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Article

Mechanistic Insights for Dry Reforming of Methane on Cu/Ni Bimetallic Catalysts: DFT-Assisted Microkinetic Analysis for Coke Resistance

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Abstract: Density functional theory (DFT) calculations have been utilized to evaluate the complete reaction mechanism of methane dry reforming (DRM) over Ni₂Cu (111) bimetallic catalyst. The detailed catalytic cycle on Ni₂Cu (111) catalyst demonstrated superior coke resistance compared to pure Ni (111) and Ni₂Fe (111) reported in the literature. Doping Cu in the Ni–Ni network enhanced the competitive CH oxidation by both atomic O and OH species with the latter having only 0.02 eV higher than the 1.06 eV energy barrier required for CH oxidation by atomic O. Among the C/CH oxidation pathways, C* + O* → CO (g) was the most favorable with an energy barrier of 0.72 eV. This was almost half of the energy barrier required for the rate-limiting step of CH decomposition (1.40 eV) and indicated enhanced coke deposition removal. Finally, we investigated the effect of temperature (800~1000 K) on the carbon deposition and elimination mechanism over Ni₂Cu (111) catalyst. Under those realistic DRM conditions, the calculations showed a periodic cycle of simultaneous carbon deposition and elimination resulting in improved catalyst stability.

Keywords: density functional theory (DFT); dry reforming of methane (DRM); Ni₂Cu (111); bimetallic catalyst; coke resistance; catalyst deactivation; and microkinetic

1. Introduction

Dry reforming of methane (DRM) has been regarded as a process to produce syngas (CO and H₂), while providing a prospective solution for mitigation of greenhouse gases (CH₄ and CO₂). The produced syngas is a valuable precursor for many other downstream applications [1,2]. It can be used directly as fuel or converted to other hydrocarbons to produce valuable ultra-clean fuels and products such as methanol, diesel, gasoline, kerosene and naphtha via Fischer-Tropsch synthesis, and other reactions [3,4]. In addition to syngas, there are ongoing efforts to make the process more economical by producing valuable byproducts such as solid carbon as added value [5,6]. Despite its numerous advantages, DRM is a highly endothermic process (Equation (1)) that requires high temperatures of around 700 °C to achieve equilibrium conversions of CH₄ and CO₂ [7]. Therefore, the reaction proceeds typically with the use of a catalyst.



Catalyst deactivation, commonly caused by a rapid accumulation of carbon or “coking,” is one of DRM’s major drawbacks. Metal catalysts such as platinum (Pt) [8], rhodium (Rh) [9], ruthenium

(Ru) [10], iridium (Ir) [11], and cobalt (Co) [12] have been used to overcome the drawbacks of coking, as well as the unfavorable reactivity of the formed carbon towards oxidation reactions. Noble metals, such as Ru and Rh, have improved catalytic activity, stability, and coke resistance [3]. However, those metals are expensive and less abundant, making their usage economically unattractive for large industrial applications [13]. On the other hand, nickel catalysts have proved catalytic activity comparable to that of noble metals and can be a cheaper alternative with greater availability. However, the use of Ni catalysts in DRM is still limited, due to their high thermodynamic potential to coke formation [14,15].

The recent developments of bimetallic Ni-transition metal catalysts [16,17] have attracted attention as an effective strategy to overcome the drawbacks of pure Ni catalysts [18]. Xu et al. [19] conducted a DFT study on DRM for Ni₂Fe overlayer of Ni (111) surface. They concluded that the surface carbon reacted with the lattice oxygen in FeO and produced CO with a low energy barrier of 0.16 eV via Mars-van Krevelen (MvK) mechanism. Their conclusion is consistent with the experimental results from Theofanidis et al. [20,21].

Cu, another example of the alloyed transition metals, acted as an active phase promoter in CH₄/CO₂ reforming. The incorporation of Cu into the Ni–Ni surface has been demonstrated to improve stability, activity, and coke resistance in DRM. According to Faro et al. [22], the partial substitution of Ni by Cu interrupts the Ni–Ni network and reduces coke formation by altering their crystal and surface features. Rahemi et al. [23] synthesized Ni–Cu/Al₂O₃ nanocatalysts to explain the effect of Cu. They found that the size of the NiO crystals affected the stability of the nanocatalysts and their activities are highly dependent on the morphology and synergies between nickel and copper. This synergistic effect is very closely related to the amount of Cu loading [23]. For instance, Wu et al. found that Cu/Ni showed a higher activity at a 1:3 loading ratio, but the higher the Cu content, the significantly lower the activation of methane. This may be due to the competitive adsorption of CH₄ and slow dissociation kinetics at the copper atoms [24]. These outcomes are supported by Wang et al., who investigated the effect of coinage metals doped on the Ni–Ni network for DRM and concluded that the adsorption energies of CH_x ($x = 0–3$) are reduced on the alloy surface [18]. Moreover, they also agreed with Liu et al. [25], who performed DFT study on CH₄ dissociation over a Ni–Cu (111) catalyst surface. Their study outcomes clearly showed that the Cu-rich surface induced better coke resistance.

Understanding the CH₄ dissociation pathway is very important to evaluate both the catalyst activity and coke resistance. An et al. [26] found that the activation energy barrier for CH → C + H and CH₄ → CH₃ + H on NiCu (111) in the DRM mechanism were 1.8 times and 1.3 times higher than Ni (111), respectively. Similarly, Wei et al. [7] studied methane dehydrogenation on the bimetallic Cu/Ni (111) surface, and observed that coke formation was reduced by increasing the CH energy barrier. Very recently, our research team (Chatla et al. [27]) conducted a DFT study to investigate the effect of Cu addition to Ni/Al₂O₃ catalysts on DRM mechanism. Our findings showed that the addition of Cu increases the activation energy barrier for CH_x dehydrogenation to carbon nearly 1.5 times, but considerably decreases the activation energy barrier for carbon elimination through carbon gasification of Ni–Cu alloy system. However, the stability of Cu/Ni alloy cannot be sufficiently explained by just the ensemble effect of Cu on the Ni metal, which can suppress the rate of carbon formation. More comprehensively, the incorporation effect of Cu into Ni on the oxidation pathway of C/CH should be considered. This factor would be more important in the stability control of Cu–Ni alloy.

In this study, density functional theory (DFT) calculations are employed to consider how the Cu-alloyed Ni (111) catalyst affects the complete catalytic cycle of DRM, focusing on the essential factors that can control the Ni–Cu catalyst ability to resist coke formation. We investigated all possible coke deposition and elimination pathways in realistic reaction conditions over Ni₂Cu (111) bimetallic system. In particular, both the effects of temperature and Cu doping on coke deposition resistance are explained by calculating the reaction rate constant over the temperature range of 800–1000 K through complete vibration analysis of the elementary reactions.

2. Results and Discussion

2.1. Adsorption Geometries and Energies on Ni₂Cu Overlayer of Ni (111) Surface

The electronic properties of Ni₂Cu overlayer of Ni (111) surface described in Figure 1 were investigated, and three different adsorption sites were identified: two top sites (Top^{Ni} and Top^{Cu}), two bridge sites (B^{2Ni} and B^{NiCu}), and two hollow sites (Hexagonal Close Packed, HCP and Face Centered Cubic, FCC).

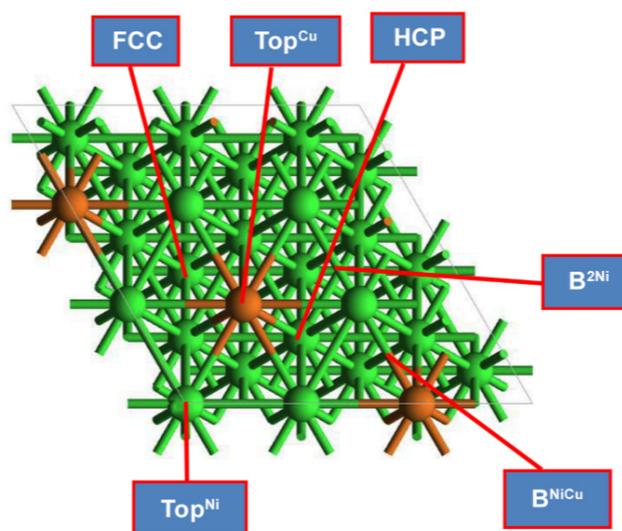


Figure 1. Schematic illustration of Ni₂Cu overlayer of Ni (111) surface. FCC, HCP, Top^{Ni}, Top^{Cu}, B^{2Ni}, and B^{NiCu} represent a face centered cubic, hexagonal close packed, Ni at the top site, Cu at the top site, Ni–Ni at the bridge site and Ni–Cu at the bridge site, respectively. Green and brown spheres represent Ni and Cu atoms, respectively.

First, optimal adsorption sites for all DRM reaction species were selected after examining all possible adsorption structures. Then, the adsorption energies of all DRM reaction species from the most stable adsorption configurations were calculated, as shown in Table 1. CH₄ species was physically adsorbed at the HCP site with a weak adsorption energy of -0.02 eV.

On the other hand, CH₃, CH₂, and CH are strongly adsorbed via C atom on the FCC site with corresponding adsorption energies of -2.17 eV, -4.99 eV, and -5.43 eV, respectively. Similarly, the H atom tends to be adsorbed to the FCC site. These results are in good agreement with Ni₂Fe overlayer [20,21] with same diagonal arrangement and pure Ni (111) surfaces [28]. In the case of CO, the adsorption is preferable on the Top^{Ni} site with E_{ads} of -1.52 eV, while the O atom is favorably bound to the FCC site with an E_{ads} of -6.34 eV. It indicates that the Cu dopant in Ni (111) network improved atomic O adsorption while reducing CO adsorption compared to both pure Ni (111) and Ni₂Fe (111) surfaces, respectively [19]. As a descriptor of coke resistance, the adsorption energy of the C atom indicates that the more strongly the carbon is adsorbed on a specific surface, the lower the coke resistance. The C atom preferentially adsorbed to HCP site with an E_{ads} of -7.04 eV and is less than the E_{ads} of -7.50 eV in a monometallic Ni catalyst [27,29,30]. This means that the Cu dopant on Ni (111) reduces coke deposition, and, as a result, it can increase the coke resistance of the catalyst surface. The adsorption of CO₂ on the Ni₂Cu (111) surface has been investigated at all possible sites. After geometry optimization, it has been found that CO₂ is physically adsorbed towards a vacuum with weak adsorption energy of -0.03 eV in parallel to the surface with C–Cu. This result agrees with Heil and [31], who used both fast ion beam and fast molecular beam techniques to study CO₂ dissociation, and found no chemisorbed CO₂ on Ni (111). Moreover, it agrees with the computational studies performed on Ni (111) and on Ni₂Fe (111) surfaces [19,32]. CO molecules prefer to adsorb at

the B^{2Ni} site with an E_{ads} of −1.52 eV. The COH* intermediate produced by the combination of C* and OH* is strongly adsorbed at the B^{2Ni} site with an E_{ads} of −4.07 eV. In the case of H₂O, it is physically adsorbed to the surface with E_{ads} of −0.06 eV. The adsorption sites and energies of the other DRM intermediates are detailed in Table 1.

Table 1. Calculated adsorption energies of all adsorbed species involved in DRM on Ni₂Cu overlayer of Ni (111) surface.

	Species	E _{ads} (eV)	Favored Adsorption Site
1	CH ₄ *	−0.02	N/A
2	CH ₃ *	−2.17	FCC
3	CH ₂ *	−4.99	FCC
4	CH*	−5.43	FCC
5	C*	−7.04	HCP
6	O*	−6.34	FCC
7	OH*	−3.28	B ^{2Ni}
8	CO*	−1.52	B ^{2Ni}
9	COH*	−4.07	B ^{2Ni}
10	CHOH*	−2.40	B ^{2Ni}
11	CO ₂ *	−0.03	N/A
12	H*	−3.60	FCC
13	H ₂ *	−0.06	N/A
14	CH ₃ O*	−2.43	B ^{2Ni}
15	CH ₂ O	−0.04	N/A
16	CH ₂ OH*	−1.87	Top ^{Ni}
17	CH ₃ OH*	−0.05	N/A
18	CHO* ^a	−2.05	Top ^{Ni}
19	COH* ^a	−4.07	B ^{2Ni}
20	H ₂ O*	−0.06	N/A
21	COOH*	−2.28	Top ^{Ni}

^a CHO is “H–C=O*” and COH* is “C–O–H*”.

2.2. DRM Reaction Mechanism

DRM turnover rate is known to be limited only by C–H bond activation, regardless of the concentration of reactants [7]. Consequently, it is expected that the CH₄ is consumed via dissociative adsorption regardless of CO₂ concentration. The resulting CH_x species are then oxidized by atomic O and OH species to form CH_xO and CH_xOH species, respectively, or they undergo further dehydrogenation.

2.2.1. CH_x Dissociation (x = 1–4)

The successive steps of CH₄ dissociation start with the physical adsorption of CH₄ (g) on the Ni₂Cu (111) surface to form CH₄* (* denotes an adsorption state). Then, the activation energy in the first step of CH₄ dissociation is found to be 1.30 eV, as shown in Figure 2. The first transition state shows the detached H atom located at the HCP site [33], and the remaining CH₃ fragment settled down at 2.08 Å to achieve maximum C–H–Ni three-center bonding [34,35]

After the dissociative adsorption of CH₄ on the Ni₂Cu (111) surface, the two subsequent dehydrogenation steps of CH₃* and CH₂* species are more facile with energy barriers of 0.75 eV and 0.49 eV, respectively. However, CH₃* dehydrogenation showed endothermicity of 0.33 eV, while CH₂* exhibited exothermicity by −0.06 eV. On the other hand, oxidations of CH₃* and CH₂* by O* or OH* are considerably difficult, due to relatively higher energy barriers than the dehydrogenation pathway mentioned above.

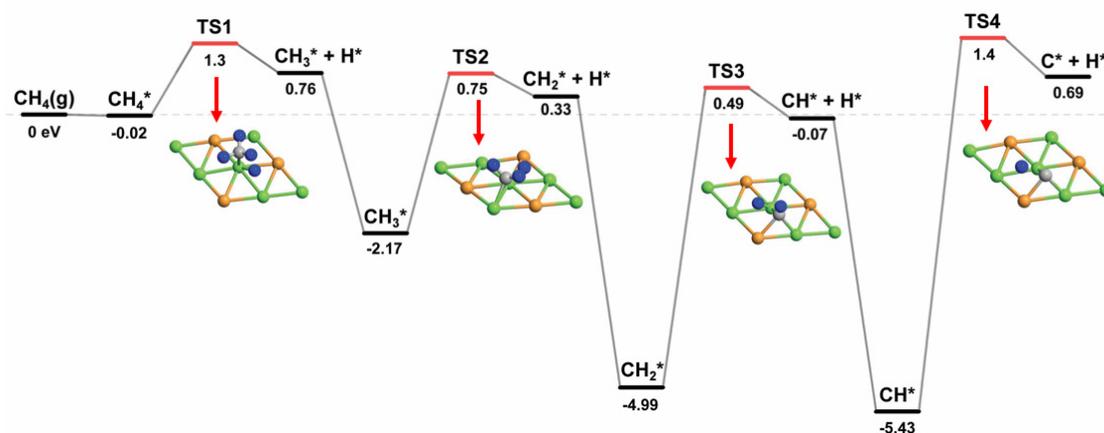


Figure 2. Activation energy profile for successive CH_4 dissociation steps. Green, brown, blue, and grey spheres represent Ni, Cu, H, and C atoms, respectively.

Figure 3 shows the activation energy barriers of all possible pathways of CH_3^* . It confirms that subsequent dissociation to CH_2^* is dominant over oxidation pathways. CH_2^* and CH_3^* oxidation can produce CH_3OH^* through CH_3^* , CH_3O^* , or CH_2OH^* intermediates. Of these intermediates, CH_2OH^* was found to be more favorable with a lower activation energy ($E_{a,r}$) of 1.10 eV, as shown in Table 2. In addition, Table 2 shows that the activation energy of the forward reaction ($E_{a,f}$) and the activation energy for the reverse reaction ($E_{a,r}$). Both of these reaction rates are calculated from Climbing-NEB method considering the enthalpy (H_f) as the energy difference between the final state (F.S) and the initial state (I.S). Next, for the CH dissociation, the activation energy ($E_{a,f}$) increases significantly to 1.40 eV, which is higher than that of CH^* oxidation by OH^* (1.08 eV) and O^* species (1.06 eV), as shown in Table 2. The conclusion of this result is that CH dissociation is the rate-limiting step.

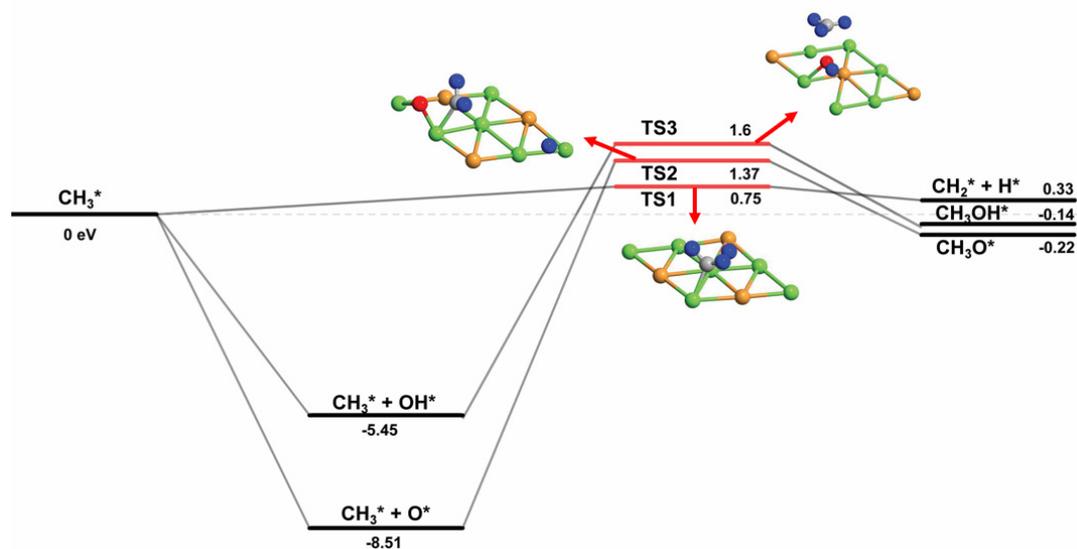


Figure 3. Activation energy profile for possible CH_3 reaction pathways. Green, brown, blue, grey, and red spheres represent Ni, Cu, H, C, and O atoms, respectively.

Table 2. Calculated activation energies of forward ($E_{a,f}$), reverse ($E_{a,r}$), and enthalpy (H_f) in an elementary reaction of dry reforming of methane (DRM).

Reaction	$E_{a,f}^+$ (eV)	H_f^+ (eV)	$E_{a,r}^+$ (eV)
$CH_4^* \rightarrow CH_3^* + H^*$	1.30	0.78	0.52
$CH_3^* \rightarrow CH_2^* + H^*$	0.75	0.33	0.42
$CH_2^* \rightarrow CH^* + H^*$	0.49	-0.06	0.55
$CH^* \rightarrow C^* + H^*$	1.40	0.69	0.71
$C^* + O^* \rightarrow CO^*$	0.72	-2.17	2.89
$CH^* + O^* \rightarrow CHO^*$	1.06	-0.30	1.36
$CHO^* \rightarrow CO^* + H^*$	0.18	-1.17	1.35
$C^* + OH^* \rightarrow COH^*$	1.13	-0.95	2.07
$H^* + H^* \rightarrow H_2$	0.73	0.57	0.16
$CH^* + OH^* \rightarrow CHOH^*$	1.08	0.24	0.84
$CHOH^* \rightarrow CHO^* + H^*$	0.60	-0.31	0.91
$CO_2^* + H^* \rightarrow COOH^*$	0.93	-0.12	1.05
$COOH^* \rightarrow CO^* + OH^*$	0.43	-0.59	1.02
$O^* + H^* \rightarrow OH^*$	0.94	-0.24	1.18
$H^* + OH^* \rightarrow H_2O^*$	0.91	-0.15	1.06
$CO_2^* \rightarrow CO^* + O^*$	1.69	0.48	1.21
$CH_3^* + O^* \rightarrow CH_3O^*$	1.37	-0.22	1.59
$CH_2^* + O^* \rightarrow CH_2O^*$	0.76	-0.43	1.19
$CHOH^* \rightarrow COH^* + H^*$	0.20	-0.53	0.73
$COH^* \rightarrow CO^* + H^*$	1.01	-1.09	2.10
$CH_3^* + OH^* \rightarrow CH_3OH^*$	1.60	-0.14	1.74
$CH_2^* + OH^* \rightarrow CH_2OH^*$	0.78	-0.10	0.88
$CH_3O^* \rightarrow CH_2O^* + H^*$	0.96	0.57	0.39
$CH_2OH^* \rightarrow CH_2O^* + H^*$	0.75	-0.07	0.82
$CH_2OH^* \rightarrow CHOH^* + H^*$	0.92	0.42	0.50
$CH_3OH^* \rightarrow CH_3O^* + H^*$	4.29	0.01	4.28
$CH_3OH^* \rightarrow CH_2OH^* + H^*$	2.46	1.39	1.10

* Zero-point energy (ZPE) corrections are not included.

Consequently, the energy barriers for CH_x ($x = 1-4$) dissociation increase in order of $CH_2 < CH_3 < CH_4 < CH$ [36], which is in line with CH_4 decomposition on pure Ni (111) and Ni_2Fe (111) systems. In addition, the energy barriers of those subsequent steps are much higher in the case of Ni_2Cu (111) than Ni (111) and Ni_2Fe (111) systems, which reduce carbon deposition from CH radical dehydrogenation [19,28,37].

2.2.2. Two Reaction Pathways for CO_2 Dissociation

According to the previous experimental studies [7,38], there are two possible routes for CO_2 dissociation. First, adsorbed CO_2^* is directly dissociated to form CO^* and atomic O^* . The latter acts as an oxidant for CH_x ($x = 1-4$), ultimately producing CO (g). In the second pathway, CH_4^* is first dehydrogenated to produce atomic H, which subsequently activates the CO_2^* to produce a $COOH^*$ intermediate. Then, the decomposition of $COOH^*$ produces CO^* and an OH^* oxidant in the following scheme.



As described above, H^* atoms released from the CH_4 dissociation pathway can either contribute towards or activate CO_2 dissociation. The potential energy profile and structure associated with CO_2 hydrogenation (or H-induced CO_2 dissociation) are shown in Figure 4. At the first step, CO_2 and H atoms are co-adsorbed on Ni_2Cu (111) surface to form a $COOH^*$ intermediate with an $E_{a,f}$ of 0.93 eV, and this reaction is exothermic by -0.11 eV. In the final state, CO and OH are co-adsorbed at the B^{2Ni} site after the breakage of $COOH^*$. For adsorbed CO^* , the C-Ni bond length is 1.89 Å, and in OH^* , the O-Ni bond length is 1.98 Å. The activation energy ($E_{a,f}$) of $COOH^*$ dissociation is 0.43 eV, and the reaction is exothermic by 0.59 eV. Previous studies of DRM on pure Ni (111) surfaces have

shown that direct CO₂ dissociation has a low energy barrier of 0.67 eV compared to 1.13 eV for the H-induced CO₂ dissociation pathway [28]. Meanwhile, the Ni₂Cu (111) surface has a lower ($E_{a,f}$) of 0.93 eV for H-induced CO₂ dissociation. Thus, doping Cu in Ni (111) network slightly favors the CO₂ hydrogenation process, producing an OH oxidant via COOH* intermediate dissociation. Comparing the direct CO₂ dissociation and the H-induced CO₂ dissociation pathways, the latter is more favorable reaction in Ni₂Cu (111) bimetallic system than in the case of Ni (111), where both atomic O* and OH* species participate as oxidants of CH_x (x = 1–3) intermediates. Similar results have been reported for the Ni₂Fe (111) surface, where both pathways were found to be competitive [19].

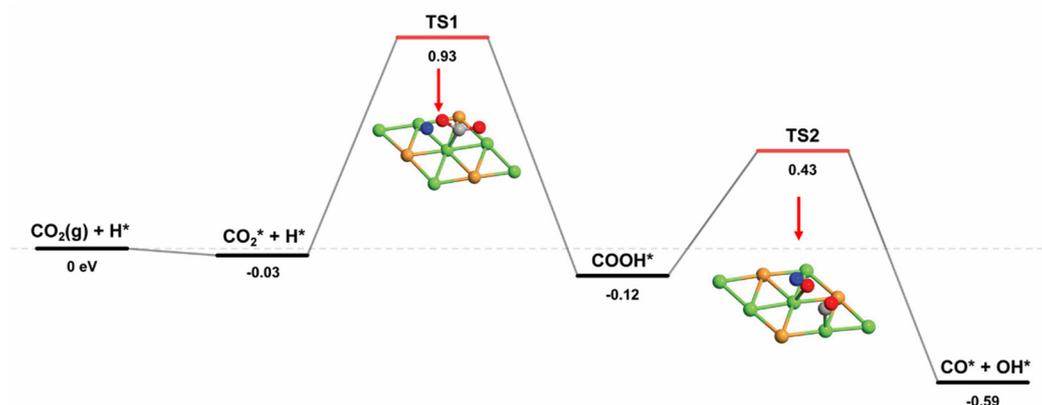


Figure 4. Activation energy profile for H-induced CO₂ dissociation (hydrogenation).

2.2.3. Oxidation of C and CH

When CH₄ dissociates into C and H, CH_x (x = 0–3) can combine with atomic O or OH species to produce CHO (H). Table 2 shows that the CH₃ and CH₂ dehydrogenation reactions are more favorable with relatively lower $E_{a,f}$ of 0.75 eV and 0.49 eV, respectively. In contrast, CH dehydrogenation has a relatively higher $E_{a,f}$ of 1.40 eV, while the reverse reaction is energetically favorable with $E_{a,r}$ of 0.71 eV. Thus, coke formation due to CH decomposition is less desirable for Ni₂Cu (111) compared to pure Ni (111) and Ni₂Fe (111) surfaces with energy barriers of 1.33 eV [19] and 1.36 eV [28], respectively. Moreover, only CH* and C* are the most stable major intermediates remaining on the surface than the kinetically unstable CH₃* and CH₂* intermediates, as discussed in Table 1. It turns out that from all possible oxidation reactions of CH_x (x = 0–3), C* + O* oxidation is the most favorable reaction.

2.2.4. Carbon elimination by C + O and C + OH

The C* + O* oxidation pathway was found to be more favorable at an $E_{a,f}$ of 0.72 eV compared to 1.59 eV and 1.58 eV for Ni (111) and Ni₂Fe (111), respectively, as shown in Figure 5.

The C* + OH* reaction pathway shows an $E_{a,f}$ of 1.13 eV compared to 1.46 eV for Ni (111) and 1.42 eV for Ni₂Fe (111) surfaces. The reverse reaction of CO* → C* + O* has an $E_{a,r}$ of 2.89 eV, which is clearly in favor of carbon elimination. These results indicate that Cu-rich surfaces can accelerate specific oxidation reactions and change surface properties to improve carbon elimination by both atomic O and even OH species. As will be explained later, temperature plays a crucial role in enhancing these oxidation steps. These results conclude that Cu doped in Ni (111) reduced coke formation by increasing the activation energy barrier of CO* and CH* dissociation, but improved carbon elimination by both atomic O* and OH* species [18,39].

This study shows that the addition of Cu can overcome the limitation of Ni (111) and Ni₂Fe (111) in terms of coke resistance, which is consistent with the results of previous calculations [26] and experimental studies [37].

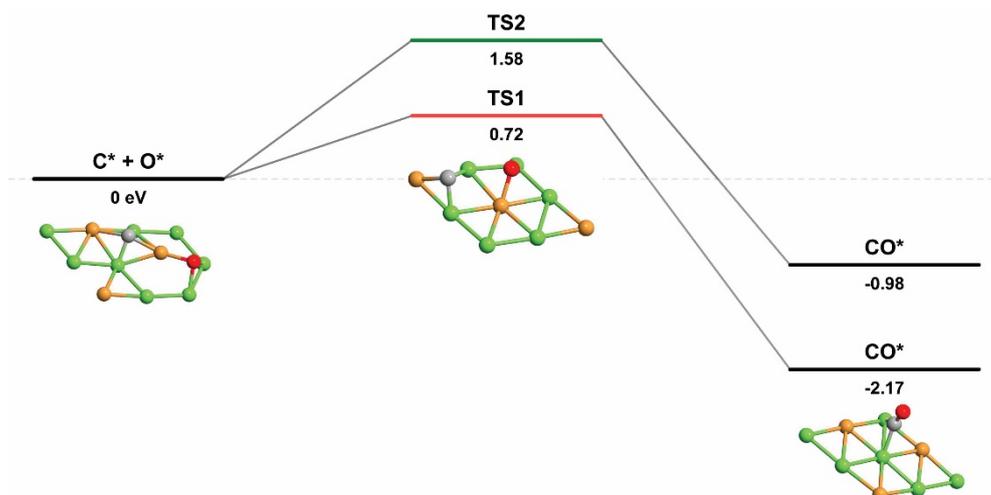


Figure 5. Comparison of activation energy profiles of $C^* + O^*$ oxidation reaction for Ni_2Cu (111) (red) and Ni_2Fe (111) (green) surfaces.

2.2.5. CH + O and CH + OH Reactions

Oxidation of CH^* by atomic O^* generated from direct CO_2 dissociation begins through co-adsorption of CH on the FCC site and an O atom on an HCP site via one Cu atom. In the transition state, atomic O moves to the B^{NiCu} site at a Ni–O distance of 1.97 Å and a Cu–O distance of 2.01 Å. CH^* settles at the B^{2Ni} site at a Ni–C distance of 1.86 Å and a Ni–H distance of 1.81 Å. At this step, the energy barrier is 1.06 eV, which is much higher than 0.47 eV for pure Ni (111) and 0.78 eV for the Ni_2Fe (111) surface [19,28].

Figure 6 shows that the $CHOH^*$ intermediate formed by co-adsorption of CH^* and OH^* at adjacent FCC and B^{2Ni} sites easily overcomes the energy barrier of 1.08 eV compared to 1.48 eV and 1.42 eV in pure Ni (111) and Ni_2Fe (111), respectively [19,28].

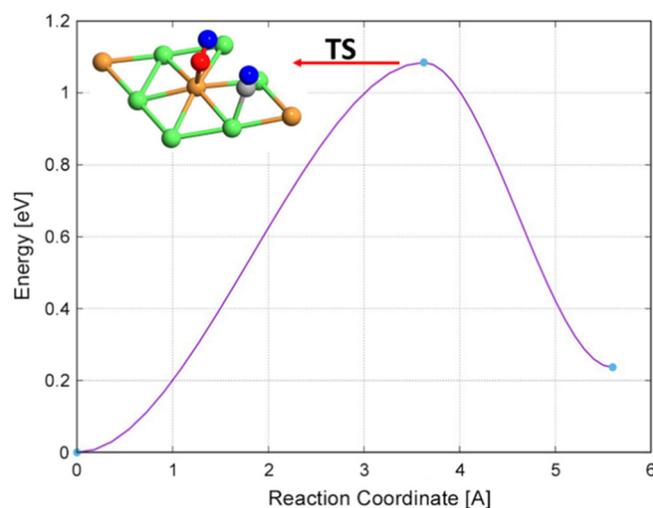


Figure 6. Activation energy profile of CH oxidation by OH. The OH is an effective oxidant that helps to skip CH dissociation. The transition state (TS) configuration shows where OH is adsorbed on the TopCu site while CH is adsorbed on the TopNi site.

2.2.6. CHOH and COH Decomposition

A stable $CHOH^*$ configuration was found at the B^{2Ni} site with the same C–Ni distance of 1.95 Å. Figure 7 shows two possible pathways for subsequent $CHOH^*$. The first pathway involves $CHOH^*$ dissociation ($CHOH^* \rightarrow CHO^* + H^*$) with an energy barrier of 0.60 eV. Then, the produced CHO^* has

a low energy barrier of 0.18 eV, which readily forms CO* and atomic H*. The second pathway follows CHOH* dissociation, which forms COH* and H* with an energy barrier of 0.20 eV, and then the COH* dissociates to CO* and atomic H* with an energy barrier of 1.09 eV.

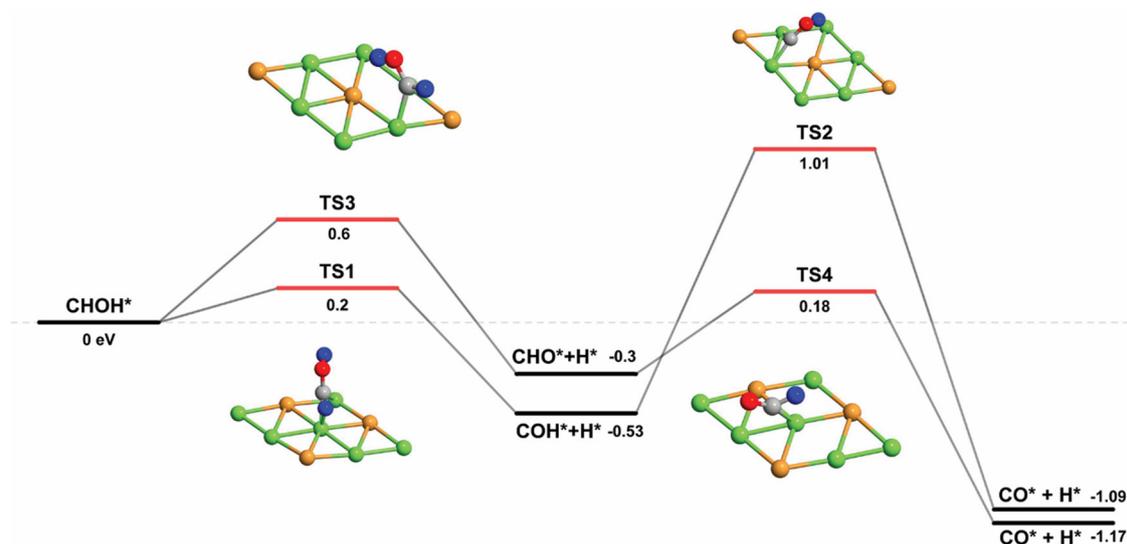


Figure 7. Activation energy profiles for two different CHOH* dissociation pathways.

From the results above, it can be concluded that the CH oxidation by atomic O (1.06 eV) and OH oxidants (1.08 eV) in the Ni₂Cu (111) system is very competitive, due to the small difference of 0.02 eV. Moreover, both oxidation pathways have a lower energy barrier than that of Ni (111) and Ni₂Fe (111) [19,28].

The energy barrier of CH oxidation by atomic O was slightly lower than that of CH oxidation by OH. Conversely, the oxidation of CH by OH showed a higher reaction rate constant in the temperature range of 800~1000K, which will be described in detail in Section 2.3.

2.2.7. H₂ and H₂O Formation

The reaction of H* + H* → H₂ (g) requires an E_{a,f} of 0.73 eV, and is an endothermic reaction at a H_f of 0.57 eV, as shown in Table 2. The H₂ (g) is physically adsorbed on the catalyst surface with an E_{ads} of -0.016 eV, which prefers the product formation in a higher reaction temperature. Hence, H₂ (g) formation in Ni₂Cu (111) catalyst is more facile than in pure Ni (111) and Ni₂Fe (111), which have relatively higher energy barriers of 0.92 eV and 1.18 eV, respectively. In the first step of H₂O* formation, the adsorbed H* and O* react to produce OH* with an E_{a,f} of 0.94 eV and exothermic reaction energy (H_f) of -0.24 eV, as shown in Table 2. Figure 8, which describes the next step, shows that the formed OH* undergoes an exothermic reaction with H* with an energy barrier of 0.91 eV. These two steps are energetically preferred over pure Ni (111) and Ni₂Fe (111) surfaces [19,28]. At high temperatures in DRM, H₂O (or steam) facilitates the physical removal of coke deposition from the catalyst surface.

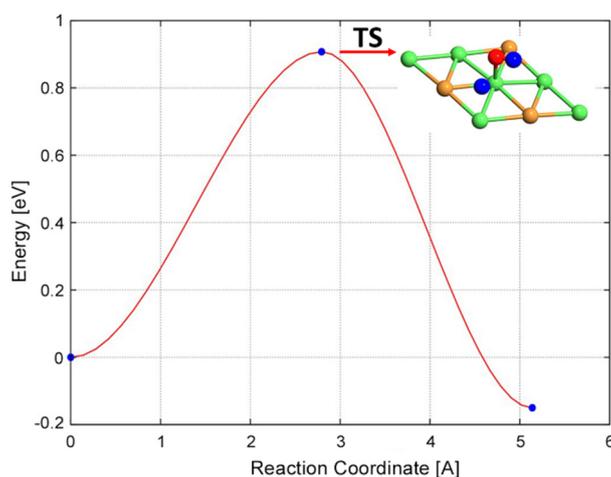


Figure 8. The energy of H₂O formation via OH* + H* reaction and configuration of transition state. The weakly adsorbed H₂O physically removes coke from the catalyst surface at high temperatures (steam).

2.3. Effect of Temperature on Carbon Deposition Resistance

One drawback of the DFT calculations used to investigate the DRM reaction is that all atoms are localized to the “minimum energy” position at zero temperature (0 K). A complete vibrational analysis is performed on the elementary reaction to overcome this problem. The analysis has two advantages; the first is that the transition state configuration as well as the activation energy barrier can be verified with a single imaginary frequency. The second advantage is that the rate constants can be calculated through the Vineyard formula [38], a crucial step in developing microkinetic models and identifying atomic models [40,41].

In this regard, the calculated vibrational frequencies are used to evaluate the rate constant at the confirmed transition states, focusing on the effect of Cu doping and temperature on coke deposition resistance. The calculations of the vibrational frequency and rate constant are described in more detail in the supplementary information. Coke deposition can come from two primary sources: CH₄ and CO₂. In the CH₄ dissociation pathway, the ratio of the rate constant of the CH oxidation pathway to the C oxidation pathway determines the carbon deposition. According to a previous study, increasing this ratio reduces carbon formation [29]. Coke can be also formed during the dissociation of CO into C* and O* in the CO₂ reaction pathway. Table 3 shows the rate constants k (s⁻¹) of carbon elimination and deposition on the Ni₂Cu (111) surface over various temperature ranges. We found that k of C* + O* (or + OH*) or CH* + O* (or + OH*) oxidation reactions increases with the increasing temperature, and the carbon deposition from CO* is negligible due to the very small k value. In addition, the rate constant of CH dissociation was lower than that of carbon oxidation ($k_{C(O)}$ and $k_{C(OH)}$) by atomic O or OH species, respectively. As the temperature increases, $k_{CH}/k_{C(O)}$ increases while $k_{CH}/k_{C(OH)}$ decreases.

Table 3. The rate constant k (s⁻¹) of carbon elimination and deposition on Ni₂Cu (111) surface at different temperature ranges.

Reactions	800 K	850 K	900 K	950 K	1000 K
CO* → C* + O*	4.36×10^{-7}	5.11×10^{-6}	4.56×10^{-5}	3.23×10^{-4}	1.88×10^{-3}
CH* → C* + H*	1.18×10^5	3.90×10^5	1.13×10^6	2.92×10^6	6.88×10^6
C* + O* → CO*	2.43×10^8	4.50×10^8	7.74×10^8	1.25×10^9	1.95×10^9
C* + OH* → COH*	5.75×10^6	1.50×10^7	3.53×10^7	7.59×10^7	1.51×10^8
CH* + O* → CHO*	6.01×10^6	1.49×10^7	3.32×10^7	6.83×10^8	1.31×10^8
CH* + OH* → CHOH*	3.28×10^7	8.27×10^7	1.88×10^8	3.93×10^8	7.62×10^8
$k_{CH}/k_{C(O)}$	0.02	0.03	0.04	0.05	0.07
$k_{CH}/k_{C(OH)}$	5.70	5.50	5.33	5.18	5.05

Figure 9 shows the temperature effect on carbon elimination reactions. The reaction of $C^* + O^*$ has the highest rate constant in all carbon elimination reactions, followed by $CH^* + OH^*$. $C^* + OH^*$ and $CH^* + O^*$ reactions have similarly low rate constants as a function of temperature. OH^* is the primary oxidizing agent for CH^* , whereas atomic O is dominant in coke removal at different temperatures. It indicates that coke deposition by atomic O is easily removed at higher temperature ranges. On the other hand, it also reveals the importance of OH species in bypassing the coke formation step from CH dissociation where $k_{CH}/k_{C(OH)} \gg k_{CH}/k_{C(O)}$, as shown in Figure 10. Comparing these results with previous studies [42,43], we can conclude that carbon elimination via $C^* + O^*$ is enhanced in Ni_2Cu (111) system over the Ni_2Fe (111) and pure Ni (111) systems [19,25,28]. It suggests that the incorporation of Cu to Ni–Ni surface can simultaneously improve carbon elimination by $C^* + O^*$ reaction, while reducing carbon deposition via CH dissociation. The higher the Cu/Ni ratio, the more it is expected to suppress catalyst activity when occupying the Ni active site. This result is consistent with the experimental results [22,24].

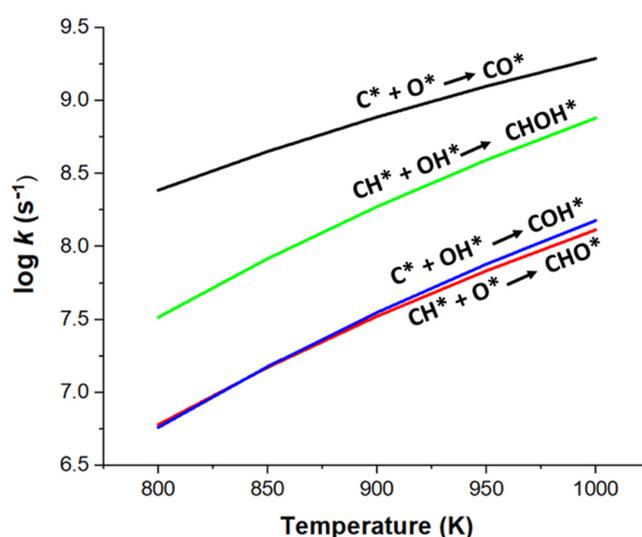


Figure 9. Rate constants of the coke removal reaction at different temperatures.

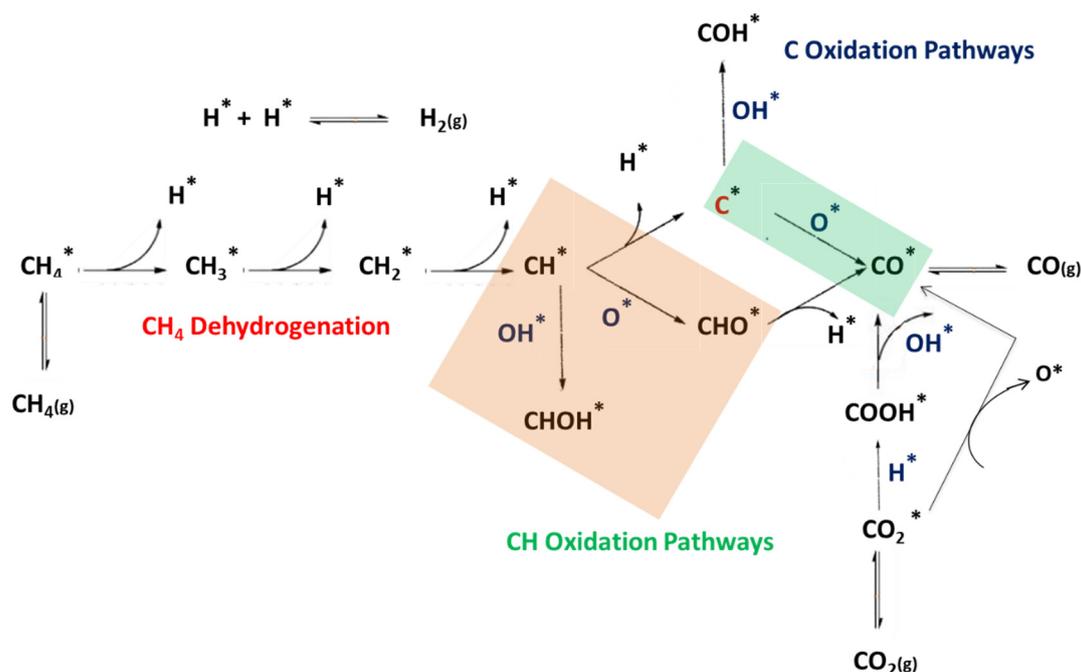


Figure 10. A schematic diagram of the DRM dominant reaction pathway on Ni_2Cu (111).

Since the carbon elimination rate by both OH and atomic O is much higher than that of carbon deposition through CH dissociation, the Ni₂Cu (111) surface is expected to exhibit higher catalytic activity. In addition, this periodic cycle of carbon deposition and elimination will result in catalyst stability.

2.4. Dominant Reaction Pathways and Rate-Limiting Steps

After determining the initial and final state of each elementary reaction of DRM, transition states are identified and confirmed by vibrational analysis. Then, zero-point energy corrections and rate constants are evaluated. As a result, the dominant reaction pathway and rate-limiting step are determined. CH₄ undergoes successive dehydrogenation steps, of which CH₃ and CH₂ dissociation more readily occur with lower energy barriers of 0.75 eV and 0.49 eV, respectively. However, CH₃ and CH₂ oxidation by atomic O or OH are energetically unfavorable due to the high energy barriers. To illustrate, CH₃ requires energy barriers of 1.37 eV and 1.6 eV while CH₂ needs 0.76 eV and 0.78 eV for oxidation by O and OH, respectively.

Consequently, CH₄ is dissociated to CH, C, and H intermediates. The main intermediate of CH₄ dissociation, CH, follows three primary pathways: (a) CH* → C* + H*, (b) CH* + O* → CHO* → CO* + H*, and (c) CH* + OH* → CHOH*. The CH dissociation, as a significant source of coke formation, is energetically and kinetically unfavorable. Therefore, CH dissociation is the rate-limiting step of CH₄ dissociation and determines the overall reaction rate. In the case of CH* oxidation pathways, both (b) and (c) are very competitive, with only a 0.02 eV difference and (b) slightly preferred with a lower energy barrier of 1.06 eV. However, the kinetic data shown in Table 3 indicate that CHOH* formation is more favorable reaction than CHO* at the temperature range 800~1000 K. Concerning CHOH*, the most preferred pathway goes through COH* formation with an energy barrier of 0.20 eV, which further dissociates into CO* and H*. From the standpoint of coke elimination, C oxidation by atomic O is a more favorable reaction with an energy barrier of 0.72 eV, which is lower than all other C and CH oxidation pathways. As for H* intermediate, H* + H* → H₂* is the most preferred pathway. In the CO₂ activation pathway, we investigated the direct CO₂ dissociation to form CO and O, and the H-induced CO₂ formation pathway to form CO* and OH*. Unlike pure Ni (111) system, the H-induced CO₂ formation pathway is the more favorable than the direct CO₂ dissociation with a lower energy barrier of 0.93 eV. Eventually, this result suggests that the doped Cu atoms promote the H-induced CO₂ formation pathway and form O and OH oxidants that remove CH and C from the Ni₂Cu (111) surface, as shown in Figure 10.

3. Computational Details

The first-principles calculations performed in this study are based on spin-polarized DFT implemented in the Vienna Ab initio Simulation Package (VASP) [28,44]. Blöchl's all-electron-like projector augmented wave (PAW) method [45] was employed to explain the interactions between the ion cores and the valence electrons. The exchange-correlation of the Kohn–Sham theory are treated by the generalized gradient approximation (GGA) [46] with Revised Perdew-Burke-Ernzerhof (RPBE), which gives more accurate chemisorption energies than the PW91 and PBE functional [47,48]. A plane-wave basis set with a kinetic energy cut-off of 400 eV is used for DFT calculations. All geometries were optimized using a force-based conjugate gradient algorithm until the forces acting on each atom converge better than 0.01 eV/Å. The optimized lattice constant for Ni is 3.523 Å, which is consistent with the experimental value of 3.524 Å [19]. Brillouin zone samplings are defined using Monkhorst-Pack scheme [39] and electronic occupancies are determined in a Methfessel-Paxton smearing method [49] with smearing energy of 0.2 eV.

Previous DFT studies on Ni catalysts considered the spin polarization of the surface magnetism to obtain more accurate total energies [50]. The Ni₂Cu (111) surface is represented as a four-layer slab with a p(3 × 3) supercell where only the bottom layer of the slab is constrained. The neighboring slabs are separated by a vacuum region of 12 Å. The first Brillouin zone of the supercell is sampled

with a $3 \times 3 \times 1$ k-point grid, which is sufficient for this cell structure. The climbing nudged elastic band [51,52] and dimer methods [53] are used to locate the transition state (TS). Total energy and band structure energy are converged to obtain accurate forces within 1×10^{-7} eV/atom during the electronic optimization. The adsorption energy (E_{ads}) is calculated as follows:

$$E_{\text{ads}} = E_{(\text{adsorbate/slab})} - E_{\text{slab}} - E_{\text{adsorbate}} \quad (3)$$

where $E_{(\text{adsorbate/slab})}$ is the total energy of the slab model with an adsorbate, E_{slab} is the total energy of the bare slab model, $E_{\text{adsorbate}}$ is the total energy of the isolated adsorbate. As agreed in the literature [54], the more negative adsorption energy indicates that the gas species is more strongly adsorbed on the surface.

The Ni structure is crystallized in a face-centered cubic (FCC) crystal lattice. We selected the (111) orientation of this lattice due to their abundance in nickel-based alloys [50]. The Cu/Ni (111) surface alloy was then constructed by replacing three nickel atoms in the topmost layer of Ni (111) by copper atoms (i.e., at the dopant coverage of 1/3 ML). The ratio (1/3 ML) was chosen from the experimental results [27] as having better carbon gasification and suitable activation energies for the CH₄ dehydrogenations, compared to high Cu loading (1.0 ML) and low Cu loading (1/9ML). The slab model surface is shown in Figure 1. Unless otherwise specified, the bottom-most layer in the slab models was constrained at the bulk position, and the top three layers, as well as the adsorbates, were allowed to relax during geometry optimization and transition state (TS) search [55]. The TS and minimum energy paths are obtained using the climbing-image nudged elastic band (Climbing-NEB) method, and confirmed by a single imaginary frequency from the vibrational analysis [56].

4. Conclusions

In this study, density functional theory (DFT) calculations were used to understand the mechanism of DRM over a Ni₂Cu (111) catalyst. In addition, carbon deposition and elimination have been investigated at the molecular level and under realistic reaction conditions. All elementary reaction steps, including CH₄ dehydrogenation, CO₂ activation, CH and C oxidations, were comprehensively described. The results showed a significant improvement in inhibiting carbon deposition compared to similar reactions on the Ni (111) and Ni₂Fe (111) surfaces. First, the energy barriers in CH₄ dissociation steps were found to be relatively increased to Ni (111) and Ni₂Fe (111) catalysts. Specifically, the CH dissociation was found to be the rate-limiting step with the highest energy barrier of 1.41 eV when compared to 1.33 eV for Ni (111) and 1.36 eV for Ni₂Fe (111) catalysts. Moreover, the source of coke had been confirmed to be from CH₄ dissociation rather than CO₂, which agrees with previous studies on Ni-based catalysts. The coke elimination through oxidation is remarkably improved by both OH and atomic O species as competitive oxidants. From the C/CH oxidation pathways, $\text{C}^* + \text{O}^* \rightarrow \text{CO}(\text{g})$ was found to be the most favorable reaction with an energy barrier of 0.72 eV. This value is less than half of similar oxidation reaction on Ni (111) and Ni₂Fe (111) catalysts. In addition, coke deposition is physically prevented by H₂O (g), which is easily formed in a Ni₂Cu (111) system. Combining the above results showed that the Ni-Ni surface with Cu atoms could improve carbon elimination (by $\text{C}^* + \text{O}^*$ reaction), while simultaneously reducing carbon deposition from CH dissociation.

The vibrational frequencies were used to evaluate the rate constant k of coke deposition and elimination reactions at typical DRM reaction temperatures. The rate constant of CH dissociation was lower than those of carbon oxidation ($k_{\text{C}(\text{O})}$ and $k_{\text{C}(\text{OH})}$) by atomic O or OH species, respectively. Their calculated values revealed the importance of OH species in bypassing the coke formation step from CH dissociation. Last, when carbon deposition occurs on the Ni₂Cu (111) surface, coke could be instantaneously removed by various oxidation reactions. In conclusion, this efficient periodic cycle of carbon deposition and carbon elimination results in a more stable catalytic performance and excellent carbon deposition resistance in DRM.

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