



Chemical structures of coal lithotypes before and after CO₂ adsorption as investigated by advanced solid-state ¹³C nuclear magnetic resonance spectroscopy

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ABSTRACT

Four lithotypes (vitrain, bright clarain, clarain, and fusain) of a high volatile bituminous Springfield Coal from the Illinois Basin were characterized using advanced solid-state ¹³C nuclear magnetic resonance (NMR) spectroscopy. The NMR techniques included quantitative direct polarization/magic angle spinning (DP/MAS), cross polarization/total sideband suppression (CP/TOSS), dipolar dephasing, CH_n selection, and recoupled C–H long-range dipolar dephasing techniques. The lithotypes that experienced high-pressure CO₂ adsorption isotherm analysis were also analyzed to determine possible changes in coal structure as a result of CO₂ saturation at high pressure and subsequent evacuation. The main carbon functionalities present in original vitrain, bright clarain, clarain and fusain were aromatic carbons (65.9%–86.1%), nonpolar alkyl groups (9.0%–28.9%), and aromatic C–O carbons (4.1%–9.5%). Among these lithotypes, aromaticity increased in the order of clarain, bright clarain, vitrain, and fusain, whereas the fraction of alkyl carbons decreased in the same order. Fusain was distinct from other three lithotypes in respect to its highest aromatic composition (86.1%) and remarkably small fraction of alkyl carbons (11.0%). The aromatic cluster size in fusain was larger than that in bright clarain. The lithotypes studied responded differently to high pressure CO₂ saturation. After exposure to high pressure CO₂, vitrain and fusain showed a decrease in aromaticity but an increase in the fraction of alkyl carbons, whereas bright clarain and clarain displayed an increase in aromaticity but a decrease in the fraction of alkyl carbons. Aromatic fused-rings were larger for bright clarain but smaller for fusain in the post-CO₂ adsorption samples compared to the original lithotypes. These observations suggested chemical CO₂–coal interactions at high pressure and the selectivity of lithotypes in response to CO₂ adsorption.

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1. Introduction

Carbon dioxide (CO₂) adsorption into coal has been widely investigated due to the potential of sequestration of CO₂ into deep, unminable coal seams as an appealing option to reduce its levels in the atmosphere and alleviate the greenhouse effects (White et al., 2005). Despite the abundant information on coal shrinkage/swelling (Reucroft and Patel, 1986; Seidle and Huitt, 1995; Walker et al., 1988) and pore characteristics (Mastalerz et al., 2008; Melnichenko et al., 2009), much less is known about chemical–structural changes in relation to CO₂ adsorption, the knowledge of which will undoubtedly enhance our understanding of CO₂–coal interaction mechanisms during CO₂ sequestration.

Coal is a heterogeneous, complex mixture of inorganic minerals and organic materials, which complicates the understanding of the

interaction mechanisms between coal and CO₂. Coal lithotypes, macroscopically recognizable coal bands, have different maceral compositions, porosity characteristics, chemical composition, and cleating, and are expected to influence CO₂ injectivity differently (Mastalerz et al., 2008). In addition, individual macerals and their associations in lithotypes may play different roles in interacting with CO₂. Therefore, understanding maceral compositions and chemical–structural properties of lithotypes is important for gaining insights into their behavior during CO₂–coal interactions.

Nondestructive solid-state ¹³C NMR techniques are widely used for coal characterization. Extensive application of ¹³C cross polarization magic angle spinning (CP/MAS) technique has significantly advanced our knowledge of coal chemical structures (Botto, 1996; Crelling et al., 1979; Hatcher et al., 1992; Mukhopadhyay and Hatcher, 1993; Pugmire, 1996; Snape et al., 1989; Suggate and Dickinson, 2004; Wilson et al., 1993). However, ¹³C CP/MAS spectra usually display two broad bands, representing the aromatic and aliphatic carbons, and consequently, provide limited opportunity for specific assignments of functional groups. For this reason, advanced solid-state ¹³C-NMR techniques were developed and applied to study coals (i.e., Botto, 1996; Hu et al., 2001; Zilm

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and Webb, 1988). We have further developed, modified and applied a series of advanced NMR techniques for the study of complex natural organic matter. Of particular utility are spectral-editing techniques that are suitable for identification of specific functional groups from the broad and overlapping spectra (Mao et al., 2007a, b, 2010a, b). For example, spectral editing techniques can selectively distinguish the signals of CH and CH₂ groups (Mao and Schmidt-Rohr, 2005; Schmidt-Rohr and Mao, 2002) and ¹H–¹³C long-range dipolar dephasing (Mao and Schmidt-Rohr, 2003) enables the estimation of degree of aromatic condensation in coal.

Our recent studies demonstrated the utility of these advanced techniques for the analyses of fossil fuels, including kerogen Type II (Mao et al., 2010a). In the present study we utilized advanced solid-state ¹³C NMR spectroscopy techniques to (i) investigate the variations in chemical structures among four lithotypes (vitrain, bright clarain, clarain, and fusain) of a high volatile bituminous coal, and (ii) determine possible changes in chemical structures of these coal lithotypes as a result of CO₂ saturation at high pressure.

2. Materials and methods

2.1. Coal lithotypes

Four coal lithotypes, vitrain, bright clarain, clarain, and fusain, were hand-picked from a core of the Pennsylvanian Springfield Coal Member (Petersburg Formation) from the Tanquary CO₂ injection site in Illinois (Morse et al., 2010). It is a high volatile bituminous coal with vitrinite reflectance (R_o) of 0.63%. Maceral compositions of these lithotypes (Table 1) demonstrate a progressive decrease in vitrinite and increase in inertinite from vitrain through bright clarain and clarain to fusain. Prior to advanced ¹³C solid-state NMR spectroscopy, high-pressure CO₂ adsorption isotherm (HPI) analyses were performed on the samples crushed to 60-mesh size, using a high-pressure volumetric adsorption instrument (Mastalerz et al., 2010). The pressure during the adsorption isotherms ranged from 25 psi to 620 psi (0.17 MPa–4.27 MPa) and the temperature was kept at 20 °C. Such temperature and pressure ranges kept CO₂ in a gas phase and prevented its phase change into supercritical fluid. The samples were moisture-equilibrated and there were nine pressure steps with several hour equilibration periods between them. The analysis and adsorption data collection followed the procedure outlined in Mavor et al. (1990).

2.2. NMR spectroscopy

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

2.2.1. Quantitative ¹³C direct polarization/magic angle spinning (DP/MAS) NMR

Quantitative ¹³C DP/MAS NMR experiments were performed at a spinning speed of 13 kHz. The 90° ¹³C pulse-length was 4 μs. Sufficiently strong ¹H decoupling at $\gamma B_1/2\pi = 72$ kHz with the two-pulse phase-modulated (TPPM) phase scheme for an acquisition time of 2 ms ensured full detection of CH₂ signals. Recycle delays (ranging

from 25 to 50 s) were determined by the cross polarization/spin-lattice relaxation time/total sideband suppression (CP/T₁-TOSS) technique to ensure all carbon nuclei were relaxed by more than 95% (Mao et al., 2000). Nonprotonated carbons (i.e. carbons with no directly attached protons) and mobile carbon fractions (such as rotating CCH₃ 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 pulse (Mao and Schmidt-Rohr, 2004). The recycle delays and numbers of scans for DP/MAS and DP/MAS with dipolar dephasing were as follows: for vitrain original, bright clarain original, and bright clarain after HPI, 50 s and 1024 scans; for clarain original, 30 s and 1024 scans; for fusain original, 30 s and 1280 scans; for vitrain after HPI, 40 s and 1280 scans; for clarain after HPI, 35 s and 1024 scans; and for fusain after HPI, 25 s and 1280 scans.

2.2.2. ¹³C cross polarization and total sideband suppression (CP/TOSS) and ¹³C CP/TOSS with dipolar dephasing

Semi-quantitative compositional information was obtained with good sensitivity using ¹³C cross polarization/magic angle spinning (CP/MAS) NMR technique, with MAS = 5 kHz, CP time = 1 ms, and ¹H 90° pulse-length = 4 μs. Four-pulse total suppression of sidebands (TOSS) (Dixon, 1982) was employed before detection, with a TPPM decoupling applied for optimum resolution. Sub-spectra for nonprotonated and mobile carbon groups were obtained by combining the ¹³C CP/TOSS sequence with a 40-μs dipolar dephasing. The numbers of scans of ¹³C CP/TOSS were 4096 for vitrain original, bright clarain original, and clarain original, and 6144 for fusain original. The recycle delay was 0.8 s for four original lithotypes. The numbers of scans of ¹³C CP/TOSS with dipolar dephasing for four lithotypes were 6144. The recycle delay was 0.8 s for vitrain original, bright clarain original, and clarain original, and 0.5 s for fusain original.

2.2.3. Spectral editing of immobile CH₂ + CH

The spectra for immobile CH₂ plus CH groups were obtained with good sensitivity using the following spectral-editing technique. First, a ¹³C CP/TOSS spectrum was recorded using a short CP time (50 μs) to emphasize protonated carbons in immobile segments. After this procedure, residual quaternary carbon peaks were observed as a result from two-bond magnetization transfer. Afterwards, a second ¹³C CP/TOSS spectrum was recorded using a short CP (50 μs) coupled with a 40-μs dipolar dephasing. The resultant spectra contained the residual signals of quaternary carbons or mobile segments (including CH₃ groups with >50% efficiency relative to the corresponding CP/TOSS spectra). This residual spectrum was then subtracted from the first CP/TOSS spectrum without any scaling. The difference spectrum represents immobile CH₂ and CH carbons, with a small CH₃ contribution (Mao and Schmidt-Rohr, 2004). The number of scans was 7168 for all four original lithotypes. The recycle delay was 1.0 s for vitrain original, bright clarain original, and clarain original, and 0.7 s for fusain original.

2.2.4. ¹H–¹³C long-range recoupled H–C dipolar dephasing experiments

The size of fused aromatic rings was estimated from the recoupled ¹H–¹³C dipolar dephasing (Mao and Schmidt-Rohr, 2003). In short, two ¹H 180° pulses per rotation period prevent MAS from averaging

Table 1
Petrographic composition (in vol.%) of the lithotypes.

	Telovit.	Detrovit.	Gelovit.	TV	Spor.	Cut.	TL	Semifus.	Fus.	Inertodet.	TI	MM
Vitrain	89.6	4.2	0.0	93.8	1.2	0.6	1.8	1.0	0.0	1.8	2.8	1.6
Bright clarain	63.8	8.2	0.0	72.0	4.2	0.0	4.2	2.6	6.2	7.8	16.6	7.2
Clarain	50.6	14.0	0.0	64.6	4.6	0.0	4.6	11.0	6.2	8.0	25.2	5.6
Fusain	4.6	0.8	0.0	5.4	1.0	0.0	1.0	6.2	81.2	6.2	93.6	0.0

Abbreviations: Telovit. – telovitrinite, Detrovit. – detrovitrinite, Gelovit. – gelovitrinite, TV – total vitrinite, Spor. – sporinite, Cut. – cutinite, TL – total liptinite, Semifus. – semifusinite, Fus. – fusinite, Inertodet. – inertodetrinite, TI – total inertinite, MM – mineral matter. These data in bold are used to correlate with the contents of different functional groups in lithotypes (see Fig. 6).

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