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Pyrolysis behaviors of two coal-related model compounds on a fixed-bed reactor

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ABSTRACT

The bibenzyl (BB) and benzyloxybenzene (BOB) were selected as coal-related model compounds, and their pyrolysis behaviors between 500 °C and 700 °C were investigated on a fixed-bed reactor. The pyrolysis products were analyzed by gas chromatography–mass spectrometer (GC–MS) and gas chromatography (GC), and the bond dissociation energy (BDE) was calculated with density functional theory (DFT) methods at B3LYP/6-31G (d) level. The results showed that the conversion in pyrolysis of BOB was higher than that of BB. The pyrolysis product distributions and BDE calculation indicate that $C_{aliphatic}$–$C_{aliphatic}$ bond dissociation is the primary step for BB pyrolysis, while $C_{aliphatic}$–O bond dissociation is the primary step for BOB pyrolysis. The differences in pyrolysis behaviors between BB and BOB indicate that the existence of oxygen atom will reduce the BDE thus being preferentially dissociated under pyrolysis. The initial radicals should be stabilized by some more reactive radicals, which lead to higher liquid yield.

1. Introduction

Coal is the main energy resource in China, and low rank coal deposits are accounting for more than 40% of the total coal reserves. About 90% of the low rank coal was consumed by power generation with direct combustion in past decades, which seriously pollutes the environment with low efficiency in energy utilization [1,2].

In order to improve the coal thermochemical conversion process, the fundamental study of coal structure and reaction mechanism during coal conversion is necessary. However, many single reactions take place simultaneously during the pyrolysis process, and the experimental results represent the total effects of all these reactions [3]. Furthermore, since different coal exhibits different coalification degree, reactivity and structure of coal should be varied [4]. As a result, it is very difficult to describe coal pyrolysis clearly. Although the structure of coal is complex, the types of weak covalent bond in coal are relatively simple. The clear understanding of the pyrolysis behavior of the typical bonds in coal will be beneficial for us to understand the pyrolysis process of the real coal.

The model compounds, which contain the main structure and property of the aromatic heterocyclic ring and simplify the macromolecule, have been widely used to study the structure and reactivity of coal. Bibenzyl (BB) has been commonly chosen as the model compound to represent the typical $C_{aliphatic}$–$C_{aliphatic}$ weak bond in coal. Thermolysis of BB in gas and liquid phases has been extensively investigated [5–8], and the results have been reviewed by Marvin L. Poutsma [9]. It is generally accepted that the homolytic cleavage of $C_{aliphatic}$–$C_{aliphatic}$ bond to form benzyl radicals is the primary process, and toluene was the primary product when there was no catalyst, while stilbene was the primary product when CaO was used as catalyst [8]. When BB was immobilized on a silica surface, the pyrolysis pathway was influenced by diffusional constraints. As a result, surface-attached 1,1-diphenylethane which originated from the rearrangement reaction was the primary product [10]. The existence of oxygen in low rank coal can seriously influence the pyrolysis behavior. The pyrolysis of benzyloxybenzene (BOB), which has the typical $C_{aliphatic}$–O weak bond, has been extensively investigated as a model for labile ether bridges [11–20]. BOB pyrolysis is initiated by homolytic scission of the weak $C_{aliphatic}$–O bond to produce benzyl and phenoxy radicals. Toluene and phenol are the dominant products. However, recombination of the incipient radicals through coupling at phenoxy ring carbons to form benzylphenol isomers was also an important pathway during the BOB pyrolysis process [18]. In order to understand the experimental results thoroughly, quantum chemistry calculation was also widely applied in the pyrolysis mechanism study of model compounds [21–26].

The studies of BB and BOB pyrolysis behavior were abundant, but very few researches were conducted on a fixed-bed reactor. However, most of the coal pyrolysis experiments are conducted on fixed-bed reactors. In order to understand the connection of pyrolysis mechanism between real coal and coal-related model compounds, the pyrolysis experiments of BB and BOB were conducted on a fixed-bed reactor with a stainless steel tube in this study. Pyrolysis pathways were proposed based on related experimental results

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and previous studies. In addition, the bond dissociation energies (BDEs) for main radical pathways were calculated with Gaussian 09 suite of programs. The quantitative analysis of the pyrolysis products combined with quantum mechanical calculations was expected to generate more information to the pyrolysis mechanism of the coal-related model compounds.

2. Experimental

2.1. Materials

BB and BOB as coal-related model compounds were purchased from J&K Chemical Ltd. and TCI, respectively. Absolute ethyl alcohol (AR) was purchased from Sinopharm Chemical Reagent Co., Ltd., China.

2.2. Pyrolysis procedure

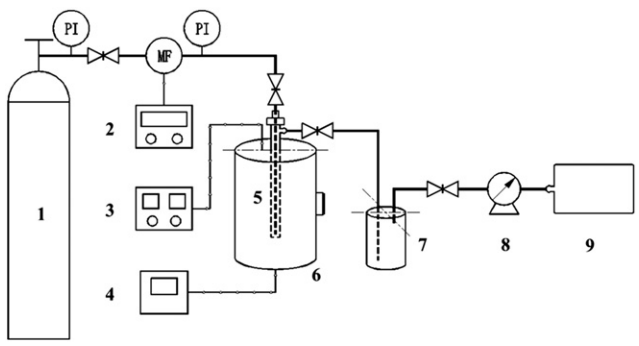
The pyrolysis experiments of model compounds were carried out on a fixed-bed reactor (shown in Scheme 1). Firstly, the desired amount of samples was placed in a stainless steel tube reactor (15 mm i.d., 220 mm length), and high-purity nitrogen was flushed to evacuate the air in the system before the pyrolysis experiment. Then the reactor was placed into the preheated furnace (500, 550, 600, 650 and 700 °C), and maintained at the desired temperature for 10 min. After that, the pyrolysis products were brought out by high-purity nitrogen to a cool trap to collect the liquids, whereas the gaseous products were collected by a gas bag. The liquid products were analyzed by gas chromatography–mass spectrometer (GC–MS) and gas chromatography (GC), while the gas products were analyzed by GC. In addition, the weight of the residual char was quantified by weighting the stainless steel tube before and after the pyrolysis. After collecting the products, the tube was heated at 750 °C in air atmosphere for 1 h to remove the residual char. Each experiment was repeated at least five times under the same conditions.

2.3. Analytical methods

Gas chromatograph (TECHCOMP GC 7890II) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) was used to quantify the gaseous products. The qualitative analysis of liquid product was carried out by GC–MS (HP6890/MS5973) with a HP-5 capillary column (0.25 mm × 30.0 m × 0.25 μm). The quantitative analysis of liquid product was carried out by GC (Agilent 6890N) with a HP-5 capillary column (0.25 mm × 30.0 m × 0.25 μm).

The conversion, yield of gas, liquid and char were calculated using the following equations:

$$\text{Conversion} = \frac{m_0 - m_e}{m_0}, \tag{1}$$



Scheme 1. Flow sheet of experimental apparatus. 1—Nitrogen cylinder, 2—mass flow meter, 3—temperature controller, 4—thermograph, 5—stainless steel tube reactor, 6—furnace, 7—cold trap, 8—wet type gas flow meter, 9—gas bag.

$$\text{Yield of gas, } Y_{gas} = \frac{m_{gas}}{m_0}, \tag{2}$$

$$\text{Yield of liquid, } Y_{liquid} = \frac{m_{liquid}}{m_0}, \tag{3}$$

$$\text{Yield of char, } Y_{char} = \frac{m_{char}}{m_0}, \tag{4}$$

where m_0 is the initial weight of BB or BOB sample before the pyrolysis, m_e is the existing weight of BB or BOB after pyrolysis, m_{gas} is total weight of the gas, m_{liquid} is total weight of the liquid including the existing BB or BOB, and m_{char} is total weight of the char.

3. Computational method

In this paper, all calculations were carried out with Gaussian 09 program [27] by using the density functional theory (DFT) method. The structures of all the reactants, intermediates and products involved in the elementary reactions were optimized with B3LYP (Becke's three parameter gradient corrected exchange functional [28] with the gradient corrected correlation functional of Lee et al. [29]) using the 6-31G (d) basis set [30], which can provide accurate geometrical parameters and energies with low computational cost.

4. Results and discussion

4.1. Pyrolysis of BB

4.1.1. Products analysis of BB pyrolysis

About 0.5 g (2.74 mmol) BB was pyrolyzed for 10 min on a fixed-bed reactor at the desired temperature. The results showed that CH_4, H_2, C_2H_4 and C_2H_6 were gas products. And benzene, toluene, ethylbenzene, styrene, diphenylmethane, trans-stilbene, 1,1-diphenylethane and phenanthrene were the principal liquid products, which account for 97.5–99.1 mol% of total liquid products. There were still two kinds of minor liquid products that had not been defined. In addition, some solid products like char, which adhered to the stainless steel tube and could not dissolve in solvent, were also produced during the pyrolysis.

As shown in Fig. 1, the conversion of BB increased from about 20 to 59 wt.% with an increase of temperature from 500 to 700 °C. The yield

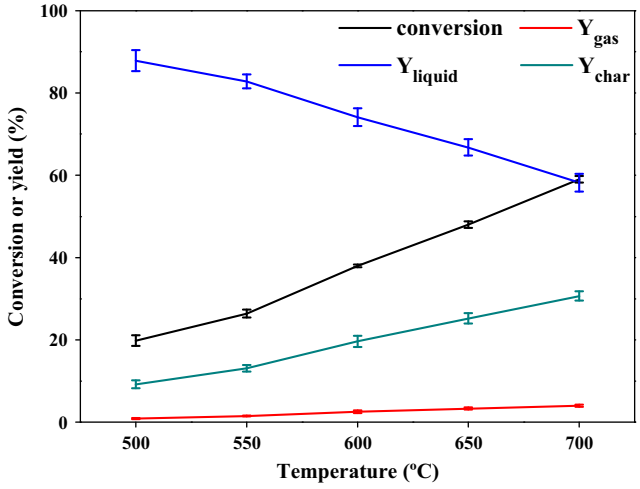


Fig. 1. Conversion, yield of gas, liquid and char at different pyrolysis temperatures for BB.