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Structural Features of a Bituminous Coal and Their Changes during Low-Temperature Oxidation and Loss of Volatiles Investigated by Advanced Solid-State NMR Spectroscopy

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Received December 9, 2009. Revised Manuscript Received February 25, 2010

Quantitative and advanced ^{13}C solid-state NMR techniques were employed to investigate (i) the chemical structure of a high volatile bituminous coal, as well as (ii) chemical structural changes of this coal after evacuation of adsorbed gases, (iii) during oxidative air exposure at room temperature, and (iv) after oxidative heating in air at 75 °C. The solid-state NMR techniques employed in this study included quantitative direct polarization/magic angle spinning (DP/MAS) at a high spinning speed of 14 kHz, cross polarization/total sideband suppression (CP/TOSS), dipolar dephasing, CH, CH_2 , and CH_n selection, ^{13}C chemical shift anisotropy (CSA) filtering, two-dimensional (2D) ^1H – ^{13}C heteronuclear correlation NMR (HETCOR), and 2D HETCOR with ^1H spin diffusion. With spectral editing techniques, we identified methyl CCH_3 , rigid and mobile methylene CCH_2C , methine CCH, quaternary C_q , aromatic CH, aromatic carbons bonded to alkyls, small-sized condensed aromatic moieties, and aromatic C–O groups. With direct polarization combined with spectral-editing techniques, we quantified 11 different types of functional groups. ^1H – ^{13}C 2D HETCOR NMR experiments indicated spatial proximity of aromatic and alkyl moieties in cross-linked structures. The proton spin diffusion experiments indicated that the magnetization was not equilibrated at a ^1H spin diffusion time of 5 ms. Therefore, the heterogeneity in spatial distribution of different functional groups should be above 2 nm. Recoupled C–H long-range dipolar dephasing showed that the fraction of large charcoal-like clusters of polycondensed aromatic rings was relatively small. The exposure of this coal to atmospheric oxygen at room temperature for 6 months did not result in obvious chemical structural changes of the coal, whereas heating at 75 °C in air for 10 days led to oxidation of coal and generated some COO groups. Evacuation removed most volatiles and caused a significant reduction in aliphatic signals in its DP/MAS spectrum. DP/MAS, but not CP/MAS, allowed us to detect the changes during low-temperature oxidation and loss of volatiles. These results demonstrate the applicability of advanced solid-state NMR techniques in chemical characterization of coal.

Introduction

Coal is the preeminent form of fossil fuels used for generating electricity. Environmentally responsible uses of coal should be based on a thorough understanding of coal chemistry and its response to external factors, such as oxidation during storage and reactions at higher temperatures. Among various techniques for characterizing coal, solid-state NMR is one of a few nondestructive approaches.¹ Our understanding of chemical structure of coal has remarkably improved over decades of extensive investigations using solid-state NMR

spectroscopy, combined with other spectroscopic methods and classical chemical analyses.^{2–11} It is well documented that coal is a heterogeneous mixture and consists largely of an organic macromolecular matrix with varying degrees of cross-linking where smaller molecular phases are embedded or adsorbed to the macromolecular network.⁵ However, the detailed structure of coal is still being debated.

The information on the structural changes of coal during storage is important. For example, oxidation of coal during storage can diminish the reactivity of coal for liquefaction or carbonization and significantly affect its industrial use.^{3,12–15}

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Small amounts of additional oxygen in functional groups reduce the capacity of coal to form a mesophase and, subsequently, strong coke.^{14,16} Using X-ray photoelectron spectroscopy (XPS), McCutcheon and Wilson¹² indicated that coal oxidation in the presence of dry air formed only minor amounts of C=O groups but the amount of C=O and C–O groups increased when coal was wet during oxidation.¹² Many questions still remain about the structural changes of coal during storage in air,¹⁷ including that of the influence of mineral alterations and bacterial activities on coal structures, which are not considered in this paper.

Recently, Schmidt-Rohr and Mao have developed, adapted, and applied many advanced solid-state NMR techniques for characterizing complex organic matter in plants, soils, water, sediments^{18–23} and also in the Murchison meteorite.²⁴ Routine ¹³C solid-state NMR spectra often consist of broad and overlapping bands in which functional groups cannot be clearly distinguished. In contrast, the advanced spectral-editing NMR techniques can selectively retain certain peaks and eliminate others, revealing specific functional groups. Also, two-dimensional ¹H–¹³C heteronuclear correlation NMR (2D HETCOR) is used to detect connectivities and proximities of different functional groups.^{19,25,26} In addition, ¹H spin diffusion can be used to detect domains or heterogeneities on a 1–50 nm scale.²⁵ The applications of these systematic techniques promise to lead to new insights into the detailed structures of coal and their changes during natural and industrial processes.

The objectives of the present study were (i) to demonstrate the utility of advanced NMR techniques in characterizing coal structure in more detail compared with routine ¹³C CP/MAS, (ii) to investigate the oxidation and outgassing effects of prolonged storage of coal at room temperature in air, and (iii) to compare the effects of storage in air at room temperature to those at 75 °C. This drying oven temperature was used to accelerate organic matter reactions in air while not approaching the temperature of combustion. Pennsylvanian-age high volatile bituminous coal from Indiana was used in this experiment. Some chemical and physical changes in this same coal as a result of room temperature storage have been recently discussed by Mastalerz et al.¹⁷

Experimental Section

Samples and Treatments. Freshly exposed and collected bituminous coal from Indiana (Lower Block Coal Member, Billings Mine) was crushed to a particle size smaller than 2 mm in diameter. The crushed coal was stirred to produce a relatively homogeneous mixture. Several aliquots of the coal sample were treated as follows. (1) A “zero exposure” split of the coal was kept under argon gas at room temperature in a sealed glass ampule until NMR analyses. (2) Another split was exposed to vacuum in a freeze-dryer for 11 days at room temperature where the coal rapidly lost its adsorbed gas content; this sample is called “evacuated” coal. (3) Other splits of the crushed coal were transferred to several glass jars that were left open to air in a dark room and were covered only with a thin layer of porous paper towels to prevent the settling of dust onto the coal. One such aliquot of coal was exposed to atmospheric oxygen at room temperature for 1 month (i.e., “1 month exposure”) and another for 6 months (i.e., “6 month exposure”). (4) One split of the coal was exposed to laboratory air at 75 °C for 11 days and is called “75 °C heated” coal.

The maceral composition of the untreated coal in volume % is 69.6% vitrinite, 16.0% liptinite, 13.6% inertinite, and 0.8% mineral matter (dominantly clay minerals).¹⁷ The relatively high liptinite Lower Block coal was selected for this study because it is more reactive than coals with higher vitrinite content from this area and, consequently, more suitable to document outgassing and oxidation reactions. The data from proximate analysis are 14.1 wt % moisture, 2.7 wt % ash, 33.5 MJ/kg (14 407 BTU/lb), 39.9 wt % volatile matter, 57.4 wt % fixed carbon, and 0.7 wt % total sulfur. The data from ultimate analysis are 83.4 wt % carbon, 5.5 wt % hydrogen, 1.6 wt % nitrogen, 8.6 wt % oxygen, and 0.7 wt % sulfur. Changes in basic chemistry, surface area, and adsorption capacity of this coal during storage at room temperature were discussed elsewhere.¹⁷

NMR Spectroscopy. All NMR measurements were performed with a Bruker Avance 400 spectrometer at 100 MHz for ¹³C using a 4 mm triple-resonance probe. “Zero exposure” coal kept under inert argon gas was measured immediately after breaking open the glass ampule.

High-Speed Quantitative ¹³C DP/MAS NMR. Quantitative structural information was obtained using ¹³C direct polarization/magic angle spinning (DP/MAS) NMR experiments performed at a spinning speed of 14 kHz. The 90° ¹³C pulse length was 4 μs. Recycle delays were tested by the cross polarization/spin lattice relaxation time-total sideband suppression (CP/T₁-TOSS) technique to make sure that at least 95% of all carbon sites were relaxed.²⁷ On that basis, a recycle delay of 30 s was used for all samples. In order to obtain quantitative information on the nonprotonated carbons (i.e., carbons that are not directly linked to hydrogens), DP/MAS ¹³C NMR with recoupled dipolar dephasing was used. The dipolar dephasing time was 68 μs and adhered to details described elsewhere.²⁸

¹³C CP/TOSS and ¹³C CP/TOSS plus Dipolar Dephasing. Qualitative compositional information was obtained with good sensitivity by ¹³C cross polarization/total sideband suppression (CP/TOSS) NMR experiments at a spinning speed of 5 kHz and a cross polarization (CP) time of 1 ms, with a ¹H 90° pulse length of 4 μs and a recycle delay of 1 s. Four-pulse total sideband suppression (TOSS)²⁹ was employed before detection, and two-pulse phase-modulated (TPPM) decoupling was applied for optimum resolution. The corresponding subspectrum with signals of nonprotonated carbons and mobile groups like rotating CH₃

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was obtained by ^{13}C CP/TOSS combined with 40 μs dipolar dephasing.³⁰

^{13}C Chemical-Shift-Anisotropy Filter. In order to separate the signals of anomeric carbons (O–C–O) from those of aromatic carbons, all of which may resonate between 120 and 90 ppm, the aromatic-carbon signals were selectively suppressed by a five-pulse ^{13}C chemical-shift-anisotropy (CSA) filter with a CSA-filter time of 35 μs .³¹

CH Spectral Editing. For selection of CH (methine), the dipolar distortionless enhancement by polarization transfer (DEPT) method was used at a spinning speed of 4 kHz.³² A 0.5 s ^{13}C T_1 -filter was applied to reduce residual CH_3 signals. The details of this technique, including the suppression of mobile-methylene signals, have been described elsewhere.³²

CH_2 Spectral Editing. Spectral editing of CH_2 signals was achieved by selection of the three-spin coherence of CH_2 groups using a ^{13}C 90° pulse and ^1H 0°/180° pulses applied after the first quarter of one rotation period with MREV-8 decoupling.³³ The spinning speed was 5.787 kHz.

Spectral Editing of Mobile CH_2 + CH. The combined spectrum of these segments can be obtained with good sensitivity in a simple spectral-editing experiment. Two spectra are recorded. The first one is a CP/TOSS spectrum with a short CP of 50 μs ; the second is a CP/TOSS spectrum with a short CP of 50 and 40 μs dipolar dephasing. The first spectrum is predominantly that of protonated carbons in mobile segments, but residual peaks of quaternary carbons result from two-bond magnetization transfer. The second one contains only the residual signals of quaternary carbons or mobile segments (including CH_3 groups with > 50% efficiency). The difference of the two spectra yields the spectrum of the CH_2 and CH carbons, with a small CH_3 contribution.²¹

Long-Range Recoupled C–H Dipolar Dephasing Experiments. Fused aromatic rings typical of charcoal and anthracite can be identified by the large number of carbons positioned far from protons. The signals of these carbons far away from protons can be selected efficiently by a recoupled dipolar dephasing technique.³⁴ In short, two ^1H 180° pulses per rotation period prevent MAS from averaging out weak CH dipolar couplings. After 0.9 ms of recoupled dipolar dephasing time, the signals of most individual aromatic rings are dephased while those of charcoal remain at the 95% level of their original signals. In order to detect nonprotonated carbons with good relative efficiency, DP/MAS as described above was used at a spinning speed of 14 kHz. The “ γ -integral” was employed to suppress sidebands up to the fourth order.³⁵ The ^{13}C 90° and 180°-pulse lengths were 4 and 8 μs , respectively. The recycle delays were 30 s. The dipolar dephasing times varied from 0.07 to 0.16 ms. Further details of this new technique have been described elsewhere.³⁴

Short- and Long-Range ^1H – ^{13}C Heteronuclear Correlation NMR (HETCOR). Two-dimensional ^1H – ^{13}C HETCOR NMR experiments²⁶ were performed at a spinning speed of 6.5 kHz. The scale on which ^1H – ^{13}C proximities were probed could be chosen by the cross polarization (CP) method and by ^1H spin diffusion before CP. One- and two-bond ^1H – ^{13}C connectivities were revealed by 0.5 ms of Lee-Goldburg cross polarization (LG-CP), which suppressed ^1H – ^1H spin diffusion during CP. The length scale of ^1H – ^{13}C proximities was probed by ^1H spin diffusion during a mixing time before CP using 2D

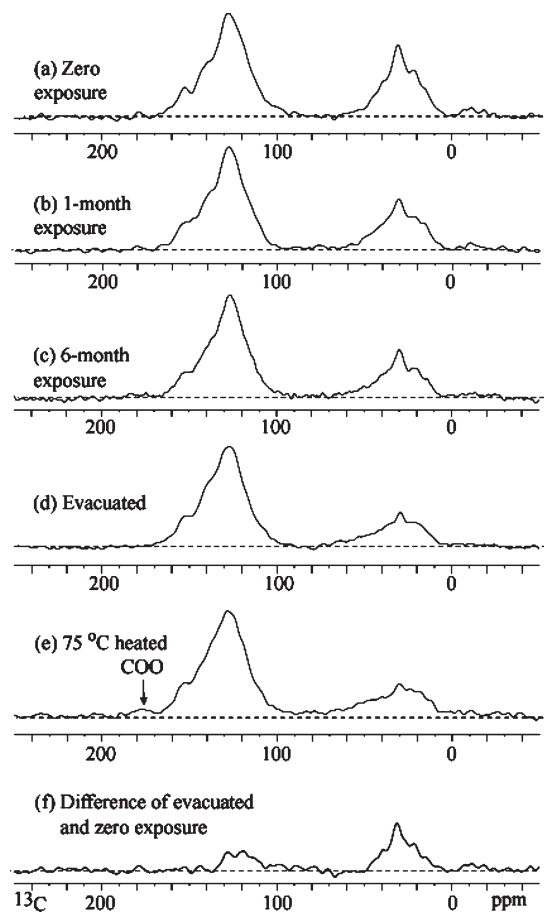


Figure 1. DP/MAS spectra of (a) “zero exposure” coal, (b) “1 month exposure” coal, (c) “6 month exposure” coal, (d) “evacuated” coal, (e) “75 °C heated” coal, and (f) difference between the spectra of “zero exposure” coal and “evacuated” coal. Recycle delay: 30 s; number of scans: 1216. 0–86 ppm integration percentages (total integration area: –50–350 ppm): 33.2% (“zero exposure” coal), 30.3% (“1 month exposure” coal), 28.0% (“6 month exposure” coal), 24.2% (“evacuated” coal), and 24.0% (“75 °C heated” coal).

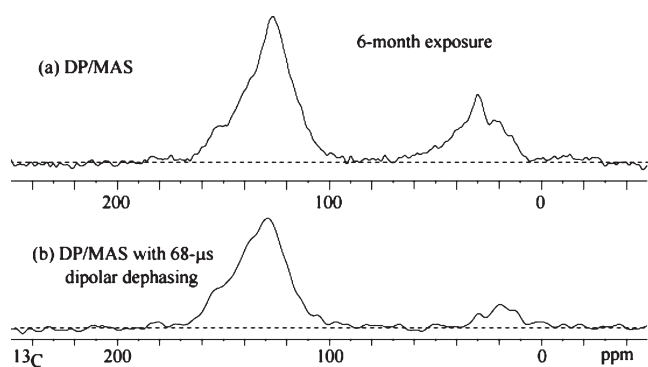


Figure 2. Quantitative ^{13}C DP/MAS NMR spectra at a spinning speed of 14 kHz of (a) DP/MAS and (b) DP/MAS with the recoupled dipolar dephasing of 68 μs . Number of scans: 1216 for (a) and 5120 for (b). Recycle delay: 30 s.

HETCOR. In addition, 40 μs dipolar dephasing was inserted in the LG-CP HETCOR to reveal multibond C–H connectivities for nonprotonated carbons. The number of scans was 1792. Ninety six t_1 increments of 5 μs were used. A more detailed discussion of the 2D HETCOR experiments has been given elsewhere.²⁶

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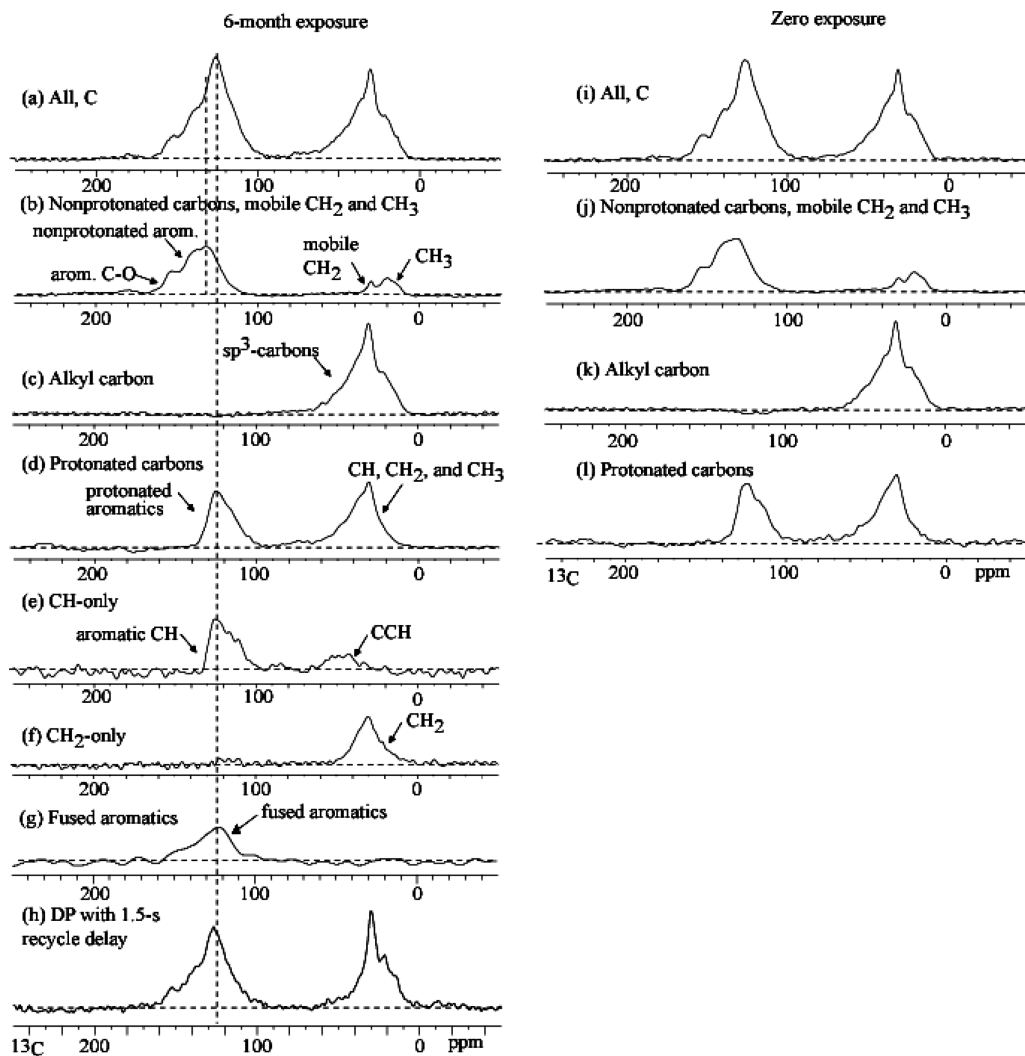


Figure 3. ^{13}C NMR spectral editing for the “6 month exposure” bituminous coal (a–h) and “zero exposure” coal (i–l). (a, i) Full CP/TOSS spectra for reference with a contact time of 1 ms. (b, j) Dipolar dephasing spectra showing nonprotonated carbons and mobile segments like CH_3 and OCH_3 with $40\ \mu\text{s}$ dephasing time. (c, k) Selection of alkyl carbons with a CSA filter, which can particularly identify OCO carbons typical of carbohydrate rings. CSA filter time: $35\ \mu\text{s}$. (d, l) Spectra for protonated carbons. These difference spectra represent the difference between a CP/TOSS spectrum with $50\ \mu\text{s}$ CP and a CP/TOSS spectrum with $50\ \mu\text{s}$ CP and $40\ \mu\text{s}$ dipolar dephasing. (e) CH-only spectrum, obtained by dipolar DEPT. Aromatic CH and CCH bands are clearly observed around 125 and 50 ppm, respectively. (f) Selection of CH_2 groups based on three-spin coherence. (g) Selection of fused-ring carbons using ^1H – ^{13}C recoupled long-range dipolar dephasing. (h) Fast-relaxation components selected by DP/MAS with a short recycle delay of 1.5 s. Number of scans (a) 4096, (b) 8192, (c) 8192, (d) 4096, (e) 34240, (f) 77558, (g) 3968, (h) 6144, (i) 4096, (j) 4096, (k) 4096, and (l) 4096. Recycle delays: all with 1 s, except (g) and (h) where recycle delays are 30 and 1.5 s, respectively.

Results and Discussion

Quantitative ^{13}C NMR Spectra. Quantitative ^{13}C DP/MAS spectra of coal samples with different time exposure to atmospheric oxygen, heating, and vacuum exhibit diagnostic changes in spectral NMR characteristics (Figure 1). The most obvious changes occur in the aliphatic region between 0 and 60 ppm where the signals of most coal volatiles are located. However, the bands in these NMR spectra are broad and assignments of specific functional groups are difficult. Before addressing details of the DP spectra, we need to employ advanced NMR techniques, especially spectral-editing and two-dimensional analyses.

Approximate peak assignments for the DP spectrum (Figure 2a) are as follows: alkyl, 0–50 ppm; O-alkyl, 50–90 ppm; aromatic C–C 90–150 ppm; aromatic C–O 150–165 ppm; COO and NC=O, 165–190 ppm; ketones, quinones, and aldehydes, 190–220 ppm. The rarity of signals

above 165 ppm indicates that contributions from COO, N–C=O, ketones, quinones, and aldehydes are negligible. To aid the interpretation of DP spectra, a series of spectral-editing techniques and two-dimensional HETCOR NMR have been used (Figures 3–6). For our systematic analysis, we usually screen all samples of a project using simple ^{13}C CP/TOSS. Subsequently, several typical samples are chosen for detailed analysis to obtain detailed structural information in an economical manner. Our study indicated that “6 month exposure” coal warranted the most detailed analyses.

Quantitative spectra of “6 month exposure” coal (Figure 2) were integrated, and the results are shown in Table 1. Cumulative aromatics and aliphatics account for 62% and 35% of the total ^{13}C NMR signals, respectively, with only 0.6% C=O and 2.4% COO. Aromatics that are nonprotonated account for 56.3% of all carbons, whereas 5.6% of total carbons are those of protonated aromatic carbons.

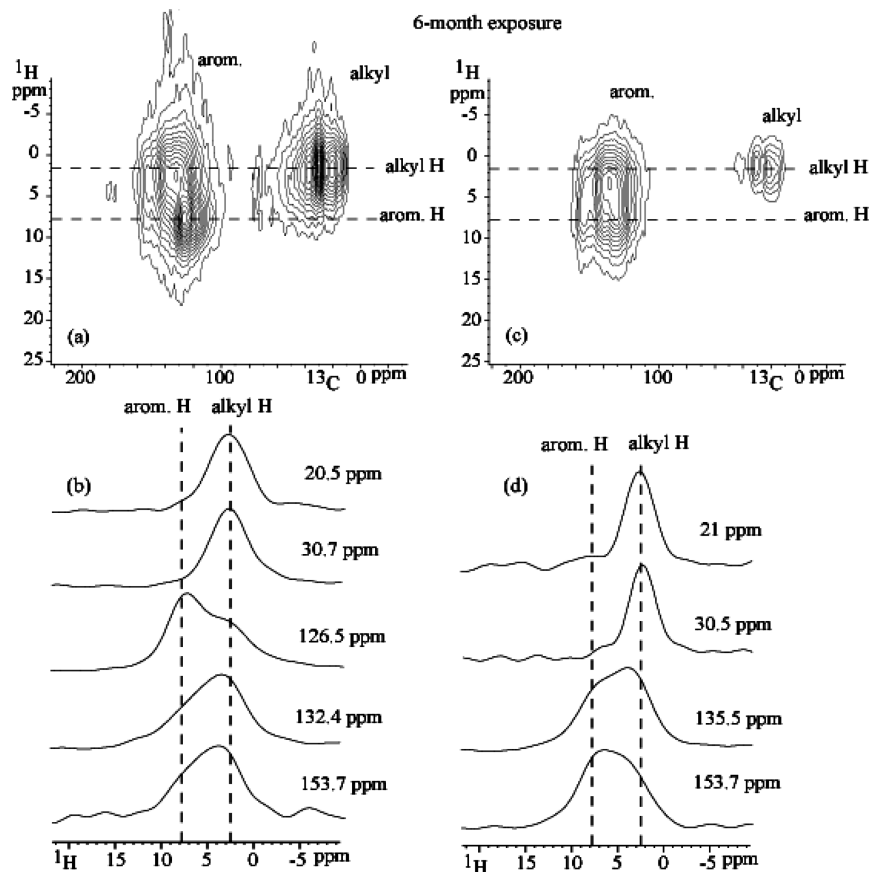


Figure 4. 2D HRTCOR spectra with a LGCP of 0.5 ms of (a) regular NMR spectrum without dipolar dephasing, (b) ^1H slices extracted at ^{13}C chemical shifts of 20.5, 30.7, 126.5, 132.4, and 153.7 ppm for (a); (c) 2D HETCOR with 40 μs dipolar dephasing, and (d) ^1H slices extracted at ^{13}C chemical shifts of 21, 30.5, 135.5, and 153.7 ppm for (c). Number of scans: 1792; recycle delay: 1 s for both (a) and (c).

Most aliphatics belong to alkyl groups, with only 5.6% present in O-alkyl groups.

Functional Groups from Spectral-Editing Techniques. In order to identify peaks reliably in “6 month exposure” coal, we acquired ^{13}C MAS NMR spectra with specially designed pulse sequences that select the signals or subspectra of specific types of chemical groups, such as nonprotonated carbons, CH (methine), CH_2 , and protonated or nonprotonated aromatic carbons. The ^{13}C CP/TOSS spectrum shows qualitative structural information and is primarily used as a reference for selective subspectra (Figure 3a). The corresponding CP/TOSS spectrum after 40 μs of dipolar dephasing exhibits only signals of nonprotonated carbons and mobile groups, including rotating CH_3 groups, which have a reduced C–H dipolar coupling due to their fast motion (Figure 3b). This spectrum shows small signals of highly mobile CCH_3 at 5–24 ppm and of CCH_2 components at ~ 30 ppm, strong signals from nonprotonated aromatic carbons around ~ 132 ppm, and a shoulder attributed to aromatic C–O around 150–160 ppm.

Only sp^3 -hybridized carbon signals remain after the ^{13}C CP/TOSS with a ^{13}C CSA filter of 35 μs (Figure 3c). This spectrum clearly demonstrates the absence of anomeric carbon signals (i.e., O–C–O from carbohydrate rings) between 90 and 120 ppm, confirming the expectation that no carbohydrates are preserved in coal. The signals of alkyl moieties CH_n with $n \geq 1$ are shown in a spectrum where the protonated aromatic band is centered around 125 ppm, along with signals from protonated nonpolar alkyls (i.e., CCH, CCH_2 , and a small contribution of residual CCH_3 ; Figure 3d). The

comparison with the dipolar-dephased spectrum indicates that protonated aromatics are clearly upfield compared with nonprotonated aromatics (see dotted lines in Figure 3b,d), with protonated aromatics around 125 ppm and nonprotonated ones around 132 ppm. The subspectrum selectively displaying methine (CH) signals (Figure 3e) was recorded with the dipolar DEPT technique.³² We observe aromatic C–H bands around 125 ppm that are identical to signals in the CH_n -only spectrum (Figure 2d), as well as CCH bands around 30–60 ppm and centered around 50 ppm. We conclude that the left shoulder of the alkyl band in the CP/TOSS spectrum (Figure 3a) primarily reflects CCH. The subspectrum of CH_2 signals displays only a dominant C– CH_2 band (Figure 2f).

Aromatic carbons in fused rings are spectroscopically selected by ^1H – ^{13}C recoupled dipolar dephasing using a dephasing time of ca. 0.9 ms and are characterized by a broadband ranging from 110 to 150 ppm (Figure 3g; further details given below in Selection of Bridge-Head Carbons.). The broad range of ^{13}C chemical shifts from fused aromatics makes it impossible to distinguish their signals from other aromatic carbons using the routine ^{13}C CP/MAS technique. The DP/MAS spectrum with a short recycle delay of 1.5 s selects signals which are of short ^{13}C spin-relaxation times (T_1 's) and can, thus, relax fast (Figure 3h). Fast-relaxation functional groups allow the acquisition of stronger signals. Compared with the fully relaxed ^{13}C DP/MAS spectrum (Figure 2a), the signals from aromatics are reduced and those of aliphatics are enhanced. As demonstrated in the dipolar-dephased spectrum, aliphatics of CCH_3 and some of CCH_2

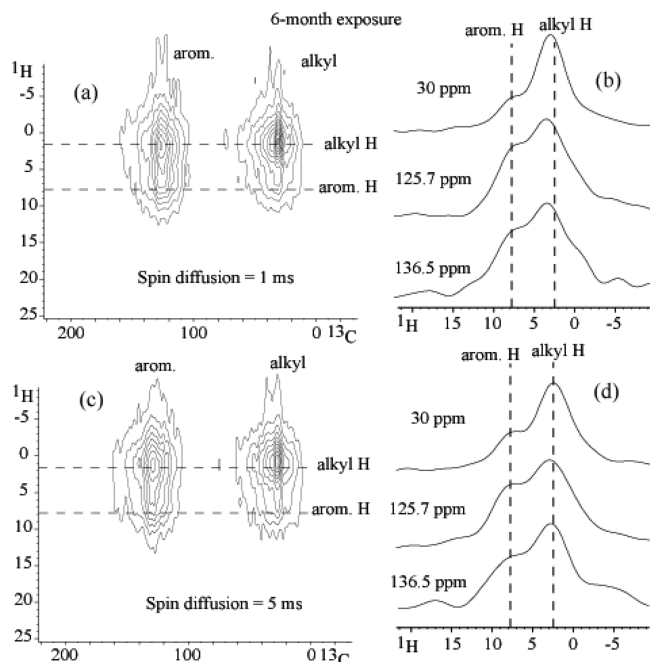


Figure 5. (a) 2D HETCOR spectrum with 1 ms of ^1H spin diffusion and (b) ^1H slices extracted at ^{13}C chemical shifts of 30, 125.7, and 136.5 ppm for (a). (c) 2D HETCOR spectrum with 5 ms of ^1H spin diffusion, and (d) ^1H slices extracted at ^{13}C chemical shifts of 30, 125.7, and 136.5 ppm for (c). Recycle delay: 1 s; number of scans: 896.

are mobile and, thus, have shorter ^{13}C T_1 's. Many aromatics also relax fast, probably due to close proximity to paramagnetic centers such as iron-containing minerals, dominantly pyrite.

In order to examine the differences between the CP-based spectral-editing NMR responses of “6 month exposure” and “zero exposure” coal samples, we also collected the relevant ^{13}C CP/TOSS, dipolar dephased, CH_n -only, and ^{13}C CSA filtered spectra for “zero-exposure” coal (Figure 3i–l). Surprisingly, the corresponding spectra of the two coal samples are almost identical, despite the fact that DP spectra express clear differences in the 0–60 ppm aliphatic region (Figure 1a,c). Although Figure 3 indicates that CP/TOSS and spectral-editing NMR responses of “6 month exposure” and “zero exposure” coals are almost identical, their DP spectra in Figure 1a,c show that the “6 month exposure” coal contains significantly fewer aliphatic carbons with signals around 0–60 ppm. This demonstrates that CP experiments failed to detect adsorbed carbon-containing gases in “zero exposure” coal, whereas DP was able to detect these gases because highly mobile, volatile matter has an extremely low CP efficiency.

Structural Information from Short-Range 2D HETCOR NMR. The spatial proximity of different functional groups can be investigated by 2D HETCOR and 2D HETCOR with dipolar dephasing. The ^1H – ^{13}C 2D HETCOR spectrum of “6 month exposure” coal with 0.5 ms of LGCP shows correlation peaks for one- and two-bond distances (Figure 4a). ^1H slices extracted at the ^{13}C peaks of 20.5, 30.7, 126.5, 132.4, and 153.7 ppm facilitate the analysis (Figure 4b). Note that a proton slice is extracted along the proton dimension at a certain ^{13}C chemical shift in a 2D HETCOR spectrum. At 20.5 and 30.7 ppm where CCH_3 and CCH_2C groups are located, the correlations of these carbons are primarily with

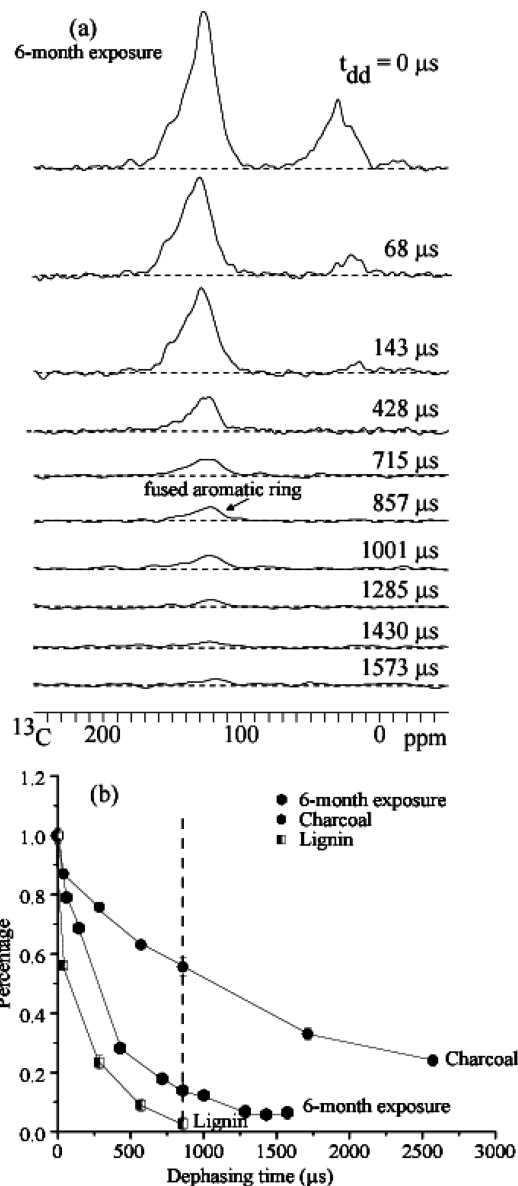


Figure 6. (a) Series of DP/MAS spectra after ^1H – ^{13}C recoupled long-range dipolar dephasing of the indicated durations t_{deph} (dipolar dephasing time). (b) Long-range dipolar dephasing curves for aromatics of 6-month exposure compared to data from ref 34 for wood charcoal and lignin. The aromatic signals were integrated between 90–150 ppm. Filled circles: wood charcoal; filled hexagons: coal; half-filled squares: lignin. Data points have been corrected for regular T_2 relaxation. Number of scans: 992; recycle delays: 30 s.

their own attached protons. Correlations at the ^{13}C chemical shift of 126.5 ppm are attributed to the contribution of protons bonded to aromatic carbons, but reduced correlation with alkyl-bonded protons is also observed. In contrast, correlation for aromatics without directly attached protons at 132.4 ppm is primarily due to alkyl-bonded protons. This suggests that these aromatics belong to alkyl-substituted aromatic moieties. The dominant protons for the slice extracted at 153.7 ppm belong to O-alkyl groups, which is consistent with the presence of aromatic CO-alkyl moieties.

The HETCOR spectrum with dipolar dephasing of “6 month exposure” coal shows nontrivial two-bond correlation peaks of carbons that have no directly bonded protons but interact with other surrounding protons (Figure 4c). Proton slices extracted at the ^{13}C chemical shifts of 21, 30.5,

Table 1. Composition of High Volatile Bituminous Coal after Exposure to Air for 6 Months (“6 month Exposure”) at Room Temperature^a

| parameter percentage | F _{C=O} | F _{COO} | F _{aro} | F _{Oaro} | F _{nao} | F _{Haro} | F _{Oalk} | F _{naik} | F _{CH} | F _{CH2} | F _{CH3} |
|----------------------|------------------|------------------|------------------|-------------------|------------------|-------------------|-------------------|-------------------|-----------------|------------------|------------------|
| | 0.6 | 2.4 | 62.0 | 6.9 | 56.3 | 5.6 | 5.6 | 29.4 | 5.5 | 14.0 | 10.0 |

^a Data were obtained from ¹³C DP NMR combined with spectral-editing techniques. F_{C=O} (220–190 ppm), F_{COO} (190–165 ppm), F_{aro} (165–90 ppm), F_{Oaro} (165–150 ppm), F_{nao} (165–90 ppm), F_{Haro} (150–90 ppm), F_{Oalk} (90–50 ppm), and F_{naik} (50–0 ppm). F_{CH}, F_{CH2}, and F_{CH3} are obtained via DP/MAS and spectral-editing techniques of dipolar dephasing, CH, and CH₂ selection. The percentages are based on integration with total signal area 100%. Note that some parameters are subfractions of others, for example, F_{naik} = F_{CH} + F_{CH2} + F_{CH3}, and thus, the percentages of all listed parameters add up to more than 100%.

Table 2. Effects of Different Coal Treatments on the Integrated NMR Signals of Aliphatic Carbons Based on Quantitative ¹³C DP/MAS Spectra

| sample integral (0–86 ppm) | “zero exposure” (sealed under argon in glass until measurement) | “1 month exposure” in air at room temperature | “6 month exposure” in air at room temperature | “evacuated” for 11 days at room temperature | “75 °C heated” for 11 days in air |
|----------------------------|---|---|---|---|---|
| | 33.2% | 30.3% | 28.0% | 24.2% | 24.0% |

135.5, and 153.7 ppm are shown in Figure 4d. Mobile CCH₃ and CCH₂ carbons at 21 and 30.5 ppm, respectively, are primarily correlated with their own attached protons. Again, the aromatic carbons without attached protons at 135.5 ppm correlate most prominently with alkyl protons, which is indicative of alkyl-substituted aromatic moieties. The slice extracted at 153.7 ppm from 2D HETCOR where aromatic C–O groups are located indicates that these carbons are correlated with alkyl protons, whereas the slice extracted at 153.7 ppm from 2D HETCOR with dipolar dephasing shows that these carbons are dominantly correlated with aromatic protons because dipolar dephasing removes most alkyl protons.

¹H Spin Diffusion and Component Mixing. The domain information on the “6 month exposure” coal can be investigated by 2D HETCOR with ¹H spin diffusion. In the absence of ¹H–¹H spin diffusion during LGCP, with 0.5 ms LGCP and no time for spin diffusion, the magnetization of aromatic and aliphatic protons is not equilibrated (Figure 4a). By introducing mixing times, ¹H spin diffusion is allowed. Spectra of 2D HETCOR with 1 ms and 5 ms spin diffusion are shown in Figure 5a,b, respectively. We extracted three proton slices at ¹³C chemical shifts of 30, 125.7, and 136.5 ppm and found that magnetization between different segments after 1 ms and 5 ms ¹H spin diffusion (Figure 5b,d) resulted in virtually identical signals for the two proton slices at ¹³C chemical shifts of 125.7 and 136.5 ppm, respectively. However, the proton slices extracted at a ¹³C chemical shift of 30 ppm were different from those extracted at ¹³C chemical shifts of 125.7 and 136.5 ppm. This indicates that spin diffusion does not equilibrate the magnetization of aromatic and alkyl ¹H within 5 ms and demonstrates domain separation of at least 2 nm. In contrast, the magnetization of humic substances is equilibrated within 1 ms.^{18,21} In other words, some of aromatics are fused, with alkyls externally attached and, thus, positioned relatively far away from alkyls in this coal; in humic substances aromatics and aliphatics are closely and randomly linked, with no specific domains such as fused-ring carbons, and therefore, their magnetizations can be quickly equilibrated.

Selection of Bridge-Head Carbons. The NMR characteristics of carbons in fused rings were selectively determined via long-range C–H recoupled dipolar dephasing. Mao and Schmidt-Rohr³⁴ demonstrated that lignin was dephased to less than 3% of its original signal after a dephasing time of ~0.86 ms, whereas the charcoal signal was retained at a 50% level. Thus, this condition provides good sensitivity for fused-ring carbons with efficient suppression of signals from only partially substituted individual aromatic rings such as those in lignin. The dephasing time for the “6 month

exposure” coal ranges from 60 to 1573 μs. The response of aromatics becomes smaller with increasing dephasing time (Figure 6a). All the signals of aliphatic carbons are dephased at 428 μs. Small responses of aromatic carbons are still observed at 1573 μs. A comparison of dephasing curves of aromatic carbons in lignin, wood charcoal,³⁴ and “6 month exposure” coal in this study demonstrates that essentially no aromatic carbon signals from lignin are left at the dipolar dephasing time of 0.86 ms, whereas 14% of the aromatic signals remain in “6 month exposure” coal and even 55% in wood char (Figure 6b).

These results show that the average size of polycondensed aromatic ring clusters in “6 month exposure” bituminous coal is relatively small (smaller than in charcoal) although most of the aromatic carbons are not directly bonded to protons, as shown in DP. Nevertheless, aromatic moieties in this coal consist of larger or more densely substituted ring systems than those found in lignin whose aromatics are of single rings.

Effect of Different Coal Treatments on NMR Spectra. In order to avoid the problem of CP efficiencies of ¹³C CP/MAS, we acquired DP/MAS spectra for all five coal samples. The combined oxidative, drying, and gas desorption effects of coal exposure to air are assessed by comparing “zero exposure” coal (Figure 1a) with the respective spectra of “1 month exposure” coal (Figure 1b) and “6 month exposure” coal (Figure 1c). Evacuation of coal only resulted in drying and desorption of gases (Figure 1d), whereas heating of coal for 11 days to 75 °C caused oxidation, drying, and gas desorption (Figure 1e). The DP/MAS spectrum of “zero exposure” coal indicates the highest percentage of aliphatic carbons in total organic carbon in all measured coals (33.2%; Table 2). After “1 month exposure” and “6 month exposure” to air, aliphatic carbon percentages of coals are reduced to 30.3% and 28.0%, respectively. We can rule out oxidation by air at room temperature as a significant factor in the reduction of aliphatic carbons because simple evacuation of coal for 11 days at room temperature lowers the percentage of aliphatic carbon to 24.2% (Table 2). We conclude that exposure to air and vacuum at room temperature causes progressive desorption of volatile aliphatic hydrocarbons from coal. Methane with a ¹³C chemical shift of –2.3 ppm is difficult to be identified in the DP/MAS spectra, with the right sideband of aromatics overlapping with it in the same region. The spectral similarities of aromatic carbons in “zero exposure”, “evacuated”, “1 month exposure”, and “6 month exposure” coals confirm that loss of volatiles at room temperature predominantly affects low-molecular aliphatic compounds (Figure 1). The loss of volatile aliphatic carbon

over 11 days from “75 °C heated” coal results in a very similar percentage of residual aliphatic carbon (24.0%) as observed for coal that was evacuated for 11 days at room temperature (24.4%) and further supports the hypothesis of severe desorption of volatile hydrocarbons. However, the DP/MAS spectrum of the “75 °C heated” coal features a small band around 176 ppm that is assigned to COO and indicates oxidation of coal. While we see these groups being generated as a result of oxidation, our study does not indicate which chemical components or functional groups are being oxidized.

The difference spectrum (i.e., the difference between two NMR spectra) between “zero exposure” coal and “evacuated” coal identifies aliphatic moieties ranging from 5 to 50 ppm and aromatic moieties from 108 to 135 ppm (Figure 6f) as organic compounds missing from “evacuated” coal. Signals around 108–135 ppm are primarily due to CO₂ adsorbed onto porous coal. Free CO₂ has an NMR signal around 124.3 ppm, but surface-adsorbed CO₂ could exhibit a broad range of ppm values that reflect different strengths of adsorption. Aliphatic signals ranging from 5 to 50 ppm are attributed to volatile hydrocarbons. The organic volatiles in coal are a mixture of short and long chain aliphatic hydrocarbons, and thus, their carbon environments are diverse; some of these hydrocarbons are absorbed in the coal matrix, resulting in relatively broad spectra, instead of sharp lines despite their high mobility. The chemical structural information of these volatiles requires further investigation.

Implications for Fossil Fuels. Our results demonstrate that advanced solid-state NMR spectroscopic techniques used in this study can contribute to a better understanding of the chemical structure of coal. The example of a series of coal samples used in this study indicates that atmospheric exposure of coal for up to 6 months at room temperature causes small changes related to oxidation and the loss of volatiles. A previous study on the same coal demonstrated changes in bulk chemistry and porosity as a result of storage at room temperature,¹⁷ whereas no systematic change in functional group distribution was detected by Fourier transform infrared (FTIR) spectroscopy within the precision of the measurements.³⁶ The advanced NMR techniques used in this study were able to detect small changes on a molecular level by documenting loss of volatiles and the formation of oxygenated groups. Different coals spanning various ranks, ages, and maceral compositions may express different responses.

The present study emphasizes superiority of advanced NMR to detect subtle differences among chemically similar coals. Advanced NMR may offer contributions to our understanding of coking properties of coal. Although there is a large body of literature on relationships between coal properties and coke quality,³⁷ important questions remain about the controls on fluidity and the plastic range of coals. Coals of similar rank, maceral composition, and functional group abundance patterns detected by FTIR can have drastically different fluidities.³⁸ The increased capabilities

of advanced NMR may yield clues beyond the capability of other spectroscopic methods.

Advanced NMR techniques can also expand our understanding of the chemical evolution of coal during maturation. The concept of nonlinear “coalification jumps” has been repeatedly expressed in coal literature;³⁷ yet, the underlying chemical properties during gradual versus sharp transitions of maturing coals remain poorly constrained. Similarly, we do not fully understand the continuity of chemical properties of coal macerals and particularly the transition from vitrinite to semifusinite or from reactive semifusinite to nonreactive semifusinite. Are underlying chemical changes gradual, as suggested by optical observations, or are they sharp, as suggested by studies of density fractions?³⁹ These questions are relevant both scientifically as well as with regard to coal utilization.

A similar set of advanced NMR techniques has been used recently to investigate a set of kerogen Type II samples from the New Albany Shale covering a wide range of maturities.⁴⁰ The study underscored the value of aromaticity as a maturity indicator and also showed that the abundances of nonprotonated and protonated aromatic carbon atoms can be used as a maturity proxy. Advanced NMR techniques can quantify “oil prone” (CH₂ and CH groups) and “gas prone” (all carbons excluding CH₂, CH, and aromaticity) carbon moieties in source rocks and, thus, contribute to a better understanding of the hydrocarbon generation potential and the quality of generated hydrocarbons from particular source rocks.

Conclusions

Using advanced spectral-editing techniques, we unambiguously detected the following functional groups in bituminous coal after “6 month exposure” to air: (1) methyl CCH₃; (2) CCH₂C, some of which are mobile; (3) CCH; (4) aromatic CH; (5) aromatic carbons bonded to alkyl groups; (6) small-size condensed aromatic systems; (7) aromatic C–O groups. We found no spectral evidence for OCH₂ or alkyl OCO groups. Four types of aromatic carbons have been identified in this coal: bonded to protons, bonded to alkyl groups, aromatic C–O groups with a hydroxyl or ether substitution, and condensed aromatic clusters with exclusive C–C bonding. ¹H–¹³C 2D HETCOR NMR experiments indicate spatial proximity of aromatic and alkyl moieties in cross-linked structures and, thus, may be suggestive of the complex macromolecular nature of coal. Proton spin diffusion experiments indicate that spatial distances between aromatics and aliphatics are > 2 nm because magnetization of aliphatic and aromatic protons is not equilibrated at a ¹H spin diffusion time of 5 ms. Nonfused aromatic carbons without directly attached protons are predominantly bonded to other aliphatic moieties, such as CCH₃ and CCH₂, and CCH. DP/MAS, but not CP/MAS, allows detection of the changes during low-temperature oxidation and loss of volatiles. Exposure to air and evacuation of coal at room temperature only resulted in drying and desorption of gases while heating of coal for 11 days to 75 °C

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caused oxidation, drying, and gas desorption. The extent of these phenomena could be slightly different for coals of different rank or type.

Acknowledgments. J.-D.M. thanks National Science Foundation Grants (EAR-0843996 and CBET-0853950) and the Donors of the Petroleum Research Fund, administered by the American

Chemical Society, Grant 46373-G2 for financial support. M.M. and A.S. acknowledge support from the U.S. Department of Energy, Basic Energy Research Grant DEFG02-00ER15032, and from the Donors of the Petroleum Research Fund, administered by the American Chemical Society, Grant 44815-AC2. We thank Susan Hatcher for providing access to the COSMIC NMR facility at ODU.