Fuel Processing Technology 96 (2012) 56–64

Contents lists available at SciVerse ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Characterization of coals and their laboratory-prepared black carbon using advanced solid-state ^{13}C nuclear magnetic resonance spectroscopy

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ARTICLE INFO

Article history:
Received 9 January 2011
Received in revised form 22 August 2011
Accepted 10 December 2011
Available online 13 January 2012

Keywords:
Lignite
Humic acid
Anthracite
Black carbon
Solid-state NMR

ABSTRACT

Lignite, anthracite, humic acid fraction of lignite, and their laboratory-prepared black carbon (BC) were characterized in detail by advanced solid state ^{13}C NMR spectroscopy to examine how the differences in chemical structures of fuels (lignite and anthracite) would affect the structures of their BC. Anthracite was almost completely dominated by aromatics (96.9%), with very minor CCH_3. Although lignite contained mostly aromatics (76.1%), significant aliphatics (21.3%) as well as small amounts of COO/N–C═O and O-alkyls were also present. In addition, anthracite had more aromatic C–C groups than lignite. Their BC samples both exhibited increased oxygenated functional groups such as COO, aromatic C−O and O-alkyl groups, and concomitant decrease of aromatic C–H and nonpolar alkyls. The ^{1}H–^{13}C recoupled long-range dipolar dephasing experiments indicated the growth of aromatic cluster sizes in BC. Although the aromaticity of anthracite was much larger than those of lignite and lignite humic acid, their aromatic cluster sizes were quite similar. The BC samples had much larger aromatic cluster sizes than anthracite despite their smaller aromaticities. Therefore, higher rank or higher aromaticity may not imply larger aromatic cluster size in coal. The structures of two BC samples were similar despite the contrasting structural differences of their original coals.

1. Introduction

Black carbon (BC), a collective term of highly condensed carbonaceous materials such as soot and char generated from incomplete combustion of biomass and fossil fuels, occurs ubiquitously and persistently in atmosphere, soils and sediments due to its widespread production and inertness in the environment [1–3]. BC has been reported to participate in various geochemical and environmental processes such as global cycling of carbon, transport and fate of organic pollutants [2,4–6]. Realization of the importance of BC has initiated great interest in its isolation, quantification, as well as characterization [2,3,5,7–9]. Formation of BC depends on fuel type, pressure, temperature, oxygen supply, and duration of combustion. Its chemical compositions and structures, therefore, are expected to vary accordingly [10,11]. Indeed, BC is understood as a combustion continuum of materials with widely different physicochemical properties [12]. Soot and char are two general groups of BC particles. While soot-BC is formed at high temperatures from the condensation of hydrocarbons in the vapor phase, char-BC is large residues produced at lower temperatures on solid fuel surfaces [10,13]. Different chemical and structural features among BC exert direct influence on their roles and fates in the environment. Therefore, structural information of BC from different sources is critical for investigating their environmental impacts and better understanding the scientific questions related to BC such as its sorption behavior.

Many techniques, including optical microscopy, scanning electronic microscopy, infrared spectroscopy, pyrolysis-gas chromatography-mass spectroscopy, and solid state ^{13}C NMR [9,10,17,18], have been applied to investigate the complex structures of BC. Among those, nondestructive ^{13}C NMR is one of the most powerful tools [19]. The wide application of ^{13}C cross polarization magic angle spinning (CP/MAS) technique has significantly advanced our knowledge of coal chemical structures [20–28] and BC [10,17,29]. Recently, we have developed, modified, and applied many advanced solid-state NMR techniques for characterizing natural organic matter. These systematic techniques can allow for identification of specific functional groups by spectral-editing techniques, detection of connectivities and proximities via two-dimensional ^{1}H-^{13}C heteronuclear correlation NMR (2D HETCOR) and 2D HETCOR combined with spectral-editing techniques, and examination of domains and heterogeneities by ^{1}H spin diffusion [30–37]. Especially, spectral editing techniques such as dipolar dephasing, CH selection, CH_2 selection and ^{13}C chemical shift anisotropy (CSA) filter permit the separation of certain carbon

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Abbreviations: LHA, lignite humic acids; LC, lignite black carbon; AC, anthracite black carbon.

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doi:10.1016/j.fuproc.2011.12.014

moieties that are otherwise overlapped in the same spectral region [32–36]. In addition, the direct polarization (DP) technique is employed to provide quantitative structural information [38].

Coal is produced and used in large quantity, and its combustion residues are released into the environment as BC. Chemothermal oxidation at 375 °C (CTO-375 method) is widely accepted by scientists in environmental science and engineering to determine BC content in soils and sediments [4,14–16]. The objectives of the present study were (1) to characterize two structurally distinct coals (anthracite and lignite) and their laboratory-prepared BC generated by CTO-375 method in detail using advanced solid-state ^{13}C NMR techniques, and (2) to examine how the differences in chemical structures of fuels (lignite and anthracite) would affect the structures of their BC. Lignite is the lowest rank of coal whereas anthracite is the highest. Since coal is a complex, heterogeneous mixture, separation of coal into sub-fractions can aid structural characterization. Extraction of humic acids is a routine, widely adopted procedure for fractionating organic matter. Therefore, we also included lignite humic acid in the present study. We were not able to characterize anthracite humic acid because we could not extract enough humic acid from this coal for NMR study.

2. Experimental section

2.1. Coal sample collection and preparation of BC

The lignite was collected from Zhalainuoer Coalfield, Inner Mongolia, and the anthracite was sampled from Rujigou Coalfield, Ningxia in China. The two coal samples were ground, sieved (<2 mm), and stored at the room temperature. Their proximate analysis and ultimate analysis are listed in Table 1 and their maceral and inorganic components are shown in Table 2. The lignite humic acid (LHA) was extracted and then purified using a method similar to the preparation of soil humic acids, as detailed elsewhere [39].

Coal samples were oven-heated to 375 °C and then held for 2 h to produce lignite black carbon (LC) and anthracite black carbon (AC). This procedure was frequently used to determine BC in soils and sediments for environmental studies in the literature [4,14–16,40]. It should be noted that the conditions used for preparing BC in laboratory in the present study may not reflect those of real-world coal combustion.

2.2. Ultimate, proximate, inorganic elemental and petrographic analyses

Elemental compositions (C, N, S, H) were measured using an elemental analyzer of Heraeus CHN-O-RAPID (Hanau, Germany). Prior to the analysis, the coal samples were demineralized to remove inorganic carbons (primarily carbonates). The proximate analysis followed the ASTM test methods [41]. Inorganic elemental composition was determined based on analysis of X-ray fluorescence (XRF) (ARL 9800XP+, Switzerland). The petrographic analyses were performed on a reflectance microscopy (NIKON E600POL-FL) (Tokyo, Japan) using both white light and fluorescence.

2.3. NMR spectroscopy

^{13}C NMR analyses were performed using a Bruker Avance III 300 spectrometer at 75 MHz (300 MHz ^{1}H frequency). All experiments were run in a double-resonance probe head using 4-mm sample rotors.

2.3.1. Quantitative ^{13}C direct polarization magic angle spinning (DP/MAS) NMR

Quantitative ^{13}C DP/MAS NMR experiments were performed at a spinning speed of 13 kHz. The 90° ^{13}C pulse-length was 4 μs. Recycle delays, ranging from 20 to 60 s, were determined by the cross polarization/spin–lattice relaxation time/total sideband suppression (CP/T_1-TOSS) technique to ensure that all carbon nuclei were relaxed by more than 95% [42]. Nonprotonated carbons and mobile carbon fractions, such as rotating CCH_3 methyl groups which have weaker C–H dipolar couplings than other groups, were quantified using a combination of DP/MAS technique with a recoupled dipolar-dephasing delay of 68 μs [38]. The recycle delays and numbers of scans for DP/MAS were 40 s and 3072 scans for lignite, 50 s and 1024 scans for LHA, 60 s and 1024 scans for LC, 25 s and 2386 scans for anthracite, and 20 s and 2432 scans for AC, respectively. The recycle delays and numbers of scans for DP/MAS with dipolar dephasing were 40 s and 1280 scans for lignite, 50 s and 1024 for LHA, 60 s and 988 scans for LC, 25 s and 1800 scans for anthracite, and 20 s and 2432 scans for AC, respectively.

2.3.2. ^{13}C cross polarization and total suppression of sidebands (CP/TOSS) and ^{13}C CP/TOSS plus dipolar dephasing

Semi-quantitative compositional information was obtained with good sensitivity using a ^{13}C CP/MAS NMR technique (MAS = 5 kHz, CP time = 1 ms, and ^{1}H 90° pulse-length = 4 μs). Four-pulse total suppression of sidebands (TOSS) [43] was employed before detection, with a two-pulse phase-modulated (TPPM) decoupling applied for optimum resolution. Sub-spectra for nonprotonated and mobile carbon groups were obtained by ^{13}C CP/TOSS sequence with 40-μs dipolar dephasing. The numbers of scans of ^{13}C CP/TOSS were 10240 for lignite, 4096 for anthracite, and 6144 for LHA, LC, and AC. The numbers of scans of ^{13}C CP/TOSS with dipolar dephasing were 7168 for lignite and 6144 for LHA, LC, anthracite, and AC. The recycle delay was 1.0 s for lignite and 0.8 s for other samples.

2.3.3. ^{13}C chemical-shift-anisotropy (CSA) filter

In many natural organic matter samples the resonances of O–C–O carbons (e.g. anomeric C in carbohydrate rings) and aromatic carbons can overlap between 120 and 90 ppm. The aromatic carbon signals were selectively suppressed using a five-pulse ^{13}C CSA filter with a CSA-filter time of 47 μs [44]. The numbers of scans were 6144 for all samples except 8192 for lignite. The recycle delay was 1.0 s.

Table 1
Data from proximate and organic elemental analysis.

Sample location	Sample	Proximate analysis (%)[a]					Ultimate analysis (%)			
		Moisture	Ash	Volatile matter	Fixed carbon	Total sulfur	C	N	S	H
Zhalainuoer Coalfield, Inner Mongolia	Lignite	17.6	5.30	36.8	40.4	0.29	71.0	4.32	0.52	4.80
Rujigou Coalfield, Ningxia	Anthracite	0.27	23.1	8.97	67.7	0.36	90.9	4.52	0.48	4.08
NA[b]	LHA		NA				63.0	2.55	0.39	1.49
NA[b]	LC		NA				7.0	3.36	0.22	2.71
NA[b]	AC		NA				53.4	3.86	0.27	3.59

[a] Air dry basis.

[b] NA: not applicable.