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HCOOH dissociation over the Pd-decorated Cu bimetallic catalyst: The role of the Pd ensemble in determining the selectivity and activity



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Pd-decorated Cu bimetallic catalysts experimentally exhibited better catalytic performance toward hydrogenation reaction than the single Pd or Cu catalyst. This study is expected to identify the role of the Pd ensemble in determining the activity and selectivity, thus, HCOOH dissociation over the Pd-decorated Cu catalysts with different surface Pd distribution is fully examined by employing density functional theory calculations, including Pd₁Cu₈, Pd₃Cu₆, Pd₆Cu₃ and Pd₉Cu₀ catalysts, which are compared to the single Pd and Cu catalysts. The results found the Pd ensemble on the Pd₆Cu₃ and Pd₉Cu₀ surfaces with the Pd/Cu ratio of 6/3 and 9/0 exhibit higher selectivity and activity toward CO₂ formation via the COOH intermediate, especially, Pd₆Cu₃ is superior to the single Pd; whereas the isolated Pd atom on the Pd₁Cu₈ and Pd₃Cu₆ surfaces with the Pd/Cu ratio of 1/8 and 3/6dominantly produce CO via the COOH intermediate. Further, the structural and electronic properties reveal the role of the Pd ensemble in determining the catalytic performance of HCOOH dissociation. Our results provide a valuable clue and evaluation method in designing low-cost catalyst with the noble metal-decorated the nonnoble metal catalysts, which can exhibit better catalytic performance by forming the surface ensemble of the noble metal.

1. Introduction

Direct formic acid fuel cells (DFAFCs) have been considered to be a promising power generates device based on its high electromotive force, mild operating conditions and easy storing compared to methanol fuel cell [1–3]. The anode catalyst is a key material of the DFAFCs, which determines the power generation efficiency and stability of the battery. Thus, an excellent anode catalyst is a key factor in the commercial application of the DFAFCs. Generally, the Pd-based and Pt-based catalysts acted as the anode catalysts have been extensively applied in the dissociation of formic acid (HCOOH) [4–6], which follows the so-called dual routes [1,5–7]:

Direct route I: HCOOH \rightarrow CO₂ + 2H⁺ + 2e⁻

Indirect route II: HCOOH \rightarrow CO_{ad} + 2H₂O

Direct route I is the dehydrogenation of OH group in HCOOH to produce the HCOO intermediate, then, HCOO dehydrogenation to form CO_2 . In contrast, the indirect route II is the dehydrogenation of HCOOH to produce the COOH intermediate, followed by its C-OH bond cracking to produce CO; alternatively, the dehydrogenation of COOH intermediate can also product CO2. Hence, enhancing the reactivity of HCOOH dehydrogenation and inhibiting CO formation are necessary for the optimization of the anode catalysts in HCOOH dissociation. The used catalyst and the applied electrode potential determine the preferences between the direct or indirect routes [1-5]. Due to the higher activity toward HCOOH dissociation on the Pd-based catalysts compared to that on the Pt-based catalysts [3,8,9], Pd-based catalysts are widely employed as the promising candidates to utilize the hydrogen of HCOOH [8,9]. It has been reported that Pd-based bimetallic catalysts, such as CuPd [10-12], AgPd [13,14], SnPd [15], AuPd [5,16], and so on, have a good catalytic activity toward HCOOH dissociation into CO₂ and inhibit CO poisoning, among them, the metal Cu promoter has been widely used and exhibits better catalytic performance, for example, He and coworkers [10] found that Cu₁@Pd₃(1 1 1) is in favor of HCOOH dissociation to form CO2 through the trans-COOH intermediate compared to CO formation. Lu et al. [12] found that for HCOOH dissociation over the carbon supported Pd-Cu catalysts, when Cu content increased, the reaction rate decreased, which reduced the production of CO. Further, when Cu is used as a base composition with other precious metal as the promoter, the catalyst also has good catalytic performance in other reactions [17-20], for example, the promoter Rh-decorated Cu

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Received 15 October 2019; Received in revised form 6 January 2020; Accepted 27 January 2020 Available online 29 January 2020 0169-4332/ © 2020 Published by Elsevier B.V. (1 1 1) surface presents higher activity toward CH₄ dissociation than the single Cu(1 1 1) surface does [18]. The density functional theory (DFT) studies by Cao and co-workers [19] concluded that the promoter Pd-decorated Cu(1 1 1) surface obviously improve the activity of propane dehydrogenation than the single Cu surface does. Based on the above reported studies [18,19], the Cu catalysts decorated with the promoter are in favor of the dehydrogenation reactions. Recently, theoretical studies about HCOOH dissociation over the Cu(1 1 1) surface [21] showed that CO is the main product. Whether the promoter Pd-decorated Cu-based bimetallic catalyst can be also applied to highlyactive and highly-selective catalyze HCOOH dissociation leading to CO₂ formation, yet, up to now, the mechanism of HCOOH dissociation on the promoter Pd-decorated Cu bimetallic catalyst is still unclear.

For the noble metal promoter decorated-non-noble metal catalysts, the arrangement of the noble metal promoter significantly alter its catalytic activity and selectivity toward the targeted reaction, which are attributed to the ensemble effect of the noble metal over the bimetallic catalyst surface [5,22-25]. Such as, Yuan and colleagues [5] found that the ensemble of Pd atoms over the Pd-decorated Au(1 1 1) surface can efficiently inhibit CO production in HCOOH dissociation. Duan and coworkers [25] found that the catalytic performance of HCOOH dissociation over three types of Pt-decorated Au(1 1 1) surfaces depended on the surface Pt ensemble. Lee et al. [22] experimentally and theoretically shows that the Pd-decorated PdAu alloy with the surface Pd ensemble exhibited the excellent catalytic activity toward HCOOH dehydrogenation. As mentioned above, the catalysts with different surface arrangements (ensembles) significantly affect its catalytic performance toward the dehydrogenation reaction. At present, the PdCu bimetallic catalysts successfully prepared in various experimental methods have performed the excellent catalytic performance for HCOOH dissociation [12,24,26], however, few studies are mentioned to explore the role of the Pd ensemble over the PdCu surfaces in determining the activity and selectivity of HCOOH dissociation.

In this study, aiming at solving above mentioned issues, different mechanisms of HCOOH dissociation on the Pd-decorated Cu catalysts with different surface Pd/Cu ratios are fully examined based on DFT calculations. Here, four types of Pd-decorated Cu surfaces, Pd_1Cu_8 , Pd_3Cu_6 , Pd_6Cu_3 and Pd_9Cu_0 , are considered to reflect the Pd ensemble effect. It is expected to give out the valuable clue for regulating the catalytic performance of the low-cost catalyst consisted of a small quantity of the noble metal and a large quantity of non-noble metal in the fuel cell.

2. Computational details

2.1. Calculation methods

All DFT calculations are implemented in the Dmol³ program package [27,28]. The ion and electrons are carried out with the projector augmented wave (PAW) method [29], the generalized-gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional [30,31] is used to describe the exchange–correlation effects, which can obtain the reliable results for the dissociation of small molecules on metal catalyst surfaces [32,33]. The integrations of the Brillouin zone are described using a $2 \times 2 \times 1$ *k*-point grid. The valence electron is expanded using the DNP function [34]. DFT-D2 functional is examined to consider the effect of van der Waals interaction. Since HCOOH dissociation often takes place at the room temperature [10,24,26,35–38], all energies are calculated at 298 K.

Aiming at obtaining the transition states (TSs) of the elementary reaction, the (LST/QST) approach is employed [39]. Moreover, the vibrational frequency with the only one imaginary frequency and TS Confirmation with the transition state connected with the reactants and products are carried out to verify the transition state.

For a elementary reaction such as $A \rightarrow B$ over the Pd-decorated Cu (1 1 1) catalyst, considering the contribution of the entropy, the

calculation formulas of the energy barrier (G_a) and reaction energy (ΔG) are as follows:

$$G_{a} = E_{TS} - E_{IS} + G_{TS} - G_{IS}$$
$$\Delta G = E_{FS} - E_{IS} + G_{FS} - G_{IS}$$

where E_{1S} , E_{FS} , and E_{TS} are the total energies of initial state (IS), final state (FS), and transition state (TS) of the elementary reaction, respectively. G_{IS} , G_{FS} , and G_{TS} are the corresponding Gibbs free energies. The formula for calculating the adsorption free energy (G_{ads}) is as

follows:

$$G_{ads} = E_{adsorbate/substrate} - E_{substrate} - E_{absorbate} + \Delta G_{ads}$$

$$\Delta G_{ads} = G_{adsorbate/substrate} - G_{substrate} - G_{absorbate}$$

where $E_{\text{substrate}}$, $E_{\text{adsorbate}}$ and $E_{\text{adsorbate/substrate}}$ correspond to the total energies of the substrate surface, the free adsorbate and the stable adsorption configuration consisted of the substrate surface with the adsorbate; $G_{\text{substrate}}$, $G_{\text{adsorbate}}$ and $G_{\text{adsorbate/substrate}}$ are the corresponding Gibbs free energies. The more negative the value G_{ads} is, the stronger the interaction between the adsorbed species and the surface is.

2.2. Surface models

It is well-known that the $(1\ 1\ 1)$ surface is mainly exposed among all exposed crystal facets of Cu catalyst and is also the most stable, which has been widely employed to model Cu catalyst [21,40–45]. The *p* (3 × 3) super cell with four-layer and the vacuum thickness of 15 Å is employed to present the Cu(1 1 1) surface.

For the Pd-decorated Cu bimetallic catalysts, aiming at identifying the effect of the surface Pd ensemble on HCOOH dissociation, the Pddecorated Cu bimetallic catalysts are modeled with different surface Pd: Cu atomic ratios over Cu(1 1 1) surface, in which the surface Cu atoms are substituted by the Pd atoms. Since previous experiment about the Pd-decorated Cu bimetallic catalyst has excluded its pattern with the nearest-neighbor arrangement [46], four types of Pd-decorated Cu (1 1 1) surfaces (Fig. 1) are examined. The one, three, six and nine surface Cu atoms on the Cu(1 1 1) is replaced by the corresponding numbers of Pd atoms to model different forms of Pd ensemble over the Pd-decorated Cu(1 1 1) surface, they are denoted as Pd₁Cu₈, Pd₃Cu₆, Pd₆Cu₃ and Pd₉Cu₀ surfaces, respectively. For the first two surfaces, the surface Pd atoms exist in the form of the isolated single atom; for the Pd₆Cu₃ and Pd₉Cu₀ surfaces, the surface Pd atoms present the ensemble form. Further, for four types of Pd-decorated Cu(1 1 1) surfaces, the absorbed species with the outmost two layers of the slab model are relaxed, other layers are fixed in the calculations.

3. Results and discussion

3.1. Adsorption and structure of the key species

All adsorption sites over the Pd-decorated Cu(1 1 1) surfaces are considered for the adsorption of key species in HCOOH dissociation, accordingly, the most stable configurations are shown in Fig. 2. Table 1 shows the preferential adsorption sites and adsorption free energies at 298 K.

3.1.1. Formic acid (HCOOH) adsorption

Experiment shows that two isomers, *trans*- and *cis*-, exist for HCOOH species [47]. The calculation results suggest that the gas phase *trans*-HCOOH has the lower total energy than the gas phase *cis*-HCOOH; moreover, the *trans*-HCOOH species has the stronger interaction with the Pd₁Cu₈, Pd₃Cu₆, Pd₆Cu₃ and Pd₉Cu₀ surfaces (-46.2, -33.8, -47.4 and -59.6 kJ·mol⁻¹) compared to the *cis*-HCOOH species (-18.4, -20.0, -34.6 and -36.1 kJ·mol⁻¹). For these surfaces, *trans*-HCOOH is preferably located at the top isolated Pd site with the carbonyl oxygen and the O-H bond points to the surface, which agree with the reported



Fig. 1. The surface morphology and the corresponding adsorption sites of the Pd₁Cu₈, Pd₃Cu₆, Pd₆Cu₃ and Pd₉Cu₀, respectively.

results for the adsorption energy and geometrical configurations of HCOOH on the Pd(1 1 1), Cu(1 1 1), Ni(1 1 1), Pt(1 1 1) and PdAu (1 1 1) surfaces [2,5,21,48]. Therefore, *trans*-HCOOH is employed to act as the initial reactant of HCOOH dissociation.

3.1.2. Formate (HCOO) adsorption

Extensive experiments confirmed the presence of HCOO species in HCOOH dissociation via the direct route [49-51]. HCOO has also two adsorption modes: bi-HCOO and mono-HCOO, the former is two O atoms of HCOO binding with the catalyst surface; the latter is one O atom of HCOO interacting with the catalyst surface. Our results found that the mono-HCOO species preferably interact with the top isolated Pd atom corresponding the stability order to of $Pd_1Cu_8 > Pd_3Cu_6 \approx Pd_6Cu_3 > Pd_9Cu_0$ (-160.3, -148.5, -149.1 and $-129.4 \text{ kJ} \cdot \text{mol}^{-1}$). The *bi*-HCOO species preferably interact with the Pd-Cu bridge site over the Pd_1Cu_8 and Pd_3Cu_6 surfaces (-244.8 and $-233.3 \text{ kJ} \cdot \text{mol}^{-1}$); while it prefers to interact with the Pd-Pd bridge site over the Pd_6Cu_3 and Pd_9Cu_0 surfaces (-208.9 and $-197.3 \text{ kJ}\cdot\text{mol}^{-1}$); the *bi*-HCOO species follows the stability order of $Pd_1Cu_8 > Pd_3Cu_6 > Pd_6Cu_3 > Pd_9Cu_0$. Hence, the stability of HCOO adsorption is closely related to surface Pd distribution; moreover, the *bi*-HCOO species has the stronger interaction with the Pd-decorated Cu surface than the *mono*-HCOO species.

3.1.3. Carboxyl (COOH) adsorption

The calculated results indicate that the gas phase *trans*-COOH has the lower total energy than the gas phase *cis*-COOH, so *trans*-COOH is selected as the key intermediate in the CO route of HCOOH dissociation. Meanwhile, *trans*-COOH species through the C atom prefers to interact with the top isolated Pd atom, which correspond to the adsorption free energies of -192.2, -192.2, -193.9 and -207.2 kJ·mol⁻¹ over the Pd₁Cu₈, Pd₃Cu₆, Pd₆Cu₃ and Pd₉Cu₀, respectively, suggesting that the surface Pd ensemble is more favorable for *trans*-COOH species adsorption.



Fig. 2. The most stable adsorption configurations of the intermediates involving in HCOOH dissociation over the (a) Pd_1Cu_8 , (b) Pd_3Cu_6 , (c) Pd_6Cu_3 , and (d) Pd_9Cu_0 surfaces. The Pd, Cu, C, H and O atoms are shown in the blue, orange, gray, white and red balls, respectively. Bond length is in Å. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.1.4. CO, CO₂, OH and H adsorption

CO is inclined to interact with the top isolated Pd atom over the Pd_1Cu_8 and Pd_3Cu_6 surfaces, whereas it interacts with the Pd-Pd bridge site and the hcp site over the Pd_6Cu_3 and Pd_9Cu_0 surfaces, respectively. The corresponding adsorption free energies are -109.2, 105.0, -119.0

and $-161.4 \text{ kJ}\cdot\text{mol}^{-1}$. Compared to that (-197.9 kJ·mol⁻¹) on Pd (1 1 1) surface [2], the Pd-decorated Cu(1 1 1) surface reduces the adsorption energy of CO, which is conducive to slow down CO poisoning.

For CO₂, CO₂ moves away from the surface of the catalysts, this is



typically weaker physisorption. Meanwhile, the angle of O-C-O and the C-O bond length are similar to those of gaseous CO_2 . The adsorption free energies are -26.6, -22.8, -30.3 and -34.9 kJ·mol⁻¹ over the Pd₁Cu₈, Pd₃Cu₆, Pd₆Cu₃ and Pd₉Cu₀, respectively.

For OH, the fcc1 site consisted of Cu atom, the fcc site consisted of Cu and Pd atoms, the Pd-Cu bridge site and the Pd-Pd bridge site are the stable adsorption sites corresponding to the Pd_1Cu_8 , Pd_3Cu_6 , Pd_6Cu_3 and Pd_9Cu_0 , respectively, accordingly, the adsorption free energies are -261.6, -229.1, -211.6 and -216.6 kJ·mol⁻¹.

For H, the 3-fold hollow sites (including hcp and fcc) are favored with the corresponding adsorption free energies of -241.8, -239.4, -239.9 and -243.2 kJ·mol⁻¹ over the Pd₁Cu₈, Pd₃Cu₆, Pd₆Cu₃ and Pd₉Cu₀ surfaces, respectively.

As presented in Scheme 1, the direct route involves the HCOO intermediate to generate CO_2 through the successive dehydrogenation; the indirect route features the COOH intermediate to produce CO through the C-O bond cracking; alternatively, the dehydrogenation of COOH can also produce CO_2 [52–54]. The *trans*-HCOOH species with the most stable configuration adsorbed over four Pd-decorated Cu (1 1 1) surfaces are used as the initial reactant for HCOOH dissociation. Table 2 lists the activation energy barrier together with reaction energy of every elementary reaction involved in HCOOH dissociation.

3.2. HCOOH dissociation over different Pd-decorated Cu(1 1 1) surfaces

Table 1

Adsorption sites and adsorption free energies ($G_{ads}/kJ \cdot mol^{-1}$) at 298 K for the most stable configurations of the adsorbed species involved in HCOOH dissociation on the Pd₁Cu₈, Pd₃Cu₆, Pd₆Cu₃ and Pd₉Cu₀ surfaces.

| Species | Pd ₁ Cu ₈ | Pd ₁ Cu ₈ | | Pd ₃ Cu ₆ | | Pd ₆ Cu ₃ | | Pd ₉ Cu ₀ | |
|-------------|---------------------------------|---------------------------------|--------------|---------------------------------|--------------|---------------------------------|--------------|---------------------------------|--|
| | sites | $G_{\rm ads}$ | sites | G _{ads} | sites | $G_{\rm ads}$ | sites | $G_{ m ads}$ | |
| trans-HCOOH | top-Pd | -46.2 | top-Pd | -33.8 | top-Pd | -47.4 | top-Pd | - 59.6 | |
| cis-HCOOH | top-Pd | -18.4 | top-Pd | -20.0 | top-Pd | -34.6 | top-Pd | -36.1 | |
| bi-HCOO | Pd-Cu bridge | -244.8 | Pd-Cu bridge | -233.3 | Pd-Pd bridge | -208.9 | Pd-Pd bridge | -197.3 | |
| mono-HCOO | top-Pd | -160.3 | top-Pd | -148.5 | top-Pd | -149.1 | top-Pd | -129.4 | |
| trans-COOH | top-Pd | -192.2 | top-Pd | -192.2 | top-Pd | -193.9 | top-Pd | -207.2 | |
| CO_2 | _ | -26.6 | _ | -22.8 | _ | -30.3 | _ | -34.9 | |
| CO | top-Pd | -109.2 | top-Pd | -105.0 | Pd-Pd bridge | -119.0 | hcp | -161.4 | |
| OH | fcc-Cu | -261.6 | fcc | -229.1 | Pd-Cu bridge | -211.6 | Pd-Pd bridge | -216.6 | |
| Н | hcp | -241.8 | fcc | -239.4 | fcc | -239.9 | hcp | -243.2 | |



Scheme 1. Proposed reaction mechanism of HCOOH dissociation on the Pd_1Cu_8 , Pd_3Cu_6 , Pd_6Cu_3 and Pd_9Cu_0 surfaces.

3.2.1. HCOOH dissociation through the HCOO intermediate

(1) The O-H bond cracking of HCOOH (HCOOH \rightarrow HCOO + H)

Along the route I, see Figs. 3-6, beginning with the trans-HCOOH species, its O-H bond cleavage through the transition state TSx-1(x = 1-4) have the energy barriers of 73.6, 66.7, 93.7 and 112.0 kJ·mol⁻¹ on the Pd₁Cu₈, Pd₃Cu₆, Pd₆Cu₃ and Pd₉Cu₀, respectively. Meanwhile, this elementary step is endothermic by 5.2, 30.4, 36.5 and 53.2 kJ·mol⁻¹, respectively. The energy barriers (93.7 and 112.0 kJ·mol⁻¹) on the Pd₆Cu₃ and Pd₉Cu₀ surfaces are close to that $(96.5 \text{ kJ} \cdot \text{mol}^{-1})$ on the Pd $(1 \ 1 \ 1) \ [2]$, indicating that the presence of the Pd ensemble over the Pd(1 1 1), Pd₆Cu₃ and Pd₉Cu₀ surfaces are not conducive to the dehydrogenation of OH group in HCOOH to HCOO. Further, the HCOO species on the Pd_1Cu_8 and Pd_3Cu_6 surfaces prefer to interact with the top isolated Pd atom in the TS1-1 and TS2-1, whereas the Pd₆Cu₃ and Pd₉Cu₀ surfaces with the Pd ensemble are not in favor of HCOO adsorption in the TS3-1 and TS4-1. Finally, the HCOO species is located at the Pd-Cu or Pd-Pd bridge sites. In addition, the Pd ensemble over the Pd-decorated Au(1 1 1) [5] is also more conducive to the dehydrogenation of OH group in HCOOH, which is opposite to that over the Pd-decorated Cu(1 1 1) in this study, indicating that the Pd ensemble effect is closely related to its connected metal type.

(2) The C-H bond cracking of HCOO (HCOO \rightarrow CO₂ + H)

Starting from the *bi*-HCOO species, it firstly goes through the TSx- $2(x = 1 \sim 4)$ to generate the *mono*-HCOO intermediate, which is a metastable state [2,48,49]; then, *mono*-HCOO dehydrogenation through the TSx- $3(x = 1 \sim 4)$ to generate CO₂ and H. In the product, CO₂ goes away from the Pd-decorated Cu surfaces, whereas the H atom is located at the 3-fold site.

bi-HCOO conversion to mono-HCOO requires the energy barriers of 99.7, 101.8, 81.9 and 80.8 kJ·mol⁻¹ on the Pd₁Cu₈, Pd₃Cu₆, Pd₆Cu₃ and Pd₉Cu₀ surfaces, the corresponding reaction energies are 84.4, 84.7. 61.2 and 69.4 kJ mol⁻¹, respectively. This step is disadvantageous in dynamics, which is similar to our previous work on PtAu catalysts [25]. This explains why only surface HCOO intermediates were observed on Pd and Pt catalyst [55,56]. Subsequently, the formation of CO₂ and H species by mono-HCOO dehydrogenation has quite low energy barriers of 18.2, 10.2, 1.9 and 12.2 kJ·mol⁻¹ with the reaction energies of -80.9, -94.8, -99.5 and -119.7 kJ·mol⁻¹, respectively. Thus, bi-HCOO dehydrogenation to form CO2 corresponds to the overall energy barriers of 102.6, 101.8, 81.9 and 80.8 kJ·mol⁻¹ with the reaction energies of 3.5, -10.1, -38.3 and -50.3 kJ·mol⁻¹ over four Pd-decorated Cu(1 1 1). Additionally, bi-HCOO \rightarrow CO₂ + H on the Pd(1 1 1) surface [2] corresponds to the overall energy barrier of 84.9 kJ·mol⁻¹, which is in line with our results on the Pd₆Cu₃ and Pd_9Cu_0 surfaces. However, that is 167.8 kJ·mol⁻¹ on the Cu(1 1 1) [21]. Above results show that the Pd-decorated Cu(1 1 1) and the single Pd(1 1 1) surfaces can enhance the catalytic activity of CO₂ generation compared to the single Cu(1 1 1) surface, especially, the Pd₆Cu₃ and Pd₉Cu₀ surfaces with the Pd ensemble. That is to say, the catalytic reactivity of HCOO dehydrogenation to produce CO2 over the Pd-decorated Cu(1 1 1) is closely related to the surface distribution of Pd atoms.

Table 2

All possible elementary reactions corresponding to the activation barriers ($G_a/kJ \cdot mol^{-1}$) and reaction energies ($\Delta G/kJ \cdot mol^{-1}$) in HCOOH dissociation on the Pd₁Cu₈, Pd₉Cu₆, Pd₉Cu₆, Pd₉Cu₀ and Pd(1 1 1) surfaces at 298 K.

| Elementary reactions | | Pd ₁ Cu ₈ | Pd ₃ Cu ₆ | Pd ₆ Cu ₃ | Pd ₉ Cu ₀ | Pd(1 1 1) [2] |
|--|------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------|
| trans-HCOOH \rightarrow bi-HCOO + H | G_{a} | 73.6 | 66.7 | 93.7 | 112.0 | 96.5 |
| | $\triangle G$ | 5.2 | 30.4 | 36.5 | 53.2 | 2.6 |
| bi -HCOO \rightarrow mono-HCOO | G_{a} | 99.7 | 101.8 | 81.9 | 80.8 | 84.9 |
| | $\triangle G$ | 84.4 | 84.7 | 61.2 | 69.4 | 61.6 |
| $mono-HCOO \rightarrow CO_2 + H$ | G_{a} | 18.2 | 10.2 | 1.9 | 12.2 | 16.1 |
| | $\triangle G$ | -80.9 | -94.8 | - 99.5 | -119.7 | - 89.1 |
| trans-HCOOH \rightarrow cis-HCOOH | G_{a} | 72.4 | 65.5 | 82.6 | 84.2 | 70.9 |
| | G | 44.4 | 30.5 | 29.5 | 41.9 | 29.4 |
| cis -HCOOH \rightarrow trans-COOH + H | G_{a} | 40.6 | 56.2 | 51.2 | 50.1 | 81.0 |
| | $\triangle G$ | -17.1 | -7.5 | -11.7 | -28.4 | -43.8 |
| trans-COOH \rightarrow CO ₂ + H | G_{a} | 107.2 | 111.9 | 71.8 | 73.0 | 105.1 |
| | G | -26.0 | -28.8 | -36.1 | -21.2 | -21.7 |
| trans-COOH \rightarrow CO + OH | G_{a} | 58.1 | 60.7 | 147.6 | 141.6 | 194.1 |
| | $\triangle G$ | -42.0 | -1.2 | -1.6 | -12.2 | -0.8 |



Fig. 3. Potential energy profiles for HCOOH dissociation via the (a) HCOO intermediate, (b) *trans*-COOH intermediate together with the partial structures of the initial states, transition states (TSs) and final states over the Pd_1Cu_8 surface. See Fig. 2 for color coding.

3.2.2. HCOOH dissociation through the COOH intermediate

(1) The C-H bond cracking of HCOOH (HCOOH \rightarrow COOH + H)

Along the route II, see Figs. 3–6, *trans*-HCOOH is firstly isomerized to *cis*-HCOOH through the TSx-4(x = 1-4), accordingly, the activation energy barriers are 72.4, 65.5, 82.6 and 84.2 kJ·mol⁻¹ on the Pd₁Cu₈, Pd₃Cu₆, Pd₆Cu₃ and Pd₉Cu₀ surfaces, respectively. The adsorption of *cis*-HCOOH is unstable compared to that of *trans*-HCOOH; however, the dehydrogenation of *cis*-HCOOH species is favored due to the C-H bond pointing toward the catalyst surface [2,11]. Hence, *cis*-HCOOH is easily dehydrogenated to produce the *trans*-COOH and H species through the TSx-5(x = 1-4) on the Pd-decorated Cu(1 1 1) surfaces. The overall energy barriers of *trans*-HCOOH \rightarrow *trans*-COOH + H are 85.0, 86.7,

82.6 and 92.0 kJ·mol⁻¹ on the Pd₁Cu₈, Pd₃Cu₆, Pd₆Cu₃ and Pd₉Cu₀, respectively, indicating that the surface Pd distribution has negligible effect for the activity of *trans*-HCOOH \rightarrow *trans*-COOH + H. However, in comparison with the (1 1 1) surfaces of Pd (110.4 kJ·mol⁻¹) [2] and Cu catalysts (36.7 kJ·mol⁻¹) [21], the promoter Pd-decorated substrate Cu could tune the catalytic activity of this reaction.

(2) The O-H bond cracking of *trans*-COOH (COOH \rightarrow CO₂ + H)

trans-COOH dehydrogenation to CO₂ occurs via the TSx-6(x = 1–4), in which the O-H bond cracking is complete, the configuration of CO₂ is initially formed, which is consistent with the previous studies on the PdAu and PtAu [5,25]. The activation energy barriers of this step are 107.2, 111.9, 71.8 and 73.0 kJ·mol⁻¹ on the Pd₁Cu₈, Pd₃Cu₆, Pd₆Cu₃



Fig. 4. Potential energy profiles for HCOOH dissociation via the (a) HCOO intermediate, (b) *trans*-COOH intermediate together with the partial structures of the initial states, transition states (TSs) and final states over the Pd_3Cu_6 surface. See Fig. 2 for color coding.

and Pd₉Cu₀ surfaces, they are exothermic by 26.0, 28.8, 36.1 and 21.2 kJ·mol⁻¹, respectively. However, this reaction on the (1 1 1) surface of Pd [2] and Cu [21] catalysts are 105.1 and 169.8 kJ·mol⁻¹, respectively. Namely, the Pd-decorated Cu(1 1 1) surfaces increase the activity of CO₂ generation by COOH dehydrogenation compared to the Cu(1 1 1); moreover, the Pd ensemble on the Pd₆Cu₃ and Pd₉Cu₀ surfaces is much favored in kinetics for the formation of CO₂.

3.2.3. CO formed via the C-OH bond cracking of trans-COOH (COOH \rightarrow CO + OH)

The formation of CO may go through the HCOO and COOH species; for the former, the generation of CO firstly goes through the hydrogen migration of HCOO species to form COOH, followed by its dehydrogenation, however, our results show that the isomerization of HCOO to COOH is unfavorable in kinetics compared with the dehydrogenation of HCOO to produce CO_2 . Alternatively, CO generation from CHO species was studied on the Pd(1 1 1) surface [2], the (1 1 1), (1 0 0) and (2 1 1) surfaces of Au [52], as well as the Pt(1 1 1) and PtAg(1 1 1) surfaces [57], however, it is found that the CO formation through the COOH species was the most advantageous in kinetics rather than that through the CHO species.

Seen from Figs. 3–6, CO species can be produced from *trans*-COOH species via the TSx-7(x = 1–4) on the Pd₁Cu₈, Pd₃Cu₆, Pd₆Cu₃ and Pd₉Cu₀ surfaces, which have the corresponding activation energy



Fig. 5. Potential energy profiles for HCOOH dissociation via the (a) HCOO intermediate (b) *trans*-COOH intermediate together with the partial structures of the initial states, transition states (TSs) and final states over the Pd₆Cu₃ surface. See Fig. 2 for color coding.

barriers of 58.1, 60.7, 147.6 and 141.6 kJ·mol⁻¹, respectively. Besides, this reaction corresponds to the activation energy barriers of 194.1 and 169.8 kJ·mol⁻¹ over the (1 1 1) surface of Pd [2] and Cu [21] catalysts, respectively. Taking the formation of CO₂ species from *trans*-COOH into account, the activation energy barriers correspond to 107.2, 111.9, 71.8, 73.0, 105.1 and 169.8 kJ·mol⁻¹ over the Pd₁Cu₈, Pd₃Cu₆, Pd₆Cu₃, Pd₉Cu₀, Pd(1 1 1) [2] and Cu(1 1 1) [21], respectively. Thus, beginning with the *trans*-COOH species, the comparison of the activation energy barrier between CO₂ and CO formation suggested that the Pd₆Cu₃, Pd₉Cu₀ and Pd(1 1 1) [2] surfaces with the Pd ensemble are not conductive to the formation of CO. However, both Pd₁Cu₈ and Pd₃Cu₆ with the isolated surface Pd atom, as well as the Cu(1 1 1) surface without Pd atom are conducive to the formation of CO, which leads to the

poisoning and deactivation of the catalyst. Similarly, the Pd ensemble on the Pd-decorated $Zn(1\ 1\ 1)$ surface also has high CO₂ selectivity and CO resistance [1]. Therefore, it is concluded that the surface Pd ensemble on the Pd-decorated Cu(1 1 1) has a great influence on the activity of CO₂ or CO formation in HCOOH dissociation, in turn affects the product selectivity of HCOOH dissociation.

3.3. General discussion

3.3.1. The effect of the Pd ensemble on the optimal route of HCOOH dissociation

For CO formation, our results showed that CO is dominantly generated by the route of the COOH intermediate in HCOOH dissociation



Fig. 6. Potential energy profiles for HCOOH dissociation via the (a) HCOO intermediate (b) *trans*-COOH intermediate together with the partial structures of the initial states, transition states (TSs) and final states over the Pd_9Cu_0 surface. See Fig. 2 for color coding.

TS4-6

7.4

trans-COOH+H

over the Pd_1Cu_8 , Pd_3Cu_6 , Pd_6Cu_3 and Pd_9Cu_0 , accordingly, the energy barriers of the rate-determining step are 85.0, 86.7, 147.6 and 141.6 kJ·mol⁻¹, respectively.

TS4-5

For CO₂ formation, on the Pd₁Cu₈ and Pd₃Cu₆ surfaces, see Figs. 3 and 4, with respect to the *trans*-HCOOH species, CO₂ generation dominantly goes through the route via the HCOO intermediates instead of that via the COOH intermediate based on the rate-determining step (102.6 vs. 107.2, 101.8 vs. 111.9 kJ·mol⁻¹). However, on the Pd₆Cu₃ and Pd₉Cu₀ surfaces (Figs. 5 and 6), the optimal route of CO₂ formation goes through the COOH intermediate instead of the HCOO intermediate on the basis of the rate-determining step (82.6 vs. 93.7, 92.0 vs.

112.0 kJ·mol⁻¹).

TS4-7

Based on above results, comparing the energy barriers of the ratedetermining step between the optimal path of CO_2 and CO formation, both Pd_1Cu_8 and Pd_3Cu_6 catalysts with the surface isolated Pd atom is favorable for CO formation. However, both Pd_6Cu_3 and Pd_9Cu_0 catalysts with the surface Pd ensemble mainly produce CO_2 through the COOH species, and effectively inhibit CO formation. As a result, the surface Pd distribution over the Pd-decorated Cu(1 1 1) can change the optimal route of CO_2 formation and further alter the selectivity of products in HCOOH dissociation.

CO+OH



Fig. 7. Potential energy profiles for the optimal route of HCOOH dissociation to form CO₂ and CO over the (a) Cu(1 1 1) [21], (b) Pd₁Cu₈, (c) Pd₃Cu₆, (d) Pd₆Cu₃, (e) Pd₉Cu₀ and (f) Pd₁Cu₁ 1 1) [2] surfaces.

3.3.2. The effect of the Pd ensemble on the selectivity and activity

To quantify the effect of the Pd ensemble on the selectivity of CO_2 over four Pd-decorated Cu(1 1 1) surfaces, the difference of activation energy barrier for the rate-determining step between CO_2 and CO formation is used as a descriptor [54,58]. The corresponding results are compared with that on the (1 1 1) surfaces of the pure Pd [2] and Cu [21] catalysts. Thus, more negative difference signifies more favorable formation of CO_2 and the lower CO production.

See the Fig. 7, the Pd₁Cu₈, Pd₃Cu₆, Pd₆Cu₃, Pd₉Cu₀, Pd(1 1 1) [2] and Cu(1 1 1) [21] catalysts have the energy barrier differences between CO₂ and CO formation of 17.6, 15.1, -65.0, -49.6, -78.6 and 84.9 kJ·mol⁻¹, respectively. Namely, the non-noble metal Cu catalyst exhibits higher CO selectivity, while the noble metal Pd catalyst shows higher CO₂ selectivity. Meanwhile, for the Cu catalyst-decorated by the noble metal Pd, both Pd₁Cu₈ and Pd₃Cu₆ catalysts with the isolated surface Pd atom are more favorable for the generation of CO, whereas both Pd₆Cu₃ and Pd₉Cu₀ catalysts with the surface Pd ensemble exhibit higher CO₂ selectivity toward HCOOH dissociation and suppresses the generation of CO, which is similar to the pure Pd catalyst. More importantly, both Pd₆Cu₃ and Pd₉Cu₀ catalysts obviously weaken CO adsorption energy in comparison with the pure Pd catalyst (-119.0, -161.4 vs. -197.9 kJ·mol⁻¹), especially, Pd₆Cu₃ catalyst. On the other hand, for the rate-determining step of CO₂ formation, the activation energy barriers are 102.6, 101.8, 82.6, 92.0, 96.5 and 141.8 kJ mol⁻¹ on the Pd₁Cu₈, Pd₃Cu₆, Pd₆Cu₃, Pd₉Cu₀, Pd(1 1 1) [2] and Cu(111) [21] surfaces, respectively, namely, compared to the pure Cu catalyst, the Pd-decorated Cu catalyst significantly increase the activity of CO2 formation, especially, both Pd6Cu3 and Pd9Cu0 catalysts with the surface Pd ensemble present higher activity of CO₂ formation in HCOOH dissociation than the pure Pd catalyst.

Further, our calculated results are also supported by some experimental conclusions, for example, the experiments by Lu *et al.* [12] have successfully prepared PdCu/C catalysts with different Pd: Cu ratios by simple impregnation reduction method, suggesting that with the increasing of Cu content in Pd-Cu/C catalyst, the activity of HCOOH dissociation decreased; moreover, the catalytic performance of PdCu/C catalyst for HCOOH dissociation was significantly better than that of Pd/C catalyst; however, when the content of Cu in PdCu/C catalyst is too high, the catalytic performance of PdCu/C catalyst will decrease since Cu has lower catalytic activity for HCOOH dissociation. Similarly, Xu and co-workers [59] have experimentally prepared a series of PdCu alloys with different Pd: Cu proportions, which found that the surface rich-Cu alloy mainly contribute to CO production, whereas the surface rich-Pd alloy dominantly produce CO_2 , and has better CO poisoning resistance. In addition, Liu *et al.* [9] have experimentally synthesized Ag-Pd nanoparticle with different Ag/Pd proportions, in which with the increasing of Pd contents, more CO_2 is produced, the rich-Pd Ag₁Pd₃ sample showed better catalytic performance and long lifetime for HCOOH dissociation at room temperature. Liu and his colleagues [60] prepared a series of PdAu/C catalysts, suggesting that a high proportion of Pd in PdAu/C catalyst can accelerate the dissociation rate of HCOOH.

As mentioned above, for Pd_1Cu_8 , Pd_3Cu_6 , Pd_6Cu_3 and Pd_9Cu_0 surfaces, with the increasing of surface Pd content, the first two surfaces are favorable for CO formation, the latter two surfaces are favorable for CO_2 formation; meanwhile, previous study has shown that $Pd(1\ 1\ 1)$ surface [2] is also favorable for CO_2 formation. Therefore, the selectivity and activity of CO_2 production will increase with the increasing of surface Pd loading over the Pd-decorated Cu catalyst; Moreover, compared to the pure Pd catalyst [2], both Pd_6Cu_3 and Pd_9Cu_0 catalysts with surface Pd ensemble, the non-precious metal Cu as the substrate decorated by a small quantity of noble metal Pd, not only reduce the cost of the catalyst and make full use of Pd effectively, but also achieve the same or higher catalytic performance.

3.3.3. The analysis of structure and electronic properties

Aiming at further illustrating the microscopic reason why the surface Pd distribution on the Pd-decorated Cu catalyst affect the catalytic performance of HCOOH dissociation, the surface structures of four Pd-decorated Cu(1 1 1) catalysts are first analyzed. As shown in Fig. 1, for the Pd₁Cu₈ and Pd₃Cu₆ catalysts, the surface Pd atoms exist in the form of the isolated single atom. However, the surface Pd atoms on the Pd₆Cu₃ and Pd₉Cu₀ catalysts are connected to form the Pd ensemble. It is concluded that the Pd-decorated Cu catalysts with the isolated single Pd atom are conducive to CO formation, whereas that with surface Pd ensemble are advantageous to CO₂ generation.

On the other hand, our results show that HCOOH dissociation over four Pd-decorated Cu catalysts mainly goes through the COOH intermediate. Moreover, the COOH intermediate can break its C-OH bond to produce CO or dehydrogenate to form CO₂, thus, the COOH intermediates play a key function in determining the product selectivity of HCOOH dissociation. Fig. 8 presents the difference charge density for the stable adsorption configurations of *trans*-COOH intermediate on four Pd-decorated Cu bimetallic surfaces, suggesting that there is strong charge transfer between the H atom and the catalyst surfaces on the



Fig. 8. The charge redistribution with the difference charge density $\Delta \rho = \rho_{COOH/PdxCuy}-\rho_{COOH}-\rho_{PdxCuy}$ for the stable adsorption configurations of *trans*-COOH intermediate on the Pd₁Cu₈, Pd₃Cu₆, Pd₆Cu₃ and Pd₉Cu₀ surfaces. The blue and yellow shaded regions represent the charge loss and charge gain, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

 Pd_6Cu_3 and Pd_9Cu_0 catalysts, which makes the cleavage of the O-H bond become easier to from CO₂, whereas this phenomenon on the Pd_1Cu_8 and Pd_3Cu_6 catalysts does not exist.

Further, the Mulliken charge analysis showed that the average charge of surface Pd atoms are -0.178 e and -0.157 e on the Pd₁Cu₈ and Pd₃Cu₆ surfaces, respectively; whereas those are -0.069 e and -0.039 e on the Pd₆Cu₃ and Pd₉Cu₀ surfaces, which is nearly close to the neutral charge on the pure Pd surface; In other words, Cu acted as an electron donor changed the electronic properties of the catalyst surface Pd atoms over the Pd-decorated Cu catalysts can high-actively and high-selectively catalyze HCOOH dissociation to form CO₂. On the other hand, as mentioned above, compared to the pure Pd catalysts, the Pd-decorated Cu catalysts, the substrate decorated by a small quantity of noble metal Pd, not only achieve the same or higher catalytic performance, but also reduce the cost of the catalyst due to the usage of Cu and make full use of Pd effectively.

4. Conclusions

In this study, the detailed mechanism of CO₂ and CO production in HCOOH dissociation over the Pd-decorated Cu catalysts with different surface Pd/Cu atomic ratios has been fully investigated using DFT calculations, which aims at understanding the role of the surface Pd ensemble in determining HCOOH dissociation's activity and selectivity. The results show that the surface Pd distribution obviously affects the optimal route and catalytic performances of HCOOH dissociation over the Pd-decorated Cu bimetallic catalysts, which is closely related to their surface structures and the corresponding electronic properties. The Pd-decorated Cu bimetallic catalysts with the surface isolated Pd atom dominantly catalyze HCOOH dissociation to form CO via the COOH intermediate, and the difference charge density show that a weak charge transfer occurs between the H atom of adsorbed trans-COOH species and the catalyst surfaces, which is unfavorable for its dehydrogenation; whereas those with the surface Pd ensemble mainly produce CO₂ through the COOH intermediate and effectively inhibit CO formation, and a strong charge transfer occurs between the H atom of

adsorbed *trans*-COOH intermediate and the catalyst surfaces, which is conducive to its dehydrogenation to from CO_2 . Further, the average charge of Pd atoms affect the catalytic performance of HCOOH dissociation, the Pd-decorated Cu catalysts with the surface Pd ensemble have smaller negative charge of every surface Pd atoms, which highactively and high-selectively catalyze HCOOH dissociation to form CO_2 . Thus, the PdCu catalysts with the surface Pd ensemble, prepared using the non-precious metal Cu as the substrate-decorated by a small quantity of noble metal Pd, not only reduce the cost of the catalyst and make full use of Pd effectively, but also achieve the same or higher catalytic performance in comparison with the pure Pd catalyst.

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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