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Résumé. - En partant des mesures physiques simples, une image est proposée de la mi-crostructure d'un gel séché monolithique de silice préparé à partir de l'orthosili-cate d'éthyle. On a mesuré la masse spécifique et la dimension des échantillons et suivi les pertes de poids au cours du séchage du gel, jusqu'à l'obtention d'un verre totalement compact. Les gaz émis pendant le chauffage ont été analysés. Les résultats sont interprétés et comparés aux études publiées sur la structure moléculaire des gels secs.

Abstract. - Using simple physical measurements, a picture was constructed of the microstructure of a dried monolithic silica gel prepared from tetraethyl orthosilicate (TEOS). The density and dimensions were measured. Weight loss was monitored during heating of the gel to a fully dense glass, and gases escaping during heating were analyzed. The results were interpreted for the dried gel and compared to published studies of its molecular structure.

1. Introduction. - When water and tetraethyl orthosilicate (TEOS) are dissolved in ethanol, the solution undergoes hydrolyzation and condensation polymerization to create complex silanols. Alkoxy groups and hydroxyl groups react to build larger units with bridging oxygens. The solution which is initially fluid becomes a vis-cous liquid which sets to a gel filling its container. This sol-gel process produces an optically transparent, amorphous shape when the appropriate combination of acid, water and temperature is used (1). The microporous dried gel can be converted to a dense inorganic glass at temperatures well below the melting temperature, which in this case for pure silica is about $1723^{\circ}C$ (2,3,4).

On closer inspection, the sol-gel process is not only an alternative method to melting, but also a method for changing the chemistry and structure of the glass. Changes in chemistry may be brought about by controlling the extent of hydrolyza-tion (5). In this way, the organic content or water content can be changed (6). Changes in structure are brought about by the interaction of hydrolyzation and polymerization.

There are really two levels of structural changes in the gels during drying and firing to an inorganic, dense glass. First, there are the changes in micro-structure in terms of pore volume and pore morphology. Second, there are the changes in molecular structure in terms of degree of cross-linking and number of bridging oxygens. The purpose of this investigation is to characterize dried and fired gels using simple physical measurements to get an idea of the effect of water on microstructure. This information can then be compared to investigations of molecular structure, where the detection of such changes is somewhat less direct.

Several suggestions that changes in molecular structure result from processing conditions have been made on the basis of various experimental techniques. For example, infrared (7,8) and visible (9) spectroscopy data have been interpreted to indicate subtle differences in molecular structure between gels and melted glasses. Nucleation and crystallization behavior have been compared for gels and melted glasses, and even when the difference in water content is taken into

consideration, there appears to be distinctly different behavior (10). More re-
cently, scanning calorimetry data have been interpreted to mean that the behavior
for a gel in the glass transition region is typical of behavior for a rapidly
quenched glass (11).

In order to relate gel microstructure to its molecular structure, gels were
prepared with four water levels representing enough water to hydrolyze to eight
times the water needed to hydrolyze a mole of TEOS. Gel density, weight loss and
shrinkage were measured after drying; then total weight loss and gas evolution
during firing were measured (12). In line with results from BET measurements (5)
and small angle x-ray scattering (13) a simple model for the gel microstructure
has been proposed and compared to gel molecular structures proposed on the basis
of infrared spectroscopy (2,7,8).

2. Experimental procedure. - All samples studied here were prepared by using a
modification of a vacuum distillation process (14). Mixtures of TEOS, ethanol and
2, 4, 8 or 16 moles of H_2O per mole of TEOS were refluxed with acid for three hours
in a three-necked flask. After cooling the reaction flask to about 5°C, the reflux
condenser was exchanged for a rush-over condenser leading to a fraction cutter and
then to a cold trap in a dry ice-acetone bath. The condenser was connected to a
mechanical pump and a vacuum of about 10 mm Hg was drawn. As primarily ethanol
was removed from the flask, the density of the solution increased. Samples were
extracted periodically and cast into 55 mm plastic Petrie dishes where the solution
gelled. The dishes were placed in the laboratory at room temperature and allowed
to dry slowly over a period of one month.

At the end of this period, the samples were uncovered and characterized for
number of fragments, radial shrinkage, weight loss on drying and dry density. For
each water level there were samples which dried in one piece. The monolithic
samples were characterized further for total weight loss during firing from 120 to
800°C, and a measure of percent weight loss for oxidation of residual organics in
air at 410°C was obtained with simultaneous thermal analysis (DTA) and thermal
gravimetry (TGA) in a Mettler thermal analyzer. The measure of organic content
was compared to the amount of gas evolved during firing which was condensed in a
cold trap and titrated for water level with Karl Fisher reagent.

In addition, four samples were selected for firing to 1000°C, thereby dupli-
cating the density of fused silica. These samples are listed in the Table. They
were heated in vacuum at 4°/min to 270°C, held in air for 60 min, heated in air
at 4°/min to 400°C and held for 60 min, and finally heated in vacuum at 4°/min
to 1000°C and held for 2 hours. The total cycle took 8 hours.

3. Experimental results. - Monolithic samples were formed when 1000 ml of reactants
were hydrolyzed with 10 ml 1N HNO_3 for 3 hours under refluxing, followed by in-
creasing the solution density to between 1.0 and 1.1 g/cm^3 by vacuum distillation,
casting the solution into plastic molds and drying at room temperature. After one
month of drying, the densities of the gels ranged from 1.5 g/cm^3 to 1.8 g/cm^3. The
dry density is plotted in Fig. 1 for the four water levels. The gel made with
eight times the water needed for hydrolysis has the lowest density. In Fig. 2 the
percent weight loss on drying is plotted on the left-hand side and the percent
radial shrinkage is plotted on the right-hand side for the four water levels. The
gel with 16 moles H_2O loses about twice as much weight and shrinks twice the dis-
tance as does the gel with 2 moles H_2O.

When the dried samples were heated in air in the thermal analyzer to 800°C,
there was an exothermic peak at 410°C. In Fig. 3 the weight loss associated with
this peak is plotted on the right-hand side along with the relative peak height on
the left-hand side. The peak height is highest for the gel with 2 moles H_2O.
Finally, in Fig. 4 the total weight loss between 120 and 800°C is plotted for
the four water levels. For this range, the gel with 2 moles H_2O loses slightly
more weight than the gels with higher water levels. The same trend is found for
the gas condensed in a cold trap which was titrated for water level. The gel with

Table: Firing behavior of samples that dry in 1 piece

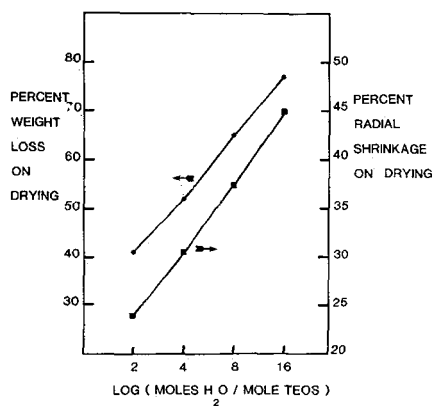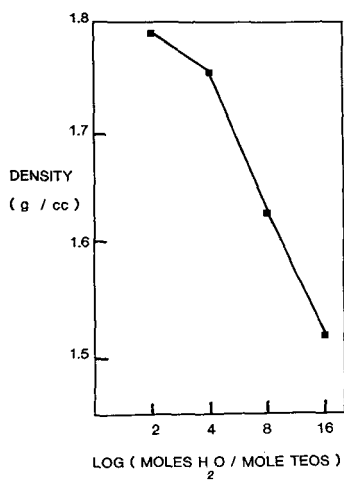| Sample	Ratio moles H_2O / moles TEOS	Electrolyte addition in g	Casting density in g/cm^3	Drying temperature °C	Comment
A	16	21 (27% HCl)	1.02	22	Cracked
B	2	9 (70% HNO_3)	1.05	22	Discolors
C	16	14.5 (70% HNO_3)	1.04	22	Cracked
D	16	14.5 (70% HNO_3)	1.05	70	Monolithic

Fig. 1 – Density of slowly dried gels for 4 water levels.

Fig. 2 – Weight loss and radial shrinkage for gels for 4 water levels.
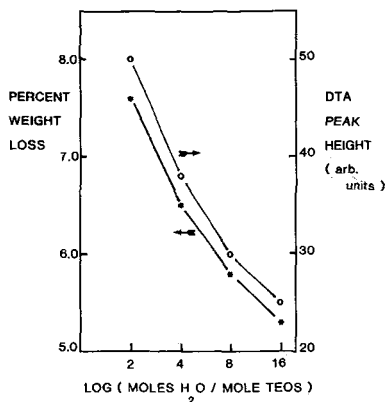
Fig. 3 – Weight loss and relative peak height from DTA for oxidation of organics in air at about 410°C for 4 water levels.
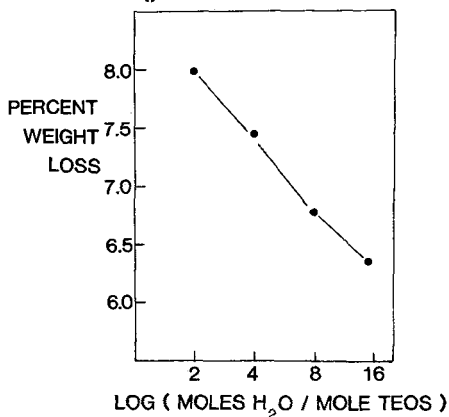
Fig. 4 – Total weight loss according to thermal gravimetry between 120 and 800°C for 4 water levels.

2 moles H_2O has more weight loss due to water than the gels with higher water levels.

The results of thermal analysis were used to design the 8 hour firing schedule. As indicated in the Table, the monolithic gel prepared with 16 moles H_2O and dried at 70°C (Sample D) has a density of 2.2 g/cm^3 and was a monolithic glass after firing. The final sample size was about 20 mm.

4. <u>Discussion and Conclusions</u>. - As expected, the gels prepared with less water had higher densities, less weight loss on drying and more residual organic than gels prepared with more water. Under acid conditions, a high water level is thought to increase the number of bridging oxygens and eliminate more alkoxy groups (5,6). When all the gels reached a dry condition in equilibrium with atmospheric moisture, they were monolithic and transparent. However, the gel with 16 moles H_2O showed less total weight loss and less weight loss due to water on firing than the gel with 2 moles H_2O. This behavior can be explained by a polymerization scheme where the high density-low water gel has low molecular weight polymers with occasional cross-links between polymers, while the low density-high water gel has larger polymers which tend to grow individually before cross-linking.

A simple geometrical model was used previously to reconcile BET (5) and SAXS (13) estimates of pore size with weight loss from elimination of hydroxyls on the surface of pores (1). Following this model, the trend towards less weight loss on firing in the low density gels would suggest a progression from cross-linked chains to cross-linked multiple chains to cross-linked sheets. Another way of looking at this is a continuum from molecular structure to microstructure.

Taking this model one step further, it has been suggested from infrared spectroscopy that a typical spectrum from a gel shows less absorption at 1100 cm^{-1} than from a melted glass, meaning either rings of large size or chains in the gel (7). This again points to the fact that in a gel the molecular structure becomes its microstructure depending on processing conditions. There is a great deal more work needed to fully characterize the structures of gels, and by comparison with gels, the structure of melted glass.

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