The effect of calcium on nitric oxide heterogeneous adsorption on carbon: A first-principles study

Lei Liu [a], Jing Jin [a, *], Yuyu Lin [a], Fengxiao Hou [a], Shengjuan Li [b]

[a] School of Energy and Power Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China
[b] School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China

A B S T R A C T

The catalytic effect of calcium on nitric oxide (NO) heterogeneous adsorption with carbon was investigated through a first-principles calculation on pristine and calcium decorated graphene models, respectively. Compared with the classical polycyclic carbon model, new graphene computational models with periodical boundary conditions are better in simulating the characteristics of solid phase carbon. The adsorption of a single NO molecule on the pristine graphene surface is physical, but it is dramatically enhanced by the calcium as the absolute value of binding energy E_b increases from 19.34 kJ/mol to 206.02 kJ/mol. In order to investigate the influence of the concentration of NO molecules, the adsorption of clusters containing two and three molecules were examined. On pristine graphene surface, E_b increases with the number of NO molecules, however, on calcium decorated one, E_b demonstrates reverse tendency. This significant difference derives from the distinct mechanisms: van der Waals interaction among the NO molecules plays a crucial role in the adsorption of NO on the pure graphene surface, while the electron transfer from the 4s- and 3d orbitals of calcium to the 2p orbitals of nitrogen and oxygen atoms contributes to the catalytic effect of calcium.

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1. Introduction

NO_x generated from burning fossil fuels are primary air pollutants and could result in acid rains and photo-chemical smog. Reburning is one of popular de-NO_x combustion technologies in coal burning because of its low investment and high reduction efficiency, which can reach as highly as 85% [1–3]. In biomass reburning, heterogeneous reduction of nitric oxide (NO) by char contributes approximately 68–79% of total NO reduction [4,5]. Recently, novel ambient temperature carbon-based solid adsorbents and low temperature SCR (selective catalytic reduction) using carbon-based catalysts have attracted more attention and are regarded as promising de-NO_x technologies [6–8]. For example, activated carbon modified by Cu [9,10] and Fe [11] have been successfully developed for NO_x removal.

With advanced experimental techniques, such as XPS (X-ray photoelectron spectroscopy) and the isotopic labeling method, the reaction mechanism and surface chemistry of NO reduction on carbon surface have been studied extensively [12–14]. The catalytic

effect of metal on the NO reduction by char has been investigated [15–19]. Illan-Gomez et al. [20,21] discovered that Ca promotes the NO reduction reaction through oxygen transition from CaO to the carbon surface.

Apart from numerous experiments, there have been many theoretical reports on NO reduction by carbonaceous materials. In his pioneering work, Kyotani et al. [22] investigated the chemisorption of NO and N_2O on zigzag or armchair edge of polycyclic carbon models using Density Functional Theory (DFT) computation. Oyarzun et al. [23] studied the reaction of NO with zigzag graphene based on polycyclic carbon models. Zhang et al. [24,25] employed similar models to explain the influence of char-bound nitrogen on NO reduction by char. Other theoretical studies on the formation and desorption of N_2 and CO in NO reaction with carbon continued using classical polycyclic carbon models [26–28]. Few first-principles studies have been published on the catalytic effect of Ca on NO reduction reaction, except for Wen et al. [29] who found that the decrease in the activation energy of NO reduction reaction is due to the appearance of Ca atom. However, since the calculation model consists of only one carbon atom, it could not describe the characteristics of the solid phase char. When considering the catalytic effect of calcium, carbon is excluded from the calculation

* Corresponding author. Tel.: +86 21 5527 7768; fax: +86 21 5527 2089.
E-mail address: alicejin001@163.com (J. Jin).

model and the interaction between the carbon and the calcium is ignored. Excluding that Oyarzun et al. [23] studied the adsorption of NO dimer on graphene, most researchers have only considered one NO molecule in computation and thus, the effect of NO molecular concentration cannot be predicted. However, gas molecule concentration or coverage rate often plays a decisive role in gas–solid adsorption [30–32].

Based on previous studies a first-principles calculation was performed to study the first step of NO reaction with carbon, that is, the adsorption of NO onto carbon surface. Being different from the existing theoretical investigations, a novel graphene model with three-dimensional periodic boundary conditions was introduced to simulate carbon surface. Metal decoration on graphene surface was employed to reveal the catalytic effect of Ca and NO cluster adsorption behavior was also investigated to illustrate the influence of the NO concentration.

2. Computational details

2.1. Computational model

Various computation models have been adopted to simulate carbon surface in previous first-principles studies on NO reduction reaction. The most widely used model, polycyclic carbon model, was first introduced by Kyotani et al. [22], where armchair and zigzag carbon models containing 4- to 9-membered rings are employed. Sendt et al. [33–35] studied O_2 and O reaction with char surface using 6-membered rings and 9-membered rings. Zhang et al. [24,25] and Zhang et al. [26] employed 5-membered rings and 7-membered rings to handle char surface, respectively. To better simulate the char surface, bigger polycyclic carbon models have been proposed. Denis et al. [36] studied the interactions of B, Mg, and Ca with carbon surface using coronene and circumcoronene models. Oubal et al. [37] used $C_{51}H_{18}$ and $C_{79}H_{22}$ to simulate the soot emitted from airplanes and Roberts et al. [38] employed 3×3, 4×4 and 5×5 carbon ring models to simulate the char surface on which the CO_2 gasification occurred. Garcia-Fernandez et al. [39] studied the adsorption between C_mH_n (m = 24, 54, 96, 150; n = 12, 18, 24, 30) and NO molecule. In summary, polycyclic carbon models are reasonable in simulating chemical reactions on the edge of carbon surface.

Another universal model simulating carbon surface is periodic boundary graphene model, which can be used to characterize solid carbon surface and always appears in the theoretical computation about H_2 storage in the carbonaceous material [40,41]. The graphene model with periodic boundary conditions has not been used to investigate NO reduction by carbon surface. According to molecular dynamic simulation [42,43], the surface of char and activated carbon can be simulated through huge polyaromatic hydrocarbon fragments, usually consisting of dozens or hundreds of carbon atoms, so merely considering the reaction of NO molecule on the edge of carbon surface is insufficient. In order to investigate the adsorption performance of carbon atoms at the center of the surface, the periodic one layer graphene surface model was adopted in this work.

Even though in coal char Ca exists in various forms, such as CaO, $CaCO_3$, $CaSO_4$, and carboxylates, and changes among these contents [44–47], a simplified computation model containing only atomic Ca was employed in this work to avoid huge computation expense. In fact, during the coal pyrolysis, the Ca containing substances might decompose and the resulting Ca atom could directly connect with the char matrix [48]. The effect of NO molecular concentration on NO reaction with carbon is studied by considering NO cluster (2 or 3 NO molecules) adsorption [49,50].

2.2. Computational method

All computations were carried out using the three-dimensional periodic boundary graphene model. A 3×3 one layer graphene model containing 25 carbon atoms (7.380 Å × 7.380 Å) was used to describe pure carbon surface. The vacuum slice was 22 Å so eliminated the interaction between two adjacent graphene layers. The geometry optimization and properties calculation were all spin unrestricted and adopted the GGA (General Gradient Approximation) method with PBE (Perdew-Burke-Ernzerhof) functional [51] for exchange and correlation interactions. TS (Tkatchenko Scheffler) method [52], a DFT-D (density functional theory with dispersion) correlation method, was adopted in this paper to consider the effect of the van der Waals interaction which is critical in physisorption. After energy convergence test, the Monkhorst-Park k-point scheme [53] for both geometry optimization and partial density of states (PDOS) calculation were $8 \times 8 \times 1$. Core electrons were treated using DFT Semi-core Psuedopots (DSPP) method [54]. The convergence criteria for geometry optimization were: 1.0×10^{-5} Ha for energy, 0.002 Ha/Å for max force, and 0.005 Å for max displacement, respectively. (Ha, or Hatree, is a unit of the energy in first-principles computation and 1 Hatree equals 2625 kJ/mol) The convergence criteria for SCF (self-consistent field method) was 1.0×10^{-6} and the smearing was 0.005 Ha. All geometry optimizations and PDOS calculations in this paper were carried out on $DMol^3$ module [55,56].

3. Results and discussion

3.1. Pristine graphene and Ca atom decorated graphene

Pristine carbon surface is investigated using a 3×3 one layer carbon atom model with periodic boundary conditions. After geometry optimization, the model keeps flat and the length of C=C conjugate bonds is 1.420 Å. As shown in Fig. 1(a). This optimized model is utilized as pristine graphene surface for calculating the adsorption of NO and calcium.

Then, Ca atom is decorated on the pristine graphene surface, with a coverage rate of Ca atom being 13.3 wt%. This coverage rate is higher than the content of calcium in real char [19], but a highly dispersed Ca computation model needs bigger graphene models and increases the computational cost.

To evaluate adsorption intensity, binding energy E_b of Ca atom on graphene surface is defined as follows.

$$E_b = E_{Ca+Graphene} - E_{Graphene} - E_{Ca} \tag{1}$$

Here, $E_{Ca + Graphene}$, $E_{Graphene}$, and E_{Ca} are the energy of Ca-decorated graphene surface, pristine graphene, and Ca atom, respectively. If the calculated E_b is negative, the adsorption reaction is exothermal; if E_b is positive, the adsorption reaction is endothermic.

After examining the adsorption on hollow, top, and bridge sites on pristine graphene surface, it is found that the adsorption on the hollow site, with the binding energy of −96.67 kJ/mol, is the most favorable, consistent with the results of Beheshti et al. [57] and Ataca et al. [58]. Since Ca atom locating on top or bridge site are unstable, only Ca atom adsorption on the hollow site is used for the calculation of NO adsorption on the Ca-decorated graphene surface.

As shown in Fig. 1(b), Ca atom locates 2.964 Å above the graphene surface. The Mulliken charge population analysis shows that the population of positively charged Ca atom is +0.490 e and those of six carbon atoms close to Ca atom are about −0.080 e, which is about 10 times higher than that of other carbon atoms. It implies