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CO₂ activation and conversion on Cu catalysts: Revealing the role of Cu surface defect types in tuning the activity and selectivity



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ABSTRACT

Cu catalysts with different defect types are widely applied in CO_2 activation and conversion, however, the underlying role of Cu surface defect types in tuning the activity and selectivity is still unclear due to the complexity of surface defect types. This work constructed a series of Cu catalysts including the perfect surface, as well as the point and line defect surfaces to reveal the role of Cu surface defect types on CO_2 activation and conversion using theoretical calculations. The results show that Cu defect types can effectively tune the activity and selectivity of CO_2 activation and conversion; the line defect Cu surfaces have higher CO_2 activation activity than the point defect and perfect surfaces. Both the line defect $Cu(1 1 1)_{LD}$ and $(5 1 1)_{LD}$ surfaces are screened out to present the highest activity toward C_1 and C_2 species formation, respectively. Moreover, Cu surfaces with different defects present an inverted volcano-type curve between *d*-band center and CO_2 activation activity, both $Cu(1 1 1)_{LD}$ and $(5 1 1)_{LD}$ with excellent activity are attributed to the moderate *d*-band center. Further, the generalized coordination number (GCN) of Cu surfaces. The results can provide the valuable structural information for the design and prediction of Cu catalysts with excellent activity and selectivity in CO_2 activation and conversion.

1. Introduction

In recent years, a large amount of experimental and theoretical studies focused on CO_2 conversion into value-added chemicals [1–3], however, CO2 conversion confronted the lower activation rate and poorer product selectivity due to CO_2 lower thermodynamic energy [3]. So the key issue needed to be solved for CO2 as carbon source is to destabilize CO₂, namely, how to enhance CO₂ adsorption and activation. Nowadays, a general method to achieve CO₂ activation is to input huge amount of energy or use high-energy starting materials [4], alternatively, to achieve low-energy input, a better way is to accelerate CO₂ charge transfer, in which CO₂ coordination activation on the metal catalysts is a representative way [5-8]. For CO₂ activation on the transition metal surfaces [9,10], Liu et al. [11] studied CO₂ adsorption on the Fe, Co, Ni, and Cu fcc(100) surfaces, suggesting that CO₂ was chemisorbed on the Fe, Co, and Ni surfaces, while it was weakly bound to Cu surface. Wang et al. [12] pointed out that CO₂ adsorption on Ni surfaces has structure sensitivity; the charge transfers together with the bending of CO₂ induced the broader d orbitals and lower LUMO energy of Ni surfaces, and thus contributed to CO₂ activation.

Normally, CO_2 moiety exists as a physisorbed linear state or chemisorbed bent state (CO_2^{δ}) over the metals, the bending state can be ascribed to the electron transfer from the metal to CO_2 ; meanwhile, the more electron transfer means the stronger binding of CO_2 [9]. Further, alkali metals as electron donors also affect electron transfer and thus promote CO_2 activation [9,12,13], for example, the negatively charged CO_2^{δ} can be easily formed on the K-modified Rh(111) surface compared to the clean Rh(111) surface, which is attributed to the enhanced electrons back-donation from the K-modified Rh to an empty $CO_2 \pi^*$ orbital [13]. Arena *et al.* [14] showed that the electron-donating character of alkali metals (Li, Na, K) altered the electronic properties of Ni active phase and thus enhanced the ability of electron transfer.

Generally, the unsaturated coordination atoms have more dangling bonds and stronger bonding ability with adsorbates, which can be used as the active sites for CO_2 reduction reaction (CO_2RR) [15]. Recent studies showed that the unsaturated coordination sites could effectively activate the inert molecules and increase reactivity, in which the defective structures with more unsaturated coordination sites present higher reactivity [16,17]. According to the spatial dimension, the defective structure can be classified into the point defects, line defects,

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interface defects and bulk defects [18,19], among them, the point and line defects are commonly observed for the metal particles [15]. The point defects with small or even atomic scale exists on the crystal surfaces, and the line defects exist with the atom arrangement deviating from the ideal lattice structure along a line, especially, the twins and stacking faults.

Although Cu catalysts have been widely applied in CO₂ activation and conversion to produce hydrocarbons and alcohols, the undistorted pure Cu was quite inactive [20,21]. Previous experimental and theoretical studies have evidenced that the presence of defects over the metal surfaces would implement an active impact on CO2 conversion, for example, the intrinsic activity for methanol synthesis increased two times over the Cu stepped and kinked sites with only 2% of overall surface sites [22]. The higher selectivity for C_{2+} products in CO₂RR over the Cu(OH)₂-D/Cu foil can be ascribed to the abundant step sites on Cu surface, which promote CO adsorption and dimerization [23]. The star decahedron Cu NPs with stacking faults and twin defects are highly active for CO₂RR [24]. Similarly, Cu nanowires with rough surface exhibit the enhanced faraday efficiency of CO₂ reduction to C₂H₄, owing to the formation of a greater density of defective sites to enrich the unsaturated coordination sites [25]. Moreover, as reported by Zhu et al. [26] and Cheng et al. [27], the product distributions of CO₂RR was closely related to Cu atomic structure. Thus, aiming at promoting CO₂ activation and conversion, more attention should be paid to the function mechanism of the defects on Cu surfaces.

Further, the selectivity of Cu catalyst is connected to the coordination number (CN) of active sites, for example, Cu(111) surface with the CN = 9 of active sites has much lower C_2 selectivity compared to Cu (100) surface with CN = 8 [28]. The stepped Cu surface with the lower CN and larger step angle were conducive to the formation of C2+ alcohols [26]. Similarly, Cu surfaces with 6-CN or 7-CN active sites enhance the local CO concentration and thereby promote the formation of C2+ alcohols [29]. The *d*-band center of Cu surface with lower coordination number is relatively near Fermi level; moreover, the more d-electron lead to the stronger interaction between Cu catalyst and adsorbates [30]. Thus, the introduction of defects corresponds to the formation of unsaturated coordination sites, which change the catalytic performance and product selectivity for CO₂RR [31]. At present, the defects can been introduced by materials modification such as selective etching, doping and in situ oxidation or reduction post-treatment [32-34]. Moreover, the defect types would affect the geometric and electronic arrangements of Cu atoms [35]. Up to now, to the best of our knowledge, the deep understandings about the underlying role of Cu surface defect types in tuning the activity and selectivity of CO2 activation and conversion over Cu catalyst is still unclear. In view of the complexity and diversity of surface defect structures, the experiment characterization is hard to identify their function toward CO₂ activation [36]. Therefore, it is necessary to identify the underlying function mechanism of different Cu surface defect types in CO2 activation and conversion over Cu catalyst at a microscopic level.

This study is designed to reveal the underlying role of Cu surface defect types in tuning the activity and selectivity of CO_2 activation and conversion over Cu catalysts using density functional theoretical calculations. Here, various types of defective Cu surfaces are constructed to reflect different Cu defect types, which are expected to clarify the function mechanism of different Cu defects in CO_2 adsorption, activation and conversion to form C_1 and C_2 species. The fundamental understanding of the defect active site and the function mechanism is beneficial for the structural design of Cu catalysts with excellent activity and selectivity in CO_2 activation and conversion.

2. Computational details

2.1. Computational methods

Density functional theory calculations were implemented using

Dmol³ code in MS 8.0, and the Perdew-Burke-Ernzerhof (PBE) with generalized gradient approximation (GGA) exchange-correlation functional were employed [37-40]. The density functional semi-core pseudopotential (DSPP) was chosen to describe Cu atoms [39]. A double numerical plus polarization (DNP) function was used for the valence electron basis set, and the adsorbates are treated with the all electron basis set. Taking the van der Waals interactions into account, DFT + D method within Grimme's scheme was applied [41,42]. During geometry optimization, the tolerances of energy and force were 2×10^{-5} Ha and 0.004 Ha/Å, and the maximum displacement was 5 \times 10 3 Å, respectively. To ensure high-quality results, a real-space global orbital cutoff radius of 5.5 Å and a smearing of 0.005 Ha was applied to the orbital occupation. According to the supercell size, the Monkhorst-Pack scheme *k*-point meshes were set to $2 \times 2 \times 1$ for the (100), (100)_{PD} and (100)_{LD} surfaces, $3 \times 3 \times 1$ for the (111), (111)_{PD} and (111)_{LD} surfaces, $3 \times 2 \times$ 1 for the (122)_LD, (211)_LD and (511)_LD surfaces, and 4 \times 2 \times 1 for $(133)_{LD}$, which are accurate and efficient for the related calculations [43]. The bottom layer was fixed with the top two layers relaxed. A vacuum layer of 12 Å along the z-direction separated the adjacent slabs.

The linear synchronous transit and quadratic synchronous transit (LST/QST) methods was used to search for a transition state [42]. To confirm the searched transition state does indeed connect the initial state and final state, TS confirmation was performed to produce a refined reaction path based on TS search. Frequency analysis was used to confirm the single imaginary frequency of transition state, and carry out the zero-point energy (ZPE) correction and the thermodynamic energies correction at a certain temperature. Electronic energies and temperature corrections are provided in the Supplementary Material.

2.2. Surfaces models

Although the industrial Cu catalysts are very complex, Cu remains metallic under the conditions of CO₂ hydrogenation [44-46], so Cu catalysts are modeled using the well-defined single crystal structures [47]. Besides, the perfect metal surfaces are hard to be observed under the realistic reaction conditions; most of Cu NPs contained various defects; the most typical among it were twins and stacking faults [48]. The defects of Cu catalysts, such as the step sites, atom vacancies and lattice strain, could affect their intrinsic activity [48,49]. Behrens et al. [22] revealed that the atomic structure of high active Cu nanoparticles in the industrial Cu/ZnO/Al $_2O_3$ catalysts is in a defective form with more planar defects. Moreover, the metastable defect structures could keep the kinetic stabilization via the heteroatom-doping or interfacial strains during the reaction conditions, which are often reflected by the longterm activity of Cu catalysts [50]. For example, the experiment by Ding et al. [51] manifested that the performance of Cu@Na-Beta catalyst with the step defects remained stable for 100 h during CO₂ conversion (H₂/CO₂ = 3/1, 300 °C, 1.3 MPa). A decahedron Cu nanocatalyst with stacking and twin defects presented high C2H4 selectivity in CO2RR, which can be kept over 50% for 12 h [23]. Li et al. [52] reported a planar defect-rich Cu catalyst, the catalytic performance of CO₂-to-C₂₊ maintained stable for 50 h. Thus, the surface Cu defect types mentioned in this study are stable under the reaction conditions, and the stabilized defects could modify the coordination environments of Cu atoms and thus behave as the active sites for CO₂ conversion.

Cu usually adopts a close-packed face-centered cubic (fcc) structure, in which the (111), (110), and (100) are the main exposed surfaces [53]. Since Cu NPs mainly present the (111) surface and a small proportion of (100) surface under typical CO₂RR process [54], both (111) and (100) surfaces are chosen to investigate CO₂ activation and conversion on Cu catalysts. Meanwhile, for the influence of Cu defect types, both the point defect and line defect surfaces are considered based on both (111) and (100) surfaces. For the perfect Cu surfaces, the (111) and (100) surfaces with three-layer $p(4 \times 4)$ supercell are chosen. For the point defect (PD) surfaces, a Cu atom on the (111) and (100) surfaces is removed to simulate the atomic-like defective surfaces, named as Cu(hkl)_{PD}. For the line defect (LD) surfaces, a row of Cu atoms on the (111) and (100) surfaces are removed, named as Cu(hkl)_{LD}. All of the optimized surface models are presented in Fig. 1a \sim f.

The formation energy (E_f) of the defect was calculated to evaluate the stability of the defective Cu catalysts according to the equation of $E_f = E_V - E_P + \mu_{host}$ [55]. For Cu(111) surface, the formation energies of the point and line defects are 0.97 and 2.79 eV, respectively. For Cu(100) surface, those for the point and line defects are 0.96 and 2.09 eV, respectively. Namely, the formation of point defect on Cu surface is thermodynamically favorable compared to that of line defect.

Further, as shown in Fig. 1g ~ j, the stepped surfaces represent another types of line defect, which was the combination of two kinds of surfaces at the terraces, kinks or steps [56,57]. In this study, the (122)_{LD}, (133)_{LD}, (211)_{LD} and (511)_{LD} surfaces were chosen and modeled using a $p(4 \times 1)$ super cell. Among them, the (133)_{LD} and (122)_{LD} surfaces can be described as n-(111)×(111) (n = 3, 4) to reflect the different terrace widths and the same surface compositions, the (211)_{LD} and (511)_{LD} surfaces can be denoted as 3-(111)×(100) and 3-(100)×(111) to reflect the same terrace widths and the different surface compositions.

3. Results and discussion

Firstly, the adsorption behavior of CO_2 on different Cu surfaces is examined to identify the possible active sites. Secondly, the mechanism of CO_2 activation to HCOO* and CO* is illustrated in detail. Finally, CO conversion to C_1 and C_2 species after CO_2 reduction is deeply investigated. The optimized structures and the calculated adsorption free energies of prominent intermediates including CO^* , O^* , H_2^* , OH^* , H^* , *mono*-HCOO*, *trans*-COOH*, *cis*-COOH*, CHO*, COH*, CH₂O*, COCO*, COCHO*, CHOCHO* are presented in Fig. S1 and Table S1, respectively.

3.1. CO₂ adsorption behavior

CO₂ molecule has higher carbon oxidation state, the extremely stable electronic structure leading to the inherent thermodynamic stability and

kinetic inertness, in turn hinder CO_2 activation on Cu surfaces under the mild conditions [58,59]. In this regard, the construction of defect active sites to enhance Cu-CO₂ adsorption ability is one of the most effective ways to induce the inert CO_2 to undergo hydrogenation reaction [17]. To elucidate the role of defect types on CO_2 activation, CO_2 adsorption behavior on the perfect and defective Cu surfaces was examined, which are compared with the previous reports to ensure the reliability. The stable adsorption configurations of CO_2 in the linear and bent states are shown in Fig. 2, the adsorption free energies and key geometrical parameters of CO_2 molecule are listed in Table 1.

3.1.1. CO_2 adsorption on the perfect Cu surfaces

The optimized C-O bond length of gas-phase CO_2 molecule is 1.176 Å, which is consistent with 1.163 Å in gas-phase molecule [60]. The bent O-C-O angle and the stretched C-O bond are employed to reflect the ability of CO_2 activation [61].

On the perfect (111) and (100) surfaces (Fig. 2a and b), the linear state CO₂ exists with the adsorption energies of -0.35 and -0.33 eV, respectively. CO₂ configuration has no significant change compared to gas phase CO₂. Previous studies [62,63] also found that the bent state CO_2^{δ} wasn't observed on Cu(111), and the linear state CO₂ has the adsorption energies of -0.35 and -0.39 eV on the (111) and (100). However, the bent state CO_2^{δ} was identified on (100) with the adsorption energy of 0.13 eV, namely, CO₂ adsorption needs the energy, and the bent state CO_2^{δ} is unstable. Both C and O atoms of CO₂ bind with Cu atoms at the 4-fold site with the C-O bond lengths of 1.224 and 1.272 Å and the bent O-C-O angle of 133.884° (Fig. 2b), which also agrees with previous results [62]. Thus, CO₂ weakly adsorbed on the perfect Cu surfaces, and CO₂ adsorption to the bent state CO_2^{δ} is unfavored thermodynamically.

3.1.2. CO_2 adsorption on the point defect Cu surfaces

On the point defect $(111)_{PD}$ and $(100)_{PD}$, the linear and bent states of CO₂ adsorption were observed, as presented in Fig. 2c and d. CO₂ exists as the linear state at the defect sites with the adsorption energies of -0.37 and -0.36 eV, respectively. Interestingly, CO₂ exists as the bent



Fig. 1. The optimized structures of Cu(hkl), Cu(hkl)_{PD} and Cu(hkl)_{LD} surfaces. Orange and blue balls stand for Cu atoms on the perfect surface and those at the defect sites, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. The stable adsorption configurations of CO_2 on the Cu(hkl), Cu(hkl)_{PD} and Cu(hkl)_{LD} surfaces. (Left: the liner state, right: the bent state). Red and gray balls stand for O and C atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

state with the C and O atoms of CO₂ bonding with the defective Cu sites, the adsorption energies are -0.30 and -0.11 eV on the $(111)_{PD}$ and $(100)_{PD}$. The C-O bond lengths of CO₂^{δ -} are 1.286 and 1.291 Å with the O-C-O angle of 120.881° on $(111)_{PD}$, those are 1.251 and 1.266 Å with the O-C-O angle of 129.714° on $(100)_{PD}$.

Thus, compared to the perfect (111) and (100) surfaces, for CO₂ adsorption to the bent state $\text{CO}_2^{\delta^2}$, both (111)_{PD} and (100)_{PD} surfaces could stabilize the bent state $\text{CO}_2^{\delta^2}$, and (111)_{PD} is better than (100)_{PD}

in terms of the energetic or geometric parameters. Namely, the introduction of point defect on the perfect Cu(111) and (100) significantly promote CO_2 adsorption and activation in thermodynamics.

3.1.3. CO_2 adsorption on the line defect Cu surfaces

On the $(111)_{LD}$ and $(100)_{LD}$, as shown in Fig. 2e and 2f, CO₂ exists as a linear state at the defect sites with the adsorption energies of -0.35 and -0.37 eV, respectively. CO₂^{δ -} exists as a bent state with the C and O

Table 1

The adsorption energy (E_{ads}/eV), C-O bond length ($d_{C-O}/Å$) and O-C-O angle ($\angle OCO/^{\circ}$) of CO₂* in the linear and bent states at the most favorable sites on the Cu(hkl), Cu(hkl)_{PD} and Cu(hkl)_{LD} surfaces.

Surfaces	Linear state			Bent state		
	E _{ads}	$d_{ ext{C-O}}$	∠0C0	E _{ads}	$d_{ ext{C-O}}$	∠0C0
Cu(111)	-0.35	1.177, 1.177	179.067	_	_	_
Cu(100)	-0.33	1.177, 1.177	179.661	0.13	1.224, 1.272	133.884
Cu(111) _{PD}	-0.37	1.176, 1.176	179.731	-0.30	1.286, 1.291	120.881
Cu(100) _{PD}	-0.36	1.177, 1.177	179.717	-0.11	1.251, 1.266	129.714
Cu(111) _{LD}	-0.35	1.176, 1.177	179.050	-0.55	1.264, 1.292	123.668
Cu(100) _{LD}	-0.37	1.177, 1.177	179.589	-0.06	1.227, 1.232	142.300
Cu(122) _{LD}	-0.36	1.177, 1.177	179.094	-0.02	1.219, 1.226	145.934
Cu(133) _{LD}	-0.35	1.177, 1.177	179.345	-0.04	1.219, 1.226	145.365
Cu(211) _{LD}	-0.38	1.176, 1.176	178.925	-0.07	1.224, 1.231	143.637
Cu(511) _{LD}	-0.37	1.176, 1.177	179.585	-0.02	1.222, 1.228	144.108

"-" represents that the bent state of CO2* cannot exist.

atoms of CO₂ adsorbed at the defective Cu sites. On $(111)_{LD}$, the bent state CO₂^{δ -} has the adsorption energy of -0.55 eV, the O-C-O angle is 123.668° with the C-O bond lengths of 1.264 and 1.292 Å. On $(100)_{LD}$, the adsorption energy of bent state CO₂^{δ -} was only -0.06 eV, the O-C-O angle is 142.300° with the C-O bond lengths of 1.227 and 1.232 Å. Thus, the bent state CO₂^{δ -} is thermodynamically favorable than the linear state on $(111)_{LD}$; the opposite thing occurs on $(100)_{LD}$. Namely, only the introduction of line defect on Cu(111) surface is an effective way for CO₂ adsorption to the bent state CO₂^{δ -}, which is better than the point defect $(111)_{PD}$ and $(100)_{PD}$ surfaces.

On the $(122)_{LD}$ and $(133)_{LD}$, CO_2 exists as a linear state with the adsorption energies of -0.36 and -0.35 eV; while $CO_2^{\delta^2}$ exists as a bent state at the step sites with the adsorption energies of -0.02 and -0.04 eV. On $(122)_{LD}$, the angle of bent state $CO_2^{\delta^2}$ is 145.934° with the C-O bond lengths of 1.219 and 1.226 Å. On $(133)_{LD}$, the angle of bent state $CO_2^{\delta^2}$ is 145.365° with the C-O bond lengths of 1.219 and 1.226 Å. On $(133)_{LD}$, the angle of bent state $CO_2^{\delta^2}$ is 145.365° with the C-O bond lengths of 1.219 and 1.226 Å. Thus, compared to the $(111)_{LD}$ and $(100)_{LD}$ with the flatted structure, the bent state $CO_2^{\delta^2}$ on the $(122)_{LD}$ and $(133)_{LD}$ with the stepped structure was unstable; and the linear state $CO_2^{\delta^2}$.

On the $(211)_{LD}$ and $(511)_{LD}$, CO_2 exists as a linear state with the adsorption energies of -0.38 and -0.37 eV, respectively; however, the bent state CO_2^{δ} has a weak interaction with Cu atoms. On $(211)_{LD}$, the adsorption energy of bent state CO_2^{δ} is -0.07 eV with the O-C-O angle of 143.637° and the C-O bond lengths of 1.224 and 1.231 Å. On $(511)_{LD}$, the adsorption energy of bent state CO_2^{δ} is -0.02 eV, the angle of CO_2^{δ} is 144.108° with the C-O bond lengths of 1.222 and 1.228 Å. Thus, for CO_2 adsorption to the bent state CO_2^{δ} , the linear state CO_2 is thermodynamically favorable than the bent state CO_2^{δ} on the $(211)_{LD}$ and $(511)_{LD}$ surfaces.



Fig. 3. Relationship between the adsorption energy and Bader charge of bent state CO_2^{δ} on the different line defect Cu(hkl)_{LD} surfaces.

As presented in Fig. 3, the adsorption energies of bent state $\text{CO}_2^{\delta-}$ are positively correlated to Bader charge of $\text{CO}_2^{\delta-}$ on the different $\text{Cu}(\text{hkl})_{\text{LD}}$ surfaces, especially, the $(1\,1\,1)_{\text{LD}}$ surface exhibits the stronger binding of CO_2 due to the more electron transfer from the defective sites to CO_2 moiety. Moreover, compared to the $(1\,1\,1)_{\text{LD}}$ and $(1\,0\,0)_{\text{LD}}$ surfaces, the $(1\,2\,2)_{\text{LD}}$, $(1\,3\,3)_{\text{LD}}$, $(2\,1\,1)_{\text{LD}}$ and $(5\,1\,1)_{\text{LD}}$ surfaces consisted of 4- $(1\,1\,1) \times (1\,1\,1)$, 3- $(1\,1\,1) \times (1\,1\,1) \times (1\,0\,0)$ and 3- $(1\,0\,0) \times (1\,1\,1)$ has relatively weaker interaction with the bent state $\text{CO}_2^{\delta-}$.

3.1.4. The influences of Cu defect site types on CO₂ adsorption

As mentioned above, CO_2 adsorption behaviors on Cu surfaces with different defect types suggested that the existence of defect sites can favor CO_2 adsorption to the bent state $CO_2^{\delta^-}$, however, the linear state CO_2 is more preferred on Cu surfaces expect for $Cu(1 \ 1 \ 1)_{LD}$. As presented in Fig. 2 and Table 1, the linear state CO_2 adsorbed on all surfaces exhibited the similar adsorption energies and configurations, CO_2 molecule was away from surfaces and keeps the geometrical structure of gas-phase CO_2 molecule, indicating that the C-O bond of CO_2 was not activated. Apparently, in terms of adsorption energies, adsorption configurations and Bader charge of $CO_2^{\delta^-}$, CO_2 has a weak interaction with the perfect Cu surfaces; the energy was required to activate CO_2 from a linear state to a bent state.

On the other hand, the bent state CO_2^{δ} is generally considered as an activation state of CO_2 , which correspond to the elongated C-O bond length and bent O-C-O angle [61] the introduction of defect sites promoted the process of CO_2 adsorption to the bent state CO_2^{δ} , and showing a structure-dependence between CO_2 adsorption and defect site types. The defects on Cu surfaces enhanced Cu coordination activation ability for CO_2 activation via accelerating the charge transfer and decreasing the energy input. However, only on $\text{Cu}(111)_{\text{LD}}$ surface, the bent state CO_2^{δ} is more preferred than the linear state, namely, the stable bent state CO_2^{δ} was effectively activated (Fig. 2e). Thus, the line defect $\text{Cu}(111)_{\text{LD}}$ surface would be the most effective way to activate CO_2 to the bent state CO_2^{δ} , while the other defect surfaces do not stabilize the bent state CO_2^{δ} .

3.2. CO₂ activation and conversion pathways on different Cu surfaces

Generally, both formate (HCOO^{*}) and carboxyl (COOH^{*}) are two possible C₁ intermediates for CO₂ hydrogenation activation on Cu-based catalysts [59–61]. Alternatively, CO₂ direct dissociation to CO^{*} on the defective surfaces with the step or kink structures is more favorable in kinetics than that on the perfect Cu surfaces [62–64], namely, the defect types can alter CO₂ activation pathway. Further, HCOO^{*} intermediate is mainly responsible for methanol formation [65–68], CO^{*} formed by COOH^{*} pathway and CO₂ direct dissociation dominantly contribute to C₁ or C₂ species [69–71]. Thus, as presented in Fig. 4, three CO₂ activation pathways, CO₂^{*} \rightarrow CO^{*}+O^{*}, CO₂^{*}+H^{*} \rightarrow mono-HCOO^{*} and CO₂^{*}+H^{*} \rightarrow trans-COOH^{*} \rightarrow CO^{*}+OH^{*}, are considered, as shown in



Fig. 4. Reaction mechanism of CO₂ activation and CO conversion on the different Cu surfaces.

Figs. S3 ~ S6. Notably, our results showed that the reaction *trans*-COOH* \rightarrow CO*+OH* goes through *cis*-COOH* intermediate.

3.2.1. H_2 dissociation on Cu surfaces

For CO₂ hydrogenation activation, H₂ dissociation is the key initial step [69], as presented in Fig. S2, the results show that the dissociation of H₂ on all considered Cu surfaces are highly exothermic, and the activation barriers of H₂ dissociation on all Cu surfaces are all about 0.5 eV, which agreed well with the previous experimental and theoretical studies [72], namely, the dissociation of H₂ into two H^{*} atoms on Cu surfaces is kinetically easy. Namely, H₂ dissociation is favorable kinetically and thermodynamically on the perfect and defective Cu surfaces, Cu catalysts exhibit highly catalytic activity toward H₂ dissociation, which can provide enough hydrogen sources for CO₂ hydrogenation.

3.2.2. CO₂ activation on the perfect Cu surfaces

On (111) surface (Fig. S3a), the overall barriers of CO_2 direct dissociation, CO_2 hydrogenation to *mono*-HCOO* or CO via COOH* pathway are 1.87, 1.15 and 1.84 eV, respectively. Correspondingly, those are 1.42, 1.03 and 1.90 eV on (100) surface (Fig. S3b). Thus, *mono*-HCOO* formation (1.15 and 1.03 eV) on the (111) and (100) surfaces is kinetically favorable than CO* formation via COOH* pathway (1.84 and 1.90 eV) and CO_2 direct dissociation (1.87 and 1.42 eV).

3.2.3. CO_2 activation on the point defect Cu surfaces

On $(111)_{PD}$, see Fig. S4a, the overall barriers of CO₂ direct dissociation, CO₂ hydrogenation to *mono*-HCOO^{*} or CO via COOH^{*} pathway are 1.22, 1.02 and 1.76 eV, respectively. On $(100)_{PD}$, see Fig. S4b, those are 1.81, 0.92 and 1.86 eV, respectively. Thus, *mono*-HCOO^{*} formation is preferred on these two surfaces.

Compared to the perfect (111) and (100) surfaces, the point defect surfaces did not change the most favorable pathways of CO_2 activation. However, the activity of CO_2 hydrogenation to *mono*-HCOO* on the (111)_{PD} and (100)_{PD} is higher than that on the perfect surfaces (1.02 and 0.92 vs. 1.15 and 1.03 eV), which can be attributed to the enhanced CO_2 adsorption ability on Cu(hkl)_{PD}. Further, CO_2 direct dissociation into CO is kinetically easier on (111)_{PD} than that on (100)_{PD} (1.22 vs. 1.81 eV) due to the presence of the stable bent state CO_2^{δ} on (111)_{PD}.

3.2.4. CO₂ activation on the line defect Cu surfaces

For CO₂ activation on Cu(hkl)_{LD}, two cases exist, one is the $(111)_{LD}$ and $(100)_{LD}$ surfaces with the flatted structure, the other is Cu surfaces

with the stepped structure.

On the $(111)_{LD}$ and $(100)_{LD}$, as presented in Figs. S5a and S5b, *mono*-HCOO* formation is still preferred compared to other two pathways (0.43 vs. 1.63, 2.05 eV; 0.71 vs. 1.91, 1.92 eV). Compared to the $(111)_{PD}$ and $(100)_{PD}$, the activity of CO₂ activation to HCOO* is higher on the $(111)_{LD}$ and $(100)_{LD}$ (0.43 and 0.71 eV).

For the $(122)_{LD}$ and $(133)_{LD}$ consisted of (111) and (111) surfaces, as shown in Figs. S6a and S6b, the formation of *mono*-HCOO* and CO* via CO₂ direct dissociation are two parallel pathways on $(122)_{LD}$ (0.88 vs. 0.87 eV), CO₂ direct dissociation to CO* is much easier in kinetics compared to CO* formation via COOH* pathway. On $(133)_{LD}$ surface, CO* formation is rather difficult through either CO₂ direct dissociation or COOH* pathway (1.66 and 1.93 eV) compared to *mono*-HCOO* formation (0.81 eV). Thus, the activity of CO₂ activation on the $(122)_{LD}$ and $(133)_{LD}$ was lower than those on the $(111)_{LD}$ and $(100)_{LD}$ (0.88/ 0.87, 0.81 vs. 0.43, 0.71 eV).

For the $(211)_{LD}$ and $(511)_{LD}$ consisted of (111) and (100) surfaces, see Figs. S6c and S6d, *mono*-HCOO* formation is predominated compared to CO* formation (0.74 vs. 0.97, 2.02 eV) on $(211)_{LD}$; while CO₂ direct dissociation to CO* is kinetically preferred than other two pathways on $(511)_{LD}$ surface (0.60 vs. 1.31, 1.90 eV).

As mentioned above, the $(511)_{LD}$ surface exhibits the highest activity of CO₂ activation among the four stepped Cu surfaces (0.60 vs. 0.88/0.87, 0.81, 0.74 eV), indicating that CO₂ activation on the stepped surface consisted of $(100) \times (111)$ is superior to that on the stepped surfaces consisted of $(111) \times (111)$ and $(111) \times (100)$.

3.2.5. The influences of Cu defect site types on CO_2 activation and its subsequent conversion

Cu catalysts are known to provide a wide product distribution in the CO_2RR , in which HCOO^{*} as a key intermediate that dominantly contributes to methanol formation [64–67]; alternatively, CO is another key intermediate that not only involves in methanol synthesis, but also contributes to the formation of C_2 species, such as ethylene and ethanol [68,69]. Meanwhile, CO may either come from the mixture feed gas or CO_2 reduction via COOH^{*} pathway/direct dissociation. Thus, the product distribution on Cu catalysts is mainly related to CO_2 activation pathways.

As shown in Fig. 5, for the perfect and point defect Cu surfaces, CO_2 hydrogenation to *mono*-HCOO^{*} is kinetically preferred than CO^{*} formation. For the line defect Cu surfaces, the same thing occurred on the $(111)_{LD}$, $(100)_{LD}$, $(133)_{LD}$ and $(211)_{LD}$. However, both *mono*-HCOO^{*} formation and CO_2 direct dissociation to CO^{*} were two parallel



Fig. 5. Free energy profiles of the most favorable pathway of CO_2 activation to $HCOO^*$ and CO^* on the $Cu(hkl)_{PD}$ and $Cu(hkl)_{LD}$ surfaces, the corresponding structures of the initial, transition and final states are presented in Figs. S3 ~ S6.

pathways on $(122)_{LD}$; CO_2 direct dissociation to CO^* is dominant on $(511)_{LD}$. Generally, CO_2 activation activity follows the order of Cu (hkl)_{LD} > Cu(hkl)_{PD} > Cu(hkl), namely, the introduced defect improved CO_2 activation activity, and the line defect Cu catalysts were identified to be the most preferred for CO_2 activation.

Thus, expect for the $(122)_{LD}$ and $(511)_{LD}$ surfaces, *mono*-HCOO^{*} is identified as the main intermediate of CO₂ activation on all other Cu surfaces, followed by its subsequent reactions to dominantly produce methanol. On $(122)_{LD}$, both *mono*-HCOO^{*} and CO^{*} can participate into methanol synthesis, alternatively, CO^{*} can also contribute to the production of C₂ species via C–C coupling. On $(511)_{LD}$, CO^{*} as the main intermediate can contribute to methanol or C₂ species.

3.3. CO conversion and C-C coupling pathways

As mentioned above, CO₂ is reduced to CO*, followed by its hydrogenation to methanol or the coupling to C₂ species, the C–C bond formation of C₂ species may goes through the coupling of CO*+CO* [73–76], CO*+COH*, CO*+CHO*, COH*+COH* [77,78] and CHO*+CHO* [79]. Our results show that CHO* formation is favored kinetically than COH* formation on different Cu surfaces (Table 2 and Fig. S7), so only three coupling pathways of CO*+CO*, CO*+CHO* and CHO*+CHO* are considered in this study. Moreover, since CH₂O* was identified as the precursor of methanol synthesis in CO hydrogenation [60,65,71], CHO* hydrogenation to CH₂O* is also considered. Thus, CO conversion to form CH₂O* and C₂ species is examined (see Figs. S8 ~ S11).

3.3.1. CO conversion on the perfect Cu surfaces

On (111) surface, as presented in Fig. S8a, beginning with the adsorbed CO* species, the overall barriers of CH_2O^* formation and the C–C coupling reactions via CO*+CO*, CO*+CHO* and CHO*+CHO* are 1.61, 2.01, 2.26 and 1.30 eV, respectively. On (100) surface, those are 1.37, 1.90, 1.65 and 1.18 eV, respectively (see Fig. S8b).

Thus, both (111) and (100) surfaces are favorable for the formation of C₂ species rather than methanol in CORR, the most preferred pathway of C₂ species formation was CHO^{*} dimerization, especially, the (100) surface exhibits higher activity of C₂ formation than (111) surface (1.18 *vs.* 1.30 eV).

3.3.2. CO conversion on the point defect Cu surfaces

On $(111)_{PD}$, see Fig. S9a, CO dimerization is the most preferred in kinetics compared to CH₂O formation, CO^{*}+CHO^{*} and CHO^{*}+CHO^{*} (1.21 vs. 1.31, 1.86 and 2.05 eV), namely, C₂ species formation is more active on $(111)_{PD}$ surface than that on the perfect (111) surface (1.21 vs. 1.30 eV). However, the $(100)_{PD}$ favors CH₂O^{*} formation rather than the C–C coupling (1.16 vs. 1.30, 1.83 and 1.81 eV, Fig. S9b), namely, the $(100)_{PD}$ surface alters product distribution (methanol) compared to the perfect (100) surface (C₂ species).

3.3.3. CO conversion on the line defect Cu surfaces

On $(111)_{LD}$ (see Fig. S10a), the overall barrier of CO dimerization is lower than those of CH₂O^{*} formation, CO^{*}+CHO^{*} coupling and CHO^{*} dimerization (1.18 *vs.* 1.22, 1.53 and 2.07 eV). On $(100)_{LD}$ (see Fig. S10b), CH₂O^{*} formation is more favorable than CO^{*}+CO^{*}, CO^{*}+CHO^{*} and CHO^{*}+CHO^{*} coupling (1.26 *vs.* 2.18, 1.55 and 3.27 eV).

On the $(122)_{LD}$ and $(133)_{LD}$, CH₂O* formation is kinetically favorable than C–C coupling via CO*+CO*, CO*+CHO* and CHO*+CHO* (1.27 vs. 1.44, 2.46 and 1.67 eV, Fig. S11a; 1.29 vs. 2.21, 2.38 and 1.38 eV, Fig. S11b). Thus, these two surfaces show a preference for C₁ species instead of C₂ species.

On $(211)_{LD}$ (Fig. S11c), CHO* dimerization is the most favorable pathways of C–C coupling (1.17 *vs.* 1.65, 1.91 eV), which is also preferred than CH₂O* formation (1.17 *vs.* 1.26 eV). On $(511)_{LD}$ (Fig. S11d), CHO* as the common intermediate leads to CH₂O* formation or CHO* dimerization with the same overall barrier of 1.09 eV, however, CHO* dimerization is favorable than CHO* hydrogenation in kinetics (0.91 *vs.* 1.01 eV) and thermodynamics (–0.59 *vs.* 0.20 eV).

Table 2

Activation energy (G_a) and reaction energy (ΔG) at 523 K of the elementary reactions involving in H₂ dissociation, CO₂ activation and CO conversion on the Cu(hkl), Cu(hkl)_{PD} and Cu(hkl)_{LD} surfaces.

Reactions	Cu(111)	Cu(100)	Cu	Cu	Cu
			$(111)_{PD}$	$(100)_{PD}$	$(111)_{LD}$
$H_{2}^{*} \rightarrow H^{*}+H^{*}$	0.53	0.52	0.50	0.48	0.50
2 .	(-0.43)	(-0.40)	(-0.34)	(-0.44)	(-0.45)
$CO_2^* \rightarrow CO^*+O^*$	1.87	1.42	1.22	1.81	2.05
-	(0.92)	(0.33)	(0.14)	(0.34)	(0.73)
$CO_2^* + H^* \rightarrow$	1.15	1.03	1.02	0.92	0.43
mono-HCOO*	(0.34)	(0.18)	(0.46)	(0.56)	(-0.52)
$CO_2^* + H^* \rightarrow$	1.84	1.90	1.76	1.86	1.63
trans-COOH*	(0.79)	(0.51)	(0.56)	(0.62)	(0.47)
trans-COOH* \rightarrow	0.59	0.61	0.61	0.61	0.56
cis-COOH*	(0.04)	(0.01)	(0.01)	(-0.02)	(-0.02)
cis-COOH* →	0.80	1.10	0.10	0.99	1.09
CO*+OH*	(-0.43)	(-0.42)	(-0.23)	(-0.81)	(-0.73)
$CO^*+H^* \rightarrow$	1.19	1.18	1.10	1.16	1.16
CHO*	(0.95)	(0.78)	(0.76)	(0.53)	(0.63)
$\rm CO^* \!\!+\! H^* \rightarrow$	2.92	3.28	3.10	3.17	3.34
COH*	(1.24)	(1.04)	(1.40)	(1.14)	(1.33)
$\rm CHO^*{+}H^* \rightarrow$	0.66	0.59	0.55	0.58	0.59
CH ₂ O*	(-0.19)	(-0.13)	(-0.35)	(-0.08)	(-0.13)
$\rm CO^*+\rm CO^* \rightarrow$	2.01	1.90	1.21	1.30	1.18
COCO*	(1.67)	(1.53)	(1.19)	(1.28)	(0.83)
$\rm CO^*{+}CHO^* \rightarrow$	1.31	0.87	1.10	1.30	0.90
COCHO*	(0.31)	(0.33)	(0.15)	(0.47)	(0.18)
$\rm CHO^*{+}\rm CHO^* \rightarrow$	0.35	0.25	1.29	1.28	1.44
CHOCHO*	(-1.33)	(-1.30)	(-0.99)	(-0.99)	(-1.70)
Reactions	Cu	Cu	Cu	Cu	Cu
Reactions	Cu (100) _{LD}	Cu (122) _{LD}	Cu (133) _{LD}	Cu (211) _{LD}	Cu (511) _{LD}
Reactions	Cu (100) _{LD}	Cu (122) _{LD}	Cu (133) _{LD}	Cu (211) _{LD}	Cu (511) _{LD}
Reactions $H_2^* \rightarrow H^* + H^*$	Cu (100) _{LD} 0.48	Cu (122) _{LD} 0.48	Cu (133) _{LD} 0.51	Cu (211) _{LD} 0.53	Cu (511) _{LD} 0.57
Reactions $H_2^* \rightarrow H^* + H^*$	Cu (100) _{LD} 0.48 (-0.42) 1.92	Cu (122) _{LD} 0.48 (-0.45) 0.88	Cu (133) _{LD} 0.51 (-0.35) 1.66	Cu (211) _{LD} 0.53 (-0.43) 0.97	Cu (511) _{LD} 0.57 (-0.24) 0.60
Reactions $H_{2}^{*} \rightarrow H^{*} + H^{*}$ $CO_{2}^{*} \rightarrow CO^{*} + O^{*}$	Cu (100) _{LD} 0.48 (-0.42) 1.92 (0.46)	Cu (122) _{LD} 0.48 (-0.45) 0.88 (0.65)	Cu (133) _{LD} 0.51 (-0.35) 1.66 (0.95)	Cu (211) _{LD} 0.53 (-0.43) 0.97 (0.44)	Cu (511) _{LD} 0.57 (-0.24) 0.60 (-0.99)
Reactions $H_2^* \rightarrow H^* + H^*$ $CO_2^* \rightarrow CO^* + O^*$ $CO_2^* + H^* \rightarrow$	Cu (100) _{LD} 0.48 (-0.42) 1.92 (0.46) 0.71	Cu (122) _{LD} 0.48 (-0.45) 0.88 (0.65) 0.87	Cu (133) _{LD} 0.51 (-0.35) 1.66 (0.95) 0.81	Cu (211) _{LD} 0.53 (-0.43) 0.97 (0.44) 0.74	Cu (511) _{LD} 0.57 (-0.24) 0.60 (-0.99) 1.31
Reactions $H_2^* \rightarrow H^* + H^*$ $CO_2^* \rightarrow CO^* + O^*$ $CO_2^* + H^* \rightarrow$ mage $HCOO^*$	Cu (100) _{LD} 0.48 (-0.42) 1.92 (0.46) 0.71 (0.38)	Cu (122) _{LD} 0.48 (-0.45) 0.88 (0.65) 0.87 (0.50)	Cu (133) _{LD} 0.51 (-0.35) 1.66 (0.95) 0.81 (0.46)	Cu (211) _{LD} 0.53 (-0.43) 0.97 (0.44) 0.74 (0.46)	Cu (511) _{LD} 0.57 (-0.24) 0.60 (-0.99) 1.31 (-0.10)
Reactions $H_2^* \rightarrow H^* + H^*$ $CO_2^* \rightarrow CO^* + O^*$ $CO_2^* + H^* \rightarrow$ mono-HCOO* $CO_2^* + H^* \rightarrow$	Cu (100) _{LD} 0.48 (-0.42) 1.92 (0.46) 0.71 (0.38) 1.91	Cu (122) _{LD} 0.48 (-0.45) 0.88 (0.65) 0.87 (0.50) 1.87	Cu (133) _{LD} 0.51 (-0.35) 1.66 (0.95) 0.81 (0.46) 1.93	Cu (211) _{LD} 0.53 (-0.43) 0.97 (0.44) 0.74 (0.46) 2.02	Cu (511) _{LD} 0.57 (-0.24) 0.60 (-0.99) 1.31 (-0.10) 1.90
Reactions $H_2^* \rightarrow H^* + H^*$ $CO_2^* \rightarrow CO^* + O^*$ $CO_2^* + H^* \rightarrow$ mono-HCOO* $CO_2^* + H^* \rightarrow$ mrans-COOH*	Cu (100) _{LD} 0.48 (-0.42) 1.92 (0.46) 0.71 (0.38) 1.91 (0.65)	Cu (122) _{LD} 0.48 (-0.45) 0.88 (0.65) 0.87 (0.50) 1.87 (0.51)	Cu (133) _{LD} 0.51 (-0.35) 1.66 (0.95) 0.81 (0.46) 1.93 (0 58)	Cu (211) _{LD} 0.53 (-0.43) 0.97 (0.44) 0.74 (0.46) 2.02 (0.50)	Cu (511) _{LD} 0.57 (-0.24) 0.60 (-0.99) 1.31 (-0.10) 1.90 (0.57)
Reactions $H_2^* \rightarrow H^* + H^*$ $CO_2^* \rightarrow CO^* + O^*$ $CO_2^* + H^* \rightarrow$ $mono-HCOO^*$ $CO_2^* + H^* \rightarrow$ $trans-COOH^*$ $trans-COOH^* \rightarrow$	Cu (100) _{LD} 0.48 (-0.42) 1.92 (0.46) 0.71 (0.38) 1.91 (0.65) 0.53	$\begin{array}{c} \textbf{Cu} \\ (122)_{\text{LD}} \end{array} \\ \hline 0.48 \\ (-0.45) \\ 0.88 \\ (0.65) \\ 0.87 \\ (0.50) \\ 1.87 \\ (0.51) \\ 0.54 \end{array}$	Cu (133) _{LD} 0.51 (-0.35) 1.66 (0.95) 0.81 (0.46) 1.93 (0.58) 0.60	$\begin{array}{c} {\bf Cu} \\ (211)_{\rm LD} \\ \hline 0.53 \\ (-0.43) \\ 0.97 \\ (0.44) \\ 0.74 \\ (0.46) \\ 2.02 \\ (0.50) \\ (0.53) \\ \end{array}$	Cu (511) _{LD} 0.57 (-0.24) 0.60 (-0.99) 1.31 (-0.10) 1.90 (0.57) 0.52
Reactions $H_2^* \rightarrow H^* + H^*$ $CO_2^* \rightarrow CO^* + O^*$ $CO_2^* + H^* \rightarrow$ $mono \cdot HCOO^*$ $CO_2^* + H^* \rightarrow$ $trans \cdot COOH^*$ $trans \cdot COOH^*$	$\begin{array}{c} Cu\\ (100)_{LD} \end{array}$ 0.48 (-0.42) 1.92 (0.46) 0.71 (0.38) 1.91 (0.65) 0.53 (-0.07)	$\begin{array}{c} Cu\\ (122)_{LD} \end{array}$ 0.48 (-0.45) 0.88 (0.65) 0.87 (0.50) 1.87 (0.51) 0.54 (-0.04)	$\begin{array}{c} Cu\\ (133)_{LD}\\ \hline 0.51\\ (-0.35)\\ 1.66\\ (0.95)\\ 0.81\\ (0.46)\\ 1.93\\ (0.58)\\ 0.60\\ (-0.03)\\ \end{array}$	$\begin{array}{c} Cu\\ (211)_{LD}\\ \hline 0.53\\ (-0.43)\\ 0.97\\ (0.44)\\ 0.74\\ (0.46)\\ 2.02\\ (0.50)\\ 0.53\\ (-0.07)\\ \end{array}$	$\begin{array}{c} Cu\\ (511)_{LD} \end{array}$ 0.57 (-0.24) 0.60 (-0.99) 1.31 (-0.10) 1.90 (0.57) 0.52 (-0.10)
Reactions $H_2^* \rightarrow H^* + H^*$ $CO_2^* \rightarrow CO^* + O^*$ $CO_2^* + H^* \rightarrow$ mono-HCOO* $CO_2^* + H^* \rightarrow$ trans-COOH* trans-COOH* cis-COOH* \rightarrow	Cu (100) _{LD} 0.48 (-0.42) 1.92 (0.46) 0.71 (0.38) 1.91 (0.65) 0.53 (-0.07) 0.51	$\begin{array}{c} Cu\\ (122)_{LD} \end{array}$ 0.48 (-0.45) 0.88 (0.65) 0.87 (0.50) 1.87 (0.51) 0.54 (-0.04) 1.09	Cu (133) _{LD} 0.51 (-0.35) 1.66 (0.95) 0.81 (0.46) 1.93 (0.58) 0.60 (-0.03) 0.62	Cu (211) _{LD} 0.53 (-0.43) 0.97 (0.44) 0.74 (0.46) 2.02 (0.50) 0.53 (-0.07) 1.01	Cu (511) _{LD} 0.57 (-0.24) 0.60 (-0.99) 1.31 (-0.10) 1.90 (0.57) 0.52 (-0.10) 1.03
Reactions $H_2^* \rightarrow H^* + H^*$ $CO_2^* \rightarrow CO^* + O^*$ $CO_2^* + H^* \rightarrow$ mono-HCOO* $CO_2^* + H^* \rightarrow$ trans-COOH* trans-COOH* cis-COOH* \rightarrow cis -COOH* \rightarrow $CO^* + OH^*$	Cu $(1 \ 0 \ 0)_{LD}$ 0.48 (-0.42) 1.92 (0.46) 0.71 (0.38) 1.91 (0.65) 0.53 (-0.07) 0.51	$\begin{array}{c} Cu \\ (122)_{LD} \end{array}$ 0.48 (-0.45) 0.88 (0.65) 0.87 (0.50) 1.87 (0.51) 0.54 (-0.04) 1.09 (-0.53)	$\begin{array}{c} Cu \\ (133)_{LD} \\ \hline 0.51 \\ (-0.35) \\ 1.66 \\ (0.95) \\ 0.81 \\ (0.46) \\ 1.93 \\ (0.58) \\ 0.60 \\ (-0.03) \\ 0.62 \\ (-0.53) \end{array}$	$\begin{array}{c} Cu\\ (211)_{LD}\\ \hline\\ 0.53\\ (-0.43)\\ 0.97\\ (0.44)\\ 0.74\\ (0.46)\\ 2.02\\ (0.50)\\ 0.53\\ (-0.07)\\ 1.01\\ (-0.53)\\ \end{array}$	Cu (511) _{LD} 0.57 (-0.24) 0.60 (-0.99) 1.31 (-0.10) 1.90 (0.57) 0.52 (-0.10) 1.03 (-0.31)
Reactions $H_2^* \rightarrow H^* + H^*$ $CO_2^* \rightarrow CO^* + O^*$ $CO_2^* + H^* \rightarrow$ mono-HCOO* $CO_2^* + H^* \rightarrow$ trans-COOH* trans-COOH* cis-COOH* $CO^* + OH^*$ $CO^* + OH^*$ $CO^* + H^* \rightarrow$	Cu (100) _{LD} 0.48 (-0.42) 1.92 (0.46) 0.71 (0.38) 1.91 (0.65) 0.53 (-0.07) 0.51 (-0.75) 1.08	$\begin{array}{c} {\bf Cu} \\ (122)_{\rm LD} \\ \hline 0.48 \\ (-0.45) \\ 0.88 \\ (0.65) \\ 0.87 \\ (0.50) \\ 1.87 \\ (0.51) \\ 0.54 \\ (-0.04) \\ 1.09 \\ (-0.53) \\ 1.01 \\ \end{array}$	$\begin{array}{c} Cu\\ (133)_{LD}\\ \hline 0.51\\ (-0.35)\\ 1.66\\ (0.95)\\ 0.81\\ (0.46)\\ 1.93\\ (0.58)\\ 0.60\\ (-0.03)\\ 0.62\\ (-0.53)\\ 0.96\\ \end{array}$	$\begin{array}{c} {\rm Cu} \\ {\rm (211)_{LD}} \\ \hline \\ 0.53 \\ (-0.43) \\ 0.97 \\ (0.44) \\ 0.74 \\ (0.46) \\ 2.02 \\ (0.50) \\ 0.53 \\ (-0.07) \\ 1.01 \\ (-0.53) \\ 1.09 \\ \end{array}$	Cu (511) _{LD} 0.57 (-0.24) 0.60 (-0.99) 1.31 (-0.10) 1.90 (0.57) 0.52 (-0.10) 1.03 (-0.31) 1.09
Reactions $H_2^* \rightarrow H^* + H^*$ $CO_2^* \rightarrow CO^* + O^*$ $CO_2^* + H^* \rightarrow$ mono-HCOO* $CO_2^* + H^* \rightarrow$ trans-COOH* trans-COOH* cis-COOH* cis-COOH* $CO^* + OH^*$ $CO^* + H^* \rightarrow$ $CO^* + H^* \rightarrow$ $CO^* + H^* \rightarrow$	Cu (100) _{LD} 0.48 (-0.42) 1.92 (0.46) 0.71 (0.38) 1.91 (0.65) 0.53 (-0.07) 0.51 (-0.75) 1.08 (0.70)	$\begin{array}{c} Cu\\ (122)_{LD}\\ \hline 0.48\\ (-0.45)\\ 0.88\\ (0.65)\\ 0.87\\ (0.50)\\ 1.87\\ (0.51)\\ 0.54\\ (-0.04)\\ 1.09\\ (-0.53)\\ 1.01\\ (0.84)\\ \end{array}$	$\begin{array}{c} Cu\\ (133)_{LD}\\ \hline 0.51\\ (-0.35)\\ 1.66\\ (0.95)\\ 0.81\\ (0.46)\\ 1.93\\ (0.58)\\ 0.60\\ (-0.03)\\ 0.62\\ (-0.53)\\ 0.96\\ (0.74)\\ \end{array}$	Cu (211) _{LD} 0.53 (-0.43) 0.97 (0.44) 0.74 (0.46) 2.02 (0.50) 0.53 (-0.07) 1.01 (-0.53) 1.09 (0.77)	Cu (511) _{LD} 0.57 (-0.24) 0.60 (-0.99) 1.31 (-0.10) 1.90 (0.57) 0.52 (-0.10) 1.03 (-0.31) 1.09 (0.48)
Reactions $H_2^* \rightarrow H^* + H^*$ $CO_2^* \rightarrow CO^* + O^*$ $CO_2^* + H^* \rightarrow$ mono-HCOO* $CO_2^* + H^* \rightarrow$ trans-COOH* trans-COOH* trans-COOH* $CO^* + OH^*$ $CO^* + OH^*$ $CO^* + H^* \rightarrow$ $CO^* + H^* \rightarrow$	Cu (100) _{LD} 0.48 (-0.42) 1.92 (0.46) 0.71 (0.38) 1.91 (0.55) 0.53 (-0.07) 0.51 (-0.75) 1.08 (0.70) 3.16	$\begin{array}{c} {\bf Cu} \\ ({\bf 122})_{{\rm LD}} \\ \hline \\ 0.48 \\ (-0.45) \\ 0.88 \\ (0.65) \\ 0.87 \\ (0.50) \\ 1.87 \\ (0.51) \\ 0.54 \\ (-0.04) \\ 1.09 \\ (-0.53) \\ 1.01 \\ (0.84) \\ 3.55 \\ \end{array}$	$\begin{array}{c} {\bf Cu} \\ ({\bf 133})_{{\bf LD}} \\ \hline 0.51 \\ (-0.35) \\ 1.66 \\ (0.95) \\ 0.81 \\ (0.46) \\ 1.93 \\ (0.58) \\ 0.60 \\ (-0.03) \\ 0.62 \\ (-0.53) \\ 0.96 \\ (0.74) \\ 2.94 \end{array}$	$\begin{array}{c} {\rm Cu} \\ {\rm (211)_{LD}} \\ \hline \\ 0.53 \\ (-0.43) \\ 0.97 \\ (0.44) \\ 0.74 \\ (0.46) \\ 2.02 \\ (0.50) \\ 0.53 \\ (-0.07) \\ 1.01 \\ (-0.53) \\ 1.09 \\ (0.77) \\ 3.29 \end{array}$	$\begin{array}{c} Cu\\ (511)_{LD}\\ \hline 0.57\\ (-0.24)\\ 0.60\\ (-0.99)\\ 1.31\\ (-0.10)\\ 1.90\\ (0.57)\\ 0.52\\ (-0.10)\\ 1.03\\ (-0.31)\\ 1.09\\ (0.48)\\ 3.07\\ \end{array}$
Reactions $H_2^* \rightarrow H^* + H^*$ $CO_2^* \rightarrow CO^* + O^*$ $CO_2^* + H^* \rightarrow$ mono-HCOO* $CO_2^* + H^* \rightarrow$ trans-COOH* trans-COOH* cis-COOH* cis-COOH* $CO^* + OH^*$ $CO^* + H^* \rightarrow$ $CO^* + H^* \rightarrow$ $CO^* + H^* \rightarrow$ $CO^* + H^* \rightarrow$ $CO^* + H^* \rightarrow$	$\begin{array}{c} {\rm Cu} \\ {\rm (100)_{LD}} \\ \hline \\ 0.48 \\ (-0.42) \\ 1.92 \\ (0.46) \\ 0.71 \\ (0.38) \\ 1.91 \\ (0.65) \\ 0.53 \\ (-0.07) \\ 0.51 \\ (-0.75) \\ 1.08 \\ (0.70) \\ 3.16 \\ (1.14) \end{array}$	$\begin{array}{c} {\bf Cu} \\ ({\bf 122})_{{\bf LD}} \\ \hline \\ 0.48 \\ (-0.45) \\ 0.88 \\ (0.65) \\ 0.87 \\ (0.50) \\ 1.87 \\ (0.51) \\ 0.54 \\ (-0.04) \\ 1.09 \\ (-0.53) \\ 1.01 \\ (0.84) \\ 3.55 \\ (1.99) \end{array}$	Cu (1 3 3) _{LD} 0.51 (-0.35) 1.66 (0.95) 0.81 (0.46) 1.93 (0.58) 0.60 (-0.03) 0.62 (-0.53) 0.96 (0.74) 2.94 (1.30)	Cu (211) _{LD} 0.53 (-0.43) 0.97 (0.44) 0.74 (0.46) 2.02 (0.50) 0.53 (-0.07) 1.01 (-0.53) 1.09 (0.77) 3.29 (1.53)	Cu $(511)_{LD}$ 0.57 (-0.24) 0.60 (-0.99) 1.31 (-0.10) 1.90 (0.57) (0.57) (0.52) (-0.10) 1.03 (-0.31) 1.09 (0.48) 3.07 (1.02)
Reactions $H_2^* \rightarrow H^* + H^*$ $CO_2^* \rightarrow CO^* + O^*$ $CO_2^* + H^* \rightarrow$ mono-HCOO* $CO_2^* + H^* \rightarrow$ trans-COOH* trans-COOH* cis-COOH* \rightarrow cis-COOH* \rightarrow $CO^* + OH^*$ $CO^* + H^* \rightarrow$ CHO* $COH^* \rightarrow$ $COH^* \rightarrow$ $CHO^* + H^* \rightarrow$ $COH^* \rightarrow$ $CHO^* + H^* \rightarrow$ $CHO^* + H^* \rightarrow$ $CHO^* + H^* \rightarrow$ $COH^* \rightarrow$	$\begin{array}{c} {\rm Cu} \\ {\rm (100)_{LD}} \\ \\ 0.48 \\ (-0.42) \\ 1.92 \\ (0.46) \\ 0.71 \\ (0.38) \\ 1.91 \\ (0.65) \\ 0.53 \\ (-0.07) \\ 0.51 \\ (-0.75) \\ 1.08 \\ (0.70) \\ 3.16 \\ (1.14) \\ 0.57 \end{array}$	$\begin{array}{c} {\bf Cu} \\ ({\bf 122})_{{\rm LD}} \\ \hline \\ 0.48 \\ (-0.45) \\ 0.88 \\ (0.65) \\ 0.87 \\ (0.50) \\ 1.87 \\ (0.51) \\ 0.54 \\ (-0.64) \\ 1.09 \\ (-0.53) \\ 1.01 \\ (0.84) \\ 3.55 \\ (1.99) \\ 0.43 \\ \end{array}$	$\begin{array}{c} {\bf Cu} \\ ({\bf 133})_{{\bf LD}} \\ \hline \\ 0.51 \\ (-0.35) \\ 1.66 \\ (0.95) \\ 0.81 \\ (0.46) \\ 1.93 \\ (0.58) \\ 0.60 \\ (-0.03) \\ 0.62 \\ (-0.53) \\ 0.96 \\ (0.74) \\ 2.94 \\ (1.30) \\ 0.55 \\ \end{array}$	$\begin{array}{c} {\rm Cu} \\ {\rm (211)_{LD}} \\ \hline \\ 0.53 \\ (-0.43) \\ 0.97 \\ (0.44) \\ 0.74 \\ (0.46) \\ 2.02 \\ (0.50) \\ 0.53 \\ (-0.07) \\ 1.01 \\ (-0.53) \\ 1.09 \\ (0.77) \\ 3.29 \\ (1.53) \\ 0.49 \end{array}$	$\begin{array}{c} {\rm Cu} \\ {\rm (511)_{LD}} \\ \hline \\ 0.57 \\ (-0.24) \\ 0.60 \\ (-0.99) \\ 1.31 \\ (-0.10) \\ 1.90 \\ (0.57) \\ 0.52 \\ (-0.10) \\ 1.03 \\ (-0.31) \\ 1.09 \\ (0.48) \\ 3.07 \\ (1.02) \\ 0.53 \end{array}$
Reactions $H_2^* \rightarrow H^* + H^*$ $CO_2^* \rightarrow CO^* + O^*$ $CO_2^* + H^* \rightarrow$ mono-HCOO* $CO_2^* + H^* \rightarrow$ trans-COOH* trans-COOH* cis-COOH* \rightarrow cis-COOH* \rightarrow $CO^* + OH^*$ $CO^* + H^* \rightarrow$ CHO^* $CO^* + H^* \rightarrow$ CHO^* $CHO^* + H^* \rightarrow$ $CHO^* + H^* - $	Cu (100) _{LD} 0.48 (-0.42) 1.92 (0.46) 0.71 (0.38) 1.91 (0.65) 0.53 (-0.07) 0.51 (-0.07) 0.51 (-0.75) 1.08 (0.70) 3.16 (1.14) 0.57 (-0.04)	$\begin{array}{c} Cu \\ (122)_{LD} \\ \hline 0.48 \\ (-0.45) \\ 0.88 \\ (0.65) \\ 0.87 \\ (0.50) \\ 1.87 \\ (0.51) \\ 0.54 \\ (-0.04) \\ 1.09 \\ (-0.53) \\ 1.01 \\ (0.84) \\ 3.55 \\ (1.99) \\ 0.43 \\ (-0.16) \end{array}$	$\begin{array}{c} Cu\\ (133)_{LD}\\ \hline 0.51\\ (-0.35)\\ 1.66\\ (0.95)\\ 0.81\\ (0.46)\\ 1.93\\ (0.58)\\ 0.60\\ (-0.03)\\ 0.62\\ (-0.03)\\ 0.62\\ (-0.3)\\ 0.96\\ (0.74)\\ 2.94\\ (1.30)\\ 0.55\\ (-0.24)\\ \end{array}$	$\begin{array}{c} {\rm Cu} \\ {\rm (211)_{LD}} \\ \\ 0.53 \\ (-0.43) \\ 0.97 \\ (0.44) \\ 0.74 \\ (0.46) \\ 2.02 \\ (0.50) \\ 0.53 \\ (-0.07) \\ 1.01 \\ (-0.53) \\ 1.09 \\ (0.77) \\ 3.29 \\ (1.53) \\ 0.49 \\ (-0.12) \end{array}$	$\begin{array}{c} Cu\\ (511)_{LD}\\ \hline 0.57\\ (-0.24)\\ 0.60\\ (-0.99)\\ 1.31\\ (-0.10)\\ 1.90\\ (0.57)\\ 0.52\\ (-0.10)\\ 1.03\\ (-0.31)\\ 1.09\\ (0.48)\\ 3.07\\ (1.02)\\ 0.53\\ (-0.28)\\ \end{array}$
Reactions $H_2^* \rightarrow H^* + H^*$ $CO_2^* \rightarrow CO^* + O^*$ $CO_2^* + H^* \rightarrow$ mono-HCOO* $CO_2^* + H^* \rightarrow$ trans-COOH* trans-COOH* \rightarrow cis-COOH* \rightarrow $CO^* + OH^*$ $CO^* + H^* \rightarrow$ $CO^* + H^* \rightarrow$ COH^* $CO^* + H^* \rightarrow$ $CO^* + H^* \rightarrow$ COH^* $CO^* + H^* \rightarrow$ COH^* $CO^* + H^* \rightarrow$ $CO^* + OO^* \rightarrow$ $CO^* + OO^* \rightarrow$	Cu (100) _{LD} 0.48 (-0.42) 1.92 (0.46) 0.71 (0.38) 1.91 (0.65) 0.53 (-0.07) 0.51 (-0.07) 0.51 (-0.75) 1.08 (0.70) 3.16 (1.14) 0.57 (-0.04) 2.18	$\begin{array}{c} {\bf Cu} \\ ({\bf 122})_{{\rm LD}} \\ \hline \\ 0.48 \\ (-0.45) \\ 0.88 \\ (0.65) \\ 0.87 \\ (0.50) \\ 1.87 \\ (0.51) \\ 0.54 \\ (-0.04) \\ 1.09 \\ (-0.53) \\ 1.01 \\ (0.84) \\ 3.55 \\ (1.99) \\ 0.43 \\ (-0.16) \\ 1.44 \\ \end{array}$	$\begin{array}{c} Cu \\ (1 3 3)_{LD} \\ \hline 0.51 \\ (-0.35) \\ 1.66 \\ (0.95) \\ 0.81 \\ (0.46) \\ 1.93 \\ (0.58) \\ 0.60 \\ (-0.03) \\ 0.60 \\ (-0.03) \\ 0.60 \\ (-0.3) \\ 0.96 \\ (0.74) \\ 2.94 \\ (1.30) \\ 0.55 \\ (-0.24) \\ 2.21 \end{array}$	$\begin{array}{c} {\rm Cu} \\ {\rm (211)_{LD}} \\ \hline \\ 0.53 \\ (-0.43) \\ 0.97 \\ (0.44) \\ 0.74 \\ (0.46) \\ 2.02 \\ (0.50) \\ 0.53 \\ (-0.07) \\ 1.01 \\ (-0.53) \\ 1.09 \\ (0.77) \\ 3.29 \\ (1.53) \\ 0.49 \\ (-0.12) \\ 1.65 \\ \end{array}$	Cu (511) _{LD} 0.57 (-0.24) 0.60 (-0.99) 1.31 (-0.10) 1.90 (0.57) 0.52 (-0.10) 1.03 (-0.31) 1.09 (0.48) 3.07 (1.02) 0.53 (-0.28) 1.83
Reactions $H_2^* \rightarrow H^* + H^*$ $CO_2^* \rightarrow CO^* + O^*$ $CO_2^* + H^* \rightarrow$ mono-HCOO* $CO_2^* + H^* \rightarrow$ trans-COOH* trans-COOH* cis-COOH* $CO^* + OH^*$ $CO^* + OH^*$ $CO^* + H^* \rightarrow$ COH^* $CO^* + H^* \rightarrow$ COH^* $COH^* + H^* \rightarrow$ $COH^* + H^* \rightarrow$ $COH^* + H^* \rightarrow$ $COH^* + H^* \rightarrow$ $COH^* + H^* \rightarrow$ $CO^* + OH^* \rightarrow$ $CO^* $	Cu (100) _{LD} 0.48 (-0.42) 1.92 (0.46) 0.71 (0.38) 1.91 (0.65) 0.53 (-0.07) 0.51 (-0.07) 1.08 (0.70) 3.16 (1.14) 0.57 (-0.04) 2.18 (1.30)	$\begin{array}{c} {\bf Cu} \\ ({\bf 122})_{{\rm LD}} \\ \hline \\ 0.48 \\ (-0.45) \\ 0.88 \\ (0.65) \\ 0.87 \\ (0.50) \\ 1.87 \\ (0.51) \\ 0.54 \\ (-0.04) \\ 1.09 \\ (-0.53) \\ 1.01 \\ (0.84) \\ 3.55 \\ (1.99) \\ 0.43 \\ (-0.16) \\ 1.44 \\ (1.23) \end{array}$	$\begin{array}{c} {\bf Cu} \\ ({\bf 133})_{{\bf LD}} \\ \hline \\ 0.51 \\ (-0.35) \\ 1.66 \\ (0.95) \\ 0.81 \\ (0.46) \\ 1.93 \\ (0.58) \\ 0.60 \\ (-0.03) \\ 0.60 \\ (-0.03) \\ 0.60 \\ (-0.03) \\ 0.60 \\ (-0.03) \\ 0.60 \\ (-0.03) \\ 0.55 \\ (-0.24) \\ 2.21 \\ (1.60) \end{array}$	$\begin{array}{c} {\rm Cu} \\ {\rm (211)_{LD}} \\ \hline \\ 0.53 \\ (-0.43) \\ 0.97 \\ (0.44) \\ 0.74 \\ (0.46) \\ 2.02 \\ (0.50) \\ 0.53 \\ (-0.07) \\ 1.01 \\ (-0.53) \\ 1.09 \\ (0.77) \\ 3.29 \\ (1.53) \\ 0.49 \\ (-0.12) \\ 1.65 \\ (1.37) \end{array}$	$\begin{array}{c} {\rm Cu} \\ {\rm (511)_{LD}} \\ \hline \\ 0.57 \\ (-0.24) \\ 0.60 \\ (-0.99) \\ 1.31 \\ (-0.10) \\ 1.90 \\ (0.57) \\ 0.52 \\ (-0.10) \\ 1.03 \\ (-0.31) \\ 1.09 \\ (0.48) \\ 3.07 \\ (1.02) \\ 0.53 \\ (-0.28) \\ 1.83 \\ (1.28) \end{array}$
Reactions $H_2^* \rightarrow H^* + H^*$ $CO_2^* \rightarrow CO^* + O^*$ $CO_2^* + H^* \rightarrow$ mono-HCOO* $CO_2^* + H^* \rightarrow$ trans-COOH* trans-COOH* cis-COOH* $CO^* + OH^*$ $CO^* + OH^*$ $CO^* + H^* \rightarrow$ COH^* $CO^* + H^* \rightarrow$ COH^* $CO^* + H^* \rightarrow$ $COH^* + H^* \rightarrow$ $CHO^* + H^* \rightarrow$ $CO^* + CO^* \rightarrow$ $CO^* + COH^* \rightarrow$ $CO^* + COH^* \rightarrow$ $CO^* + COH^* \rightarrow$	Cu (100) _{LD} 0.48 (-0.42) 1.92 (0.46) 0.71 (0.38) 1.91 (0.65) 0.53 (-0.07) 0.51 (-0.07) 0.51 (-0.75) 1.08 (0.70) 3.16 (1.14) 0.57 (-0.04) 2.18 (1.30) 0.85	$\begin{array}{c} {\bf Cu} \\ (122)_{{\rm LD}} \\ \hline \\ 0.48 \\ (-0.45) \\ 0.88 \\ (0.65) \\ 0.87 \\ (0.50) \\ 1.87 \\ (0.51) \\ 0.54 \\ (-0.04) \\ 1.09 \\ (-0.53) \\ 1.01 \\ (0.84) \\ 3.55 \\ (1.99) \\ 0.43 \\ (-0.16) \\ 1.44 \\ (1.23) \\ 1.62 \\ \end{array}$	$\begin{array}{c} {\rm Cu} \\ {\rm (133)_{LD}} \\ \hline \\ 0.51 \\ (-0.35) \\ 1.66 \\ (0.95) \\ 0.81 \\ (0.46) \\ 1.93 \\ (0.58) \\ 0.60 \\ (-0.03) \\ 0.60 \\ (-0.03) \\ 0.62 \\ (-0.03) \\ 0.96 \\ (0.74) \\ 2.94 \\ (1.30) \\ 0.55 \\ (-0.24) \\ 2.21 \\ (1.60) \\ 1.64 \\ \end{array}$	$\begin{array}{c} {\rm Cu} \\ {\rm (211)_{LD}} \\ \hline \\ 0.53 \\ (-0.43) \\ 0.97 \\ (0.44) \\ 0.74 \\ (0.46) \\ 2.02 \\ (0.50) \\ 0.53 \\ (-0.07) \\ 1.01 \\ (-0.53) \\ 1.09 \\ (0.77) \\ 3.29 \\ (1.53) \\ 0.49 \\ (-0.12) \\ 1.65 \\ (1.37) \\ 1.14 \\ \end{array}$	Cu (511) _{LD} 0.57 (-0.24) 0.60 (-0.99) 1.31 (-0.10) 1.90 (0.57) 0.52 (-0.10) 1.03 (-0.31) 1.09 (0.48) 3.07 (1.02) 0.53 (-0.28) 1.83 (1.28) 1.30
Reactions $H_2^* \rightarrow H^* + H^*$ $CO_2^* \rightarrow CO^* + O^*$ $CO_2^* + H^* \rightarrow$ mono-HCOO* $CO_2^* + H^* \rightarrow$ trans-COOH* trans-COOH* cis-COOH* cis-COOH* $CO^* + OH^*$ $CO^* + H^* \rightarrow$ $CO^* + O^* \rightarrow$ $COCO^*$	Cu $(100)_{LD}$ 0.48 (-0.42) 1.92 (0.46) 0.71 (0.38) 1.91 (0.65) 0.53 (-0.07) 0.51 (-0.75) 1.08 (0.70) 3.16 (1.14) 0.57 (-0.04) 2.18 (1.30) 0.85 (0.56)	$\begin{array}{c} {\bf Cu} \\ (122)_{{\rm LD}} \\ \hline 0.48 \\ (-0.45) \\ 0.88 \\ (0.65) \\ 0.87 \\ (0.50) \\ 1.87 \\ (0.51) \\ 0.54 \\ (-0.04) \\ 1.09 \\ (-0.53) \\ 1.01 \\ (0.84) \\ 3.55 \\ (1.99) \\ 0.43 \\ (-0.16) \\ 1.44 \\ (1.23) \\ 1.62 \\ (0.56) \\ \end{array}$	$\begin{array}{c} {\rm Cu} \\ {\rm (133)_{LD}} \\ \hline \\ 0.51 \\ (-0.35) \\ 1.66 \\ (0.95) \\ 0.81 \\ (0.46) \\ 1.93 \\ (0.58) \\ 0.60 \\ (-0.03) \\ 0.62 \\ (-0.53) \\ 0.62 \\ (-0.53) \\ 0.96 \\ (0.74) \\ 2.94 \\ (1.30) \\ 0.55 \\ (-0.24) \\ 2.21 \\ (1.60) \\ 1.64 \\ (0.45) \\ \end{array}$	$\begin{array}{c} {\rm Cu} \\ {\rm (211)_{LD}} \\ \hline \\ 0.53 \\ (-0.43) \\ 0.97 \\ (0.44) \\ 0.74 \\ (0.46) \\ 2.02 \\ (0.50) \\ 0.53 \\ (-0.07) \\ 1.01 \\ (-0.53) \\ 1.09 \\ (0.77) \\ 3.29 \\ (1.53) \\ 0.49 \\ (-0.12) \\ 1.65 \\ (1.37) \\ 1.14 \\ (0.21) \end{array}$	$\begin{array}{c} Cu\\ (511)_{LD}\\ \hline 0.57\\ (-0.24)\\ 0.60\\ (-0.99)\\ 1.31\\ (-0.10)\\ 1.90\\ (0.57)\\ 0.52\\ (-0.10)\\ 1.03\\ (-0.31)\\ 1.09\\ (0.48)\\ 3.07\\ (1.02)\\ 0.53\\ (-0.28)\\ 1.83\\ (1.28)\\ 1.30\\ (0.25)\\ \end{array}$
Reactions $H_2^* \rightarrow H^* + H^*$ $CO_2^* \rightarrow CO^* + O^*$ $CO_2^* + H^* \rightarrow$ mono-HCOO* $CO_2^* + H^* \rightarrow$ trans-COOH* trans-COOH* cis-COOH* \rightarrow cis-COOH* \rightarrow $CO^* + OH^*$ $CO^* + H^* \rightarrow$ CHO^* $CHO^* + H^* \rightarrow$ CHO^* $CHO^* + H^* \rightarrow$ $CHO^* + H^* \rightarrow$ $COCO^* + CO^* \rightarrow$ $COCOCO^*$ $COCHO^* \rightarrow$ $COCHO^*$ $COCHO^* \rightarrow$ $COCHO^* \rightarrow$	Cu (100) _{LD} 0.48 (-0.42) 1.92 (0.46) 0.71 (0.38) 1.91 (0.65) 0.53 (-0.07) 0.51 (-0.75) 1.08 (0.70) 3.16 (1.14) 0.57 (-0.04) 2.18 (1.30) 0.85 (0.56) 2.57	$\begin{array}{c} {\rm Cu} \\ {\rm (122)_{LD}} \\ \hline \\ 0.48 \\ (-0.45) \\ 0.88 \\ (0.65) \\ 0.87 \\ (0.50) \\ 1.87 \\ (0.50) \\ 1.87 \\ (0.51) \\ 0.54 \\ (-0.04) \\ 1.09 \\ (-0.53) \\ 1.01 \\ (0.84) \\ 3.55 \\ (1.99) \\ 0.43 \\ (-0.16) \\ 1.44 \\ (1.23) \\ 1.62 \\ (0.56) \\ 0.83 \\ \end{array}$	Cu (133) _{LD} (-0.35) 1.66 (0.95) 0.81 (0.46) 1.93 (0.58) 0.60 (-0.03) 0.62 (-0.53) 0.96 (0.74) 2.94 (1.30) 0.55 (-0.24) 2.21 (1.60) 1.64 (0.45) 0.64	$\begin{array}{c} {\rm Cu} \\ {\rm (211)_{LD}} \\ \hline \\ 0.53 \\ (-0.43) \\ 0.97 \\ (0.44) \\ 0.74 \\ (0.46) \\ 2.02 \\ (0.50) \\ 0.53 \\ (-0.07) \\ 1.01 \\ (-0.53) \\ 1.09 \\ (0.77) \\ 3.29 \\ (1.53) \\ 0.49 \\ (-0.12) \\ 1.65 \\ (1.37) \\ 1.14 \\ (0.21) \\ 0.40 \\ \end{array}$	Cu $(511)_{LD}$ 0.57 (-0.24) 0.60 (-0.99) 1.31 (-0.10) 1.90 (0.57) 0.52 (-0.10) 1.03 (-0.31) 1.09 (0.48) 3.07 (1.02) 0.53 (-0.28) 1.83 (-0.28) 1.83 (1.28) 1.30 (0.25) 0.043

3.3.4. The influences of defect site types on CO conversion and C–C coupling

Based on above analysis, as shown in Fig. 6, for the Cu(100)_{PD}, (100)_{LD}, as well as the (122)_{LD} and (133)_{LD} consisted of (111) and (111) surfaces, CH₂O* formation is preferred, followed by its hydrogenation to methanol. The activity of C₁ species formation follows the order of (100)_{PD} > (100)_{LD} > (122)_{LD} > (133)_{LD} (1.16, 1.26, 1.27 and 1.29 eV). Thus, the (100)_{PD} exhibits a superior activity of C₁ species formation than other three surfaces.

On the other hand, the Cu(111), (100), (111)_{PD}, (111)_{LD}, as well as the (211)_{LD} and (511)_{LD} consisted of (111) and (100) surfaces were identified to favor C₂ species formation instead of C₁ species. The activity of C₂ species formation follows the order of (511)_{LD} > (211)_{LD} > (111)_{LD}=(100) > (111)_{PD} > (111) (1.09, 1.17, 1.18, 1.18, 1.21 and 1.30 eV). The pathways of C₂ species formation on the Cu(111)_{PD} and (111)_{LD} surfaces correspond to CO^{*}+CO^{*} \rightarrow COCO^{*}, while the C–C



Fig. 6. The overall barriers of CH_2O^* formation and the C–C coupling via CO^*+CO^* , CO^*+CHO^* , CHO^*+CHO^* pathways on the Cu(hkl), Cu(hkl)_{PD} and Cu(hkl)_{LD} surfaces.

coupling take place on the Cu(111), (100), (211)_{LD} and (511)_{LD} surfaces firstly undergoes CO* hydrogenation to CHO* intermediate, followed by CHO* dimerization to C₂ species CHOCHO*. Thus, the defect types not only tuned the product distribution but also changed the most favorable C–C coupling pathways, among them, the (511)_{LD} surface exhibits the best activity of C₂ species formation.

3.4. The role of defect site types in tuning the activity and selectivity of CO_2 activation and conversion

As mentioned above, during the process of CO conversion, the product distribution is closely related to the defect site types of Cu surfaces. Similarly, the defect types also affect the product distribution of CO₂ activation and conversion, in which CO₂ conversion means the transformation of the related intermediates HCOO*, COOH* or CO* from CO₂ activation to a variety of products including C₁ products (e.g. CO, HCOOH, CH₃OH, CH₄) and C₂ products (e.g. C₂H₄, C₂H₅OH). HCOO* intermediate is mainly responsible for methanol formation, CO* formed by COOH* pathway and CO2 direct dissociation dominantly contribute to C1 or C2 species. Thus, in the process of CO2 activation and conversion, on the Cu(111), (100), (111)_{PD}, (111)_{LD} and (211)_{LD} surfaces, mono-HCOO* as the main intermediate is dominantly converted to methanol, along with a small portion of the intermediate CO* formed by COOH* pathway or CO2 direct dissociation, which can be converted to C_2 species. However, on the $Cu(100)_{PD}$, $(100)_{LD}$, $(122)_{LD}$ and (133)_{LD} surfaces, the formed mono-HCOO* and CO* intermediates are all converted to methanol. Interestingly, on (511)_{LD} surface, CO* as the major intermediate leads to the formation of C₂ species.

Previous studies reported that the product distribution of CO₂ conversion could be effectively tuned by changing the types of defect site, for example, Zhu et al [26] identified the product-specific sites of Cu foils with various facets, suggesting that Cu surfaces with the step and kink sites were more favorable for the production of C2 species than the flat Cu surfaces. Ding et al. [51] synthesized a high-performance Cu@Na-Beta catalyst with the defect Cu(221) surface, which displayed a superior activity for CO₂ hydrogenation and achieved an ethanol space-time yield of 398 mg \cdot g_{cat}⁻¹ \cdot h⁻¹ at the 300 °C and 2.1 MPa. The superior performance was attributed to a synergy between the Cu nanoparticles and Na-Beta zeolite, in which the defect Cu(221) surface provide high density of step sites for the C-C bond formation. Our calculation results showed that the formation of C2 species was easily occurred on the (511)_{LD} surface, the step sites were mainly responsible for the C-C bond formation of C₂ species, which is in accordance with the studies by Ding et al. [51].

On the other hand, the stepped Cu sites presented the superior

catalytic performance toward the C–C bond formation, for example, three types of steps sites in the oxide derived-Cu catalysts have been identified for the C–C coupling in CO₂ conversion, the planar-square and convex-square sites favor ethylene formation, while the step-square sites are favorable for alcohols formation [27]. Cu with atomic vacancies presented a 19-fold improvement for C_{2+} alcohols than the defect-free Cu NPs [80]. Thus, the catalytic performance of CO₂ conversion closely depends on the types of defect site in Cu catalysts.

As presented in Fig. 5, the line defect Cu surfaces have higher activity of CO_2 activation than the point defect surfaces, which is also better than the perfect surface. Among them, the line defect $(1\,1\,1)_{LD}$ and $(5\,1\,1)_{LD}$ surfaces are screened out to present the highest activity toward methanol and C_2 species formation, respectively. Thus, Cu defect site types play a key role in tuning the selectivity and activity of CO_2 activation and conversion.

3.5. Structural and electronic effects of different Cu surfaces

Given the fact that the product distribution of CO₂ activation and conversion on Cu catalysts are determined by the surface structures of Cu catalysts and CO₂ activation pathway, the geometric and electronic effects of different Cu surfaces for the most favorable pathway of CO₂ activation among three pathways including CO₂* \rightarrow CO*+O*, CO₂*+H* \rightarrow *mono*-HCOO* and CO₂*+H* \rightarrow *trans*-COOH* \rightarrow CO*+OH* were analyzed by the assistance of GCN model and *d*-band center.

Generally, the coordination number (CN) is used to describe the coordination environment of surface active sites and refer to the number of its nearest neighbors. However, it is not a good descriptor for the general chemical reactions due to the finiteness [26,30]. The generalized coordination number (GCN) includes the first and second nearest neighbors, which has been widely applied in CO₂RR, HER and ORR reactions on the Pt and Cu NPs [81–84]. Thus, the relationship between a more accuracy descriptor GCN and CO₂ activation activity is plotted in Fig. 7, the values of GCN for different Cu surfaces are listed in Table S2.

As listed in Table S2, all the surfaces present different GCN values, Cu (111) and (100) surfaces have higher GCN values of 7.500 and 6.667, while the GCN value was lowered at the defect sites. Moreover, as presented in Fig. 7, the activity of CO₂ activation follows the order: Cu(hkl) < Cu(hkl)_{PD} < Cu(hkl)_{LD}, which gradually increased with the decreasing of GCN values. Thus, the GCN values reflected the effect of defect sites on the activity of CO₂ activation is. More importantly, the correlation between the coordination environment of Cu atoms and product



Fig. 7. Relationship between GCN values and the activity of CO₂ activation for the most favorable pathway among three pathways including CO₂* \rightarrow CO*+O*, CO₂*+H* \rightarrow *mono*-HCOO* and CO₂*+H* \rightarrow *trans*-COOH* \rightarrow CO*+OH* on the Cu(hkl), Cu(hkl)_{PD} and Cu(hkl)_{LD} surfaces.

distribution has been confirmed experimentally and theoretically [26,27], for example, Zhu *et al.* [26] concluded that Cu(100) with 8-fold coordination show a strong positive correlation with C_2H_4 generation in CO₂RR, while the production of C_2H_5OH is preferred on the Cu atoms with smaller CN. Cheng *et al.* [27] proposed that the square sites on Cu surfaces with the lowest GCN values (5.50) dominated the formation of C–C bond rather than the vacancies or grain boundaries. Hence, GCN as an effective descriptor can be used to predict the activity of CO₂ activation over the Cu surfaces, in which the defective Cu surfaces increased the contact area between the adsorbates and surface Cu atoms due to the outspread active area, and then exhibit higher catalytic activity.

On the other hand, the *d*-band center model proposed by Nørskov et al. [85,86] has been successfully elucidate the catalytic activity of pure transition metals. Thus, the *d*-band center of different Cu surfaces is examined, the relationship between the *d*-band center and CO₂ activation activity is presented in Fig. 8, and the partial density of states (pDOS) and the *d*-band center are plotted in Fig. S12. As presented in Fig. 8, Cu surfaces with the line defect present an inverted volcano-type curve between the *d*-band center and the activity of CO₂ activation. Both the line defect $Cu(111)_{LD}$ and $(511)_{LD}$ surfaces, located at or around the bottom of the inverted volcano-type curve with the moderate d-band center from the Fermi level, exhibits the higher activity of CO₂ activation. However, the other Cu surfaces, located at two sides of the inverted volcano-type curve with the *d*-band center of either too far or too close from the Fermi level, corresponds to the weakening of CO2 activation activity. Further, for the perfect and point defect surfaces, the d-band centers are also located at two sides of the inverted volcano-type curve, so the activity of CO_2 activation is also weaker than the $Cu(111)_{LD}$ and $(511)_{LD}$ surfaces. Thus, the dependence of CO₂ activation activity on the d-band center of Cu catalysts is identified, and the introduced defects altered the position of d-band center to adjust the activity of CO2 activation.

Up to now, the underlying active site for CO₂ activation and conversion over the Cu-based catalysts remains a matter of debate since the oxidation states of Cu was susceptible to the reaction conditions [87]. At present, the understandings about the active sites for CO₂ activation and conversion mainly focus on the Cu⁺, Cu^{δ +} ($0 < \delta < 1$) and metallic Cu⁰ species [88,89]. For example, Wei *et al.* [90] proposed that the moderate valence state Cu^{δ +} ($\delta = 0.43$ and 0.51) species was more favorable for the conversion of syngas to C₂ oxygenates compared to Cu⁺ and Cu⁰ species. Yuan *et al.* [88] reported a high performance Cu/CuSiO₃ catalyst with 51.2% C₂H₄ selectivity, the synergistic effect of Cu⁰-Cu⁺ pairs contributes to the enhancement of CO₂ reduction activity, in which Cu⁰



Fig. 8. Relationship between the *d*-band center and the activity of CO₂ activation for the most favorable pathway among three pathways including CO₂* \rightarrow CO*+O*, CO₂*+H* \rightarrow *mono*-HCOO* and CO₂*+H* \rightarrow *trans*-COOH* \rightarrow CO*+OH* on the Cu(hkl), Cu(hkl)_{PD} and Cu(hkl)_{LD} surfaces.

site was responsible for CO₂ activation and the following electron transfers; while Cu⁺ site strengthens CO* adsorption to further boost C-C coupling. Chou et al. [89] has confirmed that Cu with specific oxidation state affects the formation of CO* and product selectivity during CO2 reduction. Qi et al. [91] also verified that the existence of $Cu^{\delta+}$ states over the defect-rich Cu surfaces resulted in high C_{2+} selectivity during CO₂ reduction. However, identifying the oxidation state of Cu surface in CO₂ reduction was difficult due to the complexity of Cubased catalyst [87], which contains numerous structural motifs such as grain boundaries, high-index facets, stepped terraces, corrugated surface, and so on. Thus, a simplified Cu structure with well-defined surfaces is modeled in this work. Our results showed that the Cu defect sites with $Cu^{\delta+}$ states behave as the active sites for CO_2 conversion to enrich more charge than other sites and modify the coordination environment of Cu surfaces, thus promoted CO₂ activation. The exact oxidation state of Cu surfaces will be considered in our next work.

4. Conclusions

In this study, the mechanism of CO₂ activation and conversion on Cu catalysts with two distinctive surface defect types including the point defect and line defect is fully investigated, which is compared with the perfect Cu catalyst to reveal the role of surface Cu defect types in tuning the activity and selectivity of CO2 activation and conversion. The results show that the catalytic performance of CO₂ activation and conversion could be effectively tuned by adjusting defect site types; on the Cu(111), (100), $(111)_{PD}$, $(111)_{LD}$ and $(211)_{LD}$, methanol is the dominant product via mono-HCOO intermediate, a small portion of CO intermediate can be converted to C_2 species. However, on the $Cu(100)_{PD}$, $(100)_{LD}$, $(122)_{LD}$ and $(133)_{LD}$, both mono-HCOO and CO intermediates are all converted to methanol. Interestingly, on $(511)_{LD}$, CO as the major intermediate leads to the formation of C₂ species. Moreover, the line defect Cu surfaces have higher CO2 activation activity than the point defect and perfect surfaces. Among them, both the line defect Cu(111)LD and (511)_{LD} are screened out to present the highest activity toward methanol and C₂ species formation, respectively.

The generalized coordination number (GCN) is proposed and confirmed as an effective descriptor to predict the activity of CO₂ activation and conversion on different Cu surfaces, and the smaller value of GCN corresponds to the higher activity of CO₂ activation. Moreover, Cu surfaces with the different defect types present an inverted volcano-type curve between *d*-band center and CO₂ activation activity. Both the line defect Cu(111)_{LD} and (511)_{LD} surfaces with the moderate *d*-band center exhibit higher CO₂ activation activity; whereas the other Cu surfaces with *d*-band center of either too far or too close from the Fermi level corresponds to the weakening of CO₂ activation activity. Thus, the dependence of CO₂ activation activity on the *d*-band center of Cu catalysts is identified. Our works reveal that the defect types on Cu surfaces play an important role in tuning the activity and selectivity of CO₂ activation and conversion, the variation of defect site types lead to a wide C₂/C₁ product selectivity on Cu surfaces.

CRediT authorship contribution statement

Lixuan Ma: Writing – original draft, Writing – review & editing, Formal analysis. Wantong Zhao: Formal analysis, Data curation. Baojun Wang: Data curation, Resources, Funding acquisition, Supervision. Lixia Ling: Formal analysis. Riguang Zhang: Writing – original draft, Writing – review & editing, Data curation, Conceptualization, Funding acquisition, Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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