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Activity and Synergy Effects on a Cu/ZnO(000$\underline{1}$) Surface Studied Using First-Principle Thermodynamics

Jianping Xiao*,[†,‡] and Thomas Frauenheim[†]

[†]Bremen Center for Computational Materials Science, Universität Bremen, Am Fallturm 1, 28359 Bremen, Germany
[‡]School of Engineering and Science, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany

S *Supporting Information*

ABSTRACT: Using first-principle thermodynamics, we have studied surface phase diagrams of Cu substitutional ZnO(000$\underline{1}$) surfaces under industrial conditions. On the one hand, the Cu substituted on Zn sites can promote efficient formation of oxygen vacancies on the ZnO(000$\underline{1}$) surface. It can improve the activity on the Cu/ZnO(000$\underline{1}$) surface. On the other hand, metallic monolayers containing certain Cu and Zn atoms can be also formed, accompanied by the oxygen vacancies formation. We have further investigated CO_2 adsorption and reduction on these metallic monolayers. These metallic monolayers prefer to have an intermediate binding strength with the CO_2 molecule. The intermediate binding strength was expected to be optimized for subsequent CO_2 reduction. We have performed further studies and demonstrated successfully the improved catalysis for the subsequent CO_2 reduction on these metallic monolayers. The relevant mechanism can be interpreted with the second synergy effect. The d-band states of these metallic monolayers, supported on the ZnO(000$\underline{1}$) surface, are tuned to shift upward, that is, more close to Fermi level. Therefore, these metallic monolayers indeed exhibit promoted catalysis, in comparison with reported metallic surfaces in the literature.

SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis
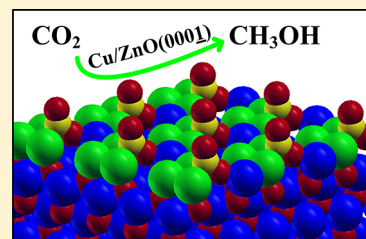
CO_2 reduction is a crucial issue for sustainable development in both environmental and energy fields. However, no material is known to be able to catalyze CO_2 reduction to fuel efficiently. $Cu/ZnO/Al_2O_3$ is an important industrial catalyst used to synthesize methanol with a gaseous H_2, CO, and CO_2 mixture. This catalytic system is also of interest for the potential capability of CO_2 capture and reduction. However, the catalysis mechanism of this catalyst is not understood yet. Hence, it is not feasible to utilize directly a Cu/ZnO-based catalyst for CO_2 reduction now.

The controversy arises regarding the nature of the methanol synthesis and the active sites on $Cu/ZnO/Al_2O_3$ catalysts. It was suggested first that ionic Cu^+ sites are the active catalytic center.[1,2] However, on the other hand, it has also been reported that the catalyst activity is a linear scaling with the metallic Cu surface area.[3] Further evidence supporting metallic Cu as the active sites was provided by experiments on single-crystalline Cu(100) and Cu(110) surfaces and polycrystalline Cu films.[4] These experiments indicate that the methanol synthesis reactions are quite sensitive to surfaces. Recently, Behrens et al.[5] reported a combinatorial study with experimental evidence and density functional calculations. It has been found there is quite different activity between pure Cu surfaces and the industrial $Cu/ZnO/Al_2O_3$ catalyst. They claimed that most Cu surfaces are not active at all; however, only a small fraction of the catalyst's surface, consisting of Zn-decorated Cu(211) steps, mainly contributes to the activity of the industrial catalyst. In addition, it has been speculated for a long time the the ZnO support can influence the activity of the catalyst. However,

synergistic effects between metallic Cu and the ZnO support have never been identified thoroughly. Frost[6] suggested that the Schottky junction effects between the metallic Cu particles and ZnO surfaces may increase the number of oxygen vacancies (V_O). However, these defects sites are also active sites when ZnO alone is used as a catalyst; there are no key reaction intermediates observed on ZnO surfaces with the presence of metallic Cu particles. Thus, the Schottky junction effects cannot explain the synergy effects sufficiently.

Moreover, Chinchen et al.[7] performed isotope labeling experiments and strongly claimed that the CO_2 is the main carbon source for methanol synthesis. However, the CO_2 adsorption and dissociation on the Cu(100) surface are not as good as expected, in comparison with other transition-metal surfaces, namely, Fe, Co and Ni(100), and homogeneous catalysts.[8] There, they claimed that the Cu(100) surface is not likely to capture the CO_2 molecule at all. Thus, there must be significant synergy effects on the heterogeneous interface between metallic Cu particles and the ZnO support.

Furthermore, the main challenge for understanding a microscopic mechanism of heterogeneous reactions is the identification of the geometry and composition of the catalyst's surface and in situ observations of the various chemical reactions under the equivalent industrial conditions.[9] Unfortunately, most experimental techniques in surface science are

difficult to perform directly at a pressure with a magnitude larger than 50 bar and a temperature higher than 500 K. However, these above experimental conditions are typically applied in industrial catalysis of the methanol synthesis.[10] Thus, what is considered to be important reaction mechanisms on the catalysts' surfaces have usually been concluded, according to chemical intuitions and extensive knowledge from experiments performed at low pressure and low temperature. However, several studies revealed the unreliability of this approach.[11] In order to improve the reliability by means of bridging the gap between these experimental temperatures and pressures and industrial ones, it is necessary to consider sufficiently these factors in first-principle calculations.

Recently, Behrens et al.[5] found that most metallic Cu surfaces are not active at all. Thus, an appropriate surface model is a critical issue for first-principle calculations to study reaction mechanisms. Fortunately, the structural evolution during activation of Cu/ZnO-based catalysts has been characterized thoroughly with several in situ experimental techniques.[12] First, Cu atoms were present in the form of substitutional Cu^{2+} in Cu/ZnO solid solution as determined with in situ resonant X-ray diffraction and electron energy loss spectroscopy. Then, the Cu atoms were extracted from the Cu/ZnO solid solution under the reductive atmosphere, forming metallic Cu crystallites. The Cu crystallites could be reoxidized by heating in air and redispersed in the Cu/ZnO solid solution, in the form of substitutional Cu^{2+} on the Zn lattice sites again. Although there was no further evidence to clarify which ZnO surfaces were involved in the above reactions, the oxygen-terminated surface should be considered first, namely, the $ZnO(000\underline{1})$ surface. This is due to the fact that this surface is the most reducible ZnO surface. As is well-known, the oxygen vacancy formation can efficiently stabilize ZnO polar surfaces by means of suppressing the macroscopic dipole moment.

In this work, we first performed first-principle thermodynamics calculations to determine the phase diagram of Cu/$ZnO(000\underline{1})$ surfaces under industrial temperature and pressure. We found that the $Cu/ZnO(000\underline{1})$ surfaces with metallic monolayers containing Cu and Zn atoms can be formed and stable. Then, CO_2 adsorption was studied thoroughly on these metallic monolayers of all reduced $Cu/ZnO(000\underline{1})$ surfaces. Because there is an intermediate binding strength between CO_2 and these metallic monolayers, we expected that the CO_2 dissociation and reduction on these metallic monolayers should be improved significantly, compared with that of pure metallic Cu surfaces. Furthermore, we investigated the CO_2 reduction on these metallic monolayers. Calculated results indicate that these metallic monolayers are indeed more active and almost optimal for CO_2 reduction, in comparison with reported surfaces in the literature, for example, Cu(100) and CuZn(211). This behavior is also quite reasonably interpreted with the d-band model. Thus, we have found two important synergy effects between the metallic monolayers and their support, namely, the $ZnO(000\underline{1})$ surface. Finally, we would propose the feasibility of CO_2 reduction on the $Cu/ZnO(000\underline{1})$ surfaces under industrial conditions.

The Cu/ZnO solid solutions were simulated with a Cu substitutional ZnO wurtzite structure. All surface structures were described by periodically repeated slabs using an extended (2 × 2) unit cell along the $[000\underline{1}]$ direction (Figure 1a). The thickness of these slabs was specified to be four Zn−O double layers with hydrogen saturated on the Zn termination. The
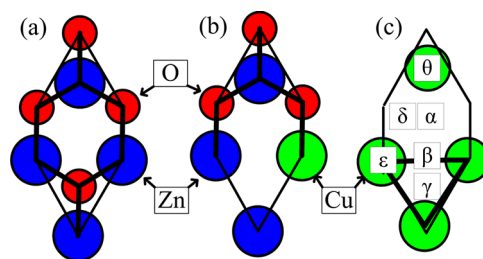

Figure 1. Top view of the studied $Cu/ZnO(000\underline{1})$ surface: (a) the perfect $ZnO(000\underline{1})$ surface, (b) Zn_3Cu_1 with an sV_O defect, and (c) the Cu_4 surface with an qV_O defects and all studied active sites of CO_2 adsorption (noted with α, β, γ, θ, δ, and ε). Bold lines indicate bonds between Cu (green), Zn (blue), and O (red) atoms.

upper four atomic layers were allowed to relax, while the atoms in the remaining layers were fixed at their bulk structures.[13]

We have considered five uniform Cu concentration gradients on the $Cu/ZnO(000\underline{1})$ surface, in the range of 0−100 atom %, denoted by the stoichiometry of the first cationic layer, namely, Zn_4, Zn_3Cu_1, Zn_2Cu_2, Zn_1Cu_3, and Cu_4, respectively. For all of these surfaces, we further considered uniform concentration gradients of oxygen vacancy (V_O) defects at 25, 50, 75, and 100%, corresponding to the nomenclature of sV_O, dV_O, tV_O, and qV_O (Figure 1), respectively. Calculated partial pressures of gaseous CO (10 bar), CO_2 (10 bar), H_2 (40 bar), and H_2O (1 bar) and the temperature (600 K) were referred to the industrial conditions.[5] Then, the formation energies of these V_O defects were calculated to determine the surface phase diagrams of the $Cu/ZnO(000\underline{1})$ surfaces. The four stable qV_O surfaces were selected for further studies of CO_2 adsorption and reduction. Studied active sites for CO_2 adsorption are represented in Figure 1c.

The surface phase diagram is a critical factor to understand the geometry and composition on the $Cu/ZnO(000\underline{1})$ surface. As the $Cu/ZnO(000\underline{1})$ surface exchanges oxygen with its surroundings, we need to determine the chemical potential of surface oxygen first. The chemical potential of surface oxygen, μ_O, varies due to the change of temperature and oxygen partial pressure, as well as the partial pressure of other reductive gases (H_2 and CO). Particularly, oxygen vacancy formation is quite sensitive to the μ_O under varying conditions. For first-principle calculations, the high-temperature and high-pressure effects can be achieved by taking into account explicitly the chemical potential change in terms of thermodynamics.[14] At a given temperature, T, and partial pressures, p, formation energies of oxygen vacancies, $\gamma(T,p)$, can be defined as

$$\gamma(T, p) = \frac{1}{A}\left[G(T, p)_d + \sum n_O\mu_O(T, p) - G(T, p)_p\right]$$

$$(1)$$

where $G(T,p)_p$ and $G(T,p)_d$ are the Gibbs free energies of perfect and defected $Cu/ZnO(000\underline{1})$ surfaces with respect to surface area, A, n_O is the number of oxygen vacancies, and $\mu_O(T,p)$ is the chemical potential of oxygen at a specific temperature, T, and pressure, p. The negative formation energies correspond to stable surface structures with certain numbers of oxygen vacancies. The Gibbs free energies of solid surfaces were replaced by the corresponding total energies, which were calculated with density functional theory (DFT) methods. In addition, we employed the ideal gas approximation to estimate chemical potentials of all gases. The chemical potential of surface oxygen can be expressed by

$$\mu_O(T, p) = \mu_O(T, p_0) + k_B T \ln\left(\frac{p}{p_0}\right) \quad (2)$$

where p_0 and k_B are the pressure in standard conditions and the Boltzmann constant. Three reactions in thermodynamic equilibrium between Cu/ZnO(000$\underline{1}$) surfaces and CO (CO$_2$), H$_2$ (H$_2$O), and O$_2$ reservoirs were considered. The $\mu_O(T,p_0)$ values were calculated in terms of thermal contributions and zero-point energy corrections. Moreover, the CO$_2$ adsorption and hydrogenation reactions were described with the following expression

$$\Delta G(T, p) = G(T, p)_a - G(T, p)_c - \sum n_i \mu_i(T, p) \quad (3)$$

Here, $G(T,p)_c$ are the Gibbs free energies of the clean Cu/ZnO(000$\underline{1}$) surfaces with various studied metallic monolayers, namely, the Zn$_3$Cu$_1$, Zn$_2$Cu$_2$, Zn$_1$Cu$_3$, and Cu$_4$ surfaces with qV_O defects. $G(T, p)_a$ are the Gibbs free energies of these surfaces with adsorbed CO$_2$ and H$_2$ molecules, and n_i is the number of adsorbates. On the one hand, the Gibbs free energies of solid surfaces are still replaced by the corresponding total energies obtained from DFT calculations. On the other hand, the chemical potential, μ_i, of gases was calculated at a certain temperature, T, and pressure, p.

For pure ZnO (Zn$_4$), the qV_O defect is not stable under the condition with a high chemical potential of surface oxygen, namely, the oxygen-rich condition. Even under industrial conditions, only the case with the lowest concentration of V_O defects (sV_O) can be stable. However, the V_O defects can be easily stabilized as long as the Cu concentration on the ZnO(000$\underline{1}$) surface is increased (see Figure 2). The detailed
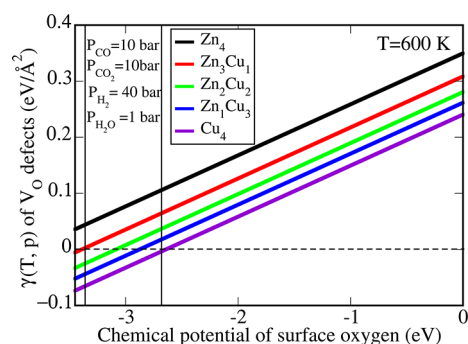
Figure 2. Surface phase diagrams of all metallic monolayers supported by the ZnO(000$\underline{1}$) surface, namely, the Zn$_4$, Zn$_3$Cu$_1$, Zn$_2$Cu$_2$, Zn$_1$Cu$_4$, and Cu$_4$ surfaces with qV_O defects, under industrial temperature and partial pressures. The dashed line refers to perfect surfaces.

$\gamma(T,p)$ data can be found in Table S2 in the Supporting Information. In Figure 3, we show the atomic structures of the metallic monolayer on all qV_O surfaces. It indicates that only the metallic Zn$_4$ monolayer is not stable under industrial conditions. The V_O defects have been identified to be active sites for methanol synthesis on the pure ZnO(000$\underline{1}$) surface.[15] Thus, the Cu can promote significantly the activity on the ZnO(000$\underline{1}$) surface by creating more V_O defects. Theoretical calculations indicate that the Cu substituted on the sites of Zn in the ZnO wurtzite structure is divalent with the electronic configuration of Cu (d^9).[16] The valence state of substituted Cu had been also validated in the subsequent experiment.[12] As the Cu (d^9) is not the most stable electronic structure, the Cu dopants prefer to be present as Cu$^+$ with less coordinated
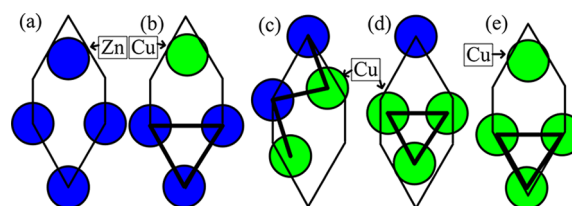
Figure 3. Top view of these metallic monolayers supported by ZnO(000$\underline{1}$) surfaces, namely, (a) Zn$_4$, (b) Zn$_3$Cu$_1$, (c) Zn$_2$Cu$_2$, (d) Zn$_1$Cu$_3$, and (e) Cu$_4$ surfaces with qV_O defects. Bold lines indicate bonds between Cu (green) and Zn (blue) atoms.

oxygen on the surface. In contrast, Zn^{2+} is quite stable with the electronic structure of Zn (d^{10}). Hence, it costs more energy to create active V_O defects by breaking Zn^{2+}−O bonds on a Cu/ZnO(000$\underline{1}$) surface, in comparison with breaking Cu^{2+}−O bonds. Therefore, we have found the first synergy effect, that is, the Cu dopants can promote the activity of the ZnO(000$\underline{1}$) surface in way of stabilizing V_O defects. Accompanied by the qV_O formation, metallic monolayers containing certain Zn and Cu atoms are formed and exposed to gas phases. As there is charge transfer from these metallic monolayers to the sublayer (O), the metallic Cu$_4$ monolayer, as well as the Zn$_3$Cu$_1$, Zn$_2$Cu$_2$, and Zn$_1$Cu$_3$ surfaces, differs significantly from pure metallic Cu surfaces. We will analyze their activity and relevant electronic structure in detail in the next paragraphs.

The binding strength between CO$_2$ and Cu surfaces determines the ability of the Cu surfaces acting as a catalyst. During catalysis, the Cu surfaces form chemical bonds with CO$_2$ and break one of the C−O bonds for its subsequent hydrogenation. The maximum in the catalytic rate requires an intermediate Cu−O bond strength, which is the optimal compromise between having a lower activation barrier for CO$_2$ dissociation (prefers a stronger Cu−O bond), and also the ability to activate further reactions with the adsorbed hydrogen (prefers a weaker Cu−C bond). The catalytic rate is a function of adsorption energy, which is reflected in terms of the volcano curve.[17] In the remainder, we will show that these metallic monolayers (Zn$_3$Cu$_1$, Zn$_2$Cu$_2$, Zn$_1$Cu$_3$, and Cu$_4$) supported with a ZnO(000$\underline{1}$) surface are indeed optimized surfaces, close to the peak of volcano curve, in comparison with reported metallic Cu surfaces.[5,8]

Liu et al.[8] have done comparative studies for CO$_2$ conversion on transition-metal (Fe, Co, Ni, and Cu) surfaces. They claimed that the CO$_2$ adsorption on the Cu(100) surface is too weak (+0.75 eV) and that the corresponding activation energy is very high. In addition, there is a stronger adsorption ability between CO$_2$ and the Ni(100) surface (−0.05 eV), as well as Co(100) surfaces (−0.42 eV). The activation energies for CO$_2$ dissociation are lower too. In contrast, the CO$_2$ is likely to overbind with the Fe (100)surface (−1.45 eV), and it results in an undesired thermodynamic sink. The activation energy for CO$_2$ dissociation rises for the Fe(100) surface. According to the classical volcano curve, as a consequence, the optimal adsorption energy for CO$_2$ conversion should be between −0.42 and −1.45 eV. All metallic monolayers on these surfaces (Zn$_3$Cu$_1$, Zn$_2$Cu$_2$, Zn$_1$Cu$_3$, and Cu$_4$) and six possible active sites (see Figure 1c) have been considered to investigate CO$_2$ adsorption thoroughly. The CO$_2$ adsorption on the metallic Cu$_4$ monolayer is considerably optimized (−1.31 eV) in comparison with above pure metallic surfaces. There are also consistent findings for metallic Zn$_1$Cu$_3$ (−0.82 eV), Zn$_2$Cu$_2$ (−1.09 eV), and Zn$_1$Cu$_3$ (−1.33 eV) monolayers. The detailed

$\Delta G(T,p)$ data for all studied active sites are available in Table S3 in the Supporting Information.

The reactions of CO_2 dissociation and hydrogenation on these metallic monolayers of Cu/ZnO(000$\underline{1}$) surfaces can be expected by analyzing relevant electronic structures. According to the d-band model, for the Cu(100) surface, when the CO_2 approaches the surface, the C-2p and O-2p orbitals interact first with Cu-4s orbitals and then switch upon coupling to the Cu-3d orbitals. As all transition metals have a half-filled 4s state in the metallic state, they do not differ significantly from one metal to another. The leading difference in this interaction is attributed to the d-band states because it is more localized. The interaction between the O-2p (and C-2p) and Cu-3d states gives rise to separated bonding and antibonding states (see Figure 4). The strength of Cu−O and Cu−C bonds is directly
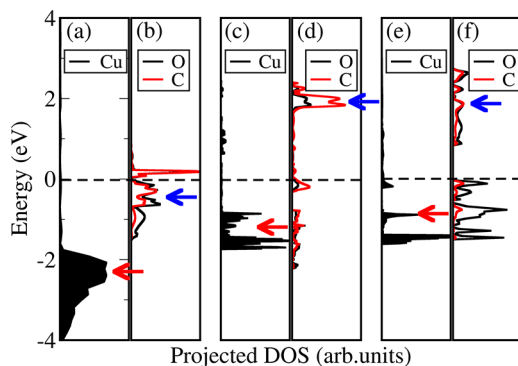

Figure 4. Projected DOS of the Cu d-band on (a) a metallic Cu(100) surface, (c) a metallic Zn_1Cu_3 monolayer, and (e) a metallic Cu_4 monolayer; the C-2p and O-2p states of adsorbed CO_2 are shown on (b) the Cu(100) surface, (d) a metallic Zn_1Cu_3 monolayer, and (f) a metallic Cu_4 monolayer. The red and blue arrows indicate the d-band center and antibonding states, respectively.

affected by the relative occupancy of bonding and antibonding states. In other words, the position of the d-band center with respect to the Fermi level determines whether the interaction is likely to be attractive or repulsive. In Figure 4, it indicates that the antibonding states of Cu−O and Cu−C interactions are considerably occupied for the Cu(100) surface. For the metallic Cu_4 and Zn_1Cu_3 monolayers, however, as the d-band centers are tuned to shift upward, it results in fewer occupied antibonding states (see Figure 4). As a result, the CO_2 adsorption on these metallic monolayers exhibits more attractive features. Therefore, these metallic monolayers with a ZnO(000$\underline{1}$) support have indeed optimized the adsorption energy close to the peak of the volcano curve, compared with that of the pure Cu(100) surface.

Besides, Behrens et al.[5] claimed that the Zn-decorated Cu(211) surface is more active rather than the pure Cu(211) surface (hereafter, we will use CuZn(211) to refer to the Zn-decorated Cu(211) surface, unless otherwise stated). We also performed further investigations of CO_2 dissociation and hydrogenation to methanol on the metallic Cu_4 monolayer in order to compare the whole process with that on the CuZn(211) surface.[5] We have obtained considerably consistent conclusions, as expected by the d-band model. The calculated results for the hydrogenation processes are shown in Figure 5. For the Cu_4 case, all reaction steps are exothermic with respect to the clean Cu_4 surface and gaseous CO_2 and H_2 phases. The second step of CO_2 hydrogenation, namely, from HCOO* +
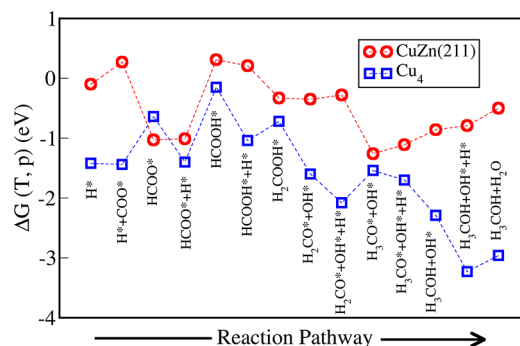

Figure 5. CO_2 reduction on a metallic Cu_4 monolayer under industrial pressure and temperature conditions is compared with reported results on a CuZn(211) surface.[5] The $\Delta G(T,p)$ scale is referred to the clean surface and gaseous CO_2 and H_2. The asterisk is to clarify the adsorbed species.

H* to HCOOH* species, is the most endothermic reaction for both CuZn(211) and the metallic Cu_4 monolayer. Obviously, the reaction on the metallic Cu_4 monolayer is more energetically favorable. Furthermore, the critical step of CO_2 dissociation is improved effectively on the metallic Cu_4 monolayer too (from H_2COOH^* to H_2CO^* + OH*). Besides, there are also more exothermic reactions for the hydrogenation process, that is, from the H_2CO^* + OH* species to CH_3OH + H_2O. Instead, there are more endothermic reactions on the CuZn(211) surface. This is exactly in agreement with the d-band model analysis.

On the one hand, the industrial catalyst is mostly prepared with a coprecipitation technique;[12] the pure Cu-covered monolayer (Cu_4) is not usually the dominant surface. On the other hand, the metallic Zn_3Cu_1 monolayer is relatively less stable in comparison with other surfaces. Therefore, the active sites of the industrial catalyst can be also contributed from the metallic Zn_2Cu_2 and Zn_1Cu_3 surfaces. We performed further investigations for the metallic Zn_2Cu_2 and Zn_1Cu_3 surfaces. It has been found that there are analogous activities for CO_2 reduction on the two surfaces too. The reaction energies of CO_2 hydrogenation are given in Table S4 of the Supporting Information. In the work of Behrens et al.,[5] they did not observe these surfaces in high-resolution transition electron microscopy (HRTEM). However, the HRTEM measurements were performed under conventional vacuum conditions, instead of conditions with a gaseous H_2 and CO_2 atmosphere. Therefore, these surfaces that we proposed are definitely reconstructed under vacuum conditions. This can explain why these surfaces that we proposed were not imaged. According to the above analyses, the CO_2 reduction is indeed feasible with the modified Cu/ZnO-based catalyst. The critical issue is to activate the modified Cu/ZnO-based catalyst before its industrial application.

In conclusion, we have employed first-principle thermodynamics to study phase diagrams and CO_2 reduction on the Cu/ZnO(000$\underline{1}$) surfaces. The calculated results suggest two synergy effects on the Cu/ZnO(000$\underline{1}$) surface. As the Cu could promote the formation of oxygen vacancies on the ZnO surface, the activity of the ZnO(000$\underline{1}$) surface can be improved significantly. Meanwhile, these metallic monolayers on the ZnO(000$\underline{1}$) surfaces have more localized d-band states, and also the Cu d-band states are tuned to shift considerably upward. This is the second synergy effect on the Cu/ZnO(000$\underline{1}$) surfaces. The CO_2 adsorption energies on these

metallic monolayers of Cu/ZnO(000$\underline{1}$) surfaces are optimized values, expected by the d-band model, close to the peak of volcano curve. The comparative studies of CO_2 adsorption and reduction have also demonstrated the optimized activity. It is in excellent agreement with the expectations of the d-band model.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The computational details, formation energies of various studied defects on all surface models, and reaction energies of hydrogenation. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: xiao@bccms.uni-bremen.de.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors have contributions equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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