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Steps Control the Dissociation of CO₂ on Cu(100)

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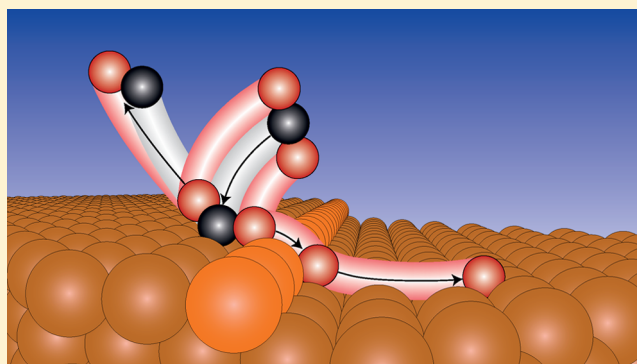
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S Supporting Information

ABSTRACT: CO₂ reduction reactions, which provide one route to limit the emission of this greenhouse gas, are commonly performed over Cu-based catalysts. Here, we use ambient pressure X-ray photoelectron spectroscopy together with density functional theory to obtain an atomistic understanding of the dissociative adsorption of CO₂ on Cu(100). We find that the process is dominated by the presence of steps, which promote both a lowering of the dissociation barrier and an efficient separation between adsorbed O and CO, reducing the probability for recombination. The identification of steps as sites for efficient CO₂ dissociation provides an understanding that can be used in the design of future CO₂ reduction catalysts.



1. INTRODUCTION

Because of global warming, there is a strong need to reduce emissions of greenhouse gases, such as CO₂, into the atmosphere. In the case of CO₂, one possible path is to convert the molecule into useful chemicals, such as methanol. The approach to recycle CO₂ will not only reduce the issues with global warming but also provide a closed carbon loop for production of essential chemicals.^{1,2}

Recycling of CO₂ is challenging because of the inertness of the molecule with high barriers for activation. To promote the development of new catalysts, it is desirable to have a fundamental understanding of the activation and dissociative adsorption of CO₂ on relevant surfaces. Industrially, Cu-based catalysts, especially combined with ZnO, play an important role for both the reversed water–gas shift reaction and methanol synthesis from CO₂. The roles of the Cu, ZnO, and Cu/ZnO interface have been discussed during the last 2 decades.^{3–9} To reach a fundamental understanding of the reaction process, it is important to study the two components also individually. Thus, the interaction and dissociation of CO₂ on copper and copper oxide surfaces have received considerable attention.^{10–22}

Rasmussen et al. observed CO₂ dissociation on Cu(100) at close to atmospheric pressures and at temperatures between 475 and 550 K.¹⁰ Exposure to CO₂ left adsorbed oxygen on the surface, while the CO resulting from the dissociation desorbed.

The determined¹⁰ dissociative sticking coefficient of CO₂ was on the order of 10^{–12}. This implies that any in situ experiments need to be performed at elevated pressures to be able to observe adsorbed oxygen. Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) has made it possible to study the dissociative adsorption of CO₂ on copper surfaces at elevated pressures, which is not possible with traditional XPS.

Using AP-XPS, Eren et al. have shown that CO₂ adsorbs dissociatively on Cu(100) at pressures in the range 0.1–10 mbar at 300 K.¹¹ Chemisorbed CO₂^{δ–} as well as adsorbed atomic oxygen were observed on the surface. Furthermore, at a coverage of 0.3 ML (MonoLayers, 1 ML = 1.53 × 10¹⁵ cm^{–2}), adsorbed oxygen was found to hinder the adsorption of CO₂, which emphasizes the need of CO in the gas mixture to remove the chemisorbed oxygen. However, the knowledge of how CO₂ interacts with pristine and oxygen-covered Cu(100) is limited and there is a need for uncovering the role of surface oxygen in this process.

We have studied the dissociative adsorption of CO₂ on Cu(100) using AP-XPS and density functional theory (DFT) calculations. In contrast to previous studies, we continuously followed the evolution of the oxygen layer, which allows for a deeper understanding of the dissociation process. In agreement

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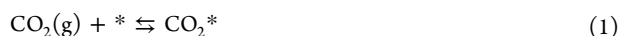
with previous studies,^{10,11} we find that CO₂ dissociates on the surface, resulting in adsorbed O, and that the rate of dissociation drops as the oxygen coverage approaches 0.25 ML. Interestingly, we find that the oxygen uptake curve is linear with different slopes in the coverage ranges of 0–0.25 and 0.25–0.45 ML. This suggests that the adsorption is unaffected by the O coverage within these ranges. To explain this behavior, we propose a model where steps dominate the CO₂ dissociation process. The calculations show that the effect of the steps is twofold; it both lowers the dissociation barrier and provides an efficient separation between adsorbed O and CO, reducing the probability for the back reaction of CO₂ formation.

2. METHODS

2.1. Sample Preparation. The Cu(100) surface was cleaned by cycles of argon ion bombardment at 1 kV, 10 mA, and 2×10^{-6} Torr for 20 min and subsequent annealing to 850 K for 20 min. The surface was considered clean when only copper was detected in the XPS.

To obtain a calibration of the oxygen coverage, the O 1s peak of the missing row (MR) structure,²³ which contains 0.50 ML of oxygen, was used as reference. This structure was prepared by saturating the clean surface with oxygen by exposure to 1200 L of O₂ at 370 K, which according to scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) gives the MR structure; see Supporting Information.

2.2. XPS Measurements. The AP-XPS experiments were conducted at Beamline 9.3.2 of the Advanced Light Source at Lawrence Berkeley National Laboratory.²⁴ The C 1s and Cu 3p spectra were measured using a photon energy of 435 eV, while O 1s was measured at 650 eV. The evolution of the oxygen coverage was monitored by measuring the O 1s region continuously, while the Cu(100) surface was exposed to 300 mTorr CO₂ at 370 K. As the surface is exposed to CO₂, adsorbed atomic oxygen appears on the surface, which originates from the following sequence of reactions:



We exclude that the oxygen uptake originates from residual O₂ gas because the observed oxygen uptake curve does not match the expected signature from O₂ gas.²⁵ After the O 1s signal saturated, the CO₂ was pumped out and O 1s, Cu 3p, and C 1s spectra were measured. The O 1s signal at UHV is then compared to the O 1s signal of the MR to achieve an oxygen coverage calibration.

The series of O 1s spectra was deconvoluted by fitting each peak using a Doniach-Sunjić function convoluted with a Gaussian as well as a linear background. After determination of the positions and line shapes of all the components, the fitting of the spectra was carried out by fixing all parameters except the intensity of the peaks. In this way, the description of the system is consistent for the entire series of spectra. For the peaks at 530.0 and 529.5 eV, the determined asymmetry parameter and fwhm of the Gaussian are 0.098 and 0.86 eV, respectively.

2.3. DFT Calculations. The calculations were performed within density functional theory (DFT) using PBE exchange-correlation functional²⁶ as implemented in the Vienna ab initio package^{27–30} and described in ref 23. Carbon, oxygen, and copper were treated with 4, 6, and 11 electrons in the valence, respectively. The (100), (611), and Cu(11 1 1) surfaces are modeled with slabs consisting of four (100) and five (stepped) layers separated by at least 15 Å of vacuum. For the (100) [stepped] surface, the top two [three] layers were allowed to relax in response to adsorption, whereas the bottom two layers were kept fixed at the bulk positions.

The calculated lattice constant of Cu in fcc bulk is 3.637 Å, in good agreement with the experimental value of 3.615 Å.³¹ The bond

lengths for carbon dioxide and carbon monoxide in gas phase are calculated to be 1.18 and 1.14 Å, respectively. This is close to the experimental values of 1.16 and 1.13 Å.

Reaction barriers were calculated using the climbing-image nudged elastic band (CI-NEB) technique as implemented in the transition-state tools module for VASP.³² All reported states in the potential energy diagram are zero-point energy-corrected. Transition states in the dissociative adsorption of CO₂ were corroborated by vibrational frequency analysis.

3. RESULTS

3.1. AP-XPS Measurements. Figure 1 shows the evolution of the O 1s spectrum as the surface is exposed to

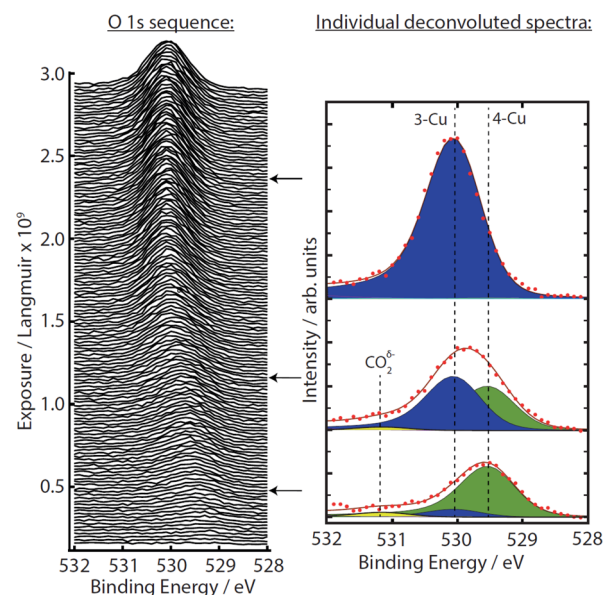


Figure 1. Measured O 1s sequence as the surface is exposed to 300 mTorr of CO₂ at a temperature of 370 K. The right side of the figure shows examples of deconvoluted spectra.

300 mTorr CO₂ at 370 K. Upon CO₂ exposure, a coverage of atomically adsorbed oxygen starts to appear, originating from CO₂ dissociation. Initially, the spectrum consists of one peak at 529.5 eV. As the oxygen coverage increases, the peak is observed to shift toward higher binding energy, reaching 530.0 eV at the saturation coverage of 0.5 ML. As reported by Eren et al.,¹¹ there is an additional peak at ~531 eV, corresponding to adsorbed CO₂^{δ−}. Under the current conditions, however, the corresponding coverage of this species is never above 0.02 ML, and as the O coverage increases, this peak, if present, is hidden in the tails of the O peaks. Hence, we do not draw any conclusions concerning the presence of the adsorbed CO₂ from these measurements, but refer to the study by Eren et al., who reported adsorbed CO₂ at low O coverages but not at 0.3 ML at room temperature.

We have in a recently published study²³ concluded that, up to a coverage of 0.25 ML, the adsorbed oxygen forms a disordered p(2 × 2) phase, with oxygen in fourfold hollow sites. This structure converts into a missing row reconstruction, where each O atom is coordinated to three Cu atoms.²³ The calculated O 1s core level shift between four- and threefold coordinated O atoms is 0.7 eV, which is in good agreement with the measured shift of 0.5 eV in Figure 1. With the two peaks at 529.5 and 530.0 eV assigned to be oxygen at the unreconstructed and reconstructed part of the surface,

respectively, the individual spectra of the O 1s sequence in Figure 1 can be deconvoluted using these peaks. Such an analysis is shown to the right in Figure 1 for three cases.

The integrated intensities of the peaks at 529.5 and 530.0 eV, as well as their sum, for the entire series of spectra are shown in Figure 2. We find that the oxygen uptake curve can

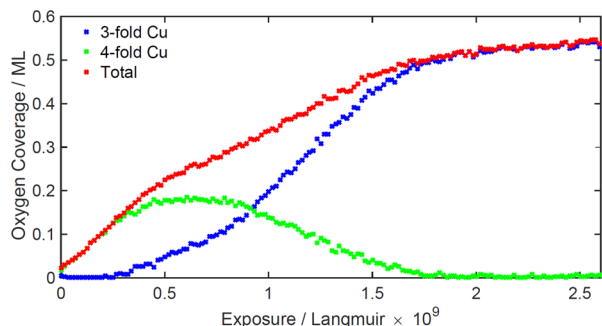


Figure 2. Evolution of adsorbed oxygen from CO_2 . The two peaks at 529.5 eV (green dots) and 530 eV (blue dots) are fitted for the entire series of spectra in Figure 1. The coverage is estimated by normalizing the integrated intensities to the MR structure.

be characterized by three regions: (i) A linear region in the coverage range up to 0.25 ML, (ii) another linear region with a gentler slope up to a coverage of 0.45 ML, and (iii) an exponentially decaying increase up to the saturation coverage of 0.5 ML. A linear uptake curve indicates that the rate of dissociative adsorption is constant and the number of sites responsible for dissociation does not depend on coverage. The change in slope at 0.25 ML shows that the rate constant is lowered by the presence of oxygen, although the active sites remain unoccupied. These effects are corroborated by the DFT calculations.

3.2. DFT Calculations. 3.2.1. Dissociative Adsorption of CO_2 on $\text{Cu}(100)$. The calculated energy landscape for the dissociation of CO_2 over $\text{Cu}(100)$ is shown in Figure 3. In agreement with previous reports,²² we find that CO_2 adsorbs as a bent activated CO_2^δ species. This is a crucial step for the dissociation process as C–O bond cleavage from linear CO_2 is associated with a barrier of ~ 3 eV. The adsorption is endothermic by 0.43 eV on the pristine surface, with respect to CO_2 in the gas phase, and has an energy barrier of 0.55 eV. This barrier is associated with both the cost of the charge transfer from the surface to the molecule and the structural distortion of the molecule and the surface. To complete the dissociation, the activated CO_2^δ is elongated and the C–O bond is broken over the adjacent bridge site. The dissociation step has a barrier of 0.83 eV and is endothermic by 0.02 eV with respect to adsorbed CO_2^δ . A configuration of $\text{CO}^* + \text{O}^*$ is left at the surface, where the CO^* molecule occupies the initial bridge site, while the oxygen atom occupies a fourfold hollow site. The CO molecule is adsorbed to the surface by 0.97 eV. Note that the barrier for desorption of CO_2 from the CO_2^δ configuration is only 0.12 eV. The entropy difference between CO_2 in the gas phase and CO in the gas phase with adsorbed O is ~ 0.08 eV in favor of CO_2 . The endothermic nature of the reaction explains the high pressure needed to drive the reaction.

The effect of adsorbed O on the CO_2 dissociation was investigated through a systematic test of the stability of

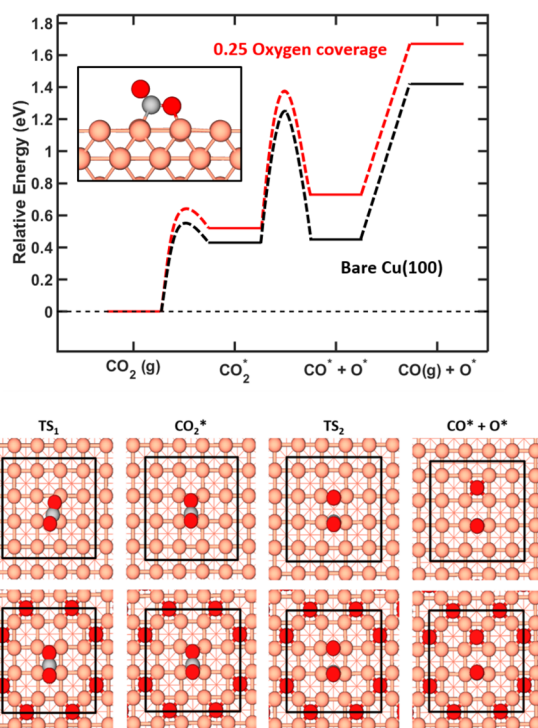


Figure 3. CO_2 dissociation on pristine and O-covered $\text{Cu}(100)$. The upper panel shows the zero-point-corrected energy diagram of the two-step dissociative adsorption process. The inset shows adsorbed CO_2 . The lower panel shows the atomic models of the dissociative process on both the pristine and O-covered $\text{Cu}(100)$. The $c(4 \times 4)$ surface cell is indicated by black lines. Atomic color codes: Cu (pink), O (red), and C (light gray).

activated CO_2^δ at an oxygen coverage of 0.083 ML. All eight possible nonequivalent configurations of CO_2 and oxygen co-adsorption in a $c(4 \times 3)$ surface cell were explored; see Figure 4. We find that the stability of CO_2 on the O-covered surface is

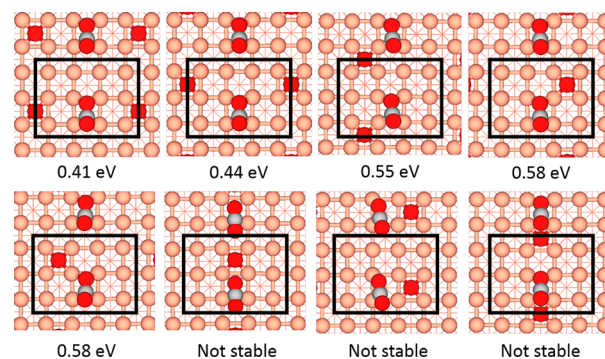


Figure 4. CO_2 on $\text{Cu}(100)$ with preadsorbed oxygen. The (endothermic) adsorption energy with respect to CO_2 in the gas phase is indicated. The $c(3 \times 4)$ surface cell is indicated by black lines. Color codes as in Figure 3.

sensitive to its relative position with respect to the adsorbed oxygen atoms. Especially, it is shown that the available number of sites for CO_2 is reduced significantly with a coverage of oxygen.

At a coverage of 0.25 ML, oxygen is predicted to form a $p(2 \times 2)$ adsorption structure.²³ According to our calculations, the chemisorbed bent CO_2^δ is not stable on this surface, which

suggests that the O coverage should saturate at 0.25 ML instead of 0.5 ML as observed experimentally (Figure 2). CO₂ may adsorb at a 0.25 ML oxygen coverage provided that the O atoms are clustered. We have considered such a configuration in Figure 3. This structure is only 0.09 eV higher in binding energy than the p(2 × 2) and might form at 370 K.²³ The structure is similar to the c(4 × 6) presented by Fujita et al.³³ CO₂ has a stable minimum when adsorbed on this structure, with an endothermic adsorption energy of 0.52 eV, which is roughly 0.1 eV higher than for the pristine surface. Although these calculations indicate that CO₂ may dissociate at Cu(100) with an O coverage higher than 0.25 ML, this possibility does not provide any explanation for the linear uptake curve as the number of sites for dissociation should decrease monotonously.

3.2.2. CO₂ Dissociation on Stepped Surface. To find an explanation for the linear uptake curve, we have investigated the dissociative adsorption of CO₂ over the stepped copper surface. As the close-packed (111) steps are expected to be the more dominant step,³⁴ we chose to study a Cu(611) surface, which has a surface unit cell comprising two (100) terraces separated by a (111) step. Figure 5 shows the corresponding

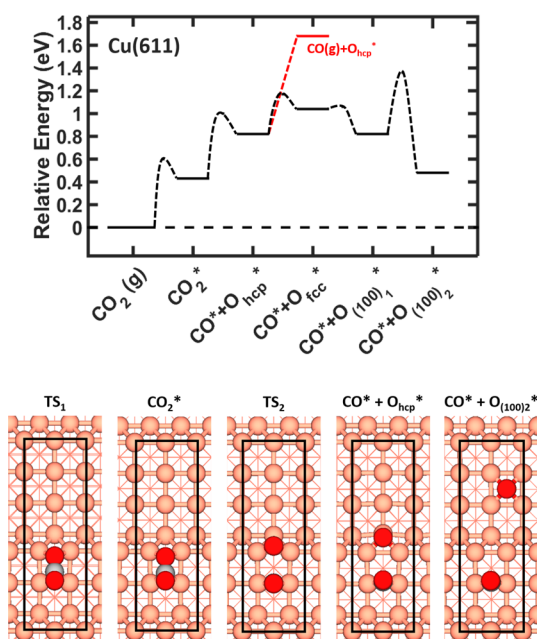


Figure 5. CO₂ dissociation on pristine Cu(611). The upper panel shows the zero-point-corrected energy diagram of the two-step dissociative adsorption process. The lower panel shows the atomic models of the dissociative process on Cu(611). The surface cell is indicated by black lines. Color codes as in Figure 3.

energy landscape and models. The dissociation process is similar to the one at Cu(100), proceeding through adsorbed CO₂^{δ−} with subsequent elongation and breaking of the C–O bond over the step. Atomic oxygen is transferred over the bridge site to occupy a threefold hollow site below the step, while CO* remains on the initial bridge site. The barrier for adsorption is slightly higher than that on Cu(100): 0.60 eV instead of 0.55 eV. The activated CO₂ has, however, the same endothermicity as on Cu(100). Dissociation of CO₂^{δ−} has a barrier of 0.57 eV and (CO* + O*) configuration is endothermic by 0.39 eV with respect to the activated CO₂.

However, diffusion of O from the threefold hollow site at the step to a fourfold position on the (100) terrace makes CO₂^{δ−} and the (CO* + O*) isoenergetic.

The barrier for CO₂ dissociation from the adsorbed state is 0.26 eV lower on the step as compared to the (100) terrace. Additionally, the barrier for CO₂ desorption is slightly higher: 0.17 eV as compared to 0.12 eV. With use of the Arrhenius expression, these differences give, at 370 K, a higher probability of CO₂ dissociation on Cu(611) as compared to that on Cu(100) by 4 orders of magnitude; see [Supporting Information](#).

In addition to lowering of the dissociation barrier, steps enable a facile separation between adsorbed CO and O. This is an important aspect as the barrier for CO and O recombination is lower than the barriers associated with diffusion of O to the terrace sites. From the threefold hollow site on the step, which is the position of O after dissociation, there is a sequence of three barriers for O to diffuse out on the lower terrace. The highest of these barriers is 0.54 eV, whereas the barrier for O diffusion on Cu(100) is 0.80 eV.

3.2.3. Avoiding Poisoning of Step Sites. Preferential CO₂ dissociation at steps would rationalize the linear uptake curves provided that the steps are not poisoned by the reaction products. Importantly, there is a thermodynamic driving force for oxygen to diffuse away from the step and instead occupy sites on the terraces. This is exemplified by calculating the stability of p(2 × 2) and c(2 × 2) types of structures on Cu(11 1 1) (Figure 6). The oxygen coverage in the two cases is 0.25

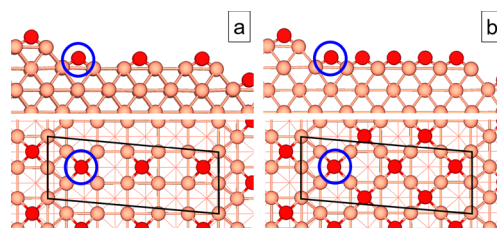


Figure 6. p(2 × 2) (a) and c(2 × 2) (b) types of structures on Cu(11 1 1). The circle highlights the oxygen atom adsorbed right below the step for which differential adsorption energies are calculated. The surface cell is indicated by black lines. Color codes as in Figure 3.

and 0.42 ML, respectively. For p(2 × 2), this is the same coverage as on the extended surface whereas the c(2 × 2) structure has a coverage of 0.5 ML on Cu(100). On Cu(11 1 1), the average oxygen binding energy is −1.86 and −1.74 eV for the low- and high-coverage case, respectively. This should be compared to the corresponding binding energies on Cu(100), which are −2.02 and −1.77 eV. The considerable reduction in stability is related to the occupation of the fourfold site below the step. The differential binding energy for this site is −1.63 and −1.32 eV for the p(2 × 2) and c(2 × 2) types of structures, respectively. The reduced binding energies on the Cu(11 1 1) surface can partly be attributed to compressive strain as Cu–Cu bond distances are reduced in the topmost surface layer.

When the coverage increases, oxygen resulting from dissociation processes on one step will by diffusion eventually reach the next lower step. This is expected to happen when the coverage approaches 0.25 ML, that is, when the surface is covered by a p(2 × 2) structure. As for Cu(100), this would block the adsorption of CO₂ and, thereby, hinder the reaction.

Still the dissociation is measured to continue until a coverage of 0.5 ML has been reached. The reason for this is most likely that the step is kept free from O through reaction with CO. As long as the dissociation rate is high enough relative to the O diffusion rate, and considering the high barrier for CO desorption, there will always be CO from another dissociation event available for reaction with the O that, by diffusion, reaches the active step sites. This will, of course, result in continuous removal of some O, and a reduced increase of the O coverage. This scenario is consistent with the change of the slope of the uptake curve when the coverage approaches 0.25 ML.

4. DISCUSSION

On the basis of our combined AP-XPS and DFT results, we suggest a model for the dissociative adsorption of CO₂ on Cu(100), where dissociation on steps dominate. The effect of the steps is twofold, both lowering the activation barrier for the dissociation and separating the resulting O and CO, thus hindering recombination. This scenario agrees with the linear behavior of the O uptake. A similar importance of steps has previously been suggested by Somorjai et al., for adsorption of CO₂ on Cu(311).¹⁷

In addition, our model is consistent with previous reports, of which the recent combined AP-XPS and HP-STM study by Eren et al. is of special interest.¹¹ Eren et al. show that CO₂ is able to adsorb on the clean Cu(100) surface; while at an O coverage of 0.3 ML, the CO₂ coverage is below the detection limit. This agrees well with our DFT calculations showing that the adsorption of CO₂ is efficiently blocked by adsorbed O such that no CO₂ adsorption can occur on the p(2 × 2) structure found to be the stable phase at 0.25 ML coverage.

The O coverage increases above 0.3 ML in both Eren's and our studies, suggesting that the adsorbed CO₂ found by AP-XPS is not involved in the reaction. This problem is solved by the reaction taking place on steps rather than the terraces, given that oxygen diffuses away from the active sites.

Another detail to take into account is that different studies have shown significantly different adsorption rates. According to ref 11, similar exposures of Cu(100) to 0.3 Torr CO₂ at room temperature for approximately 3 min at ALS Beamlines 9.3.2 and 11.0.2 results in 0.34 and 0.48 ML O coverage, respectively. This was attributed to different background pressures in the experimental chambers. We made a similar exposure for approximately 20 min, also at Beamline 9.3.2, resulting in an O coverage of about 0.06 ML; see [Supporting Information](#). We do not believe that this large difference can be explained by the experimental environment, especially since the experiments were performed at the same beamline. Instead, we believe that the difference is due to the reaction occurring at steps since the step density depends strongly on the sample preparation.

5. CONCLUSIONS

We have studied the dissociation of CO₂ over the Cu(100) using AP-XPS and DFT. Our results show that CO₂ adsorbs dissociatively on Cu(100) with a resulting O uptake that is initially unaffected by the O coverage. This is incompatible with CO₂ adsorbing on the (100) terraces, as O would block the adsorption, resulting in a gradually reduced uptake rate. Instead, we propose a model where dissociation on surface steps completely dominate. In this scenario, the steps both

lower the activation barrier for the dissociation and separate the resulting CO and O, thus hindering recombination. Furthermore, there is a thermodynamic driving force for the resulting O to diffuse away from the steps out on the terrace, leaving the active step sites available for further adsorption.

Our results emphasize the importance of steps in CO₂ hydrogenation catalysis and form a basis for further studies to establish the roles of Cu, ZnO, and the Cu/ZnO interface in industrial catalysts. Such fundamental understanding is, in turn, a prerequisite for a rational design of future catalysts aimed at reducing the emission of greenhouse gases into the atmosphere.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/jacs.8b07906](https://doi.org/10.1021/jacs.8b07906).

STM and LEED image of the missing row reconstruction, additional AP-XPS spectra, and a comparison between the theoretical dissociation rates on Cu(100) and Cu(611) (PDF)

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Notes

The authors declare no competing financial interest.

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