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A Computational Perspective on Carbon-Carbon Bond Formation by Single Cu Atom on Pd(111) Surface for CO Electrochemical Reduction

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Abstract: This study focuses on the computational characterization of electrochemical C-C bond formation through the CO and CHO coupling process utilizing a dioxo-coordinated Cu single atom site ([CuO₂]^{*}) supported on a Pd(111) surface. The stable intermediate, [CuO₂]^{*}(CO)₂, was identified as a tetradentate-and-tetrahedral species formed upon exposure to CO gaseous molecules. Electrochemically, the hydrogenation of the carbonyl group to CHO was found to be 0.87 eV, conceivably lower than the corresponding step for conventional Cu surfaces. This study observed a considerable charge transfer effect from the top layer of Pd atoms to the adsorbate moiety, especially at the TS structure. This phenomenon resulted in an accessible C-C bond formation barrier at 0.67 eV. Furthermore, the reaction energy of C-C bond formation was found to be exothermic at −0.21 eV, indicating a favorable chemical equilibrium condition. Considering the temperature effect and pressure of the gaseous molecules (CO, CO₂, O₂), the [CuO₂]^{*}(CO)₂ intermediate was substantially populated at room temperature and was found to be chemically resilient under dry ambient conditions, as suggested by the kinetic modeling results.

Keywords: carbon-carbon bond formation; single atom catalyst; CO₂ reduction reaction; density functional theory; microkinetics



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1. Introduction

Electrochemically reducing CO₂ to valuable hydrocarbons has been comprehensively explored using Cu-based electrode materials [1–3], as initially demonstrated by Hori et al. [4]. From the viewpoint of converting electric energy into chemical energy, the carbon-carbon (C-C) bond formation during the reductive mechanisms of hydrocarbon generation can be considered the most important step in terms of increasing the energy storage density. The CO dimerization reaction was assigned as the representative pathway for the electrochemical-driven multicarbon product generation observed on the common Cu(100) and Cu(111), and Cu(110) surfaces [5,6]. Other coupling pathways resulting from CO and its hydrogenated derivatives (CHO or COH) were also documented in the literature [1]. In order to enrich the electronic structure characteristics of Cu, the synthetic strategy of using bimetallic materials, including bimetallic alloys or bimetallic bifunctional interfaces, was also utilized [1,2]. The heterogeneous atomic electronic character or heterogeneous material morphologies were found to have a synergistic effect and provide outstanding catalytic performance for the carbon dioxide reduction reaction (CO₂RR). Consequently, the corresponding C-C bond formation pathway would be determined by the nature of the coupling intermediates as well as the chemical bonding properties hosted by the bimetallic surfaces.

Substitutional Cu-based alloys have been popularly pursued for the improvement of the intrinsic properties of pure Cu in CO₂RR applications. The inclusion of other transition

metals (Co, Ni, Zn, Pd, Ag, Cd, and Au) or heavy p-block elements (In, Sn, Sb, Pb, and Bi) was reported by various synthetic approaches, as recently summarized by Dickinson and Symes [7]. The reduced two-carbon-containing (C_2) products were observed for alloys incorporating transition metals with Cu, while the inclusion of oxyphilic p-block elements appeared to disfavor C-C bond formation. Okatenko et al. synthesized CuGa alloy nanoparticles, revealing a significant leap in CO_2 RR stability. These nanoparticles retained catalytic activity for over 20 h, in contrast to pure Cu nanoparticles, which deactivated within just 2 h. This increased stability was attributed to the higher oxophilicity and lower electronegativity of Ga, consequently mitigating the oxidation propensity of Cu in the alloy [8]. Therefore, synthetically controlling the distribution of heterogeneous elements in bimetallic alloys becomes one of the critical factors for the success of CO_2 RR, as evidenced by the aforementioned reports.

Forming the bimetallic bifunctional interface is the alternative approach for introducing the second type of metal element to Cu. The assembled Cu/Ag and Cu/Zn bimetallic interfaces were able to reductively convert CO_2 to C_2 products [2]. Through fine-tuning the near-surface copper composition in Ag-Cu catalysts, it has been shown to notably impact the electrochemical CO_2 reduction dynamics. More specifically, reducing the copper concentration from 99% to 45% led to a substantial boost in the Faradaic efficiency of ethanol from 5% to 23%, shifting the reaction selectivity toward ethanol over ethylene [9]. Interestingly, the combination of metal-metal oxide interfaces, e.g., Cu/ ZnO^2 , Ag/ Cu_2O^2 , and Cu/alkaline metal oxide [10], as the cathode electrode materials, was observed with the two or more carbon-containing product (C_{2+}) generation, even if the presence of metal oxide phase could naturally hinder the electron conductivity. Metal oxide surfaces also show a superior dispersive effect to stabilize the deposited secondary metal element down to the scale of the single-atom site, which is facilitated by the terminal oxyl groups. For instance, single Pt and Cu atoms have been reported to be trapped by PdO and CeO_2 support materials [11,12], respectively. However, the intrinsic electronic property of the dispersed metal atom is expected to be substantially affected by the hosting metal oxide being deviated from its original electronic capability.

Electrochemical deposition has been widely used to synthesize the bimetallic catalysts. Sn and In were reported to be electrochemically deposited on Cu materials [13,14]. The co-deposition using two types of metal elements could synthesize bimetallic materials like Ag@Cu and Pd@Cu to modify the properties of parent copper and were also shown to be electrochemically co-deposited on the carbon paper [15,16]. Intriguingly, Takashima et al. prepared Cu atomic layers on Pd nanoparticles via the underpotential deposition technique as the cathode electrode, where the Pd(111) surface was dominantly observed by the X-ray diffraction crystallography analysis, and the superior Faraday efficiency (FE) of 84% for converting CO_2 to formate production was achieved [17]. Being guided by Density Functional Theory (DFT) calculations, Zhu et al. prepared the CuPd(100) interface and observed an improved C_{2+} FE at nearly 50% over that of the pure Cu catalyst at nearly 24% [18]. Given these contradistinctive Cu-Pd bimetallic examples, the interfacial morphology and the consequential electronic structure are expected to play a critical role in understanding the catalytic performance difference. With these pioneering bimetallic materials in mind, the Cu-on-Pd combination is explored computationally in this study for the purpose of understanding the microscopic interplay between these two metallic materials. Pure Pd electrodes were shown to only electrochemically convert CO_2 to CO [19] or format [20] due to the strong CO adsorption energy and inaccessible C-C bond formation barrier. Contrastively, pure Cu surfaces have been documented in the literature for observing C_{2+} product generation from electrochemical CO_2 RR. By constructing a computational model of incorporating a single copper atom on the Pd surface under the presence of oxygen gas, that not only resembles the initial condition for electrodepositing the Cu-on-Pd electrode but conceptually represents the idea of atom-efficient bimetallic catalysts. The potential catalytic mechanics and electronic structure based upon this single Cu atom catalyst model

(Cu-SAC) would be explored by the first-principle simulations as well as the corresponding kinetic modeling.

2. Results

The diffusion barrier of the single-and-bare Cu atom on the pristine Pd(111) was predicted to be 0.15 eV by the CI-NEB calculations. Such a negligible barrier intrinsically favors the mobility of the bare Cu atom on the Pd surface and subsequently leads to Cu cluster aggregation if the density of the bare Cu atom is sufficient.

Alternatively, the oxygen atoms can be used as anchors to fix the Cu atom on the Pd(111) surface to form the Cu single-atom site in this study. The dissociation barrier of the oxygen-oxygen bond on the Pd(111) surface was reported to be almost negligible at 0.1 eV [21]. The adsorbed structures of two O₂ molecules on the current 4 × 4 Pd(111) slab model are summarized in Figure 1a–f. The corresponding formation energetics (E_{form}^O) of these O₂-adsorbed structures are calculated using Equation (1).

$$E_{form}^O = E_{slab+o} - E_{slab} - N_O \times \frac{1}{2} \times E_{O_2} \quad (1)$$

where E_{slab+O} , E_{slab} , N_O , and E_{O_2} represent the energy of the metal surface with oxygen atoms, the energy of the bare metal surface, the number of oxygen atoms, and the energy of the oxygen molecule (see the Supplementary Materials for the details of E_{O_2}). It appears that oxygen species on the Pd(111) surface prefer to be in atomic form, and that would facilitate the oxygen atom diffusion to form the chemical bond with the Cu atom.

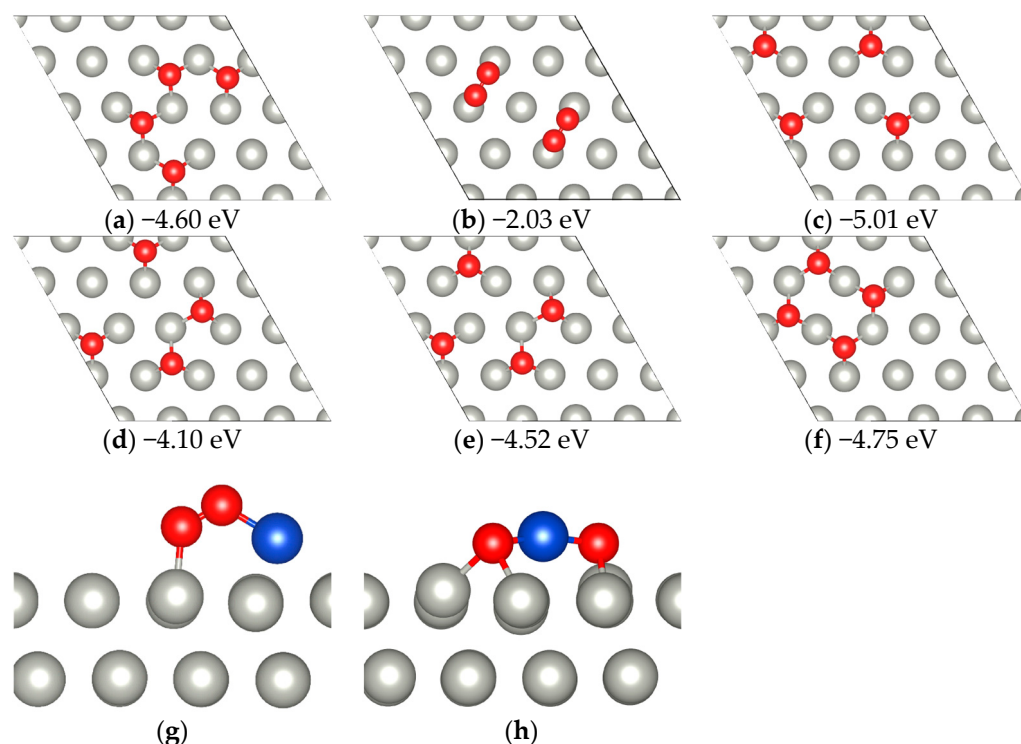


Figure 1. (a–f) The minimum structures and the corresponding formation energies of two O₂ molecule adsorbed with Cu atom on Pd(111) surface (only the top layer of Pd was shown for the purpose of clarity); (g) O₂ side-on coordination on the Cu atom; (h) dioxo-coordination Cu on Pd(111) surface forming the [CuO₂]* site. The color tubes between atoms denote chemical bonds.

The molecular oxygen may also side-on coordinate with the Cu atom, as shown in Figure 1g, where the O₂ bond length was substantially elongated from 1.16 Å (gas phase results at the current DFT setup) to 1.33 Å. The formation of the dioxo-coordinated Cu-SAC structure, denoted as [CuO₂]*, as shown in Figure 1h, was found to be 1.77 eV more

stable than that of Figure 2b. Such favorable energetics suggest $[\text{CuO}_2]^*$ formation is thermodynamically preferred for the bare single Cu atom on Pd(111) exposed to the oxygen gas.

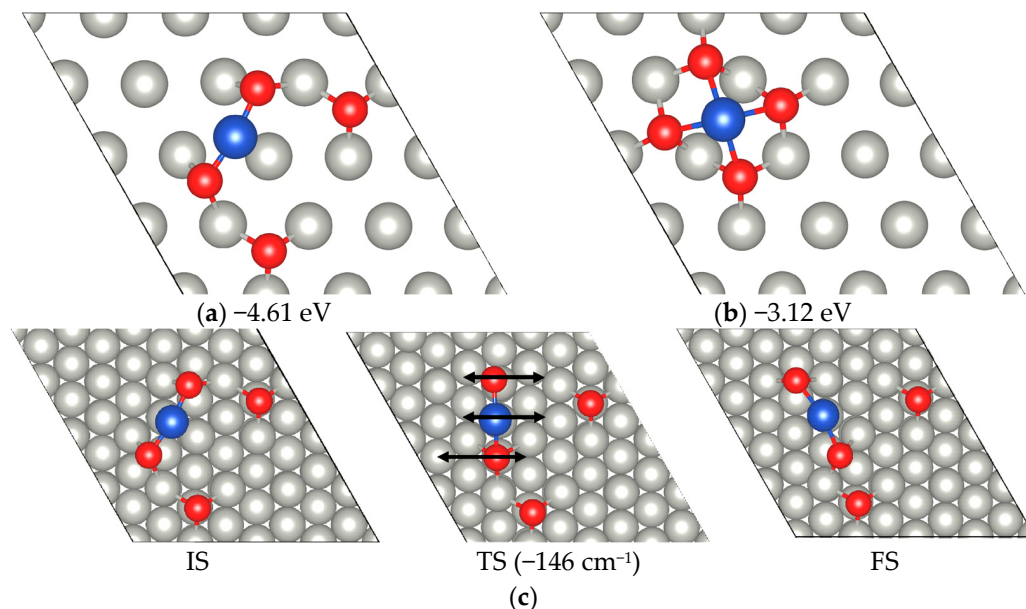


Figure 2. The minimum structures and the corresponding formation energies of (a) dioxo-coordinated Cu and (b) tetraoxo-coordinated Cu on Pd(111) surface (only the top layer of Pd was shown for the purpose of clarity); (c) the initial state (IS), TS, and final states (FS) of $[\text{CuO}_2]^*$ migration with the identified negative vibrational mode. The black arrows denote the atomic movements of the negative vibrational mode. The color tubes between atoms denote chemical bonds.

Two types of oxygen-copper coordination were identified among the various Cu + 4O models on the Pd(111) surface: dioxo-coordination and tetraoxo-coordination, as shown in Figure 2a,b, respectively, with the corresponding formation energy (E_{form}^{Cu}) calculated by Equation (2).

$$E_{form}^{\text{Cu}} = E_{\text{slab}+\text{O}+\text{Cu}} - E_{\text{slab}} - N_{\text{O}} \times \frac{1}{2} \times E_{\text{O}_2} - E_{\text{Cu}} \quad (2)$$

where $E_{\text{slab}+\text{O}+\text{Cu}}$, E_{slab} , N_{O} , and E_{O_2} represent the energy of the metal surface with oxygen atoms and Cu, the energy of the bare Pd surface, the number of oxygen atoms, and the energy of the oxygen molecule, respectively. E_{Cu} represents the energy of a single Cu atom in crystalline form. The dioxo-coordination form was identified to be thermodynamically more stable than the tetraoxo case by 1.49 eV, aligning well with the common observations of two-coordination Cu organometallic complexes in the literature [22–27]. The upper bound of the oxidation state for dioxo-coordinated Cu-SAC sites could be considered to be less than +2 due to the electronic richness of the Pd(111) surface. The diffusion barrier of the dioxo-Cu moiety was calculated to be 0.48 eV with the identified negative vibrational model at -146 cm^{-1} , as shown in Figure 2c, being notably smaller than the conventional immobile limit at 0.75 eV. However, the possible diffusion of CuO_2 units does not necessarily suggest the growth of the $(\text{CuO}_2)_n$ cluster since Cu prefers dioxo-coordination instead of tetraoxo (or more) coordination. Moreover, oxygen molecules are highly dissociable on the Pd(111) surface; $2^*[\text{CuO}_2]$ sites could not easily be converted to $[\text{OCuCuO}] + \text{O}_2$, even though the $[\text{CuO}_2]$ site is quasi-mobile. Therefore, the Cu aggregation can be substantially suppressed by the dioxo-coordination, as supported by the subsequent kinetic modeling, which includes the destruction and construction processes of the $[\text{CuO}_2]$ site under exposure to the gaseous species.

2.1. CO Dimerization Reaction on Cu-SAC

Generally, it is challenging to undergo electrochemical C-C formation at a single metal catalyst site. In the previous studies, Jiao et al. and Zhao et al. both pioneeringly provided experimental and theoretical evidence for characterizing the C-C bond formation via the cooperative effect between the single Cu atom and its coordinated carbon-based ligands [28,29]. With the synergistic effect between Pd and Cu, two CO molecules were found to bind with the $[\text{CuO}_2]^*$ site and to form an unusual tetradentate-and-tetrahedral coordinated intermediate $[\text{CuO}_2]^*(\text{CO})_2$. However, this synergistic effect was not strong enough to stabilize the C-C bond-formed species—OCCO, also known as acetylenediolate, as shown in Figure S1, where a substantial charge transfer effect from the surface materials is necessary for stabilizing such an ionic-characteristic intermediate [30]. An insightful and comparable atomistic charge analysis of CO dimerization to OCCO formation on the Cu(111) surface was demonstrated by the first-principle simulations with the explicit solvation effect [25]. With the presumption of conducting CO dimerization under quasi-dry gas/solid interface, the optimizations of the $[\text{CuO}_2]^*(\text{OCCO})$ structure were not successful and always fell back to the initial form of $[\text{CuO}_2]^*(\text{CO})_2$.

The hydrogenated CO derivative commonly undergoes the C-C bond formation process with a less demanding barrier than the parent CO dimerization process [1]. After considering one additional hydrogenation step, CO and CHO were found to coordinate with the $[\text{CuO}_2]^*$ site and form the stable $[\text{CuO}_2]^*(\text{CO})(\text{CHO})$ intermediate. The hydrogenation energy (ΔE_{hyd}) was calculated by Equation (3):

$$\Delta G_{\text{hyd}} = G_{\text{HX+site}} - G_{\text{X+site}} - \frac{1}{2} \times G_{\text{H}_2} \quad (3)$$

where the subscripts HX+site and X+site denote the hydrogenated and dehydrogenated adsorbate, respectively. The ΔG_{hyd} of converting $[\text{CuO}_2]^*(\text{CO})(\text{CO})$ to $[\text{CuO}_2]^*(\text{CO})(\text{CHO})$ was predicted at 0.87 eV for the quasi-dry scenario (without including the solvation energy contribution), being noticeably lower than the predictions of the fully solvated Cu electrode surfaces at 1.29 or 0.96 eV on Cu(111) and Cu(100) surfaces [31,32], respectively. If the homogenous solvation effect is taken into account, the predicted hydrogenation-free energy would become even smaller due to the solution environment preferentially favoring *CHO over *CO. Such a solvation preference can be supported by the dipole moments of the molecular CuCO and CuCHO species in vacuum were 2.31 and 3.46 Debye, respectively, as estimated at the B3LYP/LANL2DZ level. The current CO hydrogenation step (<0.9 eV) could be experimentally accessible with a suitable design of a proton source (e.g., the proton-accessible polymer binder) under the gas diffusion electrode setup.

Additionally, the $[\text{CuO}_2]^*(\text{CO})(\text{COH})$ intermediate was predicted to be unstable, and these optimizations led to either hydrogen dissociation (forming the surface hydroxyl species) or *COH migration to the Pd surface, as shown in Figure S2. The observation of the *COH migration can be interpreted as indicating that *COH demands to form the multi-bond character at the carbon terminal, where coordinating with the Cu-SAC site is no longer a sufficient option to satisfy its chemical bonding pattern. The *COH migration to the Pd surface could subsequently eliminate the possibility of $\text{CO} \bullet \bullet \text{COH}$ coupling on the Cu-SAC site, and the migrated *COH species may result in the generation of electrochemically reduced C1 products. Consequently, both scenarios of $[\text{CuO}_2]^*(\text{CO})(\text{COH})$ species imply that C-C bond formation through CO and COH coupling is an inaccessible process.

With the rationale provided above, $[\text{CuO}_2]^*(\text{OCCHO})$ becomes the only stable intermediate for the C-C bond formation on the Cu-SAC site. The transition state of CO and CHO dimerization was characterized by CI-NEB calculation with the identified negative vibrational mode shown in Figure S4. The mechanistic profile, TS structure, and the characteristic TS vibrational mode of C-C bond formation were schematically shown in Figure 3, starting from CO adsorption on the bare $[\text{CuO}_2]^*$ site. The adsorption energies of the first and second CO molecules are −0.66 eV and −0.65 eV, respectively. With a suitable proton source, di-carbonyl intermediates can be hydrogenated to $[\text{CuO}_2]^*(\text{CO})(\text{CHO})$. The C-C

bond formation barrier was predicted at the accessible scale at 0.67 eV in comparison with those predicted values using the common Cu surfaces [1], while this CO-CHO coupling reaction energy was predicted to be an exothermic step at -0.12 eV. Notably, the relative charge difference of the top Pd layer (see the right y-axis of Figure 3) appears to suggest that these Pd atoms transfer electron density to the adsorbate moiety to facilitate the CO-CHO couple process, particularly at the TS structure. The Bader charges of the top-layer Pd atoms of each slab model along the reaction coordinate in Figure 3 were taken into account. The origin of the relative charge transfer (labeled as 0.00) was taken with respect to the corresponding Pd atoms of the $[\text{CuO}_2]^*$ model. All of the intermediate structures along the mechanistic profile are shown in Figure 4 (top view) and Figure S5 (side view).

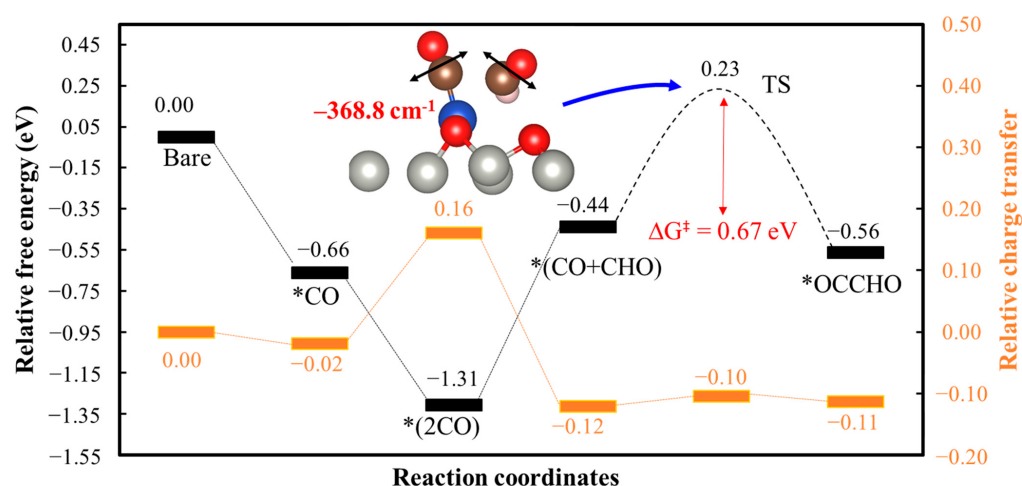


Figure 3. The predicted relative free energy profile in eV (left axis) of C-C bond formation on $[\text{CuO}_2]^*$ site, and the relative charge difference (right axis) of the Pd atoms at the top layer in respect to those of the bare $[\text{CuO}_2]^*$ model. The black arrows denote the atomic movements of the negative vibrational mode.

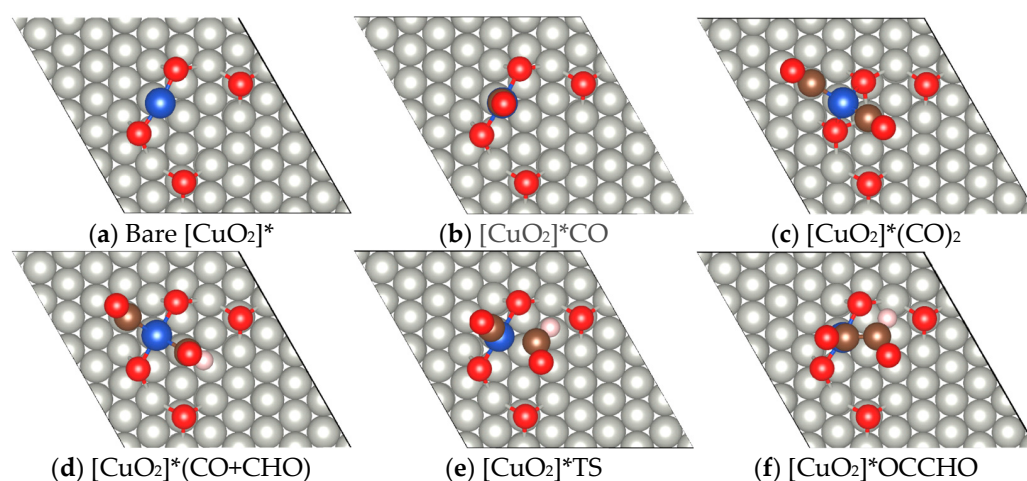


Figure 4. The top-view structures of CO + CHO coupling to $^*\text{OCCOH}$ on Cu-SAC, and TS denotes the transition state of $^*(\text{CO}\cdots\text{CHO})$.

Double hydrogenation of $[\text{CuO}_2]^*(\text{CO})(\text{CO})$ intermediate to form $[\text{CuO}_2]^*(\text{CHO})(\text{CHO})$ was found to be inaccessible, either. One hydrogen dissociation from the artificially built $[\text{CuO}_2]^*(\text{CHO})(\text{CHO})$ species was found to be highly exothermic and resulted in the formation of surface hydroxyl, as shown in Figure S3. Therefore, the $[\text{CuO}_2]^*(\text{CHO})(\text{CHO})$ species cannot be involved in the C-C formation on the $[\text{CuO}_2]^*$ site either.

2.2. Possible Side Reactions

Hydrogen evolution reaction (HER) commonly competes with CO reduction on metal surfaces due to the intrinsic and highly accessible nature of transforming protons into hydrogen gas. The free energy of forming $[\text{CuO}_2]^*\text{H}$ species from the bare $[\text{CuO}_2]^*$ site was predicted to be 0.81 eV, and that is generally comparable with the hydrogenation step of $[\text{CuO}_2]^*(\text{CO})_2$ to form $[\text{CuO}_2]^*(\text{CO})(\text{CHO})$ at 0.87 eV. However, the availability of bare $[\text{CuO}_2]^*$ sites would be significantly suppressed by the diffusivity of CO gases, as evidenced by the negative adsorption energy of CO on the $[\text{CuO}_2]^*$ site at -0.66 eV. That consequently indicates that HER could be suppressed by CO-based reduction reactions, as has also been rationalized by Bagger et al. [17,33].

CO oxidation to CO_2 , though abstracting the oxygen atom of the $[\text{CuO}_2]^*$ site, was considered to be another non-negligible side reaction to deplete the availability of the $[\text{CuO}_2]^*$ site. The corresponding oxygen-abstraction barrier was predicted at 0.58 eV as schematically shown in Figure S6. Alternatively, the degraded $[\text{CuO}_2]^*$ site, i.e., $[\text{CuO}]^*$ species, can be restored by the oxygen molecule on the Pd(111) surface. The diffusion of O_2 on Pd(111) was predicted to be barrierless and exothermically coordinated with $[\text{CuO}]^*$ species to form a superoxo intermediate— $[\text{O}_2\text{CuO}]^*$, as shown in Figure S7a,b. The oxygen-oxygen bond-breaking barrier of the superoxo intermediate to regenerate the $[\text{CuO}_2]^*$ site was predicted to be 0.30 eV, as demonstrated by Figure S7b–d. The overall stability of $[\text{CuO}_2]^*$ sites subject to the presence of CO and O_2 gaseous molecules could be kinetically maintained.

2.3. Kinetics Results

Microkinetics simulations were conducted to analyze the catalytic site coverage subject to the presumptive reaction condition to mimic the gas diffusion electrode setup based on the DFT reaction energetics schematically depicted in Figure 5. This kinetics model was constructed based on the consideration of a quasi-dry gas/solid interface and proton transfer from the electrode environment as rare events. Consequently, the contribution of the protic solvent environment was assumed to be controlled via the experimental means to assistively hydrogenate the $[\text{CuO}_2]^*\text{CO}$ or $(\text{CO})_2[\text{CuO}_2]^*(\text{CO})_2$ intermediates. Subsequently, hydrogenated species like $[\text{CuO}_2]^*(\text{CO})(\text{CHO})$ could undergo carbon-carbon formation, overcoming the predicted free energy barrier at 0.67 eV as proposed in Figure 3. With the possibility of carbon-carbon bond formation, a C_2 species could be generated using the current Cu-SAC model-like catalysts. The current kinetic modeling did not intend to predict the exact population of the electrochemically reduced C_1 or C_2 products; however, the temperature-dependent catalytic site evolution was the main concern.

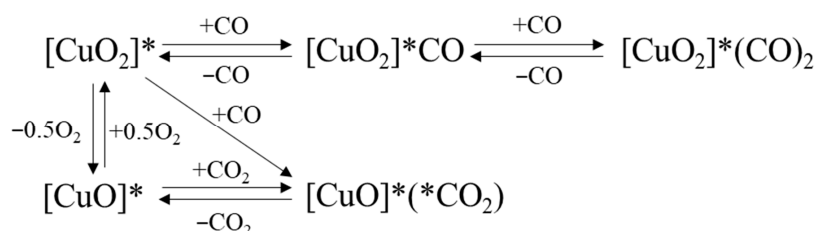


Figure 5. Reaction networks for CO reduction to C-C bond formation on $[\text{CuO}_2]^*$ site.

In order to understand the mutual effect of CO oxidation at SAC-site, CO_2 desorption, and SAC-site regeneration by O_2 , the initial partial pressures of CO, O_2 , and CO_2 were investigated in Table S1. Figure 6 provides the kinetic histograms of the SAC-site formation subject to the various initial gas pressures at 200–600 K. It appears that only the bare $[\text{CuO}_2]^*$ or $[\text{CuO}]^*$ sites can exist due to the strong molecule desorption at high temperatures, regardless of the initial gas pressure. The scenarios B, C, and E appear to favor the formation of $[\text{CuO}_2]^*(\text{CO})_2$, being substantially populated at room temperature conditions and above. The presence of O_2 gas in the system appears to support the formation of $[\text{CuO}_2]^*$ site,

which consequently facilitates the generation of $[\text{CuO}_2]^*(\text{CO})_2$, eventually leading to carbon-carbon formation if suitable hydrogenation is provided. Such an observed oxygen-philic effect implies the superior chemical resistance of Cu-SAC catalysts under dry ambient conditions. Contrastively, the absence of O_2 in the system cannot provide the regeneration of $[\text{CuO}_2]^*$ sites, and CO oxidation at the SAC site eventually inhibits the catalytic pathway, as shown in Figure 6a,d.

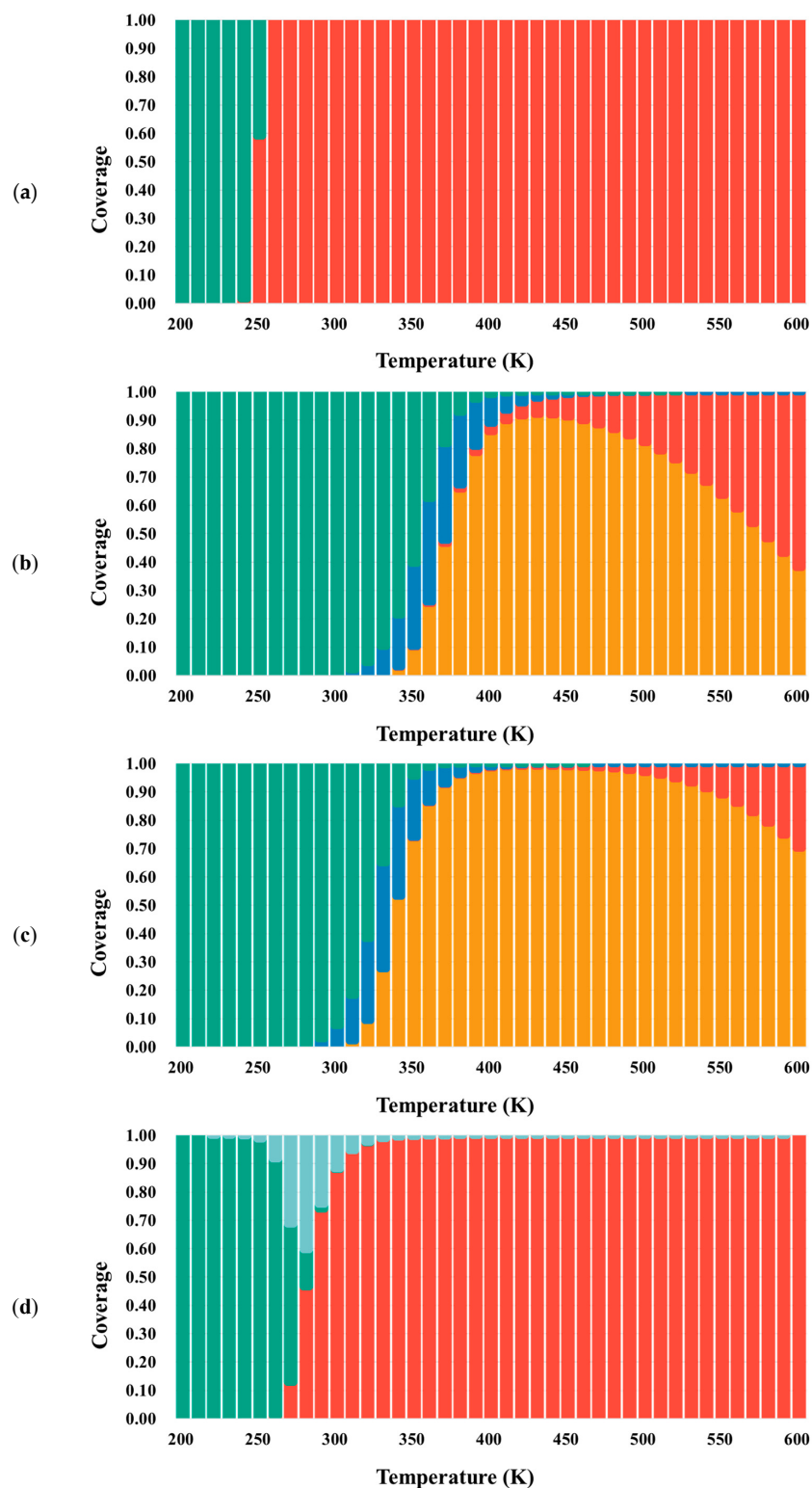


Figure 6. Cont.

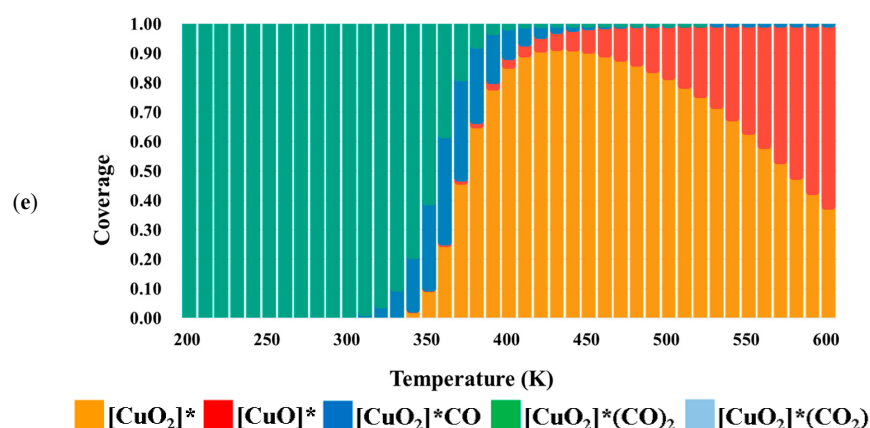


Figure 6. Kinetic modelings of the surface evolution subject to the initial gas pressures of CO, O₂, and CO₂ between 200–600 K. The pressures (in bar) of the gaseous species (CO:O₂:CO₂) are: (a) 1.0:0.0:0.0, (b) 1.0:0.1:0.0, (c) 0.1:1.0:0.0, (d) 1.0:0.0:0.1, and (e) 1.0:0.1:0.1, respectively.

3. Method

3.1. First-Principle Simulations

All of the DFT calculations were performed with the Vienna ab-initio simulation package (VASP) [34–36]. The projector augmented wave (PAW) method [37] and generalized gradient approximation (GGA) with Perdew-Burke-Ernzerh (PBE) exchange-correlation functional [38] were used. The spin polarization is considered in our calculation without constraining further atomic magnetic moments (ISPIN = 2 and MAGMOM = NIONS). The kinetic cut-off energy was 450 eV, and the Monkhorst-Pack mesh k-points that we chose were $9 \times 9 \times 9$ and $3 \times 3 \times 1$ for bulk and surface optimization, respectively. The calculated Pd lattice constant is 3.90 Å, which is consistent with the literature (3.89 Å) [39]. A $p(4 \times 4)$ Pd(111) surface with 6 layers was used for Cu-SAC and the adsorbate simulations. All of the slab models include a 15 Å thick vacuum region above the surface. For structure optimization, the bottom two layers of Pd(111) atoms are fixed, and the others are fully relaxed until the energy difference is less than 0.03 eV Å^{−1}. The climb image nudged elastic band (CI-NEB) method was used for the transition state search [40]. The adsorption energy (E_{ad}) is calculated by the following equation:

$$E_{ad} = E_{slab+adsorbate} - E_{slab} - E_{adsorbate} \quad (4)$$

where $E_{slab+adsorbate}$, E_{slab} , and $E_{adsorbate}$ represent the energy of adsorbed species on the clean surface, bare surface, and molecules, respectively. The schematic representations of all slab models were generated by VESTA [41].

3.2. Kinetic Modeling

The calculated reaction and activation energies by DFT were utilized for the kinetics analysis using the MKMCXX program [42]. The rate constants of the adsorption and desorption of molecules from the surface are described by Equations (5) and (6), respectively [43,44]:

$$k_{ads} = \frac{PA}{\sqrt{2\pi mk_b T}} S \quad (5)$$

$$k_{des} = \frac{k_b T^3}{h^3} \frac{A(2\pi mk_b)}{\sigma \theta_{rot}} e^{-E_{des}/k_b T} \quad (6)$$

where P , A , and S represent the partial pressure of the adsorbed gas, the surface area of the active site, and the sticking coefficient, respectively. The variables m , k_b , h , and T represent the mass of the molecule, Boltzmann constant, Planck constant, and reaction temperature, respectively. The variables σ and θ_{rot} are the symmetry number of molecules and the

rotational temperature of molecules, respectively. E_{des} denotes the desorption energy of adsorbed gas molecules from the surface.

4. Conclusions

In this study, electrochemical C-C bond formation by the CO and CHO coupling process using a dioxo-coordinated Cu single atom site— $[\text{CuO}_2]^*$, supported on a Pd(111) surface—is computationally characterized for the CO reduction application. A tetradentate-and-tetrahedral species— $[\text{CuO}_2]^*(\text{CO})_2$ —was identified as the stable intermediate after exposure to CO gaseous molecules. Hydrogenating the carbonyl group to CHO was predicted to be 0.87 eV electrochemically, which is conceivably lower than that of the corresponding step for conventional Cu surfaces. Consequently, this proposed pathway could be worthwhile for future experimental explorations. A substantial charge transfer effect in a synergistic manner from the top layer Pd atoms to the adsorbate moiety, particularly at the TS structure, was observed, and that was consequently attributed to the accessible C-C bond formation barrier at 0.67 eV. The reaction energy of C-C bond formation was determined to be exothermic at -0.21 eV, which is a favorable chemical equilibrium condition. Considering the temperature effect and pressure of the gaseous molecules (CO , CO_2 , O_2), the $[\text{CuO}_2]^*(\text{CO})_2$ intermediate could be substantially populated at room temperature, being chemically resilient under the dry ambient conditions.

Supplementary Materials: The following supporting materials can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics11100378/s1>, Figure S1. (a) artificially constrained initial structure $^*\text{OCCO}$. (b) fully optimized structure from (a) to form $[\text{CuO}_2]^*(\text{CO})_2$; Figure S2. The optimized structures (a) forming surface OH group and (b) migrated COH group to Pd surface from the pre-optimized initial structure of $[\text{CuO}_2]^*(\text{CO})(\text{COH})$. Both cases denote $[\text{CuO}_2]^*(\text{CO})(\text{COH})$ species cannot be a stable intermediate; Figure S3. (a) The pre-optimized initial structure of $[\text{CuO}_2]^*(\text{CHO})_2$ and (b) its optimized structure as $[\text{CuO}_2]^*(\text{CHO})(\text{CO})$ + surface H; Figure S4. The imaginary frequency mode at -368.8 cm^{-1} for TS of CO-CHO coupling. The arrows show the direction of vibrations; Figure S5. The side-view structures of CO + CHO coupling to $^*\text{OCCOH}$ on Cu-SAC, and TS denotes the transition state of $(\text{CO}\cdots\text{CHO})$; Figure S6. The reactant (a), transition state (b), and product (c) of CO oxidation on the $[\text{CuO}_2]$ site; Figure S7. The O_2 adsorption (a) and superoxo formation (b) on the $[\text{CuO}]^*$ site (the corresponding reaction energy from (a) to (b) was predicted at -0.59 eV. The reactant (b), transition state (c), and product (d) of $[\text{CuO}_2]$ site regeneration; Figure S8. Kinetic modeling results using the approximated $G_{\text{O}_2} = -9.89$ eV (other parameters kept the same as Figure 6: (a) 1.0:0.0:0.0, (b) 1.0:0.1:0.0, (c) 0.1:1.0:0.0, (d) 1.0:0.0:0.1, and (e) 1.0:0.1:0.1, respectively; Table S1. The initial partial pressure (bar) of CO_2 , O_2 and CO_2 gases in the current study; Table S2. The optimized Cartesian coordinates (in Å) of the minimum structures listed in Figure 3.

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