Application of density functional theory to the nitric oxide heterogeneous reduction mechanism in the presence of hydroxyl and carbonyl groups

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ABSTRACT

Comprehensive theoretical calculations are carried out to investigate the nitric oxide (NO) heterogeneous reduction mechanism in the presence of hydroxyl (—OH) and carbonyl (>C═O) groups. Energetics (activation energy and thermochemistry data) and kinetics (thermal rate constant) for the proposed pathways are provided by density functional theory (DFT) and conventional transition state theory (TST), respectively. The role played by —OH and >C═O has been clarified. In the presence of —OH, four stepwise reactions with the highest energy barrier of 251.7 kJ/mol are found to produce new active sites. Subsequently, a number of elementary reactions with energy barrier below 116.1 kJ/mol take place to reduce NO. The role of > C═O is to yield NCO intermediate. The formation of NCO is highly exothermic with 709.4 kJ/mol, which contributes to the elimination of carbon dioxide (CO_2) and nitrogen (N_2). The discovered mechanism is consistent with previous experimental observation that NO heterogeneous reduction is enhanced due to the presence of oxygen.

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1. Introduction

There is noticeable interest in the reaction of nitric oxide (NO) with char and/or char bound nitrogen (char(N)) in reference to their potential behavior in reducing NO emissions from combustion systems especially the fluidized bed [1–13]. Extensive experimental [14–21] efforts have been made and it seems to be clear that three reactions (R1, R2 and R3) take place to reduce NO. C_{ac} stands for the free active sites.

$$2C_{ac} + NO \rightarrow C(N) + C(O) \qquad (R1)$$

$$C_{ac} + 2NO \rightarrow N_2 + CO_2 \qquad (R2)$$

$$C(N) + NO \rightarrow N_2 + C(O) \; or \; CO \qquad (R3)$$

Quantum chemistry calculations have recently been carried out by different research teams to study the reactions R1, R2 and R3. A pioneering knowledge was proposed by the work of Kyotani and Tomita [22], in which chemisorption of NO on char active sites (R1) and potential NO reduction mechanisms (R2) were taken into account. Zhu and Lu [23] provided new insights into NO-char

reaction and found that the kinetic behaviors were largely influenced by the surface nitrogen groups. Montoya et al. [24] carried out density functional theory (DFT) calculations to investigate the pathways for the reaction R3. It was proposed that the main channels for N_2 formation were taken by direct nitrogen-nitrogen interaction between char surface nitrogen and NO molecule. Starting from a char with four active sites and two NO molecules, systematical routes on reaction R2 (including transition states and intermediates) were suggested by Kraft et al. [25,26]. Two char models, along with dimerization of NO, are selected as original reactants by Arenillas et al. [27]. They studied the NO-char reduction mechanisms and chiefly delved into the effect of temperature. To sum up, based on detailed quantum chemistry calculations, accurate information that cannot be detected experimentally is provided.

However, NO heterogeneous reduction takes place in the presence of oxygen, which largely increases the reduction rate [28]. The presence of oxygen, such as carbonyl, hydroxyl, semiquinone and epoxy, has been recognized to be helpful for NO reduction from creating new active sites. Gupta and Fan [29] carried out fixed bed experiments to investigate the NO heterogeneous reduction in the presence of oxygen and found that oxygen created active sites. These in turn reduce NO to N_2 because of the beneficial chemisorption. Experimental results of Suzuki et al. [30] informed that oxygen residing on char surface significantly promoted the char reactivity. The combination of temperature programmed desorption (TPD)

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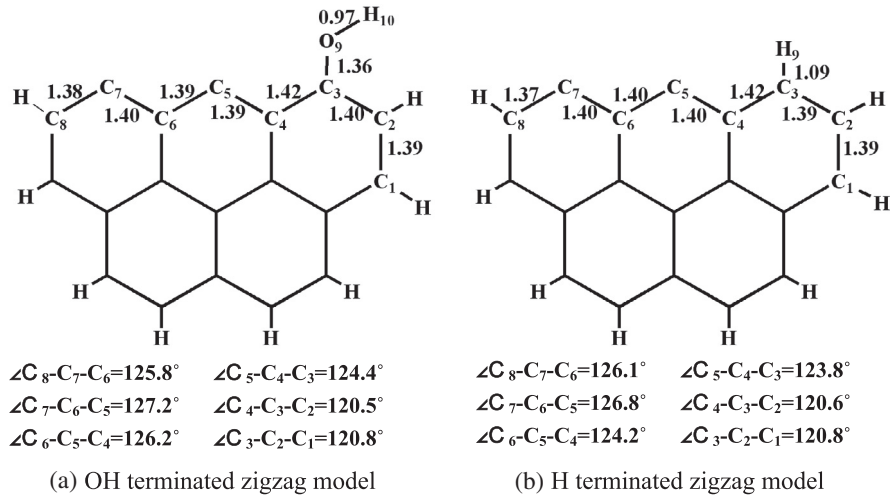 *E-mail address:* xiuminjiang@sjtu.edu.cn (X. Jiang).

Fig. 1. Modified zigzag configurations used to simulate the NO heterogeneous reduction. Bond lengths are given in angstroms.
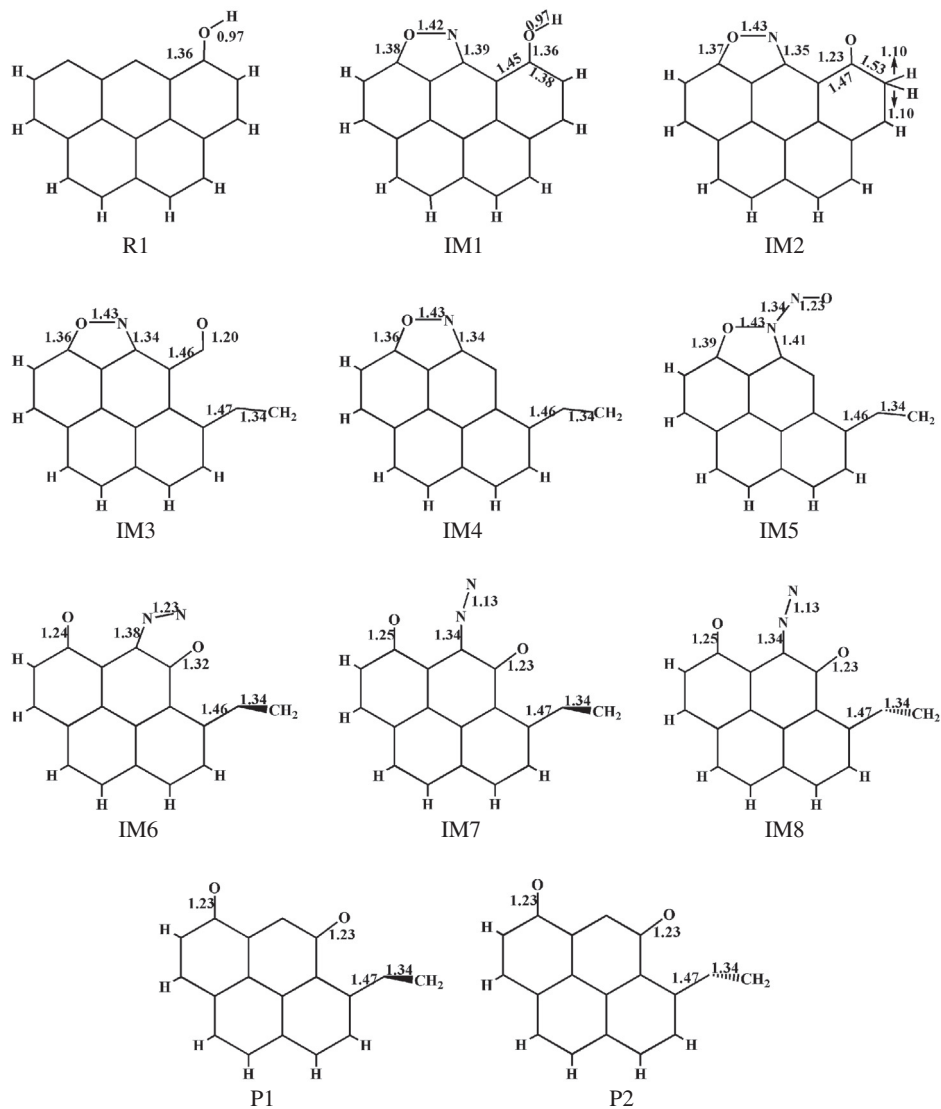

Fig. 2. Optimized equilibrium structures involved in NO heterogeneous reduction with the presence of —OH. Bond lengths are given in angstroms.