SOL-GEL PROCESSING OF CONTROLLED PORE OXIDES

C. J. Brinkerab, D. M. Smithb, R. Deshpandeb, P. M. Davisb, S. Hietala, G. C. Fryea, C. S. Ashley8 and R. A. Assink*

aSandia National Laboratories, Albuquerque, NM 87185
bCenter for Micro-Engineered Ceramics, University of New Mexico, Albuquerque, NM 87131

Abstract
In sol-gel processing the pore structure of the dry gel (xerogel) or film is a consequence of the sequential (or overlapping) gelation, aging, and drying stages. This paper demonstrates how the surface area, pore volume, and pore size are influenced by such physical and chemical factors as the size, structure and composition of the inorganic polymers, the magnitude of the capillary pressure, conditions of aging, and choice of pore fluid.

1. INTRODUCTION
The most often quoted advantages of sol-gel processing are compositional homogeneity, the ability to prepare shaped-materials such as films, fibers, and monolithic structures, and the low processing temperatures required to produce fully dense amorphous or polycrystalline ceramic materials (ref.1). Increasingly however, sol-gel processing has been used to produce porous materials for such applications as sensors, separation membranes, and catalyst supports. This paper describes several strategies we have explored to control the pore volume, surface area, and pore size distributions of dried gels (xerogels) prepared in either bulk or thin film form. We limit our discussion to silicate-based materials; however the concepts are generic and should be useful for tailoring the microstructures of any xerogel composition.

2. SOL-GEL CHEMISTRY
The sol-gel process uses inorganic or metal organic precursors (ref.1). In aqueous or organic solvents the precursors are hydrolyzed and condensed to form inorganic polymers containing M-O-M linkages. The most commonly used organic precursors are metal alkoxides (M(OR)x), where R is an alkyl group (CnH2n+1) (ref.1). Normally the alkoxide is dissolved in alcohol and hydrolyzed by the addition of water under acidic, neutral or basic conditions. Hydrolysis replaces an alkoxide ligand with a hydroxyl ligand:

\[ M(OR)_x + H_2O = M(OR)_{x-1}(OH) + ROH \] (1)

Condensation reactions involving the hydroxyl ligands produce polymers composed of M-O-M or M-(μOH)-M (where μOH refers to a bridging hydroxyl) bonds plus in most cases the by-products water or alcohol as shown below for silicate condensation:
\[
\text{Si(OR)}_3\text{OH} + \text{Si(OR)}_4 = (\text{RO})_3\text{Si-O-Si(OR)}_3 + \text{ROH} \tag{2}
\]

\[
2\text{Si(OR)}_3\text{OH} = (\text{RO})_3\text{Si-O-Si(OR)}_3 + \text{H}_2\text{O} \tag{3}
\]

The reverse of reactions 2 and 3, viz., siloxane bond alcoholysis and siloxane bond hydrolysis, promote bond breaking and reformation processes that, if extensive, permit complete restructuring of the growing polymer.

There is a considerable body of evidence based on \(^{29}\text{Si} \text{NMR} \) (ref.2-4) and small angle x-ray scattering (SAXS) (ref.5-7) data indicating that, under many synthesis procedures, condensation of silicon alkoxides results in the formation of randomly branched "polymeric" silicates described by a mass fractal dimension (D) rather than dense silica particles. The mass fractal dimension D relates an object's mass to its radius according to (ref.8):

\[
M = R^D, \tag{4}
\]

where for mass fractal objects, D is less than the dimension of space. Since in three dimensions, D < 3, the density of a mass fractal object decreases with distance, R, from its center of mass according to:

\[
\rho \propto 1/R^{(3-D)}. \tag{5}
\]

Because density is inversely related to porosity, this relationship requires that, unlike Euclidian objects, fractal objects become more "porous" as their size increases. We will show that this property may be exploited to tailor the pore structure of films deposited from fractal precursors.

3. GELATION, AGING, AND DRYING

To prepare bulk specimens, the inorganic sol (consisting of the inorganic polymers or particles plus the solvent) is normally cast in a mold and allowed to gel. Gelation occurs by a percolative process generally involving further condensation reactions (Eqs. 2 and 3) between the inorganic polymers or particles (ref.1). The gel point refers to the time at which a network forms that spans the entire volume of the sol. For percolation processes in general only a small fraction of the dispersed phase is incorporated in the spanning network at the gel point. For example, for random site percolation (of particles, porous clusters, etc.) on a three-dimensional random close-packed lattice with coordination 8, only 27% of the sites are filled at the gel point (percolation threshold). The remaining species are incorporated in the spanning network after the gel point. This process and any other changes that occur after the gel point but before complete drying are generally referred to as aging (ref.1).

The aging process may be carried out in the mother liquor (in which gelation took place) or in other liquids introduced in excess quantities and exchanged with the mother liquor by repeated washings. Aging may be used to alter the structure of the wet gel in order to tailor the microstructure of the resulting dry gel. At least three processes are involved in aging (ref.1): continued polymerization/syneresis, coarsening, and phase transformation. Polymerization involves both the addition of oligomers and polymers to the spanning network and continued condensation reactions within the spanning network. The latter cause the network to shrink and expel solvent in a process called syneresis. Polymerization reactions strengthen the gel network, thereby reducing the extent of shrinkage and pore collapse during drying. Coarsening is a process of dissolution and reprecipitation driven by differences in solubility between surfaces with
different radii of curvature (ref.1). One result of coarsening is to reduce the net curvature of the solid phase: small particles disappear and small pores are filled in. Often this has the effect of reducing the surface area and increasing the pore size of the resulting dried gel. Coarsening also strengthens the wet gel network, reducing the extent of shrinkage during drying. Phase transformations include crystallization (facilitated by dissolution and reprecipitation) and microsyneresis, in which the solid phase separates from the liquid on a local scale.

During drying (by evaporation) the gel network can at first collapse to accommodate the loss of solvent, thus preventing creation of more energetic solid-vapor interfaces associated with open pores (ref.9). This collapse is accompanied by condensation reactions that stiffen the network, inhibiting further shrinkage. At some point the network becomes sufficiently stiff that the liquid-vapor interface (initially defined by the exterior surface of the wet gel) breaks down into individual curved menisci corresponding to the exterior boundaries of the fluid-filled pores. The menisci are concave, so the liquid is in tension and network in compression. The magnitude of the capillary pressure experienced by the network depends on the surface tension $\gamma_{LV}$, the contact angle $\theta$, and the pore radius $r$ according to:

$$C_p = 2\gamma_{LV} \cos(\theta)/r.$$  \hspace{1cm} (6)

During film formation by dipping (or spinning) the deposited inorganic sol is thinned by gravitational (or centrifugal) draining accompanied by vigorous evaporation of solvent (ref.10). Unlike bulk gel formation, the drying process completely overlapped the gelation and aging processes, establishing a very short time scale (several seconds) for the sequence of events comprising film formation. Since there is little time for aging, the network remains quite compliant and is more easily compacted by the capillary pressure at the final stage of drying. The result is that films are often less porous than their bulk xerogel counterparts (ref.9).

4. EXPERIMENTAL

Silicate, multicomponent silicate, and aluminosilicate sols and gels were prepared from metal alkoxides according to the procedures documented in references 11-13, respectively. Fractal dimensions of the solvated inorganic polymers were determined by Porod analyses of small angle x-ray scattering data (ref.14). For the multicomponent silicate sols used to deposit films, aging was performed in the mother liquor (largely ethanol). Silicate gels were aged in either the mother liquor or successively in pure alcohol or water for 24 h periods, as described in ref. 15. Thin films were deposited by dip-coating (ref.10).

Surface areas and pore size distributions of wet gels were determined by a proton spin relaxation technique (ref.16). Surface areas, pore size distributions, and pore volumes of dry bulk gels were determined by classical $N_2$ adsorption-desorption methods (ref.17). Corresponding nitrogen adsorption-desorption isotherms were acquired from thin film specimens (1 cm$^2$ area x 100-200 nm thick) using a surface acoustic wave (SAW) technique developed by Frye and co-workers (ref.18). Analysis of these data allowed determination of surface area, pore volume, and pore size distribution. The refractive index ($\propto$ vol% solids) of thin film specimens was determined by ellipsometry.
5. RESULTS: Control of Pore Structure

The pore structure (pore volume, surface area, and pore size) of a xerogel or film is a consequence of sequential (or overlapping) gelation, aging, and drying processes. In this section we present several examples of how the pore structure is influenced by such factors as the size, structure, and composition of the inorganic polymers, the magnitude of the capillary pressure, and the choice of pore fluid.

5.1 Aggregation of Fractal Silicates

For fractal polymers, the polymer size and mass fractal dimension establish steric constraints that influence how efficiently the polymers pack together when they are concentrated during drying or film formation. Mandelbrot (ref. 8) has shown that if two fractal structures of radius R are placed independently in the same region of space, the number of intersections, \( M_{1,2} \), is expressed as:

\[
M_{1,2} \propto R^{D_1 + D_2 - d}
\]

(7)

where \( D_1 \) and \( D_2 \) are the respective mass fractal dimensions and \( d \) is the dimension of space. Thus in three dimensions, if each structure has a fractal dimension less than 1.5, the probability of intersection decreases indefinitely as \( R \) increases. Such structures are mutually transparent: during drying, they freely interpenetrate one another as they are forced into close proximity by the increasing concentration. This situation might be envisioned as a "network" of entangled worms: the pore size is small and has little dependence on the polymer (worm) size. Alternatively, if the fractal dimensions of both objects are greater than 1.5, the probability of intersection increases algebraically with \( R \). These structures, though porous, are mutually opaque: the branching of each polymer effectively screens its interior, inhibiting interpenetration, as in an assemblage of "tumbleweeds" deposited on a fence by the wind.

<table>
<thead>
<tr>
<th>Sample Aging Times</th>
<th>Refractive Index</th>
<th>% Porosity†</th>
<th>Median Pore Radius (nm)</th>
<th>Surface Area m²/g</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unaged</td>
<td>1.45</td>
<td>0</td>
<td>&lt;0.2</td>
<td>1.2 - 1.9</td>
<td>dense protective, electronic and optical films</td>
</tr>
<tr>
<td>0-3 Days</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>microporous films for sensors and membranes</td>
</tr>
<tr>
<td>3 Days</td>
<td>1.31</td>
<td>16</td>
<td>1.5</td>
<td>146</td>
<td>mesoporous films for sensors, membranes, catalysts, optics</td>
</tr>
<tr>
<td>1 Week</td>
<td>1.25</td>
<td>24</td>
<td>1.6</td>
<td>220</td>
<td></td>
</tr>
<tr>
<td>2 Week</td>
<td>1.21</td>
<td>33</td>
<td>1.9</td>
<td>263</td>
<td></td>
</tr>
<tr>
<td>3 Week†</td>
<td>1.18</td>
<td>52</td>
<td>3.0</td>
<td>245</td>
<td></td>
</tr>
</tbody>
</table>

* AGING OF DILUTE SOL AT 50°C AND pH3 PRIOR TO FILM DEPOSITION DETERMINED FROM N₂ ADSORPTION ISOTHERM.
† DETERMINED FROM N₂ ADSORPTION ISOTHERM.
‡ THE 3 WEEK SAMPLE GELLED. IT WAS RE-LIQUIDIFIED AT HIGH SHEAR RATES AND DILUTED WITH ETHANOL PRIOR TO FILM DEPOSITION.

Table 1. Summary of film porosities as a function of sol aging times (ref. 1). By interpolation of these data we expect that films prepared from sols aged between 0 and 3 days are microporous. Thus far we have no data to support this supposition perhaps due to condensation of water in the microporous films.
The concept of controlling pore structure through aggregation of opaque fractals is well illustrated by our investigation of film formation from a multicomponent borosilicate sol with nominal composition (wt%) 71 SiO$_2$-18 B$_2$O$_3$-7Al$_2$O$_3$-4BaO (ref.19). $^{29}$Si NMR and SAXS show that these polymers are quite highly branched and are characterized by a mass fractal dimension, $D \sim 2.4$ [(10)]. As indicated by Table 1, the vol% porosity, pore size, and surface area of films formed by dip-coating may be tailored by an aging process prior to film deposition. Aging the dilute sol causes the the average polymer size $R$ to increase. Since the density of a mass fractal object decreases with $R$ (Eq. 5), the vol% porosity of an assemblage of non-interpenetrating (opaque) fractal objects increases with $R$ (see Fig. 1). At nominally zero aging time, the polymers are small, so screening is ineffective (Eq. 7) leading to films with sufficiently small pores that there is no accessibility to N$_2$ (kinetic diameter = 0.4 nm) as indicated by Type II N$_2$ adsorption-condensation isotherms (ref. 17) acquired by the SAW technique (ref. 18). (If porous, these films have no pore openings larger than about 0.4 nm). By comparison, one week of sol aging prior to film deposition yields a highly porous film (BET surface area = 263 m$^2$/g) with a narrow distribution of pore radii centered at about 1.9 nm. Of particular interest for applications in membranes and catalysis are aging times between zero and three days. By extrapolation of the consistent trends observed for longer aging times, we expect that aging periods between 0 and 3 days would result in films that are microporous or mesoporous with pore sizes ranging from <0.4 nm to 3.0 nm, depending on the extent of aging prior to deposition.

Figure 1. Hydrodynamic radius (measured by quasielastic light scattering) of multicomponent sols as a function of aging time at 50°C and $-\mathrm{pH}$ 3 prior to film deposition and the corresponding refractive indices (proportional to density) of the deposited thin films (measured by ellipsometry). The reciprocal relationship between polymer size and density is a consequence of aggregation of mutually opaque fractals. From reference 19.
Both Figure 1 and Table 1 illustrate that unlike conventional ceramic processing, we need not avoid aggregation. In fact, growth of the polymers during aging presumably occurs by an aggregative process, and further aggregation occurs during film formation. We simply exploit these aggregation phenomena to tailor the porosity.

5.2 Capillary Pressure

The curvature of the meniscus created during drying causes the pore fluid to be in tension and the solid phase in compression. Equation 6 indicates that for spreading fluids (cos $\theta = 1$) the magnitude of the capillary pressure experienced by the solid phase varies linearly with surface tension. In order to assess the importance of the capillary pressure in determining the pore structure of dried silicate gels, we replaced the mother liquor ($\sim$90 vol% ethanol - 10 vol% water) with polar, aprotic solvents of varying surface tensions prior to drying (unlike protic solvents such as alcohol, aprotic solvents do not react with the silicate network, e.g., reverse of Eq. 2, so we can distinguish between effects of capillarity and surface chemistry). Figure 2 (ref.20) plots the BET surface areas of the dried gels as a function of the pore fluid surface tension. The surface area varies approximately linearly from about 1200 to 800 m$^2$/g as the surface tension is increased from 0 to $-35$ dyne/cm. This clearly demonstrates that the surface area may be carefully tailored by a post-gelation aging procedure, enabling us to decouple sol-gel chemistry and pore structure. Pore volume and pore size decrease with increasing surface tension in a similar manner (ref.20).

![Figure 2](image_url)

**Figure 2.** Surface area of silicate xerogels versus surface tension of pore fluid used during drying. Filled symbols are surface areas of aerogels prepared by supercritical drying ($C_p = 0$). From reference 20.

5.3 Novel Aluminosilicates

Structural studies of bulk aluminosilicate gels demonstrate remarkable effects of both composition and the magnitude of the capillary pressure on the porosity of the xerogel. At an Al:Si molar ratio of about 1:1, gels prepared in water-rich fluids dry to form xerogels with closed porosity, as indicated by $N_2$ BET surface area values close to zero and correspondingly reduced skeletal densities (ref.21) (see, Figure 3). Deviations...
Figure 3. Surface area and skeletal density vs. Al$_2$O$_3$ content for bulk xerogels in the SiO$_2$-Al$_2$O$_3$ binary. From reference 21.

Figure 4. N$_2$ isotherms for aluminosilicate xerogels (Al:Si ~ 1:1) dried in fluids with different surface tensions. From reference 13.
from this Al:Si ratio produce microporous or mesoporous xerogels. Similar trends are anticipated for supported thin films or membranes.

Figure 4 shows the effect of capillary pressure on the porosity of aluminosilicate xerogels prepared with Al:Si = 1:1 (ref.13). Reducing the surface tension of the pore fluid from about 70 to 24 dyne/cm causes the porosity to change from closed, to microporous, to mesoporous. Thus we infer that closed porosity is a consequence of the capillary pressure exerted on the solid phase during drying (as well as the Al:Si ratio) and conclude that the capillary pressure can be used to tailor the xerogel porosity.

5.4 Post Gelation Aging

A final means of tailoring porosity amenable to polymeric networks is based on structural changes that we have observed during aging bulk, wet silicate gels in various fluids (ref.15). In situ $^1$H spin relaxation measurements combined with $^{29}$Si NMR, and vibrational spectroscopy show that replacement of the original pore fluid (~90 vol% ethanol-10 vol% water) with pure ethanol results in esterification of silanol groups (reverse of Eq.1) and siloxane bond alcoholysis (reverse of Eq. 2), along with an increase in surface area, reduction in pore size, and a narrowing of the pore size distribution (ref.13). Aging in pure water caused the reverse trends. We believe this behavior is analogous to solvation or phase separation of organic polymers described as microsyneresis (see, Fig. 5) (ref.1,15). These trends are preserved in the final dried gel (ref. 15). Thus aging represents a fourth simple procedure to tailor the structure of xerogels.

Figure 5. Schematic illustration of microsyneresis during aging bulk polymeric silica gels before drying. (a) Replacement of water with ethanol causes esterification, depolymerization, and solvation of the siloxane polymers leading to a reduction in pore size and a narrowing of the pore size distribution. (b) Replacement of ethanol with water has the reverse effect, leading to larger pores and a broadening of the pore size distribution. From reference 15.

6. CONCLUSIONS

We have shown that the pore structure (surface area, pore volume, and pore size) of xerogels and thin films may be controlled by such factors as the size, structure, and composition of the inorganic polymers comprising the sol, conditions of aging, and the
magnitude of the capillary pressure exerted on the network during drying. The physical and chemical bases of these strategies are largely generic and may be exploited to tailor the pore structure for various applications such as catalyst supports, membranes, and sensors. The challenge is to develop synthetic chemical procedures that allow a rich spectrum of polymeric structures to be produced in systems other than silica.

7. REFERENCES