Reaction mechanisms for reduction of CO₂ to CO on monolayer MoS₂

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ABSTRACT

Since the reduction of CO₂ to fuels by consuming over-generated electricity, which can establish artificial carbon cycle and energy storage at the same time, extensive studies have been devoted to developing suitable catalysts for CO₂ conversion in materials science. Recently, MoS₂, a typical member of transition metal dichalcogenides, has been widely investigated for its high activity and low energy cost to catalyze CO₂ reduction. In this work, we simulate the microscopic dynamic process of the CO₂ reduction process in the framework of density functional theory (DFT). Our results reveal that Mo exposed edges of MoS₂ are inclined to adsorb CO₂ molecule and tend to catalytically reduce CO₂ to CO. CO₂ molecule is activated by two neighboring Mo atoms and the C–O double bond reconstructs in the adsorption process. The first proton/electron (H⁺ + e⁻) reaction taking place at MoS₂ edges undergoes a different pathway from that on transition metal catalyst, contributing to the product selectivity towards CO. Finally, we demonstrate that desorption of CO from MoS₂ edges is in virtue of unique diffusion process for adsorbed CO atoms.

1. Introduction

Excessive consumption of fossil fuels disturbs carbon cycle on the surface of our earth, and leads to the worse greenhouse effect. Electro-reduction CO₂ to industrial raw materials or clean fuels can establish an artificial carbon cycle, and therefore contribute to the mitigation of global warming [1–3]. Moreover, the conversion of CO₂ reduction reaction (CO₂RR) is also an economical and practical approach to store over-generated nuclear electricity, photovoltaic electricity and so on. To achieve this appealing blueprint, the key issue is to develop suitable electro-catalyst with outstanding catalytic activity, superior reliability, high product selectivity, environmental benignity, and low cost. In the last several decades, a large number of catalysts have been experimentally evaluated for CO₂RR. Some metallic electrodes, including Ag [4,5], Cu [6,7], Zn [8] and Pd [9,10], have been verified to have acceptable performance on electro-catalytic CO₂RR. Among them, copper is one of the mostly studied electro-catalysts, which has shown unique performance for CO₂RR to hydrocarbon compound at reasonable faradic efficiency, but it still needs a relatively large overpotential of ~1.0 V [11]. Ag and Pd are noble metals that are not conducive to large-scale industrial application. Furthermore, the metallic electro-catalysts produce mixed products of H₂, C₁, C₂, and C₃ hydrocarbon species [12]. These disadvantages of metallic catalysts limit their widely practical applications.

Recently, nanostructured molybdenum disulfide (MoS₂), one of the most common transition metal dichalcogenides (TMDGs), has attracted much attentions for its layered crystal structure and distinctive catalytic features [13–22]. The most stable structure of monolayer MoS₂ is trigonal prismatic polytype, and the Mo layer is sandwiched by two S layers [23] in each S-Mo-S monolayer. As an efficient catalyst, MoS₂ is widely used for hydrogen evolution reaction (HER) [15,24] and oxygen reduction reaction (ORR) [25]. Owing to the low price and high catalytic activity, MoS₂ is regarded as a more promising catalyst than noble metal for water splitting.

Unlike those for water splitting, the researches for CO₂RR over MoS₂ are still in preliminary stage. Asadi et al. first reported their study on MoS₂ catalyzing CO₂RR in 2014 [15]. They found that Mo-exposed edges of MoS₂ exhibits prominent CO₂RR performance in ionic liquid. As-reported catalytic performance of MoS₂ has the following three significant features: the overpotential of CO₂RR is extremely low, about ~54 mV (low overpotential); CO is the only carbonate product of CO₂RR (high selectivity); the semiconducting nature of MoS₂ contributes to its photochemical performance (artificial photosynthesis) [14]. Although the related experimental studies are in rapid progress,
theoretical understanding of the unique features of MoS2 catalyzing CO2RR has been of inadequacy so far. The existing calculation results based on density functional theory (DFT) have shown some explanations for the catalytic activity of MoS2 [14,17]. The d-band center of exposed Mo atoms at the edges of MoS2 is much closer to the Fermi level than that of metallic catalysts, suggesting that Mo exposed edge sites of MoS2 have strong interactions with the adsorbed species. In the MoS2, catalytic reaction pathway CO2 → COOH* → CO* → CO, the free energies of CO* and COOH* are lower than that of CO2 and CO in the gas phase, owing to the strong binding interactions between MoS2 and adsorbed CO* and COOH*. Furthermore, it is illustrated from the bow-shaped free energy curve that the first two reaction steps are exergonic and kinetically favorable.

However, there still exist some unresolved doubts about microscopic catalytic reaction process. For example, how is CO2 molecule activated at the edge of MoS2, why does the electro-catalytic reduction of CO2 select the pathway CO2 → COOH* → CO, and how does adsorbed CO diffuse and desorb from the edges of MoS2. To address these unclear issues, we present our systematically theoretical study about reaction mechanisms for the reduction of CO2 to CO on monolayer MoS2. Our work includes the following three aspects: the activation process of CO2 molecule, selectivity-determining steps of CO2 reduction to CO and dynamic process of adsorbed CO*.

We employ the first principles studies in DFT framework [26,27]. Moreover, monolayer MoS2 is chosen as the calculated model mainly for the following considerations. First, monolayer MoS2 exhibits much better catalytic CO2RR performance than that of bulk MoS2. Second, the morphology of the active edges of MoS2 are monolayer-like, as shown in the scanning transmission electron microscopy (STEM) images [14], which indicates that the monolayer model of MoS2 can fully cover the nature of bulk MoS2. Finally, monolayer MoS2 is a promising photocatalyst candidate for its semiconducting nature with about 1.9 eV direct band gap.

2. Models and computational details

The DFT [28,29] calculations were carried out using the Vienna ab-initio simulation package (VASP, version 5.4.4) [30,31]. The PBE functional [32] was employed for electronic exchange and correlation. The plane wave pseudopotential with a kinetic cutoff energy of 450 eV and Gaussian smearing method with an electronic temperature of $k_B T = 0.05$ eV were used in all our DFT calculations. During the system relaxing process, the total electronic energies and the residual forces on the atoms were converged to $10^{-6}$ eV and 0.02 eV Å$^{-1}$ respectively.

In our calculations, monolayer MoS2 model was constructed by adding a 15 Å thick vacuum slab to the c-axis direction. Unit cell of monolayer MoS2 contained two S atoms and one Mo atom. Brillouin-zone integration was conducted using a $7 \times 7 \times 1$ Monkhorst-Pack grid [33]. The lattice parameters of monolayer MoS2 were obtained by geometry optimization calculations. Our calculations yield $a = b = 3.18$ Å, in reasonable agreement with the experimental values of 3.16 Å, and the included angle of vectors $a$ and $b$ is 120°. In c direction, the distance between two nearest S atoms is 3.11 Å, well consisting with the as-reported results [34]. The Mo exposed edges were obtained by cut along the b-axis, and another 10 Å thick vacuum slab was added to avoid inter-layer interactions. The constructed Mo exposed nanoribbons included $3 \times 4$ unit cells with 24 S atoms and 12 Mo atoms. The Brillouin-zone integration on MoS2 nanoribbons was performed using a $3 \times 1 \times 1$ Monkhorst-Pack grid. The bottom four layers of the nanoribbon were fixed while the top two layers and the associated adsorbed species were allowed to relax in the geometrical optimization.

The transition state (TS) was located using the Climbing Image Nudged Elastic Band (CINEB) method [35] and was verified by vibration analyses with only one imaginary frequency. The binding energy ($E_{\text{BS}}$) of the adsorbates is defined as:

$$E_{\text{BS}} = E_{\text{Isol}} - E_{\text{Isol}} - E_{\text{ads}}.$$  

where $E_{\text{Isol}}$, $E_{\text{Isol}}$, and $E_{\text{ads}}$ are the total energy terms of optimized adsorbate + substrate, clean substrate, and gas phase adsorbate, respectively, and they can be directly obtained from the DFT calculations. The free energies ($G$) of the CO2 reduction intermediates are calculated as $G = E_{\text{Isol}} + ZPE - TS$, where $E_{\text{Isol}}$ denotes the electronic energy, ZPE the zero point energy, $T$ the temperature (20 °C in all our calculations) and $S$ the vibrational entropy. The vibrational entropy is estimated according to the vibrational frequencies determined by using the harmonic normal mode approximation:

$$S = k_B \sum_i \left[ \frac{1}{2} \left( \nu_i (e^{\nu_i} - 1) - \ln(1 - e^{-\nu_i}) \right) \right],$$

where $k_B$ is the Boltzmann constant. For each vibrational mode $x_i = h\nu_i / (k_B T)$, $\nu_i$ denotes the normal mode frequency and $h$ the Planck’s constant. For the transition state, the mode of motion along the reaction coordinate is omitted, i.e., the imaginary part of frequency is not calculated. In our practical calculations, the change of free energy ($\Delta G$) relative to the gas phase CO2 and clean substrate are more illustrative.

3. Results and discussion

In the microscopic dynamic process of CO2 electro-catalytic reduction reaction, the adsorption of CO2 on the catalyst (i.e. CO2 → CO2*) is the first step, which has a significant impact on the catalytic activity for CO2RR. The hydrogenation steps determine the selectivity of reaction pathways. The diffusion and desorption of reduction products together with the hydrogenation steps determine the efficiency of CO2RR.

3.1. Activation of CO2

The results of geometrical optimization show that the most stable adsorption site is the bridge site of two nearest exposed Mo atoms. In addition, linear CO2 molecule transforms into bent CO2 after its adsorption at the edges (as shown in Fig. 1a and d), and the O-C-O angle of bent CO2 is about 134°. To understand the bending effect further, the frontier orbitals of CO2 molecule is calculated. The highest occupied molecular orbitals (LUMO) and lowest unoccupied molecular orbitals (HOMO) are two common kinds of frontier orbitals. The HOMO and LUMO of isolated CO2 and adsorbed CO2* are shown in Fig. 1. Two parallel p orbitals of O form the π bond for isolate CO2 (Fig. 1a and b), while the frontier orbitals of bent CO2 (Fig. 1c and d) are totally different from that of isolate CO2. This phenomenon is attributed to the factors in two aspects. On one hand, the π bond in CO2 strongly depends on the linear molecule structure and the recombinant of component p-orbitals as the bending structure breaks the geometrical symmetry of CO2 molecule. On the other hand, the lone pair p electrons of O and C together with d electron of Mo form the π-d hybridized orbitals.

The projected density of states (PDOS) of CO2* and exposed Mo atoms interacting with the adsorbed CO2 are obtained by decomposing the electron density and wave function into the atomic orbital contributions. The Mo exposed edges of MoS2 exhibit the hybridization of d-orbital (Mo atoms) and p-orbitals (C and O atoms of bent CO2*), as shown in Fig. 1e. In the energy range from ~5.0 to ~3.8 eV, there are two robust orbital resonance peaks in PDOS, i.e., d-orbital of Mo and p-orbital of O, indicating the strong bonding interactions between Mo and O. Comparatively, p-orbital of C resonates more with p-orbital of O than with d-orbital of Mo in the whole energy range, which means that the hybridization of orbitals from C and Mo atoms is relatively weaker. Our PDOS results suggest that the bonding interaction between edge Mo and O breaks the strong C–O bond of CO2 and activates the adsorbed bent CO2*.

It was reported by Yu’s group that the composite TiO2@MoS2 exhibited excellent performance on catalyzing CO2RR in a slightly alkaline solution [17]. Herein, we consider the situation that CO2RR takes place in alkaline solution. In such condition, there exist two competing
3.2. Selectivity determining steps of CO2 reduction to CO

The most distinct feature of electrocatalytic CO2RR over MoS2 is the product selectivity towards CO. Unlike the product over the metal catalysts, CO is the only carbonaceous product of CO2RR over this material according to the previous experimental works [15,17,36]. To understand the reaction mechanisms for the reduction of CO2RR over MoS2, it is necessary to concern two fundamental questions: Why the selective product is CO alone and how CO2 is reduced to CO. Fig. 2 shows the possible reaction pathways of CO2RR based on previous DFT calculations [14,26–39]. Reaction step I is the adsorption of CO2, during which the CO2 molecule is activated. Step II refers to the hydrogenation process of CO2. For the CO2RR on Cu(111) [37,39], the product of this step is COOH*, while for CO2RR over MoS2, it is complicated due to the reason that the reaction takes place in two neighboring sites. So, there are two possible reactions for step II (II1 and II2). Reaction II1 is CO2* → COOH*, which is the same as that on Cu surfaces. In reaction II2, CO2* first reacts with (H++e−), forming an unstable intermediate HO-CO*, and then the intermediate product decomposes into OH* and CO* spontaneously. The proposed reaction step III is the hydrogenation of COOH*, which will happen in two different directions (i.e., reaction III1 and III2). Reaction III1 gives the same product of CO* as reaction II2, and reaction step III2 produces hydrocarbon species H3C-OH. It can be seen that both the reaction paths of I → II1 → III1 → IV1 and I → II2 → IV1 can result in the reaction CO2 → CO. We need to figure out which reaction path is more possible in experiment.

Herein, the reaction dynamics of these two paths are obtained using the CI-NEB method coded in VASP [35] program. The reactions II1: CO2* + (H++e−) → COOH* and II2: CO2* + (H++e−) → CO* + OH* generate two different intermediates. The simulated reaction progresses are shown in Fig. 3, where the transition states of reactions II1, II2, and III1 are represented as TS-II1, TS-II2, and TS-III1, respectively. The activation energy of reaction II1 is 1.92 eV as shown in Fig. 3a, larger than that of reaction II2 (~1.01 eV). Moreover, the free energy of COOH* (reaction II1) is higher than that of CO* + OH* (reaction II2). Therefore, the first hydrogenation of CO2* preferably selects reaction II2 owing to the lower activation barrier and less energy cost. The reaction CO2* → CO* needs only one step through path II2 but at least two steps through path II1 → III1. The reaction III1 will bring an additional reaction barrier of about 0.40 eV (Fig. 3a).

Given the selectivity that CO is the only carbonaceous product in CO2RR over MoS2 from previous experimental results, we further studied the hydrogenation of intermediate COOH* and CO* to clarify the underlying mechanisms. Although formation of COOH* is proved to be unfavorable in CO2RR over MoS2 according to the results and analysis above, it is still necessary to carefully study the hydrogenation process of COOH* because it’s the key reaction step to understand the formation of CO and H2 at MoC2O3 on metallic catalysts, e.g. Cu. The hydrogenation of COOH* can go along two different reaction paths, III1: COOH* + (H++e−) → CO* + H2O and III2: COOH* + (H++e−) → CO* + HO*. The activation energy of reaction III2 is about 1.47 eV, much larger than that of reaction III1 (~0.40 eV). Moreover, the free energy of COH* + OH* is about 1.0 eV, higher than that of CO* + H2O* (as shown in Fig. 4a). Our results indicate that hydrocarbon (H3C-OH) is produced by hydrogenation of CO* instead of COOH*.
features of COOH* hydrogenation over MoS2 is consistent with that over Cu-like catalysts [6,37–40].

Next, we calculate reaction dynamics of CO* hydrogenation. The possible products of reaction CO* + (H+ + e−) are COH* and CHO*. Here we only consider the reaction CO* + (H+ + e−) → COH* for its lower energy barrier [38]. The reactants CO* and H* occupy two neighbor active sites, and H* needs to traverse over a long distance to form COH*. Thus CI-NEB method is used in a strategy of H shuttling through H2O proposed in Ref. [38]. The initial state, transition state and final state are illustrated in Fig. 4c. Our calculated activation energy of reaction IV2 is 2.1 eV, which is about treble as that of the reaction on Cu (111) surface. The differences of reaction dynamics on MoS2 edges and Cu surfaces come from their different adsorption properties. The adsorption energy of H on MoS2 (~1.06 eV) is larger than that on Cu (111) (~0.52 eV) [41], thus it needs much more energy to break Mo–H bond than Cu–H bond. Therefore, the formation of hydrocarbon species (HxCyOz) is blocked by the high activation energy in reaction IV2.

3.3. Dynamic processes of adsorbed CO

For TMDCs, the strong binding effects for TM-CO (bond energy range from 0.8 to 1.1 eV) significantly prevent the CO desorption. Therefore, Asadi et al. proposed that the over-saturated binding of CO on active sites could decrease the bond energy of TM-C to 0.3–0.5 eV [14] and maintain a high turnover rate. To understand the over-saturated binding process, we conduct our calculations on the dynamics of adsorbed CO on MoS2 here.

The dynamics processes of CO* include the following: (1) CO* + * → * + CO*; (2) CO* + CO* → COCO* + *. Process (1) means that adsorbed CO* diffuses from one active site to the neighbor active site, and process (2) means that two nearest adsorbed CO* diffuse to the same active site, which can lead to the desorption of CO. The active energies of diffusion processes (1) and (2) are 0.61 eV and 0.40 eV respectively as shown in Fig. 5, both of which are smaller than bonding energy of CO*. The diffusion processes (1) and (2) are more possible to take place than the desorption process of CO* → CO + *, while less possible than the desorption process of COCO* → CO* + CO. The free energy of COCO* is larger than that of CO* + CO*, indicating that the process (2) is endothermic. Our results of the diffusion processes further prove that the diffusion processes of adsorbed CO* play important role in the desorption of CO*.

4. Conclusion

In summary, we have simulated the microscopic dynamic process of the CO2 reduction process in the framework of density functional theory. The results reveal that Mo exposed edges of MoS2 are inclined to
adsorb CO2 atoms for preferentially catalytic reduce CO2 to CO. CO2 molecule is activated by two neighboring Mo atoms and the C–O bonds reconstruct in the adsorbing process. The first proton–electron (H+ + e−) reaction taking place at MoS2 edges undergoes a different pathway from that on transition metal catalyst, contributing to the product selectivity towards CO. Finally, we demonstrate that the desorption of CO from MoS2 edges is in virtue of unique diffusion processes of adsorbed CO atoms. Our study gives reasonable explanation for electro-catalytic CO2RR over MoS2, and the understanding of high efficient and unique selectivity will provide significant insights for the design of new CO2RR catalysts.

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References


Fig. 5. Free energy diagram for two different diffusion processes.


