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Structural Characterization of Nitrogen-Enriched Coals

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A subbituminous coal and a lignite were treated with some nitrogen reagents in several solvents with the aim of obtaining enriched coal samples which could behave as active carbon precursors. This paper deals with the structural characterization of the samples obtained with urea before and after activation. The attention is focused on the identification of the main functional groups able to react with urea, on the nature of the nitrogen functions introduced in the coal network, and on the behavior of these functions during the activation. The samples were investigated by infrared spectroscopy (DRIFT), X-ray photoelectron spectroscopy (XPS). It was shown that ester/lactone and carboxylic acid groups are mainly concerned in the reaction with urea, which is solvent dependent. The identification of nitriles proved the occurrence of amides in the first step of the reaction. The participation of ketones, though to a lesser extent, suggests the possibility of further heterocyclization. The nitrogen enrichment of the coals is evidenced by XPS. On the basis of literature data, four nitrogen groups were characterized according to the binding energies. They were assigned to pyrrolic and several pyridinic forms. Their behavior during thermal treatments and steam activation is discussed.

Introduction

Recent studies were devoted to the preparation of active carbons modified by incorporation of nitrogen aiming at the development of new solid catalysts, of new catalyst support materials, and of new competitive adsorbents.

In this view, Jansen and van Bekkum studied the amination and ammoxidation of active carbons.[1] The **amination** was carried out by reaction of ammonia on carbons preoxidized with nitric acid and is expected to take place at carboxylic acid sites formed by oxidation of side groups as well as ring systems. The **ammoxidation** is a direct reaction of active carbons with ammonia–air gas mixtures and is expected to take place only at aliphatic substituents of the aromatic ring

systems. On the basis of FT/IR spectroscopy, amides, lactams, and imides are suggested as the main fixed functional groups whose heat treatment may lead to pyrroles, and pyridines, possibly through nitriles, by dehydration, decarboxylation, and decarbonylation. The products of amination and ammoxidation were studied by XPS of nitrogen N_{1S} as well as those obtained by reaction of nitric acid preoxidized carbons with organic amines. The N_{1S} binding energies (BE) of amides, lactams, imides, and tertiary amines were assigned.[2] All these BE are in the range of 399.7–399.9 eV. After heat treatment (>400 °C), pyridine and pyrrole types are most abundant due principally to the conversion of amides and N-alkyl imides since lactams and imides are persistent until 800 °C. Stöhr et al.[3] studied the enhancement of the catalytic activity in oxidation reactions (with O_2) of active carbons treated at elevated temperatures (600–900 °C) with ammonia or cyanhy-

(1) Jansen, R. J. J.; Van Bekkum, H. *Carbon* **1994**, *32*, 1507.
(2) Jansen, R. J. J.; Van Bekkum, H. *Carbon* **1995**, *33*, 1021.
(3) Stöhr, B., Boehm, H. P.; Schlögl, R. *Carbon* **1991**, *29*, 707.

dric acid. The determination of the nitrogen functionalities by XPS suggested the presence of amide and amine groups (BE 400−401 eV), and of pyridine and/or nitrile groups (BE 398 eV). The preparation of active carbon fiber (ACF) with basic properties was also investigated by Kawabuchi et al.[4] by pyrolysis of pyridine over ACF at 725 °C. It was shown that pyridine provided basic functionalities on the surface and the catalytic SO_x removal was very much enhanced. In all these experiments, having in common the introduction of nitrogen functionalities on carbon previously activated, the nitrogen enhancement does not exceed 4%.

Our interest was focused on the preparation of active carbons starting from coals enriched in nitrogen before the step of activation. Two low-ranked coals were selected: a Russian lignite from Kansk-Achinsk basin (KA) and a subbituminous Polish coal from Janina mine (J). Several nitrogen reagents such as ammonia and its derivatives were condensed at 300 °C under pressure, using different solvents, methanol, *N,N*-dimethylformamide, and *N*-methyl 2-pyrrolidinone.The preparation of the samples, their heat treatment (700−800 °C) and steam activation, and the characterization of the porosity of the chars were recently described by Bimer et al.[5] as well as their adsorption properties toward gas desulfurization.

The present paper concerns the structural characterization of the nitrogen-enriched coals, before and after carbonization and activation, with two main objectives: on the one hand, to determine what functional groups already present in the starting samples were implied in the reaction with the nitrogen derivatives, and on the other hand to identify the main nitrogen functionalities issued from this reaction and to study their behavior during the activation process. The presentation will be focused principally on the reaction with urea as it appeared to be the most interesting among the reagents used (ammonia, hydrazine, hydroxylamine, urea). The structural characterization was carried out by FT/IR spectroscopy (DRIFT) and by XPS determinations of C_{1S} and N_{1S}.

Experimental Section

The Samples. KA lignite was used after partial demineralization by HCl and without pretreatment with performic acid. As it is foreseen that carboxylic groups are mainly concerned in the reaction with the nitrogen derivatives, Janina coal was enriched in these groups by preoxidation with performic acid as already described[6] giving rise to J-OX sample. As the nitrogen introduction (see hereafter) was carried out at 300 °C, the behavior of KA and J-OX at this temperature was tested by pyrolysis at 300 °C in a tube-reactor under argon: samples KA-300 and J-300. The analytical data of all these samples are presented in Table 1.

Nitrogen Group Introduction. The preparation of the nitrogen derivatives has already been described,[5] either at ambient temperature or at 300 °C, in an autoclave. The present paper being concerned with the reaction of urea at

Table 1. Analytical Data of the Starting Coal Samples

samples	ash (%, dry)	elemental composition (%, daf)				O_{OH} (%, daf)	O_{COOH} (%, daf)
		C	H	N	O^a		
J	4.7	75.3	4.5	1.4	18.8	5.9	2.2.
J-OX	3.4	64.2	4.0	1.3	30.5	2.3	10.4
J-300	4.6	73.6	3.7	1.4	21.3	nd	nd
KA	1.9	67.9	4.3	0.8	27.0	5.2	5.9
KA-300	1.8	71.9	3.9	1.2	23.0	nd	nd

^{a} By difference.

Table 2. Yields and Ultimate Analysis of Blank Essays and Products Obtained from J-OX and KA by Treatment with Urea

samples	yields (%)	ash (%, dry)	elemental composition (%, daf)			
			C	H	N	O^a
J-F	87.0	5.1	77.9	5.3	5.1	11.7
J-M	80.6	3.7	75.3	4.6	1.3	18.8
J-UF	135.0	2.7	68.5	3.6	16.7	11.2
J-UM	86.5	3.9	72.6	4.7	7.2	15.5
KA-UF	131.2	2.1	65.2	3.6	14.1	17.1

^{a} By difference.

300 °C, in *N,N*-dimethylformamide (F) or in methanol (M), we recall here the experimental conditions: a mixture of coal sample (10 g), urea (20 g), and 100 mL of the selected solvent was placed in a 2 L autoclave. The reaction was carried out at 300 °C during 1 h. After cooling and releasing of the gases, the solvent was separated by filtration and the residue washed thoroughly with water to remove the rest of the solvent, the unreacted urea, and its byproducts. The coal products were dried in a vacuum at 105 °C and named, respectively KA-UF, J-UF, and J-UM. Blank essays were also carried out in the same conditions with the solvents alone: J-F and J-M. The analytical data are presented in Table 2.

FT/IR Spectroscopy. Diffuse reflectance spectra were recorded with a Mattson 3000 spectrometer under the conditions already described.[7] The sample to KBr ratio was 5 mg per 100 mg. Deconvoluted spectra were obtained using the standard software package on the Winfirst system. The areas under the absorption bands of selected functional groups were considered as corresponding to their weight in the system.[8] The intensities *I* of particular bands were measured from the heights of the bands. As the nitrogen derivative reagents are expected to react mainly with carboxyl, carbonyl, and ester groups, two spectral regions were selected: (1) the $\nu(NH_2)$ stretching modes in amide and amine groups, between 3500 and 3000 cm^{-1} and (2) the $\nu(C=O)$ and $\nu(C=C)$ stretching modes between 1800 and 1540 cm^{-1}.

X-ray Photoelectron Spectroscopy. XPS spectra were collected by a VG Scientific Escalab MK I system, interfaced to a VGS 5000-S data system based on a DEC PDP11/73 computer. A thin layer of fine powder of the sample was mounted on a metallic holder (1 cm²). Each sample was analyzed using a X Mg Kα nonmonochromatic radiation (1253.6 eV). Escalab was operated in the constant energy analyzer mode at a pass energy of 50 eV for the survey spectra and 20 eV for the high-resolution C_{1S} and N_{1S} spectra (pressure 10^{-8} mbar, power 10 kV × 10 mA, accumulation times 2−16, step size 1 eV (wide scan), 0.1 eV (high-resolution scan), dwell time 100 ms). The data processing software allowed smoothing, linear or Shirley type background subtraction, static charge referencing, peak fitting, and quantification. All binding energies (BE) were referenced to C_{1S} at 285 eV.

Thermal Treatments. The thermal stability of the samples was tested by pyrolysis at 450 and 600 °C during 1 h in a tube

(4) Kawabuchi , Y.; Sotowa, C.; Kuroda , K.; Kawano, S.; Whitehurst, D. D.; Mochida, I. *Proc. Eur. Carbon Conf. "Carbon 96", New Castle upon Tyne UK*, **1996**, 431.

(5) Bimer, J.; Salbut, P. D.; Berlozecki, S.; Boudou, J. P.; Broniek, E.; Siemieniewska , T. submitted for publication in *Fuel*.

(6) Salbut, P.D.; Berlozecki, S.; Bimer, J. *Fuel Process. Technol.* **1988**, *18*, 287.

(7) Krzton, A.; Cagniant, D.; Gruber, R.; Pajak, J.; Fortin, F.; Rouzaud, J. N. *Fuel* **1995**, *74*, 217.

(8) Christy, A. A.; Liang, Y. Z.; Kvalheim, O. M. *Fuel* **1992**, *71*, 125.

Table 3. Ultimate Analysis of Products Obtained from J-OX and KA by Treatment with Urea, after Carbonization and Steam Activation

	elemental composition (%, daf)			
samples	C	H	N	O[a]
J-UF 450	71.6	2.3	15.5	10.6
J-UF 600	76.0	0.3	11.6	12.1
J-UF 800	75.2	0.4	11.9	12.5
J-UF H$_2$O[b]	77.5	0.3	5.5	16.7
KA-UF 450	73.7	2.1	11.8	12.4
KA-UF 600	77.5	0.8	9.9	11.8
KA-UF 800	78.8	0.2	8.9	12.1
KA-UF H$_2$O[b]	82.5	0.0	4.4	12.1

[a] By difference. [b] 50% burnoff.

reactor under argon. The carbonization of J-UF and KA-UF by heat treatment (HTT) at 450, 600, or 800 °C and the activation of the chars by preheated steam (J-UF$_{H_2O}$) were described.[5] The relevant samples are named J-UF$_{450}$, J-UF$_{600}$, J-UF$_{800}$, and KA-UF$_{450}$, KA-UF$_{600}$, KA-UF$_{800}$ for the chars, and J-UF$_{H_2O}$, KA-UF$_{H_2O}$ for the active carbons. The analytical data are presented in Table 3.

Results

Ultimate and Functional Groups Analyses. The data reported in Tables 1 and 2 present several interesting points:

1. As expected, the performic acid treatment increases the oxygen % and particularly the COOH group contents of J-OX. As shown by IR spectroscopy (see hereafter), this group vanishes by heating at 300 °C (J-300). The reaction with urea (J-UF, J-UM, KA-UF) depletes the oxygen contents and this decrease is also observed in the blank essays (J−F, J−M).

2. The reaction with urea gives rise to a significant incorporation of nitrogen which is solvent dependent (16.7% in J-UF, 7.2% in J-UM) and a great decrease of oxygen content (30.5% in J-OX, against 11.2% in J-UF).

3. After heat treatment, a slight increase of oxygen is observed in the case of J-UF chars (HTT), this increase being more important after steam activation (J-UF$_{H_2O}$). At the opposite, a decrease of oxygen is observed for the lignite chars. In both cases, a decrease of nitrogen is observed as the severity of the heat treatment increases. Nevertheless, the nitrogen, in the active chars, remains at significant amounts (Table 3), even after treatment at 800 °C (11.9−8.9%). In the same time, the carbonization and activation give rise to a great loss of hydrogen.

4. It is also interesting to point out the yields of the reaction with urea in DMF (>100%), which are greater than those in methanol (86.5%) and with the other studied nitrogen derivatives (80−88%).[5]

Infrared Spectroscopic Data. The spectra in the **3600−3000 cm^{-1}** region are not reported. They are characterized by a large band from 3600 to 3100 cm^{-1}, overlapping more or less the kaolinite bands around 3650 cm^{-1} and being nearby the ν(CH) aromatic band around 3060 cm^{-1}. The detection of the medium or weak ν(NH$_2$) vibrations in the presence of ν(OH) vibrations is illusive in these complex materials.

The spectra in the **1800−1540 cm^{-1}** region are reported respectively for J, J-OX, J-300, J−F, J−M in Figure 1 and for J-UF and J-UM in Figure 2. As previously observed in case of a Polish gas-coking vitrain,[9] after performic acid oxidation, all the ν(C=O)

Table 4. Estimation of the Carboxylic and Ketonic Groups in the Case of Janina Coal from the Ratios $I_{\nu(C=O)}/I_{1600}$[a]

	ν(C=O) cm^{-1}	J	J-OX	J-300[b]	J-F	J-UF	J-M	J-UM
a	lactone 1760	0.54	1.01	0.92	0.26	0.26	0.65	0.56
b	ester 1741	sh	1.18	0.97	0.28	0.41	1.11	0.56
c	acid 1724	0.75	1.43	0	0.29	0.40	1.27	0.71
d	ketone 1707	0.83	1.31	1.07	0.93	0.52	1.22	1.05
e	ketone 1689	0.81	1.05	0.85 sh	0.53	0.53	0.70	0.88
f	amide 1670					0.62		
g	quinone 1660	0.84	0.89	0.82	0.89	0.79	0.85	1.04

[a] The letters a−g refer to the spectra (Figures 1 and 2). [b] In this case, the $I_{\nu(C=O)}/I_{1600}$ ratios are disturbed by aromatization secondary reactions which, by increasing I_{1600}, explain the decrease of all ratios in comparison with J-OX. The main result is the total disparition of the band at 1724 cm^{-1} and the persistence of the one at 1707 cm^{-1} in agreement with their assignment respectively to carboxylic and ketonic groups.

bonds already present in the parent coal J (Figure 1a) are located at the same wavelengths in the oxidized sample J-OX (Figure 1b). Their intensities are significantly increased, particularly for lactone, ester, acid, and ketone functions, the ν(C=O) region (1800−1640 cm^{-1}) being of greater intensity than the ν(C=C) region (1640−1550 cm^{-1}).

On the basis of previous works,[7,9] the assignments of the main bands are summarized in Table 4 where the letters a−g refer to the spectra in Figures 1 and 2. The intensities of some of the bands ν(C=O) are greatly modified either after pyrolysis at 300 °C (J-300) or after reaction with (J-UF, J-UM) or without (J−F, J−M) urea.

A semiquantitative estimation of each specific group in the different samples was made choosing the ν(C=C) band at 1600 cm^{-1} as reference and calculating the intensity ratios $I_{\nu(C=O)}I_{1600}$ on the deconvoluted spectra. It is interesting to point out the presence of a band at 1670 cm^{-1} (band f) assigned to the amide group and detected as a shoulder only in case of sample J-UF. In addition, a weak but sharp band at 2214−2220 cm^{-1} (ν(C≡N)) is significantly present in the spectra of J-UF, J-UM, and all other nitrogen-enriched samples. It remains after heating at 450 and 600 °C.

The spectrum of the lignite KA is not reported because, after deconvolution, only a large band is characterized around 1704 cm^{-1}, overlapping all the other ν(C=O) bands. As KA was treated without pretreatment with performic acid, the ν(C=O) region is of lesser intensity than the ν(C=C) region. After reaction with urea, the only characteristic features are a sharp ν(C≡N) band at 2210 cm^{-1} and a new band at 1675 cm^{-1}, assigned to the amide group. It is assumed that the difficulties occurring in the deconvolution are due to an absorption ability of these samples which disturbs the Kubelka−Munk fonction.

XPS Data. The XPS data for C$_{1S}$ are given in Table 5, in relative intensities of C$_{1S}$ peaks expressed in percent of ΣC$_{1S}$. In the same way, the N$_{1S}$ data are given in Table 6 in relative intensities of N$_{1S}$ peaks expressed in % of ΣN$_{1S}$. Furthermore, in order to estimate the increase of nitrogen enrichment in each sample, the relative intensities of XPS N$_{1S}$ peaks, expressed in percent of ΣC$_{1S}$, are also reported in parentheses in Table 6.

(9) Cagniant, D.; Bimer, J.; Salbut, P. D.; Gruber, R.; Henrion, P.; Krzton, A. *Fuel* **1994**, *73*, 871.
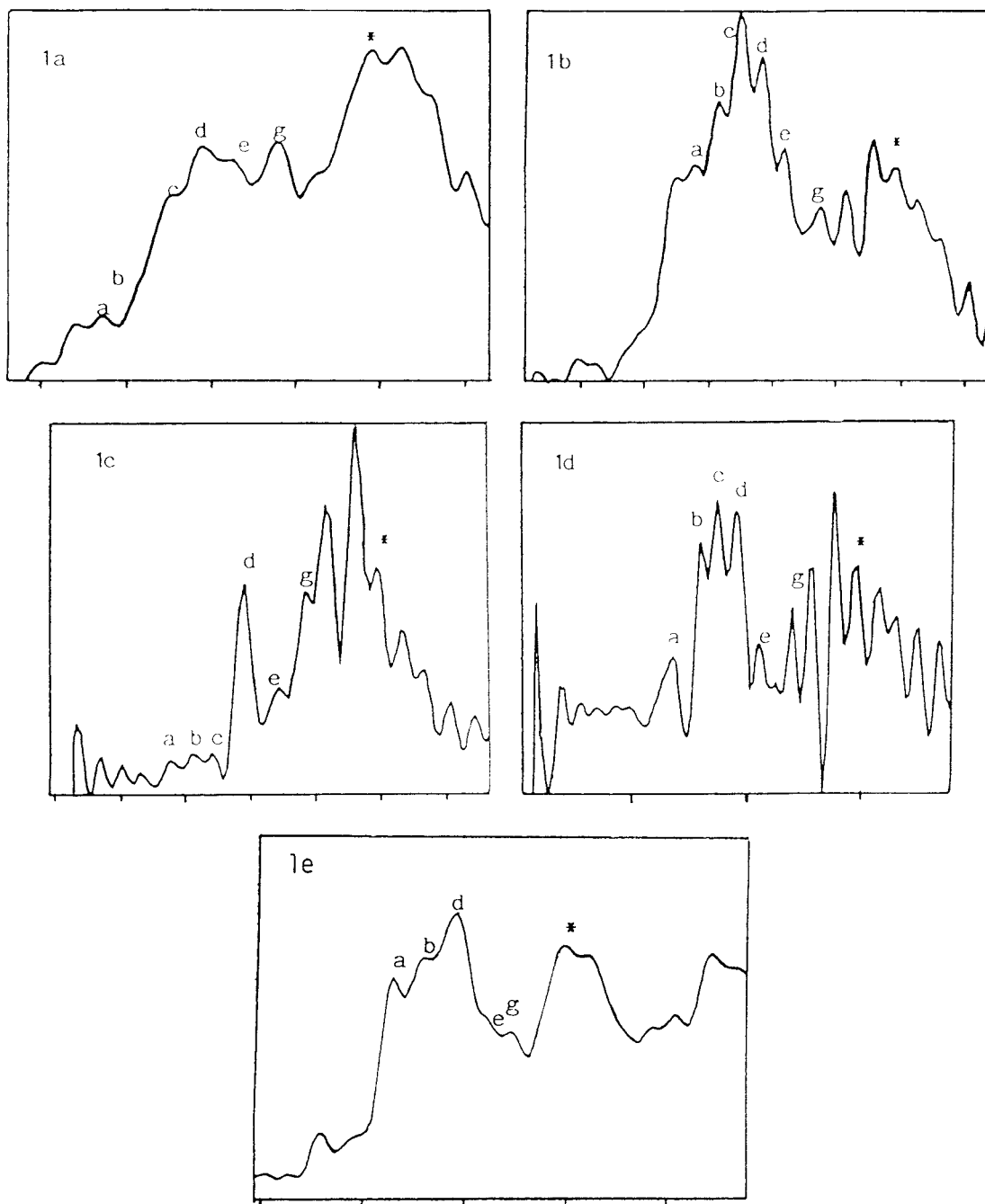
Figure 1. DRIFT deconvoluted spectra, 1800−1540 cm^{-1} region: (a) Janina coal; (b) J-OX; (c) J−F; (d) J−M; (e) J-300. (*) Reference 1600 cm^{-1}. The letters a−g as in Table 4.

The XPS spectra of N_{1S}, before and after curve fitting, are presented in Figure 3 in case of J-OX, J-UM, and J-UF and in Figure 4a,b after thermochemical treatments of J-UF and KA-UF. The six hypothetical hidden C peaks fitting the XPS unresolved C_{1S} spectra (CI to CVI) and, in the same way, the four N peaks (N6, N5, NQ, NX) fitting the XPS unresolved N_{1S} spectra were selected on the basis of the most recent literature information recalled in Tables 7−9. Surface species were referred to saturated hydrocarbon at C_{1S} at 285.0 eV. Binding energies of curve synthesis of C_{1S} and N_{1S} signals are reported in Tables 5 and 6. The estimated standard deviation of surface species was in average ±0.2 eV. All parameters of the curve fit were left free except the peak position (cf. Table 6 ± 0.2 eV), the peak

width at half-height (1.8 ± 0.2 eV), and the peak shape (mixing of 0−30% Lorentzian with Gaussian peaks).

Discussion

The discussion will be focused on the following points: the determinations of the functional groups implied in the reaction with urea, of the main nitrogen functionalities thus obtained, and of their behavior during thermochemical treatments.

Determination of the Functional Groups Implied in the Reaction with Urea. The DRIFT analysis is well suited for this purpose. The efficiency of the performic acid oxidation is obvious from the comparison of the spectra of J and J-OX. The increase
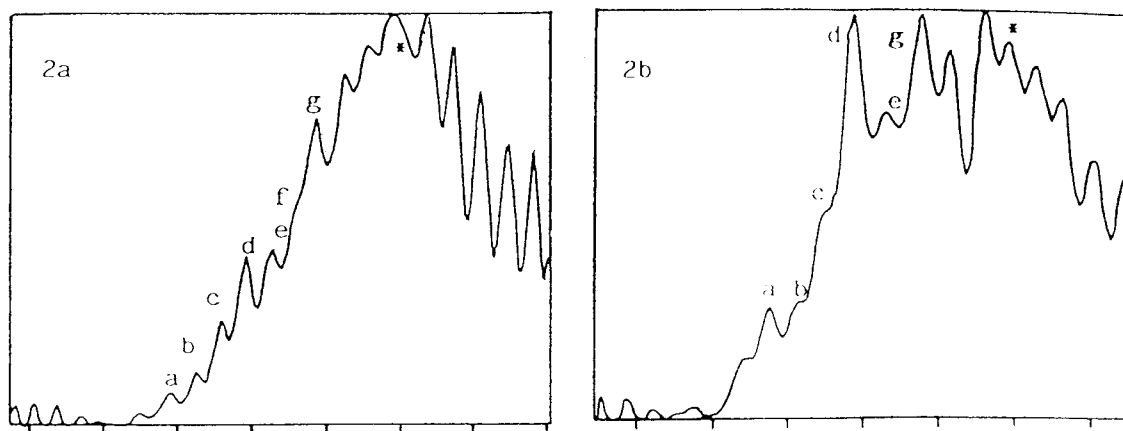
Figure 2. DRIFT deconvoluted spectra, $1800-1540$ cm^{-1} region. (a) J-UF; (b) J-UM. (*) Reference 1600 cm^{-1}. The letters a$-$g as in Table 4.

Table 5. Relative Intensities of XPS C$_{1S}$ Peaks Expressed in Percent of ΣC$_{1S}$[a]

sample	C I BE = 285.0 eV	C II 286.6 eV	C III 288.0 eV	C IV 289.2 eV	C V 290.5 eV	C VI 291.5 eV
J	89	8	1.5	0.5	0	1
J-OX	54	23	13	9	0	
J-300	81	12	4	2	0	1
J-F	80	14	3	2	0	1
J-UM	88	8	2	0	1	1
J-UF	72	18	7	0	2	1
J-UF 450	72	16	6	0	4	2
J-UF 600	74	16	6	0	2	2
J-UF 700	68	22	5	0	2	3
J-UF H$_2$O 700	66	20	6	0	5	3
KA	86	8	3	3	0	0
KA-300	83	10	5	2	0	0
KA-UF	82	13	4	0	0	1
KA-UF 450	79	12	5	0	2	2
KA-UF 600	76	13	5	0	4	2
KA-UF 700	71	17	5	0	4	3

[a] According to literature data, the number of peaks is fixed at 6 (cf. Table 7) with the following parameters: peak position ±0.2 eV, peak width at half-height 1.8 ± 0.2 eV, peak shape mixing of $0-20\%$ Lorentzian with Gaussian peaks. All binding energies were referenced to C$_{1S}$ at 285 eV.

Table 6. Relative Intensities of XPS N$_{1S}$ Peaks (atom%) and (in Parentheses) Expressed in % of ΣC$_{1S}$[a]

sample	N6 BE = 398.8 eV	N5 400.5 eV	NQ 401.3 eV	NX 403.4 eV	ΣN$_{1S}$
J	17 (0.82)	48 (2.34)	24 (1.20)	10 (0.50)	(4.85)
J-OX	21 (0.59)	40 (1.14)	27 (0.77)	11 (0.32)	(2.82)
J-300	28 (0.62)	52 (1.16)	14 (0.31)	6 (0.13)	(2.21)
J-F	19 (2.10)	64 (7.10)	14 (1.60)	2 (0.22)	(11.11)
J-UM	37 (5.13)	54 (7.49)	5 (0.75)	4 (0.56)	(13.93)
J-UF	46 (16.59)	41 (14.77)	11 (3.91)	2 (0.84)	(36.12)
J-UF 450	51 (14.41)	39 (10.88)	7 (2.02)	3 (0.77)	(28.08)
J-UF 600	50 (12.04)	33 (7.83)	12 (2.90)	5 (1.27)	(24.04)
J-UF700	51 (10.66)	24 (5.09)	18 (3.70)	7 (1.48)	(20.93)
J-UF H$_2$O 700	38 (4.72)	26 (3.20)	24 (2.97)	12 (1.41)	(12.29)
J-UF H$_2$O 800	45 (3.37)	23 (1.76)	29 (2.15)	3 (0.23)	(7.51)
KA	24 (0.46)	54 (1.03)	13 (0.25)	9 (0.17)	(1.91)
KA-300	40 (0.81)	60 (1.22)	0 (0.00)	0 (0.00)	(2.03)
KA-UF	52 (14.78)	43 (12.29)	3 (0.89)	2 (0.56)	(28.52)
KA-UF 450	55 (12.34)	31 (7.24)	8 (1.90)	5 (1.07)	(22.55)
KA-UF 600	55 (8.48)	32 (4.97)	8 (1.31)	5 (0.74)	(15.51)
KA-UF 700	52 (7.19)	29 (3.94)	14 (1.86)	5 (0.77)	(13.76)
KA-UF H$_2$O 700	41 (2.32)	24 (1.40)	28 (1.62)	7 (0.38)	(5.72)

[a] According to literature data, the number of peaks is fixed at 4 (cf. Table 8) with the following parameters: peak positions ±0.2 eV, peak width at half-height 1.8 ± 0.2 eV, peak shape mixture of $0-20\%$ Lorentzian with Gaussian peaks. All binding energies were referenced to C$_{1S}$ at 285 eV.

of lactone/ester, acid, and ketone functions can be estimated from the results presented in Table 4.

Before examination of the reaction with urea, it was necessary to take into account the role of the temperature (300 °C) and of the behavior, in the same condi-

tions, of the solvents. If the carboxylic acids are destroyed by pyrolysis alone at 300 °C, in the absence of solvents and urea (spectrum J-300, Figure 1e and Table 4), it is clear from the ratio $I_{\nu(COOH)}/I_{1600}$ that only a weak decrease (1.43 in J-OX to 1.27 in J-M) is
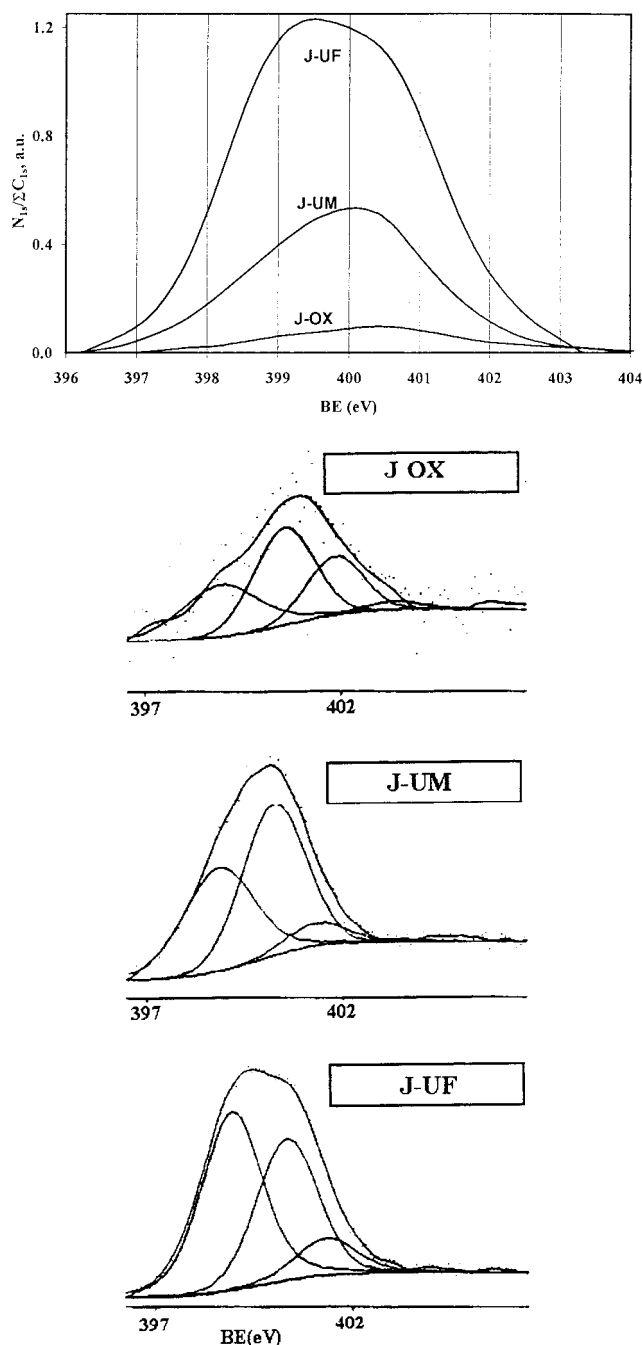
Figure 3. XPS N_{1s} spectra of J-OX, J-UM, and J-UF and relevant XPS curve resolution results.
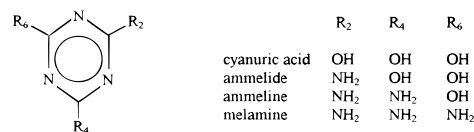
observed by heating in the autoclave at 300 °C in methanol (M), a greater decrease (1.43 in J-OX to 0.29 in J-F) being observed with *N,N*-dimethylformamide (F). The following conclusions can be drawn: if a partial decarboxylation cannot be ruled out, the results with J-M proved that in the presence of this solvent in autoclave, the carboxylic functions remain mainly present and are able to react with urea. It is the same for ester groups but lactones are partially hydrolyzed. In case of J-F the great decrease of ester/lactone and acid groups and also ketones (1689 cm^{-1}) proved the reaction of this solvent with these groups. It is suggested that DMF can have a catalytic effect on the hydrolysis of ester/lactone groups but the reaction with acids and ketones remains not clear. The reactivity of DMF is in agreement with the increase of the nitrogen amounts going

from 1.3% in J-OX and J-M to 5.1% in J-F. By analogy with the thermal behavior of formamide giving rise to CO and NH_3, the formation of *N,N*-dimethylamine could be considered and this nitrogen derivative could react also with some of the active sites of J-OX.

Concerning the Reaction with Urea, significant conclusions can be drawn in connection with the determination of the implied functional groups.

At first, **the reactivity of urea is solvent dependent** as can be seen by comparison of the results presented in Table 4 for J-UF and J-UM, the ratios being always lesser in the case of J-UF, except for quinones which seem not concerned by the reaction whatever the conditions. This observation can be related to the difference in the yields and in the nitrogen amount (Table 2), 135% and 16.7%, respectively, for J-UF and 86.5% and 7.2%, respectively, for J-UM, showing a lesser reactivity of urea in methanol than in DMF.

The second interesting point, proved by the comparison between J-OX and J-UF (or J-UM) is **the reactivity of urea with ester/lactone and acid functions** with the accompanying formation of nitrile (band around 2220 cm^{-1}) and of a new band detected around 1670 cm^{-1} as a shoulder of the quinone band at 1660 cm^{-1} and assigned to amide. Indeed, the modifications afforded in the spectrum of J-OX by reaction with urea are striking as well as the differences between the spectra of J-UF and J-UM. Another interesting point is the behavior of the ketonic band at 1707 cm^{-1} which also participates in the reaction, mainly in J-UF. More difficult is **the identification by DRIFT of the nitrogen functionalities resulting of the reaction with urea**. These difficulties are due to the complexity of the material and to the variety of the N reagents which can arise from urea itself and are able to react also with the coal. Indeed, it is clear that the main reaction is the formation of amide which implies carboxylic and ester/lactone groups. Unfortunately, this function is difficult to identify either in the 3600−3000 cm^{-1} region as explained before or in the 1800−1540 cm^{-1} region. If bands near 1660−1620 cm^{-1} are expected to be strong in pure organic compounds, they will be weak in coals and will overlap the quinonic band at 1660 cm^{-1} found in all samples. Nevertheless, it is interesting to note the shoulder at 1670 cm^{-1} assigned to amide only in the case of J-UF (Table 4). The best proof of the formation of amide is done by the weak $\nu(C\equiv N)$ vibrations present in all nitrogen-enriched coals. Amides can be formed not only with urea but also with all byproducts which can be foreseen by urea treatment in our experimental conditions. This point was already discussed [5] and several products were suggested like the following:

	R_2	R_4	R_6
cyanuric acid	OH	OH	OH
ammelide	NH$_2$	OH	OH
ammeline	NH$_2$	NH$_2$	OH
melamine	NH$_2$	NH$_2$	NH$_2$

All these triazines were identified in the byproducts of the reaction. Many other derivatives can be speculated by further reaction of amide functions with ketonic groups in suitable position, giving rise to heterocyclic
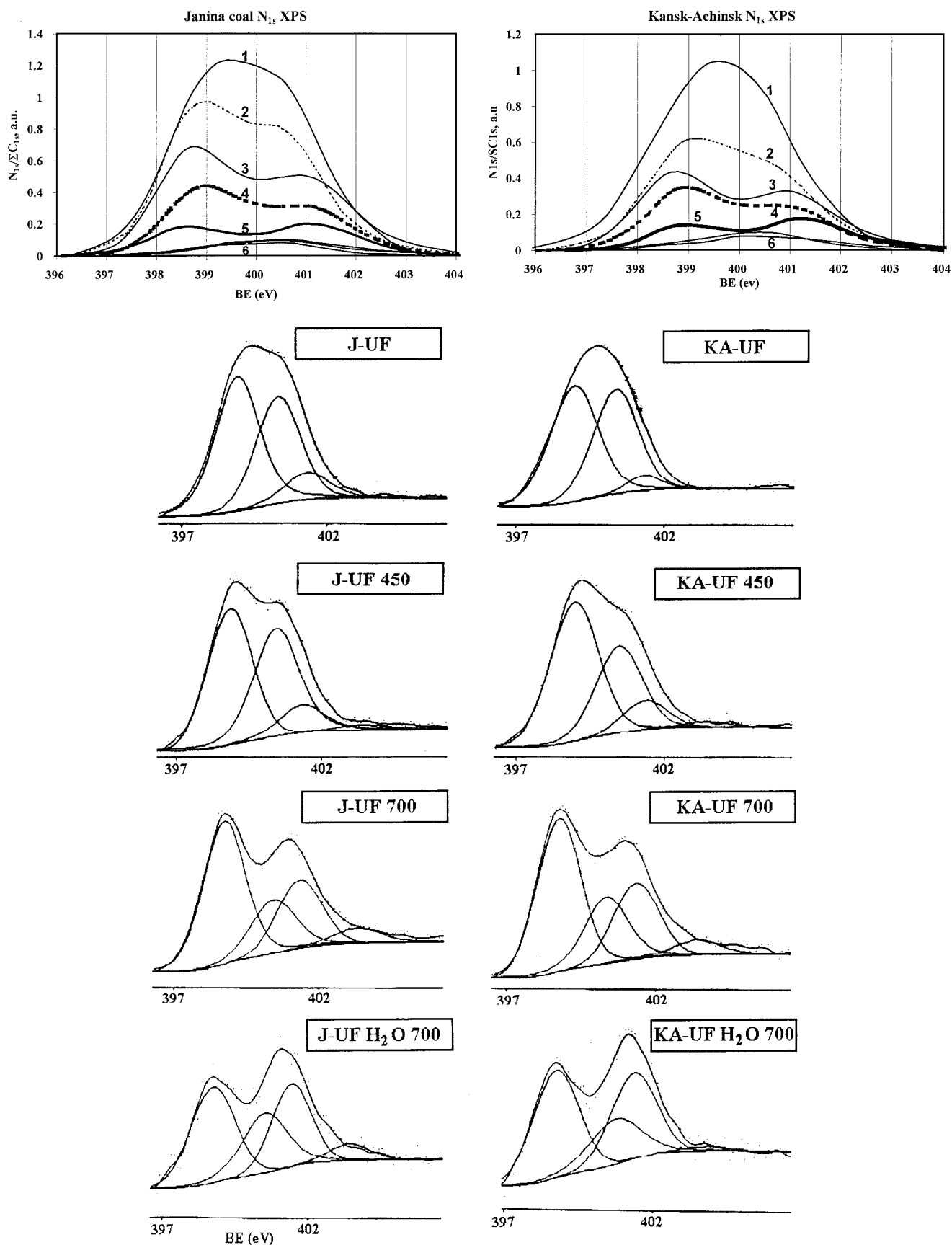
Figure 4. Variation of the XPS N_{1S} spectra according to the activation treatments and relevant XPS curve resolution results. (a) Janina coal series: (1) J-UF; (2) J-UF 450 °C; (3) J-UF 600 °C; (4) J-UF 700 °C; (5) J-UF$_{H_2O}$ 700; (6) J, J-OX, J-300. (b) Kansk-Achinsk lignite series: (1) KA-UF; (2) KA-UF 450 °C; (3) KA-UF 600 °C; (4) KA-UF 700 °C; (5) KA-UF $_{H_2O}$ 700 °C; (6) KA, KA-300.

Table 7. XPS C_{1S} Binding Energies[2,10−12] (eV)

C_{1S}	assignment	BE (eV)
C I	hydrocarbons (aliphatic,aromatic)[a]	285.0
C II	C−O single bond: ether, phenol, C associated with N	286.6
C III	C=O in carbonyl,quinone, C associated with N	288.0
C IV	carboxyl groups	289.2
C V	shake-up satellite Π−Π	290.5
C VI	shake-up satellite Π−Π	91.5

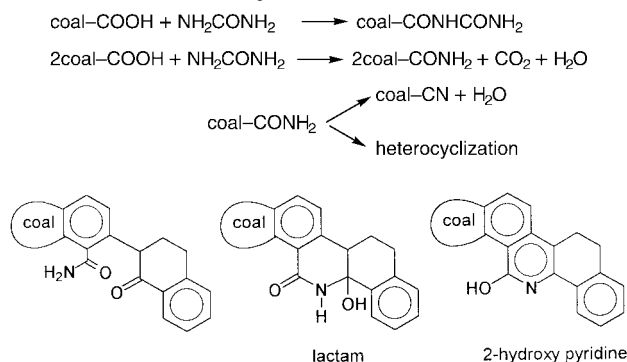[a] Nonfunctionalized carbons of polyaromatics 284.3 ± 0.1 eV, aliphatic carbons in carbon black 285.2 ± 0.2 eV.

Table 8. XPS N_{1S} Binding Energies in Carbonaceous Materials

BE (eV)	assignment	ref
398.7 ± 0.3	pyridinic nitrogen N6	13−15, 16−22, 24
399.1−(399.4)	amino groups	15, (26)
	pyridinic nitrogen	21
400.5 ± 0.3	pyrrolic nitrogen N5	13−15, 16−22, 24
401.3 ± 0.3	quaternary nitrogen N−Q	13−15, 16−22, 24
	protonated pyridinic nitrogen	13
	nitrogen in graphene layers (chars)	13
401.6 ± 0.3	protonated amines	19
401.9	methyl pyridinium	21
402−405	oxidized nitrogen N−X	13, 19, 24
402	pyridine *N*-oxide	19
402.7	pyridine *N*-oxide	18, 20, 21

Table 9. XPS N_{1S} Binding Energies in Model Compounds and in Activated Carbon Enriched by Specific Functional Groups

BE (eV)	assignment	ref
399.5−399.9	amides	2, 3
399.4−401	amines	2, 3
399.7	lactams, imides	2
397−400	nitrile	2
400.5	polyimides	23
400.6	pyridone N5	13, 17
402−403	N-protonated NQ	2
404.1	oxidized nitrogen NX	2

[a] In Tables 8 and 9, the binding energies are generally referenced to C_{1S} at 285 eV or next to 285 eV (284.8,[16] 284.6,[2,18,23,26] 280[19]). No data are done in refs 3, 20, and 21.

Scheme 1. Schematic Representation of Chemical Reactivity of Coal with Urea

coal–COOH + NH₂CONH₂ ⟶ coal–CONHCONH₂

2coal–COOH + NH₂CONH₂ ⟶ 2coal–CONH₂ + CO₂ + H₂O

coal–CONH₂ ⟶ coal–CN + H₂O

coal–CONH₂ ⟶ heterocyclization

lactam   2-hydroxy pyridine

compounds, as suggested in Scheme 1. In this view, it is interesting to point out the reactivity of the ketonic group at 1707 cm^{-1} in case of J-UF only.

In conclusion, DRIFT analysis is unable to identify nitrogen functionalities excepted amide and nitrile.

Determination of the Main Nitrogen Functionalities Obtained by Reaction with Urea. XPS is expected to be more useful for the determination of

nitrogen functionalities. It was applied either in coals,[14−18] chars,[13,14,19,22,24,25] activated carbons,[2] and nitrogen-enriched activated carbons [2,3] as well as in model compounds and their chars.[13,20,21,23] An exhaustive XPS study of the nitrogen transformations occurring in coal under different conditions of pyrolysis recently published brings up to date literature on this subject.[26] Reviewing these papers, it appears that four principal regions are noticed with peaks at binding energies (BE) of 398.7 ± 0.3, 400.5 ± 0.3, 401.3 ± 0.3, and 402−405 eV. Their assignments are summarized in Table 8. In fact, pyridinic N6, pyrrolic and pyridone N5, and quaternary pyridinic NQ and NX nitrogens are the main functionalities present in all coals and chars, in various proportions according to the rank and the carbonization procedures. A great lot of papers were devoted to the variation of these proportions during carbonization with the objective to determine how the distribution of nitrogen functionalities can affect the fractional conversion of coal and char-bound nitrogen to NO$_x$ emission.[13,14,18−22,27] In Table 9, the N_{1S} BE of various nitrogen functionalities are summarized, either for model compounds or for activated carbons submitted to the action, after preoxidation, of nitrogen reagents such as ammonia and amines, and then heat treated.[2] Unfortunately, taking into account the two large peaks N6 (398.7) and N5 (400.5) eV, it seems difficult to detect the presence of amide, amine, and nitrile in small amounts in the presence of N6 and N5 as main products. Indeed, the curve fitting of XPS spectra, considering amide contributions, was found not satisfactory by Desimoni et al.[27] to evidence the presence of this function on the surface of poly(acrylonitrile)-based fibers. In the same way, the introduction of a fifth peak at 399.6 eV (amine, amide, nitrile) was not successful in the curve fitting of the J-UF N_{1S} spectrum.

(10) Perry, D. L.; Grint, A. *Fuel* **1983**, *62*, 1024.
(11) Hontoria-Lucas, C.; Lopez Peinado, A. J.; de Lopez-Gonzales, D.; Rojas-Cervantes, M. L.; Martin-Aranda, R. M. *Carbon* **1995**, *33*, 1585.
(12) Papirer, E.; Lacroix, R.; Donnet, J. B.; Nanse, G.; Fioux, Ph. *Carbon* **1994**, *32*, 1341.
(13) Pels, J. R.; Kapteijn, F.; Moulijn, J. A.; Zhu, Q.; Thomas, K. M. *Carbon* **1995,** *33*, 1641.
(14) Kambara, S.; Takarada, T.; Toyoshima, H.; Kato, K. *Fuel* **1995**, *74*, 1247.
(15) Wojtowicz, M. A.; Pels, J. R.; Moulijn, J. A. *Fuel* **1995**, *74*, 507.
(16) Kelemen, S. R.; Gorbaty, M. L.; Vaughn, S. N.; Kwiatek, P. J. *Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1993**, *38* (2), 384.
(17) Kelemen, S. R.; Gorbaty, M. L.; Kwiatek, P. J. *Energy Fuels* **1994**, *8*, 896.
(18) Zhu, Z.; Gu, Y.; George, S. C.; Wilson, M. A.; Huggins, F. E.; Huffman, G. P. In *Coal Science*; Pajares, J. A., Tascon, J. M. D., Eds.; Elsevier Science B. V.: New York, 1995; Vol. II, p 1681.
(19) Boavida, D.; Gulyurtlu, I.; Lobo, L. S. In *Coal Science*; Pajares, J. A., Tascon, J. M. D., Eds.; Elsevier Science B. V.: New York, 1995; Vol. II, p 751.
(20) Piwowarska, Z.; Stanczyk, K.; Dziembaj, R. *Coal Science*; Pajares, J. A., Tascon, J. M. D., Eds.; Elsevier Science B. V.: New York, 1995; Vol. 2, p 1693.
(21) Bagreev, A.; Strelko, V.; Lahaye, J. *Proc. Eur. Conf. "Carbon 96", Newcastle upon Tyne, U.K.* **1996**, 527.
(22) Ohtsuka, Y.; Watanabe, T.; Mori , H.; Asami K. *Coal Science*; Pajares, J. A., Tascon, J. M. D., Eds.; Elsevier Science B. V.: New York, 1995; Vol. II, p 1689.
(23) Nakahashi, T.; Konno, H.; Inagaki, M. *Proc. Eur. Carbon Conf. "Carbon 96", Newcastle upon Tyne U.K.* **1996**, 385.
(24) Chambrion, Ph.; Suzuki, T.; Langerame, F.; Watts J. F. *J Electron Spectrosc. Relat. Phenom.* **1997**, *85*, 179.
(25) Watt, M.; Allan, W.; Flechter, Th. *Coal Science*; Pajares, J. A., Tascon, J. M. D., Eds.; Elsevier Science B. V.: New York, 1995; Vol. II, p 1685.
(26) Kelemen, S. R.; Gorbaty, M. L.; Kwiatek, P. J.; Fletcher, T. H.; Watt, M.; Solum, M. S.; Pugmire, R. J. *Energy Fuels*, **1998**, *12*, 159.

The XPS atom % data of C_{1S} (Table 5) and N_{1S} (Table 6) confirm the results obtained by DRIFT for the structural modifications of J coal going to J-OX and J-300. By comparison with literature data,[13,14] J coal itself is characterized by a greater value of NQ and lesser values of N5 (48%) and N6 (17%) than other coals of the same rank. Though it was claimed recently that there do not appear to be any strong trends in the concentration of the various nitrogen functionalities with the rank of the coal (mean values: N6 20−40%, N5 50−80%, NQ 0−20%),[28] it was also shown that NQ and N6 decrease roughly with increasing carbon content while N5 shows the opposite trend [14.]

After performic acid oxidation, going from J to J-OX, the increase of the XPS peaks (Table 5), corresponding to carbon−oxygen linkages (C II, C III, C IV) are in agreement either with the analytical data reported in Table 1 for the carboxylic group or with the DRIFT data (Table 4). In the same time, the decrease of C I (89 to 54%) evidences the oxidation of aromatic and aliphatic hydrocarbons groups. The increase of the relative proportions of quaternary nitrogen NQ at 401.3 eV (24 to 27%) is in agreement with the participation of pyridinic nitrogen associated with nearby located carboxylic groups[13,17] whose increase exceeds the decrease of phenolic groups.

After pyrolysis at 300 °C (J-300), the partial decarboxylation of carboxylic groups is proved going from J-OX to J-300, by the decrease of C IV at 289.2 eV (9 to 2%) and the decrease of NQ (0.77 to 0.31%). It is also interesting to notice the great increase of C I at 285.0 eV (54 to 81%), which can be put in relation with aromatization due to regressive side reactions during heating at 300 °C as previously reported [9] and also to the loss of carbon atoms in the oxygen functional groups. Indeed, in aromatic network a peak at 284.5 eV was assigned to C−C aromatic bond.

Concerning the reaction with urea, the XPS data bring a significant contribution to the structural modifications and to the nitrogen functionalities introduced in the coal sample matrix (J-UF, J-UM, KA-UF), starting from J-OX and KA.

At first, the case of J-F needs a discussion since the analytical data (N 5.1%) and the DRIFT analysis suggest the reaction of DMF with some active sites of J-OX. The N_{1S} spectrum (Table 6) is in agreement with the enrichment in nitrogen (ΣN_{1S} 11.11). It is striking that the main nitrogen peak with a BE of 400.5 eV is in the range of many nitrogen functions (cf. Table 9) and could correspond to amide. The C_{1S} spectrum (Table 5) is very similar to the one of sample J-300 and confirms the decrease of carboxylic groups (C IV). In addition, the results of O_{1S} XPS, expressed in % of ΣC_{1S} are presented in Table 10 with those of J-OX, J-UM, and J-UF for comparison. The curve fitting was made with the contribution of two peaks, 531.7 and 533 eV, assigned respectively to oxygen doubly bound to carbon and oxygen singly bound in aromatic structures according to literature data (ref 11 and references herein). The reactivity of the oxygenated groups present in J-OX is

Table 10. Relative Intensities of XPS O_{1S} Expressed in Percent of ΣC_{1S}

sample	O_1 BE = 531.7 eV	O_2 533.5 eV	ΣO_{1S}	O_1/O_2
J-OX	64.3	44.6	110.6	1.44
J-F	16.8	15.8	32.5	1.07
J-UM	19.8	15.0	35.5	1.32
J-UF	17.2	10.7	28.0	1.61

well evidenced if we consider the values of ΣO_{1S} which show the same trends than the O % (Tables 1 and 2).

1. The **reactivity of urea** with carboxylic groups is evidenced by the total disparition of CIV in J-UF, J-UM and KA-UF (Table 5).

2. Furthermore, the XPS N_{1S}/C_{1S} atom ratios and the N/C atomic ratios of the samples (before and after thermochemical treatments) are linearly correlated, suggesting that nitrogen is homogeneously distributed in the carbon matrix, without any strong increase or depletion of nitrogen concentrations at the surface relative to the bulk sample.[5]

3. The enrichment in all forms of nitrogen, but mainly in N6 and N5, is obvious from the relative intensities of XPS N_{1S} peaks expressed in percent of ΣC_{1S} (Table 6) which go up for example for N6 from 0.6 (J-OX) to 16 (J-UF) and from 1 (J-OX) to 15 (J-UF) for N5. Considering the nitrogen types relative proportions, the reactivity of carboxylic groups which disappeared in J-UF explains the decrease of NQ assigned to pyridine protonated through formation of a H bridge with nearby hydroxyl groups.[13,17] The decrease of NQ and also of NX explain the increase of N6 as N5 remains constant.

The same trends are also observed in the KA series.

4. The difference of reactivity of urea, according to the solvent, already suggested by the yields and the DRIFT analysis, is confirmed by XPS: the enrichment in nitrogen functionalities is significantly lesser in J-UM than in J-UF, as shown by the relative intensities of XPS N_{1S} in percent of ΣC_{1S}. Furthermore, the N_{1S} atom % of N6 and N5 are inversed going from J-UF (N6 > N5) to J-UM (N5 > N6) as clearly evidenced in Figure 1. It is suggested that DMF is more favorable to heterocyclization reactions.

In conclusion, the reaction of J-OX and KA with urea gives rise to enriched nitrogen structures with N_{1S} BE of 398.7 ± 0.3, 400.5 ± 0.3, 401.3 ± 0.3, and 402−405 eV. The first two are the most important and are assigned respectively to pyridinic (N6) and pyrrolic and pyridone (N5) heterocyclic compounds, though the presence of other nitrogen functionalities, with BE between 399 and 401 cannot be ruled out in this range according to Table 9. Among them, amide and nitrile groups were detected by DRIFT. Besides these main structures, a weak increase of quaternary nitrogen NQ and protonated NX is also observed.

Thermal Behavior of the Nitrogen Functionalities: Carbonization and Steam Activation. The fate of nitrogen functionalities in coal during pyrolysis was studied by several authors[13−16,18,19,24,26] mainly in relation with the NO$_x$ emission and, particularly, by XPS. The results are dependent on the conditions of pyrolysis. For example, Kelemen[16,17] using **low-severity pyrolysis** (400−427 °C) found that the levels of NQ went down while the forms of N6 nitrogen went up, the

(27) Desimoni, E.; Salvi, A. M.; Langerame, F.; Watts, J. F. *J Electron Spectrosc. Relat. Phenom.* **1997**, *85*, 179.
(28) Varey, J. E.; Hindmarsh, Ch. J.; Thomas, K. M. *Fuel*, **1996**, *75*, 164.

sum NQ + N6 being preserved. The decrease of NQ was correlated with the loss of oxygen (such as in COOH groups). Similar results were obtained by Wojtowicz et al.[15] But these authors using **high-severity pyrolysis** (900 °C) showed that, in chars, the originally strong N5 peak virtually disappears in favor of NQ and N6, NQ becoming the strongest peak. They explained the increase of N6 by a transformation of the original pyrrolic N5 into pyridinic forms.

The same conclusions were presented by Watt et al.[26] during rapid coal pyrolysis. Pels et al.[13] claimed that NQ in chars is unlikely to represent protonated pyridinic N since carboxylic and phenolic groups have been decomposed to gaseous molecules. They suggested that NQ represents nitrogen atoms included in polyaromatic structures with their positive charges delocalized in the π-electron system ("graphene layers"), in "center" and "valley" positions, the "top" position being a pyridinic N6 form. This hypothesis, based on the relation between BE and the electron density at the nitrogen atoms,[29] is confirmed by the MO calculations of Boutique et al.[30] Then, it can be concluded that in mild conditions NQ decreases owing to the loss of oxygen, but reappears in severely heat-treated chars due to the formation of N graphene layers. The data reported in Table 6 are in very good agreement with the above results, if we compare J-UF and its heat-treated products. The relative intensities of XPS N_{1S} peaks, expressed in percent of ΣC_{1S}, show a loss of all forms of nitrogen which increases with the severity of the treatments. The relative distribution of the nitrogen functionalities depends of the reaction conditions as evidenced by the spectra of J-UF$_{450}$, J-UF$_{600}$, J-UF$_{700}$ and J-UF$_{H_2O}$ 700 (Table 6, Figure 4a). (1) **By heat treatments**, as the pyrolysis temperature increases (450 to 700 °C), the main fact is the increase of NQ. Pyrrolic N, stable until 450 °C, disappears gradually but pyridinic N is remarkably constant. It is suggested that there is an equilibrium between the partial conversion of N5 in N6 (through oxygen loss of pyridone N) and partial conversion of N6 in NQ. (2) By **steam activation**, the losses of all forms of nitrogen are greater than by heat treatments and more particularly for N6, especially when the temperature increases. At the same time the relative proportion of NQ increases, being now greater than the one of N5, owing to the insertion of nitrogen in graphene layers. The same trends are observed in the KA series.

The predominance of pyridinic forms of nitrogen (N6, NQ) and particularly in graphene layers appears to be the most interesting feature of the chars obtained from nitrogen-enriched coals, in relation with their adsorption abilities.[5]

Conclusion

This paper has attempted to introduce nitrogen functionalities in the network of two coal samples,

acting as precursors of active carbon. The originality of the process is that the nitrogen enrichment occurs before the carbonization and activation steps. A subbituminous Polish coal (J), pretreated with performic acid, and a Russian lignite (KA) were treated with urea, in an autoclave at 300 °C, in either *N,N*-dimethylformamide (DMF) or methanol (M) as solvents. In DMF, the yields were particularly high (around 130%).

A DRIFT analysis showed that ester/lactone, carboxylic acid groups, present in the initial samples, are mainly concerned in the reaction with urea. If the formation of amides is foreseen, their identification is disturbed by the presence of other functional groups, absorbing in the range of amide I and II bands. Nevertheless, the identification of nitrile functions proved the occurrence of amides in the first step of the reaction. Furthermore, the participation of ketonic function (ν(C=O) 1707 cm^{-1}), in the reaction carried out in DMF, suggests the possibility of heterocyclization with the transient amides.

By XPS analysis, the presence of several nitrogen functionalities were detected, before and after activation. Their relative proportions were calculated from the area ratios under the peaks. This procedure,which is sufficient for the comparison of the samples, gives an estimation of the N_{1S} atom %. The nitrogen enrichment of the coal samples is well evidenced by the relative intensities of XPS N_{1S} peaks expressed in percent of ΣC_{1S}. The assignment of the nitrogen forms was made on the basis of literature data in the field of coals and chars. Four groups were characterized according to the binding energies 398.7 ± 0.3, 400.5 ± 0.3, 401.3 ± 0.3, and $402-405$ eV, assigned respectively to pyridinic N6, pyrrolic and pyridone N5, and quaternary forms of pyridine NQ and NX. It is necessary to point out that many nitrogen functions have their binding energies in the range $399-400$ eV. As they are located between the two main pyridinic N6 and pyrrolic N5 peaks, they are difficult to detect in low amounts.

The results obtained after thermochemical treatments are in agreement with recent studies showing that in chars the pyridinic forms N6 and NQ increase as the pyrrolic forms N5 decrease. This is explained by condensation reactions (i.e., carbazole derivatives) giving rise to nitrogen incorporated in graphene layers.

The efficiency of the procedure described in this paper to obtain active carbons is pointed out by the properties of the chars which are characterized by considerable effective surface area, with values up to $850-1000$ m^2/g (S_{BET}) and with excellent sulfur removal and thermal regeneration abilities.[5]

(29) Nordberg, R.; Albridge, R. G.; Bergmark, T.; Ericson, U.; Hedman, J.; Nordling, C.; Siegbahn, K.; Lindberg, B. J. *Ark. Kem.* **1967**, *28*, 257.

(30) Boutique, J. P.; Fripiat, J. G.; Delhalle, J.; Pfister-Guillouzo, G.; Ashwell, G. J.; Verbist, J. J. *J. Am.Chem. Soc.* **1984**, *106*, 4374.