The mechanism for CO2 reduction over Fe-modified Cu(100) surfaces with thermodynamics and kinetics: a DFT study†

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The adsorption, activation and reduction of CO2 over Fex/Cu(100) (x = 1–9) surfaces were examined by density functional theory. The most stable structure of CO2 adsorption on the Fe0/Cu(100) surface was realized. The electronic structure analysis showed that the doped Fe improved the adsorption, activation and reduction of CO2 on the pure Cu(100) surface. From the perspective of thermodynamics and kinetics, the Fex/Cu(100) surface acted as a potential catalyst to decompose CO2 into CO with a barrier of 32.8 kJ mol⁻¹. Meanwhile, the first principle molecular dynamics (FPMD) analysis indicated that the decomposition of the C=O bond of CO2 on the Fex/Cu(100) surface was only observed from 350 K to 450 K under a CO2 partial pressure from 0 atm to 10 atm. Furthermore, the results of FPMD analysis revealed that CO2 would rather decompose than hydrogenate when CO2 and H co-adsorbed on the Fex/Cu(100) surface.

1. Introduction

Reducing the concentration of CO2 in the atmosphere has attracted significant attention, because as the major component of greenhouse gas, excessive emissions of CO2 have contributed significantly to environment degradation in the past decades, such as global warming, and melting of glaciers. The conversion of CO2 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.¹

Because CO2 is a thermodynamically stable molecule, it is difficult to utilize CO2 as the C resource.² Currently, five ways to reduce CO2 have been reported: (i) electrocatalytic reduction,³⁴ (ii) photocatalytic reduction,³⁵–³⁷ (iii) thermal catalytic reduction,³³–³⁵ (iv) enzymatic reduction³⁸,³⁹ and (v) photoelectrocatalytic reduction.⁴⁰ In these cases, the catalyst plays a major role in CO2 activity and reduction.

Numerous experiments and theories have been used to investigate the adsorption, activation and reduction of CO2 on transition metal–based catalysts.⁴¹–⁴⁷ For instance, Fierro systematically investigated the adsorption of CO2 on the Co(100), Co(110) and Co(111) surfaces.³⁹ The results indicated that the adsorption configuration of CO2 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 CO2 into CO and O2.²² Roberts demonstrated that CO2 could be decomposed into CO on the Ni(100) surface rather than on the Ni(111) surface.²³ Ding asserted that a weak interaction was formed between CO2 and the Ni(110) surface.²⁴ Glezakou investigated the mechanism of adsorption and activation of CO2 on the Fe fcc(100) surface.²⁵ Their results indicated that CO2 on the Fe(100) surface was activated spontaneously. Wilson investigated the reduction of CO2 into CO on Co(100), Ni(100) and Cu(100) surfaces.²⁶ 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 CO2 into CO.

Except for the single metal catalysts for CO2, Great effort has been devoted to improve the catalytic performance of bimetallic catalysts for CO2 activation and catalysis.⁴⁸–⁵⁰ Nerlov pointed out that the performance of Cu–Ni bimetallic catalyst was more than 60 times greater than the pure Cu.⁵¹–⁵⁴ Liu found that the introduction of Pd, Rh, Pt, and Ni metals on the Cu(111) surface promoted the methanol production.²² Our previous reports revealed that the introduction of a second metal could improve the interaction between CO2 and the Cu(100) surface.¹¹,²³ Additionally, the results also showed that the interaction between CO2 and the Cox/Cu(100) surface was structure sensitive for the reduction of CO2 molecules and the Cox/Cu(100) surface was the potential catalyst for the reduction of CO2. The
results of Song demonstrated that the properties of CO₂ conversion on Fe–Ni and Fe–Co catalysts were similar, and CO* and HCOO* were the preferred intermediates.35,36

On the basis of these reports, in this work the density functional theory calculations was employed to understand the activation and reduction of CO₂ 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.37 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.38 Firstly, the most stable structure of Fe₃/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 CO₂ over a series of Feₓ/Cu bimetallic surfaces were analyzed. The activation energy barrier for the CO₂ reduction and the Brønsted (BEP) relationships between the kinetic parameters for CO₂ reduction on the Cu(100) surface were analyzed. The 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) (CO₂ adsorbed on the Feₓ/Cu(100) surface), namely,

\[ E_a = E_{TS} - E_{IS} \tag{2} \]

All the transition states were determined using the climbing image nudged elastic band (CI-NEB)39,40 and DIMER31,32 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 CO₂ molecule.31–35

2.3. Microkinetic model

The rate constants for CO₂ dissociation using the harmonic transition state theory46–50 was analyzed as shown in eqn (3):

\[ k = A \exp \left( - \frac{E_{act}}{RT} \right) \tag{3} \]

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:

\[ A = \sqrt{\frac{\pi \kappa^N}{\kappa^N - 1}} f_i^{TS} \tag{4} \]

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

The actual activation barrier (Eₐct), including the entropy (ATS), the zero point energy (ZPE) and enthalpy (∫C_p dT) corrections, was calculated as follows:

\[ E_{act} = E_a + \Delta ZPE - \Delta TS + \Delta \int C_p dT \tag{5} \]

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,57 respectively:

\[ ZPE = \frac{1}{2} \sum_i h f_i \tag{6} \]

\[ TS = k_b T \sum_i \ln \left( 1 - e^{\frac{h f_i}{k_b T}} \right) - \sum_i h f_i \left( \frac{1}{e^{\frac{h f_i}{k_b T}}} - 1 \right) - k_b T \tag{7} \]
\[ C_p dT = \sum_j b_j \left( \frac{1}{q_{j\ell}} - 1 \right) + k_b T \] (8)

where \( f_i \) was the vibrational frequency and \( i \) represents the different modes of vibration.

To calculate the relative concentrate \((\theta_{CO})\) of CO on the Fe–Cu bimetallic system, the steady state approximation was adopted in this work. The total amount of metal catalytic sites in the reaction was considered as a constant and the sum of the occupied \((\theta_s)\) and the free metal \((\theta_f)\) sites were defined as following eqn (9):^66

\[ \theta_{CO} + 2\theta_{CO} + \theta_f = 1 \] (9)

where \( \theta_{CO} \) was obtained by \( \theta_{CO} = K_{CO} \times P_{CO} \times \theta_s \) and \( K_{CO} = \exp \left( -\frac{E_{ads} - T\Delta S}{RT} \right) \).^61 The partial pressure \( (P_{CO}) \) of CO2 from 0 to 10 atm was set.

For the elementary reaction step \( CO_2 + k_4 CO + O \) (rate constants, \( K = \frac{k_4}{k_3} \)), according to the steady-state approximation, the equation was as follows:

\[
\frac{dCO}{dt} = k_4 \theta_{CO_2} - k_3 \theta_{CO} = 0
\] (10)

Thus,

\[ \theta_{CO} = \frac{1}{2 + \frac{1}{K} + \frac{1}{(K \times K_{CO} \times P_{CO})}} \] (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\(_x\)/Cu(100) as an example, four possible configurations for the Fe\(_x\)/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\(_x\)/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\(^{-1}\), 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 top-layer of Cu(100) surface, Cu Orange Fe green.
length was 2.014 Å (Fe$_4$/Cu(100)), 2.000 Å (Fe$_5$/Cu(100)), 1.987 Å (Fe$_6$/Cu(100)), 1.974 Å (Fe$_7$/Cu(100)), 1.961 Å (Fe$_8$/Cu(100)) and 1.965 Å (Fe$_9$/Cu(100)). Among these Fe–O$_2$ bonds, the distance of the Fe–O$_2$ bond for CO$_2$ on the Fe$_4$/Cu(100) was the longest, requiring the less energy barrier to decompose 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 Cu(100) surface could improve the bonding strength of CO$_2$ to the substrate. Compared with the adsorption energy of CO$_2$ on the pure Cu(100) ($E_{ads} = -72.4$ kJ mol$^{-1}$) and Fe fcc(100) ($E_{ads} = 139.8$ kJ mol$^{-1}$) surfaces, the binding strength of CO$_2$ on the
Table 1. Some optimized bond lengths (Å), O–C–O bond angle (degrees) and the calculated adsorption energies ($E_{ads}$, in kJ mol$^{-1}$) of CO$_2$ molecules on pure Fe(100), Cu(100) and different Fe$_x$/Cu(100) bimetallic surfaces

| System          | $d_{C-O1}$ | $d_{C-O2}$ | $\angle$O–C–O | $d_{Fe-C}$ | $d_{Fe-O1}$ | $d_{Cu-O2}$ | $d_{Fe-O2}$ | $E_{ads}$ |
|-----------------|------------|------------|---------------|------------|-------------|-------------|-------------|-----------|
| Fe$_1$/Cu(100) | 1.258      | 1.271      | 134.5         | 1.929      | 2.015       | 2.163       | —           | 84.5      |
| Fe$_2$/Cu(100) | 1.253      | 1.253      | 138.9         | 2.041 ($\times2$) $^b$ | 2.091 | —           | 2.092       | 115.9     |
| Fe$_3$/Cu(100) | 1.296      | 1.295      | 124.4         | 1.939      | 1.969       | —           | 1.971       | 135.3     |
| Fe$_4$/Cu(100) | 1.354      | 1.296      | 121.2         | 2.116/1.936 | 2.046/2.048 | 2.000       | 2.000       | 148.6     |
| Fe$_5$/Cu(100) | 1.351      | 1.299      | 121.2         | 2.160/2.050 | 2.048/2.050 | 2.000       | 2.000       | 150.8     |
| Fe$_6$/Cu(100) | 1.351      | 1.299      | 121.2         | 2.115/1.938 | 2.047/2.013 | 2.000       | 2.000       | 154.8     |
| Fe$_7$/Cu(100) | 1.361      | 1.300      | 118.3         | 2.167/1.924 | 2.028/2.009 | 2.000       | 2.000       | 150.8     |
| Fe$_8$/Cu(100) | 1.364      | 1.299      | 118.3         | 2.138/1.924 | 2.038/2.009 | 2.000       | 2.000       | 150.8     |
| Fe$_9$/Cu(100) | 1.364      | 1.299      | 118.3         | 2.157      | 2.098       | —           | —           | 72.4      |
| Fe$_{10}$/Cu(100)* | 1.322  | 1.220      | 128.4         | 2.190/1.950 | 2.040/2.080 | —           | 1.990       | 139.8     |

$^a$ The symbols O1 and O2 represent the two oxygen atoms of the CO$_2$ moiety (see Fig. 2). For the free CO$_2$ molecule, the optimized length of the C–O bond is 1.176 Å. $^b$ The number of bonds is shown in parentheses. $^c$ 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 CO$_2$ on Fe$_x$/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 Fe$_x$/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. As shown in Fig. 3(a), the value of the d-band center for the Fe$_2$/Cu(100) surface was in the range of 2.0 to 2.091 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 Fe atoms on the Cu(100) surface was calculated and shown in Fig. S3–S10.$^c$ Taking CO$_2$ on the Fe$_x$/Cu(100) surface as an example, Fig. 5(a) represents the charge density map of CO$_2$ adsorbed on the Fe$_x$/Cu(100) surface (the x-axis represents the distance from the bottom to the top of the Fe$_x$/Cu(100) system). Five high-density states orbitals of the doped Fe atoms. Furthermore, the calculated density of states (DOS) in Fig. 4 confirmed that, after CO$_2$ adsorption on Fe$_x$/Cu(100) surface, CO$_2$ tended to interact with the $\beta$-states of the substrates.

3.2.2. Bader charge analysis. As mentioned, the CO$_2$ on the substrate exhibited the bent structure, indicating that some electrons were transferred to CO$_2$ from substrate. To verify this conclusion more clearly, the charge density of CO$_2$ on the Fe$_x$/Cu(100) surface was calculated and shown in Fig. S3–S10.$^c$ Taking CO$_2$ on the Fe$_x$/Cu(100) surface as an example, Fig. 5(a) represents the charge density map of CO$_2$ adsorbed on the Fe$_x$/Cu(100) surface (the x-axis represents the distance from the bottom to the top of the Fe$_x$/Cu(100) system). Five high-density
peaks in Fig. 5(a) were observed and each peak represented the charge density of one atomic layer in the Fe₄/Cu(100) surface. Furthermore, a relatively small density peak was observed at ~9.0 Å along the x-axis, which represented the charge density of the CO₂ moiety. It was noted that an obvious interaction between CO₂ and the Fe₄/Cu(100) surface was observed at z = 7–9 Å. The charge density difference map (Δρ) in Fig. 5(b) changed from lightly positive to negative upon crossing the Fe₄/Cu(100) interface (z = 7.0–8.0 Å) and reached a minimum at z = ~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 Fe₄/Cu(100) surface to the CO₂ moiety, forming the CO₂⁻ anions.

To quantify these charge transfers, the Bader charge analysis for all systems was calculated, as shown in Table 2. As expected, CO₂ obtained some electrons from the Fe₄/Cu(100) surfaces. In general, as the coverage increased for Fe atoms, the electrons obtained by CO₂ from the surface also increased. In particular, for the Fe₉/Cu(100) surface, the transferred electrons reached the maximum (1.17 e). The atomic charges for C and O atoms of CO₂ 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 CO₂ moiety on Fe₉/Cu(100) surfaces. If the coverage was less than 4/9 ML, the p-bond between C and O atoms was weakened slightly, especially the Fe₁/Cu(100). Although the coverage was more than 3/9 ML, Fig. 6(d)–(i) clearly showed that the degree of activation for the p-bond was quite similar and was more larger than CO₂ on the Fe₁₋₃/Cu(100) surface.

### 3.2.3. Vibrational frequencies analysis

According to the Bader charge analysis, after CO₂ adsorbed on the Fe₉/Cu(100) surface, some electrons were transferred from the substrate to CO₂ 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 presents the stretching vibration frequency of C–O₁ and C–O₂ bonds in CO₂ moiety on each of the Feₓ/Cu(100) surfaces. Compared with stretching vibration frequency of a free CO₂ molecule, the stretching vibration frequency of the C–O₁ and C–

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**Fig. 4** The density of states for the top layer metallic atoms in clean Feₓ/Cu(100) and CO₂/Feₓ/Cu(100) surfaces.
3.3. Decomposition of CO$_2$ on Fe$_x$/Cu(100) surfaces

3.3.1. Transition state analysis. The minimum potential energy map for the decomposition of CO$_2$ molecules on the Fe$_x$/Cu(100) surfaces was determined using the CI-NEB and DIMER methods and shown in Fig. 7 and S11.$^\dagger$ According to the Fe$_1$/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 Fe$_x$/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 CO$_2$ decomposition on the Fe$_x$/Cu(100) surface was calculated, as shown in Fig. 7 and S11.$^\dagger$ For the Fe$_1$/Cu(100) surface, the highest reaction energy was $-4.9$ kJ mol$^{-1}$, followed by the Fe$_3$/Cu(100) surface ($-36.1$ kJ mol$^{-1}$) and the Fe$_7$/Cu(100) surface ($-43.1$ kJ mol$^{-1}$). When the coverage of Fe atoms was more than 3/9 ML, the reaction energy could be significantly increased with $-65.0$ kJ mol$^{-1}$ for the Fe$_3$/Cu(100), $-62.3$ kJ mol$^{-1}$ for the Fe$_5$/Cu(100) surface, $-70.7$ kJ mol$^{-1}$ for the Fe$_7$/Cu(100) surface, $-121.0$ kJ mol$^{-1}$ for the Fe$_9$/Cu(100) surface, $-122.5$ kJ mol$^{-1}$ for the Fe$_{11}$/Cu(100) surface, and $-127.6$ kJ mol$^{-1}$ for the Fe$_{13}$/Cu(100) surface. It was noteworthy that the reaction energy of the Fe$_x$/Cu(100) surface increased with the coverage of the Fe atom increased on the Cu(100) surface, indicating that the introduced Fe atom improved the reaction energy of CO$_2$ decomposition. It may be reasonable

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

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

$^a$ The data origin from ref. 20.
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 CO₂ decomposition from Feₓ/Cu(100) to Fe₉/Cu(100) surfaces. From the thermodynamic point of view, the negative reaction energy indicated that the Feₓ/Cu(100) surface would be favorable to decompose CO₂ into CO, especially the Fe₉/Cu(100) surface. The activation energy barrier (Eₐ) of CO₂ decomposition on the Feₓ/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 (νᵢ) was also shown in Fig. 7 and S11.† For the Fe₁/Cu(100) surface, only one TS for the C–O₁ bond decomposition was discovered. The activation energy barrier (relative to the energy of the CO₂ adsorption) of CO₂ decomposed on the Fe₁/Cu(100) surface was 45.6 kJ mol⁻¹. For the Fe₂/Cu(100) and Fe₃/Cu(100) surfaces, the activation energy barrier increased to 59.9 kJ mol⁻¹ and 63.7 kJ mol⁻¹ compared with the Fe₁/Cu(100) surface, respectively. When the coverage reached 4/9 ML, the activation energy barrier reached the minimum value (32.8 kJ mol⁻¹). The transition state of CO₂ decomposition on the Feₓ/Cu(100) surface was extremely similar to the CO₂ on the Fe₄/Cu(100) surface when the coverage was greater than 4/9 ML. The corresponding activation energy barrier from the Fe₅/Cu(100) to Fe₉/Cu(100) systems was 35.4 kJ mol⁻¹, 39.7 kJ mol⁻¹, 34.7 kJ mol⁻¹, 40.2 kJ mol⁻¹ and 35.0 kJ mol⁻¹, respectively. The results showed that the activation energy barrier of all systems exhibited an inverted “S” shape, which was decomposed on the Fe₁/Cu(100) surface was 45.6 kJ mol⁻¹. For the Fe₂/Cu(100) and Fe₃/Cu(100) surfaces, the activation energy barrier increased to 59.9 kJ mol⁻¹ and 63.7 kJ mol⁻¹ compared with the Fe₁/Cu(100) surface, respectively. When the coverage reached 4/9 ML, the activation energy barrier reached the minimum value (32.8 kJ mol⁻¹). The transition state of CO₂ decomposition on the Feₓ/Cu(100) surface was extremely similar to the CO₂ on the Fe₄/Cu(100) surface when the coverage was greater than 4/9 ML. The corresponding activation energy barrier from the Fe₅/Cu(100) to Fe₉/Cu(100) systems was 35.4 kJ mol⁻¹, 39.7 kJ mol⁻¹, 34.7 kJ mol⁻¹, 40.2 kJ mol⁻¹ and 35.0 kJ mol⁻¹, respectively. The results showed that the activation energy barrier of all systems exhibited an inverted “S” shape, which was

| System       | ν₈-CO₁/cm⁻¹ | ν₈-CO₂/cm⁻¹ |
|--------------|-------------|-------------|
| Free CO₂     | 1333        | 1333        |
| Fe₁/Cu(100)  | 1122        | 1610        |
| Fe₂/Cu(100)  | 1152        | 1152        |
| Fe₃/Cu(100)  | 1117        | 1117        |
| Fe₄/Cu(100)  | 1017        | 1305        |
| Fe₅/Cu(100)  | 1019        | 1296        |
| Fe₆/Cu(100)  | 1025        | 1283        |
| Fe₇/Cu(100)  | 989         | 1279        |
| Fe₈/Cu(100)  | 993         | 1258        |
| Fe₉/Cu(100)  | 979         | 1261        |

* The data origin from NIST database: https://webbook.nist.gov/chemistry.

Fig. 6 Charge density difference of CO₂ on Feₓ/Cu(100) (x = 1–9) surface.

Fig. 7 Calculated reaction paths of CO₂ dissociation on the Fe₄/Cu(100) surface. The zero of energy is set to the total energy of the isolated surface and CO₂ 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 Fe4/Cu(100) surface was the largest among the Fex/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 CO2 decomposition on the Fex/Cu(100) surface was minimal. In addition, Fe dopant introduced on the Cu(100) surface significantly reduced the activation energy barrier of CO2 decomposition compared with the barrier of CO2 on the pure Cu(100) surface with the barrier of 92.9 kJ mol$^{-1}$ and the Fe(100) surface with the barrier of 113.4 kJ mol$^{-1}$, especially the Fe4/Cu(100) system. Compared to CO2 on the Cox/Cu(100) surface with the barrier of 18.7 kJ mol$^{-1}$, the activation energy barrier for CO2 on the Fex/Cu(100) is more than 14.1 kJ mol$^{-1}$. The main reason is that bond strength of Fe–O (in diatomic molecules: 390.4 kJ mol$^{-1}$) is stronger than that of Co–O (in diatomic molecules: 384.5 kJ mol$^{-1}$), which led to the extra barrier formed by Fe–O bond to overcome.

Moreover, the reaction energy barrier ($\Delta E_a = E_{RS} - E_{Slab} - E_{CO_2}$) 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: $\Delta E_a = 0.43\Delta E - 2.94$ (kJ mol$^{-1}$) (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 Fe4/Cu(100) surface did not have the lowest reaction energy barrier and total reaction energy, the Fe4/Cu(100) surface had the lowest activation energy barrier for CO2 decomposition, which facilitated the decomposition of CO2.

3.3.2. Micro kinetics analysis. To further explore the mechanism of CO2 decomposition on the Fex/Cu(100) surfaces from the perspective of dynamics, a microkinetic analysis based on the DFT studies was employed on the most favorable path of CO2 decomposition. 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 CO2 decomposition on the Fex/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 CO2 decomposition on the Fex/Cu(100) surfaces increased as the temperature increased. At the same temperature, the rate constants for CO2 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 CO2 decomposition was not only increased as the increase of temperature, but the forward rate constants in all Fex/Cu(100) surface were much larger than the inverse rate constants. In addition, the equilibrium constants ($K = k_{f}/k_{r}$) of CO2 decomposition on the Fex/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 (Fe1/Cu system), G2 (Fe2/Cu and Fe3/Cu systems), G3 (Fe4/Cu, Fe5/Cu and Fe6/Cu systems), G4 (Fe7/Cu, Fe8/Cu and Fe9/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 CO2 molecule and the K of CO2 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 invers rate constants, it was unfavorable to the increase of the equilibrium constants. From
3.3.3. Effects of partial pressure of CO$_2$. Fig. 11 illustrated the impact of partial pressure of CO$_2$ towards the decomposition of CO$_2$. The results in Fig. 11(a) showed that the decomposition of 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 CO$_2$ at the low partial pressure of CO$_2$, the partial pressure of 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 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 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 CO$_2$ in the atmosphere is less than 0.03%). Therefore, when the temperature was greater than 350 K, CO$_2$ could be decomposed into CO on Fe$_4$/Cu(100) surface under the normal partial pressure of CO$_2$ in the atmosphere.

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

Fig. 12  The structures of initial structure (IS), translation structure (TS) and final structure (FS) for CO$_2$ hydrogenation to HCOO$^*$ on the Fe$_4$/Cu(100) surface.
3.4. Hydrogenation of CO₂ on Fe₄/Cu(100) surface

The mechanism of CO₂ hydrogenation on the Fe₄/Cu(100) surface was also examined in this section. There were three reaction pathways for CO₂ 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 CO₂ moiety is more favorable than that of the O atom.¹⁶⁻¹⁸ Thus, the C atom hydrogenation was considered as an important reaction pathway while CO₂ moiety was dissociated. The initial structure (IS), translation 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 translation structure had been confirmed by the single imaginary frequency with 686 cm⁻¹. It was worth noted that the calculated activation energy barrier of CO₂ hydrogenation to HCOO* was 31.8 kJ mol⁻¹, which was less than that of decomposition for CO₂ on the Fe₄/Cu(100) surface. Such the small difference suggests that CO₂ hydrogenation could also be performed during the CO₂ decomposition. To understand the relationship between hydrogenation and dissociation of CO₂, the FPMD was carried to the system with CO₂ and H co-adsorption on Fe₄/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 CO₂ would rather decompose than hydrogenate at 400 K.

4. Conclusions

The adsorption, activation and reduction of CO₂ molecule on the Fe₄/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 CO₂ molecule on the Cu(100) surface. The most stable structure for CO₂ on the Fe₄/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 CO₂ molecule interacted with the β-state orbitals of the Fe₄/Cu(100) surface. After CO₂ adsorption, some electrons were transferred from substrate to CO₂ moiety and the electrons transferred to CO₂ moiety increased with the coverage of Fe atoms increased, leading to formation of CO₂ anion. Additionally, the mechanism of CO₂ moiety decomposition on Fe₄/Cu(100) surfaces had been studied in detail. The results indicated that the activation energy barrier (Eₘₐₓ = 32.8 kJ mol⁻¹) of CO₂ decomposition on Fe₄/Cu(100) was the smallest among the Fe₄/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 CO₂ decomposition. From the viewer of kinetic, the rate constants of CO₂ on Fe₄/Cu(100) surface were close to that of the Fe₄/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 (Fe₄/Cu) > G₂ (Fe₄/Cu and Fe₄/Cu) > G₃ (Fe₄/Cu, Fe₄/Cu and Fe₄/Cu) > G₄ (Fe₄/Cu, Fe₄/Cu and Fe₄/Cu). Furthermore, our results confirmed that the lower the temperature, the more favorable it was to decompose the CO₂ molecule into CO. When the simulated temperature was in range from 350 K to 450 K, the decomposition of C–O₁ bond in CO₂ moiety was only observed. The results of partial pressure for CO₂ revealed that when the temperature was in range from 350 K to 450 K, the concentration of CO on the Fe₄/Cu(100) surface reached 49% under the partial pressure of 3 × 10⁻⁴ atm. Lastly, the mechanism of CO₂ hydrogenation on the Fe₄/Cu(100) surface was also investigated. The activation energy barrier of 31.8 kJ mol⁻¹ was slightly less than that of CO₂ decomposition. However, the results of the FPMD analysis revealed that CO₂ was decomposed to form CO*, instead of hydrogenated. Our results provide insight into the mechanism for CO₂ 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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