

THE FATE OF NITROGEN FUNCTIONALITY IN CARBONACEOUS MATERIALS DURING PYROLYSIS AND COMBUSTION USING XANES SPECTROSCOPY

*Q. Zhu, S. L. Money, A. E. Russell and K. M. Thomas
Northern Carbon Research Laboratories, Department of Chemistry,
Bedson Building, University of Newcastle upon Tyne,
Newcastle upon Tyne, NE1 7RU, United Kingdom*

Introduction

The combustion of coal for power generation leads to the release of NO_x and SO_x which contribute to acid rain. In the combustion of coal in the latest low NO_x burners the nitrogen retained in the char is the main contributor to the emissions of NO_x . The possible relations between the nitrogen functionality in coal, its conversion to nitrogen in char during pyrolysis and to NO_x during combustion are of considerable significance from an environmental perspective. Until recently the most useful technique for studying nitrogen functionality was X-ray photoelectron spectroscopy (XPS). X-ray near Edge Structure (XANES) spectroscopy has been used previously for studying nitrogen functional groups in asphaltenes^{1,2}, coals³ and carbons^{4,5}. The objective of this study was to explore the use of XANES spectroscopy for studying the chemistry of the combustion of nitrogen bound in carbons.

Experimental

1. Materials. Polynuclear aromatics, for example, carbazole and acridine were carbonised in an autoclave under an atmosphere of argon with an initial pressure of 4.1 MPa at a heating rate of 1K min^{-1} to final heat treatment temperature of 873K with a soak time of 1 hour. The carbons obtained were subjected to further heat treatments to 1073 and 1273K under a flow of argon with a heating rate of 4K min^{-1} and soak time of 1 hour at the final heat treatment temperature. Polyacrylonitrile (PAN) and acenaphthylene were carbonised in a horizontal tube furnace at a heating rate of 1K min^{-1} under a flow of argon ($\sim 100\text{ cm}^3\text{ min}^{-1}$) at atmospheric pressure. Heat treatment temperatures in the range 873 - 1273K were used. The acenaphthylene carbon (HTT 873K) was heat treated in a flow of ammonia at 4K min^{-1} to 1073K to incorporate nitrogen into the carbon structure (carbon A-N). The acenaphthylene carbon (HTT 873K) was also heated in argon to 1073K and then treated with ammonia to incorporate nitrogen (carbon A-Ar-N).

2. XANES Measurements. The XANES measurements were carried out using the High Energy Spherical Grating Monochromator (HESGM) situated on line 1.1 of the Synchrotron Radiation Source (SRS) at Daresbury Laboratory. The sample was ground to a very fine particle size, made into a slurry in carbon tetrachloride and dispersed on an aluminium plate (nitrogen studies) or platinum plate (oxygen studies). The slurry was allowed to evaporate to form a thin film. A blank plate was scanned for every run as a reference. The pressure in the electron pathway and in the sample compartment was in the range 10^{-6} - 10^{-8} Bar. All measurements were carried out at room temperature.

3. Partial Combustion Studies. The carbons were gasified in 20% O_2 /argon to a specific carbon conversion levels a 823K (PAN carbons), 873K (carbazole and acridine carbons), 923K (acenaphthylene carbons) in a thermogravimetric analyser. The sample was heated at 50 K min^{-1} in argon ($50\text{ cm}^3\text{ min}^{-1}$) to the desired combustion temperature. The gas flow was then switched to 20% O_2 /Ar and the weight change recorded. When the desired conversion level was reached the gas was switched to argon and the system cooled to room temperature. The burn-off char was designated as the name of the carbon followed by -B and a number representing the carbon conversion (%).

Results and Discussion

The XANES spectra of organic reference compounds were used as standards for the various types of nitrogen functionality. The results showed that there was a narrow energy range for the leading edge peaks for each type of nitrogen functionality¹⁻⁵. The characteristic energies for each type of functional group were used for identification for example the energies for pyridone, pyridine and pyrrolic functionalities were 399.5, 401.4 and 403.7 eV respectively.

A suite of chars derived from various nitrogen containing precursor materials (acridine, carbazole,

polyacrylonitrile) and by treating polyvinylidene (PVDC) and acenaphthylene chars with ammonia was chosen for the partial combustion studies. The nitrogen in some of these chars was characterised by X-ray photoelectron spectroscopy (XPS) in addition to XANES spectroscopy⁶. The results showed that carbons had a wide range of functionalities, CB873 (100% pyrrolic), AD873 (20% pyridinic, 58% quaternary, 21% N-X).

The combustion of acridine char AD873 to 56% carbon conversion gave a carbon (AD873-B56) which had a XANES nitrogen K edge spectrum with a new peak at 401.3 eV with a higher intensity than the pyridinic peak at 399.7 eV (see Figure 1). The new peak was assigned to pyridone functionality. The nitrogen K edge XANES spectrum of the untreated carbon CB873 had a strong peak at 403.7 eV indicative of virtually exclusively pyrrolic functionality while the XPS spectrum was consistent with the presence of 100% pyrrolic functionality. Gasification of carbazole char CB873 to 66 wt% burn-off gave CB873-B66. Partial combustion of CB873 produced a large decrease in the XANES 403.8 eV peak due to pyrrolic functionality and a new peak at 401.2 eV which indicates the presence of pyridone functionality. A peak at 399.7 eV corresponding to pyridinic functionality was also produced by partial gasification. The results indicated that the pyrrolic functionality had been converted to pyridone and pyridinic functionality. The partially gasified PAN chars showed a small increase in the peak at 401.5 eV compared with the starting material. The partially gasified acenaphthylene chars A-Ar-N-B78.5 and A-N-B48 also showed an intense peak at 401.4 eV similar to the partially gasified acridine, carbazole and PAN carbons (see Figure 1). Nitrogen was incorporated by ammonia treatment of the acenaphthylene chars whereas the other carbons were prepared by carbonization of a nitrogen containing precursor. However gasification of all the carbons, irrespective of the initial nitrogen functionality, leads to the development of a peak at 401.5 eV which is consistent with the presence of pyridone functionality.

References

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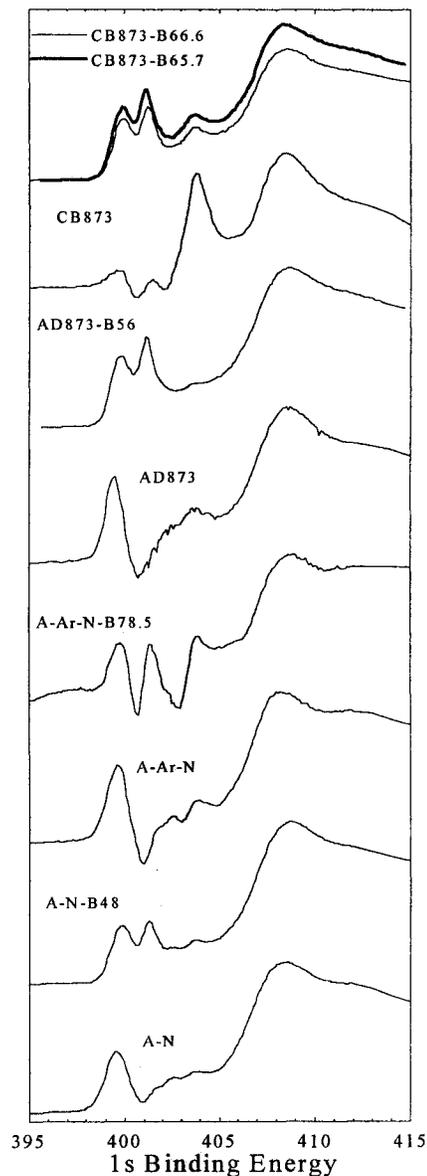


Figure 1 Nitrogen XANES spectra of partially gasified carbons