

# X.P.S. ANALYSIS FOR THE THERMAL CONVERSION OF A VINYLPIRIDINE RESIN INTO ACTIVE CARBON

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Synthetic active carbons were obtained from a porous vinylpyridine-divinylbenzene copolymer [1]. The objective of the present paper is to describe the evolution of the nitrogen groups determined by X.P.S. during the heat treatment of the vinylpyridine-divinylbenzene copolymer.

## Experimental

The initial resin containing up to 10% divinylbenzene as a crosslinking agent was heat treated according to the following conditions: oxidative carbonization (air) up to 250, 275 300 or 400°C with a heating rate of 3°C/min and a soaking time of two hours followed by pyrolysis under argon at 950°C of the different chars with a heating rate of 5°C/min and a soaking time of two hours. The samples were cooled down under argon.

The surface chemistry of the samples was determined by X.P.S. spectrometry using a Leybold LHS11 spectrometer.

## Results and discussion

Four samples numbered from 1 to 4 were examined and their elemental and functional surface compositions characterized: (i) the initial resin; (ii) the resin carbonized at 250°C; (iii) the resin carbonized at 400°C; (iiii) the char obtained at 400°C and pyrolysed at 950°C.

### « Structure » of the N1s envelope

From the different spectra seven components were individualized by fitting of the N1s envelopes corresponding to different samples. The energy gap  $\Delta[N1s(i) - N1s(1)]$  relative to pyridinic component, labeled N1s (1) and taken as an internal reference, and the « forms » of N assigned to each one are reported in table 1

Sample 1 (initial resin): On the spectrum taken after a very short exposure to ionizing radiation a single component, labeled N1s (4) at  $\Delta[N1s(4) - N1s(1)] = 2.8 \pm 0.1$  eV, is observed. It is assigned to « quaternary » methyl pyridinium  $\text{>N}^+\text{—CH}_3$ . The counter ions are the single charged methyl sulfate / sulfite species. The binding energy of the pyridinic N was set at  $399.3 \pm 0.1$  eV, according to Beamson and Briggs [2]. The anionic species degraded under the X-ray beam (volatilization as SO<sub>x</sub>) and the pyridinium N is partly converted into pyridinic N and a cyclic tertiary amine [3].

Sample 2 (carbonized at 250°C): Some anionic species (CH<sub>3</sub>-O-SO<sub>3</sub><sup>-</sup> and CH<sub>3</sub>-O-SO<sub>2</sub><sup>-</sup>) are removed and part of the methyl pyridinium is converted into pyridinic N. An optimum fit to the experimental spectrum is obtained by adding two supplementary components: the first labeled N1s (2) at  $\Delta[N1s(2) - N1s(1)] = 1.0 \pm 0.1$  eV is assigned to a

cyclic tertiary amine [8] and the second one labeled N1s (3) at  $\Delta[N1s(3) - N1s(1)] = 1.5 \pm 0.1$  eV to pyridone, i.e. pyridinic nitrogen in  $\beta$  of a phenolic -OH.

Sample 3 (carbonized at 300°C): Four components were individualized by fitting. The pyridinic N1s (1) is the most intense. The relative contribution of pyridone entities, i.e. component N1s (3), is significantly enhanced as compared to the carbonisat (250°C). Component N1s (4), at  $\Delta[N1s(4) - N1s(1)] = 2.6 \pm 0.1$  eV corresponds primarily to pyridinic N hydrogen bonded to adjacent -OH or -COOH. The fourth component, labeled N1s (5) is assigned to N pyridine oxide  $\text{>N}^+\text{—O}^-$ . The form of the spectrum is identical to those obtained by Pels and al [4] from P.A.N. char prepared at 773°K.

Sample 4 (pyrolyzed at 950°C): The nitrogen is present in 6 membered rings included in polyaromatic structures. The best fit to the profile of the experimental spectrum is obtained starting from a set of 6 components. The binding energy of pyridinic N (component N1s (1)), i.e. located at the top of edge rings of graphene layers, lies at  $398.3 \pm 0.1$  eV. The second component labeled N1s (3) at  $\Delta[N1s(3) - N1s(1)] = 1.5 \pm 0.1$  eV is assigned to pyridone. The third component labeled N1s (4) at  $\Delta[N1s(4) - N1s(1)] = 2.5 \pm 0.1$  eV corresponds to « quaternary » pyridinic N. Referring to experimental and/or theoretical investigations on model compounds, i.e. pyridine, pyrrole, benzoquinidine, pyridinium ion, pyridine N oxide [4], perinaphthene [5], and 3,5,11,13-tetraazacycl [3,3,3] azine [6], this component is assigned to pyridine N incorporated in the graphene layers (and whose effective charge is significantly higher than the one of top pyridinic N on edge rings). The component labeled N1s (5) at  $\Delta[N1s(5) - N1s(1)] = 4.1 \pm 0.2$  eV is assigned to pyridinic N oxide  $\text{>N}^+\text{—O}^-$ . The component labeled N1s (6) at  $\Delta[N1s(6) - N1s(1)] = 5.3\text{--}5.8$  eV corresponds partly to the ( $\pi \rightarrow \pi^*$ ) shake-up satellite [7] and partly to a « form » of non heterocyclic oxygenated N. The gap between binding energies of pyridinic N (in polyaromatic structures) and nitro N reaches  $7.2 \pm 0.3$  eV.

The component N1s (6) cannot be assigned to nitro N. It may correspond to entrapped NO<sub>x</sub> species.

## Conclusion

Below 300°C, the thermal treatment mainly induces the degradation of the anionic species, CH<sub>3</sub>-O-SO<sub>3</sub><sup>-</sup> and CH<sub>3</sub>-O-SO<sub>2</sub><sup>-</sup> (evolving of SO<sub>2</sub>). The methyl pyridinium type nitrogen is partly converted into pyridinic nitrogen. The carbonaceous skeleton of the resin is slightly oxidized. Essentially -OH groups from the oxidation of aliphatic chains and pyridone entities are formed.

Above 300°C, only traces of sulfur-containing groups are observed. The nitrogen is mainly pyridinic with a significant contribution of pyridone and a small one of "quaternary" species which are pyridinic nitrogen hydrogen bonded to adjacent -OH and -COOH. A small proportion of pyridine oxide is also observed. The proportion of carbon bonded to oxygen goes from 3% in the initial resin up to 26.5% in the char obtained at 400°C.

During the heat treatment at 950°C a part of the pyridinic heterocycles is destroyed and volatile nitrogen species evolve. The remaining nitrogen is included in the polyaromatic structure. After pyrolysis at 950°C and whatever the temperature of the carbonisation (from 250 to 400°C), the N1s peak exhibits the same structure. The two main components are attributed to pyridinic nitrogen (i) at the top of the border cycles of the graphene units and (ii) included in the graphitic structure and improperly named quaternary nitrogen. The small proportion of pyridone and pyridine oxide types of nitrogen are expected to be formed when the material after pyrolysis and cooling down is put into contact with the ambient air.

## References

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Table 1.

Index	$\Delta[N1s (i \neq 1) - N1s (1)]$	« Formes » d'azote
N1s (1)	/	pyridinic N
N1s (2)	+ 1.0 ± 0.1 eV	Tertiary amine N (« réduction » of $\geq N^+-CH_3$ under ionizing radiation :R.X)
N1s (3)	+ 1.5 ± 0.1 eV	Pyridone (oxidation of pyridinic heterocycles)
N1s (4)	+ 2.8 ± 0.1 eV + 2.5 ± 0.1 eV + 2.5 ± 0.1 eV	« quaternary » pyridinic N a) N methyl pyridinium $\geq N^+-CH_3$ : initial resins and chars (250 et 275°C) b) $\geq N^+-OH$ (intra and inter moléculaire H bonds): chars ( $\geq 300^\circ C$ ) c) pyridinic N incorporated in the condensed polyaromatic structural units (« center » N) Pyrolysates (950°C)
N1s (5)	+ 4.1 ± 0.1 eV	pyridine N oxide $\geq N^+-O$ : pyrolysates (post oxydation upon exposure to the ambient)
N1s (6)	+ 5.2 ± 0.1 eV	Shake-up satellites ( $\pi \rightarrow \pi^*$ ) Entrapped $NO_x$ (in the micropores)
Sat.	+ 7.4 ± 0.1 eV	Shake-up satellites ( $\pi \rightarrow \pi^*$ )