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Correlation between coal structure and release of the two organic compounds during pyrolysis

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HIGHLIGHTS

- The release principle of organic compounds is associated to coal structure during pyrolysis.
- The release amounts of PAHs and phenols has different trend as coal rank increased.
- The formation mechanisms of PAHs and phenols are proposed during coal pyrolysis.

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ABSTRACTS

A considerable amount of organic compounds could be released during coal utilization processes, and these compounds could have a significant detrimental effect on the environment and human health if freely discharged. In this study, we investigated the yields of two organic compounds (PAHs and phenols) released during the pyrolysis of coals with different ranks. And then, the formation mechanisms of PAHs and phenols are discussed by means of comparisons the correlation between release principles and coal structure. The results showed that the yields of PAHs and phenols depended to a large extent on coal structure. PAHs are formed not only by thermal breakdown of coal structure, but also by the combination of different low molecule weight compounds with each other. Monohydric phenolic carbon and aromatic ether carbon were likely to be the precursor structure of phenols. The formation of phenol, cresol and xylenol are closely related to the types of free radical (like H or CH_3) and the chemical structure of oxygenated aromatic carbon in coal during pyrolysis.

1. Introduction

A wide variety of organic compounds can be generated during the combustion, carbonization, liquefaction, or gasification of coal, including polycyclic aromatic hydrocarbons (PAHs), phenols, and polycyclic aromatic sulfur hydrocarbons (PASHs). These compounds, if freely discharged or improperly disposed of, could have a significant detrimental effect on the environment and human health. For instance, PAHs are well-known persistent organic compounds (POPs) with a high teratogenic, carcinogenic, and mutagenic potency [1,2]; and phenols in industrial wastewater can cause serious environmental problems due to its potent toxicity even at low concentration (>2 mg/L) and high oxygen demand (2.4 mg/mg of phenol) [3]. This highlights the need to better understand the release mechanism of organic compounds during coal utilization processes.

A number of studies have been conducted to quantify the amount of organic compounds, such as dioxin, furan, PAHs, alkyl PAHs and PASHs, near coal-fired power plants or in laboratory under different combustion conditions [4–9]. However, few studies have focused specifically on the relationship between the amount of organic compounds released and coal structure, and thus the mechanism responsible for the emission of organic compounds remains to be elucidated.

The application of high-power decoupling of protons, dipolar dephasing, cross polarization and magic angle spinning make it possible to obtain a high-resolution ^{13}C NMR spectrum of coal. The absorption signal of each carbon element could be observed in the ^{13}C spectrum, which helps to better understand the carbon skeleton structure of coal [10]. ^{13}C NMR spectroscopy has been widely used to determine the chemical structure of coal, tar and char [10–12], which could characterize different types of aromatic

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carbons and aliphatic carbons in coal. Therefore, coal structure was characterized by the CP/MAS ^{13}C NMR techniques in this study.

Pyrolysis is an important stage of coal conversion processes, such as combustion, carbonization, liquefaction and gasification. In this study, we investigated the yields of organic compounds (PAHs and phenols) released during the pyrolysis of coals with different ranks, based on which the relationship between the yields of compounds and coal structure was analyzed. The results might be helpful to understand the emission mechanism of organic compounds during coal conversion processes.

2. Experiments

2.1. Coal samples

Three coals with different ranks were used in this study, including lignite (A coal) from Inner Mongolia Autonomous Region of China, bituminous coal (B coal) and coking coal (C coal) from Shanxi province of China. All samples were crushed to 0.15–0.30 mm, and the proximate and ultimate analysis results were shown in Table 1.

2.2. Py-GC/MS analysis

Pyrolysis experiments were performed using a CDS Analytical Pyroprobe 5250. Coal samples of 1 mg were placed in quartz pyrolysis tubes containing quartz filler rods and plugged at either end with quartz wool. The samples were heated by a 2–3 mm diameter platinum filament in the Pyroprobe 5200, and the pyrolysis temperature was controlled by calculating the resistance of the filament at setpoint temperature and supplying the correct voltage to achieve that temperature. Each coal sample was pyrolyzed under multi-steps temperatures (400 °C, 600 °C, 800 °C, 1000 °C, and 1200 °C) with a pyrolysis heating rate of 10,000 °C/s, each for the same residence time (15 s), and GC ran automatically under each temperature step. Helium was used as the carrier gas to purge the pyrolysis products to the GC. However, it was noted that the actual sample temperature was slightly lower than the set one [13].

The GC/MS instrument used consisted of a Focus gas chromatograph and a DSQ-II mass spectrometer (Thermo Fisher, USA). Helium (>99.999%) was used as the carrier gas in GC at a constant flow rate of 1.0 ml/min and a split ratio of 100:1. TG-5MS capillary column (Thermo Fisher Scientific) was used as the GC column. The GC oven temperature was held at 40 °C for 4 min, heated to 300 °C at a rate of 3 °C/min, and then held at that temperature for 1 min. MS was operated in a SIM mode in order to reach more selectivity and sensibility for organic compounds. Organic compounds were quantified using an external standard method. The above experiments were repeated several times for each sample to ensure that the results were reproducible.

PAHs detected in this study included naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, indeno [1,2,3-c,d]pyrene, and benzo[g,h,i]perylene; Phenols included phenol, o-cresol, m-cresol, p-cresol, 2,4-xylenol, 3,4-xylenol, 2,6-xylenol, and 2-naphthol.

2.3. CP/MAS ^{13}C NMR analysis

CP/MAS ^{13}C NMR analysis was performed using a Bruker Avance III 400 MHz solid state spectrometer equipped with a triple resonance H–X–Y probe. Coal samples were packed into a 4-mm-diameter zirconia rotor. CP/TOSS sequences were recorded at a spinning speed of 5 kHz, a polarization contact time of 3 s, and a recycle delay time of 1 s. All ^{13}C chemical shifts were measured based on the standard reference materials (glycine), whose carbonyl chemical shift was at 176.03 ppm. The CP/MAS ^{13}C NMR spectra of the three coals were shown in Fig. 1, which could be divided into aliphatic carbons (0–93 ppm) and aromatic carbons (93–171 ppm). The NMR spectrum was fitted to obtain the relative proportion of different types of carbons in the three coal samples, as shown in Fig. 2. Chemical shifts, full width at half-maximum and fitting function were used as the fitting parameters. The chemical shifts for different types of carbons were summarized in Table 2 [11,14,15].

3. Results and discussion

3.1. Distributions of organic compounds during coal pyrolysis

The pyrolysis products obtained at different temperatures were quantified by GC/MS, and the yields of PAHs and phenols were shown in Fig. 3. It was evident that PAHs and phenols were released in a similar manner with temperature during the pyrolysis of the three coals. When the pyrolysis temperature is lower than 400 °C, the organic compounds were released mainly from the native compounds in coal, such as PAHs and phenols, but their amounts were quite low. Zheng-Bao Zhao et al. [16] showed that the native PAHs in the macromolecule structure of coal could be released into the environment even in the preparation and transportation processes. In addition, the release of organic compounds increased with the active thermolysis reaction, and finally reached maximum at 800 °C. For example, the amount of organic compounds released from A coal, B coal, and C coal between 600 and 800 °C accounted for 92%, 88%, and 90% of the total amount of organic compounds released during pyrolysis. However, the polycondensation reaction became the major reaction after 800 °C. The amount of organic compounds released decreased significantly after 1000 °C, accounting for only 1.0% of the total amount of organic compounds released during C coal pyrolysis, and the aromatic structures in char were highly condensed into heavy aromatic rings. Thus, pyrolysis temperature is a major determinant of the yield of organic compounds.

Fig. 3 showed that the amount of PAHs and phenols varied significantly between the three coal samples. For instance, the amount of PAHs from the pyrolysis of A coal, B coal, and C coal was about

Table 1
Proximate and ultimate analyses of coal samples.

Sample	Proximate analysis wt (%)			Ultimate analysis wt (%), daf				
	M_{ad}	A_{ad}	V_{ad}	C	H	O[a]	N	S
A coal	23.5	17.5	27.0	61.7	3.2	33.3	1.2	0.7
B coal	2.2	17.9	29.7	80.4	5.2	11.9	1.4	1.1
C coal	0.5	7.5	24.3	86.5	4.0	6.6	1.2	1.7

Note: ad: air dry; daf: dry-and-ash-free basis.
[a] By difference.