Effect of Oxidation on the Microstructure of Carbon Blacks

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The evolution during oxidation of the internal structure of soot and carbon black particles was studied using high-resolution transmission electron microscopy (HRTEM) and an image analysis system. Increasing ordering to the carbon structure with increasing oxidation is observed. Measures of the increased order are increases in the fractional coverage of a cross section of the particles with a layered structure, a decrease in the mean interlayer spacing, and a decrease in the spread of the interlayer spacing. The changing structure of the carbon black impacts its properties, such as the rate of oxidation.

Introduction

There is considerable interest in the study of the structural changes of carbonaceous materials as a function of oxidation. Davis et al.1 measured the variation of carbon dioxide surface area of various coals as a function of residence time in a flow reactor. HRTEM measurements revealed that crystallite dimensions and interlayer spacings are altered by combustion. Ishiguro et al.2 showed that oxidation alters the structure of diesel soot. The aim of our current research is to develop a better understanding of the microstructural reordering of carbon blacks with implications to their properties. The carbon blacks used in this research have already been studied and their reactivities as a function of oxidation measured.3

The methodology used in this work has already been described in detail elsewhere.4 This paper presents an application to quantify the structural changes of carbon black particles as a function of oxidation and graphitization. The technique used is based on the use of HRTEM (high-resolution transmission electron microscopy) and computational image analysis.

It is well known that carbonaceous materials like graphite, soots, coals, chars, etc., possess characteristic structural appearances which can vary from mostly random or amorphous to a perfectly ordered crystalline structure. The carbon structure has been variously described as turbostratic5 or as crumpled sheets6 to indicate that parallel layering, reminiscent of graphite, is observed over dimensions of nanometers but that these planes or crystallites show disorder over larger scales. The degree of order of such structures is strongly dependent on the thermal treatment of the material as well as the composition of the source of the carbonaceous material. The value of electron microscopy in studying the morphology of such materials has been well established,2,7,8 although only a few attempts toward quantification have been made.

Materials

The sample observed was carbon black CB330 from De gussa. One set of carbon black samples were oxidized in a thermo-gravimetric analyzer (TGA) in air at 575 °C, so that the conversion varied from 0 to 96%. Another set of carbon black samples were graphitized (Graphpac-GB by ALLTECH) and then oxidized in the TGA at 680 °C until 92% burnout was reached. The latter samples are called GB 0% and GB 92%, respectively.

For the HRTEM observation a small portion of each sample was ultrasonically dispersed in ethanol. The suspension was deposited dropwise on a copper TEM grid coated with a lacy carbon film. The examination of the samples was carried out on areas that extend over the holes in the supporting film in order to avoid interference from the amorphous carbon background film. An oriented gold crystal was used as a calibration standard and subjected to the same techniques as the carbon black samples.

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Methodology

The methodology has already been described elsewhere; however, we describe it here briefly. First, a high-resolution transmission electron microscope, operated at 200 keV, was used to record the images of each sample. (The point to point resolution of the microscope is 0.18nm, the spherical aberration coefficient $C_s$ is 0.4 mm, and the chromatic aberration coefficient $C_c$ is 0.8 mm.) These images were then digitized and stored as computer images (Figure 1a). A high-level language computer software (SEMPER), developed specifically for use with high-resolution electron microscopy, was then used to manipulate the stored images in order to extract data which could characterize physically these soots.

From these digitized images, computer-generated diffraction patterns were produced (Figure 1b). The optical diffractogram is a power spectrum calculated from the modulus of the Fourier transform. The Fourier transform (FT) of the TEM image can be used to find periodicities and is also used to extract the significant structural data from the image while eliminating unwanted characteristics, e.g., noise. After filtration, the resulting image is reverse transformed to yield a two-color "extracted structure" (Figure 1c). This is the pattern recognition phase of the technique. The extracted structure obtained in this way is not only useful for improved visualization of the internal structure but also the basis for the next step in the sequence which is statistical analysis.

The statistical analysis is aimed at identifying quantifiable structural parameters. At the current state of the research there are six parameters which can be divided into two major groups. The first three parameters are characteristic of the carbon fringes found in the transmission electron micrographs and they are called shape factors. These are circularity ($C$), elongation ($E$), and length of fringes ($L_a$).

The second set of parameters refers to the overall arrangement of the fringes. These are the orientation distribution of the fringes ($\alpha_i$), the interlayer spacing ($d_{002}$), and the fractional coverage of the extracted pattern ($F$).

The circularity, the elongation, and the fractional coverage can be computed according to eqs 1, 2, and 3, respectively:

$$C = 4\pi \frac{\text{area}}{\text{perimeter}^2}$$

(1)

$$E = \left(\frac{m_{\text{max}}}{m_{\text{min}}}\right)^{1/2}$$

(2)

$$F = \frac{\text{area of fringes}}{\text{area of view}}$$

(3)

Some of the other geometrical factors, e.g., length of fringes, their distance, which is the interlayer spacing, and the orientation of their long axis are shown in Figure 2.

Results

The different measures of the structures of carbon black particles as a function of the oxidation history of the particles are reported below.

Interlayer Spacing. Earlier studies of other authors found that when examined with a transmission electron microscope (TEM), increasing oxidation of soots results in increased orderliness of structure.\(^2\) That is, partial oxidation allows the carbon atoms to relax toward the thermodynamically favored graphitic state. Buseck et al. showed that the structure of amorphous coke becomes more orderly with increasing annealing temperatures.\(^7\) Results from our experiments support this argument. Figure 3 shows a slight but monotonic decrease in the mean values of the characteristic interlayer spacing of both the CB 330 and the GB sample as a function of burnout. The same trend can be observed in the standard deviation values. Both results show that the internal structure of the soot particles becomes more ordered as the oxidation proceeds.

Also, the graphitized carbon black has a significantly smaller mean interlayer spacing and standard deviation values than those of the nongraphitized samples. These data confirm that there is substantial ordering in the microstructure as a result of the graphitization and the
interlayer spacing of the graphitized carbon black approaches that of pure graphite as the extent of oxidation increases. (In a separate study, fluoranthene graphite was subjected to the same technique and the interlayer value was found to be 3.37 ± 0.07 Å.)

It is essential to clarify whether the parameters obtained are true measures of the sample, or characteristics of only the particular area that was examined. In order to address this question, multiple analyses have been performed on non-graphitized carbon black samples that were oxidized to different extents. Figure 4, a and b, shows the mean and standard deviation values of the interlayer spacing for the two extremes, i.e., those corresponding to the 0 and 96% burnout. Different bars represent different soot particles within the respective sample. The mean interlayer spacings corresponding to the particles within the 0% burnout sample are greater than those of the 96% burnout in all cases except one, while the standard deviation values for 0% are always greater than those for 96%. These results show the internal consistency of data taken on a particular soot sample, and the difference in both the mean spacing and its variability in going from one sample to another. The HRTEM image analysis based technique has the ability to directly measure interlayer spacing within individual soot or carbon black particles and this allows one to obtain the full distribution of that parameter within the samples. Figure 5a–d shows that the discrete characteristic spacings can be found in this way. These figures should be represented as bar graphs; however, the emphasis in this work is on the location of the peaks which is more easily noticed in the present form of the figures. The number of fringe pairs measured was 350 on average. Although Figure 5a (showing the interlayer spacing distribution for the 0% burnout CB 330 sample) seems to be noisy at first glance, careful comparison of the 38, 78, and 96% burnout sample reveals that on each of the distributions the peaks are approximately at the same locations. This result confirms that one mean value for the interlayer spacing does not describe well the material, the distribution is multimodal, and there are several characteristic interlayer spacing values.

Fractional Coverage. Figure 6 shows the fractional coverage of the extracted pattern for the 38% burnout and the 96% burnout carbon black samples, respectively. Note that any particle of the 38% burnout sample has a considerably lower fractional coverage value than does the 96% burnout sample. Both results confirm the capability of HRTEM to pick up the small but definite ordering in carbon blacks.

Discussion

Previous studies have already shown that when soft carbonaceous materials are annealed at high temperature or when graphite is disordered by neutron irradiation or mechanical grinding, a graph of the interlayer spacing versus the processing time shows a set of arrests or plateaus.9 Discrete interlayer spacing values for a variety of carbonaceous sources were reported to be about 3.38, 3.40, 3.425, 3.44, 3.49, 3.55, 3.68, and 3.87 Å.10–15 It has been hypothesized that a subset of the mentioned discrete values are unique in elemental carbons regardless of its origin.16 The most commonly used technique is X-ray diffraction (XRD). While it is possible to obtain good data from highly ordered materials, e.g., graphite, using thin samples, the examination of samples with a large amorphous component requires a substantial amount of sample. Also, the exact determination of d spacings from the diffuse diffraction patterns using a diffractometer may require the separation of the weak pattern of coherent diffracted radiation from the total measured intensity. This total measured intensity can contain large contributions from Compton scattering and other incoherent scattering processes. No simple direct measurement of the 002 spacing is possible using this technique.

The major peaks in the size distribution values of the 0% burnout sample are marked with the letters A–F on Figure 5a. Figure 5b shows the distribution for the 38% burnout carbon black. The location of the first peak (characteristic value A) is 3.28 Å, exactly the same as on the 0% sample. The same relationship is true for peak B, C, and F. Peak D of the 38% sample is shifted left as compared to the 0% sample; essentially this shift is responsible for the overall decrease of the mean interlayer spacing. The same trend, although to a lesser extent, can be noticed by comparing the two E peaks. Note that Figure 5b shows a characteristic peak between B and C, but since this is not indicated on any of the other distributions, it might be a result of experimental error. Also between peaks A and B there is a shoulder in Figure 5, a, c, and d while in Figure 5b it is a smaller peak. These peaks do not seem to be as characteristic as the others and therefore they are not marked at this stage of the study. In this paper we do not target the correct description of all possible characteristic interlayer spacing; the aim here is to show that the technique presented is capable of yielding the full distribution of interlayer spacings and thus can be a valuable tool in studying the microstructural reordering.

Figure 7 summarizes the characteristic interlayer spacings and shows that the above-mentioned trend is true regardless of which two samples are compared. The first peak corresponds to 3.28 Å in all cases. The same is true for the last peak (F), except in the 96% burnout sample where, because of the increased ordering of the structure, that peak disappeared from the distributions. As far as peaks B, C, and E are concerned, their locations are not changing or are slightly decreasing as oxidation increases. The biggest (monotonic) decrease is noticed on the location of peaks D.

The increased orderliness of the structure is highlighted in Figure 8 which shows the relative areas corresponding to the last two peaks. In Figure 5 a cutoff line indicating the area which we considered to belong to peaks E and F is shown. The monotonic decrease in the relative size of the areas shows that higher interlayer spacing values are eliminated, and hence the structure becomes more ordered.

The decrease in the mean interlayer spacing is therefore a consequence of both the decrease in the spacing corresponding to peaks such as D and the decrease in the weighting given to peaks E and F.

Figure 9 shows the interlayer spacing distribution of the 92% burnout graphitized carbon black. By comparing it to Figure 5d (96%, non-graphitized sample), the result is not surprising. As expected from the results shown in Figure 3, the distribution is less wide (standard deviation is smaller) and the mean is shifted to the left. Also, the interlayer spacing is much more uniform, and the increased orderliness yields an essentially unimodal distribution.

Relevance. It is well-known that graphites are less reactive than amorphous carbons. The HRTEM provides a means of quantifying the dependence of reactivity on structure. This has been attempted by Davis et al. who examined the burnout of various coals in a flow reactor. They found that reactivity decreases with...
conversion. They also found that the orderliness of the structure is increased, and therefore there is strong qualitative evidence that the increase in crystallinity correlates with the observed decrease in reactivity.\(^1\)

The relationship between reactivity and ordering is not necessarily simple. For CB 330 the time rate of change, \(\frac{dX}{dt}\), of carbon conversion \(X\) versus conversion is reported for a temperature of 550 °C and an oxygen partial pressure of 0.1 atm in Figure 10a. When the rate of reaction is expressed per unit of residual carbon (1 − \(X\)) the corrected rate \(\frac{dX}{dt}/(1 − X)\) is found to increase with conversion as shown in Figure 10b. This is contrary to the Davis et al. hypothesis that reactivity decreases with increases in fractional coverage.\(^1\) Another factor to be considered is the relative number of edge versus face carbon sites, a measure of which is provided by the HRTEM. The carbon blacks have fewer edge carbons than the chars studied by Davis et al.\(^1\)

The use of HRTEM provides an important added dimension in trying to rationalize the variation of carbon reactivity with conversion. This paper, in providing trend opposite to that reported by Davis et al., underlines the fact that the reactivity is governed by a multiplicity of factors.

Conclusions

The aim of this research is the development of an image analysis system that can provide verifiable and statistically significant results for the characterization of the internal structure of soot particles by the utilization of high-resolution transmission electron microscopy. This technique is believed to be an important and necessary step toward the understanding of the microstructure and its changes as a function of various factors.


parameters with implications to the material's properties. These measures of the fine structure of carbons can then be used to provide insight on the factors governing the physical and chemical properties of carbons.

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