CO catalytic oxidation on iron-embedded monolayer MoS$_2$

Dongwei Ma$^a$,*, Yanan Tang$^b$, Gui Yang$^a$, Jun Zeng$^a$, Chaozheng He$^c$, Zhansheng Lu$^d$

$^a$ School of Physics, Anyang Normal University, Anyang, Henan 455000, China
$^b$ Department of Physics and Electronic Science, Zhengzhou Normal University, Zhengzhou, Henan 450044, China
$^c$ Physics and Electronic Engineering College, Nanyang Normal University, Nanyang 473061, China
$^d$ College of Physics and Electronic Engineering, Henan Normal University, Xinxiang, Henan 453007, China

**A R T I C L E   I N F O**

Article history:
Received 15 October 2014
Received in revised form 3 December 2014
Accepted 3 December 2014
Available online 10 December 2014

Keywords:
First-principles calculations
CO oxidation
Fe-embedded monolayer MoS$_2$

**A B S T R A C T**

Based on first-principles calculations, the CO catalytic oxidation on the Fe-embedded monolayer MoS$_2$ (Fe-MoS$_2$) was investigated. It is found that Fe atom can be strongly constrained at the S vacancy of monolayer MoS$_2$ with a high diffusion barrier. The CO oxidation reaction proceeds via a two-step mechanism with the highest energy barrier of 0.51 eV, which is started by the Langmuir–Hinshelwood reaction and ended by the Eley–Rideal reaction. The high catalytic activity of the Fe–MoS$_2$ system may be attributed to the charge transfer and the orbital hybridization between the adsorbates and the Fe atom. This study proposes that embedding transition-metals is a promising way for making the basal plane of monolayer MoS$_2$ catalytically active.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

As one of the most promising two-dimensional (2D) materials, graphene, one-atom-thick layers of $sp^2$-bonded carbon, has shown exceptional physical, chemical, optical, and mechanical properties [1,2]. Recently, other 2D materials have attracted increasing attention [3]. In particular, great interest has been focused on the monolayer transition-metal dichalcogenides [4,5], such as monolayer molybdenum disulfide (MoS$_2$), which is proved to be a versatile material for a wide variety of applications owing to its unique physical, optical, and electrical properties [6–9]. Researchers have realized the growth of high-quality MoS$_2$ sheets [10–13] and have proposed and investigated possible applications, such as low-power transistors [14,15], phototransistors [16,17], sensors [17–20], hydrogen evolution reactions [21,22], and lithium ion batteries [5,23–25].

A monolayer MoS$_2$ sheet consists of three atomic layers: a Mo layer sandwiched between two S layers. Since there is no dangling bond at the basal plane terminated by S atoms, the planes of MoS$_2$ are chemically inert, like graphene, and these S atoms are not expected to be chemical activity. The catalytically active sites of MoS$_2$ are considered to be their edges, containing undercoordinated S or Mo atoms, which are expected to interact strongly with adsorbates [21,26]. The MoS$_2$-based materials are used in petrochemical hydrodesulfurization and hydrodenitrogenation processes [27]. With the aid of alkali, MoS$_2$ is also used for converting synthesis gases (syngas) to alcohol [28]. The particular optical direct band gap of the monolayer MoS$_2$ also makes it a potential candidate for an efficient and viable material for electro- and photovoltaic catalytic hydrogen evolution [22,29,30].

Creation of S vacancy could provide a facile route for making the basal plane of the MoS$_2$ layer catalytically active. More importantly, if creation of S vacancy can be performed in a controlled way, it would be possible to produce a large number of active sites on the basal plane, far more than the number provided by the edges [26]. The experiments have shown that controlled creation of S vacancy on MoS$_2$ is possible by using low-energy argon sputtering [31] or electron irradiation [32,33]. Furthermore, very recently, the potential of S vacancies serving as catalytically active sites has been explored theoretically by using density functional theory (DFT) calculations [26,34]. Ciraci et al. suggested that the MoS$_2$ triple vacancies are suitable medium for the dissociation of H$_2$O [34] and Rahman et al. [26] suggested that the S vacancies can serve as the active sites for alcohol synthesis from syngas.

Furthermore, embedding impurity species by filling the S vacancies into the monolayer MoS$_2$ could be also a promising route for making the basal plane of monolayer MoS$_2$ catalytically active. There have been numerous experimental and theoretical studies on the doping of traditional oxide catalysts, such as CeO$_2$ and TiO$_2$ [35]. Transition-metal-embedded graphene and monolayer hexagonal boron nitride (BN) have also been theoretically predicted to be good candidates for highly efficient catalysts with low cost [36–48]. Recently, we theoretically investigated the CO oxidation by Si [43] and several transition-metals (such as Pt, Al, Zn, Co, and Ni) [39,44]
embedded graphene, which shows that these embedded external elements can convert the inert graphene supports to highly active catalysts. Furthermore, it has been experimentally [49,50] and theoretically [51,52] shown that metal subnanoclusters on graphene have very high catalytic activity.

Inspired by the above findings, this work has investigated the potential of embedding transition-metals into monolayer MoS₂ as a route for making its basal plane catalytically active, by which we may significantly extend the application of this distinctive 2D material. We have chosen Fe as the dopant, since it has several unique characteristics: inexpensive, environmentally benign, readily available, and rich in the earth. The combination of Fe and MoS₂ may provide us with an earth-abundant and low-cost alternative to the precious metals catalysts [22]. The CO oxidation reaction has been investigated to examine the catalytic performance of the Fe-embedded monolayer MoS₂ (Fe-MoS₂), as Co is one of the poisonous and harmful gases in the air and its oxidation is often regarded as an important prototypical reaction for heterogeneous catalytic process [53]. Our calculated results show that Fe-MoS₂ can exhibit the catalytic behavior similar to those of the transition-metal embedded graphene or BN.

2. Computational details

All the calculations were performed with the projected augmented wave (PAW) formalism of DFT, as implemented in the Vienna Ab-initio Simulation Package (VASP) [54–56]. The generalized gradient approximation method with Perdew–Burke–Ernzerhof (PBE) for the exchange-correlation energy was used [57]. The cutoff energy for the plane-wave basis set was taken as 450 eV. The Brillouin zone integrations were performed by using Monkhorst-Pack grid of 3 × 3 × 1 [58] and a Gaussian smearing of 0.1 eV. The convergence of the total energy was considered to be achieved until two iterated steps with energy difference less than 10⁻⁵ eV. Structure optimizations were performed until the Hellmann–Feynman force on each atom was less than 0.02 eV/Å. During the optimization, all the internal coordinates were allowed to relax with a fixed lattice constant. The climbing image nudged elastic band method [59] was used to find the minimum-energy path (MEP) for the reactions. Four to eight images were inserted in between the initial state (IS) and final state (FS), and the spring force between adjacent images was 5.0 eV/Å. The geometric optimization and the search for the transition state (TS) are tested by means of frequency calculations.

The lattice parameter of monolayer MoS₂ was optimized to be 3.19 Å, which is in good agreement with the experimental (3.20 Å [60]) and theoretical values (3.18 Å [26]; 3.20 Å [61]). The bond length (S–S, 3.13 Å; S–Mo, 2.42 Å), bond angle (S–Mo–S, 80.65°), and band gap (1.50 eV) of the monolayer MoS₂ are in good agreement with the results in Ref. [61]. To simulate the Fe-MoS₂ system, a 4 × 4 supercell has been introduced, where a Fe atom is substituted for one S atom for per cell. The distance between the monolayer MoS₂ sheet and its neighboring image is about 15 Å, which is sufficient large to avoid the interactions between them.

3. Results and discussion

3.1. Structures and stability of Fe-MoS₂

Firstly, we present the results on the geometric and electronic structures as well as the magnetic properties of Fe-MoS₂. As shown in Fig. 1, the embedded Fe atom located on the S vacancy forms three bonds with the neighboring three Mo atoms. The bond length between the Fe and three Mo atoms are about 2.6 Å and the Fe atom slightly protrudes above the S plane. Meanwhile, there is about 0.37 eV transfer from the embedded Fe to monolayer MoS₂ sheet according to the Bader charge analysis [62], which is mainly accepted by the neighboring Mo atoms. The direction of electron transfer is in agreement with the values of Pauling electronegativity of two elements (Fe 1.83 vs. Mo 2.16) [63]. The electron transfer can also be verified by the charge density difference (CDD) of Fe-MoS₂. As shown in Fig. 1(a), the yellow and cyan regions represent the areas of electron accumulation and depletion, respectively. Obviously, different electron affinities of Fe and Mo determine the electron distribution around the dopants, and the transferred electron from the Fe is mainly located between the Fe–Mo bonds. The magnetic moment of the whole system is 2.29 μB and is mainly located on the Fe and its neighboring Mo atoms, which are antiferromagnetic coupling, as shown in Fig. 1(b).

To gain more insight into the electronic structure of Fe-MoS₂, the spin-polarized local densities of states (LDOS) projected on the 3d and 4s orbitals of the Fe as well as the 4d and 5s orbitals of its neighboring Mo are plotted, as shown in Fig. 1(c). When Fe atoms are located on the S vacancies, the Fe 3d and 4s orbitals are significantly broadened compared with the sharp peak of the isolated atoms, which shows the strong interaction between the Fe and its neighboring Mo atoms. Due to the charge transfer, the spin-up and spin-down DOS of the 4d orbitals of the Mo atoms are slightly asymmetric. Importantly, there are localized Fe 3d orbitals near the Fermi level, which is important to activate the adsorbed reactants as discussed later.

To see whether the S vacancy can strongly constrain the embedded Fe atom, we also calculated the adsorption of Fe on the various sites near the S vacancy. Here, the Fe adsorption energy is defined as: \( E_{\text{ads}}(\text{Fe/MoS}_2) = E(\text{MoS}_2) + E(\text{Fe}) - E(\text{MoS}_2) \), where \( E(\text{MoS}_2) \), \( E(\text{Fe}) \), and \( E_{\text{ads}}(\text{Fe/MoS}_2) \) are the total energies of the monolayer MoS₂ with a S vacancy, the free Fe atom, and the defective MoS₂ with a adsorbed Fe atom, respectively. After optimization, we have obtained two stable configurations, for which the Fe atom sits on the top of the Mo atom (the FS in Fig. 2(a)) or the center of the S–Mo–S hexagonal ring (the FS in Fig. 2(b)) of the defective monolayer MoS₂. The adsorption energy for the Fe-MoS₂ system is 4.00 eV, again indicating that Fe atom can interact strongly with its neighboring undercoordinated Mo atoms. The energy barriers for the diffusion of the trapped Fe to the top site of the Mo atom (Fig. 2(a)) and the hollow site of the S–Mo–S hexagonal ring (Fig. 2(b)) are 2.00 and 1.89 eV, respectively. The high adsorption energy for the Fe-MoS₂ system and the large energy barrier for the diffusion of the trapped Fe in the S vacancy to the nearby sites ensure the absence of the clustering problem of the embedded Fe atoms and a stable catalyst at room temperature.

3.2. Adsorption of gas molecules on Fe-MoS₂

Before investigating the CO oxidation reaction, we computed the adsorption of CO, O₂, and CO₂ on the Fe-MoS₂. Various adsorption configurations have been considered in order to find the most stable one for each adsorbate. The adsorption energy of the adsorbates is defined as: \( E_{\text{ads}}(\text{ads}) = E(\text{Fe-MoS}_2) + E(\text{ads}) - E(\text{ads/Fe-MoS}_2) \), where \( E(\text{Fe-MoS}_2) \), \( E(\text{ads}) \), and \( E(\text{ads/Fe-MoS}_2) \) are the total energies of the Fe-MoS₂ system, the free adsorbates in the gas phase, and the Fe-MoS₂ with the adsorbates, respectively.

It was found that CO and O₂ can only be physisorbed on the monolayer MoS₂ plane without any defects, while they interact strongly with Fe-MoS₂. The side views of the obtained most stable configurations for CO and O₂ adsorption are shown in Fig. 3(a) and (c), respectively. The calculated adsorption energies for CO and O₂ are 1.40 and 1.84 eV (Table 1), respectively, indicating that both of them can be readily adsorbed on Fe-MoS₂ at room temperature. Both CO and O₂ are about 1.8 Å away from the Fe atom. The bond length of the adsorbed CO (1.16 Å) is slightly changed compared with the free
one (1.14 Å), while that of the adsorbed O₂ is elongated to 1.38 Å from 1.23 Å in the gas phase, due to the significant charge transfer (0.76e) from Fe-MoS₂ to the 2π* orbital of O₂. The CDD for the adsorbed CO (Fig. 3(b)) shows that the transferred electrons from the substrate not only accumulates on the C and O ions, but also mainly on the C–Fe bond. Contrary to CO₂, as shown in Fig. 3(d), the transferred electrons from the substrate mainly accumulate around the O₂. For CO₂, the most stable adsorption site locates...
Fig. 4. Atomic configurations of the IS, TS, MS, and FS along the MEP for the CO oxidation on Fe-MoS₂ via the LH mechanism (CO + O₂ → OOCO → CO₂ + O). Both top (upper panel) and side (lower panel) views are displayed, as well as the energy change (in eV) between neighboring states.

on the Fe atom with the adsorption energy of 0.34 eV, suggesting that a CO₂ molecule is weakly adsorbed on Fe-MoS₂ and can easily desorb from the reaction site at room temperature. As expected, the atomic O strongly binds to the Fe atom with $E_{\text{ad}}$(O) of 4.85 eV, close to those of metal-embedded graphene systems [36,37]. As for the magnetic properties, the embedded Fe and its neighboring Mo atoms are still antiferromagnetic coupling for the systems with the adsorb O₂ or CO. The magnetic moment (2.00 $\mu_B$) for the Fe-MoS₂ with the adsorbed CO or O₂ is slightly reduced compared with that of the bare sheet (2.29 $\mu_B$), due to both the charge transfer and the strong interaction between the adsorbates and Fe-MoS₂. For the case of the O₂ adsorption, the magnetic moment of the embedded Fe atom is reduced by about 0.63 $\mu_B$ and that of the adsorbed O₂ is reduced to 0.23 $\mu_B$ (2 $\mu_B$ for the free O₂ molecule), which is well consistent with the significant charge transfer (0.76e) and strong interaction between O₂ and the substrate. For the case of the CO adsorption, due to the charge transfer, the magnetic moment of the Fe atom is reduced by 0.25 $\mu_B$ and the adsorbed CO also carries a small spin magnetic moment of 0.11 $\mu_B$. The properties presented above suggest that Fe-MoS₂ is a promising CO oxidation catalyst with high efficiency, which will be discussed in the following part.

Besides the monolayer MoS₂, the few-layer stacked MoS₂ are frequently observed in the experiments [24]. To check the thickness effect, we also investigated the adsorption of CO, O₂, O, and CO₂ on the Fe-embedded monolayer MoS₂ (Fe-MoS₂), for which the van der Waals density functional (vdW-DF) [64,65] was used in order to treat the long-range dispersion between the layers. The A–A’ stacking configuration of the Fe-MoS₂ is adopted, which was predicted to be the most stable in the previous calculations [66,67]. For this conformation, one type of atom is on top of the other type. The calculated binding energy and interlayer distances for the bilayer MoS₂ are 37.2 meV/atom and 6.16 Å, respectively, in good agreement with the previous results [66,67].

The calculated adsorption properties are listed in Table 1. From the table, we can see that the nearest distances and the electron transfers between the various adsorbates and the substrates are nearly same for the Fe-MoS₂ and Fe-2MoS₂. However, the adsorption energies for the Fe-2MoS₂ are always slightly larger than those for the Fe-MoS₂, which is probably due to the different calculation methods used. The calculations for the adsorption on the Fe-MoS₂ were performed by using the conventional PBE functional, while those for the adsorption on the Fe-2MoS₂ were performed by using the vdW-DF. In fact, if the structure optimizations are performed by using the vdW-DF for the systems involved in the adsorption on the Fe-2MoS₂ and then the adsorption energies are calculated by using the PBE functional, the results are almost same as those for the Fe-MoS₂, as shown in Table 1. These discussions should be applicable to the few-layer MoS₂ with more layers, due to the weak interlayer interaction. Therefore, the adsorption properties of the main adsorbates and the main conclusions of our paper should be robust with respect to the number of the layers of the few-layer MoS₂.

### Table 1

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>$E_{\text{ad}}$(eV)</th>
<th>$d$(Å)</th>
<th>$Q$(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>1.40 (1.56, 1.44)</td>
<td>1.86 (1.87)</td>
<td>0.29 (0.27)</td>
</tr>
<tr>
<td>O₂</td>
<td>1.84 (2.03, 1.85)</td>
<td>1.80 (1.80)</td>
<td>0.76 (0.76)</td>
</tr>
<tr>
<td>O</td>
<td>4.85 (5.13, 4.87)</td>
<td>1.60 (1.59)</td>
<td>0.78 (0.70)</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.34 (0.55, 0.35)</td>
<td>2.16 (2.13)</td>
<td>0.00 (0.01)</td>
</tr>
</tbody>
</table>

3.3. CO oxidation on Fe-MoS₂

Generally, there are two well-established mechanisms for the reaction of CO and O₂, namely the Langmuir–Hinshelwood (LH) and Eley–Rideal (ER) mechanisms [36–38]. For the LH mechanism, the gas-phase CO molecules directly react with the preadsorbed O₂ molecules, producing a carbonate-like CO₃ complex as intermediate state (MS). The LH mechanism involves the coadsorption of CO and O₂ molecules before reaction, the formation of a peroxo-type OOCO complex MS and the desorption of the produced CO₂ molecule. In the present study, we find that the dissociative adsorption of O₂ on Fe-MoS₂ system is energetically unfavorable, which is similar to the cases of CO oxidation on graphene doped with Au [36], Cu [38], and several non-noble metal [44]. Besides, the carbonate-like CO₃ MS formed during the ER reaction on Fe-MoS₂ is energetically more stable by 0.54 eV than the final product (the pysisorbed CO₂ and chemisorbed atomic O), indicating that the oxidation process by the ER mechanism involves the endothermic reaction and is thermodynamically unfavorable. Thus the ER mechanism is hardly possible in our case as a starting point. As previous studies [38,44], the complete CO oxidation reactions on Fe-MoS₂ may include a two-step process: the LH reaction as a starting step (CO + O₂ → OOCO → CO₂ + O) and followed by the ER
reaction (CO + O → CO₂). To search for the MEP for CO oxidation, the obtained most stable coadsorption configuration has been selected as the IS, where CO and O₂ are tilted and parallel to the Fe-MoS₂ sheet, respectively. The FS consists of a physisorbed CO₂ and a chemisorbed atomic O on Fe-MoS₂.

The local configurations of each state along the MEP for the LH reaction described above are displayed in Fig. 4 and the corresponding energies are schematically plotted in Fig. 5 with respect to the reference energy, which is the sum of the total energies of the Fe-MoS₂ and individual free CO and O₂ molecules. In addition, the structural parameters for each state along the MEP are displayed in Table 2(a). Once CO and O₂ are coadsorbed on Fe-MoS₂, the distance between the adsorbed CO and O₂ is about 2.65 Å, and both Fe–CO and Fe–O₂ distances are about 2.0 Å. The bond length of the adsorbed O₂ is elongated to 1.35 Å, while that of the adsorbed CO is slightly changed. To proceed, the O₂ molecule turns around with one of the O atom (O1) approaching the C atom of CO, while the another O atom (O2) adsorbs on the Fe atom. Reaching TS, the O–O bond length of the adsorbed O₂ is elongated to 1.39 Å, while the distance between CO and O₂ is shortened to 1.78 Å. Passing over the TS with an energy barrier of 0.51 eV, a peroxo-type OOCO complex (MS) is formed over the Fe atom. The O–O bond length of the adsorbed O₂ is further elongated to 1.54 Å, while the distance between CO and O₂ is shortened to 1.33 Å. Passing over the MS without an energy barrier, a physisorbed CO₂ molecule is formed, leaving an atomic O adsorbed on the embedded Fe atom.

After the LH reaction, we further investigated the CO oxidation by the preadsorbed atomic O through ER mechanism, for which the local configurations for each state along the MEP are shown in Fig. 6 and the corresponding structural parameters are displayed in Table 2(b). The configuration with a CO molecule about 3 Å away from the preadsorbed O on the Fe atom is chosen as the IS. The FS is simply set to the configuration of CO₂ adsorption on Fe-MoS₂. When the CO molecule approaches the preadsorbed O, the TS with the C–O₂ distance of 1.88 Å is formed. It is found that the ER process has an energy barrier of 0.26 eV, which is much smaller than that of the first CO oxidation through the LH mechanism. The adsorption energy for the FS with respect to the free CO and Fe-MoS₂ is only 0.34 eV (Table 1), therefore CO₂ can be easily desorbed from Fe-MoS₂ due to the weak interaction.

To gain deep insight into the origin of high activity of Fe-MoS₂, we investigated the electronic structure of the coadsorption configuration, i.e. the IS of the LH reaction shown in Fig. 4. Fig. 7 illustrates the spin-polarized LDOS projected onto the C–O (left panel) and O₁–O₂ atoms (right panel), as well as the Fe 3d orbital, which are critical to understand the activation of the reactants. The spin-down component of the highest d orbital of the embedded Fe is partially occupied before CO and O₂ coadsorption. Upon the CO and O₂ coadsorption, this d orbital shifts upward with respect to the Fermi level and becomes completely empty, due to the charge transfer between the Fe and the adsorbates. Bader charge analysis [62] further shows that the CO and O₂ gain 0.14 and 0.65e, respectively, less than those of the adsorbed individual molecules (Table 1), and these electrons are mainly donated by the embedded Fe atom. As

---

**Table 2**

<table>
<thead>
<tr>
<th>State</th>
<th>IS</th>
<th>TS</th>
<th>MS</th>
<th>FS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d₁(C=O)</td>
<td>1.15</td>
<td>1.17</td>
<td>1.21</td>
<td>1.18</td>
</tr>
<tr>
<td>d₂(C=O)</td>
<td>1.96</td>
<td>2.04</td>
<td>2.08</td>
<td>4.45</td>
</tr>
<tr>
<td>d₁(O=O)</td>
<td>2.65</td>
<td>1.78</td>
<td>1.33</td>
<td>1.18</td>
</tr>
<tr>
<td>d₂(O=O)</td>
<td>1.35</td>
<td>1.39</td>
<td>1.54</td>
<td>3.28</td>
</tr>
<tr>
<td>Δ(Å)</td>
<td>1.97</td>
<td>1.90</td>
<td>1.82</td>
<td>1.60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(b)</th>
<th>IS</th>
<th>TS</th>
<th>FS</th>
</tr>
</thead>
<tbody>
<tr>
<td>d₁(C=O)</td>
<td>1.14</td>
<td>1.15</td>
<td>1.17</td>
</tr>
<tr>
<td>d₂(O=O)</td>
<td>3.08</td>
<td>1.88</td>
<td>1.18</td>
</tr>
<tr>
<td>d₀(O=O)</td>
<td>1.60</td>
<td>1.66</td>
<td>2.16</td>
</tr>
<tr>
<td>Δ(Å)</td>
<td>90.7</td>
<td>119.1</td>
<td>179.9</td>
</tr>
</tbody>
</table>

---

**Fig. 5.** Schematic energy profile corresponding to the states shown in Fig. 4. All energies are given with respect to the reference energy, i.e. the sum of total energies of the Fe-MoS₂ and individual free CO and O₂ molecules.

**Fig. 6.** Atomic configurations of the IS, TS, and FS along the MEP for the CO oxidation by the atomic O preadsorbed on Fe-MoS₂ via the ER mechanism (CO + O → CO₂). Both top (upper panel) and side (lower panel) views are displayed, as well as the energy change (in eV) between neighboring states.
shown in the lower panel of Fig. 7, the transferred electrons to the CO or O2 mainly occupy the 2π* orbitals, which are unoccupied for the free molecules in the gas phase. In addition, the interaction between the adsorbates and the Fe atoms results in the broadening of the orbitals of the adsorbates. For the CO molecule, the 2π* and 5δ orbitals are significantly broadened due to the strong hybridization with the Fe 3d orbital, while for the O2 molecule, it is the 2π* orbital that has been significantly broadened. The electron transfer between the adsorbates and Fe-MoS2 and the hybridization among the orbitals lead to the elongation of the C–O and O1–O2 bonds lengths from 1.14 and 1.23 Å in the gas phase to 1.15 and 1.35 Å (the IS in Fig. 4), respectively. These electronic structures characteristics enable the strong interaction between the coadsorbed molecules and Fe-MoS2 as well as the activation of the reactants, which facilitate the CO oxidation process. In addition, the magnetic moment of the coadsorption configuration is increased to 4.00 μB, which is mainly contributed by the Fe atom and the adsorbed O2 molecule.

Overall, the highest energy barrier for the CO oxidation on Fe-MoS2 along the whole MEP including the LH and ER reactions is only 0.51 eV, which is comparable to those of other metal-embedded 2D materials, such as the Fe–graphene (0.58 eV) [37], Cu–graphene (0.54 eV) [38], and Co–BN (0.52 eV) systems [46]. Such a low energy barrier allows the reaction to proceed rapidly at room temperature [36,68,69]. As discussed above, the high thermal stability of Fe-MoS2 system and its high catalytic activity toward the CO oxidation reaction at room temperature suggest that embedding transition-metals is a promising way for making the basal plane of monolayer MoS2 catalytically active.

4. Conclusions

In summary, we have investigated the electronic structure, structural stability, and catalytic activity of the Fe-MoS2 system. It is found that the S vacancy can strongly constrains the trapped Fe atom with a high diffusion barrier (≈2.0 eV), which ensures the high stability of Fe-MoS2 at room temperature. The CO oxidation most likely occurs with the LH reaction as the starting point with a low energy barrier of 0.51 eV, which is followed by the ER reaction with an energy barrier of 0.26 eV. The high catalytic activity of Fe-MoS2 may be attributed to the charge transfer and the orbital hybridization between the adsorbates and the embedded Fe atom, which leads to the strong interaction between them and the activation of the reactants. This study suggests that embedding transition-metals is a promising method for making the basal plane of monolayer MoS2 catalytically active, through which the application of monolayer MoS2 in catalysis may be significantly extended. In addition, the adsorption properties for CO, O2, O, and CO2 on the Fe-2MoS2 are essentially same as those for these adsorbates on the Fe-MoS2, which suggests that the main conclusion of this work should be robust with respect to the number of the layers of the few-layer MoS2.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 11347186, 11147006, 11174070, U1404216, and U1404109), the Science Fund of Educational Department of Henan Province of China (Grant No. 14A140015).

References


