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Full Length Article

A study on average molecular structure of eight oil shale organic matters and radical information during pyrolysis

Xiaosheng Zhao, Zhenyu Liu, Zhenghua Lu, Lei Shi, Qingya Liu*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

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ABSTRACT

Eight oil shale samples from different mines are demineralized and characterized to understand the average molecular structure of the organic matters (OMs). The active radicals generated during pyrolysis of the OMs are quantified to evaluate the relation between average molecular structure and bond cleavage. Results indicate that all the OMs are similar to lignite in metamorphic grade and their carbon contents range from 64 wt% to 70 wt%, H/C molar ratios range from 1.0 to 1.5, and the volatile contents range from 52.7 wt% to 82.2 wt%. The aliphaticity and aromaticity of the OMs are 0.45–0.77 and 0.18–0.49, respectively. The H/C molar ratio is in direct proportion to the aliphaticity and the volatile content of the OMs while in inverse proportion to the aromaticity. Pyrolysis experiments at 420 °C in the presence of 9,10-dihydrophenanthrene (DHP) show that the active radicals generated by bond cleavage are in a range of 15.1–24.3 mmol/g in 12 min, with half of them generated in 2 min. The bonds cleaved in the pyrolysis are mainly those between α–C_{al} and β–C_{al} in C_{ar}–C_{al}–C_{al} chains and C_{al}–O. The quantity of radicals survived in the pyrolysis product (i.e. stable radicals) determined by electron spin resonance (ESR) correlates linearly with the quantity of active radicals. The probability of stable radicals' formation in the pyrolysis correlates poorly with the aromaticity of the OMs and the concentration and size of the average aromatic clusters, although the stable radicals are considered to be un-paired electrons confined in aromatic structure.

1. Introduction

With increasing consumption and shortage of petroleum resources worldwide, research and exploitation of oil shale have attracted increasing attention. Oil shale consists of organic matter (OM) and inorganic minerals [1], and the OM can be converted to shale oil through pyrolysis or retorting. Similar to pyrolysis of biomass and coal, pyrolysis of oil shale follows the radical mechanism that comprises generation of radical fragments by bond cleavage of OM and reactions of the radical fragments [2,3]. During pyrolysis, the majority of radicals generated (termed active radicals) couple and/or condense into volatiles and non-volatiles such as char, while a few radicals (termed stable radicals) are confined in non-volatiles especially in char due to steric hindrance [4–8]. It was found in reaction of biomass and coal derived tars that the quantity of stable radicals is in direct proportion to the quantity of active radicals generated and to the quantity of soot formed [9,10]. Clearly, the active radicals are reactive intermediates in pyrolysis and influence the yield and composition of pyrolysis products. Understanding the formation of active and stable radicals is a must for chemical reaction based reactor design and process development, and important in future for artificial intelligence based reactor and process design.

The behaviors of active radicals' generation and reaction are determined by the molecular structure of OM and pyrolysis conditions. The structure of OM in oil shale has been widely studied by ultimate analysis and ^{13}C NMR [11–16], and also by the stable radicals' concentration determined by electron spin resonance (ESR) because it characterizes the aromatic structure of OM as evidenced in studies of coal and asphaltene [17,18]. It is well recognized that the OM in oil shale is a three-dimensional macromolecular consisting of aromatic clusters and aliphatic chains, and the cluster size and chain length vary with the oil shale [11–16]. Given that formation of oil shale is similar to that of coal [19,20] and the average molecular structure of coal undergoes systemic changes during coalification, resulting in an increased aromaticity (f_{ar}) and decreased H/C and O/C molar ratios and aliphaticity (f_{al}) [7,21], the relation of f_{ar} or f_{al} with the H/C ratio may also be applicable to the OM of oil shale. Therefore, oil shale samples from eight geographical regions in the world are selected to study these relations with the aids of ultimate analysis, ^{13}C NMR and ESR.

Generation of active radicals through bond cleavage during

* Corresponding author.
E-mail address: qyliu@mail.buct.edu.cn (Q. Liu).

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pyrolysis of oil shale is rarely investigated except our study on Huadian oil shale [6]. It was found that the concentration of active radicals (termed $C_{R\text{-}t}$) approximates 12–26 mmol/g-OM at 380–420 °C within 30 min. Stable radicals were detectible in the pyrolysis product with a concentration (termed $C_{R\text{-}s}$) of about 10^{-6}–10^{-5} mol/g. The relation of average molecular structure of OM with $C_{R\text{-}t}$ or $C_{R\text{-}s}$ has not been established because only one sample was evaluated. This work will address this relation using eight oil shale samples.

2. Experimental

2.1. Materials

The oil shale samples used in this work include six from China, one from Burma (MM), and one from Morocco (MA). The six Chinese samples are from Huadian (HD) of Jilin Province, Beipiao (BP) of Liaoning Province, Tongchuan (TC) of Shaanxi Province, Barkol (BK) of Xinjiang Province, Longkou (LK) of Shandong Province, and Yilan (YL) of Heilongjiang Province. To avoid minerals' effect on pyrolysis of the OM, all the samples were subjected to acid treatments after being ground and sieved to below 100 mesh (0.15 mm). The detailed acid treatments procedures can be found in the literature [22,23]. Since the demineralized samples are mainly organic matters (OMs), they are termed as HDOM, BPOM, TCOM, BKOM, LKOM, YLOM, MMOM and MAOM accordingly.

2.2. Characterization of materials

2.2.1. Ultimate and proximate analyses

The ultimate analysis of the OMs was performed on an elemental analyzer (Elementar Vario EL Cube) which quantifies the samples' C, H, N and S contents. These elements are converted to CO_2, H_2O, N_2 and SO_2, respectively, and then analyzed by a TCD detector calibrated by sulfadiazine. The absolute error of the analysis is less than 0.1%.

The proximate analysis of the OMs was performed on a thermogravimetric analyzer (TG, Setsys Evolution 24, Setaram) with approximately 15 mg. Each sample was heated under an argon flow of 100 mL min^{-1} and at a rate of 10 °C min^{-1} from room temperature to 900 °C, with a 30 min stay at 110 °C for moisture removal and a 20 min stay at 900 °C. The mass losses recorded at 110 °C and between 110 and 900 °C are the contents of moisture and volatile, respectively. The sample at 900 °C was then exposed to a flow of 10% oxygen and balance argon at a rate of 100 mL min^{-1} for 1 h for complete combustion of fixed carbon. The mass of final residual was the ash content. The experimental error is less than 1.6%.

2.2.2. Solid-state ^{13}C NMR measurements

Cross-polarization magic-angle spinning (CP/MAS) ^{13}C nuclear magnetic resonance (NMR) measurement was performed at room temperature on a Bruker AV-300 spectrometer at a resonance frequency of 75.47 MHz with a resolution of less than 0.005 Hz. The contact time, MAS rotation speed, and recycle delay time were set to 1 ms, 12.0 kHz, and 0.5–1.5 s, respectively. Curve fitting of the ^{13}C NMR spectra was conducted using OriginPro 2016 software to quantify the percentages of different types of carbon in the OM by normalizing the peak areas, which yields skeletal structure parameters of the OM.

2.3. Pyrolysis experiments

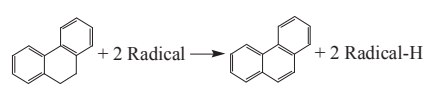
Details on the pyrolysis experiments can be found in our previous work [6]. In brief, a glass tube (Φ2 × 30 mm) containing approximately 2 mg OM or 16 mg 9,10-dihydrophenanthrene (DHP) or both of them was purged with N_2, sealed by a blast burner, and then inserted into a quartz tube preheated to 420 °C in a heating mantel. At a designated time, the glass tube was withdrawn from the heating mantel and quenched in liquid N_2.

2.4. Quantification of active radicals' concentration ($C_{R\text{-}t}$)

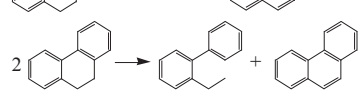
DHP reacts in a number of ways under the conditions used in this work. It converts to phenanthrene (PHE) by donating hydrogen to radicals as shown by Re. (1) or by self-reaction as shown by Res. (2) to (4) for ring opening, disproportionation and dehydrogenation, respectively. The amount of active radicals generated from OM can be estimated by the amount of PHE formed if the contribution of Res. (2)–(4) is determined and coupling of the active radicals is minimal. Our previous work showed that the contribution of Res. (2)–(4) is small and can be determined by gas chromatograph while the coupling of active radicals of OMs can be minimized using a high DHP:OM ratio, 8:1 in mass, for example [6,7].

Pyrolysis results of OM + DHP and DHP itself showed that the OM has little influence on Res. (2)–(4) by quantifying H_2 (Fig. S1 in the Supplementary material). Therefore, the amount of PHE generated during pyrolysis of DHP itself (termed $N_{PHE\text{-}blank}$, Fig. S2 in the Supplementary material) approximates the amount of PHE generated through Res. (2)–(4) during pyrolysis of OM + DHP; and then, the amount of hydrogen donated by DHP can be estimated by $2 \times (N_{PHE\text{-}total} - N_{PHE\text{-}blank})$, where $N_{PHE\text{-}total}$ is the total amount of PHE generated through Res. (1)–(4) during pyrolysis of OM + DHP. The $C_{R\text{-}t}$ can be determined by Eq. (1), where m_{daf} is the mass of OM on a dry ash-free (daf) basis (g).

The PHE were quantified using a high-performance liquid chromatography spectrometer (HPLC, Waters e2695) equipped with a Waters 2998 diode array detector (230 nm in wavelength) and an Agilent Eclipse XDB-C18 column (4.6 mm × 150 mm/5 μm). Biphenyl was the internal standard, and the mobile phase was 30% water in acetonitrile. The operating conditions can be found in our previous work [6].



(Re. 1)



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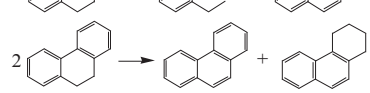

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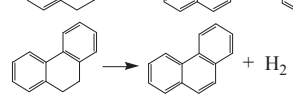

(Re. 4)

$$C_{R-t} = 2 \times (N_{PHE-total} - N_{PHE-blank})/m_{daf} \quad (1)$$

2.5. Quantification of stable radicals' concentration ($C_{R\text{-}s}$)

The OM or the pyrolysis product in the tube was subjected to ESR (JES-FA 200, JEOL, Ltd.) analysis at 25 °C to measure stable radicals. The settings of ESR are shown in Table S1 in the Supplementary material. The quantity of stable radicals (termed N_R) was determined by referencing a strong pitch standard, 1,1-diphenyl-2-picryhylhydrazyl. The $C_{R\text{-}s}$ was calculated according to Eq. (2), and duplicated measurements indicated a relative deviation of less than 5%.

$$C_{R-s} = N_R/m_{daf} \quad (2)$$

3. Results and discussion

3.1. Characterization of organic matters

3.1.1. Ultimate and proximate analyses

Table 1 shows the ultimate and proximate analyses results of the eight OMs. The samples are sequenced by H/C molar ratio from high to low as commonly done in ranking kerogen types [24,25]. It can be seen that the carbon content of the OMs ranges from 64 wt% to 70 wt%, similar to that of lignite [7,21], while the hydrogen content ranges from

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