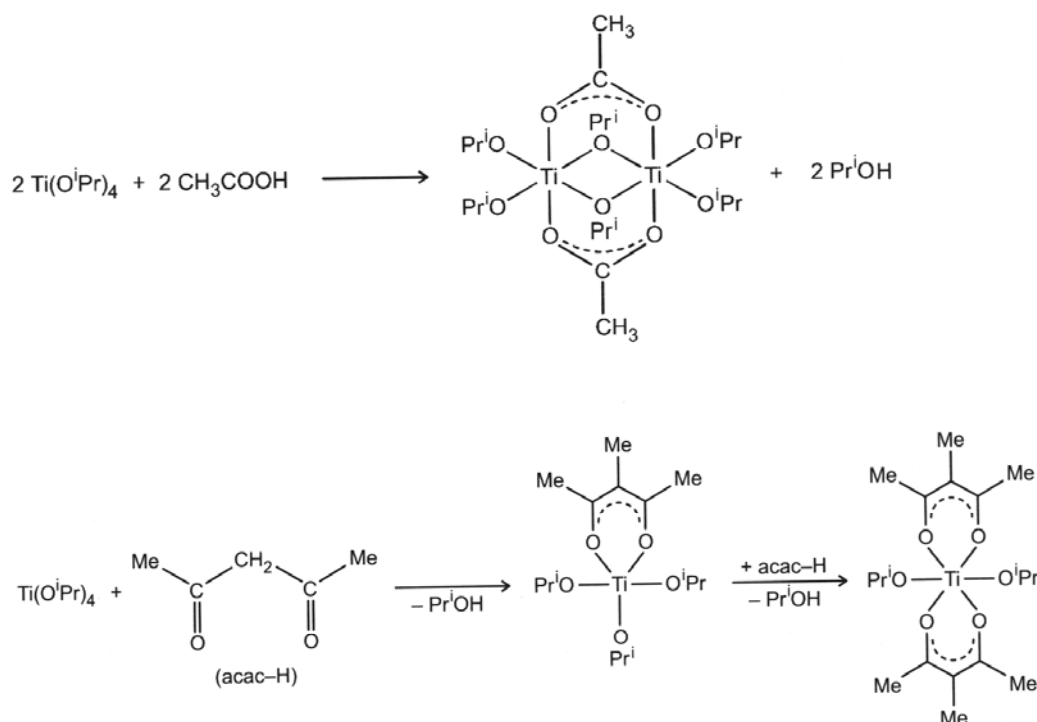
Reducing reactivity

Metal alkoxides may be polymeric (silicon alkoxides tend to be monomeric).

Polymeric species react slower than monomeric.

Small ligands result in faster reaction than large ligands

Bidentate ligands also slow down the hydrolysis.



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Inorganic-organic hybrid materials

Combining properties of organic and inorganic materials.

May be done as composites or using molecular building blocks.

- ORMOSILS: Organically modified silicates
- ORMOCERS: Organically modified ceramics
- CERAMERS: Ceramic polymers
- POLYCERAM: Polymeric ceramics

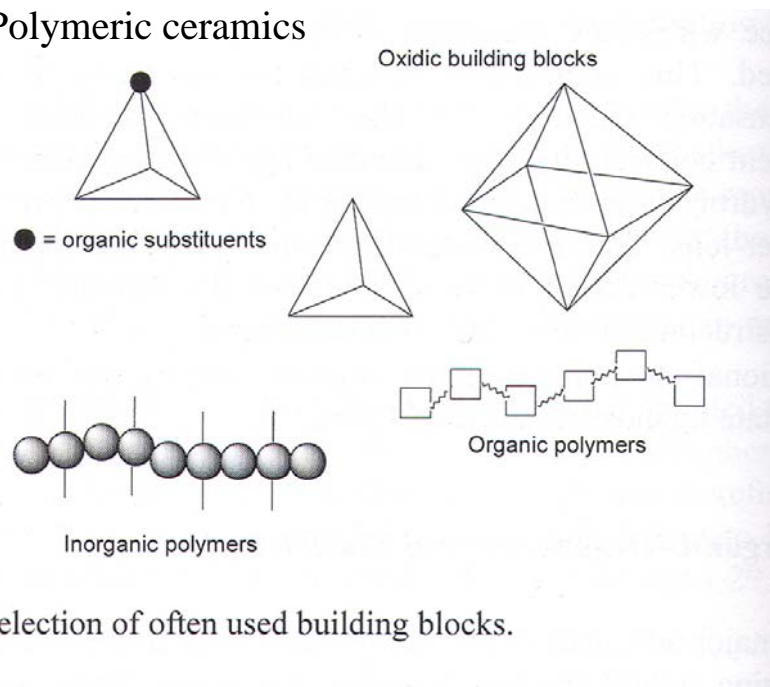


Figure 4-55. A selection of often used building blocks.

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Embedding organic molecules

Forming a gel around organic molecules (Dyes, catalytically active metal complexes, sensor compounds, biomolecules)

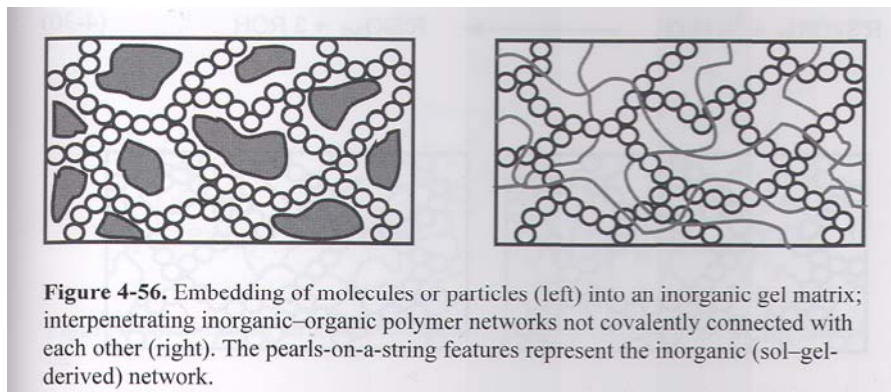


Figure 4-56. Embedding of molecules or particles (left) into an inorganic gel matrix; interpenetrating inorganic-organic polymer networks not covalently connected with each other (right). The pearls-on-a-string features represent the inorganic (sol-gel-derived) network.

Incorporation of organic groups via covalent bonding

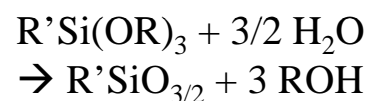
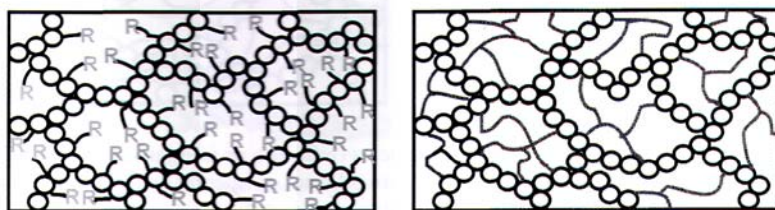


Figure 4-57. Incorporation of organic groups by covalent linkage into an inorganic gel matrix (left); dual inorganic-organic hybrid polymer networks connected with each other by covalent bonds (right). The pearls-on-a-string features represent the inorganic (sol-gel-derived) network.

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Trialkoxysilanes

Table 4-6. Some organofunctional trialkoxysilanes used for the preparation of inorganic-organic hybrid materials by sol-gel processing, and their function.

$R'Si(OR)_3$	Function
	polymerizable group for the preparation of hybrid polymers
	crosslinking (▶ glossary) sites
	group for organic polyaddition reactions; generation of hydrophilic diols by opening of the epoxide ring
	hydrophilicity, coupling sites, coordination sites for metals
	hydrophobicity
	crosslinking site in thiol-ene UV cure systems, coordination site for metals
	chromophoric substituent (non-linear optic NLO dye (▶ glossary))
	fluorescent substituent (pyrene derivative)
	coordination of transition metal complexes, catalysis

Scratch resistant coating

Mixture of vinyl and mercapto substituted trialkoxysilanes.

Formation of sol coating photochemically cured

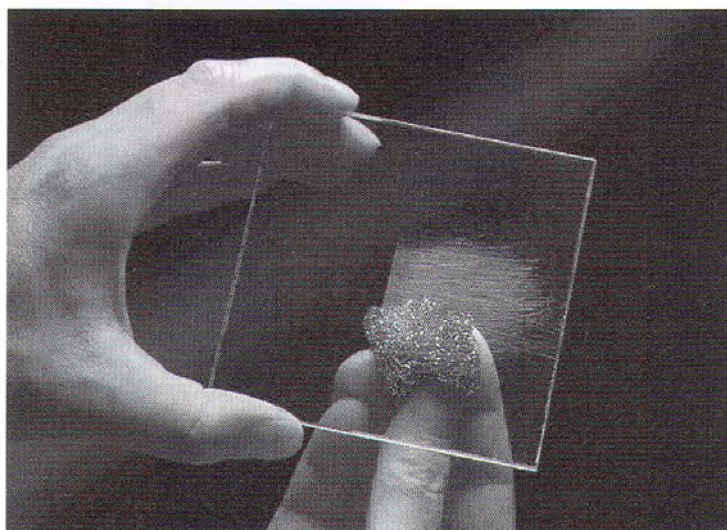
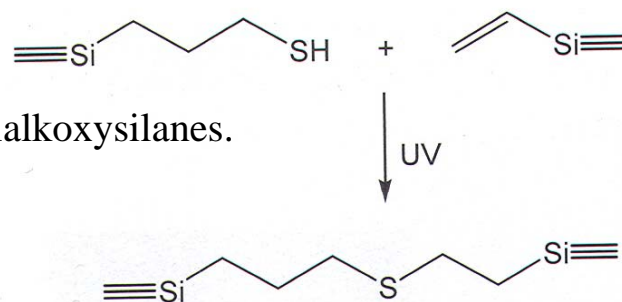


Figure 4-63. Scratch-resistant coating on polycarbonate (left half of slide coated, right half uncoated).

Surface modifications

Interface interaction:

γ_{SV} : energy of surface-vapour interaction

γ_{SL} : energy of surface-liquid interaction

γ_{LV} : energy of liquid-vapour interaction

$$\Delta E = \gamma_{SV} + \gamma_{SL} + \gamma_{LV}$$

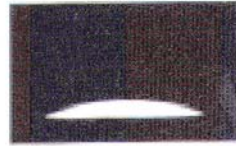
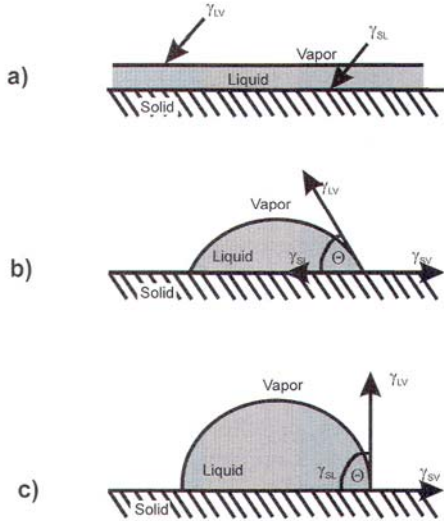


Figure 4-64. Different wetting behavior on a surface: a) the liquid spreads easily over the surface; b) the liquid wets the surface partly; and c) the liquid does not wet the surface. Corresponding to the drawings, a water droplet on a hydrophilic (b) and a hydrophobic surface (c) is shown.

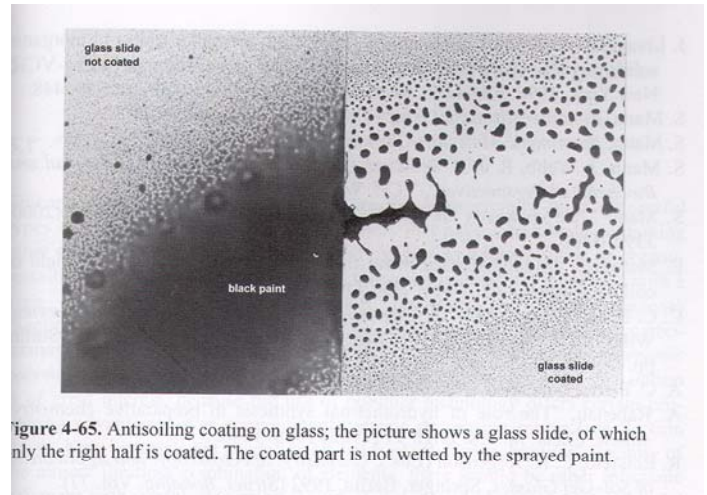


Figure 4-65. Antisoiling coating on glass; the picture shows a glass slide, of which only the right half is coated. The coated part is not wetted by the sprayed paint.