

Mechanistic insights into methanol steam reforming on PdCu(111) and PtCu(111) bimetallic catalysts

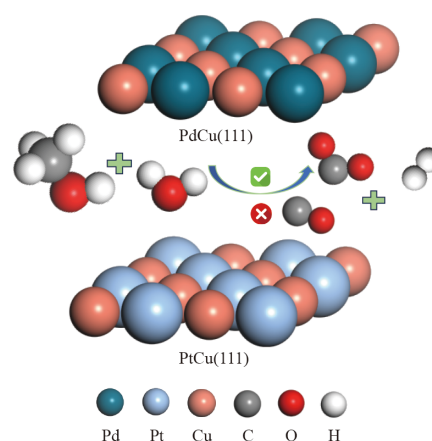
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Abstract: Methanol steam reforming (MSR) stands as a pivotal process for efficient hydrogen production. In this study, density functional theory (DFT) calculations were employed to conduct a comparative analysis of the MSR reaction mechanism on PdCu(111) and PtCu(111) bimetallic surfaces. The investigation unveiled the underlying mechanism by which alloying modulates reaction pathways and overall catalytic performance. Notably, Cu sites were found to stabilize adsorption of OH and CH₂O species, whereas Pd/Pt sites exhibited a preferential affinity for CO molecule. This spatial site separation facilitates progression along the formate pathway. PdCu(111) demonstrated superior overall catalytic performance compared to PtCu(111), with water dissociation identified as the rate-determining step (RDS), featuring an activation energy of only 0.74 eV. The bimetallic synergy breaks the inherent contradiction between the activity and selectivity of monometallic catalysts: Cu sites serve as a source of hydroxyl groups, while Pd/Pt sites enhance C–H bond cleavage efficiency, ultimately enabling high methanol conversion alongside low CO formation. From the perspectives of electronic structure and geometric configuration, this study establishes a theoretical framework to guide the rational design of high-performance bimetallic catalysts for MSR.

Key words: methanol steam reforming; PdCu(111); PtCu(111); reaction mechanism



Hydrogen is widely recognized as a quintessential clean energy carrier with potential applications across diverse fields—particularly as a fuel in fuel cells, which has garnered substantial research attention^[1–4]. However, the storage and transportation of hydrogen remain formidable challenges to its widespread utilization^[5–7]. Compared with other hydrocarbons, CH₃OH exhibits distinct advantages as a hydrogen carrier: it has the highest hydrogen-to-carbon ratio and lacks stable carbon-carbon bonds. These structural attributes enable methanol to undergo steam reforming under relatively mild temperature conditions, thereby endowing it with significant potential for efficient hydrogen production^[8–10].

Cu-based catalysts have been extensively employed in MSR reactions^[11–15], and their catalytic activity and product

selectivity can typically be modulated by incorporating appropriate promoters^[16–19] and optimizing synthesis protocols^[20–24]. Nevertheless, the inherent susceptibility of copper to sintering and deactivation at elevated reaction temperatures—stemming from its intrinsic pyrophoricity—severely constrains its long-term stability^[25–26]. In contrast, Group VIII transition metal catalysts have been developed for their exceptional thermal stability. Specifically, Pd-based catalysts exhibit catalytic activity comparable to that of Cu-based systems at high temperatures^[27–29] while maintaining performance stability over prolonged reaction periods. A critical limitation of such catalysts, however, is their propensity to generate CO, which can induce severe poisoning of fuel cell electrodes. Notably, Iwasa et al.^[30–31] demonstrated that loading Pd onto

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a ZnO support enhances MSR activity and selectivity toward CO₂. Experimental characterizations revealed that Pd particles alloy with Zn as temperature increases, forming a stable PdZn phase over a broad temperature range. Analogously, Pd/ZnO catalysts also exhibit low CO selectivity in MSR, a behavior attributed to the formation of PdZn alloys. Wang et al.^[32] further reported that PdZn alloy formation significantly improves CO₂ selectivity and overall catalytic activity, with the active phase remaining stable even at 400 °C. By contrast, catalysts that fail to form such alloy structures with ZnO (e.g., Ni, Ru, Co, Ir) typically exhibit poor methanol conversion efficiency and produce substantially higher CO concentrations, limiting their practical applicability^[33].

By integrating the advantages of Cu and Pd-based catalysts, Azenha et al.^[34] rationally designed and synthesized a high-performance PdCu bimetallic catalyst for low-temperature MSR. Compared with monometallic Pd catalysts, the PdCu catalyst displayed 1.5–2 times higher activity and significantly reduced CO formation. Additionally, its long-term stability was enhanced relative to monometallic Cu, with no detectable deactivation observed after 80 h of continuous operation at 240 °C. Complementarily, experimental studies by Mierczynski^[35] and Zhang et al.^[36] confirmed that the PdCu alloy phase markedly boosts H₂ yield during MSR. This alloy adopts a stable face-centered cubic (fcc) structure, with the exposed (111) facet serving as the primary active surface. The latter report^[36] further validated, *via* rigorous characterizations including XRD, HAADF-STEM, EDS, XAFS and XPS, that the 1:1 stoichiometric PdCu alloy exhibits excellent catalytic activity under realistic reaction conditions. These experimental findings provide a robust structural basis for the development of our computational models.

From a theoretical perspective, comprehensive reaction mechanisms for MSR on various pure metal surfaces, including Cu(111)^[37–38], Cu(110)^[39], Cu(211)^[38], Pd(111)^[37], Pt(111)^[40], Co(0001)^[41] and Ni(111)^[42] have been well-established, elucidating their respective reaction pathways and product selectivities. For alloy catalysts, systematic mechanistic investigations have also been reported for systems such as PdZn(111)^[43], PtZn(111)^[44], NiZn(111)^[44] and NiCu(111)^[45]. Given that Pt and Pd belong to the same group in the periodic table and share similar electronic configurations, we employed DFT calculations to systematically investigate MSR reaction pathways on PdCu(111) and PtCu(111) alloy surfaces. By probing the structure-performance relationship of these catalysts, this study advances our understanding of how alloy composition modulates catalytic behavior.

1 Computational methods and models

All calculations were performed using the Vienna Ab initio Simulation Package (VASP)^[46–47]. The electronic exchange-correlation interaction was described by the Perdew-Burke-Ernzerhof (PBE) functional^[48] within the framework of the generalized gradient approximation

(GGA) and core-valence electron interactions^[49] were treated *via* the projector augmented wave (PAW) method. To account for van der Waals forces between adsorbates and the catalyst surface, the DFT-D3 correction was incorporated^[50–51]. A plane-wave kinetic energy cutoff of 400 eV was employed, and the Brillouin zone was sampled with a 2×2×1 Monkhorst-Pack *k*-point mesh.

Geometric optimizations were carried out until the residual forces on all atoms converged to less than 0.02 eV/Å, with the energy difference between consecutive steps falling below 10^{−5} eV. For transition state (TS) searches, the force convergence criterion was relaxed to 0.05 eV/Å. To ensure reliability and accuracy, the climbing image nudged elastic band (CI-NEB) method^[52–54] and dimer method^[55–56] were employed in combination. TS structures were validated by the presence of exactly one imaginary vibrational frequency, whose corresponding mode strictly aligned with the bond-breaking direction involved in the reaction. Relevant energy calculations (e.g., adsorption energy (*E*_{ads}), reaction energy (ΔE) and activation energy (*E*_a)) followed the formulations reported in our previous work^[57].

Surface models of PdCu(111) and PtCu(111) were constructed using a four-layer slab with a *p*(4×4) surface supercell. The optimized lattice parameters for the PdCu(111) slab were *a* = *b* = 10.54 Å and *c* = 21.58 Å, while those for the PtCu(111) slab were *a* = *b* = 10.56 Å and *c* = 21.63 Å. A 15 Å vacuum layer was introduced along the *z*-direction to eliminate interactions between periodic images. To simulate the surface alloy structure, each slab was configured with a 1:1 stoichiometric ratio of Pd:Cu (for PdCu(111)) and Pt:Cu (for PtCu(111)). For free gas-phase molecule calculations, each molecule was placed in a 12 Å × 12 Å × 12 Å cubic supercell to avoid intermolecular interactions.

2 Results and discussion

2.1 Stable adsorption configurations of all species on PdCu(111) and PtCu(111) surfaces

All adsorbed intermediates are categorized into four classes based on the type of atoms that directly interact with the catalyst surface: (1) O-terminated intermediates: species primarily bonded to the surface *via* O atom, including: H₂O, CH₃OH, OH, CH₃O, CH₂OOH, CHOOH, CH₂OO, bi-CHOO and mono-CHOO; (2) C/O co-adsorbed intermediates: species adsorbed simultaneously through both C and O atoms, such as: CH₂O, CHO, *cis*-COOH and *trans*-COOH; (3) C-terminated intermediates: species mainly bonded to the surface *via* C atom, with CO as the representative example; (4) Other species: weakly adsorbed CO₂ on the surface. The adsorption sites considered primarily include top sites (Pd-top, Pt-top, Cu-top), bridge sites (Pd-Cu bridge, Pt-Cu bridge, Cu-Cu bridge), hexagonal close-packed (hcp) hollow sites (Cu-Pd-Pd, Cu-Pt-Pt, Cu-Cu-Pd, Cu-Cu-Pt) and fcc hollow sites (Cu-Pd-Pd, Cu-Pt-Pt, Cu-Cu-Pd, Cu-Cu-Pt), as illustrated in Figure 1.

All adsorption structures are provided in Tables S1 and S2 of the Supporting Information, where the most stable adsorption configurations on PdCu(111) and PtCu(111) surfaces are systematically depicted in Figures 2 and 3, respectively. The corresponding adsorption energies are summarized in Table 1. Detailed descriptions of each category of species are as follows.

2.1.1 Adsorption of O-terminated intermediates

On the PdCu(111) surface, H₂O preferentially adsorbs at the Cu-top site *via* the O atom with an adsorption energy of -0.48 eV. In this configuration, both O–H bonds lie parallel to the surface, with a bond length of 0.98 Å—slightly longer than the gas-phase value (0.97 Å), indicating partial activation of H₂O. On PtCu(111), the most stable H₂O adsorption occurs at the Pt-top site *via* the O atom, where both O–H bonds are parallel to the surface (bond length = 0.98 Å) and the adsorption energy is also -0.48 eV.

CH₃OH adsorbs at the Cu-top site on both PdCu(111) and PtCu(111). The average C–H bond length is 1.10 Å for both surfaces, while the O–H bond lengths are 0.97 Å (PdCu(111)) and 0.98 Å (PtCu(111)), with corresponding adsorption energies of -0.67 and -0.69 eV, respectively.

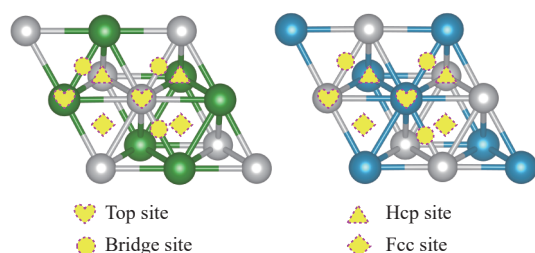


Fig. 1 Adsorption sites of intermediate species on two catalyst surfaces (The green, blue and gray balls represent Pd, Pt and Cu atoms, respectively)

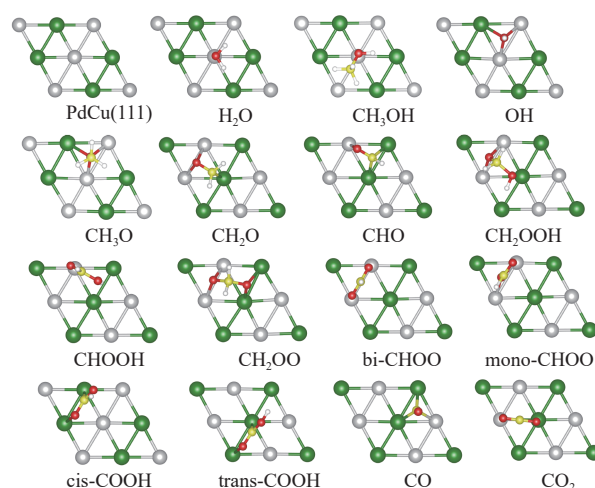


Fig. 2 Adsorption of all intermediate species on PdCu(111) catalyst (The yellow, red and white balls represent C, O and H atoms, respectively)

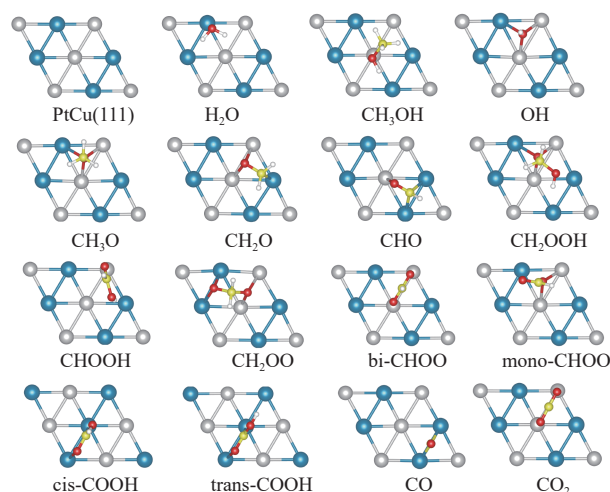


Fig. 3 Adsorption of all intermediate species on PtCu(111) catalyst

Table 1 Preferred adsorption sites and adsorption energies (E_{ads} , eV) of all intermediate species on the PdCu(111) and PtCu(111) surfaces

Specie	PdCu(111)		PtCu(111)	
	Site	E_{ads}/eV	Site	E_{ads}/eV
H ₂ O	Cu top	-0.48	Pt top or Cu top	-0.48
CH ₃ OH	Cu top	-0.67	Cu top	-0.69
OH	Cu-Cu-Pd fcc	-3.10	Cu-Cu-Pt fcc	-2.83
CH ₃ O	Cu-Cu-Pd fcc	-2.54	Cu-Cu-Pt fcc	-2.34
CH ₂ O	Cu-Cu-Pd hcp	-0.84	Cu-Cu-Pt hcp	-0.79
CHO	Cu-Pd-Pd fcc	-2.91	Cu-Pt-Pt fcc	-3.05
CH ₂ OOH	Cu-Cu-Pd hcp	-2.49	Cu-Cu-Pt fcc	-2.22
CHOOH	Cu top	-0.74	Cu top	-0.73
CH ₂ OO	Cu-Cu bridge and Pd-Pd bridge	-3.96	Cu-Cu bridge and Pt-Pt bridge	-3.44
bi-CHOO	Cu-Cu bridge by two O atoms	-3.02	Cu-Cu bridge by two O atoms	-2.75
mono-CHOO	Cu-Cu bridge by one O atom	-2.49	Cu-Cu bridge by one O atom	-2.21
<i>cis</i> -COOH	Pd-Pd-bridge	-2.85	Pt-Pt-bridge	-3.09
<i>trans</i> -COOH	Pd-Pd-bridge	-2.84	Pt-Pt-bridge	-3.09
CO	Cu-Pd-Pd hcp	-2.05	Pt-Pt bridge	-2.20
CO ₂	parallel to surface	-0.28	parallel to surface	-0.29

OH preferentially adsorbs at fcc hollow sites on both surfaces. On PdCu(111), OH is stabilized at the Cu-Cu-Pd fcc site with an average O-metal distance of 2.07 Å; on PtCu(111), it adsorbs at the Cu-Cu-Pt fcc site with an O-metal distance of 2.09 Å. The O-H bond length is 0.97 Å for both surfaces, and the adsorption energies are -3.10 eV (PdCu(111)) and -2.83 eV (PtCu(111)).

CH₃O shares the same preferred adsorption sites as OH: the Cu-Cu-Pd fcc site on PdCu(111) and the Cu-Cu-Pt fcc site on PtCu(111). The average O-metal distances are 2.07 Å (PdCu(111)) and 2.09 Å (PtCu(111)), while the average C-H bond length of CH₃O is 1.10 Å for both surfaces. Adsorption energies are -2.54 eV (PdCu(111)) and -2.34 eV (PtCu(111)).

For CH₂OOH on PdCu(111), one O atom adsorbs at the Cu-Cu-Pd fcc hollow site with an average O-metal distance of 2.13 Å; the remaining molecular moiety tilts slightly upward without direct bonding to the surface. A similar configuration is observed on PtCu(111), where one O atom occupies the Cu-Cu-Pt fcc site (O-metal distance = 2.09 Å). The adsorption energies of CH₂OOH are -2.49 eV (PdCu(111)) and -2.22 eV (PtCu(111)).

CHOOH adopts a planar, top-site adsorption configuration on both surfaces, with one O atom bound to a Cu-top site. The O-Cu distances are 2.13 Å (PdCu(111)) and 2.17 Å (PtCu(111)). In the adsorbed CHOOH, the C-H bond lengths are 1.10 Å (PdCu(111)) and 1.11 Å (PtCu(111)), while both O-H bonds measure 1.03 Å. Adsorption energies are nearly identical: -0.74 eV (PdCu(111)) and -0.73 eV (PtCu(111)).

CH₂OO, a competitive species to CHOOH, adsorbs *via* two O atoms at distinct bridge sites on both surfaces. On PdCu(111), the O atoms bind to the Cu-Cu bridge (average distance = 2.00 Å) and Pd-Pd bridge (2.17 Å), with an average C-H bond length of 1.11 Å. On PtCu(111), the O atoms occupy the Cu-Cu bridge (2.06 Å) and Pt-Pt bridge (2.16 Å), with the same average C-H bond length (1.11 Å). Adsorption energies of CH₂OO are -3.96 eV (PdCu(111)) and -3.44 eV (PtCu(111)).

CHOO exhibits two adsorption modes: bidentate (bi-CHOO) and monodentate (mono-CHOO). In bi-CHOO, both O atoms coordinate with surface metal atoms; in mono-CHOO, only one O atom binds to the substrate. On PdCu(111), the most stable bi-CHOO has both O atoms bonded to Cu atoms (adsorption energy = -3.02 eV), while the most stable mono-CHOO adsorbs *via* one O atom at the Cu-Cu bridge (-2.49 eV). On PtCu(111), a similar trend is observed. Their adsorption energies are -2.75 eV (bi-CHOO) and -2.21 eV (mono-CHOO), respectively.

2.1.2 Adsorption of C/O co-adsorbed Intermediates

On the PdCu(111) surface, the O atom of the CH₂O species occupies the Cu-Cu bridge site, with an average O-Cu bond length of 2.09 Å. The CH₂ moiety adsorbs at the Pd-atop site, forming a C-Pd bond of 2.10 Å, while the

average C-H bond length is 1.10 Å. A similar adsorption configuration is observed on PtCu(111): the C atom binds to the Pt-top site (C-Pt distance = 2.11 Å), and the O atom bridges two Cu atoms (average O-Cu distance = 2.11 Å), with an average C-H bond length of 1.10 Å. The calculated adsorption energies are -0.84 eV (PdCu(111)) and -0.79 eV (PtCu(111)).

For CHO on PdCu(111), the O atom adsorbs at the Cu-top site (O-Cu distance = 2.11 Å), while the C atom occupies the Pd-Pd bridge site (average C-Pd bond length = 2.06 Å); the C-H bond length is 1.12 Å. A similar structure is found on PtCu(111): the O atom binds to the Cu-top site (O-Cu distance = 2.10 Å) and the C atom is located at the Pt-Pt bridge site (average C-Pt bond length = 2.09 Å), with a C-H bond length of 1.11 Å. The adsorption energies are -2.91 eV (PdCu(111)) and -3.05 eV (PtCu(111)).

COOH is a competitive species relative to CHOO, existing as two configurational isomers: *cis*-COOH and *trans*-COOH. In the *cis* isomer, the O-bound H atom and C-bound O atom lie on the same side of the molecular plane; in the *trans* isomer, they are on opposite sides. Calculations indicate that both *cis*-COOH and *trans*-COOH adsorb at the Pd-Pd (PdCu(111)) or Pt-Pt (PtCu(111)) bridge sites. Their adsorption energies are -2.85 (*cis*) and -2.84 eV (*trans*) on PdCu(111), and -3.09 eV for both isomers on PtCu(111).

2.1.3 Adsorption of C-terminated Intermediates

On the PdCu(111) surface, CO is generated *via* the dehydrogenation of CHO. It adsorbs at an hcp hollow site coordinated by two Pd atoms and one Cu atom, with a C-O bond length of 1.19 Å. On the PtCu(111) surface, the C atom occupies the Pt-Pt bridge site, and the C-O bond length is also measured as 1.19 Å. The calculated adsorption energies exhibit a notable difference: -2.05 eV on PdCu(111) versus -2.20 eV for PtCu(111).

2.1.4 Adsorption of other Intermediates

CO₂ is generated *via* the dehydrogenation of either CHOO or COOH. On both PdCu(111) and PtCu(111) surfaces, the two C-O bonds of CO₂ lie parallel to the surface plane. This adsorption is classified as physisorption and exhibits the lowest adsorption energy among all studied species: -0.28 eV on PdCu(111) and -0.29 eV on PtCu(111).

2.1.5 Electronic structure analysis of key Intermediates

Based on the above results, regarding adsorption sites, most species (e.g., OH, CH₃O, CH₂O) tend to adsorb at Cu-top sites or Cu-coordinated hollow sites. This preference arises from Cu's fully occupied 3d¹⁰ electron configuration and lower d-orbital energy, which effectively mitigates

Pauli repulsion between Cu and oxygen lone pairs. In contrast, species such as CHO and CO preferentially adsorb at Pd/Pt sites (bridge or hollow sites). This selectivity stems from the higher electronegativity of Pd/Pt and their more spatially extended *d*-orbitals; their interaction with CO is dominated by strong π -backbonding, where metal *d*-electrons feed back into $2\pi^*$ antibonding orbitals of CO.

In terms of adsorption energy, intermediates like OH and CH_3O generally adsorb more strongly on PdCu than on PtCu surface. For instance, OH exhibits an adsorption energy of -3.10 eV on PdCu versus -2.83 eV on PtCu. This enhanced affinity aligns with the calculated *d*-band centers: it is located at -1.47 eV on PdCu, which is higher than that of PtCu at -1.65 eV. Conversely, intermediates such as CO and CHO bond more strongly to PtCu. Specifically, CO adsorption energies are -2.20 eV (PtCu) and -2.05 eV (PdCu), while CHO adsorption energies are -3.05 (PtCu) and -2.91 eV (PdCu). This phenomenon is attributed to Pt's unique electronic structure: in PtCu alloys, the lower electronegativity of Cu drives electron donation to Pt and the diffuse *5d* orbitals of Pt enable more effective electron feedback into the antibonding orbitals of CO and CHO.

Thus, despite the overall downshift of the *d*-band center, the local electronic and orbital properties of Pt still stabilize these intermediates.

To further validate the origins of adsorption selectivity and π feedback, we calculated the projected density of states (PDOS) for CO adsorbed on PdCu(111) and PtCu(111), focusing on interactions between CO and directly bonded metal atoms (Figure 4). Pt's *d*-band maintains a high density of states (DOS) in the -8 to -6 eV range, forming strong and effective coupling with the 3σ orbital of CO to stabilize the σ bond. In the -5 to 0 eV range, the *d*-band of Pt exhibits broad and dispersed DOS with substantial states near the Fermi level (0 eV), enabling effective overlap with CO's $2\pi^*$ orbital and strong π back-donation, directly enhancing the Pt–C bond. In contrast, Pd and Cu *d*-orbitals on PdCu show significant hybridization and overlap in the -3 to -1 eV range. Consequently, in the $2\pi^*$ -dominant range (-1 to 0 eV), the effective DOS of Pd *d*-states is drastically reduced, limiting electrons available for π back-donation and weakening orbital overlap.

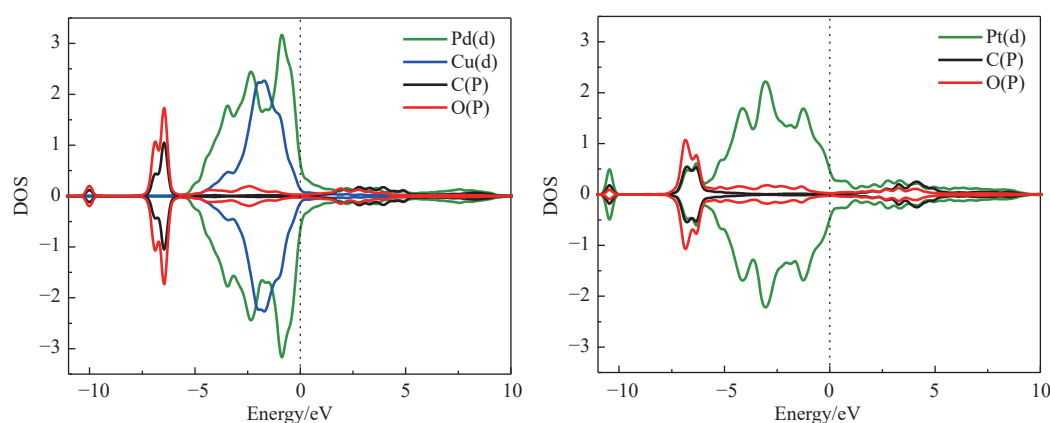


Fig. 4 Projected density of states of CO adsorbed on PdCu(111) and PtCu(111) catalysts

The electron density difference maps (Figure 5) visually confirm bonding strength differences between CO and the two alloy surfaces. In PtCu, a distinct electron accumulation bridge exists between Pt and CO's C atom, indicating sufficient electron cloud overlap and strong Pt–C bonding. In PdCu, charge distribution around Pd/Cu atoms is more dispersed, with weaker electron accumulation at Pd–C/Cu–C interfaces than in PtCu. Additionally, Cu coordination induces charge delocalization and insufficient bonding electron cloud overlap, directly reflecting weakened interfacial interactions. Bader charge analysis further supports this: in PdCu, CO's C loses 0.69 e, while two Pd atoms gain only 0.19 e, and Cu loses 0.28 e, resulting in a net system loss of 0.09 e (indicating insufficient effective bonding electrons). In PtCu, the C atom of CO loses 0.76 e and two directly bonded Pt atoms gain 0.48 e (~ 2.5 times the electron gain of Pd in PdCu), confirming abundant effective bonding electrons.

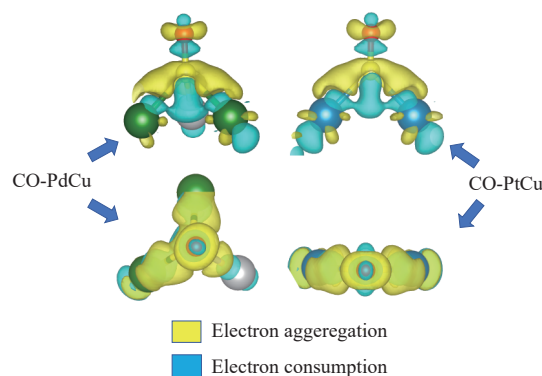


Fig. 5 Electron density difference of CO adsorbed on PdCu(111) and PtCu(111) catalysts

2.2 Elementary steps of the MSR reaction

For the MSR reaction, two primary reaction pathways are

the focus of this study, as illustrated in Figure 6: the formate pathway (Pathway 1, green arrows) and the decomposition-water gas shift (WGS) pathway (Pathway 2, blue arrows). The TS geometries of reactions occurring on PdCu(111)

and PtCu(111) surfaces are presented in Figures 7 and 8, respectively. The corresponding reaction energies, activation energies, and key bond lengths in the TS are summarized in Table 2.

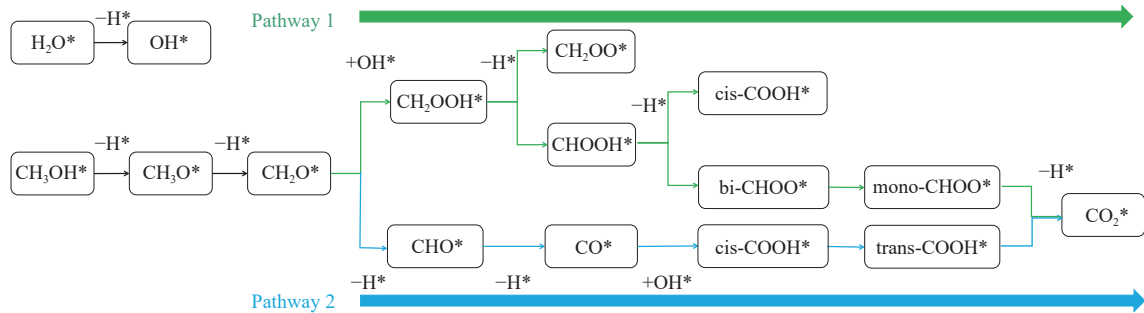


Fig. 6 Schematic illustration of the two dominant reaction pathways for MSR

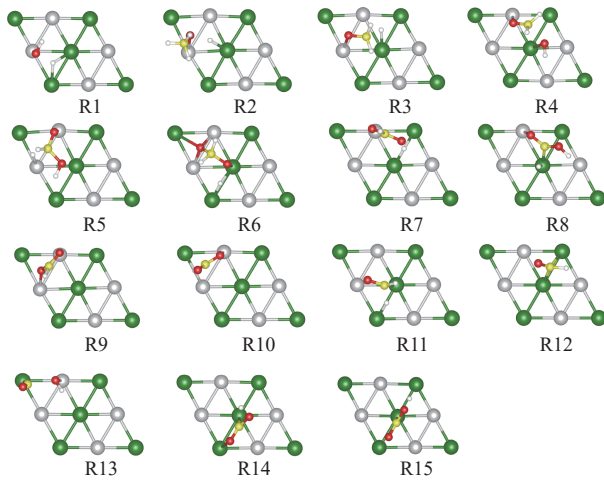


Fig. 7 Transition states of all elementary reactions on PdCu(111) catalyst

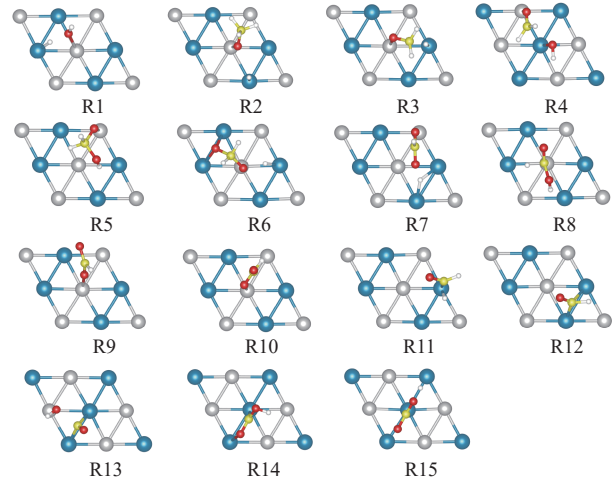


Fig. 8 Transition states of all elementary reactions on PtCu(111) catalyst

Table 2 Activation energies (E_a , eV) reaction energies (ΔE , eV) and key bond lengths (d , Å) in the transition states for all elementary reactions on PdCu(111) and PtCu(111)

Elementary step	PdCu(111)			PtCu(111)		
	E_a /eV	ΔE /eV	d /Å	E_a /eV	ΔE /eV	d /Å
R1- $\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$	0.74	-0.20	$d_{(\text{O}-\text{H})}=1.62$	0.78	0.09	$d_{(\text{O}-\text{H})}=1.46$
R2- $\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{H}$	0.64	-0.14	$d_{(\text{O}-\text{H})}=1.51$	0.93	-0.05	$d_{(\text{O}-\text{H})}=2.40$
R3- $\text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} + \text{H}$	0.66	0.04	$d_{(\text{C}-\text{H})}=1.48$	0.54	-0.11	$d_{(\text{C}-\text{H})}=1.49$
R4- $\text{CH}_2\text{O} + \text{OH} \rightarrow \text{CH}_2\text{OOH}$	0.49	-0.24	$d_{(\text{C}-\text{O})}=1.98$	0.23	-0.38	$d_{(\text{C}-\text{O})}=2.37$
R5- $\text{CH}_2\text{OOH} \rightarrow \text{CHOOH} + \text{H}$	0.63	-0.83	$d_{(\text{C}-\text{H})}=1.50$	0.56	-1.13	$d_{(\text{C}-\text{H})}=1.13$
R6- $\text{CH}_2\text{OOH} \rightarrow \text{CH}_2\text{OO} + \text{H}$	0.85	0.38	$d_{(\text{O}-\text{H})}=1.75$	0.84	0.47	$d_{(\text{O}-\text{H})}=1.68$
R7- $\text{CHOOH} \rightarrow \text{bi-CHOO} + \text{H}$	0.24	-0.25	$d_{(\text{O}-\text{H})}=1.70$	0.30	-0.31	$d_{(\text{O}-\text{H})}=2.12$
R8- $\text{CHOOH} \rightarrow \text{cis-COOH} + \text{H}$	0.69	-0.25	$d_{(\text{C}-\text{H})}=1.47$	0.72	-0.46	$d_{(\text{C}-\text{H})}=1.55$
R9- $\text{bi-CHOO} \rightarrow \text{mono-CHOO}$	0.54	0.50	—	0.63	0.51	—
R10- $\text{mono-CHOO} \rightarrow \text{CO}_2 + \text{H}$	0.13	-0.77	$d_{(\text{C}-\text{H})}=1.38$	0.28	-1.10	$d_{(\text{C}-\text{H})}=1.15$
R11- $\text{CH}_2\text{O} \rightarrow \text{CHO} + \text{H}$	0.25	-0.64	$d_{(\text{C}-\text{H})}=1.40$	0.17	-0.67	$d_{(\text{C}-\text{H})}=1.31$
R12- $\text{CHO} \rightarrow \text{CO} + \text{H}$	0.09	-1.32	$d_{(\text{C}-\text{H})}=1.15$	0.14	-1.27	$d_{(\text{C}-\text{H})}=1.17$
R13- $\text{CO} + \text{OH} \rightarrow \text{cis-COOH}$	1.12	0.70	$d_{(\text{C}-\text{O})}=1.98$	1.02	0.59	$d_{(\text{C}-\text{O})}=1.83$
R14- $\text{cis-COOH} \rightarrow \text{trans-COOH}$	0.38	-0.10	—	0.36	-0.12	—
R15- $\text{trans-COOH} \rightarrow \text{CO}_2 + \text{H}$	0.50	-0.44	$d_{(\text{O}-\text{H})}=1.46$	0.47	-0.27	$d_{(\text{O}-\text{H})}=1.50$

2.2.1 Dissociation steps of initial species

R1: We first investigated the decomposition of H_2O on PdCu(111). In the TS, OH remains adsorbed at a Cu-top site, while the dissociated H atom migrates to a Pd-Pd bridge site. The O–H bond length at this stage is 1.62 Å. Following complete dissociation, the H atom stabilizes at an hcp hollow site coordinated by two Pd and one Cu atom, while OH migrates to an fcc hollow site composed of one Pd and two Cu atoms. This step is exothermic with a ΔE of -0.20 eV and an E_a of 0.74 eV.

On PtCu(111), the reaction initiates with OH migrating to a Pt–Cu bridge site, while the H atom adsorbs at a Pt-top site (O–H bond length = 1.46 Å). In the product, the H atom stabilizes at a Cu–Pt–Pt fcc hollow site, and OH adsorbs at a Cu–Cu–Pt fcc hollow site. This step is slightly endothermic ($\Delta E = 0.09$ eV), with an E_a of 0.78 eV—comparable to the energy barrier on PdCu(111).

R2: On PdCu(111), the TS of this step closely resembles the structure of the TS for the corresponding step, with the O–H bond elongated to 1.51 Å. After reaction completion, the dissociated CH_3O adsorbs at a Cu–Cu–Pd fcc hollow site, and the H atom attaches to a Pd–Pd–Cu fcc hollow site. This step is exothermic ($\Delta E = -0.14$ eV) with an E_a of 0.64 eV.

In contrast, the TS of this reaction on PtCu(111) is more similar to the product structure, with the O–H bond elongated to 2.40 Å. In the product, CH_3O adsorbs at a Cu–Cu–Pt fcc hollow site, and the H atom adsorbs at a Pt–Pt–Cu hcp hollow site. This step is slightly exothermic ($\Delta E = -0.05$ eV) but exhibits a higher E_a of 0.93 eV, making it relatively kinetically hindered.

R3: For the reaction on PdCu(111), the product CH_2O adsorbs at a Cu–Cu–Pd hcp hollow site: the O atom bridges two Cu atoms, while the C atom sits atop a Pd atom. The dissociated H atom stabilizes at a Cu–Pd–Pd hcp hollow site, with a C–H distance of 2.63 Å. The TS is product-biased, with the C–H bond elongated to 1.48 Å. This step is slightly endothermic ($\Delta E = 0.04$ eV) with an E_a of 0.66 eV.

On PtCu(111), the TS of this reaction is also product-like (C–H bond length = 1.49 Å). Notably, this step is exothermic ($\Delta E = -0.11$ eV) with a moderate E_a of 0.54 eV.

2.2.2 Elementary steps of Pathway 1

R4: CH_2O exhibits two primary evolution pathways in the reaction: (1) combination with OH (from H_2O dissociation) to form CH_2OOH , and (2) further dehydrogenation to CHO. Here, the former is discussed first. In the initial co-adsorption structure, both CH_2O and OH adopt their most stable configurations on PdCu(111). As the reaction proceeds, the C atom of CH_2O lifts away from the Pd-top site, while the O atom of OH migrates from its original fcc hollow site to a Pd site. In this TS, the C–O distance shortens to 1.98 Å, eventually forming a stable CH_2OOH intermediate.

On PtCu(111), the reaction proceeds analogously. In the most stable reactant structure, the distance between CH_2O and OH is 2.93 Å. Upon entering the TS, the C atom of CH_2O deviates from the Pt site, indicative of nucleophilic attack by OH; the C–O distance reaches 2.37 Å at this stage. As the reaction progresses, a C–O bond forms with a final length of 1.40 Å. Energetically, this step is kinetically facile on both surfaces: PdCu(111) and PtCu(111) exhibit ΔE of -0.24 and -0.38 eV, and E_a of 0.49 and 0.23 eV, respectively.

R5: Cleavage of the C–H bond in CH_2OOH generates CHOOH, typically a planar molecule. On PdCu(111), CHOOH binds to the surface *via* one O atom coordinated to a Cu atom, while the dissociated H atom stabilizes at a Pd–Pd–Cu fcc hollow site. The C–H bond length of the TS is 1.50 Å. This step is exothermic ($\Delta E = -0.83$ eV) with an E_a of 0.63 eV. Similarly, CHOOH on PtCu(111) adopts a planar structure, with a C–H bond length of 1.13 Å in the TS; it is highly exothermic ($\Delta E = -1.13$ eV) with an E_a of 0.56 eV.

R6: On PdCu(111), dissociation of the H atom from the hydroxyl O of CH_2OOH yields CH_2OO , which stabilizes in its most favorable configuration: two O atoms occupy Pd–Pd and Cu–Cu bridge sites, respectively. The TS O–H bond length is 1.75 Å. On PtCu(111), CH_2OO adopts an analogous structure, with a TS O–H bond length of 1.68 Å. This step is endothermic (ΔE values of 0.38 eV (PdCu) and 0.47 eV (PtCu)) with comparable E_a values (0.85 and 0.84 eV, respectively). Collectively, thermodynamic and kinetic data indicate that the CH_2OO formation pathway is less favorable than CHOOH formation on both surfaces.

R7: Like CH_2OOH , CHOOH undergoes dehydrogenation *via* two competing pathways: C–H or O–H bond cleavage. We first discuss the pathway corresponding to $\text{CHOOH} \rightarrow \text{bi-CHOO} + \text{H}$. On PdCu(111), one H atom detaches from the hydroxyl O of CHOOH and migrates to a Cu–Cu–Pd fcc hollow site; the remaining bi-CHOO binds bidentately to one Pd and one Cu atom. The TS O–H bond length is 1.70 Å.

On PtCu(111), the TS O–H bond length is 2.12 Å (more elongated than on PdCu(111)). This step is exothermic on both surfaces (ΔE values of -0.25 (PdCu) and -0.31 eV (PtCu)) with low E_a values (0.24 and 0.30 eV, respectively).

R8: This step competes with R7. On PdCu(111), the *cis*-COOH product features one O atom at a Cu-top site, the C atom at a Pd–Pd bridge site, and OH pointing upward; the dissociated H atom stabilizes at a Pd–Pd–Cu fcc hollow site. In the TS, the departing H atom and C atom are co-ordinated to the same Pd atom, with an H–C distance of 1.47 Å.

On PtCu(111), *cis*-COOH has one O atom at a Cu-top site, the C atom above a Pt-top site, and the dissociated H atom at a Pt–Pt bridge site; the TS C–H bond length is 1.55 Å. This step is kinetically more hindered than bi-CHOO formation, with significantly higher E_a values (0.69 eV for PdCu and 0.72 eV for PtCu) and ΔE values of -0.25 and -0.46 eV, respectively.

R9: In bi-CHOO, the H atom is farthest from the surface. Thus, conformational rearrangement of CHOOH is required before further conversion to CO₂. On PdCu(111), bi-CHOO first migrates to a Cu-Cu bridge site ($E_a = 0.10$ eV, negligible). It then undergoes a bidentate-to-monodentate coordination transformation, with E_a (0.54 eV) nearly equal to ΔE (0.50 eV). On PtCu(111), this rotational conformation change occurs in a single step, with $\Delta E = 0.51$ eV and $E_a = 0.63$ eV.

R10: This step is kinetically facile and highly exothermic on both surfaces: $\Delta E = -0.77$ (PdCu) and -1.10 eV (PtCu), with E_a values of 0.13 and 0.28 eV, respectively. The TS C-H bond lengths are 1.38 (PdCu) and 1.15 Å (PtCu). In the product, the detached H atom stabilizes at a Pd-Pd-Cu or Pt-Pt-Cu fcc hollow site, while CO₂ desorbs to a physisorbed state (floating on the surface). The final C-H bond distances reach 3.49 (PdCu) and 3.92 Å (PtCu).

2.2.3 Elementary steps of Pathway 2

R11: This step competes with R4. On PdCu(111), the CHO product adopts its thermodynamically most stable adsorption configuration, while the dissociated H atom stabilizes at a Cu-Pd-Pd fcc hollow site (C-H distance = 2.93 Å). The TS features a C-H bond length of 1.40 Å. This step is exothermic ($\Delta E = -0.64$ eV) with an E_a of 0.25 eV. On PtCu(111), the TS is characterized by co-coordination of the dissociated H and C atoms to the same Pt atom (C-H bond length = 1.31 Å) with an E_a of 0.17 and ΔE of -0.67 eV.

R12: CO formation on PdCu(111) is highly exothermic ($\Delta E = -1.32$ eV). The TS closely resembles the reactant structure, with the key difference being a modified bond angle and a C-H bond length of 1.15 Å. The E_a of 0.09 eV is the lowest among all considered steps. Similarly, on PtCu(111), the TS's C-H bond length is 1.17 Å, with $\Delta E = -1.27$ eV and a low E_a of 0.14 eV.

R13: While CO formation is kinetically facile, its desorption energies on PdCu(111) and PtCu(111) are as high as 2.05 and 2.20 eV, respectively. Thus, we propose that adsorbed CO participates in the WGS reaction. On PdCu(111), this step is kinetically demanding ($E_a = 1.12$ eV, the highest in the reaction network), likely due to the strong co-adsorption of reactants: CO occupies a Pd-Pd-Cu site, and OH binds to a Cu-Cu-Pd site, with both species coordinated to three surface metal atoms. Breaking this stable co-adsorption structure requires overcoming a substantial barrier. In the TS, CO and OH migrate to Pd-top and Cu-top sites, respectively (C-O distance = 1.98 Å), forming *cis*-COOH ($\Delta E = 0.70$ eV, endothermic). On PtCu(111), the step is also endothermic ($\Delta E = 0.59$ eV). In the initial state, OH anchors at a Pt-Cu-Cu fcc hollow site, and CO resides at a Pt-Pt bridge site. In the TS, OH migrates to a Cu-top site (C-O distance = 1.83 Å) with an E_a of 1.02 eV—the highest barrier for PtCu(111)).

R14: The *cis*-COOH formed by direct CO-OH coupling

(H atom pointing away from the surface) is not thermodynamically stable. Thus, *cis*-to-*trans* isomerization is required before CO₂ formation. This step involves only O-H bond rotation (no bond cleavage) and is kinetically facile on both surfaces: $E_a = 0.38$ (PdCu) and 0.36 eV (PtCu), with weak exothermicity ($\Delta E = -0.10$ and -0.12 eV, respectively).

R15: In addition to the R10 pathway, CO₂ can form via dehydrogenation of *trans*-COOH. On PdCu(111), this step proceeds with moderate difficulty ($E_a = 0.50$ eV): linear CO₂ desorbs completely, and the dissociated H atom stabilizes at a Cu-Pd-Pd hcp hollow site. The TS features an H atom at a Pd-top site (O-H bond length = 1.46 Å), with $\Delta E = -0.44$ eV. On PtCu(111), the H atom dissociates from O and migrates to a Pt-top site (O-H distance = 1.50 Å), with $\Delta E = -0.27$ eV and $E_a = 0.47$ eV (comparable to that of PdCu(111)).

2.3 Discussion

2.3.1 Bonding analysis of CO and effect on the MSR reaction

To further quantitatively assess the orbital hybridization and bonding strength between metal *d*-orbitals and adsorbed CO molecular orbitals, we performed crystal orbital Hamiltonian population (COHP) analysis, with results presented in Figure 9. A positive value of -COHP indicates bonding interactions, while a negative value denotes antibonding interactions. The Integrated COHP (ICOHP) serves as a quantitative descriptor for bond strength^[58–59]: a larger absolute value corresponds to a stronger bond. Calculations show that the absolute ICOHP value for the PtCu system (-1.65 eV) is far greater than that for the PdCu system (-0.07 eV). Thus, the orbital hybridization and bonding interactions between Pt *d*-orbitals and CO molecular orbitals in the PtCu system are significantly stronger than those between Pd *d*-orbitals and CO molecular orbitals in the PdCu system.

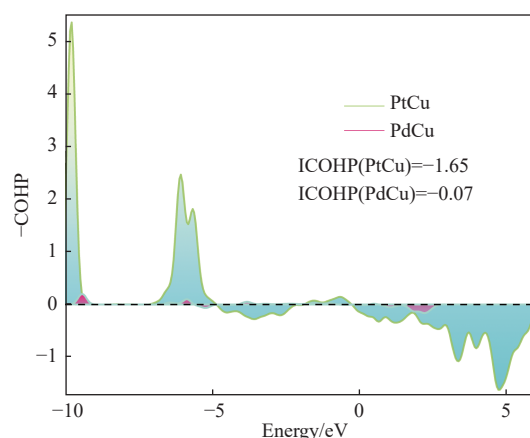


Fig. 9 COHP of CO adsorbed on PdCu(111) and PtCu(111) catalysts

Notably, despite the stronger CO adsorption on PtCu, this does not impede its subsequent conversion. The ΔE of the key elementary reaction $\text{CO} + \text{OH} \rightarrow \text{COOH}$ is slightly lower on PtCu than that on PdCu. This phenomenon can be rationalized by the reaction thermodynamics and TS stabilization principles: the reaction on PtCu exhibits less endothermicity, and the strong metal-adsorbate interaction effectively stabilizes the CO–OH TS, thereby lowering the ΔE barrier to a certain extent.

2.3.2 Optimal MSR reaction pathways on PdCu(111) and PtCu(111) surfaces

As illustrated in Figures 10 and 11, we systematically compared the energy profiles of competing pathways to further elucidate the reaction pathway selectivity of bimetallic surfaces. While the CHO pathway is kinetically favorable in the early reaction stage, the subsequent CO oxidation step presents the highest E_a barrier across the entire reaction network (typically >1.00 eV). In contrast, the formate pathway initiated by the coupling of CH_2O and OH—displays a more balanced distribution of activation energies across elementary steps. For instance, the sequential conversion of CH_2OOH to CO_2 on PdCu(111) features energy barriers mostly within the range of 0.13–0.63 eV, with no prominent high-energy bottlenecks, rendering the formate pathway kinetically dominant.

Accordingly, the optimal MSR reaction pathway on both PdCu(111) and PtCu(111) is: $\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} \rightarrow \text{CH}_2\text{OOH} \rightarrow \text{CHOOH} \rightarrow \text{CHOO} \rightarrow \text{CO}_2$. Notably, PdCu(111) outperforms PtCu(111): the RDS on PdCu(111) is water

dissociation ($E_a = 0.74$ eV), whereas that on PtCu(111) is limited by the initial O–H bond cleavage of methanol ($E_a = 0.93$ eV, a significantly higher barrier).

2.3.3 Performance comparison with pure Cu, Pd and Pt catalysts

In the MSR reaction, monometallic catalysts generally face inherent challenges. As shown in Table 3, while pure Cu(111) exhibits excellent CO_2 selectivity, its intrinsic catalytic activity is extremely low. Its RDS is the methoxy dehydrogenation step, with an E_a as high as 1.27 eV^[37]. This high energy barrier severely limits the reaction rate, making it difficult to meet the requirements for large-scale hydrogen production. Pure Pd(111) and Pt(111) have relatively high reaction activity, with RDS activation energies of 1.07 and 0.83 eV, respectively; however, both surfaces tend to directly decompose intermediates into CO instead of CO_2 ^[37,40].

However, the PdCu(111) and PtCu(111) bimetallic alloys designed in our study successfully overcome this activity-selectivity trade-off through synergistic optimization. Notably, for PdCu(111), the RDS shifts to water dissociation, with the E_a significantly reduced to only 0.74 eV, far lower than those of pure Cu and pure Pd. Meanwhile, the ΔE of this step is -0.20 eV, indicating a thermodynamically spontaneous process. This step can rapidly supply sufficient surface OH species for the reaction, which serves as a critical prerequisite for the subsequent oxidation of species such as CH_2O and CO to CO_2 .

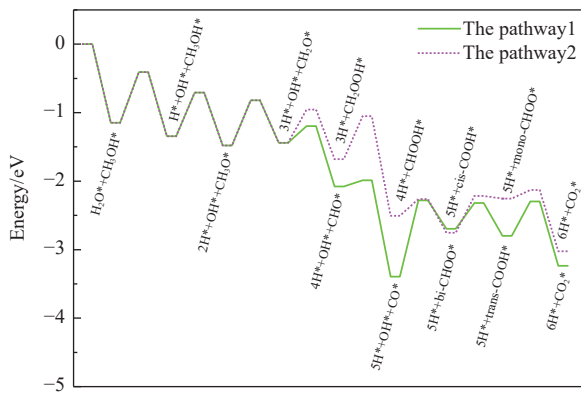


Fig. 10 Overall potential energy diagram of the MSR reaction on PdCu(111) catalyst

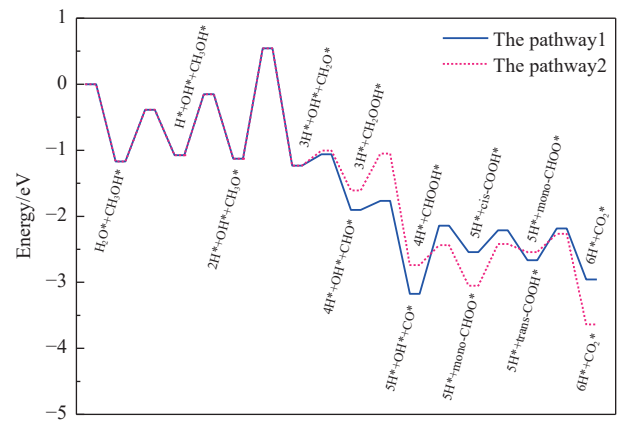


Fig. 11 Overall potential energy diagram of the MSR reaction on PtCu(111) catalyst

Table 3 Performance comparison of monometallic^[37,40] and bimetallic alloy catalysts for MSR

Catalyst	Rate-determining steps	Selectivity	E_a /eV	ΔE /eV
Cu(111) ^[37]	$\text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} + \text{H}$	CO_2	1.27	0.92
Pd(111) ^[37]	$\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{H}$	CO	1.07	0.02
Pt(111) ^[40]	$\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$	CO	0.83	0.49
PdCu(111)	$\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$	CO_2	0.74	-0.20
PtCu(111)	$\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{H}$	CO_2	0.93	-0.05

Additionally, a clear site-specific division of labor exists in the system: Cu sites exhibit stronger adsorption capacity for intermediates like OH and CH₂O, while Pd and Pt sites are more favorable for the adsorption and activation of CO molecules. This spatial separation of active sites allows formate formation to occur in the Cu region without being hindered by the presence of CO on Pd/Pt sites.

3 Conclusion

Herein, we systematically investigated the catalytic mechanism of the MSR reaction on PdCu(111) and PtCu(111) bimetallic surfaces *via* DFT calculations, with a focus on analyzing the adsorption configurations, reaction pathways, and energy evolution profiles of all intermediates. The results indicate that Cu sites exhibit strong adsorption affinity for key species such as OH, CH₃O and CH₂O, whereas Pd and Pt sites preferentially bind CO and CHO. Electronic structure analyses including PDOS, charge density difference, and COHP confirm that the 5d orbitals of Pt show stronger orbital overlap and π feedback with the 2 π^* orbital of CO, rendering this intermediate more stably adsorbed on PtCu(111). In contrast, the higher *d*-band center of PdCu(111) enhances its surface ability to adsorb and activate most intermediates.

Mechanistic studies reveal that the MSR reaction proceeds *via* an efficient formate pathway on both bimetallic catalysts, with PdCu(111) outperforming PtCu(111) in overall catalytic performance. The RDS on PdCu(111) is water dissociation ($E_a = 0.74$ eV), whereas the RDS on PtCu(111) is limited by the initial O–H bond cleavage of methanol ($E_a = 0.93$ eV, a relatively higher barrier). Both alloy catalysts overcome the inherent limitations of traditional monometallic catalysts, namely the inability to balance activity and selectivity. By integrating excellent surface water activation and adsorption properties of Cu with the superior C–H bond cleavage abilities of Pd and Pt, high methanol conversion is achieved while maintaining high CO₂ selectivity. These findings uncover the bimetallic catalytic mechanism at the atomic level, providing a reliable basis for the rational design of high-performance reforming catalysts.

Declaration of Competing Interest

The authors declare no conflict of interest.

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甲醇蒸汽重整在 PdCu(111) 和 PtCu(111) 双金属催化剂上的机理研究

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摘 要: 甲醇蒸汽重整 (MSR) 是高效制氢的关键途径。本研究采用密度泛函理论 (DFT) 计算方法, 对比分析了 MSR 在 PdCu(111) 与 PtCu(111) 双金属表面上的反应机理, 揭示了合金化效应对反应路径及整体催化性能的影响。结果表明, Cu 位点能稳定吸附羟基和甲醛物种, 而 Pd/Pt 位点可结合一氧化碳分子, 这种空间分离效应促使反应沿甲酸盐路径进行。PdCu(111) 催化剂的整体性能优于 PtCu(111), 其速率决定步骤为水分子解离, 仅需克服 0.74 eV 的能垒。双金属协同作用解决了单金属催化剂在活性与选择性之间的固有矛盾: Cu 位点提供羟基, 而 Pd/Pt 位点促进碳氢键断裂, 最终实现高甲醇转化率与低一氧化碳副产物生成。该研究从电子结构和几何构型角度出发, 为设计高性能双金属 MSR 催化剂提供了理论支撑。

关键词: 甲醇蒸汽重整; PdCu (111); PtCu (111); 反应机理

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