

NITROGEN XANES STUDIES OF ARGONNE COALS

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Keywords: XANES, nitrogen, coals

ABSTRACT

All the major forms of nitrogen in a group of Argonne coals are detected and quantified by X-ray Absorption Near-Edge Structure (XANES) studies; these forms are pyridine, pyridone, and pyrrole. In addition, there is evidence of aromatic and quarternary amines in small amounts, and virtually no saturated amines. Pyridone is found to be abundant in the low rank coals; with maturation of coals, the pyridone forms become transformed into pyridine forms. The quarternary nitrogen has been analyzed as a potential contribution to coal spectra. This compound has a distinctive peak in the nitrogen XANES spectra allowing contribution of quarternary nitrogen in the coal spectra to be determined. By this method we have found that coals generally have at most small quantities of quarternary nitrogen.

INTRODUCTION

Important natural resources such as coal often contain heteroatoms such as sulfur and nitrogen; these heteroatoms pose serious threats to the environment, as well as to effective utilization of the resources. Elucidation of the chemical structures of the heteroatom containing compounds in coals aids in the removal of the compounds, and also in understanding the complex maturation processes of these fossil fuels.

X-ray Absorption Near-Edge Structure (XANES) spectroscopy has been very versatile in direct and non-destructive studies of fossil fuel samples. Sulfur XANES studies have been performed successfully on coals(1-6), and petroleum asphaltenes(7-9). XANES studies showed that both coals and petroleum asphaltenes contain saturated and aromatic forms of sulfur; thiophenic (aromatic) is the most dominant form, followed by sulfidic (saturated) form. There are small amounts of oxidized forms in coals and asphaltenes, and unlike asphaltenes, some coals have inorganic sulfide structures present in them.

Nitrogen XANES studies have also been successfully performed on coals(10,11) petroleum asphaltenes(12), and organic parts of source rocks such as kerogens and bitumens(13). Several nitrogen model compounds have been studied to analyze the fossil fuel spectra; they are pyridine, pyridone, pyrrole, aromatic amine, porphyrin, and saturated amine. It is found that most of the nitrogen is found in aromatic forms in these fossil fuel samples, with negligible quantities of saturated forms. Pyrrolic and pyridinic are the most common forms of nitrogen in these samples. In low rank coals, considerable amounts of pyridone are also found, whereas in the high rank coals the pyridone structures are mostly replaced by pyridine structures. In addition, coals also have small quantities of aromatic amines. Some quantities of porphyrin and smaller quantities of saturated amines are present in the kerogens and bitumens in addition to the other nitrogen structures mentioned above.

Other methods which have been used in the past to elucidate the nitrogen chemical structures of fossil-fuels have been mostly destructive and indirect. Chromatographic and extraction methods have been problematic either due to high molecular weights or they are not powerful enough to study the entire sample. Several spectroscopic studies have been performed; however, they suffered mostly from resolution difficulties. X-ray Photoelectron Spectroscopy (XPS) studies on coals(14-16) and coal-related materials(17) have been informative. Earlier XPS studies on

coals(15) have shown the presence of pyridine and pyrrole; a more recent study(16) has also shown the presence of quarternary nitrogen. XPS experiments clearly could not resolve signatures arising from oxygen containing pyridone or the aromatic and saturated amine structures in coals.

In this report, preliminary XANES studies of quarternary nitrogen (pyridinium) are presented as a potential contributor to coal spectra. Several analogues of pyridinium compounds have been studied. It is found that these structures have a distinct sharp π^* resonance at 401.8 eV, and is invariant among the different analogues. The pyridinium resonance is between the pyridine and the pyridone resonances, and is distinguishable from those from other structures. The coal spectra do not show any prominent sharp feature at the pyridinium π^* energy, and at most show only small quantities of these structures. The pyridone percentage far exceeds the quarternary percentage, and the inverse connection between the pyridone and pyridine percentages is still more prominent.

EXPERIMENTAL SETUP

Nitrogen x-ray data on all the coal and model samples have been obtained at the soft x-ray beam line U4B, designed and constructed by AT&T Bell Labs(18), at the National Synchrotron Light Source at Brookhaven National Laboratory. U4B is equipped with a grating monochromator with a grating of 600 lines/mm. The sample chamber was maintained at pressures of 10^9 to 10^{10} torr by means of a turbo-molecular pump and a cryopump. The samples were mounted on pieces of nitrogen-free 3M tape and positioned on a sample holder by a load-lock system. A multichannel Ge fluorescent detector(19) was used with a 2- μ s shaping time. The energy resolution was about 140-400 meV.

The coal samples were provided by Dr. Karl Vorres from Argonne Premium Coal Sample Bank at Argonne National Laboratory(20). The coal sample suite consisted of eight samples; these samples belonged to varying ranks, starting from lignite to low-volatile bituminous. The samples were: a low-volatile bituminous coal from Pocahontas #3, VA (POC); a medium-volatile bituminous coal from Upper Freeport, PA (UF), four high-volatile bituminous coals from Pittsburgh #8, PA (PITT), Lewiston-Stockton, WV (WV), Blind Canyon, UT (UT), and Illinois #6, IL (IL), and a subbituminous from Wyodak-Anderson, WY (WY), and a lignite from Beulah-Zap, ND (ND).

The nitrogen model samples were obtained from Aldrich Chemical Company. The pyridine samples were acridine, 4,7-diphenyl-1,10-phenanthroline, phenanthridine, di-p-tolylpyridine, and 4-polyvinylpyridine-costyrene; the pyridinium samples were pyridinium dichromate, 1-ethyl-4-(methoxycarbonyl) pyridinium iodide, and pyridinium 3-nitrobenzenesulfonate; the pyridone samples were 6-(2,2-diphenyl-2-hydroxyethyl)-2(1H)-pyridone, 2-hydroxyquinoline, 1-hydroxyisoquinoline, 1-methyl-4-pentadecyl-2(1H)-quinoline; the pyrrole samples were tetrahydrocarbazole, 2-phenylindole, 9-vinylarbazole, and carbazole; the aromatic amine samples were 2-aminofluorene, and 2,7-diaminofluorene, and the saturated samples were 1,3,5-tribenzylhexahydro-1,3,5-triazine, and diaminododecane. All the coal and the nitrogen model XANES spectra were calibrated with respect to the first π^* resonance of zinc octaethylporphyrin at 399.72 eV.

RESULTS AND DISCUSSIONS

The XANES spectra of the coals show similar features with three well-resolved resonance regions(11). The feature at 401.8 eV is relatively insignificant compared to the major resonances; it occurs at the red tail-end of the second broad resonance region between 402 and 405 eV. The major resonances are much more intense; of these, the first resonance at 399.7eV varies in intensity among the different ranked coals. The lowest rank coal has a less intense resonance at 399.7eV while the same resonance in the higher rank coals is much more intense. The second resonance region, upon close inspection, shows the presence of three resonances, at \sim 402eV, \sim 403.5eV, and at \sim 405 eV. The intensity of the 402 eV also varies significantly among coals of different ranks; it is more prominent in the low rank coals than in the high rank coals. The feature at 405eV is also comparatively insignificant, and is merely a valley with varying depth, with no strong trend as a function of coal rank. All the coal spectra show a prominent resonance at 408eV.

XANES studies of different nitrogen model compounds have been performed in order to analyze the coal spectra. In the present report, spectra of six groups of model compounds have been associated with the coal spectra; they are pyridine, pyridinium, pyridone, pyrrole, aromatic amine and saturated amine. In our previous work(11) we have analyzed all the above nitrogen structures except for pyridinium. The pyridinium π^* resonances are sharp, and invariant; they are well grouped together at around 401.8 eV, consistent with our earlier results(11) of the different π^* resonances of pyridine analogues (at 399.7 eV), pyridone analogues (at 402 eV), pyrrole analogues (at 403.5 eV), and aromatic amines (at 405eV). The pyridinium π^* resonances occur at a higher energy than the pyridine π^* resonances; this is consistent with the observation in the case of sulfur structures(5), where the π^* resonances are blue shifted with more positive oxidation numbers. The π^* resonances of pyridone, on the other hand, are generally at higher energies than pyridinium resonances. Perhaps with more number of analogues a small overlap may be observed between the pyridone and pyridinium resonances. The pyrroles have higher energy π^* resonances compared to pyridine; we have explained this due to the difference of the orbital location of the lone pair of electrons at the nitrogen site. The fact that each different nitrogen structure has a characteristic π^* absorption feature distinct from that of another structure helps in the analysis of coal spectra which may contain several different nitrogen structures.

The coal spectra do not show any prominent absorption resonance at the pyridinium signature (401.8 eV). The coal spectra show only a wing at this absorption energy which is at least in part due to the pyridone resonance occurring at a higher energy. This, therefore, shows that there is at most a small amount of pyridinium present in the coals. This is consistent with the XPS results(16) which show presence of small amounts of quarternary nitrogen in these coals. In contrast, XANES results show that pyridine and pyrrole are the two major nitrogen structures in coal, consistent with XPS studies(16). XANES data also show signatures arising from pyridone, aromatic amine and saturated amine. To the best of our knowledge, unlike XANES methodology, XPS technique can not resolve features arising from pyridone, aromatic and saturated amines; XANES and XPS can therefore be considered as complimentary techniques.

Previous results(11) show that the low rank coals have a significant pyridone percentage and a low pyridine percentage; on the other hand, the opposite is true with the higher rank coals. This suggests that with maturation of coal, pyridone structures lose their oxygen content, and become transformed into pyridine. The variation of the intensity of the pyridine and the pyridone peaks as a function of coal rank is much more drastic than the small pyridinium content in the different coals.

CONCLUSIONS

XANES methodology is an excellent tool for studying heteroatom structures in coals. Nitrogen occurs mostly in aromatic forms in the coals; pyridine and pyrrole are the two most common nitrogen structures; low rank coals have a high percentage of pyridone and a small percentage of pyridine, and the opposite is true with the high rank coals. This leads to the conclusion that as coals mature, oxygen is driven away, and pyridone structures are converted into pyridine structures. XANES data do not show any prominent resonance at the quarternary nitrogen π^* energy, and low rank coals have inore significant amounts of pyridone than quarternary nitrogen structures.

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