

# XPS STUDY ON THE EVOLUTION OF NITROGEN FUNCTIONALITIES IN CHARs PREPARED FROM MODEL COMPOUNDS

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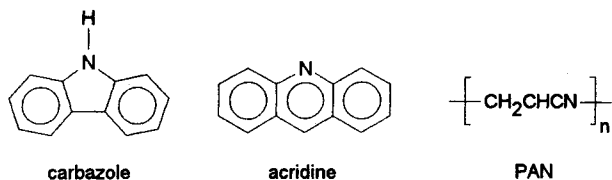
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## Introduction

In recent years the analysis of the nitrogen functionality in carbon and coals has received much attention. This is mainly due to the desire to understand the formation of nitrogen oxides,  $\text{NO}_x$  and  $\text{N}_2\text{O}$ , during the combustion of coal. During combustion both the combustion of volatiles released during pyrolysis and that of the char contribute to these emissions. This paper focuses on the chars. Two non-destructive techniques have emerged that yield information on the nitrogen in carbonaceous materials, namely X-ray Photo-electron Spectroscopy (XPS) and X-ray Absorption Near-Edge Spectroscopy (XANES) [1,2]. In XPS four peaks are observed predominantly at N 1s binding energies of 398.6 (N-6), 400.3 (N-5), 401.5 (N-Q) and 402.5-404 eV (N-X). The first two are ascribed to pyridinic and pyrrolic nitrogen functionalities, respectively. For the other two no unambiguous attributions have been made [1].

Here we present XPS results of a series of chars prepared from model compounds, acridine, carbazole and PAN, that shed more light on the nitrogen functionalities in carbons.



## Experimental

The chars were prepared by heating the samples in a closed vessel under argon at temperatures between 573 and 1273 K for 1h. After charring they were exposed to the ambient.

XPS samples were pressed in cleansed In foil. XPS measurements were carried out with an Al-K $\alpha$  source. Correction for charging was made with reference to C1s at 285.0 eV. Peak analysis was done using Gauss-Lorentzian peak shapes and Shirley type background subtraction. Recording times amounted up to 10 h.

## Results and discussion

The XPS results of the chars prepared at different temperatures are presented in figs 1-3. The deconvolution

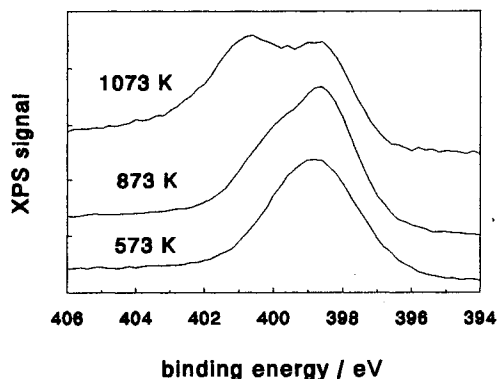


Figure 1. XPS Spectra of PAN chars

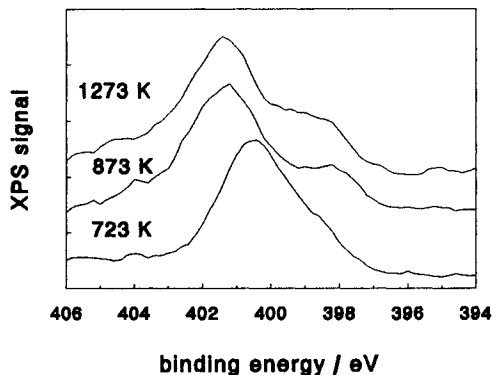


Figure 2. XPS Spectra of acridine chars

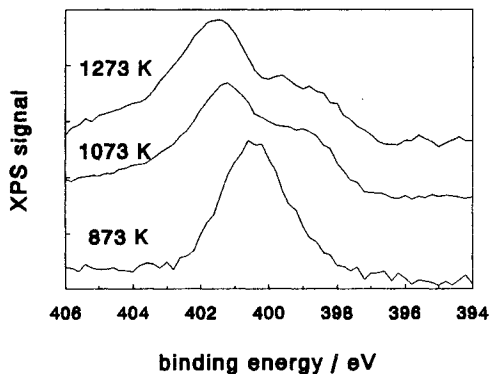


Figure 3. XPS spectra of carbazole chars

**PAN**

	N-6	N-5	N-Q	N-X
573 K	100	0	0	0
773 K	69	19	8	4
1073 K	40	29	23	9

**Acridine**

723 K <sup>a)</sup>	17	58	25	0
873 K	20	0	58	21
1273 K	21	0	61	19

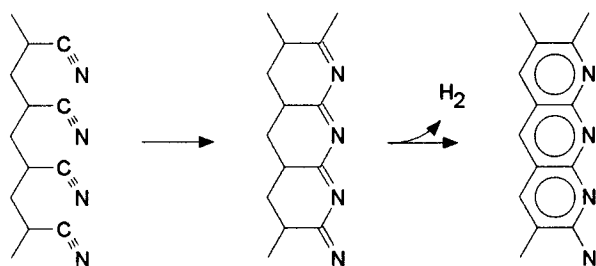
<sup>a)</sup> 50/50 mixture of acridine and carbazole

**Carbazole**

873 K	0	100	0	0
1073 K	29	10	43	18
1273 K	24	0	50	26

Table 1. Deconvolution of the XPS spectra

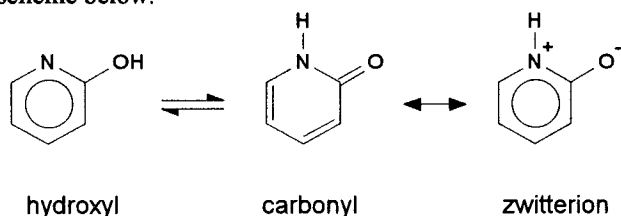
results of these spectra into the four types of nitrogen are given in table 1. With increasing temperature the amounts of N-Q increase up to 50-60% at 1273 K, of N-6 and N-X 20-30%, while N-5 is completely absent. Clearly pyrrolic functionalities are unstable at elevated temperatures. The PAN char shows a peculiar trend: N-5 seems to be produced after pyrolysis between 700-1100 K, whereas this is not expected from the cyclization and dehydrogenation mechanism:



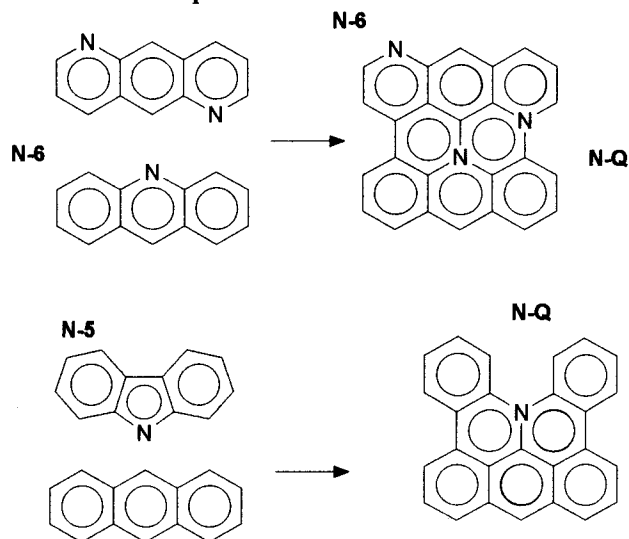
PAN

PAN char

The explanation is found in the elemental analysis, also provided by XPS. It turned out that the samples are susceptible to oxidation in the ambient air after pyrolysis, reflected in a considerable increase in the oxygen content up to 6%. This can result in pyridone-like species [2], which are located at 400.6 eV and are in fact pyridinic species that contribute to the N-5. The tautomers that result in this higher binding energy are indicated in the scheme below.



The N-Q peak is attributed to the incorporation of nitrogen in the graphene layer structure during the condensation reactions in the pyrolysis process. The location of this peak corresponds to that of quaternary nitrogen species, having a positive charge. MO calculations, using BioSym, indeed indicated that nitrogen incorporated in perinaphthene has a positive charge, which can account for the shift to higher binding energies. The incorporation during condensation reactions is exemplified as follows:



The N-X peak is at present ascribed to a pyridinic nitrogen oxide as reported by Kelemen [3] and to other nitrogen oxygen species located in this region of binding energies [1].

In view of the fairly constant composition of N-functionalities after high temperature pyrolysis, irrespective of origin, no differences in the formation of nitrogen oxides during char combustion are expected.

**Acknowledgement**

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**References**

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