

SYNTHESIS AND CHARACTERIZATION OF CARBON AEROGELS DERIVED FROM DIFFERENT POLYMERIC PRECURSORS

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INTRODUCTION

The nanoengineering of materials is an area of intensive research because small clusters of atoms (1-100 nm) often have unique properties between the molecular and bulk solid-state limits. The different properties can be explained in terms of the large fraction of atoms that are at the surface of a cluster as compared to the interior. Although the chemistry and physics of metal and semiconductor clusters, fullerenes, and nanotubes are the subject of extensive investigations, little attention has been paid to cluster-assembled porous materials such as aerogels.

Aerogels have a unique morphology in that *both* the covalently-bonded particles of the solid phase and the interconnected pores of the gas phase have nanometer-sized dimensions. This structure leads to extremely high surface areas (400-1100 m²/g) with a large fraction of the atoms covering the surface of the interconnected particles. Sol-gel polymerization conditions can be used to engineer the particle size, particle interconnectivity, and pore size in these materials.

The polycondensation of (1) melamine with formaldehyde, (2) resorcinol with formaldehyde, and (3) phenolic with furfural are three proven synthetic routes for the formation of organic aerogels. The latter two materials can also be pyrolyzed in an inert atmosphere to give carbon aerogels [1-5]. Carbon aerogels are the first electrically conductive aerogels to be synthesized, and they are finding applications as electrodes in double layer capacitors used for energy storage or capacitive deionization. In this paper, we discuss the chemistry-structure-property relationships of carbon aerogels derived from different polymeric precursors.

EXPERIMENTAL

The preparation of resorcinol-formaldehyde (RF) aerogels and their carbonized derivatives has been described previously [4]. Briefly, resorcinol (1,3 dihydroxybenzene) and formaldehyde were mixed in a 1:2 molar ratio, respectively. Deionized/distilled water was added as the diluent and sodium carbonate as the base catalyst. After stirring to form a homogeneous solution, the mixture was poured

into glass vials, sealed, and cured at elevated temperature (50-85 °C). Upon completion of the cure cycle, the crosslinked gels were exchanged with acetone and subsequently dried from supercritical carbon dioxide ($T_C = 31^\circ\text{C}$; $P_C = 7.4$ MPa). This procedure resulted in the formation of monolithic RF aerogels in cylindrical form (25 mm diameter x 60-85 mm long). The monoliths were then pyrolyzed (600-1100 °C) in flowing nitrogen to form carbon aerogels.

Phenolic-furfural (PF) gels were prepared from a commercially available polymer solution (FurCarb UP520; QO Chemicals, Inc., West Lafayette, IN) [5]. This solution was composed of approximately a 50:50 mixture of a phenolic novolak resin dissolved in furfural. The Furcarb UP520 was diluted with 1-propanol and 10 phr catalyst (a mixture of aromatic acid chlorides; Q2001; QO Chemicals, Inc., West Lafayette, IN) was added. Solutions prepared with different amounts of diluent were then poured into glass vials, sealed, and cured for 7 days at 85 °C. A small amount of syneresis was observed during the cure cycle, allowing the gels to be easily removed. PF gels were supercritically dried and pyrolyzed in the same manner as RF gels [4].

A variety of characterization techniques were used to analyze the carbon aerogels. Particle size and surface area were evaluated with transmission electron microscopy and gas adsorption techniques. Raman spectroscopy measurements were obtained in a backscattering configuration using a 488-nm excitation. Transverse magnetic susceptibility measurements were carried out in a Quantum Design magnetometer. Samples were mounted in drinking straws and scanned in a 1-T field in a temperature range of 4-300 K.

RESULTS AND DISCUSSION

The structure and properties of carbon aerogels derived from resorcinol-formaldehyde are largely controlled by three factors: (1) the [Resorcinol]/[Catalyst] (R/C) ratio of the starting solution, (2) the pyrolysis temperature, and (3) chemical activation procedures. At R/C=50, carbon aerogels have particle diameters on the order of 7-9 nm with specific surface areas of ~800 m²/g. In this type of aerogel, the particles are well-interconnected

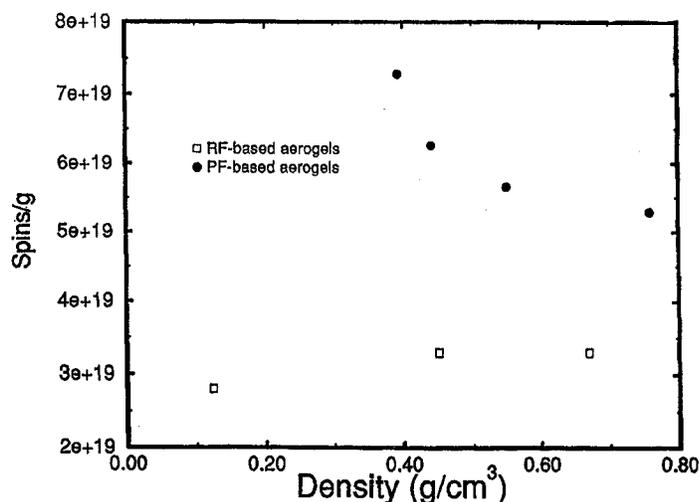
with the neck size approaching the particle diameter. In contrast, carbon aerogels synthesized at $R/C=200$, have lower surface areas ($\sim 600 \text{ m}^2/\text{g}$) and smaller necks between spherical particles of $\sim 12 \text{ nm}$ diameter. Interestingly, the specific surface area of these carbon aerogels is practically independent of the bulk density for samples prepared at the same R/C ratio. Thus, carbon aerogels with a higher bulk density simply have more interconnected particles per unit volume than their low density counterparts.

Transmission electron micrographs of carbon aerogels derived from the phenolic-furfural precursor revealed irregularly-shaped platelets with characteristic sizes of 10-15 nm. For aerogels synthesized with 10 phr catalyst, specific surface areas of $\sim 520 \text{ m}^2/\text{g}$ have been measured over a density range of 0.3-0.75 g/cc. These data suggest some similarities between the carbon aerogels derived from different organic precursors.

Raman spectroscopy was performed on carbon aerogels to probe the internal structure of the interconnected particles or platelets. In both cases, a Raman-allowed E_{2g2} peak was observed near 1580 cm^{-1} (designated as the G band) while a Raman line attributable to in-plane disorder was observed near 1360 cm^{-1} (the D band). The in-plane microcrystallite size L_a can be estimated from Knight's empirical formula, $L_a = 44 (I_G/I_D)$. For RF-based carbon aerogels pyrolyzed at $1050 \text{ }^\circ\text{C}$, L_a is approximately 25 \AA , independent of the bulk density or R/C ratio. For PF-based carbon aerogels pyrolyzed under the same conditions, L_a ranges from 25-35 Å with a slight density dependence. In both cases, the Raman data suggest that 25-35 Å wide graphene sheets are the underlying units in the carbon aerogel structure. The size of these units is largely independent of the sol-gel polymerization conditions and precursor chemistry; however, L_a is sensitive to heat treatment temperature [6,7].

Magnetic susceptibility measurements were performed on carbon aerogels from 4-300 K as a function of bulk density and polymerization conditions [7]. In the low temperature regime, Curie-like behavior was observed and the number of spins per gram was determined for each specimen. Generally, carbon aerogels synthesized at $R/C=50$ exhibited a stronger low temperature dependence, and hence a larger number of unpaired spins per gram than their $R/C=200$ and $R/C=300$ counterparts for the same sample density. These data corroborate the BET surface area measurements and suggest that the $R/C=50$ samples are more highly disordered. Preliminary data on PF-based carbon aerogels show 2-3 X more spins per gram than RF-based carbon aerogels synthesized at $R/C=200$. Figure 1 shows the unpaired spin

concentration for carbon aerogels as a function of bulk density and precursor chemistry.



SUMMARY

Carbon aerogels are a special class of porous materials whose structure and properties depend upon (1) the type of polymeric precursor, (2) sol-gel polymerization conditions, and (3) heat treatment temperature.

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