CHARACTERISATION OF PITCH-BASED CARBON FIBRES

Tim Mays, Jo Howell, Lucretia King, Brian McEnaney and Dan Edie †

School of Materials Science, University of Bath, BATH, Avon BA2 7AY, UK
† Department of Chemical Engineering, Clemson University, CLEMSON, SC 29634-0909, USA

INTRODUCTION

At Bath we are concerned with the processing, characterisation and design of activated carbons for use in applications such as natural gas storage. As part of this work we have been studying isotropic pitch fibres supplied from Clemson, for these materials are ideal precursors for high-capacity, microporous adsorbents [1, 2]. In this abstract we report initial results from a study of the influence of carbonisation temperature on the structure and reactivity of pitch-based carbon fibres. The structure of the carbon fibres was examined using x-ray diffraction (XRD) and transmission electron microscopy (TEM). The reactivity of the fibres in CO_2 was determined using thermogravimetric analysis (TGA).

PREPARATION OF CARBON FIBRES

Precursor fibres were melt-spun at Clemson from Ashland Aerocarb 80 isotropic pitch, in conditions detailed in [2]. After stabilisation in air at 250 °C for 120 min, the pitch fibres, ~ 14 μm in diameter, were supplied to Bath for study.

Previous TGA of the pitch fibres [2] showed that all pyrolysis weight losses, and hence chemical changes, occurred below 950 °C when samples were heated at 10 °C min^{-1} from 25 °C in pure, flowing He at one atmosphere pressure. Thus a series of chemically-similar carbon fibres was made by heating the pitch fibres in the above conditions to maximum heat treatment temperatures (MHTTs) in the range 990 - 2 850 °C. Samples were kept at the MHTT for 60 min for structural equilibration before cooling.

CHARACTERISATION OF CARBON FIBRES

X-ray diffraction

The carbon fibres were analysed using a Phillips PW1710 x-ray diffractometer, operating with Cu K_α radiation (wavelength = 1.5418 Å). Structural parameters estimated from diffraction spectra were the interlayer spacing, $d_{(002)}$, and L_a and L_c (crystallite sizes parallel and perpendicular to layer planes respectively).

Transmission Electron Microscopy

Thin (~ 100 nm) sections of silane-coated carbon fibres embedded in epoxy resin were cut perpendicular to the long axes of the fibres using an ultramicrotome. The sections were mounted on a Cu grid, and viewed in a Jeol 2000FX transmission electron microscope operating at 200 kV. A standard de-focusing technique was used to image graphitic lattice fringes in the sections.

Thermogravimetric Analysis

Weight losses (due to the Boudouard reaction) of carbon fibre samples exposed to CO_2 in two, different heating conditions were determined using a Setaram TGA92 thermogravimetric analyser. CO_2 was used as the oxidising gas as it is a common activating agent for adsorbent carbons.

The two heating conditions were: (i) isothermal oxidation - 10 °C min^{-1} from 25 °C to different temperatures, $T_{ox} \leq$ MHTT, in He, and then, at T_{ox}, in CO_2 until 100 % weight loss, and (ii) non-isothermal oxidation (oxidation thermogramme) - 10 °C min^{-1} from 25 °C in CO_2 until 100 % weight loss. In both cases flowing, pure gases at one atmosphere pressure were used.

It was found that, for non-isothermal oxidation, all samples were essentially burnt out before the MHTT. Thus in neither oxidation condition were extra structural changes induced due to heating above the MHTT. It was also found that isothermal weight losses were too fast to measure for $T_{ox} > 1\,200$ °C.

A simple reaction kinetics model was adopted where the isothermal oxidation rate was taken to be first order with respect to carbon, and where the rate constant was assumed to vary with T_{ox} according to the Arrhenius equation. The Arrhenius parameters A (the pre-exponential factor) and E (activation energy) were assumed to depend only on MHTT. For ease of comparison with the isothermal results, the thermogramme data for each MHTT were represented by the time, t_{40}, taken to achieve 40 % weight loss.

RESULTS AND DISCUSSION

Figure 1 displays the XRD data. Crystallite sizes are of the order of nm, and interlayer spacings are all larger than that for perfect graphite (0.3354 nm), indicating that the fibres comprise highly disordered carbons, as was expected from the isotropic nature of the pitch precursor. Figure 1 also shows that: (i) the widths of crystallites, L_a, are larger than their heights, L_c, by a factor of ~ 3; both parameters increase approximately linearly with increasing MHTT, and (ii) interlayer spacing, $d_{(002)}$, decreases sigmoidally with increasing MHTT, reaching at a constant value of ~ 0.35 nm for MHTT $> 2\,500$ °C. These observations indicate that the degree of graphitic crystallinity increases with increasing MHTT, as expected, but that the pitch precursor is essentially non-graphitisible.
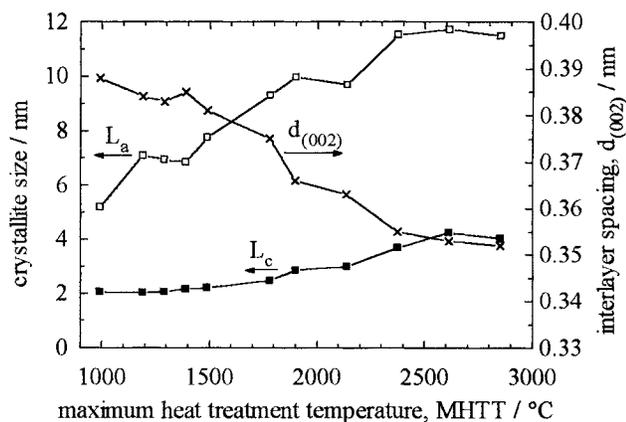

Figure 1 - XRD structure data for the carbon fibres.

Figure 2 is a TEM image (MHTT = 2 600 °C), confirming the disordered structure of the carbon fibres. Analysis of the lattice fringes in this image yielded an average value $d_{(002)} = 0.36$ nm, which is close to the interlayer spacing estimated from XRD.
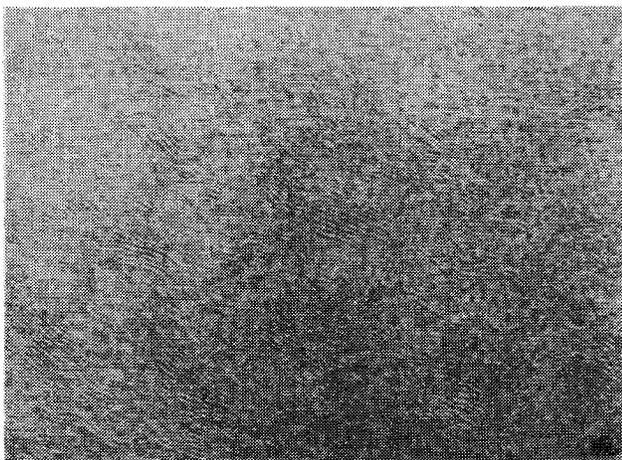

Figure 2 - TEM image (4 nm wide) of a carbon fibre.

Statistical analysis of the isothermal oxidation data suggested that: (i) the assumed, simple reaction kinetics model was reasonable, and (ii) the Arrhenius activation energy, E, depended on MHTT while the pre-exponential factor was constant (A $\sim 10^3$ min). Figure 3 is a plot of E, and t_{40} from the thermogrammes, versus MHTT.
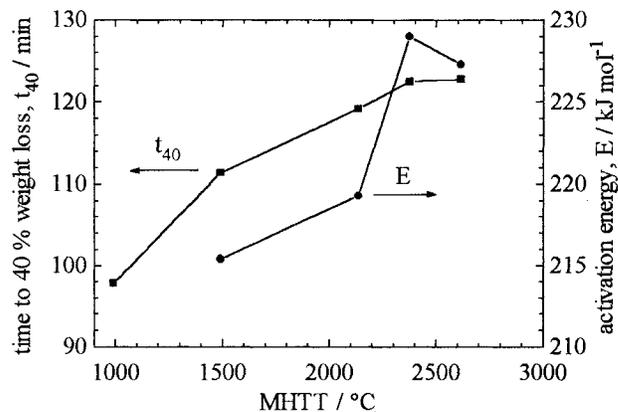

Figure 3 - TGA reactivity data for carbon fibres.

Figure 3 shows that both t_{40} and E increase, and hence reactivity of the carbon fibres in CO_2 decreases, with increasing MHTT. This supports the observations from XRD that the degree of graphitic order increases (and hence the number of active sites for oxidation - edge atoms, defects, etc. - decreases) with increasing MHTT.

CONCLUDING REMARKS

X-ray diffraction (XRD) shows that increasing the maximum heat treatment temperature (MHTT) during pyrolysis of fibres melt spun from isotropic pitch increases the degree of graphitic crystallinity of the resulting carbon fibres. However, the precursor pitch is essentially non-graphitisible. Thermogravimetric analysis confirms this result by showing that the oxidation reactivity of the carbon fibres in CO_2 decreases with increasing MHTT. Quantitative analysis of a transmission electron microscopy image yields a value of interlayer spacing that is in agreement with that from XRD. This correlation is now being studied for samples with different MHTTs.

The implications of these results for the processing, characterisation and design of microporous carbon fibres activated in CO_2 are currently being investigated.

REFERENCES

[1] T. J. Mays, et al., Proc. Carbon '94, Granada, Spain, 244 (1994).
[2] Idem, ibid., 656.