*Chem. Rev.* **2002,** *102,* 4243−4265

# Chemistry of Aerogels and Their Applications

Alain C. Pierre[†] and Gérard M. Pajonk*[,‡]

*Institut de Recherches sur la Catalyse, UPR 5401 du CNRS, Université Claude Bernard Lyon1, 2 avenue Albert Einstein,*
*69626 Villeurbanne Cedex, France, Laboratoire d'Application de la Chimie à l'Environnement, UMR 5634, Université Claude Bernard-Lyon 1,*
*43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France*

*Received November 26, 2001*

## Contents

## I. Introduction

In the present review, aerogels designate dried gels with a very high relative pore volume. These are versatile materials that are synthesized in a first step by low-temperature traditional sol−gel chemistry. However, while in the final step most wet gels are often dried by evaporation to produce so-called xerogels, aerogels are dried by other techniques, essentially supercritical drying. As a result, the dry samples keep the very unusual porous texture which they had in the wet stage. In general these dry solids have very low apparent densities, large specific surface areas, and in most cases they exhibit amorphous structures when examined by X-ray diffraction (XRD) methods. In addition, they are metastable from the point of view of their thermodynamic properties. Consequently, they often undertake a structural evolution by chemical transformation, when aged in a liquid medium and/or heat treated.

As aerogels combine the properties of being highly divided solids with their metastable character, they can develop very attractive physical and chemical properties not achievable by other means of low temperature soft chemical synthesis. In other words, they form a new class of solids showing sophisticated potentialities for a range of applications. These applications as well as chemical and physical aspects of these materials were regularly detailed and discussed in a series of symposia on aerogels,[1−5] the last of them being held in Albuquerque in 2000.[6] Reviews were also regularly published, either on both xerogels and aerogels[7] or more focused on the applications of aerogels.[8−13]

The particularly interesting properties of aerogels arise from the extraordinary flexibility of the sol−gel processing, coupled with original drying techniques. The wet chemistry is not basically different for making xerogels and aerogels. As this common basis has been extensively detailed in recent books,[14] it does not need to be reviewed. Compared to traditional xerogels, the originality of aerogels comes from

---

* To whom all correspondence should be addressed.
[†] Institut de Recherches sur la Catalyse.
[‡] Laboratoire d'Application de la Chimie à l'Environnement.

10.1021/cr0101306 CCC: $39.75

Alain C. Pierre received his Ph.D. degree from the Massachusetts Institute of Technology. In 1973 he joined industrial research for the development of new materials in the Aerospatiale Industry in France. Then, in 1987, he moved as a professor to the University of Alberta (Edmonton, Canada), to focus on research about the sol–gel process. Since 1995, he has been a professor at the University Claude Bernard-Lyon 1 in France. His current research interest is on oxide aerogels, particularly on the interface between silica and the living world and on the development of new catalysts by encapsulation of enzymes in oxide aerogels

Gerard M. Pajonk received his Ph.D. degree from University Claude Bernard Lyon 1 in heterogeneous catalysis in 1970 and spent a post-doc period at Stanford University. His scientific interests are catalysis, selective oxidations and hydrogenation reactions, spillover, and materials synthesis using sol–gel methods under the forms of xero-, aero-, and cryo-gels. He is Professor of Physical Chemistry at University Claude Bernard Lyon 1. He holds many tens of patents in catalysis as well as in materials synthesis.

the technique used to evacuate the liquid. Conventionally, the term “aerogels” has been used to designate gels dried under supercritical conditions. More recently, materials dried by other techniques such as freeze−drying, produce materials initially known as cryogels, now also termed aerogels. However, such an extension can be argued. It can only be justified if the pores actually occupy a very high percentage of a sample volume, e.g., above 90%, although no official definition exists.

All materials that can be synthesized as wet gels by the sol−gel process can then be dried by the supercritical method to obtain aerogels. New properties based upon the very open texture of these materials make them outstanding for some applications. To cite a few examples, aerogels can indeed contribute to high added value technical solutions for domestic applications such as in buildings double window glazing as transparent thermal super-insulators or for more restricted applications demanding a high degree of technology in space exploration and electronics. In any case, a striking difference appears between two classes of compounds: on one hand those wet gel monoliths which can be dried to aerogel monoliths without cracking, on the other hand those wet gels which can only be obtained as fluffy aerogel powders after supercritical drying. The former categories comprise mostly silica or the silicates where silica is a major component,[15] organic polymeric aerogels, and carbon aerogels derived from these organic aerogels. For other oxides, monolithicity with a mechanical resistance sufficient for easy handling has not really been achieved. For instance, alumina—actually boehmite AlO(OH)—monolithic gels have been made by Yoldas.[16] But these are xerogels dried by evaporation, which therefore undertake a significant contraction during drying and reach a dry specific pore volume (∼60%) much lower than silica aerogel monoliths.

In what follows, we therefore first summarize very briefly the chemistry of sol−gel processing, simply to stress out the main chemical differences between silica, carbon, and organic polymers on one hand, the other oxides on the other.

## II. Sol–Gel Processing

Sol−Gel processing designates a type of solid materials synthesis procedure, performed in a liquid and at low temperature (typically $T < 100$ °C). As previously mentioned, the physics and chemistry involved in sol−gel synthesis has been detailed in many review papers as well as in books.[17,18] The solids which were addressed were then exclusively inorganic: mostly oxides or hydroxides, formed by chemical transformation of chemical solutes termed precursors. The solid is formed as the result of a polymerization process which involves the establishment of M-OH-M or M-O-M bridges between the metallic atoms M of the precursor molecules. Such transformations are the equivalent of the polymerization process well-known to occur in organic chemistry and which consists of the establishment of direct bonds between the carbon atoms of organic precursors. Actually, the traditional division between inorganic and organic chemistry has been such that, during a long time, these two fields of sol−gel science were addressed by quite different groups of chemists, with virtually no contact between them. More recently, these two fields of chemistry have begun to merge with the development of hybrid organic−inorganic gels.[19] Moreover, supercritical drying could be applied with reasonably good success to make monoliths, not only of silicates, but also of organic polymers.

Regarding inorganic gels, that is to say mostly oxides, independent solid colloidal particles (i.e., nanoparticles with a size below a micrometer) are often formed, in a first step of the process. Each colloidal particle has a more or less densely cross-linked internal structure, as illustrated in Figure 1a. It is usually easy to maintain such particles in a dispersed state in the solvent, in which case a colloidal suspension also termed a sol is obtained. In

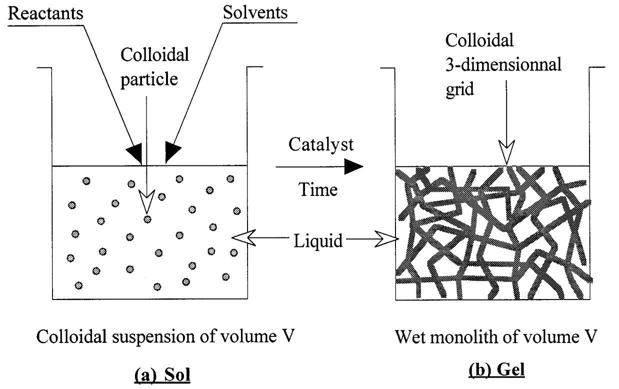


**Figure 1.** The sol−gel process: (a) sol; (b) gel. After Pajonk.[20]

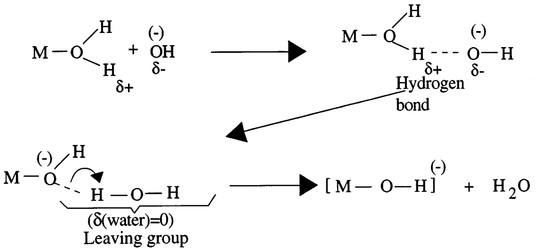
a second step, these colloidal particles can be made to link with each other, while they are still in the solvent, so as to build a three-dimensional open grid, termed a gel (Figure 1b). The transformation of a sol to a gel constitutes the gelation process, and the gels which are obtained are then termed colloidal gels. On the other hand, it is also quite possible to directly form some gels from rather linear polymer formed from a precursor solution, without the intermediate occurrence of individual particles. When this occurs, the gels are termed polymeric gels.

Historically, major milestones in the development of sol−gel processing involved the contributions of quite different fields of chemistry. The founder of Colloid Science is considered to be Graham.[21] Major contributions in understanding the physical chemistry principles involved in the kinetic stabilization of a sol by electrostatic interactions were made by Derjaguin, Landau, Verwey, and Overbeek according to a theory presently known as the D. L. V. O. theory.[22,23] As for the phenomenon of gelation itself, its understanding was independently achieved for organic gels by Flory[24] and Stockmayer.[25] Gelation is now best studied within the recent mathematical theories of percolation introduced by Hammersely,[26] as well by Monte Carlo computer simulation methods. These new methods showed that the phenomenon of gelation could be described as a particular critical phenomenon in thermodynamics. They also introduced the use of the fractal dimension to describe the network structure of gel, more particularly aerogels, which is a characteristic of some geometrical objects described in a further paragraph.[27]

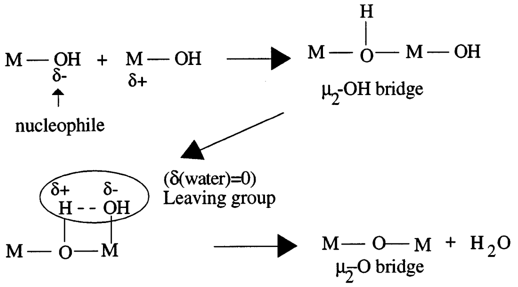
## A. Inorganic Gels

The first inorganic gels accidentally synthesized by chemists were silica gels made by Ebelmen in 1846.[28] But natural gels of an organic nature are common in the living world. As an example, the eye vitrea is a natural gel. Overall, gels are materials at the border between organic, inorganic, and biological chemistry. Aerogels, which are only at the beginning of their development, are certainly among the most amazing of these new materials because they can retain, in the dry state, the very open type of network which they had in the wet state.

The first precursors used in sol−gel processing were metallic salts $MX_n$ in which a metal M is linked to some number n of anions X. In solution in aqueous solvents, these precursors are present as ionic species in which the metal atoms exist as solvated cations $M[H_2O]_N{}^{z+}$. The reactions to form sol particles and gels comprise hydrolysis reactions which replace $H_2O$ groups by OH ones with loss of protons and, condensation reactions leading to the construction of M-OH-M “ol” bridges or M-O-M “oxo” bridges with elimination of water molecules. Several concurrent mechanisms have been proposed for these reactions. For instance, an $H_2O$ ligand can first be replaced by an $OH^-$ one by direct substitution. A proton exchange mechanism through transition hydrogen bonds according to eq 1 proposed by Livage et al.,[14] similar to that occurring in the ionization of water itself, is also possible. Next, various condensation reactions can lead to the formation of ol bridges or oxo bridges, as in the reaction mechanism in eq 2.[14]



(1)



(2)

Overall, a model termed the partial charge model was proposed by Livage et al.,[14] as a development of the electronic transfer concept developed by Sanderson.[29] This model makes it possible to establish rather satisfying numerical predictions on the complexes formed in solution. It relies on the building of transition states by nucleophilic or electrophilic attacks, followed by redistribution of the electronic cloud (i.e., modification of the polarity of each bond) among all the atoms in a given transition state. As a result, the partial charge as well as the electronegativity of each atom in this transition state are modified. When a group of near neighbor atoms in the transition state reaches an added partial charge which is an integer (e.g., −1, 0, or +1, etc.), this group of atoms becomes electronically “self sufficient”, and it separates as a leaving group. A leaving group can be an anion, a cation, or a neutral molecule such as $H_2O$ when the added partial charge ($2\delta_H + \delta_O$) reaches 0.

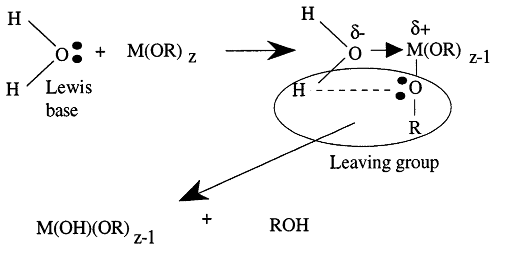
For silica gels, an important inorganic precursor was sodium metasilicate $Na_2SiO_3$, also termed waterglass, which reacts with an acid such as HCl according to reactions similar to eq 3:

$$\mathrm{Na_2SiO_3} + 2\mathrm{HCl} + (x-1)\mathrm{H_2O} \rightarrow \mathrm{SiO_2}\cdot x\mathrm{H_2O} + 2\mathrm{NaCl} \quad (3)$$

As indicated by this reaction, a salt is produced, which must be eliminated by tedious dialysis. This synthesis method was first used by Kistler to produce the first aerogels.[30] As water-glass is cheap, an industrial process based on this precursor was developed for some time by BASF.[31] The main inconvenience of these precursors is that, most frequently, they require water as the solvent, followed by dialysis to eliminate the foreign ions. This does not give much flexibility in adjusting the hydrolysis and condensation reaction rates at the desired level, hence, to tailor the texture of a gel.

The use of metallic salts as sol–gel precursors has recently seen a renewed interest with the use of organic solutions, in which an organic, slow “proton scavenger” is dissolved.[32] The metallic salt must be in its hydrated form, e.g., $\mathrm{Cr(NO_3)_3}\cdot 9\mathrm{H_2O}$. The solvent can be ethanol, and the slow proton scavenger can be propylene oxide or an epoxide (e.g., 1,2-epoxybutane, 1,2 epoxypentane, 2,3-epoxy(propyl)benzene, trimethylene oxide, glycidol, epichlorohydrin, epibromohydrin). The hydrated cation $[\mathrm{M(H_2O)_N}]^{z+}$ must be acidic, so that a slow deprotonation reaction occurs with the proton scavenger. The protonated scavenger undertakes an irreversible ring-opening reaction with the metal salt anion, while the solvated cation transforms to aquo-hydroxo species $[\mathrm{M(OH)}_x(\mathrm{H_2O})_{\mathrm{N}-x}]^{(z-x)+}$ which undertake condensation reactions later on. Nice wet gel monoliths can in this way be obtained with Cr, Fe, Al, Zr, and other cations.[32]

The second generation of precursors, which are now largely used, are alkoxides $\mathrm{M(OR)}_n$. These chemicals are compounds formed by combination of a metal M with an alkoxide group OR, where R designates an alkyl group. They are characterized by the existence of M–O polar covalent bonds in their molecules. In practice, they are often available as more or less small polymerized complexes, often in solution in their parent alcohol. Their transformation is carried out in an organic solvent and water becomes a reactant added in controlled proportion. The sol–gel reactions in which they participate are hydrolysis reactions (eq 4), which lead to the replacement of OR ligands by OH ones, followed by condensation reactions similar to those occurring with metal salts.



(4)

## B. Chemical Differences between Silica and Other Oxides Sol–Gel Chemistry

The mechanisms of hydrolysis reactions depend on nucleophilic chemical attacks on the metal M,[14] which depends on the partial positive electronic charge $\delta^+$ carried out by M. Many metal atoms such Al, Zr, and Ti carry a positive partial charge of significant magnitude, e.g., ~0.65 and 0.63 in $\mathrm{Zr(OEt)_4}$ and $\mathrm{Ti(OEt)_4}$, where Et designates an ethyl group. Hence, the nucleophilic attack of O atoms from water molecules, which carry a negative partial charge $\delta^-$, is easy. Both the hydrolysis and condensation reactions of these precursors are fast, so that it becomes difficult to experimentally measure them separately. Overall, with these precursors, it is necessary to globally reduce the gelation kinetics (hydrolysis plus condensation) to obtain gels. Moreover, the oligomers (i.e., polymers with a relatively small number of metal atoms), which are progressively formed as a result of hydrolysis and condensation reactions, are relatively packed clusters, such as the $\mathrm{Al_{13}}$ intermediate cluster in Figure 2[33] from which all alumina gels are derived.

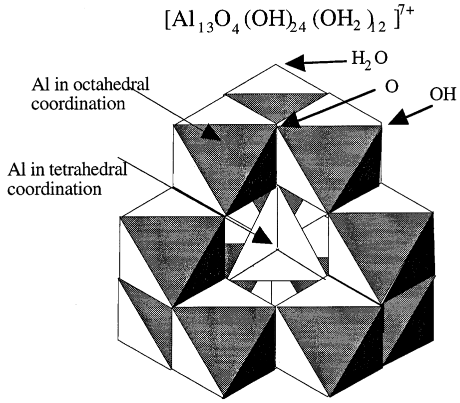


**Figure 2.** $\mathrm{Al_{13}}$ oligomer. After Henry et al.[33]

Silicon precursors, mostly alkoxides $\mathrm{Si(OR)_4}$, constitute an important exception which explains that they have been much more extensively studied than precursors of other metals M. In these alkoxides, R often is an alkyl $\mathrm{CH_3}$ group, so that the precursor is termed tetramethoxysilane, or TMOS, or an ethyl $\mathrm{C_2H_5}$, in which case the precursor is termed tetraethoxysilane, or TEOS. This exception comes from the fact that Si atoms carry a reduced partial positive charge, e.g., $\delta^+ \approx 0.32$ in $\mathrm{Si(OEt)_4}$. Hence, the global gelation kinetics of $\mathrm{Si(OR)_4}$ alkoxides can be very slow. The hydrolysis and condensation reactions of Si alkoxides therefore need to be catalyzed, either with bases which carry strong negative charges (e.g., $\mathrm{OH^-}$, but also strong Lewis bases such as $\mathrm{F^-}$ ions) or with acids (e.g., $\mathrm{H^+}$) which carry a strong positive charge and are able to attack the $\mathrm{O}(\delta^-)$ atoms from the alkoxy groups OR linked to the metal M. In practice, the relative magnitudes of the hydrolysis and condensation rates are sufficiently slow to be independently controlled. Overall, silica gels with a texture closer to the polymeric gels of organic chemistry are obtained when the hydrolysis rate is faster than the condensation rate, which requires the addition of an acid catalyst or proton donor. On the other hand, proton acceptors, i.e., bases, accelerate condensation reactions faster than hydrolysis, which favors the formation of denser colloidal silica particles and colloidal gels. The ability to control these kinetics has important consequences regarding the adapta-

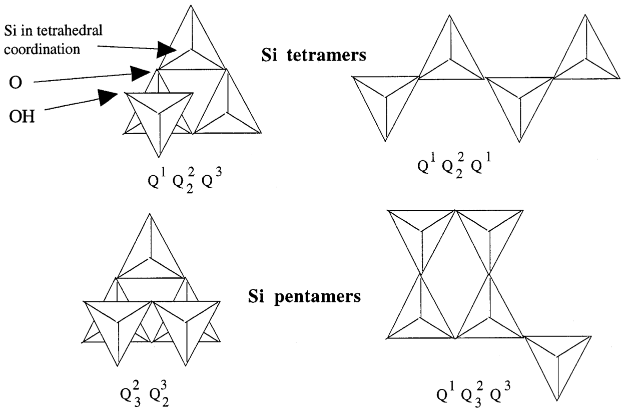


**Figure 3.** A few lower silicate oligomers. Reprinted with modification from ref 34. Copyright 1982 American Chemical Society.

tion of silica chemistry for a given type of aerogel application, as this is discussed in the related sections.

In any case, instead of building rather compact clusters such as the $Al_{13}$ polycation illustrated before, the silicon oligomer intermediates between the precursor and the final gel network can take a much more linear or open architecture, with a continuously varying degree of linearity or three-dimensional cross-linking (Figure 3). The difference in aptitude between silica and other oxides to make "random network" colloids, is quite parallel to the difference in aptitude between these oxides to build "random network" glasses. In theory, all materials can be transformed to glasses from their melt, providing they are cooled with a sufficient high cooling rate. Experimentally, an adequate cooling rate is much more easy to achieve with organic polymers and with silica than with other oxides. Similarly, a "random network" gel can in theory be achieved with any sol—gel precursor, provided the "hydrolysis" and condensation rates can be lowered to magnitudes where they can be controlled. But experimentally, this is much easier with silicon precursors than with other alkoxides.

The difference in -(M—O)- random network building ability between Si and other metals M has been related to the difference in ionic character between the Si—O bond and the M—O bonds in other oxides. An estimate of the ionic fraction $f_{\text{ionic}}$ ($0 \leq f_{\text{ionic}} < 1$) of these polar covalent bonds according to the semiempirical formula (eq 5) from Pauling:[35]

$$f_{\text{ionic}} = 1 - e^{\frac{-(\chi_M - \chi_O)^2}{4}} \tag{5}$$

where $\chi_M$ and $\chi_O$ are the Allred-Rochow electronegativities of M and O, gives ionic fractions of ~0.54, 0.64, 0.70, 0.71, and 0.78, respectively, for the oxides $SiO_2$, $Al_2O_3$, $TiO_2$, $ZrO_2$, and $Na_2O$. Roughly, $SiO_2$ is about 50% covalent. This is already sufficient to permit a wide distribution of the "Si-O-Si" angle value,[36] leading to a "random network". The ionic character is higher with the other oxides, which results in a lower bonding angle flexibility. Rather, random bonding really occurs between bigger dense colloidal particles, so that a particulate gel is made, rather than "lacy" particles interconnected by continuous siloxane type chains. Gelation is also more difficult with other oxides than with silica. In turn, this can explain a very different response to drying stresses, as discussed further on. With $Na_2O$, the ionic character is too strong, so that neither pure $Na_2O$ glass nor gel can be made. This fits with the well-known classification of Na as a "modifier " which does not participate in a random network.

## C. Alumina and Other Oxide Aerogels

The case of alumina gels is interesting. The $Al_{13}$ oligomer previously mentioned comprises one Al atom in tetrahedral coordination, while the other 12 are in octahedral coordination. This fits with the known "intermediate" random network ability of Al. That is to say, Al atoms can in part participate in a " -Si-O-Al-O-" random network where both Si and Al have a tetrahedral coordination, only to some extent. Beyond a certain proportion, further Al atoms usually act as modifier, as Na atoms do. These extra Al atoms adopt an octahedral coordination and do not participate in the random network. It must be noted that the "Al-O-Al" or "Al-OH-Al" bond angles, with Al in octahedral coordination, are not as flexible as the equivalent "Si-O-Si" angles, due to their higher ionic character and denser packing about an Al atom.

Actually, in boehmite gel monoliths as made by the Yoldas method,[16] virtually all Al atoms are in octahedral coordination. The gel random network is made by random bonding of rather dense boehmite particles, although the latter have a colloidal size in the range a few hundred nanometers. The interparticle bonding is not by a continuous covalent polymeric chain as in silica gels. Rather, as boehmite particles have a layered structure somewhat similar to that of clays, interparticle bonding is achieved by weak hydrogen bonds. Indeed, a dry gel can be dissolved again in excess water, by intercalation of water molecules. When drying is slowly done by evaporation, the particles tend to pack preferentially flat on each other (Figure 4), as illustrated by X-ray patterns with a enhanced interlayer peak.[37] As evaporation proceeds, hydrogen bonding extends on larger flat interparticles areas, which consolidates the final dry xerogel. Consequently, transparent xerogel monoliths can be obtained. On the other hand, when drying is made by the supercritical method, gel compaction does not operate. Consequently, interparticle bonding is not reinforced. It even usually becomes very weak because of the evacuation of residual polar water molecules. The dry aerogel which is obtained usually has no monolithic consistency. It collapses to a very fluffy powder upon handling.

Indeed, few attempts have been directed to the fabrication of truly monolithic aerogels containing alumina,[38−42] and the descriptions of monolithic characteristics are ambiguous. To achieve some monoliticithy in alumina aerogels, it is necessary to strengthen the initial hydrogen bonds between lamellar particles. This is made easier with new precursors in which the alkoxide has been chelated with $\beta$-diketonates such as ethylacetoacetate (etac) or acetyl

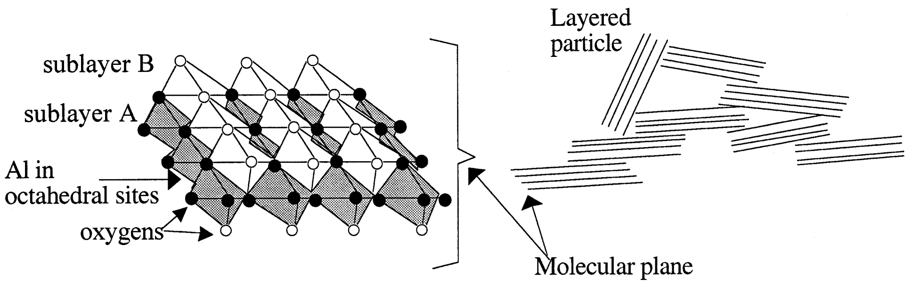


**Figure 4.** Boehmite gel structure. After Pierre.[18]

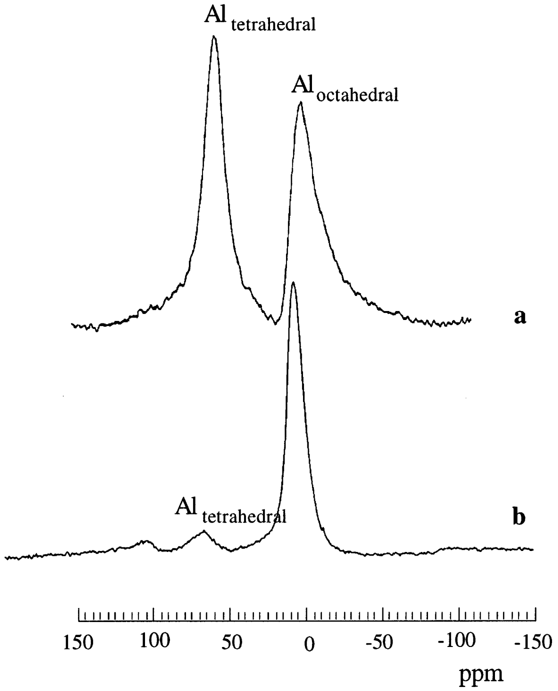


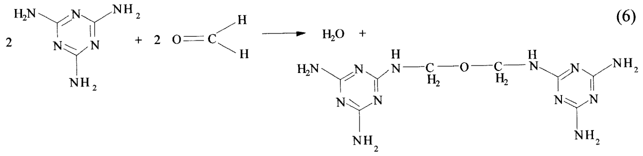
**Figure 5.** $^{27}$Al NMR data of (a) an alumino-silicate aerogel with a molar ratio Si/Al = 1.43, after Hernandez and Pierre;[43] (b) a pure alumina aerogel monolith made from an Al *sec*-butoxide and ethyl acetoacetate (etac) with a molar ratio of etac/Al = 2.1, after Pierre et al.[44]

acetoacetate (acac), not easily hydrolyzed. In this way, it has been possible to incorporate Al atoms in tetrahedral coordination in the gels, which introduces some interlamellar bonding, for instance in mixed alumina-silica aerogels.[43] Some small pure alumina aerogel monoliths could also been done, where some Al atoms are in tetrahedral coordination (Figure 5). The latter monoliths were small, extensively cracked, but could be handled with care in the best cases. They did strengthen and could be easily handled after heat treatments above 200 °C, up to 900 °C, due to partial sintering and formation of real Al−O−Al bonding between the particles. This resulted in the production of partly transparent relatively strong transition alumina aerogel pieces. Poco et al. seem to also have recently made strong alumina aerogel monoliths,[45] although the dimensions of these monoliths are not reported. In their chemical protocol, ethanol was the main solvent, and glacial acetic acid in unpublished proportions was added to introduce acetato bidentate ligands in the gel network. Supercritical drying was, moreover, done at 300 °C after a long time soaking in the supercritical fluid, so as to permit a beginning of interparticle sintering to strengthen the gel network. A similar monolithic fragility was observed in $TiO_2$ aerogels.[46−48] On the other hand, the wet gels obtained from hydrated metal salts in organic solvents with slow proton scavenger, previously mentioned, are reported to transform to nice aerogel monoliths (e.g., $Cr_2O_3$ monoliths) by supercritical drying in ethanol.[32]

## D. Organic Aerogels

Organic precursors can make organic polymers resting on strong -(C−C)- covalent bonds, even much more easily than silica precursors. Consequently, they made it possible to synthesize an interesting new class of monolithic aerogels, including aerogel particles with a size ranging from submicrometers to a few hundred micrometers, prepared by the sol−gel-emulsion technique.[49]

The most extensively studied of these materials are the resorcinol-formaldehyde (RF) and melamine-formaldehyde (MF) aerogels. They can be prepared by polycondensation of resorcinol or melamine with formaldehyde in a slightly basic aqueous solution, often with sodium hydroxide or sodium hydrogen carbonate as the gelation catalysts. The reactions are of the type shown in eq 6 for melamine.[50,51]



(6)

As with silica, small clusters of approximate size 2 nm are first formed. The latter consist of branched polymeric species characterized by a mass fractal dimension. These clusters aggregate and form particles 4−7 nm which show a surface fractal dimension. The structure is then fixed by gelation, in a temperature range from 238 to 333 K. Finally the particles surface is smoothed out by aging.[52] After supercritical drying with $CO_2$, the materials obtained have nitrogen adsorption isotherms with hysteresis loops, showing the presence of accessible mesopores, altogether with micropores.[53] In basic catalysis conditions, their typical apparent density tends to be larger than that of typical silica aerogels (0.38 up to 0.88 g cm$^{-3}$ versus 0.12−0.24 g cm$^{-3}$), while, in acidic catalysis conditions or in a double acid−base catalysis process, RF aerogels with a density as low as 0.013 g cm$^{-3}$ can be done.[54] On the other hand, a much coarser pore and cluster texture, with micron-size macropores, can be obtained by combining a very high molar ratio of resorcinol/catalyst (>1000) and a low relative molar mass content of resorcinol + formaldehyde (e.g., 30%).

Other precursors used to make organic aerogels include phenolic-furfural (PF) mixtures with poly(dimethylsiloxane) (PDMS),[50,55] 2,3-didecyloxyanthracene (DDOA) with ethanol or supercritical $CO_2$ as the solvent,[56] polyacrylonitrile (PAN),[57] or polyisocyanates.[58] The latter gels are very interesting for practical applications. They can be turned into heavily cross-linked polyurethanes (PUR), polyureas, polyurethone imines, or polyisocyanurates (PIR) aerogels and provide new thermal insulation material with good insulation characteristics both under evacuated and ambient conditions. With polyurethanes, $CH_2Cl_2$ can be used as a solvent which directly exchanges with supercritical $CO_2$. The organic aerogels which are obtained are nontransparent. They have a bulk density of 0.24 g/cm$^3$ and a specific surface area of approximately 300 m$^2$/g.[59] Finally, optically transparent aerogels can be prepared from aqueous melamine-formaldehyde solutions.[60]

## E. Carbon Aerogels

Carbon aerogels are mostly obtained by pyrolysis, at temperatures above 500 °C, of organic aerogels.[51] In this way, the organic aerogels transform to an electrically conductive carbon network. During pyrolysis, the carbon aerogels obtained from RF aerogels retain the high specific surface area (400−800 m$^2$/g), the large specific mesopore volume (>0.55 cm$^3$/g), and the isotherms with a hysteresis loop of their parent organic aerogel.[53,61] Shrinkage occurs. However, at pyrolysis temperatures below 1000 °C, a huge amount of microporosity also develops,[62,63] so that the largest specific surface area is achieved near 600 °C. In this temperature range, the pore radius of the maximum in the pore size distribution is not drastically affected.[64] Upon increase of the pyrolysis temperature up to 2100 °C, all structural characteristics observable by small-angle X-ray scattering (SAXS) start to grow drastically. Simultaneously, the micropore volume accessible to $CO_2$ almost vanishes, indicating the formation of closed micropores.[65] Overall, large pore volumes are maintained even after pyrolysis at 1800 °C.[66,67] The formation of microporosity can be enhanced by doping the parent RF aerogels with Ce or Zr. With these dopants, specific surface areas as high as 2240 m$^2$ g$^{-1}$ have been achieved,[68,69] while graphitization above 1000 °C is enhanced.[66,67]

Until recently, carbon aerogels did not exhibit fractal structures. However, a new family of carbon aerogels has been made which shows mass fractality with a mass fractal exponent of 2.5 according to Barbieri et al.[70] This result was obtained with resorcinol-formaldehyde gelation in acetone, instead of water and, with catalysis by perchloric acid, instead of sodium carbonate. Moreover, this kind of carbon aerogel displayed a bimodal distribution of pores, with micro- and macro-pores, contrary to all other types of carbon aerogels described in the literature which are mesoporous.

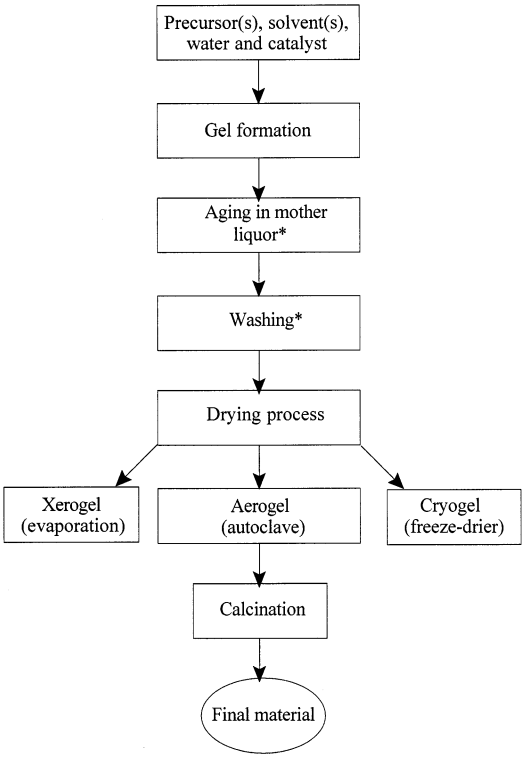


**Figure 6.** Sol-gel and drying flowchart. (*) The aging and washing steps are optional. After Pajonk.[20]

## *III. Transforming Wet Gels to Aerogels*

A general flowchart for a complete sol−gel process is shown in Figure 6. After gelation, the wet gel can optionally be aged in its mother liquor, or in another solvent, and washed. Then it must be dried.

## A. Supercritical Drying

The traditional drying technique, at the origin of the label "aerogel", is supercritical drying. This type of drying prevents the formation a liquid−vapor meniscus which recedes during the emptying of the pores in the wet gels. As this meniscus is due to the surface tension of the liquid, a capillary pressure gradient is built in the pore walls, which is able to collapse most part of the pore volume. To avoid this event, it is necessary to annihilate the liquid surface tension and one convenient way to do so is to transform this liquid in a supercritical fluid with a null surface tension. Supercritical evacuation of the liquid-phase impregnating the porous volume of the wet gel permits the recovery of a kind of "dry solid image" of the wet material. This drying procedure releases the porous texture quite intact by avoiding the pore collapse phenomenon.

Practically, supercritical drying consists of heating the wet gel in a closed container, so that the pressure and temperature exceeds the critical temperature, $T_c$, and critical pressure, $P_c$, of the liquid entrapped in the pores inside the gel. Initially investigated by Kistler et al.,[30] the synthesis of monolithic silica aerogels from tetraethoxysilane (TEOS) by supercritical drying in methanol was applied by Peri[71] in order to study the surface chemistry of these materials. Then, the technique has been largely developed

**Table 1. Critical Point Parameters of Common Fluids**[73]

| fluid | formula | $T_c$ (°C) | $P_c$ (MPa) |
|---|---|---|---|
| water | $H_2O$ | 374.1 | 22.04 |
| carbon dioxide | $CO_2$ | 31.0 | 7.37 |
| Freon 116 | $(CF_3)_2$ | 19.7 | 2.97 |
| acetone | $(CH_3)_2O$ | 235.0 | 4.66 |
| nitrous oxide | $N_20$ | 36.4 | 7.24 |
| methanol | $CH_3OH$ | 239.4 | 8.09 |
| ethanol | $C_2H_5OH$ | 243.0 | 6.3 |

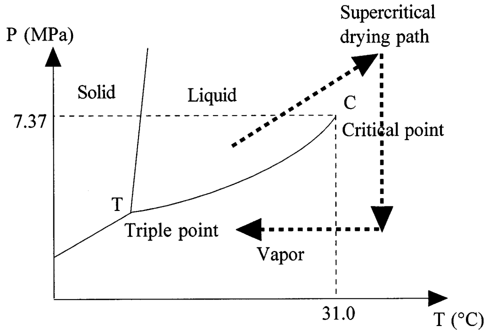


**Figure 7.** Example of a possible cold supercritical drying path in the Pressure (P) Temperature (T) phase diagram of $CO_2$ .

by the Teichner group, who directly performed supercritical drying within the alcohol in which the alkoxides were hydrolyzed. By operating in this manner, alcogels were obtained.[72] The critical conditions are very different depending on the fluid which impregnates the wet gel. A few values are given in Table 1.

Presently, one distinguishes high-temperature supercritical drying (or HOT) in alcohol from low-temperature supercritical drying (COLD) in $CO_2$. Both methods are different in the sense that the hot method is accompanied by a kind of a rather poorly controlled aging process during the temperature and pressure increase used to attain the chosen supercritical conditions. The resulting materials thus are generally hydrophobic since their surfaces are covered by alkoxy groups. In the case of silica synthesis, these alkoxy groups result from the reaction of the silanol groups with the alcohol selected to make the alcogels. On the other hand, the cold method does not favor such processes, and as a consequence, it leads to more hydrophilic solids.

A possible supercritical drying path in the phase diagram of $CO_2$ is presented in Figure 7, while an autoclave to perform supercritical drying with alcohol and the corresponding temperature and pressure program schedule are, respectively, illustrated in Figures 8 and 9. Various detailed procedures regarding the sample drying preparation protocol, the heating-pressurization path, the atmosphere above the samples, the nature of the liquid, the duration of the many steps have been investigated. They were summarized by Pajonk.[74] For silica, the aerogels obtained typically have a pore volume above 90% of the sample volume and a specific surface area which in some cases can exceed 1000 $m^2/g$. For other oxides, the corresponding specific pore volume and surface area are usually significantly lower than for silica except for carbon aerogels.

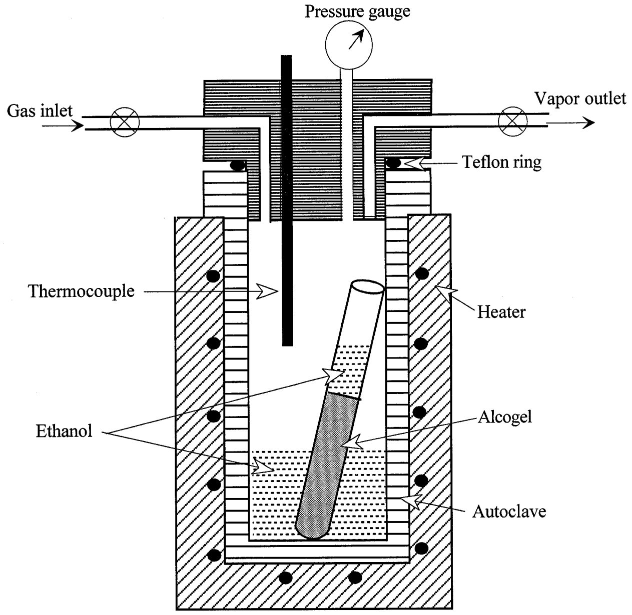


**Figure 8.** Schematic illustration of an autoclave for supercritical drying with ethanol. After Pajonk.[20]

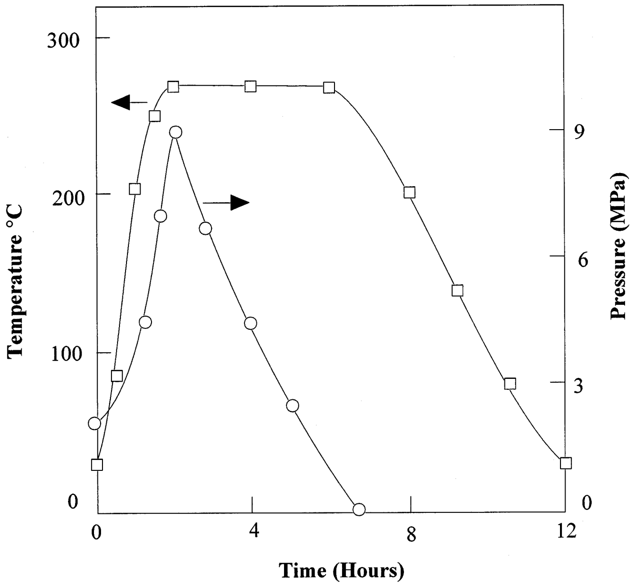


**Figure 9.** Flow diagram of the supercritical drying process with alcohol. After Pajonk.[20]

## B. Other Drying Techniques

Organic wet gels made in organic solvents can sometimes be dried by solvent evaporation at ambient pressure with moderate shrinkage.[60,75] Surfactants can also be added to the liquid to decrease the capillary stresses. The gel can be made hydrophobic by silylation to change the liquid−solid contact angle and annihilate the capillary liquid tension, as done the first time by Smith et al.[76]

Other techniques than supercritical drying can also be used to obtain high surface area and pore volume materials. One of them concerns the addition of "drying control chemical additives" (DCCA) such as glycerol, formamide, dimethyl formamide, oxalic acid, and tetramethylammonium hydroxide.[77−80] In this way, brittle but uncracked dry monoliths can be obtained, with a relative pore volume up 97.4%,[81]

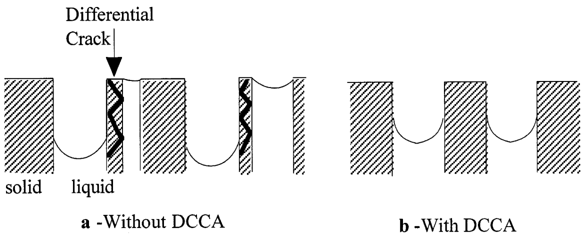


**Figure 10.** Effect of formamide on the pore size distribution of gels. After Hench.[81]

equivalent to the best aerogels obtained by supercritical drying. The explanation provided for this drying behavior is that a uniform pore size distribution is formed, with pores which can be relatively large (basic formamide) or small (oxalic acid). In turn, this minimizes the differential drying shrinkage (Figure 10). Chemically, with formamide, such a structure is related to a lower hydrolysis rate so that the condensation kinetics is relatively enhanced by comparison with hydrolysis. Consequently, bigger silica nanoparticles are formed and linked to each other by bigger and stronger necks, resulting in a lower shrinkage.

A promising technique which can be applied on a large scale for industrial purposes, is known as “ambient-pressure drying”. This method relies on a passivation of the pore surface, inside the gel, so as to impede further formation of new siloxane bonds by condensation reactions when the gel network is compressed under the drying stresses. Such a passivation can be induced by silylation for instance with trimethylchlorosilane as done by Smith et al.[82] At the end of the solvent evaporation process, an aerogel monolith is no longer submitted to capillary stresses so that it can resume its wet size by a spring-back effect. More recently, Schwertfeger applied the technique, in hexamethyldisiloxane as the solvent, to hydrogels made from sodium silicate (water glass), making it a very cheap process.[83] Other preparation methods before drying rest on ion exchange treatments.[84]

Another concurrent technique is freeze-drying, as done for instance with *tert*-butyl alcohol.[61,85] In this method, the gel liquid is first frozen and thereafter dried by sublimation.[21,84,86] Therefore, the formation of a liquid−vapor meniscus is prevented. The materials obtained are then also termed cryogels. Their surface area and mesopore volume tend to be smaller than those of aerogels, although they remain significant. Nevertheless, the gel network may eventually be destroyed by the nucleation and growth of solvent crystals, which tend to produce very large pores.[87] To attenuate this event, a rapid freeze process known as flash freezing has been developed. It is also important that the solvent has a low expansion coefficient and a high pressure of sublimation.

## IV. Texture and Structure of Aerogels

As previously mentioned, gel networks are often described as fractal geometrical architecture.[27] It is possible to distinguish mass fractals from surface fractals. In the former case, the mass $M$ of a gel inside a sphere of radius $R$, centered at a random point in the gel network, is a statistical function of $R$ of the type

$$M \approx R^{f} \qquad (7)$$

where $f$ is not an integer and hence is termed the fractal dimension. For a surface fractal object, the surface area $A$ follows the law

$$A \approx R^{fs} \qquad (8)$$

Actually, a gel can only be fractal in a limited range of magnitude of the radius $R$, roughly in the so-called intermediate range 1−50 nm, which in details depends on the material. However, in this limited range, $f$ can be as low as ∼1.9 for acid-catalyzed gels.[17] At macroscopic dimensions, a gel always has a uniform density. The fractal dimensions can be experimentally determined by small-angle X-ray scattering (SAXS) and by adsorption of molecules of different cross-sectional area. In the first type of data, at so-called intermediate angles, the scattered intensity $I(k)$ follows a Porod law of the type (eq 9)

$$I(k) \approx k^{-2f+f_s} \qquad (9)$$

where $k$ is the wave vector defined at a scattering angle $\theta$, for an X-ray wavelength $\lambda$ by

$$k = 4\pi/\lambda \sin(\theta/2) \qquad (10)$$

In adsorption experiments, the mass $w$ adsorbed at low pressure follows a law of the type

$$w \approx \sigma^{-(f_{s,a}/2)} \qquad (11)$$

where $f_{s,a}$ is the surface fractal dimension for adsorption of an adsorbate with cross -sectional area $\sigma$. Also, the volume $V_p(r)$ of pores smaller than $r$ should depend on $r$ according to the following equation

$$\frac{dV_p(r)}{dr} \approx r^{2-f_s} \qquad (12)$$

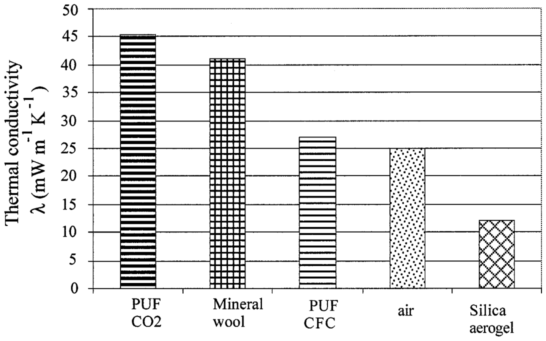
Basically, aerogels should not differ very much from xerogels. Supercritical drying mostly affects only the larger pores which involve network dimensions beyond the fractal scale. The general literature on sol−gel therefore gives experimental values for gels at large, which support various theoretical fractal models summarized by Brinker and Scherer.[17]

The texture and structure of aerogels make them interesting for some applications. However, some adaptation was often needed to best fit them with a given application. This in turn required chemical synthesis studies which are briefly summarized in the following paragraphs.

## V. Chemical Adaptation of Aerogels to Thermal Insulation

### A. Summary of the Insulation Properties

Aerogels are among the best known thermal insulating materials.[88] Moreover, they can be made very transparent although they are also very brittle. The



PUF CFC : Polyurethane foam - Chlorohydrofluorocarbon

PUF CO2 : Polyurethane foam - Carbon dioxide

**Figure 11.** Typical order of magnitude of the thermal conductivity of silica aerogel compared to other insulating materials, for 10 mm thick slabs. Reprinted with permission from ref 89. Copyright 2001 Institute of Materials.

low conductivity of aerogels originates in a very high porosity (95−98%) and thus a low solid conductivity $\lambda_s$. This contribution to the thermal conductivity scales as the aerogel density $\rho$ as[10]

$$\lambda_s \approx \rho^\gamma, \text{ with } \gamma \approx 1.2-1.8 \qquad (13)$$

Typically, for a monolithic silica aerogel with an approximate density $\rho$ of 120 kg m$^{-3}$, $\lambda_s$ is about 5 mW m$^{-1}$ K$^{-1}$.[10] Moreover, the extremely small pore size (lower than the mean free path of air) causes a very low gaseous thermal conductivity $\lambda_g$ due to Knudsen effect. At ambient pressure, $\lambda_g$ does not exceed 10 mW m$^{-1}$ K$^{-1}$.[20] This gas conductivity can be minimized by lowering the gas pressure within the aerogel. Overall, at room temperature, for silica aerogels with an approximate density of 150 kg m$^{-3}$ the thermal conductivity $\lambda$ is about 15 mW m$^{-1}$ K$^{-1}$ in air and 10 mW m$^{-1}$ K$^{-1}$ under vacuum (Figure 11). In air, this compares with values of about 35 mW m$^{-1}$ K$^{-1}$ for polyurethane foam, mineral wool and expanded polystyrene.[13]

Aerogel granules as well as large size monoliths were investigated for daylight transparent thermal insulation in the European JOULE II and III (HILIT project) and the two French ADEME programs (PACTE projects).[90] Glass panels with dimension 55 × 55 × 2 cm were made by the Airglass Ltd. company in Sweden, as part of the European EUROSOL program.[90] Hydrophobic silica aerogels with an acceptable transparency were also made from a mixture of methyltrimethoxysilane (MTMS) and tetramethoxysilane (TMOS).[89,91,92]

Silica is nonflammable. They let enter the visible and UV radiation from the sun daylight but they do not let the infrared radiation from a heated house pass through.[93,94] In terms of transparency, they show very high solar as well as light transmittances. Figure 12 shows the optical properties of such aerogels in terms of solar transmittances against wavelengths. However, they all show a tendency to scatter the transmitted light, resulting in a reduced optical quality. This phenomenon is considered as being the main obstacle to incorporating the material in clear glazing, although a significant improvement has been observed during the last five years.[96]

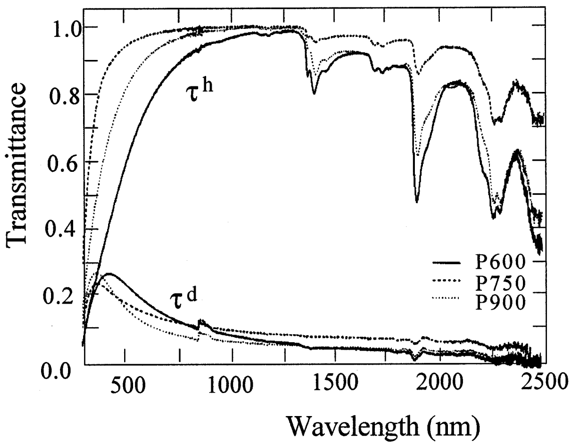


**Figure 12.** Hemispherical and diffuse normal transmistances of $P_{600}$, $P_{750}$, and $P_{900}$ aerogel series, for a common precursor volume fraction in solution, $x_{prec} = 0.5$. After Rigacci et al.[95]

Besides window insulation, silica aerogels can be used to insulate cooling or heating systems, including piping, for heat or cold storage applications[13,97,98] as well as car windshield defrost in cold weather conditions.[99] Uncooled monolithic thin film infrared imaging devices based on lead zirconate titanate materials coated on silica aerogels have also been designed. The low thermal conductivity of the aerogel attenuates the thermal noise and results in a significantly faster temporal response and a visible reduction in scattering.[100] Novel types of furnaces for the controlled temperature gradient growth of monocrystalline metals or semiconductors, such as InSb, have been demonstrated. With a transparent silica aerogel crucible, the crystallization front can directly be controlled with a IR camera. Aerogels offer a much better control of the solidification process than the classical method. A nearly one-dimensional temperature field and a nearly planar crystallization front can be achieved.[101,102] Finally, transparent silica aerogel is also interesting in the production of hollow spheres for inertial confinement fusion.[103]

## B. Chemistry of Monolithicity

Chemically, it is necessary to reinforce the mechanical properties of silica aerogels without loosing their main properties, especially when they are to be used as thermal superinsulent and transparent materials for window insulation. The transparency of silica aerogels is an important advantage for this kind of high added value technical applications. Such a goal can be met by applying a double step process to the already wet gel before the supercritical evacuation step. First, a washing of the wet gel is applied with a solution of ethanol and water which is then followed by an aging step consisting in placing the former washed gel in contact with a solution of ethanol containing the silicon precursor; tetramethyl orthosilicate (TMOS), tetraethyl orthosilicate (TEOS), or polyethoxydisiloxane (PEDS) as described by Einarsrud et al.[104] The stiffness of wet gels is greatly increased by this particular treatment without loosing the permeability properties. This type of final aging corresponds to the continuation of the creation

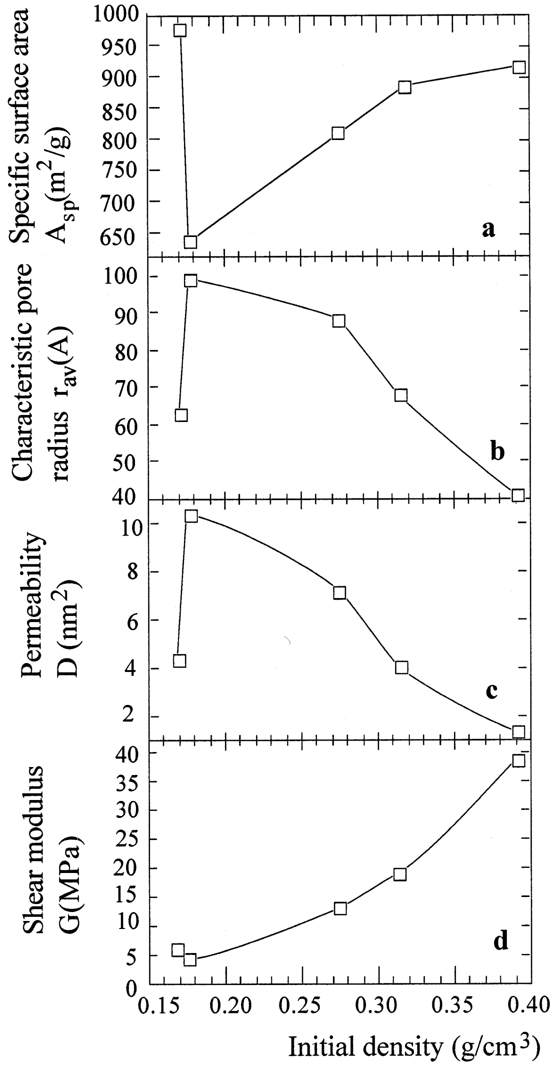


**Figure 13.** (a) Shear modulus, $G$ (±1.68 MPa); (b) characteristic pore radius $r_{av}$ (±5% Å); (c) permeability, $D$ (±0.55 $nm^2$); (d) surface area (20 $m^2$/g) of wet silica aerogels versus initial density. The gels were aged in 70 vol % $P_{750}$/ethanol at 70 °C for 0−24 h after washing in 20 vol % $H_2O$/ethanol for 24 h at 60 °C. The lines are guides for the eye. After Einasrud et al.[104]

of additional siloxane bridges through the condensation−polymerization mechanism already mentioned in a previous section of this paper, which increases the overall mechanical quality of the material as shown in Figures 13 and 14, where shear modulus, permeability, characteristic pore size, BET surface area, and modulus of rupture were respectively estimated. On the basis of SAXS measurements, it could be seen that there were no major differences of structure between nontreated, washed, and aged silica aerogels as demonstrated in Figure 15. The dried silica exhibited mass fractality with an average mass fractal exponent equal to 1.9, suggesting an aggregation mechanism pertaining to the DLCA-like model (diffusion-limited cluster aggregation).

## C. Chemistry of Hydrophobicity

A second quality is required in order to be used in a sustainable manner, i.e, silica aerogels must exhibit good hydrophobic properties with time on stream. One pertinent method to reach this goal is to co-gel some silicon precursor containing at least one non-polar chemical group, such as a $CH_3$−Si bond, with the normal silicon precursor. Hydrophobic aerogels

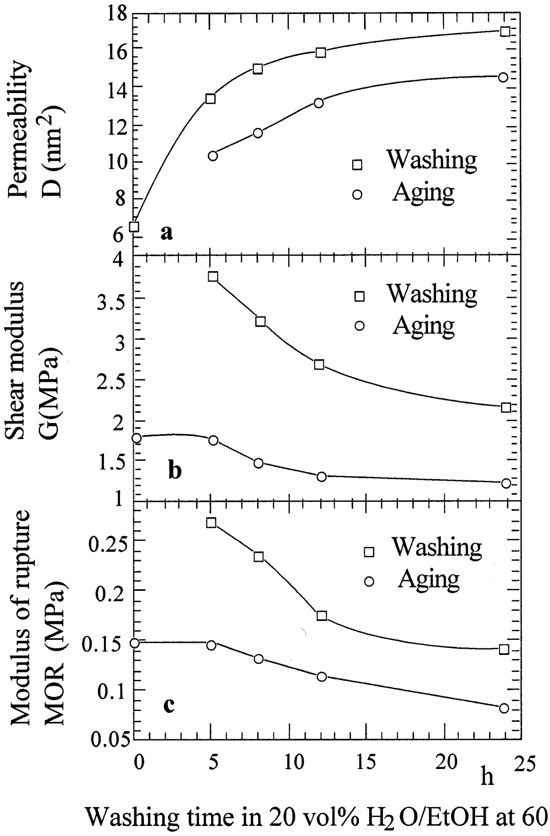


**Figure 14.** (a) Permeability, $D$ (±0.51 $nm^2$); (b) shear modulus, $G$ (±0.07 MPa); (c) modulus of rupture, MOR (±0.04 MPa) of wet silica aerogels as a function of washing time in 20 vol % $H_2O$/ethanol at 60 °C. Data for washed only gels are given (open symbols) as well as data after aging in 35 vol % $P_{750}$ for 7 h at room temperature (closed symbols). The lines are guides for the eye. After Einasrud et al.[104]

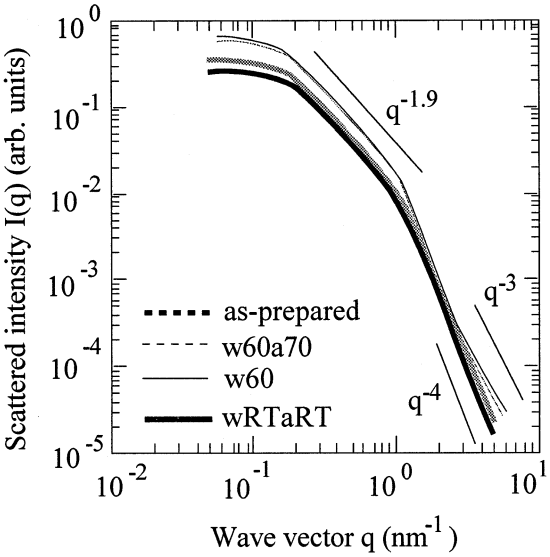


**Figure 15.** Log−Log plot of the SAXS intensity versus the scattering vector **q** of as-prepared, washed and washed/aged silica aerogels dried under direct supercritical $CO_2$ conditions. After Einasrud et al.[104]

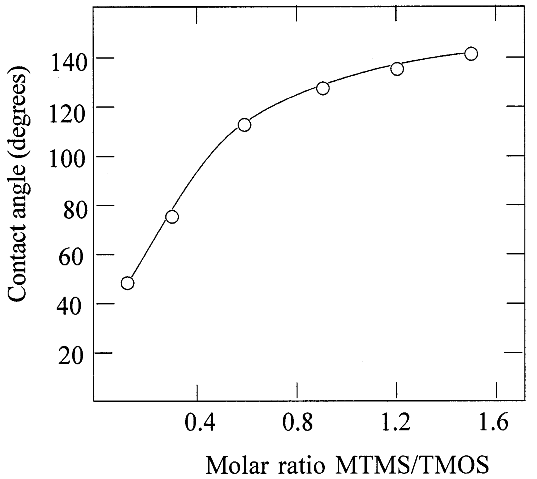
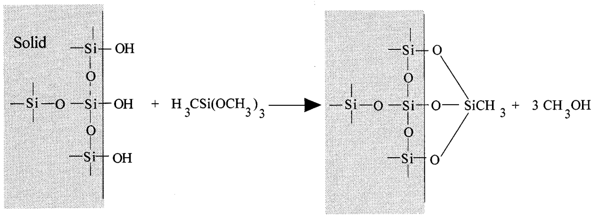


**Figure 16.** Contact angle of a water droplet with the aerogel surface versus MTM/TMOS molar ration. After Venkatsewara Rao and Pajonk.[92]

were synthesized by Schwertfeger et al. from methyltrimethoxysilane (MTMS) and TMOS by hydrolysis in basic conditions followed by supercritical drying in methanol.[105,106] In these high-temperature drying conditions, the aerogel surface was dehydrated, and these authors found that aerogels made from more 20% MTMS would float on water and hence were hydrophobic. However, for a higher proportion of MTMS, the condensation degree of silica was reduced. As the hydrolysis and condensation rates of MTMS are much lower than those of TMOS, a quasi two-step gelation process was achieved. Indeed, as this was well shown by Hüsing et al., this particular gelation occurs in two-steps: first, the TMOS reacts and then the MTMS is grafted through the silanol surface groups of the gel giving surface Si-0-Si-$CH_3$ functions.[107] The methyl groups in MTMS could also be replaced by other types of functionalities with similar hydrophobization and gel structure results.[107]

The hydrophobization of silica aerogels with MTMS can be summarized by reaction 14, according to which



(14)

the gel network is due to TMOS as described by Venkateswara Rao and Pajonk.[92]

These authors showed that, provided the molar ratio of MTMS/TMOS was fixed around 0.7, good optical and hydrophobic properties were obtained when the temperature of treatment did not exceed 200 °C. Figure 16 shows the contact angle recorded when the molar ratio MTMS/TMOS changed between 0 and 1.65 while Figure 17 gives the infrared spectra versus heat treatments showing that the methyl groups are responsible of the hydrophobic properties of the so-obtained silica aerogels. Similar results were obtained by co-gelling TMOS with trimethylethoxysilane (TMES) whose chemistry is summarized in

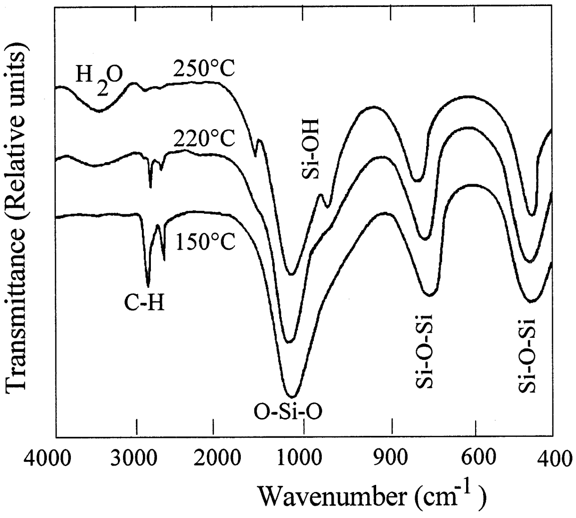


**Figure 17.** Infrared spectra of the aerogels prepared with MTM/TMOS molar ratio of 0.8 at different temperatures. After Venkatsewara Rao and Pajonk.[92]

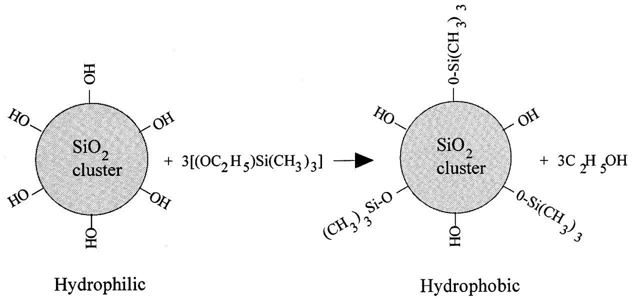


**Figure 18.** Hydrophobisation of silica particles with trimethylethoxysilane (TMES). After Venkatsewara Rao et al.[108]

Figure 18.[108] One can notice that the choice of methoxy or ethoxy methyl-silicon precursors allowed the use of these molecules as co-gelation ones, which is not the case for instance with hexamethyldisilazane (HMDS) which can only be reacted once the silica aerogel has been recovered from the autoclave. Again, infrared analysis confirmed the hydrophobic role of the external Si-$CH_3$ groups. For aerogels differing by their respective TMES/TMOS molar ratio, a higher TMES/TMOS resulted in a very good hydrophobic material but exhibited poor optical transparency principally due to an enlargement of the pore size (Rayleigh diffusion).

## D. New Chemical Developments in Organic, Hybrid Organic-Silica Aerogels, and Other Related Materials

Monolithic organic aerogels have a thermal conductivity of the same order of magnitude as silica aerogels at room temperature.[109] The main advantages, compared to silica aerogels, is that they are less brittle and the radiation component is minimized as the temperature increases. This is the case with polyurethane aerogels made in $CH_2Cl_2$, which are nontransparent but have a low thermal conductivity. Hence, they are considered as new insulating materials for the appliance industry, where energy requirements are becoming more and more stringent.[110]

The strength of silica aerogels can also be quite significantly increased by adding inorganic powder or organic binders, while the thermal conductivity can be maintained below 20 mW $m^{-1}$ $K^{-1}$ at room temperature in air.[111] This technique moreover attenuates the radiation component of thermal conductivity, at higher temperatures. Granules can for instance be opacified with $TiO_2$ or carbon black[109] or bound with a thermoplastic such as polyvinylbutyrate (PVB) or an aqueous polymer dispersion such as vinyl acetate-ethene.[12] With PVB, an application of a 1 bar pressure in the melting range temperature of the polymer can form a compact with good thermal insulation performances and reasonable strength.[112] Such plates 9 mm thick with ~50% PVB are excellent to cover the inner floor of houses. They are able to support ceramic tiles, while they offer an excellent footfall sound attenuation characteristic.[12]

Finally, siliceous mesostructured cellular foams (MCF) with well-defined ultralarge mesopores can also be made by templating a sol with oil-in-water microemulsions before gelation. Their texture consists of uniform spherical and interconnected cells measuring approximately 25−40 nm in diameter. BET surface areas up to 1000 $m^2/g$ and porosity of ≥80% can be achieved. The cell size can be chemically controlled by adding various swelling agents and by varying the aging temperature. The MCF materials resemble aerogels, but offer the benefits of a facilitated synthesis in combination with well-defined pore and wall structure, thick walls, and high hydrothermal stability.[113]

## *VI. Application of Aerogels for Acoustic Insulation*

Overall, aerogels are excellent acoustic insulators. The acoustic propagation in aerogels depends on the interstitial gas type and pressure, the aerogel density, and more generally its texture on the preparation procedure.[114] The energy transferred from the gas to the solid phase is in part lost to the acoustic propagation and, thus, reduces the amplitude and velocity of the acoustic wave.[115] This longitudinal acoustic velocity is typically on the order of 100 m $s^{-1}$.[10,116] This property makes silica aerogels suitable for applications in acoustic impedance $\lambda/4$ matching layers in ultrasonic transducers, range finders, speakers.[117,118] Their application in house floor covering for footfall sound insulation was previously mentioned.[12] Other applications concern the acoustic insulation of transportation and machinery. Besides, silica aerogels are investigated for applications in anechoic chambers.[12,114,119,120]

## *VII. Chemical Adaptation of Aerogels for Optical Applications*

### A. Chemistry of Homogeneous Porous Texture

As mentioned in the previous section, silica aerogels are extremely porous materials which can be made transparent. Optical applications depend on their homogeneity. Inhomogeneities in the nanometer range are responsible for Rayleigh scattering, which makes a sample appear yellowish when light is observed by transmission through it, while it appears bluish when light is observed by reflection against a dark background. Inhomogeneities in the micrometer range are responsible for a blurred optical deformation of images.[13] These problems have been attenuated by empirical chemical synthesis screening. Typically, aerogels made from TMOS in methanol, in particular by a two-step procedure (acid-catalyzed hydrolysis followed by base-catalyzed condensation), can produce sufficiently good samples, with an optical transmittance up to 93% at a wavelength of 900 nm[91,121] (Figure 19). Silicon precursors prehydrolyzed with an acid catalyst and a substoichiometric water molar ratio $w = H_2O/Si < 2$, such as the polyethoxydisiloxane (or PEDS-$P_x$ where $x = 1000w$), are also available on the market[95] and make it possible to control a more uniform porous texture, as is needed for optical applications. One type of applications is due to their refractive index which is very close to 1. It concerns in particular Cherenkov counters, described further on. The refractive index of silica aerogels is related to their density $\rho$ (kg $m^{-3}$) by the eq 15[122]

$$n - 1 = (2.1 \times 10^{-4})\rho \qquad (15)$$

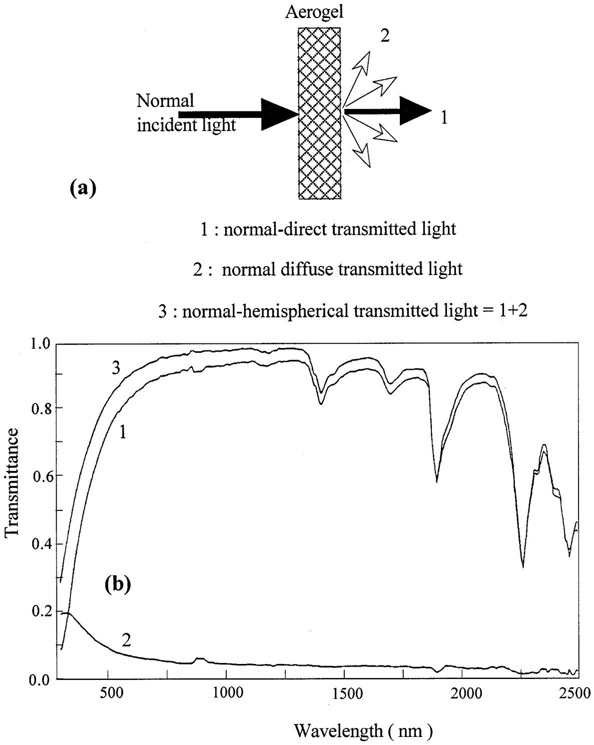


**Figure 19.** (a) Representation of *n*-hemispherical (direct + diffuse) transmittance through aerogel samples and (b) optical transmittance spectra of silica aerogel in the ultraviolet (UV)−visible near-infrared (NIR) region, after optimizing supercritical drying parameters. Reprinted with permission from ref 91. Copyright 1998 Institute of Materials.

A second type of application is that silica aerogels can entrap all kinds of molecules or dopants with special fluorescent properties. A third group of applications combines both properties of transparency and thermal insulation and was described in the previous section.

## B. Aerogels in Cherenkov Counters

It was shown very early by the Teichner group,[123] that low-refractive-index silica aerogel constitutes a convenient medium for the Cherenkov counters, which are used for electrically charged particle identification in high-energy physics experiments. This is, also, tied to a major problem of cosmology, which requires the identification of anti-matter and matter particles in the cosmic rays. The principle of Cherenkov counters rests on the fact that electrically charged elementary particles, which travel across the radiator medium with a velocity "*v*" higher than the velocity of light "*c*" in this medium, themselves emit a light. An analysis of this light can therefore be used to derive the velocity of a particle and hence its nature.

Cherenkov counters can be of two types. In the threshold type, particles are identified according to whether light is emitted or not when they travel across the radiator material. The number of photons collected *N* depends on *v*, *c*, and *n* as indicated in the following equation:

$$N = K\left(1 - \frac{1}{(\beta n)^2}\right) \qquad (16)$$

where $\beta = v/c$, $K$ is a proportionality coefficient, and $\beta n \geq 1$.

To separate pions from kaons with a momentum of the order of 3 GeV/c, radiator materials must have a refractive index of <1.03. This can be achieved with silica aerogels. Such aerogel counters were actually installed in the BELLE detector at the KEK B−Factory in Japan. For this piece of equipment, over a thousand highly transparent aerogel plates with dimensions 24 mm × 12 cm × 12 cm were made, which represented a total aerogel volume of approximately 2 $m^3$. Their refraction index *n* was in the range 1.01−1.03. Because water modifies their refractive index, they were also made completely hydrophobic by aging in hexamethyldisilazane.[122] They could operate without any problem under magnetic fields of up to 1.8 T and could resist to an irradiation up to 9.8 Mrad.[122,124,125] Variants of this type of counter have been developed for the KEDR detector in Russia.[126−131]

The second type of Cherenkov counters are termed Ring Imaging Cherenkov (RICH) counters, because the light emitted by the particles originates from a cone-shaped electromagnetic shock wave with angle:

$$\theta = \frac{1}{\beta n} \qquad (17)$$

Hence, RICH-type Cherenkov counters calculate the velocity of particles from the cone angle. They also use aerogel radiators.[132,133] For instance, silica aerogel tiles with a refractive index of 1.03 and dimensions 11 cm × 11 cm × 1 cm, have been developed by the Matsushita Electric Works (Japan), for use in the RICH counter of the HERMES experiment at the DESY−HERA German electron synchrotron (Figure 20). This counter is able to determine the contributions of the different quark flavors to the nucleon spin and to identify pions, kaons and protons over a large kinematic range.[135,136] A detector of this type was launched in a balloon at an altitude of about 10 000 m to observe anti-particles, such as anti-protons, in the cosmic rays. Similar counters are being considered to search for anti-matter in the space.[122]

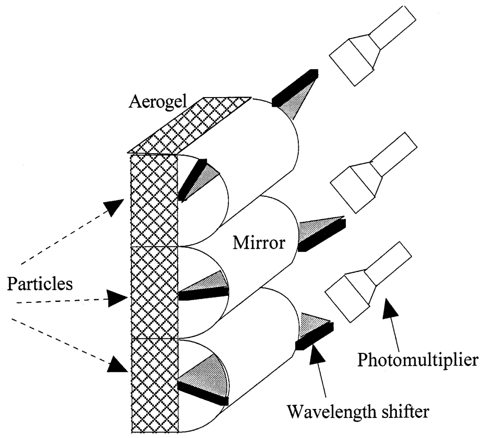


**Figure 20.** Aerogel Cherenkov counter with wavelength-shifter readout. After Poels.[134]

Another application of silica aerogels, due to their refractive index close to that of air, is as a cladding film on optical fibers. The film thickness is typically on the order of 20 μm. It maximizes the collection angle at the fiber ends and can improve the light trapping fraction by a factor of 4.[137] Similarly, aerogel coating on solar cells improves their efficiency, because Fresnel scattering losses are attenuated and more light reaches the active surface.[138]

## C. The Chemistry of Luminescent Arogels

Photoluminescent materials based on silica aerogels can be made by encapsulation of various photoluminescent dopants during the gelation process. The chemical problem here is to retain the dopants inside the gel network even after washing and supercritical drying, while maintaining its luminescent properties. Chemically, the dopant can be adsorbed (hydrogen bonds), fixed by reversible electrostatic attraction, irreversibly covalently bonded, or just physically entrapped, such as in a hydrophilic pocket surrounded by hydrophobic gel.

The span of encapsulated molecules is very large. It comprises C-60 to C-70 fullerenes, which emit an intense visible light with a blue shift by comparison with the free dopant. The latter effect is due to a quantum confinement by the gel network. Here again, the luminescent properties depend on the aerogel chemical preparation procedure.[139,140] A fluorescent dye such as the *N*-(3-trimethoxysilylpropyl)-2,7-diazapyrenium bromide (DAP), was covalently bonded to the gel network.[141] Another dopant, 1,4-bis[5-phenyl-2−oxazolyl]-benzene (or POPOP), has been used to enhance the detection of the Cherenkov light in the SAPHIR program.[142] Luminescent scintillators, made by saturated impregnation of $SiO_2$ aerogel under argon, with 1-methylnaphthalene-based liquid scintillators, have also been investigated for application in high-energy physics.[143] Another

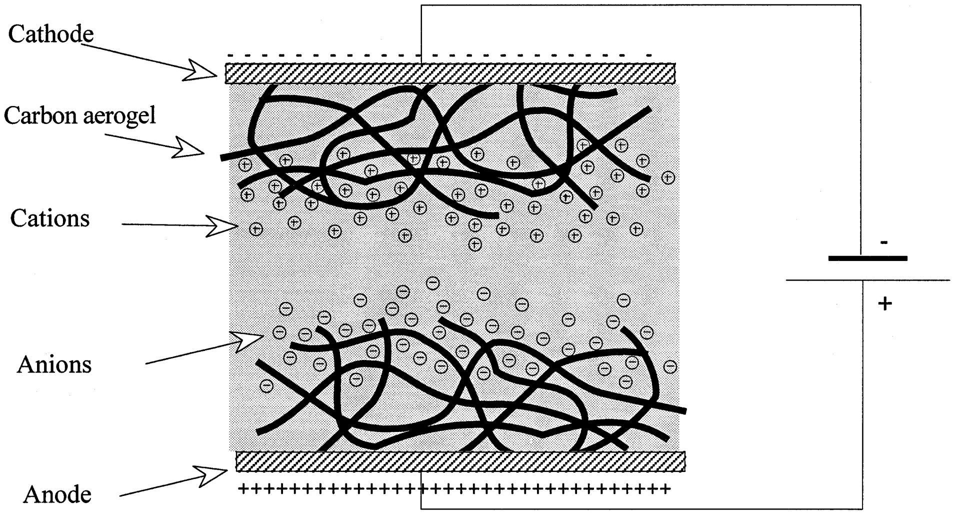


**Figure 21.** Representation of a carbon aerogel double layer supercapacitor.

different type of dopant consists of about 6 nm sized nanocrystalline ZnO particles, which provide strongly green-yellow fluorescent aerogels at about a wavelength of 500 nm.[144] Dopants can even be simple cations introduced with salts such as aluminum nitrate. In high-temperature ethanol supercritical drying conditions, the $Al^{3+}$ cations from the salt break some Si−O−Si bonds to build Si−O−Al ones. This also results in an increased formation of oxygen vacancies near some silicon atoms, by comparison with pure silica aerogels. In turn, this can drastically increase the green luminescent intensity which is due to a small proportion of 2-fold coordinated Si atoms in the Al doped silica gel.[145] The design of lasers using aerogels is possible, for instance by encapsulation of lanthanides[146] or other special dyes.[147] Besides silica, alumina aerogels made by complexation with ethylacetoacetate show an intense blue emission band in the wavelength range 400−800 nm, after annealing at 500 °C.[148]

## *VIII. The Chemistry of Electrical Applications*

### A. Batteries

The chemical problem here is to be able to reversibly intercalate ions in the aerogel network. A large amount of small ions can indeed be intercalated because of the very porous texture of oxide aerogels. Moreover, as the latter are good thermal insulents, they can be applied in high-temperature electrical batteries.[13,97] The most studied oxides are vanadium oxide,[149] manganese oxide,[150] and molybdenum oxide aerogels[151] in which lithium ions are intercalated. A $V_2O_5$ aerogel is an amorphous material which consists of a highly interconnected solid network with a surface area up to 450 $m^2/g$, and a specific pore volume as much as 2.3 $cm^3/g$. Up to 5.8 equiv of lithium/mol of $V_2O_5$ aerogel can be inserted by means of chemical or electrochemical lithiation.[152] These materials may function as high capacity (500−600 mAh/g), high-energy positive electrodes in lithium batteries.[153] Besides $Li^+$, the polyvalent cations $Mg^{2+}$, $Zn^{2+}$, and $Al^{3+}$ can also be reversibly intercalated.[154]

The kinetics and the cycle performance of these positive electrodes must still be improved, although progress is being made in this direction.[155] In particular, hybrid vanadium pentoxide/polypyrrole (PPy/$V_2O_5$) aerogels were made by simultaneous polymerization of pyrrole and vanadium alkoxide $VO(OC_3H_7)_3$, using pyrrole−water−acetone mixtures. The aerogels obtained were monolithic, with a green-black coloration, a specific surface area from 150 to 257 $m^2\ g^{-1}$, and densities between 0.1 and 0.2 g $cm^{-3}$. They were sufficiently strong to be cut without fracturing, but their electrical conductivity decreased as the polypyrrole content increased. TEM studies showed they were comprised of fibers similar to those of $V_2O_5$ aerogels, but with a shorter chain length.[156]

Other possible compositions comprise $AgI-Al_2O_3$ composite aerogels, with a maximum room-temperature conductivity of $2.8 \times 10^{-3}$ S $cm^{-1}$. Here also, the conductivity is higher in the aerogel than in the corresponding xerogel, showing that the pore size distribution of aerogels is more effective than that of xerogels for enhancing the ionic conductivity.[157]

### B. Capacitor Electrodes

Here again, the chemical problem is to reversibly immobilize a large quantity of electrical charge carriers. Moreover, the aerogel itself must conduct electricity, which explains that these properties were mostly studied with carbon aerogels. The latter were investigated for applications as double layer electrodes in supercapacitors, pseudocapacitors, capacitive deionization units, and fuel cells.[158−160] They have a low electric resistance ($10^{-3}$−$10^{-2}$ Ω.m)[161] and, because of their high specific surface area, they can store more electrical energy than conventional capacitors (Figure 21). Typical specific capacitance for RF derived carbon aerogels is 45 F $g^{-1}$ in an aqueous electrolyte, or even higher depending on the experimental setup.[159,160] Their stored energy can be released very rapidly to provide an instant power up to 7.5 kW $kg^{-1}$.[158] More recently, carbon aerogels obtained by pyrolysis of polyacrylonitrile (PAN) aerogels have made it possible to achieve specific capacitances as high as 130 F $g^{-1}$ in a 5 M KOH aqueous media, with a stored energy density of approximately 15 kJ $kg^{-1}$ and a power density of approximately 1.4 kW $kg^{-1}$.[57] On the other hand, the ion storage potential of carbon aerogels make them good candidates for the deionization medium, for instance, the efficient removal of NaCl, as well as metals (Cu, Zn, Ni, Cd, Cr, Pb, U), from water.[9,159] Given their high specific pore volume, they can store a large amount of these solutes. Morover, they can easily be regenerated by applying an inverse voltage.

Carbon aerogels can also be impregnated with a metal vapor, for instance of ruthenium, for applications in electrocatalysis and power sources. The resulting nanostructure is composed of highly dispersed Ru particles (approximately 2−3 nm in diameter) attached to the carbon aerogel surface and homogeneously distributed throughout the material. A high proportion of Ru can be deposited (>50 wt %). These Ru particles themselves oxidize with water to produce hydrous $RuO_2$ which increase the specific capacitance of the carbon aerogels to values greater than 250 F/g.[162] Ruthenium dioxide is an important electrode material. High surface areas can be achieved in mixed $(Ru-Ti)O_x$ aerogels. These aerogels display a low specific capacitance, which can be explained by their high crystallinity degree. However, all RuOx domains in the aerogel are voltammetrically addressable.[163]

## C. Dielectric Materials

Thin film silica aerogel is investigated as super-low dielectric constant material for ultra-large-scale integrated circuits. It is considered that they could more than double computer speed.[164] Such films can for instance be made by using TMOS-based solution mixed with dimethyl sulfoxide, dried in supercritical carbon dioxide after coating. A relative dielectric constant as low as 1.1 can be obtained.[165] No intrinsic breakdown of $SiO_2$ aerogel films was observed under an electric field of up to 1 MV $cm^{-1}$. This property maintained after annealing at 450 °C. However, early breakdown was observed after annealing at 700 °C, which was attributed to a random enhancement of the electric field at the irregular asperity of the rough interface with the metallic surface of the capacitor structure.[166] It is possible to modify the surface of the aerogel, for instance with hexamethyldisilazane (HMDS), to obtain electret materials (i.e., materials which produce a permanent external electric field) as good as porous poly(tetrafluoroethylene) (PTFE).[167]

The dielectric properties of organic aerogels make them applicable in the capacitive part of low pass filters. Their complex dielectric constant $\epsilon$ shows losses due to relaxation phenomena, attributable to water adsorbed at the inner surface of the samples, in the range of frequency from 1 Hz to 50 kHz. This is different with silica aerogels which do not show losses.[168]

## D. Piezoelectric Materials

For ultrasonic applications in gases, porous piezoelectric transducers with low acoustic impedance are required. Such highly porous piezoceramics can be prepared by sol−gel processing, supercritical drying, and subsequent firing. As an example, lead zirconium titanate (PZT) aerogels with composition $PbZr_{0.53}Ti_{0.47}O_3$ can be obtained as monoliths with porosities up to 90 vol % and specific surface area above 300 $m^2$ $g^{-1}$. During drying, metallic lead is formed as an intermediate phase. Then, during thermal treatment at 600 °C, the aerogels dried in carbon dioxide tend to disintegrate, while those supercritically dried in 2-propanol transform to monolithic polycrystalline PZT with a porosity exceeding 70% and an enhanced mechanical stability. To facilitate their polarization, the coercive field strength can be lowered with dopants, for instance with 2 mol % neodymium, which does not affect the material porosity.[169−171] Finally, aluminosilicate aerogels present some piezoelectric properties which are better than those of xerogels and can be explained by the gel structure.[172]

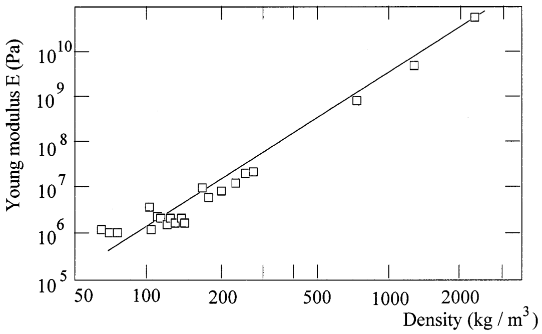


**Figure 22.** Young modulus as a function of silica aerogel density. Reprinted with permission from ref 173, with modification. Copyright 1988 Elsevier Science.

## IX. Application of Aerogels Due to Their Mechanical Properties

A distinctive characteristic of silica aerogels is that they are extremely light, brittle materials, yet sufficiently strong to be handled. Their compressive strength, tensile strength, and elastic modulus are very low, and they largely depend on the network connectedness and aerogel density (Figure 22). Indeed, as previously mentioned, a gel can however be aged in alkoxide solutions to chemically stiffen its network, especially the necks between colloidal particles. Aging treatments make gels more resistant to capillary stresses and improve their mechanical properties. It can increase their shear modulus by up to 23 times.[174] Typically, aerogels can easily be compressed, in particular by the capillary stresses during adsorption or desorption in mercury porometry, thermoporometry, and nitrogen adsorption.[175] The magnitude of the contraction can reach 50%.[9] When their macroporosity is measured using a mercury porosimeter, two phenomena can be observed as the applied pressure increases. In a lower pressure range, no intrusion at all is detected and only a crushing of the aerogel occurs. Above a certain pressure threshold, mercury intrusion is then really observed.[176] Therefore, precaution must be taken when this technique is applied to all fragile materials and especially with aerogels or aerogel-like materials of low bulk densities. Besides, the mechanical properties are sensitive to the synthesis chemistry of the gel, the environment, and the storage history.[177] With age, the compressive strength and elastic moduli increase while the strain at fracture decreases. The environment is responsible for subcritical crack growth, which proceeds by a stress corrosion mechanism analogous to that observed in dense silica glass subjected to alkaline aqueous solutions. Crack growth can be considerably reduced in hydrophobic aerogels,[178] although an apparently fully hydrophobic character does not totally impede water molecules from reaching the crack tip.[179]

The fragility of aerogels may explain why they do not seem to have been used or even studied for application in filtration membranes, contrary to xerogel oxides which have been extensively studied and used mostly as coatings on a ceramic support.[180] Despite their low density and brittle characteristics, the mechanical properties of silica aerogels are interesting for some applications. The easy compressibility can advantageously be used in kinetic energy absorber materials.[11] Much energy can be absorbed during a shock compression.[181] Silica and carbon aerogels actually constitute low shock impedance materials, useful to confine few eV plasmas, to capture freezing states of minerals generated in 100 Mbar shock pressures, or in fluid mixing studies requiring X-ray induced shocks.[11,181,182] Hybrid silica aerogels can also be made by mixing silicon alkoxide with hybrid precursors such as polydimethyl siloxane (PDMS), and the gels obtained have a more rubber-like flexibility. With 20% PDMS, they can be elastically compressed by 30%.[183]

## *X. Cosmic (Comet) Dust Collection by Silica Aerogels*

Since 1987, the Jet Propulsion Laboratory has developed with Tsou[184] a new technique for collecting comet dust. Indeed comet dust collection is of great interest for planetary scientists. These small comet particles, with dimensions of the order of the micron (from 0.1 to 100), travel space at speeds of many tens of kilometers per second. For this reason they are called hypervelocity particles. It is necessary to capture them intact, i.e., without melting, and this can only be achieved by transparent silica aerogels. To be a good device, the aerogel monolith must offer a wide range of specific qualities such as a suitable mesoporosity, a good transparency in order to easily locate the extraterrestrial particles, a wide span of low apparent densities, high internal surface areas, a very high cleanliness, good launch and landing robustness (they are embarked in space shuttles such as the Spacelab module, space laboratories, balloons, etc.), a very low thermal conductivity coefficient, a very good resistance to very rapid thermal cycling from 200 to −100 °C for instance, a good stability toward magnetic and UV radiation, a good stability versus ionic erosion, and of course very low mass. All these requirements are fully met by pieces of silica aerogels made by a “two-step acid−base catalysis gel” (TSABG) and prepared at the Lawrence Livermore National Laboratory. At the present time, they are irreplaceable comet dust capture medium. Such silica aerogel are also part of the Stardust project, with the mission to provide back to Earth in 2006, samples of a recently deflected comet named Wild-2 which will be encountered in 2004 and also contemporary interstellar samples. Silica aerogels were also engaged in the recent PATHFINDER MARS mission to insulate the Sojourner Mars Rover. During the night, the temperature dropped down to −67 °C while the temperature inside the Rover measured 21 °C, which permitted the protection of the very sensitive electronics from freezing. A similar program termed European Retrieval Carrier (EURECA) satellite is being studied.[184] Other applications of this type are being considered, for instance to collect aerosol particles,[185] to protect space mirrors, or to design tank baffles.[11,12]

## *XI. Aerogels as Additives or Encapsulation Medium*

### A. Chemical Applications

Aerogel particles can be used as filler of other materials, to provide them with some hardness, resistance to wear, or some thickening characteristics. This is the case with paints, varnishes, and elastomers in tires.[12] On the other hand, aerogels can be used as carriers of diverse components, for instance pigments. In pharmacy and agriculture, where many applications require a progressive release of active agents, aerogel particles can operate as nanovessels to carry substances as diverse as fungicides, herbicides, pesticides. As colloidal abrasives, they even show some insecticide properties as they remove the protecting lipid layer on insects, which die more rapidly.[186] Partially sintered aerogels, which are mechanically stronger to resist capillary stresses, are convenient to store or transport liquids such as rocket fuel.[7] Hazardous liquids such red fuming nitric acid and unsymmetric 1,1-dimethyl hydrazine (UDMH), both used as rocket fuels, have been stored with silica aerogels.[187] Different tasks consist in adsorbing or extracting some chemical components, for instance to treat wastewater, to confine radioactive waste,[11] or to filter gases.[188] In chemistry, silica, alumina, and carbon aerogels impregnated with $CaCl_2$, LiBr, and $MgCl_2$ have been tested as water sorbents for heat storage at low temperature. Their energy storage ability $E$ measured by a differential scanning calorimetry (DSC) technique can be as high as 4.0 kJ/g for naturally saturated sorbents, which is much higher than for common sorbents such as zeolites and unimpregnated silica gels.[189]

Resorcinol-formaldehyde (RF) aerogels can also be templated with $SiO_2$, $Al_2O_3$, or $TiO_2$ nanoparticles.[190] Upon carbonization in an inert atmosphere between 500 and 900 °C, the oxide component helps to develop mesoporosity.[191] Etching the $SiO_2$ particles with HF then produces nanoporous carbons with pore sizes predominantly in the range of 10−100 nm. These carbons exhibit very high pore volumes of $>4$ $cm^3/g$ and surface areas up to 1000 $m^2/g$. Their adsorption capacities for bulky dyes is over 10 times higher than that of commercial activated carbon.[192]

## B. Aerogels for Inertial Confinement Fusion (ICF)

Borate, organic, and carbon aerogels were used for some time in inertial confinement fusion experiments (ICF) as target microspheres containing the fuel.[193] These aerogels were stable to radiation and could be wetted by deuterium and tritium. Hollow silica aerogel droplets for ICF target experiments were proposed by Kim et al.,[194] Jang et al.,[195] and Kim and Jang[196] 10 years ago for the fusion of mixtures of liquid deuterium and tritium using a powerful laser beam of the Nova or Supernova type at the Lawrence Livermore National Laboratory. Tetraethoxysilane (TEOS) was selected as precursor and gelled in ethanol containing aqueous nitric acid. The droplets were generated by a double nozzle reactor. Hair et al.[197] more recently showed that even organic aerogels such as a copolymer resorcinol/formaldehyde having been supercritically dried with respect to liquid $CO_2$ exhibited good qualities for ICF targets in terms of cell size (0.1 $\mu$m) and density (0.05−0.1 g/cm$^3$) and $Z$ value, under cryogenic conditions. Overturff et al.[198] succeeded in making transparent foam shell targets from resorcinol and formaldehyde in organic solvents of low solubility in water which prevented the densification of the foam. The fabrication of these low-density foam shells was detailed in the papers of Schroen-Carey et al.[199] and Lambert et al.,[200] respectively. The requirements were to make spherical organic copolymer shells of a diameter of 1−2 mm with a cryogenic liquid or solid layer of deuterium−tritium mixture in the inside surface with a thickness of 80−100 $\mu$m.

## C. Silica Aerogels for Nuclear Waste Storage

Silica aerogels have been proposed by Reynes et al.[201] for the storage of long life actinide wastes because they are chemically very stable with time on stream and possess a very large porous volume per cm$^3$. They can easily be converted into vitreous silica after a low temperature (at about 1000 °C) and short heat treatment. The authors[201,202] impregnated the porous aerogels by a solution of the “actinide salts” simulated by neodyme nitrate, and after evacuation of the liquid phase, they were sintered as a composite glassy material containing the nuclear wastes under the form of neodyme oxide. The storage was improved from the point of view of permeability by adding a pyrogenic (fumed) silica, namely aerosil, of large pore dimensions into the TEOS precursor solution in the sol−gel step, in such a way to synthesize a so-called composite aerogel. Up to a solution of 20% of nitrate in weight, the results showed their total capture by the composite aerogel system. The experimental results also indicated that these aerogels were able to store the simulated nuclear waste much longer than the conventional borosilicate glass.[202,203]

## D. Applications in Fundamental Sciences

Aerogels offer an opportunity to perform original studies. Because of their high specific surface area, they can for instance be used as a means of introducing strong perturbations in fluids near their critical temperature. In aerogels, the gel network acts as an impurity for the fluids which strongly interact with the solid surface. Hence, large fluid NMR signals with long polarization lifetimes can be recorded, revealing a very weak specific wall relaxation.[204] This effect can be used to study either the gel itself or the fluid. The gel network was for instance studied by impregnation with liquid $^{131}$Xe near its critical temperature ($T_c$ of approximately 289 K). Magnetic resonance images were obtained, which made it possible to differentiate between aerogels with a different density or hydration level.[205] Regarding studies on the fluid properties, much work has been devoted to superfluid $^4$He,[206−208] phase separation of $^3$He-$^4$He mixtures,[209,210] and more recently to $^3$He near its critical temperature.[211−214] It was found that the perturbations due to the gel network affect the fluid long range order properties. The superfluid state in $^3$He can only be maintained at temperatures between $T_c^a$ and $T_c$, where $T_c$ is the bulk $^3$He superfluid critical temperature and $T_c^a < T_c$ depends on the aerogel and the pressure. With neon, the critical temperature slightly lowers, and the coexistence region becomes more narrow.[215] Similarly, if an aerogel is impregnated with a nematic liquid crystal, the gel network randomness destroys the crystal long-range order and transforms the liquid crystal into a glassy state.[216]

## XII. Application of Aerogels in Catalysis

Sol−gels have characteristics which make them good materials for applications in catalysis, and review papers have been published on this subject.[217−219] Catalytic reactions can be of the redox or of the acid−base type. In the latter case, as in all oxides, different types of Brönsted or Lewis acid sites may coexist. To incorporate more or stronger acid sites, a classical technique consists of substituting dopant cations with a valence state different from that of the host oxide. As an example, trivalent $Al^{3+}$ cations can be substituted for tetravalent $Si^{4+}$ cations in $SiO_2$, in such a way that they occupy a tetrahedral Si site. Sol−gel processes make it possible to incorporate such Al atoms in tetrahedral coordination ($Al^{tet}$ atoms) in a silicate network with a high specific surface area, hence to create many such surface sites. Redox catalytic sites are due either to transition metal atoms (Cu, Fe, Mo, V) able to change their valence state or to noble metals (Pt, Pd, Ir, ...). The former ones explains that transition metal oxide aerogels were mostly investigated for catalytic reactions. For the latter metals, an oxide aerogel can be used as a support. In all cases, a major advantage of aerogels is their high specific surface area, which makes it possible to increase the number of active sites per gram of material. Moreover, the pore texture of sol−gel oxides presents a relatively good resistance to thermal coarsening, at least at temperatures fitted to fine organic synthesis.

However, compared to traditional xerogels, aerogels are more recent materials for use in this field. The types of chemical reactions involved with them comprise selective oxidation such as with $NiO-Al_2O_3$ and $NiO-SiO_2-Al_2O_3$[220,221] nitroxidation with $NiO-Al_2O_3$,[217] selective reduction with $Fe_2O_3-Cr_2O_3-$

$Al_2O_3$,[222] polymerization with $TiCl_4-Al_2O_3$,[223] and selective hydrogenation as in the Fischer Tropsch reaction with $Fe_2O_3-SiO_2$ and $Fe_2O_3-Al_2O_3$.[224,225] Selective hydrogenation is mostly due to metal catalysts, and sol−gels are efficient as supports, such as with $Cu-Al_2O_3$, $Ni-SiO_2$, $Ni-MoO_2$, and $Pd-Al_2O_3$.[226−229] However, active metal particles supported on oxide aerogels can also be prepared directly from a multicomponent aerogel. To obtain the metal particles, supercritical drying must be performed in a reducing environment, that is to say either in alcohol, by replacing $N_2$ with $H_2$ before heating the autoclave, or by flushing the autoclave with $H_2$ at approximately 200 °C. In these conditions, oxides such as NiO, CuO, PbO, $V_2O_5$ are reduced to finely divided metal particles with a size a few nanometers.[230−233] Colloidal gold particles, 5−100 nm in size, were also obtained by a similar process.[234] For organic synthesis, sol−gel catalysts often have a high selectivity, but their activity is not outstanding.

Aerogels can be applied to the protection of the environment, in particular to reduce the emissions of pollutants in the exhaust gases from automobiles. These main pollutants are CO, residual hydrocarbons designated by HC, and nitrogen oxides designated by $NO_x$. Hence, catalysts are needed to achieve the clean combustion of hydrocarbons. Possibly, it is desirable to simultaneously eliminate the three types of pollutants, in a so-called "three-way catalysis", so that only $CO_2$, $H_2O$, and $N_2$ are released in the atmosphere. For diesel engines, it is moreover necessary to favor the catalytic combustion of engine soot. In practice, the catalysts which are needed must operate at a temperature from 900 to 1200 °C, in conditions where most aerogels lose their high specific surface area. In particular, oxide sintering is promoted by $H_2O$ present in engine exhaust gases. Also, at these temperatures, chemical reactions between the support and the active catalytic phases commonly occur. Despite these problems, a relative success has so far been achieved in the clean combustion of methane with aerogels derived from the hexaaluminate $BaAl_{12}O_{19}$ doped with Mn, Cr, Fe, Ni, or Co.[235−237] This compound has a structure derived from cubic spinel, and its densification is attenuated because of its lamellar texture.

Other chemical synthesis catalysts, which operate at milder temperatures, can be made by grafting organometallic complexes on the inner walls of aerogels. Perhaps, the most recent and interesting result in this domain concerns the biocatalysts made by encapsulation of enzymes in silica aerogels.[238,239] The best success presently is with encapsulated lipases which can be used for esterification reactions. Biosensors made by encapsulation of other biocatalysts are also being studied.[240]

## XIII. Silica Aerogel and Life Science

The first example summarized below deals with biocatalysis, and the second one depicts a process to detect viral particle by immobilized bacteria. Buisson et al.[238,239] described the in situ encapsulation of the *Pseudomonas cepacia* lipase into a hydrophobic silica aerogel (Figure 23) and tested the resulting solid in the reaction of esterification of lauric acid by 1-octanol. It is well-known that enzymes need to adopt special conformations in order to be active, i.e., that once encapsulated into the porous silica aerogel matrix, no strong interactions between the enzyme and the "solid solvent" are expected to build up. The authors observed that, contrary to the same silica matrix, but in the form of a xerogel, the aerogel type possessed a much higher activity in the reaction test. The explanation proposed was that in the aerogel matrix, the lipase was able to adjust its good conformation due to the highly developed porous network (large controlled meso- and macropores).

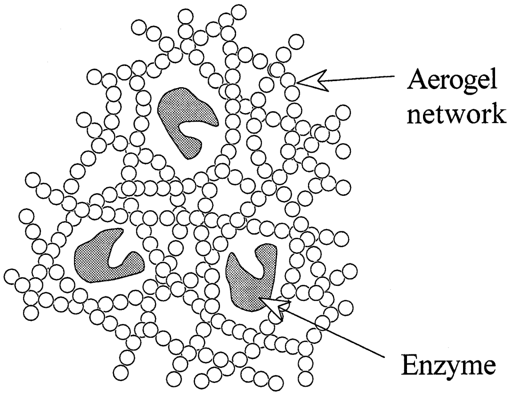


**Figure 23.** Representation of the encapsulation of enzymes in silica aerogels. After Buisson et al.[239]

The second example is related to the use of silica macroporous aerogels as biosensors involving the detection of a bacteriophage by a bacteria entrapped into the aerogel. Power et al.[240] described a solid biosensor prepared and tested under the form of an aerosol of aerogel containing *Escherischia coli* and the green fluorescent protein (GFP), the latter being obtained from the jellyfish called *Aequorea Victoria*. The GFP is a very interesting "bio-reporter". When a virus, like the bacteriophage T7 polymerase promoter also under the form of an aerosol, contacts the bacteria, a green fluorescence light is emitted. Silica aerogels offer the advantage to immobilize the sensor part of the detector which can then give an easy detectable and even quantified response to a biological organism existing as an aerosol in the environment. These two kinds of experiments clearly demonstrate that silica aerogels are biocompatible materials.

## XIV. Further Potential Developments in the Chemical Synthesis of Aerogels

As seen all along this review, the chemistry is very different between, on one hand, silica, organic, and carbon aerogels, which can easily be made as monoliths, and on the other hand, other materials which are essentially obtained as powders. In the future, new chemical developments may attenuate this difference. Recently, new generations of precursors have appeared which provide more flexibility to control the reaction kinetics of alkoxides other than those of Si. These precursors have been designed to reduce their overall transformation rates, by partially replacing some OR ligands by ligands of a different nature.

Such ligands include oxo ligands, which give oxo-alkoxides, and organic ligands, which provide organometallic bonds C−M. The latter case is particularly well developed in the case of Si for which an abundant list of $R'Si(OR)_3$ precursors, where R′ is an organic group or chain (with an end methyl, ethyl, propyl, phenyl, amine, epoxy, thio group, etc.), is available in the chemical catalogues. But such compounds begin to appear for other metals. They offer the possibility to functionalize gels, for instance to make them hydrophobic, graft other molecules (inorganic, organic, or bio-organic), or to synthesize hybrid organic−inorganic gels, if the R′ chain can itself be polymerized. Reviews of these hybrid gels have been published,[19,241] although their drying to aerogels remains to be done. For metals other than Si, bidentate chelated ligands L, which cannot be easily hydrolyzed as previously mentioned for Al precursors, have provided interesting new precursors $[M(OR)_xL_y]_n$.[242,243] The most elaborate recent precursors are complex macromolecular clusters which may comprise several metal atoms M of a different nature, and several types of ligands in their molecular structure. New compounds of this type appear in increasing number, but very few have been investigated for sol−gel applications.[14]

## XV. Conclusions

This review only gives a very limited idea of the chemistry involved in the synthesis of aerogels. Silica by itself is a remarkable inorganic oxide with a very rich chemistry, which can be tailored to a range of applications in fundamental science and high technology. Moreover, some recent developments in the preparation of “aerogel-like” materials at ambient pressure, which eliminates the use of the autoclave as recently described by Land et al.,[244] will really open new fields of applications at the industrial level and require further chemical studies. Aerogels, in the general sense, whatever their nature—organic, inorganic, simple, or composite—really deserve to be viewed as a new class of chemically designed architecture and much remains to be done for materials other than silica.

## XVI. References

(1) Fricke, J., Ed. *Aerogels*; Proceedings of the First International Symposium, Wurzburg, FRG, Sept. 23−25, 1985, Springer-Verlag, Berlin, 1986.
(2) Vacher, R.; Phalippou, J.; Pelous, J.; Woignier, T., Eds. Proceedings of the Second International Symposium on Aerogels (ISA2). *Rev. Phys. Appl. Colloq.* **1989**, 24−C4.
(3) Fricke, J., Ed. Proceedings of the Third International Symposium on Aerogels (ISA 3). *J. Non-Cryst. Solids* **1992**, *145*.
(4) Pekala, R. W.; Hrubesh, L. W., Eds. Proceedings of the Fourth International Symposium on Aerogels (ISA 4). *J. Non-Cryst. Solids* **1995**, *186*.
(5) Phalippou, J.; Vacher, R., Eds. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*.
(6) Ashley, C. S.; Brinker, C. J.; Smith, D. M., Eds. Aerogels 6; Proceedings of the Sixth International Symposium on Aerogels (ISA6), Albuquerque, NM, 8−11 October 2000. *J. Non-Cryst. Solids* **2001**, *285*.
(7) Gesser, H. D.; Goswani, P. C. *Chem. Rev.* **1989**, *89*, 765.
(8) Fricke, J.; Emmerling, A. *Struct. Bonding (Berlin)* **1992**, 77 (*Chem., Spectrosc. Appl. Sol−Gel Glasses*, 37).
(9) Fricke, J; Emmerling, A. *J. Sol-Gel Sci. Technol.* **1998**, *13*, 299.
(10) Burger, T; Fricke, J. *Chem. Phys.* **1998**, *102*, 1523.
(11) Hrubesh, L. W. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 335.
(12) Schmidt, M.; Schwertfeger, F. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 364.
(13) Husing, N.; Schubert, U. *Angew. Chem., Int. Ed.* **1998**, *37*, 23.
(14) Livage, J.; Henry, M.; Sanchez, C. Sol-Gel Chemistry of Transition Metal Oxides. *Prog. Solid State Chem.* **1988**, *18*, 259.
(15) Woignier, T.; Phalippou, J.; Zarzycki, J. *J. Non-Cryst. Solids* **1984**, *63*, 117.
(16) Yoldas, B. E. *J. Mater. Sci.* **1975**, *10*, 1856.
(17) Brinker, C. J.; Scherer, G. W. *Sol−Gel Science. The Physiscs and Chemistry of Sol−Gel Processing*, Academic Press, New York, 1990.
(18) Pierre, A. C. *Introduction to Sol-Gel Processing*, Kluwer, Boston, 1998.
(19) Sanchez, C.; Ribot, F. *New J. Chem.* **1994**, *18*, 1007.
(20) Pajonk, G. M. *Heterog. Chem. Rev.* **1995**, *2*, 129.
(21) Graham, T. *J. Chem. Soc.* **1864**, *17*, 318.
(22) Derjaguin, B. V.; Landau L. D. *Acta Physicochim. URSS* **1941**, *14*, 633.
(23) Verwey, E. J. W.; Overbeek, J. T. G. *Theory of the Stability of Lyophobic Colloids*; Elsevier, Amsterdam, 1948.
(24) Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3083, 3091, 3096.
(25) Stockmayer, W. H. *J. Chem. Phys.* **1943**, *11*, 45.
(26) Hammersley, J. M. *Proc. Cambridge Philos. Soc.* **1957**, *53*, 642.
(27) Mandelbrot, B. B. *Fractals: Form, Chances and Dimensions*; Freeman, San Francisco, 1977.
(28) Ebelmen, M. *Ann. Chim. Phys.* **1846**, *16*, 129; Ebelmen, M. *C. R. Acad. Sci., Paris* **1847**, *25*, 854.
(29) Sanderson, R. T. *Science* **1951**, *114*, 670
(30) Kistler, S. S. *J. Phys. Chem.* **1932**, *36*, 52.
(31) Broecker, F. J.; Heckmann, W.; Fischer, F.; Mielke, M.; Schroeder, J.; Stange, A. Proceedings of the Second International Symposium on Aerogels (ISA2). *Rev. Phys. Appl. Colloq.* **1989**, 10.
(32) Gash, A. E.; Tillotson, T. M.; Satcher, J. H., Jr.; Hrubesh, L. W.; Simpson, R. L. Aerogels 6; Proceedings of the Sixth International Symposium on Aerogels (ISA6), Albuquerque, NM, 8−11 October 2000. *J. Non-Cryst. Solids* **2001**, *285*, 22.
(33) Henry, M.; Jolivet, J. P.; Livage, J. *Struct. Bonding*, **1992**, *77*, 154.
(34) Harris, R. K.; Knight, C. T. G.; Hull, W. E. in *Soluble Silicates*; Falcone, J. S., Jr.; ACS Symp. Series, Americam Chemical Society, Washington, DC 1982; vol. 194, p 79.
(35) Pauling, L. *The Nature of Chemical Bonds*; Cornell University Press, Ithaca, NY, 1960.
(36) Mozzi, R. L.; Warren, B. E. *J. Appl. Cryst.* **1969**, *2*, 164.
(37) Pierre, A. C.; Uhlmann, D. R. *Mater. Res. Soc. Symp.* **1986**, *73*, 481.
(38) Mizushima, Y.; Hori, M. *J. Mater. Res.* **1993**, *8*, 2993.
(39) Mizushima, Y.; Hori, M. *J. Non-Cryst. Solids* **1994**, *167*, 1.
(40) Horiuchi, T.; Osaki, T.; Sugiyama, H.; Masuda, H.; Horio, K.; Suzuki, T.; Mori, T.; Sago, T, *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2573.
(41) Komarneni, S.; Roy, R.; Selvaray, U.; Malla, P. B.; Breval, E. *J. Mater. Res.* **1993**, *8*, 3163.
(42) Osaki, T.; Horiuchi, T.; Sugiyama, T.; Susuki, K.; Mori, T. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 111.
(43) Hernandez, C.; Pierre, A. C. *J. Sol-Gel Sci. Technol.* **2001**, *20*, 227.
(44) Pierre, A.; Begag, R.; Pajonk, G. *J. Mater. Sci.* **1999**, *34*, 4937.
(45) Poco, J. F.; Satcher, J. H., Jr.; Hrubesh, L. W. Aerogels 6; Proceedings of the Sixth International Symposium on Aerogels (ISA6), Albuquerque, NM, 8−11 October 2000. *J. Non-Cryst. Solids* **2001**, *285*, 64.
(46) Pietro, J. J.; Rolison, D. R. Aerogels 6; Proceedings of the Sixth International Symposium on Aerogels (ISA6), Albuquerque, NM, 8−11 October 2000. *J. Non-Cryst. Solids* **2001**, *285*, 13.
(47) Dagan, G.; Tomkiewicz, M. *J. Phys. Chem.* **1993**, *97*, 12651.
(48) Campbell, L. K.; Na, B. K.; Ko, E. I. *Chem. Mater.* **1992**, *4*, 1329.
(49) Lee, H. J.; Song, J. H.; Kim, J. H. *Mater. Lett.* **1998**, *37*, 197.
(50) Pekala, R. W. *J. Mater. Sci.* **1989**, *24*, 3221.
(51) Tamon, H.; Ishizaka, H. *J. Colloid Interface Sci.* **2000**, *223*, 305.
(52) Tamon, H.; Ishizaka, E. *J. Colloid Interface Sci.* **1998**, *206*, 577.
(53) Zhang, S. Q.; Wang, J.; Shen, J.; Deng, Z. S.; Lai, Z. Q.; Zhou, B.; Attia, S. M.; Chen, L. Y. *Nanostruct. Mater.* **1999**, *11*, 375.
(54) Barral, K. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 46.
(55) Lee, K. N.; Lee, H. J.; Kim, J. H. *J. Supercrit. Fluids* **2000**, *17*, 73.
(56) Placin, F.; Desvergne, J. P.; Cansell, F. *J. Mater. Chem.* **2000**, *10*, 2147.
(57) Gouerec, P.; Miousse, D.; Tran-Van, F.; Dao, L. H, *J. New Mater. Electrochem. Syst.* **1999**, *2*, 221.

(58) Biesmans, G.; Randall, D.; Francais, E.; Perrut, M. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 36.
(59) Biesmans, G.; Mertens, A.; Duffours, L.; Woignier, T.; Phalippou, J. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 64.
(60) Nguyen, M. H.; Dao, L. H. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 51.
(61) Tamon, H.; Ishizaka, H.; Yamamoto, T.; Suzuki, T. *Carbon* **1999**, *37*, 2049.
(62) Bock, V.; Emmerling, A.; Fricke, J. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 69.
(63) Petricevic, R.; Reichenauer, G.; Bock, V.; Emmerling, A.; Fricke, J. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 41.
(64) Tamon, H.; Ishizaka, H.; Araki, T.; Okazaki, M. *Carbon* **1998**, *36*, 1257.
(65) Reichenauer, G.; Emmerling, A.; Fricke, J.; Pekala, R. W. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 210.
(66) Maldonado-Hodar, F. J.; Moreno-Castilla, C.; Rivera-Utrilla, J.; Hanzawa, Y.; Yamada, Y. *Langmuir*, **2000**, *16*, 4367.
(67) Kuhn, J.; Brandt, R.; Mehling, H.; Petricevic, R.; Fricke, J. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 58.
(68) Bekyarova, E.; Kaneko, K. *Langmuir* **1999**, *15*, 7119.
(69) Bekyarova, E.; Kaneko, K. *Adv. Mater.* **2000**, *12*, 1625.
(70) Barbieri, O.; Ehrburger-Dolle, F.; Rieker, T. P.; Pajonk, G. M. M.; Pinto, N.; Venkateswara Rao, A. Aerogels 6; Proceedings of the Sixth International Symposium on Aerogels (ISA6), Albuquerque, NM, 8−11 October 2000. *J. Non-Cryst. Solids* **2001**, *285*, 109.
(71) Peri, J. B. *J. Phys. Chem.* **1966**, *70*, 2937.
(72) Nicolaon, G. A.; Teichner, S. J. *Bull. Soc. Chim. Fr.* **1968**, 1900, 1906.
(73) Matson, D. W.; Smith, R. D. *J. Am. Ceram. Soc.* **1989**, *72*, 871−881.
(74) Pajonk, G. M. in *A short history of the preparation of aerogels and carbogels, in Sol−Gel Processing and Applications*; Attia, Y. J., Ed.; Plenum Press, New York, **1994**; p 201.
(75) Saliger, R.; Bock, V.; Petricevic, R.; Tillotson, T.; Geis, S.; Fricke, J. *J. Non-Cryst. Solids* **1997**, *221*, 144.
(76) Smith, D. M.; Deshpande, R.; Brinker, C. J. Better Ceramics Through Chemistry V. *Mater. Res. Soc. Symp. Proc.* **1992**, *271*, 567.
(77) Chen, H.; Ruckenstein, E. *J. Colloid Interface Sci.* **1991**, *145*, 581.
(78) Chan, J. B.; Jonas, J. *J. Non-Cryst. Solids* **1990**, *126*, 79.
(79) Roger, C.; Hampden-Smith, M. J. *J. Mater. Chem.* **1992**, *2*,1111.
(80) Zarzycki, J.; Prassas, M.; Phalippou, J. *J. Mater. Sci.* **1982**, *17*, 3371.
(81) Hench, L. L. in *Science of Ceramic Chemical Processing*; Hench L. L., Ulrich, D. R., Eds.; Wiley, New York, **1986**; p 52.
(82) Schwertfeger, F.; Frank, D.; Schmidt, M. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 24.
(83) Smith, D. M.; Stein, D.; Anderson, J. M.; Ackermann, W. Proceedings of the Fourth International Symposium on Aerogels (ISA 4). *J. Non-Cryst. Solids* **1995**, *186*, 104.
(84) Tretyakov, Y. D.; Shlyakhtin, O. A, *J. Mater. Chem.* **1999**, *9*, 19.
(85) Tamon, H.; Ishizaka, H.; Yamamoto, T.; Suzuki, T. *Carbon* **2000**, *38*, 1099.
(86) Klvana, D.; Chaouki, J.; Repellin-Lacroix, M.; Pajonk, G. M. Proceedings of the Second International Symposium on Aerogels (ISA2). *Rev. Phys. Appl. Colloq.* **1989**, 29.
(87) Kocklenberg, R.; Mathieu, B.; Blacher, S.; Pirard, R.; Pirard, J. P.; Sobry, R.; VandenBossche, G. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 8.
(88) Yoldas, B. E.; Annen, M. J.; Bostaph, J. *Chem. Mater.* **2000**, *12*, 2475.
(89) Venkateswara Rao, A.; Pajonk, G. M.; Haranath, D. *Mater. Sci. Technol.* **2001**, *17*, 343.
(90) Pajonk, G. M. *Prog. Colloid Polym. Sci.*, **2002** (submitted for publication).
(91) Venkateswara Rao, A.; Haranath, D.; Pajonk, G. M.; Wagh, P. B. *Mater. Sci. Technol.* **1998**, *14*, 1194.
(92) Venkateswara Rao, A.; Pajonk, G. M. Aerogels 6; Proceedings of the Sixth International Symposium on Aerogels (ISA6), Albuquerque, NM, 8−11 October 2000. *J. Non-Cryst. Solids* **2001**, *285*, 202.
(93) Wolff, B.; Seybold, G.; Krueckau, F. E. (BASF-G), Eur. Pat. Appl. EP 0340707, 1989; *Chem. Abstr.* **1990**, *112*, P82924x.
(94) Quenard, D.; Chevalier, B.; Sallee, H; Olive, F.; Giraud, D. *Rev. Metall. Cah. Inf. Tech.* **1998**, *95*, 1149.
(95) Rigacci, A.; Ehrburger-Dolle, F.; Geissler, E.; Chevalier, B.; Sallée, H.; Achard, P.; Barbieri, O; Berthon, S.; Bley, F.; Livet, F.; Pajonk, G. M.; Pinto, N.; Rochas, C. Aerogels 6; Proceedings of the Sixth International Symposium on Aerogels (ISA6), Albuquerque, NM, 8−11 October 2000. *J. Non-Cryst. Solids* **2001**, *285*, 187.
(96) Duer, K.; Svendsen, S. *Sol. Energy* **1998**, *63*, 259.
(97) Fricke, J.; Arduini-Schuster, M. C.; Büttner, D.; Ebert, H.-P.; Heinemann, U.; Hetfleisch, J.; Hümmer, E.; Kuhn, J. *Therm. Conduc.* **1990**, *21*, 235.
(98) Fricke, J.; Lu, X.; Wang, P.; Büttner, D.; Heineman, U. *J. Heat Mass Transfer* **1992**, *35*, 2305.
(99) Zobel, W.; Strähle, R. *Proc. Inst. Mech. Eng. IMechE Conf.* **1995**, *379*, C496/017.
(100) Ruffner, J. A.; Clem, P. G.; Tuttle, B. A.; Brinker, C. J.; Sriram, C. S.; Bullington, J. A. *Thin Solid Films* **1998**, *332*, 356.
(101) Tscheuschner, D.; Ratke, L. *Cryst. Res. Technol.* **1999**, *34*, 167.
(102) Alkemper, J.; Sous, S.; Stocker, C.; Ratke, L. *J. Cryst. Growth* **1998**, *191*, 252.
(103) Pajonk, G. M. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 307.
(104) Einasrud, M. A; Nilsen, E.; Rigacci, A.; Pajonk, G.,M.; Buathier, S.; Valette, D,; Durant, M.; Chevalier, P; Nitz, P.; Ehrburger-Dolle, F. Aerogels 6; Proceedings of the Sixth International Symposium on Aerogels (ISA6), Albuquerque, NM, 8−11 October 2000. *J. Non-Cryst. Solids* **2001**, *285*, 1.
(105) Schwertfeger, F.; Glaubitt, W.; Schubert, U. Proceedings of the Third International Symposium on Aerogels (ISA 3). *J. Non-Cryst. Solids* **1992**, *145*, 85.
(106) Schwertfeger, F.; Hüsing, N.; Schubert, U. *J. Sol-Gel Sci. Technol.* **1994**, *2*, 103.
(107) Hüsing, N.; Schubert, U.; Misof, K.; Fratzi, P. *Chem. Mater.* **1998**, *10*, 3024.
(108) Venkateswara Rao, A.; Kulkarni, M. M.; Pajonk, G. M.; Amalnerkar, D. P.; Seth, T. *J. Sol-Gel Sci. Technol.* **2002** (in press).
(109) Lu X.; Wang P.; Arduini-Schuster, M. C.; Kuhn J.; Büttner, D.; Nilsson, O.; Heinemann, U.; Fricke J. Proceedings of the Third International Symposium on Aerogels (ISA 3). *J. Non-Cryst. Solids* **1992**, *145*, 207.
(110) Biesmans, G.; Randall, D.; Francais, E.; Perrut, M. *Cell. Polym.* **1998**, *17*, 17.
(111) Deng, Z. S.; Wang, J.; Wu, A. M.; Shen, J.; Zhou, B. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 101.
(112) Smith, D. M.; Maskara, A.; Boes, U. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 254.
(113) Schmidt-Winkel, P.; Lukens, W. W.; Yang, P. D.; Margolese, D. I.; Lettow, J. S.; Ying, J. Y.; Stucky-GD, *Chem. Mater.* **2000**, *12*, 686.
(114) Forest, L.; Gibiat, V.; Woignier, T. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 287.
(115) Conroy, J. F. T.; Hosticka, B.; Davis, S. C.; Smith, A. N.; Norris, P. M. *Microscale Thermophys. Eng.* **1999**, *3*, 199.
(116) Gross, J.; Fricke, J. Proceedings of the Third International Symposium on Aerogels (ISA 3). *J. Non-Cryst. Solids* **1992**, *145*, 217.
(117) Gronauer, M.; Fricke, J. *Acustica* **1986**, *59*, 177.
(118) Gerlach, R.; Kraus, O.; Fricke, J.; Eccardt, P.-C.; Kroemer, N.; Magori, V. Proceedings of the Third International Symposium on Aerogels (ISA 3). *J. Non-Cryst. Solids* **1992**, *145*, 227.
(119) Gross, J.; Zimmermann, A.; Fricke, J. Proceedings of the Fourth International Symposium on Aerogels (ISA 4). *J. Non-Cryst. Solids* **1995**, *186*, 238.
(120) Gibiat, V.; Lefeuvre, O.; Woignier, T.; Pelous, J.; Phalippou, J. Proceedings of the Fourth International Symposium on Aerogels (ISA 4). *J. Non-Cryst. Solids* **1995**, *186*, 244.
(121) Tajiri, K.; Igarashi, K. *Sol. Energy Mater. Sol. Cells* **1998**, *54*, 189.
(122) Sumiyoshi, T.; Adachi, I.; Enomoto, R.; Iijima, T.; Suda, R.; Yokoyama, M.; Yokogawa, H. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 369.
(123) Cantin, M.; Casse, M.; Koch, L.; Jouan, R.; Mestran, P.; Roussel, D.; Bonnin, F.; Moutel, J.; Teichner, S. J. *Nucl. Instrum. Methods* **1974**, *118*, 177.
(124) Sumiyoshi, T.; Adachi, I.; Enomoto, R.; Iijima, T.; Suda, R.; Leonidopoulos, C.; Marlow, D. R.; Prebys, E.; Kawabata, R.; Kawai, H.; Ooba, T.; Nanao, M.; Suzuki, K.; Ogawa, S.; Murakami, A.; Khan, M. H. R. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1999**, *433*, 385.
(125) Iijima, T.; Adachi, I.; Enomoto, R.; Suda, R.; Sumiyoshi, T.; Leonidopoulos, C.; Marlow, D. R.; Prebys, E.; Kawai, H.; Kurihara, E.; Nanao, M.; Suzuki, K.; Unno, Y.; Ogawa, S.; Murakami, A.; Khan, M. H. R. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2000**, *453*, 321.

(126) Buzykaev, A. R.; Danilyuk, A. F.; Ganzhur, S. F.; Kravchenko, E. A.; Onuchin, A. P. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2000**, *433*, 396.

(127) Gougas, A. K.; Ilie, D.; Ilie, S.; Pojidaev, V. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2000**, *421*, 249.

(128) Barnykov, M. Y.; Buzykaev, A. R.; Danilyuk, A. F.; Ganzhur, S. F.; Goldberg, I. I.; Kolachev, G. M.; Kononov, S. A.; Kravchenko, E. A.; Mikerov, V. I.; Muraviova, T. M.; Minakov, G. D.; Onuchin, A. P.; Sidorov, A. V.; Tayursky, V. A. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1998**, *419*, 584.

(129) Buzykaev, A. R.; Danilyuk, A. F.; Ganzhur, S. F.; Gorodetskaya, T. A.; Kolachev, G. M.; Kravchenko, E. A.; Mikerov, V. I.; Minakov, G. D.; Onuchin, A. P.; Shamov, A. G.; Tayursky, V. A. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 381.

(130) Suda, R.; Watanabe, M.; Enomoto, R; Iijima, T.; Adachi, I.; Hattori, H.; Kuniya, T.; Ooba, T.; Sumiyoshi, T.; Yoshida, Y. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1998**, *406*, 213.

(131) Barnyakov, M. Y.; Bobrovnikov, V. S.; Buzykaev, A. R.; Danilyuk, A. F.; Ganzhur, S. F.; Goldberg, II; Kolachev, G. M.; Kononov, S. A.; Kravchenko, E. A.; Minakov, G. D.; Onuchin, A. P.; Savinov, G. A.; Tayursky, V. A. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2000**, *453*, 326.

(132) da-Cunha, J. P.; Neves, P.; Lopes, M. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2000**, *452*, 401.

(133) Nappi, E. *Nucl. Phys. B, Suppl.* **1998**, *61B*, 270.

(134) Poelz, G. *Aerogels*; Proceedings of the First International Symposium, Wurzburg, FRG, Sept. 23−25, 1985, Springer-Verlag, Berlin, 1986, 176.

(135) Aschenauer, E.; Bianchi, N.; Capitani, G. P.; Carter, P.; Casalino, C.; Cisbani, E.; Coluzza, C.; De Leo, R.; De Sanctis, E.; De Schepper, D.; Djordjadze, V.; Filippone, B.; Frullani, S.; Garibaldi, F; Hansen, J. O.; Hommez, B.; Iodice, M.; Jackson, H. E.; Kaiser, R.; Kanesaka, J.; Lagamba, L.; Muccifora, V.; Nappi, E.; Nowak, W. D.; O'Neill, T. G;; Potterveld, D.; Ryckbosch, D.; Sakemi, Y.; Sato, F.; Schwind, A.; Suetsugu, K.; Shibata, T. A;. Thomas, E.; Tytgat, M.; Urciuoli, G. M.; Van de Kerckhove, K.; Van de Vyver, R.; Yoneyama, S.; Zhang, L. F. *Nucl. Instrum. Methods Phys. Res., Sect. A*, **2000**, *440*, 338.

(136) Sakemi, Y. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2000**, *453*, 284.

(137) Sprehn, G. A.; Hrubesh, L. W.; Poco, J. F.; Sandler, P. H. U.S. Patent, US5684 907, 1997; *Chem. Abstr.* **1997**, *127*, P339050n.

(138) Hrubesh, L. W.; Poco, J. F. *J. Non-Cryst. Solids* **1995**, *188*, 46.

(139) Zhou, B.; Wang, J.; Zhao, L.; Shen, J;; Deng, Z. S.; Li, Y. F. *J. Vac. Sci. Technol., B* **2000**, *18*, 2001.

(140) Shen, J.; Wang, J.; Zhou, B.; Deng, Z. S.; Weng, Z. N.; Zhu, L.; Zhao, L.; Li, Y. F., Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 315.

(141) Leventis, N.; Elder, I. A.; Rolison, D. R.; Anderson, M. L.; Merzbacher, C. I. *Chem. Mater.* **1999**, *11*, 2837.

(142) Bockhorst, M.; Heinloth, K.; Pajonk, G. M.; Begag, R.; Elaloui, E. Proceedings of the Fourth International Symposium on Aerogels (ISA 4). *J. Non-Cryst. Solids* **1995**, *186*, 388.

(143) Vasilchenko, V. G.; Golovkin, S. V.; Solovev, A. S. *Instrum. Exp. Techn.* **1998**, *41*, 61.

(144) Mo, C. M.; Li, Y. H.; Liu, Y. S.; Zhang, Y.; Zhang, L. D. *J. Appl. Phys.* **1998**, *83*, 4389.

(145) Li, Y. H.; Mo, C. M.; Yao, L. Z.; Liu, R. C.; Cai, W. L.; Li, X. M.; Wu, Z. Q.; Zhang, L. D. *J. Phys.: Condens. Matter* **1998**, *10*, 1655.

(146) Tillotson, T. M.; Sunderland, W. E.; Thomas, I. M.; Hrubesh, L. W. *J. Sol-Gel Sci. Technol.* **1994**, 1, 241.

(147) Charlton, A.; McKinnie, I. T.; Meneses-Nava, M. A.; King, T. A. *J. Mod. Opt.* **1992**, *3*, 1717.

(148) Sun, X. T.; Yao, L. Z.; Mo, C. M.; Shi, G.; Cai, W. L.; Zhang, Y. M.; Zhang, L. D. *J. Mater. Sci. Technol.* **2000**, *16*, 315.

(149) Giorgetti, M.; Passerini, S.; Smyrl, W. H.; Berrettoni, M. *Chem. Mater.* **1999**, *11*, 2257.

(150) Passerini, S.; Coustier, F.; Giorgetti, M.; Smyrl, W. H. *Electrochem. Solid-State Lett.* **1999**, *2*, 483.

(151) Dong, W.; Dunn, B. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 135.

(152) Passerini, S.; Le, D. B.; Smyrl, W. H.; Berrettoni, M.; Tossici, R.; Marassi, R.; Giorgetti, M. *Solid State Ionics* **1997**, *104*, 195.

(153) Owens, B. B.; Passerini, S; Smyrl, W. H. *Electrochim. Acta* **1999**, *45*, 215.

(154) Le, D. B.; Passerini, S.; Coustier, F.; Guo, J.; Soderstrom, T.; Owens, B. B.; Smyrl, W. H. *Chem. Mater.* **1998**, *10*, 682.

(155) Long, J. W.; Swider Lyons, K. E.; Stroud, R. M.; Rolison, D. R. *Electrochem. Solid-State Lett.* **2000**, *3*, 453.

(156) Wong, H. P.; Dave, B. C.; Leroux, F.; Harreld, J.; Dunn, B.; Nazar, L. F. *J. Mater. Chem.* **1998**, *8*, 1019.

(157) Tadanaga, K.; Imai, K.; Tatsumisago, M.; Minami, T. *J. Electrochem. Soc.* **2000**, *147*, 4061.

(158) Mayer, S. T.; Pekala, R. W.; Kaschmitter, J. L. *J. Electrochem. Soc.* **1996**, *140*, 446.

(159) Pekala, R. W.; Farmer, J. C.; Alviso, C. T.; Tran, T. D.; Mayer, S. T.; Miller, J. M.; Dunn, B. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 74.

(160) Saliger, R.; Fischer, U.; Herta, C.; Fricke, J. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 81.

(161) Pekala, R. W.; Alviso,C. T. Novel Forms of Carbon. *Mater. Res. Soc. Symp. Proc.* **1992**, *270*, 3.

(162) Miller, J. M.; Dunn, B. *Langmuir* **1999**, *15*, 799−806.

(163) Long, J. W.; Swider, K. E.; Merzbacher, C. I.; Rolison, D. R. *Langmuir* **1999**, *15*, 780.

(164) Zunger, A. *MRS Bull.* **1998**, *23*, 8.

(165) Kawakami, N.; Fukumoto, Y.; Kinoshita, T.; Suzuki, K.; Inoue, K. *Jpn. J. Appl. Phys., Part 2* **2000**, *39*, L182.

(166) Jo, M. H.; Park, H. H. *Appl. Phys. Lett.* **1998**, *72*, 1391.

(167) Cao,Y.; Xia, Z. F.; Li, Q.; Shen, J.; Chen, L. Y.; Zhou, B. *IEEE Trans. Dielectr. Electr. Insul.* **1998**, *5*, 58.

(168) Geis, S.; Muller, B.; Fricke, J. *J. Porous Mater.* **2000**, *7*, 423.

(169) Lobmann, P.; Glaubitt, W.; Geis, S.; Fricke, J. *J. Sol-Gel Sci. Technol.* **1999**, *16*, 173.

(170) Lobmann, P.; Glaubitt, W.; Muller, G. *J. Mater. Sci.* **1998**, *33*, 2371.

(171) Lobmann, P.; Glaubitt, W.; Geis, S.; Fricke, J. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 130.

(172) Sinko, K.; Cser, L.; Mezei, R.; Avdeev, M.; Peterlik, H.; Trimmel, G.; Husing, N.; Fratzl, P. *Phys. B* **2000**, *276*, 392.

(173) Fricke, J. *J. Non-Cryst. Solids* **1988**, *100*, 169.

(174) Einasrud, M. A.; Dahle, M.; Lima, S.; Hæreid, S. Proceedings of the Fourth International Symposium on Aerogels (ISA 4). *J. Non-Cryst. Solids* **1995**, *186*, 96.

(175) Scherer, G. W.; Smith, D. M.; Qiu, X.; Anderson, J. M. Proceedings of the Fourth International Symposium on Aerogels (ISA 4). *J. Non-Cryst. Solids* **1995**, *186*, 316.

(176) Pirard, R.; Blacher, S.; Brouers, F.; Pirard, J. P. *J. Mater. Res.* **1995**, *10*, 2114.

(177) Parmenter, K. E.; Milstein, F. *J. Non-Cryst. Solids* **1998**, *223*, 179.

(178) Despetis, F.; Etienne, P.; Phalippou, J. *Phys. Chem. Glasses* **2000**, *41*, 104.

(179) Etienne, P.; Despetis, F.; Phalippou, J. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 266.

(180) Bhave, R. R. *Inorganic Membranes; Synthesis, Characteristics and Applications*, Van Nostrand Reinhold, New York, 1991.

(181) Holmes, N. C.; Radousky, H. B.; Moss, M. J.; Nellis, W. J.; Henning, S.; *Appl. Phys. Lett.* **1984**, *45*, 626.

(182) Amendt, P.; Glendining, S. G.; Hammel, B. A.; Landen, O. L.; Murphy, T. J.; Suter, L. J.; Hatchett, S.; Rosen, M. D.; Lafittte, S.; Desenne, D.; Jadaud, J. P. *Phys. Plasmas* **1997**, *4*, 1862.

(183) Kramer, S. J.; Rubio Alnso, F.; Mackenzie, J. D. Better Ceramics through Chemistry VII: Organic/Inorganic Hybrid Materials. *Mater. Res. Soc. Symp. Proc.* **1996**, *435*, 295.

(184) Tsou, P. Proceedings of the Fourth International Symposium on Aerogels (ISA 4). *J. Non-Cryst. Solids* **1995**, *186*, 415.

(185) Guise, M. T.; Hosticka, B.; Earp, B. C.; Norris, P. M. Proceedings of the Fourth International Symposium on Aerogels (ISA 4). *J. Non-Cryst. Solids* **1995**, *186*, 317.

(186) Loschiavo, S. R. *J. Econ. Entomol.* **1988**, *81*, 1237.

(187) Pajonk, G. M.; Venkateswara Rao, A. *Recent Res. Dev. Non-Cryst. Solids* **2001**, *1*, 1.

(188) Emmerling, A.; Gross, J.; Gerlach, R.; Goswin, R.; Reichenauer, G.; Fricke, J.; Haubold, H. G. *J. Non-Cryst. Solids* **1990**, *125*, 230.

(189) Aristov, Y. I.; Restuccia, G.; Tokarev, M. M.; Cacciola, G. *React. Kinet. Catal. Lett.* **2000**, *69*, 345.

(190) Moreno-Castilla, C.; Maldonado-Hodar, F. J. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4818.

(191) Maldonado-Hodar, F. J.; Moreno-Castilla, C.; Rivera-Utrilla, J. *Appl. Catal., A* **2000**, *203*, 151.

(192) Han, S. J.; Sohn, K.; Hyeon, T. *Chem. Mater.* **2000**, *12*, 3337.

(193) Pekala, R. W.; Kong, F. M. Proceedings of the Second International Symposium on Aerogels (ISA2). *Rev. Phys. Appl. Colloq.* **1989**, 33.

(194) Kim, N. K.; Kim, K.; Payne, D. A.; Upadhye, R. S, *J. Vac. Sci. Technol., A* **1988**, *7*, 1181.

(195) Jang, K. Y.; Kim, K.; Upadhye, R. S. *J. Vac. Sci. Technol., A* **1990**, *8*, 1732.

(196) Kim, K. K.; Jang, K. Y. *J. Am. Ceram. Soc.* **1991**, *74*, 1987.

(197) Hair, L. M.; Pekala, R. W.; Stone, R. E.; Chen, C.; Buckley, S. R, *J. Vac. Sci. Technol., A* **1988**, *6*, 2559.

(198) Overstuff, G. E.; Cook, R.; Letts, S. A.; Buckley, S. R. *Fusion Technol.* **1995**, *28*, 1803.

(199) Schroen Carey, D.; Overstuff, G. E.; Reibold, R.; Buckley, S. R.; Letts, S. A.; Cook, R. *J. Vac. Sci. Technol., A* **1995**, *13*, 2564.

(200) Lambert, S. M.; Overstuff, G. E.; Wilmeski, G.; Letts, S. A.; Schroen-Carey, D.; Cook, R. C. *J. Appl. Polym. Sci.* **1997**, *63*, 2111.

(201) Reynes, J.; Woignier, T.; Phalippou, J.; Dussossoy, J. L. in *Proc. of the fifth Meeting on Supercritical Fluids (I.S.A.S.F.)*; Perrut, M; Subra, P., Eds.; Nice, France, 1998; vol. 1, p 57.

(202) Woignier, T.; Reynes, J.; Phalippou. J.; Dussossoy, J. L.; Jacquet-Francillon, N. Proceedings of the Fifth International Symposium on Aerogels (ISA 5). *J. Non-Cryst. Solids* **1998**, *225*, 353.

(203) Reynes, J.; Woignier, T.; Phalippou, J. Aerogels 6; Proceedings of the Sixth International Symposium on Aerogels (ISA6), Albuquerque, NM, 8−11 October 2000. *J. Non-Cryst. Solids* **2001**, *285*, 323.

(204) Tastevin, G.; Nacher, P. J.; Guillot, G. *Physica B* **2000**, *284 Part 1*, 291.

(205) Pavlovskaya, G.; Blue, A. K.; Gibbs, S. J.; Haake, M.; Cros, F.; Malier, L.; Meersmann, T. *J. Magn. Reson.* **1999**, *137*, 258.

(206) Chan, M. H. W.; Blum, K. J.; Murphy, S. Q.; Wong, G. K. S.; Reppy, J. D. *Phys. Rev. Lett.* **1988**, *61*, 1950.

(207) Maynard, R.; Deutscher, G. *Europhys. Lett.* **1989**, *10*, 257.

(208) Snow, W. M.; Sokol, P. E. *J. Low Temp. Phys.* **1990**, *80*, 197.

(209) Ma, J.; Kim, S. B.; Hrubesh, L. W. *J. Low Temp. Phys.* **1993**, *93*, 945.

(210) Yoon, J.; Mulders, N.; Hrubesh, L. W.; Chan, M. W. H. *Czech. J. Phys.* **1996**, *46*, 157.

(211) Venkalaramani, P.; Sauls, J. A. *Physica B* **2000**, *284 Part 1*, 297.

(212) Hanninen, R.; Thuneberg, E. V. *Physica B*, **2000**, *284 Part 1*, 303.

(213) Cousins, D. J.; Bauerle, C.; Bunkov, Y. M.; Chen, A. S.; Collin, E.; Godfrin, H. *Physica B* **2000**, *284 Part 1*, 311.

(214) Porto, J. V.; Parpia, J. M. *Phys. Rev. B, Condens. Matter* **1999**, *59*, 14583.

(215) Tan, H. W.; Beamish, J. R. *Physica B*, **2000**, *284 Part 1*, 389.

(216) Feldman, D. E. *Phys. Rev. Lett.* **2000**, *84*, 4886.

(217) Pajonk, G. M. *Appl. Catal.* **1991**, *72*, 217.

(218) Ward, D. A.; Ko, E. I. *Ind. Eng. Chem. Res.* **1995**, *34*,421.

(219) Cauqui, M. A.; Rodriguez Izquierdo, J. M. *J. Non-Cryst. Solids* **1992**, *147*−*148*, 724.

(220) Astier, M.; Bertrand, A.; Bianchi, D.; Chenard, A.; Gardes, G. E. E.; Pajonk, G.; Taghavi, M. B.; Teichner, S. J.; Villemin, B. Preparation of Catalysts. In *Studies in Surface Science and Catalysis*; Delmon, B.; Jacobs, P. A.; Poncelet, G., Eds.; Elsevier, Amsterdam, 1976; vol. 1, p 315.

(221) Matis, G.; Juillet, F.; Teichner, S. J. *Bull. Soc. Chim. Fr.* **1976**, 1633.

(222) Willey, R. J.; Lai, H.; Peri, J. B. *J. Catal.* **1991**, *130*, 319.

(223) Fanelli, A. J.; Burlew, J. V.; Marsh, G. B. *J. Catal.* **1988**, *116*, 318.

(224) Blanchard, F.; Pommier, B.; Reymond, J. P.; Teichner, S. J. *J. Mol. Catal.* **1982**, *17*, 171.

(225) Blanchard, F.; Pommier, B.; Reymond, J. P.; Teichner, S. J. Preparation of Catalysts III. In *Studies in Surface Science and Catalysis*; Poncelet, G.; Grange, P.; Jacobs, P. A., Eds.; Elsevier, Amsterdam, 1983; vol. 16, p 395.

(226) Taghavi, M. B.; Pajonk, G. M.; Teichner, S. J. *J. Colloid Interface Sci.* **1979**, *71*, 451.

(227) Klvana, D.; Chaouki, J.; Kusohorski, D.; Chavarie, C.; Pajonk, G. M. *Appl. Catal.* **1988**, *42*, 121.

(228) Astier, M.; Bertrand, A.; Teichner, S. J. *Bull. Soc. Chim. Fr.* **1980**, 218.

(229) Armor, J. N.; Carlson, E. J.; Zambri, P. M. *Appl. Catal.* **1985**, *19*, 339.

(230) Lacroix, M.; Pajonk, G.; Teichner, S. J. New Horizons in Catalysis. In *Studies in Surface Science and Catalysis*; Seiyama, T.; Tanabe, K., Eds.; Elsevier, Amsterdam, 1981; vol. 7, p 279.

(231) Gardes, G. E. E.; Pajonk, G. M.; Teichner, S. J. *Bull. Soc. Chim. Fr.* **1976**, 1327.

(232) Astier, M.; Bertrand, A.; Teichner, S. J. *Bull. Soc. Chim. Fr.* **1980**, 191.

(233) Pajonk, G.; Taghavi, M. B.; Teichner, S. J. *Bull. Soc. Chim. Fr.* **1975**, 983.

(234) Anderson, M. L.; Morris, C. A.; Stroud, R. M.; Merzbacher, C. I.; Rolison, D. R. *Langmuir* **1999**, *15*, 674.

(235) Machida, M.; Eguchi, K.; Arai, H. *Chem. Lett. (Japan)* **1986**, 1993.

(236) Machida, M.; Eguchi, K.; Arai, H. *Chem. Lett. (Japan)* **1987**, 767.

(237) Yan, L. C.; Thompson, L. T. *Appl. Catal., A* **1998**, *171*, 219.

(238) Pierre, M.; Buisson, P.; Fache, F.; Pierre, A. *Biocatal. Biotransform.* **2000**, *18*, 237.

(239) Buisson, P.; Hernandez, C.; Pierre, M.; Pierre, A. C. Aerogels 6; Proceedings of the Sixth International Symposium on Aerogels (ISA6), Albuquerque, NM, 8−11 October 2000. *J. Non-Cryst. Solids* **2001**, *285*, 295.

(240) Power, M.; Hosticka, B.; Black, E.; Daitch, C.; Norris, P, Aerogels 6; Proceedings of the Sixth International Symposium on Aerogels (ISA6), Albuquerque, NM, 8−11 October 2000. *J. Non-Cryst. Solids* **2001**, *285*, 303.

(241) Schubert, U.; Hüsing, N.; Lorenz, A. *Chem. Mater.* **1995**, *7*, 2010.

(242) Livage, J.; Sanchez, C. Proceedings of the Third International Symposium on Aerogels (ISA 3). *J. Non-Cryst. Solids* **1992**, *145*, 11.

(243) Kickelbick, G.; Schubert, U. *Chem. Ber.* **1997**, *130*, 473.

(244) Land, V. D.; Harris, T. M.; Teeters, D. C. *J. Non-Cryst. Solids* **2001**, *283*, 11.

CR0101306