SiO$_2$ Aerogels

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Abstract This chapter focuses on one of the most studied aerogel materials, silica aerogels. It aims at presenting a brief overview of the elaboration steps (sol–gel synthesis, aging, and drying), the textural and chemical characteristics (aggregation features, porosity, and surface chemistry), the main physical properties (from thermal, mechanical, acoustical, and optical, to biological, medical, etc.), and a rather broad panel of related potential applications of these fascinating nanostructured materials. It cannot be considered as an exhaustive synopsis but must be used as a simple tool to initiate further bibliographic studies on silica aerogels.

2.1. Elaboration

2.1.1. Sol–Gel Synthesis

The physics and chemistry involved in the synthesis of silica gels were detailed in books [1, 2], and many reviews on aerogels with particular focus on silica aerogels have already been published [3–10]. Schematically, a nanostructured solid network is formed in a liquid reaction medium as a result of a polymerization process, which creates siloxane bridges ($\equiv$Si–O–Si$\equiv$) between Si atoms delivered by precursor molecules. Such transformations are the equivalent of a polymerization process in organic chemistry, where direct bonds between the carbon atoms of organic precursors are established leading to linear chains or branched (crosslinked) structures, depending on the type of reactive monomers and crosslinkers used. Dispersed solid colloidal silica particles (i.e., nanoparticles with a size well below 1 $\mu$m) or “more or less” linear oligomers are formed in the early stage of the sol–gel process. In the second stage, these elementary objects can link with each other while still in the solvent, such as to make up a three-dimensional (3D) open network structure termed a gel, only limited by the container. The continuous transformation of a sol to a gel constitutes the gelation process. The brutal change from the liquid to the solid stage is termed the sol–gel transition. The gels that are obtained are termed either colloidal or polymeric depending on the nature of the building blocks of which the network is composed.
of and whether they are nanoparticulate or more linear (polymer-like). For both stages, the driving reactions are hydrolysis and water and/or alcohol condensation.

For silica gels, a first important precursor is sodium metasilicate Na$_2$SiO$_3$, also termed waterglass [11, 12], which was previously used by Kistler to produce the first silica aerogels reported in the literature [13]. This precursor reacts with an acid such as HCl according to the reactions of the type shown in (2.1) below. A salt is produced, which must be eliminated by tedious dialysis or by exchange for H$^+$ through an acidic ion exchange column [14].

\[
Na_2SiO_3 + 2HCl + (x - 1)H_2O \rightarrow SiO_2 \cdot xH_2O + 2NaCl \quad (2.1)
\]

At present, some of the brand new works conducted on the silica system in aqueous solution concern the use of agricultural wastes, such as rice hull ash, as an inexpensive silica source [15, 16].

However, the Si precursors most frequently used nowadays are alkoxides of the Si(OR)$_4$ type, in which R and OR designate alkyl and alkoxide groups, respectively. Often, R is a methyl group CH$_3$ (or Me). An often used precursor is hence termed TetraMethOxySilane (or TMOS) [17]. Another common material has four ethyl rests C$_2$H$_5$ (or Et) as R groups, in which case the precursor is termed TetraEthOxySilane (or TEOS) [18]. The first inorganic gels synthesized were indeed silica gels made by Ebelmen from such precursors in 1846, except that they were not dried by a supercritical method to produce aerogels [19]. A much larger list of alkoxide-derived precursors and mixtures of them are used today, comprising, for instance, polyethoxysiloxane (PEDS) [20, 21], methyltrimethoxysilane (MTMS) [22, 23], methyltriethoxysilane (MTE) [24], 3-(2-aminoethylamino) propyltrimethoxysilane (EDAS) [25], N-octyltriethoxysilane [26], dimethyldiethoxysilane [27], and perfluoroalkylsilane (PFAS) [28]. Some precursors (such as EDAS) include built-in chemical functionality, which can then be used to modify the resulting gel materials with appropriate chemical synthetic strategies.

All these precursors are characterized by the existence of Si–O polar covalent bonds. This bond can in a first approximation be described as being ≈ 50% covalent, according to a description introduced by Pauling [29]. Such a characteristic explains the differential ability to build a random – (M–O) – network, between Si atoms and other cations M. The covalent character of the Si–O bond is sufficient to permit a wide distribution of the Si–O–Si angle values [30], leading to a “random 3D network” similar to the network known to prevail in silica glass.

In real life, Si alkoxides are often available as complexes in solution in their parent alcohol and are typically polymerized to a smaller or larger extent. Even if some monolithic but quite dense aerogel-like materials can be synthesized through ultrasonic-assisted solventless sol–gel routes (Chap. 20) [31, 32], their polymerization is mostly carried out in an organic solvent through simultaneous hydrolysis (2.2) and polycondensation of water (2.3) and alcohol (2.4) so that water becomes a reactant added in controlled proportion to drive the hydrolysis reaction (2.2).

\[
\equiv Si - OR + H_2O \rightarrow \equiv Si - OH + R - OH \quad (2.2)
\]
\[
\equiv Si - OH + HO - Si \rightarrow \equiv Si - O - Si \equiv +H_2O \quad (2.3)
\]
\[
\equiv Si - OR + HO - Si \rightarrow \equiv Si - O - Si \equiv +R - OH \quad (2.4)
\]

The hydrolysis mechanisms involve first a nucleophilic attack of oxygen lone pairs of the H$_2$O molecule on the Si atoms [33]. Because of the polarized Si–O bonds, the silicon atoms hold a partial positive electronic charge δ+, which in turn determines the kinetics of the nucleophilic attack and hence of the overall hydrolysis reaction. In alkoxides, the Si atoms carry a relatively moderate partial positive charge (e.g., δ+ ≈ 0.32 in Si(OEt)$_4$ by
comparison with ≈ 0.65 and 0.63, respectively, in Zr(OEt)₄ and Ti(OEt)₄ [33]). As a result, the global gelation kinetics of Si(OR)₄ alkoxides is very slow, unless the hydrolysis and condensation steps of Si are catalyzed either by bases that carry strong negative charges (e.g., OH⁻, but also strong Lewis bases such as F⁻ ions) or by acids (e.g., H⁺) in which case the reaction mechanism changes completely. In practice, the relative magnitudes of the hydrolysis and condensation rates are sufficiently slow to permit a relatively independent control. Overall, silica gels with a texture closer to that of polymeric gels derived from organic chemistry are obtained if the hydrolysis rate is faster than the condensation one. This is usually the case under acidic catalysis. In the literature, a large range of acids have proven to be useful catalysts, including HCl [27, 34], HF [3, 20, 28], or carboxylic acids [22, 34, 35].

On the other hand, proton acceptors, i.e., bases, accelerate the condensation reactions more than hydrolysis, which then favors the formation of denser colloidal silica particles and colloidal gels. Aqueous NH₃ is the basic catalyst most frequently used [22, 36, 37], but a Lewis base such as NaF or NH₄F also has its advantages, in particular when used with precursors such as MTMS [23, 38].

Additional parameters that affect the properties of the final aerogel are the nature of the solvent, which most typically is an alcohol [21, 27, 28, 34, 37] but can be acetone [35] or ethyl acetoacetate [20]. In addition, there is also the molar ratio “Si-precursor to water” as well as the concentration of Si precursor in the solvent and the catalyst nature and concentration, which are important parameters too. In short, these parameters rule the nanostructuration of the resulting gel (primary particles size, pores size distribution, fractality, tortuosity, density, etc.). To better control this nanostructuration, researchers have developed two-step processes so that they can successively favor one or another type of catalysis [39], a trick which is used, for example, to elaborate ultralight silica aerogels [40] or to achieve a good compromise between low thermal conductivity and high optical transparency [41]. The latter aerogels were synthesized first with H₂SO₄ catalysis of TEOS in ethanol under a substoichiometric molar ratio H₂O/TEOS = 1.8, followed by a second catalysis step with HF in ethylacetoacetate. Subsequent ²⁹Si NMR studies have shown that the intermediate precondensed species were rather polymeric, while the final gels were more colloidal (Figure 2.1). More recently, new developments are focused on the use of new classes of nonaqueous polar solvents such as

Figure 2.1. High-resolution scanning electron micrographs (HR-SEM) of silica aerogels synthesized by a two-step process (first catalysis with H₂SO₄ followed by HF catalysis) (courtesy of Grillon F, MINES ParisTech, Evry, France and Rigacci A).
2.1.2. Ageing

Before drying, silica gels are often aged via different processes. The aim of this step generally is to mechanically reinforce the tenuous solid skeleton generated during the sol–gel process. The majority of studies dedicated to these strengthening treatments were performed by Prof. Mari-Ann Einarsrud and coworkers at NTNU University, Trondheim, Norway [20, 46]. *Aging* schematically consists in taking advantage of *syneresis* and/or *Ostwald ripening* mechanisms by modifying the composition of the liquid phase contained in pores of the silica gel. Adding water [47] and/or monomeric alkoxy silanes such as TEOS [11, 20, 38, 46, 48–50] can significantly enhance surface reactions and primarily those involving the residual hydroxy/alcoxy groups. Consequently, supplementary *condensation* reactions and *dissolution/reprecipitation* of silica can occur. The associated kinetics depends on the pH and the nature of the solvent. Generally, the particles “neck” area, the average pore size, and the apparent density of the gel increase through aging treatments. If properly controlled, these morphological changes can significantly improve the mechanical properties (*E, K, MOR...*) and the liquid permeability (*D*). In one case, for example, an augmentation of the shear modulus by up to 23 times was reported [51].

Recently, it has been shown that other types of successful *aging* treatments exist to simultaneously increase the permeability and mechanical properties. These include, for example, the addition of larger precursor molecules, e.g., polyethoxydisiloxanes [20] or simply adding a dilute HF solution without additional silica precursor [50] (Figure 2.2). It has also been demonstrated that monitoring the temperature and simply performing a thermal *aging* of the wet gel in water can be a key factor to decrease the gel microporosity before drying [52].

![Figure 2.2. Permeability of silica wet gels (i.e., before drying) as a function of HF concentration in the aging bath composed of ethanol (SPL1, white marks) or ethylacetocetate (SPL2, solid marks) containing 3 vol% water. After [50].](image)
2.1.3. Drying

Capillary stresses inevitably occur whenever gas–liquid menisci appear at the pore boundaries, during evaporation of the pores’ liquid. Even if the siloxane bonds have approximately 50% covalent character, which makes the silica gels much more capable of resisting to evaporative effects than other oxide gels, particular attention must be paid to this really tricky step. As illustrated in a number of review articles [53, 54], three main routes are commonly used for drying:

1. Freeze-drying (which necessitates to bypass the triple point)
2. Evaporation (which implies crossing the liquid–gas equilibrium curve)
3. Supercritical drying (which necessitates to bypass the critical point)

In general, freeze-drying and evaporation applied to finely nanostructured silica gels have not yet proved to produce monolithic aerogels. Freeze-drying leads to cracked pieces or even powder-like products [55]. Evaporation without specific surface (e.g., sylilation [56]) and/or aging [46] treatments results in “dense” (e.g., \( \rho > 0.25 \text{ g cm}^{-3} \) [57]) and even cracked materials, so-called xerogels, as discussed in the preceding Chap. 1 (Figure 2.3). As shown by Phalippou et al. [58], the densification during evaporation comes from the condensation of remaining reactive silica species [see (2.3) and (2.4)]. When submitted to capillary stresses, initially far distant hydroxyl and/or alkoxy groups can come close enough to one another to react and generate new siloxane bonds, thus leading to irreversible shrinkage (Figure 2.4), because of the inherent flexibility of the silica chains.

Supercritical drying, on the other hand, permits to eliminate capillary stresses. Hence, this process produces monolithic silica aerogels of rather large dimensions (Figure 2.5), if required by a targeted application [59] (Figure 2.6).

Figure 2.3. Appearance of cracks during evaporative drying under ambient conditions (here observed with mesoporous silica wet gels impregnated with ethylacetoacetate at times \( t_1 = 5 \text{ min} \) and \( t_2 = 20 \text{ min} \), respectively, after the beginning of evaporation \( t_0 \)). Courtesy of Rigacci A.

Supercritical drying can be performed (1) in organic solvents in their supercritical state (generally alcohol as the pore liquid and consequently above 260°C if ethanol is used) according to a so-called HOT process [61] or (2) in supercritical CO\(_2\) at a temperature slightly above the critical temperature of CO\(_2\) ~31°C according to a so-called COLD process. Application of the COLD process to silica gels was investigated by Tewari et al. [62]. For this purpose, the liquid that impregnated the wet gels had to be exchanged with CO\(_2\), either in the normal liquid state [18] or directly in the supercritical state [63]. Indeed,
Figure 2.4. Comparison of the shrinkage behavior, from the wet (upper photographs) to the dry (lower photographs) states, occurring during evaporative drying of native, e.g., untreated (left-hand side) and sylilated (right-hand side) silica gels. Courtesy of Rigacci A.

Figure 2.5. Monolithic silica aerogels obtained after supercritical CO$_2$ extraction. Courtesy of Rigacci A.
the interdiffusion of CO₂ with methanol or ethanol, and with it the exchange, is slow and is significantly accelerated when CO₂ is in the supercritical state [64, 65].

However, although perfect monolithic silica aerogels can be elaborated by both HOT and COLD supercritical drying routes, the supercritical way could remain too time-consuming to be widely exploited on an industrial scale to produce this type of samples. Indeed, the low gel permeability results in rather slow CO₂ washing and vessel depressurization steps [66, 67], in particular for thick gel plates. To speed up the CO₂ washing, simple molecular diffusion must be assisted by forced convection, for example, by integrating compression–decompression cycles into the process [68]. However, if an accelerated depressurization is required, gels must be significantly strengthened prior to drying. If not, they will experience cracks even at low depressurization rates (Figure 2.7).

Figure 2.6. Large monolithic silica aerogel monoliths integrated in demonstration glazing (left side) and window (right side) prototypes [60]. Courtesy of K.I. Jensen and J.M. Schultz, DTU, Lyngby, Copenhagen.

Figure 2.7. Typical depressurization crack (perpendicular to the largest surface) experimented by the silica gel during supercritical drying (illustrated here on a 1 cm thick wet silica tile having a liquid permeability between 5 and 10 nm², dried with supercritical CO₂ at 313 K and 90 bar, and submitted to an autoclave depressurization of 0.15 bar min⁻¹). Courtesy of Rigacci A.
To accelerate the supercritical drying process, a “rapid supercritical extraction method,” in which the silica sol or the precursors were directly gelled inside the container under HOT supercritical conditions, was investigated in the mid-1990s by Poco et al. [69] and subsequently by Gross et al. [70], Scherer et al. [71], and Gauthier et al. [72]. Even though successful in the case of small samples, this technique does yet not permit to elaborate large crack-free, low-density monolithic silica aerogels. Currently, to try solving the fluid exchange difficulties associated with the standard supercritical CO₂ routes, one of the major challenges concerns the direct synthesis of the silica gel in supercritical CO₂ by a water-free process [73–75].

Because the supercritical drying methods have remained considerably costly, some specific subcritical [76] and ambient pressure drying methods were developed to synthesize silica aerogels. In this case, the capillary stresses depend on surface tension and viscosity of the pore liquid, drying rate, and wet gel permeability. In order to reduce their negative impact on the drying, Drying Control Chemical Additives (DCCA) such as polyethylene glycol (PEG) [17, 77], polyvinyl alcohol (PVA) [78, 79], glycerol [80], or surfactants [81] have been used. They interfere with the hydrolysis products of the respective Si precursors and permit to control the pore size and pore volume as well as their distribution. In any case, one of the key points relies on the introduction of incondensable species in the system via the sylilation of the silica gel [56] or the use of specific Si precursor such as MTMS [22] in order to promote a so-called spring-back effect when the solvent front retreats and capillary stresses are released [54]. To conclude, after some trial and error ambient pressure drying was applied with great success to the synthesis of silica aerogels from alkoxides [82–84], as well as from waterglass [11, 56], and is today the most promising manufacturing technique for SiO₂ aerogels. Densities below 0.1 g cm⁻³, for a total specific pore volume sometimes larger than that of CO₂-dried samples, could be obtained, something which would have been unimaginable 20 years ago.

2.1.4. Synthesis Flexibility

Besides these synthesis and processing methods, it must be emphasized that the flexibility of sol–gel processes permits to enlarge the selection of silica aerogel-based materials, which is currently accessible. Bulk architecture can be tailored by templating techniques [85]. The gel chemistry can be modified by grafting, either during [86] (Figure 2.8) or after gelation [87]. Composites and nanocomposites can be elaborated by impregnation of foams (Figure 2.9) or fibrous networks (Figure 2.10), by dispersion of particles [88], powders [89], or polymers [90], or by synthesis of mixed silica-based oxides [91, 92]. Organic silica hybrids [93] can also be made either by many techniques such as cogelation and crosslinking [94] or by reaction with functionalized particles [95].

After the drying stage, a wide panel of posttreatments can also be applied to increase the huge application potential of silica aerogel-based materials. For example, chemical modifications by grafting in solution after re-impregnation [96] or in a gaseous atmosphere [97], skeleton coating by chemical vapor infiltration [98], impregnation of the bulk porosity with reactive species (Figure 2.11), embedding in polymers (Figure 2.12), mechanical engineering by milling, cutting, laser micromachining [100], and thermal processing such as sintering [101] can be performed to target specific applications.
2.2. Main Properties and Applications of Silica Aerogels

2.2.1. Texture

Silica aerogels are amorphous materials. They have a skeletal density, as measured by Helium pycnometry [102] \( \approx 2 \text{ g cm}^{-3} \), close to that of amorphous silica (2.2 g cm\(^{-3}\)). They typically have a pore volume above 90% of their whole monolith volume. Some ultraporous
Figure 2.9. Scanning electron microscopy of an organic–inorganic composite obtained by impregnation of a cellular open-cell organic foam with a silica sol. *Courtesy of Repoux M., MINES ParisTech, CEMEF, Sophia Antipolis, France and Rigacci A.*

Figure 2.10. Blanket-type composite obtained by casting of a silica sol on an unwoven mineral fiber network. *Courtesy of Repoux M, MINES ParisTech, CEMEF, Sophia Antipolis, France and Rigacci A.*

Figure 2.11. Polarized light microscopy of polyacrylate–silica aerogel composites obtained by photopolymerization of octylcyanobiphenyl liquid crystal infiltrated in the porosity of the aerogel (in the cliche, liquid crystal and silica aerogel are, respectively, the brilliant and opaque phases). *Courtesy of Pesce da Silveira N (UFRGS, Porto Alegre, Brazil) and Rigacci A.* [99].
and ultralight silica aerogels can be synthesized by two-step process, and a density as low as 0.003 g cm$^{-3}$ has been reported [40]: these are the lightest silica aerogels that can be found in the literature.

Silica aerogels are usually largely mesoporous, with interconnected pore sizes typically ranging from 5 to 100 nm and an average pore diameter between 20 and 40 nm. Micropores (i.e., pore sizes < 2 nm) become significant in aerogels synthesized under acid catalysis conditions or having undergone particular treatments [52]. The associated specific surface area is rather high, typically from 250 to 800 m$^2$ g$^{-1}$ and can exceed 1,000 m$^2$ g$^{-1}$ [28].

Figure 2.12. Photography (top) and scanning electron microscopy (bottom) of sylilated silica aerogel beads embedded by a polymer. Courtesy of Rigacci A.
As already underlined in the first part of the text, the mesoporosity can be controlled through the sol–gel process conditions, for example, when a two-step catalysis is applied to standard alkoxides such as TMOS [36, 82, 103]. If these simple tetra-alkoxides are mixed with a more exotic functionalized Si precursor, differences in the hydrolysis and condensation rates of the two precursors may drastically influence the final texture of the material. For example, when the functionalized precursor carries basic moieties such as an amine in 3-(2-aminoethylamino)propyltrimethoxysilane (EDAS), 3-aminopropyltriethoxysilane (AES), or 3-aminopropyltrimethoxysilane (AMS), these functionalized precursors can act as nucleation centers for condensation and can lead to generation of large macropores [104, 105].

The architecture of silica gel networks is often described as that of a fractal geometry [106] and it is possible to distinguish mass from surface fractalities. In the former case, the mass $M$ of a gel inside a sphere of radius $R$, centered about a random point in the gel network, is a statistical function of $R$ of the type (2.5):

$$M \approx R^f,$$

where $f$ is termed the fractal dimension because this is not an integer.

For a surface fractal object, the surface area $A$ follows the law (2.6):

$$A \approx R^{f_S}$$

The fractal dimension can be experimentally determined by adsorption of molecules of different cross-sectional area, by small or ultra-small-angle X-ray scattering (SAXS/USAXS) or by small-angle neutron scattering (SANS) spectroscopy [35, 107]. These experimental results support various theoretical fractal models summarized by Brinker and Scherer [1, 108] (Chap. 24). In theory, true fractal structures can only exist near the gel point. In real silica gels, a fractal description only applies over a limited length scale range from one to hundreds of nm, which in detail depends on the exact structure of the aerogel. Silica aerogels made by Einarsrud et al., for instance, had a fractal network in the microporous range with an average mass fractal exponent $f \approx 1.9$ consistent with a “Diffusion Limited Cluster Aggregation” (DLCA) model [20]. SAXS/USAXS and SANS are also widely used to characterize elementary particles and/or distributions of clusters that constitute the silica skeleton as well as other structural features such as the specific surface area. These results generally give larger values than their BET analogues (Chap. 21).

Even if solid and porous networks of silica aerogels are essentially tailored during the sol–gel step, posterior treatments also influence the overall structure of the materials. As already mentioned in Sect. 2.1.3, some shrinkage occurs during evaporative drying due to the presence of intense capillary stresses, but this also sometimes holds for supercritical drying. Indeed, some irreversible shrinkage also occurs due to the restructuration of the gel network by dissolution–reprecipitation of SiO$_2$ in supercritical media and also because of the stresses during solvent exchange processes [35, 40]. All these kinds of shrinkages affect the porous network, but when applied to a wet gel, supercritical drying mostly affects the larger pores that involve network dimensions beyond the fractal scale, while drying by evaporation to obtain a xerogel in addition leads to a drastic shrinkage of the mesopores. Furthermore, concerning supercritical drying, the silica aerogels obtained by the HOT process tend to possess a lower specific microporosity but a similar specific mesoporosity to those obtained by the COLD process [35, 109, 110].
The porous network characteristics (specific pore volume, mean pore size, pore size distribution, etc.) reported in the literature are usually obtained either by adsorption of nitrogen [111] or by non-intrusive mercury porosimetry [112] and are discussed in detail in Chap. 21. An example of pore size distribution obtained by non-intrusive mercury porosimetry is presented in Figure 2.13.

![Figure 2.13. Pore size distribution of a 0.15 g cm$^{-3}$ silica aerogel obtained by non-intrusive mercury porosimetry on samples synthesized in alcohol via a two-step process with TetraEthOxySilane (using a buckling constant $k_f$ of 28 nm MPa$^{1/4}$). Courtesy of Rigacci A.](image)

### 2.2.2. Chemical Characteristics

After drying, untreated (e.g., not sylilated) silica aerogels contain residual reactive groups (e.g., alkoxy and hydroxyl groups). Fourier-transformed infrared spectra (FTIR) reveals a silanol surface coverage (≡Si–OH) of typically 4–6 groups per nm$^2$ [113], which gives them a certain hydrophilic behavior. This parameter is influenced by the specific sol–gel conditions used as well as by the drying route. Concerning drying, silanol groups condense during evaporation while HOT supercritical processing induce re-esterification of the silanol functionalities. This makes both xerogels and aerogels more hydrophobic after drying is complete.

Indeed, for many applications, it is necessary that aerogels be hydrophobic to not absorb (even adsorb) water vapor. The methods to prepare hydrophobic silica aerogels were intensively studied by many authors (Schwertfeger et al. [56], Schuth et al. [114], Venkateswara Rao et al. [115–119], Lee et al. [14], Kim and Hyun [120], Shi et al. [121], and Hwang et al. [12]). Good reviews of the methods to synthesize such materials and of the characteristics achieved are presented in Chaps. 3 and 4. Briefly, to elaborate hydrophobic silica aerogels, the pore surface must be covered with nonpolar side functions such as ≡Si–CH$_3$, which can be introduced by several methods. For instance, a silicon precursor containing at least one nonpolar chemical group, of the type RSi(OR')$_3$ where R and R' are alkyl groups, can be cogelled in various proportions with TMOS or TEOS. For example, when some hybrid gels are synthesized with TMOS and MTMS, the silanol concentration can be decreased. MTMS, for instance, is more difficult to condense than TMOS. Hence, the gel network is then mostly made by TMOS, while in the second stage ≡Si–CH$_3$ end groups cover the pore surface [122]. Of course, hydrophobization can also be realized after supercritical
drying, for instance, by treating the aerogel with hexamethyldisilazane (HMDS) [123], but it is now far less studied than silylation in solution. As already mentioned in Sect. 2.1.3 dedicated to drying, these silylation methods permit to promote spring-back effect and to obtain ambient-dried aerogel while giving them specific surface properties.

2.2.3. Physical Properties and Some Related Applications

Thermal Conductivity

One of the major characteristics of silica aerogels is their very low thermal conductivity, typically of the order of 0.015 W m\(^{-1}\) K\(^{-1}\) at ambient temperature, pressure, and relative humidity. These values are significantly lower than the conductivity of air under the same conditions, e.g., 0.025 W m\(^{-1}\) K\(^{-1}\). Thus, silica aerogels are among the best-known thermal insulating materials [124]. Besides, silica is nonflammable and silica aerogels are amorphous.

Moreover, silica aerogels can be made optically transparent, although they are also very brittle. Consequently, they present an amazing application potential for opaque or transparent insulating components [125, 126] as well as daylighting devices, if they can be mechanically reinforced. The physics governing their thermal properties, as well as their use in thermal insulation (Chap. 26) and the first related commercial products (Part XV), is described later in the handbook (Chap. 23). As an example for a high-tech product, it shall be underlined that silica aerogels find ever increasing use as thermal insulator in the aeronautical and aerospace domains [127]. They were, for instance, used in the recent PATHFINDER MARS mission to insulate the Sojourner Mars Rover. During the mission, the nocturnal temperature dropped down to \(-67\)°C, while a stable inside temperature of 21°C was maintained. This permitted to protect the Rover’s very sensitive electronics from damage by the cold. For a similar program termed European Retrieval Carrier (EURECA) satellite, the use of aerogels has been investigated [128].

Of course, it must be underlined here that applications in space are not at all limited to thermal insulation. Indeed, silica aerogels can be applied to collect aerosol particles [129], to protect space mirrors, or to design tank baffles [130, 131]. The applications in space were reviewed by Jones [132] (Part XI). The most recent project, Stardust, successfully returned to earth in January 2006. This mission provided samples of a recently deflected comet named Wild-2, which are being examined in various laboratories all over the world.

Optical Properties

The optical transmission and scattering properties of silica aerogels constitute another group of important characteristics, sometimes in conjunction with their thermal properties when a transparent thermal insulation is targeted, such as in windows. A first review of this subject was published by Pajonk [133]. More recent works comprise those of Buzykaev et al. [134], Danilyuk et al. [135], Venkastewara Rao et al. [115], Jensen et al. [136], Schultz et al. [59], and Adachi et al. [137]. The transparency and visible light transmittance of silica aerogels can be high, although they all tend to scatter the transmitted light to some extent, which reduces their optical quality [138]. The Rayleigh scattering due to the solid gel network heterogeneities in the nanometer range is responsible for a yellowish coloration of silica aerogel observed in transmission and a bluish coloration when observed in reflection mode against a dark background. The scattering due to heterogeneities in the
micrometer range is responsible for a blurred deformation of optical images [139]. A two-step gelation catalysis procedure, previously described, was found to give satisfactory transparency results. Typically, aerogels made from TMOS in methanol can be obtained with an optical transmittance ratio up to 93% (for ~1 cm thick aerogels) at a wavelength of 900 nm [140, 141]. Silicon precursors prehydrolyzed with an acid catalyst and a substoichiometric water molar ratio \( w = n_{\text{H}_2\text{O}}/n_{\text{Si}} < 2 \) are available on the market [124, 142] and make it possible to control a more uniform porous texture, as is needed for optical applications. Transparency ratio up to 90% together with specific extinction coefficient of the order of 15 m\(^{-1}\) [143] can be obtained with 1 cm thick aerogels synthesized with such prepolymerized precursors (Figure 2.14).

The refractive index of silica aerogels increases with their density \( \rho \) (kg m\(^{-3}\)) according to (2.7) [144]:

\[
 n - 1 = 2.1 \times 10^{-4} \rho.
\]  

Hence, \( n \) is very close to 1 [145], which makes aerogels excellent materials to apply in the radiator of Cerenkov counters [146]. In a Cerenkov counter, the radiator is a low-density medium such as an aerogel slab, in which electrically charged elementary particles travel with a velocity “\( v \)” higher than the velocity of light “\( c \)” and from where they radiate (emit) photons. An analysis of these photons can therefore be used to derive the velocity of the particles and hence their nature. This was one of the well-known historical uses of silica aerogels. Kharzheev published a recent review on the use of silica aerogels, for this type of application, with a description of their optical and physical characteristics [147]. Moreover, a summary of the operational experience from 1998 to 2007, with silica aerogel tiles used in RICH-type Cerenkov counters, for the HERMES experiment at the DESY – HERA facility, was published by de Leo [148]. The average refractive index value \( n \) of these tiles at a wavelength of 633 nm was equal to 1.0304 ± 0.0004. The aerogel optical quality was characterized by its light attenuation length \( \lambda \) at 400 nm. This characteristic is defined as...
the distance into an aerogel, where the probability that a photon having this wavelength has not been absorbed has dropped by $1/e$ (where $e = 2.71828$). Clearly, this property depends on the aerogel density and it increased from $A \approx 1$ cm in the 1980s, to $\approx 2$ cm in the early 1990s, to reach $\approx 4.5$ cm in recent larger aerogel tiles ($20 \times 20 \times 4$ cm$^3$).

**Acoustic Properties**

The acoustic properties of silica aerogels are closely related to their thermal insulation properties. The acoustic propagation in aerogels depends on the interstitial gas nature and pressure, the aerogel density, and more generally the texture [149]. Silica aerogels are indeed excellent acoustic insulators. The propagation of an acoustic wave is attenuated both in amplitude and velocity because the wave energy is progressively transferred from the gas to the aerogel solid network, over the entire aerogel workpiece thickness [150]. The longitudinal acoustic velocity is typically of the order of 100 m s$^{-1}$ [151, 152], which makes silica aerogels suitable for applications in acoustic devices.

**Mechanical Properties**

A fourth group of important characteristics has to deal with their mechanical properties (Chap. 22). The compressive strength, tensile strength, and elastic modulus of silica aerogels are very low and largely depend on the network connectivity [153] and aerogel density [154]. Indeed, silica aerogels can easily be elastically compressed when the porous texture is studied, for example, by the capillary stresses that they are subjected to during nitrogen adsorption or desorption [155] or by compression during mercury porometry and thermodorometry [83, 156]. The magnitude of the contraction can reach $\approx 50\%$ by length [157].

As previously mentioned, many synthetic routes are investigated with the goal to strengthen silica aerogels, the most popular approaches of which are aging [51] and hybridization. For example, hybrid silica aerogels can be made for strengthening purposes by mixing a silicon alkoxide with hybrid precursors such as polydimethyl siloxane (PDMS). Gels obtained in this way are termed ORMOSIL hybrids. They have a more rubber-like flexibility. With 20% (by mass) PDMS, they can be elastically compressed to 30% (by volume) with no damage [158]. Some flexible silica aerogels with superhydrophobic properties were also made from MTMS by A. Venkateswara Rao et al. [116]. At last, polymeric crosslinking of the silica skeleton can also permit to drastically increase the initial mechanical characteristics [159].

In addition, the mechanical properties are sensitive to the synthesis chemistry of the gel, the environment, and the storage history [160]. With age, the compressive strength and elastic moduli increase while the strain at fracture decreases. The environment is responsible for subcritical crack growth, which proceeds by a stress corrosion mechanism analogous to the phenomenon observed in dense silica glass subjected to alkaline aqueous solutions. Crack growth can be considerably reduced in hydrophobic aerogels [161], although an apparently fully hydrophobic character does not totally impede water molecules from reaching the crack tip [162].

In spite of their low density and brittle characteristics, the mechanical properties of silica aerogels are quite promising for some rare but specific applications. As an illustration, their good compressibility can be used advantageously for absorbing the kinetic energy
involved in a compressive shock [134, 163]. Silica aerogels are useful low shock impedance materials to confine few eV plasmas, to capture frozen states of minerals generated under high shock pressures, or as medium to study the mixing of fluids requiring X-ray-induced shocks [134, 163, 164].

Dielectric Properties

The relative dielectric constant of silica aerogels can be as low as 1.1 [165]. Hence, thin film silica aerogels could be and are being considered as super-low dielectric constant material for integrated circuits in computers. It is also possible to modify the surface of silica aerogel to obtain good electret materials (i.e., materials that produce a permanent external electric field) [166].

Entrapment, Release, Sorption, and Storage

The combination of a high specific pore volume, with – in some specific cases – a relatively resistant solid SiO$_2$ network, can also be advantageously used to entrap a large variety of molecules or nanoparticles. The entrapped species can be luminescent molecules or particles [167–172].

Hollow silica aerogel droplets were also proposed by Kim et al. [173], Jang et al. [174], and Kim and Jang [175] for the inertial confinement of fluids (ICF), namely, mixtures of liquid deuterium and tritium, as the target in fusion experiments under a powerful laser. The droplets were generated by a double nozzle reactor; they were stable to radiation and could be wetted by deuterium and tritium. In aerogels, the gel network acts as an impurity for the fluids that strongly interact with the solid surface. Hence, large fluid NMR signals with long polarization lifetimes can be recorded, revealing a very weak specific wall relaxation [176]. This effect can be used to study either the gel itself or the trapped fluid. The gel network was, for instance, studied by impregnation with liquid $^{131}$Xe near its critical temperature ($T_c$ of approximately 289 K). Magnetic resonance images were obtained, which made it possible to differentiate between aerogels of different densities and hydration levels [177]. As far as studies on fluid flow are concerned, the interaction between superfluid $^3$He and the silica aerogel network has received significant attention and was reviewed by Halperin et al. [178]. The solid network introduced disorders in these interactions, thus allowing us to suppress the superfluid transition temperature.

Similarly, when an aerogel is impregnated with a nematic liquid crystal, the gel network randomness destroys the crystal long-range order and transforms the liquid crystal into a glassy state [179].

Biomaterials can also be successfully immobilized inside aerogels. Besides an early study by Antczak et al. [180], Pierre et al. [181, 182] described the in situ encapsulation of the Pseudomonas cepacia lipase into a hydrophobic silica aerogel on which they tested various enzyme catalyzed esterification and transesterification reactions. The authors observed that, contrary to the same silica matrix but in the form of an ambient-dried aerogel, the material showed a much higher activity. Because of the larger pore size, each lipase molecule was indeed able to operate as a free isolated molecular catalyst, while agglomeration of the catalyst was made impossible by dispersion in the aerogel network. Bacteria can also be trapped inside aerogels and still remain alive. Power et al. [183] described a biosensor under the form of an aerosol composed of aerogel dust particles, containing
*Escherichia coli* and the Green Fluorescent Protein (GFP) obtained from the jellyfish *Aequorea Victoria*. When a virus, like the bacteriophage T7 polymerase promoter also under the form of an aerosol, contacted the bacteria, a green fluorescent light was emitted.

The controllable pore size and high specific pore volume of silica aerogels make them also ideal candidates for releasing medical drugs or agriculture chemicals (fungicides, herbicides, and pesticides) [184] in a controlled fashion. Hydrophilic silica aerogels can be loaded with chemicals during the sol–gel synthesis process or by posttreatment of dried aerogels [185].

Inversely, aerogels can be used to adsorb or extract some chemical compounds, for instance, to treat waste water, to confine radioactive waste [134], or to filter gases [186]. Silica aerogels were proposed by Reynes et al. [187] for the storage of long life actinide wastes because they are chemically very stable with time on stream and they possess a very large relative pore volume. Besides, aerogels could easily be converted to vitreous silica after a short heat treatment at \( \approx 1,000^\circ\text{C} \) [188, 189]. The experiments also showed that these aerogels were able to store the waste much longer than the conventional borosilicate glass.

Silica aerogels impregnated with CaCl\(_2\), LiBr, and MgCl\(_2\) salts have been tested too as water sorbents for heat storage at low temperature. Their energy storage ability \( E \) measured by differential scanning calorimetry (DSC) can reach 4.0 kJ g\(^{-1}\), which is much higher than for common sorbents such as zeolites and unimpregnated silica gels [190]. Partially sintered aerogels, which are mechanically stronger to resist capillary stresses, are convenient to store or transport liquids such as rocket fuel [191]. Hazardous liquids such as red fuming nitric acid and unsymmetric 1,1-dimethyl hydrazine (UDMH), both used as rocket fuels, have been stored with silica aerogels [192].

Aerogel particles can also be used as the dispersed phase in composite materials, such as elastomers for tires or paints. The incorporation of aerogels will provide them with additional hardness, resistance to wear, and also exert a thickening effect on the mixture [135]. As colloidal abrasives, they even show some insecticide properties because they remove the protecting lipid layer on insects [193].

### 2.3. Conclusion

Clearly, silica aerogels occupy a dominant place within aerogels. They are used in many important applications and several chapters of this handbook are dedicated to some of them (Chaps. 26, 28, 30–34) or to a detailed review of important properties that sustain these applications (Chaps. 21–23). These fields are still rapidly growing, primarily because of their potential impact in sustainable technology developments. Moreover, new possible applications are appearing such as CO\(_2\) sequestration, as recent studies have shown that enhanced carbonation reactions could be observed in SiO\(_2\)-based aerogels under ambient conditions [89]. The amazing class of silica aerogel materials has for a long time been considered as the most fascinating examples of nanostructured porous materials. It appears now that a massive commercialization may be imminent while fundamental studies still continue.

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