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Water catalyzed pyrolysis of oxygen functional groups of coal: A density functional theory investigation

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ABSTRACT

The pyrolysis mechanism of carboxylic and hydroxyl groups which are present in the coal has been investigated with the help of density functional theory calculations. The role of water in the pyrolysis reaction mechanisms has also been investigated by the calculation of activation energy barriers. The activation energy barriers for the water mediated reactions are less when compared to thermal pyrolysis process. The results show the significant decrease in the energy barriers for decarboxylation reactions than the hydroxyl groups in the presence of water. Therefore, water can significantly decrease the oxygen content in the non-coking coals with high content of carboxylic groups.

1. Introduction

Steel industry is the main consumer of coke and it needs significant increase in the coke production. The properties of coke are necessary for blast furnace applications and hence there is a significant demand for the production of good quality coke with high carbon content and porosity. The coke with good quality can be produced only from coking coals that are blended at high proportion. The availability of sources for coking coals is limited. The rise in cost and reduced disposal of coking coals demands the production of new sources for prime coals. Non-coking coals attract interest in making of coke due to their availability and less cost. Among all the types of coals, non-coking coals are taken as the lowest rank of coal because of their relatively low heat content. The content of water, sulfur and metal elements is high in non-coking coals when compared to coking coals. The important requirement for the composition of coal blends is the production of good quality coke [1]. However, the non-coking coals are usually not suited for the coke production in commercial perspective due to their properties.

Several methods have been developed to increase caking propensity of non-coking coals such as addition of various additives and biomass [2–6]. These methods are useful to increase the usage of non-coking coals in coke-making process. Thermal treatment of low rank vitrinite coal initiates the depolymerization reactions in the vitrinite network

and it leads to the formation of low molecular weight products [7]. The new products are not efficient to form large anisotropic domains. In addition to additive methods, the pretreatment of coal also plays important role to increase the caking properties. Hydrothermal pretreatment of low rank coal can improve solvent extraction yields and change the caking properties of coal [8–10]. Water treatment of three Argonne Premium coals at 600 K shows the increase in the extraction yields [11]. The same has been found in the case of hydrothermal treatment of bituminous coal at suitable conditions [12]. Previous study found that promoted formation of coke in the hydrothermal treatment of non-coking coal [13]. The decrease in the total content of oxygen and hydroxyl oxygen were higher in hydrothermal treatment of coal compared to thermal pyrolysis. The reduction of oxygen content may improve the solubility of the treated coals. The content of oxygen and oxygen functional groups in low rank is higher when compared to coking coals. These oxygenated groups are responsible for the formation of cross linked chars. In the pyrolysis process, oxygenated functional groups consume much active hydrogen and subsequent decrease in the caking properties. Hence, hydrothermal treatment of low rank coal is useful to modify their caking properties and to create source for coke making. Hydrothermal treatment of sub bituminous coal with high content of oxygen shows the increase in solvent extraction yields and caking properties. The effect of base in the hydrothermal treatment of non-coking coals has been shown in the earlier study [14]. The basic nature

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enhances the reduction of oxygen functional group content by removing the hydroxyl groups from coal molecules. Oxygen functional groups in coal are categorized such as carboxylic, hydroxyl, carbonyl and ether. The contribution of oxygen from the carboxylic and hydroxyl groups is more compared to others. Several experimental and computational studies have been performed on the pyrolysis of oxygen functional groups [15–19]. Liang et al. has explored the mechanism involved in the water treatment of coal [20]. The impact of hydrothermal treatment on the chemical structure of lignite coal has been studied using ReaxFF simulations [20].

Oxygen functional groups are involved in the formation of hydrogen bonds with each other and the hydrogen bonds are responsible for the rigidity of coal. During the pyrolysis process, the hydrogen bonded oxygen functional groups undergo cross linking reactions [21]. The cross linking reactions affect the further pyrolysis process products. Therefore, understanding the crosslinking reactions of oxygen functional groups present in non-coking coal is important. The knowledge about the mechanisms involved in the hydrothermal treatment of coal is not clear yet. Therefore, in this investigation the influence of water on the pyrolysis of single and hydrogen bonded oxygen functional groups have been studied using density functional theory. The results show that the water has promoted the pyrolysis process of carboxylic groups and thus decreases the oxygen content in the non-coking coal which would be useful for the caking properties.

To understand the complicated pyrolysis process of coal macromolecules, several model structures have been developed for both coking and non-coking coals [22,23]. Several models have been used to understand the pyrolysis process. The model has shown that The selected models of non-coking coals have high content of oxygen groups. The oxygen functional groups involved in intra- and inter- molecular hydrogen bonds. The study of pyrolysis of macromolecules is very complicated and difficult. Therefore, in this study the small fragments have been chosen as considered in the previous studies. Various model systems have been considered for the non-coking coal which are depicted in Fig. 1.

2. Computational details

The models presented in Fig. 1 were used to study the mechanistic aspects of pyrolysis involved in oxygen functional groups in the presence and absence of the water molecules. All the geometries were optimized using density functional theory (DFT) based Becke's three parameter hybrid exchange functional and the Lee Yang Parr correlation functional (B3LYP) along with 6-31G* basis set [24–27]. To ensure the optimized geometries corresponding to the true minima on the potential energy surface (PES), vibrational analysis was carried out at the same level of theory (B3LYP/6-31G*). The standard transition state theory (TST) was employed to trace the transition state (TS) structures from the initial geometries. The TSs were characterized by single imaginary frequency criteria and subsequent intrinsic reaction coordinate (IRC) calculations were performed to confirm the correlation between the TS and the corresponding minima on the minimum energy path (MEP) of a reaction [28,29]. All the calculations were performed with the help of Gaussian 09 package [30]. The rate constants for all reactions presented in Table 1 were calculated using Eyring equation as given below to describe the variation of the rate of reaction with temperature.

$$k = \frac{k_B T}{h} e^{-\frac{E_a}{RT}} \quad (1)$$

where, E_a is the Gibbs free energy of activation, k_B is Boltzmann's constant, and h is Planck's constant.

3. Results and discussion

3.1. Unimolecular decarboxylation

The isolated benzoic acid (BA) can undergo decarboxylation reaction through various possible reaction pathways. The decarboxylation of BA has been adopted from the literature which results benzene and CO_2 through the formation of four membered transition state. The decarboxylation is initiated from the elongation of C (COOH) – C (Benzene) bond and the transfer of hydrogen (OH) to benzene ring. The corresponding activation barrier of this particular reaction is of 59.20 kcal/mol and the rate constant is of $k = 7.13 \times 10^{-29} \text{ s}^{-1}$ which indicates, the reaction is very slow under standard reaction conditions. This result is in close agreement with the previous reports [21]. As the activation barrier is large, the decarboxylation of BA may takes place at higher temperatures (Fig. 2a).

3.2. Intra-molecular coupling reactions of carboxylic acid

As coal is a solid macromolecule, the carboxylic acid groups cannot change their positions rapidly as in the liquid phase. Hence, inter- and intra-molecular hydrogen bonded carboxylic groups can undergo reactions. Similar studies have been reported for the bimolecular coupling of inter-hydrogen bonded carboxylic groups using benzoic acid [22]. Here, we have considered the models such as N-2, PB-2 and BP-2 for the coupling reactions of intra-molecular hydrogen bonded carboxylic groups. The possible mechanism for the coupling of intra-hydrogen bonded carboxylic groups is the formation of anhydride by subsequent removal of water molecule from two carboxylic acid groups. The detailed reaction mechanism with geometries and reaction energy profile is depicted in Fig. 2b. The activation energy for this concerted reaction is 37.48 kcal/mol with rate constant $6.66 \times 10^{-15} \text{ s}^{-1}$. The rate of reaction increases ($10.70 \times 10^{-2} \text{ s}^{-1}$) drastically with rise in temperature (600 K). The transition state involves simultaneous formation of O–H (COOH-1) bond and breaking of C–O bond (COOH-2) to form water molecule and corresponding anhydride.

During the course of this reaction, the water molecule moves away from the complex and the unsaturated carbon of one carboxylic acid attacks the other COOH group at unsaturated oxygen. This reaction leads to the formation of the product containing three rings which is more stable than the two membered reactant (N-2). Further, to understand the coupling reactions involved in various dicarboxylic acid moieties, the coupling reactions for PB-2 and BP-2 have been investigated. The proposed mechanisms for PB-2 and BP-2 are similar to N-2 and are shown in Fig. 2c and d.

The mechanism is similar to the anhydride formation in N-2 but differs in the activation energy barriers involved in the reaction. The activation energy barriers are 48.52 and 53.56 kcal/mol for PB-2 and BP-2, respectively and the corresponding rate constants are 1.51×10^{-24} and $8.69 \times 10^{-28} \text{ s}^{-1}$. The activation barriers of PB-2 and BP-2 are higher than the activation barrier involved in the case of N-2 by 11.14 and 26.08 kcal/mol, respectively. Hence, the activation energy is significantly affected by the chemical environment around the intra-hydrogen bonded carboxylic groups. From the previous report [22] it is clear that, the inter-molecular hydrogen bonded dicarboxylic acids have activation energy barriers (≈ 36.00 kcal/mol) which are lower than those of intra-molecular hydrogen bonded carboxylic acid coupling reactions (≈ 38.00 – 54.00 kcal/mol, Fig. 2). This indicates that the bimolecular coupling of inter-molecular hydrogen bonded carboxylic acid groups undergo anhydride formation at relatively low temperatures when compared to intra-molecular hydrogen bonded dicarboxylic moiety. The moieties N-2, PB-2 and BP-2 are structurally different with respect to the separation of both the carboxylic groups. From the calculations it is observed that, if the separation of carboxylic groups is more, then the anhydride formation between them requires higher activation energy. The carboxylic groups as such in N-2 undergo reaction at relatively lower

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