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Cost-Effective Palladium-Doped Cu Bimetallic Materials to Tune Selectivity and Activity by using Doped Atom Ensembles as Active Sites for Efficient Removal of Acetylene from Ethylene

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The catalytic activity and selectivity of cost-effective noble-metal-doped common metal materials strongly depend on the doped atom ensemble in specific arrangements to provide active sites. In this study, aiming at insight into the doped atom ensembles as active sites for tuning the selectivity and activity towards the target reaction, different doped noble metal Pd atom ensembles for cost-effective Pd-doped Cu catalysts act as active sites to investigate the activity and selectivity towards the efficient removal of acetylene from ethylene by using density functional theory calculations. The results show that an ensemble composed of one surface and its joint sub-layer Pd atoms in the Cu catalyst as active sites enhance both the selectivity and activity of C_2H_4 formation caused by adjusting the catalyst surface electronic structure. Moreover, the surface d-band center of the Pd-doped Cu catalyst can act as an effective "descriptor" for the rapid screening of catalytic activity in the design of improved catalysts with the noble-metal-doped common metal. Further, the ensemble composed of one surface and its joint sublayer doped Pd atoms as active sites in the cost-effective Pd-doped Cu bimetallic catalysts is an efficient approach to finely tune the activity and selectivity towards the efficient removal of acetylene from ethylene.

1. Introduction

In heterogeneous catalysis, cost-effective noble-metal-doped common metal materials have been widely used, in which the "ensemble effect" with a very limited number of noble atoms often acts as active site, and usually plays an essential role in catalytic reactions.[1–3] Especially, the catalytic activity and selectivity of bimetallic catalysts with a small amount of noble metal in the common elements strongly depend on "ensemble effects" that describe the synergistic behavior of different constituents in specific arrangements.[2, 4] Thus, identifying the structure and nature of such ensembles as active sites is an ef-

fective approach to understand and enhance the catalytic performance of bimetallic catalysts.[5–10]

Nowadays, cost-effective noble metal Pd-doped Cu bimetallic catalysts have started to be applied in the efficient removal of acetylene from ethylene by C_2H_2 hydrogenation to C_2H_4;[11–15] in this catalytic reaction, C_2H_2 wastes that degrade the Ziegler–Natta catalysts for C_2H_4 polymerization are converted into industrial feed stock C_2H_4. Even doping a very small quantity of noble-metal Pd into a Cu catalyst can exhibit a higher activity and selectivity towards C_2H_2 hydrogenation to

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C_2H_4 than the pure Cu or Pd alone.[1,14,15] For Pd-doped Cu bi-metallic catalysts, one arrangement leading to an "ensemble effect" that has attracted attention is an ensemble of surface Pd atoms acting as active sites;[1] the other is an ensemble composed of surface and sublayer Pd atoms acting as active sites.[3,14,16,17]

Although demonstrated experimentally,[1,14,15] the theoretical understanding of this catalytic reaction is lacking, and the actual structure and nature of active sites in Pd-doped Cu bi-metallic catalysts catalyzing C_2H_2 hydrogenation, whether as a result of an ensemble of surface Pd atoms as active sites or an ensemble composed of surface and sublayer Pd atoms as active sites, still remains unclear. Further, the ensemble effect on the activity and selectivity towards C_2H_4 formation is also unknown. Up to now, it is still difficult to elucidate the structure and nature of the active site(s) and the ensemble roles by using experiments alone. Fortunately, calculations using density functional theory (DFT) can be used to understand the details of catalytic phenomena, the structure and nature of active sites, the ensemble role of atomic arrangement, and the mechanistic details. Such detailed knowledge can be used to design catalysts with superior performance and specific experiments to better understand mechanistic details.[18–25]

This study was designed to make progress in understanding the catalytic performances of the cost-effective Pd-doped Cu bimetallic catalysts towards efficient removal of acetylene from ethylene, and gain insight into the effects of doped noble-metal atom ensembles as active sites on the catalytic activity and selectivity by using density functional theory (DFT) calculations. Here, different types of doped Pd atom ensembles as active sites, including the ensemble of surface Pd atoms and the ensemble composed of surface–sublayer Pd atom configurations, are considered. The results not only find the ensemble arrangements that are most suitable to enhance the activity and selectivity of active sites towards C_2H_4 formation over Pd-doped Cu bimetallic catalysts, but also provide an efficient approach to tune the selectivity and activity of cost-effective bimetallic catalysts using a very limited quantity of noble-metal atoms doped into the common elements in industrially key hydrogenation reactions.

2. Computational Details

2.1. Computational method

DFT calculations were performed by using the Dmol³ program package in Materials Studio 5.5,[26,27] the generalized gradient approximation (GGA) with the exchange-correlation functional PBE proposed by Perdew–Burke–Ernzerhof[28,29] was employed. In the computation, 2.0×10^{-5} Ha, 4.0×10^{-3} Ha Å^{-1}, and 5.0×10^{-3} Å were set for the energy convergence, maximum force, and maximum distance. To expand the valence electron function, the double numerical basis set with a polarization d-function (DNP) was selected.[30] A $3\times3\times1$ k-point sampling in the surface Brillouin zone was used for analyzing Cu(111) and Pd-doped Cu surfaces. The orbital cutoff range was set as medium quality, and 0.005 Hartree was set for the smearing value. An

effective core potential (ECP) is used for Cu and Pd atoms and all-electron basis sets for other atoms.

To obtain accurate activation barriers of elementary reactions involved in the selective hydrogenation of C_2H_2, the transition state (TS) of every elementary reaction was searched by using the complete LST (linear synchronous transit)/QST (quadratic synchronous transit) method.[31,32] All transition states were confirmed by ensuring only one imaginary frequency, and by using TS confirmation to show that the transition state is connected with the reactant and product.

Oligomerization of C_2H_2 can be effectively inhibited by high H_2/C_2H_2 ratios and high temperatures, reducing the formation of "green oil",[4,15,33,34] so a high temperature of 425 K used in experiments is considered. Contributions of zero-point vibrational energy (ZPE), thermal energy, and entropy to the molar Gibbs free energy have been included. The entropies of gaseous H_2, C_2H_2, and C_2H_4 species under standard conditions are taken from experimental databases, and are used for calculating the entropies at 425 K. The total pressure is set to 1.0 atm along with an H_2/C_2H_2 ratio of 10:1, leading to partial pressures of H_2, C_2H_2, and C_2H_4 of 0.1, 0.01, and 0.89 atm, respectively, similar to experimental conditions used for comparison.[33]

Further, it is found that the Pd-based catalysts during the C_2H_2 hydrogenation reaction can form Pd hydride and Pd carbide owing to the formation of subsurface species like C and H species, which can affect the selectivity of C_2H_2 hydrogenation.[33,35–37] Hu et al. have proved that the subsurface H atoms on the Pd catalyst can improve the selectivity of ethylene more than the pure Pd catalysts.[38] However, for CuPd catalysts, recent works from Gapipaud et al.[39] and Friedrich et al.[40] suggest that CuPd mixtures do not form a hydride phase for Cu/Pd bulk ratios of 0.5 and above. Interestingly, Anderson et al.[15] by using temperature-programmed reduction (TPR) measurements found that on CuPd catalysts, there is no Pd-hydride for the CuPd ratios 100:1, 50:1, 25:1, and 10:1. Thus, the formation of Pd-hydride is difficult on CuPd catalysts, and the effect of Pd-hydride formation on the hydrogenation of C_2H_2 is not considered in this study. Detailed descriptions of the calculations of Gibbs free energies of gaseous and adsorbed species, and the reactions are presented in the Part 1 of the Supporting Information.

2.2. Surface model

For the Cu catalyst, the (111) surface is the most stable and has the most dominantly exposed crystal facets with the lowest surface energy,[41–43] so it is generally chosen as the representative surface for experimental and theoretical studies.[3,14,41–43] Cu(111) is cleaved from the bulk with the lattice constant of 3.615 Å, and it is modeled by a four-layer $p(3\times3)$ periodic slab with nine atoms in each layer (Figure 1 (a)). The vacuum gap is set to 15 Å to separate the slabs, which is large enough to avoid interactions between the slabs.

To probe the ensemble effect of surface Pd atoms as the sites controlling the activity and selectivity in the selective hydrogenation of C_2H_2 over Pd-doped Cu bimetallic catalysts, Cu atoms on the outmost layer are replaced by Pd atoms to con-
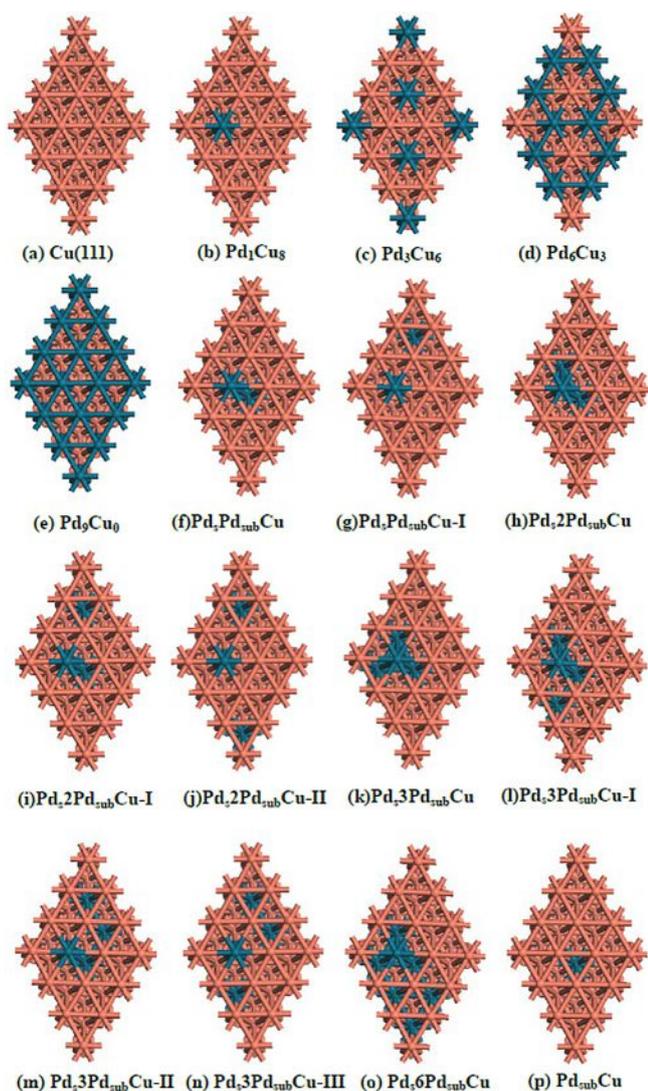
Figure 1. Surface structures with the different distributions of surface and sublayer Pd ensembles incorporated into a Cu surface.

struct PdCu bimetallic surfaces with different Pd geometrical distributions (Figure 1 (b)–(e)). The nearest-neighbor arrangement is not considered as such a pattern has been firmly excluded by the experiments,[14] so four PdCu(111) surface configurations are likely, that is, six, three, and one outmost layer Cu atoms on the Cu(111) surface replaced by Pd atoms, which are named as Pd_6Cu_3, Pd_3Cu_6, and Pd_1Cu_8, respectively. Meanwhile, all nine outmost layer Cu atoms on Cu(111) replaced by Pd atoms is also considered, and denoted as Pd_9Cu_0. In addition, it should be noted that the Pd-Cu-Cu trimer ensemble appears on the Pd_1Cu_8 and Pd_3Cu_6 surfaces, and the Pd-Cu dimer ensemble appears on the Pd_6Cu_3 surface, which can also present the effect of Pd-Cu-Cu trimer and Pd-Cu dimer ensembles on the formation of ethylene.

A specific aim of the calculations is to examine the ensemble when surface and sublayer Pd atoms interact to create active sites that drive the activity and selectivity in C_2H_2 hydrogenation. As such, a series of PdCu bimetallic surfaces involving both the surface and sublayer Pd atoms are studied (Fig-

ure 1 (f)–(o)), all surface-sublayer Pd-doped Cu catalysts are based on the Pd_1Cu_8 surface, which is found to have the highest selectivity towards C_2H_4 formation in the results presented below.

Cu atoms in the sublayer of Pd_1Cu_8 are replaced with Pd atoms to construct PdCu bimetallic surfaces with different sublayer Pd geometrical distributions, which leads to different connection modes between one surface Pd atom and the sublayer Pd atoms. In addition, the case of a $Pd_{sub}Cu$ surface with one Cu atom in the sublayer replaced by one Pd atom is also considered (Figure 1 (p)).

During the calculations, the top two layers of the PdCu bimetallic surfaces together with the adsorbed gaseous species were allowed to relax, whereas the bottom two layers were fixed at their bulk structure, resembling the unperturbed bulk atoms.

3. Results and Discussion

3.1. Proposed mechanism for the selective hydrogenation of C_2H_2

For the selective hydrogenation of C_2H_2, two key factors affect the selectivity of C_2H_4 formation: one is the over-hydrogenation of C_2H_2 to ethane; the other is the formation of "green oil" through the polymerization of C_2H_2.[15,33,34] Previous experiments have shown that when the temperature is 425 K, and the H_2/C_2H_2 ratio is high,[15] the formation of "green oil" can be inhibited. Introducing Pd into the Cu(111) surface decreases the activation barrier of H_2 dissociation to 0.29 eV from the range 0.45–0.50 eV on the Cu(111) surface.[3] To focus this study specifically on C_2H_2 over-hydrogenation to ethane, the temperature is set to 425 K and the H_2/C_2H_2 ratio is set to 10:1.

Three potential pathways are examined to determine the optimal pathway in the selective hydrogenation of C_2H_2,[33] as shown in Figure 2, the first path, the C_2H_4 desorption pathway, is that C_2H_4 is formed via the C_2H_3 intermediate; C_2H_4 then readily desorbs from the catalyst surface instead of being hydrogenated to ethane. The latter two paths are the over-hydrogenation of C_2H_2 via C_2H_4 or CH_3CH intermediates to form C_2H_5, followed by its hydrogenation to ethane, which are denoted as the C_2H_4 and CH_3CH intermediate pathways, respectively. Thus, when the C_2H_4 desorption pathway is the preferred pathway, the corresponding catalyst exhibits a better se-
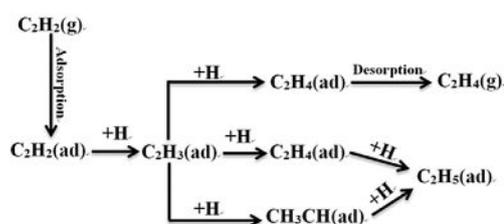
Figure 2. Three possible reaction pathways involved in the selective hydrogenation of C_2H_2 via C_2H_4 desorption pathway, as well as CH_3CH and C_2H_4 intermediate pathways, respectively; (ad) and (g) stand for the adsorbed and gas-phase states, respectively.

lectivity towards C_2H_4 formation. If either the C_2H_4 or $CHCH_3$ intermediate pathways is the preferred pathway, the primary product of C_2H_2 hydrogenation is ethane, and the catalyst will have a poor selectivity towards C_2H_4 formation.

3.2. Adsorption of C_2H_x ($x = 2$–5) and H species

The adsorption of C_2H_x ($x = 2$–5) and H species in the selective hydrogenation of C_2H_2 on Cu(111) and Pd-doped Cu surfaces is examined explicitly as a potentially important set of reaction pathways.[44,45] The most stable adsorption configurations of these species are presented in Figures S3–S5 (in the Supporting Information) and the adsorption free energies at 425 K are listed in Table 1.

Table 1. The adsorption free energies of H and C_2H_x ($x = 2$–5) species involved in the selective hydrogenation of C_2H_2 over different Pd-doped Cu surfaces at 425 K.

Surfaces	Adsorption free energy [kJ mol^{-1}]					
	H	C_2H_2	C_2H_3	C_2H_4	CH_3CH	C_2H_5
Cu(111)	240.7	147.0	201.2	68.1	292.8	111.3
Pd_1Cu_8	243.1	156.5	196.7	89.5	303.6	131.6
Pd_3Cu_6	233.6	144.4	201.6	86.1	288.9	132.4
Pd_6Cu_3	231.4	136.2	206.9	79.8	323.4	132.3
Pd_9Cu_0	237.0	141.9	228.8	92.8	370.5	147.0
$Pd_sPd_{sub}Cu$	246.5	155.5	225.7	100.7	312.6	145.0
$Pd_sPd_{sub}Cu$-I	244.7	160.8	216.0	92.9	316.3	129.3
$Pd_s2Pd_{sub}Cu$	247.6	162.6	214.4	108.0	316.3	153.1
$Pd_s2Pd_{sub}Cu$-I	249.2	164.1	232.5	103.6	317.4	137.8
$Pd_s2Pd_{sub}Cu$-II	246.8	167.5	218.9	105.3	303.6	139.3
$Pd_s3Pd_{sub}Cu$	244.3	165.8	209.3	103.7	318.5	149.4
$Pd_s3Pd_{sub}Cu$-I	224.3	162.0	216.7	106.5	312.1	139.2
$Pd_s3Pd_{sub}Cu$-II	249.8	167.8	217.9	98.2	314.0	129.4
$Pd_s3Pd_{sub}Cu$- III	236.9	163.4	203.8	83.2	301.9	122.3
Pd_s6Pd_{sub}	244.7	168.6	215.5	115.4	330.6	152.3
$Pd_{sub}Cu$	240.6	145.7	201.0	63.8	294.8	114.8

The feed gas in the C_2H_2 process typically contains 0.1–1% C_2H_2 and 89% C_2H_4.[33] Thus, only when the adsorption ability of C_2H_2 is much stronger than that of C_2H_4, one can realize the removal of trace amounts of C_2H_2 from a large amount of C_2H_4. In addition, it is noted that besides the hydrogenation reaction of C_2H_2 to C_2H_4 for the removal of trace amounts of C_2H_2 from a large amount of C_2H_4, the adsorbent-based separation of C_2H_2 from C_2H_4 has also been well demonstrated as an energy- and cost-efficient strategy,[46,47] which is not considered in this study.

The results show that the adsorption ability of C_2H_2 on Pd-doped Cu surfaces is much stronger than that of C_2H_4, which favors the adsorption, activation, and hydrogenation of trace C_2H_2. Further, the adsorption free energy of C_2H_4 on the Pd-doped Cu surface is higher than that on the Cu(111) surface, inhibiting C_2H_4 desorption, which can contribute to the Pd-based catalyst having a lower selectivity towards C_2H_4 formation.

3.3. C_2H_2 hydrogenation on Cu(111) and Pd-doped Cu(111) surfaces

3.3.1. C_2H_2 hydrogenation on the Cu(111) surface

As shown in Figure 3, C_2H_2 hydrogenation to C_2H_3 via transition state TS1-1 is exothermic (6.1 kJ mol^{-1}) with an activation free energy of 121.6 kJ mol^{-1}. This is lower than the adsorption free energy of C_2H_2 (147.0 kJ mol^{-1}), suggesting that C_2H_2 hydroge-
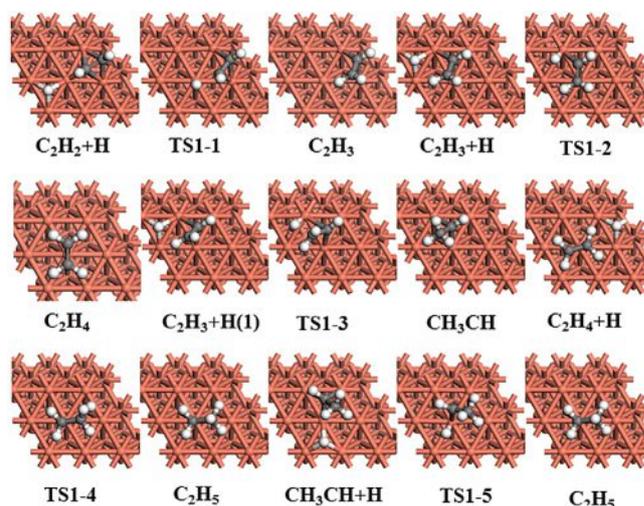
Figure 3. Free energy profiles of three pathways involved in the selective hydrogenation of C_2H_2 on a Cu(111) surface together with the structures of initial states (ISs), transition states (TSs), and final states (FSs).

nation is more favorable than its desorption. C_2H_3 hydrogenation to C_2H_4 via TS1-2 has an activation free energy of 78.1 kJ mol^{-1}, and is exothermic by 76.7 kJ mol^{-1}; then, C_2H_4 desorption from the surface has a free energy of 68.1 kJ mol^{-1}. C_2H_4 hydrogenation to C_2H_5 via TS1-4 has the activation and reaction free energies of 81.1 and -17.0 kJ mol^{-1}, respectively.

Alternatively, C_2H_3 hydrogenation to C_2H_5 via the CH_3CH intermediate has the activation free energies of 101.4 and 61.5 kJ mol^{-1} via TS1-3 and TS1-5 with the reaction energies of -12.3 and -81.4 kJ mol^{-1}, respectively. The activation free energies of C_2H_3 hydrogenation to C_2H_4 and CH_3CH (78.1 and 101.4 kJ mol^{-1}) are much lower than the adsorption free energy of C_2H_3 (201.2 kJ mol^{-1}), suggesting that C_2H_3 hydrogenation can proceed without its desorption. CH_3CH hydrogenation is more favorable than its desorption as the activation free energy of CH_3CH hydrogenation is much lower than its adsorption free energy (61.5 vs. 292.8 kJ mol^{-1}).

C_2H_3 is the common intermediate of three pathways studied, so identifying which pathway is the most favorable is of specific interest. Starting from $C_2H_3 + H$ species (Figure 3), the overall activation free energies of three pathways are 72.0, 72.0, and 95.3 kJ mol^{-1}, respectively, indicating that the CH_3CH intermediate pathway is unfavorable. However, C_2H_4 prefers to desorb from the catalyst surface rather than being hydrogenated to C_2H_5 (68.1 vs. 81.1 kJ mol^{-1}), namely, the C_2H_4 desorption pathway is the optimal pathway to form gaseous C_2H_4, and therefore the Cu(111) surface exhibits a better selectivity towards C_2H_4 formation.

For the selective hydrogenation process of C_2H_2, besides C_2H_4 over-hydrogenation to ethane, the high molecular weight oligomeric species such as oligomers from C_2H_2 polymerization is the very important issue.[48] These oligomers and polymers are commonly referred to as C_{4+}, and the liquid part of C_{4+} is named "green oil";[49] moreover, previous studies[34,50,51] have proposed that 1,3-butadiene may be the precursor for green oil formation. Thus, the formation of 1,3-butadiene is examined. The hydrogenation–coupling pathway and coupling–hydrogenation pathway are used to investigate the formation of 1,3-butadiene.[52]

As shown in Figure S18 (in the Supporting Information), the $C_2H_3+C_2H_3$ pathway is the most favorable reaction pathway to form 1,3-butadiene on the Cu(111) surface, this pathway has the overall activation free energy of 209.1 kJ mol^{-1}, which is higher than that the formation of ethylene (121.6 kJ mol^{-1}), suggesting that the formation of C_2H_4 is much easier than the formation of 1,3-butadiene over the Cu(111) surface. Moreover, when Pd is doped into Cu catalysts, it enhances the dissociation of H_2,[3] which is more favorable for the hydrogenation of C_2H_2, and inhibits the coupling reaction to 1,3-butadiene, which means that Pd-doped Cu catalysts are more favorable for the formation of C_2H_4 instead of the formation of 1,3-butadiene.

3.3.2. C_2H_2 hydrogenation on the Pd-doped Cu(111) surface

Similar to the Cu(111) surface, on Pd_9Cu_0, Pd_6Cu_3, Pd_3Cu_6, and Pd_1Cu_8 surfaces, starting from C_2H_3+H species (Figure S6 in the Supporting Information), the pathways via the C_2H_4 intermediate are more favorable than that via the $CHCH_3$ intermediate. Moreover, C_2H_4 prefers desorption from the catalyst surface over its hydrogenation on Pd_6Cu_3, Pd_3Cu_6, and Pd_1Cu_8 surfaces, which exhibits a better selectivity towards C_2H_4 formation. However, the Pd_9Cu_0 surface more readily results in C_2H_2 over-hydrogenation to ethane as C_2H_4 prefers to be hydrogenated instead of desorbing. In addition, the Pd_9Cu_0 surface with a Pd monolayer supported on Cu(111) has a similar catalytic performance with Pd catalysts; both exhibit a poor selectivity towards C_2H_4 formation.[33,53–59]

As the number of doped Pd atoms over the Cu(111) surface increases, the activation free energy of C_2H_2 hydrogenation decreases, suggesting that the catalytic activity of PdCu bimetallic catalyst in C_2H_2 hydrogenation is enhanced, which agrees with the experimental facts that Pd catalyst exhibits a higher catalytic activity in C_2H_2 hydrogenation.[19,33,50]

3.3.3. The selectivity towards C_2H_4 formation on Cu(111) and Pd-doped Cu(111) surfaces

As mentioned above, as the CH_3CH intermediate pathway is less likely to occur, it has little effect on the selectivity towards C_2H_4 formation; as a result, both C_2H_4 hydrogenation and its desorption determine the selectivity towards C_2H_4 formation. In this study, aiming at quantitatively evaluating the selectivity towards C_2H_4 formation over Cu-based catalysts, the difference between the activation free energy of C_2H_4 hydrogenation and

the absolute value of C_2H_4 adsorption free energy, ΔG_a, is obtained according to Equation (1), which has been widely used.[33,60,61]

$$\Delta G_a = G_a - |G_{ads}| \tag{1}$$

Where G_a is the activation free energy of C_2H_4 hydrogenation, and G_{ads} is the adsorption free energy of C_2H_4. The more positive ΔG_a is, the better the selectivity towards C_2H_4 formation is.

As listed in Table 2, according to the value of ΔG_a (kJ mol^{-1}), the selectivity towards C_2H_4 formation follows the order Pd_1Cu_8 (49.7) > Pd_3Cu_6 (34.1) > Cu(111) (13.0) > Pd_6Cu_3 (8.1) > Pd_9Cu_0 (−3.0), suggesting that when one or three Pd atoms as the monomer is doped into a Cu(111) surface, Pd_1Cu_8 and Pd_3Cu_6 surfaces present a better selectivity towards C_2H_4 formation than a Cu(111) surface does. Whereas Pd_6Cu_3 and Pd_9Cu_0 surfaces exhibit poorer selectivity towards C_2H_4 formation than a Cu(111) surface does, especially, the Pd_9Cu_0 surface presents a similar selectivity with Pd catalysts; both have a good selectivity towards ethane instead of C_2H_4.

Table 2. Hydrogenation activation free energy (G_a in kJ^{-1} mol^{-1}) and the adsorption free energy (G_{ads} in kJ^{-1} mol^{-1}) of C_2H_4, the differences (ΔG_a in kJ^{-1} mol^{-1}) between G_a and G_{ads}, as well as the reaction rate (r in s^{-1} site^{-1}) of C_2H_2 hydrogenation to C_2H_4 over different Pd-doped Cu surfaces at 425 K.

Surfaces	G_a	G_{ads}	ΔG_a	r
Cu(111)	81.1	68.1	13.0	1.00×10^{-2}
Pd_1Cu_8	139.2	89.5	49.7	5.79×10^{1}
Pd_3Cu_6	120.2	86.1	34.1	4.88×10^{1}
Pd_6Cu_3	87.9	79.8	8.1	4.27×10^{3}
Pd_9Cu_0	89.8	92.8	-3.0	5.01×10^{4}
$Pd_sPd_{sub}Cu$	132.9	100.7	32.2	1.06×10^{9}
$Pd_sPd_{sub}Cu$-I	124.5	92.9	31.6	3.85×10^{2}
$Pd_s2Pd_{sub}Cu$	153.8	108.0	45.8	9.78×10^{5}
$Pd_s2Pd_{sub}Cu$-I	125.5	103.6	21.9	4.93×10^{0}
$Pd_s2Pd_{sub}Cu$-II	125.0	105.3	19.7	5.07×10^{0}
$Pd_s3Pd_{sub}Cu$	125.1	103.7	21.4	9.73×10^{0}
$Pd_s3Pd_{sub}Cu$-I	113.8	106.5	7.3	6.30×10^{1}
$Pd_s3Pd_{sub}Cu$-II	139.6	98.2	41.4	2.57×10^{0}
$Pd_s3Pd_{sub}Cu$-III	119.2	83.2	36.0	7.00×10^{-1}
$Pd_s6Pd_{sub}Cu$	145.7	115.4	30.3	1.00×10^{1}
$Pd_{sub}Cu$	106.1	63.3	42.8	3.94×10^{-3}

3.3.4. The activity of C_2H_4 formation

Aiming at quantitatively describing the catalytic activity of Pd-doped Cu catalysts in C_2H_2 hydrogenation to C_2H_4, on the basis of the two-step model reported by Hu et al.[62,63] (see details in Part 2 of the Supporting Information), the reaction rate can be obtained, in which the coverage of adsorbed species in the selective hydrogenation of C_2H_2 is considered.

The reaction rates (s^{-1} site^{-1}) of C_2H_2 hydrogenation to C_2H_4 (see Table 2) show that the catalytic activity follows the order: Pd_9Cu_0 (5.01×10^4) > Pd_6Cu_3 (4.27×10^3) > Pd_1Cu_8 (5.79×10^1) > Pd_3Cu_6 (4.88×10^1) > Cu(111) (1.00×10^{-2}), namely, with the increasing number of doped Pd atoms over a Cu(111) surface, the catalytic activity of a Pd-doped Cu(111) surface increases.

3.3.5. The ensemble effects of surface Pd atoms as active sites on the activity and selectivity

Projected density of states (pDOS) is calculated to deeply illustrate the effects of the surface Pd ensemble on the activity and selectivity of C_2H_4 formation, the d-band center of Pd_1Cu_8, Pd_3Cu_6, Pd_6Cu_3, and Pd_9Cu_0 surfaces is shown in Figure 4 (details in Figure S16 in the Supporting Information), the results show that as the number of doped Pd atoms increases, the catalytic activity of C_2H_4 formation increases, accordingly, the d-band center is far from the Fermi energy level. According to the values of ΔG_a, the selectivity towards C_2H_4 formation decreases, which is attributed to the increasing catalytic activity in C_2H_4 hydrogenation to C_2H_5, and therefore in ethane formation. In addition, the findings by Pallassana and Neurock[64] on C_2H_4 hydrogenation suggest that the C—H bond activation of ethyl and ethylene is primarily guided by electron-back donation to the antibonding σCH* orbital, the catalytic activity of C—H bond formation increases on Pd catalyst surfaces where the d-band is far from the Fermi level. These also agree with the previous studies about CH_x hydrogenation to CH_4.[65–67]

The above results show that over Pd-doped Cu(111) surfaces, the higher the selectivity towards C_2H_4 formation is, the lower the activity towards C_2H_4 formation is. Moreover, compared with Cu(111), both Pd_1Cu_8 and Pd_3Cu_6 surfaces with only surface single-atom Pd monomer sites present a high selectivity and a relatively low activity in C_2H_4 formation, whereas Pd_6Cu_3, Pd_9Cu_0, and Pd(111) surfaces exhibit a low selectivity and a relatively high activity owing to the existence of surface Pd dimer and trimer sites. These results also mean that the Pd-Cu-Cu trimer ensemble over Pd_1Cu_8 and Pd_3Cu_6 surfaces is of benefit for the selectivity toward C_2H_4 formation, and the Pd-Cu dimer ensemble is of benefit for the activity of C_2H_4 formation. Our results agree with the theoretical and experimental studies by Feng et al.[68] that the (110) surface of $Pm\bar{3}m$ PdIn with single-atom Pd sites shows high selectivity for C_2H_2 hydro-

genation to C_2H_4, whereas the (111) surface of $P4/mmm$ Pd_3In with Pd trimer sites shows low selectivity. Thus, the catalytic activity and selectivity of C_2H_4 formation over a Pd-doped Cu(111) surface markedly depend on the Pd geometrical distribution, namely, the surface Pd ensemble effect.[7,9]

Overall, for the surface ensemble, these surface ensemble models can also present the surface Pd segregation over the Cu(111) surface, a Pd-doped Cu(111) surface with the reduction of contiguous Pd sites as active sites is highly efficient in C_2H_2 hydrogenation to C_2H_4, which can suppress ethane formation as a result of the surface Pd ensemble. Particularly, the Pd_1Cu_8 surface with the single-atom Pd sites and the smallest surface Pd ensemble significantly enhances the selectivity towards C_2H_4 formation. However, it is noted that the activity and selectivity in C_2H_2 hydrogenation to C_2H_4 cannot be tuned simultaneously by a surface Pd ensemble effect over a Cu(111) surface. In addition, the formation energy (kJ mol^{-1})[69–71] (details in the Part 6 of the Supporting Information) shows that the stability of Pd-doped Cu(111) with different surface Pd ensembles follows the order: Pd_9Cu_0 (10.9) < Pd_6Cu_3 (−4.1) < Pd_3Cu_6 (−20.9) < Pd_1Cu_8 (−24.5), indicating that the formation of the Pd_1Cu_8 surface is the most favorable, and it is the most stable among the four Pd-doped Cu(111) surfaces.

3.4. C_2H_2 hydrogenation on the sublayer Pd-doped Pd_1Cu_8 surface

As discussed above, the Pd_1Cu_8 surface exhibits the highest selectivity towards C_2H_4 formation; however, its catalytic activity is moderate. Moreover, it is difficult to simultaneously achieve high selectivity and activity by the Pd ensemble effect over Pd-doped Cu(111) surfaces. Fortunately, a previous study[3] clearly showed that the ensemble composed of the surface and contiguous sublayer Pd atoms over a Cu(111) surface as active sites can effectively enhance the catalytic activity of H_2 dissociation.

In this section, based on the Pd_1Cu_8 surface, we turn our attention to the ensemble composed of the surface and sublayer Pd atoms as active sites, and its effect on the activity and selectivity of C_2H_4 formation. As shown in Figure 1, the sublayer Pd-doped Pd_1Cu_8 surfaces with one, two, three, and six sublayer Cu atoms replaced by Pd atoms are examined, in which the surface and sublayer Pd atoms may be either joined together or unconnected to each other. Moreover, two differences exist between the ensemble of surface joint Pd atoms and that of one surface and its joint sublayer Pd atoms, one is the structure of the models, which represent different ensembles; the other is the electronic properties of the models, which change the catalytic activity and selectivity.

3.4.1. One-sublayer Pd-doped Pd_1Cu_8 surface

For the one-sublayer Pd-doped Pd_1Cu_8 surface, as shown in Figure 1 (f) and (g), two types of surface models exist according to the connection pattern be-
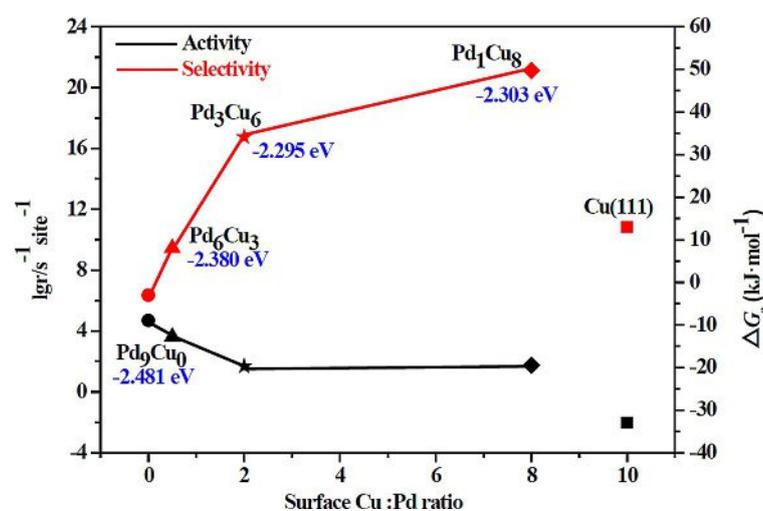
Figure 4. The relationship for the selectivity and the reaction rate of C_2H_2 hydrogenation to C_2H_4 as a function of surface Cu/Pd ratio over different Pd-doped Cu(111) surfaces, and the values of $\lg r$ and ΔG_a on the y axis are employed to represent the catalytic activity and selectivity of the catalyst, respectively.

tween the surface and sublayer Pd atoms, one is a $Pd_sPd_{sub}Cu$ surface with one surface Pd atom connecting only one sublayer Pd atom; the other is a $Pd_sPd_{sub}Cu$-I surface where one surface Pd atom does not connect with only one sublayer Pd atom.

On $Pd_sPd_{sub}Cu$ and $Pd_sPd_{sub}Cu$-I surfaces, the C_2H_4 desorption pathway is favorable to form gaseous C_2H_4 (Figure S8 in the Supporting Information). As listed in Table 2, the selectivity is towards C_2H_4 formation with the ΔG_a on $Pd_sPd_{sub}Cu$ and $Pd_sPd_{sub}Cu$-I surfaces being 32.2 and 31.6 kJ mol^{-1}. The activity of C_2H_4 formation on the $Pd_sPd_{sub}Cu$ surface is much larger than that on the $Pd_sPd_{sub}Cu$-I surface (1.06×10^9 vs. 3.85×10^2 s^{-1} site^{-1}). Thus, the $Pd_sPd_{sub}Cu$ surface exhibits a high activity and selectivity in C_2H_2 hydrogenation to C_2H_4.

3.4.2. Two-sublayer Pd-doped Pd_1Cu_8 surface

For the two-sublayer Pd-doped Pd_1Cu_8 surface, as shown in Figure 1(h)–(j), three types of surface models exist: the $Pd_s2Pd_{sub}Cu$ surface is that with one surface Pd atom connected with two sublayer Pd atoms; $Pd_s2Pd_{sub}Cu$-I surfaces have one surface Pd atom connected with only one sublayer Pd atom; the $Pd_s2Pd_{sub}Cu$-II surface is where one surface Pd atom does not connect with any sublayer Pd atoms.

The C_2H_4 desorption pathway is still the favored pathway to form gaseous C_2H_4 on these three surfaces (Figure S10 in the Supporting Information). As listed in Table 2, the ΔG_a on the $Pd_s2Pd_{sub}Cu$ surface is 45.8 kJ mol^{-1}, which is higher than those on $Pd_s2Pd_{sub}Cu$-I and $Pd_s2Pd_{sub}Cu$-II surfaces (21.9 and 19.7 kJ mol^{-1}). The reaction rate on the $Pd_s2Pd_{sub}Cu$ surface (9.78×10^5 s^{-1} site^{-1}) is much larger than those on $Pd_s2Pd_{sub}Cu$-I and $Pd_s2Pd_{sub}Cu$-II surfaces (4.93×10^0 and 5.07×10^0 s^{-1} site^{-1}). Thus, the $Pd_s2Pd_{sub}Cu$ surface exhibits a high activity and selectivity towards C_2H_4 formation.

3.4.3. Three-sublayer Pd-doped Pd_1Cu_8 surfaces

As shown in Figure 1(k)–(n), four types of surface models are considered, $Pd_s3Pd_{sub}Cu$, $Pd_s3Pd_{sub}Cu$-I, and $Pd_s3Pd_{sub}Cu$-II surfaces, where one surface Pd atom is connected with three, two, and one sublayer Pd atoms, respectively. The $Pd_s3Pd_{sub}Cu$-III surface is where one surface Pd atom does not connect with any sublayer Pd atom.

The C_2H_4 desorption pathway is still the favorable pathway to form gaseous C_2H_4 on these surfaces (Figure S12 in the Supporting Information). As listed in Table 2, the ΔG_a (kJ mol^{-1}) follows the order $Pd_s3Pd_{sub}Cu$-II (41.4) > $Pd_s3Pd_{sub}Cu$-III (36.0) > $Pd_s3Pd_{sub}Cu$ (21.4) > $Pd_s3Pd_{sub}Cu$-I (7.3). The reaction rates on $Pd_s3Pd_{sub}Cu$, $Pd_s3Pd_{sub}Cu$-I, $Pd_s3Pd_{sub}Cu$-II, and $Pd_s3Pd_{sub}Cu$-III surfaces are competitive, with the corresponding values of 9.73×10^0, 6.30×10^1, 2.57×10^0, and 7.00×10^{-1} s^{-1} site^{-1}, respectively. Thus, taking the activity and selectivity into consideration, the $Pd_s3Pd_{sub}Cu$-II surface exhibits a better catalytic performance towards C_2H_4 formation.

3.4.4. Six-sublayer Pd-doped Pd_1Cu_8 surfaces

Aiming at examining the effect of the number of sublayer Pd atoms on the catalytic performance of C_2H_4 formation, a six-sublayer Pd-doped Pd_1Cu_8 surface with one surface Pd atom connecting three sublayer Pd atoms, $Pd_s6Pd_{sub}Cu$ surface, is considered (Figure 1(o)). The results show that the C_2H_4 desorption pathway is more favorable than the other two pathways (Figure S14(a) in the Supporting Information). Both ΔG_a and the reaction rate are 30.3 kJ mol^{-1} and 1.00×10^1 s^{-1} site^{-1}, respectively.

3.4.5. The ensemble effect composed of surface and sublayer Pd atoms as active sites on the activity and selectivity in C_2H_4 formation

As discussed above, for one-, two-, three-, and six-sublayer Pd-doped Pd_1Cu_8 surfaces, there is good selectivity towards C_2H_4 formation with the ΔG_a values of 32.2, 45.8, 41.4, and 30.3 kJ mol^{-1}, respectively. $Pd_sPd_{sub}Cu$, $Pd_s2Pd_{sub}Cu$, $Pd_s3Pd_{sub}Cu$-II, and $Pd_s6Pd_{sub}Cu$ surfaces exhibit high activity for C_2H_4 formation, the reaction rates are 1.06×10^9, 9.78×10^5, 2.57×10^0, and 1.00×10^1 s^{-1} site^{-1}, respectively. The ΔG_a and r on the Pd_1Cu_8 surface are 49.7 kJ mol^{-1} and 5.79×10^1 s^{-1} site^{-1}.

As shown in Figure 5, as the number of sublayer Pd atoms increases, the d-band center (details in Figure S17 in the Supporting Information) approaches the Fermi level, and the catalytic activity decreases. The selectivity towards C_2H_4 formation presents a volcanic curve; the highest selectivity appears on the $Pd_s2Pd_{sub}Cu$ surface, which is close to that on the Pd_1Cu_8 surface. Clearly, compared with the Pd_1Cu_8 surface, both $Pd_sPd_{sub}Cu$ and $Pd_s2Pd_{sub}Cu$ surfaces significantly enhance the catalytic activity of C_2H_4 formation, whereas $Pd_s3Pd_{sub}Cu$-II and $Pd_s6Pd_{sub}Cu$ surfaces do not improve the catalytic activity of C_2H_4 formation. Thus, the catalytic activity of sublayer Pd-doped Pd_1Cu_8 surfaces in C_2H_4 formation markedly depends
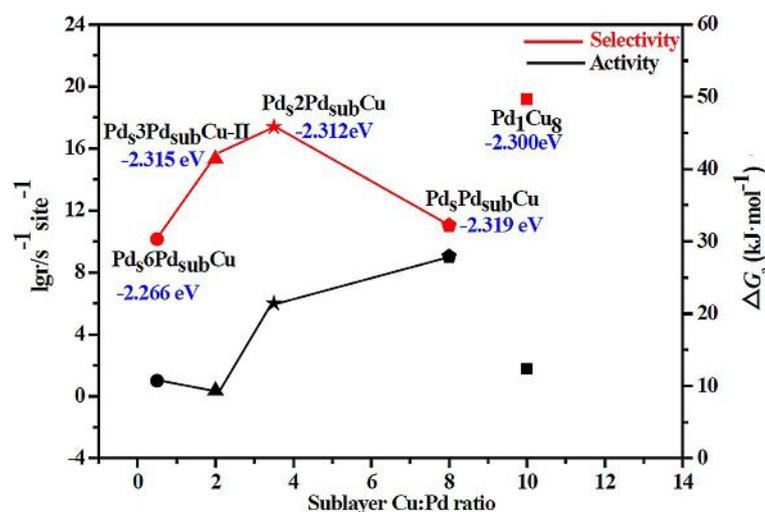
Figure 5. The relationship between the selectivity and the reaction rate of C_2H_2 hydrogenation to C_2H_4 as a function of the surface Cu/Pd ratio over different Pd-doped Pd_1Cu_8 surfaces, and the values of lg r and ΔG_a on the y axis are employed to represent the catalytic activity and selectivity of the catalyst, respectively.

on the number of sublayer Pd atoms, n. Only when $n \leq 2$ do both $Pd_sPd_{sub}Cu$ and $Pd_s2Pd_{sub}Cu$ surfaces with the joint surface–sublayer Pd ensembles exhibit an excellent catalytic activity for C_2H_4 formation, suggesting that only the joint surface–sublayer Pd ensembles play a role as the active sites in C_2H_2 hydrogenation to C_2H_4, namely, the catalytic activity depends on the ensemble arrangement.

3.5. General discussions

These calculations elucidate the activity and selectivity of C_2H_2 hydrogenation to C_2H_4 on Pd-doped Cu surfaces with a particular focus on the ensemble of surface Pd atoms and the ensemble composed of surface and sublayer Pd atoms. The ensemble of surface Pd atoms is an effective way to tune the selectivity towards C_2H_4 formation. The Pd_1Cu_8 surface with the smallest surface Pd ensemble as active sites exhibits the highest selectivity towards C_2H_4 formation ($\Delta G_a = 49.7$ kJ mol^{-1}). On the other hand, the activity of the Pd_1Cu_8 surface is still relatively low ($r = 5.79 \times 10^1$ s^{-1} site^{-1}) compared with the Cu(111) surface ($\Delta G_a = 13.0$ kJ mol^{-1}, $r = 1.00 \times 10^{-2}$ s^{-1} site^{-1}); one isolated Pd atom doped into the sublayer of a Cu(111) surface ($Pd_{sub}Cu$ surface) was examined (see Figure S14(b) in the Supporting Information), suggesting that the C_2H_4 desorption pathway is more favorable than other two pathways: the ΔG_a towards C_2H_4 formation is 42.8 kJ mol^{-1}, the reaction rate is 3.94×10^{-3} s^{-1} site^{-1}. However, compared with the reaction rate on the Cu(111) surface (1.00×10^{-2} s^{-1} site^{-1}), the $Pd_{sub}Cu$ surface is much less reactive, which is similar to the Pd_1Cu_8 surface. Thus, one isolated Pd atom on a surface or sublayer of Cu(111) does not contribute to the high catalytic activity.

The ensemble composed of one surface Pd atom and its joint sublayer Pd atoms is an effective way to tune the catalytic activity for C_2H_4 formation. A very small quantity of Pd doped into the surface and sublayer and joined together exhibits strong catalytic activity ($r = 1.06 \times 10^9$ and 9.78×10^5 s^{-1} site^{-1} for $Pd_sPd_{sub}Cu$ and $Pd_s2Pd_{sub}Cu$). Moreover, the Pd_1Cu_8 surface with the smallest surface Pd ensemble as active sites still keeps a relatively good selectivity towards C_2H_4 formation ($\Delta G_a = 32.2$ and 45.8 kJ mol^{-1}), which is close to the selectivity of C_2H_4 formation on the single Pd_1Cu_8 surface ($\Delta G_a = 49.7$ kJ mol^{-1}).

For Pd-doped Cu bimetallic catalysts, the higher catalytic activity corresponds to the lower surface d-band center of the bimetallic catalyst. As the d-band center can be more efficiently obtained than the reaction rate, the surface d-band center of Pd-doped Cu bimetallic catalysts can be used as a good "descriptor" for the corresponding catalytic activity of C_2H_4 formation. This is quite useful for rapid screening of catalytic activity in the design of improved catalysts, including Pd-doped Cu bimetallic catalysts and other precious metal-doped common metal bimetallic catalysts.

Therefore, only the ensemble composed of a surface and joint sublayer Pd atoms over a Pd-doped Cu surface is responsible for the enhanced catalytic activity and selectivity in C_2H_2 hydrogenation to C_2H_4, which can be experimentally realized by a Cu catalyst doped with a very small quantity of Pd into the surface and sublayer to join together. It has been also ex-

perimentally confirmed that a small quantity of Pd atoms incorporated into the surface and sublayer of Cu(111) can be developed.[3,14,16,17] Our results not only give guidance for improving the catalytic performances of Cu-Pd alloy systems, but also provide an effective method for the design of other precious-metal-doped common metal catalysts in industrially key hydrogenation reactions.

4. Conclusions

Extensive DFT calculations have been used to elucidate the activity and selectivity for the selective hydrogenation of C_2H_2 over Pd-doped Cu catalysts with different ensemble effects, identifying the specific active sites. For almost all Pd-doped Cu surface–sublayer configurations, the C_2H_4 desorption pathway is the most favorable for gaseous C_2H_4 formation. The catalytic activity of C_2H_2 hydrogenation to C_2H_4 increases with increasing Pd/Cu ratios on the surface or in the sublayer, and the surface reactivity increases, the further the d-band center of a Pd-doped Cu surface is from the Fermi energy level. The surface Pd ensemble is more sensitive to the selectivity, and the sublayer Pd ensemble is more sensitive to the activity in C_2H_2 hydrogenation to C_2H_4. The ensemble composed of a surface and joint sublayer Pd atoms over a Pd-doped Cu surface contributes to the enhanced catalytic activity and selectivity in C_2H_2 hydrogenation to C_2H_4, which can be experimentally realized by a Cu catalyst doped with a very small quantity of Pd into the surface and sublayer to join together.

This detailed understanding for the mechanisms of enhanced activity and selectivity in C_2H_2 hydrogenation to C_2H_4 shows that the performance of Pd-doped Cu catalysts can be tuned by controlling the doped Pd atom ensemble effects, which can provide an effective method for the design of bimetallic catalysts with the precious-metal-doped common-metal motif for industrially key hydrogenation reactions.

Conflict of interest

The authors declare no conflict of interest.

Keywords: acetylene hydrogenation · activity · Cu-based catalyst · ensemble effect · selectivity

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