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Research article

The relationship between benzene carboxylic acids from coal via selective oxidation and coal rank

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ABSTRACT

The oxidation of coal to produce benzene carboxylic acids (BCAs) was widely researched. However, the relationship between coal rank and BCAs from coal is unknown. In this study, 8 kinds of coal with different ranks were investigated and the effect of coal rank on the BCA yield distribution was studied. The results indicate that with the increase of coal rank, the yield of BCAs increases, and the structure of coal becomes more and more difficult to be degraded. In addition, BCA yield distribution varies significantly with the increase of coal rank. The results of ^{13}C NMR show that with increasing coal rank, the fraction of aromatic carbon (f_a) and mole fraction of aromatic bridgehead carbon in aromatic carbon (X_b) both are increased gradually, and alkyl-substituted degree of aromatic ring (δ) and average methylene chain length (C_n) both are decreased. More and more parent structures of phthalic acid, trimellitic acid, hemimellitic acid and prehnitic acid exist in the coal with the increase of coal rank. When the carbon content of coal is >87%, the structure of coal has a mutation property that more and more circular catenations of aromatic rings exist in the structure of coal.

1. Introduction

Benzene carboxylic acids (BCAs, including 12 types, whose structures are shown in Scheme 1) are highly valuable and widely used in the polymer industry and the pharmaceuticals industry. BCAs are obtained currently from diminishing petroleum reserves. As petroleum resources drying up, coal as an abundant energy and resource to replace petroleum is drawing more and more attention all over the world. It is well known that coal contains lots of aromatic structures, which provide a possibility to produce BCAs from coal. Therefore, the production of BCAs from coal will be very promising.

The production of BCAs from coal via oxidation has been widely studied [1–8]. In 1937, Juettnuer et al. [9] reported that coal could be oxidized to yield abundant mellitic acid using alkaline permanganate and nitric acid as oxidant. Many researchers [10–12] studied the oxidation of low rank coal in hydrogen peroxide and obtained lots of carboxylic acids. Liu et al. [13] investigated the oxidation of Shengli lignite with NaOCl aqueous solution after the lignite was pretreated with H_2O_2 aqueous solution. The results indicated that the pretreatment with H_2O_2 significantly increased the yields of alkanoic acids, alkanedioicacids, and benzene carboxylic acids and enhanced the formation of compounds with molecular weight from 300 to 500 amu. As for the above the researches on coal oxidation, oxidants are expensive in the processes, which limit their applications. Since oxygen is inexpensive, easily available and suitable as oxidant, the alkali-oxygen oxidation of coal was reasonably accepted. Franke et al. [1] investigated alkali-oxygen oxidation of several coals in an alkali/coal mass ratio of 6.71 at a temperature of 250 °C, and obtained a high total yield of water-soluble poly(carboxylic acid)s. Okuwaki et al. [14] reported that coal could be oxidized with O_2 in 25 mol/kg sodium hydroxide solution, and 20–24% (based on carbon) yields of volatile acids were obtained. In our previous work [4,15–17], we also conducted the oxidation of several coals with O_2 in alkali aqueous solution and obtained high yields of BCAs. The results indicated that 12 kinds of BCAs had different yield distributions.

In addition, oxidation has also been used to study the structure of coal [18–22]. Detailed analyses of ruthenium ion catalyzed oxidation products from bituminous and brown coals were conducted by using FD/MS and ^{13}C NMR. The results indicated that coals contained relatively large condensed aromatic rings with alkyl side chains or bridges, which were easily converted to aromatic polycarboxylic acids [18]. In 1998, Nomura et al. [23] evaluated the structure of Zaozhuang bituminous on the basis of ruthenium-catalyzed oxidation. The ruthenium-catalyzed oxidation offered information regarding aliphatic functionalities and bridge types and the results also suggested the presence of some types of molecular units. In 1999, Hayashi et al. [24] determined the quantitative relationship between the decrease in the number of bridges and clusters and the increase in the proportion of low-

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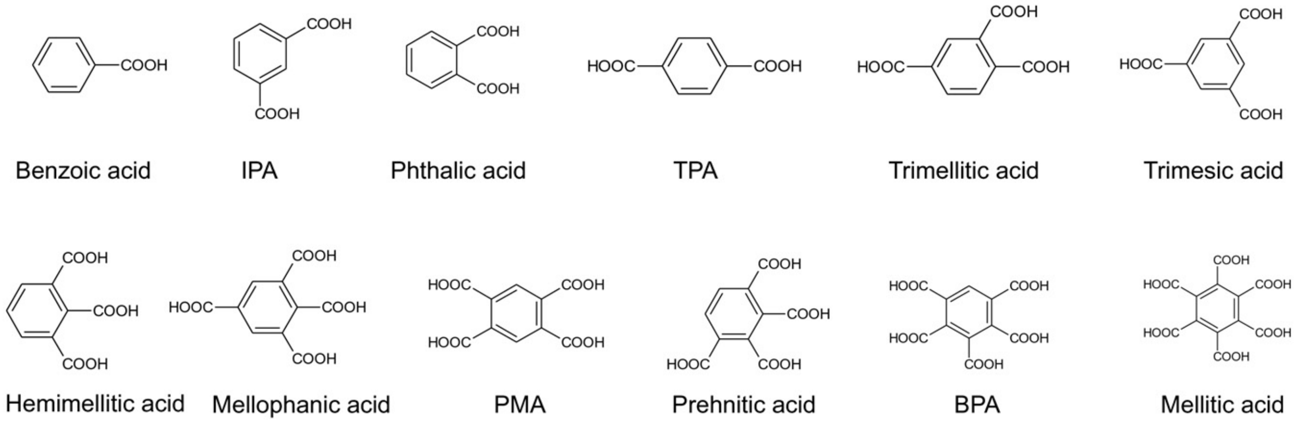

Scheme 1. The structure of BCAs obtained from selective oxidation of coal. Abbreviations: BPA, benzene pentacarboxylic acid; IPA, isophthalic acid; PMA, pyromellitic acid; TPA, terephthalic acid.

molecular-mass network fragments by means of oxidative degradation in $NaCO_3$ aqueous solution.

As mentioned above, when coal oxidation was studied, low rank coals were always selected to produce BCAs or investigated for their structural features. There are few studies focused on the effect of coal rank on the oxidation of coal and the relationship between the yield distributions of BCAs and coal rank or coal structure.

In this work, the oxidation of 8 coals with different ranks was studied to investigate the effect of coal rank on the coal oxidation. ^{13}C NMR was used to analyze the coal samples, and various structural parameters of coals were obtained. On the basis of above results, the effect of coal rank on the oxidation of coal, and the relationship between the yield distributions of BCAs and coal rank or coal structure were investigated. It was found that coal rank had a significant influence on BCA total yields and the yield distributions of 12 BCAs.

2. Experimental

2.1. Raw coals and reagents

Eight coals with different ranks were collected from different coal mines in China. Table 1 shows their proximate and ultimate analyses. The coal samples were pulverized to pass a 200 mesh sieve before use. Sodium hydroxide (NaOH, 98%, AR), concentrated sulfuric acid (H_2SO_4, 98%, AR), phosphoric acid (H_3PO_4, ≥ 85%, AR), acetonitrile (C_2H_3N, 99.9%, GR) and isopropanol (C_3H_7OH, 99.9%, GR) were purchased from Beijing Chemical Plant. Oxygen (O_2, 99.995%) was supplied by Beijing Haipu Gases Co., Ltd. (Beijing, China). All reagents were used without further purification.

Table 1
Proximate and ultimate analyses of 8 coals.

Coal	Proximate analysis/%			Ultimate analysis/% in daf basis				
	M_{ad}	A_d	V_{daf}	C	H	N	O[a]	S
XLT	16.40	12.12	36.24	73.7	3.9	1.3	20.1	1.0
XLHT	1.55	16.83	33.26	80.9	5.2	1.8	10.4	1.8
YZ	2.70	2.72	42.28	81.5	5.9	1.3	8.6	2.7
KL	0.98	12.51	27.94	85.5	4.3	1.2	7.9	1.0
XZ	7.81	2.73	28.92	85.6	4.2	1.0	9.0	0.2
PDS	0.60	19.68	12.99	88.4	4.1	1.2	5.9	0.4
HB	0.60	7.26	12.53	90.0	3.7	1.2	4.7	0.4
TX	0.38	1.78	7.03	91.9	2.1	0.9	5.0	0.1

XLT: Xiaolongtan lignite; XLHT: Xilinhaote lignite; YZ: Yunzhong bituminous; KL: Kailuan bituminous; XZ: Xuanzhong bituminous; PDS: Pingdingshan bituminous; HB: Hebi anthracite; TX: Taixi anthracite.

ad: air-dry basis; d: dry basis; daf: dry-and-ash-free basis. *M*: moisture; *A*: ash; *V*: volatile matter content.

[a] By difference.

2.2. Experiment of coal oxidation

The oxidation of coals were carried out in a high-pressure batch reactor made from Hastelloy (HC276), supplied by Haian Petroleum Scientific Research Co., Ltd., Jiangsu, China. The reactor has an inner volume of 50 cm^3 and is equipped with a magnetic stirrer. In a typical experiment, 1.00 g coal, 3.00 g NaOH, and 20.0 cm^3 distilled water were loaded into the reactor. Next, the reactor was sealed and purged with O_2. After that, O_2 was charged into the reactor to a desired pressure. Then, the reactor was submerged into a heating furnace and heated at 13–15 °C/min to a desired reaction temperature controlled by a temperature controller and monitored by a K type thermocouple with an accuracy of ± 1 °C. When the desired temperature was reached, the reaction time was recorded. During the reaction, the mixture was stirred at a constant speed of 500 rpm. After the reaction, the reactor was transferred into a cold water bath to rapidly stop the reaction. When the reactor reached room temperature, the mixture in reactor was transferred into a beaker. The unreacted residues were filtered, and the filtrate acidity was adjusted by titrating with concentrated sulfuric acid to $pH = 1.5$. The filtrate was diluted for further analysis. The residues were washed with distilled water and dried in air.

2.3. Analysis of BCA products

Filtrate samples were analyzed using a high-performance liquid chromatography (HPLC, Waters 2695, USA). BCA compositions in samples were obtained using the following method. A binary gradient elution procedure was used for HPLC analysis of BCAs. The mobile phase was acetonitrile and 0.1% (volume fraction) phosphoric acid aqueous solution, and the stationary phase was C18 bonded by silica gel (Waters XBridge C18, 5 μm). A UV detector at 235 nm was used to quantify the products. The mobile phase flow rate was 1 cm^3/min, and the column temperature was at 35 °C. The gradient elution procedure was shown as follows: the initial volume ratio of acetonitrile to phosphoric acid aqueous was 5:95, the ratio was increased to 20:80 linearly over 10 min and then maintained for 2 min, and finally the ratio was decreased to 5:95 over 2 min.

2.4. ^{13}C NMR analysis of coal samples

Structural parameters of various carbons in coals were obtained by ^{13}C NMR. All CP/MAS ^{13}C NMR spectra were obtained on Bruker AV-300 spectrometer with a ^{13}C frequency of 67.8 MHz. Chemical shift of ^{13}C was calibrated by adamantine (an external standard substance). The cross-polarization contact time was 2 ms, and the cycle time was 7 s.