Lawrence Berkeley National Laboratory

Recent Work

Title

PROCESS CONSIDERATIONS IN MONOLITHIC AEROGELS

Permalink

<https://escholarship.org/uc/item/7dn439qv>

Authors

Hung, A. J.
Lofftus, K.D.

Publication Date

1988-09-01

c.2

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

APPLIED SCIENCE DIVISION

RECEIVED
LAWRENCE
BERKELEY LABORATORY

FEB 2 1990

LIBRARY AND
DOCUMENTS SECTION

To be published as a chapter in **Better Ceramics
through Chemistry III**, C.J. Brinker, D.E. Clark,
and D.R. Ulrich, Eds., Materials Research Society,
Pittsburgh, PA, 1988

Process Considerations in Monolithic Aerogels

A.J. Hunt and K.D. Lofftus

September 1988

APPLIED SCIENCE
DIVISION

LBL-26289
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

PROCESS CONSIDERATIONS IN MONOLITHIC AEROGELS

ARLON J. HUNT AND KEVIN D. LOFFTUS

Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

ABSTRACT

This paper describes important process considerations in the preparation of supercritically evacuated alcogels called aerogels. Aerogels are fine grained, open pore, low density materials that possess a variety of unusual properties and have a number of diverse applications. Factors influencing the microstructure and uniformity of alcogel monoliths are discussed. The effects of hydrolysis rate, diffusion, condensation, dispersion medium, and electrostatic interactions on particle formation and gelling are outlined. These effects are illustrated with the preparation of zirconia, mullite precursors, and silica alcogels. A theoretical model of particle interaction based on the combination of van der Waals and electrostatic double layer forces is used to interpret gelation and homogeneity. Solvent substitution and supercritical drying processes are discussed.

INTRODUCTION

Sol-gel processing and supercritical drying can be used to produce monolithic or powder aerogel. In monolithic form, aerogel is a low density, open pore solid typically characterized by very high surface area, transparency to visible light, low thermal conductivity, low sound velocity, and complex microstructure. This unusual combination of properties makes aerogel a unique material suited for a diverse array of applications: insulating transparent glazings (e.g., windows, appliance doors, solar collector covers, etc.), Cherenkov detectors, catalyst substrates, filters, membranes, acoustic delay lines, and oxide ceramic precursors. Control of the sol-gel and solvent removal processes is necessary to produce materials with the required characteristics for these applications. Factors effecting the composition, uniformity, porosity, density, and microstructure must be understood for control of these processes. The goals of this research are to (1) explore the hydrolysis and condensation of alkoxides, (2) control the chemistry of the gel to produce gels with specifically tailored properties, (3) develop improved solvent removal methods, and (4) characterize the materials during and after their preparation.

PROCESS CONSIDERATIONS

Sol-gel processing may be used to produce diverse forms of material by varying the process conditions. Isodispersed sols, gels, gelatinous precipitates, and fine precipitates may be produced. All these materials may be supercritically dried to produce aerogels. To obtain a desired material, control must be exercised over two different regimes during preparation. These are the molecular short range interactions dominated by chemical forces and the longer range physical forces acting between condensed particles. Both share common phenomena such as Brownian motion and van der Waals forces, but the details are distinctly different in each regime.

In the molecular regime, any one or combination of the following processes can occur: production of the molecular monomer (e.g. hydrolysis of a metal alkoxide), polymerization, condensation, growth, redissolution, surface modification, and Ostwald ripening. Processes that occur in the particulate regimes are aggregation, dispersion, reprecipitation, and aging (rearrangement). Obviously growth, redissolution, Ostwald ripening, and surface modification occur in the particulate processes and hydrolysis and condensation can influence aggregation so a complete separation of the regimes is not always possible. However, it is helpful to differentiate these processes to reduce confusion in cases where quite different effects may occur in each regime of the same system.

Control of Condensation and Growth

Iler[1] discusses many of the issues of condensation and growth in the context of the silica system. The discussion here applies to the general area of the evolution of a metal oxide gel from an alkoxide precursor. A hydrated oxide species is produced as hydrolysis occurs and polymerization takes place. Mostly cyclic and random polymers or oligomers form and interact with monomers to grow. The core of the oligomer can condense and eventually form particle nuclei. Small Angle X-ray Scattering (SAXS) [2] show that silica particles are incompletely condensed in acidic solutions but are fully dense in basic solutions consistent with "polymer" and "particle-like" characteristics of these gels in the chemical regime.

The relative rates of hydrolysis and diffusion of the monomer determines whether a single nucleation burst or continuous nucleation occurs. As a nucleus is formed, the local monomer concentration is reduced to nearly the saturation level. Monomers from the surrounding supersaturated solution diffuse towards this nucleus. The mass balance between the production of new monomers by hydrolysis and depletion by diffusion can be characterized by a nucleation length from the existing nuclei at which supersaturation levels would nucleate new particles.

The growth rate of monomers on the particles plays a significant role in the balance between nucleation and growth. Like polymerization, growth of silica in acidic solutions is slow, resulting in higher monomer concentrations at the surface and slower diffusion rates. Continuous nucleation occurs in this system until the hydrolysis nears completion and small (2-3 nm) particles form. In basic solutions, growth is rapid and larger particles are formed (typically 10-15 nm)[1]. However, under some catalyst conditions, basic solutions can produce smaller particles.

Control of Aggregation and Dispersion

In systems normally stabilized by electrostatic repulsion, hydrolysis and condensation may occur so rapidly that only part of the equilibrium surface charge can be maintained at any one time. According to the DLVO (Derjaguin, Landau, Vervay, Overbeek) theory[3], this effect reduces the electrostatic energy barrier of and allows aggregation to occur during hydrolysis creating precipitates. We find that precipitates tend to form at pH 8 to 9 for high tetraethylorthosilicate (TEOS) concentrations unless the process is slowed down by reducing the water and catalyst concentrations.

For oxides with extremely low saturation concentrations such as alumina and zirconia, it is very difficult to prevent precipitation. The hydrolysis rate can be controlled by using vapor transport of water into the alkoxide solution. Blanchard[4] used ambient moisture on mixed alkoxides including zirconium alkoxide with limited success. With a controlled atmosphere, the hydrolysis rate of zirconium propoxide can be reduced to the point where no precipitation occurs. In many experiments, we have observed that the water released from the initial nucleation accelerates the hydrolysis producing more water. In some cases, this autocatalytic effect did not occur for six days and resulted in a partially settled precipitate surrounded by a transparent gel.

A more detailed look at DLVO theory reveals that the composition of the dispersion media (the excess solvents and water) plays an important role in the stabilization of the sol. Calculations show that decreasing the dielectric constant of a solvent such as increasing the ethanol in a water-ethanol mixture will increase the repulsive potential at a constant surface charge density. However, at constant double layer potential, the decrease in dielectric constant with composition lowers the repulsion as illustrated in Figure 1. This effect occurs because of the influence of the dielectric constant on the charge potential relationship at the surface. Except for when the surface charge is near its maximum value, the chemical equilibrium between the surface and solution maintains a constant double layer potential and this controls the stability of the sol.

The effect of the dielectric constant of the solvent on processing was observed experimentally. When a portion of the propanol originally present in a zirconia sol was replaced with ethanol (having a higher dielectric constant), it was much easier to obtain a transparent gel with no precipitate. In a series of tests on base catalyzed TEOS, replacement of some ethanol with either methanol or propanol increased the homogeneity of the gels for increased dielectric constant of the mixtures. The clearest gels indicate the greatest homogeneity while a precipitate is the extreme inhomogeneous.

Figure 1. Energy barrier between two silica spheres of radius 3 nm at 12.6 mV potential and 0.001 M ionic strength showing the effect of substitution of ethanol for water.

Figure 2. Potential energy between two silica spheres of radius 3nm: a. 12.6 mV 0.001 M, b. 37.8 mV 1.0 M, and c. 37.8 mV 0.1 M.

geneity. The results of increasing the concentration of the more polar solvent in the mixture (i.e. propanol to methanol) on scattering can be seen in Table I.

Stable sols of alumina are difficult to obtain because aluminum alkoxides have fast hydrolysis rates and are solid for the more nonpolar alcohols and alumina has a low saturation concentration. However, based on precipitates from the hydrolysis of aluminum tri-*sec*-butoxide (ATBO), alternate processing methods can be used. Repeptization of the alumina precipitates was performed at high temperatures in acidic solutions to form sols that gelled when cooled[5,6]. As the alkoxide to water ratio was increased, repeptization became more difficult because of the increased concentration of alcohols. This difficulty was overcome by changing the pH to increase the electrostatic repulsion. Very high density alumina gels were obtained at HCl concentrations of 5 molar. The alcohols formed a second liquid phase containing no particles which was decanted to leave a high density sol that gelled when cooled. These gels repeptized and regelled when any solution was added to the top of the beaker. This can be interpreted as gelation in a secondary minimum where no bonds form between particles that was enhanced by high ionic strengths at high potentials. Figure 2 illustrates the character of the potential well responsible for this behavior. It also illustrates that for very small particles, the primary attractive potential well can be eliminated by high potentials.

TABLE I
Solvent Substitution Effects in Silica Gels

3 ml TEOS 1.80x10 ⁻³ M NH ₄ F			6.25 ml H ₂ O 1.33x10 ⁻² M NH ₄ OH	
EtOH ml	MeOH ml	PrOH ml	Gel Time hr	Scattering at 90° Relative to CS ₂
4.75	8.1	0	5.25	4.07
8.35	4.5	0	3.25	5.07
11.95	0.9	0	2.5	9.38
4.75	0	8.1	144	35.8
8.35	0	4.5	11	12.6
11.95	0	0.9	3.25	7.14

Mixed Gels and Composites

To make mullite precursors from TEOS and ATBO, it was found that direct hydrolysis of a mixed solution was unsuccessful because of the large differences in hydrolysis rates. Instead, the alumina was reprecipitated under conditions that were slow to gel when cooled. By using a combination of acetic and chloroacetic acids, it was possible to achieve good reprecipitation yet have a pH buffering effect that prevented rapid gelation upon cooling and mixing with a prehydrolyzed TEOS solutions.

We prepared composite materials of mixed oxides and nonoxides. Nonoxide powders may not develop a surface charge in aqueous solutions and must be dispersed by other means. Nonpolar solvents reduce van der Waals attractions between particles as well as the electrostatic repulsion at constant potential. Some neutral solids can be dispersed in nonpolar solvent[7,8], but these dispersions are incompatible with aqueous sols stabilized by electrostatic repulsion. To obtain a composite gel, steric stabilization of the neutral powder in a polar solvent was required. As an example, a silicon nitride powder was dispersed in isopropanol and water with acetic acid and FC431 (a 3M surfactant) and mixed in a mullite precursor sol as it gelled to obtain a monolithic gel of fair quality. In selecting a solvent, other properties must be considered. Formamide is often used but it also effects the hydrolysis rate[9,10].

From Microgels to Gels

Once it has been established how to obtain a gel rather than a precipitate, the quality of the gel can be improved. Long range inhomogeneities cause light scattering in silica aerogels[11]. This is confirmed by surface area measurements and TEM micrographs. The formation of low density microgel networks from spherical particles can be explained by DLVO theory applied to aggregates. As two charged spheres aggregate, the repulsive energy barrier for the aggregation with a third sphere is higher on the side of the aggregate than on the end. As aggregation with single spheres continue, longer chains of particles form[12,13]. These chains then aggregate to form microgels. If the charge repulsion is high enough, the chains will aggregate perpendicular to each other, making the microstructure more uniform than that composed of randomly aggregated chains. Random aggregation occurs in acid catalyzed TEOS gels and the difference as compared to base catalyzed gels can be seen in both clarity and gelation [14]. The TEM micrographs in Figure 3 of acid and base catalyzed aerogels show different residual porosity between the microgels, 25% for acid compared to 10% for the base, even though the acid gel has twice the density. Also apparent in these micrographs is the larger size of these pores in the acid gels which scatter 10 or 15 times more light than base gels.

Further, observations of aging behavior are also explained by the microstructure of the gel. Acid gels have little charge to prevent rearrangement of the microgels by thermal vibrations. The unconnected chains and microgel surfaces next to large pores will slowly condense. These gels will shrink as they age even when kept under alcohol. On the other hand, highly charged base gels remain resilient and unshrunk for years if the solvent is maintained.

Solvent Exchange and Supercritical Drying

The last step in sol-gel processing is the removal of the solvent to get a dry stable solid. If air dried, an alcogel will collapse due to the force exerted by the surface tension of the liquid-vapor interface on the gel's small pores. When dried slowly under a controlled atmosphere, a monolithic high density xerogel is obtained. To maintain the open porosity of the gels, they are often supercritically dried as powders or monoliths. This procedure is facilitated by the substitution of the solvent to obtain a favorable critical point[15]. For instance, excess water must be removed for supercritical drying in alcohol or carbon dioxide. As new solvent replaces the old, the ionic strength of the solution drops and, if the equilibrium reaction of protons or hydroxyl ions with the charged surface is slow to adjust, the repulsion is increased and the gels swell. Once this reaction nears equilibrium, the repulsion can drop to below the initial level because of the decrease in the concentration of ions. Added to this, the more favorable solvents

Figure 3. TEM micrographs of resin impregnated silica aerogel thin sections. Base catalyzed TEOS, left; acid catalyzed TEOS, right. XBB 883-2557

for supercritical drying are nonpolar and do not support ionic charges changing the charge potential relationship as discussed above. This is reflected in Figure 1 as a decrease in the energy barrier at constant ionic strength for the substitution of water by ethanol. This effect is more dramatic for decreasing ionic strengths of the dispersion media and for nonpolar solvents such as liquid carbon dioxide.

Other concerns in supercritical drying of monolithic aerogels also arise from the solvent-solvent interactions. Although completely miscible, diminution of molar volume can occur upon mixing[16]. This is caused by the high interaction energy between ethanol and carbon dioxide. Under pressures required to maintain liquid carbon dioxide at room temperature, this volume diminution represents a high interaction energy and analysis of Fick's second law (the flux of a species is proportional to its free energy gradient) reveals that negative diffusion can result[17]. Another way of looking at this for the liquid carbon dioxide-ethanol system is that the density of the mixture reaches a maximum at about 60% carbon dioxide at room temperature and, rather than force expansion at this pressure, increased carbon dioxide concentrations will form a new phase and the average density of the two phases is greater than that of their mixture. Since carbon dioxide is nearer its critical point and is more compressible than ethanol, the density maximum can be shifted or even eliminated by dropping the temperature and raising the pressure. Two-phase formation was observed down to about 3 °C at 800 psi and 8 °C at 1200 psi.

There are other ways around the two-phase formation other than going to low temperatures and high pressures. Since ethanol and carbon dioxide are completely miscible, they can be mixed either by internal stirring or by a circulating pump. Whether or not a gel can survive the mechanical forces induced by the mixing depends upon the exchange rate of carbon dioxide for ethanol and upon the nature of the gel's strength. Another way of avoiding two-phase formation is by using other solvents than ethanol before the carbon dioxide substitution[18]. Properties of the intermediate solvent should be similar to carbon dioxide but it should be nonpolar and completely soluble in both carbon dioxide and ethanol, as well as being a liquid at room temperature and pressure.

To prevent shrinkage using the solvent substitution method, the fluid exchanges should be done gradually. This is because the gels allow diffusion and not convective mixing due to concentration derived density gradients. In some gels, a steep concentration gradient can be supported that acts like a interface to cause forces similar to surface tension which are capable of collapsing the gels. Under some conditions, it was possible to get fairly uniform shrinkage without fracturing the gel. As much as 50% linear (87.5% volumetric) shrinkage has been observed on 1.25 inch silica gels without any cracks appearing.

SUMMARY

There are many considerations in sol-gel production of a material. Both chemical and particulate interactions play important roles in obtaining a nearly stable sol that will make a uniform gel. Hydrolysis can be controlled to prevent precipitation. The particulate interactions depend greatly upon the nature of the dispersing solvent and determine the microstructure, aging, and drying behavior of gels. Polar solvents are good for electrostatic stabilization and reptitization of oxides where as nonpolar solvents or steric stabilization are required to disperse nonoxides. Exchange of solvents in the gel can make elimination of shrinkage easier and aid supercritical drying.

ACKNOWLEDGEMENTS

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Conversion and Utilization Technologies Program and Office of Solar Heat Technologies, Passive and Hybrid Solar Division of the United States Department of Energy under Contract No. DE-AC03-76SF00098.

REFERENCES

1. R. Iler, *The Chemistry of Silica: Solubility, Polymerization, Colloidal and Surface Properties, and Biochemistry* (John Wiley & Sons, New York, 1979) pp. 213-44.
2. D.W. Schaefer, *MRS Bulletin*, **12** (2), 22-27 (1988).
3. A. W. Adamson, *Physical Chemistry of Surfaces*, 4th ed. (John Wiley & Sons, New York, 1982) pp. 244-247.
4. N. Blanchard, et. al., *J. of Non-Crystalline Solids*, **82**, pp. 205-209, (1968).
5. B.E. Yoldas, *Ceramic Bulletin*, **54** (3), pp. 289-290, (1975); *J. of Materials Sci.*, **10**, pp. 1856-1860, (1975).
6. A.F.M. Leenaars and A.J. Burggraaf, *J. of Colloid Interface Sci.*, **105** (1), pp. 27-40, (1985).
7. A. Bleier, *J. of the Am. Cer. Soc., Communications*, **66** (5), pp. C79-C81, (1983).
8. P.D. Calvert, et. al., *Better Ceramics Through Chemistry II*, edited by C. J. Brinker, D. E. Clark, and D. R. Ulrich (Mater. Res. Soc. Proc. **73** Pittsburgh, PA 1986) pp. 579-584.
9. I. Artaki, T.W. Zerda, and J. Jonas, *Materials Letters*, **3** (12), pp. 493-496, (1985).
10. G. Orzel, R. W. Gould, and L. L. Hench, *Better Ceramics Through Chemistry II*, edited by C. J. Brinker, D. E. Clark, and D. R. Ulrich (Mater. Res. Soc. Proc. **73** Pittsburgh, PA 1986) pp. 289-294.
11. A.J. Hunt and P. Berdahl, *Better Ceramics Through Chemistry*, edited by C. J. Brinker, D. E. Clark, and D. R. Ulrich (Mater. Res. Soc. Proc. **32**, Pittsburgh, PA 1984) pp. 275-280 (LBL-16579).
12. A.L.G. Rees, *J. Phys. Chem.*, **55**, pp. 1340-1344 (1951).
13. I.L. Thomas and K.H. McCorkle, *J. of Colloid and Interface Sci.*, **36** (1), pp. 110-118 (1971).
14. P.H. Tewari, A.J. Hunt, K.D. Lofftus, and J.G. Lieber, *Better Ceramics Through Chemistry II*, edited by C. J. Brinker, D. E. Clark, and D. R. Ulrich (Mater. Res. Soc. Proc. **73** Pittsburgh, PA 1986) pp. 195-205 (LBL-20499).
15. P. H. Tewari, A. J. Hunt, and K. D. Lofftus, *Materials Letters*, **3** (9,10), pp. 363-367 (1985).
16. L.C.W. Baker and T.F. Anderson, *J. Am. Chem. Soc.*, **70**, pp. 2071-2074 (1957).
17. G. H. Geiger and D. R. Poirier, *Transport Phenomena in Metallurgy* (Addison-Wesley Publishing Co., Reading, MA, 1980) pp. 441-442.
18. J. Bastacky (private communication).

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720