AEROGELS

1. Introduction

Aerogels, solid materials that are so porous that they contain mostly air, were first prepared in 1931. Kistler used a technique known as supercritical drying to remove the solvent from a gel (a solid network that encapsulates its solvent) such that, as stated in his paper in *Nature*, "no evaporation of liquid can occur and consequently no contraction of the gel can be brought about by capillary forces at its surface (1)." In the six decades since then, there have been significant advances made both in the use of new precursors to form gels and in the removal of solvent from them. These advances have greatly simplified the preparation of aerogels and, in turn, improved their economic viability for commercial applications. Increasingly an aerogel is defined in terms of its properties and not the way in which it is prepared.

Almost all applications of aerogels are based on the unique properties associated with a highly porous network. Envision an aerogel as a sponge consisting of many interconnecting particles. The particles are so small and so loosely connected that the void space in the sponge, the pores, can make up for over 90% of the sponge volume. As an example, a silica aerogel contains particles that are of the order of 10 nm and each particle is connected to two or three other particles on average. Such a material has a typical density of about 100 kg/m^3 and accessible surface area of about 1000 m^2/g.

The ability to prepare materials of such low density, and perhaps more importantly, to vary the density in a controlled manner, is indeed what make aerogels attractive in many applications such as thermal insulation, detection of high energy particles, and catalysis. Thus, this article begins with a discussion of sol–gel chemistry used to form the wet gel. The intention is not to discuss in detail the fundamental chemistry involved, but to provide the basic principles that explain the formation of a porous network and the effect of preparative variables on its microstructure (often referred to as nanostructure because the relevant length scale is on the order of nanometer), ie, factors that impact on density. The general applicability of these principles are illustrated by examples of inorganic, organic, and inorganic–organic gels.

The section on preparation and manufacturing continues to focus on the microstructure of a gel, in particular its evolution during the removal of solvent. In addition to the original supercritical drying used by Kistler, there are now safer and more cost-effective methods that do not involve supercritical drying. More importantly, these methods ensure that the products possess the defining characteristics of an aerogel (ultrafine pores, small interconnected particles, and high porosity).

This article also aims at establishing the structure–property–application relationships of aerogels. Selected examples are given to show what some desirable properties are and how they can be delivered by design based on an understanding of the preparation and preservation of a gel's microstructure.

2. Sol–Gel Chemistry

2.1. Inorganic Materials. Sol–gel chemistry involves first the formation of a sol, which is a suspension of solid particles in a liquid, then of a gel, which is a diphasic material with a solid encapsulating a solvent. A detailed description of the fundamental chemistry is available in the literature (2–4). The chemistry involving the most commonly used precursors, the alkoxides ($M(OR)_m$), can be described in terms of two classes of reactions:

Hydrolysis

$$-M-OR + H_2O \longrightarrow -M-OH + ROH$$

Condensation

$$-M-OH + XO-M- \longrightarrow -M-O-M + XOH$$

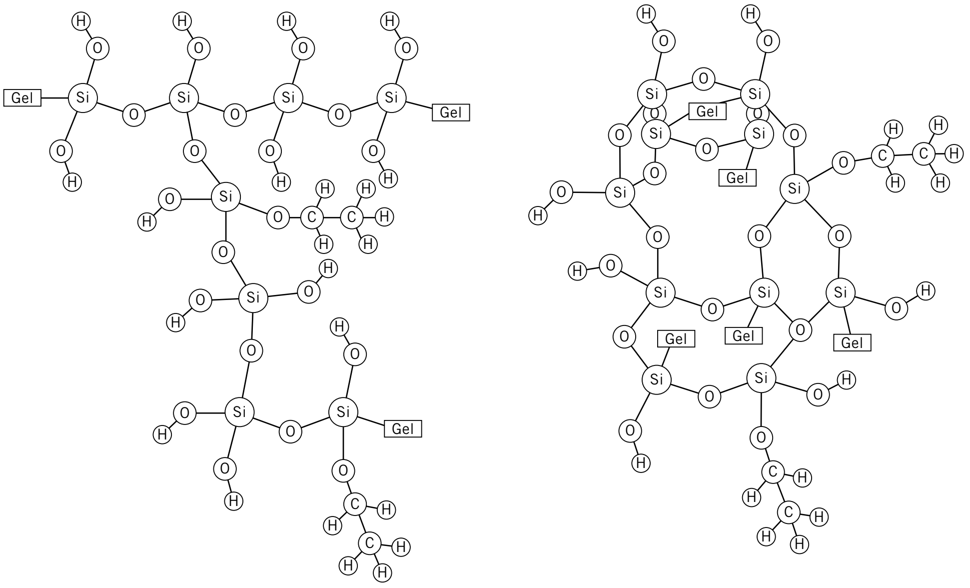
where X can either be H or R, an alkyl group.

The important feature is that a three-dimensional gel network comes from the condensation of partially hydrolyzed species. Thus, the microstructure of a gel is governed by the rate of particle (cluster) growth and their extent of crosslinking or, more specifically, by the *relative* rates of hydrolysis and condensation (3).

The gelation of silica from tetraethylorthosilicate (TEOS) serves as an example of the above principle. Under acidic conditions, hydrolysis occurs at a faster rate than condensation and the resulting gel is weakly branched. Under basic conditions, the reverse is true and the resulting gel is highly branched and contains colloidal aggregates (5, 6). Furthermore, acid-catalyzed gels contain higher concentrations of adsorbed water, silanol groups, and unreacted alkoxy groups than base-catalyzed ones (7). These differences in microstructure and surface functionality, shown schematically in Figure 1, result in different responses to heat treatment. Acid- and base-catalyzed gels yield micro- (pore width less than 2 nm) and meso-porous (2–50 nm) materials, respectively, upon heating (8). Clearly an acid-catalyzed gel which is weakly branched and contains surface functionalities that promote further condensation collapses to give micropores. This example highlights a crucial point: *the initial microstructure and surface functionality of a gel dictates the properties of the heat-treated product*.

Besides pH, other preparative variables that can affect the microstructure of a gel, and consequently, the properties of the dried and heat-treated product include water content, solvent, precursor type and concentration, and temperature (9). Of these, water content has been studied most extensively because of its large effect on gelation and its relative ease of use as a preparative variable. In general, too little water (less than one mole per mole of metal alkoxide) prevents gelation and too much (more than the stoichiometric amount) leads to precipitation (3, 9). Other than the amount of water used, the rate at which it is added offers another level of control over gel characteristics.

The principles discussed so far are valid for silicates as well as nonsilicates, although there are more data available for the former. The alkoxides of



(a) (b)

Fig. 1. Schematics of (**a**) acid-catalyzed and (**b**) base-catalyzed silica gels showing the differences in microstructure and surface functional groups. Reproduced from Ref. 7. Courtesy of the American Ceramic Society.

transition metals tend to be more reactive than silicon alkoxides because both hydrolysis and condensation are nucleophilic substitution reactions and their cations have a more positive partial charge than silicon (3). This difference in reactivity presents both a challenge and an opportunity in the preparation of two-component systems. In a two-component system, the minor component can either be a network modifier or a network former. In the latter case, the distribution of the two components, or mixing, at a molecular level is governed by the *relative* precursor reactivity. Qualitatively good mixing is achieved when two precursors have similar reactivities. When two precursors have dissimilar reactivities, the sol–gel technique offers several strategies to prepare well-mixed two-component gels. Two such strategies are prehydrolysis (10), which involves prereacting a less reactive precursor with water to give it a head start, and chemical modification (11), which involves slowing down a more reactive precursor by substituting some of its alkoxy groups with bulkier, less reactive groups such as acetate. The ability to control microstructure *and* component mixing is what sets sol–gel apart from other methods in preparing multicomponent solids.

2.2. Organic Materials. The first organic aerogel was prepared by the aqueous polycondensation of resorcinol with formaldehyde using sodium carbonate as a base catalyst (12). Figure 2**a** shows that the chemistry is similar to the sol–gel chemistry of inorganic materials. Subsequent to the reaction between resorcinol and formaldehyde, the functionalized resorcinol rings (ie, those possessing–CH_2OH groups) condense with each other to form nanometer-sized clusters, which then crosslink to form a gel. The process is influenced by typical

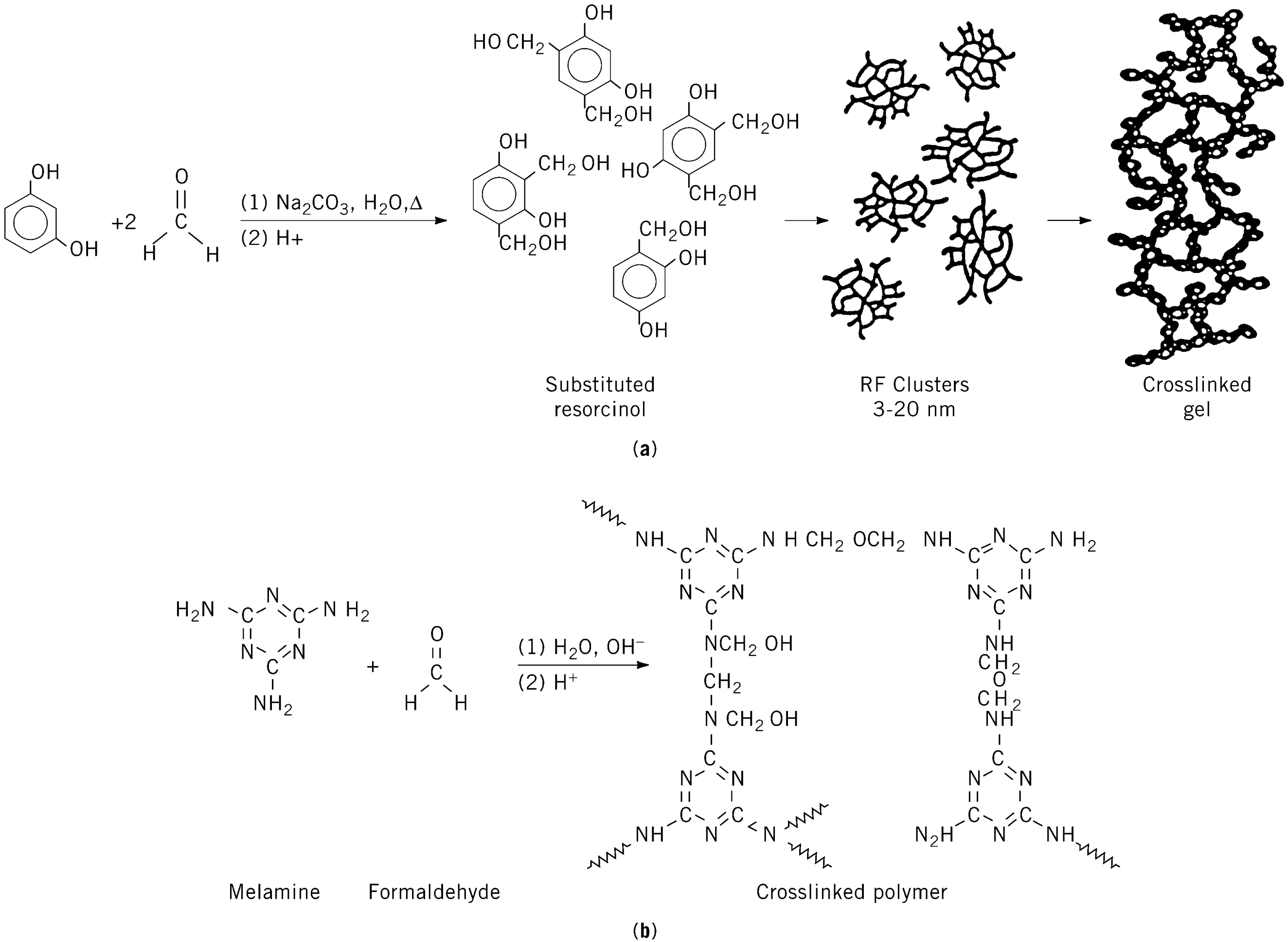


Fig. 2. The sol–gel polymerization of resorcinol with formaldehyde (**a**) and (**b**) of melamine with formaldehyde. Reproduced from Refs. 13 and 14, respectively. Courtesy of the Materials Research Society.

sol–gel parameters such as pH, reactant concentration, and temperature. The resorcinol–catalyst molar ratio turns out to be the dominant factor that affects the microstructure of the gel (13).

Resorcinol–formaldehyde gels are dark red in color and do not transmit light. A colorless and transparent organic gel can be prepared by reacting melamine with formaldehyde using sodium hydroxide as a base catalyst (14). The chemistry, shown in Figure 2**b**, involves first the formation of $-CH_2OH$ (hydroxymethyl) groups and then the formation of $-NHCH_2NH-$ (diamino methylene) and $-NHCH_2OHC_2H-$ (diamino methylene ether) bridges through cross-linking reactions. The solution pH is again a key parameter, it is necessary to add hydrochloric acid in the second part of the process to promote condensation and gel formation.

Both the preparations of resorcinol–formaldehyde and melamine–formaldehyde gels are aqueous-based. Since water is deleterious to a gel's structure at high temperatures and immiscible with carbon dioxide (a commonly used supercritical drying agent), these gels cannot be supercritically dried without a tedious solvent-exchange step. In order to circumvent this problem, an alternative synthetic route of organic gels that is based upon a phenolic–furfural reaction using an acid catalyst has been developed (15). The solvent-exchange step is eliminated by using alcohol as a solvent. The phenolic–furfural gels are dark brown in color.

Carbon aerogels can be prepared from the organic gels mentioned above by supercritical drying with carbon dioxide and a subsequent heat-treating step in an inert atmosphere. For example, the following heating schedule has been used in flowing nitrogen (13, 15): 22 to 250°C in 2 h, held at 250°C for 4 h, 250 to 1050°C in 9.5 h, held at 1050°C for 4 h, and cooled to room temperature in 16 h. This treatment results in a volume shrinkage of the sample of 65–75% and a mass of 45–50%. Despite these changes, the carbon aerogels are similar in morphology to their organic precursors, underscoring again the importance of structural control in the gelation step. Furthermore, changing the sol–gel conditions can lead to aerogels that have a wide range of physical properties. As a specific example, surface area for the phenolic–furfural aerogels is about $385 \pm 16\ m^2/g$ over a density range of $100–250\ kg/m^3$, whereas the corresponding carbon aerogels have surface areas of $512 \pm 40\ m^2/g$ over a density range of $300–450\ kg/m^3$.

2.3. Inorganic–Organic Hybrids. One of the fastest growing areas in sol–gel processing is the preparation of materials containing both inorganic and organic components. The reason is that many applications demand special properties that pure materials can seldom provide. The combination of inorganic and organic materials is, thus, an attractive way to deliver materials that have desirable physical, chemical, and structural characteristics. In this regard, sol–gel chemistry offers a real advantage because its mild preparation conditions do not degrade organic polymers, as would the high temperatures that are associated with conventional ceramic processing techniques. The voluminous literature on the sol–gel preparation of inorganic–organic hybrids can be found in several recent reviews (16–20) and the references therein; only a qualitative sketch is given in this section.

There are several ways to classify inorganic–organic materials, all of which depend on the strength of interaction between the two components. The interaction can range from nonexistent or weak, such as organic species embedded (or entrapped) in an inorganic network, to very strong, such as systems involving covalent bonds. For weakly interacting systems, the general observation is that most molecules can be entrapped in sol–gel matrices and, once entrapped, these molecules retain most of their characteristic physical and chemical properties (18). The entrapment of bioorganic materials such as enzymes, whole cells, antibodies, and other proteins (21) falls into this category.

For strongly interacting systems, chemical bonding can be induced by using functionalized precursors. There are three basic types of precursors: inorganically functionalized preformed organic polymers, organically functionalized oxides, and precursors containing both inorganic and organic functional groups. Examples of commonly used precursors are organofunctional metal alkoxides $(RO)_n$–E–X–A (19) and bridged polysilsesquioxanes (20). In $(RO)_n$–E–X–A, A is a functional organic group and X is a hydrolytically stable spacer linking A and the metal alkoxide which provides the inorganic function. The use of such precursors has allowed the control of very small domain sizes, often in the nanometer range, in the preparation of inorganic–organic materials (16,19,20). The challenge is to achieve a high degree of mixing of the two phases, thus, enabling the manipulation of interfacial properties at a molecular level. Another promising strategy to provide better homogeneity between the two phases is to form the inorganic and organic phases simultaneously, leading to what is known as a simultaneous interpenetrating network (16).

All the methods described so far involve introducing the organic phase prior to the formation of a solid phase. There is an interesting alternative to prepare a nanocomposite by a sequential approach (22). In this approach a silica aerogel was first prepared, then carbon was deposited in it by the decomposition by hydrocarbons (eg, methane, acetylene) at a temperature range of 500–850°C. This example demonstrates the feasibility of preparing hybrid materials by depositing an inorganic or organic phase onto an organic or inorganic substrate, respectively.

3. Preparation and Manufacturing

3.1. Supercritical Drying. The development of aerogel technology from the original work of Kistler to about late 1980s has been reviewed (23). Over this period, supercritical drying was the dominant method in preparing aerogels and, for this reason, aerogels are synonymous with supercritically dried materials. As noted earlier, supercritical drying could be an insufficient definition of an aerogel because it might not lead to the defining characteristics. Kistler used inorganic salts and a large amount of water in his work (1,24), making the subsequent salt removal and solvent-exchange steps time-consuming (water has to be removed because it would dissolve the gel structure at high temperatures). A significant time savings came when alkoxides were used as precursors in organic solvents, thereby requiring a minimum amount of water and eliminating the tedious solvent-exchange step (25,26). The introduction of carbon dioxide, which has a lower critical temperature and pressure than alcohols, as a supercritical drying agent allowed the drying step to be done under milder conditions and improved

Table 1. **Important Developments in the Preparation of Aerogels**

Decade	Developments
1930	using inorganic salts as precursors, alcohol as the supercritical drying agent, and a batch process; a solvent-exchange step was necessary to remove water from the gel
1960	using alkoxides as precursors, alcohol as the supercritical drying agent, and a batch process; the solvent exchange step was eliminated
1980	using alkoxides as precursor, carbon dioxide as the drying agent, and a semicontinuous process; the drying procedure became safer and faster. Introduction of organic aerogels
1990	producing aerogel-like materials without supercritical drying at all; preparation of inorganic–organic hybrid materials

its safety (27). The development of a semicontinuous drying process further facilitated the preparation of aerogels (28). Together these advances, summarized in Table 1, have made possible the relatively safe supercritical drying of aerogels in a matter of hours. In recent years, the challenge has been to produce aerogel-like materials without using supercritical drying at all in an attempt to deliver economically competitive products. This topic will be discussed in more detail later.

As stated earlier, the main idea behind supercritical drying is to eliminate the liquid–vapor interface inside a pore, thereby removing the accompanying capillary pressure which acts to collapse a gel network. The value of this approach is demonstrated by the fact that aerogels do have higher porosities, higher specific surfaces areas, and lower apparent densities than xerogels, materials that are prepared by evaporative drying. However, it is incorrect to think that a gel remains static during supercritical drying. Rather, supercritical drying should be considered as part of the aging process, during which events such as condensation, dissolution, and reprecipitation can occur. The extent to which a gel undergoes aging during supercritical drying depends on the structure of the initial gel network. For example, it has been shown that a higher drying temperature changes the particle structure of base-catalyzed silica aerogels but not that of acid-catalyzed ones (29). It is also known that gels that have uniform-sized pores can withstand the capillary forces during drying better because of a more uniform stress distribution. Such gels can be prepared by a careful manipulation of sol–gel parameters such as pH and solvent or by the use of so-called drying control chemical additives (DCCA) (30). Clearly, an understanding of the interrelationship between preparative and drying parameters is important in controlling the properties of aerogels.

The most widely studied supercritical drying variable is temperature simply because different solvents have different supercritical temperatures. Specifically, since alcohols have higher supercritical temperatures than carbon dioxide, there have been many recent reports on the effect of drying agent on the textural properties and crystallization behavior of aerogels (31–33). These results demonstrate nicely the accelerated aging that a gel undergoes at high temperatures and pressures. For this reason carbon dioxide is the drying agent of choice if the goal is to stabilize kinetically constrained structure, and materials prepared by this low-temperature route are referred to by some people as *carbogels*. In general, carbogels are also different from aerogels in surface functionality, in particular hydrophilicity, which impacts on the moisture sensitivity of these materials and their subsequent transformations under heat treatment.

It is less well known, but certainly no less important, that even with carbon dioxide as a drying agent, the supercritical drying conditions can also affect the properties of a product. For example, in the preparation of titania aerogels, temperature, pressure, the use of either liquid or supercritical CO_2, and the drying duration have all been shown to affect the surface area, pore volume, and pore size distributions of both the as-dried and calcined materials (34,35). The specific effect of using either liquid or supercritical CO_2 is shown in Figure 3 as an illustration (36).

Other important drying variables include the path to the critical point, composition of the drying medium, and depressurization (37). The rates of heating and depressurization are especially important in the preparation of monoliths because if the pore liquid does not have sufficient time to flow out of the gel network, it could lead to excessive stresses that cause cracking (38,39). The container of a gel is by itself a source of stresses by preventing the radial expansion and flow of liquid. Quantitative models describing these phenomena are available and have been tested against experimental data for silica gels (38–40).

For some applications it is desirable to prepare aerogels as thin films that are either self-supporting or supported on another substrate. All common coating methods such as dip coating, spin coating, and spray coating can be used to prepare gel films. However, for highly porous films (ie, porosity $> 75\%$), special care is necessary to minimize the rate of solvent evaporation both during and after gel formation. One way to do so is to perform the coating processes within an enclosure that is filled with the saturated vapor of the working solvent and a partial pressure of ammonium hydroxide that catalyzes the gelation of the films (41). The subsequent supercritical drying step can be done in either alcohol or carbon dioxide. The choice depends on the desired properties of the aerogels and, in the case of supported films, the thermal stability of the substrate materials.

In all the processes discussed above, the gelation and supercritical drying steps are done sequentially. Recently a process that involves the direct injection of the precursor into a strong mold body followed by rapid heating for gelation and supercritical drying to take place was reported (42). By eliminating the need of forming a gel first, this entire process can be done in less than three hours per cycle. Besides the saving in time, gel containment minimizes some stresses and makes it possible to produce near net-shape aerogels and precision surfaces. The optical and thermal properties of silica aerogels thus prepared are comparable to those prepared with conventional methods (42).

3.2. Ambient Preparations.

Supercritical drying with alcohols incurs high capital and operating costs because the process is run at high temperatures and pressures and needs to remove a large amount of pore liquid. Carbon dioxide allows drying to be done under milder conditions but its use is limited to miscible solvents. Thus, economic and safety considerations have provided a strong motivation for the development of techniques that can produce aerogel-like materials at ambient conditions, ie, without supercritical drying. The strategy is to

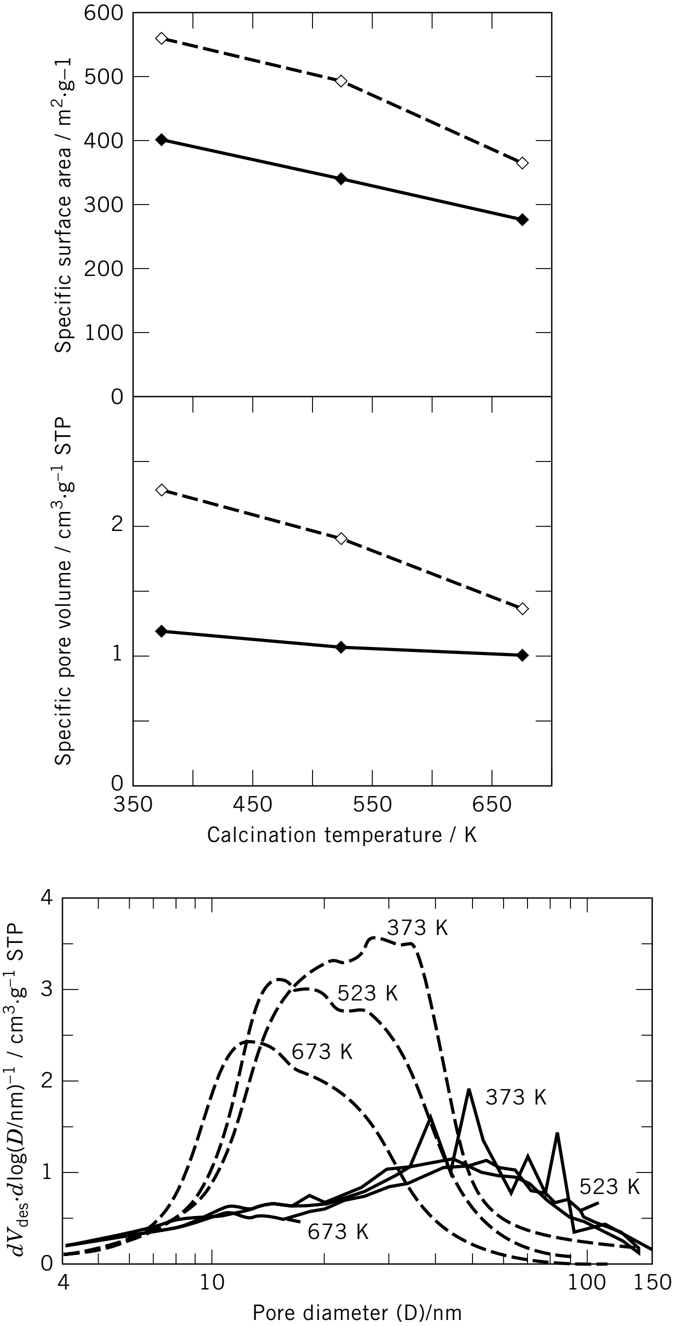


Fig. 3. Effect of using either liquid or supercritical carbon dioxide on the textural properties of titania aerogels calcined at the temperatures shown. (—), dried with liquid carbon dioxide at 6 MPa and 283 K; (- - -), dried with supercritical carbon dioxide at 30 MPa and 323 K. Reproduced from Ref. 36. Courtesy of Marcel Dekker, Inc.

minimize the deleterious effect of capillary pressure which is given by:

$$P = 2\sigma \cos(\theta)/r$$

where P is capillary pressure, σ is surface tension, θ is the contact angle between liquid and solid, and r is pore radius.

The equation above suggests that one approach would be to use a pore liquid that has a low surface tension. Indeed, two-step acid–base or acid–acid catalyzed silica gels have been made, aged in ethanol or water, washed with various aprotic solvents, and finally evaporatively dried at 323 K for 48 hours and then at 383 K for 48 hours (43). The aprotic solvents used and their corresponding surface tension in N/m at room temperature (shown in parentheses) are tetrahydrofuran (23.7×10^{-3}), acetone (23.7×10^{-3}), cyclohexane (25.3×10^{-3}), acetonitrile (29.3×10^{-3}), nitromethane (32.7×10^{-3}), and 1:4 dioxane (33.6×10^{-3}). For both the acid-catalyzed and base-catalyzed gels, it was found that increasing surface tension causes a decrease in surface area and total pore volume. However, for acid-catalyzed gels with an intermediate water wash, the micro pore volume increases with increasing surface tension. It was suggested that the water wash leads to a hydroxylated surface which, upon further condensation, gives a stiffer network and consequently a larger fraction of micropore volume. The important point is that with a pore liquid that has a sufficiently small surface tension, ambient pressure aerogels can have comparable pore volume and bulk density to those prepared with supercritical drying (Fig. 4) (44).

For base-catalyzed silica gels, it has been shown that modifying the surface functionality is an effective way to minimize drying shrinkage (44,46). In particular, surface hydroxyl groups, the condensation of which leads to pore collapse, can be "capped off" via reactions with organic groups such as tetraethoxysilane and trimethylchlorosilane. This surface modification approach (also referred to as surface derivatization), initially developed for bulk specimens, has recently been applied to the preparation of thin films (47,48). The process involves the following steps: (*1*) prepare a base-catalyzed gel, (*2*) wash the gel with hexane, (*3*) replace the surface hydroxyls with organosilicon groups, (*4*) reliquify the surface-modified gel with ultrasound, (*5*) dip-coat the redispersed sols onto a silicon substrate, and (*6*) heat treat the film in air at 450°C. During drying these materials exhibit reversible shrinkage in a gradual dilation, or "spring-back," of the film. The extent of spring-back is a function of processing conditions. Films with porosity in the range of 30–99% can be prepared via a proper control of the washing, surface modification, dip-coating, and heat treatment conditions (48).

In changing surface hydroxyls into organosilicon groups, surface modification has an additional advantage of producing hydrophobic gels. This feature, namely the immiscibility of surface-modified gel with water, has led to the development of a rapid extractive drying process shown in Figure 5 (49). The basic idea is to submerge a wet gel into a pool of hot water that is above the boiling point of the pore fluid. After the pore fluid boils out of the gel, the gel floats to the surface because it is not wetted by water and can be easily recovered. Other working fluids, such as ethylene glycol and glycerol, can be used instead of water as long as they have a high boiling point and do not wet the gel. This

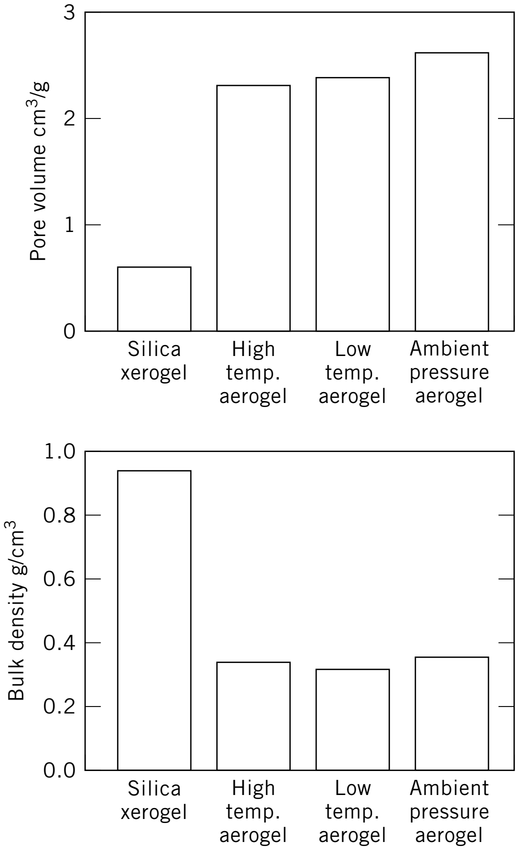


Fig. 4. Comparison of physical properties of silica xerogels and aerogels. Note the similar properties of the aerogels prepared with and without supercritical drying. Reproduced from Ref. 44. Courtesy of the Materials Research Society.

ambient pressure process offers improved heat transfer rates and, in turn, greater energy efficiency without compromising desirable aerogel properties.

Another approach to produce aerogels without supercritical drying is freeze drying, in which the liquid–vapor interface is eliminated by freezing a wet gel into a solid and then subliming the solvent to form what is known as a *cryogel*. Some potential problems are that cracks may develop in the frozen gel and sublimation, if done too fast, can melt the solvent. Cryogels of silica and nickel oxide–alumina have similar, but not identical, properties to aerogels of the same materials (50). In general, there has not been a lot of study on freeze drying and the limited data available suggest that it might not be as attractive as the above ambient approaches in producing aerogels on a commercial scale.

4. Properties

A detailed discussion of the properties of aerogels can be found in several recent review articles (51–55) and the references therein. This section provides a

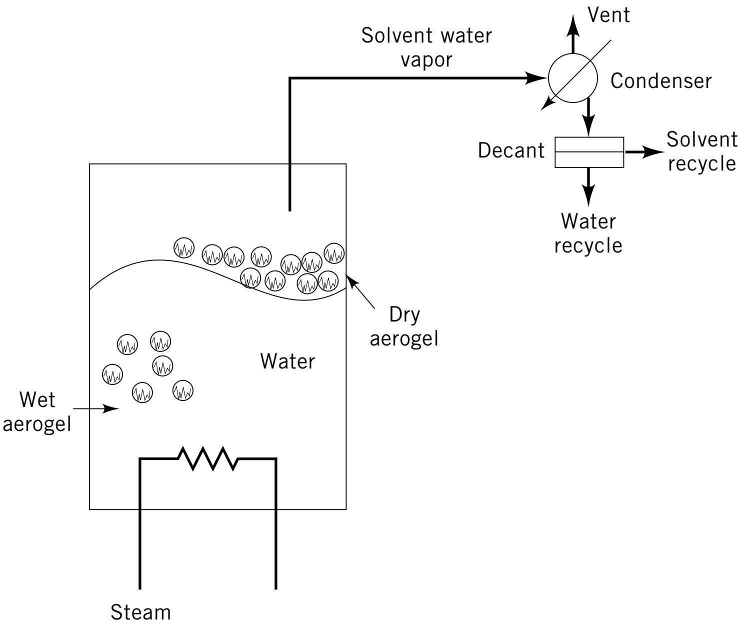


Fig. 5. Schematic diagram of an extractive drying process that produces aerogels at ambient pressure. Reproduced from Ref. 49. Courtesy of the Materials Research Society.

physical basis for these properties by focusing on the microstructure of an aerogel. The intent is to provide a bridge between the two previous sections, which discuss the preparative and drying parameters that affect microstructure, and the next one, which outlines the potential applications made possible by unique structural features. The emphasis is on silica aerogels because they have been the most extensively characterized.

All properties of aerogels are related to the extremely high porosity of these materials. Consider an aerogel as consisting of strings of pearls; each pearl is a structural unit and connected to only two to three other units on average. The size of each structural unit depends on the gelation and drying conditions and varies between 1 to 100 nm in diameter. Correspondingly, pore sizes in an aerogel range from 1 to 100 nm. For silica aerogels skeletal (ie, the solid phase) densities, ρ_s, of 1700–2100 kg/m^3 have been reported, whereas the overall densities, ρ, are in the range of 3–500 kg/m^3 (54). The fact that the overall density is much lower than the skeletal density suggests that an aerogel is full of open space, or pores. Quantitatively the porosity, P, is given by

$$P = 1 - (\rho/\rho_s)$$

Thus, the porosity of an aerogel is in excess of 90% and can be as high as 99.9%. As a consequence of such a high porosity, aerogels have large internal surface area and pore volume.

Since the pores in an aerogel are comparable to, or smaller than, the mean free path of molecules at ambient conditions (about 70 nm), gaseous conduction of heat within them is inefficient. Coupled with the fact that solid conduction is suppressed due to the low density, a silica aerogel has a typical thermal conductivity of 0.015 W/(m·K) without evacuation. This value is at least an order of magnitude lower than that of ordinary glass and considerably lower than that of CFC (chlorofluorocarbon)-blown polyurethane foams (54).

The low density and high porosity of aerogels lead to several other unique properties. Sound travels in silica aerogels at a longitudinal velocity of 100–300 m/s (the corresponding value in ordinary glass is about 500 m/s) (56). The low sound velocity and low density combine to give a low acoustic impedance, which is the product of the two quantities. Silica aerogels also have a refractive index that is very close to unity, meaning light can enter and leave a piece of aerogel without appreciable reflective losses and refractive effects. And for porosity larger than 0.7, silica aerogels have a very low dielectric constant (less than 2) (57). Finally, compared to silica glass, silica aerogels have an extremely small Young's modulus (10^6–10^7 N/m^2, several orders of magnitude less than nonporous materials), and thus, can be compressed easily (51).

From a practical viewpoint it is not only the low density of aerogels but also the variability of density over a wide range that offers interesting possibilities. As discussed in "Inorganic Materials," a silica gel can be formed under either acidic or basic conditions. Densities that can be formed under either acidic or basic conditions. Densities that can be obtained with these one-step processes are in the range of 25–500 kg/m^3. To produce ultralow-density silica aerogels, a two-step process has been developed to extend the lower limit to 3 kg/m^3 (58). In the first step, either tetramethyl- or tetraethyl-orthosilicate is reacted with a substoichiometric amount of water to form a partially hydrolyzed, partially condensed silica precursor. After distilling off the alcohol solvent, this precursor is stored in a nonalcoholic solvent. The second step involves the further hydrolysis of the precursor under basic conditions to form a gel. The ability to vary density over two orders of magnitude is significant because almost all the properties discussed in this section vary with density. Specifically (52,54), the following:

Property	Value
refractive index	$n = 1 + 2.1 \times 10^{-4}\ \rho$; ρ in kg/m^3
sound velocity	$v_s \propto \rho^{\beta}$
Young's modulus	$Y \propto \rho^{\alpha}$
where for silica	$\beta = (\alpha - 1)/2$
	$\alpha = 3.6$; $\beta = 1.3$

Note that scaling exponents depend on preparative conditions.

Table 2 summarizes the key physical properties of silica aerogels. A range of values is given for each property because the exact value is dependent on the preparative conditions and, in particular, on density.

5. Applications

5.1. Thermal Insulation. In addition to their low thermal conductivity, as discussed in the section above, silica aerogels can be prepared to be highly

Table 2. **Typical Values of Physical Properties of Silica Aerogels**

Property	Values
density, kg/m^3	3–500
surface area, m^2/g	800–1000
pore sizes, nm	1–100
pore volume, cm^3/g	3–9
porosity, %	75–99.9
thermal conductivity, $W/(m\cdot K)$	0.01–0.02
longitudinal sound velocity, m/s	100–300
acoustic impedance, $kg/(m^2\cdot s)$	10^3–10^6
dielectric constant	1–2
Young's modulus, N/m^2	10^6–10^7

transparent in the visible spectrum region. Thus, they are promising materials as superinsulating window-spacer. To take further advantage of its high solar transmission, a silica aerogel layer sandwiched between two glass panes can be used to collect solar energy passively. Figure 6 shows a specific arrangement in which an insulating layer of transparent silica aerogel is placed in front of a

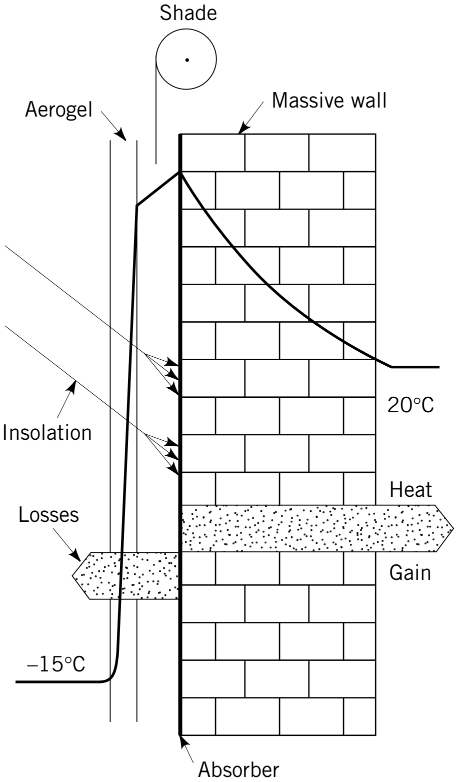


Fig. 6. Schematic diagram showing the use of transparent silica aerogel in passive solar collection. Reproduced from Ref. 53. Courtesy of Elsevier Science-NL.

brick wall, the surface of which is painted black. Solar radiation collected at the black surface is mostly transferred as heat into the house because heat loss through the aerogel layer is minimal. A shade is put into place to prevent overheating if necessary (53). The same principle applies when silica aerogels are used as insulating covers for solar panels.

The thermal conductivity of silica aerogels can be further reduced by minimizing the radiation leakage with an opacifier such as carbon black (54). The introduction of an opacifier makes the material opaque and unsuitable for window insulation. On the other hand, opaque silica aerogels can be used as insulating materials in appliances such as refrigerators and freezers. Compared with CFC-blown insulating foams, which could release chlorine into the atmosphere, silica aerogels pose no such environmental hazard and are nonflammable. Moreover, the thermal conductivity of opaque silica aerogels is a weak function of temperature (52), making them useful as insulating materials for heat-storage systems. Another promising application of silica aerogels is as a filler in vacuum panel because they do not require a high vacuum for good thermal performance. The high surface area of these materials further allow them to act as a "getter" by adsorbing gases in the panel.

The commercial viability of silica aerogels as thermal insulators depends on the ability to produce them at a competitive price. After all, in the 1950s, the production of Monsanto's Santocel stopped after a lower-cost process to manufacture fumed silica was developed (59). Recently an initial economic analysis that consists of six factors in the manufacturing of aerogels: starting material, solvent, energy, wage, equipment, and facility was published (60). The results show that the dominant cost is the cost of the starting material and that aerogels could be competitive with commercial insulating materials on a cost per R value basis. Indeed, BASF has developed a silica aerogel which has the registered trademark Basogel (61). Since supercritical drying, even with carbon dioxide at a lower temperature, is an energy-intensive process, NanoPore, Inc. is developing an ambient approach to make silica aerogels (49,59). Technological progresses in the next several years will be critical in determining whether aerogels can capture a significant share of the commercial insulation market, which is probably their largest potential area of application. At least two U.S. companies are currently developing aerogels as insulating materials. Aspen Systems manufactures silica aerogels in the forms of powders, monoliths, and blankets. Their present (1996) price range is from $100 to $2,000 per cubic foot, depending on the size of the order (62). Aerojet Corporation has collaborated with different end-users in evaluating the market potential of organic aerogels (59), which have even lower thermal conductivities than their silica counterparts.

5.2. Catalysis. Kistler explored the catalytic applications of aerogels in the 1930s because of the unique pore characteristics of aerogels (24), but this area of research stayed dormant for about three decades until less tedious procedures to produce the materials were introduced (25,26). Three recent review articles summarize the flurry of research activities since then (63–65). Table 3 is a much abbreviated list of what has been cited in these three articles to demonstrate simply the wide range of catalytic materials and reactions that have been studied.

Table 3. **Example of Materials and Reactions Involving Catalytic Aerogels**

Materials	Reactions	Examples
Type I, simple oxides		silica, alumina, titania, zirconia
Type II, mixed oxides		nickel oxide–alumina, titania–silica, zirconia–silica, chromia–alumina
Type III, ternary oxides		nickel–oxide–silica–alumina, magnesia–alumina–silica, titania–silica–vanadia, alumina–chromia–thoria
Type IV, supported metals		palladium–alumina, ruthenium–silica, platinum–titania, palladium–silica–alumina
Type V, doped oxides (dopant not an oxide)		zirconia–sulfate, zirconia–phosphate, niobia–phosphate, $TiCl_4$–alumina
Types I, II, III, IV	partial oxidation	isobutylene to methyacrolein, acetaldehyde to acetic acid
Type IV	hydrogenation	cyclopendiene to cyclopentene, benzene to cyclohexane
Types I, II, V	isomerization	1-butene to *cis*- and *trans*-2-butene, *n*-butane to isobutane
Type II	epoxidation	1-hexene and cyclohexene to the corresponding epoxides
Type IV	hydrotreating	hydrodenitrogenation and hydrodesulfurization
Type V	polymerization	ethylene to polyethylene
Types II and III	nitric oxide reduction	reduction of NO by ammonia to nitrogen

Most of the studies on catalytic aerogels reported in the open literature involve testing powder samples in experimental reactors. For the potential scale-up to commercial operations, aerogels have several limitations which, ironically, arise from their unique properties. First, even though aerogels have high specific surface area, they also have low densities. The product of the two quantities, which is surface area per unit volume, does not offer a significant advantage over other materials that have been used as adsorbents or catalysts. Second, the low thermal conductivity of aerogels means that it would be difficult to transfer heat in or out of a catalytic packed bed. Third, aerogels are fragile and do not withstand mechanical stress well. Attempts have been made to overcome the last two limitations by supporting or combining aerogels with materials that are either more thermally conducting or more rigid (63). Finally, as in the case of thermal insulation, catalytic aerogels need to be cost-competitive, even though the economic pressure is not as severe because the cost of a catalyst is usually a small fraction of the value of its derived products.

It is commonly believed that catalytic aerogels are interesting because their composition, morphology, and structure can be controlled at a microscopic level. But this feature is generic to any sol–gel-derived materials, so perhaps what set aerogels apart is that during solvent removal, there is another level control over the physical and chemical properties of the products. For example, supercritically dried materials are usually mesoporous and, as such, should be good catalysts for liquid-phase reactions for which there could be diffusional limitations. And for multicomponent materials, the distribution (or mixing state) of the various components could be better preserved without compromising the integrity of the porous network. A nice illustration of these effects is the recent results on epoxidation (66–68).

For the epoxidation of olefins over catalysts containing titania and silica, two factors are considered to be crucial: the accessibility of large pores for the bulky olefins (containing six to ten carbons) and the presence of Ti–O–Si linkages. It has been shown (66–68) that both of these desirable properties can be obtained only by supercritically drying an optimized gel at low temperatures with carbon dioxide. High temperature supercritical drying led to the segregation of titania and destruction of Ti–O–Si linkages. Conventional evaporative drying maintained the density of Ti–O–Si linkages but resulted in microporous xerogels that were inactive. Figure 7 (69) illustrates these observations for the epoxidation of cyclohexene. Besides reporting similar results for other olefins such as cyclododecene, norbonene, and limonene, these researchers were able to establish a semiquantitative correlation between activity and Ti–O–Si connectivity.

The Ti–O–Si linkages in titania–silica also have a large impact on the acidic properties of this mixed oxide. It was recently demonstrated that, over the entire composition range, the extent of mixing as controlled by prehydrolysis changes the acid site density, acid site type (Lewis versus Brønsted), and 1-butene isomerization activity of titania–silica aerogels (70). In fact, these observations appear to be general for other mixed oxide pairs in that sol–gel chemistry affords a higher degree of control over the intimacy of molecular-scale mixing that is not available by other preparative methods (71). Intimate mixing is actually undesirable in some instances, as shown for the selective catalytic reduction of NO with NH_3 (72). For this system, titania crystallites are believed to be good for stabilizing a two-dimensional overlayer of vanadia. Still, for this reaction the role of oxide–oxide interactions in affecting surface acidic properties remains critical (73). The fact that multicomponent materials of specific pore characteristics can be prepared to be either well-mixed or poorly-mixed, depending on the application, represents a unique advantage of catalytic aerogels.

5.3. Scientific Research. There are some applications that require such specific and unique properties that an aerogel is the only alternative. In these situations price is no longer a factor and aerogels have been and will continue to be produced for scientific purposes. One example is the use of silica aerogel monoliths as radiators in Chernekov counters, or detectors, in high energy physics and nuclear astrophysics experiments (23). In order to measure precisely the momentum of elementary particles, which are produced by particle interactions in high energy accelerators, over different momentum ranges, it is necessary to vary the refractive index of radiators. The reason is that a charged particle produces light in passing through a medium only if its velocity is higher than the velocity of light in that medium (52). As pointed out in the section "Properties", the refractive index of silica aerogels is related to density. Thus, by varying the density from about 50 to 300 kg/m^3, which is easily attainable with the

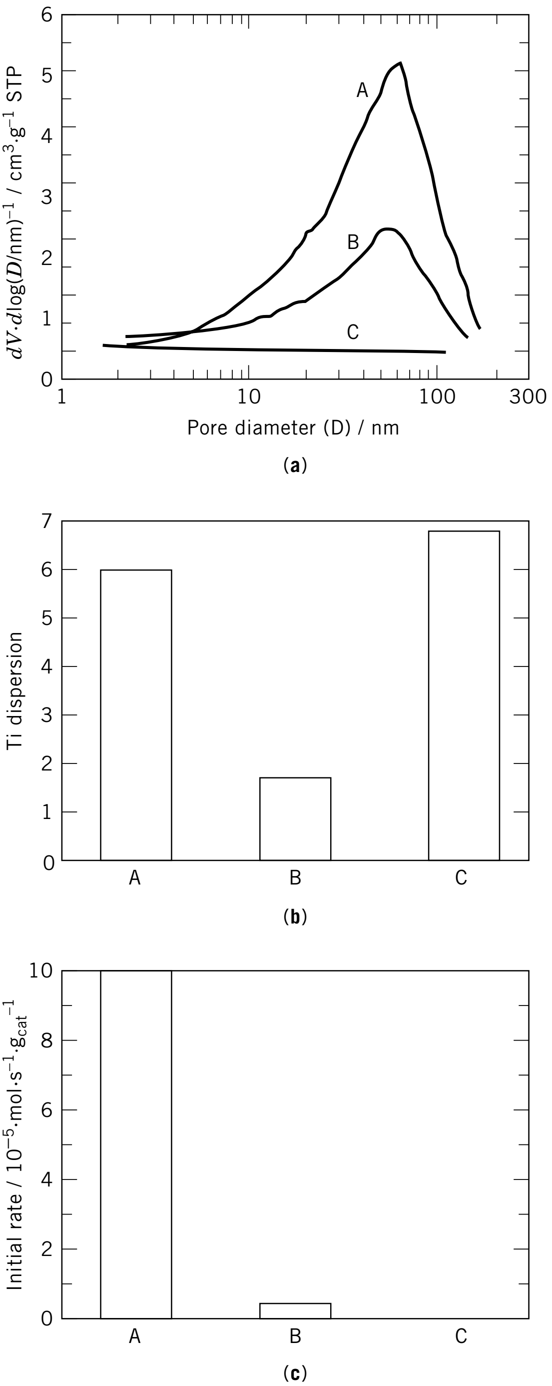


Fig. 7. The effect of preparation on the pore size distribution (**a**), titanium dispersion (**b**), and the activity for epoxidation of cyclohexene (**c**) of titania–silica containing 10 wt % titania and calcined in air at 673 K. Sample A, low-temperature aerogel; Sample B, high-temperature aerogel; Sample C, aerogel. Reproduced from Ref. 69. Courtesy of Marcel Dekker, Inc.

control of sol–gel chemistry, materials of indices of refraction between 1.01 and 1.06 can be delivered to measure low values of momentum. Indeed, two large blocks of silica aerogels have been prepared as particle detectors for use in the CERN Intersecting Storage Rings and the Deutsches Electronen-Synchrotron (DESY) (23).

Aerogels are also among the few materials that can capture cosmic particles intact (74). When a spacecraft approaches a source (eg, the corona of a comet), the cosmic particles have relative speeds of the order of tens of km/s. These hypervelocity particles tend to melt or vaporize upon collision with a solid. Mesoporous materials that are of very low density can capture these particles relatively intact, but a silica aerogel is the only one that allows the captured particles to be located easily because of its transparency. In fact, as a particle enters a silica aerogel at hypervelocity, it creates a carrot-shaped tract that points to where the particle stops. The high surface area of an aerogel provides the added advantage of adsorbing any volatiles that are either in space or generated during capture.

Panels of silica aerogels have already been flown on several Space Shuttle missions (74). Currently a STARDUST mission has been planned by NASA to use aerogels to capture cometary samples (>1000 particles of >15 micron diameter) and interstellar dust particles (>100 particles of >0.1 micron diameter). The mission involves the launch of a spacecraft in February 1999 to encounter the comet Wild 2 in December 2003 and to return the captured samples to earth in January 2006. Silica aerogels of ultralow density, high uniformity, and high purity need to be prepared to meet the primary objectives of the mission. Furthermore, there are challenges to produce nonsilicate aerogels of the same high quality and aerogels that can perform chemical as well as physical capture.

Besides being used as a tool for scientific research, silica aerogels can be the cause for new scientific phenomena. For example, the long-range correlations of the disorder in silica aerogels are believed to be responsible for the intriguing observations of the superfluid transitions in ^{4}He and ^{3}He and on the ordering of ^{3}He–^{4}He mixtures (75).

5.4. Other Applications. There are several other applications that take advantage of the unique properties of silica aerogels shown in Table 2. In a piezoceramic ultrasound transducer, the signal is reduced as sound waves cross the interface of two materials that have very different acoustic impedances (eg, the acoustic impedances of air and piezoelectric ceramics differ by several orders of magnitude). With its tunable acoustic impedance, a layer of silica aerogel sandwiched between a piezoceramic and air minimizes the mismatch and enhances the signal (54). The low dielectric constant of silica aerogels suggests their usefulness as layer materials in integrated circuits. For silica aerogels to replace the currently used silica glasses, several issues such as the control of porosity, mechanical strength, thermal stability, and process integration problems need to be addressed (57). Finally, silica aerogels are effective dehydrating agents because of their high capacity for absorbing moisture and chemical inertness. For household insect control, silica aerogels work by absorbing waxes from the cuticle of insects, which then die from dehydration; their potency can be enhanced with the doping of insecticides (76).

The introduction of organic aerogels has led to interesting areas of applications. Recent data (77,78) showing the thermal properties of these materials and, more importantly, how these properties can be varied with preparative conditions, should help their further development as thermal insulators. Carbon aerogels are also promising electrode materials in electrochemical double-layer capacitors. Large specific capacities and capacitance densities have been demonstrated in a device consisting of two carbon aerogel wafers; this performance is attributed to the high specific surface area and contiguous structure of the carbon electrode (79). These results are encouraging for the use of carbon aerogels in building low cost, high power, and high energy density capacitors (often referred to as "supercapacitors"). Another potential application of carbon–aerogel electrodes is the capacitive deionization of water. In a recently developed process, water with various anions and cations is pumped through an electrochemical cell consisting of a stack of carbon aerogel electrodes (80). The large specific surface area of the electrodes allows the electrostatic capture of ions. After water is purified, the cell can be regenerated by a simple electrical discharge.

6. Summary

As of 1996 the commercial market for aerogels remained very small. However, aerogels have the potential of being marketable both as a commodity chemical (eg, in thermal insulation) and as a specialty chemical (eg, in electronic applications) because of their unique and tailorable properties. The next few years will be critical in assessing whether aerogels can penetrate and grow in either end of the market, as the field is changing rapidly with the development of cost-competitive technologies and novel applications.

BIBLIOGRAPHY

"Aerogels" in *ECT* 4th ed., Suppl. Vol., pp. 1–22, by Edmond I. Ko, Carnegie Mellon University.

CITED PUBLICATIONS

1. S. S. Kistler, *Nature*, **127**, 741 (1931).
2. C. J. Brinker and G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press, New York, 1990.
3. J. Livage, M. Henry, and C. Sanchez, *Prog. Solid State Chem.* **18**, 259 (1988).
4. R. C. Mehrota, *J. Non-Cryst. Solids* **145**, 1 (1992).
5. H. D. Gesser and P. C. Goswami, *Chem. Rev.* **89**, 765 (1989).
6. R. K. Iler, *The Chemistry of Silica*, John Wiley & Sons, New York, 1979, Chapt. 3.
7. J. Y. Ying, J. B. Benziger, and A. Navrotsky, *J. Am. Ceram. Soc.* **76**, 2571 (1993).
8. B. Handy, K. L. Walther, A. Wokaun, and A. Baiker, in P. A. Jacobs, P. Grange, and B. Delmon, eds., *Preparation of Catalysts V*, Elsevier, Netherlands, 1991, 239–246.
9. E. I. Ko, in G. Ertl, H. Knözinger, and J. Weitkamp, eds., *Handbook of Heterogeneous Catalysts*, VCH, Germany, 1997, Vol. 1, Sec. 2.1.4.

10. B. E. Yoldas, *J. Mater. Sci.* **14**, 1843 (1979).
11. J. Livage and C. Sanchez, *J. Non-Cryst. Solids* **145**, 11 (1992).
12. U.S. Pat. 4,873,218 (Oct. 10, 1989); U.S. Pat. 4,997,804 (Mar. 5, 1991), R. W. Pekala.
13. R. W. Pekala and C. T. Alviso, *Mat. Res. Soc. Symp. Proc.* **270**, 3 (1992).
14. R. W. Pekala and C. T. Alviso, *Mat. Res. Soc. Symp. Proc.* **180**, 791 (1990).
15. R. W. Pekala, C. T. Alviso, X. Lu, J. Gross, and J. Fricke, *J. Non-Cryst. Solids* **188**, 34 (1995).
16. B. M. Novak, *Adv. Mater.* **5**, 422 (1993).
17. C. Sanchez and F. Ribot, *New J. Chem.* **18**, 1007 (1994).
18. D. Avnir, *Acc. Chem. Res.* **28**, 328 (1995).
19. U. Schubert, N. Hüsing, and A. Lorenz, *Chem. Mater.* **7**, 2010 (1995).
20. D. A. Loy and K. J. Shea, *Chem. Rev.* **95**, 1431 (1995).
21. D. Avnir, S. Braun, O. Lev, and M. Ottolenghi, *Chem. Mater.* **6**, 1605 (1994).
22. W. Cao, X. Y. Song, and A. J. Hunt, *Mat. Res. Soc. Symp. Proc.* **349**, 87 (1994).
23. A. J. Ayen and P. A. Iacobucci, *Rev. Chem. Eng.* **5**, 157 (1988).
24. S. S. Kistler, S. Swan, Jr., and E. G. Appel, *Ind. Eng. Chem.* **26**, 388 (1934).
25. S. J. Teichner, *CHEMTECH*, **21**, 372 (1991).
26. S. J. Teichner, G. A. Nicolaon, M. A. Vicarini, and G. E. E. Gardes, *Adv. Colloid Interface Sci.* **5**, 245 (1976).
27. U.S. Pat. 4,610,863 (Sept. 9, 1986), P. H. Tewari and A. J. Hunt.
28. U.S. Pat. 4,619,908 (Oct. 28, 1986), C. P. Cheng, P. A. Iacobucci, and E. N. Walsh.
29. P. Wang, A. Emmerling, W. Tappert, O. Spormann, J. Fricke, and H. G. Haubold, *J. Appl. Cryst.* **24**, 777 (1991).
30. D. R. Ulrich, *J. Non-Cryst. Solids* **100**, 174 (1988).
31. D. M. Smith, R. Deshpande, and C. J. Brinker, *Mat. Res. Symp. Proc.* **271**, 553 (1992).
32. G. Cogliati, M. Guglielmi, T. M. Che, and T. J. Clark, *Mat. Res. Symp. Proc.* **180**, 329 (1990).
33. M. Beghi, P. Chiurlo, L. Costa, M. Palladina, and M. F. Pirini, *J. Non-Cryst. Solids* **145**, 175 (1992).
34. C. J. Brodsky and E. I. Ko, *J. Mater. Chem.* **4**, 651 (1994).
35. D. C. M. Dutoit, M. Schneider, and A. Baiker, *J. Porous Mater.* **1**, 165 (1995).
36. M. Schneider and A. Baiker, *Catal. Rev.-Sci. Eng.* **37**(4), 529 (1995).
37. G. W. Scherer, in A. S. Mujumdar, ed., *Drying*, Elservier, the Netherlands, 1992, 92–113.
38. G. W. Scherer, *J. Non-Cryst. Solids*, **145**, 33 (1992).
39. G. W. Scherer, *J. Sol-Gel Sci. Tech.* **3**, 127 (1994).
40. T. Woignier, G. W. Scherer, and A. Alaoue, *J. Sol-Gel Sci. Tech.*, **3**, 141 (1994).
41. L. W. Hrubesh and J. F. Poco, *J. Non-Cryst. Solids*, **188**, 46 (1995).
42. J. F. Poco, P. R. Coronado, R. W. Pekala, and L. W. Hrubesh, *Mat. Res. Soc. Symp. Proc.* **431**, 297 (1996).
43. R. Deshpande, D. M. Smith, and C. J. Brinker, *Mat. Res. Soc. Symp. Proc.* **271**, 553 (1992).
44. C. J. Brinker, R. Sehgal, N. K. Raman, S. S. Prakash, and L. Delattre, *Mat. Res. Soc. Symp. Proc.* **368**, 329 (1995).
45. D. M. Smith, R. Deshpande, and C. J. Brinker, *Mat. Res. Soc. Symp. Proc.* **271**, 567 (1992).
46. D. M. Smith, R. Deshpande, and C. J. Brinker, *Ceram. Trans.* **31**, 71 (1993).
47. S. S. Prakash, C. J. Brinker, A. J. Hurd, and S. M. Rao, *Nature* **374**, 439 (1995).
48. S. S. Prakash, C. J. Brinker, and A. J. Hurd, *J. Non-Cryst. Solids* **190**, 264 (1995).
49. D. M. Smith, W. C. Akerman, R. Roth, A. Zimmerman, and F. Schwertfeger, *Mat. Res. Soc. Symp. Proc.* **431**, 291 (1996).

50. D. Klvana, J. Chaouki, M. Repellin-Lacroix, and G. M. Pajonk, *J. Phys. Colloq.* **C4**, 29 (1989).
51. H. D. Gesser and P. C. Goswami, *Chem. Rev.* **89**, 765 (1989).
52. J. Fricke and A. Emmerling, *J. Am. Ceram. Soc.* **75**(8), 2027 (1992).
53. J. Fricke, *J. Non-Cryst. Solids* **147/148**, 356 (1992).
54. J. Fricke and J. Gross, *Mater. Eng.* **8**, 311 (1994).
55. T. Heinrich, U. Klett, and J. Fricke, *J. Porous Mater.* **1**, 7 (1995).
56. J. Fricke, *Sci. Amer.* **256**(5), 92 (1988).
57. D. M. Smith, J. Anderson, C. C. Cho, G. P. Johnston, and S. P. Jeng, *Mat. Res. Soc. Symp. Proc.* **381**, 261 (1995).
58. T. M. Tillotson and L. W. Hrubesh, *J. Non-Cryst. Solids* **145**, 45 (1992).
59. C. M. Caruana, *Chem. Engr. Prog.* (June 11, 1995).
60. G. Carlson, D. Lewis, K. McKinley, J. Richardson, and T. Tillotson, *J. Non-Cryst. Solids* **186**, 372 (1995).
61. G. Herrmann, R. Iden, M. Mielke, F. Teich, and B. Ziegler, *J. Non-Cryst. Solids* **186**, 380 (1995).
62. *http://www.aspensystems.com/aerogel.html*
63. G. M. Pajonk, *Appl. Catal.* **72**, 217 (1991).
64. G. M. Pajonk, *Catal. Today*, **35**, 319 (1997).
65. M. Schneider and A. Baiker, *Catal. Rev.-Sci. Eng.* **37**(4), 515 (1995).
66. D. Dutoit, M. Schneider, and A. Baiker, *J. Catal.* **153**, 165 (1995).
67. R. Hutter, T. Mallat, and A. Baiker, *J. Catal.* **153**, 177 (1995).
68. R. Hutter, T. Mallat, and A. Baiker, *J. Catal.* **157**, 665 (1995).
69. From Ref. 65, p. 544.
70. J. B. Miller, S. T. Johnston, and E. I. Ko, *J. Catal.* **150**, 311 (1994).
71. J. B. Miller and E. I. Ko, *Catal. Today*, **35**, 269 (1997).
72. B. E. Handy, A. Baiker, M. Schramal-Marth, and A. Wokaun, *J. Catal.* **133**, 1 (1992).
73. R. J. Willey, C. T. Wang, and J. B. Peri, *J. Non-Cryst. Solids* **186**, 408 (1995).
74. P. Tsou, *J. Non-Cryst. Solids* **186**, 415 (1995).
75. M. Chan, N. Mulders, and J. Reppy, *Physics Today* (Aug. 30, 1996).
76. http://www.ent.agri.umn.edu/academics/classes/ipm/chapters/ware.htm
77. X. Lu, R. Caps, J. Fricke, C. T. Alviso, and R. W. Pekala, *J. Non-Cryst. Solids* **188**, 226 (1995).
78. V. Bock, O. Nilsson, J. Blumm, J. Fricke, *J. Non-Cryst. Solids* **185**, 233 (1995).
79. S. T. Mayer, R. W. Pekala, and J. K. Kaschmitter, *J. Electrochem. Soc.* **140**(2), 446 (1993).
80. J. C. Farmer, D. V. Fix, G. V. Mack, R. W. Pekala, and J. F. Poco, *J. Electrochem. Soc.* **143**(1), 159 (1996).

EDMOND I. KO
Carnegie Mellon University