SOL–GEL TECHNOLOGY

1. Introduction

Sol–gel technology is a field of growing importance and the subject of textbooks (1,2). In practice, although organic gels exist, this field really designates a group of processing techniques to synthesize materials in which one component at least is inorganic. Nevertheless, a large variety of organic–inorganic hybrid or even biochemical–inorganic hybrid materials are now being developed. When made by sol–gel processing, all these materials are achieved after a succession of transformations beginning with chemical compounds known as precursors. The first chemical step, which is carried out in liquid medium at near room temperature, transforms these precursors to a dispersed colloidal state. The latter can be either a sol or a polymeric solution. In the second step, the previous dispersed colloidal state is made to transform to an interconnected colloidal state known as a gel. In a third step, a gel usually needs to be dried. Finally, it may possibly be transformed to a dense ceramic by thermal treatment at higher temperatures.

2. Overview of Sol–Gel Technology

2.1. Main Definitions.

A dispersed colloid is a divided state of solid matter, such that each individual colloidal particle can be maintained in suspension, either in a liquid or in a gas. The driving force responsible for such a suspended state is provided by the local thermal energy, that is to say the local temperature, which keeps the colloidal particles under constant and random agitation known as Brownian motion. This thermal driving force must be of a magnitude larger than the action of gravity, which means that each particle must have a very small mass. In practice, this condition can be satisfied with a range of particles with very different shapes. Colloidal particles are often nearly spherical with a size that depends on the nature of the material, typically $<0.2\,\mu m$ with oxides. Or they can be plate-like particles with an extent in the plate that can exceed $1\,\mu m$ while the thickness is typically $<0.1\,\mu m$, such as occurring in some clay suspensions. Or they can be more linear polymeric molecules often observed in organic chemistry, with an individual mass similar to that of the previous spherical oxide particles. In both former examples, a sol designates a stable suspension of colloidal particles within a liquid, while in the third one it designates a stable solution of colloidal polymers. When colloidal particles are suspended in a gas, such a dispersed state is usually referred to as an aerosol, in which case each colloidal particle may itself be a liquid colloidal droplet, as in fog.

In a sol, collisions between colloidal particles or polymers subjected to Brownian motion are frequent. The evolution in time of a sol will depend on the results of such collisions. One first possibility is that two particles may be able to rapidly establish bonds between each other during a collision, in which case relatively dense aggregates are progressively built. This phenomenon is known as coagulation or flocculation. When each floc has reached a mass such that the force of gravity significantly exceeds the driving force of Brownian motion, it segregates in the lower part of the reactor containing the sol to form a precipitate. Many materials preparations described in the scientific literature occur by

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such a “precipitation” technique (or coprecipitation when several different components are made to precipitate) and should not be described as sol–gel. A second opposite evolution occurs when no bonds have time to establish between particles during collisions. In this case, a sol is said to be stable. Nevertheless, this is a stability of “kinetic” nature, that is to say a metastable state, not a thermodynamically stable one. Aggregation can indeed occur at a rate that largely depends on the nature of particles and medium where they are suspended. Hence, a sol may precipitate after a time scale that may range from a few seconds to hundred of years. In an exploratory laboratory research, kinetic stability for a few days or at least a few hours is often sufficient. However, industrial applications often require stability on a much longer time scale to be practical.

The formation of a gel, or gelation, corresponds to a state of aggregation intermediate between coagulation and sol stabilization. In this case, bonds form between colloidal particles or polymeric molecules so as to favor architectures that must be largely, but not completely, linear. Indeed, some branching points are necessary to insure the formation of a unique three dimensional (3D) very open solid grid. Although the latter grid remains completely impregnated with the liquid medium from the sol, it is so porous that no precipitation occurs under gravity. Rather, the full liquid sol transforms to a single and uniform solid mass that does not flow any more, as in a “jelly”. It is termed a “gel”. A gel has a wet feel, although it can be cut to solid geometrical shapes, eg, a cube. The ease to transform a sol to a gel largely depends on the type of colloidal particles in suspension. Such a transition very easily occurs with polymeric solutions or lacy colloidal particle, in particular in organic chemistry and with silica. The time scale is here also very variable and can range from a few seconds to months. Gelation is more complicated with spherical dense colloidal oxide particles, eg, ZrO_2, TiO_2 and many other complex oxide compositions. In some dry gels termed aerogels, the pore volume inside the solid network can be as high as 99.8% (3), which corresponds to a solid of density about three times that of ambient air. Such solids are sometimes described as solid smoke. They can be very transparent and the trajectory of a visible light beam can easily be seen across an entire monolith, as across smoke.

2.2. Historical Background. Sols and gels are two forms of matter that exist naturally, in particular in biology where they comprise the eye vitrea, blood, serum, and milk, but also in materials science with some clay and silica gels (4). Graham is usually considered as being the founder of colloidal materials science, in 1861. However, the oldest sols prepared in a laboratory were made of gold colloidal particles, by Faraday in 1853 (5). The first stable silica gels made in a laboratory were by Ebelmen in 1846 (7,8). During the century that followed, an extremely large range of different oxides, as well as complex mixed oxide compositions and some non-oxides have been synthesized by sol–gel, although studies based on silicates outnumbered all other compositions (2).

The scientific background on which rests the modern expertise in sol–gel technology, is made of contributions from very different fields of science. The latter domains regard the formation of colloidal particles, sol stabilization, coagulation, precipitation, and gelation, as well as recent coordination chemistry developments to synthesize new precursors from which more elaborate sol–gel materials can be designed. A better understanding of the formation of colloidal particles of controlled size, by nucleation and growth from solutions of precursors, was proposed by La Mer (9). This knowledge was applied with success to the growth of a large variety of monodispersed colloidal particles (particles of uniform size), by Matijevic (8–12). One possible method to control the coagulation or the stabilisation of a sol depends on purely electrostatic interactions. Full understanding of this aspect of colloids was developed by Derjaguin, Landau, Verwey and Overbeek (13), in a theory presently gathered under the appellation of D.LV.O theory according to the names initials of these scientists. The latter theory was distinguished by the attribution of a Nobel Prize in physics.

It is also possible to control the coagulation by grafting various organic polymers on colloidal particles. In this case, interactions between the grafted polymers and the solvent are critical. The steric theory that unifies the underlying science (14) is derived from a theory on the behavior of polymer solutions, by Flory (15,16) and by Huggins (17). The former scientist was granted the Nobel Prize in chemistry. Next, Flory (18) and separately Stockmayer (19), established a precise definition of the gelation phenomenon, for polymer solutions undergoing growth by condensation reactions. The gel point was defined as the critical value ξ_c of the extent of condensation reactions, where for the first time a 3D continuous network was formed. This network was only limited by the size of the container, but the value of ξ_c was itself independent of the container size. In more recent mathematical developments, the theory of Flory and Stockmayer were shown to coincide with one of the possible percolation models, invented by Hammersley (20). The gel network architecture just after gelation was shown to be best described by a fractal geometry, introduced in mathematics by Mandelbrot (21). For dense colloidal particles, other mathematical simulation techniques termed diffusion limited aggregation (DLA) models, based on the random fractal aggregation of such particles were developed with success (22). For practical applications, gel drying is also very critical and important technological developments have brought new possibilities. This is the case of the supercritical drying investigated for the first time by Kistler (23). This technique led to the production of aerogels with an extremely high pore volume, up to 99.8% as previously mentioned. Also, doping of sols with chemical additives to control gelation and drying, in particular surfactants (24), led to the discovery of micellar materials.

Recent sol–gel key developments are largely depending on progress in pure chemical synthesis, especially in coordination chemistry. The task is to develop precursors with new ligands, such that homogeneous gelation can indeed occur with exotic compositions. It is also necessary to design sol–gel materials with new surface functionalities, eg, to make them hydrophobic. Other applications require grafting or immobilizing various chemical compounds, eg, molecular catalysts, enzymes, or other biomolecules, in gels. Naturally, organic molecules themselves able to undertake polymeric gelation could be grafted, which lead to the development of quite interesting hybrid organic–inorganic materials, which do not exist in Nature (22).

2.3. Range of Applications. The first industrial interest for sol–gel materials (25) followed by their commercialization as coatings (26), appeared about a century after publication of the first scientific papers on such materials (6–8). Nevertheless their quite original properties slowly made them attractive for a large variety of different applications, leading to more extensive basic research (2). One of the first advantages of sol–gel materials was their high specific pore volume and specific surface area. In a dry state, they could be used as absorbents or desiccants. This property also made them interesting for applications in heterogeneous catalysis (27). The sol–gel material could itself be a catalyst, eg, a transition metal oxide, eg, NiO, or used as a support of a catalyst, eg, γ-alumina used as a support of platinum. A second advantage was the high purity of the materials that could be obtained by sol–gel processing, by comparison with traditional ceramics processing. This advantage was used to synthesize nuclear oxide fuels, eg, ThO_2, in the shape of spherical particles of several μm in diameter and of uniform size. With silica, Stöber also discovered the possibility to directly grow spherical silica powder of uniform size, within a liquid medium (28). The sol–gel processing technology was then extended to a large variety of simple or complex oxides for applications as optical, dielectric, or piezoelectric materials; ionic or electronic semiconductors; superconductors (2). With high temperature traditional ceramics, only the equilibrium thermodynamic phases tend to form. Since the sol–gel processing involves much lower processing temperatures, the formation of new metastable phases with interesting technical properties is common, eg, in mixed-oxide systems, eg, $BaO-TiO_2$.

A key problem of sol–gel processing was the breaking of gels during drying. To avoid this drawback and obtain net shape monoliths, drying had to be controlled. This task was easier on monoliths with small dimensions, of the order of 0.1 to a few hundreds of microns (μm). Hence, the sol–gel technology was more readily applied either to the formation of powder of controlled size or to surface coatings. The formation of fibers was more difficult, because not only the net shape must be controlled, but the formation of radial flaws that lower the mechanical properties of such fibers must be avoided. Yet, the sol–gel technology was interesting because fibers could be made with new compositions not feasible by the melt processing. Also, sintering often occurred at a lower temperature than in conventional processing. To obtain uncracked larger monoliths, the control of drying is much more involved. One solution, developed by Hench, was to add drying control chemical additives (DCCA) in silica sols (29). Optical lenses with a few centimeters in diameter and a perfect optical surface finish could be directly fabricated. Another solution consisted in drying wet gels by supercritical drying techniques. The dry gels produced by this technique are termed aerogels (3). They have themselves found a range of new applications described further in this article.

The difficulty to dry large size monoliths is not a concern for the most recent applications. Indeed, it can now be considered that some of the largest potential applications of sol–gel materials are in nanotechnology, in particular in sensors and biosensors as summarized in the section properties and applications of Sol–gel Materials. Gels can be efficient immobilization media of molecular catalysts, including enzymes, as well as full living cells.

3. Sol–Gel Process Steps

3.1. Overview.

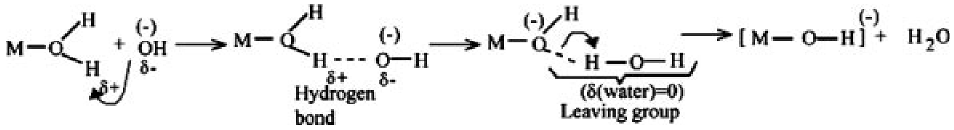
Many variations exist in sol–gel processing, because the technique needs to be adapted to the nature, final shape, and function of a ceramic part. Nevertheless, the central art of sol–gel technology consists in achieving a successful gelation step as illustrated in Fig. 1. First, chemical compounds known as the precursors must be selected and dissolved in a selected liquid solvent, where they will be chemically transformed. These chemical transformations often aim at first forming either a sol of colloidal particles or a solution of oligomers (small polymers). A sol is a fluid, so that it can be cast in a mold and possibly be stored for a certain time before further casting.

Gelation is performed after either casting in a mould, or applying various shaping techniques, eg, spraying on a surface, dipping, or spinning through a set of rotating nozzles. To achieve gelation, the chemical transformations in a sol must be allowed to proceed until a single and interconnected network forms, only limited by the walls of the container. The first time such a network is observed is the gel point, previously defined. From this point, and as chemical transformations keep proceeding, a wet gel exists. A wet gel behaves as a solid and it already has the shape of the desired final object: spherical powder, fiber, coating, or small monolith. Yet, it is extremely porous and impregnated with the solvent from the sol. A wet gel also is a very weak solid. It is often necessary to strengthen it before drying, eg, by aging it in appropriate liquid medium conditions. Another step in sol–gel art is drying: A very critical step as previously mentioned. In many instances, a dry gel finally needs to be thermally treated to be densified. The various steps of this outline are reviewed in more detail in the next sections.

3.2. Chemical Precursors and Their Transformation

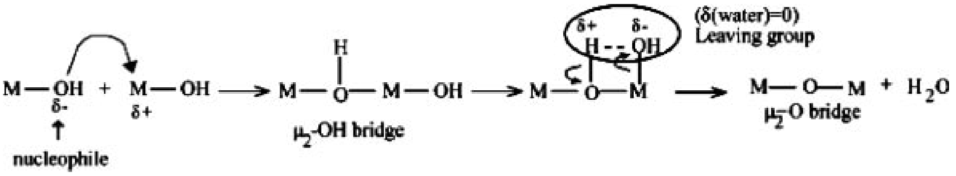
Simple Oxides. The simplest types of precursors are metal salts MX_n in which a number, n, of anions, X, are linked to the metal, M. In aqueous media, such precursors are dispersed as ions where the cationic species are solvated complexes $[M(H_2O)_N]^{z+}$, of charge z^+, built by coordination of N of water molecules to M. Depending on the metallic salt, some of the anions, X, may also remain coordinated to M, that explains the variety of materials which can be obtained with different precursors of a given metal M.

Depending on the liquid medium conditions, eg, the pH, the above complexes can be gradually hydrolyzed by reaction with free water. As a result, some of the aquo H_2O ligands of a metal complex are replaced by hydroxo OH ones. Several mechanisms have been proposed, eg, the direct transfer of one H atom from a water molecule coordinated to M, to an OH^- anion, after establishing a transitory hydrogen bond between these two molecular groups, as proposed in equation 1 (30).



(1)

In further spontaneous steps, two metal atoms, M, can be linked by either an “ol” (ie, M–(OH)–M) or an “oxo” (ie, M–O–M) bridge, eg, μ_2-O, shown in equation 2.



(2)

Such transformations depend on the partial charge carried by each atom in a complex, either negative δ^- or positive δ^+. In a theoretical model known as the partial charge model, it is considered that transformations proceed through transition states made by nucleophilic or electrophilic attacks between the complexes in solution. This is followed by modification of the polarization of each bond in this transition state. Each time the added partial charges of a group of neighbor atoms in this transition state reaches an integer charge (eg, -1, 0, or $+1$), this group of atoms becomes self-sufficient and leaves the complex. For example, a water molecule becomes a leaving group, each time the added partial charge of two neighbor hydrogen atoms plus one oxygen atom ($2\delta_H + \delta_O$) reaches the value 0.

For silica, an important inorganic salt-type precursor is sodium metasilicate, Na_2SiO_3, also termed water glass. This precursor reacts with an acid, eg, HCl, to produce a polymeric form of silicic acid, $Si(OH)_4$. The latter acid can end in the formation of hydrated silica gel, according to reaction 3.

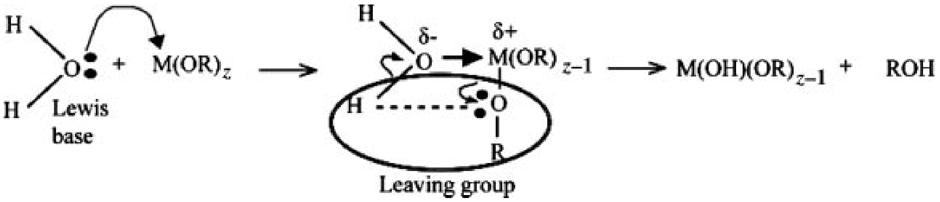
$$Na_2SiO_3 + 2\ HCl + (x\text{-}1)H_2O \rightarrow SiO_2xH_2O + 2\ NaCl \qquad (3)$$

Reaction 3 also shows that another metallic salt, presently NaCl, is liberated. This is always the case when metallic salts are used as sol–gel precursors. When pure sol–gel materials are desired, this salt must be eliminated by dialysis, which can be a tedious task. Hence, other types of sol–gel precursors, eg, the alkoxides described below, are now usually preferred. Nevertheless, metal salts are cheap and industrial processes were developed (31).

With other metal salts, hydrolysis and condensation are usually extremely rapid, so that agglomeration of particles followed by their precipitation readily occurs. Nevertheless, with hydrated acidic salts, eg, $Cr(NO_3)_3 \cdot 9H_2O$, an organic solvent, eg, ethanol, can be used. In this case, a slow proton scavenger, eg, an epoxide (propylene oxide, 1,2-epoxybutane, epichlorohydrin), can slowly replace some aqua ligands by hydroxo ones. Condensation reactions can then slowly proceed, ending in the formation of a gel monolith (32). Still, the anions must be eliminated.

Anionic impurities are absent from carboxylates, $M(O_2CR)_n$; β-diketonates, $M((O)CRCHCRC(O))_n$; alkoxides, $M(OR)_n$; or oxoalkoxides, $MO(OR)_n$ (33,34). Alkoxides are certainly the favorite sol–gel precursors. These compounds can be synthesized by direct or indirect reaction between M and an alcohol, ROH. Many alkoxides are soluble in an appropriate organic solvent. When this is not the case, it is possible to modify the nature of OR ligands coordinated to the metal atoms, in order to make the alkoxide soluble in some organic solvent. This precursor synthesis chemistry is also very useful to adjust the precursors hydrolysis and condensation rates in order to obtain a gel. The simplest metal alkoxides are methoxides, ethoxides, propoxides (normal or secondary), and butoxides (normal, secondary or tertiary), respectively, synthesized with methanol, ethanol, normal, or *sec*- propanol, *n, sec*- or *tert*- butanol. The two most frequently used silicon alkoxides are the methoxide and the ethoxide, termed TMOS (tetramethylorthosilicate) and TEOS (tetraethylorthosilicate), respectively. The main alkoxides of Si, Al, Ti, and Zr are commercially available at affordable cost. Otherwise, alkoxides can be synthesized in the laboratory. Structurally, their molecules are characterized by the existence of polar covalent M–O bonds. Their hydrolysis is carried out in an organic solvent, and water becomes a reagent added in proportions and at a rate that must be precisely controlled.

For most alkoxides of cations other than Si, the classical hydrolysis mechanism is driven by a nucleophilic attack of the oxygen atom from one water molecule onto the metal atom M in the alkoxide. The former O atom carries a negative partial charge, while the cation M carries a positive partial charge δ^+. Such nucleophilic attacks eventually replace alkoxy OR groups by OH, according to a mechanism, eg, the one illustrated in equation 4. Condensation reactions involving species carrying OH groups follow, similarly to those occurring with salts. In the end, a solid oxide network is progressively built:



(4)

Important differences in magnitude exist between the partial charges δ^+ carried by the metal atoms, depending on their nature and ligands. The magnitude of δ^+ is, respectively, 0.32, 0.63, and 0.65 in the ethoxides of Si, Ti, and Zr (30). Consequently, the hydrolysis of silicon ethoxide is slow, while that of Ti and Zr ethoxides is fast. Indeed, the latter alkoxides are spontaneously hydrolyzed by air humidity, to form dense colloidal white particles. It is necessary to slow down this hydrolysis rate, so as to favor condensation to more linear oligomers and induce homogeneous gelation. On the other hand, with Si, hydrolysis and condensation must be accelerated to obtain a solid. A catalyst is an additive that brings high partial charges to favor nucleophilic or electrophilic attacks on an OR group coordinated to Si. It can be an H^+ ion brought by a Brønsted acid, an OH^- ion brought by a Brønsted base, or a strong Lewis base, eg, a fluoride anions F^- brought by NaF. In practice, the hydrolysis and condensation reactions of Si alkoxides are sufficiently slow to be independently controlled. Acid catalysis favors the hydrolysis of Si precursors, while base catalysis favors condensation. When the catalytic conditions are such that hydrolysis is faster than condensation, polymeric silica gels are obtained.

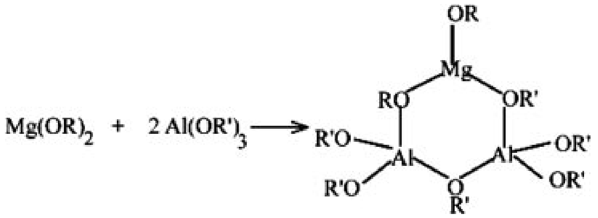
When condensation is faster than hydrolysis, colloidal gels made by interconnection of denser colloidal silica particles are formed. Two-step catalysis is possible, eg, acid followed by base catalysis, so that a large range of different silica network architectures can be designed. The gelation time and gel texture depend very much on many parameters, including the nature of solvent and Si precursor, the catalysts, the molar proportion of water to silicon. Extensive data have been reported (1,35).

Overall, ^{29}Si nuclear magnetic resonance (NMR) studies have shown that much more linear oligomers can be formed with silicon precursors than with precursors of other metals. The situation is quite analogous to the ability to make a random glass network by quenching an oxide melt. Glass making is easier with SiO_2 than with many other metal oxides. With Al alkoxides, eg, a well-known relatively stable intermediate oligomer is a compact Al_{13} polycation having the so-called Keggin structure (32). Nevertheless boehmite, AlO(OH), gels can be relatively easily made in acidic conditions by the so-called Yoldas method (36), because these polycations combine to form lamellar oligomers. The latter ones slowly aggregate in colloidal particles with a layered atomic structure. Bonding between the planar faces of two particles is insured by hydrogen bonds. Overall, a rather tight packing of the colloidal particles against each other occurs during solvent evaporation. This gives rather mechanically strong dry xerogels with a layered structure, although they are soluble in water. On the other hand, supercritically dried alumina aerogels are extremely weak, contrary to silica aerogels, because extensive hydrogen bonding on large areas is prevented from occurring (37). In order to recover a more random gel network structure and achieve the formation of stronger alumina gels, the initial Al alkoxides have to be modified. For example, some alkoxy OR groups can be replaced by ligands that do not hydrolyze. For this purpose, chelating β-diketonates, eg, ethylacetoacetate (etac) and acetyl acetoacetate (acac), are often used (38). The complexing reaction with acetylacetone can be written as equation 5.

$$\mathrm{Al(OR)_3} + x\ \mathrm{acacH} \rightarrow \mathrm{M(OR)_{3\text{-}x}(acac)}_x + x\ \mathrm{ROH} \tag{5}$$

These ligands suppress some possible condensation directions. They introduce more linearity in the oligomers and the possibility of random branching. Similar modifications of the coordination shell about the metal atom in the precursor, was applied to the synthesis of ZrO_2 and TiO_2 gels (39). In these oxides, the colloidal particles formed do not display a layered structure as observed in boehmite. The result of hydrolysis–condensation reactions of the modified precursors depends on the molar hydrolysis ratio $r_H = (H_2O)/(M)$ and the molar complexation ratio $x = (acac)/(M)$. In the case of $Ti(OR)_4$ alkoxides, sols transforming to gels could be obtained for $2 < r_H < 20$ and $0.15 < x < 1$.

Complex Oxides. In the case of a complex oxide, eg, the spinel $MgAl_2O_4$, a crude strategy consists in mixing chemical precursors of each simple oxide, MgO and Al_2O_3. However, homogeneous cogelation does not readily occur. In a more elaborate strategy, a so-called double-metal alkoxide can be synthesized in which both cations are present with the same stoichiometric ratio as in the target oxide. The main advantage of this technique is that a more homogeneous distribution of the Mg and Al atoms is achieved in the gel. This avoids the necessity of heating the gel at high temperature in order to accelerate the interdiffusion of both cations and form the target phase. In the case of spinel, such a double alkoxide can be obtained by refluxing a magnesium alkoxide and an aluminium alkoxide in the same solvent, according to reaction (6–8, 40).



(6)

The synthesis of new complex alkoxides is a subfield of coordination chemistry (34). Some of these alkoxides are sufficiently stable to not dissociate during hydrolysis and condensation reactions.

When double alkoxides appropriate for a target complex oxide are not available, it is always possible to first mix simple alkoxides and reflux them in a common solvent, so as to favor the formation of mixed-metaloxane bonds M−O−M′. Hydrolysis is performed in a second step. This technique has been applied to synthesize a number of oxides, including mullite, Al_2SiO_5; the zirconate, $SrZrO_3$; the simple titanates, $PbTiO_3$, $BaTiO_3$, and $SrTiO_3$; and the complex titanate of lead, lanthanum, and zirconium known as PLZT (2,41). Nevertheless, the formation of double metaloxane bonds is rarely proven. Besides, the alkoxides of two different metal rarely have the same hydrolysis rate. For example, when an alkoxide of Si is mixed with an alkoxide of Al or Ti, the former one hydrolyzes much more slowly than the latter one. Hence, two separate simple oxides are successively formed. To avoid such segregation, it is possible to partially prehydrolyze the slowest reacting alkoxide. Or the fastest reacting alkoxide can be made less reactive by modifying its ligands, eg, replacing OR groups by chelating ones.

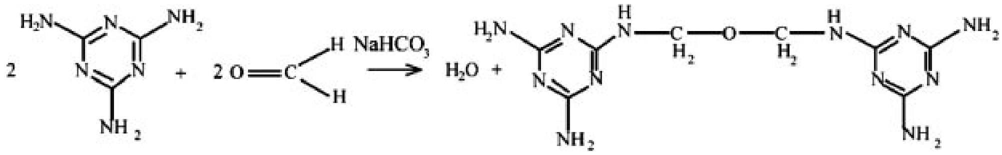
Ceramics Other Than Oxides. Although sol–gel processing of ceramics other than oxides has been much less studied, it is also possible to some extent (2). Both SiC and Si_3N_4 ceramics can be synthesized from siloxanes, silanes, and silazanes, and some of these processes can be made in liquid medium, in a manner similar to sol–gel, although it is usually termed ceramics polymer processing. The component $Si(NH)_2$, for example, is a precursor of Si_3N_4, which can be produced by liquid medium reaction between $SiCl_4$ and liquid NH_3 at −50°C. Such an ammonolysis reaction is quite similar to hydrolysis with water. The silazane, (H_2SiNH), polymers can be prepared by ammonolysis of dichlorosilanes (eg, H_2SiCl_2) in solution in benzene. Often, the products obtained when refluxing chlorosilane solutions with NH_3 in dry organic solvents, undergo cross-linking within their solvent at moderate temperatures (60−130°C), or in the presence of humid air at room temperature. The SiC containing fibers can be made by hydrolysis of Si alkoxides in which one alkoxy group, OR, has been replaced by an organic group, R′, directly linked to Si. Such precursors of formula $R'Si(OR)_3$ can be hydrolyzed to form functionalized silica gels, in which the R′ groups remain directly attached to the silica gel backbone. Chlorosilanes of formula $R'SiCl_3$ can also be used. After heat treatment at 1200°C, the Si-R′ groups are replaced by Si–C ones, which corresponds to the formation of mixed carbide and oxide ceramic of the formula SiC_xO_y.

A sulfide gel, eg, GeS_2, could be made by direct sulfidation of $Ge(OEt)_4$ by H_2S in solution in a dry organic solvent (42). The SH ligands have an electron-donor ability intermediate between that of OH and that OEt. Hence, thiolysis reactions, eg, equation 7, are possible. Any trace of residual water must be avoided, to avoid the formation of GeO_2 gel.

$$2\ H_2S + Ge(OEt)_4 \rightarrow GeS_2 + 4EtOH \tag{7}$$

Other gels of WS_3 and ZnS could be made by this technique from $W(OEt)_6$ and $Zn(Ot\text{-}Bu)_2$ (43) as well as TiS_2 and La_2S_3 particles. Sulfide powders were also obtained by thiolysis of organometallic compounds, MR_n, in an organic solvent (2).

Carbon gels constitute another class of interesting materials applicable as electrical conductors. They can be derived from organic gels by pyrolysis $> 500°C$. The most frequent organic gels used as precursors are made by condensation reactions of resorcinol–formaldehyde (RF) or melamine–formaldehyde (MF) (44,45). Other compositions can be made, eg, mixtures of phenolic furfural reactants with poly(dimethylsiloxane)(PDMS) (44). The type of polycondensation reaction occurring between melamine and formaldehyde is illustrated in reaction 8.



(8)

Usually, pyrolysis is performed on organic aerogels dried by the supercritical method. Although some significant shrinkage occurs during pyrolysis, the gel can retain a high specific surface area (400–800 m^2/g) and a significant specific mesopore volume ($>0.55\ cm^3/g$), depending on the thermal treatment procedure that is applied.

Hybrid Organic–Inorganic Gels. The chemistry of silicon alkoxides is extremely rich. As previously mentioned, alkoxy, OR, groups can be replaced by a large variety of other organic ligands, so that extended catalogues of functionalized organosiloxanes are now commercially available. Moreover, organic ligands can themselves undertake gelation by polycondensation. Consequently, new types of gels could be developed, comprising an organic component, as well as an inorganic one. These gels are often simply termed hybrids. They have been reviewed in several articles (46–48) and they are divided into two classes. Class I includes hybrids in which organic molecules or low molecular weight organic polymers are embedded in an inorganic matrix to which they are linked by weak hydrogen or van der Waals bonds. Class II comprises hybrids in which the organic and inorganic components are bonded to each other by strong covalent bonds.

To synthesize class I hybrids, the hydrolysis and condensation of alkoxides can be performed in solutions containing both the alkoxides and a soluble organic polymer. A porous oxide gel network can also be simply impregnated with the organic compound. The former technique is commonly applied to immobilize a dye or an enzyme in a gel matrix, mostly made of silica (49,50). Often, the weak interaction between the immobilized molecules and the oxide network improves the thermal stability of the dye, without affecting its other properties. This technique has also been used to mix an organic polymer with an alkoxide and produce a number of mixed silica–organic polymer materials, in which the polymers establish links between the silica nanocores, as illustrated in Fig. 2a. This is the case of poly(*N*-vinyl pyrrolidone)-silica hybrid (or PVP–SiO_2), poly(-methylmethacrylate) (PMMA)–SiO_2, Poly(*n*-butylmethacrylate)–TiO_2, and polyphosphazene–MO_x, where M can be Si, Ti, Al, or Zr. The opposite can also be done. For example, metal cation complexes can be dispersed in a solution containing organic monomers, eg, acrylamide. Addition of a radical transfer agent, eg (N,N,N',N'-tetraethylenediamine) initiates the polymerization of acrylamide to polyacrylamide, in which the complex cations are entrapped (2).

In other hybrids, the organic and inorganic components can each undertake polymerization and form two interpenetrating networks, as illustrated in Fig. 2**b**. Examples of this type of materials are the *ormosils* made by interpenetration of a silica gel network and an organic polymer network of polypyrrole, polyaniline, or polyparaphenylene. In order to avoid segregation by precipitation of the organic polymer, a radical polymerization process can be selected for the organic component. Or cyclic organic monomers can be selected that undertake a ring-opening polymerization when the alcohol is liberated by hydrolysis of the alkoxide (2). In sols or gels made of colloids with a layered structure, eg, a clay, layered phosphates, and V_2O_5, ordered hybrids can be made by intercalation of organic molecules in between the atomic layers of the colloid.

Class II hybrids require either the design of organic precursors that display some reactivity toward inorganic precursors or the grafting of organic functionalities on inorganic precursors, before gelation.

The first possibility was mostly studied with silicon precursors and, to a much lower extent, titanium ones. The organic polymers comprise polysaccharides, cellulosic polymers, polystyrenes, polyimides, polybutadiene, polyethylene oxides, and poly(methylmethacrylates). The characteristics and properties of the hybrids that can be made depend on many parameters: the nature of organic functionalities, their proportion, the hydrolysis ratio, the solvent, the temperature, and the use of a catalyst. Phase separation between the organic and the inorganic components may occur on a micrometer scale and provide composites with interesting mechanical properties. This is the case of the composites known as “ceramer”, made by embedding of inorganic polymers in an organic matrix (2).

The second possibility is a consequence of the synthesis of precursors mostly derived from silicon alkoxides by functionalization with various organic groups. In particular, the trialkoxysilanes, $R'Si(OR)_3$, are used to produce hydrophobic silica gels. Dialkoxysilanes only make linear silica polymers, but they can be grafted on Zr, Ti, Al, and V alkoxides, in order to synthesize mixed M–O–Si materials, where M is one of these metals (51). Inorganic clusters can also be functionalized with various organic groups able to undertake polymerization, eg, $((CH_3)_2HSi)_8Si_8O_{20}$ and $(CH_2{=}CH(CH_3)_2Si)_8Si_8O_{20}$. Large TiO_2 clusters could also be functionalized with methacrylate and dispersed in an aqueous micellar solution of a surfactant containing some methacrylate monomers. Other oxo inorganic clusters are based on Sn, Ti, or Zr (46). Core shell hybrid materials were obtained (2). Gelation can eventually be achieved by the intermediate of the polymeric shell (Fig. 2**c**).

3.3. Gelation and Shaping

Chemical Phenomena Leading to Gelation. With polymeric solutions, gelation is naturally achieved after a gel time t_g that depends on the precursor solution, when the condensation reactions described before are allowed to proceed. Before t_g, the polymer solution is a fluid and its viscosity η can be measured. This viscosity increases drastically and eventually reaches the limit of a viscometer used to measure it, when nearing t_g. Mathematically, η tends toward an infinite value. After t_g, a solid is formed. It no longer flows. In other words an elastic shear modulus G can be measured (Fig. 3) (18,19).

This type of gelation mechanism is now well described by mathematical percolation models (20). The continuous solid network just after gelation has a geometrical architecture known as fractal. That is to say, the mass M of this network contained in a circle or a sphere of radius R with centre chosen at random, statistically follows the law:

$$M = R^f \tag{9}$$

In this equation, the exponent f is not an integer number. Hence, it is termed the fractal dimension of the network (21). All planar models have the same fractal dimension, $f \sim 1.89$, while the value for all 3D models is $f \sim 2.6$.

With denser colloidal particles, gelation is a particular type of agglomeration driven by the interactions between particles. These interactions can be of electrical nature, with contributions from dipolar attractions and electrostatic repulsion due to the electrical charges adsorbed on the surface of particles (13). For each type of colloid, a zero-point charge (zpc), also called isoelectric point (iep) can be defined. This point is a pH for which the colloidal particles carry a net zero electrical charge. The zpc drastically depends on the nature of the colloid. For example, it is ~ 2.5 for SiO_2 and ~ 9 for Al_2O_3. The operation of peptization consists in bringing the pH of a sol in a range where the colloidal particles carry a significant net electrical charge either negative or positive, hence at a pH far enough from the zpc so as to repel each other and remain dispersed in the solvent. Once in a peptized state, aggregation can be controlled by adding another type of electrolyte termed indifferent, because it does not adsorb on the colloidal particles, and hence it does not modify their surface charge. Yet, such an indifferent electrolyte modifies the electrical environment in the liquid around each particle. Eventually, in the double-layer model, a critical coagulation concentration (ccc) of indifferent electrolyte can be reached, where immediate and dense coagulation of the particles occurs. The main result of the DLVO theory is that, for an electrolyte with ions pf valence z:

$$\mathrm{Ccc} \sim z^{-6} \tag{10}$$

Some polymers with a solubility in the solvent that depends on temperature, also can be adsorbed on colloidal particles. In this case, sol peptization or coagulation is governed by steric interactions. The polymer solubility is characterized by the Flory θ temperature of the couple polymer–solvent (15–17). In most cases, for $T > \theta$, the polymer is soluble in the solvent. Such polymer molecules adsorbed on the colloidal particle tend to expand and minimize any polymer–polymer contact, a situation that makes the sol stable (10). On the other hand, when $T < \theta$, polymer–polymer contacts are favored. The polymer molecules tend to collapse on each other, which also induces coagulation of the particles on which they are adsorbed.

Colloidal gelation is a case intermediate between dense immediate coagulation and sol stabilization. For colloidal gelation to occur, agglomeration between the particles must occur at a relatively low speed. The colloidal particles must also have a very low mass and an internal structure that is not fully dense, with some internal linear polymerization being favored, eg, by chelation of the precursor. Such conditions do not favor the immediate formation of dense aggregates that would immediately coagulate. Rather, computer simulations show that the addition of small oligomers that are transported by the random Brownian motion towards an aggregate, are likely to favor the growth of lateral branches. Overall, fractal aggregates slowly grow and their very open texture prevents their precipitation. When such aggregates meet each other, a gel network is obtained. Models based on such a mechanism are known as diffusion limited aggregation (DLA) models. The fractal dimension of such aggregates ($f \sim 1.67$ for planar models, $f \sim 2.5$ in 3D models) is even lower than that of previously described polymeric gels. This indicates that DLA colloidal gels are even more “lacy” than polymeric ones. In practice, this type of gelation prevails for most oxides, including with some SiO_2 colloidal gels. The real gels that are best described by percolation are polymeric SiO_2 gels or organic gels.

Mechanical Strengthening of Wet Gels. A wet gel is a very weak material. Two types of spontaneous mechanisms can make it stronger while in the wet stage.

A first one is the syneresis. The weak branches of the gels are very flexible just after gelation. Hence, they can move by viscoelastic deformation. Eventually, two hydroxyl M–OH on different side branches may meet each other and undergo condensation to build new metaloxane M–O–M bonds. These new bonds strengthen the gel network, while a slow and irreversible shrinkage inside the mother liquor can be observed. This is also a homothetic shrinkage: A monolith keeps its initial shape (2).

A second mechanism is aging in various liquids. When performed in the mother liquor, independent oligomers not yet linked to the gel backbone may aggregate as side branches and reinforce thin necks. The gel network is also submitted to a dissolution–reprecipitation mechanism. The convex surfaces of colloidal particles slowly dissolve and reprecipitate on the thin concave necks between two particles. The rapidity of the latter mechanism depends on the liquid in which the gel is aged and the solubility limit of the solid constituting the gel network, in this liquid.

Drying Gels. A wet gel can be dried by evaporation of the liquid present in its pores. In this case, liquid meniscuses form at the exit of each pore, so that the liquid in the gel pores is subjected to a hydrostatic tension. The magnitude of the tensile stress is given by equation 11, assuming this is a pore with cylindrical exit.

$$\sigma_r = 2\,\gamma \cos(\theta)/r_{\mathrm{pore}} \tag{11}$$

In this equation, γ is the liquid surface tension, θ its wetting angle with the gel solid network surface, and r_{pore} is the pore radius.

To balance the liquid tension, the gel solid network is subjected to compressive stresses, which make the gel shrink (Fig. 4). Shrinkage can be extremely important, up to 80% in volume. It is more important in polymeric gels with micropores of very small radius than in gels with coarser pores. A gel dried in such conditions is termed a xerogel. A xerogel monolith will very easily tend to break to small pieces, when evaporation is too fast. In order to avoid this, it is necessary to slow down the evaporation rate so that the gel network has time to relax by viscoelastic deformation, under the mechanical stresses imposed by the liquid tension. The response of the gel depends largely on its permeability coefficient D and its hydrodynamic relaxation time τ, as this was analyzed in details by Scherer (52).

To offset this problem, several techniques have been developed. A gel may be prepared for a better resistance to shrinkage by modifying the wetting angle θ between the liquid in the pores and the solid network. In particular, the solid surface may be made hydrophobic ($\theta > 90^\circ$) by coating the network surface by hydrophobic groups, eg, CH_3. Such functionalities can be brought by a precursor, eg, methyltrimethoxysilane, $Si(OCH_3)_3\ (CH_3)$,or methylchlorosilane, $ClSi(CH_3)_3$ (53). Or the liquid surface tension γ may be decreased, either by synthesis of the gel in an organic solvent, or by adding so called drying chemical control additive (DCCA), eg, formamide (29). Dry gels with limited shrinkage and a relative pore volume up to 97.4% can be obtained by these techniques. They are often termed "ambient pressure drying aerogels", or "ambigels". Tensioactives are interesting additives. They led to the discovery of new types of micellar silicates in which an ordered array of spherical, cylindrical or layered micelles give materials with a very well ordered mesoporous texture (24).

Traditional aerogels are made by another technique: supercritical drying (54), first explored by Kistler (23). For this purpose, a wet gel is placed with an excess of solvent into an autoclave (Fig. 5). After closure of the autoclave, the liquid is brought beyond its critical point by heating along a pathway that is plotted in Fig. 6 for ethanol. The supercritical fluid is evacuated as this is done with a gas. Enough liquid must be placed in the autoclave, so that no liquid–gas meniscus can form at the exit of gel pores, before reaching the critical point (55). The minimum mass of alcohol to add corresponds to the solvent density at the critical point. For ethanol, eg, an autoclave must contain a minimum of 27.63-g ethanol for 100 cm^3 of autoclave volume. A few critical point values are given in Table 1 (56).

The critical point of CO_2 is at low temperature. With this fluid, a COLD process can be directly applied to synthesize aerogels in which biomolecules, eg, enzymes, have been encapsulated (49). Nevertheless, liquid CO_2 cannot be directly exchanged with water or methanol, so that dialysis in an intermediate common solvent, eg, acetone, is needed. In HOT processes, high temperature supercritical drying can be directly performed in ethanol, a very interesting method for gels synthesized in this solvent as no liquid exchange is required. An esterification reaction, the reverse of reaction (4), occurs in alcohol at high temperature. This makes an aerogel much less hydrophilic when dried by a HOT process, than when dried by a COLD process. In both processes, when dry monoliths without defects are desired, many processing details are important. Cracking may be due to heating, because of a differential dilatation of the liquid in the pores. The gel response depends on its permeability D, as in drying by evaporation. It may also be due to a too fast supercritical fluid evacuation, which may induce a significant adiabatic cooling. If the liquid–gas coexistence line happens to be crossed during cooling, liquid–gas meniscuses will again form and break the monolith. When the alcohol contains some water, which is often the case with gels made in methanol, the critical pressure and temperature are increased. To a first approximation, a linear relationship, proportional to the estimated water content can be applied to calculate T_c and P_c.

A related technique to supercritical drying is lyophilization or cryodrying. The frozen solvent is evacuated from the gel by sublimation after freezing. Nevertheless, the growth of solvent crystals usually induces gel network distortions. Hence, this technique is not as efficient as supercritical drying to obtain perfect monoliths (55).

Thermal Transformation of Dry Gels. In contrast to traditional ceramics powder processing that directly requires heating at high temperature to be synthesized, usually $>1000°\mathrm{C}$, the sol–gel process provides a dry material at low temperature, in most cases $\sim 100°\mathrm{C}$. Hence, new types of transformations are observed during heating at intermediate temperatures, from 100 to 1000°C, before reaching the traditional high temperature equilibrium phases (2).

The first group of thermal transformation are chemical in nature. They involve the surface groups, in particular physically adsorbed water molecules, surface hydroxyl groups chemically bound to an oxide solid network and organic groups either adsorbed or chemically bound to the solid network. The dehydration of oxide gels always proceeds by successive steps at increasing temperatures. In most cases, two main steps can be observed: first, the departure of adsorbed water; and second the departure OH chemically bound to the oxide network. For example, in alumina gels, adsorbed water leaves between 25 and 140°C, while the Al–OH bound hydroxyls, which are part of the boehmite gel structure, require a temperature of the order of 400°C (2). At higher temperatures, only isolated residual chemically bound OH remain, because the material undergoes densification. A similar sequence is observed in silica gels. These transformations can be followed by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) as in Fig. 7.

The residual organic groups can come from the precursor or the solvent. Regarding the alkoxide residues, the main difference with water is that the OR groups can leave as alcohol molecules, or they can be decomposed to leave a carbon residue. Organic residuals are particularly frequent when hydrolysis is done in substoichiometric conditions. Their decomposition is often strongly exothermic, in contrast to dehydration. In titania gels, these exothermic reactions can induce ignition near 400°C (57).

A second group of transformations, which may occur concurrently with chemical reactions, are various phase transformations. In a temperature range from

400 to 900°C, anions, eg, the oxygen anions, are not very mobile. Only the cations, which are smaller than the anions can undergo significant diffusion. Consequently, metastable phases are often formed from a dry gel by so-called "topotactic" transformations, in particular order–disorder transformations. No nucleation of a new phase can be observed, but rather the progressive cooperative transformation of the whole solid, in which the anions are relatively inert. Such phase transformations are well known in boehmite gels, which successively transform to a series of transition aluminas (γ, δ, τ) in which the oxygen anions maintain a packing akin to fcc (2). Their occurrence is best described in Transformation, Time, Temperature (TTT) diagrams. An example is illustrated in Fig. 8a for alumina (58). Formation of the thermodynamically stable phase, α-alumina, eventually occurs by nucleation and growth at high temperature, > 1200°C. In sol–gel multication systems, the cations of a different nature are often well mixed at a very fine scale, if not at the atomic scale. Hence, they only have to diffuse for short distances to form new crystalline phases. This explains why the sol–gel technique often allows the synthesis of complex metastable phases, not feasible by traditional ceramic powder processing. In silica gels, which consist of more or less extensively cross-linked polymers, these topotactic transformations are proceeding by progressive polymer relaxation in a material which remains amorphous (Fig. 8b) (59).

A third type of evolution is progressive densification. Because densification begins to operate concurrently with the two previous types of transformations, it is important to monitor the heating rate so that all residual groups that should leave the gel do not remain trapped inside closed pores. Otherwise, bloating may occur, or even explosions, as when nitrate and ammonia groups are present. At moderate temperatures, densification appears as a progressive modification of the pore texture. Micropores disappear while larger ones keep developing by an Ostwald ripening-type process. Overall, the specific surface area and specific pore volume continuously decrease. In silica gels, polymeric relaxation progressively gives place to a cooperative viscous flow phenomenon, as the temperature increases. Densification by viscous flow follows laws that were well described by Scherer (60). In practice, a silica gel progressively transforms to a dense glass as a continuous topotactic amorphous transformation. In Fig. 8b, in the plot of small angle X-ray scattering, the small angle diffusion at $2\theta < 3°$ due to porosity is progressively attenuated, while the maximum near 22°, due to random Si–O–Si glass network, is just slightly shifted as the temperature increased.

In crystalline phases derived from sol–gel, sintering follows the same mechanisms as in traditional ceramics processing. Atoms move by diffusion inside the crystalline phase, via interfaces or in the vapor phase. The driving force is the interface energy. The latter translates into mechanical pressure (or tension) gradients in the material just under an interface, depending on its local curvature. Two types of interfaces exist in a material: pore surfaces and grain boundaries. Hence, elimination of the pores by sintering occurs concurrently with grain growth. Depending on the texture, in sol–gel materials as in traditional ceramics, the sintering mechanism may dominate all along a thermal treatment process, in which cases densification ends in a fully dense material. Or the grain growth mechanism may take over at some point. Abnormal grain growth then occurs, in which case densification stops (2).

4. Properties and Applications of Sol–Gel Materials

4.1. Structure and Properties of Dry Gels. Most silica xerogels have an extremely porous structure. Typically, pores constitute 60–70% of the monolith volume, a proportion that can reach up to 99.8% in aerogels. In other oxide gels, the pore volume is usually lower, although still very high. Their specific surface area is usually very high, typically hundreds of m^2/g and up to 1000 m^2/g in some silica aerogels. Regarding the pore size distribution, gels may contain micropores with a diameter < 2 nm, mesopores, with a radius from 2 to 50 nm according to the IUPAC convention and larger pores. For example, Fig. 9 shows electron transmission micrographs of the gel network in a SiO_2 aerogel made from TMOS and a Y_2O_3 aerogel made from a metallic salt in alcohol that are both mostly mesoporous (60,61)).

When the pore size is smaller than the visible light wavelength, oxide gels are transparent. This transparency can make them directly applicable in some optical applications. Otherwise, they are often white or with some coloration, depending on surface groups. The highly porous network also gives outstanding thermal and sound insulation properties. The thermal conductivity comprises a contribution by the solid network, λ_s, a contribution by the gas phase in the pores λ_g and a radiation contribution λ_r. The solid network contribution depends on the gel apparent density ρ_s according to the relationship $\lambda_s \sim \rho_s{}^{\alpha}$, where $\alpha \sim 1.6$ for bulk samples and 0.9 for thin films. The parameter λ_s ranges from 10^{-3} to 1.4 W m^{-1} K^{-1} as the gel density increases from 80 to 270 kg m^{-3} (58). The gas phase contribution does not exceed 10^{-3} W m^{-1} K^{-1} at ambient pressure, because of the very small pore size. It is lower in aerogels where vacuum is established. The radiation contribution is negligible with visible wavelength. It becomes significant with infrared radiations of wavelengths from 7 to 30 μm, hence at high temperatures. Overall, the thermal conductivity of a silica aerogel is typically of the order of 1.5 10^{-2} W m^{-1} K^{-1} in air and 10^{-2}W m^{-1} K^{-1} in vacuum. The mechanical properties of silica aerogels are characterized by a low Young's modulus E_y, increases from 10^6 to 10^{10} Pa, when the apparent density increases from 100 to 1000 kg/m^{-3}. This corresponds to brittle ceramics, although they can be elastically (hence reversibly) compressed by a large magnitude (eg, up to 50%), (64).

The surface groups of a gel can also be the origin of some properties. For example, a dry gel can be made hydrophobic if a precursor carrying hydrophobic functionalities, eg, methyltrimethoxysilane, $(CH_3)Si(OCH_3)_3$ (or MTMS), is mixed with a precursor, eg, TMOS. The hydrolysis products of MTMS will bind to the silica network constructed by TMOS and replace silanol Si–OH surface groups with hydrophobic $Si{-}CH_3$ ones. Aerogel monoliths that float on water can be prepared. They do not adsorb humidity and, for a molar ratio MTMS/TMOS = 0.7, transparent hydrophobic materials can be obtained. Other hydrophobic surface groups can also be used (35,65).

4.2. Applications of Dry Gels. Dry xerogel monoliths for application in chromatograph columns have been reviewed by Siouffi (66). Oxide sols can be cast inside capillary columns before gelation, possibly with various additives. The pore size distribution, which must combine macropores for an easy global flow and mesopores to separate the various molecules in a solvent, are important parameters, as well as the gel surface functionalities. For this purpose, porous silica monoliths with a hierarchical pore structure could be designed (67).

In a different field, large silica gel cylinders derived from chlorosilanes with polymeric additives have been developed as optical fiber preforms (68). In this case, the chemical purity and composition of the gel monolith is a key characteristic.

Other applications have emerged for silica aerogels and have been reviewed (55). These materials have outstanding thermal and sound insulation characteristics. Besides, they can be made translucent, if not transparent, hydrophobic, and are nonflammable. Aerogel granules were investigated as daylight transparent thermal insulation panels to use in buildings or as insulators in cooling or heating systems, eg, piping, car windshield defrost, or novel types of furnaces. Silica aerogel crucibles make it possible to control the crystallization of semiconductors with great precision with an infrared camera. Their outstanding sound insulation properties make them applicable in $\lambda/4$ acoustic impedance matching layers in ultrasonic transducers, range finders, and speakers. They were also found quite interesting for in house floor acoustic insulation and in anechoic chambers. Two-step hydrolysis (acid-catalyzed hydrolysis followed by base catalysis condensation), has made it possible to synthesize transparent aerogel monoliths with a uniform size in the nanometer range. Thousands of such monoliths of dimensions 24 mm × 12 cm × 12 cm with an index of refraction $n < 1.03$ were produced for application in Cherenkov counters. Luminescent or fluorescent ZnO particles or molecules, eg, lanthanides, fullerenes, and other molecular dyes, can be entrapped inside silica aerogels to which they can eventually be covalently bonded. A blue shift of the luminescent light is often observed due to a quantum confinement of the dopant inside the gel network.

Regarding electrical application (55), silica aerogels are insulators and they are investigated as superlow dielectric constant materials, with a relative dielectric constant as low as 1.1, for ultralarge scale integrated circuits. Piezoelectric transducers with a low impedance require very porous piezoceramics, eg, lead zirconium titanate (PZT). Such crystalline ceramics with a pore volume up to 70% can be prepared by heat treatment of PZT aerogels. High porosity, high temperature, and high capacity electrical batteries can also be made by reversibly entrapping a high density of small cations, eg, Li^+. The type of aerogels used for this application comprise vanadium oxide, manganese oxide and molybdenum oxide. Carbon aerogels are electrical conductors. They can be made with a high specific surface area, so as to store a very high electrical surface charge that can be released at a fast rate. Hence, they are quite interesting as electrode materials in supercapacitors, fuel cells, and capacitive deionization units used to remove NaCl or metal cations from water. They can also be impregnated with a metal, eg, Ru, by vapor deposition, to produce efficient electrocalysts.

Mechanically, it was mentioned that aerogels are very weak materials. Nevertheless, they also have a low Young's modulus. Hence, their elastic deformation can be very high, up to 50% deformation and they find applications as kinetic energy absorbers in low shock impedance parts to confine plasma. Or they can be used to capture freezing states of materials generated under high shock pressure. One of the most spectacular application was the use of large aerogel blocks to capture hypervelocity (tens of Km/s) comet dust with a size from from 0.1 to 100 μm, such as in the recent STARDUST space mission. Each dust particle penetrated up to a distance that depended on its velocity and size, and it could be easily localized inside an aerogel block for analysis, given their transparency. For space missions, silica aerogels also proved to be very efficient thermal insulators, to protect the satellite equipment in the PATHFINDER MARS mission (55).

Aerogels can be used as fillers in paints and elastomers (tires) to provide thickening and abrasion resistance. They can be applied as carrier of diverse active agents that need to be progressively released, eg, herbicides. Or they can be used to store dangerous liquids, eg, acids used in rocket fuels, to retain pollutants from water, store radioactive waste, or even contain nuclear fluid used in nuclear fusion experiments (55).

Gels or partially sintered materials are also very interesting as heterogeneous catalysts or supports of heterogeneous catalysts (27). Active metal particles supported on aerogels can be directly prepared from mixed transition oxide gels, in reducing conditions (55). The immobilization of complex molecular catalysts inside gels is a field of research that is currently expanding, including the immobilization of enzymes or even full living cells (49).

4.3. Applications of Ceramics Parts made by Sol–Gel.

The field of sol–gel processing has rapidly extended during the last 6 years and a detailed account of the applications is within the reach of this article. The readers interested in particular sol–gel applications are encouraged to read books that were dedicated to such purpose, in particular the *Handbook on Sol–Gel Technologies for Glass Producers and Users* edited by Aegerter and Mennig (27), and the *Handbook of Sol–Gel Science and Technology Processing, Characterization and Applications*, Vol. III, *Applications of Sol–Gel Technology*, edited by Sakka (69).

Powders. Sol–gel made particles with a controlled size from 5 nm to several hundred microns can now be prepared on industrial scales, in particular by microemulsion techniques (72,73). The addition of surfactants more over makes it possible to form powders with an ordered array of cylindrical mesopores (24).

Thin Films. Sol–gel coatings can be made by several techniques (27,72). A flat panel can be dipped in a sol, or a sol can be sprayed on it. A liquid sol film can also be made by spin coating. Dipping is the most frequently applied method. The film thickness is usually < 1 μm because of the formation of cracks. Nevertheless, organically modified silica gels termed *ormosils* have made it possible to dry films up to 10 μm thick in one single step by spin coating. With dip coating, the film thickness ε is linked to the sol viscosity η and density ρ, and the velocity v at which a plate is drawn out of the sol by the relationship:

$$\varepsilon = k\,\eta v/\rho g \qquad (12)$$

where k is a constant that depends on the type of sol and g is the gravity constant.

Sol–gel coating may be considered as the most promising field of applications for the sol–gel technology. The surface to be coated can be a glass, a metal, eg, steel or a plastic. Sol–gel coating can provide chemical durability, alkali resistance, increased strength to glasses (78), scratch resistance to plastics (74). Metals also can be protected from corrosion or oxidation. Sol–gel coatings can be used as intermediate layers for the metallization of dielectrics (75). The coloration of glasses, metals and plastics can be adjusted, in particular by dispersion of noble metal colloids in the gel (76). Oxide coatings have been largely studied for optical applications, with a great variety of complex oxide combinations (2,27,72). For example, it is possible to independently adjust the reflectivity and the visible light absorbency. The refractive index can be tuned in a very large range, from close to 1 with aerogels to > 2 with CeO_2, HfO_2, and Ta_2O_5. Antireflective coatings of thickness $\lambda/4$ have been developed for various applications (77). For other applications, sol–gel coatings can be made conducting (78), transparent and conducting (79), hydrophobic (80) or hydrophilic (81), resistant to high temperatures (82). The coating materials can have ferroelectric (83), photochromic (84), electrochromic (85), electrooptical (86), thermochromic (87), gasochromic (87), photovoltaic (89), or self-cleaning (90) properties.

Another important application of sol–gel coatings is for ceramic filtration membranes (91). These are usually supported membranes, in Al_2O_3, TiO_2, or CeO_2. The sol–gel filtration membrane itself is deposited on the inner surface of a porous cylindrical support with large pores, made by traditional ceramics processing. For this purpose, a sol is forced to pass through the support under high pressure. The colloidal sol particles deposit as a thin layer with mesopores or micropores, on the internal surface of the support (2). Free-standing films can be made by scrapping off a gel film formed over a solid surface, a nonwetting surface, eg, Teflon or a dense liquid that is immiscible with water. A sol film in a state close to gelation can be pulled out of a slit, or lifted with a wire to which it is attached by wetting, just prior to gelation (59).

Fibers. Fibers can be made by spinning, baiting with a glass rod, extrusion, or directional freezing, of a sol. Depending on the process, either short or continuous fibers can be made. The sol viscosity and structure are important. A sol appropriate for making fibers must be composed of polymeric oligomers, as linear as possible. An organic gelling additive, eg, poly(vinyl alcohol) (PUA) may be added to the sol. The drying stresses are important to avoid, since they can very easily introduce small surface flaws on the fibers, which will decrease their mechanical resistance. Otherwise sol–gel processing is a low temperature inexpensive process, which can be applied to refractory oxides, eg, Al_2O_3, or SiO_2 glasses with a relatively high Al_2O_3, TiO_2, or ZrO_2 content (2,92).

Monoliths. Sol–gel ceramic monoliths can be made by direct sintering of monolithic gels. Or they can be made by traditional powder processing techniques, eg, hot pressing and sintering, from sol–gel derived powders. The first method is very challenging because, as previously mentioned, drying stresses easily induce cracks. Consequently, only the synthesis of small monoliths has been attempted, mostly based on silica xerogels. The best success was achieved by Hench and co-workers (93) with neat net shape optical lenses, 10 cm in diameter and a few millimeters (mm) in thickness, by addition of drying control chemical additives (DCCA). Bioactive glass monoliths were also made by these authors in the SiO_2–CaO–P_2O_5 system. Such glasses can bond to living tissues, by a dissolution regeneration process, when placed in a living body (94). The second method is more common. It is usually applied to all kinds of technical ceramics, eg, titanates, zirconates, mullite, spinel, yttria stabilized zirconia, and sodium ionic conductors (2). The use of sol–gel powders often lowers to some extent the sintering temperature. It permits to make parts with a smaller grain size, an improved purity and technical performance better than with traditional powders.

Monoliths are much easier to make with hybrid organic–inorganic materials (66,95). They can be made homogeneous; or with a controlled porosity, transparent colorless, or with a given color depending on an embedded dye. Glass rods with a refractive index varying with a parabolic profile (r-GRIN glass) from the center to the external surface, have been developed for microoptics applications (96). Dyes can be selected for their luminescent, photochromic, or non-Linear Optics (NLO) characteristics (97). Heterogeneities often form and the mechanical properties depend on the size of these heterogeneities and on the bonding between the two phases. When the bonds between the organic and the inorganic components are strong, outstanding mechanical properties can be achieved. This is the case for hybrid composites made from polydimethylsiloxane (PDMS)–TEOS or polyimide–SiO_2 composites that also have NLO properties. Other composites are based on SiO_2, combined with polyamide, polystyrene, and poly(methyl methacrylate), poly(vinyl acetate), polycarbonate, and poly(tetramethylene oxide). Several hybrids are being investigated for their ionic conduction properties, eg, the SiO_2–polyethylene glycol hybrids.

Nanotechnologies. Sol–gel materials are well suited to the development of new nanotechnologies. A first domain of potential applications is optical communication technologies (98). Nevertheless, to be industrially accepted, the sol–gel technique must bring a significant processing cost improvement by comparison with existing technologies, mostly melting ad chemical or physical vapor deposition. Actually, sol–gel has not yet achieved full acceptance because some problems need to be solved in an economical manner. In particular, traces of foreign elements or OH groups must be economically eliminated from silica-based optical fibers (98). The formation of flaws when drying fibers must also be eliminated. But work in this direction is intense and is achieving some success (98). This is the case for sol–gel cladding developed for silica optical fibers. Also, a gradient in the refraction index between the core and the cladding can be easily adjusted by doping with fluorine, or sol–gel germanium oxide (98). Specialty, fibers can be made by doping silica with rare earths, eg, erbium, for applications in amplifiers, lasers, dispersion-compensating fibers, Raman fiber, polarization-maintaining fibers, and highly nonlinear optical fibers (99). Hybrid gels are well suited to the fabrication of planar lightwave circuits (PLC), with an appropriate thickness, by masking techniques, eg, used in large-scale chip integration (100). Gels bearing phenyl or methyl groups make it possible to tune the refraction index up 1.55 (101). Other devices made by sol–gel are actively studied, in particular electrooptical devices based on PLZT or other titanates and tunable photonic crystals. Photonic crystals are the optical equivalent of bandgap semiconductors, used in all sorts of electronic components (102). They can be fabricated from an ordered packing of monodispersed microspheres, either polymeric or SiO_2 microspheres made by the Stöber process (28). The latter packing can be used as templates to incorporate high refractive index material, eg,

TiO_2, or a semiconducting material, eg, CdSe, and produce an inverse opal crystal characterized by the existence of an "optical bandgap" (98).

Potentially, a large number of possibilities are offered by the hybrid materials having a nanostructure comprising inorganic oxo groups linked by organic chains. Such materials can offer original photochromic properties, nonlinear optical response, or electroluminescent behavior (103). Several products were reported to be commercialized, in particular TV sets with hybrids made by encapsulation of indigo dyes in a SiO_2/ZrO_2 matrix (104) and special glassware (105). Hybrid sols could also be used as precursors of ceramic membranes, eg, ZrO_2 nanomembranes, TiO_2 photocatalytic coatings, and antistatic SnO_2 coatings (46).

Inorganic or hybrid materials with an organized texture, eg, a uniform mesoporosity, can be designed by self-assembling procedures. The latter can make use of surfactants, amphiphilic block copolymer linkers between the inorganic clusters, liquid crystals, and various biomolecular templates (106). Ordered hydrophobic cylindrical mesostructures were made, eg, by combining a silicon alkoxide $Si(OR)_4$ with $C_6F_5(CH_2)_2{-}Si(OR)_3$ in an organic solvent. Other ordered structures were made with polyethylene–polypropylene amphiphilic copolymer linkers. Deoxyribonucleic acid (DNA) has been used to design programmed assemblies of gold colloidal particles. Magnetic nanoclusters of Mn and Cr applicable for information storage at the molecular level, were also incorporated in silica mesoporous materials. Organic thermoreversible physical gels, made of fibers or ribbons, could also be used to template the formation of fibrous silica or alumina with a fibrous texture, including a chiral texture (107). Another important application domain of nanotechnologies is the development of biosensors for medicinal applications, summarized in a further paragraph.

Bioinorganic Applications. A large number of biomolecules can be immobilized in sol–gel materials by covalent grafting or by encapsulation, a technique where the biomolecule is added in a sol prior to gelation. The main reason is that sol–gel encapsulation can be made near room temperature and at a pH brought close to seven just prior to biomolecule addition. Among them, many enzymes were entrapped for application in biocatalysis (49,108,109).

Medicinal Applications. Sol–gel encapsulation now extend to antibodies, nucleic acids, phospholipids, polysaccharides and whole living cells coming from plants, algae, and bacteria, that keep their viability after encapsulation (110). Encapsulated biomolecules are compatible with *in situ* analysis techniques, eg, ultraviolet (uv)–visible absorption, fluorescence, or electrochemical measurements (111). The most frequently investigated enzymes for sol–gel encapsulation in biosensors are glucose oxidase (GOx) and Horse Radish Peroxidase (HRP) (49,109). Sols containing dispersed biomolecules can be incorporated before gelation in chromatograph columns (41) or the microwells of titration plates. The latter ones can be applied in immunoassay biosensors by encapsulation of antibodies or antigens. Antigen–antibody coupling in a living body is then analyzed by the colorimetric enzyme-linked immunosorbent (immunoadsorbent) assay (ELISA) procedure (112). Other biosensor designs involve micron sol–gel pads deposited on the tip of optical fibers, on micron-sized gold-coated cantilever quartz balance, or inside capillary chromatograph columns. In each case, the silica sol contains a sensing molecule, eg, a fluorescent dye or an enzyme, or a range of different chemical sensing or biosensing molecules. These sensing molecules can be entrapped inside the gel, or possibly grafted to this gel network after gelation. Because the gel network is very porous, the sensor obtained can be used to determine any target reactant molecule or pollutant, which emits an optical or an electrical signal, or a mechanical deflection, when reaching the sensing molecules entrapped inside the gel network.

A second field of important research is drug delivery. It was shown that sol–gel nanoparticles are biocompatible and controllably resorbed in living fluids (113). By modifying the gel chemistry and porous texture, encapsulated medicinal drugs can be released *in vivo* at a controllable rate, on periods up to 6 months (114). A mesoporous silica gel layer can also be deposited on Fe_3O_4 nanoparticles, offering the possibility to guide the drug carrier with a magnet (115). Hollow silica nanospheres, by templating on alginate, are also studied (116,117).

Finally, a very innovative field concerns the design of artificial living tissues, with sol–gel encapsulated cells. An artificial pancreas for *in vivo* use has been designed by encapsulation of living Langerhans islets (118), as well as artificial livers by encapsulation of hepatocytes, through which the patients plasma can circulate (119).

5. Economic Aspects

According to a study by the British Bank of Commerce (BCC) (120), the world market for sol–gel products was $1 billion in 2006 and it is expected to grow to $1.4 billion by 2011. These numbers correspond to an average annual growth rate (AAGR) of 6.3%. The U.S. share of this market is expected to be $500 million by 2011 with an AAGR of 8.7%. During this period, the expected AAGR for optical and electronic applications is expected to range from 12 to 15%. The aerogels market expansion is even more remarkable. It increased from $24.8 million in 2004 to $62.2 million in 2006, driven mostly by thermal insulation. The aerogel AAGR up to 2011 is projected to be 78.5%, with applications expending to textiles, fuel cells, and catalysts.

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A. C. PIERRE
Université Cladube Bernard Lyon 1

Table 1. **A Few Fluid Critical Points**

Fluid	T_c, °C	P_c, MPa
water	374.1	22.04
methanol	239.4	8.09
ethanol	243.0	6.3
carbone dioxide	31.0	7.37

[a] Ref. 56.

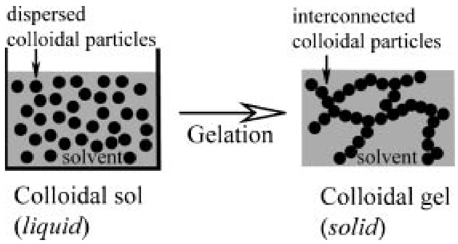


Fig. 1. Sol to gel transformation.

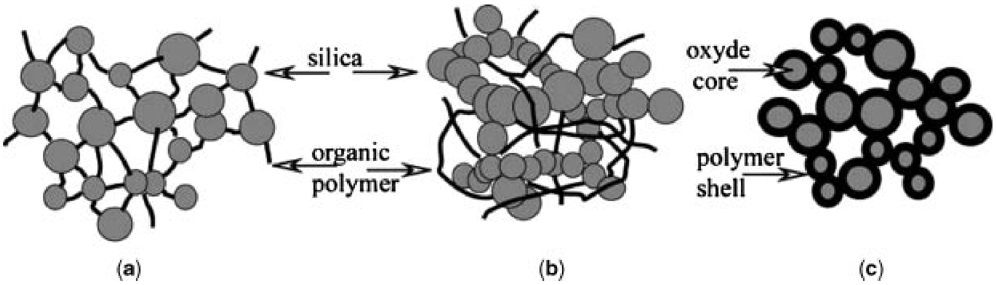


Fig. 2. Hybrid organic–inorganic gel networks with: (**a**) inorganic cores interconnected by polymers; (**b**) interpenetrating networks; (**c**) core-shell particles.

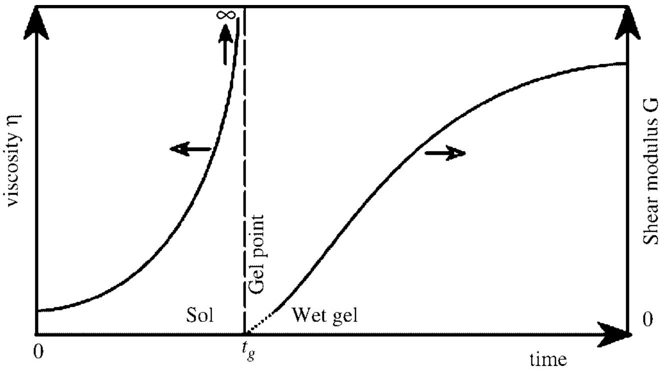


Fig. 3. Evolution of the viscosity and shear modulus, as a function of time, for a precursor solution undertaking polymeric gelation.

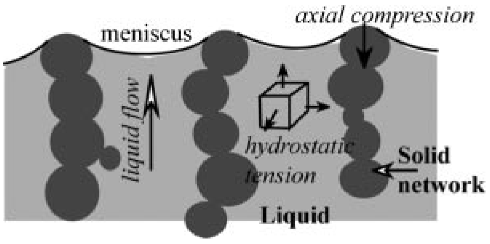


Fig. 4. Stresses in a gel dried by evaporation.

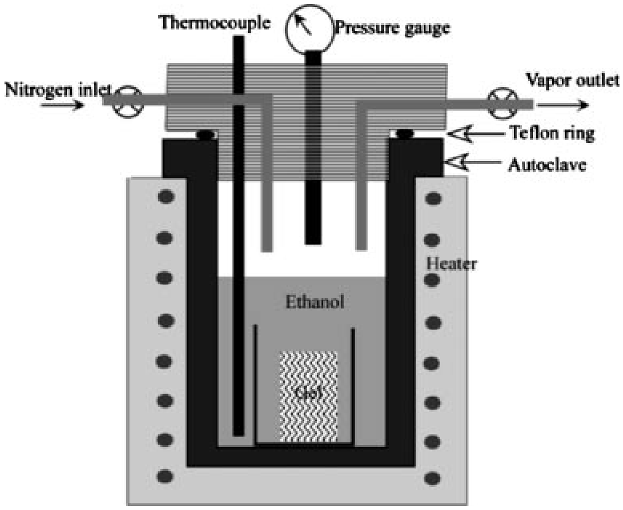


Fig. 5. Schematic illustration of an autoclave used to dry an aerogel by the supercritical method with ethanol.

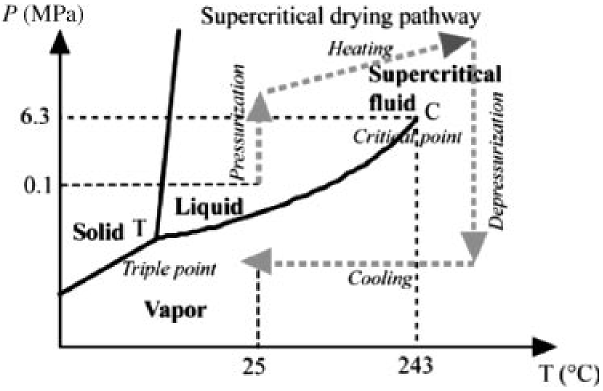


Fig. 6. Simplified supercritical drying pathway in the pressure (P) temperature (T) phase diagram of ethanol.

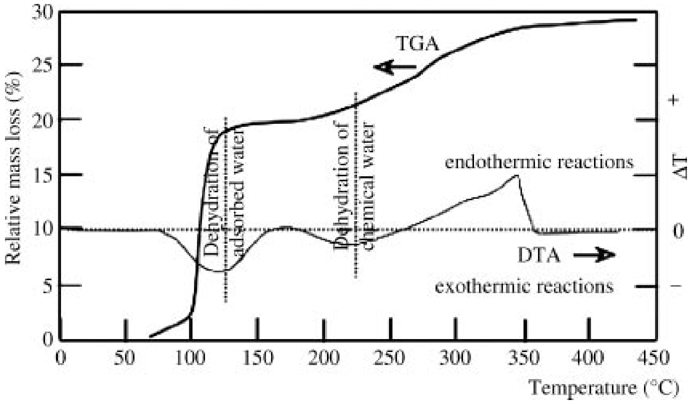


Fig. 7. Thermogravimetric and differential thermal analysis of PLZT made by the sol.

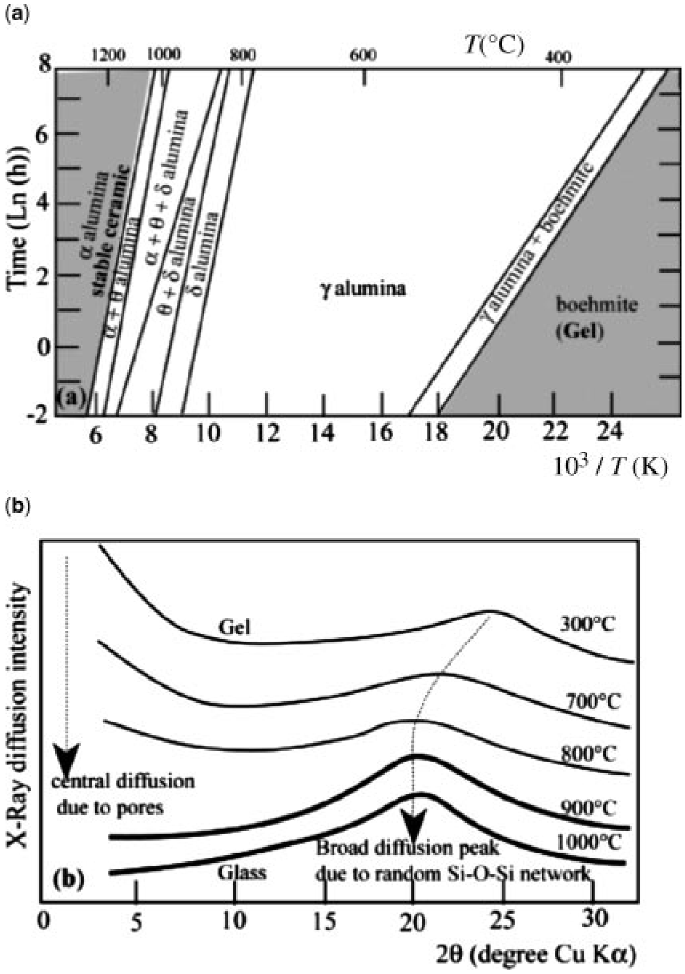
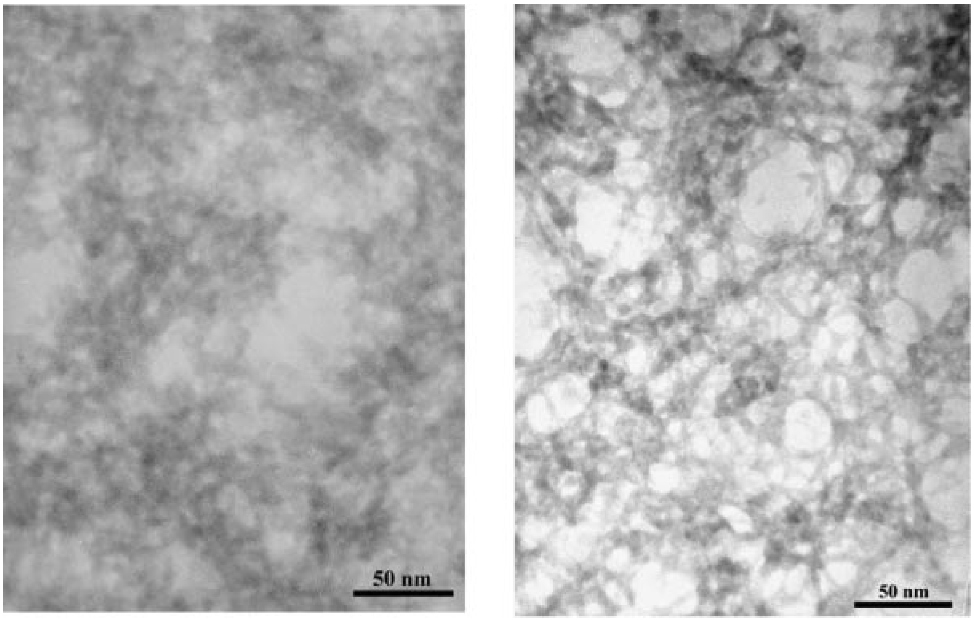


Fig. 8. Topotactic transformations: (**a**) TTT diagram of transition aluminas formed from boehmite gels. (Adapted from Ref. 58); (**b**) X-ray diffraction patterns of 10% TiO_2–SiO_2 gels, at increasing temperatures. (Adapted from Ref. 59).



(**a**) SiO_2 aerogel (**b**) Y_2O_3 aerogel

Fig. 9. Electron transmission micrographs of SiO_2 and Y_2O_3 aerogels. (Unpublished photographs from work in Refs. 61 and 62).