Effects of the oxygen substituent on the pyrolysis of phenyl ethers on a fixed-bed reactor

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Anisole, phenyl ethyl ether (PEE) and benzyloxybenzene (BOB) with different oxygen substituents were selected as coal-related phenyl ether model compounds, and their pyrolysis behaviors at 500, 600 and 700 °C on a fixed-bed reactor were compared. 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 pyrolysis experimental results and theoretical calculations suggest that the $C_{aliphatic}$—O bond dissociation is an initial radical step of these model compounds. However, the substituents that connect to the oxygen atom make the model compounds have their own pyrolysis characteristics. The conjugate action generated from the two benzene rings in BOB weakens the BDE. And the existence of β-H allows the phenyl ethers to form phenols through non-radical reaction at low temperature. In addition, the further reactions of phenoxy radicals affect the final composition of products.

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1. Introduction

In China, the low rank coal deposits account for about more than 40% of the total reserves. In consideration of environment protection, the effective conversion and clean utilization of low rank coal rather than direct combustion is very important. Pyrolysis, as one of the most important coal utilization processes, can be used for upgrading low rank coal and obtaining a liquid product [1,2]. As known, the organic portion of coal predominantly consists of polycyclic aromatic, hydroaromatic, and heterocyclic clusters joined together into a cross-linked three-dimensional network by short aliphatic and ether linkages [3]. The oxygen content in low rank coal is relatively high, and it mainly exists as ether linkage. Due to the complexity, heterogeneity and variability of coal, the direct analysis of pyrolysis behavior of ether linkage is difficult. Consequently, the study of simpler model compounds has the potential to provide detailed mechanistic insights into the pyrolysis behavior of low rank coal. Generally, phenyl ethers often serve as model compounds for the low rank coal and lignin [4–9].

Anisole is the simplest and most selected ether model compound, and its pyrolysis behavior has been studied. Ten products of anisole decomposition were quantified after a 2 min pyrolysis at 723 K by Schlosberg et al. [10] in 1980s. The pyrolysis of anisole was also studied in a perfectly stirred reactor over the temperature range 850–1000 K at low pressure ($16–120 \times 10^{-3}$ atm), and the yields of the main products as functions of temperature at two residence times (0.14 and 0.95 s) were reported [11]. In order to study the pyrolysis behavior of anisole, a hyperthermal nozzle and a flow tube reactor followed by analysis by mass spectrometry and FTIR spectroscopy were used [12]. Phenoxy and cyclopentadienyl radicals were found to be important intermediates in the decomposition of anisole. With the use of a hyperthermal tubular reactor and a reflection photoionization mass spectrometer, Scheer et al. [13,14] have studied the pyrolysis of anisole using both single photon ionization (PIMS; 118.2 nm) and 1 + 1 resonance-enhanced multiphoton ionization (REMPI). Their results confirm that the first step in the decomposition of anisole is the loss of the methyl group to form a phenoxy radical, followed by the ejection of CO to yield a cyclopentadienyl radical. A new kinetic mechanism validated against the experimental data from the previous study [15,16] was proposed by Hemings et al. in a recent research [17]. More recently, anisole pyrolysis and stoichiometric oxidation were studied in a jet-stirred reactor coupled with gas chromatography

and mass spectrometry [18]. The results show that anisole mainly decomposes to phenoxy and methyl radicals in both pyrolysis and oxidation conditions. The decomposition of phenoxy radicals is the main source of cyclopentadienyl radicals, which are the main precursor of naphthalene and heavier PAH. Phenyl ethyl ether (PEE) and benzyloxybenzene (BOB) are the other two frequently selected ether model compounds, whose structures are similar to the anisole that has the typical O—$C_{aliphatic}$ bond. The pyrolysis behaviors of PEE and BOB have also been studied in detail [1,19–25]. The above literature reviews show that the O—$C_{aliphatic}$ bond dissociation, which leads to two radicals, is the initial step for all the above selected ether model compounds. However, the detailed pyrolysis behaviors of phenyl ethers are different with the change of the substituent. Although the pyrolysis behaviors of single ether model compound have been studied, the study about the influence of the substituent on the pyrolysis of phenyl ethers is scarce.

In this study, anisole, PEE and BOB were selected as model compounds to study the substituent effects on the pyrolysis of phenyl ethers. The pyrolysis experiments were conducted on a fixed-bed reactor with a stainless steel tube. In addition, the bond dissociation energies (BDEs) for main radical pathways were calculated with *Gaussian 09* suite of programs. Based on the experimental and theoretical analyses, the similarities and differences in the pyrolysis behaviors of three model compounds were summarized, and the substituent effects of phenyl ethers were obtained.

2. Experimental

2.1. Materials

Anisole and PEE were purchased from J&K Chemical Ltd., and BOB was purchased from Tokyo Chemical Industry (TCI). 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. 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, 600 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. All the results presented are the averages of the repeated experiments.

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 products 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:

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

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

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

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

where m_0 and m_e is the weight of model compound (anisole, PEE or BOB) before and after pyrolysis, respectively. m_{gas}, m_{char} and m_{liquid} is total weight of the gas, char and liquid (including the existing model compound after pyrolysis), respectively.

2.4. Computational method

In this paper, all calculations were carried out with *Gaussian 09* program [26] by using the density functional theory (DFT) method. The structures of all the reactants, intermediates, transition states and products involved in the reactions were optimized with B3LYP (Becke's three parameter gradient corrected exchange functional [27] with the gradient corrected correlation functional of Lee et al. [28]) using the 6-31G (d) basis set [29], which can provide accurate geometrical parameters and energies with low computational cost.

3. Results and discussion

3.1. Comparison of pyrolysis results of the phenyl ether model compounds

The conversion and yield of liquid products, gas products and char were calculated, and the pyrolysis results are shown in Fig. 1. The mass balances during the pyrolysis of model compounds are 95.6 ± 1.6 wt.%.

As shown in Fig. 1a, the conversions of all the model compounds increase with raising the temperature. The conversions increase with raising the pyrolysis temperature, while all the yields of liquid decrease (Fig. 1b). This result may be attributed to further reactions, such as carbonization and polymerization, resulting in the increase of gas and char yields (Fig. 1c and d). Further reactions will be more active at higher temperature. That is, further reactions are not beneficial for the efficient conversion of model compounds into liquid products. As illustrated in Fig. 1, the temperature effect on the pyrolysis of BOB is weaker than that of anisole and PEE. The conversion of BOB is much higher than that of anisole and PEE, while anisole and PEE have almost the same conversion regardless of temperature. At 500 °C, the conversion of BOB is about eight times to that of anisole or PEE, which means the pyrolysis of BOB is much easier than that of anisole or PEE. Among the three model compounds, the gas yield of PEE is the highest, while its char yield is the lowest. The liquid products of anisole is the lowest at 700 °C, while its char yield is the highest. The possible pyrolysis pathways will be discussed in Section 3.3 in detail. The detailed discussions will explain the temperature effect on the pyrolysis of the three model compounds.

3.2. The pyrolysis products analysis

3.2.1. The pyrolysis products analysis of anisole

As illustrated in Fig. 2, the production of methane, hydrogen, ethylene, ethane and carbon monoxide increases with raising the pyrolysis temperature, and methane is the principal gas product. It can be found from Fig. 3 that phenol, benzene, naphthalene,