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A density functional theory study on the decomposition of aliphatic hydrocarbons and cycloalkanes during coal pyrolysis in hydrogen plasma

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Abstract

To get deep understanding of the reaction mechanism of coal pyrolysis in hydrogen plasma, the decomposition reaction pathways of aliphatic hydrocarbons and cycloalkanes, which are two main components in volatiles from coal, were investigated. Methane and cyclohexane were chosen as the model compounds. Density functional theory was employed, and many reaction pathways were involved. Calculations were carried out in Gaussian 09 at the B3LYP/6-31G(d,p) level of the theory. The results indicate that the main pyrolysis products of methane and cyclohexane in hydrogen plasma are both hydrogen and acetylene, and the participation of active hydrogen atoms makes dehydrogenation reactions more favorable. H_2 mainly comes from dehydrogenation process, while many reaction pathways are responsible for acetylene formation. During coal pyrolysis in hydrogen plasma, three main components in volatiles like aliphatic hydrocarbons, cycloalkanes and aromatic hydrocarbons lead to the formation of hydrogen and acetylene, but their contributions to products distribution are different.

Key words

coal pyrolysis; thermal plasma; density functional theory; aliphatic hydrocarbons; cycloalkanes

1. Introduction

Coal pyrolysis in thermal plasma has been proved to be an effective, direct and clean way to produce acetylene (C_2H_2) by many researches [1−8]. In this process, coal particles are injected into thermal plasma reactor and pyrolysis reactions take place. After the pyrogas is quenched by water or other quenching media, hydrogen and light hydrocarbons such as acetylene, ethylene and methane are produced. Several institutions have run pilot-plant tests on coal pyrolysis in thermal plasma. In the 1980s, AVCO used a prototype of 1 MW plasma reactor to produce acetylene from coal, and water was used for quenching. A high acetylene concentration in pyrogas of 12 vol% was achieved, and the energy cost for acetylene was about 10.5 kW·h/kg [9,10]. Xinjiang Tianye Co. has been working on the pilot-plant tests using 2 MW and 5 MW V-shaped plasma torch since 2007. The highest acetylene concentration was 9.4 vol% on 2 MW plasma reactor, and the energy cost for acetylene was about 10.6 kW·h/kg [6,11]. All these previous researches and pilot-plant tests prove that the acetylene production from coal pyrolysis has a competitive cost with current technology, and notably the technology produces little waste. It is believed that thermal plasma is a promising technology for coal utilization and chemicals production, and this process is technologically feasible and economically favorable.

Before further attempts on scaling-up and process optimization on coal pyrolysis in thermal plasma, the understanding of pyrolysis mechanism is necessary. The two-steps mechanism proposed by Baumann and Bittner is widely accepted to describe coal pyrolysis process in thermal plasma [4,12]. According to this mechanism, pyrolysis starts with the vaporization of volatiles (including aliphatic hydrocarbons, cycloalkanes, aromatic hydrocarbons, and etc.) from coal, and then these volatiles further decompose into acetylene, hydrogen and other light hydrocarbons. Shuang et al. [13] have studied the heat transfer and devolatilization process during the first step through CFD simulation, based on the data obtained from the 2 MW scale-level pilot-plant tests run by Xinjiang Tianye Co. A mechanism model is established to describe heat transfer, release of volatiles and reactions. Aromatic hydrocarbons play very important roles in the formation of acetylene, and their reaction mechanism in thermal plasma has been studied in our previous work through density functional theory (DFT)

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calculation [14]. Therein, benzene is chosen as model compound for aromatic hydrocarbons. Calculation results indicate that the dehydrogenation of benzene ring is responsible for the additional hydrogen gas, and the decomposition of phenyl radical leads to the formation of acetylene.

To get a complete reaction mechanism of coal pyrolysis in thermal plasma, we need to study the reaction mechanism of other two volatiles from coal in hydrogen plasma. Thus, in this work, the reaction pathways of methane and cyclohexane (c-C_6H_{12}) in hydrogen plasma have been investigated using DFT method. The aliphatic hydrocarbons in volatiles are mainly composed of methane, ethylene and propane, and methane is most abundant. The reaction pathways of ethylene and propane have also been studied in our previous work [15], and the main products of ethylene and propane pyrolysis are acetylene and hydrogen. So methane is chose as the model compound of aliphatic hydrocarbons here. And cyclohexane (c-C_6H_{12}) is a common model compound for cycloalkanes because of its simplicity [16,17].

2. Method of calculation

All the DFT calculations were carried out using the Gaussian 09 suit of program [18]. B3LYP with the 6-31G(d, p) basic set, a widely used hybrid density functional method [19,20], was employed to optimize the geometries of all the reactants and products, and their electronic energies (E_0) were gained. At the same level of theory, the vibrational frequencies of reactants and products were calculated to obtain zero-point energy (ZPE) corrections (E_{ZPE}). Thus, the ground state energies (E) of reactants and products can be obtained by: $E = E_0 + E_{ZPE}$. And the enthalpy for reaction is the relative energy between product and reactant: $H = E_{product} - E_{reactant}$. Transition states (TSs) of reactions were searched using QST2 method and then optimized using TS method. And the activation energy for reaction is defined as the relative energy between transition state and reactant: $E_a = E_{TS} - E_{reactant}$. Transition state was confirmed by checking imaginary frequency in Gaussian View and running IRC calculation. For correct transition state, there is only one imaginary frequency, and IRC calculation will lead back to reactant and product.

3. Results and discussion

3.1. The generation of hydrogen plasma

Hydrogen is used as the working gas of plasma generator here. The electric arc between cathode and anode can heat hydrogen gas to a temperature as high as $2000-3500\,^{\circ}C$ when hydrogen gas runs through, and hydrogen molecules decompose into active hydrogen atoms. This process, $H_2 \rightarrow 2H\cdot$, requires a high energy of 103.4 kcal/mol, as discussed in our previous work [14,15]. Thus, thermal plasma jet is generated and then enters the reaction zone. In reaction zone, plasma will transfer the energy from electric arc to coal particles and supply the energies needed for further reactions of volatiles.

3.2. The decomposition of methane

The initiation step of the decomposition of methane is described as following [21]:

$$CH_4 \rightarrow CH_3\cdot + H\cdot \quad (1)$$

$$CH_4 + H\cdot \rightarrow CH_3\cdot + H_2 \quad (2)$$

Then $CH_3\cdot$ can continue to dehydrogenate into $CH_2\cdot$, $CH\cdot$ and C (carbon black) at the end [22]. The potential energies profiles of this dehydrogenation pathway are shown in Figure 1. Some reported calculation results [22] (inside the parenthesis) and experimental results [23] (inside the bracket) are also presented, in order to show the accordance of our results with the existing results. The structures of species (red atom for C and blue atom for H) with some important structure parameters (bond length in Å and angle in degree) are also given in Figure 1. It can be seen that the reaction routes with the participation of active hydrogen (mainly from thermal plasma) are more favorable, which are marked by red lines. This kind of reactions is called hydrogen abstraction reaction, and they are the main reaction pathways of methane dehydrogenation.

It has been reported that there is a reaction route for the thermal coupling of methyl radical at high temperature as following [21]:

$$2CH_3\cdot \rightarrow C_2H_6 \rightarrow C_2H_4 + H_2 \rightarrow C_2H_2 + H_2 \quad (3)$$

All these reactions can be explained by a free radical mechanism. The combination of methyl radical into ethane is exothermic by 86.3 kcal/mol, and this result is quite close to the calculation result (88.5 kcal/mol) [22] and experimental result (87.5 kcal/mol) [24]. Then ethane starts to lose hydrogen atom by the following reactions:

$$C_2H_6 \rightarrow C_2H_5\cdot + H\cdot \quad (4)$$

$$C_2H_6 + H\cdot \rightarrow C_2H_5\cdot + H_2 \quad (5)$$

Reaction (4) is a direct C–H bond breaking process, and it is strongly endothermic by 99.0 kcal/mol. With the participation of active hydrogen atom, Reaction (5) is slightly exothermic by 4.4 kcal/mol with a small activation energy barrier of 4.7 kcal/mol. Experimental activation energy for Reaction (5) is 5.2 kcal/mol [23]. Then ethyl radical ($C_2H_5\cdot$) continues to dehydrogenate into ethylene. The decomposition of ethyl radical into ethylene and further decomposition of ethylene into acetylene and hydrogen have been discussed in our previous work. Ethyl radical loses three more hydrogen atoms, and three hydrogen abstraction reactions are the most possible reaction routes [15].

Thus, the main reaction pathways for the decomposition of methane can be summarized as following:
Dehydrogenation:

$$CH_n\cdot + H\cdot \rightarrow CH_{n-1}\cdot + H_2 \ (n = 4, 3, 2, 1)$$

Thermal coupling:

$$2CH_3\cdot \rightarrow C_2H_6$$