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Electrochemical interfacial influences on the deoxygenation and hydrogenation reactions in CO reduction on Cu(100) surface

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Electroreduction of CO₂ to hydrocarbons on copper surface has attracted much attention in the last decades for providing a sustainable way for energy store. During the CO₂ and further CO electroreduction processes, the deoxygenation that is C-O bond dissociation, and hydrogenation that is C-H bond formation, are two main types of surface reactions catalyzed by copper electrode. In this work, by performing the state-of-the-art constrained *ab initio* molecular dynamics simulations, we have systematically investigated the deoxygenation and hydrogenation reactions involving two important intermediates, COH_{ads} and CHO_{ads}, under various conditions of (i) on Cu(100) surface without water molecules, (ii) at the water/Cu(100) interface and (iii) at the charged water/Cu(100) interface, in order to elucidate the electrochemical interfacial influences. It has been found that the electrochemical interface can facilitate considerably the C-O bond dissociation *via* changing the reaction mechanisms. However, the C-H bond formation has not been affected by the presence of water or electrical charge. Furthermore, the promotional roles of aqueous surrounding and negative electrode potential in the deoxygenation have been clarified, respectively. This fundamental study provides an atomic level insight into the significance of electrochemical interface towards electrocatalysis, which is of general importance in understanding electrochemistry.

1. Introduction

Electrocatalytic reduction of CO₂ into hydrocarbon fuels is a promising process with a carbon cycle for the sustainable energy storage.¹ Since it was reported by Hori et al. for the first time, it has attained remarkable interests in recent years, due to the advantages of the electroreduction of CO₂ on copper electrodes in aqueous electrolytes at ambient temperature with a high faradic efficiency.¹⁻⁵ Copper electrode was experimentally found to be able to reduce CO₂ into hydrocarbons (methane and ethylene) uniquely,⁶⁻⁹ and the reaction mechanisms were extensively investigated.¹⁰⁻¹⁵ It was found that CO was not only the first reduced product but also a new starting species that could be further reduced to the final products of hydrocarbons. The rate-determining step was suggested to be the electron transfer to the adsorbed CO, and the adsorbed COH was proposed to be the crucial intermediate.¹⁰⁻¹⁵ To advance our understanding of the experimental findings, density functional theory (DFT) calculations were employed widely for investigating the mechanisms in CO₂ reduction at the atomic level.¹⁶⁻²⁵ Norskov's group has developed a computational hydrogen electrode model to map out the free energy diagrams from

CO₂ to CH₄ including about 40 elementary steps on Cu(111).¹⁷ Nie et al. described the roles of the kinetics of elementary steps and the whole reaction network on Cu(111).^{19,20} Calle-Vallejo et al. proposed a CO dimerization mechanism at low overpotentials on Cu(100) from calculations, and Montoya et al. systematically calculated the same process at a charged water layer on Cu(111) and Cu(100).^{21,22} Goddard's group calculated the formation of C1 and C2 species on both Cu(111) and Cu(100) with considering pH effect.^{23,24} We previously revealed that adsorbed COH was favorable kinetically but CHO was favorable thermodynamically in CO activation on Cu(100).²⁵ In fact, the mechanism to explain how copper catalyzes CO₂ to hydrocarbons still remains controversial and requires further studies.

Hori et al. carried out the CO₂ electroreduction over a series of Cu single crystal planes, it was found that the activity on Cu(100) and Cu(111) single crystal surfaces is comparable, e.g., a current density of 5 mA cm⁻² was achieved at a reduction potential of -1.4 V (vs SHE) on Cu(100) and -1.5 V (vs SHE) on Cu(111), respectively.^{7,8} Recently, Cu(100) was identified experimentally to be a very important surface in CO₂ electroreduction. Schouten et al. found that the behaviors of Cu polycrystalline and Cu(100) were very much alike in terms of the remarkable selectivity towards ethylene, suggesting that the dominating facet of Cu polycrystalline was actually Cu(100) instead of Cu(111).²⁶ Kim et al. also observed the reconstruction of Cu(111) to Cu(100) but no further transformation from Cu(100) in CO₂ electroreduction under operando electrochemical scanning tunneling microscopy.²⁷

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Some theoretical approaches based on DFT calculations and molecular dynamics (MD) simulations have been developed to model the electrochemical interface which is central for electrocatalysis.^{22-25,28-38} To avoid the introduction of artificial counter-charge, H atoms were usually introduced into the water layer. Since the H atoms could separate into protons and electrons, one may vary the surface charge and the potential by changing the concentration of protons.^{25,36,37} DFT calculations performed in aqueous surrounding would be extremely challenging and extraordinary time-consuming since the water structures would be fluctuating in dynamics at the interface. In fact, it has been proved that without the appropriate dynamics for water structure, calculation of the work function hardly matched the experiments.³³ Importantly, the presence of aqueous surrounding has a great impact on thermodynamics and kinetics of electrocatalytic reactions,³⁸ and thus MD study is highly expected for describing the roles of solution in electrochemistry. However, most of the previous theoretical works were performed by using the vacuum model or static water structure.^{17-19,20,21} Further investigation of this process using a liquid water/solid catalyst interface model with explicit water molecules is expected in understanding electrocatalysis.

During the CO electroreduction to hydrocarbon fuels, the deoxygenation (i.e., C-O bond dissociation) and hydrogenation (i.e., C-H bond formation) are the two main types of surface reactions catalyzed by copper electrode.^{4,5} Without deoxygenation, the final products would be methanol (CH₃OH) resulting from hydrogenation, instead of methane/ethylene (CH₄/C₂H₄). It is well known that the electrochemical interface has two crucial features: the aqueous surrounding and the electrode potential, in comparison with the traditional gas/solid interface in heterogeneous catalysis. However, very few investigations were focused on elucidating the significance of electrochemical interface at the atomic level, although it is very important for fundamentally understanding the reaction mechanism in electrocatalysis.

In this contribution, we present a detailed study on how the electrochemical interface affects the energetics and mechanisms of surface catalytic reactions at the atomic level, by performing the state-of-the-art constrained *ab initio* MD simulations. On the basis of the calculation involving two crucial intermediates, COH_{ads} and CHO_{ads}, under various conditions of (i) on Cu(100) surface without water molecules, (ii) at the water/Cu(100) interface and (iii) at the charged water/Cu(100) interface, it was found that the electrochemical interface can dramatically change the mechanism in C-O bond dissociation and facilitate remarkably the dissociation. However, the C-H bond formation has not been affected by the presence of water or electrical charge. Furthermore, the promotional roles of aqueous surrounding and negative electrode potential in the deoxygenation have been clarified, respectively. This fundamental study provides an atomic level insight into the significance of electrochemical interface towards electrocatalysis.

Fig. 1. Models of the charged water/Cu(100) interfaces including 20 water molecules, a solvated proton (H⁺), adsorbed COH (COH_{ads}) and CHO (CHO_{ads}). Orange: Cu; grey: C; red: O; white: H. (the same colors are used in the paper.)

2. Computational details

All the electronic structure calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) with Perdew-Burke-Ernzerh (PBE) functional of exchange-correlation. The projector-augmented-wave (PAW) pseudopotentials were utilized to describe the core electron interaction.³⁹⁻⁴⁶ A four-layer Cu(100) slab was modeled by *p*(3×3) unit cell with 36 atoms. The bottom two layers were fixed and the top two layers were fully relaxed during all the *ab initio* MD simulations. The cut-off energy was set as 400 eV and a 3 × 3 × 1 Monkhorst-Pack k-point sampling was utilized for high accuracy. We employed the constrained *ab initio* MD method which was well established on the basis of thermodynamic integration by Sprik and others to calculate the free energy of reactions in aqueous surrounding.⁴⁷⁻⁴⁹ For each state, we performed *ab initio* MD simulation for 6 ps (1 fs per step, 6000 steps) at a constant room temperature (T = 300 K) within the canonical (NVT) ensemble by Nosé-Hoover thermostat method. Usually, we found that the interatomic force could be converged after at least 3 ps in a MD duration and 6 ps was long enough for the convergence of interatomic forces. We selected 1000 samples from the last 1 ps of each MD simulation to do the average of the interatomic force.

The water/Cu(100) interface contains 20 water molecules with a density of water layer at 1 g cm⁻³ which was kept constant during the MD simulation. Considering that the water layer was relatively thin (~12 Å) and the bottom of Cu slab would affect the water structure, a vacuum layer of 7 Å was added above the water layer to avoid the interaction between water molecules and the bottom of Cu slab. In order to simulate the

charged interface, one extra H atom was placed in the water layer, which spontaneously separates into H^+ in solution and an electron ending up at the slab. The models used in this work are displayed in Fig. 1. From our previous calculation, one can see that the corresponding electrode potential in neutral system (potential of zero charge) is -0.63 (vs SHE), comparing with the experimental value of -0.54 V (vs SHE).²⁵ For the charged interface model including H^+ , the corresponding electrode potential is -2.04 V (vs SHE), more negative than the onset potential of -1.4 V (vs SHE) in CO_2 electroreduction on Cu(100).⁸ Using the water/Cu(100) interface and the charged water/Cu(100) interface can help to decouple the effects of aqueous surrounding and electrode potential for investigating them respectively.

3. Results

3.1 C-O bond dissociation in COH

Firstly, we calculated the C-O bond dissociation in COH_{ads} yielding C_{ads} under three different conditions: on Cu(100) without water molecules, at the water/Cu(100) interface and at the charged water/Cu(100) interface, respectively. Fig. 2 displays the free energy profiles against the C-O bond distance of COH_{ads} respectively. Fig. 3 presents the key structures along the reaction paths. On Cu(100) without water molecules, reaction 1 with the formation of C_{ads} and OH_{ads} on surface is allowed thermodynamically with the reaction free energy being 0.05 eV. But the free energy barrier was calculated to be as high as 1.17 eV (see the red line in Fig. 2), implying that this reaction is not favorable kinetically at the room temperature. The distance of C-O bond is $\sim 2 \text{ \AA}$ at the transition state, and the structures are presented in Fig. 3a.

Interestingly, at the water/Cu(100) interface, although the thermodynamics changes a little, with a reaction energy of -0.10 eV, the C-O bond in the COH_{ads} could be effectively activated. The calculated free energy barrier is much reduced to 0.74 eV from the value of 1.17 eV found in vacuum. It is clear from Fig. 2 (see the blue line) that the free energy reaches the peak position of 0.74 eV under aqueous surrounding, where the C-O bond is lengthen to $\sim 2.0 \text{ \AA}$.

Fig. 2. Free energy profiles for the deoxygenation of COH_{ads} under different conditions.

Fig. 3. Structures in the deoxygenation of COH_{ads} obtained from *ab initio* MD simulations under different conditions. (a): on Cu(100) without water molecules; (b): at water/Cu(100) interface; (c): at charged water/Cu(100) interface.

Afterwards, the free energy decreases and finally reaches a value of -0.10 eV where the C-O bond is fully broken. Under aqueous surrounding, water molecules are able to stabilize the dissociating OH group *via* hydrogen bonding, which is quite different from the structures in vacuum that the dissociating OH_{ads} binds to nearby Cu surface free site, as illustrated in Fig. 3b. One surface adsorbed water molecule ($\text{H}_2\text{O}_{\text{ads}}$) passes one H to the dissociating OH group in solution (OH^- anion), resulting in the formation of OH_{ads} on surface and $\text{H}_2\text{O}_{\text{aq}}$ in solution. This process can be written as reaction 2.

Moreover, at the charged water/Cu(100) interface, it was amazingly found that the C-O bond in COH_{ads} can be readily broken with a much reduced free energy barrier of 0.34 eV only, which is much lower than the value of 1.17 eV and 0.74 eV obtained in the absence and presence of water molecules. As shown in Fig. 3c, the C-O bond dissociation occurs accompanying with the coupled proton and electron transfer ($\text{H}^+ + \text{e}^-$) simultaneously. When the C-O bond is lengthened to $\sim 1.9 \text{ \AA}$, H^+ has been transferred to the O-end in COH_{ads} forming the structure of $[\text{C}_{\text{ads}} \cdots \text{H}_2\text{O}_{\text{aq}}]$. After that, the C-O bond breaks with releasing one water molecule into solution at the same time, which can be written as reaction 3. Such a concerted mechanism that H^+ reacts with the dissociating OH group forming $\text{H}_2\text{O}_{\text{aq}}$ directly can further lower the barrier to an extremely low value of 0.34 eV, indicating that the C-O bond dissociation rate is fast enough.

In comparison with previous work, Nie et al. have proposed a carbon formation mechanism through the hydrogenation to the O-end in COH_{ads} .¹⁹ However, we found that the formation of O-H bond would not induce the C-O bond dissociation. Instead, when H^+ approaches the O at the distance of $\sim 1.3 \text{ \AA}$, the original O-H bond breaks and a new O-H bond forms, overcoming a barrier as low as 0.05 eV, that is, the initial H is replaced by the new H. Such a low barrier indicates a fast proton transfer process. The free energy profile and the structures are displayed in Fig. 4.

Fig. 4. Free energy profiles for H^+ attacking the O of COH_{ads} with the key structures. Yellow: attacking H^+ .

3.2 C-O bond dissociation in CHO

The dissociation of CHO_{ads} on $\text{Cu}(100)$ without water molecules is endothermic by 0.45 eV, overcoming a large barrier of 1.47 eV at the room temperature (see the red line in Fig. 5), indicating that the breaking of C-O bond is rather energetically unfavourable in both kinetics and thermodynamics in reaction 4. The dissociating O_{ads} stays at the bridge site on surface at the transition state when the C-O bond length is elongated to ~ 1.9 Å at the transition state from 1.31 Å at the initial state. Finally, O_{ads} and CH_{ads} both move to the hollow sites as illustrated in Fig. 6a.

An interesting phenomenon was noticed at the water/ $\text{Cu}(100)$ interface that an adjacent $\text{H}_2\text{O}_{\text{ads}}$ is readily dissociated to OH_{ads} by passing one H to the O in CHO_{ads} , when the C-O bond is lengthened to ~ 1.6 Å. At the C-O bond distance of ~ 1.9 Å, the C-O bond is broken and finally, two OH_{ads} adsorbs at the bridge sites as reaction 5. The key structures with water molecules are displayed in Fig. 6b. As a general common sense, the hydrogenation of double bond is an effective approach for lowering the dissociation barrier. As a consequence, the reaction energy in reaction 5 is -0.32 eV and the free energy barrier is 1.04 eV, which is apparently promoted after the O in C-O double bond being hydrogenated (see the blue line in Fig. 5), in comparison with the data obtained in vacuum ($\Delta G = 0.45$

Fig. 5. Free energy profiles for the deoxygenation of CHO_{ads} under different conditions.

Fig. 6. Structures in the deoxygenation of CHO_{ads} obtained from *ab initio* MD simulations under different conditions. (a): on $\text{Cu}(100)$ without water molecules; (b): at water/ $\text{Cu}(100)$ interface; (c): at charged water/ $\text{Cu}(100)$ interface.

eV, $E_a = 1.47$ eV). However, although the thermodynamics already allows the C-O bond to be broken, the reaction rate is still very slow.

At the charged water/ $\text{Cu}(100)$ interface in the presence of H^+ , once the C-O bond is lengthened to ~ 1.4 Å, the O in CHO_{ads} can be protonated to OH forming a structure of $[\text{CH}\dots\text{OH}_{\text{ads}}]$. The reaction free energy is thus further reduced to 0.70 eV with more exothermic of -0.71 eV in reaction 6 (see the green line in Fig. 5). It can be clearly seen from Fig. 6c that the OH_{ads} is stabilized by surface Cu site during the dissociation process, which is different from the fact that the OH_{ads} in COH_{ads} enters into aqueous solution directly. Comparing with the reaction 5 where hydrogen comes from an adjacent $\text{H}_2\text{O}_{\text{ads}}$, H^+ in solution can directly attack the O in CHO_{ads} at negative potentials.

3.3 Hydrogenation of COH and CHO

The formation of C-H bond by the assault of H^+ in solution was identified not feasible, but H^+ has to adsorb on surface as H_{ads} ($\text{H}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}}$) firstly and then the C-H formation follows the Langmuir-Hinshelwood mechanism.²⁵ The hydrogenation of COH_{ads} yielding CHOH_{ads} as reaction 7 and that of CHO_{ads} yielding HCHO_{ads} as reaction 8 were calculated, respectively. The free energy profiles are plotted against the C-H bond distance in Figs. 7 and 9, and the key structures along the reaction paths are displayed in Figs. 8 and 10.

In the hydrogenation of COH_{ads} without water molecules, the reaction free energy is -0.07 eV with a barrier of 0.51 eV. COH_{ads} and H_{ads} both adsorb initially at the hollow sites and move gradually to the bridge sites. At the transition state, the C-H bond distance is ~ 1.8 Å. The new produced CHOH_{ads} stays at the bridge site. In the presence of aqueous solution, the reaction energy is -0.11 eV and the energy barrier is 0.52 eV, which are much close to the data obtained in vacuum. The OH

Fig. 7. Free energy profiles for the hydrogenation of COH_{ads} under different conditions. Fig. 8. Structures in the hydrogenation of COH_{ads} from *ab initio* MD simulations under different conditions. (a): on Cu(100) without water molecules; (b): at water/Cu(100) interface.

group in COH_{ads} and CHOH_{ads} can form hydrogen bonds with water molecules.

In the hydrogenation of CHO_{ads} without water molecules, the reaction energy is -0.39 eV and the barrier is 0.41 eV. With the presence of water molecules, the reaction energy and barrier are close to those ($\Delta G = -0.44$ eV, $E_a = 0.38$ eV) obtained in vacuum. It can be thus seen that water molecules have little effect on the C-H bond formation process whatever in COH_{ads} or CHO_{ads} . The surface reaction which follows the Langmuir-Hinshelwood mechanism without electron transfer was reported to be insensitive to the electrode potential.⁵⁰ Therefore, to decrease the time-consuming MD calculations, the hydrogenation barriers at the charged water/Cu(100) interface are expected to be close to those with water molecules.

3.4 Free energy barriers and charge analysis

The barriers obtained in C-O bond dissociation and C-H bond formation at three different interfaces are compared in Fig. 11. It can be obviously seen that the C-O bond dissociation reactions are rather sensitive towards the structures of interfaces, but the hydrogenation reactions are not. The deoxygenation barriers in COH_{ads} are 1.17 eV, 0.74 eV and 0.34 eV but the hydrogenation barriers are 0.51 eV and 0.52 eV respectively. Likewise, the deoxygenation barriers in CHO_{ads} are 1.47 eV, 1.04 eV and 0.7 eV but the hydrogenation

barriers are 0.41 eV and 0.38 eV respectively. The energetic difference

Fig. 9. Free energy profiles for the hydrogenation of CHO_{ads} under different conditions. Fig. 10. Structures in the hydrogenation of CHO_{ads} from *ab initio* MD simulations under different conditions. (a): on Cu(100) without water molecules; (b): at water/Cu(100) interface.

in the hydrogenation reaction are less than 0.04 eV. Table 1 shows the Bader charge analysis results in COH_{ads} , CHO_{ads} , CHOH_{ads} and HCHO_{ads} without and with the presence of water molecules. It was found that O in C-O bond is negatively charged of around -1.2 e, however, H in C-H bond is nearly electro-neutrality (~ 0.07 e). This data may explain why C-O bond is easily affected by water molecules *via* hydrogen bonding while C-H bond is not. In addition, Table 1 also shows evidently that with the presence of water can make O more negatively charged by around 0.1 e.

4. Discussion

4.1 Effect of the aqueous surrounding

In the deoxygenation reactions, we have demonstrated that water plays not only being a solvent molecule but also as a reactive molecule to participate in the surface reactions. The presence of aqueous solution has a great impact on mechanisms and energetics, indicating that an interfacial model with some explicit water molecules should be used in the calculation of electrocatalytic reactions or aqueous heterogeneous catalysis for understanding the reaction mechanisms properly at atomic scale. In this section, we discuss the effect of aqueous surrounding in details, in order to rationalize the phenomenon at the water/Cu(100) interface. In

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general, aqueous surrounding is beneficial to the deoxygenation reaction by stabilizing the transition states *via*

Table 1. Bader charges analysis (in e) of H of C-H bond and O of C-O bond in COH_{ads} , CHO_{ads} , CHOH_{ads} and HCHO_{ads} under two conditions: Cu(100) without water molecules and the charged water/Cu(100) interface.

		H	O
Cu(100)	COH_{ads}	/	-1.13
	CHO_{ads}	0.06	-1.04
	CHOH_{ads}	0.08	-1.12
	HCHO_{ads}	0.06	-1.07
water/Cu(100)	COH_{ads}	/	-1.2
	CHO_{ads}	0.07	-1.15
	CHOH_{ads}	0.07	-1.23
	HCHO_{ads}	0.07	-1.08

different pathways and as a result, the free energy barriers are remarkably reduced.

In COH_{ads} deoxygenation, it was found that water can eliminate the electronic repulsion between C_{ads} and OH_{ads} at the transition state and transfer proton in the formation of OH_{ads} . (i) At the transition state, because of the co-adsorption of C_{ads} and OH_{ads} at the same Cu site as shown in Fig. 3a, the electronic repulsion was calculated to be 0.59 eV between the dissociating C_{ads} and OH_{ads} leading to a contribution to the high barrier of 1.17 eV. However, under aqueous surrounding, water molecules are able to stabilize the dissociating OH_{ads} *via* hydrogen bonding, that is, they could provide new sites for OH adsorption as shown in Fig. 3b. Thus, the dissociating OH_{ads} does not need to stay on surface but could directly enter solution as anion (OH^-), resulting in eliminating the strong electronic repulsion (0.59 eV). (ii) After the dissociating OH group entering solution, one surface water molecule passes one H to the OH^- anion rapidly *via* hydrogen bond network, leading to the formation of OH_{ads} .

In CHO_{ads} deoxygenation, water is identified to stabilize the bridge O_{ads} at the transition state and activate the C-O double bond. (i) Once O_{ads} was moved from the hollow to bridge site, it readily reacted with a neighboring $\text{H}_2\text{O}_{\text{ads}}$, generating two bridge OH_{ads} . The reaction, $\text{O}_{\text{ads}} + \text{H}_2\text{O}_{\text{ads}} \rightarrow 2\text{OH}_{\text{ads}}$, was calculated to be a highly exothermic process of -0.91 eV without a distinct barrier, implying that the bridge O_{ads} is rather unstable at the water interface. This data may explain why the C-O bond dissociation and water dissociation occur simultaneously as a one-step reaction. (ii) After the O of C-O double bond being hydrogenated, the distance of C-O bond is elongated from 1.31 Å to 1.40 Å, indicating that it has already been activated.

4.3 Effect of the electrode potential

On Cu(100) without and with the presence of water molecules, the C-O bond dissociation follows the Langmuir-Hinshelwood mechanism as the reactions 1, 2, 4, and 5 without involving the electron transfer, which is not affected by electrode potential. However, at negative potentials, the C-O bond dissociation was found to accompany with the coupled proton and electron transfer, which can be regarded as a concerted process (reactions 3 and 6). This type of reaction is indeed strongly

affected by the electrode potential, and a large negative electrical potential would accelerate the reaction rate. Therefore, the electrode potential plays a vital role in adjusting

Fig. 11. Comparisons of the free energy barriers (in eV) in C-O bond dissociation and C-H bond formation under different conditions.

the deoxygenation barriers. One important experimental phenomenon is consistent with our results that copper electrode was found to be easily poisoned by graphitic or amorphous carbon formed during electrolysis.¹⁰⁻¹² Modulation of electrode potential could effectively avoid the poisoning carbon formation,^{51,52} indicating that the carbon species formation resulting from deoxygenation can be controlled by shifting the potential.

It is worth mentioning that the electrode potential is kept constant during the coupled proton and electron transfer in reality. Due to the computational limitation, the size of our model in this simulation is relatively small, resulting in the electrode potential would change significantly in the coupled proton and electron transfer. The realistic electrocatalytic reactions should occur under constant potential condition. Using constant charge is just an approximation to control the electrode potential for studying the potential effect, however, the potential cannot be kept strictly before and after the reactions. This crucial issue is still a big challenge within the current DFT framework and some errors are inevitable leading to an approximate description of the electrocatalytic reactions. Nevertheless, it could help us to generally understand the realistic reaction mechanism at the electrochemical interface. We have shown that the disappearance of H^+ results in an increase in the electrode potential from -2.04 V (vs SHE) to -

0.63 V (vs SHE) and thus, the barrier is actually lower than 0.34 eV in COH_{ads} and 0.70 eV in CHO_{ads} .

In alkaline solution, the cation is Na^+ , which is surrounded by numbers of water molecules in the OHP layer. At very negative potentials, the presence of Na^+ near surface would block the surface reactions to some extent by hindering the mass transportation. Na^+ usually would not participate the reactions directly due to the highly chemical stability, and thus we do not consider Na^+ in our calculations. Additionally, the coupled proton and electron transfer in alkaline solution ($\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}^* + \text{OH}^-$) is different from that in acidic solution ($\text{H}^+ + \text{e}^- \rightarrow \text{H}^*$), where proton comes from water resulting in the formation of OH^- simultaneously. Although the equilibrium potentials with respect to the reversible hydrogen electrode (RHE) are same, the kinetics behaviours are different.

4.4 Significance of electrochemical interface

We notice an interesting issue that, the major products are methanol (CH_3OH) from CO_2 reduction by gaseous H_2 over copper catalysts in the industrial methanol synthesis process, however, negligible methanol was detected in the CO_2 electroreduction over copper electrode.^{4,5} It could be an indication that the methanol/hydrocarbons selectivity is determined by the deoxygenation. That is, without a fast deoxygenation process, the final product of CO_2 reduction have to be CH_3OH in the industrial methanol synthesis. On the other hand, once the deoxygenation process is fast enough, the final products of CO_2 reduction turn out to be hydrocarbon fuels. The electrochemical interface involved here having two important features of aqueous surrounding and large negative potential can effectively facilitate the deoxygenation reactions. Without the assistance of the electrochemical interface, the C-O bond can hardly be broken due to the high barriers, and methanol is expected to be the final product. However, once carbon species are generated on surface, the final products should be hydrocarbons.

5. Conclusions

In this work, the deoxygenation, i.e., C-O bond dissociation, and hydrogenation, i.e., C-H bond formation, as the two main types of surface reactions catalyzed by copper electrode during CO electroreduction, were investigated, respectively. COH_{ads} and CHO_{ads} as the two important intermediates were taken as examples under three different conditions: (i) on Cu(100) without water molecules, (ii) at the water/Cu(100) interface and (iii) at the charged water/Cu(100) interface. By performing the state-of-the-art constrained *ab initio* MD simulations, we have elucidated the electrochemical interfacial influences. The main conclusions are summarized below:

(i) The C-O bond dissociation barrier in COH_{ads} is 1.17 eV without water molecules, one near Cu surface site accepts the dissociating OH_{ads} . Aqueous surrounding can stabilize the dissociation OH leading to a reduced barrier of 0.74 eV. At negative potentials, the coupled proton and electron transfer can further lower the barrier to 0.34 eV.

(ii) A high barrier of 1.47 eV is obtained in CHO_{ads} without water molecules. At the water/Cu(100) interface, one $\text{H}_2\text{O}_{\text{ads}}$ is observed to pass one H to the O of C-O bond during the dissociation, lowering the barrier to 1.04 eV. At negative potentials, proton transfer can help reduce the barrier to 0.70 eV.

(iii) The effects of aqueous surrounding on the hydrogenation reactions with C-H bond formation are not noticeable, since the differences in free energy barriers and reaction energies are less than 0.04 eV. Bader charge analysis shows that O in C-O bond is negatively charged but H in C-H bond is electro-neutrality, which may explain why the C-O bond dissociation is easily affected by the presence of water molecules.

(iv) The effects of aqueous surrounding in the deoxygenation reactions involving the two intermediates are revealed, respectively. For COH_{ads} , water molecules eliminate the electronic repulsion between C_{ads} and OH_{ads} at the transition state and transfer proton from $\text{H}_2\text{O}_{\text{ads}}$ to the dissociation OH group. For CHO_{ads} , the bridge O_{ads} at the transition state is stabilized by $\text{H}_2\text{O}_{\text{ads}}$ dissociation and at the meantime, the C-O double bond is activated.

(v) At negative potentials, the C-O bond dissociation accompanies with the coupled proton and electron transfer. Such a reaction is strongly affected by the electrode potential. A large negative electrical potential is expected to facilitate the deoxygenation reactions.

This fundamental study provides an atomic level insight into the significance of electrochemical interface towards electrocatalysis, which is of general importance in understanding electrochemistry.

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