

AN ^{19}F AND ^{13}C NMR STUDY OF CF_x PREPARED BY VARIABLE TEMPERATURE FLUORINATION OF CHARCOAL WITH ELEMENTAL FLUORINE.

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Key Words: charcoal, fluorine, carbon monofluoride, nmr

Abstract

The preparation of CF_x by elemental fluorination of charcoal is studied using solid state ^{13}C and ^{19}F NMR spectroscopy. ^{19}F - ^{13}C CP/MAS NMR experiments are 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, CF_2 and CF_3 . These species are assigned and quantified using dipolar dephasing and variable contact time experiments. NMR results are presented along with gravimetric and ESCA results to provide new insights into charcoal structure and fluorination.

Introduction

Probing heterogeneous carbonaceous solids with selective reagents is a useful approach to study their chemical and physical properties.¹ Elemental fluorine is a particularly effective probe, adding to unsaturated carbon, and displacing O and H from organic materials.^{2,3} Fluorine is easily detected by ^{19}F NMR spectroscopy.⁴ It also provides a useful polarization source for investigating carbon structure by ^{19}F - ^{13}C CP NMR spectroscopy.⁵

Here we describe changes in the structure of charcoal as it is converted to CF_x by reaction with elemental fluorine. These studies demonstrate the utility of fluorine as a probe and provide insight into the fluorination process in more complex solids. Both radical and ionic mechanisms are reported upon elemental fluorination of model organic compounds.^{2,3} CF_x made from graphite is reported as a solid lubricant and as an excellent cathode material for Li batteries.⁶ Gravimetric, NMR and ESCA analyses are used to investigate charcoal structure and the fluorination process.

Experimental

Preparation of CF_x . Coconut-based activated charcoal (6x16 mesh size) was provided by Calgon Carbon Corporation. The microstructure is that of graphite, consisting of stacked planar platelets of fused aromatic carbon.⁷ The C-C bond distance is 0.141 nm and the interplatelet distance is 0.335 nm. According to the manufacturer's data a large portion of the micropore volume consists of pores in the range 1.5 to 2.0 nm and a system of macropores larger than 100 nm. A suite of ten CF_x samples were prepared over the temperature range -80 to 350°C using the following method. Ten to fifteen gram batches were loaded into a passivated-nickel U-tube reactor (1/2" OD) having monel bellows vacuum valves at each end. The activated charcoal was pre-conditioned by heating to 200 - 250°C under helium flow. The reactor was then fully immersed in a thermostatic bath to maintain the desired fluorination temperature. To minimize formation of gaseous products and to better control the highly exothermic reaction, dilute fluorine gas was used. A 5 % by volume F_2/He

gas mixture was prepared in three liter batches in a passivated-nickel tank. The preparative manifold has a titanium getter to remove water, oxygen or nitrogen impurities. Dilute fluorine was introduced into the reactor at a very low flow rate. A temperature difference of $<3^{\circ}\text{C}$ 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.

NMR Spectroscopy. NMR spectroscopy was performed on 50-100 mg samples in a Bruker MSL-100 (2.35 T) spectrometer. The samples were spun at 5 kHz in a doubly tuned single coil magic angle spinning probe. Single pulse ^{19}F spectra were obtained at 94.200 MHz and MAS = 12 kHz. ^{13}C spectra were obtained at 25.184 MHz by ^{19}F - ^{13}C cross polarization (CP) with ^{19}F decoupling during acquisition. Dipolar dephasing (DD) delays in the range of 0-100 μs were used to aid in assignment of fluorinated species, while 0-2 ms delays were used for graphitic carbons. To obtain quantitative CP data, variable contact time (VCT) experiments were performed.⁸ Signal intensity (I) is acquired vs. contact time (τ) over a wide range of contact times (25 μs to 100 ms), and fit to equation (1) to

$$I = \frac{I_0}{T_{\text{CF}}} * \frac{e^{-(\tau/T_{1\rho})} - e^{-(\tau/T_{\text{CF}})}}{(1/T_{\text{CF}}) - (1/T_{1\rho})} \quad (1)$$

obtain I_0 , T_{CF} and $T_{1\rho}$. I_0 represents the $T_{1\rho}$ relaxation-independent intensity of the resonance, while T_{CF} and $T_{1\rho}$ are the time constants associated with the buildup and decay of intensity. Fitting is accomplished by least squares minimization. Composition of each carbon type is reported as a percentage of total observed carbon. The precision of the percentage composition reported are on the order of $\pm 5\%$.

ESCA Analysis. ESCA data were obtained using a PHI (Perkin Elmer) 5000 series XPS spectrometer equipped with a dual anode (Al: $h\nu = 1486.6$ eV and Mg: $h\nu = 1253$ eV). The Al anode was utilized at a power of 400 W (15 kV). The instrument was operated in the fixed analyzer transmission (FAT) mode with a pass energy of 17.9 eV for high resolution scans. Pressure was $< 1.0 \times 10^{-7}$ torr.

Results and Discussion

NMR Analysis. ^{13}C NMR spectra of charcoal fluorinated at different temperatures are presented in Figure 1. Four distinct resonances are observed, assigned to graphitic C, CF, CF_2 and CF_3 species. In the -80°C spectrum, the downfield feature found at 129 ppm is initially assigned to graphitic carbon (C). This chemical shift is consistent with model fused aromatic carbons (121-133 ppm). Its relatively slow signal accrual ($T_{\text{CF}} > 100 \mu\text{s}$) and decay ($T_{\text{DD}} \approx 500 \mu\text{s}$) indicate that these carbons are at least 0.3 nm (2-3 bonds) from fluorine nuclei. The resonance observed at 86 ppm is assigned to CF. Fast signal accrual and dephasing (T_{CF} and $T_{\text{DD}} \approx 50 \mu\text{s}$) confirm that these carbons are strongly coupled (directly bonded) to fluorine. A third resonance (CF_2) becomes apparent at 112 ppm in charcoal fluorinated at higher temperatures. A fourth resonance (136 ppm) is observed only in the charcoal fluorinated at 250°C and is assigned

to CF_3 . A ^{19}F spectrum of the charcoal fluorinated at $250^\circ C$ (Figure 2) supports these ^{13}C CF_x assignments. The broad feature in the region -60 to -220 ppm contains unresolved isotropic peaks which are flanked by spinning sidebands outside this range. The isotropic peaks indicate the presence of CF (-170 ppm), CF_2 (-128 ppm) and CF_3 (-85 ppm).

The relative percentages of each carbon type in the ^{13}C spectra are listed in Table 1. The F/C atomic ratio indicates the extent of fluorine incorporation. Fluorination is evident even at $-80^\circ C$, but is not complete until $350^\circ C$. CF , CF_2 , and CF_3 percentages determined by ^{13}C NMR and ^{19}F NMR are comparable (within 5 %), supporting structural assignments and justifying the fitting procedure used to quantify species in CP spectra. CF_3 is lost upon fluorination at $350^\circ C$, indicating platelet degradation above $250^\circ C$. Carbons at the platelet edge produce CF_2 rather than CF upon fluorination. The CF_2/CF ratio is a measure of edge to bulk carbon and is thus useful in determining platelet size. A simple hexagon-shaped model platelet with 5 aromatic rings per side (assuming a C-C distance of 0.14 nm) has an edge to bulk carbon ratio of 0.20 and a 2.2 nm diameter. The CF_2/CF ratio obtained by NMR studies of the $250^\circ C$ material is 0.19 ± 0.09 . A platelet diameter of 2 ± 1 nm is obtained if a hexagonal shape is assumed. Small angle neutron scattering experiments gave a platelet size of roughly 2 nm.

Two graphitic carbon species are assigned to the 129 ppm resonance based on VCT results. This bimodal character is revealed in a plot of intensity vs. contact time for the charcoals fluorinated at $-80^\circ C$, $23^\circ C$ and $65^\circ C$ (Figure 3). Bulk graphitic carbon (C_b), with $T_{CF} = 5$ ms and $T_{1\rho} = 30$ ms, dominates the $-80^\circ C$ plot. It consists of carbon further than 0.32 nm from fluorine nuclei. At higher preparation temperatures, an increasing amount of graphitic carbon displays $T_{CF} = 0.2-1$ ms and $T_{1\rho} = 1-5$ ms. This species becomes dominant at $65^\circ C$ as indicated by the change in lineshape and is defined as interfacial graphitic carbon (C_i). C_i is adjacent to CF with a C_i-C-F distance estimated at 0.24 nm. Fluorine must be widely dispersed in small CF clusters at $-80^\circ C$ to account for the percentage C_i observed. The C_i/CF ratio is an indicator of CF cluster size. It shows the growth of CF regions in the graphitic plates with increasing temperatures. Initially, 2-3 F/cluster are indicated, increasing to about 8 F/cluster at $23^\circ C$, and >40 F/cluster at $180^\circ C$.

ESCA Analysis. Results of ESCA analyses are given in Table 2. The generation of fluorinated carbon species follow trends observed in the NMR data, although relative percentages are lower by 10-20 %. CF_2 is detected even at $-80^\circ C$, but is never more than 4 %. Two species of graphitic carbon are also observed. Bulk graphitic carbon (CC), analogous to C_b , is initially the dominant species but is entirely consumed at $250^\circ C$. $C(CF)$ is analogous to C_i . Its concentration (35-40 %) is remarkably constant over the sample temperature range. The ratio $C(CF)/CF$ follows trends observed for C_i/CF . CF_2/CF is nearly constant at 0.11 throughout the temperature range. Assuming a hexagon-shaped platelet, the platelet diameter that produces this ratio is about 4 nm.

Comparison of Analyses. Gravimetric analysis is the most direct measure of fluorine incorporation into charcoal. The F/C ratios determined by attributing net weight gain to fluorine (See Tables 1 & 2) are very similar to results from NMR and ESCA. Gravimetry does not take into account weight loss from the displacement of edge oxygen and hydrogen by fluorine. This atomic replacement can lower the F/C ratio measured

gravimetrically by as much as 20 %. Differences in F/C ratios are generally within experimental error except at 250°C where the F/C ratio from the ESCA analysis is significantly lower than the NMR result. The F/C ratio is very sensitive to CF₂ and CF₃ concentrations which are consistently lower in the ESCA results. This lower ratio is most pronounced in studies of the sample fluorinated at 250°C where the CF₂ and CF₃ concentrations is greatest. An F/C ratio of 1.1-1.25 is calculated for fluorinated charcoal with platelets roughly 2-3 nm, a value more consistent with NMR results.

Structural Features and Fluorination Mechanism. Charcoal consists of planar fused aromatic carbon platelets having an average diameter on the order of 2-4 nm. The platelet interlayer distance (0.33 nm) is large enough for F₂ to diffuse between platelets. F₂ is not limited to surface reaction in micropore void spaces. The platelets separate to 0.57 nm upon complete fluorination.⁶ Paramagnetic sites were detected based on NMR observations. Carbonaceous materials generally contain free electron spin density as a result of their aromatic character and/or the presence of trace amounts of metals. A ¹H-¹³C CP experiment was attempted on the original charcoal used in this study to search for edge functionality. Edge sites in this material are assumed to consist of hydrogen and oxygen containing functional groups. Edge resonances were not detected, but the experiments did confirm the presence of free spin density. The probe tuning characteristics changed significantly with this material, an effect sometimes observed for conductive or paramagnetic materials. A ¹H-¹³C CP spectrum could not be obtained. The spinning sample also slowed significantly (4953 Hz to 4860 Hz) when the probe was raised into the magnetic field. This effect was reversible. ¹⁹F T_{1ρ} time constants were on the order of 50 ms for the charcoal fluorinated at -80°C, a value common for diamagnetic materials. The free spin density present in the charcoal had evidently been quenched by fluorine reaction at -80°C. At higher CF_x preparation temperatures, ¹⁹F T_{1ρ} grows significantly shorter (to 1 ms for the 250°C material) and returns to 50 ms for the 350°C material. Iron is also present in this charcoal (1 %) as a possible paramagnetic source. Demineralization did not remove the paramagnetic sites, so we conclude that iron is not the source of free spin density in the charcoal or its fluorination products. The tuning, spinning, and T_{1ρ} behavior strongly suggest the presence of paramagnetic organic radicals.

Summary

Carbon monofluoride is prepared by elemental fluorination of charcoal. Two graphitic and three fluorinated carbon species are quantified in NMR studies and confirmed by ESCA analysis. Fluorination occurs to a limited extent at -80°C by a radical mechanism. Small widely dispersed CF regions grow larger and more numerous when charcoal is fluorinated at higher temperatures. CF_{1.1-1.2} is produced above 250°C. The charcoal platelet has an average diameter on the order of 2-4 nm and is stable to at least 250°C.

Acknowledgments

This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy, under Contract No. DE-AC05-84OR21400 with Lockheed Martin Energy Research. The ESCA analysis was done by Joeseph Fiedor.

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Table 1. Composition and ratios of carbon components in fluorinated charcoal as determined by ¹⁹F-¹³C CP/MAS NMR

Carbon Component	Fluorination Temperature							
	-80	0	23	65	120	180	250	350
C _i	27%	38%	33%	36%	29%	21%	0%	0%
C _b	57%	37%	33%	21%	17%	5%	0%	0%
C (=C _i + C _b)	84%	75%	66%	57%	46%	26%	0%	0%
CF	16%	25%	34%	39%	48%	67%	81%	78%
CF ₂				4%	6%	8%	15%	22%
CF ₃							4%	0%
C _i /CF	1.64	1.50	0.96	0.91	0.61	0.31	0	0
CF ₂ /CF				0.10	0.12	0.11	0.19	0.28
F/C by NMR	0.16	0.25	0.34	0.47	0.59	0.82	1.19	1.22
F/C by Wt.	0.27	0.32	0.38	0.45	0.50	0.77	0.91	

Table 2. Composition and ratios of carbon components in fluorinated charcoal as determined by ESCA Analysis

Carbon Component	Fluorination Temperature						
	-80	0	23	65	120	180	250
C(CF)	38%	39%	34%	39%	43%	38%	35%
CC	43%	39%	36%	13%	9%	10%	0%
Total C	81%	78%	70%	52%	52%	48%	35%
CF	19%	18%	22%	32%	44%	47%	60%
CF ₂	2%	2%	2%	4%	4%	4%	4%
CF ₃	0%	0%	0%	0%	1%	1%	1%
C(CF)/CF	2.00	2.17	1.55	1.22	0.98	0.81	0.58
CF ₂ /CF	0.11	0.11	0.09	0.13	0.09	0.09	0.07
F/C by ESCA	0.24	0.26	0.30	0.42	0.53	0.56	0.77
F/C by Wt.	0.27	0.32	0.38	0.45	0.50	0.77	0.91

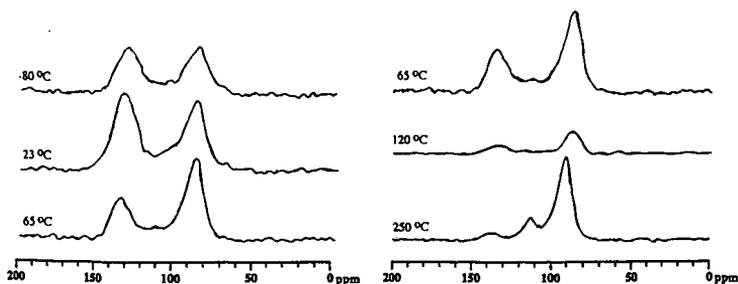


Figure 1. ^{19}F - ^{13}C CP/MAS NMR spectra of charcoal fluorinated at various temperatures. Typically 20k scans were signal averaged using a 2.5 ms contact time and a 2 s recycle delay.

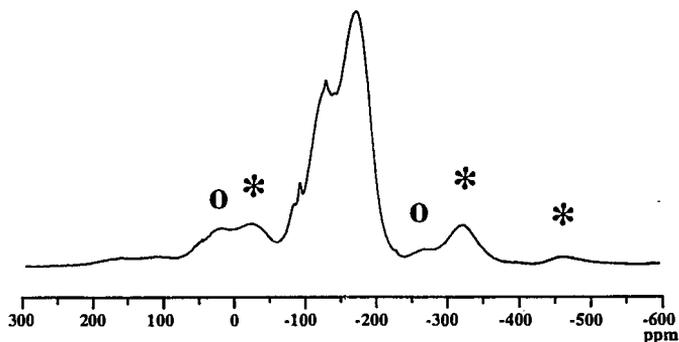


Figure 2. ^{19}F MAS NMR spectrum of charcoal fluorinated at 250°C. Spin rate is 12 kHz (127 ppm). * indicates spinning sidebands of the CF peak (-170 ppm). O indicates sidebands of the CF_2 peak (-128 ppm).

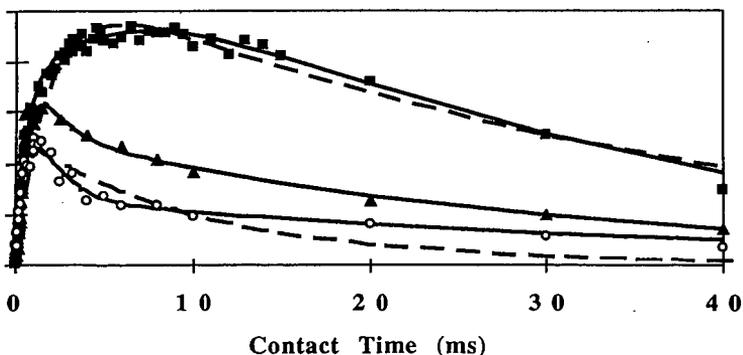


Figure 3. Graphitic carbon intensities from ^{19}F - ^{13}C CP/MAS NMR studies plotted vs. contact time for several fluorinated charcoal samples: (■) -80°C, (▲) 23°C, (○) 65°C. Two component fits are displayed as solid lines. Selected one component fits are displayed as dashed lines.