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Thermodynamic and kinetic evaluation of the reaction between NO (nitric oxide) and char(N) (char bound nitrogen) in coal combustion

Hai Zhang, Jiaxun Liu*, Jun Shen, Xiumin Jiang

Institute of Thermal Energy Engineering, School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

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ABSTRACT

Using pyridine nitrogen as representative of nitrogen-containing char model, detailed theoretical calculations based on DFT (density functional theory) and conventional TST (transition state theory) are carried out to investigate the thermodynamics and kinetics of the heterogeneous interaction between NO (nitric oxide) and char(N) (char bound nitrogen) during coal combustion. Focus is directed on NO chemisorption of direct nitrogen–nitrogen interaction and N_2 desorption from medium chemisorbed surface. It is suggested that side-on chemisorption is a low barrier (2.3 kJ/mol) and high exothermic (178.5 kJ/mol) step, while N-down chemisorption is a high barrier (105.2 kJ/mol) and moderate exothermic (64.4 kJ/mol) step. Worth noticing is that NO chemisorption on char(N) surface is different from that on char surface, largely because there is no unpaired σ electrons located at N atom. After chemisorption, four stepwise reactions with the highest energy barrier of 266.3 kJ/mol are found to produce separated N_2. The overall NO reduction rate is expressed as $7.6 \times 10^5 \times \exp\left(-\frac{9606}{T}\right)$. Reaction rate of rate-limiting step involved in N_2 desorption is 2×10^0 s^{-1} at 1000 K, indicating it can tempestuously take place above 1000 K. The calculated results lend credit to previous experimental phenomenon.

1. Introduction

NO (nitric oxide) reduction with char or char(N) (char bound nitrogen) is of great significance in coal combustion field [1]. Broadly speaking, it can be described by reactions R1 and R2. R1 belongs to gas-phase NO reduction on char surface. R2 is a gas–solid interaction between NO and char(N).

$$C_{ac} + 2NO \rightarrow N_2 + CO_2 \quad \text{(R1)}$$

$$C(N) + NO \rightarrow N_2 + C(O)\ or\ CO \quad \text{(R2)}$$

Conspicuous advances have been made up to now towards understanding the reaction mechanisms [2,3], the effect of microstructure and surface chemistry [4,5], and the catalysis of metals [6]. Nonetheless, the heterogeneous NO reduction leading to the formation of N_2 is quite complicated, including NO chemisorption on char/char(N) surface, rearrangement and migration of surface functional groups and N_2 desorption from the medium surface, which can not be observed in experiments. Quantum chemistry calculations impart a promising alternative method to testify the mechanisms propounded on the basis of experimental observations. This has brought about a quantity of theoretical calculations [7–12]. Working on the systematical routes containing intermediates and transition states, Kraft et al. [8,9] characterized a series of reactions giving rise to N_2. An analysis of the potential energy surface evidenced that NO chemisorption on char surface was a good-sized driving force for the generation of N_2. This two works followed a reported literature [7] dealing with chemisorption approaches on both zigzag and armchair char models and the authors pointed out that side-on chemisorption as determined by enthalpy change was the most thermally favorable. Recent advance [10] in linking the role of temperature to the heterogeneous reduction mechanism clearly demonstrated that N_2 was the main reduction product at low temperature, as temperature increased, N_2 and CO_2 emission coexisted.

The understanding of NO heterogeneous reduction reaction R1 has been significantly promoted so far by combination of quantum chemical calculations and experimental observations from the

* Corresponding author. Tel.: +86 21 34205521.
E-mail address: liujx@sjtu.edu.cn (J. Liu).

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available literature. Contrarily, in regard to reaction R2, the theoretical estimation of the N_2 formation behavior is still lacking. Montoya et al. [12] proposed that the main channels for N_2 formation were taken by direct nitrogen–nitrogen interaction between char(N) and NO, unfortunately neither intermediates nor transition states were characterized thus the conclusions drawn may be questioned. A contribution from quantum chemical calculations is obviously indispensable towards understanding the heterogeneous reduction between NO and char(N).

The previous work showed the potential triplet energy surface for the reaction between NO and char(N) [13]. In this study, the authors thus have characterized by quantum mechanical calculations at the DFT (density functional theory) level all the singlets for direct nitrogen–nitrogen interaction, including NO surface chemisorption, rearrangement and migration of surface functional groups, as well as the N_2 desorption from medium surface. Thermodynamics encompassing these processes is considered. Kinetics for the individual reactions and overall NO reduction reaction are evaluated with conventional TST (transition state theory) and steady state approximation, respectively. Finally, the calculated results are validated by comparisons with the generalized experimental phenomenon. Many organic reactions involve reactive unsaturated species (carbynes, nitrenes, carbenes, char model, etc.) involve spin crossover phenomena and are the topic of intense investigations. On the basis of this work, two states reactivity of NO reduction by char(N) will be focused.

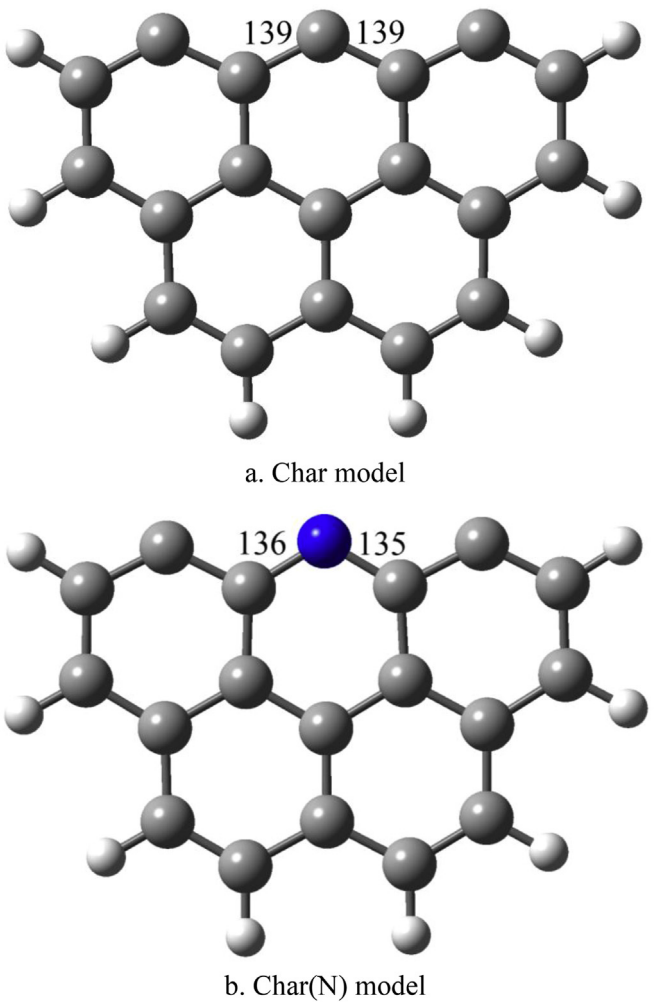

Fig. 1. Two models discussed in the present work. Bond lengths in picometers.

2. Computational details

2.1. Physical model

Coal, consisted of polycyclic aromatic hydrocarbons with some functional groups working as bridges, is a species of highly intricate matrix with cross-connected molecular systems. When subjected to severe pyrolysis, it is stacked irregularly by three to seven benzene rings, as evidenced in Ref. [14]. Mondragón and co-workers [11] selected the five six-membered benzene rings (see Fig. 1a) to investigate the NO-char reactions with the presence of H_2O and O_2. Considering an electron cannot delocalize efficiently through single bond, the reactivity of the edges of the carbonaceous model in many cases comes from the local structure of the unsaturated atom instead of the model size [15]. It is therefore reasonable to select the five six-membered benzene rings.

The fate of organically bound nitrogen residing in char is of great importance to establish an appropriate char bound nitrogen model. It is found that pyridinic, pyrrolic and quaternary complexes as characterized by existing XPS analysis are the most important N-containing groups [16]. However, at temperatures higher than 1273 K, pyridinic-N at the graphene edge is the most abundant nitrogen functional form [17], which is mainly due to the high stability of pyridinic-N [18]. Therefore, traditional plane zigzag configuration containing pyridinic-N (shown in Fig. 1b) is applied to model char(N). Edge atoms on the upper side are unsaturated for chemisorption. Eight terminating H atoms are added, according to Mondragón et al. [11], in order to preserve the sp^2 hybridization of other edge carbon atoms. Using pyridinic-N as a nitrogen containing carbonaceous model, Espinal and co-workers [19] studied the NH_3 evolution mechanism, Montoya et al. [12] investigated the reaction between NO and char(N), and Zhang et al. [20] evaluated the reaction between O_2 and char(N). Mechanisms proposed by calculated results showed good agreement with experimental phenomenon.

2.2. Chemical method

DFT provides an efficient way to quantitatively determine the electronic properties, geometries and reaction energies. This promising method depends on its ability to consider electron exchange and correlation with acceptable computational cost. The interaction between NO and char(N) is therefore investigated by DFT at the level of B3LYP/6-31 G(d). The B3LYP, together with 6–31 G(d) basis set, can provide excellent performance between calculated results and experimental observations in the simulation of carbonaceous surface [12,13,15,19,20]. B3LYP stands for Beck's three-parameter functional with a Lee–Yang–Parr gradient-corrected correlation functional. In order to enable polarization of the carbon orbitals, a set of 'd' functions is inserted in the basis set. The spin contamination observed in calculations with unrestricted wavefunctions is minor as compared to other methods [21]. Also, it has acceptable small effects on the thermodynamics of carbonaceous surface. The thermodynamics considered here is determined by the following steps: (a) geometry optimization for location of the reactants, intermediates, transition states and products; (b) frequency analyses for all the species to guarantee that correct number of imaginary frequencies is acquired, namely, zero for equilibrium structures and only one for transition states; (c) the vibrations associated with the transition states are monitored, if there exists any ambiguity about the vibrational modes, the minimum energy paths by IRC (intrinsic reaction coordinate)

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