

# Aerosol Synthesis of Low Density High Surface Area Aerosol Gels

*C.M. Sorensen, R. Dhaubhadel and A. Chakrabarti*  
*Department of Physics*  
*Kansas State University*

## I. Introduction

We have recently discovered a novel method to produce porous materials with high specific surface area and extremely low density [1]. We were led to this discovery by our recent work that demonstrated gelation of soot aerosols in flames [2-5]. Our method involves the gelation of nanoparticles in the aerosol phase to create a material that we have named an "aerosol gel." So far we have produced aerosol gels of carbon. The initial aerosol is composed of nanometer sized carbon particles produced rapidly by exploding in a chamber any one of a number of hydrocarbons with oxygen. The nanometer particles so produced quickly aggregate and then gel to form the aerosol gel. The materials we have made have densities as low as 2.5 mg/cc, roughly twice the density of air and lower than any known material. The aerosol gel is significantly different than ordinary soot and carbon black. It is a new material that has not been described before.

The current state of the art for manufacture of low density, porous materials is the sol-gel/supercritical-drying production of well-known aerogel and xerogel materials [6,7]. We believe our aerosol gelation method is a significant advancement over this state of the art because: 1) there is no need for a supercritical drying step as for aerogels, and 2) the aerosol gel method should be applicable to any material.

## II. Aerosol Gelation

Any system of particles undergoing aggregation can form a gel if the combining particles do not coalesce, and if the time to reach the gel point is shorter than other time scales that can deter gel formation such as gravitational setting. Non-coalescence is necessary so that the aggregating particles will form a non-dense (ramified) fractal aggregate with fractal dimension,  $D$ , less than the spatial dimension,  $d$ . When  $D < d$ , the average cluster separation to cluster size ratio falls with time during aggregation until the separation equals the size. Then the clusters jam together to form a gel. This scenario describes the general features of all gelation phenomena from gelatin in water to hydrolysis and subsequent gelation of silica in solutions as precursors to aerogels.

A simple argument can be used to calculate approximately the time it takes to gel. A reasonable approximation for when the particulate system gels is when the monomer or primary particle number density in the average cluster is equal to the primary particle number density in the entire system, i.e.,

$$n(c)=n(s). \tag{1}$$

For a fractal aggregate (cluster) the number of primary particle of radius "a" in a cluster of radius R is approximately

$$N = (R/a)^D. \tag{2}$$

Then the primary particle density in the cluster is

$$\begin{aligned}
n(c) &= N / V \\
&\approx N / R^d \\
&= R^{D-d} / a^D.
\end{aligned} \tag{3}$$

The system primary particle number density is related to the particulate volume fraction  $f_v$  by

$$f_v = n(s)a^d. \tag{4}$$

Then Eqs.(1), (3) and (4) yield the size of the cluster at the gel point

$$R_{gel} = a f_v^{\frac{1}{D-d}}. \tag{5}$$

For  $d=3$  and the DLCA  $D=1.8$  this is

$$R_{gel} = a f_v^{-5/6}. \tag{6}$$

The gel time is the time to grow to  $R_{gel}$ . Kinetics of growth are governed by the Smoluchowski equation which in its simplest form is

$$\frac{dn_c}{dt} = -K n_c^2. \tag{7}$$

In (7)  $n_c$  is the number density of clusters and  $K$  is the aggregation constant. The long time solution to (7) is

$$n_c(t) = (Kt)^{-1}. \tag{8}$$

The cluster and primary particle number densities are related by

$$n(s) = N n_c. \tag{9}$$

$n(s)$  is a constant and  $N$  and  $n_c$  vary with time. The gel time can be found by setting the number of primary particle per cluster  $N$  to its value at the gel point through Eqs.(2) and (5)

$$N_{gel} = (R_{gel}/a)^D. \tag{10}$$

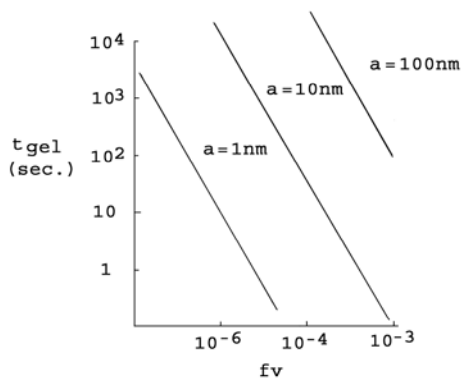
Then combining Eqs.(4), (5), (8), (9) and (10) one can find the gel time

$$t_{gel} = K^{-1} \frac{a^3}{f_v^{\frac{D-d}{d}}}. \tag{11}$$

For  $d=3$  and  $D=1.8$  (11) becomes

$$t_{gel} = K^{-1} \frac{a^3}{f_v^{2.5}}. \tag{12}$$

Equation (12) is full of meaning. It says that if  $a$  is small and  $f_v$  is large, i.e., if there is a lot of finely divided matter, the system will gel fast. Moreover, the functionalities on  $a$  and  $f_v$  are very strong. Equation (12) is plotted in Fig. 1. For the aggregation constant  $K$  the value for air at STP is used,  $K = 3 \times 10^{-10} \text{ cm}^3/\text{s}$  [8]. Figure 1 shows that an aerosol can gel quickly, 100s or less, if  $a \leq 10 \text{ nm}$  for  $f_v \sim 10^{-4}$ . Coarser aerosols at lower  $f_v$  have huge gel times and essentially never gel.

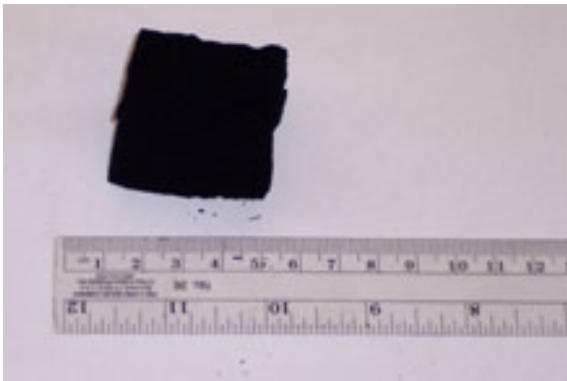


**Figure 1.** Time for gel to form.

The conditions for rapid gel formation,  $f_v \geq 10^{-4}$  and  $a \sim 10\text{nm}$ , can be obtained with rapid, gas phase reaction. Any gas at STP if converted directly to a solid will yield a solid  $f_v$  of about  $10^{-3}$  (recall that gases are about 1,000 times less dense than the condensed phase). Rapid reactions from the gas to the solid phase will drive the system deep into a supersaturated regime. Thus rapid and uniform nucleation to small particles will occur.

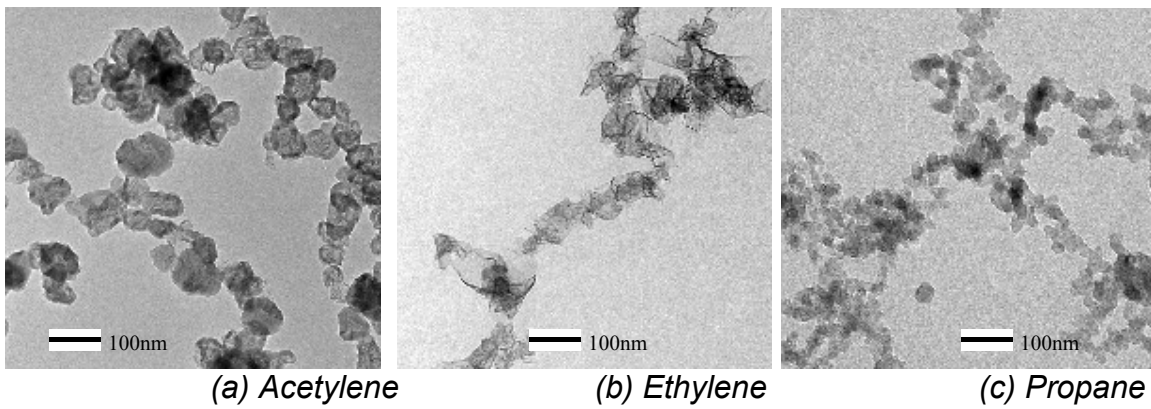
#### IV. Low Density Carbon Aerosol Gels

To produce carbon aerosol gels a mixture of a hydrocarbon and oxygen in various proportions between the lower and upper explosive limits is introduced into a thick walled, 4 or 16 liter, aluminum chamber. Liquid fuels are introduced as micron sized liquid drop aerosols. After exploding the fuel-oxygen mixture with an electric spark, the chamber can be opened to obtain a dark black and fluffy carbon layer on the inner surfaces of the chamber. The material, pictured in Fig. 2, is very light and elastic with a density as low as 2.5 mg/cc. It can withstand ca. 200 times its weight before it is crushed. The aerosol gel can be compressed to densities as high as 300 mg/cc.



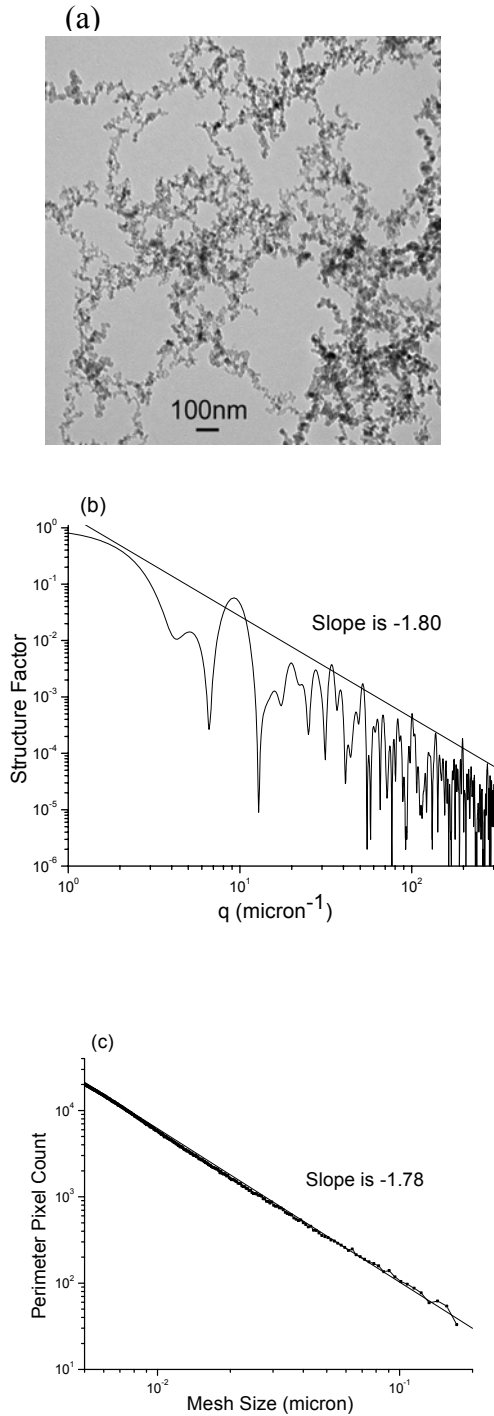
**Figure 2.** Carbon aerosol gel, density = 2.5 mg/cc.

Transmission Electron Microscope (TEM) pictures of the aerosol gel show that the primary particles are graphitic in nature and are more or less polygonal in structure. Sometimes thin surfaces with thick borders are seen. The TEM pictures for acetylene, ethylene and propane hydrocarbon precursors are shown in Figure 3 (a), (b) and (c), respectively.

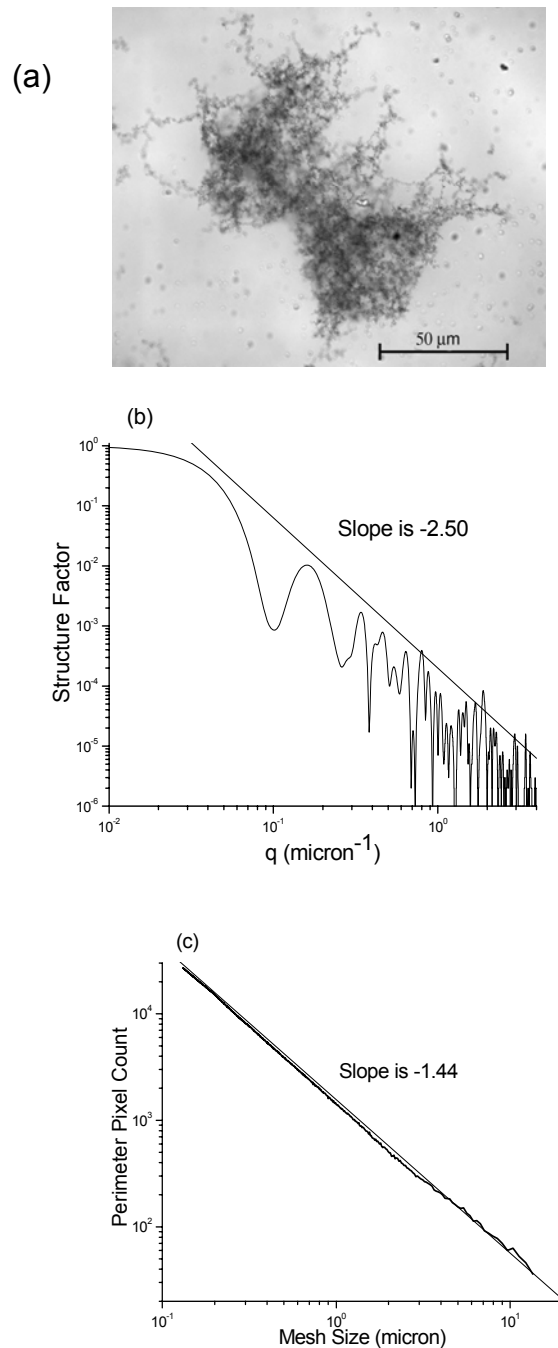


**Figure 3.** TEM pictures of aerosol gels.

Cluster morphology was determined from the TEM pictures by three different methods: correlation function, structure factor and perimeter analyses. Two representative examples among the pictures used for the cluster morphology analysis are presented in Figs. 4 and 5. When analyzed on the scale of the primary particle size ( $\sim 50\text{nm}$  diameter) up to ca. 1 micron, the clusters were found to have a fractal dimension of  $1.75 \pm 0.05$  via all three analyses. Analysis of cluster morphology over length scales from ca. 1 micron to 50 microns with the perimeter analysis method, which is the only viable method when  $D > 2$ , yielded a fractal dimension of  $D = 2.5 \pm 0.2$ . These results imply superaggregates with DLCA and percolation morphologies consistent with previous results for aerosol gelation in flames and in our simulations.



**Figure 4.** (a) TEM picture of soot clusters, note scale bar, (b) structure factor of and (c) perimeter analyses of part (a). The fractal dimension measured is equal to the negative slope of either graph and is found to be  $\sim 1.8$ .



**Figure 5.** (a) TEM picture of a large soot cluster, note scale bar, (b) structure factor of and (c) perimeter analyses of part (a). The fractal dimension is equal to the slope in the structure factor analysis. The perimeter analysis slope yields the perimeter fractal dimension, 1.44. The mass fractal dimension is found via Eq. (4) to be 2.42.

XRD analysis showed graphitic carbon. Scherrer analysis of line broadening yielded crystallite sizes of 4 nm.

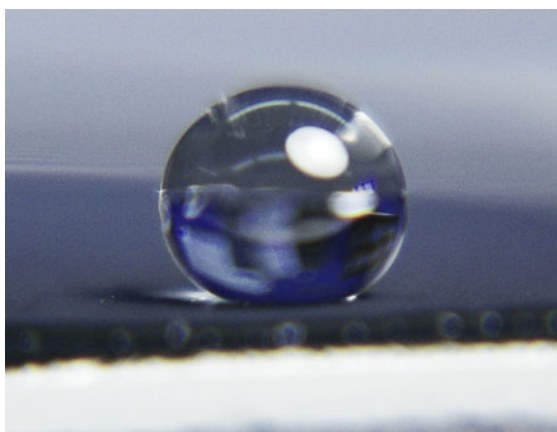
Thermal gravimetric analysis showed no volatiles up to 600°C.

BET analysis results for several aerosol gels are given in Table 1.

**Table 1.** Specific surface areas of soot aerosol gels obtained for selected fuels.

Hydrocarbon Fuel	Specific Surface Area (m <sup>2</sup> /g)
Acetylene	400
Ethylene	310
Propane	140

The material is very hydrophobic as shown in Fig. 6.



**Figure 6.** A ca. 2mm water droplet on the surface of a carbon aerosol gel.

## REFERENCES

1. "Creation of Ultralow Density Porous Materials via Aerosol Gelation: Aerosol Gels," patent pending.
2. C.M. Sorensen, W.B. Hageman, T.J. Rush, H. Huang, and C. Oh, "Aerogelation in a Flame Soot Aerosol," *Phys. Rev. Lett.* **80**, 1782-1785 (1998).
3. C.M. Sorensen, W.G. Kim, D. Fry, D. Shi and A. Chakrabarti, "Observation of Soot Superaggregates with a Fractal Dimension of 2.6 in Laminar Acetylene/Air Diffusion Flames," *Langmuir* **19**, 7560-7567 (2004).
4. W. Kim, C.M. Sorensen, A. Chakrabarti, "Universal Occurrence of Soot Aggregates with a Fractal Dimension of 2.6 in Heavily Sooting Laminar Diffusion Flames," *Langmuir* **20**, 3969-3977 (2004).
5. W. Kim, C.M. Sorensen, D. Fry, A. Chakrabarti, "Aggregates, Superaggregates and Gel-Like Networks in Laminar Diffusion Flames," *J. Aerosol Science*, accepted.
6. C.J. Brinker and G.W. Scherer, Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing (Academic, Boston, 1990).
7. Aerogels – Airy Materials: Chemistry, Structure, and Properties", N. Hüsing and U. Schubert, *Angewandte Chemie International Edition* **37**, 22-45 (1998).
8. S.K. Friedlander, "Smoke, Dust and Haze," Wiley-Interscience New York, 195 (1977).