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# The mechanism for CO<sub>2</sub> reduction over Fe-modified Cu(100) surfaces with thermodynamics and kinetics: a DFT study†

Mei Qiu,<sup>a</sup> Yi Li<sup>b</sup> and Yongfan Zhang<sup>c</sup>

The adsorption, activation and reduction of CO<sub>2</sub> over Fe<sub>x</sub>/Cu(100) ( $x = 1-9$ ) surfaces were examined by density functional theory. The most stable structure of CO<sub>2</sub> adsorption on the Fe<sub>x</sub>/Cu(100) surface was realized. The electronic structure analysis showed that the doped Fe improved the adsorption, activation and reduction of CO<sub>2</sub> on the pure Cu(100) surface. From the perspective of thermodynamics and kinetics, the Fe<sub>4</sub>/Cu(100) surface acted as a potential catalyst to decompose CO<sub>2</sub> into CO with a barrier of 32.8 kJ mol<sup>-1</sup>. Meanwhile, the first principle molecular dynamics (FPMD) analysis indicated that the decomposition of the C–O1 bond of CO<sub>2</sub> on the Fe<sub>4</sub>/Cu(100) surface was only observed from 350 K to 450 K under a CO<sub>2</sub> partial pressure from 0 atm to 10 atm. Furthermore, the results of FPMD analysis revealed that CO<sub>2</sub> would rather decompose than hydrogenate when CO<sub>2</sub> and H co-adsorbed on the Fe<sub>4</sub>/Cu(100) surface.

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## 1. Introduction

Reducing the concentration of CO<sub>2</sub> in the atmosphere has attracted significant attention, because as the major component of greenhouse gas, excessive emissions of CO<sub>2</sub> have contributed significantly to environment degradation in the past decades, such as global warming, and melting of glaciers. The conversion of CO<sub>2</sub> as a C resource to synthesize more valuable chemical raw materials not only solves the major crisis of global greenhouse gases and energy shortage, but also provides great opportunities and challenges for exploring novel catalysts and developing a modern catalytic industry.<sup>1</sup>

Because CO<sub>2</sub> is a thermodynamically stable molecule, it is difficult to utilize CO<sub>2</sub> as the C resource.<sup>2</sup> Currently, five ways to reduce CO<sub>2</sub> have been reported: (i) electrocatalytic reduction,<sup>3-8</sup> (ii) photocatalytic reduction,<sup>9-11</sup> (iii) thermal catalytic reduction,<sup>12-15</sup> (iv) enzymatic reduction<sup>16,17</sup> and (v) photo-electrocatalytic reduction.<sup>18</sup> In these cases, the catalyst plays a major role in CO<sub>2</sub> activity and reduction.

Numerous experiments and theories have been used to investigate the adsorption, activation and reduction of CO<sub>2</sub> on transition metal-based catalysts.<sup>19-27</sup> For instance, Fierro

systematically investigated the adsorption of CO<sub>2</sub> on the Co(100), Co(110) and Co(111) surfaces.<sup>19</sup> The results indicated that the adsorption configuration of CO<sub>2</sub> on the substrate was sensitive, especially the Co(110) surface. The experimental results of Rasmussen showed that the Cu(100) surface was able to decompose CO<sub>2</sub> into CO and O<sub>2</sub>.<sup>22</sup> Roberts demonstrated that CO<sub>2</sub> could be decomposed into CO on the Ni(100) surface rather than on the Ni(111) surface.<sup>23</sup> Ding asserted that a weak interaction was formed between CO<sub>2</sub> and the Ni(110) surface.<sup>24</sup> Glezakou investigated the mechanism of adsorption and activation of CO<sub>2</sub> on the Fe fcc(100) surface.<sup>25</sup> Their results indicated that CO<sub>2</sub> on the Fe(100) surface was activated spontaneously. Wilson investigated the reduction of CO<sub>2</sub> into CO on Co(100), Ni(100) and Cu(100) surfaces.<sup>26</sup> The calculated results revealed an interesting trend between reaction energy and the total reaction barrier from Fe to Cu and that reactions tended to be less exergonic. Additionally, Co and Ni were more favorable to decompose CO<sub>2</sub> into CO.

Except for the single metal catalysts for CO<sub>2</sub>, Great effort has been devoted to improve the catalytic performance of bimetallic catalysts for CO<sub>2</sub> activation and catalysis.<sup>27,28</sup> Nerlov pointed out that the performance of Cu–Ni bimetallic catalyst was more than 60 times greater than the pure Cu.<sup>29-31</sup> Liu found that the introduction of Pd, Rh, Pt, and Ni metals on the Cu(111) surface promoted the methanol production.<sup>32</sup> Our previous reports revealed that the introduction of a second metal could improve the interaction between CO<sub>2</sub> and the Cu(100) surface.<sup>33,34</sup> Additionally, the results also showed that the interaction between CO<sub>2</sub> and the Co<sub>n</sub>/Cu(100) surface was structure sensitive for the reduction of CO<sub>2</sub> molecules and the Co<sub>4</sub>/Cu(100) surface was the potential catalyst for the reduction of CO<sub>2</sub>. The

<sup>a</sup>Department of Chemistry, College of Science, Jiangxi Agricultural University, Nanchang, Jiangxi, 330045, China. E-mail: qium@jxau.edu.cn

<sup>b</sup>State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, 350002 Fuzhou, Fujian, 350002, China

<sup>c</sup>College of Chemistry, Fuzhou University, Fuzhou, Fujian, 350116, China

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results of Song demonstrated that the properties of CO<sub>2</sub> conversion on Fe–Ni and Fe–Co catalysts were similar, and CO\* and HCOO\* were the preferred intermediates.<sup>35,36</sup>

On the basis of these reports, in this work the density functional theory calculations was employed to understand the activation and reduction of CO<sub>2</sub> on the Cu(100) surface with embedded small Fe atoms. The result of a recent STM experiment showed that small Co clusters can be formed in the first layer of the Cu(100) surface through the vacancy-mediated diffusion of Co atoms.<sup>37</sup> The similarity of the Co/Cu(100) and Fe/Cu(100) epitaxial systems suggests that the diffusion of embedded Fe atoms also leads to the formation of small nanostructures.<sup>38</sup> Firstly, the most stable structure of Fe<sub>x</sub>/Cu(100) ( $x = 1-9$ ) was generated using the first principle molecular dynamics (FPMD) method. Then the adsorption energetics and geometry, vibrational frequencies analysis, charge transfers and d-band center of CO<sub>2</sub> over a series of Fe<sub>x</sub>/Cu bimetallic surfaces were analyzed. The activation energy barrier for the CO<sub>2</sub> reduction and the Brønsted–Evans–Polanyi (BEP) relationships between the kinetic parameters for CO<sub>2</sub> reduction over the Fe<sub>x</sub>/Cu(100) systems were investigated. And then the optimal temperature and partial pressure for CO<sub>2</sub> reduction on the Fe<sub>4</sub>/Cu(100) surface was explored in detail. Lastly, the hydrogenation of CO<sub>2</sub> and residual CO or O was considered in the paper.

## 2. Computation details

### 2.1. Method

All of the density functional theory (DFT) calculations using the Vienna *ab initio* simulation package (VASP)<sup>39–41</sup> were according to projector-augmented wave DFT (PAW-DFT).<sup>42–44</sup> The Perdew–Burke–Ernzerhof (PBE) functional based on the generalized gradient approximation was employed.<sup>45</sup> The kinetic energy cutoff of 400 eV for the plane-wave expansion was set. In all systems, the effects of dipole correction, spin polarization in the surface normal direction and the van der Waals correction were considered by using DFT-D2 method.<sup>46,47</sup> Geometrical structure was optimized until the energy change and the maximum force were less than 10<sup>−6</sup> eV and 0.02 eV Å<sup>−1</sup>, respectively. The 5 × 5 × 1 *k*-points with Monkhorst–Pack method were used.<sup>48</sup>

### 2.2. Surface model

Previous studies reveal that the Cu(100) surface is the most potential value to be reduction of CO<sub>2</sub> molecule among Cu(100), Cu(110) and Cu(111) surfaces.<sup>34</sup> Thus, the Cu(100) surface with a  $p(3 \times 3)$  supercell and five atomic layers was employed. For the Fe<sub>x</sub>/Cu(100) ( $x = 1-9$ ) surfaces, Cu atoms on top-layer of the pure Cu(100) surface were substituted by several Fe atoms. In the geometry optimizations, the top three layers were completely relaxed in all directions and the bottom two layers were fixed in their bulk position. The vacuum of 15 Å between the adjacent slabs was set along the *c*-axis direction to avoid periodic interactions.

The adsorption energy ( $E_{\text{ads}}$ ) for the CO<sub>2</sub> molecule on the Fe<sub>x</sub>/Cu(100) surface was defined eqn (1), as follows:

$$E_{\text{ads}} = E_{\text{CO}_2} + E_{\text{Slab}} - E_{\text{CO}_2/\text{Slab}} \quad (1)$$

where,  $E_{\text{CO}_2}$ ,  $E_{\text{Slab}}$  and  $E_{\text{CO}_2/\text{Slab}}$  represent the total energy of the free CO<sub>2</sub> molecule in the gas phase, the clean surface and the slab with adsorbed CO<sub>2</sub>, respectively. Therefore, a negative value of  $E_{\text{ads}}$  indicates an endothermic adsorption and a positive value refers to an exothermic adsorption.

The reduction of CO<sub>2</sub> on the Fe<sub>x</sub>/Cu(100) surface was involved in the formations of CO and HCOO, namely, CO<sub>2</sub>(g) → CO\* → CO\* + O\* and CO\* → H\* + HCOO\* (where X\* represents X species adsorbed on substrate). The corresponding activation energy barrier was calculated from the relative energy of the transition state (TS) with respect to the sum of the energies of the initial structure (IS) (CO<sub>2</sub> adsorbed on the Fe<sub>x</sub>/Cu(100) surface), namely,

$$E_a = E_{\text{TS}} - E_{\text{IS}} \quad (2)$$

All the transition states were determined using the climbing image nudged elastic band (CI-NEB)<sup>49,50</sup> and DIMER<sup>51,52</sup> methods and performed a vibrational frequency analysis to confirm that the predicted transition state to the first-order saddle point in the reaction path. Additionally, the Bader charge analysis using the code developed by Henkelman and co-workers was employed to quantify the charge transfer between the substrates and CO<sub>2</sub> molecule.<sup>53–55</sup>

### 2.3. Microkinetic model

The rate constants for CO<sub>2</sub> dissociation using the harmonic transition state theory<sup>56–58</sup> was analyzed as shown in eqn (3):

$$k = A \exp\left(-\frac{E_{\text{act}}}{RT}\right) \quad (3)$$

where,  $A$  represents the pre-exponential factor. According to the harmonic transition state theory, the pre-exponential factor ( $A$ ) can be estimated using the following formula:

$$A = \frac{\prod_{i=1}^{3N} f_i^{\text{IS}}}{\prod_{i=1}^{3N-1} f_i^{\text{TS}}} \quad (4)$$

where  $f_i^{\text{IS}}$  and  $f_i^{\text{TS}}$  were the vibrational frequencies at the IS and the TS. Note that the imaginary frequency in TS was excluded.

The actual activation barrier ( $E_{\text{act}}$ ), including the entropy ( $\Delta\text{TS}$ ), the zero point energy (ZPE) and enthalpy ( $\int C_p dT$ ) corrections, was calculated as follows:

$$E_{\text{act}} = E_a + \Delta\text{ZPE} - \Delta\text{TS} + \Delta \int C_p dT \quad (5)$$

where,  $S$  and  $C_p$  represent the entropy and the heat capacity, respectively. The zero point energy, entropy and enthalpy correction are calculated as follows,<sup>57</sup> respectively:

$$\text{ZPE} = \frac{1}{2} \sum_i h f_i \quad (6)$$

$$-\text{TS} = k_b T \sum_i \ln\left(1 - e^{-\frac{h f_i}{k_b T}}\right) - \sum_i h f_i \left(\frac{1}{e^{\frac{h f_i}{k_b T}}} - 1\right) - k_b T \quad (7)$$



$$\int C_p dT = \sum_i h f_i \left( \frac{1}{e^{-\frac{h f_i}{k_b T}} - 1} \right) + k_b T \quad (8)$$

where  $f_i$  was the vibrational frequency and  $i$  represents the different modes of vibration.

To calculate the relative concentration ( $\theta_{CO}$ ) of CO on the Fe–Cu bimetallic system, the steady state approximation was adopted in this work.<sup>59</sup> The total amount of metal catalytic sites in the reaction was considered as a constant and the sum of the occupied ( $\theta_x$ ) and the free metal ( $\theta_*$ ) sites were defined as following eqn (9):<sup>60</sup>

$$\theta_{CO_2} + 2\theta_{CO} + \theta_* = 1 \quad (9)$$

where  $\theta_{CO_2}$  was obtained by  $\theta_{CO_2} \times K_{CO_2} \times P_{CO_2} \times \theta_*$  and  $K_{CO_2} = \exp\left(-\frac{E_{ads} - T\Delta S}{RT}\right)$ .<sup>61</sup> The partial pressure ( $P_{CO_2}$ ) of  $CO_2$  from 0 to 10 atm was set.

For the elementary reaction step  $CO_2 \xrightarrow{k_+} CO + O$  (rate constants,  $K = \frac{k_+}{k_-}$ ), according to the steady-state approximation, the equation was as follows:

$$\frac{dCO}{dt} k_+ \theta_{CO_2} - k_- \theta_{CO} = 0 \quad (10)$$

Thus,

$$\theta_{CO} = \frac{1}{2 + 1/K + 1/(K \times K_{CO_2} \times P_{CO_2})} \quad (11)$$

### 3. Results and discussion

The most stable structure of the different coverage ( $n$ ) for Fe dopant on the top-layer of the Cu(100) surface was discussed briefly.

If  $n > 1/9$  ML, more than one possible structure of Fe could be doped in the Cu(100) surface. Optimal doping structure for the different coverage of Fe dopant was predicted after extensive study of the various arrangements of Fe atoms embedded in the top-layer of the Cu(100) surface. Taking  $Fe_4/Cu(100)$  as an example, four possible configurations for the  $Fe_4/Cu(100)$  surface, namely: M1 ~ M4, (see Fig. 1), were considered. In the M1 model, four Fe atoms tended to gather together and form

a square nanocluster. For the M2 and M3 structure, the four Fe atoms exhibited the T- and Z-type structure, respectively. In the M4 structure, it was seen as the  $Fe_3$  trimer and an isolated Fe atom. The calculated relative energies (Fig. 1) indicated that the energetically most favorable configuration among the M1 ~ M4 models was the M1. The most stable structure for the  $Fe_x/Cu(100)$  surfaces was determined by the similar approach and shown in Fig. S1.† Interestingly, from the perspective of thermodynamic, Fe dopant tended to arrange together when the  $n$  values increased from 1/9 to 1 ML. Therefore, we focused on the adsorption, activation and reduction of  $CO_2$  molecule on the most stable configuration for the  $Fe_x/Cu(100)$  surfaces.

#### 3.1. Adsorption configurations of $CO_2$ on $Fe_x/Cu(100)$ surfaces

The most stable structure of  $CO_2$  on the  $Fe_x/Cu(100)$  ( $x = 1-9$ ) surface was presented in Fig. 2, including  $CO_2$  on the pure Cu(100) and Fe fcc(100) surfaces. It was clearly observed in Fig. 2 that the adsorption behavior of  $CO_2$  on the  $Fe_x/Cu(100)$  surface was sensitive to the coverage of Fe atoms when the coverage of Fe atoms was less than 4/9 ML (Fig. 2(a)–(c)). While the coverage was more than 4/9 ML (Fig. 2(d)), the adsorption configuration of  $CO_2$  on the  $Fe_x/Cu(100)$  surface (Fig. 2(e)–(i)) was similar to the structure of  $CO_2$  on the  $Fe_4/Cu(100)$  surface. Herein, it was worth noting that the O atoms in the  $CO_2$  molecule tended to bind with the Fe atoms on the substrate *via* forming Fe–O adsorption bonds because the strength of the Fe–O bond was stronger than the Cu–O bond (*e.g.*, in a diatomic molecule, the dissociation energies of the Fe–O bond and Cu–O bond were about 390.4 and 269.0 kJ mol<sup>−1</sup>, respectively), indicating that the introduced Fe atoms were the major center of  $CO_2$  adsorption and activation.

After  $CO_2$  adsorption, some electrons were transferred from the substrate to  $CO_2$  moiety, leading to the bent structure with the O–C–O bond angle from 118° to 135° (Table 1). Furthermore, the C–O1 bond and the C–O2 bond was stretched to about 1.253 to 1.364 Å and 1.253 to 1.300 Å, respectively. Especially the C–O1 bond, its distance was gradually elongated by 0.2 Å compared with the distance of 1.176 Å in gas-phase  $CO_2$  molecule when the coverage of the Fe atoms was more than 3/9 ML, which meant that the C–O1 bond was activated after  $CO_2$  adsorption. Meanwhile, it was also noticed that when the coverage of the Fe atoms was more than 3/9 ML, the extra interaction between the O2 atom in the  $CO_2$  moiety and the Fe atom was established and the corresponding Fe–O2 bond

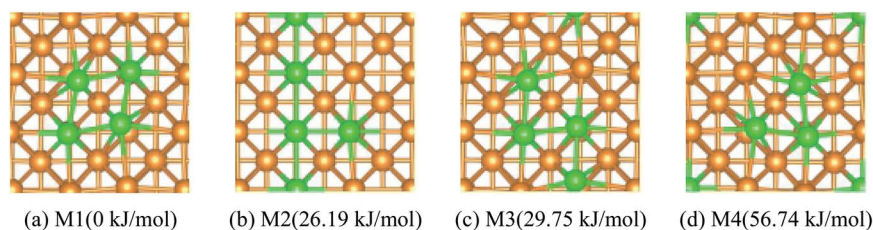


Fig. 1 Top views and the relative energies for four different arrangements of four Fe atoms embedded in the toplayer of Cu(100) surface, Cu Orange Fe green.



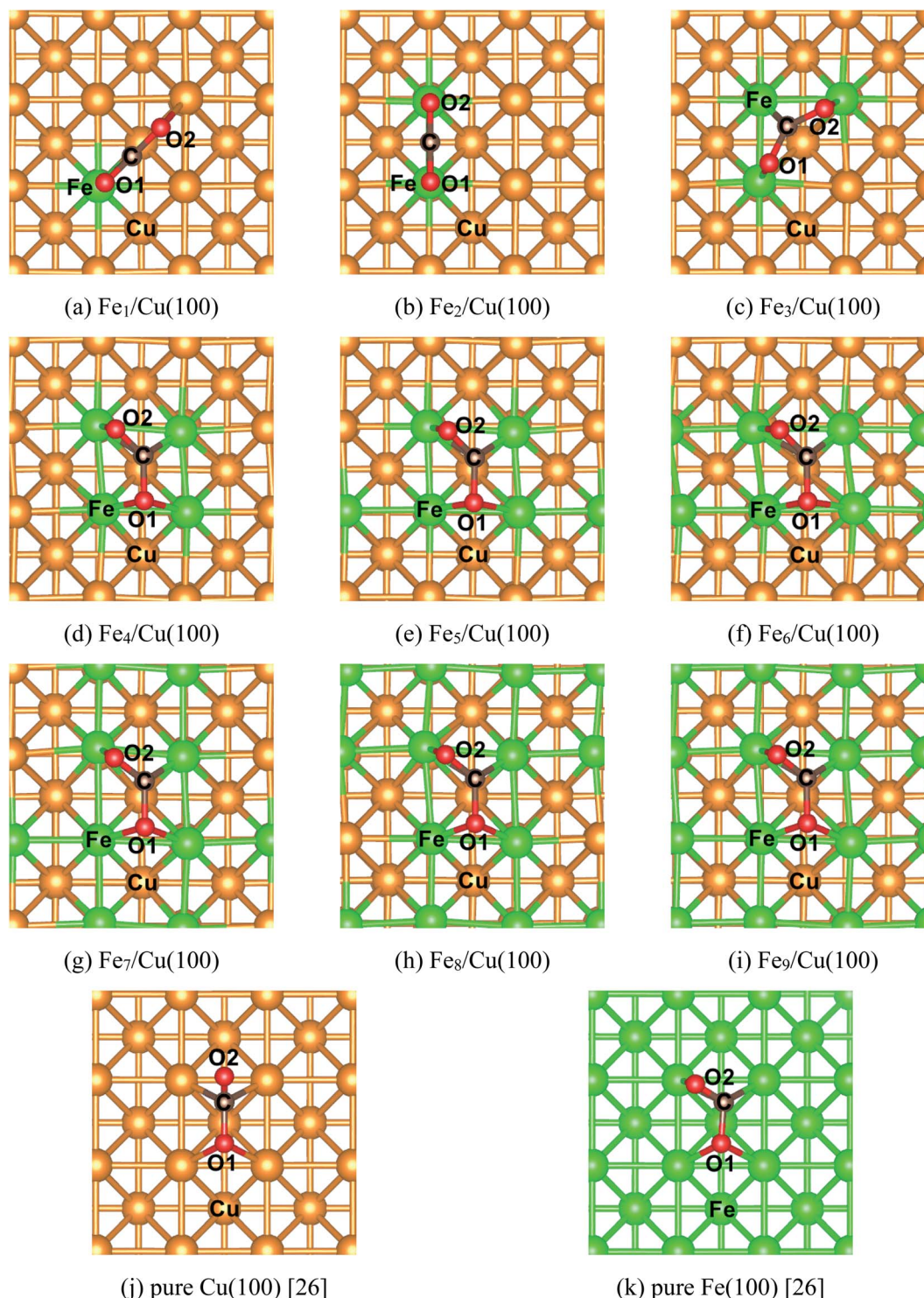


Fig. 2 Top views of the most stable configurations of  $\text{CO}_2$  adsorbed on the different  $\text{Fe}_x\text{Cu}(100)$  surfaces, as well as on the pure  $\text{Cu}(100)$  and  $\text{Fe}(100)$  surfaces with fcc structure.

length was 2.014 Å ( $\text{Fe}_4/\text{Cu}(100)$ ), 2.000 Å ( $\text{Fe}_5/\text{Cu}(100)$ ), 1.987 Å ( $\text{Fe}_6/\text{Cu}(100)$ ), 1.974 Å ( $\text{Fe}_7/\text{Cu}(100)$ ), 1.961 Å ( $\text{Fe}_8/\text{Cu}(100)$ ) and 1.965 Å ( $\text{Fe}_9/\text{Cu}(100)$ ). Among these Fe–O2 bonds, the distance of the Fe–O2 bond for  $\text{CO}_2$  on the  $\text{Fe}_4/\text{Cu}(100)$  was the longest, requiring the less energy barrier to decompose  $\text{CO}_2$ . The calculated adsorption energy (see Table 1) increased

monotonously as an increase of the coverage for Fe atoms, suggesting that introducing Fe atoms in the pure  $\text{Cu}(100)$  surface could improve the bonding strength of  $\text{CO}_2$  to the substrate. Compared with the adsorption energy of  $\text{CO}_2$  on the pure  $\text{Cu}(100)$  ( $E_{\text{ads}} = -72.4 \text{ kJ mol}^{-1}$ ) and  $\text{Fe fcc}(100)$  ( $E_{\text{ads}} = 139.8 \text{ kJ mol}^{-1}$ ) surfaces,<sup>26</sup> the binding strength of  $\text{CO}_2$  on the



**Table 1** Some optimized bond lengths (Å), O–C–O bond angle (degrees) and the calculated adsorption energies ( $E_{\text{ads}}$ , in  $\text{kJ mol}^{-1}$ ) of  $\text{CO}_2$  molecules on pure Fe(100), Cu(100) and different  $\text{Fe}_x/\text{Cu}(100)$  bimetallic surfaces

System	$d_{\text{C-O1}}^a$	$d_{\text{C-O2}}$	$\angle \text{O-C-O}$	$d_{\text{Fe-C}}$	$d_{\text{Fe-O1}}$	$d_{\text{Cu-O2}}$	$d_{\text{Fe-O2}}$	$E_{\text{ads}}$
$\text{Fe}_1/\text{Cu}(100)$	1.258	1.271	134.5	1.929	2.015	2.163	—	84.5
$\text{Fe}_2/\text{Cu}(100)$	1.253	1.253	138.9	$2.041 (\times 2)^b$	2.091	—	2.092	115.9
$\text{Fe}_3/\text{Cu}(100)$	1.296	1.295	124.4	1.939	1.969	—	1.971	135.3
$\text{Fe}_4/\text{Cu}(100)$	1.356	1.293	121.3	2.113/1.936	2.039/2.040	—	2.014	145.3
$\text{Fe}_5/\text{Cu}(100)$	1.354	1.296	121.2	2.116/1.936	2.046/2.048	—	2.000	148.6
$\text{Fe}_6/\text{Cu}(100)$	1.351	1.299	121.2	2.160/2.050	2.048/2.050	—	1.987	153.0
$\text{Fe}_7/\text{Cu}(100)$	1.362	1.296	118.5	2.115/1.938	2.047/2.013	—	1.974	147.4
$\text{Fe}_8/\text{Cu}(100)$	1.361	1.300	118.3	2.167/1.924	2.028/2.009	—	1.961	154.8
$\text{Fe}_9/\text{Cu}(100)$	1.364	1.299	118.3	2.138/1.924	2.038/2.009	—	1.965	150.8
纯 Cu(100) <sup>c</sup>	1.322	1.220	128.4	2.157	2.098	—	—	−72.4
纯 Fe(100) <sup>c</sup>	1.340	1.290	120.5	2.190/1.950	2.040/2.080	—	1.990	139.8

<sup>a</sup> The symbols O1 and O2 represent the two oxygen atoms of the  $\text{CO}_2$  moiety (see Fig. 2). For the free  $\text{CO}_2$  molecule, the optimized length of the C–O bond is 1.176 Å. <sup>b</sup> The number of bonds is shown in parentheses. <sup>c</sup> The data origin from the ref. 20.

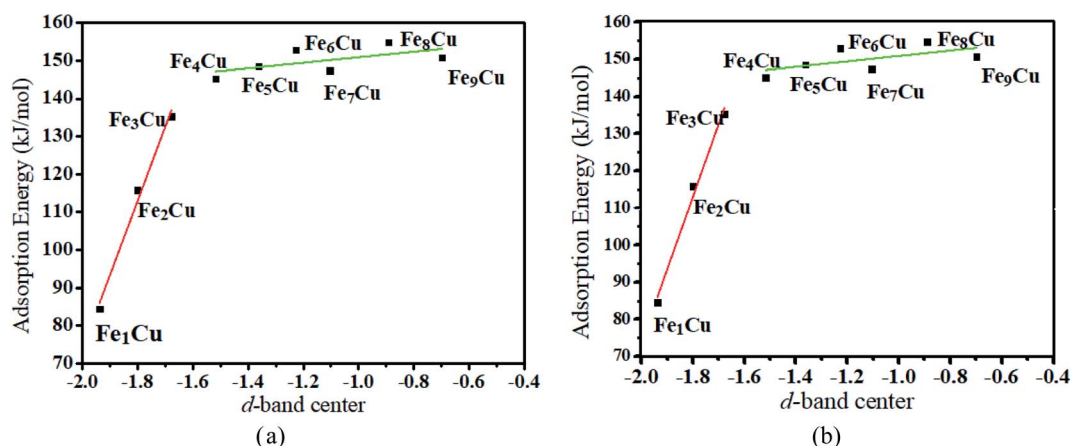
substrate was enhanced while the coverage of Fe atoms was more than 3/9 ML.

### 3.2. Electronic structures of $\text{CO}_2$ on $\text{Fe}_x/\text{Cu}(100)$ surfaces

**3.2.1. D-Band center analysis.** To interpret a variation in adsorption energy as an increase of coverage for Fe atoms, the position of the d-band center of the  $\text{Fe}_x/\text{Cu}(100)$  surface was calculated. As well-known, the d-band center model was used widely to understand the bond formation on a transition metal surface, this is, the higher the d-band center, the stronger the adsorption bond.<sup>33</sup> As shown in Fig. 3(a), the value of the d-band center for the  $\text{Fe}_x/\text{Cu}(100)$  surface was in the range of 2.0 to −0.7 eV and tended to increase with an increase of Fe atoms on the Cu(100) surface. Although the coverage exceeded 3/9 ML, the variation of adsorption energy was small as the increase of position of the d-band center because of the same structure of the  $\text{CO}_2$  on  $\text{Fe}_x/\text{Cu}(100)$  surface. Furthermore, to gain a deeper understanding of the active state of the  $\text{Fe}_x/\text{Cu}(100)$  surface, the

position of the d-band center for alpha ( $\alpha$ ) and beta ( $\beta$ ) states in 3d-orbitals was extracted from the total position of the d-band center. As shown in Fig. S2† and 3(b), the trend of the variation of the d-band center for  $\beta$ -states orbitals was consistent with that of the total d-band center, which meant that  $\text{CO}_2$  was adsorbed on the  $\text{Fe}_x/\text{Cu}(100)$  surface by interaction with the  $\beta$ -states orbitals of the doped Fe atoms. Furthermore, the calculated density of states (DOS) in Fig. 4 confirmed that, after  $\text{CO}_2$  adsorption on  $\text{Fe}_x/\text{Cu}(100)$  surface,  $\text{CO}_2$  tended to interact with the  $\beta$ -states of the substrates.

**3.2.2. Bader charge analysis.** As mentioned, the  $\text{CO}_2$  on the substrate exhibited the bent structure, indicating that some electrons were transferred to  $\text{CO}_2$  from substrate. To verify this conclusion more clearly, the charge density of  $\text{CO}_2$  on the  $\text{Fe}_x/\text{Cu}(100)$  surface was calculated and shown in Fig. S3–S10.† Taking  $\text{CO}_2$  on the  $\text{Fe}_4/\text{Cu}(100)$  surface as an example, Fig. 5(a) represents the charge density map of  $\text{CO}_2$  adsorbed on the  $\text{Fe}_4/\text{Cu}(100)$  surface (the x-axis represents the distance from the bottom to the top of the  $\text{Fe}_4/\text{Cu}(100)$  system). Five high-density



**Fig. 3** Relationship between (a) the total d-band center (b) the d-band center for beta-orbitals of different  $\text{Fe}_x/\text{Cu}(100)$  surface and the adsorption energies of  $\text{CO}_2$  molecule.



peaks in Fig. 5(a) were observed and each peak represented the charge density of one atomic layer in the  $\text{Fe}_4/\text{Cu}(100)$  surface. Furthermore, a relatively small density peak is observed at  $\sim 9.0$  Å along the  $x$ -axis, which represented the charge density of the  $\text{CO}_2$  moiety. It was noted that an obvious interaction between  $\text{CO}_2$  and the  $\text{Fe}_4/\text{Cu}(100)$  surface was observed at  $z = 7-9$  Å. The charge density difference map ( $\Delta\rho$ ) in Fig. 5(b) changed from lightly positive to negative upon crossing the  $\text{Fe}_4/\text{Cu}(100)$  interface ( $z = 7.0-8.0$  Å) and reached a minimum at  $z = \sim 8.6$  Å. Then it changed from negative to positive in the region ( $z = 8-9$  Å). This evolution indicated that the electrons flowed from the  $\text{Fe}_4/\text{Cu}(100)$  surface to the  $\text{CO}_2$  moiety, forming the  $\text{CO}_2^-$  anions.

To quantify these charges transferred, the Bader charge analysis for all systems was calculated, as shown in Table 2. As expected,  $\text{CO}_2$  obtained some electrons from the  $\text{Fe}_x/\text{Cu}(100)$  surfaces. In general, as the coverage increased for Fe atoms, the electrons obtained by  $\text{CO}_2$  from the surface also increased. In particular, for the  $\text{Fe}_9/\text{Cu}(100)$  surface, the transferred electrons reached the maximum (1.17e). The atomic charges for C and O

atoms of  $\text{CO}_2$  moiety were also included in Table 2. It was obviously evident in Table 2 that the transferred electrons were significantly concentrated on C atom.

Fig. 6 displays the charge density difference for  $\text{CO}_2$  moiety on  $\text{Fe}_x/\text{Cu}(100)$  surface. If the coverage was less than  $4/9$  ML, the  $\pi$ -bond between C and O1 atoms was weakened slightly, especially the  $\text{Fe}_1/\text{Cu}(100)$ . Although the coverage was more than  $3/9$  ML, Fig. 6(d)–(i) clearly showed that the degree of activation for the  $\pi$ -bond was quite similar and was more larger than  $\text{CO}_2$  on the  $\text{Fe}_{1-3}/\text{Cu}(100)$  surface.

**3.2.3. Vibrational frequencies analysis.** According to the Bader charge analysis, after  $\text{CO}_2$  adsorbed on the  $\text{Fe}_x/\text{Cu}(100)$  surface, some electrons were transferred from the substrate to  $\text{CO}_2$  moiety and concentrated on the C atom, which weakened the C–O bond and further caused a red shift of the vibrational frequency for C–O bond, especially the C–O1 bond. Table 3 present the stretching vibration frequency of C–O1 and C–O2 bonds in  $\text{CO}_2$  moiety on each of the  $\text{Fe}_x/\text{Cu}(100)$  surface. Compared with stretching vibration frequency of a free  $\text{CO}_2$  molecule, the stretching vibration frequency of the C–O1 and C–

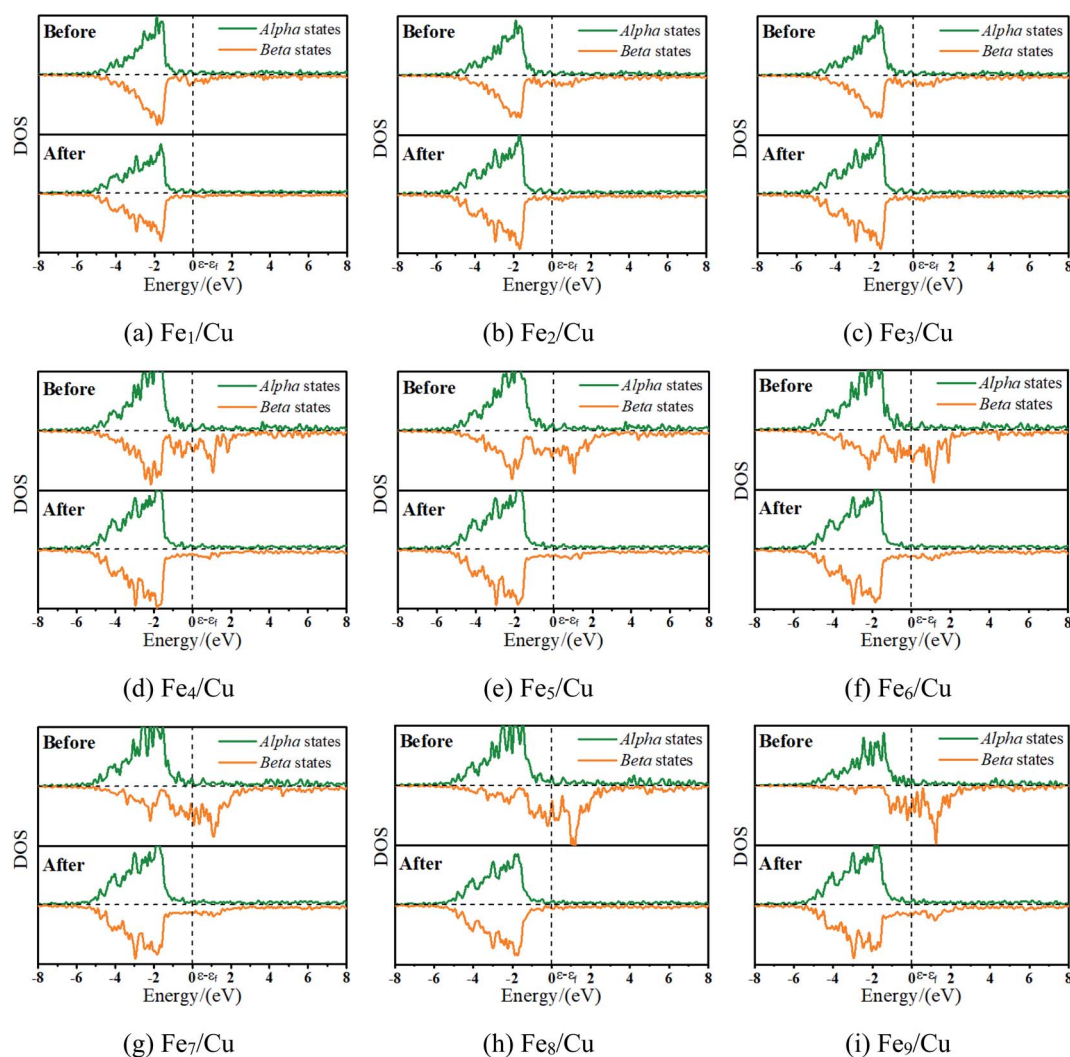


Fig. 4 The density of states for the toplayer metallic atoms in clean  $\text{Fe}_x/\text{Cu}(100)$  and  $\text{CO}_2/\text{Fe}_x/\text{Cu}(100)$  surfaces.



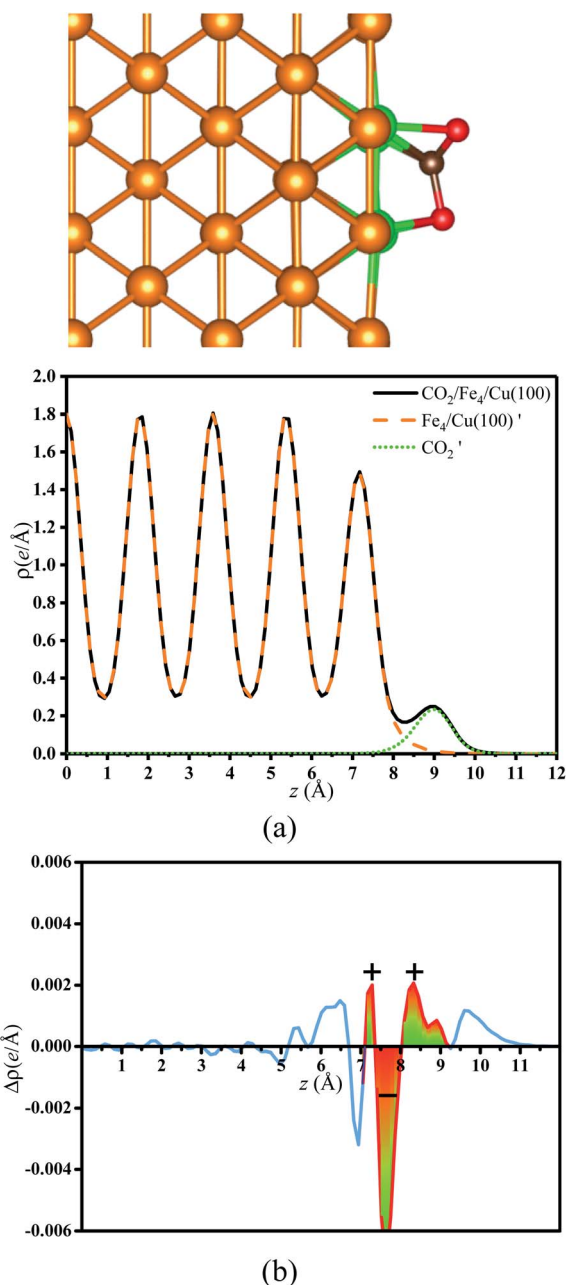


Fig. 5 (a) Charge density curves of isolated  $\text{Fe}_4/\text{Cu}(100)$  surface,  $\text{CO}_2$  moiety and  $\text{CO}_2/\text{Fe}_4/\text{Cu}(100)$  surface. (b) Charge density difference curve of  $\text{CO}_2/\text{Fe}_4/\text{Cu}(100)$  surface:  $\Delta\rho(z) = \rho_{\text{CO}_2/\text{Fe}_4/\text{Cu}(100)}(z) - \rho_{\text{CO}_2}(z) - \rho_{\text{Fe}_4/\text{Cu}(100)}(z)$ .  $\text{Fe}_4/\text{Cu}(100)$  surface denotes from the  $\text{CO}_2/\text{Fe}_4/\text{Cu}(100)$  system and  $\text{CO}_2$  is the bent  $\text{CO}_2$  moiety of the same  $\text{CO}_2/\text{Fe}_4/\text{Cu}(100)$  system.

O2 bonds was red-shifted when the  $\text{CO}_2$  was adsorbed on the  $\text{Fe}_x/\text{Cu}(100)$  surface. However, the variation of the stretching vibration frequency for C–O2 bond decreased lightly when the coverage was more than 3/9 ML. Compared with the stretching vibration frequency ( $1333\text{ cm}^{-1}$ ) of the gas  $\text{CO}_2$  molecule, the reducing value of the stretching vibration frequency for the C–O1 bond was  $211\text{ cm}^{-1}$  ( $\text{Fe}_1/\text{Cu}(100)$ ),  $181\text{ cm}^{-1}$  ( $\text{Fe}_2/\text{Cu}(100)$ ),  $216\text{ cm}^{-1}$  ( $\text{Fe}_3/\text{Cu}(100)$ ),  $316\text{ cm}^{-1}$  ( $\text{Fe}_4/\text{Cu}(100)$ ),  $314\text{ cm}^{-1}$  ( $\text{Fe}_5/\text{Cu}(100)$ ),  $308\text{ cm}^{-1}$  ( $\text{Fe}_6/\text{Cu}(100)$ ),  $344\text{ cm}^{-1}$  ( $\text{Fe}_7/\text{Cu}(100)$ ),  $340\text{ cm}^{-1}$  ( $\text{Fe}_8/\text{Cu}(100)$ ) and  $354\text{ cm}^{-1}$  ( $\text{Fe}_9/\text{Cu}(100)$ ), respectively.

Table 2 Bader charges (e) of the  $\text{CO}_2$  moiety, the carbon and oxygen atoms of different  $\text{Fe}_x/\text{Cu}(100)$  surfaces and the free  $\text{CO}_2$  molecule

	C	O1	O2	$\text{CO}_2$ moiety
$\text{CO}_2$	1.94	−0.97	−0.97	0
$\text{Fe}_1/\text{Cu}(100)$	1.29	−1.07	−0.99	−0.77
$\text{Fe}_2/\text{Cu}(100)$	1.24	−1.01	−1.01	−0.78
$\text{Fe}_3/\text{Cu}(100)$	1.14	−1.03	−1.04	−0.93
$\text{Fe}_4/\text{Cu}(100)$	0.98	−1.06	−1.04	−1.12
$\text{Fe}_5/\text{Cu}(100)$	0.90	−1.02	−1.00	−1.13
$\text{Fe}_6/\text{Cu}(100)$	0.96	−1.08	−1.02	−1.14
$\text{Fe}_7/\text{Cu}(100)$	0.92	−1.03	−1.04	−1.15
$\text{Fe}_8/\text{Cu}(100)$	0.94	−1.08	−1.02	−1.16
$\text{Fe}_9/\text{Cu}(100)$	0.94	−1.08	−1.03	−1.17
Pure $\text{Cu}(100)^a$	1.47	−1.10	−1.00	−0.63
Pure Fe fcc(100) <sup>a</sup>	1.02	−1.12	−1.05	−1.16

<sup>a</sup> The data origin from ref. 20.

Among these frequencies, the variation of the stretching vibration frequency of the C–O1 bond adsorbed on the  $\text{Fe}_9/\text{Cu}(100)$  surface reached its maximal value, which was consistent with the variation in bond length and the number of transferred charges after adsorption. Thus, the more electrons were transferred to the  $\text{CO}_2$  molecule, the longer the C–O1 bond length was and the easier the stretching vibration frequency for the C–O1 bond was to redshift.

### 3.3. Decomposition of $\text{CO}_2$ on $\text{Fe}_x/\text{Cu}(100)$ surfaces

**3.3.1. Transition state analysis.** The minimum potential energy map for the decomposition of  $\text{CO}_2$  molecules on the  $\text{Fe}_x/\text{Cu}(100)$  surfaces was determined using the CI-NEB and DIMER methods and shown in Fig. 7 and S11†. According to the  $\text{Fe}_1/\text{Cu}(100)$  surface shown in Fig. S11(a),† the O atom bonded to three Cu atoms and one Fe atom (4-fold site), whereas the CO moiety was adsorbed between two adjacent Cu atoms. On all other  $\text{Fe}_x/\text{Cu}(100)$  surfaces, the O atom was still bonded to four metal atoms to form the 4-fold site and the C atom of CO moiety was co-adsorbed to the substrate with an incline through the Fe–C adsorption bond. The reaction energy (H) of  $\text{CO}_2$  decomposition on the  $\text{Fe}_x/\text{Cu}(100)$  surface was calculated, as shown in Fig. 7 and S11.† For the  $\text{Fe}_1/\text{Cu}(100)$  surface, the highest reaction energy was  $-4.9\text{ kJ mol}^{-1}$ , followed by the  $\text{Fe}_3/\text{Cu}(100)$  surface ( $-36.1\text{ kJ mol}^{-1}$ ) and the  $\text{Fe}_2/\text{Cu}(100)$  surface ( $-43.1\text{ kJ mol}^{-1}$ ). When the coverage of Fe atoms was more than 3/9 ML, the reaction energy could be significantly increased with  $-65.0\text{ kJ mol}^{-1}$  for the  $\text{Fe}_4/\text{Cu}(100)$ ,  $-62.3\text{ kJ mol}^{-1}$  for the  $\text{Fe}_5/\text{Cu}(100)$  surface,  $-70.7\text{ kJ mol}^{-1}$  for the  $\text{Fe}_6/\text{Cu}(100)$  surface,  $-121.0\text{ kJ mol}^{-1}$  for the  $\text{Fe}_7/\text{Cu}(100)$  surface,  $-122.5\text{ kJ mol}^{-1}$  for the  $\text{Fe}_8/\text{Cu}(100)$  surface and  $-127.6\text{ kJ mol}^{-1}$  for the  $\text{Fe}_9/\text{Cu}(100)$  surface. It was noteworthy that the reaction energy of the  $\text{Fe}_x/\text{Cu}(100)$  surface increased with the coverage of the Fe atom increased on the  $\text{Cu}(100)$  surface, indicating that the introduced Fe atom improved the reaction energy of  $\text{CO}_2$  decomposition. It may be reasonable

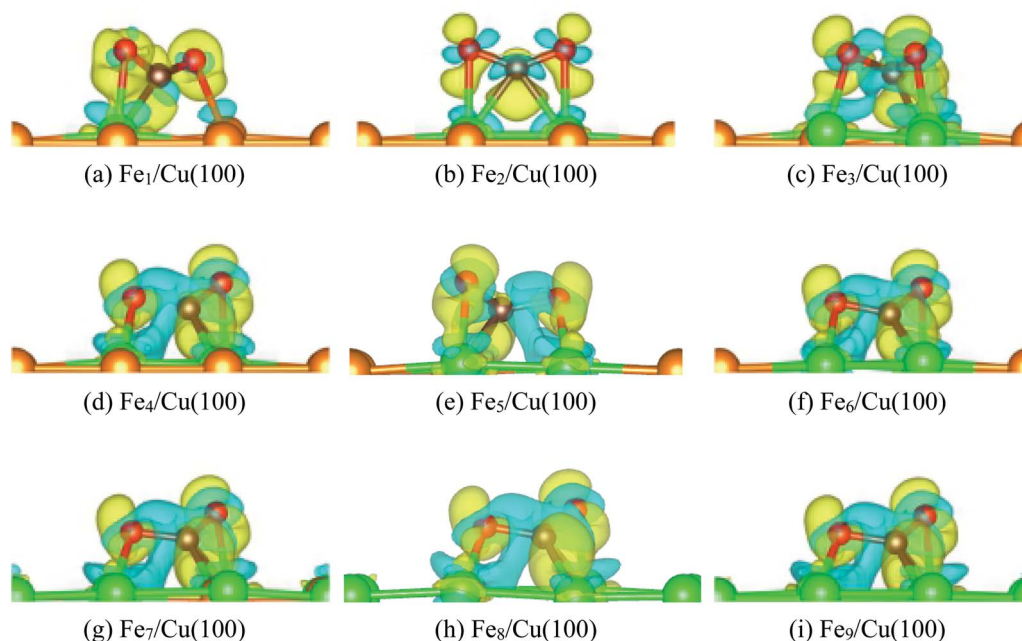


Fig. 6 Charge density difference of CO<sub>2</sub> on Fe<sub>x</sub>/Cu(100) ( $x = 1-9$ ) surface.

that, as the coverage of Fe atoms increased, the number of Fe–O bonds increased and the strength of Fe–O bond was stronger than that of Cu–O bond, thereby reaction energy was increased for CO<sub>2</sub> decomposition from Fe<sub>1</sub>/Cu(100) to Fe<sub>9</sub>/Cu(100) surfaces. From the thermodynamic point of view, the negative reaction energy indicated that the Fe<sub>x</sub>/Cu(100) surface would be favorable to decompose CO<sub>2</sub> into CO, especially the Fe<sub>9</sub>/Cu(100) surface.

The activation energy barrier ( $E_a$ ) of CO<sub>2</sub> decomposition on the Fe<sub>x</sub>/Cu(100) surface was determined and shown in Fig. 7 and S11.† In addition, the vibration frequencies of all transition states were calculated to ensure that the predicted TS corresponds to the first-order saddle point in the reaction path and the imaginary frequency ( $\nu_i$ ) was also shown in Fig. 7 and S11.† For the Fe<sub>1</sub>/Cu(100) surface, only one TS for the C–O1 bond

decomposition was discovered. The activation energy barrier (relative to the energy of the CO<sub>2</sub> adsorption) of CO<sub>2</sub> decomposition on the Fe<sub>1</sub>/Cu(100) surface was 45.6 kJ mol<sup>−1</sup>. For the Fe<sub>2</sub>/Cu(100) and Fe<sub>3</sub>/Cu(100) surfaces, the activation energy barrier increased to 59.9 kJ mol<sup>−1</sup> and 63.7 kJ mol<sup>−1</sup> compared with the Fe<sub>1</sub>/Cu(100) surface, respectively. When the coverage reached 4/9 ML, the activation energy barrier reached the minimum value (32.8 kJ mol<sup>−1</sup>). The transition state of CO<sub>2</sub> decomposition on the Fe<sub>x</sub>/Cu(100) surface was extremely similar to the CO<sub>2</sub> on the Fe<sub>4</sub>/Cu(100) surface when the coverage was greater than 4/9 ML. The corresponding activation energy barrier from the Fe<sub>5</sub>/Cu(100) to Fe<sub>9</sub>/Cu(100) systems was 35.4 kJ mol<sup>−1</sup>, 39.7 kJ mol<sup>−1</sup>, 34.7 kJ mol<sup>−1</sup>, 40.2 kJ mol<sup>−1</sup> and 35.0 kJ mol<sup>−1</sup>, respectively. The results showed that the activation energy barrier of all systems exhibited an inverted “S” shape, which was

Table 3 The stretching vibration of the C–O1 and C–O2 bonds in CO<sub>2</sub> moiety on Fe<sub>x</sub>/Cu(100) surface and free CO<sub>2</sub>

System	$\nu_{\text{C-O1}}/\text{cm}^{-1}$	$\nu_{\text{C-O2}}/\text{cm}^{-1}$
Free CO <sub>2</sub> <sup>a</sup>	1333	1333
Fe <sub>1</sub> /Cu(100)	1122	1610
Fe <sub>2</sub> /Cu(100)	1152	1152
Fe <sub>3</sub> /Cu(100)	1117	1117
Fe <sub>4</sub> /Cu(100)	1017	1305
Fe <sub>5</sub> /Cu(100)	1019	1296
Fe <sub>6</sub> /Cu(100)	1025	1283
Fe <sub>7</sub> /Cu(100)	989	1279
Fe <sub>8</sub> /Cu(100)	993	1258
Fe <sub>9</sub> /Cu(100)	979	1261

<sup>a</sup> The data origin from NIST database: <https://webbook.nist.gov/chemistry>.

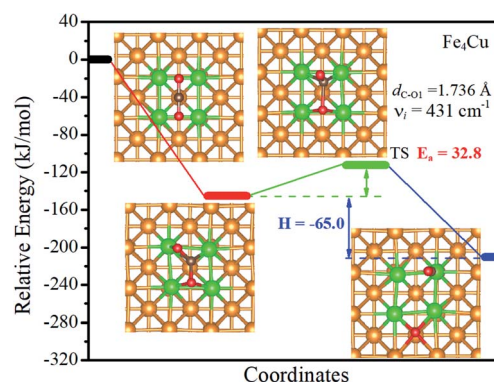


Fig. 7 Calculated reaction paths of CO<sub>2</sub> dissociation on the Fe<sub>4</sub>/Cu(100) surface. The zero of energy is set to the total energy of the isolated surface and CO<sub>2</sub> molecule in the gas phase.



consistent with the variation in the distance between Fe and O2 atoms, that is, the shorter the distance of the Fe–O2 adsorption bond, the larger the activation energy barrier. For instance, the length (2.014 Å) of the Fe–O2 adsorption bond formed on the Fe<sub>4</sub>/Cu(100) surface was the largest among the Fe<sub>x</sub>/Cu(100) system, which indicated that the O2 atom may need to consume less additional energy to “escape” out of the substrate. Therefore the activation energy barrier of CO<sub>2</sub> decomposition on the Fe<sub>4</sub>/Cu(100) surface was minimal. In addition, Fe dopant introduced on the Cu(100) surface significantly reduced the activation energy barrier of CO<sub>2</sub> decomposition compared with the barrier of CO<sub>2</sub> on the pure Cu(100) surface with the barrier of 92.9 kJ mol<sup>−1</sup> and the Fe(100) surface with the barrier of 113.4 kJ mol<sup>−1</sup>, especially the Fe<sub>4</sub>/Cu(100) system.<sup>26</sup> Compared to CO<sub>2</sub> on the Co<sub>4</sub>/Cu(100) surface with the barrier of 18.7 kJ mol<sup>−1</sup>,<sup>33</sup> the activation energy barrier for CO<sub>2</sub> on the Fe<sub>x</sub>/Cu(100) is more than 14.1 kJ mol<sup>−1</sup>. The main reason is that bond strength of Fe–O (in diatomic molecules: 390.4 kJ mol<sup>−1</sup>) is stronger than that of Co–O (in diatomic molecules: 384.5 kJ mol<sup>−1</sup>), which led to be the extra barrier formed by Fe–O bond to overcome.

Moreover, the reaction energy barrier ( $\Delta E_a = E_{TS} - E_{slab} - E_{CO_2}$ ) and the total reaction energy ( $\Delta E = E_{ads} + H$ ) followed a linear relationship for the C–O bond scission and the BEP relationship was established:  $\Delta E_a = 0.43\Delta E - 2.5$  (kJ mol<sup>−1</sup>) (see Fig. 8). This BEP relationship played an important role in estimating the reaction barrier of the C–O bond scission on other metal surfaces. Furthermore, the results in Fig. 3 showed an increasing trend as the number of Fe-dopants increased. It was worth noting that although the Fe<sub>4</sub>/Cu(100) surface did not have the lowest reaction energy barrier and total reaction energy, the Fe<sub>4</sub>/Cu(100) surface had the lowest activation energy barrier for CO<sub>2</sub> decomposition, which facilitated the decomposition of CO<sub>2</sub>.

**3.3.2. Micro kinetics analysis.** To further explore the mechanism of CO<sub>2</sub> decomposition on the Fe<sub>x</sub>/Cu(100) surfaces from the perspective of dynamics, a microkinetic analysis based on the DFT studies was employed on the most favorable path of

CO<sub>2</sub> decomposition.<sup>62,63</sup> In the microkinetic model, the temperatures ranging from 250 to 1000 K was adopted to investigate its impact.

The zero point energy, entropy and enthalpy corrections for the activation energy barrier ( $E_a$ ) were considered to accurately describe the reaction at high temperatures (from 250 to 1000 K) in this section. The obtained results were presented in Tables S2–S19.† The forward and reverse rate constants of the elementary reaction steps for CO<sub>2</sub> decomposition on the Fe<sub>x</sub>/Cu(100) surfaces at temperature ranging from 250 to 1000 K were displayed in Fig. 9. The Fig. 9 showed that the forward rate constants and inverse rate constants for the CO<sub>2</sub> decomposition on the Fe<sub>x</sub>/Cu(100) surfaces increased as the temperature increased. At the same temperature, the rate constants for CO<sub>2</sub> dissociation increased with an increase in the coverage of dopant Fe atom, indicating that the doped Fe significantly improved the rate constants. Moreover, it was further noting that the both forward rate constants and inverse rate constants for CO<sub>2</sub> decomposition was not only increased as the increase of temperature, but the forward rate constants in all Fe<sub>x</sub>/Cu(100) surface were much larger than the inverse rate constants. In addition, the equilibrium constants ( $K = k_f/k_r$ ) of CO<sub>2</sub> decomposition on the Fe<sub>x</sub>/Cu(100) surfaces were also considered as a critical parameter. As shown in Fig. 10 and in Tables S11–S19,† the  $K$  decreased as the temperature increased, which meant that the increase in the inverse rate constants was greater than the positive rate constants as the temperature increased. The nine curves for  $K$  (equilibrium constants) were divided into four groups, *i.e.* G1 (Fe<sub>1</sub>/Cu system), G2 (Fe<sub>2</sub>/Cu and Fe<sub>3</sub>/Cu systems), G3 (Fe<sub>4</sub>/Cu, Fe<sub>5</sub>/Cu and Fe<sub>6</sub>/Cu systems), G4 (Fe<sub>7</sub>/Cu, Fe<sub>8</sub>/Cu and Fe<sub>9</sub>/Cu systems). In each group the equilibrium constants were close to each other, which was agreement with the variation in the BEP relationship. According to the  $K$ , the order of the four group was G4 > G3 > G2 > G1 at the same temperature. Thus, the doped Fe atom was favorable to be activation and decomposition of CO<sub>2</sub> molecule and the  $K$  of CO<sub>2</sub> decomposition increased as the coverage of the Fe atom increased. Moreover, although increasing temperature was favorable to the increases of the forward rate constants and inverse rate constants, it was unfavorable to the increase of the equilibrium constants. From

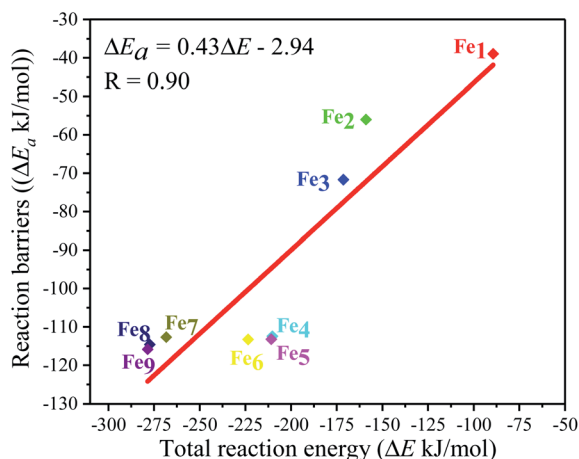


Fig. 8 Brønsted–Evans–Polanyi (BEP) relationship for the C–O1 bond scission of CO<sub>2</sub> on the Fe<sub>x</sub>/Cu(100) ( $x = 1-9$ ) surfaces.

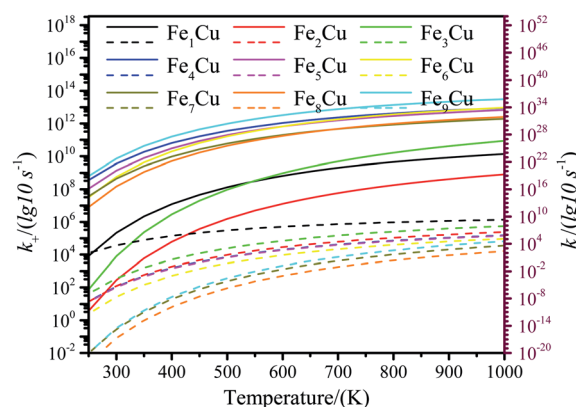


Fig. 9 The forward and reverse rate constants for CO<sub>2</sub> decomposition on the Fe<sub>x</sub>/Cu(100) surfaces at temperature from 250 K to 1000 K. (The solid line represents the positive equilibrium constants and the dashed line is the inverse equilibrium constants).



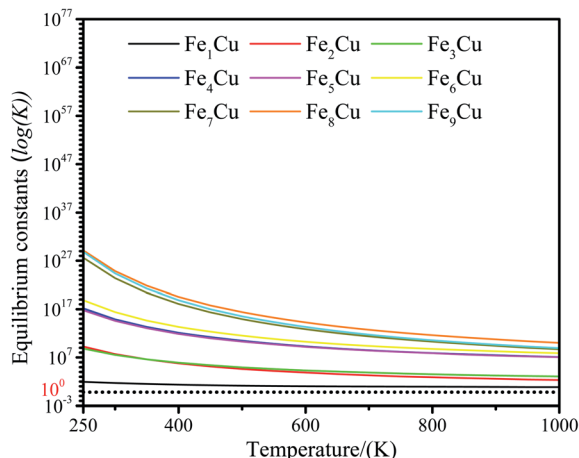


Fig. 10 Equilibrium constants for  $\text{CO}_2$  decomposition on the  $\text{Fe}_x/\text{Cu}(100)$  surface at temperature from 250 to 1000 K.

the perspective of dynamics, this results indicated that the lower the temperature for  $\text{CO}_2$  decomposition, the more favorable the decomposition of  $\text{CO}_2$  on the  $\text{Fe}_x/\text{Cu}(100)$  surface.

**3.3.3. Effects of partial pressure of  $\text{CO}_2$ .** Fig. 11 illustrated the impact of partial pressure of  $\text{CO}_2$  towards the decomposition of  $\text{CO}_2$ . The results in Fig. 11(a) showed that the decomposition of  $\text{CO}_2$  into CO at partial pressure from 0 to 10 atm was not obviously observed when the temperature was less than 300 K. While the concentration of CO reached 50% at the partial pressure of 0.5 atm when the temperature is higher than or equal to 300 K. To further explore the decomposition of  $\text{CO}_2$  at the low partial pressure of  $\text{CO}_2$ , the partial pressure of  $\text{CO}_2$  from 0 atm to 0.01 atm was studied and the results were shown in Fig. 11(b). It was seen in Fig. 11(b) that when the temperature is below 300 K, the decomposition reaction of  $\text{CO}_2$  was not observed at the partial pressure from 0 atm to 0.01 atm; The relative concentration of CO increased with the partial pressure of  $\text{CO}_2$  increased when the temperature was at 350 K; if the temperature was greater than 350 K, the concentration of CO reached 49% at the partial pressure of 0.0003 atm (in general, the partial pressure of  $\text{CO}_2$  in the atmosphere is less than 0.03%). Therefore, when the temperature was greater than 350 K,  $\text{CO}_2$  could be decomposed into CO on  $\text{Fe}_4/\text{Cu}(100)$  surface under the normal partial pressure of  $\text{CO}_2$  in the atmosphere.

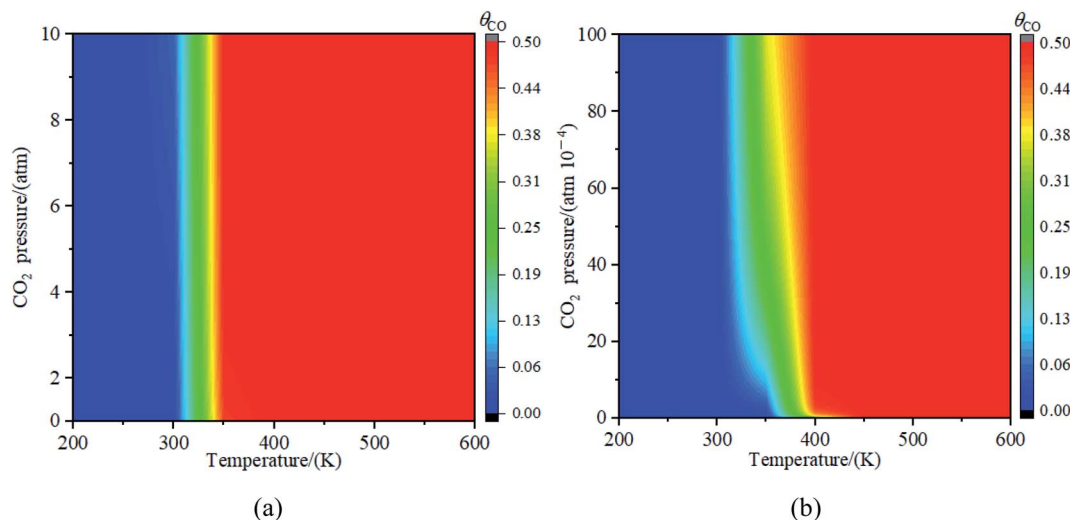


Fig. 11 The concentration of CO on  $\text{Fe}_4/\text{Cu}(100)$  surface with the partial pressure for  $\text{CO}_2$  (a) from 0 to 10 atm and (b) from 0 to 0.01 atm.

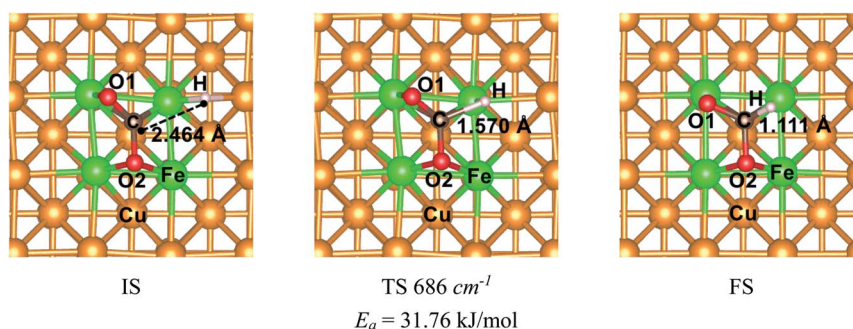


Fig. 12 The structures of initial structure (IS), transition structure (TS) and final structure (FS) for  $\text{CO}_2$  hydrogenation to  $\text{HCOO}^*$  on the  $\text{Fe}_4/\text{Cu}(100)$  surface.



### 3.4. Hydrogenation of CO<sub>2</sub> on Fe<sub>4</sub>/Cu(100) surface

The mechanism of CO<sub>2</sub> hydrogenation on the Fe<sub>4</sub>/Cu(100) surface was also examined in this section. There were three reaction pathways for CO<sub>2</sub> hydrogenation: the C atom was attacked by H atom and the O1 and O2 atom was attacked, respectively. However, our previous works reveal that the hydrogenation of the C atom in CO<sub>2</sub> moiety is more favorable than that of the O atom.<sup>16,33,34</sup> Thus, the C atom hydrogenation was considered as an important reaction pathway while CO<sub>2</sub> moiety was dissociated. The initial structure (IS), transition structure (TS) and finally structure (FS) was presented in Fig. 12. In Fig. 12, the distance between C and H atoms was changed from 2.464 Å in the IS to 1.570 Å in the TS, and then to 1.111 Å in the FS. The transition structure had been confirmed by the single imaginary frequency with 686 cm<sup>-1</sup>. It was worth noted that the calculated activation energy barrier of CO<sub>2</sub> hydrogenation to HCOO\* was 31.8 kJ mol<sup>-1</sup>, which was less 1.0 kJ mol<sup>-1</sup> than that of decomposition for CO<sub>2</sub> on the Fe<sub>4</sub>/Cu(100) surface. Such the small difference suggests that CO<sub>2</sub> hydrogenation could also be performed during the CO<sub>2</sub> decomposition. To understand the relationship between hydrogenation and dissociation of CO<sub>2</sub>, the FPMD was carried to the system with CO<sub>2</sub> and H co-adsorption on Fe<sub>4</sub>/Cu(100) surface at temperature from 250 to 450 K. The radial distribution function of C–O suggests that the broad peak was observed from 2.5 to 3.5 Å in Fig. S15(a)† and it was not found for the peak of C–H in Fig. S15(b)† and O–H in Fig. S15(c)† from 1.0 to 1.5 Å at 400 K. This means that CO<sub>2</sub> would rather decompose than hydrogenate at 400 K.

## 4. Conclusions

The adsorption, activation and reduction of CO<sub>2</sub> molecule on the Fe<sub>x</sub>/Cu(100) ( $x = 1-9$ ) had been investigated by the density functional theory based on the first principle. The results indicated that the introduction of dopant Fe atom could enhance the adsorption and activation of CO<sub>2</sub> molecule on the Cu(100) surface. The most stable structure for CO<sub>2</sub> on the Fe<sub>x</sub>/Cu(100) surface was sensitive to the coverage of the Fe dopant. The electronic structural analysis, including d-band center, Bader charge, vibrational frequencies, showed that CO<sub>2</sub> molecule interacted with the  $\beta$ -state orbitals of the Fe<sub>x</sub>/Cu(100) surface. After CO<sub>2</sub> adsorption, some electrons were transferred from substrate to CO<sub>2</sub> moiety and the electrons transferred to CO<sub>2</sub> moiety increased with the coverage of Fe atoms increased, leading to formation of CO<sub>2</sub><sup>-</sup> anion. Additionally, the mechanism of CO<sub>2</sub> moiety decomposition on Fe<sub>x</sub>/Cu(100) surfaces had been studied in detail. The results indicated that the activation energy barrier ( $E_a = 32.8$  kJ mol<sup>-1</sup>) of CO<sub>2</sub> decomposition on Fe<sub>4</sub>/Cu(100) was the smallest among the Fe<sub>x</sub>/Cu(100) surfaces. The major reason was that, if coverage was more than 4/9 ML, the extra formed Fe–O2 bond played an handle role for CO<sub>2</sub> decomposition. From the viewer of kinetic, the rate constants of CO<sub>2</sub> on Fe<sub>4</sub>/Cu(100) surface were close to that of the Fe<sub>9</sub>/Cu(100) surface and the equilibrium constants analysis revealed that the servers of the equilibrium constants were divided into the four

group, and the order of the four groups was G1 (Fe<sub>1</sub>/Cu) > G2 (Fe<sub>2</sub>/Cu and Fe<sub>3</sub>/Cu) > G3 (Fe<sub>4</sub>/Cu, Fe<sub>5</sub>/Cu and Fe<sub>6</sub>/Cu) > G4 (Fe<sub>7</sub>/Cu, Fe<sub>8</sub>/Cu and Fe<sub>9</sub>/Cu). Furthermore, our results confirmed that the lower the temperature, the more favorable it was to decompose the CO<sub>2</sub> molecule into CO. When the simulated temperature was in range from 350 K and 450 K, the decomposition of C–O1 bond in CO<sub>2</sub> moiety was only observed. The results of partial pressure for CO<sub>2</sub> revealed that when the temperature was in range from 350 K to 450 K, the concentrate of CO on the Fe<sub>4</sub>/Cu(100) surface reached 49% under the partial pressure of  $3 \times 10^{-4}$  atm. Lastly, the mechanism of CO<sub>2</sub> hydrogenation on the Fe<sub>4</sub>/Cu(100) surface was also investigated. The activation energy barrier of 31.8 kJ mol<sup>-1</sup> was slightly less than that of CO<sub>2</sub> decomposition. However, the results of the FPMD analysis revealed that CO<sub>2</sub> was decomposed to form CO\*, instead of hydrogenated. Our results provide insight into the mechanism for CO<sub>2</sub> decomposition and hydrogenation on bimetallic surfaces from the perspective of thermodynamics and kinetics, which was important for the design and optimization of novel Cu-based bimetallic catalysts.

## Conflicts of 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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