
DENSITY FUNCTIONAL THEORY INVESTIGATION OF METHANE STEAM REFORMING ON NI(111) AND PD₁-CU(111) SINGLE-ATOM ALLOY SURFACES

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ABSTRACT

Density functional theory (DFT) calculations were performed to investigate the elementary reaction steps involved in methane steam reforming on Ni(111) and Pd₁-Cu(111) single-atom alloy catalyst (SAAC) surfaces. The reaction pathway includes methane and water dissociation, oxidation of CH* by adsorbed oxygen to form CHO*, and subsequent dehydrogenation of CHO* to CO. The objective of this study is to evaluate the catalytic potential of the Pd₁-Cu(111) SAAC as a carbon-tolerant alternative to conventional Ni catalysts while maintaining high reforming activity. The results show that methane activation on Pd₁-Cu(111) proceeds with an activation barrier of 0.97 eV, which is 0.32 eV lower than that on Ni(111), indicating enhanced CH₄ activation. In contrast, water dissociation is less favourable on Pd₁-Cu(111), with an activation barrier 0.39 eV higher than that on Ni(111). Notably, the formation of surface carbon from CH* is kinetically inhibited on the Pd₁-Cu(111) SAAC because of its substantially higher activation barrier, thereby suppressing coke formation. Overall, these findings demonstrate that the Pd₁-Cu(111) single-atom alloy effectively promotes methane activation while minimizing carbon deposition, highlighting its promise as a highly active and coke-resistant catalyst for methane steam reforming.

Keywords: Density functional theory; Methane steam reforming; Single atom alloy; Ni catalyst)

1. INTRODUCTION

Methane steam reforming (MSR), $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$, remains the principal industrial route to hydrogen and syngas, which underpin ammonia synthesis, methanol production, and emerging hydrogen-energy technologies (Blaylock et al., 2009). Nickel-based catalysts dominate commercial MSR because Ni combines high intrinsic activity for C–H bond activation with low cost and broad availability. However, the strong methane-activation capability of Ni also promotes sequential dehydrogenation of CH_x intermediates, particularly at low-coordination sites, leading to surface carbon accumulation and the nucleation of graphitic coke. Carbon deposition blocks active sites, alters the catalyst surface, and ultimately accelerates deactivation (Wang et al., 2017). Thermal sintering of Ni under reforming conditions further compromises catalyst stability (Che et al., 2017). These limitations have therefore driven the search for catalyst architectures that retain efficient C–H activation while suppressing the elementary steps responsible for carbon formation.

Single-atom alloys (SAAs), in which isolated catalytically active metal atoms are embedded in a less reactive host-metal surface, offer a distinctive strategy for addressing this challenge (Ibrahim et al., 2023). Site isolation can electronically and geometrically modify the reactivity of the active atom while restricting ensembles of contiguous reactive sites required for multidentate adsorption, extensive dehydrogenation, and carbon–carbon coupling (Hannagan et al., 2020). Among emerging SAA platforms, Pd–Cu systems are particularly attractive for reforming chemistry. Although Cu exhibits limited activity toward methane activation, isolated Pd atoms can provide highly reactive sites for C–H bond cleavage within an otherwise relatively inert Cu matrix (Cao et al., 2015). At the same time, the spatial isolation of Pd atoms may limit the contiguous ensembles that facilitate deep dehydrogenation and coke-precursor formation (Cao et al., 2015). Pd₁-Cu(111) thus provides a well-defined model system for determining whether single-atom site isolation can preserve the methane-activation

characteristics required for MSR while mitigating the carbon-forming chemistry inherent to conventional Ni surfaces.

The overall MSR mechanism comprises a complex network of competing elementary reactions, including CH₄ activation, H₂O dissociation, sequential CH_x dehydrogenation, oxidation of carbon-containing intermediates, and CO formation (Blaylock et al., 2011). Consequently, overall catalytic performance cannot be rationalized solely from adsorption properties or a single apparent activation barrier. Periodic density functional theory (DFT) provides a direct means of resolving these elementary processes and quantifying their reaction energies and kinetic barriers at the atomic scale (Ibrahim et al., 2024). Despite increasing interest in single-atom catalysts for hydrocarbon conversion, the mechanistic relationship between methane activation and carbon suppression on Pd₁-Cu(111) remains insufficiently established. In particular, a direct comparison of the competing CH* oxidation pathway toward CO and CH* dehydrogenation pathway toward surface carbon on Pd₁-Cu(111) and Ni(111) is lacking. Establishing this competition is essential for determining whether Pd₁-Cu(111) can overcome the activity–coking trade-off that constrains Ni-based MSR catalysts. A coke-resistant, highly active MSR catalyst is of direct relevance to Nigeria and other gas-endowed African economies, where methane steam reforming underpins existing and planned syngas, ammonia/fertilizer, and hydrogen-energy value chains built on the region's substantial natural gas reserves; catalysts that resist deactivation by carbon deposition can improve the operating economics and reliability of such reforming processes, supporting broader sustainable-energy and industrial-development objectives (Omuboye & Nweke-Eze, 2026).

This study addresses that gap using periodic DFT calculations to map the complete elementary reaction network of MSR on Ni(111) and Pd₁-Cu(111), directly comparing activation barriers for methane activation, water dissociation, and coke-forming dehydrogenation. The novelty of this work lies in demonstrating, at the mechanistic level, that Pd₁-Cu(111) simultaneously lowers the barrier for methane activation and kinetically suppresses surface carbon formation relative to Ni(111), establishing a mechanistic basis for its use as a coke-resistant reforming catalyst.

2. METHODOLOGY

Periodic, spin-unrestricted DFT calculations were performed using the DMol³ code (Delley, 2010). Exchange–correlation effects were treated within the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional. Self-consistent field convergence was set to a threshold of 10^{−5} Ha for the total electronic energy, and geometry optimizations were converged to a maximum force criterion of 0.005 Ha Å^{−1}. Brillouin-zone integration was performed using a 4 × 4 × 1 Monkhorst–Pack k-point mesh.

The Ni(111) and Pd₁-Cu(111) single-atom alloy (SAA) surfaces were modelled using a p(3 × 3) periodic supercell of a four-layer slab. For the Pd₁-Cu(111) SAA, a single Pd atom was substituted for a Cu atom in the topmost layer of the Cu(111) slab, embedding an isolated Pd site within the Cu host. During optimization, the two uppermost slab layers were allowed to relax fully, while the two lower layers were fixed at their bulk-optimized positions to approximate bulk-like behaviour. Periodic slab images were separated by an 18 Å vacuum region along the surface normal to eliminate spurious interactions between periodic replicas.

Transition states (TS) for each elementary reaction step were located using the linear synchronous transit (LST) and quadratic synchronous transit (QST) methods, followed by conjugate-gradient refinement. Each optimized TS was confirmed by vibrational frequency analysis, requiring exactly one imaginary frequency along the reaction coordinate, corresponding to the reaction pathway. Zero-point energy (ZPE) corrections, reported as ΔE^{ZPE} and E_a^{ZPE} in Table 1, were obtained from the vibrational frequencies computed for each initial, transition, and final state and added to the corresponding electronic-energy differences. The activation energy (E_a) and reaction energy (ΔE) for each elementary step were calculated as:

$$E_a = E_{TS} - E_{IS} \quad (1)$$

$$\Delta E = E_{FS} - E_{IS} \quad (2)$$

where E_{IS}, E_{TS}, and E_{FS} are the total electronic energies of the slab system in the initial, transition, and final states, respectively. All reported E_a and ΔE values correspond to electronic-energy differences. The zero point energy (ZPE) was calculated using the following equation 3.

$$ZPE = \sum hv/2$$

Where h is Planck's constant and v is the vibrational frequency. Adsorbed species are denoted throughout using an asterisk (*) to indicate surface-bound intermediates: CH_4^* , CH_3^* , CH_2^* , CH^* , C^* , H_2O^* , OH^* , O^* , HCO^* , COH^* , CO^* , COOH^* , and CO_2^* , consistent with standard surface-science notation.

3. RESULTS AND DISCUSSION

The reaction mechanisms of MSR on Ni(111) and Pd1–Cu(111) single-atom alloy (SAA) surfaces were systematically investigated. The kinetic parameters associated with the individual reaction steps were determined and are summarized in Table 1.

Table 1: Activation energy and reaction energy of the reaction steps in MSR

	elementary reaction step	Ni(111)		Pd1-Cu(111)	
		ΔE^{ZPE}	E_a^{ZPE}	ΔE^{ZPE}	E_a^{ZPE}
		(eV)	(eV)	(eV)	(eV)
R1	$\text{CH}_4 + * \rightarrow \text{CH}_4^*$	-0.11		-0.11	
R2	$\text{H}_2\text{O} + * \rightarrow \text{H}_2\text{O}^*$	-0.41		-0.37	
R3	$\text{CH}_4^* + * \rightarrow \text{CH}_3^* + \text{H}^*$	0.20	1.29	0.59	0.97
R4	$\text{CH}_3^* + * \rightarrow \text{CH}_2^* + \text{H}^*$	0.15	0.78	0.15	1.11
R5	$\text{CH}_2^* + * \rightarrow \text{CH}^* + \text{H}^*$	-0.21	0.40	0.41	0.92
R6	$\text{CH}^* + * \rightarrow \text{C}^* + \text{H}^*$	0.69	1.39	1.22	1.77
R7	$\text{H}_2\text{O}^* + * \rightarrow \text{OH}^* + \text{H}^*$	-0.22	0.71	0.14	1.10
R8	$\text{OH}^* + * \rightarrow \text{O}^* + \text{H}^*$	-0.19	1.07	0.63	1.26
R9	$\text{CH}^* + \text{O}^* \rightarrow \text{HCO}^* + *$	0.11	1.20	-1.72	0.41
R10	$\text{C}^* + \text{OH}^* \rightarrow \text{COH}^* + *$	-0.89	0.86	-1.36	0.77
R11	$\text{C}^* + \text{O}^* \rightarrow \text{CO}^* + *$	-1.92	1.08	-3.23	0.73
R12	$\text{HCO}^* + * \rightarrow \text{CO}^* + \text{H}^*$	-1.19	0.11	-0.66	0.40
R13	$\text{COH}^* + * \rightarrow \text{CO}^* + \text{H}^*$	-1.12	0.76	-1.35	0.75
R14	$\text{CO}^* + \text{OH}^* \rightarrow \text{COOH}^* + *$	0.63	1.40	0.46	0.69
R15a	$\text{CO}^* + \text{O}^* \rightarrow \text{CO}_2^* + *$	0.66	1.08	-	-
R15b	$\text{CO}^* + \text{O}^* \rightarrow \text{CO}_{2,\text{phys}}^* + *$	-	-	-1.04	0.45
R16a	$\text{COOH}^* + * \rightarrow \text{CO}_2^* + \text{H}^*$	-0.02	0.71	-	-
R16b	$\text{COOH}^* + * \rightarrow \text{CO}_{2,\text{phys}}^* + \text{H}^*$	-	-	-0.46	0.91
R17	$\text{CO}_2^* \rightarrow \text{CO}_{2,\text{phys}}^*$	-0.29	0.12	-	-
R18	$\text{CO} + * \rightarrow \text{CO}^*$	-1.64		-1.09	
R19	$\text{CO}_2 + * \rightarrow \text{CO}_{2,\text{phys}}^*$	-0.1		-0.09	
R20	$2\text{H}^* \rightarrow \text{H}_2^* + 2^*$			0.36	0.73

3.1 Elementary reaction step kinetics

3.1.1 CH_4 Dehydrogenation

The initial C–H bond activation in methane represents a critical step in MSR because it initiates the sequential dehydrogenation of CH_4 and ultimately generates surface carbon species. On the Pd1–Cu(111) single-atom alloy (SAA) surface, CH_4^* dehydrogenation to CH_3^* is endothermic by 0.59 eV and proceeds with an activation energy of 0.97 eV. This barrier is 0.32 eV lower than that calculated for Ni(111), indicating that isolated Pd atoms embedded in the Cu surface facilitate the initial C–H bond cleavage relative to the parent Ni surface.

The subsequent dehydrogenation sequence, $\text{CH}_3^* \rightarrow \text{CH}_2^* \rightarrow \text{CH}^* \rightarrow \text{C}^*$, remains endothermic on $\text{Pd}_1\text{-Cu(111)}$, with reaction energies of 0.15, 0.41, and 1.22 eV, respectively. The corresponding activation energies are 1.11, 0.92, and 1.77 eV. Notably, Ni(111) exhibits lower barriers for $\text{CH}_3^* \rightarrow \text{CH}_2^*$ and $\text{CH}_2^* \rightarrow \text{CH}^*$ by 0.33 and 0.52 eV, respectively, demonstrating that Ni is kinetically more effective for these intermediate dehydrogenation steps. In contrast, the final $\text{CH}^* \rightarrow \text{C}^*$ step requires a 0.23 eV higher activation energy on $\text{Pd}_1\text{-Cu(111)}$ than on Ni(111) . Thus, although $\text{Pd}_1\text{-Cu(111)}$ promotes the initial activation of methane, the subsequent conversion of CH^* to atomic carbon is less kinetically favorable on the SAA surface. This distinction is important because the balance between facile methane activation and carbon formation can strongly influence both reforming activity and carbon accumulation.

3.1.2 H_2O^* Dissociation

Water activation constitutes another essential elementary process in MSR because it provides surface OH^* and, subsequently, O^* -containing species required for carbon oxidation and CO_2 formation. Previous DFT calculations by Blaylock and co-workers (2011) reported that H_2O^* dissociation on Ni(111) is exothermic by 0.28 eV with an activation energy of 0.90 eV [Blaylock et al., 2011]. In the present calculations, $\text{H}_2\text{O}^* \rightarrow \text{OH}^* + \text{H}^*$ on Ni(111) is also exothermic, with a reaction energy of -0.22 eV, while the corresponding activation energy is 0.71 eV. In contrast, H_2O^* dissociation on $\text{Pd}_1\text{-Cu(111)}$ is endothermic by 0.14 eV and requires an activation energy 0.39 eV higher than that on Ni(111) . The subsequent $\text{OH}^* \rightarrow \text{O}^* + \text{H}^*$ step exhibits activation energies of 1.01 and 1.11 eV on Ni(111) and $\text{Pd}_1\text{-Cu(111)}$, respectively. The Ni(111) value is consistent with previous DFT calculations reported by Du and co-workers (Du et al., 2017). These results indicate that, unlike the initial C-H bond cleavage in CH_4 , water activation is kinetically more favorable on Ni(111) . Consequently, the overall reforming performance of $\text{Pd}_1\text{-Cu(111)}$ may depend strongly on the availability and reactivity of adsorbed hydroxyl species.

3.1.3 COH^* and HCO^* Formation

Following methane dehydrogenation, surface carbon-containing intermediates can undergo oxidation through reactions with oxygen-containing species. The oxidation of CH^* to HCO^* on $\text{Pd}_1\text{-Cu(111)}$ is highly exothermic, releasing 1.82 eV, and proceeds with a relatively low activation energy of 0.41 eV. This barrier is 0.79 eV lower than that calculated for Ni(111) , indicating that the SAA surface strongly facilitates this oxidation route. COH^* can alternatively form through the recombination of C^* and OH^* . The strongly exothermic character of this reaction on both surfaces indicates that COH^* formation is thermodynamically favourable, although its overall contribution to MSR must also be assessed from the corresponding kinetic barriers.

3.1.4 CO^* Formation

CO^* represents a key product intermediate in MSR and can form through several competing pathways. One route involves the recombination of C^* and O^* , whereas alternative routes proceed through the decomposition of HCO^* or COH^* . On Ni(111) , $\text{C}^* + \text{O}^* \rightarrow \text{CO}^*$ is strongly exothermic, with a reaction energy of -1.92 eV, but requires an activation energy of 1.08 eV, consistent with previous theoretical studies. The corresponding barrier on $\text{Pd}_1\text{-Cu(111)}$ decreases to 0.73 eV, demonstrating that the SAA surface facilitates CO^* formation through direct C-O coupling. The decomposition of HCO^* provides another kinetically accessible route. On Ni(111) , $\text{HCO}^* \rightarrow \text{CO}^* + \text{H}^*$ is exothermic and has a very low activation energy of 0.11 eV, consistent with the value reported for Ni-based surfaces by Blaylock and co-workers [Blaylock et al., 2011]. On $\text{Pd}_1\text{-Cu(111)}$, however, the barrier increases by 0.34 eV, indicating that HCO^* decomposition is less favorable on the SAA. COH^* decomposition to CO^* also proceeds with a moderate activation energy on $\text{Pd}_1\text{-Cu(111)}$, calculated as 0.75 eV, while the reaction remains exothermic by 0.35 eV. Collectively, these results demonstrate that $\text{Pd}_1\text{-Cu(111)}$ favors direct C-O coupling over HCO^* decomposition, whereas Ni(111) provides a particularly facile pathway through HCO^* .

3.1.4 COOH^* and CO_2^* Formation

COOH^* formation represents a subsequent oxidation pathway toward CO_2^* . On Ni(111) , the interaction of CO^* with OH^* to form COOH^* is endothermic by 0.63 eV and requires an activation energy of 1.40 eV. On $\text{Pd}_1\text{-Cu(111)}$, the same reaction is substantially more accessible, with a lower activation energy of 0.69 eV and a smaller endothermicity of 0.46 eV. Thus, the SAA surface

significantly facilitates COOH* formation relative to Ni(111). CO₂* can subsequently form through either direct oxidation of CO* by O* or dissociation of COOH* via O–H bond cleavage. On Ni(111), the CO* + O* → CO₂* pathway is endothermic by 0.66 eV and has an activation energy of 1.09 eV, in agreement with previous calculations [Blaylock et al., 2009]. In striking contrast, CO oxidation on Pd₁-Cu(111) is exothermic by 1.04 eV and requires only 0.45 eV of activation energy. Although COOH* dissociation to CO₂* is also exothermic on Pd₁-Cu(111) by 0.46 eV, the direct CO* oxidation pathway remains kinetically preferred because it proceeds with the lower activation barrier. These results highlight a pronounced mechanistic difference between the two surfaces: Ni(111) relies more strongly on sequential COOH*-mediated oxidation, whereas Pd₁-Cu(111) promotes direct CO oxidation to CO₂*. This altered reaction landscape illustrates how isolated Pd atoms can modify both the thermodynamics and kinetics of oxygen-assisted carbon oxidation on Cu-based SAA surfaces.

4. CONCLUSION

Periodic density functional theory calculations were employed to elucidate and compare the elementary reaction network of methane steam reforming on Ni(111) and Pd₁-Cu(111) single-atom alloy surfaces. The results identify a key mechanistic advantage of Pd₁-Cu(111) as it lowers the CH₄* activation barrier to 0.97 eV, 0.32 eV below that of Ni(111), while increasing the barrier for the coke-precursor-forming CH* → C* step to 1.77 eV. This combination facilitates methane activation while kinetically suppressing surface carbon formation. Pd₁-Cu(111) nevertheless exhibits a clear water-activation penalty, with higher barriers for both H₂O* → OH* and OH* → O* formation, potentially limiting the availability of oxygen-derived intermediates. Importantly, once generated, these species promote a low-barrier CH* → HCO* pathway, redirecting reactive carbon away from C* accumulation and toward CO formation. However, because water dissociation is itself less favorable on Pd₁-Cu(111), the supply of OH*/O* needed to sustain this carbon-oxidation route may itself become rate-limiting under working conditions, so the coke-suppression advantage identified here should be regarded as a mechanistic, elementary-step result rather than a demonstrated gain in overall turnover frequency; a full microkinetic treatment would be required to establish the net effect on catalytic performance. Overall, Pd₁-Cu(111) emerges as a mechanistically promising, potentially carbon-tolerant alternative to conventional Ni catalysts. These findings provide a molecular basis for designing SAA catalysts that balance methane activation, water dissociation, and coke resistance under realistic MSR conditions.

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