

STRUCTURE AND REACTIVITY OF VAPOR-GROWN CARBON FIBERS

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Introduction

Vapor-grown carbon fibers (VGCF) are produced from a hydrocarbon source and hydrogen in the presence of a catalyst. Due to the high temperatures involved (>1000 °C), an in-situ study of the growth process has not yet been performed. Nevertheless, most authors agree with a mechanism involving the initial production of a carbon filament, over which pyrolytic carbon is deposited in concentric layers. Therefore, VGCF present the annular structure of a tree [1-3]. Only a few studies have dealt with the oxidation of this material [4,5], but our preliminary results have demonstrated that VGCF are more reactive to air oxidation than PAN or pitch fibers, and that the mode of attack by air is different in the case of VGCF [6].

In the present work we have studied the controlled gasification of VGCF with air and carbon dioxide in order to highlight the intimate structure of this kind of fiber. In addition, the reactivity of VGCF's has been correlated with their diameter and surface chemistry.

Experimental

A batch process has been used for production of VGCF in a tubular reactor externally heated by an electric furnace. A mixture of hydrogen and methane was supplied through mass flow controllers and passed over a support impregnated with the catalyst, placed inside the reactor. The experimental conditions were the following: - An ethanolic solution of the catalyst precursor, $\text{Fe}_3(\text{CO})_{12}$, was sprayed onto a piece of Grafoil®, which was subsequently dried in an oven at 100 °C. Inside the reactor, the support was heated from room temperature to 950 °C at 15 °C/min under an atmosphere of 70% H_2 and 30% CH_4 (catalyst reduction stage), then the temperature was raised to 1150 °C at 3°C/min (filament growth stage), and finally a thickening stage was accomplished at 1150°C. The duration of this last stage determined the diameter of the VGCF produced.

The gasification of VGCF was studied with a Mettler M-3 thermobalance. In the isothermal mode, the sample (5 mg) was flushed with nitrogen under a flow of 100 cm^3/min , and heated at 20°C/min up to the reaction temperature. Then, air or carbon dioxide was admitted at the same flow rate. In the dynamic mode, the sample was flushed with air (100 cm^3/min) and heated at 5°C/min from room temperature up to 900 °C. In both cases, the weight loss was monitored as a function of time.

Temperature programmed desorption (TPD) experiments were carried out in a U-shaped tubular microreactor, placed inside a vertical furnace. The procedure employed consists of heating the VGCF sample (150 mg) at 5 °C/min from room temperature to 1100 °C under helium flow (25 cm^3/min). A quadrupole mass spectrometer was used to monitor, continuously, the evolution of gases (CO , CO_2 , H_2 and water vapor).

Nitrogen adsorption isotherms at 77K were determined with a Coulter Omnisorp 100 CX apparatus. SEM observations were performed with a JEOL JSM 630 IF microscope. X-ray diffraction measurements were made on a D-5000 Siemens spectrometer, using $\text{Cu K}\alpha$ radiation. X-ray photoelectron spectra (XPS) were obtained with a ESCALAB 200 A VG Scientific spectrometer.

Results and Discussion

Four types of VGCF were studied, denoted FC3, FC6, FC12 and FC40 according to their mean diameters of 3 ± 1 , 6 ± 2 , 12 ± 4 and 40 ± 8 μm , respectively. These different mean diameters were obtained by adjusting the duration of the CVD carbon coating performed at 1150 °C.

The gasification of these fibers with air at 700 °C is completed in a few minutes whatever the diameter. However, when the gasification rates (weight loss normalized by the initial mass of the sample) are plotted as a function of time, different profiles emerge according to the fiber diameter. These profiles were deconvoluted into the same four peaks, with different intensities, for each type of fiber. This result seems to indicate that we can describe the gasification of VGCF in terms of four components, presenting different reactivities.

In order to obtain further insight into these components, we have interrupted the oxidation experiments of FC6 at different levels of burn-off, and subsequently observed the oxidized fibers by SEM. Burn-off levels of 25, 50 and 75% were chosen, since they correspond to the positions of the first three peaks present in the gasification rate curve; no observation was done for the last peak, which corresponded to an almost complete gasification (burn-off of 98.3%).

In the first stage, the attack of the fiber surface occurs by pitting, and some large holes (diameter up to 1 μm) are the only traces of reaction.

In the next stage, there is a non-localized kind of attack which creates defects or holes of small depth and diameter on the surface.

Finally, at 75% burn-off, it is clearly observed that a less reactive inner core is present in the fiber, this part just starting to be attacked as the outer shell is already seriously oxidized. In the case of FC6, the diameter of this inner core is about one third of the total fiber diameter.

In addition to these observations, we were able to detect clearly the filament present in the core of the VGCF [7]. Therefore, the structure of these fibers can be described in terms of a central nanometric filament, a micrometric inner core, and an outer shell, and these parts have different reactivities.

The formation of very large pores by a pitting mechanism was observed after gasification by air in the temperature range from 400 to 900 °C as well as by carbon dioxide in the temperature range from 800 to 1200 °C. This mode of attack was attributed to the presence of iron on the surface or in the bulk of the fibers, which can act as a gasification catalyst [8].

We have demonstrated the presence of a certain partial pressure of iron in the gas phase during the VGCF growth process, although we were not able to detect it on the fibers by XPS or EDS. But it is worth noting that the sensitivity of these methods is not high enough if the iron concentration or particle size are very small. Nevertheless, we could detect iron in the residue left after gasification. The presence of iron in VGCF has also been previously reported [4].

The second gasification stage can be attributed to the uncatalyzed gasification of carbon, which can occur at active sites on the surface. Similarly, the third stage corresponds to the uncatalyzed gasification of the inner core of the VGCF.

From the Arrhenius plots corresponding to the gasification of VGCF with air, it was shown that, whatever the fiber diameter, oxidation occurs in zone I below 760 °C (chemical reaction control and absence of diffusion limitations). The activation energies determined were in the range of 38-40 kcal/mol.

Surface area measurements performed on FC12 at 0% burn-off ($S_{\text{BET}}=1.8 \text{ m}^2/\text{g}$) and at 25% burn-off ($S_{\text{BET}}=3.5 \text{ m}^2/\text{g}$) have confirmed that no significant microporosity, which could control the reaction rate, develops at the beginning of the reaction. At higher temperatures, and whatever the fiber diameter, the rate of reaction reaches a constant value, indicating that the reaction occurs in zone III (film diffusion regime).

Temperature programmed oxidation has shown that small diameter VGCF are in fact more reactive than large diameter ones. This may be explained by the higher specific surface area (geometric) of smaller fibers, since there is no development of any microporosity.

Temperature programmed desorption experiments have confirmed this hypothesis, as the quantities of oxygenated products released are much higher in the case of FC3 when compared to FC12.

The TPD profiles for both FC3 and FC12 show two CO₂ peaks, one at 340 °C and another, of greater intensity, at 600 °C. One CO peak is also observed at higher temperature (>1000 °C). What is remarkable is the small amount of CO evolved in comparison to CO₂, whereas the opposite is normally observed with the other types of fiber [9]. We have tentatively attributed this result to the presence of iron, which could catalyze the CO disproportionation reaction. Indeed, when the fibers are previously washed with hydrochloric acid, the CO₂ peak located at 600 °C disappears from the TPD profile, and the first mode of attack (large holes) is no longer observed upon gasification.

Typical surface compositions of FC12 before and after gasification (to 50% burn-off) were determined by XPS, showing that only a moderate increase in the concentration of surface oxygen groups is achieved by reaction.

Conclusions

Selective oxidation has been used to investigate the inner structure of VGCF, and three regions of different reactivity were identified: a central carbon filament, an inner core and an outer shell.

The particular mode of attack of oxygen or carbon dioxide on the surface of these fibers may be caused by the presence of traces of the iron catalyst used.

Smaller fibers gasify faster due to their higher specific surface area.

Acknowledgements

This work was supported by the EEC under contract n° CHRXCT940457.

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