Promotional Effect of Surface Hydroxyls on Electrochemical Reduction of CO₂ over SnO_x/Sn electrode

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ABSTRACT: Tin oxide (SnO_x) formation on tin-based electrode surfaces during CO_2 electrochemical reduction can have a significant impact on the activity and selectivity of the reaction. In the present study, density functional theory (DFT) calculations have been performed to understand the role of SnO_x in CO_2 reduction using a SnO monolayer on the Sn(112) surface as a model for SnO_x . Water molecules have been treated explicitly and considered actively participating in the reaction. The results showed that H_2O dissociates on the perfect SnO monolayer into two hydroxyl groups symmetrically on the surface. CO_2 energetically prefers to react with the hydroxyl, forming a bicarbonate ($\text{HCO}_3(\text{t})^*$) intermediate, which can then be reduced to either formate (HCOO^*) by hydrogenating the carbon atom or carboxyl (COOH^*) by protonating the oxygen atom. Both steps involve a simultaneous C-O bond breaking. Further reduction of HCOO^* species leads to the formation of formic acid in the acidic solution at $\text{pH} < 4$, while the COOH^* will decompose to CO and H_2O via protonation. Whereas the oxygen vacancy (V_O) in the oxide monolayer maybe formed by the reduction, it can be recovered by H_2O dissociation, resulting in two embedded hydroxyl groups. The results show that the hydroxylated surface with two symmetric hydroxyls is energetically more favorable for CO_2 reduction than the hydroxylated V_O surface with two embedded hydroxyls. The reduction potential for the former has a limiting-potential of -0.20 V (RHE), lower than that for the latter (-0.74 V (RHE)). Compared to the pure Sn electrode, the formation of SnO_x monolayer on the electrode under the operating conditions promotes CO_2 reduction more effectively by forming surface hydroxyls, thereby, providing a new channel via COOH^* to the CO formation, although formic acid is still the major reduction product.

KEYWORDS: DFT, electrochemical reduction, CO_2 , SnO_x , hydroxyl, bicarbonate.

1 Introduction

The reliance on fossil fuel of modern society has resulted in a global CO₂ level that is not sustainable. Therefore, developing a sustainable technology to reduce and convert CO₂ to value-added products, including CO, methanol and other products, has attracted great attention over the past few decades [1]. Among the methods for CO₂ reduction, electrochemical reduction has the unique advantages of operating at a relatively low temperature and interfacing easily with the electricity from a variety of renewable sources (e.g. solar or wind) [2, 3].

Electrochemical reduction of CO₂ can be realized on various electrode materials, especially the metal electrodes [3-6]. The major products for CO₂ reduction are carbon monoxide (CO) [7-12], methanol (CH₃OH) [13-16], formic acid (HCOOH) or formate (HCOO⁻) [17-24], and hydrocarbons, primarily methane (CH₄) and ethylene (CH₂CH₂) [25-31], depending on electrode materials and operating conditions. Among the metals, tin has been widely studied for CO₂ reduction. The tin electrode has a high overpotential for the hydrogen evolution reaction (HER), making it attractive for CO₂ reduction [32]. Formic acid, or formate in basic solutions, was reported as the dominant product with a wide range of Faradaic efficiencies [17, 19, 20, 33]. However, most metal electrodes, including tin, exhibit a high overpotential for CO₂ reduction. In addition, degradation and corrosion of metal electrodes make them easily deactivated [32, 34].

Electrochemical reduction of metal oxides to metal particles or oxidizing metal electrodes to a thin metal oxide film in a controllable fashion have been used to optimize the activity for CO₂ reduction [7, 34-38]. It is generally considered that the active site for CO₂ reduction on tin electrodes is the metallic tin surface. However, a native tin oxide film can be formed rapidly when the tin electrode is exposed to air [39]. Several groups investigated the electrochemical

reduction of CO_2 on electrodes based on tin oxides. Kanan's group compared electrochemical reduction of CO_2 on the clean tin surface and the composite SnO_x/Sn thin-film catalyst [40]. They showed that on the clean tin electrode only the hydrogen evolution reaction could be activated. On the other hand, formate and carbon monoxide were the main products on the SnO_x/Sn catalyst. These results indicated that tin oxide is responsible for CO_2 reduction on a tin-based electrode with highly enhanced activity. Baruch et al. studied the reduction of CO_2 on the tin electrodes with a mixed Sn/SnO_x thin film by using in situ attenuated total reflectance infrared (ATR-IR) spectroscopy [41]. They detected the surface-bound tin-carbonate species and considered it as the active intermediate for CO_2 reduction in aqueous solutions. They also suggested that SnO_2 should be first reduced to SnO before being active for CO_2 reduction. Lee et al. demonstrated that the HCO_3^- species was an important intermediate for HCOO^- formation [42], while another work suggested the oxide layer thickness on the tin electrode could influence the Faradaic efficiencies for HCOO^- and CO formation [18]. Even though tin oxides may be reduced partially during the electrochemical process, SnO_x still persist on the surface [17, 40, 43]. All those studies suggested that the tin oxide could exist on the tin electrode and resulted in the enhancement of the activity for electrochemical CO_2 reduction. However, how SnO_x affects the CO_2 electrochemical reduction activity is still unclear.

In this work, density functional theory (DFT) calculations were performed to gain an insight into the mechanism of electrochemical reduction of CO_2 on a monolayer SnO on $\text{Sn}(112)$. The model is based on our previous study of electrochemical reduction of CO_2 on $\text{Sn}(112)$ [44]. We examined the stability of possible intermediates formed along the pathways of CO_2 reduction and constructed free energy diagrams. Our results show that CO_2 can be reduced along different pathways. We found the hydroxyl groups formed on the oxide surface play an important role in

determining the activity and selectivity of the electrodes towards CO₂ reduction and the bicarbonate (HCO₃^{*}) species is the crucial intermediate.

2 Methods

All calculations were performed using the Vienna Ab Initio Simulation Program (VASP) package [45]. Projector-augmented wave (PAW) method with the Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional was used. The cutoff energy of the plane wave basis set is 400 eV.

Lattice parameters with $a = 5.92 \text{ \AA}$ and $c = 3.23 \text{ \AA}$ for bulk Sn, determined in our previous work [44], were used to construct the slabs for electrochemical studies. These parameters are in good agreement with the experimental lattice parameters of $a = 5.84 \text{ \AA}$ and $c = 3.18 \text{ \AA}$ [46]. The SnO monolayer slab was built on the basis of a four-layer Sn(112) slab with a (2×4) surface cell. Half of the Sn atoms in the top layer was replaced by the oxygen atoms. Slabs were separated by a 15 Å vacuum in the z-direction. The O atoms and the Sn atoms in the top three layers were allowed to relax to get the optimized SnO/Sn(112) structure. The SnO/Sn(112) surface and each adsorbate were optimized using 4×4×1 k-point grid and the convergence criteria for electronic self-consistence was set at 5×10^{-6} eV. The bottom layer was fixed in their positions of optimized surface slab, while the remaining layers and the adsorbates were allowed to relax. The configurations of SnO/Sn(112) surface structure after optimization are shown in **Fig. 1**. Clearly, the formation of the SnO monolayer makes the Sn(211) surface more corrugated. It has been reported that the stepped surface is more active for C-O bond activation and we anticipate the corrugated SnO monolayer benefits CO₂ adsorption and activation [47].

Fig. 1. The top view and side view of the optimized structure for SnO/Sn(112) surface model (shown in four unit cells. Gray= Sn, red= O.).

In this work, we again adopt the computational hydrogen electrode (CHE) method proposed by Nørskov and coworkers to calculate the free energies of adsorbates for the CO₂ reduction reaction [48]. Based on this method, the reference electrode is set to reversible hydrogen electrode (RHE), i.e. the chemical potential of one electron-proton pair equals half molecule of hydrogen gas at the standard pressure [$(\text{H}^+ + e^-) \rightleftharpoons 1/2\text{H}_2(\text{g})$]. The free energy of each intermediate in the reaction at potential U ($\neq 0$) should be shifted by eU , as shown below, where e is the elementary charge and U is the electrode potential.

$$\Delta G_n(U) = \Delta G_n(U = 0) + eU$$

Experimentally, the electrochemical CO₂ reduction reaction usually occurs in an aqueous solution as the medium provides the proton necessary for the hydrogenation reaction. In most theoretical studies, the solvent effect has not been considered [26, 30, 49]. Several recent studies included explicit water molecules to account for the solvation effect but the computation cost is

high [50, 51]. Herein, we employed the implicit solvent model developed by Henning and Arias [52-54]. The implicit solvent models are based on joint density functional theory (JDFT), which replaces solvent molecules with a continuum dielectric medium. As the average solvent molecular configurations were embedded in the parameters of solvent model, the increase in computation cost is minimal. Lim et al. studied the electrochemical conversion of CO₂ on various electrodes and concluded that the implicit solvation model is good enough to capture the solvent effect [55]. Wang and Liu compared the reaction energies of formic acid oxidation at the Pt/H₂O interface by employing both the implicit solvation model and the model with several explicit water molecules and found the difference between these two models was less than 0.20 eV [56]. Therefore, it is reasonable to believe that the implicit solvation model used in present study is appropriate for exploring the reaction mechanism of CO₂ reduction on the SnO/Sn(112) surface. In this study, water with a dielectric constant $\epsilon_b=80$ was chosen as the solvent. Zero point vibrational energy (ZPVE) and entropy corrections based on the harmonic approximation were applied to all species [57]. It has been shown that the PBE functional overestimates the energy of CO by ~ 0.51 eV [49]. Therefore, the energy of CO (g) will be corrected by -0.51 eV, while no correction is applied for other species. Additional deviation may be caused by the variations of chemical potential in the tin oxide film and polarization of the adsorbates. We neglect those deviations in the work as their effect is likely minimal [58].

The activation barrier for proton-electron transfer is generally considered negligible for the reactions involved in the electrochemical reduction of CO₂ [59]. Therefore, most studies of electrochemical reduction only focus on the thermodynamic trend of the reaction. However, other molecules except hydrogen, such as CO₂ and H₂O, participate in the reduction reaction. Therefore, we calculate the reaction energy barriers for selected elementary steps that involve

CO₂ and H₂O molecules to determine the favorable mechanism. All barrier calculations were performed using the climbing image nudged elastic band (CINEB) method with more than 5 images. Every transition state configuration was confirmed by frequency calculations.

3. Results and discussion

3.1. CO₂ reduction on the SnO/Sn(112) surface

To investigate the pathway of CO₂ reduction on SnO/Sn(112), we start with CO₂ and H adsorption.

3.1.1. CO₂ adsorption

It is generally believed that the electrochemical reduction of CO₂ on a metal electrode starts with CO₂ adsorption on the electrode surface via combination of one electron to form CO₂⁻. However, this step does not occur easily as the formation of CO₂⁻ requires a high potential of ~ -1.90 V SHE (Standard hydrogen electrode) [60]. We have shown that the CO₂ adsorption on the Sn(112) surface is highly unlikely as the adsorption of CO₂ on Sn(112) is highly endothermic [44]. In contrast, CO₂ adsorption on the SnO/Sn(112) surface is feasible. As shown in **Fig. 2**, CO₂ can adsorb on the surface by forming a carbonate-like species. This step is only slightly endothermic with a reaction free energy of 0.16 eV. At the transition state, the CO₂ molecule bends while approaching the H adatom. The <O-C-O angle becomes 149.8° and the distance between the H adatom and C atom of CO₂ is 1.90 Å. The activation barrier for CO₂ adsorption is moderate, ~0.52 eV. The reduction of the CO₂* species will produce either HCOO* or COOH* intermediates with activation barriers of 1.19 eV or 0.73 eV, respectively. Our results show that the formation of HCOO* requires a high free energy of 0.81 eV, while the reaction free energy for COOH* formation is 0.53 eV lower than that for HCOO*. Therefore, the most favorable

pathway for CO₂ adsorption and reaction on the surface is through the COOH* intermediate. It is obvious that the COOH* intermediate maintains a carbonate-like (CO₃*) structure. As the CO₃* structure is symmetric and stable on the surface, it is highly unlikely to break one of its C-O bonds. As a result, further hydrogenation of the carbon atom of COOH* will produce HCOOH* adsorbate rather than form HCOOH and desorb from the surface. This step is thermodynamically unfavorable with an increase in free energy by 0.48 eV. Adding hydrogen to the oxygen atom of COOH* will cause the formation of the H₂CO₃ species, which consumes the surface oxygen atom and creates an oxygen vacancy (V_o) in the SnO monolayer on Sn(112). On the other hand, one hydrogen can also be transferred to the hydroxyl group of COOH*, forming water and causing CO₂ to desorb as a molecule. The desorption of water and CO₂ molecules also leave an oxygen vacancy on the SnO/Sn(112) surface. The reaction free energy of the latter pathway is -

Fig. 2. Free energy diagram and optimized structures for CO₂ reduction on SnO/Sn(112) surface starting from CO₂ adsorption, at 0 V (RHE). (Gray= Sn, red= O, blue= C, white= H.)

0.28 eV and energetically more favorable. Therefore, we conclude that initial CO₂ adsorption on the SnO/Sn(112) surface under electrochemical reduction condition does not reduce CO₂ but results in the formation of an oxygen vacancy.

3.1.2. Proton reduction and adsorption

Reduced proton may adsorb on either the oxygen or Sn atoms of the SnO/Sn(112) surface. As shown in **Fig. 3**, proton adsorption and reduction step is thermodynamically unfavorable both on tin and oxygen atoms. Reaction free energies are 0.35 eV on tin atom and 0.09 eV on oxygen atom, respectively. The Bader charge for (-Sn)H* is -1.20 |e|, and for (-O)H* is +1.00 |e|, while

Fig. 3. Free energy diagram and optimized structures for CO₂ reduction on SnO/Sn(112) starting from proton reduction, at 0 V (RHE). (Gray= Sn, red= O, blue= C, white= H.)

the embedded hydroxyl $(-\text{O})\text{H}^*$ has a charge of $-1.10 |e|$ [61, 62]. As a result, the hydrogen adsorbed on oxygen atom is difficult to directly react with CO_2 . It is more likely that the hydroxyl groups participate in the reduction of CO_2 , which will be discussed in section 3.3. Following the formation of $(-\text{Sn})\text{H}^*$, CO_2 molecule combines with the surface hydrogen atom to produce the formate (HCOO^*) species. The formation of HCOO^* is an exothermic step. Once HCOO^* is formed, it can be easily combined with one electron to form HCOO^- in basic solutions [63]. This pathway of HCOO^* formation is similar to the electrochemical reduction of CO_2 on Sn(112) [44]. On the other hand, the formation of SnO_x thin film on a tin electrode could influence the CO_2 reduction mechanism, making it different from the mechanism on metallic Sn. Further reduction of $(-\text{O})\text{H}^*$ by adding a second proton-electron pair will produce a water molecule without involving CO_2 . Water desorption will leave an oxygen vacancy (V_O) in the SnO monolayer similar to the case of CO_2 adsorption. The activation barrier for V_O formation is 0.23 eV, which can be easily surmounted at room temperatures. Alternatively, the second proton-electron pair may be transferred to another surface oxygen atom, forming another $(-\text{O})\text{H}^*$ hydroxyl-like structure. The barrier for a proton transfer step is also small [59]. For example, Petersen et al. stated that the barriers for a proton transferring from the (water) solution to the accessible atom are small (<0.25 eV) [49]. Pan et al. reported the barrier for protonation of an activated CO_2 by a surface hydroxyl ranges from 0.42-0.53 eV [64]. Therefore, proton transfer is not expected to be the rate-limiting step and alters the reaction mechanism.

Upon the proton reduction and adsorption on the Sn site, CO_2 molecule could directly react with $(-\text{Sn})\text{H}^*$ forming COOH^* species. The COOH^* would dissociate into CO and H_2O via further reduction. However, the calculated reaction free energy for the COOH^* formation is

+0.85 eV, higher than the HCOO* formation at -0.20 eV. As a result, the HCOO* is expected to be the main intermediate following (-Sn)H* formation.

3.1.3 CO₂ adsorption and reaction on the defective SnO/Sn(112) surface

Our results suggest that the SnO monolayer could be reduced by generating an oxygen vacancy on SnO/Sn(112) upon either CO₂ adsorption or proton reduction. This is consistent with the previous experimental observation that the tin oxide film will be reduced in the initial period of the electrochemical reduction of CO₂ [17, 18]. To investigate the reactions on the reduced SnO/Sn(112) overlayer, we studied the CO₂ reduction process using the surface with one oxygen vacancy, i.e., the V_O surface.

The optimized structures of initial, transition and final states for CO₂ dissociation to CO on V_O surface are shown in **Fig. 4(a)**. One oxygen atom of the CO₂ molecule approaches the V_O site. On the V_O site, the adsorbed CO₂ is in a bidentate configuration, i.e. bent by forming a O_{CO2}-Sn_{surf} bond and a C_{CO2}-Sn_{surf} bond. The lengths of O_{CO2}-Sn_{surf} and C_{CO2}-Sn_{surf} bonds and <O-C-O angle in adsorbed CO₂* are 2.30 Å, 2.37 Å and 135.5°, respectively. The dissociation of CO₂ releases a CO molecule via the C-O bond-breaking, resulting in the remaining oxygen atom occupying the oxygen vacancy site and shortening the O-Sn bond distance to 2.19 Å. The healed surface has almost the identical structure to the initial one. The activation barrier for CO₂ dissociation is high, approximately 0.78 eV.

As shown in **Fig. 4(b)**, H₂O can be dissociated to form two hydroxyl groups on SnO/Sn(211). At the transition state, the breaking of the O-H bond is coupled with the formation of two O_{water}-Sn_{surf} bonds on the oxygen defective site, forming one hydroxyl group. The distances of the two O_{water}-Sn_{surf} bonds are 2.23 Å for O₁-Sn₁ and 2.20 Å for O₁-Sn₂. The other hydrogen would combine with the next tin atom at a distance of 1.80 Å, which is then transferred to the nearby surface oxygen to form an embedded hydroxyl group. The distances of the O₂-H₂, O₂-Sn₁ and O₂-Sn₂ bonds in the final state are 0.98 Å, 2.41 Å and 2.26 Å, respectively. The hydroxyl groups bind the same two tin atoms, resulting in a distorted diamond-like -O-Sn-O-Sn- planar structure with O₁H₁* and O₂H₂* pointing to the opposite side of the plane. The distortion makes the four O-Sn bonds in the quadrilateral have different distances. The structure is similar to the 2(-)H* structure formed from proton reduction and adsorption on the surface. Bader charge analysis

Fig. 4. Optimized initial, transition and final state structures of CO₂ dissociation (a) and H₂O dissociation (b) on V_O surfaces. (Number on atoms are to clarify the discussion on text. Gray= Sn, red= O, blue= C, white= H.)

showed that the O_1H_1^* species has a charge of $-1.13 |e|$, while the charge of O_2H_2^* is $-1.08 |e|$. The dissociation of H_2O on the V_O surface is easier with a barrier of 0.53 eV , lower than the barrier of CO_2 dissociation ($\sim 0.78 \text{ eV}$). We also examined the possible intermediate of dissociated H_2O combine with surface tin atoms. However, the free energy of 0.76 eV for $(-\text{Sn})\text{H}^*$ formation is much higher than 0.21 eV for $(-\text{O})\text{H}^*$ formation. Combining with the kinetic considerations, it is evident that H_2O dissociation is preferable on the V_O surface. As a result, the hydroxylated $\text{SnO}/\text{Sn}(112)$ surface will be formed.

3.1.4 H_2O dissociation on $\text{SnO}/\text{Sn}(112)$ surface

Following proton reduction or CO_2 adsorption on the initial $\text{SnO}/\text{Sn}(112)$ surface, an oxygen vacancy may be produced via two proton-electron pairs transfer. On the reduced surface, dissociation of H_2O could happen, forming two embedded hydroxyl groups. In fact, the Pourbaix diagram indicates that the Sn surface will be dominated by hydroxides ($\text{Sn}(\text{OH})_2$ or $\text{Sn}(\text{OH})_4$) in basic aqueous [65]. In order to take different types of hydroxyl groups into account, we studied the H_2O dissociation process on the initial $\text{SnO}/\text{Sn}(112)$ surface. The optimized structures of initial, transition and final states are shown in **Fig. 5**. In the initial state, H_2O approaches the surface oxygen to form a $\text{H}_{\text{water}}-\text{O}_{\text{surf}}$ hydrogen bond with a distance of $1.98 \text{ \AA}$. The reaction

Fig. 5. Optimized initial, transition and final state structures for H_2O dissociation on initial $\text{SnO}/\text{Sn}(112)$ surfaces. (Gray= Sn, red= O, blue= C, white= H.)

barrier is 0.29 eV which is easy to overcome. During the transition state, $H_{\text{water}}-O_{\text{surf}}$ bond becomes even shorter (1.89 Å), accompanied by lengthening of $H_{\text{water}}-OH_{\text{water}}$ bond. The OH_{water} binds the near surface tin atom. The structure after optimization has two symmetric OH^* species which are stable on the surface with a low free energy of -0.35 eV. The four O-Sn bonds with an almost same distance of 2.19 Å form a quadrilateral and both hydroxyl groups point to the same side of the plane. We have also tested the situation of leaving the H atom of H_2O adsorbed on surface tin atom. However, the process has a much higher barrier of 1.18 eV, making it an unlikely event.

3.2 Surface structure transition during electrochemical reduction

The catalytic activities of Sn electrodes have been reported to vary significantly, depending on the preparation methods and experimental conditions, which indicate that the activity of electrode depends on the surface structures [32, 40, 43]. To test the main intermediates during the electrochemical reduction conditions, we compare the stability of different surface structures which have been mentioned in former sections.

With one proton-electron transfer, the hydrogen adatom may be formed on the surface via $H-Sn_{\text{surf}}$ or $H-O_{\text{surf}}$ bond

A water molecule can dissociate to produce a hydroxyl group and a proton on the initial $SnO/Sn(112)$ surface. The proton that adsorbs on the surface oxygen atom will form a new hydroxyl group.

where * presents an active surface site. The free energies of these reactions as a function of potentials are shown in **Fig. 6(a)**. It can be seen that, at negative potentials, hydroxyls formation from H_2O dissociation is favorable until -0.22 V (RHE). At even lower potentials, H^* species will prefer to adsorb on surface oxygen atoms to form embedded hydroxyl groups. Therefore, simple proton reduction and adsorption, or water dissociation are both possible to form OH^* groups on the surface, resulting in a hydroxylated surface as the favorable structure.

In the presence of CO_2 , H^* may further react with CO_2 to form other intermediates, see **Fig. 6(b)**. Hydrogenation of the C atom of CO_2 will produce formate

While carboxyl species may be produced if proton-electron add on O atom of CO_2

Formation of the formate species is thermodynamically more favorable than that of the carboxyl.

Fig. 6. The reaction free energies of main intermediates on SnO/Sn(112) surface as a function of potentials.

Following the formation of the embedded hydroxyl groups or CO₂ adsorption on the surface, further reduction may generate one oxygen vacancy (V_O)

As shown in **Fig. 6(b)**, below potential 0 V (RHE), HCOO* will be the main adsorbate, which is the important intermediate to form formic acid. In addition, the surface may be reduced by transfer of two proton-electron pairs to form one water molecule. Correspondingly, as shown in section 3.1.3, water can also dissociate on the V_O surface to form two embedded hydroxyl groups. The free energy cost for further reduction of the surface becomes higher, therefore, the surface may be partially reduced at negative potentials and OH* surfaces should be the dominant structures. The result is in good agreement with the experiments [41, 43, 66]. In the following section, we will focus on investigating the mechanism for CO₂ reduction on the hydroxylated surfaces.

3.3 CO₂ reduction on the hydroxylated surface

There are two types of hydroxylated surfaces during the electrochemical reduction of CO₂ on SnO/Sn(112) surface. The symmetric OH* surface is formed through H₂O decomposition on initial SnO/Sn(112) surface, while two embedded OH* species form after H₂O decomposition on the V_O surface. **Fig. 6** shows that the symmetric OH* surface is more likely to be formed at a negative potential less than -0.22 V (RHE), while the embedded OH* groups are favorable at even more negative potentials.

Fig. 7 shows the lowest free energy pathway for CO₂ reduction on the symmetric OH* surface to form formate and carbon monoxide with the corresponding configurations. As noted above, H₂O is likely to decompose into two symmetric OH* species. The reaction free energy of this step is downhill by -0.35 eV, and the barrier is only 0.29 eV. The two symmetric OH* groups coadsorb on the same tin atoms and form a rhombus like structure. The two OH* have the same configuration with the same Bader charge of -1.10 |e|, indicating that the OH* species is likely an electron donor and promote CO₂ reduction. As the CO₂ molecule approaches one of the OH* species, one side O-Sn bond will be broken, allowing CO₂ insertion while the CO₂ molecule bends slightly with a <O-C-O angle of 176.7°. At the same time, the proton will transfer from the

Fig. 7 Free energy diagram for CO₂ reduction on symmetric OH* surface at 0 V (RHE), starting from H₂O decomposition on initial SnO/Sn(112) surface. The optimized intermediate structures after symmetric OH* surface formed are also shown in the figure. (Gray= Sn, red= O, blue= C, white= H.)

bottom oxygen atom to the top oxygen atom to form the bicarbonate ($\text{HCO}_3(\text{t})^*$) intermediate. We have also considered the possible intermediate of $\text{HCO}_3(\text{b})^*$ by keeping a proton on the bottom oxygen atom that binds the tin atom. However, the $\text{HCO}_3(\text{b})^*$ species is highly unstable and either spontaneously goes back to CO_2 and H^* or transforms to $\text{HCO}_3(\text{t})^*$. Therefore, we only consider the CO_2 reduction following the $\text{HCO}_3(\text{t})^*$ intermediate. Hydrogenating the C atom coupled with C-O bond breaking of $\text{HCO}_3(\text{t})^*$ will lead to the formate (HCOO^*) species. In the meantime, the proton is transferred to the bottom O atom to reform the OH^* species. Alternatively, protonation at the bottom O atom will lead to breaking the C-O bond and result in the carboxyl (COOH^*) intermediate. The OH^* species will be reproduced following COOH^* formation. The formation of HCOO^* has a relatively lower energy of -0.20 eV than that for COOH^* formation. It can be seen that the potential-limiting step is COOH^* formation with a free energy change of 0.20 eV, which requires a potential of -0.20 V (RHE) to make this reaction channel accessible. Further reduction of COOH^* at O atom will produce CO and H_2O .

As shown in section 3.1, the $\text{SnO}/\text{Sn}(112)$ surface may be reduced partially by CO_2 or H adsorption to generate an oxygen vacancy in the monolayer. H_2O dissociation can fill the vacancy and form two embedded OH^* species. This step is endothermic with a barrier of 0.53 eV. **Fig. 8** shows the free energy diagram for CO_2 reduction in the presence of the embedded OH^* species. Similar to the pathway shown in **Fig. 7**, CO_2 could also be inserted into the HO-Sn bond to form a bicarbonate-like species. At the transition state, CO_2 bends with a $\angle\text{O-C-O}$ angle of 130.5° . The $\text{O}_1\text{-Sn}_2$ bond will be broken while the $\text{O}_1\text{-C}_{\text{CO}_2}$ bond forms. The O_1H_1^* group departs from the Sn_1 atom and approaches the nearby Sn_3 atom. Hydrogen atom (H_1) also prefers to bond with the top oxygen atom, forming $\text{HCO}_3(\text{t})^*$. However, $\text{HCO}_3(\text{t})^*$ formed with the embedded OH^* surface has a relatively higher barrier (~ 0.75 eV) than that with symmetric OH^*

surface (~ 0.47 eV). The subsequent reduction of $\text{HCO}_3(\text{t})^*$ to HCOO^* or COOH^* has the reaction free energy of -0.11 eV and 0.74 eV, respectively. Next, HCOO^* can be reduced and desorb to the aqueous solution in the form of HCOO^- , while further reduction of COOH^* will generate CO and H_2O . The largest endothermic step is the reduction of $\text{HCO}_3(\text{t})^*$ to form COOH^* , which results in the formation of CO but requires a potential below -0.74 V (RHE), much lower than the potential required on the pristine surface with symmetric OH^* (-0.20 V (RHE)). Consequently, the symmetric OH^* surface formed by H_2O dissociation on SnO monolayer is more favorable for CO_2 reduction than the surface with the embedded OH groups, especially for CO formation.

Compared with CO_2 reduction on pure tin electrodes, the presence of SnO_x promotes the reaction activity by lowering the overpotential and changing product distribution [40, 44]. From thermodynamic consideration, HCOO^* formation is more favorable than COOH^* , resulting in a higher selectivity for formic acid than carbon monoxide. The result is consistent with the experimental observations that formate is the main product while carbon monoxide can be produced with a lower Faradaic efficiency for CO_2 electrochemical reduction on SnO_x/Sn electrodes [17, 18, 40, 41]. On the other hand, the formation of SnO_x on the Sn electrode opened up new reaction channels to other products, including CO. This is in direct contrast to CO_2 electrochemical reduction on Sn(112) as we reported previously: COOH^* is unlikely to form on the Sn(112) surface. CO formation in that case has to follow the HCOO^* intermediate [44]. Again, it has been shown that the formation of CO only accounts for a small amount as the Faradaic efficiency is lower than 10% for CO_2 electrochemical reduction on the Sn electrodes [17, 67]. This is because the HCOO^* can be easily reduced and desorbs from the surface, reducing the possibility of further reduction to CO. As shown in **Fig. 7** and **Fig. 8**, the

Fig. 8 Free energy diagram for CO₂ reduction on OH* surface formed by H₂O dissociation on V_O surface at 0 V (RHE), starting with V_O surface formation. The optimized intermediate structures after OH* surface formed are also shown in the figure. (Gray= Sn, red= O, blue= C, white= H.)

mechanism on SnO is different from that on pure Sn. The HCOO* and COOH* species on SnO/Sn(112) originate from the same HCO₃(t)* intermediate. The overpotential for CO formation is as low as -0.20 V (RHE) on SnO/Sn(112), which is lower than the potential (-0.58 V (RHE)) required on the Sn(112) electrode [44]. Therefore, under the potential lower than -0.20 V (RHE), HCOO* and CO can be produced simultaneously. In addition, change in the thickness or morphology of SnO_x may further enhance CO formation [7, 18].

We find that HCOO⁻ and CO desorption from the surface will recover the hydroxylated surface and complete the reaction cycle. Therefore, the dominant mechanism for CO₂ reduction on the SnO/Sn(112) surface is very likely to proceed through the bicarbonate (HCO₃(t)*) species on the hydroxylated surface. The HCO₃(t)* species would be the key intermediate to form

HCOO* and CO, and the formation of COOH* is the potential-limiting step for CO₂ reduction [41]. It should also be noted that H₂ may be produced by protonation of H* adatom. However, under the electrode potentials predicted in this work, it will facilitate the more stable surface structures, i.e. OH* species, and suppressing the hydrogen evolution reaction (HER).

4. Conclusions

DFT calculations were used to study the effect of SnO_x formation on the tin electrode for the electrochemical reduction of CO₂. Various reaction pathways of CO₂ reduction were explored on the SnO/Sn(112) model surface. Our calculated free energy diagrams suggested that the existence of SnO monolayer lead to the formation of hydroxyls on the SnO surface, either symmetrical or embedded. On the hydroxylated SnO layer, CO₂ can insert into the OH* species and form a bicarbonate (HCO₃*) species, a key reaction intermediate for CO₂ reduction on the oxidized surfaces. Reduction of HCO₃* will produce HCOO* or COOH*, although the formation of HCOO* is energetically more favorable. Further reduction of COOH* will generate CO and H₂O. This is also consistent with previous experimental observation that the formation of the surface-bound tin-carbonate species in the presence of SnO_x is an active intermediate for CO₂ reduction to HCOO* [41]. Moreover, the reaction pathway via HCO₃(t)* and COOH* opens a new channel for complete CO₂ reduction to CO. As a result, we conclude that the formation of SnO_x monolayer on the Sn electrode would promote the CO₂ reduction to CO.

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