

# SUPERINSULATING MONOLITHIC SILICA AEROGELS VIA SUPERCRITICAL CO<sub>2</sub> EXTRACTION FOR HIGH TEMPERATURE APPLICATIONS

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Monolithic and transparent silica aerogels were synthesized by two step sol-gel method using TEOS (Tetraethylorthosilicate) as precursor, HCl and NH<sub>4</sub>OH as catalysts and ethanol as solvent. The alcogels were dried using supercritical CO<sub>2</sub> extraction method. The effects of several sol-gel parameters including TEOS concentration, gelation and aging temperature on both transparency and thermal conductivity were investigated. First, TEOS concentration, which was found to have a significant effect on optical properties, was varied from 20 to 70 % by weight and the sol having 60 % TEOS was found to be the most transparent one. The alcogels were aged in 50% water-ethanol solutions at 298, 323, 343 K among them 323 K aged sample was the best in terms of transparency. After these parameters were optimized for maximum transparency and minimum thermal conductivity, the effect of supercritical CO<sub>2</sub> extraction temperature, pressure and duration on pore size distributions and transparency were studied to relate these two properties. The extraction temperature was varied from 308 to 358 K and the pressure was varied from 80 to 300 MPa. It was observed that higher temperatures lead to better properties in terms of transparency. The drying duration was related to the drying conditions and the alcogel size. After drying step the aerogels were heat treated which increased transparency of the monolith beyond a certain temperature. For the transmittance measurements of the monoliths a UV-VIS spectrophotometer was used. Moreover the refractive indexes were determined by a laser method. The thermal insulation property was characterized via hot-wire method. Long term stability against high temperature tests were performed by subjecting the monoliths up to 1073 K for extended periods and also by subjecting the monoliths to rapid heating and cooling cycles.

## Introduction:

Environmental concerns including global warming have become a driving force for researchers to find ways to decrease energy consumption in the world. Improving thermal insulation is a promising way of decreasing the energy consumption without reducing life standards. Development of advanced insulation materials that are transparent are important for reducing high heat losses in buildings or in white goods. Particularly, an improvement in thermal insulation of oven windows can result in significant reduction of energy usage in houses. Silica aerogels are promising materials for such window insulation applications due to their low thermal conductivity and high transparency among other insulation materials[1]. They exhibit thermal conductivities that are lower than 20 mW/K·m<sup>-1</sup> where air has a thermal conductivity of 24.1 mW/K·m<sup>-1</sup> under same conditions [2].

Yoldas et al.[3] studied the applicability of silica aerogels which were produced via ambient pressure drying for thermal insulation applications. Optimized amounts of reactants which were calculated by a computer design for low thermal conductivity were used during synthesis. However, the resulting aerogels were cracked during drying, which made it impossible to use them as large panels, but when the aerogels were grinded the properties did not change. Studies about using granulated silica aerogel for insulation panels [4], [5] led to the development of panels with thermal conductivity of lower than 0.4 W/ (m<sup>2</sup>K) and for a 50 mm panel a transparency of %17-%45. But when silica aerogel granules are used between two glass layers, thermal conductivity and light transmission work against each other such that, when the panel thickness increases, thermal conductivity decreases but transparency decreases as well. Using monolithic transparent aerogels between two glass layers instead of granulate form can be a solution in such cases. K.I. Jensen et al. [6] achieved to synthesize and apply monolithic silica aerogels for windows of buildings. They obtained monolithic silica aerogel with a thickness of

15 mm, a center heat-loss coefficient of  $<0.7\text{Wm}^{-2}\text{K}^{-1}$  and a solar transmittance of 76% for glazing prototypes. But a material that will be used for self cleaning ovens should be resistant to high temperatures (up to  $650\text{ }^{\circ}\text{C}$ ). A recent study showed that treating alcogels with a trialkyl silation agent before ambient pressure drying makes it possible to obtain silica aerogels stable up to  $350\text{ }^{\circ}\text{C}$  with low thermal conductivity ( $0.09\text{ w/m K}$ ) [7]. Carlos Folgar et al.[8] has recently worked on microstructural evolution in silica aerogels during thermal process from room temperature to  $1500\text{ }^{\circ}\text{C}$ . This study shows that temperature affects the pore volume, density and surface area which are expected to be stable enough for oven window applications.

This study is about development of transparent monolithic silica aerogels with a low thermal conductivity that are stable at high temperatures for a long time and resistant to high temperature swings.

### Materials and Methods:

Silica aerogels were synthesized via two step sol-gel method using TEOS (FLUKA purun:>98.0%(GC) ) as the precursor. HCl was used as hydrolysis catalyst and  $\text{NH}_3$  (ALDRICH 2.0M in ethanol) was the condensation catalyst. TEOS was diluted with ethanol at different concentrations. Subsequently, water and acid catalyst were added to start hydrolysis under continuous stirring. Condensation started with the addition of the base catalyst and the sol was taken into syringes for complete gelation. After the sol lost its fluidity and became a hydrogel, it was transferred into different aging solutions. The remaining water in hydrogels due to condensation reaction and aging solution which would cause problems at the drying step was removed by solvent exchange using ethanol. Supercritical drying was performed using a 50 ml high pressure vessel which is heated by circulating fluid through internally machined channels. The vessel is equipped with two sapphire windows for continuous observation. The contents of the vessel was stirred using a magnetic stirbar. A stainless steel screen was placed in the middle of the vessel to separate the magnet and samples.  $\text{CO}_2$  was pumped into the vessel with a syringe pump at constant flow rate; and pressure was controlled by a back pressure regulator which is heated with a water bath. (Fig.1)

The dimensions of cylindrical aerogels were measured using a caliper and they were weighed using an analytical balance for density calculation. UV-vis spectrophotometer was used to measure the transmittance values in the visible region. The weight loss of the samples during heat treatment was measured via Thermal Gravimetric Analysis (TGA).

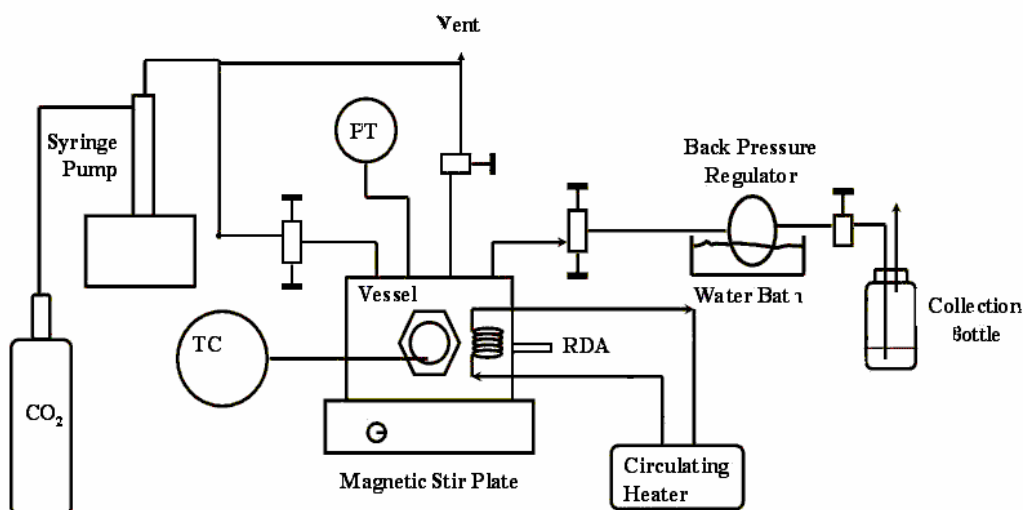


Figure 1. Supercritical extraction set-up.

## Results:

In the first set of experiments, the TEOS concentration was varied from 20 to 70 % and was found to have a significant effect on optical properties. After four days of solvent exchange with ethanol, these gels were extracted at 298K at 1600 psig and then the temperature was increased to 313 K at 1600 psig. The vessel was then depressurized. It can be seen from Table 1 that increasing the TEOS conc. did not affect the density of the aerogels prepared from these sols significantly. This behavior can be explained by the differences in their shrinkage values. One can expect the densities of the aerogels to increase more than observed due to higher silica amount within same volume. But the samples shrink less with increasing TEOS concentration. In order to obtain aerogels with low densities, one has to not only start with a dilute sol but also minimize shrinkage. The transparencies of the samples were affected significantly with the change in the TEOS concentration. The transparency of the aerogels increased with increasing TEOS concentration up to 60%. The transparency of the sample obtained with 70% TEOS was less than the sample obtained with 70% TEOS concentration. The solution with 60% TEOS by weight is close to the miscibility line of the ternary phase diagram of the system TEOS-ethanol-water at 298K [9], which becomes miscible with the addition of HCl. After 70 %, the sol was not miscible even after HCl addition.

Table 1. Concentration effect on shrinkage

TEOS conc. (%Wt)	Density (g / cc)	Shrinkage (%)
20	0.099	19
30	0.164	25
40	0.195	19
50	0.165	10
60	0.149	9
70	0.203	14

When gelation occurs, the reactions are not complete. Aging is done after gelation to obtain a stronger alcogel which can resist the capillary forces during the drying process. Some other experiments were carried out with different aging solutions. Hydrogels obtained from the same sol were aged in, TEOS-ethanol, water-ethanol and pure ethanol solutions. Then they were placed into pure ethanol after a certain period of time for solvent exchange. After drying, it seemed that TEOS- ethanol solution does not have a significant effect on the amount of shrinkage; on the other hand water had a strengthening effect on gel structure so that it decreased diameter shrinkage values from 26% to 19%. It was shown that using water as the aging solution lead to gels that are mechanically stronger and also that have less external and micropore surface area which decrease shrinkage during drying [10]. The gels in this study were not optically characterized. For the purposes of this study, transparency is an important property as mechanical strength so optical properties were considered while choosing the optimum aging solution and temperature. Aging the gels in 50% water-ethanol at 323K led to transparent monolithic aerogels with reasonable shrinkage values. Also the solvent exchange with ethanol was performed at 323K within 24h instead of 3-4 days at room temperature. Performing aging and solvent exchange at same temperature and in 2 days makes procedure more practical and faster.

Table 2. Effect of aging parameters.

TEOS conc. (%Wt)	Aging solvent	Density (g / cc)	Shrinkage (%)
30	eth+water 20%	0.195	29
30	eth+water 50%	0.164	25
40	Eth	0.240	26
40	Eth+water 50%	0.195	19
40	Eth+TEOS 20%	0.25	26

Drying is the critical step for aerogel production being an energy and time consuming step. Simulations were done to estimate the effect of drying temperature on the duration of drying.

When the pores are assumed to be cylindrical and the drying procedure was treated as diffusion in a capillary with a moving boundary, flux is given by,

$$N_A = -D_{ab} \left[ \frac{dC_A}{dz} \right] \quad (1)$$

where  $N_A$  is the flux,  $D_{ab}$  is the binary diffusion coefficient of ethanol and carbon dioxide,  $C_A$  is the concentration of ethanol in  $CO_2$ . Flux is used to estimate the drying time which is given by the following formula

$$\left( \frac{S * \rho}{M_A} \right) \frac{dz}{dt} = \frac{D_{ab} * C_A}{h - z_t} \quad (2)$$

where  $S$  is the cross-sectional area of the pore,  $\rho$  is the density of ethanol at these conditions,  $M_A$  is the molecular weight and  $h$  is the length of the pore. In derivation of equation (2), the concentration of ethanol at surface of the gel was assumed to be 0 due to continuous  $CO_2$  flow during extraction and the concentration of ethanol at the interphase in the pore was assumed to be the solubility of ethanol in supercritical  $CO_2$ .

After integration this equation takes the form,

$$h^2 = \frac{D_{ab} * C_A * M_A * t}{\rho} \quad (3)$$

The binary diffusion coefficient of ethanol and carbon dioxide was calculated at different conditions using Schmidt number coloration proposed by Funazukuri and Wakao [11];

$$Sc^+ = \frac{Sc}{Sc^*} = 1 + \exp \left[ \sum_{i=0}^5 a_i \left( \frac{v_0}{v} \right)^i \right] \quad (4)$$

$$Sc^* = \frac{5}{6} \left[ \frac{\sigma_1 + \sigma_2}{2\sigma_2} \right]^2 \left[ \frac{2M_1}{M_1 + M_2} \right]^{1/2} \quad (5)$$

where,  $Sc$  is Schmidt number at high pressure and  $Sc^*$  is at atmospheric pressure at the same temperature,  $v$  is molar volume of solvent,  $\sigma_1$  and  $\sigma_2$  are the hard sphere diameters of solute and solvent respectively.  $v_0$  is the hard sphere closest packed volume of solvent molecules which can be calculated for carbon dioxide as;

$$v_0 = \frac{1}{1.384} \left( \sum_{i=0}^4 c_i T^i \right) \quad (6)$$

Then  $D_{ab}$  is calculated using the formula;

$$D_{ab} = \frac{V}{\rho * Sc} \quad (7)$$

where  $V$  is the viscosity and  $\rho$  is the density. According to the simulations  $D_{ab}$  values increased with temperature at constant pressure.

From these calculations the drying time was found to increase as temperature increased at constant pressure.

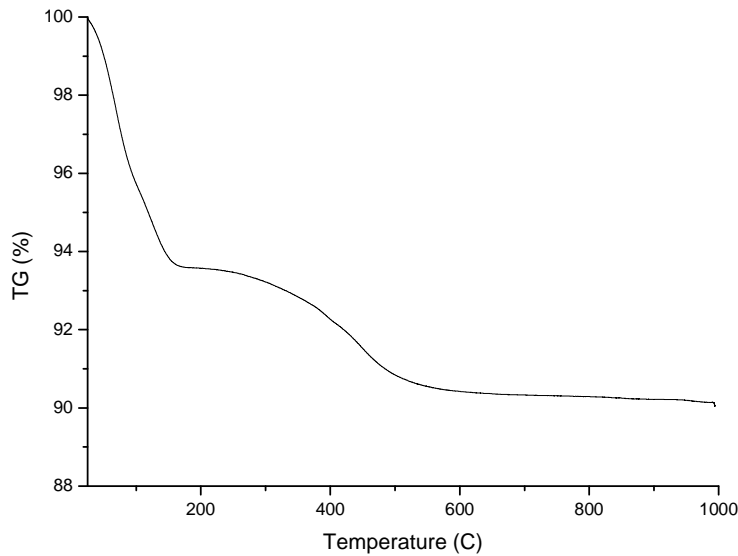
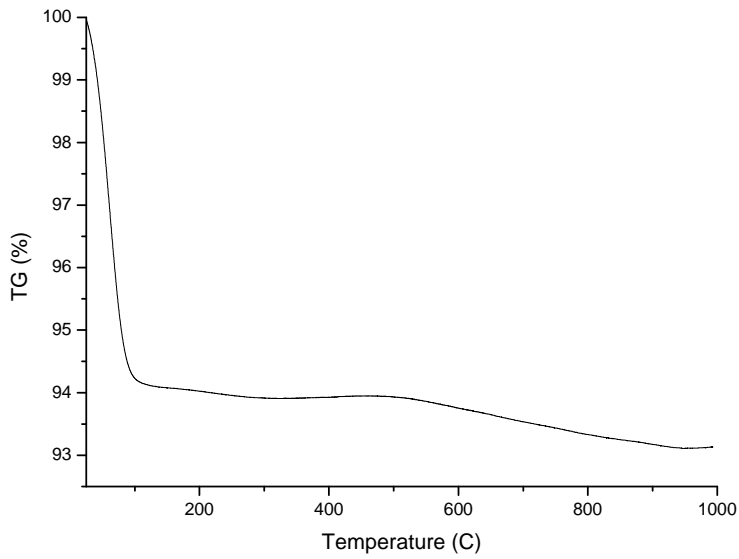


Figure 2. TGA of 2 samples a) heat treated and b) directly after drying.

Figure 2 shows the TGA of two aerogel samples that have been prepared by identical synthesis and drying procedures. One of them was heat treated in a tube furnace at 673K for 4h, and the other one was not heat treated. TGA was performed in oxygen atmosphere. The 6% weight loss up to 100C<sup>0</sup> observed in both samples indicates that this loss is due to the adsorbed water. It can be said that samples regain nearly 6% of their weight by water absorption from air fast. The loss around 300C<sup>0</sup> is believed to be due to the unreacted TEOS or some organic end groups such as CH<sub>3</sub>. Once these groups are released by heat treatment the sample does not loose weight at these temperatures any more. The samples are stable up to 1000 C and do not crack.

### Conclusion

Monolithic transparent silica aerogels were synthesized for use in high temperature applications. Reactant concentrations and aging conditions were optimized. A model was developed to predict the effect of drying conditions on the drying time. The experimental results showed the same trend which

was as the temperature increased drying time decreased. TGA of the samples showed the stability of the aerogels up to 1200K and the necessity of heat treatment after drying which also increased transparency.

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