



CO oxidation on Ni doped and Ni-M (M = Ca, Sc, V, Cu) bimetal-doped graphene: A first-principles study

Peng-Fei Yuan*, Hui Liu, Qiang Sun, Yu Jia

International Joint Research Laboratory for Quantum Functional Materials of Henan Province, and School of Physics and Engineering, Zhengzhou University, Henan 450001, China

ARTICLE INFO

Keywords:

CO oxidation
Bimetal-dope
Single atom catalyst
First principles calculation

ABSTRACT

CO oxidation over atomic Ni doped and Ni-M (M = Ca, Sc, V, Cu) bimetal-doped graphene (Ni@graphene and Ni-M@graphene, respectively) were investigated by first-principles method. For atomic Ni@graphene, O₂ is adsorbed first and then reacts with CO (gas phase) directly to release the first CO₂. The barrier is about 0.432 eV. The remaining O atom would react with CO (gas phase) directly and release the second CO₂ with a barrier of 0.368 eV. If another metal atom was doped at the opposite site of Ni atom, the reaction path does not change. However, the calculated reaction barriers are all higher for the first CO₂ release but lower for the second. The CO and O₂ co-adsorption structures are all energetically unfavorable. The reason is that the LUMO orbital of the O₂ pre-adsorbed structure is mainly located on the two O atoms, and thus will have a maximum overlap with the CO HOMO orbital. D-band model can explain the different adsorption energies for CO and O₂.

1. Introduction

Carbon monoxide (CO) is one of the major contributors to air pollution due to inadequately combusted fuels, either from vehicles or industrial emissions. One of the effective ways of mitigating the issue is to transform CO to CO₂ via $\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2$ at ambient conditions. The main challenge is the high energy barrier that prohibits this reaction from occurring at low temperatures. This is also the technological reason why catalytic oxidation of CO is a prototype reaction in heterogeneous catalysis [1]. The scientific reason is that CO oxidation is relatively simple and can be used as a model system to address general questions in heterogeneous catalysis [2]. Traditionally, these catalysts are always based on noble metals, such as Au, Pt, Pd and Rh [3–6], which are limited in reserves and are expensive. The development of low cost alternatives becomes an important issue for this purpose.

One of the ways of reducing cost is to reduce the size of the catalyst, down to nanoparticles, atomic clusters and even a single atom, i.e. a single-atom catalyst (SAC) [7]. The first practical fabrication of isolated single Pt atoms anchored onto iron oxide (FeO_x) nanocrystallites, Pt₁/FeO_x, was obtained in 2011 [8]. This catalyst exhibits very high activity and stability for both CO oxidation and preferential oxidation of CO in H₂. With this seminal work, some other SACs were reported, for example, Pt₁/θ-Al₂O₃ [9], Ir₁/FeO_x [10,11], and Pt₁/graphene [12]. These all exhibit significantly improved catalytic activity over their traditional counterparts. Actually, the catalytic activity of single atoms

has been studied theoretically for several years. As early as 2009, the Au-doped graphene is shown to have effective catalytic activity for CO oxidation based on the first-principles calculations [13]. The results show that the first step of CO oxidation is most likely to proceed with the Langmuir-Hinshelwood (LH) reaction, and the barrier is 0.31 eV; the second step of the oxidation would be the Eley-Rideal (ER) reaction with a much smaller barrier of 0.18 eV. In the following years, other metals, such as Cu, Ag, Pt and Fe, were investigated. The support is also extended from graphene, *h*-BN, to silicone, etc. [14–25]. More recently, a new mechanism for CO oxidation was proposed theoretically, involving an Au-doped *h*-BN monolayer catalyst [26]. A tri-molecular ER reaction is obtained, where an O₂ molecule is activated by two pre-adsorbed CO molecules. The formed OCOAuOCO intermediate dissociates into two CO₂ molecules simultaneously with a barrier of 0.47 eV. Hence, even for the simple CO oxidation, there are still much to be understood before a SAC is widely used.

Another method of reducing catalyst cost is to use non-noble metals or nonmetals [27–30]. Nickel is not only an inexpensive replacement for noble metals but also enables new reaction and catalytic systems [31]. Ni-based catalysts have been widely used in many reactions such as the reforming of alcohols, hydrogenation reactions and also oxidation processes [32]. In 2010, low-temperature CO oxidation on Ni (111) was investigated theoretically and experimentally [33,34], where it is noted that the chemisorbed CO and O on Ni(111) do not react to form CO₂ between 100 K and room temperature. However, Ni

* Corresponding author.

E-mail address: pfyuan@zzu.edu.cn (P.-F. Yuan).

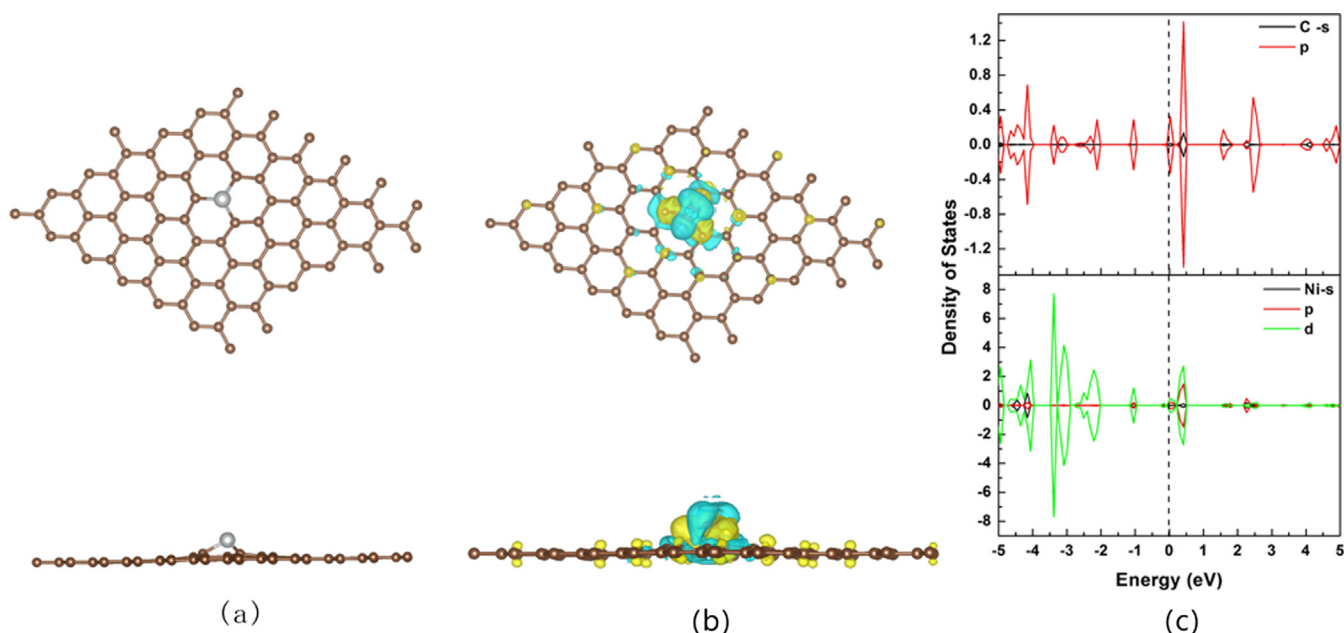


Fig. 1. (a) The optimized structure of Ni doped graphene. Up: top view; down: side view. (b) The calculated charge difference distribution of Ni doped graphene. Up: top view; down: side view. (c) The calculated density of states projected on Ni atom and the C atom.

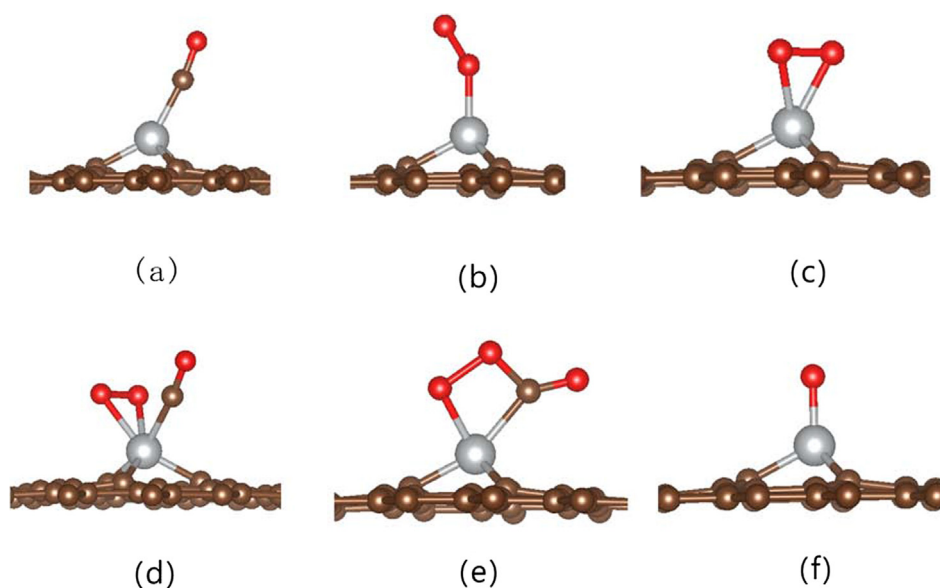


Fig. 2. Optimized structures for (a) CO adsorption; (b) O_2 adsorption (O2-1); (c) O_2 adsorption (O2-2); (d) CO and O_2 co-adsorption; (e) meta-stable phase; (f) O atom adsorption.

(1 1 1) is oxidized when O_2 is adsorbed at a low temperature close to 100 K and that loosely bound oxygen reacts with CO to form CO_2 . The calculated barrier changes from 0.5 to 1.43 eV at different levels of O coverage. If the oxidation occurs on NiO(1 1 1) between the adsorbed CO and the lattice apex O, the barrier is at least 0.9 eV. If O_2 adsorbs on an NiO(1 1 1) surface prior to CO adsorption, the barrier can be reduced to 0.47 eV and this is the possible mechanism for the experimental observation of low temperature CO oxidation [33,34].

Most recently, CO oxidation on Ni-doped graphene (Ni atom at a single vacancy site in graphene) was investigated by first-principle calculations. The results show that CO oxidation will happen *via* LH mechanism with energy barrier 0.63 eV [35]. Because graphene is a single atomic layer material, it is possible to dope another metal atom in the opposite site at the same vacancy site, and then affect the catalytic properties of Ni atom. Previous theoretical studies have shown that

both-side doping can change the hydrogen storage properties of g-CN sheet [36]. Recently development in roll-to-roll production of graphene [37] also indicated that both side doping in single layer graphene is possible. So in this work, Ni and Ni-M bimetal-doped graphene (on the single vacancy site) were investigated as a non-noble single atom catalyst for CO oxidation. Previous work has shown that the d-electrons have great effect to catalytic property. So, Ca, Sc, V and Cu were selected as doping atoms, respectively representing elements with none, a few, half-filled and fully-filled d-electrons. Such bimetal-doped system is able to tune the catalytic property of Ni effectively. The electronic structures, including density of states, HOMO/LUMO orbital and d-band center, are used to investigate the mechanistic insights at different conditions.

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