Solid-State ^{15}N NMR Spectroscopy of Coal

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Solid-state ^{15}N NMR is applied in a study of various coal samples to evaluate the forms of nitrogen in coal. The spectra display the main signal intensities in the region of pyrrole and indole derivatives. No signals assigned to pyridine derivatives were identified. This contradicts the most common belief that pyridine-like structures comprise the major form of nitrogen in coal. The successful application of ^{15}N NMR spectroscopy to coal samples may help to provide a new level of understanding of coal-nitrogen chemistry.

Introduction

The chemical nature of nitrogen in coal has long been of interest for a variety of reasons. First, nitrogen containing structures in coal are involved in the release of NO_x during coal combustion.¹ Second, many nitrogen-containing polycyclic aromatic compounds in coal and coal-derived liquids are mutagenic and/or carcinogenic.² Third, nitrogen functional groups have a major effect on fuel stability, refinery catalysts, and the solubility of coal-derived liquids.³ Finally, nitrogen compounds are believed to play an important role in linking together the macromolecular subunits of the coal structure.⁴ Although nitrogen in coal is believed to occur principally in pyridine and pyrrole analogs, its distribution in functional groups is not well understood.⁵

There are, in principle, two approaches that can be used to investigate the chemical structure of nitrogen associated with the macromolecular coal network.⁶ The first involves the degradation of the macromolecular network into numerous small molecules by thermolytic methods. The initial structures are then inferred by identifying the fragment structures. The main problem with this approach is that in heterogeneous organic mixtures such as coal, secondary reactions (rearrangement, cracking, hydrogenation, and polymerization) occur simultaneously and in unpredictable ways. Therefore, conclusions regarding the original structure of the sample have to be drawn with extreme caution.

A second strategy for characterizing nitrogen structures in coal is to apply nondestructive spectroscopic methods that allow the examination of the coal as a whole in the solid state. Recently, X-ray photoelectron spectroscopy (XPS) has been applied for this purpose.^{7,8} Unfortunately, XPS suffers from a lack of resolution and

is limited to examination of the surface of the coal. Only recently have promising spectra of nitrogen compounds in coal and asphaltenes been obtained by X-ray absorption near-edge structure (XANES),⁹ and the data support the concept that nitrogen in coal occurs mostly in pyridinic and pyrrolic compounds. Although the spectra obtained with this method show better resolution than those obtained from XPS, signals of pyridinic and pyrrolic structures cannot be adequately resolved.

An alternative, nondestructive spectroscopic technique for examination of nitrogen in solid macromolecules is solid-state ^{15}N nuclear magnetic resonance (NMR) spectroscopy. While solid-state ^{13}C NMR has emerged as perhaps one of the most powerful tools for the analysis of carbon structures in coal, ^{15}N NMR suffers from severe sensitivity problems. Due to the fact that the most abundant nucleus, ^{14}N , possesses a quadrupole moment which results in poorly resolved spectra with very broad resonance lines, high-resolution solid-state NMR is limited to the ^{15}N isotope. The low natural abundance of ^{15}N (0.36%) and its negative gyromagnetic ratio means that, in an NMR experiment, the ^{15}N isotope is about a factor of 50 less sensitive than the ^{13}C nucleus. This along with the low nitrogen concentrations of less than 2% in most coals may have been the reason that the application of ^{15}N NMR was thought not to be possible. The successful application of ^{15}N NMR for the study of organic matter in soil systems^{10,11} suggested that solid-state ^{15}N NMR spectra could be obtained from coals. In the present paper we report the first solid-state ^{15}N NMR spectra of bituminous and subbituminous coals.¹²

Experimental Section

The three coal samples used in the study were obtained from the Penn State Coal Sample Bank and Data Base and have been characterized thoroughly (Table 1) by standard chemical methods.¹³

The solid-state ^{13}C NMR spectra were obtained on a Chemagnetics M-100 spectrometer at a frequency of 25.04 MHz

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Table 1. Description of the Coal Samples Studied¹³

sample	PSOC 1362	PSOC 1517	PSOC 1382
location	Lawrence County, PA	Mahoning County, OH No. 5	Moffat County, CO
description	Pennsylvanian, Allegheny Group, Freeport Formation	Pennsylvanian, Allegheny Group, Kittanning Formation	Upper Cretaceous, Mesaverde Group, Williams Fork Formation
Elemental Analysis (dmmf)			
carbon (%)	84.0	83.6	75.8
hydrogen (%)	6.0	5.4	5.0
nitrogen (%)	2.0	1.9	2.0
sulfur (%)	0.8	1.3	0.4
oxygen (%)	7.1	7.8	16.8
ash (% dry)	5.1	4.8	6.5
rank	high-volatile A bituminous (hvAb)	high-volatile B bituminous (hvBb)	subbituminous A (subA)
Maceral Composition (white light, vol %, mineral free)			
total vitrinite	81.0	87.2	87.3
fusinite	3.0	1.7	3.0
semifusinite	6.5	3.1	3.5
macrinite	0.8	0.5	1.2
micrinite	4.4	3.8	4.1
sclerotinite	0.0	0.0	0.0
total inertinite	14.7	9.1	11.8
sporinite	4.1	3.0	0.7
resinite	0.2	0.7	0.2
alginite	0.0	0.0	0.0
cutinite	0.0	0.0	0.0
total liptinite	4.3	3.7	0.9

with magic-angle spinning at 3.5 kHz (CPMAS technique). The radio-frequency field strength of the decoupler was 50 kHz. The ¹³C NMR chemical shifts were calibrated to the tetramethylsilane scale. A single Hartmann-Hahn contact time of 1 ms, a repetition time of 0.5 s, and an acquisition time of 18 ms were applied. A line broadening of 20 Hz was used. Approximately 20 000 scans were accumulated.

Solid-state ¹⁵N NMR spectra were obtained on a Chemagnetics CMC-300 spectrometer at a frequency of 30.2 MHz using the CPMAS technique with magic-angle spinning of 3.6 kHz, a contact time of 1 ms, an acquisition time of 20 ms, and a pulse delay of 100 ms. The radio-frequency field strength of the decoupler was also 50 kHz. The chemical shifts were referenced to external nitromethane. Approximately 1 500 000 scans were accumulated. A line broadening of 150 Hz was used. A more detailed discussion of the relevant relaxation times and their influence upon the relative intensities is provided in Knicker and Lüdemann¹⁰ and Knicker et al.¹⁴

Results and Discussion

Figure 1 shows the solid-state ¹⁵N NMR spectra of a subbituminous A coal (PSOC 1382) and a high-volatile B bituminous coal (PSOC 1517). Both spectra are characterized by a narrow resonance line at -345 ppm that is due to the added reference glycine¹⁵ and a broad signal in the chemical shift region between -120 and -270 ppm, peaking at -240 ppm. This peak can be assigned to pyrrolic nitrogen compounds.¹⁶ The broadness of the signal indicates extensive substitution and variable cross-linking of the pyrrolic ring system in the coal network. In general, resonance lines of unsubstituted pyrroles are expected at -235 ppm. The broad

Figure 1. Solid-state ¹⁵N and ¹³C NMR spectra of a subbituminous coal (coal PSOC 1382) and a high-volatile bituminous coal (PSOC 1517). A detailed description of the coal is given in Table 1. The asterisks refers to the internal reference glycine.

shoulder at the low-field side (-120 to -210 ppm) of the broad peak at -240 ppm may originate from pyrrolic nitrogens in which the lone pair electrons have been delocalized by substitution or from imidazoles. Unsubstituted indolic or carbazolic nitrogens show higher electron density and, therefore, a higher magnetic shielding as compared to nitrogen in pyrroles. Resonance lines from carbazole and indole nitrogens may contribute to the high-field shoulder (-240 to -280 ppm) of the broad peak at -240 ppm. Indolic nitrogens usually show signals in the chemical shift range between -230 and -260 ppm.¹⁶ Farrow et al.¹⁷ measured

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a nitrogen chemical shift at -262 ppm for carbazole dissolved in dimethyl sulfoxide (DMSO).

It is generally believed that nitrogen in coal occurs not only in pyrrolic but also in pyridinic structures. In a solid-state ^{15}N NMR spectrum, resonance lines of unsubstituted pyridinic nitrogen are expected to occur in the chemical shift range between -40 and -90 ppm. Neat pyridine shows a resonance line at -62 ppm while aqueous pyridine absorbs at -84 ppm¹⁶. In the solid-state ^{15}N NMR spectra of coals presented here no signals can be distinguished from the noise in the chemical shift area assigned to unsubstituted pyridinic nitrogen. Protonation or N-alkylation of pyridinic nitrogen leads to a dramatic increase of the magnetic shielding of up to 100 ppm or more. Resonance lines originating from such pyridinium compounds may contribute to the weak signal in the chemical shift region between -100 and -200 ppm. However, if we assign this signal to pyridinium ions in coal compounds, then it implies that a complete proton transfer has occurred from a strong acidic moiety with $pK_a < 4$.¹⁸ In coal, such strong acidic groups can exist as carboxylic acid functional groups on condensed aromatic ring systems. Evidence for the protonation of pyridinic nitrogen by strong acidic carboxyl functional groups was previously given by solid-state ^{15}N NMR studies of pyridine absorption on coals displaying various degrees of oxidation.¹⁹ The formation of pyridinium nitrogen was observed by an ^{15}N NMR resonance line at -150 ppm whose intensity increased as a function of the carboxyl content of the coal samples.

The existence of acidic carboxylic groups or oxygen-substituted aromatic carbons in the examined coals is readily shown by solid-state ^{13}C NMR spectra (Figure 1). Carboxylic carbons are expected to give resonance lines in the chemical shift region between 220 and 160 ppm. In the ^{13}C NMR spectra shown in Figure 1 no signals can be identified in this chemical shift region. Therefore, we can conclude that, in the coal samples examined here, few, if any, acidic carboxylic groups are available for the formation of pyridinium ions. The main signal intensities in these spectra are found in the chemical shift region between 160 and 100 ppm which is assigned to aromatic carbon. Alkyl substituted, unsubstituted, and protonated aromatic carbons can be observed between 140 and 100 ppm and are the main contributors to the signal intensity of the broad and intense resonance line at 130 ppm. Oxygen-substituted aromatic carbons give signals in the region between 160 and 140 ppm and may add to the intensity of the low-field shoulder of the peak at 130 ppm.

Solid-state ^{15}N NMR spectra are usually obtained as double resonance spectra after simultaneously irradiating ^1H and ^{15}N radio-frequency fields during a contact time t . During t , magnetization is transferred from the proton spin system to the ^{15}N spin system. The efficiency of the magnetization transfer depends upon the cross polarization time T_{NH} and the proton spin-lattice relaxation time in the rotating frame $T_{1\rho\text{H}}$. T_{NH} , however, is dependent upon heteronuclear dipolar interactions between the nitrogen nucleus and its neighboring protons. This interaction decreases as a function

Figure 2. Solid-state ^{15}N NMR spectra of a subbituminous coal (PSOC 1362) obtained at a contact time of 1 and 2.5 ms.

of the distance between the two interacting nuclei. Because pyridinic compounds do not have nitrogen with directly bonded protons, their T_{NH} is expected to be longer than that of compounds where the nitrogen has directly bonded protons. In a cross polarization experiment, however, full signal intensity can only be obtained if the magnetization transfer is completed before $T_{1\rho\text{H}}$ becomes effective, when $T_{\text{NH}} \ll T_{1\rho\text{H}}$.²⁰

In heterogeneous mixtures such as coals, individual components will display their own cross polarization dynamics. The maximal signal intensity for each component is not reached at the same optimal contact time t_{opt} . For functional groups with no directly bonded protons t_{opt} is expected to be longer than for groups with one or two protons in their immediate vicinity. In order to obtain quantitative data one must be assured that t_{opt} is approximately the same for all the nitrogen-containing structures or that t_{opt} spans a broad range of times. For the ^{15}N spectra obtained here an averaged contact time t_{average} of 1 ms was used. According to recent ^{15}N NMR studies of soil organic matter^{10,14} t_{average} of 1 ms was determined to yield quantitative spectra. Ripmeester et al.¹⁹ found that the relative intensities of ^{15}N -enriched pyridine and pyridinium ions sorbed on coal were virtually independent of t 's between 1 and 5 ms indicating that t_{opt} occurred over a broad range of times.

In spite of these indications that a t of 1 ms should yield quantitative data, the absence of signals for pyridinic compounds in the coals examined here may be that the chosen t of 1 ms is too short for complete magnetization transfer. Therefore, solid-state ^{15}N NMR spectra of one coal were obtained at t of 1 and 2.5 ms (Figure 2). Both spectra show their main signal intensity at -240 ppm and a downfield shoulder at -175 ppm. While the signal at -240 ppm decreases with increasing t , no intensity loss can be observed for the signal at -175 ppm. Also, no additional signals can be identified in the region of pyridinic structures. These results indicate that too short a contact time is not an explanation for missing pyridinic signals. A longer t of 2.5 ms only results in a signal intensity loss for nitrogen compounds suspected of having strong dipolar interactions.

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In solid-state NMR experiments on coals the presence of free radicals can efficiently shorten $T_{1\rho H}$.²⁰ If $T_{1\rho H}$ has been affected by free radicals and has decreased such that $T_{NH} > T_{1\rho H}$, then a significant reduction in signal intensity will be detected resulting in nonquantitative behavior. Several studies have shown that pyridinic compounds adsorbed on coal, γ -alumina and zeolites can be detected by CPMAS solid-state ^{15}N NMR spectroscopy.^{19,21,22} Although these studies do indicate that pyridinic nitrogen is detectable by CPMAS solid-state ^{15}N NMR, we cannot completely exclude the fact that the cross polarization dynamics of pyridinic compounds in coal may preclude their observation.

Summary and Conclusions

This paper has attempted to introduce solid-state ^{15}N NMR into the investigation of nitrogen functional groups in coal. Three coals, two subbituminous A coals and a high-volatile B bituminous coal, were examined. The main signals detected in the solid-state ^{15}N NMR spectra in the chemical shift region between -120 and -270 ppm peaking at -240 ppm are most likely assigned to pyrrolic compounds. No signal can be distinguished from the noise in the chemical shift region typical for unsubstituted pyridinic structures. A comparison of solid-state ^{15}N NMR spectra obtained at a contact time of 1 and 2.5 ms showed that the application of a contact time of 2.5 ms only results in a decrease of the signal intensity of unsubstituted pyridinic compounds. No signal assignable to pyridinic nitrogen can be identified in either spectra. Under the assumption that cross polarization dynamics do not remove the pyridinic signal in the solid-state ^{15}N NMR spectra, the results of this study suggest that in these coals, pyridinic compounds are not a major component of the coal nitrogen. However, with the low signal to noise ratio of these spectra some of the pyridine intensity may be hidden and not distinguishable from the noise. Even

after considering the low signal to noise ratio and the possibility that some of the coal pyridinic compounds occur in pyridinium forms, these spectra lead to the conclusion that in the coals examined here not more than 25% of the nitrogen is contained in pyridinic compounds. This contradicts recent studies obtained with X-ray absorption near-edge structure spectroscopy (XANES) which suggested a pyridinic nitrogen content of 47 and 53% for pyrrolic nitrogen.⁹ On the other hand, the results obtained here are consistent with those obtained from X-ray photoelectron spectroscopy (XPS) applied to examine the nitrogen functionality of coals as a function of rank.⁷ In the XPS study it was found that the pyrrolic form predominates in bituminous coal and that the proportion of pyridinic nitrogen increases with rank. This suggests that six-membered heterocyclic structures are more stable in the later stages of coalification. Whether this can be confirmed by ^{15}N NMR will be the objective of future work on coal samples of higher and lower rank.

This investigation has demonstrated that, in spite of the low natural abundance of the ^{15}N isotope and its low sensitivity, solid-state ^{15}N NMR can be applied to whole coal samples. Although these preliminary studies on the native coal material currently suffer from a modest signal-to-noise-ratio, further optimization of NMR spectroscopic parameters, the application of higher magnetic field NMR instruments, and the use of high-volume sample tubes²³ may lead to an improvement of the quality of coal ^{15}N NMR spectra. Although much work is still necessary with respect to quantification problems, solid-state ^{15}N NMR spectroscopy on coal may help to provide a new level of understanding of coal-nitrogen chemistry.

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