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Full Length Article

Theoretical study of the CO formation mechanism in the CO_2 gasification of lignite

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ABSTRACT

Reactive force field (ReaxFF) molecular dynamics simulations of lignite and lignite-CO_2 models were performed to investigate the CO formation mechanism of CO_2 gasification process of lignite. A C++ program was developed to assess ReaxFF trajectories and to analyze elementary reactions involved in the mechanism. Calculated product distribution and relative amounts of main gas products show good agreement with reported experimental observations. We found that the CO formation pathways in the CO_2 gasification of lignite begin with the chain carbon radical (R_n), which is formed by C—H/C—C bond cleavage reactions of aromatic moieties in the lignite or produced semicoke at high temperatures. These chain carbon radicals can react with CO_2, forming oxidized carbon radicals, such as R_n-O-C-O, R_n-CO_2 and R_n-O. Among these radicals, R_n-O and R_n-O-C-O are important precursors of CO. They produce CO molecules by releasing their C-O moieties at the end. The thermodynamic properties of these elementary reactions were obtained by density functional theory calculations at the B3LYP/6-311 + G(2d,2p) level. The calculated overall enthalpy and entropy changes could clearly explain the experimental data. The density functional theory results show that most of these elementary reactions are endothermic and entropy increasing. High gasification temperatures are favorable for the reactions.

1. Introduction

Gasification is a clean technology for low-rank lignite with effective carbon utilization. It refers to the process where coal/char reacts with gasification agents and converts the useful components in coal to gas products (e.g. CO, H_2 and CH_4). The gas products can be used as not only a source of energy (e.g. power generation), but also as a carbon source for the synthesis of chemicals (e.g. methanol and alkenes) [1]. For the gasification of lignite, O_2, H_2O and a mixture of both are always used as the gasification agents [2,3]. Nowadays, the replacement of gasification agents by CO_2 in the lignite gasification process has attracted increasing attention [4,5]. This is because the CO_2 gasification of lignite is an effective way to reduce the phenolic wastewater in traditional gasification processes [6] and is an efficient technology for utilizing the carbon element of the major greenhouse gas CO_2.

To date, only a few investigations have reported the reactivity and kinetic models of CO_2 gasification. These studies have focused on the factors that influence the formation of the main product, CO, e.g. coal particle size, temperature and pressure [7–9]. It is found that improving the CO_2 pressure can accelerate the gasification reaction and increase CO production. Skodras [1] performed an isothermal CO_2 gasification of Greek lignite in a fixed bed reactor, and concluded that the conversion was sensitive to temperature due to carbon-CO_2 reactions. Moreover, they found that the presence of CO could reduce the gasification reaction rate. It is also reported that CO_2 is helpful for nitrogen and sulfur transfer from coal to the gas phase in the gasification process. Wang [10] investigated the effect of CO_2 on sulfur removal during the pyrolysis process of two raw coals. They found that CO_2 is beneficial for the H_2S, COS and SO_2 release of coal. However, few investigations have reported the microscopic reaction mechanism of CO_2 gasification, and in particular, the production pathways for its gas products. Understanding this is critical to the evaluation of the CO_2 gasification and increasing the yield of CO. The lack of knowledge regarding the interaction between CO_2 and coal/char is due to the complexity of the CO_2 gasification reaction. Current analysis methods cannot distinguish the types and relative amounts of a certain radical intermediate generated by CO_2 and the coal/char reaction [11,12].

Molecular dynamics simulations based on the reactive force field (ReaxFF) [13] could be a complementary method for studying the mechanisms of coal reactions, including CO_2 gasification. Extensive studies have been conducted in this field and have confirmed that ReaxFF simulations could successfully describe the mechanisms of coal

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reactions, such as pyrolysis [14–17], hydropyrolysis [18,19], oxidation [20] and hydrothermal treatment [21,22]. Recently, Li [23] simulated pyrolysis reactions with a 4976-atom bituminous coal using the ReaxFF method. Their simulation results show a gas generation sequence that is identical with experimental results [24]. The formation pathways of methyl and hydroxyl radicals, precursors of methane and H_2O, are also obtained [25]. Zhan [26] carried out ReaxFF simulations to investigate the mechanism of the initial reaction process of subbituminous coal pyrolysis. The formation mechanism for typical products, like CH_4 and H_2, was further confirmed by density functional theory (DFT). Our group also studied lignite pyrolysis processes in H_2 and O_2 atmospheres using ReaxFF simulations and traced the radical intermediates in the sulfur- and nitrogen-transfer reactions [27–29]. Thus, ReaxFF simulations have proved to be an effective method for complicated coal chemical reactions under various conditions.

In the present work, we report ReaxFF simulations and DFT calculations concerning the CO_2 gasification process of lignite. The calculations aim to provide a microscopic view of the elementary reactions between CO_2 and lignite model molecules at a high temperature by tracking the corresponding atoms. In particular, we focus our attention on the formation pathways of the main product of lignite gasification, CO. This work is expected to be beneficial for the understanding of the fundamental reactions of CO_2 gasification and even the carbon solution loss reaction in the caking process of lignite.

2. Computational details

2.1. Construction of lignite and lignite-CO_2 models

The molecular model provided by Wolfrum [30] was selected as the structural unit in the following simulations. We modified its unreasonable or unstable substructures and further removed metal atoms due to the limitation of the force field (see *Fig. S1, Supporting information*). The final structure unit is shown in Fig. 1a ($C_{225}H_{182}N_4S_3O_{36}$, abbreviated as **W**). Then, the lignite model was built according to the molecular weight of **W** and the bulk density of lignite. We added 14 optimized **W** molecules (Fig. 1b) to a 55.0 Å × 55.0 Å × 55.0 Å cubic box ($C_{3150}H_{2548}N_{56}S_{42}O_{504}$, abbreviated as **L**, density of ~0.5 g/cm^3) using the Packmol program [31], and optimized its geometry with the Dreiding force field [32] in the Lammps program [33,34] (see Fig. 2a). In the actual process of CO_2 gasification, the CO_2 is added to the reaction system continuously. The excess CO_2 serves the functions of both the reactant and carrier gas. Here, we placed 14 **W** molecules and 270 CO_2 molecules into a 55.0 Å × 55.0 Å × 110.0 Å box to build the model for CO_2 gasification of lignite ($C_{3420}H_{2548}N_{56}S_{42}O_{1044}$, abbreviated as **LC**). The following simulation results show that the CO_2 molecules are adequate for the gasification reaction (Section 3.1). The geometry of **LC** was also optimized with the Dreiding force field. To reduce the intermolecular stresses in **L** and **LC**, the following steps were performed repeatedly until the total energies of the two models reached the steady state: (1) each model was heated from 0 to 900 K with the isothermal-isochoric (NVT) ensemble; (2) maintained at 10 MPa and 900 K with the isothermal-isobaric (NPT) ensemble and (3) annealed from 900 to 298 K at 0.1 MPa with the NVT ensemble.

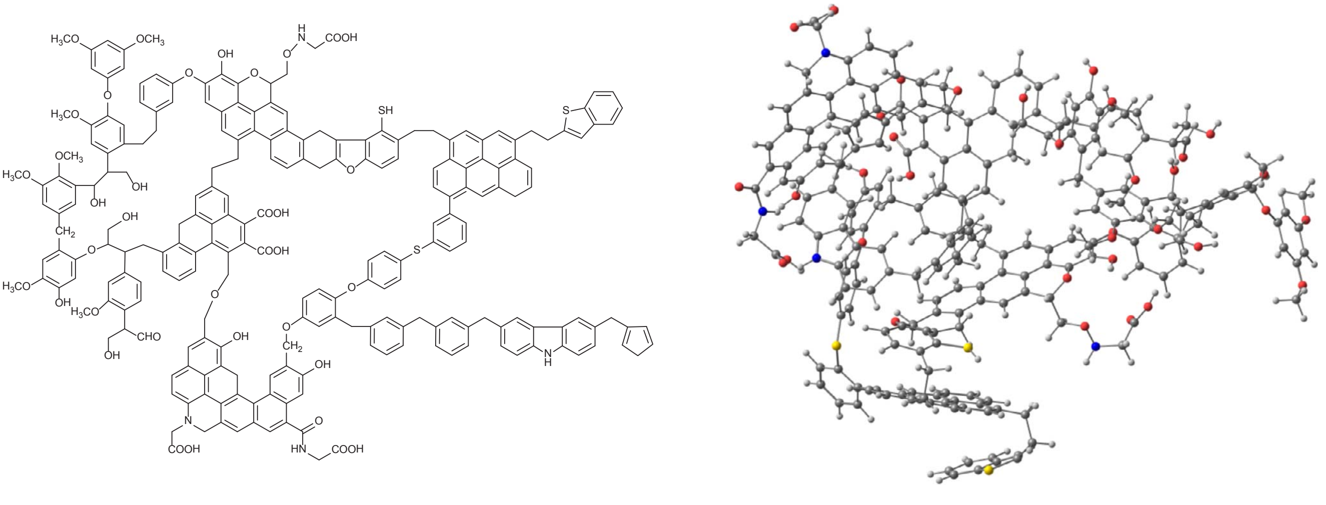
2.2. ReaxFF parameters

Since both **L** and **LC** contain C, H, O, N and S elements, the C/H/O/N/S parameters reported by Pitman and Kamat [35] are selected in all the following simulations. To determine the simulation temperature, we performed a series of ReaxFF simulations of **LC** at 1500, 2000, 2500 and 3000 K. It was found that the solid portion of **LC** is vaccinated only at 3000 K (see *Fig. S2, Supporting information*). Therefore, the simulation temperature was set to 3000 K. Although this is obviously much higher than the reaction temperature in CO_2 gasification experiments ($>$ 900 K) [11,12], it is necessary for the elementary reactions to complete in a few nanoseconds without changing the reaction mechanism. Previous studies also confirmed that increasing temperature in ReaxFF simulations has no significant effect on the simulation results [15,25,26]. ReaxFF simulations were performed with NVT ensembles at 3000 K for 1 ns. During this timeframe, both **L** and **LC** could reach equilibrium. The time step was 0.25 fs. The bond order and nonbonded cut off were 0.3 and 10 Å, respectively. We trace all corresponding atoms in the **L** and **LC** systems and analyze the simulation trajectories using a C++ code.

We then performed test runs of **LC** at 3000 K to obtain meaningful statistical data from the ReaxFF simulations. The results show that the average CO number of two trajectories agree well with those with three trajectories (see Fig. S3, Supporting information), meaning that if there are more than two trajectories, the results show convergence. To improve the accuracy, we ran the simulation four times for each system. All the simulation results were obtained by summing the results of the four trajectories.

2.3. DFT calculations

Optimizations and vibration analysis calculations of all the model molecules involved in the CO formation process were carried out by



(a) (b)

Fig. 1. (a) Two-dimension structure and (b) three-dimension geometry of **W** molecule.