



CO oxidation catalyzed by silicon carbide (SiC) monolayer: A theoretical study



Nan Wang^a, Yu Tian^a, Jingxiang Zhao^{a,*}, Peng Jin^{b,**}

^a Chemistry and Chemical Engineering College, Harbin Normal University, Harbin, 150025, PR China

^b Key Laboratory of Micro- and Nano-scale Boron Nitride Materials of Hebei Province, School of Materials Science and Engineering, Hebei University of Technology, Tianjian, 300130, PR China

ARTICLE INFO

Article history:

Received 14 December 2015

Received in revised form 24 April 2016

Accepted 25 April 2016

Available online 26 April 2016

Keywords:

CO oxidation

SiC nanosheet

Density functional theory

Metal-free catalysts

ABSTRACT

Developing metal-free catalysts for CO oxidation has been a key scientific issue in solving the growing environmental problems caused by CO emission. In this work, the potential of the silicon carbide (SiC) monolayer as a metal-free catalyst for CO oxidation was systematically explored by means of density functional theory (DFT) computations. Our results revealed that CO oxidation reaction can easily proceed on SiC nanosheet, and a three-step mechanism was proposed: (1) the coadsorption of CO and O₂ molecules, followed by (2) the formation of the first CO₂ molecule, and (3) the recovery of catalyst by a second CO molecule. The last step is the rate-determining one of the whole catalytic reaction with the highest barrier of 0.65 eV. Remarkably, larger curvature is found to have a negative effect on the catalytic performance of SiC nanosheet for CO oxidation. Therefore, our results suggested that flat SiC monolayer is a promising metal-free catalyst for CO oxidation.

© 2016 Published by Elsevier Inc.

1. Introduction

CO oxidation, although seemingly a simple chemical reaction, plays an important role in solving the growing environmental problems caused by hazardous CO gas. Noble transition metals (TM) and their alloys or oxides are commonly used catalysts for CO oxidation [1–16]. For example, Liu et al. demonstrated that nanosized gold clusters can effectively facilitate the CO oxidation [17]. Su et al. disclosed that CO oxidation can easily take place on the Ag(111) and Au(111) surfaces [18]. However, the shortcomings such as high cost, scarce sources, and high reaction temperature for efficient operation of these noble metals seriously prohibit their practical applications. Therefore, searching for metal-free catalysts with low cost and high efficiency for CO oxidation at mild conditions is highly desirable.

Recently, graphene-based catalysts have been widely employed for CO oxidation and are considered to be the most promising alternatives of the traditional noble metal-based catalysts due to their unique properties such as high surface-to-volume ratio, good thermal and mechanical

stability as well as high conductivity [19–21]. In particular, both experimental and theoretical studies have shown that graphene is an ideal support for TM nanoparticles and it endows the anchored TM nanoparticles with high stability and tunable electronic properties, thus improving their catalytic performance for CO oxidation. For instance, Yoo et al. [22] suggested experimentally that small Pt clusters supported by graphene exhibit high catalytic activity for CO oxidation. Theoretically, Au–[23–28], Fe–[29,30], Cu–[31] and Pt–embedded graphenes [32] are all proposed can effectively facilitate CO oxidation.

On the other hand, the layered silicon carbide (SiC) monolayer has recently attracted considerable attention due to its outstanding properties such as high mechanical strength, saturated carrier mobility, high thermal stability and thermal conductivity [33–35]. Compared with graphene, SiC monolayer has a much higher chemical reactivity towards foreign adsorbates [36–38], rendering it potential metal-free catalysts. Indeed, Zhang et al. [39] reported that SiC nanosheet exhibited superior catalytic performance for the oxygen reduction reaction occurred at cathodes in fuel cells. Feng et al. [40] demonstrated that SiC nanosheet can serve as the metal-free catalysts for NO reduction.

Since SiC nanosheet possesses unusual chemical activity, an interesting question then arises naturally: can SiC monolayer be utilized as a potential catalyst for CO oxidation? To address this issue, in this work, we examined the adsorption of various intermediates of CO oxidation on SiC monolayer by means of

* Corresponding author.

** Corresponding author.

E-mail addresses: xjz_hmily@163.com (J. Zhao), china.peng.jin@gmail.com (P. Jin).

comprehensive density functional theory (DFT) computations. Our results demonstrated that the CO oxidation can easily occur on SiC nanosheet due to a small energy barrier of 0.65 eV, and the detailed mechanism was proposed: (1) CO and O₂ molecules are firstly co-adsorbed on the SiC monolayer, followed by (2) the first CO₂ molecule is released, leaving an atomic O on the catalyst surface, and (3) the SiC monolayer is recovered for the next catalytic cycle by introducing a second CO molecule, which step is identified to be the rate-determining one. Therefore, our computations suggested that SiC monolayer is a promising metal-free catalyst for CO oxidation. Although O₂ adsorption on SiC nanosheet is involved both in this work and in Zhang et al.'s computations [39], the research targets are completely different: we focus mainly on CO oxidation, while oxygen reduction was studied in their report [39].

2. Computational models and methods

All the calculations were carried out by using the spin-polarized density functional theory (DFT) methods implemented in the DMol³ code [41,42]. The generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) [43] exchange–correlation functional, which is the most popular method in materials and surface science, was used to describe the exchange and correlation effects. The double numerical plus polarization (DNP) basis set was employed. The Grimme approach [44] was adopted to describe the dispersion corrections between various species involved in CO oxidation and the SiC monolayer. Differences between DFT exchange–correlation functionals in the description of short to medium-range dispersion interaction were taken into account by a suitable modification of the correction potential through the parameters S_6 , where S_6 was set as 1 [44]. Self-consistent field (SCF) calculations were performed with a convergence criterion of 10^{−6} au on the total energy. To ensure high-quality results, the real-space global orbital cutoff radius was set as high as 4.60 Å.

We employed a hexagonal 5 × 5 supercell, which includes 25 Si and 25C atoms. The *x* and *y* directions were set to be parallel to the plane of the SiC nanosheet, while the *z* direction was perpendicular to the plane with a sufficient length of 20 Å to avoid the interaction between the SiC monolayer and its periodic images. The Brillouin zone integration was performed with 5 × 5 × 1 *k* points. To study the minimum-energy pathway (MEP) for CO oxidation, linear synchronous transit (LST/QST) and nudged elastic band (NEB) tools in DMol³ code were used [45,46]. The vibrational frequencies for each obtained structure along the MEP [28–30] were calculated at the same level to ensure that every transition state has a single imaginary frequency and each local minimum has no imaginary frequency.

The adsorption energy of various CO oxidation species, including O₂, CO, O, and CO₂, on SiC monolayer was defined as: $E_{\text{ads}} = E_{\text{adsorbate/SiC}} - (E_{\text{SiC}} + E_{\text{adsorbate}})$, where $E_{\text{adsorbate/SiC}}$, E_{SiC} , and $E_{\text{adsorbate}}$ represent the total energy of the adsorption systems, SiC monolayer, and the isolated adsorbate, respectively. According to the definition, a negative adsorption energy means an exothermic process.

3. Results and discussion

3.1. The adsorption of various species of CO oxidation on SiC nanosheet

Firstly, we studied the adsorption of various intermediates in CO oxidation on SiC monolayer. To obtain the most favorable adsorption configuration for each adsorbate, various adsorption sites in SiC monolayer were considered, including the top of C or Si atom, the bridge of Si–C bond, and the hexagonal Si₃C₃ ring.

Table 1

Adsorption energy E_{ads} of various adsorbates on the SiC sheet, the charge transfer (Q)^a, and the shortest distance (d) between the adsorbate and SiC sheet.

Adsorbate	E_{ads} (eV)	Q (e)	d (Å)
O ₂	−0.54	−0.28	1.51
CO	−0.15	−0.00	3.67
CO + O ₂	−2.71	−0.30	1.55
CO ₂	−0.14	−0.28	1.60
O	−1.01	−0.24	1.53

^a The charge transfer is calculated through Hirshfeld population analysis.

Our DFT results revealed that a O₂ molecule favors to attach to the SiC monolayer by (2 + 2) cycloaddition, i.e., the O–O bond approaches to one Si–C bond to form a four-membered ring (Fig. 1a). The lengths of the newly formed Si–O and C–O bonds are 1.74 and 1.51 Å, respectively. According to the Hirshfeld population analysis [47], about 0.28 e charge are transferred from SiC nanosheet to O₂ molecule (Table 1). The transferred charge occupies the half-filled O₂ – 2π* orbitals and makes the O₂ activated with elongated O–O bond (from 1.23 Å to 1.51 Å). The corresponding adsorption energy is −0.54 eV, suggesting that the O₂ molecule is chemisorbed on the SiC nanosheet. Notably, the computed structural parameters and energetics of O₂ molecule on SiC nanosheet are in good agreement with Zhang et al.' study [39], indicating that the employed methods and models in this work are accurate enough to describe the behavior of adsorbate on SiC nanosheet. Recent experiments revealed that the thickness of synthesized 2D layered SiC nanosheet is between 0.5 and 1.5 nm [48], and the sheet is energetically more favorable than cubic SiC sheets when its layer number (*N*) is less than 4 [39]. Thus, we also computed the adsorption of O₂ molecule on SiC nanosheets with different layer numbers (*N* = 2 and 3). The adsorption energies of O₂ on layered SiC nanosheets are −0.47 and −0.51 eV for *N* = 2 and 3, respectively, and the values are very close to that of the SiC monolayer (−0.54 eV). Thus, the chemical reactivity of layered SiC nanosheets is nearly independent on their layer numbers.

To get a deeper understanding on the mechanism of O₂ activation, we computed the partial density of states for O₂ adsorbed SiC monolayer. As shown in Fig. 2, the O₂–2p orbitals have an obvious hybridization with the C–2p states and Si–3p states at −8.22–0.11 eV and 2.50–3.80 eV due to the charge transfer from SiC monolayer to O₂ molecule. Overall, the above results reveal that O₂ molecule can be effectively activated on the SiC monolayer, which phenomenon would facilitate its subsequent reduction reactions.

Previous theoretical study showed that the chemisorbed O₂ molecule on Pt surfaces immediately undergoes the O–O bond dissociation to form two separated O atoms [49,50]. Then, will the O–O bond of the adsorbed O₂ on SiC sheet also dissociate? To address this question, we examined the dissociation pathway of the adsorbed O₂ molecule. Two possible final states are considered, namely the two separated O atoms reside on either the same (Int.1) or different hexagonal Si₃C₃–ring (Int.2). The energy barriers of the two reactions (i.e., O₂* → Int.1 and O₂* → Int.2) are calculated to be 0.32 and 0.35 eV, respectively (Figure S1 in Supporting Information), which, together with the large exothermicity of about −1.60 eV, suggest that the chemisorbed O₂ molecule is ready to dissociate on SiC monolayer.

For the CO adsorption, the end-on configuration is energetically the most favorable with an adsorption energy of −0.15 eV, which is much smaller than that of O₂ molecule (−0.54 eV). Thus, when the CO/O₂ mixture is injected as the reaction gas, the SiC nanosheet may be firstly covered by O₂ molecule. The CO molecule is nearly parallel to the sheet surface with a mutual distance of 3.67 Å (Fig. 1b). The small adsorption energy and long distance indicate a weak van der Waals interaction between the CO molecule and SiC monolayer, which is further confirmed by the small charge transfer of

Download English Version:

<https://daneshyari.com/en/article/443275>

Download Persian Version:

<https://daneshyari.com/article/443275>

[Daneshyari.com](https://daneshyari.com)