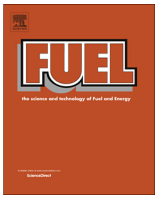
Fuel 189 (2017) 195–202

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



Full Length Article

Distribution of hydroxyl group in coal structure: A theoretical investigation

Lu Li [a,b], Hongjun Fan [b,*], Haoquan Hu [a,*]

[a] *State Key Laboratory of Fine Chemicals, Institute of Coal Chemical Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China*
[b] *State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*

HIGHLIGHTS

- The most plausible position for hydroxyl group in coal is that with lowest energy.
- Hydroxyl substituted on the pyridine ring show the most preference.
- The hydroxyl groups are inclined to form hydrogen bond in coal structure.

ARTICLE INFO

Article history:
Received 6 December 2015
Received in revised form 27 July 2016
Accepted 19 October 2016
Available online 26 October 2016

Keywords:
Coal structure
Hydroxyl group
DFT calculations

ABSTRACT

Coal structure is very complicated. The ratio of various functional groups in coal may be studied by existing analysis techniques, but the connections of these functional groups are still mostly unknown. In this work we assume that the most stable position for a certain group could be the most plausible position for that group in the coal structure, then with the help of Density Functional Theory (DFT) calculations we have studied the most plausible position for hydroxyl group in coal. We found the order of preferential position for hydroxyl group is: (1) pyridine rings; (2) polycyclic aromatic hydrocarbons; (3) monocyclic aromatic hydrocarbons; (4) monocyclic heteroatomic molecules (pyrrole, furan and thiophene); (5) alicyclic rings. Besides, double substituted hydroxyl groups on pyridine and polycyclic aromatic ring are possible. Hydroxyl groups tend to be in the positions where they can form hydrogen bond. Electron donating and withdrawing groups do not obviously change the preference of hydroxyl group unless there is hydrogen bond formed.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Coal structure is very complicated and highly depends on the origin, history, and age or rank of the particular coal. Nonetheless, insights of the macromolecular structure of coal at molecular level are helpful for improving the efficiency of coal processing technology. A lot of coal molecular structure models have been proposed over the past few decades [1–3], and several representational coal macromolecular structure model are well known such as Fuchs and Sandoff [4], Given [5], Wiser [6] and Shinn [7]. The coal molecular structure could be derived with the help of a variety of sources, including elemental composition, carbon and hydrogen ratios, and developed analytical techniques such as nuclear magnetic resonance (NMR) [8–12], FTIR [13–15], X-ray photoelectron spectroscopy (XPS) [16–18], X-ray diffraction (XRD) [19,20], and high-resolution transmission electron microscopy (HRTEM) [21–27], which all provided additional insights to the coal structure.

There are a surprisingly large number of coal molecular models have been published over the last decades. The first coal model was presented by Fuchs and Sandoff in 1942 [4], this model pave the way for further advancements of generating a two dimension structure representation. The three dimension space-filling coal models would not appear until Spiro [28]. With the advances in computational power, software tools and analytical techniques, numerous models are beginning to emerge and these models are being applied broadly, which range from swelling behaviors of coal observed in solvents and gases [29–31] to pyrolysis [32–34], liquefaction [7,35], char formation [36–38], and spontaneous combustion [39–41].

Coal molecular structures are usually constructed using organic molecular fragments which are created to match the observed properties of coal, including elemental distribution, H/C ratio, functional group composition, etc. The large amount of fragments and

---

* Corresponding authors.
E-mail addresses: fanhj@dicp.ac.cn (H. Fan), hhu@dlut.edu.cn (H. Hu).

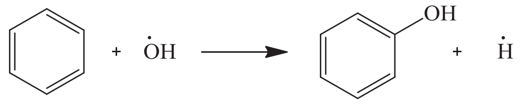
http://dx.doi.org/10.1016/j.fuel.2016.10.091
0016-2361/© 2016 Elsevier Ltd. All rights reserved.

possible connections will inevitably result in numerous possible structure models since the crosslinks and functional groups position are uncertain. The molecular models of coal structure revealed the preferences and interests of the chemists who constructed them with knowledge of chemistry.

The connections of the functional groups in coal are very important for its properties. Unfortunately, there is still no effective method to get the accurate information. Since the coal have been formed under extremely high pressure in millions of years, we think it is reasonable, at least at some extent, to assume that the most stable position for a certain functional group could be the most plausible position in coal structure. The stability of the groups at various positions can be estimated by Density Functional Theory (DFT) calculations. Therefore, with this assumption, we proposed a way to study the possible position for the functional groups in coal. Considering the oxygen is the most predominant heteroatom in coal, and the phenolic hydroxyl appears to be the most abundant oxygen functional group [7,42], in this work we studied the possible position of hydroxyl group in coal structure using this protocol. The hydroxyl substitution energy (HSE) has been taken as the criterion for the relative stability of hydroxyl group at various positions on the coal fragments. With the help of DFT calculations, the order of preference for hydroxyl group has been proposed. We found the most likely position for hydroxyl group is on pyridine ring, then on the polycyclic aromatic hydrocarbons (PAHs), and the alicyclic rings are the most unlikely position.

2. Computational method

Although different coals could have very different molecular structures, the fragment structure for certain rank coal is more or less the same. In this work, we selected several typical fragment structures, summarized in Table 1, which are usually used to construct coal model structure in literatures [6,43]. The HSE of hydroxyl substituted reaction on the fragments (take hydroxyl substituted on benzene as example, Reaction 1) was used to depict the stability of hydroxyl at certain position, which was used as criterion for evaluating the degree of stability for hydroxyl at various positions of coal fragment structures. The more negative the HSE is, the more likely the position is for hydroxyl substitution.



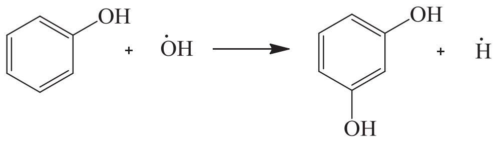
(Reaction 1)

The HSE can be calculated by Eq. (1):

$$\mathrm{HSE} = H(\mathrm{C_6H_6O}) + H(\dot{\mathrm{H}}) - H(\mathrm{C_6H_6}) - H(\dot{\mathrm{O}}\mathrm{H}) \quad (1)$$

where H is the enthalpy of the related species.

Double hydroxylation is also studied. The HSE for the second hydroxylation is defined as that for the second hydroxylation reaction (take second hydroxyl substituted on benzene as example, Reaction 2).



(Reaction 2)

The HSE of second hydroxylation reaction can be calculated by Eq. (2):

$$\mathrm{HSE} = H(\mathrm{C_6H_6O_2}) + H(\dot{\mathrm{H}}) - H(\mathrm{C_6H_6O}) - H(\dot{\mathrm{O}}\mathrm{H}) \quad (2)$$

All calculations were carried out with Gaussian 09 program [44]. Considering the large amount of the fragment molecules, we selected M06-2X [45] method to balance the accurate results with computational economy to the greatest extent [46]. The M06-2X/cc-pVDZ was used for all geometry optimizations and vibrational frequency calculations. Single-point energies on the optimized structures were calculated at M06-2X/cc-pVTZ level. The zero point energy (ZPE) and thermal corrections for enthalpies at 298 K ($H_{298\mathrm{K}}$) was obtained from the vibrational frequencies calculations. The enthalpy was calculated using Eq. (3) [47].

$$H_{298\mathrm{K}} = \mathrm{E} + \mathrm{ZPE} + H_{\mathrm{trans}} + H_{\mathrm{rot}} + H_{\mathrm{vib}} + \mathrm{RT} \quad (3)$$

where E is electronic energy, H_{trans}, H_{rot}, and H_{vib} represents the translational enthalpy, rotational enthalpy, and vibrational enthalpy, respectively, and the values are calculated with the equilibrium statistical mechanics with harmonic oscillator approximation using unscaled vibrational frequencies under standard temperature.

3. Results and discussion

3.1. Single hydroxylation on the fragments

A comprehensive test set of singly hydroxylated fragments was examined. Hydroxylation can take place at different positions on the fragments structure, and all potential substituted carbon sites are indicated in Table 1. The computed HSE are summarized in Fig. 1. Among the model compounds we have studied, the most favorite substituted site is the ortho-position of N in pyridine ring, including pyridine (**12**), substituted pyridine (**25**), and pyridine fragment in the polycyclic aromatic molecules (**13**, **14**, **18**). The HSE varies from −11.9 to −9.2 kcal/mol. In cases of having two different ortho-positions such as structure **14** (**14-2** and **14-8**) and **18** (**18-2** and **18-10**), there are few differences between two sites, and the sites **14-8** and **18-10** are slightly favorable. As a comparison, the HSE of para- (−4.0 to −3.5 kcal/mol) and meta-position (−0.7 to 3.3 kcal/mol) of pyridine ring is much higher, indicating that they are not the preferred position for hydroxyl.

The most favorable substitute sites for PAHs are **4-2**, **5-2**, **6-2**, **7-1**, **8-11**, respectively. The species **4-2**, **5-2**, and **6-2** can be described as naphthalene-like structures, and their HSE values are very similar (−1.8 kcal/mol for **4-2**, −2.0 kcal/mol for **5-2**, and −2.1 kcal/mol for **6-2**). The species **7-1**, **8-11** are illustrated as pyrene-like structures, they also have similar local environment as in the four- and five-membered ring PAHs (−2.1 kcal/mol for **7-1**, −2.5 kcal/mol for **8-11**). The hydroxyl substituted on benzene requires a higher energy with the value of −1.7 kcal/mol. These show that PAHs are more favorable to hydroxyl substitution than monocyclic benzene. The substituted monocyclic aromatic molecules (**3**, **21**, **22**, **23**, **24**) show lower HSE value than benzene, ranging from −2.4 to −1.8 kcal/mol for the best favorable position. The observed phenomenon can be rationalized by the effect of p-π conjugation between the hydroxyl group and the aromatic ring, where hydroxyl is an electron donating group. The stronger the p-π conjugation is, the easier for hydroxyl substitution, and vice versa. The hydroxyl substituted on pyridine is the most favorable due to the strong electron attracting effect of nitrogen atom, which makes the strong p-π conjugation between the hydroxyl group and pyridine ring. The PAHs have more electrons to participate in the

Download English Version:

https://daneshyari.com/en/article/6475675

Download Persian Version:

https://daneshyari.com/article/6475675

Daneshyari.com