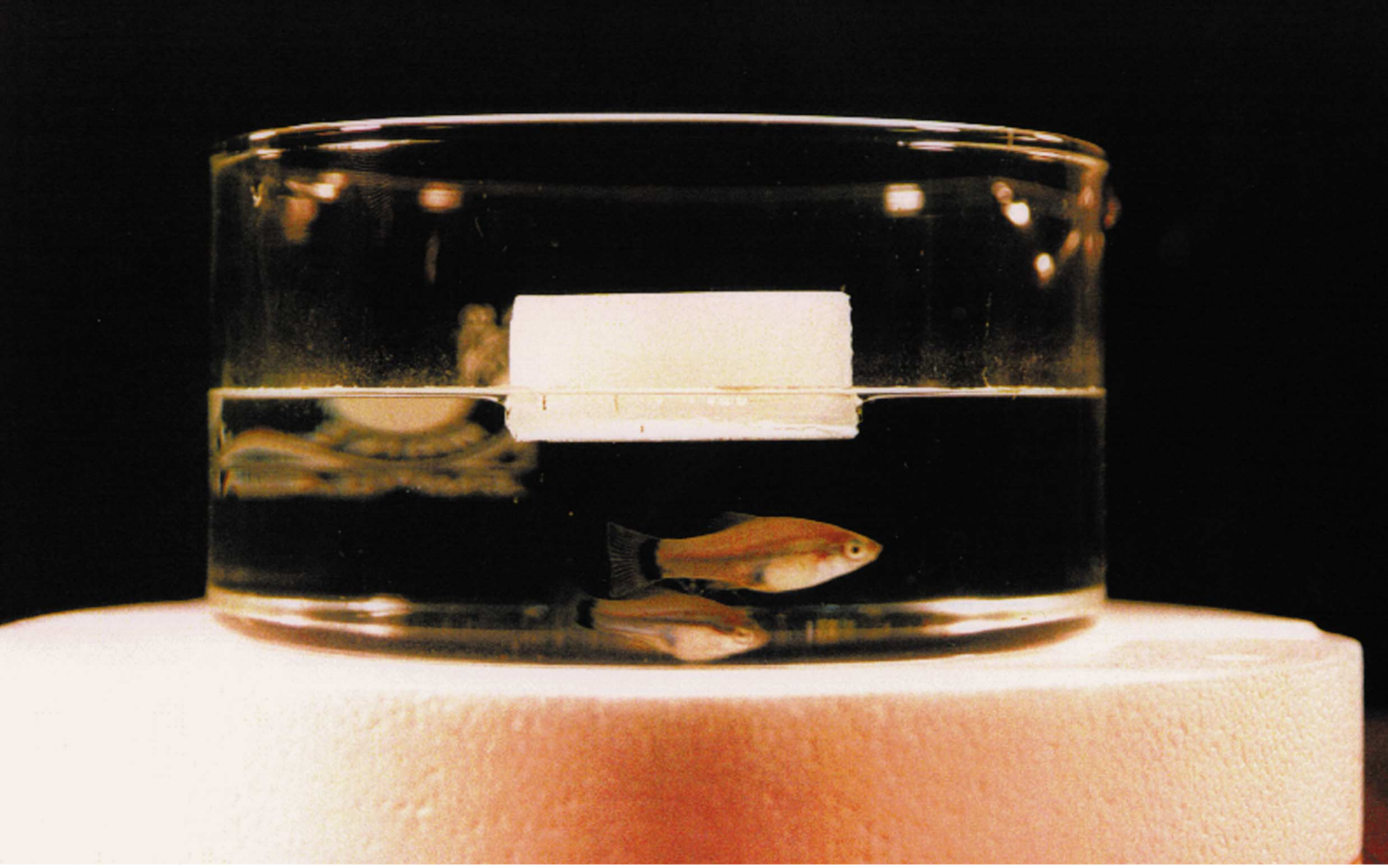

Two of the fascinating characteristics of aerogels—highly porous materials made, for example, from SiO_2 and air—are demonstrated by these pictures: In their hydrophobic form the aerogels float on water for months, and under suitable conditions one obtains plates that are translucent even with a thickness of about 2 cm.

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Aerogels—Airy Materials: Chemistry, Structure, and Properties

Nicola Hüsing* and Ulrich Schubert*

Aerogels are unique among solid materials. They have extremely low densities (up to 95% of their volume is air), large open pores, and a high inner surface area. This results in interesting physical properties, for example extremely low thermal conductivity and low sound velocity combined with high optical transparency. They are prepared from molecular precursors by sol–gel processing. The initially formed gels have a spongelike solid network filled with liquid. Special drying techniques must be applied to exchange the pore liquid with air while maintaining the filigrane solid network. Supercritical drying is most common. However, recently developed methods allow removal of the liquid in a classical way after chemical modification of the inner surface of the gels. The structure of the gel network, and thus the physical properties of aerogels, decisively depend on the choice of the precursors and the chemical reaction parameters for preparing the gels. Therefore, the later material properties are predetermined at the beginning of the preparation process. In this review, connections between the underlying sol–gel chemistry, the structure of the gels, and the resulting properties of the materials will be shown, which are the basis for a chemical "design" of aerogel properties.

Keywords: aerogels · materials science · mesoporosity · nanostructures · sol–gel processes

1. Introduction

Whipped egg whites or solid bubble bath are closest in appearance to aerogels. In principle, the name says everything: the main component of this material is air which is surrounded by a very filigrane, solid network. This network can be constructed in a way that the resulting aerogels have a density that is only three times that of air.

If an aerogel is given to a chemist, a physicist, or a materials scientist, each of them would discover interesting properties which individually are also observed in other materials. For example, SiO_2 aerogels have a high transparency that is close to that of glass, a thermal conductivity corresponding to that of polystyrene or polyurethane foams, or very high specific surface areas, which are also found in charcoal. The unique feature of aerogels is the combination of these physical properties in one material which can have different chemical compositions. Important aspects for various applications are thus combined, for example, for heat insulation (Figure 1), optical applications, sensors, catalysts, or catalyst carriers.

What exactly is an aerogel? The term aerogel is not uniformly used in the literature, and there are two different definitions:

1) First, all materials prepared from wet gels (see below) by a special drying process, the supercritical drying technique, were called aerogels irrespective of their structural properties. With the development of new drying techniques (e.g., the possibility of drying under conventional conditions, see Section 3.3), this definition no longer appears appropriate.
2) According to the alternative definition, materials in which the typical structure of the pores and the network is largely maintained (which is not always the case for supercritical drying) while the pore liquid of a gel is replaced by air are called aerogels. However, it is not always clear to what extent the structure was maintained. Rearrangement and shrinkage in the gel body during drying are normal phenomena! In many publications attention is not paid to this issue.

In this review we will mainly follow the second definition, which better applies to the special properties of this class of materials. However, we do not generally exclude materials which correspond only to the first definition.

There are already some excellent reviews on aerogels,[1] most of which focus on physical properties or applications. Here, we want to present these fascinating materials from a more chemical point of view. Aerogels are an excellent example for how important chemistry is for the development of new materials. We want to use aerogels as an example to demonstrate that the intimate knowledge and understanding of the chemistry of precursors and the chemistry of the formation of the solid are indispensible for the deliberate optimization and tailoring of materials properties.

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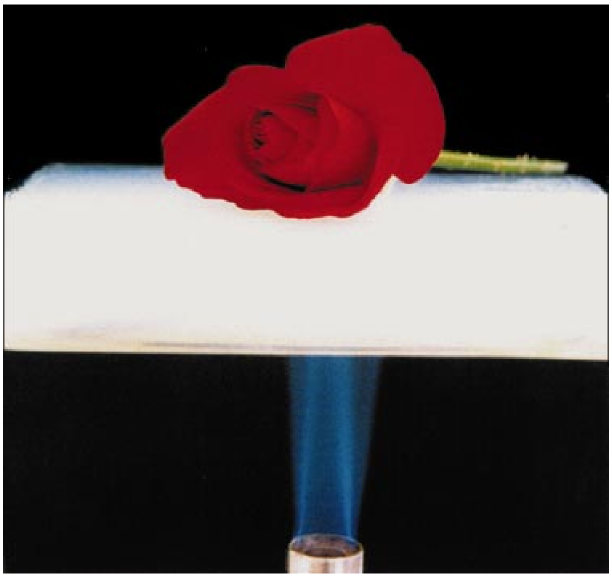

Figure 1. Aerogels have excellent insulating properties, as shown here for a silica aerogel tile.

Until recently, the chemical approach for developing materials with novel properties mainly consisted of preparing substances with a new chemical composition, that is, in an attempt to correlate the macroscopic properties and the chemical building blocks. The importance of the controlled synthesis of pore structures was only recently realized. A topical example is the family of mesoporous molecular sieves with regular channel systems (the M41S family).[2] Several emerging technologies depend on the development of engineered porous materials.[3] Nevertheless, deliberate tailoring of pores is still a major challenge in materials chemistry.

Materials are porous if they contain cavities, channels, or interstices that are deeper than they are wide.[4] The pores may be regularly arranged, as in molecular sieves. However, the more common situation is an irregular pore structure, as obtained by cross-linking of polymer chains, aggregation or agglomeration of small particles, or selective removal of elements of a solid (e.g. by etching or pyrolysis). The physical properties of a porous solid and its reactivity are effectively influenced by the kind, shape, and size of the pores. Some technical terms are defined in Table 1. The unique materials properties of aerogels result from the special arrangement of their solid network, which is schematically shown in Figure 2 for a SiO_2 aerogel.[6]

The structures of aerogels are characterized by well-accessible, cylindrical, branched mesopores. Other mesoporous materials are fumed silica, Vycor glass, carbon soot, or mesoporous molecular sieves. Among them, aerogels are

Table 1. Definition of terms used to characterize porous solids.

Term	Explanation
porosity	ratio of the pore volume to the volume occupied by the particles or powder
pore shape	ink-bottle, cylindrical, funnel, or slit-shaped
accessibility of the pores	closed, blind, or through pores
pore size,[5] dominating transport mechanisms	*micropores*: <2 nm, activated transport *mesopores*: 2–50 nm, Knudsen diffusion, surface diffusion along the pore walls, capillary transport *macropores*: >50 nm, molecular diffusion
density	skeletal density: density of the solid network bulk density: mass per total volume (volume = solid phase + closed pores + open pores)

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Nicola Hüsing, born in Rheda-Wiedenbrück (Germany), received her Diplom in chemistry and in 1997 her Ph.D. at the Universität Würzburg (Germany). Her dissertaion was on the chemical modification of aerogels. Since 1994 she has been working as a research and teaching assistant at the Institut für Anorganische Chemie der Technischen Universität Wien (Austria). A research scholarship from the Deutschen Akademischen Austauschdienst allowed her to stay with Professor J. Zink at the University of California in Los Angeles (USA) for six months in 1996 to investigate enzymes trapped in inorganic gels. She was awarded an Erwin–Schrödinger scholarship of the Fonds zur Förderung der wissenschaftlichen Forschung for postdoctoral research in 1997/98 with Dr. J. Brinker at the Advanced Materials Laboratory in Albuquerque (USA) in the area of novel porous materials. In 1997 she received the Harry Kloepfer Aerosil Award, which was sponsored by the Degussa AG and awarded by the Gesellschaft Deutscher Chemiker. Her research interests are porous sol–gel materials.

Ulrich Schubert, born in Regensburg (Germany), studied chemistry at the Technische Hochschule München (Germany), and received his Ph.D. in 1974. His dissertation was on reactions of carbene complexes. After a postdoctoral year at Stanford University (USA) with Professor W. S. Johnson, he finished his Habilitation at the Technische Universität München in 1980 on the structural chemistry of metal complexes. From 1982 to 1994 he held the position of Associate Professor of Inorganic Chemistry at the Universität Würzburg. Since 1989 he also served in different positions at the Fraunhofer-Institut für Silikatforschung in Würzburg. In 1994 he was appointed ordinary Professor of Inorganic Chemistry at the Technische Universität Wien. The current research interests of his group center around applied fundamental research on sol–gel processes, the activation of silicon– and tin–element bonds by transition metal complexes, and the structural chemistry of molecular inorganic compounds.

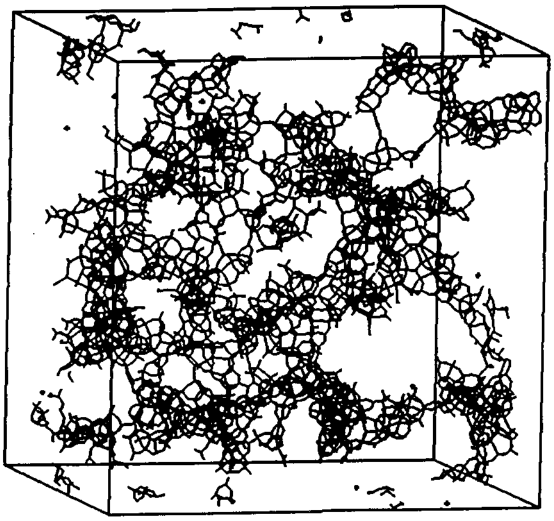


Figure 2. Schematic description of the structure of a silica aerogel (reproduced with friendly permission from ref. [6]).

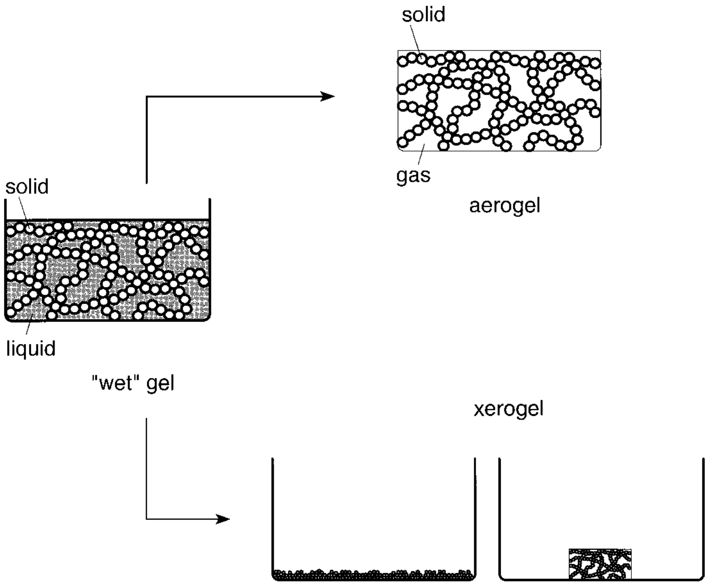


Figure 3. Shrinkage upon drying of a wet gel body to give an aerogel (top) and a xerogel (bottom) as a powder (left) and a monolith (right).

unique owing to their extremely high porosity (low density) and high specific surface area, and the possibility of making monoliths. Aerogels can also be obtained as granulates or powders. The bulk density of aerogels is in the range of 0.004 – 0.500 $g\,cm^{-3}$ owing to the high porosity (for comparison, the density of air is 0.00129 $g\,cm^{-3}$).

The pore structure of aerogels is formed by the controlled condensation of small (polymeric or colloidal) primary particles with a diameter of 1 – 3 nm, as discussed in detail in Section 2. Generation and aggregation of the particles is controlled by chemical processes, usually the sol – gel process, which has been extensively treated in books,[7, 8] conference proceedings,[9–11] and several reviews.[12, 13]

To begin, we want to explain some terms related to the sol – gel process which will be frequently used throughout this review. In a *sol* colloidal particles with diameters in the range of 1 – 1000 nm are dispersed in a liquid. A *gel* consists of a spongelike, three-dimensional solid network whose pores are filled with another substance (usually a liquid). When gels are prepared by hydrolysis and condensation of metal or semimetal alkoxides or other hydrolyzable metal compounds (through the sol stage), the pore liquid mainly consists of water and/or alcohols. The resulting ("wet") gels are therefore called *aquagels*, *hydrogels*, or *alcogels*. When the pore liquid is replaced by air without decisively altering the network structure or the volume of the gel body,[14] *aerogels* are obtained (or *cryogels* when the pore liquid is removed by freeze-drying). A *xerogel* is formed upon conventional drying of the wet gels, that is, by increase in temperature or decrease in pressure with concomitant large shrinkage (and mostly destruction) of the initially uniform gel body (Figure 3).

The large shrinkage of a gel body upon evaporation of the pore liquid is caused by capillary forces acting on the pore walls as the liquid retreats into the gel body. This results in the collapse of the filigrane, highly porous inorganic networks of the aquagels or alcogels. Therefore, other drying methods had to be developed to prepare aerogels (see Section 3). Kistler, who prepared the first aerogels in 1931, used the solvent in the supercritical state for drying.[15] The chemical composition of the gel networks included oxides of silicon, aluminum, tin, thorium, iron, and tungsten as well as organic compounds such as cellulose, cellulose nitrate, and gelatine. Therefore, the first publication on aerogels ended very optimistically: *"…and we see no reason why this list may not be extended indefinitely"*.

Despite the optimistic and encouraging prediction of Kistler, the application-oriented research and development of aerogels only started in the late 1960s, concomitant with the rapid development of the sol – gel process. They found their first application in particle detectors for high-energy physics (Çerenkov detectors). The continuing and steadily increasing interest, both in applied fundamental research and technical applications, is demonstrated by the increasing number of publications each year and the regular international symposia since 1985.[16]

2. Network Formation and Structure

Formation of the highly porous three-dimensional network is one of the key steps in the preparation of aerogels. It is remarkable that this can be achieved for inorganic, inorganic – organic, and purely organic systems under controlled conditions despite a typical solid content of only 1 – 15 vol %. Network formation is an excellent example for the influence of chemical parameters, in particular the kind of precursors and the reaction conditions, on the resulting microstructure. The microstructure, for their part, influences the macroscopic properties of the resulting solid. "Design" of the materials properties therefore requires mastering of the fundamental chemical processes. This is especially important for aerogels, because the network formed by wet chemical processes can be preserved nearly unchanged by the special drying techniques

(Section 3). Therefore, some possibilities for structural investigations should be mentioned at this point. In a simplifed manner we consider the structure of an aerogel, which is easier to investigate by physical methods, to be approximately equal to that of the corresponding wet gel. We thus want to link the chemical processes for the network formation with the structure of the (aero)gels.

The gathering of information on the structure of aerogels requires methods which cover the length scale from the lower nanometer (structure of the primary particles) to the micrometer range (linking of the particles).[17] No technique can provide the complete information, and a clearer picture only emerges by combining different methods. Some common methods for determining the structure of aerogels are listed in Table 2.

There are several other techniques for gaining structural information. For example, NMR spectroscopy was used to follow the evolution of the structure from the molecular precursors to the gel,[30] or to determine the pore diameters or fractal dimensions.[31] Mechanisms of the network formation can be derived from the fractality—that is, the self-similarity—of the structure.[32] Atomic force microscopy (AFM) was recently used to obtain information on the atomic structure at the surface.[33]

The irregular, branched three-dimensional gel network is usually formed by condensation of colloidal particles. There are two principal possibilities:

1. Solid gels are dissolved (peptized) and the obtained sols (colloids) then reaggregated under different conditions.
2. Sol particles are formed by chemical reactions from dissolved molecular precursors. Their condensation results in the formation of a gel. Most aerogel syntheses follow this route, with two variations:

a) Hydrolysis and subsequent condensation reactions are initiated starting from aqueous solutions of ionic precursors by changing the pH or the temperature.

b) Precursor molecules in an organic solvent are transformed into species capable of undergoing condensation. For example, the reaction of metal or semimetal alkoxide groups (E−OR) with water results in the formation of hydroxy groups (E−OH), which can then condense to form E-O-E units. Gel formation starting from multifunctional organic precursors proceeds similarly.

The production of inorganic and inorganic–organic aerogels is shown schematically in Figure 4. Some parameters are also listed with which the sol–gel process and therefore the properties of the resulting aerogels can be influenced and varied. Organic aerogels are produced similarly.

The solvent plays an important role in sol–gel processes. It not only serves to homogenize the precursors in the initial stage, but also influences the particle- and network-forming reactions to a very high degree due to its polarity and viscosity. In the preparation of aerogels it has an additional function, as shown in Figure 4. Since gelation results in only a marginal change in volume and the drying process during the aerogel production is performed (by definition) in a way that shrinking is minimal, the volume of the aerogel body (and thus its density) is determined by the volume of the reaction solution. Therefore, the density of aerogels is simply modified by varying the precursor concentration in the starting solution.

In principle, the structures of all covalently bonded gels are between those of colloidal and polymeric gels, which constitute the two extremes with regard to both the microstructure and the resulting properties (Figure 5). The three-dimensional network in both structural types is formed by connecting primary particles (clusters[34]). In colloidal gels, dense colloidal particles are interconnected like a string of pearls (Figure 5a). In polymer gels, linear or branched polymer chains are formed by condensation of small clusters (rings, cages) instead of dense particles (Figure 5b). There are several theoretical models for the aggregation of the clusters to three-dimensional networks.[7, 35]

Because the microstructure strongly depends on the preparation conditions, each aerogel has its own structural characteristics. It is difficult to compare different aerogels in spite of similar structural features. We therefore restrict ourselves in the following sections to discussing some basic concepts for network formation that are exemplarily for different chemical systems.

2.1. Inorganic Aerogels

Nearly all metal or semimetal oxides are known to form gels, and many served for the production of aerogels. A complete listing of all known inorganic aerogels would be beyond the scope of this review. For this reason, we restrict

Table 2. Typical methods for structurally characterizing aerogels and the structural information available from them.

Method	Structural information	Remarks/problems
N_2 adsorption and desorption according to Brunauer, Emmett and Teller (BET)[18]	specific surface area, distributions of pore radii,[19] interactions of adsorbents and adsorbates	only pores are detected which are accessible for N_2, structural changes by the N_2 pressure during the measurements results in falsification of the values for the pore radii[20]
helium pyknometry[21]	skeletal density	
mercury porosimetry[22]	pore volumina	compression of the network by the applied pressure instead of penetration of Hg into the matrix[23, 24]
electron microscopy [scanning, transmission, and scanning transmission electron microscopy (SEM, TEM, and STEM, respectively)]	particle sizes, form and arrangement of the particles (morphology)	sintering processes due to the high energy of the electron beam
light scattering (LS),[25] small-angle X-ray scattering (SAXS),[26, 27] small-angle neutron scattering (SANS)[28, 29]	particle and cluster sizes, fractal dimensions, surface area	inverse relation of the scattering vector and the structural dimension, information from the Angstroem to the micrometer range

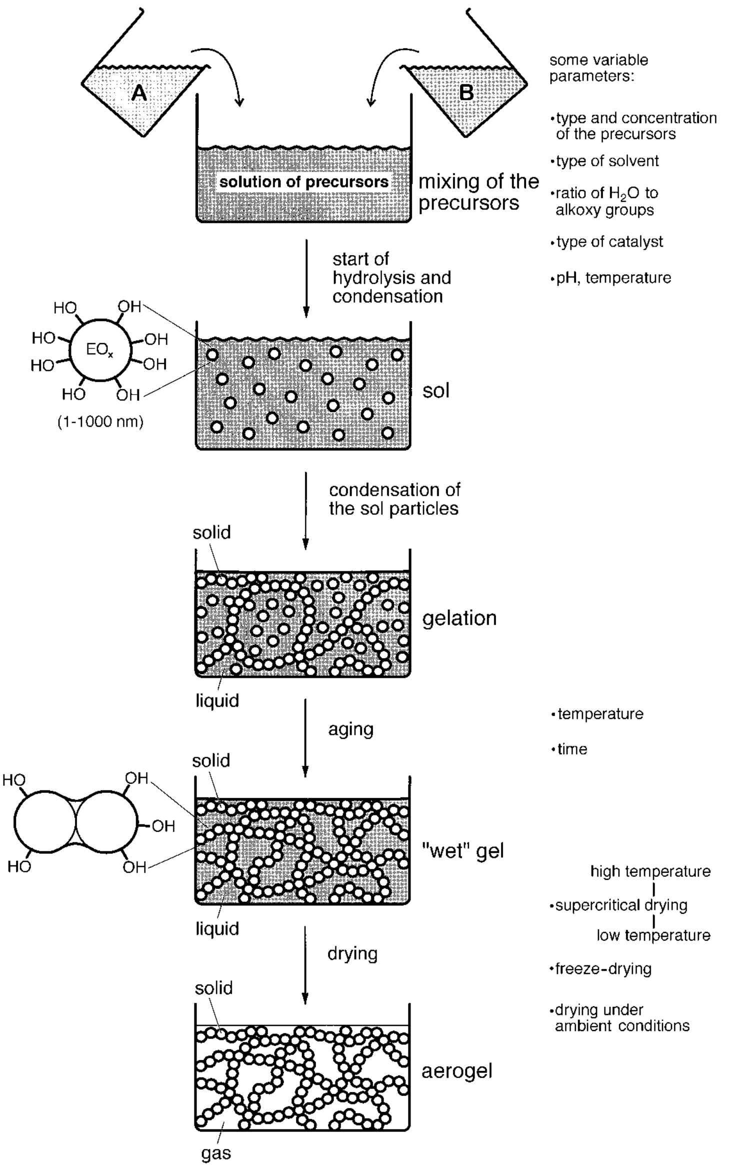


Figure 4. General scheme for preparing aerogels by sol–gel processing and some typical variable parameters.

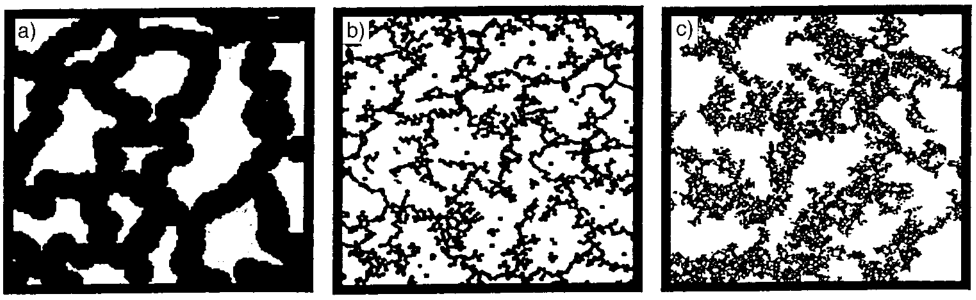


Figure 5. Two-dimensional structures of aerogels: a) colloidal, b) polymeric, and c) with a rough surface (see Section 2.1.1; reproduced with friendly permission from ref. [44]).

ourselves to some examples which we believe to be important or representative. A semantic aspect should be pointed out first. The term "SiO_2 gel" (correspondingly for other gels) is only used to characterize the type of inorganic skeleton. SiO_2 gels and aerogels often have the composition $SiO_x(OH)_y$ or, if they are prepared from alkoxides, $SiO_x(OH)_y(OR)_z$, where the values of y and z can be (but must not be) rather high. For example, in aerogels made from $Si(OMe)_4$ under basic conditions and then supercritically dried with methanol, 30% of the silicon atoms still carry a methoxy substituent ($z = 0.3$ in this case).[36]

2.1.1. SiO_2 Aerogels

Silica gels certainly belong to the best investigated materials in inorganic chemistry. Therefore, it is not surprising that Kistler used SiO_2 gels in 1931 for his first attempts to exchange the liquid in gels for air.[15] For this purpose he allowed water glass, an aqueous solution of sodium silicate, to react with hydrochloric acid [Eq. (1)].

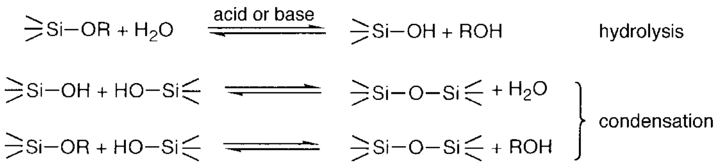
$$\text{"}Na_2SiO_3\text{"} + 2\,HCl \xrightarrow{H_2O} [SiO_2 \cdot x\,H_2O] + 2\,NaCl \qquad (1)$$

To convert the aquagels into aerogels he first had to remove the formed NaCl by several washing cycles. Then the water had to be exchanged for another solvent, because supercritical drying of the aquagels resulted in their complete peptization. Kistler showed impressivly that the liquid of the gels can be removed without destroying the gel structure. One of the reasons why it took 30 years for the aerogels to become interesting for industrial applications was certainly the time-consuming preparation, which took more than a week.

A decisive simplification and acceleration of the synthesis was achieved by Teichner et al. in the 1960s.[37] They dissolved tetramethoxysilane (TMOS) in methanol and added a defined amount of water to start the hydrolysis and condensation reactions [Eq. (2)]. The pore liquid now mainly consisted of alcohol, and therefore the wet alcogels could be dried supercritically without the awkward solvent exchange.

$$Si(OCH_3)_4 + H_2O \xrightarrow{CH_3OH} [SiO_2 \cdot H_2O/CH_3OH] \qquad (2)$$

The chemical reactions during sol–gel processing of alkoxysilanes can be formally described by three equations (Scheme 1). Condensation already occurs even if not all of the OR groups are hydrolyzed. Small oligomers (clusters) are initially formed by the condensation reactions and then the sol particles which eventually form the oxidic gel network. However, all intermediate species still contain Si–OR and/or Si–OH groups. Hydrolysis therefore takes place parallel to condensation during all steps of the sol–gel process.



Scheme 1. Chemical reactions for the sol–gel process of alkoxysilanes.

Parameters which influence the hydrolysis and condensation and whose deliberate variation are used for "materials design" are, inter alia, the kind and concentration of the precursors, the relative concentration of the components in the precursor mixtures, the kind of the solvent, the ratio of H_2O to alkoxy groups, the temperature, and the pH value.

A variety of physical-chemical measurements and also some computer simulations were performed to determine the influence of these parameters on the network formation of SiO_2 aerogels.[16, 38–42] For example, Schaefer et al. showed with in situ SAXS experiments that variation of the mentioned parameters strongly influences the silicate structures on a length scale of 1–20 nm.[43] Schaefer and Keefer postulated kinetic models for the growth of gel networks based on SAXS data.[44, 45] Although probably not universal, they are currently the only basis for a preparative design of aerogel structures in the nanometer range. Two of the most important models are shown in Figure 6.

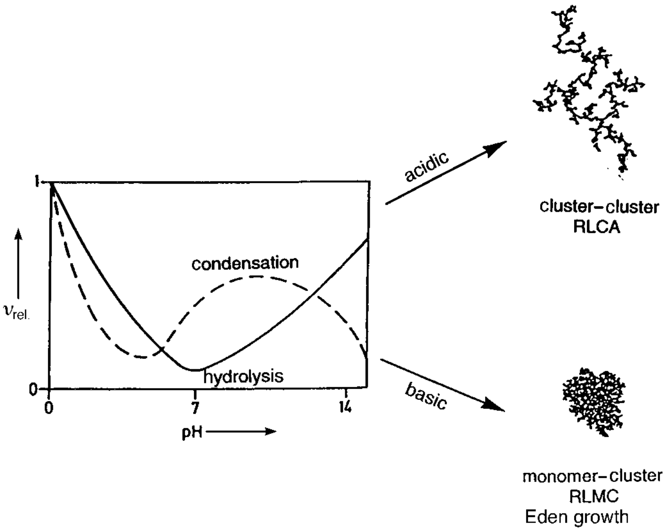


Figure 6. Dependency of the hydrolysis and condensation reaction on the pH, and derived models for kinetic growth of gel structures based on RLCA and RLMC growth (according to ref. [7, 35]). $v_{rel.}$ = relative rate of reaction.

The pH value is the decisive parameter for the relative rates of hydrolysis and condensation of tetraalkoxysilanes $Si(OR)_4$. Under acidic conditions (pH 2–5) hydrolysis is favored, and condensation is the rate-determining step. A great number of monomers or small oligomers with reactive Si–OH groups is simultaneously formed. Under these conditions, reactions at terminal silicon atoms are favored for electronic reasons. This results in polymerlike gels which are formed from chains with few branches; that is, small clusters condense to give a polymerlike network with small pores. This process is called reaction limited cluster aggregation (RLCA).

In contrast, hydrolysis is the rate-determining step under basic conditions. Due to a different mechanism, reaction at the central silicon atoms of an oligomer unit is favored. The resulting network is characterized by big particles and large pores ("colloidal" gels). Hydrolyzed species are immediately consumed because of the faster condensation. Condensation of clusters with each other is relatively unfavorable because it requires inversion of configuration at one of the silicon atoms involved in the reaction.[7] Therefore, the clusters grow mainly by condensation of monomers. This model is called reaction limited monomer cluster growth (RLMC) or Eden growth.[46, 47] It would ideally result in equally dense structures. However, for tetraalkoxysilanes this simple model must be slightly modified. Not all the four branching points are equal, because $Si(OR)_{4-x}(OH)_x$ is initially formed from $Si(OR)_4$ ("poisoned" Eden growth). Condensation is inhomogeneous owing to the presence of Si–OR groups at the growth front, and rough structures are obtained (see Figure 5c). Therefore, the kind of inorganic network formed upon condensation not only depends on the absolute rates of the individual reactions but also on the relative rates of hydrolysis and condensation.[48, 49]

The preparation of aerogels from polymeric gels is more difficult, because diffusion processes are strongly inhibited by the smaller pores. Complete removal of the pore liquid is therefore more difficult and results in greater shrinkage upon drying.[50] For this reason SiO_2 aerogels are usually prepared by base-catalyzed reaction of tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS), usually with ammonia as the catalyst.

A modification of this procedure was developed by Brinker et al:[51] $Si(OR)_4$ is first prehydrolyzed with a small amount of water under acidic conditions. This results in the formation of small clusters of silicic acid. In a second step (which must not necessarily immediately follow the first) a defined amount of aqueous acid or base is added. Networks formed by this two-step procedure have a structure similar to that of the RLCA model; that is, they have polymeric character. The probable explanation is that the reactive clusters formed in the first step as structure-forming units are strongly responsible for the formation of the network, independent of the kind of catalyst used in the second step. The main difference caused by base or acid catalysis in the second step is the stiffness of the resulting network. The former results in a stiffening which stabilizes the gels. With this two-step procedure a more deliberate control of the microstructure and thus the particle and pore sizes of the SiO_2 gels is possible.

The group of Hrubesh used the two-step sol–gel process to vary the density of aerogels within a larger range.[52, 53] When aerogels are made by simple base- or acid-catalyzed reactions their density is restricted to 0.030–0.300 $g\,cm^{-3}$, because the alcohol formed during hydrolysis shifts the equilibrium towards species with alkoxy groups. This results in long gelation times. Tillotson and Hrubesh removed the alcohol by destillation after the first step and replaced it by an aprotic solvent (e.g. acetonitrile). Deliberate dilution, base-catalyzed hydrolysis of the remaining Si–OR groups, and condensation of the SiO_2 particles resulted in the formation of a three-dimensional network and a solid with a density of only 0.004 $g\,cm^{-3}$.[53]

In principle, the work of Pajonk et al. is also based on a two-step procedure. They synthesized oligomeric polyethoxysiloxanes of a certain size from TEOS by adding an exact amount of water. These defined oligomers were then used as precursors for sol–gel processing to form the three-dimensional network.[54-56]

The preparative routes to SiO_2 aerogels described so far have one thing in common: an alkoxysilane was used as the precursor. For technical applications, in which large amounts of aerogels are needed, alkoxysilanes are too expensive. Therefore, BASF, Hoechst, and others use a procedure in which a solution of aqueous sodium silicate is ion-exchanged and then hydrolyzed under acidic conditions.[57, 58] For the production of Basogel, the aerogel product of BASF, a two step-procedure was applied. A solution of sodium silicate is mixed with sulfuric acid in the first step. Small hydrogel or aquagel droplets are formed by spraying. The metal salts are then extracted, and the water is exchanged for an organic solvent.[59] The gel droplets are then supercritically dried. The procedure of Hoechst and Nanopore, an American company, will be discussed with the drying methods.

Henkel patented a procedure in 1991 with which silicic acid is transfered into an organic solvent, and condensation is then performed under acidic, neutral or basic conditions. These wet gels are also potentially suited for producing aerogels.[60]

The transition from sol to gel is reached when a continuous network is formed (gel point). An extremely important aspect of the preparation of inorganic gels is that the chemical reactions are not finished with the formation of the gel network. First, the pore liquid is initially a sol. That is, it contains condensable particles or even monomers which slowly condense to the existing basic network. Second, there are structural rearrangements in the gel network for mainly two reasons. The gel network is originally still very flexible, and neighboring E–OH or E–OR groups can approach each other and undergo condensation ("aging"). Furthermore, hydrolysis and condensation are in principle reversible. Therefore, mass is dissolved from thermodynamically unfavorable regions, and the solutes condense to thermodynamically more favorable regions, in particular in pores, crevices, and particle necks ("Ostwald ripening"). This process results in the reduction of the net curvature, disappearance of small particles, and filling of small pores. Aging and ripening increase the stiffness of the gels (see Figure 4). This is an important aspect, particularly for aerogels, to which we will return when discussing the drying methods.

Because of the described differences in the structure of the primary particles and the network formation, which are caused by the different reaction mechanisms, the macroscopic properties of SiO_2 aerogels differ within a wide range. This is a very good example for the correlation between precursor chemistry and the properties of the final materials (see Section 5.1). "Typical" structural data therefore have only limited relevance. Nevertheless, some data for SiO_2 aerogels are listed in Table 3 to exemplify their properties.

Table 3. Important structural properties of SiO_2 aerogels

Property	Range	Typical value
bulk density [$g\,cm^{-3}$]	0.003–0.500	0.100
skeletal density [$g\,cm^{-3}$]	1.700–2.100	
porosity [%]	80–99.8	
mean pore diameter [nm]	20–150	
inner surface area [$m^2\,g^{-1}$]	100–1600[61]	600
refractive index	1.007–1.24	1.02
thermal conductivity λ (in air, 300 K) [$W\,m^{-1}\,K^{-1}$]	0.017–0.021	1.02
modulus of elasticity E [MPa]	0.002–100	1
sound velocity c_L [$m\,s^{-1}$]	< 20 to 800	100
acoustic impedance Z [$kg\,m^{-2}\,s^{-1}$]		10^4

2.1.2. Metal Oxide Aerogels

The principles for network formation of SiO_2 gels also hold for non-silicate inorganic gels. Aqueous solutions of salts or molecular precursors in organic solvents, again usually alkoxides, can be employed for sol–gel processing.

Metal alkoxides of, for example, titanium, zirconium, tin, or aluminum are much more reactive towards water than alkoxysilanes. This is due to the lower electronegativity and higher Lewis acidity as well as the possibility of increasing the coordination number. Table 4 lists some properties that are important for the reactivity of different tetravalent alkoxides. Reactivity in hydrolysis reactions decreases in the order $Si(OiPr)_4 <<< Sn(OiPr)_4, Ti(OiPr)_4 < Zr(OiPr)_4 < Ce(OiPr)_4$.

Table 4. Electronegativity EN, ionic radius r for the coordination number four, preferred coordination number CN, and the degree of coordinative unsaturation of the central atom (CN – N) for some tetravalent ($N = 4$) alkoxy compounds.[62]

Alkoxide	EN[a]	r [Å][63]	Preferred CN	CN – N
$Si(OiPr)_4$	1.74	0.40	4	0
$Sn(OiPr)_4$	1.72	0.69	6	2
$Ti(OiPr)_4$	1.32	0.56	6	2
$Zr(OiPr)_4$	1.22	0.73	7	3
$Ce(OiPr)_4$	1.08	1.02[b]	8	4

[a] Allred–Rochow electronegativities. [b] For the coordination number six.

The reactivity towards water is so high for many of these alkoxides that precipitates are spontaneously formed. Whereas the reactivity of alkoxysilanes has to be promoted by catalysts, the reaction rates of metal alkoxides must be moderated to obtain gels instead of precipitates. The most common method is the addition of acetic acid or acetylacetone to the precursor solution. This results in substitution of part of the alkoxy groups by acetate or acetylacetonate. Other chelating or bridging ligands can also be used. The new molecular compound $[M(OR)_y(L)_x]_n$ (L = bidentate anionic ligand, Figure 7) shows a different reactivity, structure, and functionality than the unsubstituted alkoxide $M(OR)_{y+x}$ as a function of the kind and number of the ligands.

Complexation allows the chemical design of the precursors, with which the properties of the sol–gel materials can be deliberately influenced. Not only are new building blocks introduced, but the average degree of condensation is also

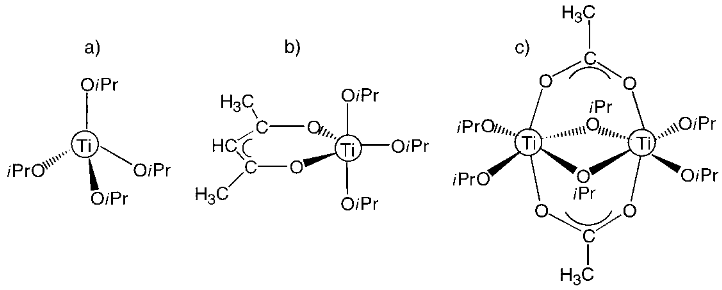


Figure 7. Molecular structure of a) $Ti(O\textit{i}Pr)_4$, b) the acetylacetonate derivative $[Ti(O\textit{i}Pr)_3(acac)]$, and c) the acetate derivative $[Ti(O\textit{i}Pr)_3(OAc)]_2$.

changed. Since the bidentate ligands are located at the surface of the oxo clusters, the size and structure of the primary particles can be engineered by deliberately varying the ratio of alkoxide to ligand.[64, 65]

Typical examples of metal oxide aerogels of some elements or combinations of elements will be discussed in the following. Compared to aerogels with a silicate network, only little work was done to elucidate their network formation and structure. One of the most important differences is the possibility of forming crystalline primary particles. As a general rule, the crystalline portion is favored by a large excess of water in the hydrolysis reaction.

Alumina

The preferred precursors for the synthesis of Al_2O_3 aerogels are $Al(O\textit{s}Bu)_3$ (ASB) and $Al(O\textit{t}Bu)_3$ (ATB). ASB has the advantage of being soluble in 2-butyl alcohol, whereas other aluminum alkoxides are insoluble in the corresponding alcohol. There are different possibilities for handling this problem.[66] The alkoxide can be dissolved in benzene followed by addition of pure water (two liquid phases are formed) or water dissolved in the corresponding alcohol. Alternatively, a dispersion of the alkoxide in the corresponding alcohol can be prepared, and water is added afterwards. Teichner et al investigated the basic chemistry of aluminum alkoxides in the context of preparing Al_2O_3 aerogels.[67–69] They found that one of the most important parameters is the relative amount of water, which allows control of the surface area, the pore volume, and the portion of crystalline (boehmite) and amorphous units in Al_2O_3 aerogels.

Mizushima and Hori prepared Al_2O_3 aerogels from ethylacetylacetonate-modified ASB.[70] They were able to interrupt the process at the sol stage owing to the better control of the hydrolysis and condensation reactions, to remove the solvent, and to modify the alumina particles. A hybrid network between alumina and organic units was prepared by cross-linking with, for example, hexamethylenediisocyanate (Figure 8), which has a lower density and a broader pore-radii distribution than an unmodified alumina aerogel.[71]

Markel et al. prepared Al_2O_3 aerogels by a different method.[72] They amalgamized the surface of metallic aluminum and then oxidized it with O_2. A layer of Al_2O_3 fibers oriented perpendicular to the metal surface was formed, which the authors called an aerogel.

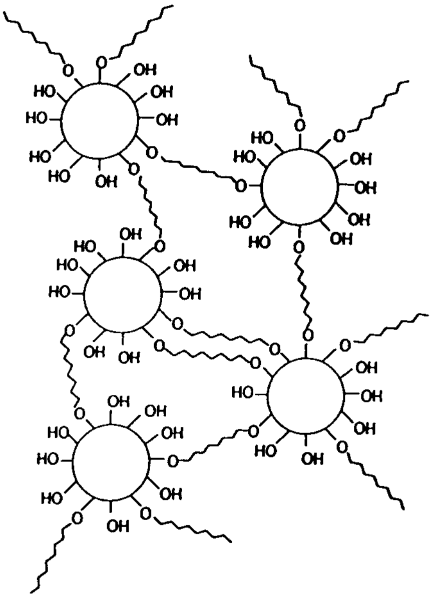


Figure 8. Schematic representation of an alumina gel cross-linked with hexamethylenediisocyanate (reproduced with friendly permission from ref. [71]). The large circles represent particles of hydroxylated alumina, and the snakelike lines $C(O)NH(CH_2)_6NHC(O)$ chains.

Titania and zirconia

The first TiO_2 and ZrO_2 aerogels were prepared by Teichner et al. as early as 1976.[67] Until today, the propoxides and butoxides of these metals are mainly used as precursors.[1f,73–75]

TiO_2 aerogels can be prepared totally amorphous or with a network of anatase primary particles.[76] Zhu and Tomkiewicz were able to elucidate the microstructure and morphology over two length scales and three density regions by combining SAXS, SANS, N_2 sorption, and electron microscopy: the size and density of the nanoparticles (clusters) and the mesoparticles, and the bulk density of the whole network. Figure 9 schematically shows the network model derived from these measurements. Mesoparticles with a diameter of about 50 nm aggregate to give a three-dimensional network. They are formed by aggregation of the crystalline nanoparticles of about 5 nm in diameter.

As with the alumina gels, the amount of water added for hydrolysis is decisive for the structure of zirconia aerogel networks. Addition of substoichiometric amounts of water results in an amorphous network, whereas a structure composed of crystalline, monoclinic ZrO_2 particles is obtained with an excess of water.[1c, 67] Vesteghem et al. gelled $Zr(O\textit{n}Pr)_4$ in 1-propanol in the presence of acetic acid. The acetate ligand remained in the aerogel.[77]

Zeng et al. investigated the fractal dimension of amorphous and partially crystalline ZrO_2 aerogels.[78, 79] From the results of SAXS measurements (values for d_f [mass fractality] close to 2) they concluded that the aerogels have a branched, polymerlike fractal structure, which is analogous to that of the silicate systems investigated by Keefer and Schaefer,[45, 46] consisting of small primary particles with an average diameter of 5.2 nm (partially crystalline) or 2.5 nm (amorphous). Other one-component oxide aerogels are listed in Table 5.

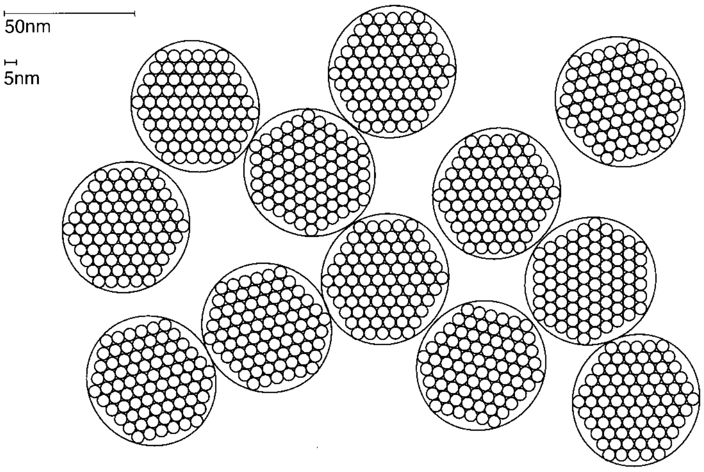


Figure 9. Schematic representation of the structure of partially crystalline TiO_2 aerogels (reproduced with friendly permission from ref. [76c]).

Table 5. Examples of purely inorganic aerogels, precursors for their preparation, and potential applications.

Aerogel	Precursor	Application
V_2O_5	$VO(O\textit{i}Pr)_3$,[80] $VO(OEt)_3$[81]	cathode in lithium batteries
Cr_2O_3	$Cr(NO_3)_3$,[82] $CrCl_3$,[83] $Cr(OAc)_3$[84, 85]	oxidizing properties, fluorination of hydrocarbons with HF
Fe_2O_3	$FeCl_3$,[82, 83] $[Fe(acac)_3]$[86–88]	
MoO_2	$[MoO_2(acac)_2]$[67, 89, 90]	electrocatalysis
Nb_2O_5	$Nb(OEt)_5$[91–94]	isomerizations, solid acids

Binary and ternary oxide aerogels

Compared to other methods for preparing multicomponent oxides, the sol–gel method offers the best control over the resulting properties of the materials by varying the processing parameters.[37, 89, 95, 96] When precursors that undergo hydrolysis and condensation at similar rates are combined, mixed metal oxides are obtained which are homogeneous at the molecular level. With increasing differences in the reaction rates, the microstructure of the product becomes more heterogeneous and phase separation may even occur. In particular, the "core-shell" phenomenon is observed. The faster reacting compound forms sol particles which are "coated" by the slower reacting component. There are several possibilities for avoiding this effect: The reaction rate of the faster reacting component can be moderated by the bidentate ligands discussed above. Alternatively, the slower reacting precursor can be prehydrolyzed, and the faster reacting component added afterwards.[97] The network in the thus prepared aerogels is analogous to that of the one-component oxide aerogels.

Typical binary or ternary systems consist of SiO_2, TiO_2, ZrO_2, or Al_2O_3 combined with NiO, CuO, ThO_2, PbO, or Fe_2O_3. A complete compilation is beyond the scope of this review. Some aerogels are exemplarily listed in Table 6. Mixed oxide aerogels for catalytic applications are summarized in reviews by Pajonk and Baiker.[1c, e]

The structural composition of Al_2O_3/SiO_2 (mullite) systems, prepared from the alkoxides in the presence of bidentate ligands, was thoroughly investigated by Heinrich et al.[101] The interpretation of the SAXS data again led to the postulation of a RLCA-related network. SiO_2 building blocks are partially incorporated into the alumina clusters and partially integrated onto the surface of these particles. The Si–OH groups at the surface of the clusters serve as condensation sites between the particles (Figure 10).

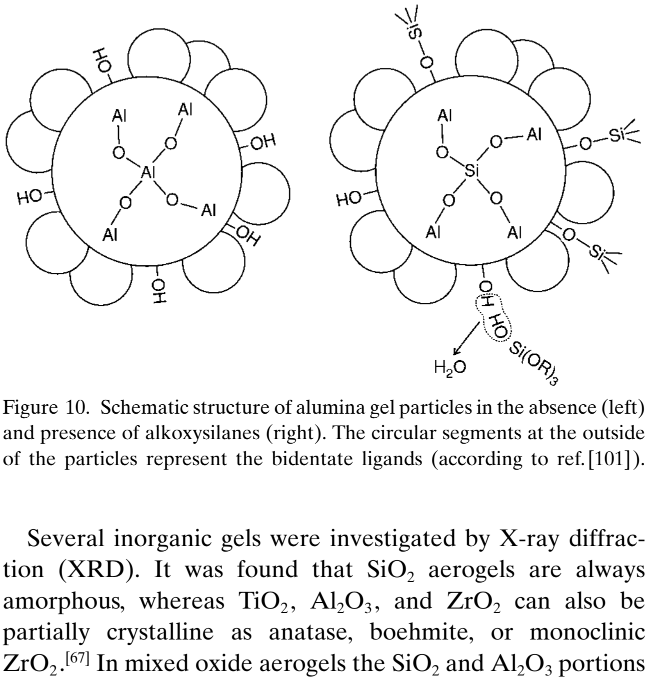


Figure 10. Schematic structure of alumina gel particles in the absence (left) and presence of alkoxysilanes (right). The circular segments at the outside of the particles represent the bidentate ligands (according to ref. [101]).

Several inorganic gels were investigated by X-ray diffraction (XRD). It was found that SiO_2 aerogels are always amorphous, whereas TiO_2, Al_2O_3, and ZrO_2 can also be partially crystalline as anatase, boehmite, or monoclinic ZrO_2.[67] In mixed oxide aerogels the SiO_2 and Al_2O_3 portions

Table 6. Examples of binary and ternary oxide aerogels.

Aerogel	Precursor	Application
TiO_2/SiO_2	$(Ti(O\textit{i}Pr)_4 + acac) + Si(OMe)_4$[98, 99]	epoxidation of olefins
Al_2O_3/SiO_2[100]	$(AlCl_3$ + ethylene oxide$) + Si(OEt)_4$,[83] $Al(OAc)_3$, $[Al(acac)_3]$	catalyst support
$3\,Al_2O_3/2\,SiO_2$ (mullite)	(ASB + β-diketone) + $Si(OEt)_4$[101]	preparation of very pure ceramics
Fe_2O_3/SiO_2,[102] Fe_2O_3/Al_2O_3	$[Fe(acac)_3] + Si(OMe)_4$ and ASB	Fischer–Tropsch syntheses
V_2O_5/MgO	$[V(acac)_3] + Mg(OMe)_2$[103]	ammonia synthesis
PbO/Al_2O_3, PbO/ZrO_2	$Pb(OAc)_2$ + ASB[104] and $Zr(O\textit{i}Pr)_4$[105]	nitroxidation of hydrocarbons to nitriles
BaO/Al_2O_3	$Ba[Al(O\textit{s}Bu)_4]_2$ + ASB, Ba(1,3-butandiolate) + ASB[106]	car-exhaust catalysis
$x\,Li_2O/(1-x)\,B_2O_3$	$B(OBu)_3 + LiOMe$[107]	
$PbTiO_3$	$Pb(OAc)_2 + Ti(O\textit{i}Pr)_4$[108, 109]	model systems for piezoelectric lead zirconate/titanate (PZT) aerogels
$NiO/Al_2O_3/MgO$	$Ni(OAc)_2$ + ASB + $Mg(OMe)_2$	nitroxidation
$NiO/SiO_2/MgO$	$Ni(OAc)_2 + Si(OR)_4 + Mg(OMe)_2$[110]	
$2\,MgO/2\,Al_2O_3/5\,SiO_2$ (cordierite-like)	$Si(OEt)_4$ + ASB + $Mg(NO_3)_2$[77]	

are always amorphous.[87, 88, 110–112] However, crystalline aluminates are observed, for example $NiAl_2O_4$.

The structural data of some non-silicate aerogels are listed in Table 7. We want to emphasize again that this is only a selection, because particularly for these aerogels the structural parameters differ decisively with the preparation conditions.

Metals in Metal Oxide Aerogels

A second metal component in the gels must not necessarily yield a binary oxide aerogel. The use of alcohols for supercritical drying (see below) can, under the applied conditions, result in the conversion of easily reducible oxides into metals, because alcohols have reducing properties. Metal particles can also be generated by subsequently reducing the aerogels with hydrogen at high temperatures or by mixing hydrogen into the autoclave during supercritical drying.[118] Aerogels are particularly well suited as carriers for catalytically active metals because of their high porosity. Detailed discussions are found in reviews on aerogels as catalysts.[1c, e]

To incorporate metal components into the gel matrix, the formed aerogels can be impregnated with solutions of the corresponding metal salts (two-step process).[119, 120] Alternatively, suitable metal salts can be added to the precursor solution, which results in the incorporation of the metal compounds into the gel during sol–gel processing.[121] The first metal-containing aerogels, Pt/SiO_2 and Ni/SiO_2, were prepared by Foster and Keyes in this manner with water glass as the source of SiO_2.[82]

The number of examples of metal-doped aerogels and, correspondingly, the number of catalytic reactions in which these materials are employed increase every year. Table 8 gives a short selection.

2.2. Inorganic–Organic Hybrid Aerogels

Materials in which organic molecules or building blocks are combined with structural elements of ceramic materials have only been known for a short time. There are several reasons for modifying oxide aerogels with organic groups. Most importantly, the spectrum of properties of aerogels is widened or improved without influencing the existing positive properties, such as good heat insulation, transparency, and high surface area. For example, the hydrophobicity and the elastic properties of SiO_2 aerogels can be improved relative to unmodified SiO_2 aerogels by incorporating organic groups.[36, 129]

There are only limited possibilities for subsequently doping or modifying aerogels with organic compounds; they will be discussed in Section 4. A more general route is the integration of organic molecules or groups already during sol–gel processing. There are several options for doing this (Figure 11). Embedding molecules into gels without chemical bonding (Figure 11, top right) is achieved by dissolving the molecules in the precursor solution. The gel matrix is formed around them and traps them. Such doped wet gels can, in principle, be converted into aerogels, but the probability is very high that the organic groups are washed out during supercritical drying, which is usually used, and the associated rinsing processes. Bockhorst et al. were able to incorporate a fluorescent dye (POPOV) into the gel network. However, the extent of leaching during aging and drying was relatively high.[130] Although fullerenes C_{60} and C_{70} were also incorporated into SiO_2 aerogels, there is no information on how well the fullerenes are entrapped.[131]

Novak et al. investigated networks built analogously to those in Figure 11, top left (interpenetrating, but not con-

Table 7. Typical structural data of some non-silicate aerogels.

Aerogel	Density [$g\,cm^{-3}$]	Porosity [%]	Pore radii [nm]	BET surface area [$m^2\,g^{-1}$]	Particle morphology [nm]
TiO_2[113]	0.3–1	78–90	1–25	316–690	
ZrO_2[67, 77, 81, 94]	0.2–0.3	84–96	10	81–480	2.5–5.2
Al_2O_3[67, 70, 114]	0.13–0.18		5	123–616	22–25 (platelike)
Al_2O_3/SiO_2[101, 115, 116]	0.06–0.21		12		1–5[a]
V_2O_5[81 a, 117]	0.04–0.1	96		140–400	< 10 nm (fibrous)
V_2O_5/GeO_2[81 b]	0.08	96			
Cr_2O_3[111]	0.15–0.54			516–785	
PbO/TiO_2[108]	0.7	77	1–4	260	45 ± 10

[a] Controllable by the amount of added β-diketone.[116]

Table 8. Examples for metal-doped aerogels.

Aerogel	Precursor for the metal	Application
1. Impregnation		
Cu/SiO_2, Cu/MgO	$[Cu(NH_3)_4](OH)_2$ in alcohol[119]	
$Cu/ZnO/Al_2O_3$	$Cu(OAc)_2$[122]	hydrogenation
Pt/MoO_2	$H_2[PtCl_6]$ in MeOH[120]	hydrogenation
Pd/Al_2O_3, Pd/CeO_2, $Pd/BaO/Al_2O_3$	$PdCl_2$[123, 124]	car-exhaust catalysis
2. Sol–gel method		
Pt/TiO_2	$PtCl_2$, $[Pt(acac)_2]$, $(NH_4)_2[PtCl_6]$[125]	hydrogenation
Pd/Al_2O_3	$Pd(OAc)_2$[126]	car-exhaust catalysis
V/SiO_2	$V(O\textit{i}Pr)_3$	
Cu/SiO_2	$Cu(OAc)_2$[127]	
Pt/Al_2O_3	$H_2[PtCl_6]$[128]	dehydrocyclization

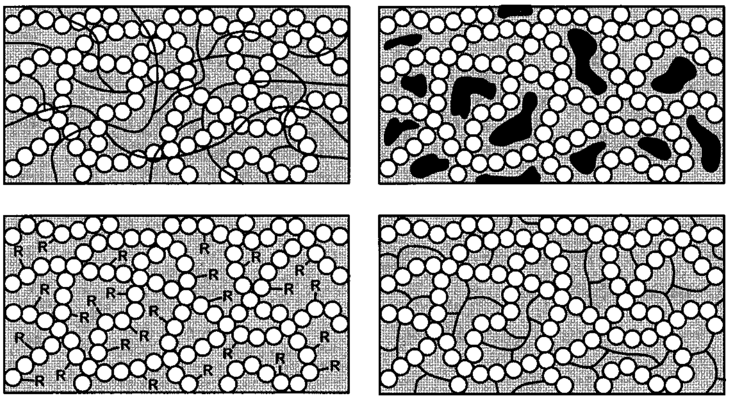


Figure 11. Inorganic–organic hybrid networks obtained by sol–gel processing. Top left: interpenetrating inorganic and organic networks; top right: incorporation of organic molecules (enzymes, dyes, etc.); bottom left: modification (functionalization) of oxidic materials with organic substituents; bottom right: dual networks.

nected networks). The organic polymer was generated in situ during the sol–gel reaction by radical polymerization of a vinyl monomer. The aerogel obtained by supercritical drying with CO_2 consists of interpenetrating inorganic and organic networks (Figure 12).

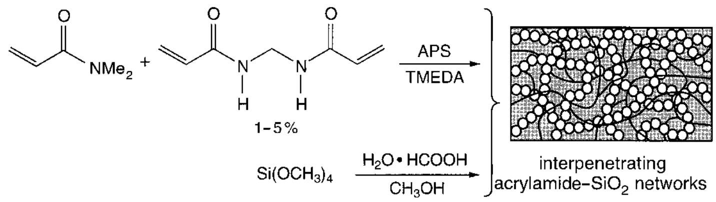


Figure 12. Formation of two interpenetrating networks (inorganic–organic) by simultaneous sol–gel reaction and polymerization of *N,N*-dimethylacrylamide (in the presence of *N,N*′-methylenebisacrylamide (APS = ammonium persulfate); according to ref. [132]).

Attempts to perform the sol–gel process in solutions of organic polymers usually failed, because the polymer was washed out during supercritical drying. The only success was observed with organic polymers capable of forming hydrogen bonds to the surface silanol groups of the inorganic matrix, such as poly(2-vinylpyridine).[132]

The more important modifications of aerogels are based on covalent bonding of the organic groups (Figure 11, bottom). In silicate systems precursors can be used in which the (functional) organic group is bonded through a hydrolytically stable Si–C link to the network-forming "inorganic" part of the molecule. Compounds of the type $R'Si(OR)_3$, in which R′ is the organic group modifying the inorganic gel, are usually employed. This kind of linkage is not possible for non-silicate systems because of the hydrolytic instability of M–C bonds. However, the organic groups can be introduced with bidentate ligands (Section 2.1.2). The preparation of organically modified xerogels is described in several reviews.[62, 133, 134]

In the remainder of this section we want to concentrate on organically modified SiO_2 aerogels, because these are best investigated. Schwertfeger et al. performed the sol–gel process with a mixture of a tetraalkoxysilane and an organically substituted trialkoxysilane $R'Si(OR)_3$ [Eq. (3)].[36, 129] The

$$x\,R'\text{–Si(OR)}_3 + (1-x)\,\text{Si(OR)}_4 + H_2O \xrightarrow{CH_3OH} [R'_x\text{–SiO}_{(2-0.5x)}\cdot H_2O/CH_3OH] \qquad (3)$$

R′-substituted silanes (R′ = alkyl, aryl) condense in a kind of two-step process to the network formed from the tetraalkoxysilane under alkaline conditions, because the rate of hydrolysis and condensation of $R'Si(OR)_3$ is slower than that of the corresponding tetraalkoxysilane $Si(OR)_4$. Thus, they modify the inner surface without influencing the typical aerogel properties. The process is similar to the formation of the core-shell structures mentioned in Section 2.1.2. for the preparation of multicomponent oxide aerogels. This kind of network formation was verified by Hüsing et al. by Raman spectroscopy. The spectra clearly show that $Si(OR)_4$ hydrolyzes and condenses before $R'Si(OR)_3$. The R′-substituted silane units therefore condense to the then existing network much later (hours to days).[135, 136] These results are confirmed by NMR spectroscopic investigations, which additionally show the inverse trends for acid-catalyzed mixed sol–gel systems.

The integration of functional organic groups into the aerogel matrix allows further extension of the application spectrum of SiO_2 aerogels (for example, towards catalysts or sensors) because now the chemical properties can also be varied.[136–140] Figure 13 shows a selection of functional organic groups which were already

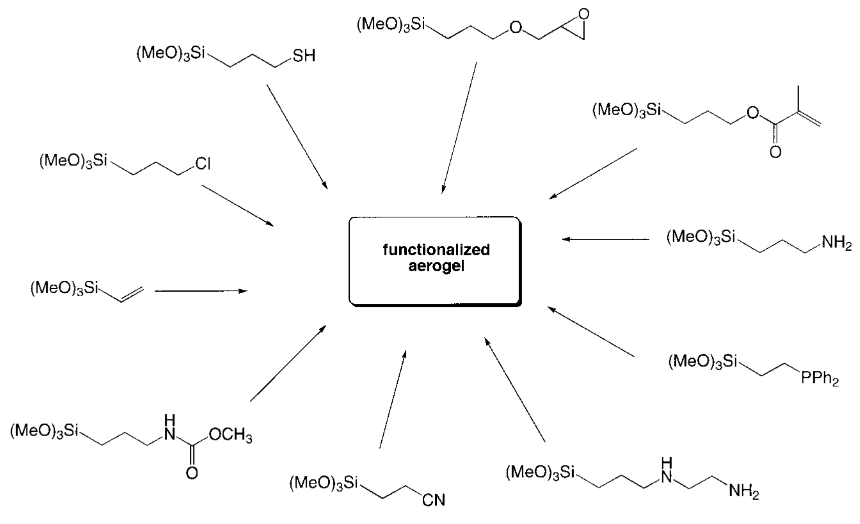


Figure 13. Silane precursors with organic substituents that were used for preparing functionalized aerogels.

successfully incorporated into aerogels. A two-step sol–gel mechanism was also established for most of these groups. Surprisingly, structural variations (porosity, inner surface area) in the functionalized aerogels are not induced as much by the properties of the functional group than by indirect influences on the sol–gel process. The trialkoxysilane basically acts as a co-solvent in the first phase of the reaction. Therefore, the tetraalkoxysilane is more diluted at this stage (resulting in a decrease in the network density), and a larger amount of water and catalyst is available for its reaction (resulting in larger particles).[140]

In another approach, the morphology (pore sizes, surface) of the aerogels is not tailored by the reaction conditions of sol–gel processing but instead by linking of the $Si(OR)_3$ groups in the precursors. Organic groups of variable length (for example saturated or unsaturated hydrocarbon chains, or polyaryls) substituted with $Si(OR)_3$ groups at both ends are used. An inorganic oxidic network in which the hydrocarbon chains bridge the inorganic building blocks is formed during sol–gel processing (Figure 14).

Loy et al. used precursors of the type $(RO)_3Si(CH_2)_n$-$Si(OR)_3$ with $n = 2, 6, 8, 10, 14$ without adding $Si(OR)_4$ for sol–gel processing under both basic and acidic conditions. They showed that the length of the spacer n decisively influences the later aerogel structure.[141] Ethylene- and hexamethylene-modified gels are highly porous and have high specific surface areas (about 700 m^2g^{-1}). The specific surface area decreases with increasing length of the spacer. The tetradecylmethylene-modified "aerogel" is nonporous, and SEM micrographs show a distinctly different morphology (whether this gel really is an aerogel is not discussed here, see Section 1).

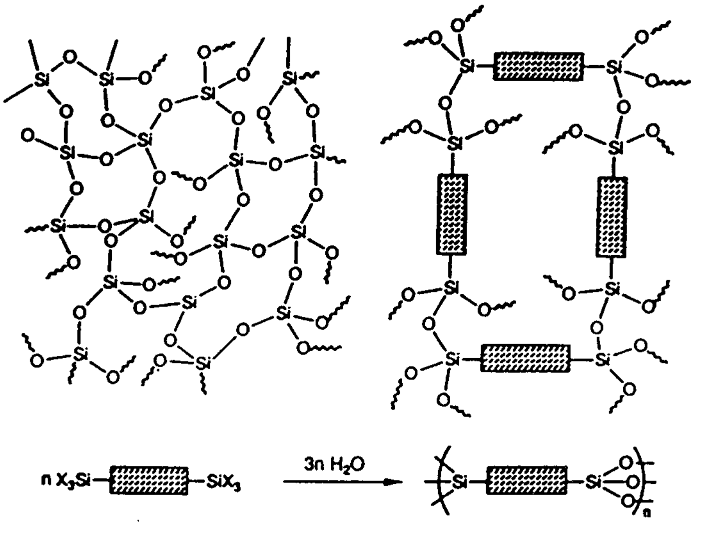
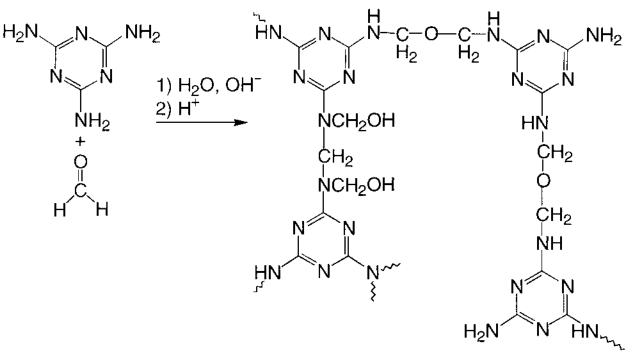


Figure 14. Schematic representation of silica gel (left) and inorganic–organic hybrid silsesquioxanes (right) as well as their syntheses (bottom, with drawings of the arenediyl, alkanediyl, and alkynediyl spacers; reproduced with friendly permission from ref. [141]).

2.3. Organic Aerogels

An interesting alternative to the inorganic aerogels was developed by Pekala et al. starting in 1987.[142] Purely organic aerogels were synthesized by polymerization of multifunctional organic monomers in dilute solution followed by supercritical drying.[143–145] Resorcinol/formaldehyde (RF) and melamine/formaldehyde (MF) were the first precursor mixtures for this organic sol–gel chemistry. Gelation was initiated by Na_2CO_3 or NaOH. The gels were then treated with dilute acid to increase the degree of cross-linking and, thus, to stabilize the network.

Resorcinol is a trifunctional monomer which can add up to three equivalents of formaldehyde. These substituted resorcinol derivatives then condense with formation of nanometer-sized clusters which then cross-link through groups at the surface (e.g. CH_2OH). For the polymerization of melamine with formaldehyde, either the monomers or MF polymers with low molecular mass can be used. Equation (4) shows the possible polymerization reactions.[146]



(4)

Topical developments in the area of organic aerogels are based on the polymerization of furfural with a phenolic Novolak resin (prepared by the reaction of phenol with formaldehyde) to give the "PF gels". A decisive advantage over RF or MF polymerization is that alcoholic solutions can be used, and the laborious solvent exchange before drying is avoided.[147]

The most important parameters for the synthesis of purely organic gels are the catalyst concentration and the pH of the solution. Their structure and properties—such as density, specific surface area, or particle and pore sizes—can be deliberately influenced by these variables.

Despite the structural differences originating from the different precursors, organic aerogels have some common properties. These include accessible pores with small diameters (≤ 50 nm), high specific surfaces (400–1000 m^2g^{-1}), and a solid matrix which is formed from either connected colloidal particles or polymeric chains of about 10 nm in diameter.

RF and MF aerogels are built from linked colloidal particles formed during sol–gel processing. The size and number of the clusters strongly depends on the ratio of resorcinol to catalyst (R:C). Typical values are in the range of 50–300. High catalyst concentrations (for example R:C = 50) result in particles with diameters of 3–5 nm that are connected to each other through broad particle necks (polymeric gels). If the R:C ratio is increased, the particle are larger in diameter (11–14 nm) and cross-link like pearls on a string (colloidal gels). The structure of MF gels was investigated by Ruben by high-resolution transmission electron microscopy.[146] Table 9 shows some representative data for organic aerogels.

Table 9. Some typical structural data and properties of organic aerogels.

Parameter	RF aerogel	MF aerogel	PF aerogel[147]
density [$g cm^{-3}$]	0.03 – 0.06	0.10 – 0.80	0.10 – 0.25
surface area [$m^2 g^{-1}$]	350 – 900	875 – 1025	385
pore diameters [nm]	≤ 50	≤ 50	
particle morphology [nm]	3 – 20	2 – 10	irregular shape, ca. 10 nm
application	precursor for carbon aerogels	–	precursor for carbon aerogels
color	dark red, transparent	colorless, transparent	dark brown

Pekala and Schaefer tried to apply kinetic models for network formation, developed for inorganic gels, to organic RF aerogels.[148] However, no fractal character was found for these gels in SAXS experiments. Nanophase separation, both initiated and limited by the cross-linking, was discussed as an alternative explanation for the network formation.[3]

3. Drying Methods

Evaporation of the liquid from a wet gel is very complex, and different stages can be distinguished. At the first stage, the gel shrinks by the volume that was previously occupied by the liquid. The liquid flows from the interior of the gel body to its surface. If the network is compliant, as for gels derived from alkoxides, the gel deforms (Figure 15).

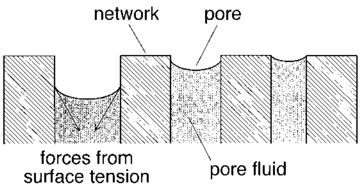


Figure 15. Representation of the contracting surface forces in pores of different size during drying. At the same pressure the curvature of all menisci in the pores is the same. For this reason the larger pores empty first (according to ref. [7]).

Upon shrinkage, OH groups at the inner surface approach and can react with each other. For example, new siloxane bridges are formed in SiO_2 gels. As drying proceeds the network becomes increasingly stiffer and the surface tension in the liquid rises correspondingly, because the pore radii become smaller. The second stage of the drying process begins when the surface tension is no longer capable of deforming the network and the gel body becomes too stiff for further shrinkage. This is the "critical point".[149] At this stage the tension in the gel becomes so large that the probability of cracking is at its highest. At the second stage of drying, the liquid/gas interface retreats into the gel body. Nevertheless, a contiguous funicular liquid film remains at the pore walls; that is, most of the liquid still evaporates from the exterior surface of the gel body. At the third stage of drying this film is raptured. Eventually only isolated pockets contain liquid, which can leave the network only by diffusion into the gas phase.[7, 150]

Two processes are important for the collapse of the network: First, the slower shrinkage of the network in the interior of the gel body results in a pressure gradient which causes cracks. Second, larger pores empty faster than smaller ones during drying; that is, if pores with different radii are present, the meniscus of the liquid drops faster in larger pores (see Figure 15). The walls between pores of different size are therefore subjected to uneven stress and crack.

The parameters influencing these capillary forces are well investigated, and strategies were developed to avoid cracking. Important options are, inter alia, the pore size (larger pores are more advantageous because the capillary force is inversely proportional to the pore radius),[151, 152] aging (the network becomes stiffer), or addition of tensides (reduction of the surface energy leads to a decrease in the capillary forces), organic templates, or drying-control chemical additives (DCCA).[153–157] Crack-free xerogels can be obtained by exact control of these parameters; however, large shrinkage cannot be avoided.

This situation is not sufficient for the production of aerogels. Methods have to be found to conserve the pore structure of the wet gels, that is, to avoid shrinkage. In the following sections possibilities are discussed with which the above-mentioned processes during drying and the occurrence of capillary forces can be avoided.

3.1. Supercritical Drying

In this procedure the solvent is put into the supercritical state, and therefore there are no liquid/gas interfaces in the pores during drying. The wet gel is placed in an autoclave and covered with additional solvent. Drying out of the samples (which would lead to the formation of cracks), is thus avoided, and the critical volume V_c is reached. After the autoclave is closed, the temperature is slowly raised resulting in an increase in pressure (pathway A in Figure 16). Both the

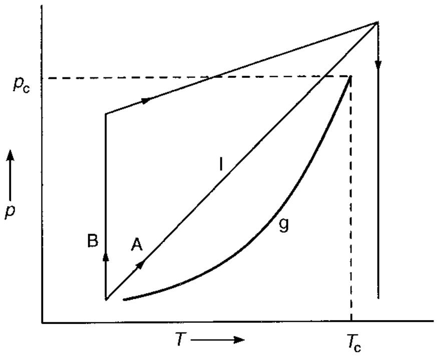


Figure 16. Schematic representation of the principle of supercritical drying. At the critical point (T_c, p_c) the densities of the liquid (l) and the gas (g) are equal. Supercritical drying can be performed along pathway A or B.

temperature and the pressure are adjusted to values above the critical point of the corresponding solvent (T_c, p_c) and kept there for a certain period of time. This ensures that the autoclave is completely filled with the supercritical fluid. The fluid is then slowly vented at constant temperature, which results in a drop in pressure. When ambient pressure is reached, the vessel is cooled to room temperature and then opened. Drying is often performed in a way that the vessel is prepressurized with nitrogen to avoid evaporation of the solvent (pathway B in Figure 16).[158] The phase boundary between the liquid and the gas must not be crossed during drying.

In principle, different organic solvents can be used for drying. The critical constants of the most common drying fluids are listed in Table 10. Supercritical drying is performed either "hot" (organic solvents) or "cold" (CO_2) depending on T_c.

Table 10. Critical constants for some solvents.

Solvent	T_c[°C]	p_c[Mpa]	V_c[$cm^3 mol^{-1}$]
methanol	240	7.9	118
ethanol	243	6.3	167
acetone	235	4.7	209
2-propanol	235	4.7	
H_2O	374	22.1	56
CO_2	31	7.3	94
N_2O	37	7.3	97

3.1.1. Drying in Organic Solvents ("Hot")

The pore liquid, which is usually an alcohol or acetone owing to the preparation conditions, is used as the supercritical fluid. About 250 °C and 5–8 MPa are needed to put the solvent in the supercritical state. Problems arise from the combination of high temperatures and high pressure as well as the flammability of these solvents. In August 1984 the main gasket in the lid of a 3000-L pressure vessel for the production of 60 × 60 cm^2 aerogel tiles failed in a pilot plant in Lund (Sweden). More than 1000 liters of methanol were released, and a big explosion destroyed the whole building.[159]

In addition to the risks connected with supercritical drying in organic fluids, rearrangement reactions in the gel network are highly probable because of the high temperatures. For example, in SiO_2 aerogels a modification of the surface may occur upon conversion of Si–OH into Si–OR groups, or processes such as during aging and ripening of the gels are accelerated. Small pores are thus filled, and particle necks strengthened. As a consequence, the resulting aerogels have a lower specific surface area, a narrow pore-radii distribution (elimination of microporosity), and a stiffer network.[160–163] Organically modified aerogels are particularly sensitive to the high temperatures, and functional organic groups may be destroyed during drying.[164] Phase separation and loss of stoichiometry (SiO_2/B_2O_3, SiO_2/B_2O_5)[165] or crystallization (SiO_2/TiO_2)[166] may occur in multicomponent gels.[1e, 167]

3.1.2. Supercritical Drying with CO_2 ("Cold")

An alternative to drying in organic solvents is the use of liquid carbon dioxide.[168-170] This method was developed by biologists for electron microscopy[171] and has the advantage of a very low critical temperature at a moderate critical pressure. However, a time-consuming solvent exchange is necessary. The time required for exchanging the original pore liquid for liquid CO_2 is determined by the diffusion of carbon dioxide into the gel, and is therefore dependent on the dimensions of the gel body. Another requirement is the miscibility of the pore liquid with carbon dioxide. For example, water and CO_2 are immiscible, and therefore an intermediate solvent exchange (e.g. water for acetone) is necessary.[107]

Structural changes, as observed during supercritical drying with alcohols, take place to a minor extent with CO_2. Therefore, the network of the wet gel can be conserved almost unchanged.

A modification of this method and its application in a continuous plant in which CO_2 is recycled was described by van Bommel et al.[172, 173] Heating and cooling of the autoclave is avoided by exchanging the solvent with CO_2 that is already in the supercritical state.

Brodsky and Ko showed that deliberate structural changes can be induced in SiO_2/TiO_2, ZrO_2, and Nb_2O_5 aerogels by varying the temperature above T_c during supercritical drying with CO_2. For example, the ratio between crystalline and amorphous regions, which is important for catalytic applications, can thus be influenced.[174]

3.2. Freeze-Drying

Another possibility for avoiding phase boundaries between the liquid and gas phases during drying is freeze-drying. The pore liquid is frozen and then sublimed under vacuum.

Several attempts were made to use this method for producing aerogels.[175–177] However, aging periods have to be extended to stabilize the gel network, the solvent must be exchanged for another with a low expansion coefficient and a high pressure of sublimation, and low freezing temperatures should be achieved by addition of salts. Another disadvantage is that the network may be destroyed by crystallization of the solvent in the pores. Cryogels are therefore only obtained as powders.

3.3. Ambient-Pressure Drying

To make aerogels interesting for larger scale commercial applications, one must avoid the most expensive and risky part of the preparation: supercritical drying. Therefore, the interest in alternative ways for exchanging the pore liquid in the gels by air is very high. However, with the above-mentioned processes (Sections 3.1 and 3.2) during drying in mind, the intention already appears to face a contradiction.

The capillary forces exerted by the meniscus of the pore liquid and the pressure gradient upon the large shrinkage of the network are the main reasons for the collapse of the filigrane structure (see Section 3). To dry aerogels at ambient conditions (subcritical drying), one has to strengthen the network to avoid its collapse (irreversible shrinkage). Additionally or alternatively, the contact angle between the pore liquid and the pore walls has to be influenced by deliberate modification of the inner surface and variation of the solvent to minimize the capillary forces.

Smith, Brinker, and Deshpande published the first synthesis of SiO_2 aerogels dried at ambient pressure in 1992.[178] In principle, their procedure involves a series of solvent-exchange processes and a modification of the inner surface.[179] The water/alcohol mixture in the pores of the gel is first exchanged for a water-free solvent, and the Si–OH groups at the surface are silylated (e.g. with chlorotrimethylsilane). The reactivity of the gel surface is thus reduced, and the surface hydrophobized. The actual drying process is performed after another solvent exchange. As expected, the gel shrinks strongly during evaporation of the solvent from the pores. However, no irreversible narrowing of the pores with formation of Si-O-Si bonds is possible because of the silylation. The gel therefore expands to nearly its original size after reaching the critical point. This is called the "spring-back effect". One of the prerequisites for this procedure is the strengthening of the network by exact control of the aging conditions. The network of the modified gels must be stable enough to tolerate a reversible shrinkage to 28% of its original volume![180]

Einarsrud et al. obtained similarly good results with another strategy.[181, 182] They increased the strength and stiffness of the network drastically by aging the wet gels in solutions of tetraalkoxysilanes in aqueous alcohols, and were thus able to avoid shrinkage during drying completely. The monomers added during aging mainly condense in the smallest pores and at the particle necks; the microporosity of the gels is thus lost. The gels can also be dried at ambient pressure between 20 and 180 °C because of the stiffer network.

The technique of ambient-pressure drying for preparing aerogels is still in its infancy, but is a highly topical area in which many research activities are concentrated. Since companies like Hoechst and Nanopore have taken over this method developed by Smith et al., a technically much simpler and therefore less expensive method is available. This makes the industrial application of aerogels economically interesting.[183]

4. Modification of Aerogels after Drying: Is There Chemistry after the Critical Point?

Chemical modifications are still possible even after drying. The intention of this section is to show some possibilities for improving or modifying the property profile of aerogels, in particular with respect to special applications. The examples show that this is another approach for chemically modifying aerogels which until now, however, was hardly used.

The subsequent doping of an aerogel host with active components appears attractive because of the high porosity of aerogels. However, follow-up treatment with a liquid phase is difficult because wet gels are formed again. As discussed in Section 2.1.2 aerogels can be doped with metals by impregnation with a suitable metal salt. The metal salt has to be introduced in alcoholic solution, and then the solvent has to be removed again in another supercritical drying step in order not to prevent destruction of the aerogel network.[122]

Another, more general possibility for subsequently modifying aerogels is their reaction with gaseous compounds. Early attempts were performed with gaseous dichlorodimethylsilane or other silylation reagents to remove the reactive silanol groups at the surface of the network and thus to hydrophobize the aerogel permanently.[184] There are now better possibilities for hydrophobation. However, doping with compounds from the gas phase is increasingly an attractive option. Even a homogeneous distribution in monoliths can be achieved.

Hunt et al. intensively investigated the reaction of aerogels with gaseous reactants, and called this method chemical vapor infiltration (CVI). Originally, the intention of this approach was to improve the thermal properties of aerogels by incorporation of carbon (see Section 5.2).[185–187] For this purpose, the aerogels were allowed to react with acetylene, methane, propane, xylol, or furfuryl alcohol in a stream of an inert gas at high temperatures. The temperatures necessary for pyrolysis depend on the gas and varied between 350 and 850 °C. The aerogels strongly favor decomposition of the organic compounds. Carbon is deposited as graphite on the inner surface of the aerogels, and even nanometer-sized carbon fibers, rings, and tubes were found.

The CVI method appears to be broadly applicable. Its potential is clearly visible for reactions in which new products are formed by chemical, thermal, or photolytic treatment. Cao et al. were able to prepare SiO_2/Si nanocomposites by decomposition of gaseous silanes (such as SiH_4 or $HSiCl_3$) in SiO_2 aerogels, which then showed photoluminescence upon irradiation with ultraviolet light.[188] Analogous reactions with ferrocene resulted in the deposition of iron particles in the aerogel matrix, which then displayed interesting magnetic properties.[188] Reaction of SiO_2 aerogels with $[W(CO)_6]$ and subsequent thermal decomposition of the metal carbonyl in the aerogel resulted in metallic tungsten particles. WN or WS_2 particles in aerogels were formed by follow-up treatment of the metal-doped aerogels with ammonia or sulfur. SiO_2 aerogels were analogously treated with gaseous $[Fe(CO)_5]$. Under an oxidizing atmosphere amorphous iron oxide/SiO_2 aerogels were formed, which were transformed into Fe_3O_4/SiO_2 (by reaction with additional $[Fe(CO)_5]$) or Fe_9S_{10}/SiO_2 aerogels (by reaction with H_2S).[189] Organic compounds can also be sublimed into the network through the gas phase as shown for a porphyrine derivative.[190]

Besides the treatment of aerogels with gaseous compounds, pyrolysis of organic groups which are part of the aerogel structure is another possibility for modifying aerogels. Schwertfeger et al. pyrolyzed the organic groups of inorganic–organic hybrid aerogels (see Section 2.2). They were thus able to coat the aerogel network with carbon nanostructures.[186a]

Pyrolysis reactions are most important for preparing carbon aerogels, which are of particular interest because they are the first electrically conducting aerogels.[191] They can be made by pyrolysis of resorcinol/formaldehyde or phenol/furfural aerogels under an inert atmosphere (1050 °C/N_2). Their structure and morphology basically corresponds to that of their precursors; that is, there are colloidal or polymeric gels (Table 11). The colloidal gels have spheric particles with

Table 11. Typical structural data of carbon aerogels.

skeletal density [g cm^{-3}]	2.06
density [g cm^{-3}]	0.05 – 0.80
specific surface area [m^2 g^{-1}]	600 – 800
pore size [nm]	< 50
particle morphology [nm]	3 – 20, amorphous
appearance	black, opaque

diameters of 12 – 15 nm which are loosely connected by graphitic ribbons. The polymeric gels have smaller particles (7 – 9 nm) connected by broad particle necks. Two factors mainly influence the properties of carbon aerogels: the ratio of precursor to catalyst during the preparation of the organic gels and the pyrolysis temperature.

5. Properties and Applications

SiO_2 aerogels are currently the aerogels with the highest potential for applications. They are not only the best investigated with regard to their preparation, structure, and properties, but can also be prepared with lower costs than other aerogels (cheaper precursors). There are already commercial applications. The development of the sol – gel process for non-silicate materials has recently boomed. One of the consequences is that the number of possibilities for varying aerogels becomes considerably larger. Non-silicate aerogels (see Section 2.1.2) increasingly play an important role, particularly in the search for new catalysts. In the case of organic aerogels, mainly their pyrolysis products (carbon aerogels) offer interesting new applications.

Since the main focus of this review is on the chemistry of aerogels, only a short overview on the properties of aerogels and the resulting applications will be given. Comprehensive information on these topics can be found in more physically oriented reviews.[1]

5.1. Optical Properties

The optical properties of SiO_2 aerogels and the derived inorganic – organic hybrid aerogels vary between transparent and translucent, depending on the preparation conditions. This means that the structure-forming units are smaller than the wavelength of visible light. However, inhomogeneities in the network in the nanometer range result in Rayleigh scattering. Therefore, aerogels appear yellowish under light and bluish against a dark background (see page 22). The portion of Rayleigh scattering correlates directly with the homogeneity of the gel network in the nanometer range. Objects that are viewed through an aerogel tile appear slightly blurred. Inhomogeneities in the micrometer range at the exterior surface of the aerogel body are responsible for this phenomenon.[192]

Numerous attempts were made to influence the optical properties of SiO_2 aerogels deliberately for their application in Çerenkov detectors (see below) or for transparent heat insulation. A transparency as high as possible is required for both applications. Initially, there were more physically oriented approaches to solving this problem, such as investigating the influence of the drying process, of water adsorbed to Si–OH groups, or of adsorbed organic components. It was found, for example, that supercritical drying with CO_2 results in more transparent materials than drying with organic fluids.[169, 193] Heating the aerogels also improves their transparency due to desorption of water and burning of organic components.[1d, 194]

However, these efforts are like putting the cart before the horse. Since scattering phenomena caused by inhomogeneities in the network are responsible for an insufficient transparency, it appears more logical to influence the transparency at its origin by optimizing the sol – gel parameters.[195, 196]

Russo and Hunt tried to quantify scattering in SiO_2 aerogels. They prepared aerogels from TMOS or TEOS under various conditions to determine the optimal precursor composition and gelation conditions.[196] They showed that transparency can be improved by lowering the concentration of water and the reaction temperature. Furthermore, base catalysis is more favorable, and aerogels prepared from TMOS show about nine times less scattering than the corresponding aerogels from TEOS. However, these are not necessarily general trends but instead specific statements for the investigated systems. The correlation of scattering measurements with other structural investigations (N_2 sorption according to Brunauer, Emmett, and Teller) was not successful.

Emmerling et al. investigated the pH dependence of the transparency of gels from TMOS. They showed that there are two distinct extinction minima (high transparency) at pH 1 and 13. They concluded from the correlation of these results with those from SAXS measurements that the particle diameter has to be kept small to improve the optical quality. Interestingly, the transparency was improved in this case when more than a stochiometric amount of water was used for hydrolysis and condensation.[197, 198] In subsequent work the same group correlated the transparencies of SiO_2 aerogels prepared in one step from TMOS, gels from water glass, and gels from the two-step synthesis with the nanostructure of their networks (SAXS, Ultra(U)-SAXS). Aerogels from water glass showed the lowest transparency because of the larger particles and the presence of sodium ions. The aerogels prepared in two steps were distinctly more transparent than gels prepared in one step, probably because smaller clusters are formed during the acid-catalyzed first step.[197]

The latter results were confirmed by Cao and Hunt.[199] They also showed that aerogels prepared by the two-step process (acid hydrolysis and subsequent base-catalyzed condensation) are more transparent than the corresponding aerogels prepared in one step (acid or base catalysis).

Çerenkov detectors

Çerenkov radiation is emitted by charged particles such as piones, muones, or protons if they move faster than light in a medium. A cone-shaped electromagnetic shock wave is formed, from which light is emitted. The velocity of the particles can be calculated from the cone angle. Since the speed of light depends on the refraction index of the medium, media with different refraction indices were searched. SiO_2 aerogels with refraction indices between 1.007 and 1.024 offer a range not covered by the previously used compressed gases or liquids. Aerogels as solid materials additionally allow easier construction of the detectors and are therefore ideal materials for this application.[200, 201] They are now installed in several Çerenkov detectors worldwide, and the amount of aerogel tiles produced for this application is impressive. For example, 1000 liters of SiO_2 aerogels were produced by Henning for an experiment at the CERN in Geneva, and Poelz et al. equipped a detector (TASSO) at the German Electron Synchrotron (DESY) in Hamburg with 1700 liters of SiO_2 aerogel.[16a]

5.2. Thermal conductivity

The thermal conductivity of aerogels is extraordinarily low. It is made up of three components: thermal transportation by the gas phase, by the solid phase, and by radiation. Figure 17 schematically shows the contribution of these components depending on the bulk density. The solid conductivity clearly increases with increasing density, whereas the reverse is true for the gas and radiative transport. The minimum for the total thermal conductivity is at a density of about 0.150 $g cm^{-3}$.[200] Heat transport by the gas phase can be avoided by evacuation of the system. For example, an evacuated SiO_2 aerogel at about 300 K shows a thermal conductivity of only 0.010 $W m^{-1} K^{-1}$, compared to 0.020 $W m^{-1} K^{-1}$ in air.[202] This is not a special property of SiO_2 aerogels. Thermal conductivities as low as 0.012 $W m^{-1} K^{-1}$ were measured for non-evacuated organic RF aerogels.[203]

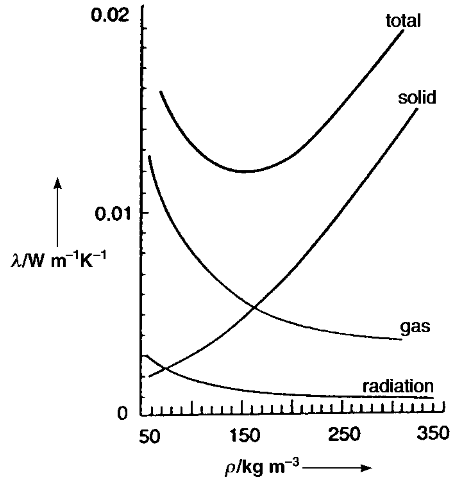


Figure 17. Composition of the thermal conductivity of aerogels: gas, solid, and radiation transport λ depending on the density ρ of the material (reproduced with friendly permission from ref. [200]).

Another possibility for reducing the thermal conductivity of SiO_2 aerogels is to reduce the radiative heat transport. This is more important at high temperatures, because the radiation maximum is then in a wavelength range in which SiO_2 does not sufficiently absorb (3–5 μm). Reduction of the thermal conductivity at these temperatures is possible by doping the aerogels with infrared opacifiers, such as carbon soot or TiO_2. These compounds can be mixed in a highly dispersed form to the precursor solution during sol–gel processing or to the sol.[203] Another possibility is the generation of carbon in the aerogel by pyrolysis of organic gases or covalently bonded organic groups of hybrid aerogels (see Section 4). The latter method leads to a particularly efficient decrease in the thermal conductivity (0.012 $W m^{-1} K^{-1}$ in air at 300 K), because the aerogel skeleton is partially covered with nanometer-sized carbon structures.[204] The improvement of heat-insulation properties is a continuing topic of intense research.[16]

Aerogels have the lowest thermal conductivities of all solids (Figure 18). There is no question that they belong to the best heat-insulation materials currently available. Additional advantages are their nonflammability and transparency (see page 22 and Figure 1). However, a big problem for the insulation of windows is the production of large aerogel panels.[205] Conventional window systems cannot be equipped with the commonly prepared granulate, which is not transparent due to the roughness of its surface; they can only be used for "daylight windows" (for example bathroom, staircase, or ceiling windows). The scattering of the sunlight in the granulate layer is here rather advantageous, because a diffuse lighting of the rooms is achieved.

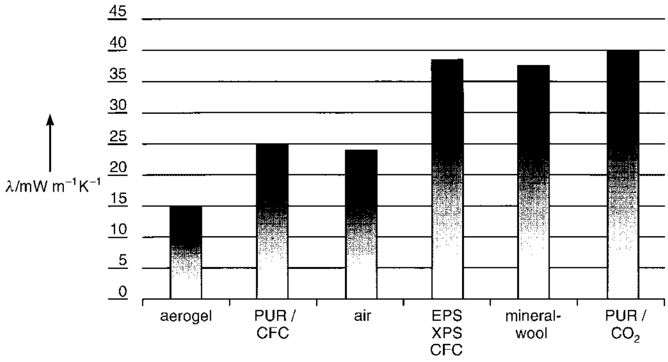


Figure 18. Comparison of the thermal insulation properties of some commercially available insulating materials. PUR: polyurethane foam, CFC: chlorofluorohydrocarbons; EPS, XPS: expanded and extruded polystyrene (reproduced with friendly permission from ref. [183]).

In addition to transparent thermal insulation, applications for a variety of other insulation problems are conceivable for which the transparency of the insulating material is not necessary, for example in cooling or heating systems and high-temperature batteries.[206, 207] Aerogels can also be utilized for the passive use of solar energy, for example for paneling house walls (Figure 19) or for coating solar-energy collectors.[208, 209] In the Cité Solaire in Ardon (Switzerland) a house was built using an aerogel granulate as a translucent insulating material. A layer of the transparent aerogel allows the penetration of the sun's radiation to the blackened wall, but not the escape of the heat generated there.[210]

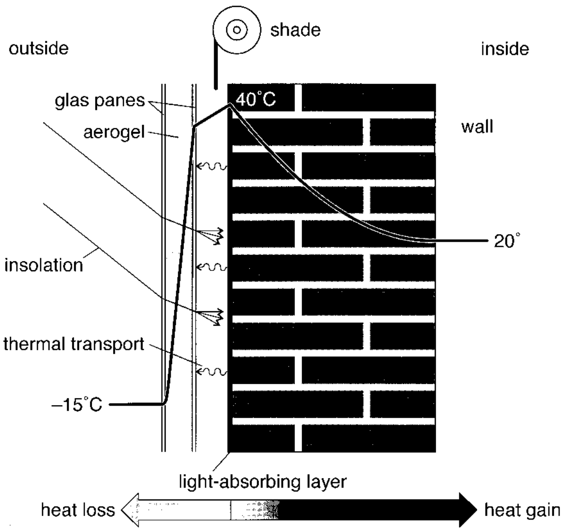


Figure 19. Concept for energy saving by passive use of the solar energy (reproduced with friendly permission from ref. [200]).

5.3. Hydrophobicity

One of the big problems of unmodified SiO_2 aerogels, in particular for technical use, is their long-term stability under a humid atmosphere. Owing to the large number of silanol groups on the inner surface of the material, adsorption and capillary condensation of water and eventually cracking of the gel body by the resulting capillary forces results. Approaches to hydrophobize aerogels permanently were therefore investigated quite early. The possibility of allowing an aerogel to react subsequently with a silylating reagent, such as chlorotrimethylsilane, has the disadvantage of a complicated processing procedure. This kind of modification is only possible by the gas phase (see Section 4).

Hydrophobation at the alkogel stage is time-consuming, since the diffusion rate of the silylating reagent into the pores is a limiting factor. However, this process is a key step in the prevailing ambient-pressure drying of aerogels (see Section 3.3); that is, aerogels prepared by this method are inherently hydrophobic.

Schwertfeger et al. prepared permanently hydrophobic aerogels with a one-step process using a mixture of a tetraalkoxysilane and an organically substituted trialkoxysilane for sol–gel processing (see Section 2.2).[36] They were able to prepare aerogels that floated on water for months (see full-page picture on page 22) while retaining the typical aerogel network.

5.4. Mechanical and Acoustic Properties

Mechanical properties have many aspects. Among others, rigidity, brittleness, and form stability as well as the method of investigation have to be considered. Although the rigidity of aerogels is low because of their structure and the brittleness of the SiO_2 particles, it is sufficient for most applications. The compressive strength of monolithic SiO_2 aerogels is between 0.15–0.30 $N\,mm^{-2}$, depending on the density, with an elastic compression of about 2–4%. The rigidity in vacuum is distinctly higher. The tensile strength is about 0.020 $N\,mm^{-2}$.[211]

One of the decisive parameters for the mechanical properties is the connection of the network in the nanometer range, which strongly depends on the preparation conditions. For example, aerogels prepared under acidic or neutral conditions are about twice as stiff as the corresponding samples prepared under base-catalyzed conditions.[212] Investigations of organically modified aerogels showed that the elastic properties of SiO_2 aerogels can also be improved by chemically modifying the precursors. Ultrasound measurements were used for these investigations. The longitudinal sound velocity is connected with one of the elastic constants (which correlates with the Youngs modulus), and the density of the aerogel. The reason for the improved elastic properties of hybrid aerogels is probably that the presence of alkyl or aryl groups at the surface of the secondary particles impairs stiffening of the particle necks by Ostwald ripening.[137]

Kramer et al. were able to prepare aerogels with very good elastic properties by cocondensation of flexible polydimethylsiloxanes (PDMS) with TEOS. An elastic compression of up to 30% was observed for aerogels into which 20 wt% of PDMS was incorporated.[213]

The particular network structure of aerogels results in impressive acoustic properties which, as mentioned above, correlate with the elastic properties.[214] The sound velocities in SiO_2 aerogels of 100–300 $m\,s^{-1}$ are among the lowest for inorganic solids (this is noteworthy when one considers that sound velocities of 5000 $m\,s^{-1}$ were measured in quartz glass).[215, 216]

The product of density and sound velocity is the acoustic impedance. Since both are low, SiO_2 aerogels have the lowest impedances of all solid materials ($Z = 10^4 - 10^5\,kg\,m^{-2}s^{-1}$). This allows interesting applications. For example, aerogels can be used as $\lambda/4$ layers for matching the high acoustic impedance of piezo ceramics to the low impedance of air. The efficiency of these devices is considerably increased by decreasing the reflexion losses at this interface.[217, 218]

5.5. Applications in Catalysis

All the advantages of sol–gel processing for preparing catalysts or catalyst supports—in particular the controllable dispersion of the active component and the possibility of deliberately influencing the microstructure—also apply for aerogels. Additionally, typical structural properties predestinate them for these applications: the extremely high inner surface (which is easily accessible because of the open porosity), the large pore volumes, the excellent temperature stability, and the high selectivities in catalytical processes. Nearly all oxides relevant for catalytical applications can be prepared as aerogels. This is also true for binary and ternary compositions, mixtures of metal oxides, or metal particles on oxide carriers. Furthermore, aerogels can be prepared as powders, granulates, or monolithes, either amorphous or with crystalline portions (see Section 2).

Despite these advantages, the use of aerogels in catalysis has only been increasingly investigated since 1974. The number of publications rises drastically every year. Considerable progress was achieved in solving problems originating from the low density and the low thermal conductivity, that is, pressure drops and bad heat dissipation in the catalyst bed. For example, heat-dissipating materials can be added, or the aerogels can be deposited already during their preparation (i.e. in the autoclave) on a carrier (such as Raschig rings, metal tubings, cordierite honeycombs, wire mesh screens, boiling stones, and others).[84]

It is impossible to list all the investigated systems here; they are summarized in more specialized reviews by Pajonk[1c] as well as Schneider and Baiker.[1e] The following incomplete selection is intended to give an impression of the numerous possibilities: nitroxidation of hydrocarbons to nitriles (NiO/Al_2O_3 with SiO_2 and MgO, PbO/ZrO_2),[105, 112] hydrogenation of nitrobenzene to aniline and of toluene to methylcyclohexane (Ni/SiO_2, Pd/Al_2O_3),[126] hydrogenation and hydrogenolysis after hydrogen "spillover" activation (ZrO_2, SiO_2, MgO, Al_2O_3),[219] isomerizations (Nb_2O_5, Nb_2O_5/SiO_2),[91, 92] Fischer–Tropsch syntheses (Fe_2O_3/Al_2O_3, Fe_2O_3/SiO_2),[102] polymerization of ethene or propene ($TiCl_4/Al_2O_3$),[220] $deNO_x$ reactions ($Fe_2O_3/Cr_2O_3/Al_2O_3$, Pt/C),[143, 221] catalysis for combustion of car exhaust (Pd/Al_2O_3, Pt/Al_2O_3, $Pd/Al_2O_3/SiO_2$),[124, 222] and fluorinations (Cr_2O_3).[85]

5.6. Aerogel Films

Films (coatings) are one of the most important applications of sol–gel materials. Completely dense or partially densified films are prepared in most cases. However, there are numerous applications in which porous films are required. Aerogels with their high porosity and the resulting unique physical properties are highly interesting for such applications. Although aerogels can in principle also be prepared as films, supercritical drying is here a very delicate issue. Nevertheless, aerogel films were synthesized in some laboratories.[223, 224] The possibilities provided by ambient-pressure drying (see Section 3.3) eliminate the principal obstacles for preparing highly porous films.[225–227] The development and use of aerogel films is clearly just in its infancy.

Applications of aerogels as $\lambda/4$ layers for acoustic impedance matching or as catalytically active layers on carriers were already mentioned. Other examples for the application of aerogel films from the Lawrence Livermore National Laboratory in California are optical coatings for solar cells because of their low refractive index (aerogel films prepared for this purpose are subsequently fixed to the surface of the solar cell).[228] The currently used glass layers with high refractive indices can thereby be replaced by aerogels. More light reaches the active surface because of the lower Fresnel scattering losses. The efficiency of the solar cell is thus increased. Thermal applications are also interesting. For example, IR detectors can be coated to obtain a kind of shield against the heat radiating from the substrate.

Other applications for which aerogel films can compete with existing technologies are in microelectronics; here, the low dielectric constant of aerogels plays a particularly important role. With a value of lower than 2.0, they offer important progress in the velocity of electric curcuits. In addition, the dielectric constant is easily controlled because it is directly correlated with the porosity and thus the density of the materials.

This is only a short list of interesting possible applications for highly porous films. Many more will certainly emerge in the future.

5.7. Carbon Aerogels

Carbon aerogels are very well suited as electrode materials because of their low electric resistance ($< 40\ m\Omega\,cm$), their controllable pore-radii distribution (1–50 nm), and their high specific surface area. When a voltage is applied, a thin polarization layer with high capacity is formed on the large surface area. More charge can be stored than with conventional capacitors, because the surface area per volume is very high for aerogels. Compared with other materials (carbon powder or fibres), aerogels have the big advantage that they can be prepared as monoliths.[191]

5.8. Other Applications

Aerogels can be sintered at low temperatures and can therefore be processed to extremely pure and totally homogeneous glasses.[229, 230] The inner surface area and the porosity decrease during sintering. The pore structure can therefore be modified in a controlled way by partial sintering. This was used, for example, for producing gas filters with pores in the range of 20–100 nm.[231] Partially sintered aerogels can resist the tensions of a gas/liquid interface because their texture is strengthened during sintering. They can therefore be used for the storage, thickening, or transport of liquids, for example rocket fuels; in this case the low weight of aerogels is particularly advantageous.[1b]

There are no limits to the fantasy required to find other potential applications of aerogels. The concluding examples show that also exotic applications can be considered: SiO_2 aerogels are suitable as ecologically sound insecticides against pests in grain and seeds or on the ground, such as mites, ticks, cockroaches, or silver fish.[232,233] As a chemically inert dust with small particles and a high specific surface area, aerogels can remove the protecting lipide layer of insects by abrasion or adsorption. They are then killed by rapid loss of body liquid.

SiO_2 aerogels are currently one of the standard media for collecting cosmic dust,[234] and they are fixed on the outside of spacecrafts.[235] Aerogels have the advantage that they are extremely light with a unique mesostructure which is also transparent. This enables a "soft landing" of very fast extraterrestrial particles hitting with a velocity of more than $3\ km\,s^{-1}$, and also allows their later investigation by optical methods.

6. Final Remarks

The preparation of aerogels is "nanotechnology", because their unique optical, thermal, acoustic, and mechanical properties originate from the combination of a solid matrix (with a certain chemical composition) and nanometer-sized pores filled with air. We wanted to show in this review that there is a direct connection between the chemistry of the sol–gel process and the structure of the gels on one hand, and between the structure and the properties of the aerogels on the other. The choice of the precursors and the chemical reaction parameters already determines the physical properties of the final materials.

Physical research currently dominates the area of aerogels. The unique physical phenomena were and are intensively investigated, and are already well understood in many cases. In contrast, most aerogels are prepared empirically. Although the chemical principles are known, we are far away from a chemical "design" of aerogel properties and from an understanding of structure–property correlations. There is thus a wide field for applied chemical research. This is particularly true for the transfer of the physical effects investigated for simple systems, mostly SiO_2, to chemically more complex systems. Porous materials with totally new combinations of properties and applications can be expected by the combination of new chemical compositions with deliberately prepared micro- and nanostructures.

A big push forward can be expected in the next few years. The possibilities originating from ambient-pressure drying will provide strong impetus to preparative chemical research, because aerogels can now be prepared with standard laboratory equipment. The new drying methods have made the preparation process much "more chemical". There is now room for more extensive chemical modifications of the profile of properties of aerogels.

The new drying methods are also a big step forward from an economic point of view. Apart from special applications in which material costs only play a minor role, the rather high price of supercritically dried aerogels has hindered a broader range of applications. The most important area for the application of aerogels are all kinds of thermal and acoustic insulation. There is no doubt about the physical and ecological advantages (nontoxic, nonflammable, readily disposable) of SiO_2 aerogels over most other materials on the market. However, according to a study of the Austrian Academy of Science,[236] the period of amortization for aerogel insulation is relatively long when one considers the materials and energy streams over the whole preparation process (including the production of the precursors), even for favorable applications such as daylight elements. The new drying techniques will probably make the technical preparation much cheaper and will thus make aerogels more competitive.

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