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The cost-effective Cu-based catalysts for the efficient removal of acetylene from ethylene: The effects of Cu valence state, surface structure and surface alloying on the selectivity and activity



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HIGHLIGHTS

- A two-step model was employed to obtain the reaction rates of C₂H₂ selective hydrogenation.
- The valence state change of Cu(II) → Cu(I) → Cu(0) affects the selectivity of C₂H₄ formation.
- Both Cu(I) and Cu(0) catalysts should be considered under the realistic conditions.
- Cu(I) and Cu(0) catalysts focus on the defective and the stable (111) surfaces, respectively.
- The selectivity and *d*-band center meets the volcano curves for alloyed Cu(0) catalysts.

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GRAPHICAL ABSTRACT



ABSTRACT

Cost-effective Cu-based catalysts with high activity and selectivity towards C_2H_4 formation are vital for the efficient removal of C_2H_2 from C_2H_4 in industry. A comprehensive understanding about the effects of Cu-based catalyst properties, including the valence state, surface structure and surface alloying, on the selectivity and activity towards C_2H_4 formation is essential for developing any novel Cu-based catalysts. In this work, C_2H_2 hydrogenation to C_2H_4 over various Cu-based catalysts, including Cu(0), Cu(1), Cu(II), and alloyed MCu(M = Ni, Pd, Pt, Au), were systematically investigated. The results indicated that the activity and selectivity of Cu catalysts with different oxidation states towards C_2H_4 formation are very different. Cu(I) led to the highest selectivity, while Cu(0) led to the highest activity. Moreover, the catalytic performances of Cu(I) and Cu(0) catalysts are closely related to their surface structures, especially their defective and stable (111) surfaces. For the most stable Cu(0) catalyst in reducing atmosphere, the activity and selectivity towards C_2H_4 formation on M-doped Cu(111) (M = Ni, Pd, Pt, Au) surface are affected by the surface *d*-band center, PdCu(111) surface with *d*-band center at the middle site has the best activity of Cu-based catalysts and the selectivity of C_2H_2 hydrogenation towards C_2H_4 formation are determined by the valence state, surface structure, and surface *d*-band center of Cu catalysts. The catalytic activity and selectivity of all active surface structure, and surface *d*-band center of Cu catalysts.

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characteristics. The results are considerably beneficial to the development of new generation of Cu-based catalysts in the selective hydrogenation of C_2H_2 .

1. Introduction

Ethylene (C₂H₄) as a very important raw material in the production of polymers [1,2] is commonly produced through thermally cracking petroleum fractions, which inevitably contain about 0.1–1% acetylene (C₂H₂). The dilemma for the industrially critical technology is that the unavoidable impurity, C₂H₂, simultaneously is a poison to the catalyst in the process of C₂H₄ polymerization [3,4]. Thus, it is crucial to remove C₂H₂ from the feedstock of C₂H₄. The state-of-the-art solution is the selective hydrogenation of C₂H₂ to C₂H₄ [5,6]. However, there are two challenges with the low selectivity of C₂H₂ hydrogenation to C₂H₄ and then to C₂H₆ that negatively affects the subsequent polymerization of C₂H₄ due to deactivating-catalyst "green oil" formation via C₂H₂ polymerization [7–9].

Pd-based catalysts modified by the promoter Cu [10–12], Ag [13–20], Ga [21–24], Au [25,26], Zn [27], Ni [28], and Pb [29] were the most commonly utilized catalysts for the selective hydrogenation of C_2H_2 . Among them, the promising promoter was Cu promoter. It can enhance the performance of Pd-based catalysts, and increase C_2H_4 selectivity. In addition, Cu was widely doped to other metals (Au, Ni) in VIII and IB groups to improve the catalytic performance towards C_2H_2 hydrogenation to C_2H_4 [30,31]. More importantly, Kyriakou et al. [32] found that the Cu catalyst doped with a small quantity of promoter Pd exhibits a higher C_2H_4 selectivity in C_2H_2 hydrogenation than the pure Cu or Pd alone does. Cu/Al₂O₃ catalyst modified with Pd [33,34] with Cu:Pd ratio of 50:1 demonstrated high activity and selectivity towards C_2H_2 hydrogenation to C_2H_4 . Thus, developing cost-effective Cu-based catalysts for the efficient removal of C_2H_2 from C_2H_4 is of great significance.

For Cu-based catalysts, Cu₂O showed a higher activity during syngas conversion to methanol than elemental Cu does [35-37]. Also, Cu(I) is capable in strongly adsorbing C₂H₂ at low temperature [38], which is beneficial to the hydrogenation or conversion of C₂H₂. Cu₁Au₃/SBA-15 catalyst has characteristics of high activity for C₂H₂ hydrogenation resulting from Cu(I) in Cu₂O [30]. Moreover, CuO-La₂O₃/AC containing both CuO and Cu₂O species confirmed by TPR and XRD characterizations [39,40] is a great catalyst for oxidative methanol carbonylation. Reductions of CuO to Cu₂O and then Cu with H₂ occur at \sim 360 K and at 780 K, respectively [41]. C₂H₂ hydrogenation on Cu-based catalysts usually occur in 423–523 K range [34]. Under the conditions, H₂ may simultaneously participate in both reduction and hydrogenation. As a result, co-existence of different valence state Cu-based catalysts, including Cu(0), Cu(I), and Cu(II), could be advantageous [34]. However, both the valence states of Cu-based catalysts and their corresponding active surfaces that dominantly contribute to the high-performance in C₂H₂ hydrogenation to C₂H₄ have not been identified yet.

MCu bimetallic catalysts had received intensive attention. The synergistic effect of bimetallic catalysts on C_2H_2 hydrogenation is different from that of individual metals. CuNi synthesized by doping Cu to Ni(111) surface resulted in the increased activity of the catalyst [31]. As another example, ternary Cu-Ni-Fe catalyst [42] had a relatively high selectivity towards the formation of alkenes. Also, SBA-15 supported Au-Cu bimetallic catalyst with Cu: Au ratio of 1: 3 achieved an elevated C_2H_2 conversion and C_2H_4 selectivity within 433–473 K [30]. Doping a small amount of Pd onto Cu catalysts made them more active and selective for C_2H_2 hydrogenation to C_2H_4 [32]. Thus, the alloy surfaces could considerably contribute to the high yield of C_2H_4 under the given conditions.

This study was designed to make progress in investigating the effects of Cu-based catalyst material properties, including the valence

state, surface structure and the alloying effect, on the catalytic activity and selectivity towards the efficient removal of C_2H_2 from C_2H_4 using density functional theory (DFT) calculations. Firstly, different valence states (0, I, and II) of Cu catalysts and their corresponding exposed surfaces (the perfect and their defective surfaces containing lower coordinated Cu atoms) are examined to illustrate the effects of valence state and surface structure on C_2H_2 hydrogenation to C_2H_4 . Also, the alloy effects of Ni, Pd, Pt, and Au-doped Cu bimetallic catalysts on C_2H_2 hydrogenation to C_2H_4 are determined. Finally, the potential of a promising Pd-doped Cu(111) catalyst is compared with that of Pd(111) reportedly better than Pd(100) and Pd(211) [43] in viewpoints of C_2H_4 selectivity.



Fig. 1. Surface models and the corresponding adsorption sites of Cu(111), (110), (100) and (211) surfaces. Orange balls stand for Cu atoms.



Fig. 2. Surface models and the corresponding adsorption sites of the perfect and defective $Cu_2O(111)$, (110) and (100) surfaces, respectively. The red and black balls denote O atoms and oxygen-vacancy sites, respectively.

2. Computational details

2.1. Computational methods

All DFT calculations were implemented in Dmol³ program package of Materials Studio 8.0 [44,45]. The exchange-correlation functional PW91 was used to calculate the electronic structure with generalized gradient approximation (GGA) [46-48]. The valence electron functions were expanded into a set of numerical atomic orbitals by a doublenumerical basis with polarization functions (DNP) [49,50]. The effective core potential (ECP) method was employed to describe the interaction between the atomic cores and electrons for metal atoms [51], other atoms were treated with an all-electron basis set. Methfessel---Paxton smearing of 0.005 Ha was adopted. A $4 \times 4 \times 1$ Monkhorst-Pack grid was used for Cu, Pd, Cu₂O and alloyed surfaces, while a $3 \times 3 \times 1$ Monkhorst-Pack grid was performed for CuO surface. All energies obtained in our calculations included the zero-point vibrational energy. In addition, the adsorption and hydrogenation of C2H4 species (the key step of the whole process to determine the selectivity towards C₂H₄ formation) on different types of Cu-based catalysts were calculated by using dispersion-corrected (DFT-D2) method to describe the dispersion interaction, suggesting that DFT-D2 method is not suitable for our investigated system (see Part 1 of Supplementary material).

The transition state (TS) of every elementary reaction was searched using complete LST (Linear Synchronous Transit)/QST (Quadratic Synchronous Transit) method [52–54] in order to obtain the accurate activation barrier of C_2H_2 hydrogenation. Moreover, all transition states were confirmed by only one imaginary frequency, and TS Confirmation shows that transition state was associated with both reactant and product.



Fig. 3. Surface models and the corresponding adsorption sites of the perfect and defective CuO(111), (110) and (100) surfaces, respectively.

On the other hand, since high H_2/C_2H_2 ratio and temperature can effectively inhibit the oligomerization of C_2H_2 , and further reduced the extent of "green oil" [33,34,43], a high temperature of 520 K was examined. The entropic contribution is considered including the adsorption and desorption of the adsorbed species, as well as the reactions. The reference values of the entropies of gaseous H_2 , C_2H_2 , and C_2H_4 species under standard conditions (298 K, 1 atm) were used [55], which were used for calculating the entropies at 520 K and 1 atm. The total pressure was set to 1.0 atm, while the partial pressures of H_2 , C_2H_2 , and C_2H_4 were 0.1, 0.01, and 0.89 atm, respectively, which were close to the experimental conditions used by others [43,56]. All the thermodynamic values in this study were calculated with the conditions of 520 K and 1 atm unless the different conditions are mentioned.

According to the transition state theory by Eying [57], the activation free energy $(\Delta_r^{\neq} G_m^{\Theta})$ and reaction free energy $(\Delta_r G_m^{\Theta})$ of the elementary reactions at 520 K occur on Cu-based catalyst were calculated on the basis of Eqs. (1) and (2).

$$\Delta_r^{\neq} G_m^{\Theta} = E_{elec}(TS) + G_m^{\Theta}(TS) - E_{elec}(R) - G_m^{\Theta}(R)$$
⁽¹⁾

$$\Delta_r G_m^{\Theta} = E_{elec}(P) + G_m^{\Theta}(P) - E_{elec}(R) - G_m^{\Theta}(R)$$
⁽²⁾

where $E_{elec}(TS)$, $E_{elec}(R)$ and $E_{elec}(P)$ were the electron energies of transition state, reactant and product, respectively. $G_m^{\Theta}(TS)$, $G_m^{\Theta}(R)$ and $G_m^{\Theta}(P)$ were the corresponding corrections for the standard free energies at a finite temperature (520 K). $E_{elec}(R)$ and $E_{elec}(P)$ can be obtained from a geometry optimization of reactant and product, while $E_{elec}(TS)$ can be calculated from TS search using DMol³. On the other hand, once the structures of transition state, reactant and product were determined, the results of a vibrational analysis calculation can be used to compute important thermodynamic properties such as enthalpy (H), entropy (S), free energy (G) and heat capacity at constant pressure (C_p) as a function of temperature. In our calculation, the values of $G_m^{\Theta}(TS)$,



Fig. 4. The top views of (a) NiCu(111), (b) PdCu(111), (c) PtCu(111), (d) AuCu(111), and (e) Pd(111) alloyed surfaces. The dark blue, cyan, bluish violet and yellow balls denote Ni, Pd, Pt and Au atoms, respectively.



Fig. 5. The proposed mechanism for the selective hydrogenation of C_2H_2 via CHCH₃ and C_2H_4 intermediates, as well as C_2H_4 desorption pathways, respectively; (ad) and (g) stand for the adsorbed and gas phase states, respectively.

 $G_m^{\Theta}(R)$ and $G_m^{\Theta}(P)$ at a finite temperature (520 K) can be directly obtained from the data in DMol³ output document of frequency analysis.

The adsorption free energy (G_{ads}) at 520 K was calculated according to the Eq. (3).

$$G_{ads} = E_{elec}(sub) + G_m^{\Theta}(sub) + E_{elec}(mol) + G_m^{\Theta}(mol) - E_{elec}(all) - G_m^{\Theta}(all)$$
(3)

where $E_{elec}(all)$ was the total electron energy of adsorbate–substrate system in its equilibrium state, $E_{elec}(sub)$ was the electron energy of the substrate, and $E_{elec}(mol)$ was the electron energy of the isolated adsorbate in gas phase; $G_m^{\oplus}(all)$, $G_m^{\oplus}(sub)$ and $G_m^{\oplus}(mol)$ were the corresponding corrections for the standard free energies at a finite temperature (520 K). According to this definition, a large positive value of G_{ads} represents a stronger adsorption between the adsorbates and substrate.

2.2. Computational models

Cu, Cu₂O, and CuO catalysts were employed to model different valence states of Cu(0), Cu(I), and Cu(II) catalysts, respectively. Three dominantly exposed low-index surfaces (111), (110) and (100) of Cu, Cu₂O, and CuO catalysts were considered to represent different surface

structures of Cu(0), Cu(I), and Cu(II) catalysts, respectively, which can reasonably present the catalytic performance of Cu, Cu₂O, and CuO catalysts [58–61]. Moreover, the corresponding defective surfaces of Cu, Cu₂O, and CuO with lower coordinated Cu atoms were also examined, in which Cu catalyst corresponds to the stepped Cu(211) surface with (100)-type step, both Cu₂O and CuO catalysts correspond to the oxygen-vacancy surfaces due to the existence of reducing gas H₂; one oxygen-vacancy can be easily formed in the selective hydrogenation of C₂H₂ [41]. These surfaces were confirmed to be the dominant defective surfaces of metal and metal oxides in reality [62–65]. On the other hand, for the alloy effects, M(Ni, Pd, Pt, Au)-doped Cu(111) surfaces were considered. In addition, Pd(111) surface was also examined to facilitate the comparison of catalytic performance with alloyed Cu surfaces.

For the flat Cu(111), (100), (110) and Pd(111) surfaces, as well as Ni, Pd, Pt and Au-doped Cu(111) alloyed surfaces, a four-layers p (3 × 3) unit cell were used with the top two layers relaxed during optimization [43,59,66,67]. For the stepped Cu(211) surface, an eight-layers $p(2 \times 3)$ unit cell was employed with the three bottom layers constrained in the bulk position [68]. The MCu(111)(M = Ni, Pd, Pt, Au) alloyed surface were modeled with one surface Cu atom replaced by one Ni, Pd, Pt and Au atoms, respectively.

Table 1

Adsorption free e	energies of ($C_{2}H_{x}(x = 2-4)$	species at 520 K on	different types of	Cu-based catalysts.
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Surfaces	Adsorption free energies $(G_{ads}/kJ \cdot mol^{-1})$					
	C ₂ H ₂	C_2H_3	C_2H_4	CHCH ₃		
Cu(111)	158.5 (148.2)	230.5 (219.1)	63.0 (50.3)	290.7 (293.3)		
Cu(110)	151.2 (163.1)	259.8 (243.7)	97.3 (80.9)	342.1 (315.1)		
Cu(100)	188.4 (170.7)	242.5 (235.1)	77.2 (59.9)	293.1 (297.4)		
Cu(211)	162.1 (157.0)	269.5 (266.1)	96.0 (81.7)	316.0 (320.6)		
Cu ₂ O(111)-perfect	136.1 (118.9)	256.8 (250.7)	118.0 (115.1)	329.3 (351.2)		
Cu ₂ O(111)-defective	255.4 (259.8)	269.4 (282.6)	131.0 (119.5)	398.4 (416.7)		
Cu ₂ O(110)-perfect	80.6 (31.5)	253.5 (254.0)	49.7 (29.3)	324.2 (341.6)		
Cu ₂ O(110)-defective	152.9 (153.7)	305.8 (320.1)	86.8 (74.7)	386.0 (408.5)		
Cu ₂ O(100)-perfect	160.1 (205.9)	400.1 (422.6)	191.8 (229.1)	532.6 (577.0)		
Cu ₂ O(100)-defective	298.4 (308.1)	398.9 (402.5)	306.9 (316.6)	507.3 (516.2)		
CuO(111)-perfect	47.3 (45.6)	276.3 (268.2)	56.1 (62.7)	401.6 (398.0)		
CuO(111)-defective	189.0 (184.3)	294.5 (285.9)	131.5 (120.1)	293.2 (308.3)		
CuO(110)-perfect	56.8 (30.7)	318.1 (314.2)	172.2 (180.1)	486.9 (500.0)		
CuO(110)-defective	66.1 (71.6)	333.5 (320.1)	158.9 (172.4)	444.2 (462.5)		
CuO(100)-perfect	493.9 (487.4)	595.1 (594.3)	327.6 (341.5)	635.1 (645.2)		
CuO(100)-defective	490.1 (486.1)	576.5 (569.1)	323.0 (341.4)	597.0 (612.9)		
NiCu(111)	207.4 (203.3)	274.0 (261.2)	116.3 (106.7)	338.0 (343.5)		
PdCu(111)	159.1 (153.4)	235.8 (229.9)	92.7 (86.7)	294.6 (306.2)		
PtCu(111)	163.6 (160.8)	262.5 (253.9)	92.8 (88.5)	310.6 (322.9)		
AuCu(111)	142.0 (136.0)	226.7 (216.7)	62.8 (51.1)	286.7 (289.6)		
Pd(111)	218.0 (215.7)	288.4 (292.1)	127.9 (121.0)	388.5 (375.8)		

^{*} The values in the parenthesis are the adsorption energies at 0 K.

For Cu₂O(111) and (110) surfaces, a $p(2 \times 2)$ unit cell with six and seven atomic layers was employed, respectively, the three bottom layers were fixed [69–73]. For Cu₂O(100) surface, a $p(2 \times 3)$ unit cell with seven atomic layers was employed, the three top layers were relaxed.

For CuO(111) and (100) surfaces, the six-layered surface model with a $p(3 \times 2)$ and (2×2) super-cells were employed, respectively, which have been widely used in the previous studies [74–77]. In all calculations, the three bottom layers were kept fixed to maintain the bulk structure, while the three top atomic layers of the substrate and the adsorbed species were allowed to relax. For CuO(110) surface, a p (2 × 3) unit cell with four atomic layers were employed, and the two top layers were relaxed. The defective CuO and Cu₂O surfaces were modeled with removing one surface O atom.

A vacuum space of 15 Å was added perpendicular to all surfaces avoiding the interactions between the periodic slabs. All catalyst surface models and the corresponding adsorption sites are shown in Figs. 1–4. The surface reconstructions are considered when calculations are performed for all surface models. All Cu catalyst surfaces are firstly optimized; then, all the associated adsorption and reaction are considered over the optimized surfaces.

3. Results and discussion

3.1. The proposed possible mechanism of C_2H_2 selective hydrogenation

As shown in Introduction, the formations of ethane and "green oil" are two crucial aspects in the selective hydrogenation of C_2H_2 . Previous studies [33,34,43] found that both high H_2/C_2H_2 ratio and high temperature were enough to suppress the oligomerization of C_2H_2 . Thus, the oligomerization of C_2H_2 to "green oil" is not considered, which will be examined in our future work. In this study, only the crucial factor of ethane formation was considered to identify its effect on the selectivity of C_2H_2 hydrogenation to C_2H_4 . For ethane formation, except for C_2H_4 over-hydrogenation to ethane, CHCH₃ formation ($C_2H_2 + H \rightarrow$ CHCH₃) followed by its hydrogenation to ethane via C_2H_5 intermediate also affected the selectivity of C_2H_2 hydrogenation to C_2H_2 hydrogenation to C_2H_3 .

As shown in Fig. 5, aiming at identifying the selectivity of C_2H_2 hydrogenation to C_2H_4 on Cu-based catalysts, starting from C_2H_2 hydrogenation, three pathways have been considered to determine the

optimal pathway in the selective hydrogenation of C_2H_2 : the first is C_2H_4 formation via C_2H_3 intermediate, subsequently, C_2H_4 easily desorbs from the catalyst surface, which is named as C_2H_4 desorption *pathway*. The latter two pathways are C_2H_5 formation via C_2H_4 or CHCH₃ intermediates, which are denoted as C_2H_4 or CHCH₃ *intermediate pathways*, respectively. In three cases above, when the optimal pathway goes through C_2H_4 desorption pathway, the catalyst exhibits a better selectivity towards C_2H_4 formation rather than C_2H_6 . However, when the optimal pathway goes through C_2H_4 or CHCH₃ intermediate pathway to form C_2H_5 , the product of C_2H_2 hydrogenation is ethane by C_2H_5 hydrogenation, namely, the catalyst presents a poor selectivity towards C_2H_4 formation.

3.2. Effect of surface structure on C_2H_4 formation over Cu(0) catalyst

3.2.1. The adsorption of $C_2H_x(x = 2-4)$ species

Under the realistic conditions of the selective hydrogenation of C_2H_2 , there are about 0.1-1% C_2H_2 and 89% C_2H_4 in the feed gas [3,4,43], suggesting that only when the adsorption ability of C_2H_2 is much stronger than that of C_2H_4 , the removal of trace C_2H_2 from C_2H_4 -rich feed gas can be realized. Thus, the adsorptions of C_2H_2 and C_2H_4 on Cu catalyst, including Cu(111), (110), (100) and (211) surfaces, are investigated, as listed in Table 1.

On Cu(111), (100) and (211) surfaces, C_2H_2 prefers to adsorbing at the "4-fold diagonal hollow" site, which agrees with the experimental and theoretical results reported in literature [79–82]. On Cu(110) surface, the "4-fold aligned hollow" site is preferred for C_2H_2 adsorption, which well agrees with previously reported results on Cu(110) surface [82]. Meanwhile, the most stable adsorption configurations of C_2H_4 on different Cu surfaces are similar. C_2H_3 prefers to adsorbing at the bridge sites on different Cu surfaces, while CHCH₃ prefers to adsorb at the fcc sites on Cu(111) surface, and the bridge site is the most stable sites on other three Cu surfaces (see Fig. S2 and Table 1). As shown in Fig. 6, the adsorption free energy of C_2H_2 is much larger than that of C_2H_4 , suggesting that the trace C_2H_2 in C_2H_4 -rich feeding gas is more favorable to sorption than C_2H_4 , which is beneficial to C_2H_2 hydrogenation on Cu(0) catalyst.

3.2.2. Selectivity of C_2H_4 formation on different Cu surfaces

As shown in Fig. 5, when CHCH₃ intermediate pathway is difficult



Fig. 6. Adsorption free energies of C_2H_2 and C_2H_4 species with the most stable adsorption configurations on different types of Cu, Cu₂O, CuO, MCu(111)(M = Ni, Pd, Pt, Au) and Pd(111) surfaces at (a) 520 K, (b) 0 K; (-p) and (-d) stand for the perfect and the defective surfaces, respectively.

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to occur, the selectivity of C_2H_2 hydrogenation to C_2H_4 on Cu-based catalysts is mainly controlled by C_2H_4 hydrogenation and its desorption, which determines the surface concentration of C_2H_4 [17]. Previous studies [17,43,83–85] found that determining barrier differences between C_2H_4 desorption and its hydrogenation is the simplest way to compare the selectivity. Nørskov et al. [17] and Hu et al. [43] confirmed that the catalyst with a high selectivity towards C_2H_4 formation should have a relatively high hydrogenation barrier and a low desorption barrier of C_2H_4 .

Since the difference between the desorption barrier and the absolute value of adsorption energy is relatively small, these two values are approximately equal [31,86–88]. Thus, in this study, the differences between the activation free energy of C_2H_4 hydrogenation and the absolute value of C_2H_4 adsorption free energy is adopted to compare the selectivity of C_2H_4 formation at 520 K on different surfaces, which is denoted as ΔG_a in Eq. (4):

$$G_a = G_{a,hydr} - |G_{ads}| \tag{4}$$

where $G_{a,hydr}$ and G_{ads} are the activation free energy of C_2H_4 hydrogenation and the adsorption free energy of C_2H_4 , respectively. This equation indicates that the more positive ΔG_a is, the better the selectivity of the catalyst has towards C_2H_4 formation.

The free energy profiles for the three pathways of CHCH₃ intermediate, C_2H_4 intermediate and C_2H_4 desorption on Cu(111), (211), (110) and (100) surfaces are shown in Fig. 7. In order to clearly present the reaction mechanism of C_2H_2 selective hydrogenation on different valence states of Cu catalysts, Cu(111) surface is used as an example to illustrate the mechanism of C_2H_2 hydrogenation in detail, as shown in Fig. 7(a) and Fig. S6(a), the optimized co-adsorption configurations of C_2H_2 and H is chosen as the initial state of C_2H_2 hydrogenation ($C_2H_2 + H \rightarrow C_2H_3$), and the most stable adsorption configuration of C_2H_3 is regarded as the final state. C_2H_2 hydrogenation can



Fig. 7. Free energy profiles of the pathways $C_2H_3 + H \rightarrow CHCH_3$ (red), $C_2H_3 + H \rightarrow C_2H_4$ (black) and C_2H_4 desorption (blue) at 520 K on (a) Cu(111), (b) Cu(211), (c) Cu(110), and (d) Cu(100) surfaces. The labeled (g) in the free energy profiles stand for gas phase state; others without label represent the adsorbed state; these notations are used throughout this paper.

Table 2

Activation free energies (G_a) of C₂H₄ hydrogenation to C₂H₅, the differences of free energy (ΔG_a) between the activation free energy of C₂H₄ hydrogenation and the absolute value of C₂H₄ adsorption free energy, as well as the corresponding adsorption free energies (G_{ads}) of C₂H₄ at 520 K on different types of Cu, Cu₂O, CuO, MCu(111)(M = Ni, Pd, Pt), and Pd(111) surfaces.

Surfaces	$G_{\rm a}/{\rm kJ}\cdot{\rm mol}^{-1}$	$G_{\rm ads}/{\rm kJ\cdot mol^{-1}}$	$\Delta G_{\rm a}/{\rm kJ}\cdot{\rm mol}^{-1}$
Cu(111)	96.7	63.0	33.7
Cu(211)	124.8	96.0	28.8
Cu(110)	70.8	97.3	-26.5
$Cu_2O(111)$ -defective	196.5	131.0	65.5
Cu ₂ O(110)-defective	151.8	86.8	65.0
CuO(111)-defective	164.6	131.5	33.1
NiCu(111)	135.9	116.3	19.6
PdCu(111)	132.5	92.7	39.8
PtCu(111)	114.6	92.8	21.8
Pd(111)	76.4	127.9	-51.5

form C_2H_3 *via* a transition state TS1-1. This elementary reaction has the activation and reaction free energies of 115.8 and $-27.5 \text{ kJ} \cdot \text{mol}^{-1}$, respectively. The activation free energy of C_2H_2 hydrogenation (115.8 kJ·mol⁻¹) is smaller than its adsorption free energy (158.5 kJ·mol⁻¹), which is favorable to C_2H_2 hydrogenation instead of C_2H_2 desorption, and consequently beneficial to the selective hydrogenation of C_2H_3 . Then, for the elementary reactions $C_2H_3 + H \rightarrow C_2H_4$ and $C_2H_3 + H \rightarrow CHCH_3$, C_2H_3 hydrogenation can form C_2H_4 and CHCH₃ *via* TS1-2 and TS1-4 with the activation free energies of 86.2 and 228.8 kJ·mol⁻¹), the activation free energies (86.2 and 228.8 kJ·mol⁻¹) of C_2H_3 hydrogenation to C_2H_4 and CHCH₃ are low,

suggesting that C_2H_3 hydrogenation can proceed without C_2H_3 desorption. Further, for $C_2H_4 + H \rightarrow C_2H_5$ and $CHCH_3 + H \rightarrow C_2H_5$, the most stable adsorption configuration of C_2H_5 is chosen as the final state, and the optimized co-adsorption configurations of $C_2H_4 + H$ and $CHCH_3 + H$ are regarded as the initial states, respectively; these two reactions occur through TS1-3 and TS1-5 to form C_2H_5 with the corresponding reaction free energies of -27.8 and -77.1 kJ·mol⁻¹, and the activation free energies of 96.7 and 70.9 kJ·mol⁻¹, respectively. The activation free energy of C_2H_4 hydrogenation (96.7 kJ·mol⁻¹) is higher than its adsorption rather than being hydrogenated. However, the adsorption free energy of $CHCH_3$ (290.7 kJ·mol⁻¹) is much larger than the activation free energy of $CHCH_3$ (290.7 kJ·mol⁻¹), thus $CHCH_3$ prefers to be hydrogenated to C_2H_5 instead of its desorption.

Similar to what occurs on Cu(111) surface, C₂H₂, C₂H₃, and CHCH₃ hydrogenations are more favorable than their desorption on other Cu surfaces. On Cu(111) and (211), as shown in Fig. 7(a) and (b), CHCH₃ intermediate pathway has slight contribution to C₂H₄ formation. Moreover, C₂H₄ desorption instead of its hydrogenation is favorable to C₂H₄ formation. The ΔG_a of C₂H₄ on Cu(111) and (211) surfaces are 33.7 and 28.8 kJ·mol⁻¹, respectively, as shown in Table 2. Thus, Cu (111) and (211) surfaces have high selectivity towards C₂H₄ formation. However, hydrogenation is more likely for C₂H₄ because its ΔG_a is -26.5 kJ·mol⁻¹ on Cu(110) surface as shown in Fig. 7(c). On Cu(100) surface in Fig. 7(d), CHCH₃ intermediate pathway (80.6 kJ·mol⁻¹) has almost the same overall activation free energy as C₂H₄ desorption pathway (79.1 kJ·mol⁻¹) does; thus, CHCH₃ formation followed by its hydrogenation to ethane leads to low C₂H₄ selectivity.



Reaction coordinate

Fig. 8. Free energy profiles for the selective hydrogenation of C_2H_2 to gas phase C_2H_4 on Cu(111), (211) and the defective $Cu_2O(111)$, (110), CuO(111) surfaces with C_2H_4 easy desorption rather than being hydrogenated at (a) 520 K, (b) 0 K; (ad) and (g) stand for the adsorbed and gas phase states, respectively.

Table 3

The exponential energetic terms $(kJ \cdot mol^{-1})$ in the denominator of Eq. (5) and the corresponding reaction rates at 520 K $(r/s^{-1} \text{ site}^{-1})$ for the selective hydrogenation of C_2H_2 to C_2H_4 .

Surfaces	G_R^{ad}	G_R^{de}	G_P^{de}	$G_R^{ad} - G_R^{de} + G_P^{de}$	r
$\begin{array}{c} Cu(111)\\ Cu(211)\\ Cu_2O(111)-defective\\ Cu_2O(110)-defective\\ CuO(111)-defective\\ NiCu(111)\\ PdCu(111)\\ PtCu(111)\\ PtCu(111)\\ Pd(111)\\ Pd(111)\\ \end{array}$	117.6 117.6 117.6 117.6 117.6 117.6 117.6 117.6 117.6 117.6	258.9 293.6 337.6 329.0 393.4 325.8 244.6 231.6 238.4 399.0	115.8 154.9 162.6 117.8 146.4 134.2 45.7 54.9 139.4 110.4	- 25.5 - 21.1 - 57.4 - 93.6 - 129.4 - 74.0 - 81.3 - 59.1 18.6 - 171.0	$\begin{array}{c} 2.52 \times 10^{0} \\ 2.98 \times 10^{-4} \\ 5.02 \times 10^{-2} \\ 1.59 \times 10^{0} \\ 2.13 \times 10^{-3} \\ 3.58 \times 10^{-2} \\ 2.78 \times 10^{7} \\ 3.31 \times 10^{6} \\ 1.07 \times 10^{-2} \\ 8.80 \times 10^{0} \end{array}$

3.2.3. Activity of C_2H_4 formation on Cu surfaces

With the purpose of quantitatively describing the catalytic activity of Cu surfaces towards C_2H_4 formation, according to the studies by Hu et al. [89,90], the Eq. (5) obtained from two-step model is adopted to calculate the reaction rate, and the coverage of the species is considered.

$$r = \frac{k_B T}{h} \frac{\left(1 - \frac{P_P}{P_R} e^{\frac{\Delta G}{P_R}}\right)}{\frac{P^{\Theta}}{P_R} e^{\frac{G_R^{dd} - G_R^{de} + G_P^{de}}{RT}} + e^{\frac{G_R^{de}}{RT}}}$$
(5)

where $P_{\rm R}$, $P_{\rm P}$, and $P^{\rm o}$ are the partial pressures of reactant and product, and the standard pressure, respectively, *T* is the temperature, $k_{\rm B}$ is the Boltzmann constant, *h* is the Planck's constant, *R* is the universal gas constant, G_R^{ad} and G_R^{de} are the effective free energy of reactant adsorption and desorption, respectively; G_P^{de} is the effective free energy of product desorption, and ΔG is the activation free energy change of



Fig. 9. Free energy profiles of the pathways $C_2H_3 + H \rightarrow CHCH_3$ (red), $C_2H_3 + H \rightarrow C_2H_4$ (black) and C_2H_4 desorption (blue) at 520 K on the perfect (a) $Cu_2O(110)$, (b) $Cu_2O(111)$, and the defective (c) $Cu_2O(111)$, (d) $Cu_2O(110)$ surfaces.

overall reaction. All free energies are obtained at 520 K. The detailed descriptions about two-step model are shown in Part 5 of Supplementary material.

In Eq. (5), ΔG is the intrinsic property of the reaction at 520 K, which can be calculated from DFT calculations, T, $P_{\rm R}$ and $P_{\rm P}$ are the reaction conditions, $k_{\rm B}$, h and R are just constants. Thus, it is important to calculate the values of $G_R^{ad} - G_R^{de} + G_P^{de}$ and G_P^{de} in order to determine the reaction rate of C_2H_2 hydrogenation to C_2H_4 .

As mentioned in Section 3.2.2, since only both Cu(111) and Cu (211) surfaces present a high selectivity towards C_2H_4 formation, the catalytic activity of Cu(111) and (211) surfaces towards C_2H_4 formation is discussed. As shown in Fig. 8, the adsorption of reactants (C_2H_2 and H_2) at 520 K needs to overcome an adsorption free energy of 117.6 kJ·mol⁻¹, while the adsorption of reactants at 0 K is spontaneous.

Table 3 lists the exponential energetic terms in the denominator of Eq. (5) at 520 K obtained from Fig. 8(a). The results show that the different surfaces of Cu(0) catalyst have the same value of G_R^{ad} (117.6 kJ·mol⁻¹) but different values of G_R^{de} and G_P^{de} . Moreover, the value of $G_R^{ad} - G_R^{de} + G_P^{de}$ is considerably lower than G_P^{de} , and therefore, the effect of G_P^{de} on the reaction rate is much larger than that of $G_R^{ad} - G_R^{de} + G_P^{de}$ for Cu(211) surface is larger by 39.1 kJ·mol⁻¹ than that for Cu(111) surface. As a result, the reaction rate (2.98 × 10⁻⁴ s⁻¹·site⁻¹) on Cu(211) surface is lower by four orders of magnitude than that on Cu(111) surface (2.52 × 10⁰ s⁻¹ site⁻¹). Therefore, G_P^{de} can be selected to evaluate the activity of Cu surface towards C₂H₄ formation, and the results of G_P^{de} and reaction rates show that the order of catalytic activity of Cu surface is Cu(111) > Cu (211).

3.2.4. The effect of Cu surface structure on the selectivity and activity towards C_2H_4 formation

Over Cu(111), (110), (100) and (211) surfaces with different surface structure, the adsorption of C_2H_2 species is much stronger than

that of C_2H_4 species, which ensures the strong adsorption of trace C_2H_2 in C_2H_4 -rich feed gas.

Both Cu(110) and (100) surfaces show poor selectivity towards C_2H_4 formation. Cu(111) and Cu(211) surfaces have good selectivity towards C_2H_4 formation. Cu(111) surface with the weakest C_2H_4 adsorption ability presents the highest selectivity for C_2H_4 formation among four Cu(0) surfaces, which agrees with the previous results [32] that the weak binding of intermediates on Cu(111) surface results in a high selectivity towards C_2H_2 hydrogenation. Moreover, Cu(111) surface has a higher reaction rate. Thus, the surface structure of Cu(0) catalyst obviously affects the selectivity and activity towards C_2H_4 formation, and Cu(111) surface presents the best catalytic activity and selectivity among four different surfaces of Cu(0) catalyst.

3.3. Effect of surface structure on C_2H_2 hydrogenation to C_2H_4 on Cu(I) catalyst

3.3.1. The adsorption of $C_2H_x(x = 2-4)$ species

The adsorption free energies of $C_2H_x(x = 2-4)$ species and their favorable configurations are summarized and presented in Table 1 and Fig. S3, respectively. As shown in Fig. 6, except for the perfect and defective $Cu_2O(100)$ surfaces, C_2H_2 is more favorable to adsorption than C_2H_4 , and results in the possible hydrogenation of trace C_2H_2 in C_2H_4 -rich feed gas. Thus, only the selective hydrogenation of C_2H_2 on $Cu_2O(111)$ and $Cu_2O(110)$ surfaces are considered.

3.3.2. Selectivity of C₂H₄ formation on Cu₂O surfaces

As shown in Fig. 9, on the perfect $Cu_2O(110)$ surface, C_2H_2 favors desorption instead of hydrogenation, suggesting that C_2H_2 fails to be hydrogenated into C_2H_3 . On the perfect $Cu_2O(111)$ surface, C_2H_4 tends to hydrogenate to ethane instead of its desorption, which exhibits a poor selectivity towards C_2H_4 formation.

Both the defective Cu₂O(111) and (110) surfaces show better



Reaction coordinate

Fig. 10. Free energy profiles of the pathways $C_2H_3 + H \rightarrow CHCH_3$ (red), $C_2H_3 + H \rightarrow C_2H_4$ (black) and C_2H_4 desorption (blue) at 520 K on the (a) defective CuO(111), and (b) perfect CuO(100) surfaces.

selectivity towards C_2H_4 formation; the corresponding ΔG_a values are 65.5 and 65.0 kJ·mol⁻¹, indicating that the defective $Cu_2O(111)$ and (110) surfaces have almost the same selectivity towards C_2H_4 formation.

3.3.3. Activity of C_2H_4 formation on Cu_2O surfaces

As mentioned above, only the defective Cu₂O(111) and (110) surfaces exhibit better selectivity towards C₂H₄ formation, as listed in Table 3, the values of G_p^{de} are far larger than $G_R^{ad}-G_R^{de}+G_P^{de}$. Therefore, G_p^{de} is selected to evaluate the activity of Cu₂O surface towards C₂H₄ formation. Based on reaction rates, from the perspective of the activity of Cu₂O(110) surface for C₂H₂ hydrogenation to C₂H₄, the defective Cu₂O(110) surface (1.59 × 10⁰ s⁻¹ site⁻¹) is better than the defective Cu₂O(111) surface (5.02 × 10⁻⁵ s⁻¹ site⁻¹).

3.3.4. The effect of Cu_2O surface structure on the selectivity and activity towards C_2H_4 formation

 C_2H_2 has lower adsorption and hydrogenation capabilities on the perfect and defective Cu₂O(100) surfaces than $C_2H_4.\ C_2H_4$ over-hydrogenation to ethane occurs on the perfect Cu₂O(111) surface. C_2H_2 desorption is easier than its hydrogenation on the perfect Cu₂O(110) surface. Thus, these four surfaces lead to poor selectivity towards C_2H_4 formation.

The defective $Cu_2O(111)$ and (110) surfaces are characterized with higher selectivity and activity for C_2H_2 hydrogenation to C_2H_4 . Both surfaces lead to similar selectivity towards C_2H_4 formation, while the defective $Cu_2O(110)$ surface leads to higher catalytic activity. Thus, the oxygen-vacancy on Cu(I) catalyst is in favor of C_2H_4 formation.

3.4. Effect of surface structure on C_2H_2 hydrogenation to C_2H_4 on Cu(II) catalyst

3.4.1. The adsorption of $C_2H_x(x = 2-4)$ species

Table 1 and Fig. S4 present the adsorption free energies of C₂ species and its corresponding stable adsorption configurations on different CuO surfaces, respectively. As shown in Fig. 6, since the adsorption free energy of C₂H₄ is larger than that of C₂H₂, trace C₂H₂ in feed gas fails to be adsorbed, which makes C2H2 hydrogenation become almost impossible on the perfect CuO(111) and (110) surfaces, as well as the defective (110) surface. Whereas the adsorption free energy of C_2H_2 is larger than that of C_2H_4 at 520 and 0 K on the defective CuO(111) and (100) surfaces, as well as the perfect (100) surface. Moreover, both the perfect and defective CuO(100) surfaces present almost the same adsorption free energies and stable adsorption configurations of C₂ species, suggesting that the adsorption of C₂ species on CuO(100) surface is not affected by the existence of oxygen-vacancy. Since O_{SUF} site is the stable adsorption site of C₂ species, the existence of oxygen-vacancy reduces the number of adsorption active sites for C₂ species; as a result, only C2H2 hydrogenation on the perfect CuO(100) surface is considered. Thus, only both the defective CuO(111) and perfect (100) surfaces are discussed in this section.

3.4.2. Selectivity of C_2H_4 formation on CuO surfaces

On the defective (111) and perfect (100) surfaces, C_2H_2 , C_2H_3 , and CHCH₃ species have higher probability in hydrogenation than in desorption. As presented in Fig. 10, C_2H_4 and ethane are the final products of C_2H_2 hydrogenation on the defective (111) and perfect (100) surfaces, respectively, suggesting that the defective CuO(111) surface is desirable for C_2H_4 formation ($\Delta G_a = 33.1 \text{ kJ} \cdot \text{mol}^{-1}$), while the perfect CuO(100) surface is preferable for ethane formation.

3.4.3. Activity of C_2H_4 formation on CuO surfaces

Above results indicate that only the defective CuO(111) surface exhibits a good selectivity towards C_2H_4 formation among six different CuO surfaces, thus, only the activity of the defective CuO(111) surface is discussed, as listed in Table 3, the reaction rate on the defective CuO (111) surface is $2.13 \times 10^{-3} \, \text{s}^{-1}$ site⁻¹.

3.4.4. The effect of CuO surface structure on the selectivity and activity towards C_2H_4 formation

The adsorption free energy of C_2H_4 is higher than that of C_2H_2 on the perfect CuO(111), (110), and the defective (110) surfaces, which makes C_2H_2 adsorption and hydrogenation almost impossible in C_2H_4 -rich feed gas.

On the perfect and defective CuO(100) surfaces, ethane is the dominant product. The defective CuO(111) surface leads to a high selectivity towards C_2H_4 formation. Thus, like Cu₂O(111) and (110) surfaces, only the presence of oxygen-vacancy over CuO(111) surface in Cu(II) catalyst can significantly improve the selectivity towards C_2H_4 formation.

3.5. Effect of Cu valence state and surface structure on selectivity and activity in C_2H_4 formation

As mentioned above, our results indicate that Cu(II), Cu(I) and Cu (0) catalysts lead to a good selectivity to catalyze C_2H_2 hydrogenation to C_2H_4 . Zhong et al. [91] showed that on the supported CuO/SiO₂ and Cu/SiO₂ catalysts, the individual Cu(II) or Cu(0) catalysts present a better selectivity towards C_2H_4 formation, which agree with our calculated results. Up to now, few experimental studies can validate our calculated results on the individual Cu(I) catalyst, only Lee et al. [30] experimentally showed that the presence of Cu(I) in Cu₂O leads to a high activity in C_2H_2 hydrogenation over Cu₁Au₃/SBA-15 catalyst; meanwhile, Cu(I) exhibits a strong interaction with C_2H_2 , which makes C_2H_2 hydrogenation possible [38]; these experiments support the fact



Fig. 11. Free energy profiles of the pathways $C_2H_3 + H \rightarrow CHCH_3$ (red), $C_2H_3 + H \rightarrow C_2H_4$ (black) and C_2H_4 desorption (blue) at 520 K on (a) NiCu(111), (b) PdCu (111), (c) PtCu(111), and (d) AuCu(111) surfaces.



Fig. 12. Free energy profiles of the pathways $C_2H_3 + H \rightarrow CHCH_3$ (red), $C_2H_3 + H \rightarrow C_2H_4$ (black) and C_2H_4 desorption (blue) at 520 K on Pd(111) surface.(For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

that the existence of Cu(I) presents a high activity in C_2H_2 hydrogenation, which also agrees with our calculated results. Therefore, our results can provide a reliable guide for the design of efficient Cu catalysts in the selective hydrogenation of C_2H_2 .

Based on above results about the catalytic performance in C_2H_2 hydrogenation to C_2H_4 on different valence states and surface structures of Cu(0), Cu(I), and Cu(II) catalysts, our results can identify that the catalytic performances of Cu(II), Cu(I) and Cu(0) catalysts in C_2H_2 hydrogenation to C_2H_4 are closely related to their surface structures, Cu

(II) catalyst only focuses on the defective CuO(111) surface, and Cu(I) catalyst focuses on the defective Cu₂O(111) and (110) surfaces; Cu(0) catalyst only focuses on the stable and dominantly exposed Cu(111) surface.

To determine the stabilities of various Cu catalysts, the exposed ratios of the facets of Cu, Cu₂O and CuO can be obtained via the Wulff construction based on surface energies. As an approximation, the surface energies of numerous facets under vacuum condition (Table S2) were calculated. As shown in Fig. S1 and Table S2, the results indicate that the most stable (111) surface account for the largest percentage (> 70%) of the total exposed surface areas of for Cu, Cu₂O, and CuO catalysts. Accordingly, the (111) surface determines the overall performance of the total surface for CuO, Cu₂O, and Cu.

As mentioned above, since the (111) surface is proved to be the dominantly exposed surface, and possess the highest stability among different CuO, Cu₂O, and Cu surfaces, the catalytic performance should be closely related to the (111) surface [59,74-76]. Thus, CuO(111), $Cu_2O(111)$, and Cu(111) surfaces representing different valence states are addressed to identify the effect of Cu valence state on the selectivity towards C2H4 formation, and the oxygen-vacancy CuO and Cu2O surfaces are considered as the intermediate state in the reduction reactions of CuO \rightarrow Cu₂O and Cu₂O \rightarrow Cu. Thus, the process of CuO(111)-perfect \rightarrow CuO(111)-defective \rightarrow Cu₂O(111)-perfect \rightarrow Cu₂O(111)-defective \rightarrow Cu(111) is employed to simulate the reduction process of $CuO \rightarrow Cu_2O \rightarrow Cu$ with different Cu valence state and surface structure. Firstly, since the adsorption free energy of C₂H₂ is lower than that of C₂H₄, the perfect CuO(111) surface almost has no selectivity towards C_2H_4 formation. Then, the defective CuO(111) surface is formed along with the reduction process, and presents a better selectivity towards C₂H₄ formation. Subsequently, the perfect Cu₂O(111) surface exhibits



Reaction coordinate

Fig. 13. Free energy profiles for the selective hydrogenation of C_2H_2 to gas phase C_2H_4 on NiCu(111), PdCu(111), PtCu(111), AuCu(111) surfaces with C_2H_4 easy desorption rather than being hydrogenated, as well as Pd(111) surface with C_2H_4 being hydrogenated rather than its desorption at (a) 520 K, (b) 0 K; (ad) and (g) stand for the adsorbed and gas phase states, respectively.



Fig. 14. The variation tendency of the activity (black) and selectivity (red) as a function of surface *d*-band center in the selective hydrogenation of C_2H_2 to C_2H_4 on Cu(111), MCu(111)(M = Ni, Pd, Pt, Au), and Pd(111) surfaces.

a poor selectivity towards C_2H_4 formation due to the over-hydrogenation of C_2H_2 to ethane. Further, with the increasing of reduction degree, the formed defective $Cu_2O(111)$ surface presents a better selectivity towards C_2H_4 formation. Finally, after the complete reduction, Cu(111)surface also exhibits a high selectivity towards C_2H_4 formation. These results indicate that along with the change of valence state and surface structure in the reduction process of $Cu(II) \rightarrow Cu(I) \rightarrow Cu(0)$, the intermediate states of reduction reaction $Cu(II) \rightarrow Cu(I)$, $Cu(I) \rightarrow Cu(0)$ and Cu(0), *i.e.*, the defective CuO(111) and $Cu_2O(111)$ surfaces, as well as Cu(111) surface, present a better selectivity towards C_2H_4 formation.

The selectivity towards C_2H_4 formation of Cu(0), Cu(I) and Cu(II) is in the order of Cu(I) > Cu(0) > Cu(II), although the order of catalytic activities of three Cu catalysts for C_2H_4 formation are Cu(0) > Cu (I) > Cu(II). Thus, both Cu(0) and Cu(I) should be especially considered under the realistic experiments or Cu(I) should be the focus of the defective surface study and Cu(0) should be the focus of stable and dominantly exposed (111) surface evaluation.

3.6. Effect of surface alloying on the selectivity and activity in C_2H_4 formation on MCu(111) (M = Ni, Pd, Pt, Au) surfaces

Above results indicate that in C_2H_2 hydrogenation to C_2H_4 , Cu(0) catalyst, as the most stable substance among Cu, Cu₂O and CuO catalysts in reducing atmosphere [92–98], mainly focuses on the stable and dominantly exposed Cu(111) surface. Moreover, Cu(0) catalyst exhibits a higher catalytic activity than Cu(II) and Cu(I) catalysts. However, compared to Pd catalyst, Cu(0) catalyst still has a relatively low activity. Thus, aiming at improving activity and maintaining high selectivity, the effects of promoters Ni, Pd, Pt, and Au on the selectivity and activity in C₂H₄ formation over Cu(111) surface are examined. Pd (111) is also considered to facilitate a comparison with MCu(111) (M = Ni, Pd, Pt, Au) surfaces.

3.6.1. The adsorption of $C_2H_x(x = 2-4)$ species

As shown in Fig. 6, since the adsorption free energies of C_2H_2 are much larger than those of C_2H_4 over MCu(111)(M = Ni, Pd, Pt, Au) and Pd(111) surfaces, trace C_2H_2 in C_2H_4 -rich feed gas can be fully adsorbed over these surfaces at 520 and 0 K. Meanwhile, as listed in Table 1, the adsorption free energies of C_2 species on MCu(111) (M = Ni, Pd, Pt) are higher than those on Cu(111), while those on AuCu(111) are lower than those on Cu(111).

3.6.2. Selectivity of C_2H_4 formation on MCu(111) and Pd (111)surfaces

On MCu(111)(M = Ni, Pd, Pt, Au) and Pd(111) surfaces, C_2H_2 , C_2H_3 , and CHCH₃ species likely hydrogenate rather than desorption. As shown in Fig. 11(a)–(c), MCu(111)(M = Ni, Pd, Pt) surfaces exhibit a high selectivity towards C_2H_4 formation because C_2H_4 desorption pathway is more favorable than other two pathways. The ΔG_a (see Table 2) are 19.6, 39.8 and 21.8 kJ·mol⁻¹, respectively, and the ΔG_a on Cu(111) surface is 33.7 kJ·mol⁻¹. AuCu(111) surface (see Fig. 11(d)) presents a relatively low selectivity towards C_2H_4 formation because both CHCH₃ intermediate and C_2H_4 desorption pathways are two parallel pathways with the same overall activation free energy. Pd(111) surface (see Fig. 12) with the ΔG_a of -51.5 kJ·mol⁻¹ presents a low selectivity towards C_2H_4 to ethane, which agrees with the reported results on Pd catalyst [6,43,99,100].

Therefore, PdCu(111) has the highest value of ΔG_a (39.8 kJ·mol⁻¹) among different Cu alloyed surfaces, which is also larger than that of Cu (111) surface (33.7 kJ·mol⁻¹). Although AuCu(111) surface presents a relatively low selectivity towards C₂H₄ formation, it still much better than Pd(111) surface. In summary, the selectivity towards C₂H₄ formation is in the order of PdCu(111) > Cu(111) > PtCu (111) > NiCu(111) > AuCu(111) > Pd(111).

3.6.3. Activity of C_2H_4 formation on MCu(111)(M = Ni, Pd, Pt, Au) surfaces

Above mentioned MCu(111)(M = Ni, Pd, Pt) surfaces exhibit a better selectivity towards C_2H_4 formation. As presented in Fig. 13 and Table 3, the reaction rate of C_2H_2 hydrogenation to C_2H_4 on Cu(111) surface ($2.52 \times 10^0 \text{ s}^{-1} \text{ site}^{-1}$) is significantly high when Cu(111) surface is alloyed with Pd and Pt (2.78×10^7 and

 $3.31\times10^6\,s^{-1}\,site^{-1})$, while it decreases after the surface is doped with Ni $(3.58\times10^{-2}\,s^{-1}\,site^{-1})$. In addition, the reaction rates of C_2H_4 formation on AuCu(111) and Pd(111) are 1.07×10^{-2} and $8.80\times10^0\,s^{-1}\,site^{-1}$, respectively. Thus, PdCu(111) is the most active surface towards C_2H_4 formation, even when individual Cu(111), Pd (111) surfaces, and MCu(111) surfaces are included for comparison.

3.6.4. The effects of surface alloying on the selectivity and activity in C_2H_4 formation

Fig. 14 presents the variation in selectivity and activity as a function of the surface *d*-band center over various Cu-based catalysts, in which the values of lgr and ΔG_a in Y axis are employed to represent the activity and selectivity, respectively. In addition, due to the low selectivity of AuCu(111) towards C₂H₄ formation, its ΔG_a qualitatively falls between NiCu(111) and Pd(111) surfaces in spite of the mean-inglessness of the value.

From Fig. 14, two roughly volcano types of curves are observed on the promoter-doped Cu catalysts. Obviously, both AuCu(111) and Pd (111) surfaces present a low selectivity towards C₂H₄ formation due to the lowest and highest *d*-band centers, respectively. PdCu(111) surface with the surface d-band center at a medium site exhibits the best catalytic activity and selectivity towards C₂H₄ formation among all MCu (111) alloyed surfaces, as well as Cu(111) and Pd(111) surface. Kyriakou et al. [32] explored a catalyst with doping a small quantity of Pd into Cu catalyst, in which Cu is the dominant component and Pd is the promoter, it exhibits the higher C₂H₄ selectivity compared to the pure Cu or Pd alone. McCue et al. [33,34] prepared Cu/Al₂O₃ catalyst modified with Pd by co-impregnation, sequential impregnation and a colloidal approach, when the Cu:Pd ratio sets at 50:1, it presents 80% selectivity to C₂H₄ formation and more than 99% conversion. These reported experiments confirm that the promoter Pd-doped Cu catalyst presents high selectivity towards C₂H₄ formation, and support our calculated results, which provide an explanation at an electronic level for PdCu bimetallic catalysts with the high activity and selectivity towards C₂H₄ formation observed experimentally [32-34,101].

As a result, the selectivity of the promoter-doped Cu(0) catalysts towards C_2H_4 formation has a correlation with the surface *d*-band centers, when the surface *d*-band center is located at a medium range, the catalysts exhibit a better selectivity towards C_2H_4 formation. More importantly, on the basis of these correlations, we not only predict the selectivity towards C_2H_4 formation on all active Cu(0) catalyst surfaces by analyzing their surface properties, but also deduce the promoters with the best catalytic performance towards C_2H_4 formation using *d*band centers as a "descriptor".

4. Conclusions

The fundamental relationship between the properties of Cu-based catalysts and their performances on C2H2 hydrogenation to C2H4 is successfully understood by using computation chemistry. The challenges with these catalysts and their applications in removal of C₂H₂ for green and efficient C₂H₄ polymerization are identified. Also, the solutions for overcoming the challenges are proposed. Furthermore, the results achieved in this research not only benefit the targeted research the removal of C₂H₂ from C₂H₄ but also development of new Cu-based catalysts for other desired or undesired chemical conversions. Firstly, Cu based materials have been considered to be promising catalysts due to their acceptable prices but high performances. The oxidation states of the Cu materials determine their catalytic performances not only in the studied process but also in various other processes. Also, it is expected that the discovered intrinsic relationships between the oxidation states of Cu and their roles in catalysis could also shed light on other multi oxidation state metal based catalysis research. Finally, reaction pathways set for the Cu-based catalytic C2H2 conversion research are instrumental to other metal-catalyzed hydrocarbon conversion.

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Appendix A. Supplementary data

The differences between DFT and DFT-D calculations (Part 1), surface energy and Wullf construction for different surfaces (Part 2), the most stable adsorption configurations of $C_2H_x(x = 2-4)$ species (Part 3), free energies and the corresponding structures for the pathways of C_2H_4 desorption, C_2H_4 and CHCH₃ intermediates (Part 4), two-step model and the adsorption free energy barrier (Part 5), and surface *d*-band center (Part 6) are presented in detail.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2018.06.083.

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