Part One
Sol–Gel Chemistry and Methods
1
Chemistry and Fundamentals of the Sol–Gel Process

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1.1 Introduction

The structure of oxide glasses produced from melts consists of dense amorphous networks of connected polyhedra. An alternative way to obtain such networks is a “bottom-up” approach, that is, connecting molecular building blocks such as SiO$_4$ tetrahedra and TiO$_6$ octahedra with each other in a stepwise manner. Contrary to glass formation from melts, where the thermodynamically favorable crystalline structure is avoided by fast enough cooling, fast and (nearly) irreversible reactions are the reason for the amorphous network structures in sol–gel materials. Sol–gel materials are therefore metastable solids that are formed in kinetically controlled reactions from molecular precursors, which constitute the building blocks for the later materials. An immediate consequence is that all reaction parameters, including the precursor properties, have a decisive influence on the structure and thus the properties of sol–gel materials [1].

- A sol is a stable suspension of colloidal particles (nanoparticles) in a liquid. The particles can be amorphous or crystalline, and may have dense, porous, or polymeric substructures. The latter can be due to aggregation of subcolloidal chemical units.
- A gel consists of a porous, three-dimensionally continuous solid network surrounding and supporting a continuous liquid phase (“wet gel”). In most sol–gel systems for the synthesis of oxide materials, gelation (i.e., formation of the gels) is due to the formation of covalent bonds between the sol particles. Gel formation can be reversible when other bonds are involved, such as van der Waals forces or hydrogen bonds. The structure of a gel network depends to a large extent on the size and shape of the sol particles.

The easy agglomeration or aggregation of fine particles (sol particles) is caused by attractive van der Waals forces and/or minimization of the total surface or interfacial energy of the system. In order to prevent aggregation (i.e., to stabilize the sols), repulsive forces of comparable dimensions are required that must be overcome during gelation. Stabilization can be achieved by adsorbing an organic layer ("steric barrier") or by creating electrostatic repulsion between the particles. This shows the great influence of organic additives and especially ionic species on the gelation behavior, as will be discussed later in more detail. The stability and coagulation of sols is of utmost importance to sol–gel chemistry. Gelation can also be induced by rapid evaporation of the solvent, which is especially important for the preparation of films or fibers.

Drying of the initially obtained wet gels by evaporation of the pore liquid gives rise to capillary forces that cause shrinkage of the gel network, often by a factor of 5–10. The resulting dried gels are called xerogels. Due to the drying stress, monolithic gel bodies are often destroyed and powders are obtained. When a wet gel is dried in a way that the pore and network structure of the gel is retained, the resulting dried gel is called an aerogel.

In the following, the chemical and physical principles behind the individual steps of sol–gel processing will be discussed in more detail.

1.2 Hydrolysis and Condensation Reactions

1.2.1 Silica-Based Materials

The basic chemical principle behind sol–gel processing of silica-based materials is the transformation of Si–OR- and Si–OH-containing species to siloxane compounds by condensation reactions. From a structural point of view, this corresponds to connecting SiO$_4$ tetrahedra (or RSiO$_3$ tetrahedra in hybrid materials) by corner sharing. To obtain a stable gel, the number of siloxane bonds (Si–O–Si) has to be maximized and consequently the number of silanol (Si–OH) and alkoxo (Si–OR) groups has to be minimized.

The most common precursors are aqueous solutions of silicates ("water glass") and silicon alkoxides, Si(OR)$_4$, mostly tetramethoxysilane (TMOS) or tetaethoxysilane (TEOS). Water glass solutions contain complex mixtures of different monomeric and oligomeric silicate species (i.e., species with negatively charged, nonbridging oxygen atoms), with an approximate average composition of M$_2$SiO$_3$ (M = Na, K). The equilibrium compositions of such “metasilicate” solutions are highly dependent on the concentration, pH, metal counterion, temperature, and so on. The point of zero charge (PZC) of Si–OH-containing species is between pH 1.5 and 4.5; the higher the degree of condensation of the silica species, the lower the PZC (the acidity of surface M–OH groups generally depends somewhat on the particle size). Acidifying a solution to a pH below the PZC
means that the siliceous species are positively charged, and increasing the pH above the PZC means that the species are negatively charged (Eq. (1.1)). The silicate species in water glass solutions are stable only under strongly alkaline conditions, because the anionic species reject each other.

\[
\begin{align*}
\text{Si--OH} + \text{H}^+ & \rightarrow \text{Si--OH}_2^+ \\
\text{Si--OH} + \text{OH}^- & \rightarrow \text{Si--O}^- + \text{H}_2\text{O}
\end{align*}
\] (1.1)

The chemical reactions during sol–gel processing can be formally described by three equations (Eq. (1.2)). In alkoxide-based systems, hydrolysis reactions of Si–OR groups must precede condensation to generate the Si–OH groups, which are necessary for condensation. The fact that the reactive groups must be created in the first place is an important difference to typical organic polymerization reactions. Condensation (i.e., formation of Si–O–Si units) takes place by either alcohol or (more often) water elimination.

\[
\begin{align*}
\equiv\text{Si--OR} + \text{H}_2\text{O} & \rightarrow \equiv\text{Si--OH} + \text{ROH} & \text{Hydrolysis} \\
\equiv\text{Si--OH} + \equiv\text{Si--OR} & \rightarrow \equiv\text{Si--O--Si} + \text{ROH} & \text{Condensation} \\
\equiv\text{Si--OH} + \equiv\text{Si--OH} & \rightarrow \equiv\text{Si--O--Si} + \text{H}_2\text{O} & 
\end{align*}
\] (1.2)

The most important differences between the two precursor types are the following:

- Gelation is initiated in aqueous silicate systems by pH changes, and in alkoxide precursor systems by addition of water (hydrolysis reactions to generate Si–OH groups).
- A mixture of a Si(OR)$_4$ in water and alcohol would react very slowly. Therefore, acid or base catalysis is necessary to start the hydrolysis and condensation reactions of alkoxysilanes.
- The solvent in water glass-based reactions is always water, while the alkoxides are employed either neat or dissolved in an organic solvent. Since many alkoxysilanes are immiscible with water, alcohols are often used to homogenize the reaction mixture (mostly the same alcohol as liberated by the hydrolysis reactions to avoid alcohol exchange reactions).
- Alkoxide-based systems are more complex because more parameters influence the sol–gel reactions (see below). This gives more possibilities to control the texture and properties of the obtained materials.

The use of silicon alkoxides also allows introducing organic groups, by means of organo-substituted derivatives. While sol–gel processing of tetraalkoxysilanes, Si(OR)$_4$, results in the formation of silica, SiO$_2$, alkoxysilanes of the type R’Si(OR)$_3$ (R’ = any hydrolytically stable organic moiety) result in the so-called silsesquioxanes, R’SiO$_{3/2}$. In practice, however, alkoxysilane mixtures are processed in most cases, by which any proportion of the organic group(s) R’ can be introduced. Specific aspects of processing alkoxysilane mixtures will be discussed later. Diorganodialkoxysilanes, R$_2$Si(OR)$_2$, are rarely used, because their hydrolytic
polycondensation does not result in network structures, but instead in chain structures (as in silicones).

The reaction mechanisms are the same for both silicate and alkoxy silane precursors. However, from a mechanistic point of view, reactions under acidic or basic conditions have to be considered separately. Under acidic conditions, that is, at a pH below the PZC, the oxygen atom of a $\equiv\text{Si}−\text{O}^−$, $\equiv\text{Si}−\text{OH}$, or $\equiv\text{Si}−\text{OR}$ group is protonated in a rapid first step (Eq. (1.3)). A good leaving group (water or alcohol) is thus created. In addition, electron density is withdrawn from the central silicon atom, rendering it more electrophilic and thus more susceptible to attack by water (in hydrolysis reactions) or silanol groups (in condensation reactions).

\[
\equiv\text{Si}−\text{OX} + H^+ \rightarrow \equiv\text{Si}−\text{O}^−H^X
\]

\[
Y−OH + \equiv\text{Si}−\text{O}^−H^X \rightarrow Y−\text{O}−\equiv\text{Si} + \text{HOX}
\]  

(1.3)

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

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

Under basic conditions, the reaction proceeds by nucleophilic attack of either an $\text{OH}^−$ (in hydrolysis reactions) or a $\equiv\text{Si}−\text{O}^−$ ion (in condensation reactions) to the silicon atom with an $\text{SN2}$-type mechanism (Eq. (1.4)). The entering $\text{OH}^−$ or $\equiv\text{SiO}^−$ group is formed by deprotonation of water or a $\equiv\text{Si}−\text{OH}$ group. Under strongly alkaline conditions, the $\text{Si}−\text{O}−\text{Si}$ bonds can be cleaved again by $\text{OH}^−$.

\[
\equiv\text{Si}−\text{OX} + \text{YO}^− \rightarrow \equiv\text{Si}−\text{O}^−Y^X \rightarrow \text{YO}−\equiv\text{Si} + \text{OX}^−
\]  

(1.4)

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

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

Inductive effects of the substituents attached to a silicon atom are very important, because they stabilize or destabilize the transition states or intermediates during hydrolysis and condensation. The electron density at the silicon atom decreases in the following order:

\[\equiv\text{Si}−\text{R}’ > \equiv\text{Si}−\text{OR} > \equiv\text{Si}−\text{OH} > \equiv\text{Si}−\text{O}−\text{Si}.\]

For acid catalysis, the electron density at the silicon atom should be high because the positive charge of the transition state (Eq. (1.3)) is then stabilized
1.2 Hydrolysis and Condensation Reactions

best. Therefore, the reaction rates for hydrolysis and condensation under acidic conditions increase in the same order as the electron density. For base catalysis, a negatively charged intermediate has to be stabilized (Eq. (1.4)). Therefore, the reaction rates for hydrolysis and condensation increase in the reverse order of the electron density.

This has several consequences, for example:

- As hydrolysis and condensation proceed (increasing number of OH and OSi units attached to a specific silicon atom), the silicon atom becomes more electrophilic. This means, for example, that in acidic media monomeric Si(OR)$_4$ hydrolyzes faster than partially hydrolyzed Si(OR)$_{4-x}$(OH)$_x$ or oligomeric species (which have more Si–O–Si bonds), and vice versa in basic media.
- More branched (i.e., more highly condensed) networks are obtained under basic conditions and chain-like networks under acidic conditions, because reactions at central silicon atoms (i.e., atoms with two or three Si–O–Si bonds) are favored under acidic conditions, and reactions at terminal silicon atoms (i.e., atoms with only one Si–O–Si bond) under basic conditions.
- Organically substituted alkoxysilanes R'Si(OR)$_3$ react faster than the corresponding Si(OR)$_4$ under acidic conditions and slower under basic conditions.
- The acidity of a silanol group increases with the number of Si–O–Si bonds at the silicon atom. This is one of the reasons why the PZC changes with the degree of condensation.

An important feature of the chemistry of silicon alkoxides is that hydrolysis and condensation reactions compete with each other during all steps of the sol–gel process. Figure 1.1 shows the reaction possibilities of a hypothetical trisiloxane intermediate as an example. It can react by either hydrolysis or condensation, and these reactions can occur on chemically different silicon atoms. Note that monomeric species (“cluster–monomer” aggregation leading to extension by one Si–O unit), oligomeric species (“cluster–cluster” aggregation), or even siliceous structures can be involved in the intermolecular condensation reactions (≡Si– in Figure 1.1d and e can be the silicon atom of a monomeric or oligomeric species or of a particle). The situation is even more complex, since each possibility shown in Figure 1.1 has a different reaction rate, which is influenced to a different degree by the reaction parameters. The same is true for the different intermediates that are formed as hydrolysis and condensation reactions proceed; that is, each intermediate has its own set of kinetic parameters. For practical purposes, the absolute rate constants are not too decisive, but instead the relative rates of the hydrolysis and condensation reactions (see below). It is important to understand that we are discussing not a static, but a continuously changing system as network formation proceeds.

As indicated in Figure 1.1c, not only linear or branched structures can be formed, but closed structures as well. Many three-dimensional cage compounds, the so-called spherosilicates (Figure 1.2), with either closed or partially open
cages, have been isolated. Such structures can also be substructures of the networks formed during sol–gel processing. Cage compounds (RSiO$_{1.5}$)$_n$, the so-called POSS (polyhedral oligomeric silsesquioxanes), can be similarly obtained from R’Si(OR)$_3$. Both POSS and spherosilicates are interesting building blocks for materials syntheses for their own [2].

From what has been said, it is obvious that the systems are very complex and many different routes from the molecular precursor to the final silica gel are possible. The chemical parameters discussed in the following determine which route is taken. Because of this complexity, a detailed understanding (and awareness) of the parameters influencing the reaction rates and thus the structure evolution is necessary in order to tailor the texture and properties of sol–gel materials. The most important parameters influencing hydrolysis and condensation (and their relative rate) are

- the kind of precursor(s),
- the pH (OH$^-$ or H$^+$ catalysis), or other catalysts,
1.2 Hydrolysis and Condensation Reactions

1.2.1 Precursor(s)

Different from water glass as a precursor, the Si—OR groups of silicon alkoxides must first be hydrolyzed before condensation reactions can take place. In addition to the inductive effects discussed above, the hydrolysis rates of alkoxysilanes are also influenced by steric factors. Any branching of the alkoxo group or increasing of the chain length lowers the hydrolysis rate of the alkoxysilanes. It means that the reaction rate decreases in the order Si(OMe)₄ > Si(OEt)₄ > Si(OⁿPr)₄ > Si(OⁱPr)₄.

1.2.1.1 Precursor(s)

As discussed above, the reaction mechanisms for acid or base catalysis are very different. Furthermore, the reaction rates for hydrolysis and condensation of silicon alkoxides have different pH dependence (Figure 1.3). The minimal reaction rate for hydrolysis is at pH 7, and for condensation at around pH 4.5. The latter corresponds to the PZC of silica. At pH < 5, hydrolysis is favored, and condensation is the rate-determining step. A large number of monomers or small oligomers with reactive Si—OH groups are simultaneously formed. In contrast, hydrolysis is the rate-determining step at pH > 5, and hydrolyzed species are immediately consumed because of the faster condensation. Catalysis by fluoride ions is similar to that of hydroxide ions (basic conditions).

The pH is an especially important parameter to control the texture of gels from water glass solutions. At intermediate pH, the reaction rate of condensation is proportional to the concentration of the OH⁻ ions (see Eq. (1.4)). At pH
lower than about 2, the silicic acid species are positively charged, and according to the mechanism given in Eq. (1.3), the reaction rate of the condensation is proportional to the concentration of H\(^+\). Under strongly alkaline conditions, the solutions contain mainly anionic species. For this reason, the rate of Si-O-Si cleavage or redissolution of particles is high at high pH (see Figure 1.3).

1.2.1.3 Alkoxo Group/H\(_2\)O Ratio (\(R_w\))
The overall reaction for sol–gel processing of tetraalkoxysilanes implies that two equivalents of water (\(R_w = 2\)) are needed to convert Si(OR)\(_4\) to SiO\(_2\). Four equivalents of water (\(R_w = 1\)) are needed for the complete hydrolysis of Si(OR)\(_4\) if no condensation would take place. Increasing the water proportion (i.e., lowering \(R_w\)) generally favors the formation of silanol groups over Si-O-Si groups. The \(R_w\), together with the kind of catalyst, thus strongly influences the properties of the silica gels.

1.2.1.4 Solvent
A solvent may be necessary to homogenize the reaction mixture of alkoxide-based systems, especially at the beginning of the reaction. Polarity, dipole moment, viscosity, and protic or nonprotic behavior of the solvent influence the reaction rates and thus the structure of the final sol–gel material. Polar and particularly protic solvents (H\(_2\)O, alcohols, and formamide) stabilize polar species such as [Si(OR)\(_x\)(OH)\(_y\)]\(_n\) by hydrogen bridges. The latter generally play a very important role in sol–gel systems. Nonpolar solvents (tetrahydrofuran and dioxane) are sometimes used for organotrialkoxysilanes, R’Si(OR)\(_3\), or incompletely hydrolyzed alkoxide systems.

1.2.1.5 Electrolytes
Increasing the electrolyte concentration in a colloidal dispersion compresses the electrical double layer around the particles, because the number of charges required to balance the surface charge is now available in a smaller volume surrounding the particle. The colloid will eventually coagulate because the attractive
force between the particles is unchanged, while the repulsive barrier is reduced. Therefore, the presence of electrolytes (salts) has a strong influence on the gelation behavior. To render sol–gel processes reproducible, special care has to be taken (especially in alkoxide-based systems) not to introduce unwanted salt contaminations in the system, for example, through the water used for hydrolysis of alkoxides. An often neglected source of ionic species is the counterions of the acids or bases needed for catalysis. The reason why ammonia is mostly used as a base is that it is not ionic. Acids are more problematic, because anionic species (the counterions) are inevitably introduced and influence the reaction rates and the gelation behavior.

1.2.2 Metal Oxide-Based Materials

Any metal oxide can, in principle, be prepared by sol–gel processing. There are two important differences between silicon (as a semimetal) and typical main group or transition metals that are highly relevant for sol–gel chemistry [3]:

- Metals are more electropositive (Lewis acidic) than silicon and therefore more susceptible to a nucleophilic attack.
- The preferred coordination number of silicon is 4, and is thus equal to its valence (+IV). For metals, especially transition metals, on the other hand, the preferred coordination number is higher than their valence. The increase of the coordination number beyond the valence is reached by interaction with any nucleophilic (Lewis basic) entity in the system, as will be discussed in more detail below.

The comparison of the SiO₂ and TiO₂ polymorphs may illustrate one of the structural consequences. Both metal atoms are in the +IV oxidation state. However, silicon is always 4-coordinate (tetrahedral SiO₄ building blocks), while titanium in rutile is 6-coordinate (octahedral TiO₆ building blocks). The only way to connect SiO₄ tetrahedra with each other in a thermodynamically stable way is via shared corners. This results in the overall composition SiO₂ (= SiO₄/2, because all oxygen atoms bridge two silicon atoms). In the TiO₂ polymorphs, the two oxygen atoms per formula unit have to occupy six coordination sites to fulfill the coordination number requirement of the Ti atoms. The stoichiometry MO₂ can only be obtained if each oxygen atom coordinates to three titanium atoms (= TiO₆/3). In the rutile structure, strings of edge-sharing octahedra are connected with the corners of a neighboring string through the three-coordinate oxygen atoms (Figure 1.4). This leaves lesser degrees of freedom for the long-range arrangement of the polyhedra in the rutile structure compared with crystalline SiO₂ (only corner-sharing polyhedra). A practical consequence is that sol–gel processing of titania often results in semi- or microcrystalline materials, whereas silica gels are always amorphous. Similar considerations apply to all silica- and titania-(metal-)based materials.
As in silicate sol–gel processes, inorganic or metal–organic (alkoxide) precursors can be used. Many metal salts are hydrolytically unstable; that is, they form oxide/hydroxide precipitates from aqueous solutions upon pH changes. This is due to the fact that water molecules coordinated to metal ions are more acidic than those in the noncoordinated state due to charge transfer from the oxygen to the metal atom. The series of equilibria shown in Eq. (1.5) is more easily shifted to the right than in water itself when the pH is increased (i.e., if a base is added).

\[
\begin{align*}
M-\text{O} & \quad \text{H}^+ \\
(n) & \quad \text{M-} \quad \text{OH} \\
(n-1) & \quad \text{M-} \quad \text{OH} \\
(n-2) & \quad \text{M} \quad \text{O} \\
\end{align*}
\]

Condensation reactions, that is, formation of M–O–M links with concomitant cleavage of H$_2$O, require the presence of M–OH units (as for silica, Eqs. (1.3) and (1.4)). This means that the equilibria in Eq. (1.5) must be shifted in the M–OH regime, which depends on the valence of the metal and the pH. This is schematically shown in Figure 1.5. There are three possibilities to shift the equilibria in the M–OH regime:

1) Raising the pH corresponds to moving from left to right in Figure 1.5 for a given valence (Z). For example, when aluminum salts are dissolved in water, the hydrated cation [Al(H$_2$O)$_6$]$^{3+}$ exists only below pH 3. As the pH is increased, the water ligands are deprotonated, and the ions [Al(OH)$_x$(H$_2$O)$_{6-x}$]$^{(3-x)+}$ are formed. Mononuclear species with $x = 0$–4 are stable only in very dilute solutions; at higher concentrations, poly-nuclear species are formed by condensation reactions, that is, by formation of Al–O–Al links. Alternatively, the solution can simply be aged at elevated temperatures. A higher temperature promotes dissociation of protons from the hydrated metal ions.

2) Solutions of metallate ions, such as titanates, vanadates, niobates, tantalates, or tungstates, form gels when acidified (right to left in Figure 1.5 for a given valence).
3) Solutions of oxide species with the metal in high oxidation states can be reduced to give gels (top-down in Figure 1.5 at a given pH); one of the best-known examples is the formation of MnO$_2$ gels from MnO$_4$. As in the case of silica-based sol–gel processes, M–OH groups can also be created by hydrolysis of M–OR groups, that is, by addition of water to metal alkoxides. As outlined above, metal alkoxides are stronger Lewis acids than silicon alkoxides, and the formation of higher coordinated species is easier. Nucleophilic attack at the metal is thus facilitated, and the hydrolysis rates are strongly increased. For example, the hydrolysis rate of Ti(OR)$_4$ is about $10^5$ times faster than that of Si(OR)$_4$ with the same alkoxide substituents. The reactivity of some tetravalent isopropoxides in hydrolysis reactions increases in the following order [4]:

\[
\text{Si(OiPr)$_4$} < \text{Sn(OiPr)$_4$} < \text{Ti(OiPr)$_4$} < \text{Zr(OiPr)$_4$} < \text{Ce(OiPr)$_4$}.
\]

The reactivity of many metal alkoxides toward water is so high that precipitates are often formed spontaneously upon addition of water. While the reactivity of alkoxy silanes has to be promoted by catalysts, the reaction rates of metal alkoxides must be moderated to obtain gels instead of precipitates (see below).

In principle, the same parameters influence the rates of the hydrolysis and condensation reactions of metal alkoxides as those already discussed for silicon alkoxides (apart from the fact that no catalyst is needed). An additional factor is the degree of oligomerization of the alkoxide precursors. Silicon alkoxides are always monomeric, while metal alkoxides can associate through $\mu_2$- or $\mu_3$-OR bridges (the subscript denotes the number of metal atoms coordinated to the bridging ligand). The reason for the association is, as discussed above, that the
preferred coordination number is higher than their valence. Coordination expansion occurs by association via OR bridges. The degree of association depends on the following:

- **Size of the groups R**: larger groups R favor smaller units because of steric hindrance. For example, Ti(OEt)\textsubscript{4} in ethanol has a trimeric structure, while Ti(O'Pr)\textsubscript{4} is monomeric in isopropanol solution.

- **Size of the metal**: the tendency to oligomerize increases with the size of the metal. For example, the average degree of oligomerization (the oligomerization processes are equilibria) of M(OEt)\textsubscript{4} is 2.4 for M = Ti, 3.6 for Zr and Hf, 4.0 for Sn, and 6.0 for Th [5].

The degree of oligomerization influences not only the solubility of the metal alkoxides (highly associated oligomers may even be insoluble) but also the reaction kinetics. Coordinatively unsaturated species have a higher reactivity in hydrolysis and condensation reactions. For example, monomeric Ti(O'Pr)\textsubscript{4} is hydrolyzed more rapidly than trimeric Ti(OEt)\textsubscript{4} despite the larger alkoxo ligands.

Association via alkoxide bridges is not the only way to reach a higher coordination number. When the alkoxides are dissolved in polar solvents such as alcohols, addition of solvent molecules may occur and compete with association. For example, hydrolysis of Zr(O'nPr)\textsubscript{4} in PrOH is very fast and results in a precipitate, while hydrolysis of the same alkoxide in cyclohexane gives a homogeneous gel. The explanation of this difference is that OR-bridged oligomeric species are formed in cyclohexane solution, while an alcohol molecule is coordinated to Zr(O'nPr)\textsubscript{4} in n-propanol solution (Figure 1.6). Upon hydrolysis, the coordinated ROH is more easily cleaved than the OR bridge. The structures of M\textsubscript{2}(OR)\textsubscript{8}(ROH)\textsubscript{2} [6] show that both ways of reaching higher coordination numbers, that is, oligomerization through OR bridges and coordination of neutral Lewis bases, can occur simultaneously. Note that the coordinated ROH molecules are stabilized by hydrogen bonds. Neither association to oligomeric species nor solvate formation is observed for silicon alkoxides.

The high reactivity of metal alkoxides can be moderated by chemical modifications. The general approach is to replace one or more alkoxo ligands by groups that are less easily hydrolyzed than the remaining OR groups and additionally block coordination sites at the metal. The most common ligands are carboxylate

![Figure 1.6 Schematic structure of $M_2(OR)_8(ROH)_2$ ($M$ = Ti, Zr, and Hf).](image-url)
or β-diketonate groups, but any other anionic bidentate ligands (BLs) can also be used, such as β-ketoesterates, aminoalcoholates, oximates, phosphonates, and sulfonates [7] The bi- or (tri-)dentate ligands can be chelating or bridging and are introduced by reactions of metal alkoxides with acidic compounds (BL–H) (Eq. (1.6)). In practical sol–gel processes, the isolation of the derivatives M(OR)$_x$–n(BL)$_n$ is not necessary; the compounds BL–H are just added to the precursor mixture. Note that the term “chemical additives,” which is often used for the compounds BL–H, is misleading, because a new derivative is formed in situ.

$$M(OR)_x + n \text{BL–H} \rightarrow M(OR)_{x–n}(\text{BL})_n + n \text{ROH} \quad (1.6)$$

The new precursor, M(OR)$_{x–n}$(BL)$_n$, can also oligomerize through OR bridges for the same reasons as discussed above. It has a different reactivity and different building block properties than M(OR)$_x$. The situation is comparable to alkoxysilanes: Si(OMe)$_4$ has a different reactivity than MeSi(OMe)$_3$ and leads to different network structures. The introduction of organic groups (e.g., BL) has several consequences on hydrolysis and condensation reactions:

- The substitution of a monodentate ligand (OR$^–$) by a bidentate ligand (BL$^–$) blocks an additional coordination site at the metal. This reduces the reactivity in hydrolysis and condensation reactions, where a nucleophile must be coordinated to the metal in a transition state or an intermediate.

- Substitution leads to a lower degree of condensation (fewer M–O–M links per metal atom possible). The formation of gels instead of precipitates is thus facilitated and different gel structures are obtained.

- Inductive effects of the BL may also influence the reactivity (similarly to the influence of groups R on the reactivity of silicon alkoxides discussed above).

- The bidentate ligand may stereochemically direct the site of nucleophilic attack (e.g., cis or trans to the coordinated BL) during hydrolysis and condensation reactions and thus influence the microstructure and texture of the gels (see below).

- Organic groups change the polarity (hydrophilicity/hydrophobicity) of the precursor and the resulting gels. Hydrogen bonding plays a tremendous role in sol–gel chemistry; polarity changes also influence the network of hydrogen bonds.

- Functional or nonfunctional organic groups can be introduced by the bidentate ligands. In the methacrylate derivative in Figure 1.7, for example, the functional organic group (methacrylate group) is connected to the (dimerized) Ti(OR)$_3$ moiety by means of a β-ketoesterate ligand. With regard to materials syntheses, this compound would be analogous to the often used methacrylate-substituted silane (MeO)$_3$Si(CH$_2$)$_3$OC(O)CMen=CH$_2$. While Si–C bonds are hydrolytically stable and thus allow introducing organic substituents into the gel materials, metal–carbon bonds in transition metals are usually cleaved by water and therefore hydrolytically stable bidentate groups must be used as linkers.
As was discussed for silicon precursors (Figure 1.2), closed structures (oxo clusters) can be formed as well by the condensation reactions, and the same remarks apply with regard to their importance in sol–gel processes. Figure 1.8 shows an example of a cluster obtained by hydrolysis of an organically substituted zirconium alkoxide derivative.

Although the use of $\text{M(OR)}_{x-n}(\text{BL})_n$ compounds is very similar to that of $\text{R}’\text{Si(OR)}_3$, there is one important chemical difference. The $\text{M(OR)}_{x-n}(\text{BL})_n$ derivatives are coordination compounds, which means that they are prone to coordination/decoordination equilibria. A compound $\text{M(OR)}_y(\text{BL})$, for example, may be in equilibrium with $\text{M(OR)}_{y+1} + \text{M(OR)}_{y-1}(\text{BL})_2$. This does not affect the practical sol–gel procedures, but may have structural consequences for the final material. While a group $\text{R}’$ stays at the silicon atom with which it was introduced upon sol–gel processing of $\text{R}’\text{Si(OR)}_3$, the BL ligands may migrate to other atoms and accumulate in certain areas, for example, at the surface of sol particles.

The mechanisms of condensation reactions of metal alkoxides are similar to those of silicon alkoxides (Eqs. (1.3) and (1.4)) in a sense that an $\text{M}–\text{OH}$ group undergoes nucleophilic attack to another metal atom. Due to the higher propensity of metal atoms to interact with nucleophilic agents, base or acid catalysts are not needed in most cases, as has been discussed before. There is an important stereochemical difference, however. When a silica network grows, the question that decides the texture of the obtained gels is whether condensation occurs preferentially at the end of a chain of corner-sharing $\text{SiO}_4$ tetrahedra or at a central atom. For transition metals, this issue is more complicated and hardly understood in detail in most cases. First, the coordination polyhedra of transition metals must also share edges and faces to satisfy the coordination requirements of the metal (see Figure 1.4). Second, hydroxo or aquo ligands coordinated to the same metal may be chemically nonequivalent due to the effect of different trans ligands. For example, an aquo ligand trans to an M=O unit is a better leaving group than that trans to an M–OH group. The nucleophilicity of OH groups or the acidity of hydroxo and aquo ligands is also influenced by the trans ligands.

Third, the counterion ($X$) of a metal salt precursor ($\text{MX}_n$) can compete with the aquo ligands for coordination to the metal center and can act similarly to
the BL in modified metal alkoxide precursors. An anionic counterion (X) may remain coordinated to the metal through all stages of the overall process and even turn up in the final product. Its (complete) removal may be difficult and may require special postsynthesis procedures. Hydrolysis and condensation reactions may thus proceed differently when different salts of the same metal are employed. A strong metal–anion interaction (coordination) can influence sol–gel processing in the same ways as the bidentate ligands discussed above. When metal oxides are prepared by sol–gel processing of metal salt precursors (MXₙ), the choice of the metal salt must therefore be well considered.

1.3 Sol–Gel Transition (Gelation)

1.3.1 Hydrolytic Sol–Gel Processes

The crystalline state of a solid compound is thermodynamically more favorable than the amorphous state. In order that crystallization can occur, however, (crystalline) nuclei must be formed and growth of the nuclei must be possible. If either nucleation or crystal growth is inhibited under a given set of experimental conditions, amorphous materials are formed, which include glass-like materials and gels. The formation of amorphous networks (i.e., networks without a three-dimensional order) is particularly favored if there are many degrees of freedom for the mutual arrangement of the building blocks (see Figure 1.4 and associated discussion).

This is the reason why silica-based materials form gels more easily than other oxides, and consequently the chemistry of silica gels is particularly well
investigated. The following discussion of gelation is thus focused on silica, but is analogous for other materials.

In the initial stage of sol–gel reactions, small three-dimensional oligomeric particles are formed. Figure 1.9 schematically shows the structural development of silica gels from molecular precursors. Whether the initially formed primary (nano)particles aggregate once they have reached a certain size or continue to grow depends on the experimental conditions. Aggregation of the primary particles may lead to (larger) secondary particles (features at the descending branches in the left part of Figure 1.9). Whether the particles (with a polymeric or dense substructure) may remain suspended in solution (i.e., form a stable sol) or aggregate to form a three-dimensional network (i.e., a wet gel) again depends on the system and the experimental conditions. The basic chemical processes (hydrolysis and condensation), however, are the same. In nonsilicate systems, the network-forming (nano)particles may be crystalline or semicrystalline.

As the sol particles aggregate and condense, the viscosity of the sol gradually increases. The sol–gel transition (gel point) is reached when a continuous
network is formed. Before the gel point has been reached, the colloidal dispersion behaves like a more or less viscous liquid. At the gel point, the viscosity increases sharply, and a form-stable, elastic gel body is obtained. From a practical point of view, the gel time \( t_{\text{gel}} \) (time at which the gel point is reached after starting hydrolysis and condensation reactions) is determined by turning the reaction vessel upside down. Since all liquid is retained in the gel body, no liquid can flow out of the vessel. For the same reason, the volume of the gel in this stage is the same as that of the original precursor solution.

Typical \( t_{\text{gel}} \) values for Si(OEt)\(_4\) are 92 h with 0.05 mol of HCl or 107 h with 0.05 mol of NH\(_4\)OH as the catalyst. Without a catalyst, \( t_{\text{gel}} \) would be about 1000 h [11]. The \( t_{\text{gel}} \) is generally lowered by all parameters that increase the rate of condensation reactions, as discussed above. These parameters thus allow to deliberately influence the gel times.

A wet gel, by definition, consists of a continuous solid network, the pores of which contain a liquid phase. At the gel point, however, unbound oligomers of various sizes or even monomeric species are still dissolved or dispersed in the pore liquid. This is important for the aging of gels (see below).

The simplest picture of gelation is that the particles grow by aggregation or condensation until they collide to give clusters of particles. (Note that in the models describing gelation, the term “cluster” is used equivalent to “particle” or “oligomeric species.”) The clusters become bigger and bigger by repeated collisions. This process produces clusters of various sizes. In this picture, which is mathematically described by the percolation theory, the gel is formed when the last link between two giant clusters of particles is formed. This is called the “spanning cluster,” that is, a cluster that reaches across the vessel that contains it. Note that the bond resulting in the formation of the spanning cluster is not different from the previously formed bonds; that is, gelation is not a special thermodynamic event.

An alternative description of gelation is given by kinetic growth models. These also explain the different microstructures upon changing the reaction conditions. Depending on the conditions, growth in silicate systems may occur predominantly by condensation of clusters with monomers or with other clusters. The rate of the condensation reactions may be diffusion or reaction limited.

As has been discussed before, hydrolysis of silicon alkoxides is faster than condensation under acidic conditions. Since all species are hydrolyzed at an early stage of the reaction, they can condense to form small oligomeric species (clusters) with reactive Si–OH groups. Under these conditions, reactions at terminal silicon atoms are favored (see above). This results in polymer-like gels; that is, small clusters undergo condensation reactions with each other to give a polymer-like network with small pores.

Monomer–cluster growth, on the other hand, requires a continuous source of monomers. Hydrolysis is the rate-determining step under basic conditions. The hydrolyzed species are immediately consumed by reaction with existing clusters because of the faster condensation reactions. Furthermore, the rate of hydrolytic cleavage of (terminal) Si–O–Si bonds is much higher than that under acidic conditions.
conditions. This additionally ensures that a source of monomers is available. Condensation of clusters among each other under these conditions is relatively unfavorable because this process requires inversion of one of the silicon atoms involved in the reaction. Reaction at central silicon atoms of an oligomer unit is favored under basic conditions (see above). The resulting network therefore has a particulate character with big particles and large pores (colloidal gels).

The formation of larger particles, mainly in aqueous systems, is also favored by Ostwald ripening by which small particles dissolve and larger particles grow by condensation of the dissolved species. Solubility of a particle is inversely proportional to its radius. The solubility of nanoparticles (<5 nm) therefore is rather high. Growth stops when the difference in solubility between the smallest and the largest particles in the system becomes only a few ppm. Solubility depends on the given conditions (temperature, pH of the solution, etc.). At higher temperatures, larger particles are obtained because the solubility of silica is higher.

One of the advantages of amorphous materials is that their chemical composition is not bound to given stoichiometries. Thus, mixtures of different molecular precursors, that is, building blocks of different composition, can be coprocessed. This option is mainly used to prepare inorganic–organic hybrid materials or mixed oxides. If two or more different metal alkoxides are coprocessed, be it alkoxide mixtures of different metals or mixtures of parent alkoxides and their organically modified derivatives, one has to take their different reaction rates into account. Sol–gel materials from precursor mixtures with a random distribution of the building blocks as they are often drawn in schemes are wishful thinking in most cases. In reality, phase separation will occur; the question is on what scale. Materials being considered to be homogeneous to the naked eye or even a microscope may have inhomogeneities on the micro- or nanometer scale; that is, they may, for example, contain structural features related to the spherolite/POSS or metal oxide clusters discussed before. If mixtures of organotrialkoxysilanes R’Si(OR)₃ and tetraalkoxysilanes are used, the organically substituted compounds react faster than the Si(OR)₄ in acid-catalyzed systems and slower in base-catalyzed systems (Figure 1.10) due to the different mechanisms and transition states [12]. Therefore, materials with a different structure will be obtained by working in solutions of different pH.

![Figure 1.10](image-url) When a Si(OMe)₄/R’Si(OMe)₃ mixture is reacted under base-catalyzed conditions, the gel network is initially formed from Si(OR)₄ because it reacts faster. The R’SiO₂⁻ units then condense onto the network. In an acidic medium, the situation is reversed.
If the difference in reaction rates is very high, macroscopic phase separation may occur. For example, if water is added to a mixture of Si(OR)\(_4\) and Ti(OR)\(_4\), titania will precipitate while (partially) hydrolyzed alkoxysilanes are still dissolved. The reason is the about 10\(^5\)-fold higher reactivity of Ti(OR)\(_4\). Several strategies have been developed to avoid *macroscopic* phase separation in multi-precursor systems:

- Prehydrolysis of the faster reacting component with a substoichiometric proportion of water leads to clusters/nanoparticles onto which the slower reacting component may condense. After addition of the latter, the rest of water is added.
- Moderating the reactivity of the faster reacting precursor (mostly metal alkoxides) by means of “chemical additives” such as acetylacetone or acetic acid. Chemically speaking, these “additives” convert the parent metal alkoxides *in situ* to substituted derivatives M(OR)\(_{x-n}\)(BL)\(_n\) (Eq. (1.6)) with a lower reactivity, as discussed before. To obtain purely inorganic materials (mixed oxides), the organic groups must be removed by some postsynthesis treatment (see below).
- A more recent approach is linking two different metal alkoxide moieties by means of a (hydrolytically stable) organic group. Due to this link, the system cannot undergo macroscopic phase separation, even if the reactivity of the two moieties is very different. An example is shown in Figure 1.11, where a β-diketonate-substituted alkoxysilane was coordinated to Ti(OR)\(_4\). While a mixture of Si(OR)\(_4\) and Ti(OR)\(_4\) spontaneously phase separates upon addition of water, transparent gels are obtained with the bimetallic precursor. Due to the different reactivity of the Si(OR)\(_x\) and Ti(OR)\(_x\) groups, however, Ti/O nanoparticles are initially formed, which are surrounded by the organic groups. In a later stage of the reaction, the silica network is formed around the Ti/O particles [13]. Note the analogy to diblock copolymers.

![Figure 1.11](image.png)

*Figure 1.11*  Titanium alkoxide derivative with a β-diketonate-substituted silane as a ligand, as a precursor for a silica–titania mixed oxide.
1.3.2
Nonhydrolytic Sol–Gel Processes [14]

The conventional (hydrolytic) sol–gel process is based on the hydrolysis and condensation of molecular precursors, leading to oxide networks. The oxo ions originate from water that is added as a reagent or may be formed in situ by water-producing reactions, such as ester formation and aldol condensation. Variations of these reactions have been developed, in which the oxo groups are formed by alkyl chloride, ether, or ester elimination instead of water or alcohol elimination (Eq. (1.2)) in the traditional sol–gel process. This process has been termed the nonhydrolytic sol–gel process because no water is added and the oxygen atoms originate from an organic O-donor. The basic reactions are given in Eq. (1.7).

\[
\equiv M – OR + M′ – X \\
\| \\
\equiv M – X + M′ – OR
\]

\[
\rightarrow \equiv M – O – M\equiv + R – X \quad (X = Cl, OR, OOCR) \quad (1.7)
\]

Condensation occurs at temperatures between 20 and 100 °C; sometimes, a catalyst is needed (FeCl₃ is often used). The kinetics of nonhydrolytic sol–gel processes depends on the nature of the metal, the nature of the oxygen donor, electronic effects of the group R, and the composition of the initial metal alkoxide/metal chloride (carboxylate) mixture, but is generally slower than that for aqueous processes. Noteworthy features of this method are that nonhydrated oxides without residual hydroxo groups are obtained, due to the aprotic conditions, and that in bimetallic systems the metals M and M′ have an alternate order (no phase separation), due to the reaction mechanism (Eq. (1.7)). A limitation of nonhydrolytic processes is that the M/M′ ratio is not freely selectable if fully condensed products are targeted. For this reason, sol–gel processes of mixed metal systems are sometimes initiated by nonhydrolytic reactions (to obtain a high homogeneity) and then completed by hydrolytic reactions (to obtain complete hydrolysis and condensation).

1.3.3
Inorganic–Organic Hybrid Materials [15]

One of the major advances of sol–gel processing is undoubtedly the possibility of synthesizing hybrid inorganic–organic hybrid materials, where organic and inorganic building blocks are combined. Sol–gel processing is a very suitable way to make such materials due to the mild processing conditions. The high-temperature synthesis route to ceramic materials, for example, does not allow the incorporation of thermally labile organic moieties. There are a wide range of
possibilities to vary the composition and structure, and thus the properties of hybrid materials:

- chemical composition of the organic and inorganic moieties,
- ratio of the inorganic to organic components,
- kind of interaction between organic and inorganic moieties,
- structure of the building blocks, and
- distribution of the building blocks (random, block-like, etc.).

Two different approaches can be used for the incorporation of organic groups into an inorganic network by sol–gel processing, namely, embedding of organic molecules into gels without chemical bonding (class I hybrid materials) and incorporation of organic groups through covalent bonding to the gel network (class II hybrid materials).

Embedding of organic molecules is achieved by dissolving them in the precursor solution. The gel matrix is formed around them and traps them, and the organic and inorganic entities interact only weakly with each other. A variety of organic or organometallic molecules can be employed, such as dyes, catalytically active metal complexes, sensor compounds, or even biomolecules or small particles. If sol–gel processing of alkoxides is performed in the solution of an organic polymer, the inorganic network (formed by sol–gel processing) and the organic network interpenetrate but are not bonded to each other. The presence of organic compounds may of course influence gelation because of polarity changes in the system.

Very important sol–gel materials are obtained when functional or non-functional organic groups are covalently linked to oxide networks (class II materials). In silicate systems, it is mostly done by using organotrialkoxysilanes, R'Si(OR)3, as precursors for sol–gel processing. Nearly any organic group R' can be employed; the only requirement is that the group R' must be hydrolytically stable. Since Si–C bonds are hydrolytically stable, the organic groups are retained in the final material after sol–gel processing. In the case of metal alkoxides, the bidentate ligands discussed before can be used to introduce organic groups (see Figure 1.7 for an example). The influence of organic groups on the hydrolysis and condensation reactions was already discussed in Section 1.3.

One of the most important issues is that each pending organic group results in a lower cross-linking density of the resulting inorganic network. For example, processing of Si(OR)4 results in four network-forming Si–O–Si bonds per silicon, but only three when R'Si(OR)3 is processed. For this reason, organotrialkoxysilanes are typically coprocessed with tetraalkoxysilanes or metal alkoxides to obtain the properties characteristic of highly cross-linked networks. An alternative is the use of compounds (RO)2Si–R”–Si(OR)3 (or analogous metal alkoxide derivatives) [16]. This allows incorporation of organic groups without lowering the network connectivity, because one Si–O–Si entity is replaced by Si–R”–Si. The groups R” can range from simple alkylene or arylene groups to more complex entities, as shown in Figure 1.12.
1.4 Aging and Drying

The sharp increase in viscosity at the gel point freezes in a particular network structure. Thus, gelation is structurally related to glass-forming processes. However, this structure may change considerably with time, depending on the temperature, solvent, or pH conditions. It is very important to realize that the chemical reactions leading to network formation are not finished with gelation, and structural rearrangements take place in the wet gels. This phenomenon increases the stiffness of the gels and is called aging. Aging is due to several processes:

- The network of a wet gel still contains a continuous liquid phase. The pore liquid initially is a sol; that is, it contains condensable particles or even monomers, which eventually condense to the existing network. This causes gradual changes in the structure and properties of the gels.
- The gel network originally is still very flexible. This allows neighboring M—OH or M—OR groups to approach each other and to undergo condensation reactions, causing contraction of the network and expulsion of pore liquid. This spontaneous shrinkage of some gels is called syneresis and continues as long as the gel network exhibits sufficient flexibility. The driving force is the reduction of the large solid–liquid interface in the gels.
- Mass is dissolved from thermodynamically unfavorable regions, mostly regions with a high positive curvature or small particles. The solutes condense to thermodynamically more favorable regions, particularly in pores, crevices, particle necks, and so on. This process (“ripening” or “coarsening”) results in the reduction of the net curvature, disappearance of small particles, and filling up of small pores.

Controlled aging is an important step when monoliths are prepared. For most practical sol–gel processes, aging plays an indirect role. For example, when films
or coatings are deposited, gelation occurs concomitant with or immediately after the deposition process. This is mostly followed by a drying or hardening step (see below). In order to obtain coatings with reproducible properties, the period between deposition and drying/hardening, during which aging occurs, must be kept constant.

The evaporation of the liquid from a wet gel by temperature increase or pressure decrease, that is, conventional drying, proceeds in three stages:

1) The gel shrinks by the volume that was previously occupied by the liquid. The liquid flows from the interior of the gel body to its surface. If the network is compliant, the gel deforms. Upon shrinkage, OH groups at the inner surface approach each other and can react with each other and new $M-O-M$ bridges are formed. As drying proceeds, the network becomes increasingly stiffer and the surface tension in the liquid rises correspondingly because the pore radii become smaller.

2) This stage of the drying process begins when the surface tension is no longer capable of deforming the network and the gel body becomes too stiff for further shrinkage. The tension in the gel becomes so large that the probability of cracking is highest. In this stage of drying, the liquid/gas interface retreats into the gel body. Nevertheless, a contiguous funicular liquid film remains at the pore walls; that is, most of the liquid still evaporates from the exterior surface of the gel body.

3) In this stage, the liquid film is ruptured. Eventually, liquid is only in isolated pockets and can leave the network only by diffusion via the gas phase.

Two processes are important for the collapse of the network. First, the slower shrinkage of the network in the interior of the gel body results in a pressure gradient that causes cracks. Second, larger pores will empty faster than smaller pores during drying; that is, if pores with different radii are present, the meniscus of the liquid drops faster in larger pores. The walls between pores of different size are therefore subjected to uneven stress, and crack (Figure 1.13).

![Figure 1.13](image-url) Contracting surface forces in pores of different size during drying.
For these reasons, xerogel powders are usually obtained when wet gel bodies are conventionally dried. Although strategies were developed to obtain crack-free xerogel bodies, the large shrinkage cannot be avoided. Due to the shrinkage problem, one of the most important applications of sol–gel materials is for films and coatings, where shrinkage is easier to control.

Methods have been developed by which the porous network structure is retained upon drying, the most important being drying with supercritical fluids and the so-called ambient-pressure drying, where formation of Si–O–Si bridges is prevented by hydrophobization of the pore walls. The obtained materials are called aerogels (because the pore liquid is replaced by air) [17] and will be treated in Chapter 18.

1.5 Postsynthesis Processing

The final step in the synthesis of many (but not all) sol–gel materials is some postsynthesis treatment after or concomitant with drying, depending on the intended properties or uses.

- If purely inorganic materials are targeted, the gels are heated in air or in an inert atmosphere at not too high temperatures to remove residual organic groups or organic compounds that were deliberately added during synthesis, such as “chemical additives,” porogens, and templates.
- Higher temperatures are needed for crystallization. Although crystalline materials are not the prime target of sol–gel processing (see Section 1.1), the processing advantages (as for producing films or fibers) might nevertheless render sol–gel processing the method of choice.
- A very important subclass of inorganic–organic hybrid materials includes those with dual polymer networks, where the inorganic network structures are linked by organic groups or polymer fragments. Such hybrid materials are commonly prepared from R’Si(OR)3, or related metal alkoxide derivatives (as in Figure 1.7), where R’ is capable of undergoing polymerization or cross-linking reactions. The methacrylate-substituted silane (MeO)3Si(CH2)3OC(O)CMe=CH2 is often used for this purpose. After sol–gel processing, the organic part of the dual network is formed in a separate processing step by standard organic reactions of the pending groups R’, such as polymerization and addition reactions. This can be induced by thermal or photochemical treatment of the gels.

1.6 Concluding Remarks

The outcome of sol–gel reactions can be summarized in seemingly simple equations, such as Si(OR)4 + 2H2O → SiO2 + 4ROH. Looking at sol–gel processes in
detail shows, however, that the chemistry behind can be very complex. This results in an ambivalent situation: one side of the coin is that the many chemical and processing parameters allow producing materials with a huge variety of compositions, textures, and forms by deliberate variation of these parameters. The other side of the coin is that development and optimization of new sol–gel materials still has to rely on empiricism and expert knowledge due to the complexity of chemical reactions. Very reliable and reproducible sol–gel processes have been developed in the past, also on an industrial scale, but only a few of them are understood in detail (although the general principles are known). The notion that sol–gel materials can be deliberately “designed” from the scratch, that is, by assembling defined molecular building blocks according to a chemical blueprint, is wishful thinking for the time being, but a goal that is worth to pursue in the future.

References


