Subsurface oxide plays a critical role in CO₂ activation by Cu(111) surfaces to form chemisorbed CO₂, the first step in reduction of CO₂

Marco Favaro<sup>a,b,c,1</sup>, Hai Xiao<sup>d,e,1</sup>, Tao Cheng<sup>d,e</sup>, William A. Goddard III<sup>d,e,2</sup>, Junko Yano<sup>f</sup>,<sup>1,2</sup>, and Ethan J. Crumlin<sup>b,2</sup>

<sup>a</sup>Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, CA 94720; <sup>b</sup>Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720; <sup>c</sup>Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720; <sup>d</sup>Joint Center for Artificial Photosynthesis, California Institute of Technology, Pasadena CA 91125; <sup>e</sup>Materials and Process Simulation Center, California Institute of Technology, Pasadena CA 91125; and <sup>f</sup>Molecular Biophysics and Integrated Bioimaging Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

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A national priority is to convert CO₂ into high-value chemical products such as liquid fuels. Because current electrocatalysts are not adequate, we aim to discover new catalysts by obtaining a detailed understanding of the initial steps of CO₂ electroreduction on copper surfaces, the best current catalysts. Using ambient pressure X-ray photoelectron spectroscopy interpreted with quantum mechanical prediction of the structures and free energies, we show that the adsorption of a thin suboxide of a close-packed Cu surface is essential to bind the CO₂ in the physisorption configuration at 298 K, and we show that this suboxide is essential for converting to the chemisorbed CO₂ in the presence of water as the first step toward CO₂ reduction products such as formate and CO. This optimum suboxide leads to both neutral and charged Cu surface sites, providing new insights into how to design improved carbon dioxide reduction catalysts.

CO₂ reduction | suboxide copper | ambient pressure XPS | density functional theory | M06L

The discovery of new electrocatalysts that can efficiently convert carbon dioxide (CO₂) into liquid fuels and feedstock chemicals would provide a clear path to creating a sustainable hydrocarbon-based energy cycle (1). However, because CO₂ is highly inert, the CO₂ reduction reaction (CO₂RR) is quite unfavorable thermodynamically. This makes identification of a suitable and scalable catalyst an important challenge for sustainable production of hydrocarbons. We consider that discovering such a catalyst will require the development of a complete atomistic understanding of the adsorption and activation mechanisms involved. Here the first step is to promote initiation of reaction steps.

Copper (Cu) is the most promising CO₂RR candidate among pure metals, with the unique ability to catalyze formation of valuable hydrocarbons (e.g., methane, ethylene, and ethanol) (2). However, Cu also produces hydrogen, requires too high an overpotential (>1 V) to reduce CO₂, and is not selective for desirable hydrocarbon and alcohol CO₂RR products (2). Despite numerous experimental and theoretical studies, there remain considerable uncertainties in understanding the role of Cu surface structure and chemistry on the initial steps of CO₂RR activity and selectivity (3, 4). To reduce CO₂ to valuable hydrocarbons, a source of protons is needed in the same reaction environment (2), with water (H₂O) the favorite choice. Thus, H₂O is often the solvent for CO₂RR, representing a sustainable pathway toward solar energy storage (1). However, we lack a comprehensive understanding of how CO₂ and H₂O molecules adsorb on the Cu surface and interact to first dissociate the CO₂ (5, 6). An overview of the various surface reactions of CO₂ on Cu(111) is reported in Fig. 1, illustrating the transient carbon-based intermediate species that may initiate reactions.

Previous studies using electron-based spectroscopies observed physisorption of gas-phase g- CO₂ at 75 K, whereas a chemisorbed form of CO₂ was stabilized by a partial negative charge induced by electron capture (CO₂<sup>-</sup>) (Fig. L4) (7, 8). The same experiments showed that no physisorption is observed upon increasing the temperature of the Cu substrate to room temperature (r.t.) (298 K) (Fig. 1B). Previous ex situ studies performed in ultrahigh vacuum (UHV) (about 10<sup>-9</sup> Torr) after relatively low CO₂ exposures [from a few to hundreds of Langmuir (L)] at temperatures between 100 K and 250 K did not reveal CO₂ dissociation or adsorption on clean Cu(100) (9), Cu(110) (10), and Cu(111) (11). However, Nakamura et al. (12) showed that when the exposure is increased to sensibly higher values (pressures ranging between 65 Torr and 1,300 Torr for hundreds of seconds), a nearly first-order dissociative adsorption of CO₂ on clean Cu(110) can be detected between 400 K and 600 K (with an activation energy of about 67 kJ·mol<sup>-1</sup>), according to the reaction CO₂<sub>ads</sub> → CO<sub>ads</sub> + O<sub>ads</sub> (where O<sub>ads</sub> stands for surface adsorbed oxygen). A similar phenomenology was also observed by Rasmussen et al. (9) on clean Cu(100) for CO₂ pressures of about 740 Torr and temperatures in the range of 475–550 K (finding an activation energy of about 93 kJ·mol<sup>-1</sup>). On the other hand, a recent study by Eren et al. (13) performed at much lower CO₂ partial pressures (between 0.05 Torr and 10 Torr) revealed that CO₂ can dissociatively adsorb on Cu(100) and Cu(111) with the consequent formation of surface oxygen as well. Indeed it has been suggested that the CO₂ might dissociate more easily on preoxidized Cu surfaces (3), but there is little evidence to support this important concept. Activation of CO₂ via assumed chemisorbed CO₂ species was reported also on Cu stepped surfaces (11, 14), but direct in situ proof of the existence of such species on Cu(111) is lacking. These uncertainties and discrepancies indicate the importance of determining the initial species.

Significance

Combining ambient pressure X-ray photoelectron spectroscopy experiments and quantum mechanical density functional theory calculations, this work reveals the essential first step for activating CO₂ on a Cu surface, in particular, highlighting the importance of copper suboxide and the critical role of water. These findings provide the quintessential information needed to guide the future design of improved catalysts.

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1M.F. and H.X. contributed equally to this work.

2To whom correspondence may be addressed. Email: wag@wag.caltech.edu, jyano@lbl.gov, or ejcrumlin@lbl.gov.

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formed while exposed to realistic gas pressures of CO₂ and H₂O (13, 15).

To advance this understanding, we investigated in detail the initial steps of CO₂ adsorption both alone and in the presence of H₂O on Cu(111) and suboxide surfaces (Cu₆₃₋₁₅,O) via in situ probing of the electronic structure of the surface and reaction products, using ambient pressure X-ray photoelectron spectroscopy (APXPS) performed with soft X-rays (200–1,200 eV) at the solid/gas interface. These studies are complemented with molecular structures and binding free energies of the reaction products, using density functional theory (DFT) to study the gas-phase CO₂ that stabilizes a physisorbed linear CO configuration (g-CO₂, Fig. 1C). In addition, H₂O in the gas phase (g-H₂O), aided by small amounts of suboxide, drives CO₂ adsorption through the transition from the linear physisorbed state to a bent chemisorbed species (b-CO₂), which with the aid of H₂O promotes the initial reduction of CO₂ to formate (HCOO−, Fig. 1D).

The Cu surface exposing mainly the Cu(111) orientation was prepared in situ from a polycrystalline sample, by repeated argon (Ar) sputtering (normal incidence, 2 keV, 45 min) and annealing cycles in hydrogen (0.15 Torr) at 1,100 K (60 min), to obtain a typical 1 × 1 reconstruction as shown by the low-energy electron diffraction (LEED) pattern in Fig. 2A (17). Scanning electron microscopy (SEM) measurements Fig. 2A confirm that this sputtering and annealing procedure leads to crystalline regions with tens of micrometers mean sizes. The characterized sample surface location remained unchanged throughout the APXPS experiments. The collected spectra were averaged over a beam spot size of ~40.8 mm in diameter. Although we cannot exclude possible contributions from the presence of grain boundaries, averaging the data over the large probed area led to an eventual grain boundary contribution less than 1% of the overall measured signal, which is below the detection limit. Therefore, their physical/chemical features were not captured in the spectra and do not constitute the focus of this study.

During the APXPS experiments (Fig. 2B) performed at r.t. (298 K), CO₂ was first introduced at 0.7 Torr on the pristine metallic Cu(111) surface. For the other experimental conditions and investigated surfaces (see Table 1 and Supporting Information for further details), the CO₂ partial pressure (p(CO₂)) was kept at 0.35 Torr whereas the total pressure (p(total)) was kept constant at 0.7 Torr by codosing H₂O. The APXPS measurements were performed while dosing CO₂ on both metallic Cu(111) and Cu₆₃₋₁₅,O surfaces, whereas CO₂ and H₂O were codosed on metallic Cu(111), Cu₆₃₋₁₅,O, and Cu₆₃₋₂₅,O suboxide surfaces (18). The sample surface was clean and no evident Cu or O-based contaminations were observed after the cleaning procedure, as shown in Fig. S1. In addition, the in situ mass analysis of the reactants (O₂, CO₂, and H₂O) using a conventional quadrupole mass spectrometer (QMS) mounted on the analysis chamber (and operating at a partial pressure of about 10⁻⁶ Torr), did not reveal CO cross-contaminations of the gases. However, Fig. S2 shows that, concomitantly with the gas dosing
To disentangle the role of oxygen on the surface and subsurface regions, we carried out a similar analysis on O 1s core-level spectra (Fig. 2D). The analysis performed on C 1s was used to help the interpretation of the O 1s spectral envelope while also accounting for the different relative abundances. As with C 1s, we partition the O 1s spectral window into three regions. At low BEs, we identify the states of O bonded as follows: (i) surface adsorbed O (Cu-O$_{ads}$) on metallic Cu and on suboxidic Cu$_x$O$_{sub}$ structures (Cu$_x$O$_{adss}$) at 531.0 eV and 529.6 eV, respectively (15, 25–27); (ii) subsurface adsorbed O (O$_{sub}$) on metal Cu (Cu-O$_{sub}$) at 529.8 eV (27) (as we discuss in a later section, such a presence of suboxide plays an important role in stabilizing the l-CO$_2$); and (iii) for Cu$_{O_x}$O the O 1s is centered at 530.3 eV (15, 18, 25). It is noteworthy that O$_{ads}$ groups on the Cu surface can serve as nucleation sites for hydroxylation when in the presence of H$_2$O. However, the detection of eventual Cu-OH groups via photoelectron chemical shift identification is compromised by the fact that in the same spectral range (530.6–530.8 eV) several oxygen-based species overlap (such as formate, C-(OH), and O-R species with R = −CH$_3$, −CH$_2$CH$_2$). On the other hand, the presence of the C 1s spectral counterpart of formate and C-(OH) (well discriminated in BE) allows us to build up a consistent and reliable fitting. Therefore, although we cannot completely exclude the presence of surface Cu-OH, its concentration is most likely below the detection limit of the technique (about 0.02 ML). C-O bonds fall instead in the middle region, namely between 530.8 eV and 532.0 eV. Within this range, from lower to higher BE, we identify chemisorbed CO$_2$, C-(OH), and formate (HCOO−) overlapping at 530.8 eV; l-CO$_2$ at 531.4 eV; and carbonates at 531.8 eV (15, 25). Finally, at high BE we observed adsorbed H$_2$O (H$_2$O$_{ads}$) at 532.4 eV (15, 25).

The difficulty in discriminating between Cu$^0$ and Cu$^+$ using Cu core levels has been well established and is clearly evidenced from Fig. S5A, reporting the Cu 3p photoelectron spectra. To overcome this limitation, the various Cu surfaces were characterized by means of the Cu Auger L$_{2,3}$M$_{4,5}$M$_{4,5}$ transition and the valence band (VB) as described in Discussion and as reported in Figs. S3B and S6.

It is important to note that the BE of the aforementioned chemically shifted components for C 1s and O 1s do not change with the experimental conditions (within the spectral resolution, ~0.15 eV), with an exception only for the adsorbed CO$_2$, where the adsorption configuration (b-CO$_2$ vs. l-CO$_2$) depends on the experimental conditions. In particular, we observe an important decrease by ~0.50 eV (Fig. 2B) of the C 1s BE when CO$_2$ is codosed with H$_2$O on the metallic Cu(111) surface (Fig. S2). This work was inspired by similar experiments previously reported by Deng et al. (15), where they dosed CO$_2$ and H$_2$O separately and together on a polycrystalline (nonoriented) Cu sample. The authors observed the presence of an adsorbed CO$_2$ species at r.t. (with the corresponding C 1s centered at BE = 288.4 eV), which they labeled as a negatively charged adsorbed CO$_2^−$.

We believe their adsorbed CO$_2$ species could actually be attributed to the l-CO$_2$ configuration observed and computed in this work. Interestingly, however, the authors did not observe a new component in the adsorbed CO$_2$ spectral region (287.9–288.5 eV i.e., the b-CO$_2$), passing from the exposure to pure CO$_2$ to CO$_2$+H$_2$O. In addition, we observe only a weak presence of reaction products between CO$_2$ and H$_2$O codosed at r.t. (Fig. 2 C and D), whereas Deng et al. (15) observed the significant development of the methoxy group spectral component (−OCH$_3$, BE = 285.2 eV) when codosing CO$_2$ and H$_2$O. These differences might be attributed by the higher experimental gas pressures used in this study, as well as potentially different investigated surface structures formed by different surface cleaning and annealing procedures. Overall, these differences can potentially lead to a different surface reactivity. The results reported by Deng et al. (15) have been obtained on a polycrystalline surface

<table>
<thead>
<tr>
<th>Experimental condition</th>
<th>Surface structure</th>
<th>Gas environment</th>
<th>Total pressure, Temperature, Torr, K</th>
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<tbody>
<tr>
<td>A</td>
<td>Metallic Cu(111)</td>
<td>CO$_2$</td>
<td>0.7</td>
</tr>
<tr>
<td>B</td>
<td>Metallic Cu(111)</td>
<td>CO$_2$+H$_2$O (1:1)</td>
<td>0.7</td>
</tr>
<tr>
<td>C</td>
<td>Cu$_{O_x}$</td>
<td>CO$_2$+H$_2$O (1:1)</td>
<td>0.7</td>
</tr>
<tr>
<td>D</td>
<td>Cu$_{O_x}$</td>
<td>CO$_2$</td>
<td>0.7</td>
</tr>
<tr>
<td>E</td>
<td>Cu$_{O_x}$</td>
<td>CO$_2$</td>
<td>0.7</td>
</tr>
</tbody>
</table>

(for pressures exceeding 10$^{-6}$ Torr), uptake of carbon contaminations readily occurred [the corresponding binding energy (BE) being centered at 285.1 eV). Therefore, we cannot completely exclude eventual side reactions and interplay between carbon contaminations and the copper surface.

To understand how interactions between the catalyst surface and CO$_2$ determine the mechanisms of the initial CO$_2$ reduction steps, we established the experimental conditions under which a chemisorbed CO$_2$ state can be stabilized. This provides the basis for tailoring novel catalysts with improved electrochemical performance toward the CO$_2$RR.

Previously it was difficult to probe these early steps experimentally because r.t. studies require pressures of CO$_2$ high enough to stabilize a physisorbed configuration sufficiently to allow detailed investigations of various adsorption dynamics, but this high-pressure gas makes it difficult to use electron-based spectroscopies. Our use of APXPS overcomes this difficulty (19–21). To discriminate between physisorbed and chemisorbed CO$_2$, we monitor the spectral BE shifts of the corresponding C 1s and O 1s photoelectron peaks as a function of the different surfaces and experimental conditions. Physisorption mediated by weak van der Waals (vdW) interactions [surface binding energies of a few millielectronvolts, comparable to $k_BT = 25.7$ meV at 298 K (7)] generally leaves the adsorbate electronic structure unchanged compared with its gas-phase configuration (7, 22–24). In contrast, the chemical bonding needed to form chemisorbed CO$_2$ on the Cu surface redistributes the electronic density in the adsorbate, leading to appreciable BE shifts compared with the physisorbed state (8).

The adsorption state of CO$_2$ and the overall surface chemistry of the various systems were monitored by multipeak deconvolution on both the C 1s and O 1s photoelectron spectra (Fig. 2 C and D), using chemically shifted components sensitive to the initial state effects. Fig. S3 A and B reports the integrated peak areas of the chemically shifted components for C 1s and O 1s deconvolution, respectively, normalized by the total area under the peaks over the entire BE range. C 1s and O 1s photoelectron spectra were acquired under APXPS conditions at photon energies of 387 eV and 632 eV, respectively. Because the kinetic energy of the escaping C 1s and O 1s photoelectrons is about 100 eV, the probed depth, 3λ (λ is the electron mean free path) is about 1.2 nm, from the topmost layer (Fig. 2B).

The deconvoluted C 1s spectra (see Supporting Information for further details) exhibit two main spectral regions: (i) At low BEs we see chemical species that can be associated as graphitic carbon (284.5 eV), sp$^2$ (C-C) carbon (285.2 eV), and C-O(H) bonds (286.3 eV), based on the literature values (15). (ii) At higher BEs we see spectral fingerprints of higher oxidized carbon structures and adsorbed CO$_2$, where deconvolution of the spectra indicates the presence of formate (HCOO−) (287.3 eV), chemisorbed (denoted b-CO$_2$ for bent), and physisorbed CO$_2$ (denoted l-CO$_2$ for linear) (287.9 eV and 288.4 eV, respectively) and carbonate (−CO$_3^2$−) (289.4 eV) (15). Finally, a sharp peak centered at about 293.3 eV corresponds to the photoelectron emission of g-CO$_2$ (Fig. S4).
likely exposing extended grain boundaries and coexistence of different surface orientations, whereas the present study was performed on an oriented surface. Our experimental results can be explained in terms of two different adsorption configurations of CO$_2$: (i) physisorbed linear CO$_2$ (l-CO$_2$) above 0.150 Torr (Fig. 3) stabilized by small amounts of residual O$_{sub}$, and (ii) chemisorbed CO$_2$ (c-CO$_2$) that is formed only after adding H$_2$O, but also requires O$_{sub}$.

For pure CO$_2$ on pristine metallic Cu(111) (Fig. 2 C and D, experimental condition A), we observe experimentally a weakly adsorbed l-CO$_2$ at 298 K with a pressure of 0.7 Torr CO$_2$. This does not agree with our DFT calculations, performed at the M06L level, including the electron correlation required for London dispersion (vdW attraction) (16). We find an electronic binding energy of $\Delta E = -0.36$ eV and an enthalpy of binding of $\Delta H(298 \text{ K}) = -0.30$ eV [after including zero-point energy (ZPE) and specific heat]; however, due to the large decrease in entropy from the free CO$_2$ molecule, the free energy for l-CO$_2$ is uphill by $\Delta G(298 \text{ K}, 0.7 \text{ Torr}) = +0.27$ eV. These energetics would require pressures of 33 atm ($\approx 2.5 \times 10^{-3}$ Torr) for the adsorbed l-CO$_2$ to be observed at 298 K on pure metallic Cu(111). This is in line with previous experimental observations reported in the literature (also Fig. 1), where only l-CO$_2$ was observed on metallic Cu(111) surface at 298 K (7).

On the other hand, our DFT calculations show that very small amounts of suboxide (one suboxide O per every four surface Cu in our calculations, but likely much smaller levels are sufficient) lead to a negative free energy of $\Delta G(298 \text{ K}, 0.7 \text{ Torr}) = -0.12$ eV, which would stabilize physisorbed l-CO$_2$ at our experimental conditions. Indeed, our experiments find evidence for small amounts ($\approx 0.08$ ML) of surface suboxide on our freshly prepared Cu(111) (Fig. 2D, experimental condition A). Such subsurface adsorbed O (denoted Cu-O$_{sub}$) has been observed often near the Cu surface, most likely resulting from oxygen impurities in the chamber (28) or partial dissociative adsorption of CO$_2$ (13). Interestingly, even if CO$_2$ is still in a linear configuration (similar to the gas phase), we observe experimentally that the O 1s and C 1s core-level BEs of the adsorbed l-CO$_2$ shift downward by $\approx 4.9$ eV compared with g-CO$_2$ (Fig. S4). This important shift means that an actual interaction is taking place between the adsorbate and the surface (7, 22), although the adsorption state still resembles physisorption.

To interpret these findings, we investigated in detail the influence of O$_{sub}$ on the formation of l-CO$_2$, using various levels of DFT calculations. These calculations are discussed in detail in Supporting Information. It is well known that standard DFT approaches (e.g., generalized gradient approximation (GGA) and local-density approximation (LDA)) do not account for London dispersion, which is usually included with empirical corrections (29). However, there is no rigorous basis for the empirical vdW correction for Cu. Instead we use the M06L version of DFT that includes both kinetic energy and exchange correlation functions optimized by comparing to a large benchmark of known vdW clusters with accurately known bonding energies (16). Further details are presented in Computational Details of DFT Calculations, Dataset S1, and Tables S1 and S2.

**Physisorbed CO$_2$ on Cu(111)**

Fig. 3A shows the predicted surface structure for 1/4 monolayer (ML) equivalents (MLE) of CO$_2$ on metallic (O$_{sub}$-free) Cu(111). The physisorbed l-CO$_2$ molecules have a C-O bond distance of 1.64 Å compared with 1.163 Å in gas phase and O-C-O angles of 179°, with an equilibrium distance of 3.11 Å from the C atom of CO$_2$ to the Cu surface, characteristic of weak vdW interactions. The quantum mechanical (QM) electronic bond energy to the surface is $\Delta E = -0.36$ eV with $\Delta H(298 \text{ K}) = -0.30$ eV enthalpy of bonding (after including ZPE and specific heat). However, the large decrease in entropy from the free CO$_2$ molecule leads to a free energy for physisorbed CO$_2$ that is unfavorable by $\Delta G(298 \text{ K}, 0.7 \text{ Torr}) = +0.27$ eV, which would require a pressure of 33 atm to observe at 298 K.

**Physisorbed CO$_2$ with O on Cu(111)**

The experimentally observed O 1s shifts indicate a small amount of surface and/or subsurface adsorbed O (denoted O$_{ads}$ and O$_{sub}$, respectively) is present in our pristine Cu(111). Compared with

![Fig. 3. Predicted structures for 1/4 ML of physisorbed l-CO$_2$ on various Cu surfaces (Cu, light blue; C, brown; O, red, but O$_{sub}$ is marked in orange). (A–D) Top and side views of (A) pristine Cu(111), $\Delta G = +0.27$ eV, $\rho_{l-CO_2} = 33$ atm; (B) Cu(111) with 1/4 ML O$_{sub}$ (row 1 of Table 2) $\Delta G = -0.21$ eV, $\rho_{l-CO_2} = 3$ atm; (C) Cu(111) with 1/4 ML O$_{sub}$ (row 2 of Table 2) $\Delta G = -0.39$ eV, $\rho_{l-CO_2} = 2 \times 10^{-7}$ Torr; and (D) Cu(111) with 1/4 ML of both O$_{sub}$ and O$_{ads}$ (row 3 of Table 2), $\Delta G = -0.13$ eV, $\rho_{l-CO_2} = 7$ Torr. Both C and case D are consistent with experiment.

![Fig. 4. M06L predicted structures for chemisorbed b-CO$_2$ with H$_2$O on Cu(111) with different levels of O$_{sub}$. $\Delta G$ is reported for 298 K, and $\rho_{l-CO_2} = 0.35$ Torr for H$_2$O and CO$_2$. (A–C) Top and side views with chemical illustration of predicted structures (A) on pristine Cu(111), $\Delta G = +1.07$ eV; (B) on Cu(111) with 1/4 ML O$_{sub}$, $\Delta G = -0.06$ eV; and (C) on Cu(111) with 1/2 ML O$_{sub}$, $\Delta G = +0.28$ eV.

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<th>Method</th>
<th>Structure</th>
<th>Predicted $\delta O_{ads}$ and $\delta O_{sub}$</th>
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<tr>
<td>DFT</td>
<td>1/4 ML O$_{ads}$</td>
<td>$\delta O_{ads} = -2.2$ eV, $\delta O_{sub} = -1.3$ eV</td>
</tr>
<tr>
<td>DFT</td>
<td>1/4 ML O$_{sub}$</td>
<td>$\delta O_{ads} = -0.3$ eV, $\delta O_{sub} = -1.5$ eV</td>
</tr>
<tr>
<td>DFT</td>
<td>1/4 ML O$<em>{ads}$ + 1/4 ML O$</em>{sub}$</td>
<td>$\delta O_{ads} = -0.4$ eV, $\delta O_{sub} = -1.6$ eV</td>
</tr>
<tr>
<td>APXPS</td>
<td>0.06 ML O$<em>{ads}$ + 0.08 ML O$</em>{sub}$</td>
<td>$\delta O_{ads} = -0.4$ eV, $\delta O_{sub} = -1.6$ eV</td>
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the O 1s BE of O in the l−CO₂ configuration, we observe an experimental shift (ΔO_ads) of −0.4 eV for O_ads and an experimental shift (ΔO_ads) for O_ads of −1.6 eV. To deduce the nature of this O_ads, we consider the three cases reported in Table 2.

For computational convenience we assumed a 2 × 2 surface cell, but the experimental O_ads coverage is about 0.08 MLE. For the 2 × 2 unit cell, our DFT calculations find two cases with O 1s BE consistent with experiment. Fig. 3C with one O_ads per cell leads to a BE = −1.35 eV whereas Fig. 3D with one O_ads and one O_ads leads to BE = 0.31 and 1.54 eV. Referencing to gas-phase O₂ (standard conditions), Fig. 3D is ΔG = −2.34 eV more stable than Fig. 3C. For case Fig. 3C we predict ΔG = −0.39 eV bonding for l−CO₂ (a pressure threshold of 2 × 10⁻⁷ Torr), whereas Fig. 3D leads to ΔG = −0.13 eV with a pressure threshold of 7 Torr, both consistent with experiment.

Simultaneous dosing of CO₂ in the presence of H₂O leads to a dramatic change in the character of the surface CO₂, showing clearly the adsorption characteristics for chemisorbed b−CO₂. For a Cu(111) surface that includes some surface suboxide, the DFT calculations lead to several local minima (Fig. 4): (i) physisorbed l−CO₂ plus H₂O_ads, (ii) chemisorbed b−CO₂ plus H₂O_ads (Fig. 4 A–C), (iii) reacted COOH plus OH₂ads (Fig. S7 A), and (iv) HCOOH plus surface O_ads (Fig. S7B). In the case of Cu(111) without O_ads (Fig. 4A), the C atom of b−CO₂ is chemically bonded to a surface Cu¹⁺, whereas the two O atoms accommodate the partial negative charge transferred from the Cu surface, with one stabilized by hydrogen bonding to H₂O_ads. However, this b−CO₂ leads to a QM binding energy of ΔE = −0.23 eV, but including vibrational and entropy contributions we find b−CO₂ is unstable, with ΔG(298 K, 0.7 Torr) = 1.07 eV, which agrees with our experiments.

When the O_ads is increased to 1/4 ML (Fig. 4B), we find that the C atom is chemically bonded to two surface Cu¹⁺, one O atom is chemically bonded to one Cu⁰ center, and the other O atom is stabilized by the surface Cu⁺ pulled up by H₂O_ads. This b−CO₂ leads to ΔG(298 K, 0.7 Torr) = −0.06 eV, which is stable in agreement with our experiments.

However, increasing the O_ads to 1/2 ML, we predict that ΔG(298 K, 0.7 Torr) = +0.28 eV, which is unstable. Here the C atom is chemically bonded to a surface Cu⁺ that shares an O atom bearing a partial charge (stabilized by a hydrogen bonding to H₂O_ads on surface Cu⁰.). Our experiments also show that increased levels of O_ads decrease the binding of b−CO₂. Thus, we find that chemisorbed b−CO₂ is stable only for the case in Fig. 4B with 1/4 ML O_ads. Having more O_ads or none at all destabilizes b−CO₂. We explain this in terms of the distinct interactions of Cu⁰ and Cu¹⁺ induced by the Cu(111)O_ads=0.25.

This result of an optimum O_ads for b−CO₂ is in agreement with our experiments for CO₂ and H₂O codoping on the Cuₓ=0.25O and Cuₓ=1.5O suboxide structures, which shows both b−CO₂ and l−CO₂, but with a l−CO₂/b−CO₂ ratio of 3.8 and 5.3 for Cuₓ=0.25O to the Cuₓ=1.5O structure, respectively (the ratio was determined from both C 1s and O 1s spectra) (Fig. S3 A and B). In addition, Fig. S8 reports the experimental results of exposing the Cuₓ=1.5O structure to 0.7 Torr of 1:1 CO₂ and O₂. In this case we do not observe chemisorbed b−CO₂, but only physisorbed l−CO₂ and its conversion to surface −CO₂ (carbonate).

The DFT calculations predict that on Cu(111)O_ads=0.25, b−CO₂ can react with H₂O_ads to form formate plus OH₂ads, but the product is unstable in our conditions, with ΔG(298 K, 0.7 Torr) = +0.20 eV, making it endothermic from b−CO₂ in Fig. 4B by ΔG(298 K, 0.7 Torr) = +0.26 eV [it is 0.43 eV endothermic for Cu(111)O_ads=0.5]. On the other hand, our DFT calculations predict that this formate can extract an H from the −OH to form formic acid plus O_ads, which is stable with ΔG(298 K, 0.7 Torr) = −0.05 eV.

We expect that learning how to tune the character of the surface atoms (Cu⁺ vs. Cu⁰ in this case) to manipulate these relative energetics of l−CO₂ plus H₂O, l−CO₂ plus H₂O_ads, physisorbed plus OH₂ads, and formic acid plus O_ads, may allow us to design modified systems aimed at accelerating these reaction steps. For example, we hypothesize that other subsurface anions such as S or Cl might favorably modify the energetics by changing the charges and character of the surface atoms and/or replacing some Cu with Ag, Au, or Ni with different redox properties.

Activation of the inert linear l−CO₂ molecule requires enforcing a bent b−CO₂ configuration (30) with great chemical stabilization, but pristine Cu(111) and corresponding derivatives with O_ads and/or O_ads do not deliver sufficient stabilization, as shown in our calculations. Thus, forcing CO₂ to have the necessary angle (120° ~140°) and appropriate distance (~2 Å) to the pristine Cu surface, we find no stable local minimum; all of the initial bent CO₂ structures relax into the stable l−CO₂ physisorption state.

However, the presence of modest amounts of O_ads generates a mixture of surface Cu⁺ and Cu⁰ atoms that combines with H₂O_ads to stabilize the b−CO₂ structure reported in Fig. 4B. We conclude that this configuration of surface atoms and H₂O is responsible for stabilizing b−CO₂ and opening up the possibility of forming formate, formic acid, etc. This elucidates the first reduction step of CO₂.

This combination of APXPS experiments and DFT calculations enabled us to obtain a detailed understanding of the initial steps of CO₂ activation by H₂O on a Cu surface. We find that a modest level of O_ads between the top two Cu layers is essential for stabilizing physisorbed l−CO₂.

This unexpected finding may explain a general observation empirically derived in the literature from the catalytic performance of Cu oxides for CO₂RR: It is known that Cu catalysts previously treated to generate surface oxides generally show improved activity compared with the pristine metallic surface (3, 6, 31). From our experimental results and theoretical predictions, we conclude that the topmost layer needs to expose metallic centers, because CO₂ can efficiently chemisorb only on such centers (Fig. 4B) to form the activated molecular substrate for subsequent reduction to formate and other products. However, we find that the presence of a subsurface oxide structure is also needed to promote H₂O chemisorption onto a Cu⁺ center. This enables the electronic communication between adsorbed CO₂ and H₂O, favoring the transition from a linearly physisorbed l−CO₂ to a bent chemisorbed b−CO₂. From Fig. 4B, reactions to formate and formic acid are possible but not favored under our conditions.

These results provide the insight that subsurface oxide plays a critical role in the initial steps for activating CO₂, providing a foundation for the rational development of unique active electrocatalysts.

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