



Insights into the functional group transformation of a chinese brown coal during slow pyrolysis by combining various experiments



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HIGHLIGHTS

- Combined NMR experiments were used to characterize the brown coal char.
- Higher resolution NMR provided unique structural insight of coal char.
- Two distinct transformation intervals of brown coal were clarified.
- Aromatic cluster increased with removal of amorphous carbon.

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ABSTRACT

The effects of heat treatment on the structural transformation of a Chinese brown coal were studied using Fourier transform infrared spectroscopy (FT-IR), high resolution solid-state nuclear magnetic resonance (SSNMR), and Raman spectroscopic techniques. The wide applicabilities of ¹³C dipolar-decoupling magic-angle-spinning (DDMAS), ¹H MAS, ¹H–¹H homonuclear double-quantum (DQ) MAS and ¹H–¹³C cross-polarization heteronuclear correlation (CP-HETCOR) SSNMR approaches that directly probed the proton and carbon spatial interactions within functional groups of Shengli (SL) brown coal char were tentatively demonstrated. Two distinct transformation intervals, as a function of pyrolysis temperature, were clarified in the SL brown coal char. The initial decomposition (at <300 °C) of coal, with slight change in either functional groups or microstructures, may be caused by the loss of adsorbed gaseous materials and partial scission of weak bonds (such as methylene and ether bridges). Moreover, the progressive dehydrogenation and splitting off of side-chains at 400–700 °C resulted in the drastically cracking of aliphatic groups. However, a significant amount of oxygen-containing functional groups were also found, such as heterocyclic, phenolic hydroxyl groups and crystalline hydrates. The thermal treatment was a crystallite-perfecting process, during which the fraction of the amorphous carbon in the coal chars, determined by Raman spectroscopy, was gradually decreased with increase in the heat-treatment temperature; however, the carbon crystallite size did not show any apparent change.

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1. Introduction

The microstructure or molecular structure of coal char usually has quite significant effects on its properties. Although, many studies have been conducted to understand the structural variations in coal char during pyrolysis, it is still very important to systematically elucidate the transformation behaviors of coal using improved technologies throughout the pyrolysis processes.

Numerous nondestructive techniques can be applied to study the changes in the functional groups of coal char and provide

useful information during pyrolysis; however, each of them has its own limitations and thus cannot completely explain the structural transitions in coal char. For example, X-ray photoelectron spectroscopy (XPS) [1] and X-ray absorption near edge spectroscopy (XANES) [2] have been proved to provide functionality determination of coal chars; but, they are mainly valid for surface analysis. FT-IR spectroscopy is widely used to obtain the cross-linked molecular information of organic substances present in coal char; whereas, there are some difficulties in obtaining quantitative information in FT-IR spectra [3–5]. Raman spectroscopy has been extensively used to characterize the structural features of coal-derived products by correlating the Raman bands to structural parameters, out of which only the G (graphite) and D (defect)

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bands are able to investigate the coal char laminar structures and its correlation to other properties [6–9]. Nonetheless, these Raman bands are still ineffective in analyzing the specific functional group changes.

In recent years, the advancements in the solid-state nuclear magnetic resonance (SSNMR) have been extensively used for characterizing the coal char structures [10–12]. In particular, it has been proven to be capable of assessing information about the carbon- and hydrogen-containing groups' features in char using suitable techniques [4,13–18]. By means of the ^{13}C dipolar-dephasing MAS experiment, the same increasing trend of aromatic cluster sizes of bio-chars with increasing temperature and quantitative changes of different aromatic carbon forms and aromatic cluster size as a function of heat treatment temperature were constructively elucidated [11]. ^1H SSNMR techniques are expected to provide unique structural insights for a diverse range of molecular systems. Studies using the ^1H NMR analyses provided the evidence on the increases in the aromaticity and decreases in the peripheral aliphatic groups during the devolatilization of a bituminous coal [19]. A higher quantitative accuracy with these methods is achieved by using higher magnetic-field NMR at the same pulse contact time [20]. The advances in radio frequency console technologies under ultra-high magnetic-field have led to the development of combined rotation and multiple pulse spectroscopy (CRAMPS) NMR, which has improved reliability [21–23]. The enhanced resolution offered by the two-dimensional (2D) ^1H – ^1H double-quantum (DQ) NMR approach combining MAS with homonuclear decoupling pulse sequences is being increasingly applied in the identification of proton distribution [24–27]. Such DQ recoupling techniques extract important structural information by restoring the through-space dipole–dipole couplings, which depends on the inverse cube of the distances between the interacting nuclei [24,28]. In other recent applications, one of the simplest techniques used in the structural determination of coal char is the ^1H – ^{13}C cross-polarization heteronuclear correlation (CP-HETCOR); applying 2D ^1H – ^{13}C correlation techniques, a rapid ^1H and ^{13}C assignment of unknown structures in coal char may be obtained [10,29]. The homonuclear DQ and HETCOR experiments are based on through-space dipolar interactions to generate DQ coherences and magnetization transfer, respectively; thus, specific information regarding internuclear proximities becomes available using such 2D correlation experiments [30,31]. Moreover, a high-magnetic-field NMR will greatly enhance the resolution of half-integer nuclei, allowing for increased structural analysis. Therefore, these NMR experiments are strongly suggested to obtain more valuable information for elucidating the detailed spatial correlations among the various carbon and hydrogen functional groups in coal char.

This study uses FT-IR, Raman, and SSNMR (combining ^{13}C dipolar-decoupling (DD) MAS, ^1H MAS, ^1H – ^{13}C CP-HETCOR, and ^1H – ^1H homonuclear DQMAS experiments) for integrally probing the functional groups and structural changes in coal char during its slow pyrolysis.

2. Experimental

2.1. Samples

The Shengli (SL) brown coal was collected from the sixth seam of Shengli deposit west #1 mine located in Inner Mongolia, China. The as-received coal samples were crushed and ground to fine powders and then dried at 105 °C for 1 h in air. The coal samples were heat treated in a tube bomb reactor (open system mode with a constant N_2 gas flow) to the target temperatures (i.e., 200, 300, 400, 500, 600, and 700 °C) with a 20 °C/min heating rate. The

Table 1
Proximate analysis and ultimate analysis of SL brown coal.

Ultimate analysis					Proximate analysis			
C_{daf} (wt%)	H_{daf} (wt%)	N_{daf} (wt%)	S_{daf} (wt%)	O_{daf} (diff.) (wt%)	FC_{db} (wt%)	V_{db} (wt%)	Ash_{db} (wt%)	H/C
73.76	3.90	0.88	0.82	20.64	43.31	34.46	22.24	0.70

Note diff.: by different; daf.: dry ash free; db.: dry basis.

results of the proximate and ultimate analyses of SL brown coal are shown in Table 1.

2.2. FT-IR analysis

The FT-IR analyses for the raw and as-prepared samples were carried out on an FT/IR-615, JASCO (JASCO Ltd., Japan) spectrometer using the transmission mode. For preparing pellets, the sample (ca. 1 mg) was further ground to a powder with a particle size of $\sim 75\ \mu\text{m}$ and mixed with KBr (ca. 200 mg). The sample pellets were prepared using the normal KBr procedure and were dried in an oven at 60 °C for 12 h. All the spectra were obtained at a resolution of $4\ \text{cm}^{-1}$ in the 4000 – $400\ \text{cm}^{-1}$ wave number range, and 32 scans per spectrum were performed.

2.3. SSNMR analyses

2.3.1. Quantitative ^{13}C DD MAS

The ^{13}C DDMAS experiments were performed using a JEOL ECA-400 (JEOL Ltd., Japan) (9.4 T, 400 MHz for ^1H NMR) SSNMR. The well-established high-power DDMAS allows high-resolution ^{13}C NMR spectra to be obtained routinely [12].

The sample (ca. 400 mg) was packed into a zirconia rotor using a 3.2 mm CP/MAS probe. The high-resolution ^{13}C NMR spectra were obtained at a frequency of 100.56 MHz with a 15 kHz MAS speed to give spectra in which the spinning sideband intensities were less than 5% of the central aromatic band intensities. The 30° pulse length was ca. 4 μs , and the smaller pulse angle was for the shorter repetition time. The ^1H decoupling field was ca. 39 kHz. Recycle delays of raw coal and chars prepared at 200, 300, 400, 500, 600, and 700 °C were 40, 30, 40, 30, 40, 30, and 30 s respectively, which were determined to ensure that all the carbon nuclei were relaxed by more than 95%. Over 20,000 transients and 2048 data points for all samples were collected with an acquisition time of 50 ms. The ^{13}C NMR chemical shift was indirectly calibrated through the methyl moiety of hexamethylbenzene peak observed at chemical shift of $\delta = 17.36\ \text{ppm}$. To quantify the relative proportion of different carbon types in the samples, curve fitting of the ^{13}C NMR spectrum was conducted to eight Gaussian peaks and four Lorentzian peaks (for the spectrum of Fig. 4a) by adjusting the full width at half-maximum (FWHM) and chemical shifts.

2.3.2. Quantitative ^1H MAS spectrum

The spectra were obtained on a JEOL ECA-800 spectrometer operating at a ^1H frequency of 800 MHz, and a sample spinning speed of 20 kHz. Recycle delay of 5 s were used. All the spectra were acquired with a ^1H 90° pulse length of 1.5 μs and a dead time interval of 2.5 μs . A pulse repetition rate of 10 Hz was used on all the samples allowing for full ^1H relaxation and pulse recovery. Approximately 32 transients were averaged for each free induction decays, comprising 128 data points. The ^1H chemical shift was externally referenced to tetramethylsilane with a ^1H chemical shift at $\delta = 0\ \text{ppm}$. The line shape analyses were also performed to resolve curve into two Gaussian peaks and one Lorentzian peak (designated for the O-alkyl-H peak) [32].

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