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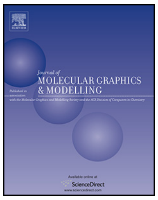

A comparative theoretical study of CO oxidation reaction by O_2 molecule over Al- or Si-decorated graphene oxide

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ABSTRACT

Using density functional theory calculations, the probable CO oxidation reaction mechanisms are investigated over Al- or Si-decorated graphene oxide (GO). The equilibrium geometry and electronic structure of these metal decorated-GOs along with the O_2/CO adsorption configurations are studied in detail. The relatively large adsorption energies reveal that both Al and Si atoms can disperse on GO quite stably without clustering problem. Hence, both Al- and Si-decorated GOs are stable enough to be utilized in catalytic oxidation of CO by molecular O_2. The two possible reaction pathways proposed for the oxidation of CO with O_2 molecule are as follows: $O_2 + CO \rightarrow CO_2 + O_{ads}$ and $CO + O_{ads} \rightarrow CO_2$. The estimated energy barriers of the first oxidation reaction on Si-decorated GOs, following the Eley–Rideal (ER) reaction, are lower than that on Al-decorated ones. This is most likely due to the larger atomic charge on the Si atom than the Al one, which tends to stabilize the corresponding transition state structure. The results of this study can be useful for better understanding the chemical properties of Al- and Si-decorated GOs, and are valuable for the development of an automobile catalytic converter in order to remove the toxic CO molecule.

1. Introduction

Graphene is a novel form of carbon in which a single layer of carbon atoms are formed in a honeycomb lattice and shows outstanding electronic, optical and mechanical properties [1–4]. Therefore, owing to these characteristics and also its large specific surface area, graphene has attracted considerable interest over the last few years [5–7]. For instance, it can be used for the adsorption and removal of toxic gases such as NO_2, NH_3 and CO [8–10]. However, the lack of chemically active defect sites on pristine graphene leads to the weak interaction between gas molecules and the surface, which hinders the wide use of this material in practical sensing applications. Graphene oxide (GO) is a derivative of graphene sheet that has emerged recently as a novel class of carbon-based nanomaterials [11–13]. Generally, there are many studies about the preparation and the electrochemical applications of GO [14,15]. Numerous studies have also indicated that the GO can be served as a high performance molecular sensor, such as for nitrogen oxides (NO_x, $x = 1 - 3$) [16,17], NH_3 [18] and SO_2 [19]. Hou and coworkers [20] studied the catalytic oxidation of NO into NO_2 over GO surface at room temperature, theoretically. They found that the hydroxyl groups of the surface can enhance the adsorption of NO molecule. This was due to the weak covalent interaction between the nitrogen atom of the NO molecule and the carbon atom of the surface. Then, the NO molecule can be oxidized by epoxy groups with rather low barrier energy, which helps to explain the low temperature catalytic oxidation of GO. Moreover, it is found that different metal-decorated GO such as Ti [21] Li, Al [22] or Pd [17] can significantly increase the adsorption of gas molecules and their catalytic decompositions. For example, Lv et al. [23] theoretically investigated the adsorption and decomposition of N_2O molecule on Al-decorated GO at the presence of electric field, recently. They found that the physically adsorbed N_2O molecule could be decomposed into N_2 and O species which are bonded on the GO surface exothermally.

Carbon monoxide (CO) is one of the main contributors to atmospheric pollution, chiefly originated from the car exhaust and inadequate combustion of fuel cells as well as industrial emissions. So, the catalytic oxidation of this gas molecule to CO_2 has been a considerable topic due to its importance for the environment [24–26]. In the past few decades, numerous studies have been devoted to the CO oxidation reaction by O_2 molecule as the most common oxidizing agent [27,28]. Of particular interest is the oxidation of CO by O_2 over noble metal surfaces such as Pd [26,29,30] Rh, Au, Ag [31,32] or Pt [33,34]. According to the recent studies [7,35–38], it has been found that the oxidation of CO into CO_2 can be better performed over carbon-based materials such as metal-doped

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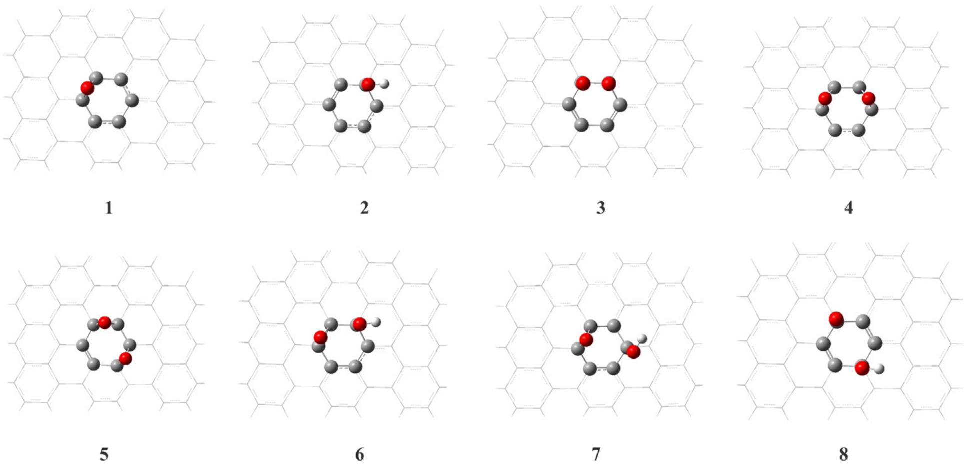

Fig. 1. Optimized structures of different GO models.

graphene sheet. For instance, Song et al., [39] studied the CO oxidation reaction mechanisms over Cu-doped graphene via a two-step mechanism of (a) $CO + O_2 \rightarrow OOCO \rightarrow CO_2 + O$ and (b) $CO + O \rightarrow CO_2$. They revealed that the high activity of Cu-embedded graphene may be attributed to the electronic resonance among electronic states of CO, O_2, and the Cu atom.

To the best of our knowledge, no study has been reported on the mechanisms of the CO oxidation reaction over Al- or Si-decorated GOs. Therefore, it motivated us to find out whether these surfaces can act as a promising candidate for the oxidation of CO to CO_2 molecule. So, in this study, we focus on the geometry and catalytic properties of Al- or Si-decorated GOs as an oxidizing catalyst toward the oxidation of CO by molecular O_2. Also, the probable oxidation mechanisms of CO to CO_2 molecule are studied using density functional theory (DFT) calculations. The results of this study can be useful for better understanding the chemical properties of metal decorated-GOs and are worthy for the development of an automobile catalytic converter in order to remove the toxic CO gas.

2. Computational details

All geometry optimizations and frequency calculations were performed at the M06–2X/6–31G* level of theory, using the Gaussian 09 suite of programs [40]. The M06-2X is a global–hybrid meta–GGA density functional which has been exclusively designed to treat medium-range correlation energy, non-covalent interactions, and reaction barriers [41–44]. The Al- and Si-decorated GOs were adopted as the substrate to investigate the oxidation of CO molecule. The simulation cell consists of a 4 × 4 graphene supercell with a vacuum width of 20 Å above the graphene layer to minimize the interlayer interaction. The adsorption energies (E_{ads}) of the O_2 and CO molecules adsorbed over Al- or Si-decorated GOs were calculated as the following equation:

$$E_{ads(A)} = E_{A-M} - E_M - E_A \qquad (1)$$

where E_{A-M}, E_M and E_A are the total energies of the adsorbate–substrate (A–M) system, the substrate (M) and adsorbate (A), respectively. The triplet spin state of molecular oxygen was used for all adsorbed configurations.

It should be noted that to check the thermodynamic feasibility of the adsorption process, the change of enthalpy (ΔH) and free-energy (ΔG) were obtained at 298.14 K and 1 atmosphere from the frequency calculations according to the following equations:

$$\Delta H = \sum_{\text{products}} (\varepsilon_0 + H_{corr}) - \sum_{\text{reactants}} (\varepsilon_0 + H_{corr}) \qquad (2)$$

Table 1
Calculated adsorption energies (kcal/mol) of a single Al or Si atom over different GO models.

GO model	Al	Si
1	−86.6	−173.5
2	−72.3	−139.0
3	−91.5	−148.0
4	−148.3	−214.9
5	−136.0	−190.1
6	−96.0	−197.6
7	−182.3	−207.2
8	−124.0	−197.6

$$\Delta G = \sum_{\text{products}} (\varepsilon_0 + G_{corr}) - \sum_{\text{reactants}} (\varepsilon_0 + G_{corr}) \qquad (3)$$

where ε_0 is the total electronic energy, H_{corr} and G_{corr} are thermal corrections that should be added to ε_0 to obtain the enthalpy and Gibbs free energy, respectively.

3. Results and discussion

3.1. Al-/Si-decorated GOs

According to the most well-known GO model suggested by Lerf and Klinowski [45,46], GO consists of a hexagonal carbon network having both sp^2 and sp^3 hybridized carbon atoms with epoxy and hydroxyl groups on its "basal" plane, whereas the edges are mostly functionalized by carboxyl and carbonyl groups. Hence, in the current study, only hydroxyl and epoxy groups are regarded for anchoring metal atoms. We investigate many different GO models, including one epoxy (**1**), one hydroxyl (**2**), double epoxies (**3**–**5**) and epoxy/hydroxyl groups (**6**–**8**). The relaxed structures of these GO models are depicted in Fig. 1. In order to find the most stable adsorption configurations, a single Al or Si atom was initially placed at different position above the epoxy or hydroxyl groups. Fig. S1 of Supporting information shows the optimized metal-decorated GOs. The corresponding adsorption energies are listed in Table 1.

Considering the adsorption energies of the resulting complexes, some interesting results can be extracted. From Table 1, one can see that for a given GO model, the Si atom always has a larger (more negative) adsorption energy than the Al atom. This can be attributed to the larger charge-transfer effects between the Si atom and epoxy or hydroxyl group of the surface (Fig. S1). Besides, the tendency of the Al or Si atom to bind over the epoxy group is larger than over the hydroxyl group. For example, the calculated adsorption energy for the Si atom over substrate **1** is −173.5 kcal/mol, which is