FULLERENES IN THE CARBON BLACK FURNACE

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Introduction

This research is the first known report of the major role fullerenes, particularly C60, plays in the precursor chemical reactions in the formation and nucleation of carbon black in a combustion furnace (1). The role of polynuclear aromatic hydrocarbons (PAHs) as the basic structural units of the crystallite blocks in primary particles of carbon black is well-established. Until now the PAH reaction pathway was considered to be the fundamental chemical mechanism in the formation of carbon black (2). However, it has been theorized that fullerenes could play a role in the chemical mechanism of carbon black by forming from PAHs' containing pentagonal rings (3). Recent analytical experiments in model flames systems confirm this precursor/reaction pathway (4).

Precursor chemical formation, nucleation and growth mechanisms of carbon black produced in a combustion furnace have been studied systematically. Experimental and conventional carbon blacks were compared. The experimental carbon blacks (CCC, Sunray, TX) were designed using conventional and Continex Low Hysteresis Carbon Black processes with short residence times. There were two basic research premises: 1) the precursor chemical species present in the gaseous phase at the time of the reaction quench represents the basic molecular units in the formation of carbon black and 2) the experimental carbon materials represent a unique opportunity to study carbon black formed by the combustion process at the point of nucleation and subsequent early primary particle growth formation.

Experimental

Carbon blacks, N339 and XB were extracted by ASTM Method D4527, substituting a 72 hr extraction time. The toluene soluble extractables were removed and analyzed quantitatively for 17 PAH standards by HPLC. Qualitative analyses were performed by Time of Flight Static Ion Mass Spectroscopy (ToF/SIMS), for < 800amu.

Carbon blacks XB, XB2 and XB3 were studied by HRTEM with crystallinity mapping of the treated data Specifically, samples of nucleation and early growth sites were compared for short residence time experimental carbon blacks.

Results and Discussion

The detailed results of the extract analyses have been reported elsewhere (1,5). The quantitative results are summarized in Table 1. Only 7% of the extract of N339 could be accounted for by the 17 standard compounds, which had molecular weights <400amu. In contrast, the short residence time XB had 27% of the total extract is accounted for by the 17 standards.

Table 1. Summary Table of Quantitative LC Results for the Standard PAH Compounds*
*in μg extract/gram carbon black

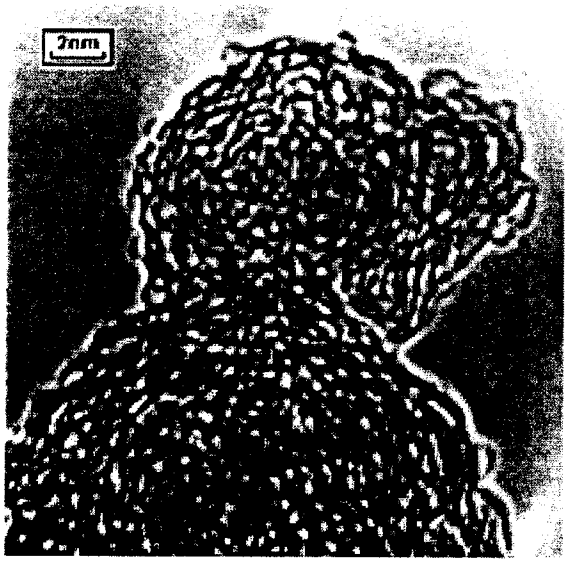
COMPOUND	*N339*	*XB*
NAPHTHALENE	10.32	17.78
ACENAPHTHALENE	0.12	44.38
ACENAPHTHENE	14.15	0.23
FLUORENE	11.08	46.67
PHENANTHRENE	0.32	13.99
ANTHRACENE	0.02	0.02
FLUORANTHENE	5.77	95.98
PYRENE	52.28	582.18
BENZO[a]ANTHRACENE	3.93	1.71
CHRYSENE	1.15	0.79
BENZO[b]FLUORANTHENE	0.58	13.51
BENZO[k]FLUORANTHENE	0.19	5.74
BENZO[a]PYRENE	3.59	35.28
BENZO[g,h,I]PERYLENE	24.14	113.03
DIBENZO[a,h]ANTHRACENE	3.71	20.51
INDENO[1,2,3-c,d]PYRENE	3.24	48.74
CORONENE	47.8	49.55
Total Identified	**182.39**	**1090.09**
Total Extracted	**2507.3**	**3969.77**
Identified Percentage (wt%)	**7.27**	**27.46**

Low molecular weight compounds are found in higher abundance in the XB extract. An interesting point is made if the data are reduced into semi-volatile and nonvolatile PAHs, as in Table 2. When the % nanomoles of the total PAHs containing pentagonal rings (C5) in each 72 hour extraction is calculated, it becomes obvious that the C5 ring-containing compounds are the dominant species in the case of the short residence time carbon black, XB, compared to N339 with a longer residence time.

Table 2. PAHs Containing Pentagonal Rings in Total Extract Based on Semi and Nonvolatile Compounds*

Percent C5 Rings (3 Day Total)	2-3 rings	4 rings	5 rings	6-7 rings
N339	65.94%	9.22%	9.97%	4.54%
XB	72.77%	14.11%	26.79%	23.34%

* % nanomoles extract/gram carbon black



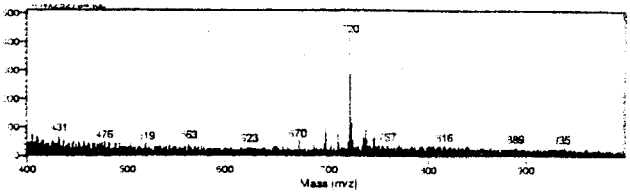
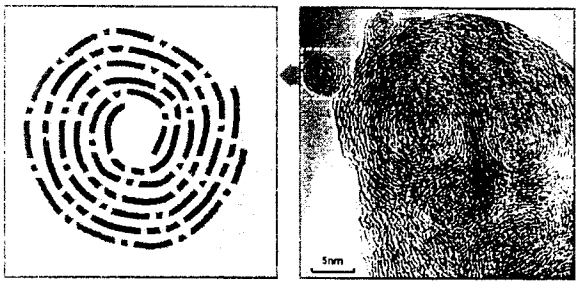


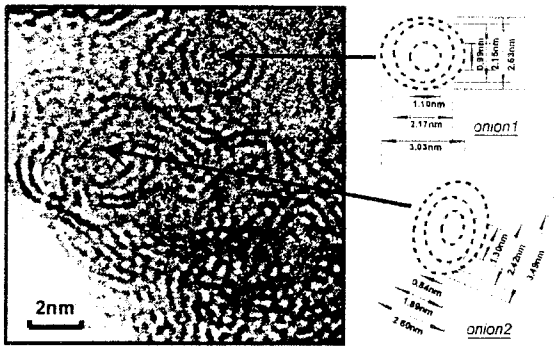
Figure 1. a) HRTEM data of primary particles of XB illustrating hemispherical nanostructures on the surface of the carbon black; b)ToF/SIMS spectra showing the presence of C60 in the toluene extract of XB (1).

The data correlate well with the ToF/SIMS spectrum of C60 in the same XB toluene extract. The presence of C60 in short residence time carbon black toluene extracts have been confirmed by other MS techniques on several experimental carbon blacks.

The HRTEM data support the concept of fullerenic-type species functioning in a fundamental chemical pathway in the formation of carbon blacks, in addition to PAH graphene sheet formation. The data given in Figure 2 show two nucleation mechanisms, a) the icospiral and b) a nano-onion with a fullerenic-size species functioning as nucleation sites. In both cases, the photomicrographs represent the earliest growth of primary particles captured in a combustion carbon black furnace.



(a)



(b)

Figure 2. a) XB2 bi-icospiral nucleation center; 2) XB3 nano-onion fullerenic nucleation center (6).

Conclusions

C60 has been identified in the toluene extracts of experimental carbon blacks using ToF/SIMS. This is the first report of C60 positively identified in carbon blacks and their organic extracts. The pentagonal-ring containing PAH compounds appear to function as precursor species in competitive chemical pathways in the formation of fullerenes and very high molecular weight PAHs in the carbon black furnace. The HRTEM data show C60 plays an integral role in the nucleation processes in the formation of carbon black in the combustion furnace.

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