Research Article

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CH₄ dissociation on the Pd/Cu(111) surface alloy: A DFT study

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Abstract: The periodic four-layered model of the pure Cu (111) surface has been considered, and the effect of doping with palladium on CH₄ dissociation has been investigated. The most stable adsorption geometries of CH_x species ($x = 1-4$) and H atom on the PdCu(111) and pure Cu(111) surfaces have been obtained. Their computed adsorption energy results on the pure Cu(111) surface have been compared with the previously reported studies. Then, transition state geometries of CH₄ dehydrogenation steps on both surfaces were calculated by the climbing image nudged elastic band method. Finally, the relative energy diagram for CH₄ complete dehydrogenation has been represented. The results show that the PdCu(111) surface is more favorable than the Cu(111) surface in terms of the activation energies. The addition of Pd atoms to the Cu (111) surface significantly improves the catalytic activity. This knowledge can enable an efficient catalyst design at a lower cost using different strategies.

Keywords: CH₄ dissociation, Cu(111) surface, PdCu(111) surface, adsorption, activation energy, DFT calculations

1 Introduction

One of the most basic examples of the transition from hydrocarbon-based compounds to renewable energy sources is natural gas. As it is known, natural gas is a fuel mainly containing methane, and the chemical formula of methane is CH₄. Its heat of combustion is -890 kJ/mol. Moreover, it has a high energy content compared to other hydrocarbon fuels. Due to the advantageous properties of the CH₄ molecule, it has been extensively studied for new applications and hydrogen production techniques [1,2]. The

CH₄ dissociation reaction is usually based on sequential hydrogen decomposition (or dissociation). The CH_x species occurring at each stage of the reaction deactivate the catalysts [3–5]. Therefore, catalysts modified with transition metals are often used to improve catalysts' activity and stability in the reaction. These catalysts are usually bimetallic or alloy groups. As the nickel and nickel-based catalysts are of low cost and have high catalytic effect, they have been often used for the dissociation reaction of CH₄, which include Ni [6], Ni/ γ -Al₂O₃ [7], Sn/Ni [8], Ni–M (M = Cu, Ru, Rh, Pd, Ag, Pt, and Au) [9], Ni/Fe-catalyzed carbon [10], pure and gold-alloyed Ni(111) [11], Ni(100) [12], NiPd [13], NiCu [14], NiM(111) (M = Co, Rh, Ir) [15], NiCo [16], MgO(001)-supported Ni₄ [17], Ni(111) and Ru (0001) [18], Pt–Ni [19], Ni, Pd, Pt, and Cu [20]. The aforementioned results have shown that while bimetallic catalyst groups such as NiPt and NiPd have high catalytic activity on CH₄ dissociation reaction, NiAu, NiSn, and Ni can be classified as catalysts or catalyst groups with low activity.

Zhao et al. [21] have revealed that the Pd-doped Ni catalyst has high stability and that the Ni(211) and Pd/Ni (211) surfaces are more favorable for CH₄ dissociation than the Ni(100) and Pd/Ni(100) surfaces in terms of reaction energetics. Khettal et al. [22] have reported that the W–Cu(100) surface is more active thermodynamically and kinetically than other Cu-based catalysts for CH₄ dissociation. Recently, Pd- and Cu-based catalysts have been extensively used for CH₄ dissociation reaction. Rahmani et al. [23] have found that the activation barrier of the oxygen-covered surface of Cu(111) on CH₄ dissociation reaction is lower than that of oxygen-covered surfaces of Ni(111). Meng et al. [24] have examined partial methane oxidation on two single atom alloy catalysts (A-model Pd/Cu(111) and D-model Pd/Cu(111)). They found that CH₄ dissociation (CH₄ → CH₃) is the rate-determining step (RDS) of reaction on both catalysts and the activation energy values of RDS on these surfaces are very close to each other.

Solymosi et al. [25] have investigated the decomposition of methane on supported Pd catalysts and found that a significant part of hydrogen is dissolved through Pd

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crystals. Hou et al. [26] have studied the effects of Pd/Pt bimetal supported by the γ -Al₂O₃ surface on methane activation. They discovered that CH₄ adsorption depends on the ratio of Pd/Pt. Moreover, the Pd-3Pt/ γ -Al₂O₃ surface has been found to have the best catalytic activity among the modeling surfaces with 3Pd-Pt/ γ -Al₂O₃, 2Pd-Pt/ γ -Al₂O₃, and Pd-3Pt/ γ -Al₂O₃. Li et al. [27] have proposed two possible reaction mechanisms on Ni(111) and Cu(111) surfaces. These reaction mechanisms are H-abstraction reaction ($\text{CH}_x + \text{H} \rightarrow \text{CH}_{x-1} + \text{H}_2$) and direct dehydrogenation reaction ($\text{CH}_x + \text{H} \rightarrow \text{CH}_{x-1} + 2\text{H}$). They have shown that the direct dehydrogenation reaction on the Cu(111) surface is more favored than that on the Ni(111) surface. In the present research, the effect of Pd atoms doped onto different layers of the Cu(111) surface on CH₄ dehydrogenation reaction has been studied. First, the adsorption mechanisms of CH_x species and H atom on the PdCu(111) and pure Cu(111) surfaces were considered. Then, the activation and reaction energies for sequential dehydrogenation steps on the PdCu(111) and pure Cu(111) surfaces were calculated by the nudged elastic band method.

2 Methods

2.1 Computational method

All calculations were carried out via Quantum espresso code based on the density functional theory (DFT). For *ab initio* electronic structure calculations, the projector augmented wave potentials were used. The Perdew–Burke–Ernzerhof exchange–correlation functional [31] was used for the computation. The spin polarization term is used for accurate identification of total magnetization values. The Brillouin zone integrations were performed on a grid of sampling of $4 \times 4 \times 1$ *k*-points of the Monkhorst–Pack. The charge density and the wave functions were expanded with kinetic cutoffs of 60 and 600 Ry, respectively, for the Cu(111) and PdCu(111) surfaces. Relaxations in material optimizations were introduced using the BFGS quasi-Newton algorithm. In all calculations, van der Waals (vdW) interaction was defined by the DFT-D2 force-field approach. The force on each atom and energy convergence during geometric optimization were less than 1×10^{-5} eV/Å and 1×10^{-6} eV. The transition state geometries and activation energies between reactants and products on the reaction pathway were obtained using the climbing image nudged elastic band (CINEB) method.

2.2 Surface model

Examining the catalyst's active role in the CH₄ dissociation reaction is necessary to understand the individual binding nature of atomic or molecular species adsorbed by surfaces. The catalyst effect on a chemical reaction has often been investigated on M(111) surfaces, where M denotes transition metals. In this context, the catalytic effect of the Cu(111) surface on decomposition reactions has been studied in the literature [24,27,28]. Besides, a periodically repeating four-layered (2×2) supercell can be constructed to analyze the adsorption mechanism of atomic and molecular structures (adsorbed species) on the PdCu(111) surface. Herein, the top two layers were relaxed, and the bottom layers were fixed at their ideal bulk positions. A 14 Å vacuum in the slab model was applied to prevent undesirable interactions between periodically repeating supercells. The Cu atoms in the second layer of the periodic slab model were substituted by Pd atoms.

Adsorption energy, E_{ads} , between the surface and adsorbed species was calculated as follows:

$$E_{\text{ads}} = E_{\text{adsorbates/slab}} - (E_{\text{adsorbates}} + E_{\text{slab}}), \quad (1)$$

where $E_{\text{adsorbates/slab}}$ is the total energy of the surface and the adsorbed species. $E_{\text{adsorbates}}$ is the total energy of adsorbates, which was isolated in the $12 \times 12 \times 12$ cubic box. E_{slab} is the total energy of the metal slab.

3 Results and discussion

3.1 Adsorption mechanism of CH_x ($x = 0-4$) species and H atom

In this section, the most stable geometries of CH_x ($x = 0-4$) species and H atom on PdCu(111) are represented. The possible adsorption sites on the PdCu(111) surface are shown in Figure 1. The Cu atoms have been labeled as Cu_(*n*) ($n = 1 \rightarrow 5$).

Figure 1 indicates that the PdCu(111) surface has four high symmetric adsorption sites. The fcc and hcp sites are the threefold hollow sites of three Cu atoms. The bridge site is the twofold hollow site of two Cu atoms. The top site is above the Cu atom.

The preferred sites of CH_x ($x = 0-4$) species and H atom were determined on the pure Cu(111) surface. The results have been compared to the previously reported

Figure 1: The possible adsorption sites of the PdCu(111) surface. The Cu and Pd atoms are shown in orange and dark blue colors, respectively.

studies [27,28]. The adsorption geometries of CH_x ($x = 0-4$) and H on the PdCu(111) surface are given in Figure 2.

3.2 Adsorption mechanism of CH_4 on the PdCu(111) and pure Cu(111) surfaces

The adsorption of the CH_4 molecule on transition metal surfaces is usually a physisorption process.

CH_4 is adsorbed onto the PdCu(111) surface by vdW interaction. The bond lengths and adsorption energies of CH_x ($x = 1-4$), C, and H on the PdCu(111) and Cu(111) surfaces are given in Table 1. The most stable configuration of CH_4 is shown in Figure 2a. In this configuration,

Table 1: Adsorption energies (E_{ads} , eV) and bond lengths for the most stable adsorption structures of CH_x ($x = 1-4$), C, and H on the PdCu(111) and Cu(111) surfaces

Species	E_{ads} (eV)		Bond lengths (Å)
	Cu(111)	PdCu(111)	Adsorbed
CH_4	-0.01	0.02	C-H1 = 1.10 C-H2 = 1.10 C-H3 = 1.10 C-H4 = 1.10
CH_3	-1.83	-1.84	C-H1 = 1.10 C-H2 = 1.10 C-H3 = 1.10
CH_2	-3.86	-3.62	C-H1 = 1.10 C-H2 = 1.11
CH	-5.38	-5.45	C-H = 1.09
C	-5.34	-5.10	C-Cu(1) = 1.84 C-Cu(2) = 1.84 C-Cu(3) = 1.84
H	-2.77	-2.66	H-Cu(1) = 1.72 H-Cu(2) = 1.72 H-Cu(3) = 1.71

three H atoms are parallel to the surface, and the other H atom is perpendicular to the C atom.

The adsorption energy of the CH_4 molecule was found to be -0.01 eV. CH_4 on the pure Cu(111) surface has low adsorption energy. The adsorption energy of CH_4 was calculated as -0.02 eV on the PdCu(111) surface, which is very close to the data in previous studies [27,28].

Figure 2: The stable adsorption geometries of CH_x ($x = 0-4$) and H on the PdCu(111) surface. (a) CH_4 , (b) CH_3 , (c) CH_2 , (d) CH, (e) C, (f) H.

3.3 Adsorption mechanism of CH₃ on the PdCu(111) and pure Cu(111) surfaces

The adsorption of CH₃ onto the PdCu(111) surface has been considered on the fcc and hcp sites. Because CH₃ does not exhibit a stable behavior on the top and bridge sites, CH₃ interacts with the nearest neighbor Cu atoms on the fcc site. The adsorption energies of CH₃ on the fcc and hcp sites are -1.84 and -1.81 eV, respectively. For CH₃, the most stable geometry is at the fcc site (shown in Figure 2b). The bond lengths of C–H(1), C–H(2), and C–H(3) are 1.107, 1.106, and 1.107 Å, respectively.

The adsorption energies of CH₃ on the pure Cu(111) surface are -1.83 eV on the fcc site and -1.82 eV on the hcp site. These outputs are in good agreement with the literature results [27,28]. The bond lengths of C–H(1), C–H(2), and C–H(3) are 1.107, 1.106, and 1.107 Å, respectively. Compared to the PdCu(111) surface, there is no significant difference in the bond lengths of CH₃ on the pure Cu(111) surface.

3.4 Adsorption mechanism of CH₂ on the PdCu(111) and pure Cu(111) surfaces

The adsorption of CH₂ on the PdCu(111) surface has been investigated on all possible sites. Two stable geometries have been obtained. The calculated adsorption energies of the CH₂ are -3.62 eV on the fcc site and -3.58 eV on the hcp site. The most stable geometry of CH₂ is shown in Figure 2c. In this stable geometry, the H(1) atom is directly bonded to the Cu(3) surface atom, and the H(2) atom is relatively vertical on the bridge site. The bond lengths of C–H(1) and C–H(2) are 1.102 and 1.118 Å, respectively.

The adsorption energies of CH₂ on the pure Cu(111) surface are -3.86 eV on the fcc site and -3.78 eV on the hcp site. This result obtained on the fcc site is consistent with the study reported by Li et al. [27]. The bond lengths of C–H(1) and C–H(2) are 1.102 and 1.121 Å, respectively. The bond length of C–H(2) on the pure Cu(111) surface is more elongated by 0.003 Å than the PdCu(111) surface, and the bond length of C–H(1) is the same on both surfaces. Moreover, the CH₂ binds stronger on the pure Cu(111) surface compared to the PdCu(111) surface.

3.5 Adsorption mechanism of CH on the PdCu(111) and pure Cu(111) surfaces

When CH was being optimized on top and bridge sites of the PdCu(111) surface, it tended to move to the fcc or hcp sites, on which the adsorption energies of CH were calculated to be -5.45 and -5.40 eV, respectively. Therefore, the most stable geometry of CH is at the fcc site. The preferred geometry of CH is presented in Figure 2d. The bond length of C–H is 1.096 Å. CH prefers the fcc site on pure Cu(111), and the adsorption energy of CH is -5.38 eV, in agreement with previous studies [27,28]. The bond length of C–H on pure Cu(111) is 1.097 Å.

3.6 Adsorption mechanism of C and H on the PdCu(111) and pure Cu(111) surfaces

C and H atoms were optimized in all active sites on the PdCu(111) surface. The adsorption energy of H atom is close to each other on the fcc, hcp, bridge, and top sites. The most stable geometry of H is the fcc site (shown in Figure 2f). The adsorption energy of H on the fcc site is -2.66 eV. The C atom prefers to occupy the threefold hollow site of three Cu atoms denoted as the fcc site, and the adsorption energy of C at the fcc site is -5.10 eV. The preferred geometry of the C atom is plotted in Figure 2e.

The adsorption geometries of C and H atoms on the pure Cu(111) surface are similar to those on the PdCu(111) surface. Their most stable adsorption sites are at the fcc sites. The adsorption energies of C and H atoms are -5.34 and -2.70 eV, respectively. These adsorption energies are in good agreement with the literature results [27,28].

4 Transition states for the dissociation reaction of CH₄

In this section, sequential dehydrogenation of the CH₄ reaction is studied on the PdCu(111) and pure Cu(111) surfaces. According to the reaction mechanism considered, the reaction path has occurred through the same route on both surfaces. The most stable geometries of the initial and final states were selected to determine transition states (TS). Then, CH_x dissociated to CH_{x-1} and H. The total energy of the system with CH_{x-1} ($x = 1-4$)

species and H atom at an infinite distance was considered as the initial state of the next dehydrogenation step [11,30].

For the reaction of $\text{CH}_x \rightarrow \text{CH}_{x-1} + \text{H}$ on surfaces, the activation energies (E_a) and reaction energy (E_r) were calculated with the following formulas:

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

$$\Delta E_r = E_{\text{FS}} - E_{\text{IS}}, \quad (3)$$

where E_{IS} and E_{FS} are the total energies of surface together with the adsorbed CH_x and the dissociated $\text{CH}_{x-1} + \text{H}$ species, respectively; E_{TS} is the total energy of transition states.

According to the calculations, the activation energies of all possible reaction steps for CH_4 dehydrogenation are summarized in Table 2. Moreover, the pure Cu(111) surface results are in good agreement with the previously reported data [27,28].

4.1 Transition states for $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$ reaction

CH_4 sequential dehydrogenation reaction begins with a breakaway of a single H from the CH_4 molecule. This transition state is called TS1, and the related initial state, transition state, and final state geometries are shown in Figure 3, respectively. Moreover, H atoms attached to the CH_4 molecule have been labeled as H(n) ($n = 1 \rightarrow 4$).

CH_4 on the NiPd(111) surface has been adsorbed to the surface by vdW interaction. This geometry was selected as the initial state of the first dehydrogenation step (Figure 3a). CH_3 has been placed at the fcc site for the final state, and H has been located at the hcp site based

on the information that it has nearly the same stability at every site on the surface. The co-adsorbed geometry of CH_3 and H is represented in Figure 3c. In the transition state (TS1), the dissociated H(4) atom moved to the top site. As shown in Figure 3b, the distance between H(4) and C atom is 1.930 Å. In the final state, this value increases to 3.10 Å. The activation and reaction energies of the first dehydrogenation step ($\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$) were calculated to be 0.84 and 0.34 eV, respectively. This reaction is endothermic by 0.34 eV.

Similar to the above first dehydrogenation step of CH_4 dissociation, the reaction path was created for the pure Cu(111) surface. The calculated activation and reaction energies of the first dehydrogenation step are 1.32 and 0.72 eV, respectively, which are nearly the same as that on the pure Cu(111) surface [27].

4.2 Transition states for $\text{CH}_3 \rightarrow \text{CH}_2 + \text{H}$ reaction

In the second dehydrogenation step, removal of a single H atom from the CH_3 molecule has been investigated. The initial, transition, and final states on the PdCu(111) surface are plotted in Figure 4. The fcc site was selected as the initial state for CH_3 . For the final state, the co-adsorbed species CH_2 and H have been placed at the fcc and hcp sites, respectively. In the transition state (TS2), H (1) and H(2) atoms moved toward the bridge site and top site, respectively. The dissociated H(3) atom migrates toward the top site. Moreover, the distance between H(3) and C atoms is 2.12 Å. In the final state, this value increases to 3.05 Å (Figure 4c).

The activation and reaction energies were calculated to be 1.11 and 0.52 eV, respectively. This reaction is endothermic. On pure Cu(111), the activation and reaction energy values are 1.24 and 0.54 eV, respectively. Moreover, the obtained activation energy value on the pure Cu(111) surface is in agreement with the result (1.26 eV) of Li et al. [28].

4.3 Transition states for $\text{CH}_2 \rightarrow \text{CH} + \text{H}$ reaction

In the third step of the dehydrogenation reaction, CH_2 adsorbed on the PdCu(111) surface starts breaking down into CH and H species. For CH_2 , the fcc site on the surface was selected as the initial state (Figure 5a).

Table 2: Activation energies (eV) of sequential dehydrogenation of CH_4 on the pure Cu(111) and PdCu(111) surfaces

Surface	$\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$	$\text{CH}_3 \rightarrow \text{CH}_2 + \text{H}$	$\text{CH}_2 \rightarrow \text{CH} + \text{H}$	$\text{CH} \rightarrow \text{C} + \text{H}$
Cu(111) (vdW) in this study	1.32	1.24	0.87	2.03
Cu(111) (vdW)	1.31 ^a	1.26 ^a	0.93 ^a	1.97 ^a
Cu(111)	1.54 ^b	1.34 ^b	0.96 ^b	1.98 ^b
(no vdW)	1.57 ^c	1.36 ^c	0.94 ^c	1.84 ^c
PdCu(111) (vdW) in this study	0.84	1.11	0.80	1.98

^a Ref. 27. ^b Ref. 28. ^c Ref. 29.

Figure 3: The optimized initial and final state geometries and the transition state geometry of $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$ dehydrogenation step on PdCu(111). (a) CH_4 , (b) TS1, (c) $\text{CH}_3 + \text{H}$.

Figure 4: The optimized initial and final state geometries and the transition state geometry of $\text{CH}_3 \rightarrow \text{CH}_2 + \text{H}$ dehydrogenation step on PdCu(111). (a) CH_3 , (b) TS₂, (c) $\text{CH}_2 + \text{H}$.

Figure 5: The optimized initial and final state geometries and the transition state geometry of $\text{CH}_2 \rightarrow \text{CH} + \text{H}$ dehydrogenation step on PdCu(111). (a) CH_2 , (b) TS₃, (c) $\text{CH} + \text{H}$.

The co-adsorbed geometry of CH and H is shown in Figure 5c, and they have been placed at the fcc and hcp sites, respectively, as the final state.

In the transition state (TS₃), the dissociated H(2) atom migrated toward the top site (Figure 5b). The calculated distance C–H(2) is 1.96 Å. In the final state, the H(2) atom exceeding over the activation energy is at a distance of 2.97 Å from the C atom (shown in Figure 7c). The

reaction energy was calculated to be 0.38 eV. This reaction is endothermic. The activation energies of the third dehydrogenation step on the PdCu(111) and pure Cu(111) surfaces were calculated to be 0.80 and 0.87 eV, respectively, which is approximate to that (0.93 eV) on pure Cu(111) [28]. Moreover, the obtained reaction energy value on the pure Cu(111) surface is 0.56 eV and endothermic.

Figure 6: The optimized initial and final state geometries and the transition state geometry of $\text{CH} \rightarrow \text{C} + \text{H}$ dehydrogenation step on PdCu(111). (a) CH, (b) TS_4 , (c) C + H.

4.4 Transition states for $\text{CH} \rightarrow \text{C} + \text{H}$ reaction

In the final step of the dehydrogenation reaction, the CH molecule's most stable adsorption site is presented in Figure 6a. In this geometry, the C atom is bound to the nearest surface atoms, and the H atom is in the perpendicular position to the C atom. CH adsorbed to the fcc site on PdCu(111) was selected as the initial state. In the final state geometry, C and H atoms have been placed at the fcc and hcp sites (Figure 6c).

In the transition state (TS_4), the H atom migrated toward the top site of the PdCu(111) surface (Figure 6b). The calculated distance C–H is 1.97 Å. The reaction energy is 0.54 eV, and this reaction is endothermic. The activation energies of the final dehydrogenation step on the PdCu(111) and pure Cu(111) surfaces were calculated to be 1.97 and 2.03 eV, respectively, which is approximate to that (1.98 eV) on pure Cu(111) [28]. Moreover, the calculated reaction energy value on the pure Cu(111) surface is 0.61 eV and endothermic. According to the activation

energies of both surfaces, the relative energy diagram is given in Figure 7 by Table 3.

The activation energies of the first dehydrogenation step ($\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$) are 1.32 and 0.84 eV, respectively, on pure Cu(111) and PdCu(111). The activation energies of the second dehydrogenation step ($\text{CH}_3 + \text{H} \rightarrow \text{CH}_2 + 2\text{H}$) are 2.72 and 1.48 eV, respectively, on pure Cu(111) and PdCu(111). The activation energies of the third step ($\text{CH}_2 + 2\text{H} \rightarrow \text{CH} + 3\text{H}$) are 2.86 and 1.71 eV on pure Cu(111) and PdCu(111), respectively. The activation energies of the last step ($\text{CH} + 3\text{H} \rightarrow \text{C} + 4\text{H}$) are 4.10 and 3.18 eV, respectively, on pure Cu(111) and PdCu(111). As mentioned above, the activation energies of all dissociation steps are much lower on the PdCu(111) surface. We can see that the highest activation energy is CH dissociation. In other words, the RDS of the reaction is the final step for both surfaces.

Based on the CH_4 complete dissociation, we can see that the bonding mechanism between Pd and Cu atoms improves the catalytic activity of reaction, so the reaction route should be on the surface where Pd atoms take an active role. Moreover, the adsorption energies of the CH_x ($x = 1-4$) on both surfaces point out that these molecules are more weakly adsorbed onto the PdCu surface than the Cu(111) surface. This trend in adsorption energies can be a reason for the decreases in activation energies.

Figure 7: Relative energy diagram of CH_4 complete dehydrogenation on the pure Cu(111) and PdCu(111) surfaces.

Table 3: Relative energy diagram results for CH_4 dissociation on the Cu(111) and PdCu(111) surfaces

Reaction steps	Activation energies (E_a , eV)	
	Cu(111)	PdCu(111)
$\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$	1.32	0.84
$\text{CH}_3 + \text{H} \rightarrow \text{CH}_2 + 2\text{H}$	2.72	1.48
$\text{CH}_2 + 2\text{H} \rightarrow \text{CH} + 3\text{H}$	2.86	1.71
$\text{CH} + 3\text{H} \rightarrow \text{C} + 4\text{H}$	4.10	3.18

5 Conclusion

In this study, the sequential dehydrogenation reaction of CH₄ has been studied through DFT calculations on the PdCu(111) and pure Cu(111) surfaces. The adsorption energies and the most stable adsorption geometries were calculated on both surfaces. The obtained results show that CH_x ($x = 0-4$) species and H atom on PdCu(111) are more weakly adsorbed than that on the pure Cu(111) surface. Then, all possible states of the reaction mechanism are given in Table 1. The transition states of each dehydrogenation reaction step have been investigated by the CINEB method. The results have revealed that the PdCu(111) surface is more active than the pure Cu(111) surface. Significantly, the first step of the dehydrogenation on PdCu(111) is lower by 0.48 eV than the pure Cu(111) surface. The second and third steps are lower, approximately 0.1 eV than the pure Cu(111) surface. The final step occurs in the same way on both surfaces.

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