

THE FLUORINATION OF CHARCOAL WITH ELEMENTAL FLUORINE.

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Introduction

The Molten Salt Reactor Experiment was operated at the Oak Ridge National Laboratory from 1965 to 1969 to test the concept of a high temperature homogeneous fluid fueled reactor. At the completion of the project the fuel salt was solidified in drain tanks where it has remained for the past 28 years. Large charcoal beds (U-tubes of 6 inch diameter and 24 feet length) connected to the drain tanks have since been found to contain deposited uranium from migration of UF_6 . Gas samples from a gas line between the MSRE drain tanks and the charcoal beds indicated the presence of 350 mm Hg F_2 , 70 mm Hg UF_6 and smaller amounts of other gases. Oxidizing fluorine gases such as F_2 and UF_6 are known to react with activated charcoal to produce carbon fluorides of varying properties. Of particular concern is the realization that these C-F compounds are explosive under some circumstances when heated or otherwise shocked. Because of these considerations there is a need to fully understand the C-F chemistry in the charcoal beds so that the hazard can be fully evaluated and finally a means of nullifying this hazard through chemical treatment can be developed.

Charcoal was fluorinated to prepare a graded series of CF_x products to model the charcoal beds. The fluorination of carbonaceous solids may be accomplished in a manner that exploits both the substitution of carbon-hydrogen bonds and

the addition of fluorine to unsaturated bonds.¹ This conversion can be effected by conducting the fluorination at low temperature and F_2 concentration, then increasing the reaction severity in stepwise fashion. This reaction was used to prepare a series of related fluorocarbons, CF_x , $0.25 < x < 1$, from charcoal. This paper reports the spectroscopic characterization of these materials. The average structural properties of CF is assessed using ^{19}F - ^{13}C cross polarization (CP)/MAS ^{13}C NMR² and ^{19}F MAS NMR spectroscopies.^{3,4}

Experimental

CF_x was prepared by fluorination of coconut-based activated charcoal (6x16 mesh size) provided by Calgon Carbon Corporation.

A suite of ten CF_x samples was prepared over the temperature range -80 to 350 °C using the following method. Ten to fifteen gram batches of charcoal were loaded into a passivated-nickel U-tube reactor (½" OD) having Monel bellows vacuum valves at each end. The charcoal was pre-conditioned by heating to 200-250 °C under flowing helium (99.99 % from Air Products). The reactor was then fully immersed in a bath to maintain the desired fluorination temperature. Reactions below ambient temperatures were carried out in a methanol/dry-ice bath (-78 °C) or in a water/ice bath (0 °C). A thermostatic bath was used to heat the reactor to elevated temperatures. At the highest temperatures,

a hollow tube furnace was used. To minimize formation of gaseous products and to better control the highly exothermic reaction, dilute fluorine gas was used. A 5 % by volume F₂/He gas mixture was prepared in three liter batches in a passivated-nickel tank. Dilute fluorine was introduced into the reactor at a very low flow rate. A temperature difference of <3 °C was maintained between the charcoal and reactor wall by controlling gas flow. Flow was maintained for several days until these temperatures equalized. Finally, pure fluorine was slowly flowed for several hours to ensure complete reaction. The reaction vessel was then purged with helium and transferred to a dry-helium glove box for disassembly and storage of the fluorinated product.

Results and Discussion

¹⁹F-¹³C CP/MAS NMR experiments were used to determine the extent of fluorination vs. reaction temperature. Four types of carbon species are observed over the temperature range -80 °C to 350 °C, assigned to graphitic carbon (C), CF, CF₂ and CF₃. These species are assigned and quantified using dipolar dephasing and variable contact time experiments. The fluorinated carbons are fully polarized in tenths of milliseconds, while polarization transfer among graphitic carbon is slower and is explained by a two component model. One component cross-polarizes in less than 1 ms and is assigned to sp² carbons adjacent to fluorinated carbons, i.e., interface carbon. The other component cross-polarizes on the order of milliseconds, and is assigned to more remote carbon species, i.e., bulk graphitic carbon. The fraction of CF, CF₂ and CF₃ found in the ¹⁹F-¹³C cross polarization

experiments are confirmed by direct measurement of the ¹⁹F NMR spectrum. The NMR results are consistent with gravimetric and ESCA analyses. An average graphitic carbon platelet size of 2-4 nm is proposed from these measurements.

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