

NITROGEN XANES STUDIES OF FOSSIL FUELS.

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All the major nitrogen chemical structures, present in coals of varying ranks have been quantitatively determined using nitrogen X-ray Absorption Near-Edge Spectroscopy (XANES). XANES spectra of these samples exhibit several distinguishable resonances which can be correlated with characteristic resonances of particular nitrogen chemical structures thereby facilitating analysis of these complicated systems. Aromatic nitrogen compounds abound in the coals; no evidence of saturated amine is found. Pyrroles, pyridines, pyridones, and aromatic amines are found in coal; of these, pyrrolic structures are the most prevalent. The low rank (high oxygen) coals have large quantities of pyridone and smaller quantities of pyridine; this suggests that with increasing maturation of coal, pyridone loses its oxygen and is transformed into pyridine. Aromatic amines are present at low levels in coals of all rank. Preliminary studies on kerogens and bitumens indicate the presence of pyrrole, pyridone, pyridine, and aromatic amine structures; some saturated amine may also be present. Other models containing multiple oxygen and nitrogen sites have been investigated and they may be present in bitumens and low rank coals in small quantities.

INTRODUCTION

Coal is a valuable natural resource. The origin of the organic part of coal stems from plant materials, which over geological time, become compacted, and mature into coal beds due to severe physical conditions such as heat and pressure. Heteroatoms such as nitrogen and sulfur present in fossil fuels pose major problems in the effective usage of the resource. Heteroatoms in coals often act as catalyst poisons; upon combustion of coal, heteroatoms evolve gases which are harmful to the environment. Heteroatoms also help in the determination of solubility and chemical properties of coal. Heteroatoms also provide markers to follow evolution of the chemistry of coal with maturation.

The rank of coal by definition is a measure of the degree of metamorphism of coal beds, higher rank indicating greater maturation. During the process of maturation, moisture and chemically bound oxygen are expelled from coal beds, and consequently, higher rank coals have lower oxygen and moisture content than lower rank coals. Aromaticity increases with maturation; carbon aromaticity can range from 90% in a high rank coal to 40% in a low rank coal. Oxygen, which is the major heteroatom present in coals, occur as furan analogues, phenolic analogues, and etheric groups. Sulfur is present in coals both in aromatic and saturated forms. X-ray Absorption Near-Edge Structure (XANES) spectroscopy has been used for the last ten years to successfully determine the major sulfur chemical forms present in coals(1-4). Thiophenic (aromatic) sulfur is the dominant type, followed by sulfidic (saturated) type of sulfur. Oxygen containing sulfur forms such as sulfoxides, sulfones and sulfates are also found in coals, as well as mineral pyritic sulfur(2,4).

Kerogens are the organic insoluble, and bitumens are the organic soluble fractions of oil shales. The maturation process is somewhat similar to coal maturation; however, the maturation process of kerogen results in the production of crude oil. The H:C ratio of both immature kerogens and bitumens is typically ~1.5. Most of the carbon exists in aliphatic forms, and nitrogen and oxygen are present in greater amounts than sulfur.

Nitrogen has been difficult to study in fossil fuels; the high molecular weight of coals hinder chromatographic measurements, and the low concentrations of nitrogen in coal make spectroscopic measurements difficult. X-ray photoelectron studies in coal

have been informative, but the limited energy resolution hinders determination of all major forms of nitrogen(5,6). Nitrogen studies have also been difficult in kerogens and bitumens; insolubility of kerogens and complex structures of both kerogens and bitumens exacerbate the analysis of their nitrogen chemistry. XANES methodology is direct and nondestructive and has already been successful in determining the different nitrogen chemical functionalities in coal (7,8) and petroleum asphaltenes(9).

The present study determines all principal nitrogen structures of coals of varying ranks; this study has also been extended to provide preliminary information about immature kerogens and bitumens. Pyrrole and pyridine are found in these samples; in addition, presence of pyridones and aromatic amines, and very small amounts of saturated amines are also found. In the low rank coals, there is less or no pyridine but considerable amounts of pyridone; in the high rank coals the pyridones lose the oxygen and become converted into pyridines. Aromatic amines, and very small amounts of saturated amines are found in both the immature kerogens and bitumens. The XANES spectra of the kerogens and bitumens suggest the presence of pyrroles, pyridones, pyridines, and aromatic amines, and perhaps small amounts of saturated amines. During the maturation process of oil shales while some biomarkers remain unaltered, several starting chemical functionalities in immature oil shales alter significantly in the production of crude oil. Our present data on the immature kerogens and bitumens suggest that there may be considerable quantities of pyridone present in them; in that case, these structures disintegrate upon reaching the crude oil stage, as our previous studies on petroleum asphaltenes(9) did not show any occurrence of pyridone structures.

EXPERIMENTAL SECTION

Our nitrogen XANES data have been collected at beamline U4B at National Synchrotron Light Source at Brookhaven National Lab; this beamline has been constructed by AT&T Bell Labs(10). We used a monochromator consisting of a grating of 600 lines/mm, and a multi-element fluorescent Ge detector(11). The pressure inside the beampipe leading to the sample chamber, as well as the sample chamber was on the order of 10^{-9} - 10^{-10} torr; a cryopump and a turbo-molecular pump were used to maintain such high vacuum conditions. Samples were placed on nitrogen-free Scotch tape and were positioned inside the chamber by means of a load-lock system.

Our sample suite consisted of several coals, kerogens, bitumens, and nitrogen model compounds. The coals were obtained from Argonne National Laboratory Coal Sample Bank, IL(12), the kerogens and the bitumens were obtained from Western Research Institute, WY, and the model compounds from Aldrich Chemical Company. The models were used as received, without any further purification.

RESULTS AND DISCUSSIONS

Figure 1 plots the nitrogen XANES of several coals of varying ranks; the plots are in the order of increasing rank from the bottom to the top of the figure. Three principal regions are noticed, at ~400 eV, 402-405 eV, and 408 eV; the second region can be decomposed into three regions, at 402 eV, 403.3 eV, and 405 eV. The first resonance region at 400 eV varies considerably in intensity among the different coals, the intensity gradually increases as we move from a lower rank coal to a higher rank coal. The resonance feature at 402 eV, on the other hand, grows in intensity as we move from a higher rank to a lower rank coal. This suggests that as coal matures, the nitrogen structure identifiable with the 402 eV resonance feature transforms into a structure whose characteristic resonance is at 400 eV. The resonance feature at 403.3 eV in all the spectra varies less dramatically within different samples, and the 405 eV resonance intensity is rather small for all the plots.

Figure 2 shows the XANES plots of several kerogens and bitumens. Here we notice the three distinct resonance regions also observed in the coal plots, where the second region can be decomposed into three features. The peaks at 400 eV and ~403 eV are well pronounced in all the kerogen and bitumen spectra, the feature slightly shifted from 402 eV is very well pronounced in the bitumens, and the exact origin of such a peak is still under investigation.

XANES plots of a high rank coal, a low rank coal, a kerogen, a bitumen and analogues of five different nitrogen structures are shown in figure 3. The first resonance in the fossil-fuel spectra match well with the π^* resonance of pyridine, suggesting the presence of pyridine in these samples. The second resonance feature in the fossil-fuel spectra matches well with π^* resonance energy of the pyridone molecule. This suggests the presence of such structures in the fossil-fuel samples. The spectrum of a high rank coal has an intense pyridine peak, but a barely discernible shoulder for the pyridone signature; the opposite situation exists in the spectrum of the low rank coal, where the pyridine peak is absent, and a strong pyridone peak is present. This leads to the argument that as coals mature, oxygen is driven away, and the pyridone in a low rank coal loses its oxygen when it reaches a high rank stage and is transformed into pyridine(8). Among the kerogen and bitumen, the peak around 402 eV is relatively strong; this may be partly due to the presence of pyridone structures, as well as other oxygen nitrogen structures, and the issue is still under investigation. The kerogen and bitumen samples are immature, and considerable amounts of pyridone, as well as other oxygen containing molecules are not unexpected to be present in these samples. The third resonance in the fossil-fuel spectra corresponds in energy with the π^* resonance of the pyrrole molecule. The four fossil-fuel samples show intense pyrrole resonances, and the intensity is more or less uniform in all the four spectra. The smaller resonance feature at 405 eV in the fossil-fuel spectra can be attributed to the presence of aromatic amines, since the spectrum of an amine has a broad resonance in this region. The saturated amine spectrum shows an absence of a π^* resonance, but the presence of a σ^* resonance, which occurs at 408 eV. All the four types of fossil-fuel samples show resonances at this energy, which suggests that there may be some amount of saturated amine structures present in them.

Different nitrogen structures show π^* (or σ^*) resonances at well separated energies, as shown in figure 3. Several analogues of different structures of nitrogen have been studied previously(8,9), and it is found that all analogues belonging to the same structure exhibit π^* resonances at energies close to each other ($\Delta E \sim 0.5 eV$), but well separated from the π^* resonances of the spectra of other structures ($\Delta E \sim 2 eV$). This has been explained by means of the behavior of the lone pair of electrons at the nitrogen site in the molecule. When the electrons are involved in the π -cloud of the six-membered aromatic ring, as in pyrroles and pyridones, the nitrogen site is left slightly positive, and these structures show higher energy π^* resonances. In contrast, in pyridines, the lone pair of electrons are involved in the sp^2 orbital and the nitrogen site is left slightly negative; these structures show lower energy π^* resonances than pyrroles and pyridones.

A least-squares fitting program has been used in order to analyze the coal spectra. All the spectra of models and the coal samples were first normalized with respect to the respective step heights, and were then fit to a sum of several different Lorentzian peaks and an arc-tangent step. The peaks represent bound to bound electronic transitions, and the step represents transition to the continuum. Figure 4(a) shows a typical fitted spectrum of a nitrogen model compound (9-vinylcarbazole), and figure 4(b) shows the fitted spectrum of a coal (PITT). The first seven resonance features of the fossil-fuel spectra were identified to five different types of nitrogen; in order to maintain consistency, all the model and fossil-fuel spectra were fit with the same set of parameters. The relevant peaks were: 399.8 eV, $\Delta v = 0.8 eV$ (pyridine), 401.9 eV, $\Delta v = 0.97 eV$ (pyridone), 402.6 eV, $\Delta v = 1.3 eV$ and 403.7 eV, $\Delta v = 1.9 eV$ (pyrrole), 405.0 eV,

$\Delta v=2.0$ eV (aromatic amine), and 406.2 eV, $\Delta v=1.4$ eV and 407.9 eV, $\Delta v=2.9$ eV (all models including saturated amines). A continuum resonance was included to produce better fits to the data but were not used in our analysis procedure; its location was 412.8 eV, $\Delta v=3.2$ eV. The step was positioned at 408 eV, with a width of 1.5 eV. Average area values of the normalized peaks in the spectra of all analogues belonging to the same nitrogen structure were determined; these values were then used to analyze the coal spectra. For instance, the resonance at 400 eV in the fossil-fuel spectra was attributed to pyridine structure, and the pyridine contribution in the coal spectra was determined; in a likewise manner, other nitrogen contributions were also determined. Care was taken to subtract from the fossil-fuel spectra any secondary contribution arising from a different structure at the same energy as the π^* resonance of the primary structure in consideration. After determining secondary contributions from pyridines, pyridones, and pyrroles at 405 eV, the valley at this energy in the coal spectra was assumed to be "filled in" due to the presence of aromatic amine, and the aromatic amine contribution was determined. The 408 eV resonance was attributed as due to the presence of saturated amines.

Table 1 lists the percentages of the different nitrogen structures present in the coals. All the nitrogen in coals are aromatic in nature, with pyrrolic type being the most dominant. Substantial quantities of pyridinic structures are also found in the high rank coals. The low rank coals have smaller amounts of pyridine and larger amounts of pyridone, as opposed to the high rank coals; this leads to the argument that as coal matures from a low rank stage to a high rank stage, pyridone loses its oxygen and become transformed into pyridine structures. Small quantities of aromatic amine are found in all the coals.

We estimate the errors in the percentages listed in the above tables to be within 12%; there are several sources for such errors. First of all, the ratio of the intensity to the step height of different analogues of the same structure can vary significantly as seen previously, and an average value for the π^* area may introduce some errors. Secondly, the aromatic amine determination is not unique, since the aromatic amine analogues exhibit spectra with broad π^* resonances, and we have assumed that the valley at 405 eV in the fossil-fuel spectra is "filled up" due to the presence of aromatic amine in the fossil-fuel samples. Furthermore, the assignment of peaks in the fossil-fuel spectra to different nitrogen structures is somewhat arbitrary, and a slightly different position would perhaps generate a slightly different set of numbers. However, the trends would remain the same in the percentage values noted above.

CONCLUSIONS

Five different nitrogen structures have been determined by XANES methodology in several coals of different ranks. Coals have only aromatic nitrogen structures with pyrrolic types being the most dominant. Low rank coals have significant amounts of pyridone and smaller (or no) quantities of pyridine; as these coals mature over geological time to a higher rank stage, the pyridone structures lose their oxygen and become transformed to pyridine types. Aromatic amine is the other form of nitrogen found in these coals. The immature kerogens and bitumens have spectra similar to those of coals, although trends in the intensities of the different resonances among the different kerogen and bitumen spectra are not evident. The peak ~ 402 eV in the bitumen samples may arise from pyridone, as well as some other nitrogen structures; the matter is still under investigation

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Table 1. Percentages of different nitrogen structures found in coals of different ranks.

Samples	C	H	O	N	Pyridine	Pyridone	Pyrrrole	Aniline
POC	91.81	4.48	1.66	1.34	18	8	66	8
UF	88.08	4.84	4.72	1.60	18	8	66	8
PITT	84.95	5.43	6.90	1.68	20	8	65	9
WV	85.47	5.44	6.68	1.61	20	16	55	9
UT	81.32	5.81	10.88	1.59	17	15	60	8
L	80.73	5.20	10.11	1.43	20	19	54	7
WY	76.04	5.42	16.90	1.13	10	29	51	10
ND	74.05	4.9	19.13	1.17	2	42	50	6

* Mass fraction from K. S. Vorres, Users Handbook for the Argonne Premium Coal Sample Program, Argonne National Lab.

Normalized by nitrogen content

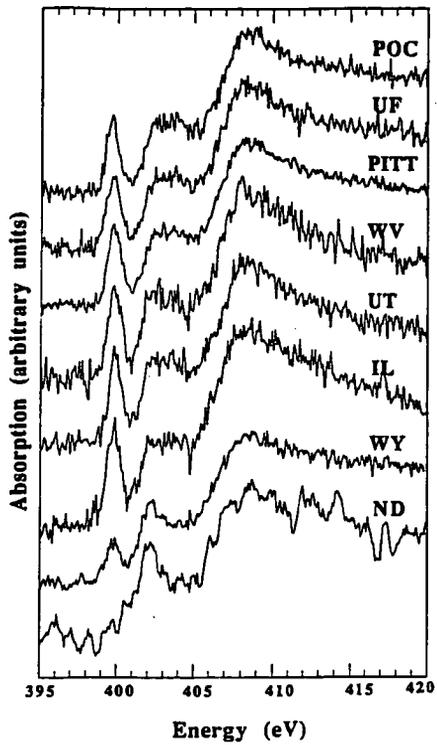


Figure 1. Nitrogen XANES of different coals. The plots are shown in order of coal rank, the higher rank being at the top.

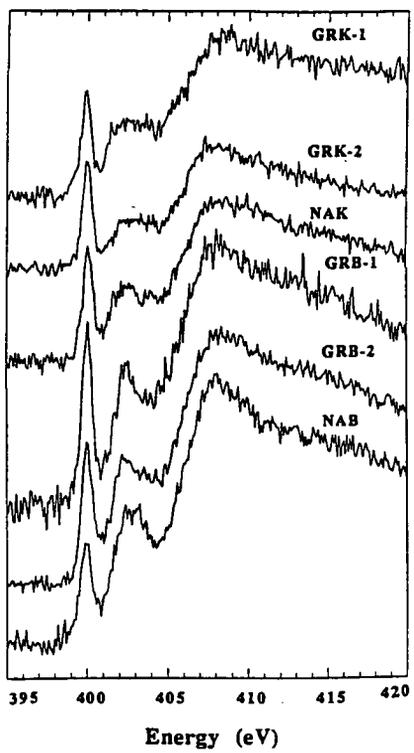


Figure 2. Nitrogen XANES of several kerogens and bitumens.

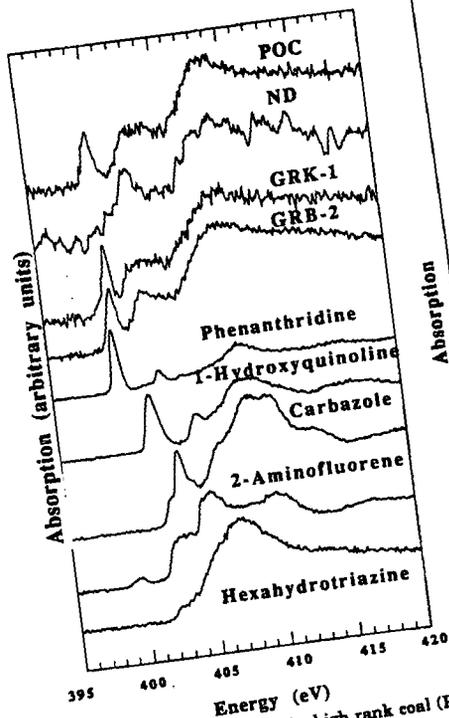


Figure 3. Nitrogen XANES of a high rank coal (POC), a low rank coal (ND), a kerogen (GRK-1), a bitumen (GRB-2), and five different nitrogen structures.

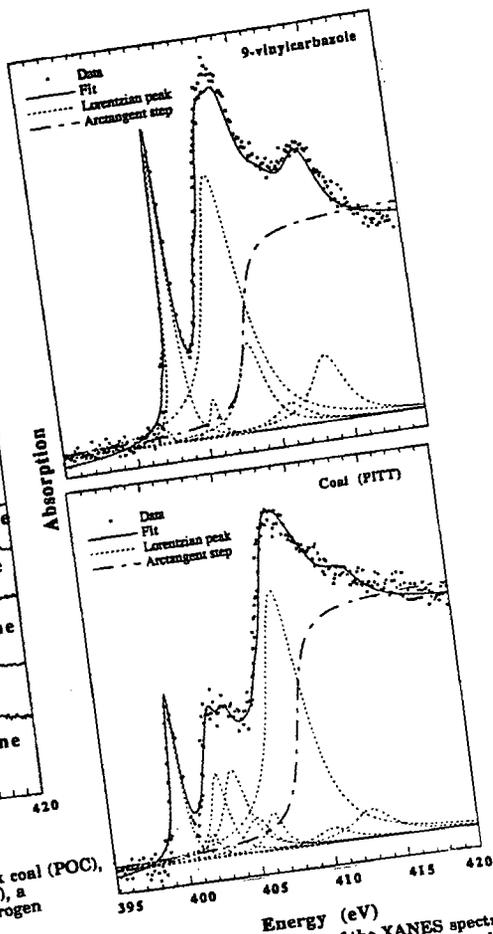


Figure 4. Least squares fit of the XANES spectra of a nitrogen model compound (9-vinylcarbazole) and a coal (PITT).