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Photoemission studies of fluorine functionalized porous graphitic carbon

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Porous graphitic carbon (PGC) has unique properties desirable for liquid chromatography applications when used as a stationary phase. The polar retention effect on graphite (PREG) allows efficient separation of polar and non-polar solutes. Perfluorinated hydrocarbons however lack polarizabilty and display strong lipo- and hydrophobicity, hence common lipophilic and hydrophilic analytes have low partition coefficiency in fluorinated stationary phases. Attractive interaction between fluorinated stationary phase and fluorinated analytes results in strong retention compared to non-fluorinated analytes. In order to change the selectivities of PGC, it is necessary to develop a bonded PGC stationary phase. In this study, we have synthesized perfluorinated, PGC using hepatadecafluoro-1-iodooctane, under different temperature conditions. Surface functionalization of the raw material was studied using photoelectron spectroscopy (PES). Results indicate the existence of fluorine containing functional groups, $-$CF, $-CF_2$ along with an intercalated electron donor species. Multiple oxygen functional groups were also observed, likely due to the presence of oxygen in the starting material. These oxygen species may be responsible for significant modifications to planer and tetrahedral carbon ratios.©2012 American Institute of Physics. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3691888]

I. INTRODUCTION

Porous graphitic carbon (PGC) is widely used as a chromatographic stationary phase. It is chemically stable and inert, hence robust against aggressive mobile phases and extreme temperature conditions.[1] PGC is thermally conductive and thermally stable,[2] resistive to extreme *p*H values,[1] and it possesses unique polarization properties.[1,2] These unique properties of PGC are exploited in different applications of liquid chromatography (LC).[1] Highly oriented pyrolytic graphite structure (HOPG) consists of planar carbon layers with ABAB registration held together through van der Waals interactions.[3] PGC is different from HOPG as it is composed of intertwined graphitic ribbons. These intertwined sheets have interplanar distances matching those of graphite, but there is no registry between the sheets. This structure is responsible for the high rigidity and mechanical stability of PGC.[4] The porosity and particle size of PGC are directly related to chromatographic performance and can be controlled in the production process[1,4] Numerous studies[5–8] suggest that the polarizability, planar character, and the electronic density of solutes affect the retention on PGC. This particular behavior, known as the polar retention effect on graphite (PREG), is a charge-induced attraction of polar analytes with the π network of PGC.[9] The planar surface of PGC favors the polar retention of solutes with planar conformation.[9] Consequently, PGC demonstrate better selectivity toward geometrical isomers and other closely related compounds.[1]

The selectivity of PGC can be changed by developing a bonded PGC phase.[10] The work described below focuses on a perfluorinated bonded stationary phase. Perfluorinated hydrocarbon (R_f) stationary phases are lipophobic and hydrophobic, have low polarizability, and are electronegative with good thermal and chemical stability. Furthermore, R_f phases can have different separation mechanisms depending on the type of analytes to be separated and the chosen mobile phase conditions.[10] R_f phases show better selectivity toward fluorine containing analytes. Solvophobic fluorine-containing molecules tend to repulse away from the mobile phase and are retained in the stationary phase through fluorine-fluorine interactions.[10] As a result, R_f phases display the ability to resolve fluorinated compounds according to their fluorine content. In general, a fluorinated stationary phase has weaker retention toward hydrocarbon molecules, shows improved performance in many chromatography methods, gives better reproducibility, and demonstrates longer lifetime compared to non-fluorinated phases.[1] Combining R_f and PGC to develop a perfluorinated bonded PGC stationary phase may allow for different selectivities along with superior overall performance.

We have synthesized fluorinated PGC samples under different temperature conditions. Samples were analyzed using photoelectron spectroscopy (PES). PES investigates the energy distribution of the electrons emitted from compounds when illuminated by photons under ultra high vacuum conditions. This technique is surface sensitive as the probe depth is limited by the low inelastic mean free path (IMFP) of the photoelectrons in solids.[11] In this experiment, valence band photoemission spectra were measured at electron kinetic energies centered around 185 eV where the calculated IMFP is 6.19 Å.[12] The core level spectra were measured at a kinetic energy of approximately 81 eV where the calculated IMFP is 4.39 Å.[12] A sample layer of thickness three times the IMFP absorbs 95% of the emitted photoelectrons. Consequently, the

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