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The bond cleavage and radical coupling during pyrolysis of Huadian oil shale

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HIGHLIGHTS

- The quantities of total radicals and bonds cleaved at 380–440 °C are determined.
- The bond cleavage can be described by first-order reaction.
- The amounts of total and stable radicals show a good linear relation.
- Coupling of around 2500 active radicals yields one stable radical.
- Not all the bond cleavage results in a mass loss.

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ABSTRACT

Pyrolysis of an oil shale starts with cleavage of covalent bonds to generate radical fragments which is followed by coupling of the radical fragments to form volatiles (shale oil and gas) and char. The radical's reaction determines the distribution, composition and quality of pyrolysis products. However, information about the bond cleavage and the radicals' reaction during oil shale pyrolysis is very limited in the literature. This paper studies the quantities of total radicals and bonds cleaved in pyrolysis of the organic matter in Huadian oil shale (HDOM) at 380–440 °C. The kinetics of the bond cleavage is established and the behavior of radicals' coupling is discussed. It is found that the quantities of cleavable bonds in HDOM are 0.62×10^{-2}, 0.87×10^{-2}, 1.10×10^{-2} and 1.33×10^{-2} mol/g at 380, 400, 420 and 440 °C, respectively. The bond cleavage can be described by the 1st-order reaction kinetics with an activation energy (E_a) of about 90.10 kJ/mol and a pre-exponential factor of 5.23×10^5 min^{-1}. Since not all the bond cleavage yields a mass loss, the activation energy determined for the bond cleavage is different from that for the devolatilization reported in the literature. The number of stable radicals confined in the pyrolysis products shows a good linear relation with that of total radicals generated during pyrolysis and one stable radical is formed among around 2500 radicals generated from HDOM.

1. Introduction

Oil shale is a complex mixture of organic matter and inorganic minerals [1]. Pyrolysis is the major technology to convert its organic portion to liquid and gas. It is well recognized that pyrolysis of the organic matter starts with cleavage of covalent bonds to generate radical fragments and then the radicals couple together or recombine to form volatiles and char [2–8]. Formation of radicals has been investigated for many years with the aid of electron spin resonance (ESR) or electron paramagnetic resonance (EPR) spectrometers.

Many studies reported the presence of radicals in the char and shale oil [7–10]. Wang et al. [8] found that the radical concentrations of shale oil and semi-coke increased with increasing the pyrolysis temperature. He et al. [4–6] reported that the radicals in pyrolysis oil have a negative effect during transportation, storage and refining because they increase viscosity with time and promote coking. The radicals can also be found commonly in oil shale [7–11] but their effect on the yield of shale oil from pyrolysis was found to be minute [11].

In spite of many literatures on radicals, the radicals studied were the stable ones that are confined in large structures and can be measured by ESR. The studies of coal and biomass pyrolysis indicated that the quantity of stable radicals are far less than the total amount of radicals generated in pyrolysis by bond cleavage [2,3]. Because most of the radicals are too active, their lifespan is

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too short, in nanoseconds [12], to be detected by ESR. These short-life radicals, termed active radicals, play a dominant role in determination of pyrolysis products but their behavior has not been reported due to lack of suitable instrumentations.

Liu et al. [2,3] recently reported a method to quantify the concentration of active radicals and the number of bonds cleaved during pyrolysis of coal and biomass by introducing a radical scavenger or a hydrogen donor, 9,10-dihydrophenanthrene (DHP). Reference to this method, this work takes Huadian oil shale, a major oil shale resource in China, as an example to estimate the quantities of active radicals and the bonds cleavable during pyrolysis in a temperature range of 380–440 °C. The kinetics of bond cleavage is also established. The concentration of stable radicals in the pyrolysis product is also measured by ESR and correlated with that of the active radicals. This fundamental information reveals in-depth behavior in oil shale pyrolysis and is useful in understanding the structure-reactivity relation in oil shale conversion.

2. Experimental

2.1. Materials

The oil shale used in this work was from Dachengzi Mine located in Huadian of Jilin province in China and is termed HDOS. It was ground and sieved to smaller than 100 mesh (0.15 mm) and some of them were subjected to acid treatments to remove the minerals [13,14]. The acids used include HCl (6 N), HNO_3 (20 wt%) and a mixture of HF (40 wt%) and HCl (6 N) at a volume ratio of 2. All the acid treatments were carried out at a HDOS/acid ratio of 1 g: 10 mL under stirring in a nitrogen atmosphere. The HCl treatment was at 70 °C for 12 h, the HNO_3 treatment was at 25 °C for 2 h while the HCl + HF treatment was at 70 °C for 8 h. In each step, the acid insoluble matters were separated from the acid solution by filtration, washed with deionized hot water (60 °C) to neutral and finally dried at 110 °C for 24 h under a vacuum. The acid-treated oil shale, termed as HDOM, were sieved to smaller than 100 mesh in size for pyrolysis experiment. The proximate and ultimate analyses and Fischer assay results of HDOS and HDOM are shown in Table 1.

2.2. Pyrolysis experiment

The pyrolysis experiment was carried out in a glass tube reactor of $\Phi 2 \times 30$ mm. The glass tube containing 2 mg HDOM and 0–16 mg DHP was purged with N_2, sealed by a blast burner and then inserted into a quartz tube of $\Phi 3 \times 30$ mm. The quartz tube was then immersed in a preheated metal block. The pyrolysis temperature was 380–440 °C which covers the main cleavage range of aliphatic carbon bonds, C_{al}-C_{al} [15], and avoids significant decomposition of DHP. At a designated time, the quartz tube along with the reactor was withdrawn from the furnace and quenched quickly in a liquid N_2 bath. It took about 2 min for the sample to reach the pyrolysis temperatures (The temperature curves are shown in Fig. S1 in the Supplementary material). The time used in the iso-thermal kinetics study therefore was set zero at 2 min.

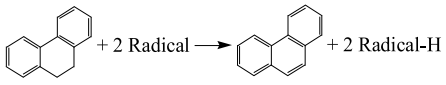
2.3. ESR measurement

The quartz tube containing the glass reactor was subjected to ESR (JES-FA 200, JEOL, Ltd.) analysis at 25 °C to measure the concentration of stable radicals in the pyrolysis product. The operation parameters of the 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 (DPPH). The concentration of radicals (termed $C_{R\text{-}S}$) of the sample was calculated by Eq. (1), where m_{daf} is the mass of HDOM on dry-ash-free basis (g). All the tests were performed three times to ensure repeatability. Results indicated that the relative deviation of $C_{R\text{-}S}$ was less than 5%.

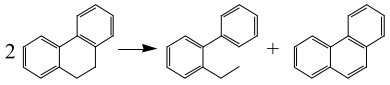
$$C_{R-S} = N_R / m_{daf} \quad (1)$$

2.4. Determination of the quantity of hydrogen donated by DHP

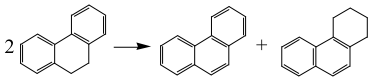
DHP converts to phenanthrene (PHE) after donating hydrogen to radicals, as shown in Re. (1). It may also convert to PHE by ring-opening, disproportionation and/or dehydrogenation reactions as shown in Res. (2)–(4), which are accompanied by the formation of 2-ethyl-biphenyl (EBP), 1,2,3,4-tetrahydrophenanthrene (THP) and hydrogen (H_2), respectively. The amount of hydrogen donated by DHP (termed Q_H) to one gram HDOM can be determined by Eq. (2), where N_{PHE} is the amount of PHE generated in pyrolysis process and so forth.



Re.(1)



Re.(2)



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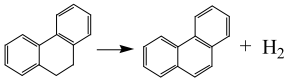

Re.(4)

Table 1
Proximate and ultimate analyses and Fischer Assay result of Huadian oil shale (HDOS) and its organic matter (HDOM).

Sample	Proximate analysis (wt%)			Ultimate analysis (daf. wt%)					Fischer Assay (ad. wt%)			
	M_{ad}	A_d	V_{daf}	C	H	O*	N	S	Char	Oil	Water	Gas
HDOS	4.28	75.32	93.27	60.16	8.13	26.37	1.44	3.90	86.97	7.21	2.39	3.37
HDOM	1.30	10.86	70.74	63.52	7.29	25.50	3.13	0.56	44.16	29.54	7.85	18.45

* By difference.