AEROGELS: UNIQUE MATERIAL, FASCINATING PROPERTIES AND UNLIMITED APPLICATIONS

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Abstract

This chapter follows a chapter in the sixth volume of this book series focused on fascinating ultra-porous materials referred to as aerogels. That chapter focused on applications in thermal insulation and catalysis. In this chapter, the production process for these sol-gel-derived materials is presented, and the characterization techniques are reviewed. In recent years much progress has been made in commercialization of aerogel materials and a summary of many potential applications, ranging from acoustic impedance matching layers to biosensors, is provided.
1 INTRODUCTION

Aerogels belong to an unusual class of low density, microporous, open-cell materials that possess extraordinary physical properties. They are sometimes referred to by the nickname “frozen smoke” in reference to their hazy, nebulous appearance. At first glance, aerogels look like fog that has been molded into a distinct shape [1]. In room light, aerogels appear slightly blue; yet, when a light source is viewed through them, they appear yellowish, evidence that the color is due to Rayleigh scattering off the micropores. S. S. Kistler developed aerogels in 1931 and was able to produce samples with densities ranging from 0.02 to 0.1 g/cm$^3$ [2].

Typical silica aerogels consist of approximately 95% air, while the remaining 5% is a thin, wispy matrix of silica. The unique microstructure leads to many extraordinary properties. Aerogels have the lowest density, lowest thermal conductivity, lowest dielectric constant, lowest acoustic velocity, and lowest refractive index of any known solid [3]. The solid thermal conductivity of aerogels can be two to three orders of magnitude smaller than that of bulk silica glass [4]. In the 1980s, the energy crisis spawned considerable interest in aerogel research in the U.S. and Europe due to its potential use as a thermal insulator [5].

An international symposium on aerogels has been held every three years since 1985. As a review of the symposium proceedings shows, the focus has evolved over time [6–11]. The early symposia focused on production and characterization techniques, while later symposia included significant emphasis on potential applications. The most recent symposium, held in 2003 in Alexandria, VA, included a great deal of discussion about commercialization efforts and applications.

The sixth volume of this book series includes a chapter on “Aerogels: Applications, Structure, and Heat Transfer Phenomena” by Richter, Norris, and Tien [12]. That chapter includes a detailed discussion of the production and characterization techniques used at the time, as well as a discussion of potential applications, with particular attention given to thermal insulation and catalysis. There is also a detailed discussion of the heat transfer mechanisms in aerogels. The interested reader is referred to that volume for more details in any of these areas. This current work will only briefly describe the production technique and the resulting properties, and will provide an update of current activities in the field and a summary of advances made since 1996.

2 PRODUCTION PROCESS

When Kistler discovered aerogels in 1931, he was seeking to demonstrate that it is possible to remove the liquid from a wet gel without damaging the solid component. Kistler discovered the key to deriving a microporous solid from a wet gel; the liquid filling must be transformed into a supercritical fluid before being removed from the porous solid. In this manner, the surface-tension forces resulting from the evaporating fluid at the liquid-vapor interface are avoided and the tenuous solid remains
unharmed [13]. The resulting material is called an aerogel and is one of the most extraordinary room-temperature solids known to humanity.

The most common method used to produce porous silica gels is the sol-gel process, where a solution of silicate monomer undergoes polymerization as shown in Figure 1 [14, 15]. The term sol refers to a colloidal suspension of solid particles that, under the proper conditions, condenses with one another or with an unreacted precursor to form an irregular, noncrystalline, three-dimensional network that spans the entire volume of a vessel. The resulting network can be described as a gel when a path can be traced from one boundary point of the vessel to another without leaving the solid phase, although further condensation may still be occurring. The gel network is commonly very porous (sometimes in excess of 99%) and is often denoted by the interstitial fluid. The fluid phase in hydrogels is thus water or aqueous solution, in algogels it is alcoholic solutions, and in aerogels it is air or other gases. The gelation reaction can occur in any number of solvents and is commonly driven by changes in pH or stoichiometry of the reactions. Unlike many organic polymer hydrogels, inorganic gels are mechanically robust and solvent exchange produces minimal changes in gel dimensions. Under controlled reaction conditions, the sol-gel process is amenable to various shapes (beads, fibers, thin films, bulk monoliths) and sizes.

The solid backbone of the network can be many from any of a number of materials, but sol-gel processing is most common with metal oxides, and most specifically with silica, alumina, titania, and zirconia. The solid component is commonly derived from the hydrolysis/condensation of the respective alkoxy metalla. The hydrolysis reaction refers solely to the substitution of alkoxy groups with hydroxyl groups or water on individual metal centers, while condensation is the chain-lengthening reaction that releases water or alcohol derived from hydroxyl groups on neighboring molecules.

As the process of polymerization continues, a solid silicate network separates out
Figure 2 Complex aerogel pore structure describing macro-, meso-, and microporosity in addition to surface silanol groups.

of the solution (gel point). The solid is still “soaking” in the alcohol solution; this biphasic system is usually referred to as the alcogel. If the alcogel is allowed to dry under atmospheric conditions, the solid matrix shrinks to form a xerogel. During evaporation, capillary pressure develops within the pores of the gel and draws the pore walls together. This results in significant volumetric shrinkage and a reduction in porosity. Supercritical drying, on the other hand, essentially preserves the structure of the initial liquid-filled gel and is capable of producing large monolithic pieces. By taking the interstitial liquid supercritical, the capillary pressure is brought to zero and the gel micro- and macrostructure are preserved during removal of the supercritical fluid. The super-critical drying step is a time consuming and often dangerous procedure, however. Ethanol or methanol drying requires elevating the temperature to over 250°C while maintaining high pressure. This poses a significant safety issue and explosions have been reported on more than one occasion. An alternative technique was reported by Tewari et al. in 1983 [17]. In this procedure, the alcohol within the gel is replaced with liquid carbon dioxide and the CO₂ exchange is followed by supercritical drying, which can be accomplished at much less extreme conditions (< 40°C and 1050 psi). However, depending on the volume of the sample and the pore size, the solvent exchange procedure can be quite time consuming.

The physical microstructure of sol-gel-derived metal oxides is highly dependent upon the production conditions. Reactant stoichiometry, temperature, catalyst, polarity of the reaction solution, and/or surfactant concentration all significantly influence the physical properties of the final gel. Figure 2 shows the three regimes of pore size that evolve during polymerization: micropores (< 2 nm), mesopores (2 to 100 nm), and macropores (> 100 nm). Statistical control over the evolution of pore size can be accomplished by varying the reaction conditions [14]. For example, aerogels produced using tetraethoxysilane (TEOS), ethanol, and water in the presence of an acid (HCl) or base (NH₃) catalyst result in a pore size distribution ranging from less than 2 to 10–50 nm [18]. At the other extreme, macroporous aerogels with pore sizes ranging between 3 and 10 μm can be produced by using tetramethoxysilane (TMOS) as precursor in the presence of acetic acid and using a polymer to form a template for gelation [19]. Acid-catalyzed aerogels made with TMOS and methanol possess surface areas as low as 200 m²/g [20], while homogeneous silica aerogels prepared
from silicon alcoholates in alcoholic solutions are known to possess surface areas as high as 1600 m²/g [21].

By varying the precursors and catalysts, the microstructure of the gels can be influenced and optimized for use in specific applications. Figure 3 shows scanning electron microscopy (SEM) photographs of two very different gel microstructures. The gel in Figure 3a is a two-step acid-base catalyzed TEOS-based gel that has smaller macropores (on the order of 100 nm) and appears more condensed, but possesses a higher surface area due to the larger and more numerous micropores of this type of aerogel. While the microstructure of the resulting gel is specific to the particular reaction conditions, some general conclusions can be drawn. In general, gels formed under acidic conditions tend to be “polymeric” in nature (as in Figure 3b), where condensation of unreacted alkoxy silicate occurs preferentially at the end of long chains that grow until they entangle and condense with one another. On the other hand, sol-gels formed under basic conditions tend to form larger clusters that condense with one another as particles. Surfactant concentration and solution polarizability can also have a significant influence upon gel microstructure, and phase separation may occur during the gelation reaction and this leads to unique microstructural features [22].

For enhanced performance in specific applications, the aerogel surface can also be functionalized or the material can be doped. Doping can occur by a variety of techniques. For example, any alcohol-soluble compound can be added to the sol prior to gelation. This technique has been used to dope silica aerogels with carbon black to produce opacified silica aerogels for optimized thermal behavior at high temperatures [23]. Functionalization of sol-gel-derived metal oxides is quite easy due to both the reactive surface and liquid precursor of the solid. The increased reactivity
of sol-gel-derived materials removes the need for traditional activation steps, and the liquid precursor guarantees even perfusion of a wide variety of silane coupling agents that can be introduced at various times during the sol-gel production process [24,25]. Furthermore, by alternating condensation and functionalization steps, it is possible to pattern three-dimensional structures with functionalization domains [26]. The most common approach to surface functionalization involves silane coupling agents that, despite difficulty with reproducibility, are widely available and the subject of much research due to their commercial importance [27].

It should also be noted that conventionally prepared aerogels are hydrophilic in nature. They absorb moisture from the environment, which causes deterioration over time and, ultimately, failure. This vastly reduces the potential for applications that require exposure to the atmosphere. This problem has been recently overcome by preparing hydrophobic aerogels by suitable changes made during the sol-gel preparation procedure [28,29].

An alternative to the supercritical drying process was reported in 1995 [30]. It has been shown that adding surface groups to the inorganic gel as the pore fluid is withdrawn makes drying shrinkage reversible, resulting in a gel that springs back to its porous state. Aerogel films of up to 98.5% porosity have been prepared, using this approach. By derivatizing the hydroxylated surface of the inorganic gel with organosilanes via standard silylation routes, processing conditions can be established to achieve reversible drying shrinkage for thin-film samples [30].

While this current work concentrates on silica aerogels, there are other types. For example, Livage et al. (1988) provides an excellent review of transition metal gels [31]. They report on successful production and application of aerogels based on alumina, zirconia, titania and other transition metal oxides. Aerogels can also be organic, as first reported in 1989 [32]. Pekala and Alviso (1989) prepared aerogels by the polycondensation of resorcinol with formaldehyde. They also demonstrated the ability of these gels to undergo pyrolysis in an inert environment to produce electrically conductive carbon aerogels, which find a variety of innovative applications [33].

3 PROPERTIES OF AEROGELS

Due to their complex microstructure, aerogels have many fascinating properties that can be used in numerous applications. Table 1 provides a summary of the commonly quoted material properties for low-density silica aerogels. As previously noted, however, the material properties are highly dependent upon the production process. Following the table is a brief description of some of the commonly used characterization techniques.
Table 1 Properties of silica aerogel (Ernest Orlando Lawrence National Laboratory published values)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>0.003 – 0.35 g/cm³</td>
</tr>
<tr>
<td>Internal surface area</td>
<td>200 – 1600 m²/g</td>
</tr>
<tr>
<td>Mean pore diameter</td>
<td>~ 20 nm</td>
</tr>
<tr>
<td>Solidity</td>
<td>0.13 – 15%</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.2</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>$10^6 – 10^7$ N/m²</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>~ 1.1</td>
</tr>
<tr>
<td>Speed of sound through bulk sample</td>
<td>100 m/s</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.017 W/mK</td>
</tr>
</tbody>
</table>

3.1 Structural Characterization

Characterization of the pore size, specific surface area, and structural properties of aerogels requires the use of either wavelengths or particles on the size scale of the microstructural features. Thus, gas molecules, X rays, neutrons, light, and electrons are frequently used. The most commonly applied techniques are briefly reviewed.

3.1.1 Gas Adsorption. The most commonly used technique for measuring the specific surface area, the mesopore size distribution, and the total mesopore volume of aerogels is gas adsorption. In this technique, a sample is cooled to cryogenic temperatures and then exposed to an analysis gas, most commonly nitrogen, at a series of controlled pressures. With each incremental pressure, the number of gas molecules adsorbed on the surface increases. The equilibrium pressure and universal gas law can be used to calculate the quantity of gas adsorbed. With increasing pressure, the thickness of the adsorbed film increases, covering first the smaller pores followed by the larger pores. This is followed by the desorption process where the molecules from the adsorbed surface are slowly liberated. Once again, the quantity of gas liberated can be calculated. Hence, adsorption and desorption isotherms are obtained that yield information on the surface characteristics of the aerogel. The specific surface area is calculated from the adsorption isotherm by the Brunauer–Emmett–Teller (BET) method [34]. In order to obtain accurate results for the mean mesopore size for highly porous aerogels, it is necessary to allow sufficient time for proper equilibration. As reported by Reichenauer and Scherer [35], many previous nitrogen sorption studies led to misleading results that did not accurately detect the total pore volume for low-density aerogels. They report that run times of up to 150 hours are required for 2 mm sized samples with porosities greater than 90%.

3.1.2 Small-Angle Scattering (SAS). SAS is the most powerful and reliable technique for studying the microstructure of aerogels. In this technique, radiation is elastically scattered by inhomogeneities of the sample, and the resulting
scattering pattern is analyzed to provide information about the size, shape, and orientation of some component of the aerogel structure. The main aspect of division among SAS techniques is the type of radiation used. Hence, there are SAXS and SANS experiments using X-rays and neutrons, respectively. Scattering of X-rays is caused by differences in electron density, while scattering of neutrons is caused by differences in scattering power of different nuclei. The porosity and surface area can be determined from the scattering intensity. Response of scattering intensity with change in scattering vector is then analyzed in order to obtain morphological information. Frick and Emmerling [36] report on application of this technique for study of aerogels and include a description of the experimental procedure as well as a discussion of the information that can be obtained.

Scattering techniques have been widely used to make many fundamental studies of the influence of processing conditions or production techniques on the microstructure of aerogel materials. SAXS and SANS techniques have been applied to examine fractal behavior at specific length scales and to study change in structure with respect to processing variables [37]. These experiments show that silica aerogels are made of a disordered but homogeneous array of fractal clusters resulting from the aggregation of primary particles [38]. SANS experiments performed on two types of silica aerogels during isothermal gas adsorption revealed differences in long-range texture despite similarities in mesopore diameter [39]. SANS has been used to study the effect of adding a biopolymer to a silica aerogel [40]. Silica aerogels of different densities with different catalysts prepared under different conditions have been studied using SAXS [41]. Properties of silica aerogels densified by isostatic compression and thermal sintering have also been studied using SAXS [42].

### 3.1.3 Optical Transmission Techniques

Some properties of transparent aerogels can be characterized by the measurement of the angular distribution of scattered light [43]. Yang et al. prepared TEOS-based silica thin films and used Fourier-transform infrared (FTIR) spectroscopy to identify unmodified and modified silica, and to observe compositional changes in films upon heating [44]. Transmission spectrum of TMOS-based gels supercritically dried using ethanol, methanol, and CO₂ measured in the wavelength region of 200–2500 nm showed that hydroxyl groups exist on the surface before and after heat treatment [45]. Analysis of the transmission spectra also showed that solar transmittance improved due to heat treatment. Since silica aerogels show significant IR transmission within the infrared (IR) optical window, 2000–2800 cm⁻¹, IR emission spectroscopy has also been used to characterize their thermal properties [46].

### 3.1.4 Electron Microscopy

While high-resolution electron microscopy, including both scanning electron microscopy and tunneling electron microscopy (TEM), is a technique often used to image the microstructure of aerogels and to estimate the pore size, this can be a difficult task. Owing to the very low thermal conductivity of aerogels, exposure to a beam of highly energetic electrons can lead
to sintering, which would severely alter the microstructure. To negate this charging effect, samples to be characterized are first coated with a thin metal film. This coating distorts the microstructure, however, and makes it impossible to determine ultimate particle sizes due to the thickness of the coating. Hu et al. provide an example of a study using TEM to image the microstructure of a new-type silica-biopolymer aerogel [40]. They report on the TEM-measured fractal dimension and its comparison to small-angle scattering results.

3.2 Mechanical Characterization

Mechanical property measurements are a bit more straightforward with the major experimental difficulties lying in sample preparation and small force measurement. Mechanical properties have been measured by classic three-point bending [47], uniaxial compression [48], ultrasonic techniques [49], and more recently, atomic force microscopy [50]. Atomic force microscopy (AFM) allows direct measurement of local elastic sample properties by force spectroscopy. Stark et al. [50] determined the elastic properties of a sample from the relation between an indentation made on the sample by the AFM tip and the loading force. By applying a maximum load of 50 nN to a commercially available aerogel powder of heap density 110 kg/m$^3$, the Young's modulus was determined to be 6 MPa.

3.3 Acoustical Characterization

Acoustic properties of aerogels are also of interest and are frequently measured under different conditions. Putselyk et al. [51] measured sound transmission and attenuation in aerogel samples of fixed length and diameter. Their aim was to characterize the high-frequency oscillation modes of the aerogel and determine how these modes vary with temperature. Gibiat et al. [52] presented acoustic properties of aerogels in both the ultrasonic and audible range. They report that classical theory fails to completely describe wave attenuation in aerogels. Properties of Pb(Zr$_{0.53}$Ti$_{0.47}$)O$_3$ (PZT) aerogels were studied by Geis at al. [53]. Aerogels were prepared with PZT as the backbone. The elastic moduli, dielectric permittivities, dielectric charge constants, porosity, and surface area were determined with a view to application as ultrasonic transducers. More acoustical studies on alcogels during their formation can be found in the works of Forest et al. [54].

3.4 Thermal Characterization

Several techniques are available to determine the thermal conductivity of aerogels. Zeng et al. [55] developed a thin-film heater apparatus using a 10 nm thick gold film for uniform spatial distribution of heat. Tests were conducted on opacified silica
aerogels and thermal conductivity values of 10 – 15 mW/mK were reported. Haranath et al., [56] used the transient, hot-wire probe method to determine thermal conductivity of silica aerogels prepared by varying molar ratios of TMOS, water, methanol, and catalyst. This method yielded a maximum thermal conductivity of 0.1 W/mK and a minimum of less than 0.02 W/mK for the various compositions considered. Other measurements of thermal conductivity have been made using heat-flux meters [57], hot disk thermal constant analyzers [58], and a laser-flash apparatus [59].

4 HEAT TRANSFER IN AEROGELS

Thermal energy transport through aerogels is known to occur through three mechanisms: solid conductivity, gaseous conductivity, and radiative (infrared) transmission. Convection is suppressed owing to the small size of the pores. The three modes of heat transfer are coupled and obtaining a solution requires numerically solving a complex integro-differential equation. However, if the medium may be assumed to be optically thick, linear superposition can be applied and the combined thermal conductivity of an aerogel can be expressed as the sum of the individual contributions [60].

While the solid conductivity of silica is relatively high, silica aerogels consist of a very small amount of silica, roughly on the order of 1 – 10%. In addition, the solid skeleton is a three-dimensional (3D) network of very small particles linked together in a very tortuous path, which impedes heat transfer. Further, many of these networks result in dead ends terminating the solid medium. Thus, the solid conductivity of aerogel is only about 1/1000 that of bulk silica [13].

Aerogels are open-pore structures and, thus, heat transfer by gaseous conduction must be considered. The inherently fine pore structure of aerogel, however, means that the mean pore diameter is similar in size to the mean free path of nitrogen and oxygen molecules at standard atmospheric temperatures and pressures. The mean free path of air at ambient conditions (T = 300 K, P = 100 kPa) is about 70 nm, which is comparable in size to the pore diameters. Thus, convection is not fully developed, even at atmospheric pressure, and the gaseous conductivity decreases even further with increasing aerogel density or with decreasing gas pressure [61]. For example, under ambient conditions, the thermal conductivity of a typical bulk silica aerogel might be on the order of 0.017 W/mK, while under the effects of even a modest vacuum, the same aerogel’s thermal conductivity could be lowered to about 0.008 W/mK [62]. For comparison, free nonconvecting air has a thermal conductivity of 0.03 W/mK and fiberglass insulation (ρ = 16 kg/m^3) has a thermal conductivity of 0.046 W/mK [63].

The contribution of radiation to the total thermal conductivity of aerogels is significant at ambient temperature and increases considerably at higher temperatures, becoming the predominant mode of heat transfer. This form of heat transfer occurs due to the weak absorption region in the near infrared, which transmits thermal radiation significantly when the spectrum is shifted toward shorter wavelengths [64].

The use of aerogels as heat insulators is an example of their application in the building industry. The thermal conductivity of aerogel, which is a measure of its ability to conduct heat, is lower than that of many other materials, making it an effective insulator. However, the cost of producing aerogels may limit their widespread use. Further research is needed to improve the production process and make aerogels more affordable for commercial use.
The extinction of thermal radiation by the IR photons is caused by absorption only and not scattering, since the pore sizes are much smaller than the IR wavelengths. While silica aerogel is not a very good absorber of IR energy in the wavelength range between 3 – 8 μm, a large decrease in radiation heat transfer can be accomplished by opacifying the aerogel. Zeng et al. [65] showed that 8% of carbon in silica aerogel reduced heat transfer by 1/3 at ambient temperature, while nonopacified aerogel had heat transfer 10 times higher than aerogel opacified with optimal amounts of carbon. If the aerogel medium can be regarded as optically thick, the radiative heat transfer process can be regarded as a diffusion process through a homogeneous medium [66]. However, if the optical thickness of the medium is low, then heat transfer is treated as a step-by-step photon transfer within the specimen on a scale which is small compared to the geometrical dimensions of the medium [67].

5 APPLICATIONS

The versatility of the sol-gel process and the resulting tailormade of the aerogel properties make the potential applications of aerogels almost limitless. Their amazing thermal properties make them obvious candidates for a variety of applications as thermal insulators [68], while their large accessible inner surface area make them ideal for catalytic applications [69]. Other less obvious applications include micrometeroid collectors in space [70], environmentally favorable insecticides [71], thickening agents [72], acoustic impedance-matching layers [52], and the list continues. A few of the applications of aerogels are reviewed here with numerous references given for the interested reader.

5.1 Windows

Windows have long been known to be a major source of heat loss in homes and commercial buildings. Energy loss due to windows accounts for a reported $20 billion annually in the United States. Due to their very low thermal conductivities, aerogels promise to be an excellent alternative to conventional window panels. In an early investigation, the microstructure and optical properties of transparent silica aerogels were examined by Rubin and Lampert [73] and the energy transfer through hypothetical aerogel windows was calculated. It was concluded that an aerogel window could have significantly lower thermal conductance than a multipane glass window of equal transmittance. More recently, superinsulating windows have been constructed, using triple-glazing systems with low-emissivity coatings and noble gas filling the gap between the transparent layers, that result in thermal conductivity values lower than 1 W/mK [74]. It was observed that while increasing the layers of glazing would further reduce thermal conductance, this would result in a negative impact on the total energy balance of the window, not to mention the loss of solar transmittance. Evacuating the space between the panels leads to further reduction in conductance, but the edge seal holding the vacuum becomes critical.
Optical and thermal characterization experiments were performed on aerogels by Duer and Svendsen [74] to show the possibility of constructing glazings with thermal conductance less than 0.5 W/mK and a total solar energy transmittance of greater than 0.75. Starting with TEOS or TMOS as precursor mixed with alcohol and different catalysts, aerogels were synthesized and found to have pore sizes in the 10–20 nm range (~ 1/40 wavelength of visible light). The material under atmospheric pressure was found to have a thermal conductivity of 0.015 W/mK. These two properties further solidified the position of aerogels as prime candidates for insulation material in windows. It has been noted that sol-gel chemistry plays a vital role in the transparency of aerogels [75]. Studies have shown that the optical transparency of a 20 mm thick aerogel panel can be varied between 25 and 80%, and the thermal conductivity can be varied from 0.014 to 0.021 W/mK [76]. These studies were conducted by Cabot Corporation with a view to making the applications of aerogels for daylighting commercially feasible. Panels made using this technology are currently being employed by Kalwall in their high-tech translucent building systems.

5.2 Thermal Insulation

In addition to windows, aerogels can be used in a wide variety of thermal insulation applications and as insulation in solar energy devices. Solar energy can be converted to process heat to provide temperatures of 100 to 150°C by using flat-plate collectors. A reduction in heat conduction of approximately 50% was observed when unpacked aerogel was used in glazings for flat-plate collectors [77]. In addition, the space between the panels was filled with krypton to offer further reduction in heat loss. Shallow solar pond water heaters have been widely used in Japan to provide hot water for the early afternoon [78]. In order to prevent the rapid decrease in water temperature after sunset, silica aerogel surface insulation can be used to reduce heat losses from the surface of the tank. An aerogel-glazed window, constructed by packing granular aerogels between two panels and filling the space in between with krypton gas, was integrated into solar walls in a building to serve dual purposes. In addition to insulation, the diffusely scattering aerogel system offered daylighting inside the building [79]. Application of aerogels for daylight scattering has also been addressed by Beck et al. [80].

For many potential applications of aerogel thermal insulators, a major drawback is their brittleness. While a small block of low-density silica aerogel is capable of withstanding the load of a brick more than 100 times its own weight, it shatters upon impact from a very light load. This brittleness, combined with a lack of flexibility, restricts aerogels from being used in many applications. Preparation of defect-free monoliths with no cracks is also a major concern, but can be overcome by careful processing. Various research groups are working to eliminate these drawbacks and further enhance the potential applicability of aerogels for thermal insulation applications that do not require visible transparency. Adding fibers to a sol before gelation is a method used to strengthen the aerogel matrix. This aids in thermal insulation
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5.3 Catalytic Applications

A catalyst is a substance that accelerates the rate at which a chemical reaction approaches equilibrium, while remaining unaffected by the reaction. The unique and tailorable morphological and chemical properties of aerogels offer interesting opportunities for application in catalysis. Two of the most important properties of an aerogel that allow for its use in catalysis are its high porosity and specific surface area. Selectivity is the ability of a catalyst to shift the distribution of the products of a chemical reaction toward a desired component. Aerogel catalysts are expected to exhibit high activity and selectivity paired with a long lifetime, provided the relevant physical and chemical properties of the aerogel are adapted to the specific catalytic application. The internal surface area of an aerogel is larger than its external surface area. Reaction catalysis happens predominantly on the internal surface. This requires that the reactants be able to diffuse through the surface of the aerogel, through the pores, and access the internal surface. In order to facilitate active diffusion of the reactant molecules, the proper design of pore structure is crucial. The chemical and structural properties of the aerogel also influence catalytic activity and selectivity. Therefore, other properties, such as size, external shape, density, mechanical strength, etc., have to be adapted to the reaction type.

Alumina aerogels find application as catalyst supports in high-temperature catalytic combustions where the catalyst needs to be able to survive sintering at 1400°C [85]. This requires improvement of the thermal and structural properties of alumina. Silica aerogels are also popular supports for heterogeneous catalysis [85]. They are generally considered chemically inert, but can be activated under certain circumstances. Other popular catalysts are aerogels synthesized from titania, zirconia, niobium, tin, manganese, and copper [69, 85, 86]. Pyrolyzed carbon aerogels are elec-
trically conductive and display large volumetric surface areas, and find application in electrocatalyst electrode synthesis. In addition, composites of the elements listed above are also frequently used in catalysis applications. The review by Pajonk [69] offers several reactions where aerogel materials are employed. Hydrocarbon combustion, methane and methanol synthesis, and hydrogenation and hydrogenolysis reactions are only a few of the many found in the review.

In environmental applications, aerogels as catalysts can be used in preventing the formation of pollutants and treating those that have already been formed [69]. Pure alumina aerogels and barium hexaaluminate aerogels are used in flameless combustion (or catalytic combustion) reactions. Vanadia-titania aerogels and vanadia-silica aerogels are used for the selective reduction of NO by NH₃ (SCR). Copper oxide aerogels and titania-silica aerogels can be used in waste treatment. Smith et al. [87] analyzed aerogels with silver nanoparticles for use in gas catalysis applications. More recently, Suh et al. [88] have analyzed nickel-alumina composite aerogels for application in liquid-phase hydrogenation catalysis.

5.4 Low Dielectric Constant Substrates

Low dielectric constant materials are required for reduction of power dissipation in ultralarge-scale integrated devices. Owing to their very low dielectric constant, silica aerogels find application as thin films in intermetal dielectrics [82]. The highly porous nature of silica aerogel is the key to the realization of low dielectric constants in these applications [89]. A method for ambient-pressure preparation of aerogel films with thickness less than 5 μm with a dielectric constant lower than 2 for a pore volume of approximately 60% is described by Mezza et al. [90]. The relationship between the dielectric constant and microstructure of nanoporous silica aerogels was investigated numerically by Xiao et al. using ANSYS [91]. It was concluded that while porosity is the major factor in determining the dielectric constant of the aerogel film, the effect of other factors, such as pore shape, pore size, and pore size distribution, are weak in comparison. The use of ambient-pressure-dried silica aerogel films has also been explored by Park et al. [92]. Having established that the low dielectric constant of aerogels can be employed in GaAs-based devices, methods to improve the properties of the surface and interface without degrading aerogel properties are presented [92].

5.5 Filters and Gas Adsorption Media

Owing to their large internal surface area, which is accessible via open pores, aerogels can be used as filters and gas adsorption media. In order to overcome the brittleness of the aerogels, use of partially densified samples has been suggested [93]. Similar studies on application of aerogels in aerosol filtration have also been undertaken by Hosticka et al. [94]. Instead of pure aerosol filtration, the aerogel could be
used to facilitate the detection of chemicals and organisms within the environment by employing microorganisms immobilized within the aerogel [95].

5.6 Micrometeoroid Collectors

A unique application of aerogels is in STARDUST, a U.S. cometary sample return mission using aerogel collectors [70]. Capturing fresh interstellar grains is of great interest and a major challenge in the astrophysics community. These grains possess isotopic information on their birth elsewhere in the galaxy. However, distinguishing between terrestrial grains that may originate from rocket emissions and extraterrestrial grains is an expensive and time-consuming process. In order to identify extraterrestrial grains among grains captured using the aerogel collectors, a novel doped aerogel, which turns fluorescent in the red after baking, was manufactured for use as a collector. Owing to the impact of the hypervelocity extraterrestrial grains on the aerogel collectors, a fraction of their kinetic energy is converted to local heating, offering the opportunity to identify them [70].

5.7 Acoustic Impedance Matching Layers

Since the acoustic impedance of aerogels is essentially tunable over the range between the acoustic impedance of air and many solid materials, it provides an ideal material for maximizing acoustic transmission between different media. This tuning has been done primarily through manipulation of the production reaction conditions, and a wide range of sol-gel densities and acoustic velocities have been achieved. Thin films are employed on the surface of ceramic transducers to serve as acoustic impedance matching layers to increase sending and receiving of airborne acoustic waves [52]. As another example, aerogel films can serve as impedance matching layers for air-coupled medical ultrasound imaging [52,96–101].

5.8 Cherenkov Counters

Perhaps the most common application of aerogels to date is in Cherenkov counters. A charged particle traversing a medium with refractive index \( n \), with a velocity \( v \), exceeding the velocity of light, \( c/n \), in that medium emits Cherenkov radiation. The Cherenkov effect can be used to identify particles of fixed momentum by means of threshold Cherenkov counters. Ring-imaging Cherenkov counters have become extremely useful in the fields of elementary particles and astrophysics. A low-refractive-index material, such as silica aerogel, is required by a threshold-type Cherenkov detector. Many research groups have presented different techniques for synthesis and characterization of hydrophobic, crack-free, very transparent samples where the loss of photons due to scattering and absorption has been
minimized [102–105]. In more recent years, optimization of the silica aerogel to further suit its use as Cherenkov counters has also been achieved [106–108].

5.9 Storage Media

Aerogels are being considered as storage media for nuclear waste [109]. The idea is to soak an aerogel in the nuclear waste and then sinter it, so that the nuclear waste is trapped inside the aerogel. The use of a composite aerogel is suggested, owing to its higher mechanical strength and relatively large permeability. In a similar application, aerogels have been proposed as a solution for the confinement of helium in scientific space missions where liquid helium is used as a coolant [110]. Liquid helium is used in transporting accelerometers in certain space missions because their ultimate performance is ensured only with thermal stability and at temperatures low enough to suppress Brownian noise. Even a submillimeter motion of the helium free surface results in the amplification of gravitational disturbances beyond the range of the accelerometers. Aerogels have been suggested as an alternative medium to transport helium owing to their porous nature. Experiments show that when the aerogel is partially filled with liquid helium, surface tension and capillary forces act against gravity to ensure liquid helium distribution. However, work needs to be done on the effect of thermal gradients on helium motion [110].

5.10 Electrochemical Applications

Recent evidence has shown that tailoring the properties of the aerogel may enable their use in electrochemical applications [111]. Studies conducted on vanadium oxide aerogels, molybdenum oxide aerogels, manganese oxide aerogels, mixed-phase ruthenium oxide-titanium oxide aerogels, organic/inorganic hybrid aerogels, and electrically conductive composite aerogels have shown that these conductive oxide aerogels possess electrochemical properties that make them suitable for use in cation-insertion battery materials, ultracapacitors, and fuel cells. Studies on the electrochemical response of titania-silica aerogel thin films deposited on substrates have been studied to show the possibility of electrochemically modifying the aerogels in a controllable way [112]. Silica aerogels have also been prepared by doping with magnetically aligned iron particles [113]. Using the same methods, ferromagnetic and paramagnetic particles may be embedded in nonsilica-based aerogels to create composite aerogels for different applications [113].

5.11 Aerocapacitors

In other storage applications, carbon materials are used to store electrochemical energy in capacitors [114]. Carbon aerogels are obtained by the pyrolysis of organic aerogels based on resorcinol-formaldehyde (RF) or phenol-furfural (PF) precursors
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The idea is to use aerogel to trap and filter waste to allow for proper drainage for further applications. Liquid waste can be filtered to remove their dissolved solids, which are then a very low form of aerogel that allows for the range of aerogel applications in various fields. Aerogel technology can be used to create a barrier against bacteria or be used as a material on the surface for bacterial growth.

via the sol-gel process [115]. Aerocapacitors employing thin films can provide specific capacitances in excess of 45 Farads per gram of material [114]. The advantages of carbon aerogels for capacitor applications are high surface area, low density, high porosity, and high pore volume.

5.12 Biosensor Applications

Recent research has shown the potential to use macroporous aerogels as a biocompatible scaffold for the immobilization of cells and for the development of cell-based biosensors [95]. Aerogels are ideal for this application due to the adjustable pore size and the extremely large surface area. Power et al. [95] demonstrated the ability to use Escherischia coli (pET-gfp) bacteria-doped gels in the form of thin disk-shaped filters in an aerosol collection system to detect bacteriophage (see Figure 4). This work shows that virus particles can penetrate the structure of macroporous silica gels and trigger a detectable response in immobilized bacteria. In the future, bacteria with specific biological functions could be doped into the gel and the doped gel could then be used as a collection media and detector of specific aerosols in the environment.

6 OUTLOOK

While aerogels were invented in the 1930s, they have been limited to scientific exploration in the lab for most of the past, with the notable exception being their use in Cherenkov counters. The main reason for the lack of more widespread interest in
these remarkable materials has often been said to be the relatively high cost of producing the materials [116]. While aerogels are still not common in the marketplace, commercialization of aerogels has advanced more in the past few years than in the past several decades. Several companies are now successfully exploiting the many desirable properties of aerogels in a variety of applications.

NanoPore, Inc. employs silica, titania, and/or carbon aerogels for thermal insulation, vacuum insulation panels, insulated shipping containers, as specialty adsorbents, and in the form of thin films in microelectronics. Keller Companies, Inc. in conjunction with Cabot Corporation has developed aerogel granules whose transmittance and thermal properties can be controlled. These granules are then sandwiched between panels and used for daylighting systems. Aspen Systems, Inc. manufactures and distributes relatively low-cost flexible aerogel blanket products, along with other aerogel products, to customers in the aerospace, apparel, cryogenics, and technical insulation markets. Aerogel-based materials manufactured by NanoScale Materials, Inc. are commercially available for applications, such as neutralization of chemical warfare agents and hazardous materials, air filtration, enhancing physical properties of paints and industrial coatings, acid gas treatment, transparent UV attenuation, and polishing applications.

Scientific research in the area of aerogel technology now seems to be primarily devoted to nanoeengineering of the material. Some are focusing on efforts directed at influencing the developing microstructure or at templating the material, while others focus on creation of nanocomposite materials employing aerogel technology. While the field has progressed greatly since Kistler's time, there remains much to be learned about how the microstructure and the resulting properties of these unique materials can be predictably and reproducibly influenced and optimized for specific applications.

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