

Article

Mechanisms of Methanol Steam Reforming on Ni₁/ZnO and Pd₁/ZnO Single-Atom Catalysts: Insights from Density Functional Theory

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Abstract

On-demand hydrogen can be generated through methanol steam reforming. Isolated metal atoms hosted on ZnO may provide a lower-cost catalytic platform for this reaction. Density functional theory calculations were applied to examine the complete methanol steam reforming pathways over Ni₁/ZnO and Pd₁/ZnO single-atom catalysts, and the associated kinetics were evaluated using transition-state theory. H₂O and CH₃OH prefer Zn-top sites, with nearly identical adsorption energies on both catalysts, whereas most other intermediates bind more strongly to Pd₁/ZnO as the Pd d-state centroid lies closer to the Fermi level. Formaldehyde (CH₂O) governs product selectivity. The weaker C–3c–O orbital interaction on Ni₁/ZnO favors the direct CO₂-forming pathway without a CO intermediate, for which the rate-determining barrier is 0.844 eV. On Pd₁/ZnO, the CO-mediated and direct CO₂-forming pathways have comparable limiting barriers of 1.152 and 1.190 eV, respectively. The rate constant for the CHO rearrangement required before CO formation is only 6.704 s^{−1} on Ni₁/ZnO, making CO formation kinetically unfavorable. Taken together, the calculations show that Ni₁/ZnO provides higher intrinsic activity and CO₂ selectivity than Pd₁/ZnO as well as the reference Pt₁/ZnO and Cu₁/ZnO system. This work provides a mechanistic basis for designing efficient single-atom methanol-reforming catalysts.

Keywords: methanol steam reforming (MSR); mechanistic pathway; Ni₁/ZnO; Pd₁/ZnO

1. Introduction

Hydrogen is widely regarded as a sustainable energy carrier [1–3], with important applications in technologies such as proton-exchange membrane fuel-cell (PEMFC) systems [4–8], where its chemical energy can be converted efficiently. However, hydrogen storage and transportation remain difficult because hydrogen is a gas under ambient conditions. In situ methanol reforming therefore offers a practical route for producing hydrogen at the point of use [9]. Among these reforming routes, MSR combines relatively simple equipment with the production of high-purity hydrogen and limited byproduct formation. It has consequently become a widely used technology for hydrogen generation. Unlike reforming routes based on hydrocarbons including methane and ethanol, the MSR process also avoids carbon–carbon bond formation, which simplifies the reaction network, and it proceeds under relatively mild conditions [10,11].



Received: 28 July 2026

Revised: 12 August 2026

Accepted: 17 August 2026

Published: 20 August 2026

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Copper formulations remain the conventional catalytic choice for MSR [12]. They exhibit strong activity together with CO₂ preference but can sinter and deactivate as temperature is raised [13,14]. Group VIII metals, including Pd, generally provide better thermal stability [10]. However, monometallic Pd tends to produce substantial amounts of CO, which can poison PEMFC electrodes [15]. The limited reserves and high cost of noble metals also restrict their large-scale use. Nickel is a non-noble metal with promising catalytic potential for MSR [16,17]. For example, Ma et al. found that Ni-modified β -Mo₂C maintained higher long-term catalytic activity and stability than Mo₂C modified with the same amounts of Fe or Co [18].

ZnO is an important support for methanol steam reforming. Although bare ZnO provides favorable CO₂ selectivity, its intrinsic activity remains low [19]. Noble- and non-noble-metal species are therefore added to improve the activity of ZnO. Studies have shown that forming PdZn alloys on ZnO improves catalytic performance relative to monometallic Pd [20–26]. Similarly, Ni-Zn combinations increase both activity and CO₂ selectivity relative to pure Ni or pristine ZnO. Men et al. showed that methanol conversion and product distribution depend strongly on catalyst composition. Their experimental evidence indicated that Ni-Zn mixed catalysts gave the best overall performance, whereas Zn-free Ni catalysts were much less active [27]. Although these alloy systems have provided valuable mechanistic insights, the absence of lattice oxygen sites means that the spatial constraint and confinement effects offered by oxide supports cannot be captured by alloy models.

Research on atomically dispersed catalysts has expanded rapidly in heterogeneous catalysis in recent years [28–34]. Previous studies showed that isolated Pt and Au atoms can be stabilized on ZnO as active sites for MSR [35]. For example, incorporating an isolated Pt atom (Pt₁) increased the turnover frequency to 1000 times that of bare ZnO, showing the pronounced influence of an isolated metal atom on ZnO reactivity. Qie et al. investigated Cu₁/ZnO and Pd₁/ZnO single-atom catalysts using density functional theory (DFT) calculations on the ZnO(100) surface, confirming that both Cu and Pd atoms can be stably anchored at zinc vacancy sites, with the single-atom catalysts exhibiting lower activation barriers than pure ZnO and corresponding alloy catalysts [36]. Chen et al. studied a series of CeO₂-supported noble metal single-atom catalysts (Pt₁, Pd₁, Rh₁, and Ru₁/CeO₂) for MSR and revealed an “ensemble reaction pool” mechanism, where the metal single atoms and adjacent oxygen vacancies work synergistically to promote the tandem reaction [37]. More recently, Zhang et al. reported phase-interface-anchored Cd single-atom catalysts on P25 TiO₂, achieving 100% methanol conversion and ultralow CO concentration (~0.1 mol%) with stability exceeding 150 h, demonstrating the potential of single-atom catalysts beyond conventional noble metals [38]. However, none of these studies have addressed the MSR performance of non-noble Ni on the ZnO(100) surface. Because Ni, Pd, and Pt are all Group 10 metals, Ni₁/ZnO and Pd₁/ZnO models were constructed and evaluated using the same computational conditions. This comparison isolates the intrinsic catalytic differences between the two metal centers and provides an atomic-scale basis for developing low-cost, CO₂-selective ZnO-supported isolated-metal catalysts in MSR.

2. Results

2.1. Description of Adsorption Sites

A three-layer ZnO(10 $\bar{1}$ 0) periodic slab model with a (4 × 2) supercell was employed, and the single-atom catalysts were constructed by embedding isolated metal atoms at surface Zn-vacancy sites. According to Figure 1, the outermost surface layer mainly exposes three-coordinated Zn (3c-Zn) and three-coordinated O (3c-O) atoms. The Ni₁/ZnO slab is used as a representative model to illustrate four types of surface adsorption sites. Top sites are located above Zn, Ni, or Pd atoms. Metal–metal bridge (TMs–bridge) sites occur

between Zn–Zn, Ni–Zn, or Pd–Zn pairs, while metal–O bridge (TM–O bridge) sites occur between Zn–O, Ni–O, or Pd–O pairs. Three-atom (TMs–O) sites involve O–Ni–Zn or O–Pd–Zn ensembles. The most stable structures of all species on Ni₁/ZnO and Pd₁/ZnO are presented in Figures 2 and 3, respectively. Their associated adsorption energies (E_{ads}) are summarized in Table 1.

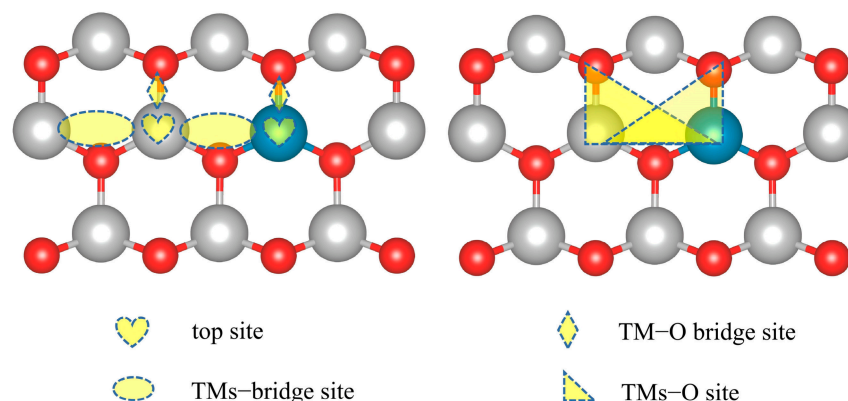


Figure 1. Representative adsorption sites on the Ni₁/ZnO surface model. Color code: blue, Ni; gray, Zn; red, O.

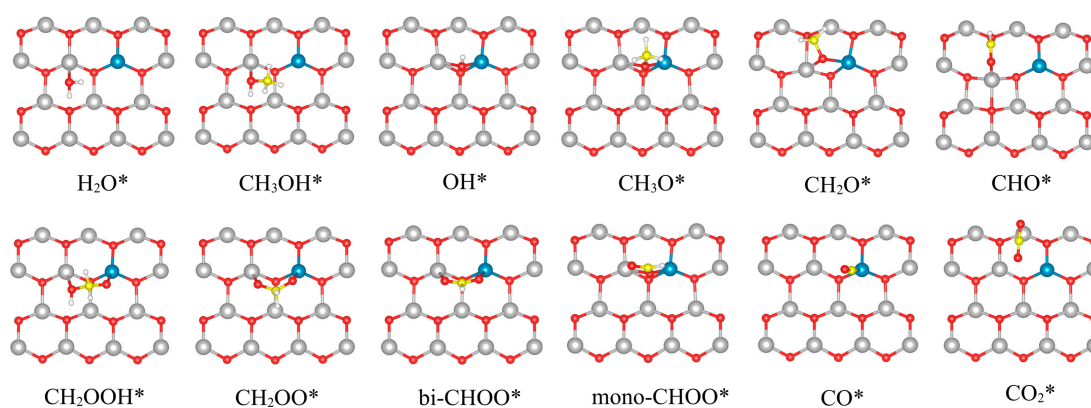


Figure 2. The most stable structures of all species on Ni₁/ZnO. Color code: blue, Ni; gray, Zn; red, O; yellow, C; white, H. The asterisk (*) denotes a surface-adsorbed species.

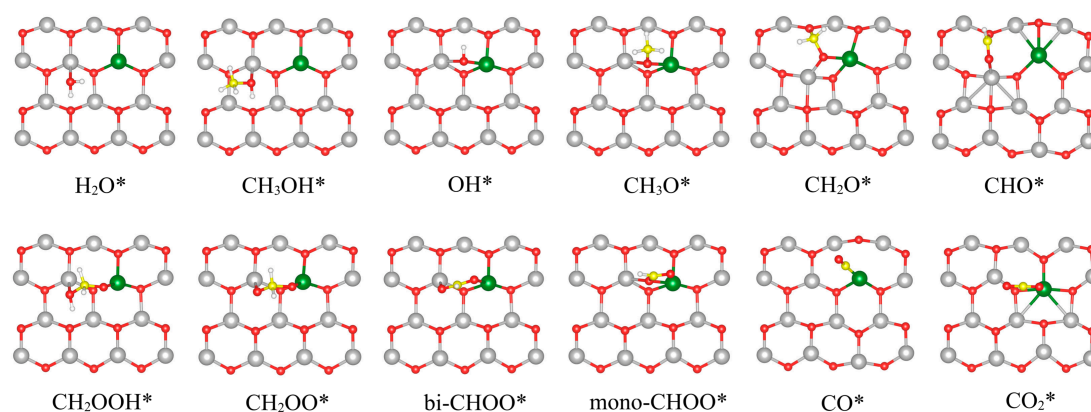


Figure 3. The most stable structures of all species on Pd₁/ZnO. Color code: green, Pd; gray, Zn; red, O; yellow, C; white, H. The asterisk (*) denotes a surface-adsorbed species.

Table 1. Preferred sites and corresponding adsorption energies (E_{ads} , eV) for all intermediates on Ni_1/ZnO and Pd_1/ZnO .

Species	Ni_1/ZnO		Pd_1/ZnO	
	Preferred Site	E_{ads}	Preferred Site	E_{ads}
H_2O^*	Zn top site	−1.225	Zn top site	−1.222
CH_3OH^*	Zn top site	−1.370	Zn top site	−1.358
OH^*	Zn–Ni bridge site	−2.571	Zn–Pd bridge site	−3.175
CH_3O^*	Zn–Ni bridge site	−1.998	Zn–Pd bridge site	−2.558
CH_2O^*	O–Zn–Ni site	−1.107	O–Zn–Pd site	−1.664
CHO^*	O–Zn site	−2.947	O–Zn site	−3.296
CH_2OOH^*	Zn–Ni bridge site	−2.601	Zn–Pd bridge site	−2.630
CH_2OO^*	Zn–Ni bridge site	−2.987	Zn–Pd bridge site	−2.990
bi- CHOO^*	Zn–Ni bridge site	−2.829	Zn–Pd bridge site	−2.922
mono- CHOO^*	Zn–Ni bridge site	−2.029	Zn–Pd bridge site	−2.544
CO^*	Ni top site	−0.839	Pd top site	−1.184
CO_2^*	Parallel to surface	−0.364	Parallel to surface	−0.617

The asterisk (*) denotes a surface-adsorbed species.

2.2. Preferred Adsorption Structures of the Intermediates

H_2O^* : On Ni_1/ZnO , the most stable H_2O configuration is adsorbed through its O atom at a Zn-top site. Both H atoms point toward one surface three-coordinate O atom and the Ni atom, respectively. The two O–H distances are 1.055 and 0.974 Å, whereas the gas-phase H_2O bond length is 0.973 Å. Adsorption at the Ni-top site was also examined and was 0.276 eV less favorable than the preferred geometry.

On Pd_1/ZnO , the lowest-energy H_2O structure is similar to that on Ni_1/ZnO and is also located at a Zn-top site. The two O–H distances are 1.056 and 0.974 Å, respectively. Binding of H_2O on the Pd-top site was also calculated and was 0.295 eV less favorable than the most stable configuration.

CH_3OH^* : Similar to H_2O , CH_3OH adsorbs most stably via the O atom above a Zn-top position of Ni_1/ZnO . Its O–H distance reaches 1.041 Å, which is 0.069 Å longer than the gas-phase reference of 0.972 Å. The methyl group points toward the Ni center, whereas the average value for the three C–H bonds equals 1.101 Å, close to the gas-phase value equal to 1.102 Å. This comparison indicates that the O–H linkage is activated considerably more strongly than the C–H bonds. Adsorption at the Ni-top site was also considered and was 0.253 eV less favorable than the most stable configuration.

On Pd_1/ZnO , the adsorbed CH_3OH molecule has an O–H distance of 1.040 Å together with an average C–H distance of 1.100 Å. Adsorption at the Pd-top site was 0.277 eV less favorable than the most stable configuration. Thus, Zn sites govern the adsorption of both initial reactants, consistent with the reported behavior of Pt_1/ZnO [35].

OH^* : On Ni_1/ZnO , the OH species formed by H_2O dissociation preferentially occupies a Ni–Zn bridge position via O atom. The O–Ni and O–Zn distances are 2.109 and 1.921 Å, respectively. The O–H length is 0.975 Å, and E_{ads} is −2.571 eV. OH adsorption at a Zn–Zn bridge site was also examined, giving $E_{\text{ads}} = -2.322$ eV. On Pd_1/ZnO , Pd–Zn and Zn–Zn bridge sites were both considered. The corresponding O–H distances are 0.982 and 0.986 Å, and the corresponding adsorption energies are −3.175 and −2.716 eV, respectively. Both values are more negative than those on Ni_1/ZnO .

CH_3O^* : CH_3O is formed directly by cleavage at the O–H linkage of CH_3OH . On Ni_1/ZnO , the most stable CH_3O configuration is also adsorbed through its O atom at a Ni–Zn bridge site. The respective O–Zn and O–Ni separations are 2.167 and 1.892 Å, respectively. A Zn–Zn bridge configuration was also considered and was 0.375 eV less

favorable. On Pd₁/ZnO, adsorption at Pd–Zn and Zn–Zn bridge sites was evaluated, giving E_{ads} values of -2.558 and -2.019 eV, respectively.

CH₂O*: On Ni₁/ZnO, the most stable CH₂O configuration has its O atom adsorbed at a Zn–Ni bridge position, where the O–Zn and O–Ni separations are 1.979 and 2.178 Å, respectively, while the C center also interacts with a surface 3c–O site at a distance of 1.465 Å. The two C–H bond lengths measure 1.107 and 1.105 Å.

On Pd₁/ZnO, the average separation from the O atom of CH₂O to the Zn and Pd atoms is 2.057 Å. The C center also interacts with a surface O atom at a distance of 1.409 Å. The two C–H bond lengths measure 1.108 and 1.106 Å, respectively.

CHO*: The most stable CHO configuration on Ni₁/ZnO is located at a Zn–O bridge site. Its O atom coordinates with a Zn center at a distance equal to 2.012 Å, whereas the C center interacts with a surface 3c–O site at a distance equal to 1.292 Å. Another relevant configuration places CHO at a Zn–Ni bridging geometry, where C and O interact with Ni and Zn, respectively.

The most stable CHO configuration on Pd₁/ZnO closely resembles the geometry on Ni₁/ZnO. Corresponding distances from the O center to a 3c–Zn site, and from C to a 3c–O site, are 2.018 and 1.293 Å, respectively. CHO adsorption at a Zn–Pd bridge site was also considered, giving $E_{\text{ads}} = -2.604$ eV. The strong adsorbate–surface interaction causes some deformation of both the Ni₁/ZnO and Pd₁/ZnO surfaces.

CH₂OOH*: CH₂OOH is formed by coupling CH₂O with OH generated from H₂O dissociation. On Ni₁/ZnO, the two O atoms of CH₂OOH are located above the Ni and Zn atoms at separations of 1.843 and 2.061 Å, respectively. The hydroxyl H atom points toward a surface 3c–O atom, whereas the O–H distance is 1.021 Å. For Pd₁/ZnO, the most stable CH₂OOH configuration is likewise adsorbed through its two O atoms at a Zn–Pd bridge site, and the O–H distance is 1.004 Å.

CH₂OO*: CH₂OO is obtained by dehydrogenation of CH₂OOH. On Ni₁/ZnO, its most stable configuration resembles that of CH₂OOH after removal of the hydroxyl H atom. The two remaining O atoms remain bonded to Ni and Zn at distances of 1.945 and 1.829 Å, respectively. On Pd₁/ZnO, CH₂OO is similarly adsorbed through its two O atoms at a Pd–Zn bridge site, with distances of 1.912 and 1.897 Å.

CHOO*: The CHOO species has two stable adsorption modes. In bidentate CHOO (bi-CHOO), the two O atoms bind separately to two metal atoms. On Ni₁/ZnO, the O atoms occupy the top positions of both Zn and Ni atoms, with interatomic distances of 2.010 Å and 1.966 Å, respectively; on Pd₁/ZnO, these distances decrease to 2.004 Å and 2.036 Å. In monodentate CHOO (mono-CHOO), only one O atom occupies a bridging position between two metal centers. The average distances between O atom and surface metal atoms are 2.057 Å on Ni₁/ZnO and 2.108 Å on Pd₁/ZnO, respectively.

CO*: On Ni₁/ZnO, the most stable CO configuration is adsorbed via its C atom on the Ni-top position. The C–O distance is 1.155 Å, and E_{ads} is -0.839 eV. Adsorption at the Zn-top site was also considered, giving E_{ads} of -0.568 eV and a C–O distance of 1.142 Å. On Pd₁/ZnO, the most stable CO configuration is likewise adsorbed through its C atom at a Pd-top position, where the C–O distance is 1.156 Å and E_{ads} is -1.184 eV. At the Zn-top site, the C–O distance remains 1.141 Å and E_{ads} is -0.565 eV.

CO₂*: On Ni₁/ZnO, CO₂ is physisorbed and retains its linear geometry, with an average C–O separation of 1.177 Å. Its separation from the surface is 3.369 Å, and its E_{ads} value of -0.364 eV is the least negative value, indicating weak surface binding. On Pd₁/ZnO, CO₂ lies parallel to the Pd–O–Zn direction. The average C–O distance remains 1.177 Å, while the computed adsorption strength is also relatively weak at -0.617 eV.

2.3. Adsorption Characteristics and Electronic Structures of the Intermediates

2.3.1. Characteristics of the Adsorption Sites

The optimized configurations can be divided into two adsorption types. The first includes H_2O and CH_3OH , whose most stable configurations are formed by coordination of their O atoms to surface Zn sites of the ZnO support. H_2O adsorption on Ni_1/ZnO was selected as a representative example for charge-density-difference and Bader-charge analyses (Figure 4a,b). For the Zn-top geometry, the O atom in H_2O gains 1.317 e, while the adjacent Zn atom loses 1.236 e. At the Ni single-atom site, the water O center accepts 1.286 e, whereas the Ni center donates 1.082 e. The larger interfacial charge redistribution at the Zn site is consistent with the greater thermodynamic stability of this adsorption configuration. The adsorption of H_2O and CH_3OH is therefore governed mainly by the ZnO support rather than by the isolated dopant atoms.

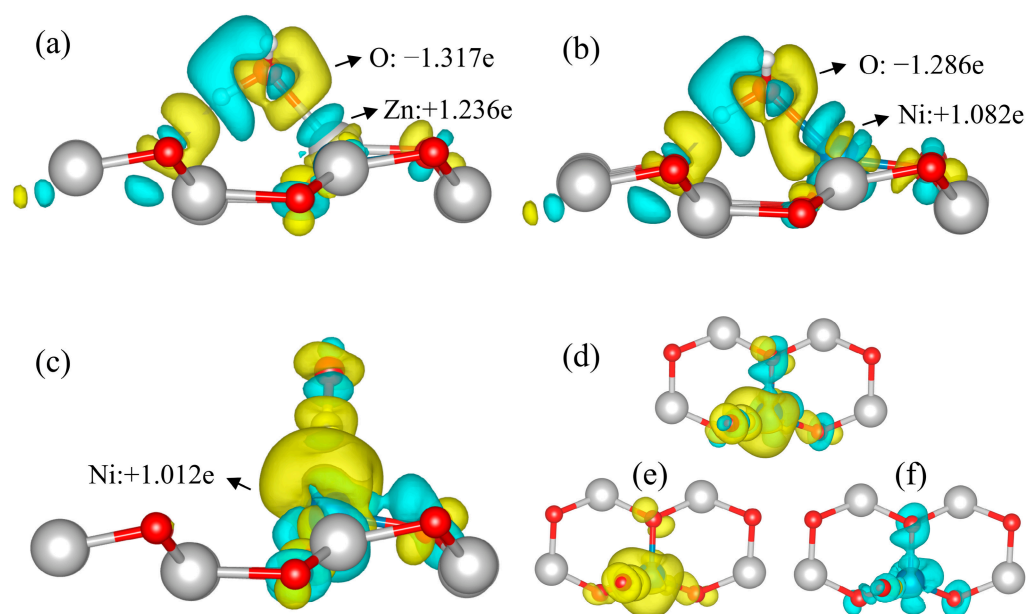


Figure 4. Charge-density differences and Bader charges for H_2O and CO adsorption on Ni_1/ZnO . (a) H_2O adsorbs on the top of Zn atom on Ni_1/ZnO . (b) H_2O adsorbs on the top of Ni atom on Ni_1/ZnO . (c) The side view of CO adsorbs on Ni_1/ZnO . (d) The vertical view of CO adsorbs on Ni_1/ZnO . (e) The positive section in charge density difference in CO adsorbs on Ni_1/ZnO . (f) The negative section in charge density difference in CO adsorbs on Ni_1/ZnO . Color code: blue, Ni; gray, Zn; red, O; yellow, C; white, H.

The second adsorption type includes most reactive intermediates. These species, including CO , preferentially bind to the doped Ni or Pd atom. Take Ni_1/ZnO as an example, unlike atoms on bulk metal surfaces, the supported Ni atom transfers 1.012 e to the highly electronegative three-coordinated lattice O atoms of ZnO and therefore carry a net positive charge (Figure 4c–f). This electronic modification suppresses metal-to-ligand electron back-donation to the $\text{CO } 2\pi^*$ antibonding level, resulting in weaker CO adsorption than on pristine $\text{Ni}(111)$ [39] surface.

2.3.2. Adsorption-Energy Trends and Their Electronic Origin

Figure 5 summarizes the calculated adsorption energies and shows a consistent trend for Ni_1/ZnO and Pd_1/ZnO . Relatively stable species, including H_2O , CH_3OH , and CO , adsorb more weakly ($E_{\text{ads}} > -1.4$ eV), whereas reactive intermediates such as OH , CH_3O , and CHO bind strongly, generally with adsorption energies below -2.0 eV.

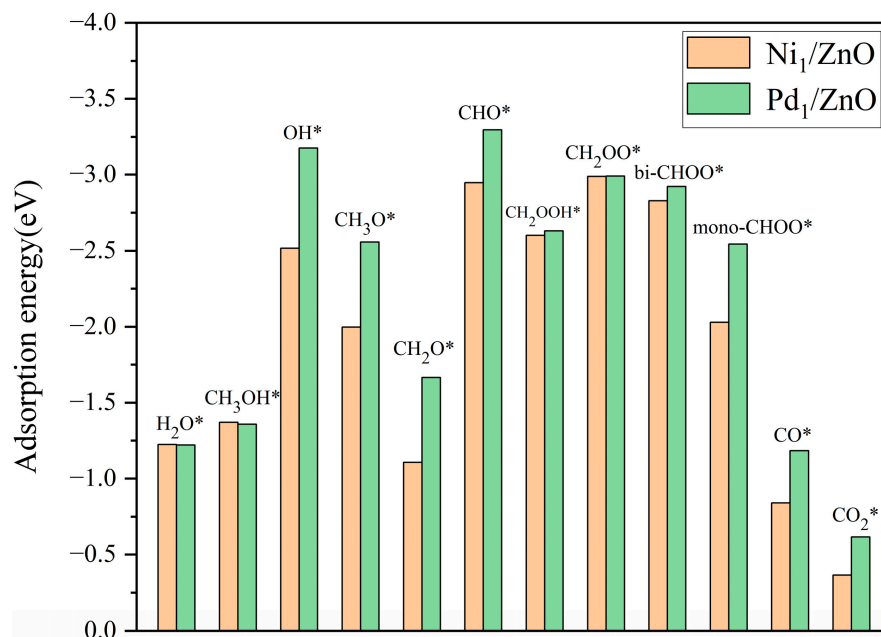


Figure 5. Adsorption energies of all intermediates on Ni₁/ZnO and Pd₁/ZnO. The asterisk (*) denotes a surface-adsorbed species.

The most stable H₂O and CH₃OH configurations occur at Zn-top sites on the ZnO support, indicating that their adsorption is controlled primarily through the electronic and structural attributes of the oxide. Their interactions with the isolated Ni or Pd atoms are therefore limited, which explains the nearly identical adsorption energies on Ni₁/ZnO and Pd₁/ZnO. By contrast, most other intermediates, including OH, CH₃O, CHO, and CO, adsorb more strongly on Pd₁/ZnO. As shown in Figure 6, the Pd d-band center (ϵ_d : −1.305 eV) lies nearer in energy to the Fermi level than the Ni d-state centroid (ϵ_d : −1.744 eV), providing more states around the Fermi energy together with stronger orbital hybridization with the intermediates. This electronic difference is consistent with the systematically more negative adsorption energies of metal-coordinated intermediates on Pd₁/ZnO.

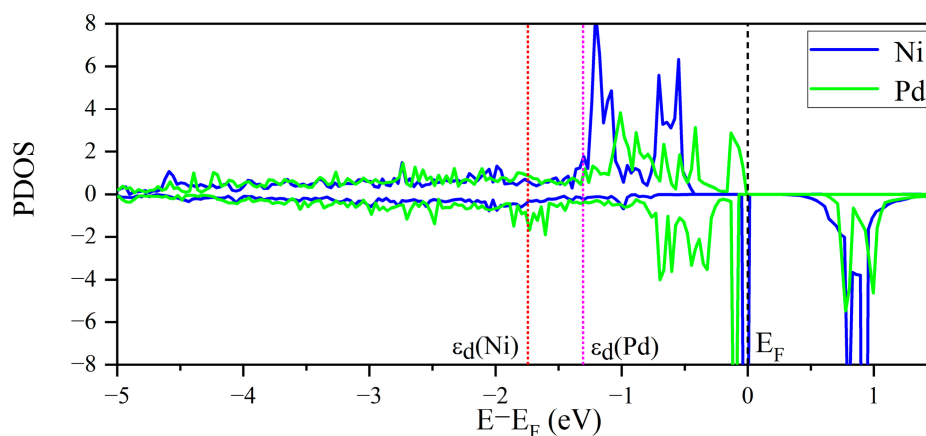


Figure 6. Projected densities of states (PDOS) of Ni 3d as well as Pd 4d states in Ni₁/ZnO and Pd₁/ZnO, respectively.

2.4. Elementary Steps in the MSR Reaction

The overall product MSR selectivity is mainly controlled by the reaction involving the CH₂O intermediate. As shown in Figure 7, two pathways can proceed from CH₂O: (1) the formate-mediated direct CO₂ pathway (green lines) and (2) direct dehydrogenation

followed by the water-gas shift (WGS) pathway (purple lines). Each elementary step was evaluated on Ni₁/ZnO and Pd₁/ZnO. Activation barriers, reaction energies, and key bond distances within the transition states are listed in Table 2. The TS structures are shown in Figures 8 and 9 and are described below.

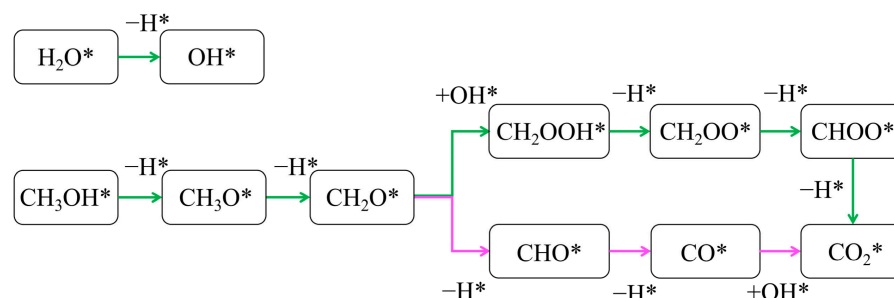


Figure 7. Two possible pathways for the MSR reaction. The asterisk (*) denotes a surface-adsorbed species.

Table 2. Activation barriers (E_a , eV), reaction energies (ΔE , eV), and key bond distances (d , Å) in the TS on Ni₁/ZnO and Pd₁/ZnO.

Elementary Steps	Ni ₁ /ZnO			Pd ₁ /ZnO		
	E_a	ΔE	d	E_a	ΔE	d
R1: H ₂ O* → OH* + H*	0.601	0.455	2.211	0.341	0.285	1.943
R2: CH ₃ OH* → CH ₃ O* + H*	0.694	0.492	2.117	0.418	0.295	2.054
R3: CH ₃ O* → CH ₂ O* + H*	0.609	−0.820	1.356	0.671	−0.975	1.366
R4: CH ₂ O* + OH* → CH ₂ OOH*	0.844	−0.438	2.802	1.190	0.205	2.484
R5: CH ₂ OOH* → CH ₂ OO* + H*	—	0.141	—	0.144	0.120	1.297
R6: CH ₂ OO* → bi-CHOO*	0.795	−3.074	1.267	0.003	−3.181	1.238
R7: bi-CHOO* → mono-CHOO*	0.794	0.776	—	0.780	0.356	—
R8: mono-CHOO* → CO ₂ * + H*	0.500	−1.393	1.326	0.896	−1.572	1.183
R9: CH ₂ O* → CHO* + H*	0.971	−0.475	1.373	0.980	−0.915	1.429
R10: CHO* rearrangement	1.550	0.987	—	1.152	0.621	—
R11: CHO* → CO* + H*	0.292	−1.269	1.209	0.407	−1.519	1.243
R12: CO* + OH* → CO ₂ * + H*	0.374	−1.545	1.757	0.709	−1.301	1.774

The asterisk (*) denotes a surface-adsorbed species.

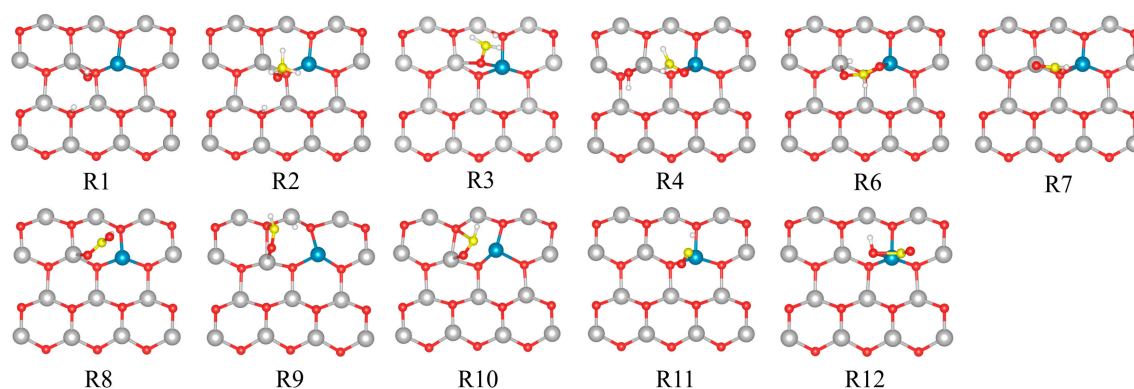


Figure 8. The structures of TS in all elementary steps on Ni₁/ZnO catalyst. Color code: blue, Ni; gray, Zn; red, O; yellow, C; white, H.

R1: H₂O first dissociates into OH and H. On Ni₁/ZnO, one O–H bond is initially cleaved while the released H atom migrates toward a surface 3c–O atom. The O–H distance within the TS equals 2.211 Å. A similar process occurs on Pd₁/ZnO, where the

corresponding O–H separation is 1.943 Å. In the product state, OH occupies a Zn–Pd bridge position, whereas H attaches to a surface 3c–O atom.

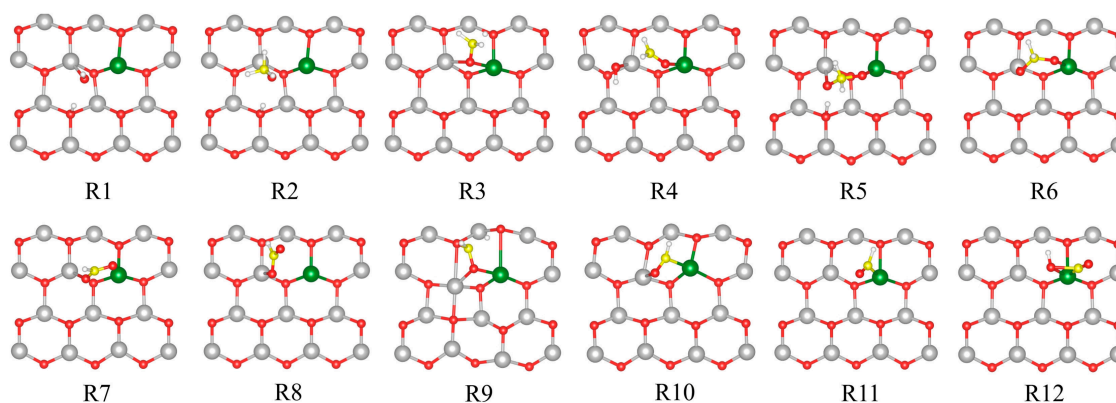


Figure 9. The structures of TS in all elementary steps on Pd₁/ZnO catalyst. Color code: green, Pd; gray, Zn; red, O; yellow, C; white, H.

R2: The preceding structural analysis showed that average C–H lengths for adsorbed CH₃OH on Ni₁/ZnO and Pd₁/ZnO are similar to the gas-phase values, indicating little C–H activation. Therefore, only CH₃OH → CH₃O + H was considered in this step. On Ni₁/ZnO, the O–H distance within the TS equals 2.117 Å. The resulting methoxy species moves to a Ni–Zn bridge site, whereas the dissociated H species attaches to a surface three-coordinate O atom. On Pd₁/ZnO, the corresponding O–H distance in the TS is 2.054 Å.

R3: On Ni₁/ZnO, a H atom gradually moves away from the C center of CH₃O and migrates toward the 3c–O site bonded to Ni. At the same time, the C atom moves toward another O atom bonded to Zn, reaching a distance of 1.454 Å. The C–H distance in the TS reaches 1.356 Å. The corresponding C–H distance on Pd₁/ZnO equals 1.366 Å.

R4: In the initial state, OH occupies a bridge site between two adjacent Zn atoms. CH₂O binds through its O atom at a Ni–Zn bridge site, while its C center interacts with a neighboring surface 3c–O site. In this TS, both species move from their initial positions. OH migrates toward a Zn-top site, and CH₂O becomes coordinated only through its O atom on the Ni-top position. The emerging C–O separation is 2.802 Å. The TS on Pd₁/ZnO has a similar geometry, with a corresponding C–O separation of 2.484 Å. These energies in Table 2 show that this coupling step has a relatively high barrier. Because both C and O centers of adsorbed CH₂O remain coupled to the surface, rather than only the O atom, access of OH to the C atom is restricted, which increases the barrier to nucleophilic attack.

R5: For this dehydrogenation step on Ni₁/ZnO, no TS could be located because CH₂OOH spontaneously converted to CH₂OO during optimization. The process is slightly endothermic but proceeds without a detectable energy barrier. On Pd₁/ZnO, a TS was obtained, with an O–H distance of 1.297 Å.

R6: Formation of bi-CHOO is highly exothermic on both Ni₁/ZnO and Pd₁/ZnO. The key C–H bond distances within the TS measure 1.267 and 1.238 Å, respectively. On both catalysts, the removed H species ultimately attaches to a surface three-coordinate O atom.

R7: On both catalysts, the CHOO species formed from CH₂OO initially adopts a planar bidentate geometry in which the H center is directed away from the catalyst surface. Conversion from bi-CHOO to mono-CHOO is therefore required before CO₂ formation. This rearrangement does not require cleavage of a chemical bond.

R8: On Ni₁/ZnO, the CO₂ molecule formed from mono-CHOO is positioned well above the catalyst surface, while H remains attached to a surface 3c–O site. The C–H distance of TS is 1.326 Å. On Pd₁/ZnO, the product CO₂ remains adsorbed at the surface,

with one O atom bound to Zn and the C atom interacting with Pd. The C–H distance within the TS is 1.183 Å.

R9: Dehydrogenation of CH₂O provides a competing route to CH₂OOH formation. On Ni₁/ZnO, one H atom gradually moves away from the C center of CH₂O and shifts toward the 3c–O site bonded to Ni. The O atom of CH₂O shifts concurrently from the Ni–Zn bridge site toward a Zn-top site. The C–H distance within the TS is 1.373 Å. The barrier is higher than that for CH₂OOH formation, so direct CH₂O dehydrogenation is less favorable on Ni₁/ZnO.

On Pd₁/ZnO, however, the same step is strongly exothermic. Its TS remains reactant-like, with partial removal of one H atom and a C–H distance of 1.429 Å. The barrier remains below that for CH₂OOH formation. Accordingly, in contrast to Ni₁/ZnO, direct CH₂O dehydrogenation is favored on Pd₁/ZnO.

R10: The CHO intermediate formed by direct dehydrogenation of CH₂O occupies the Zn–3c–O bridge site on both Ni₁/ZnO and Pd₁/ZnO. Direct C–H cleavage is inaccessible from this initial geometry. Activation of the C–H bond first requires CHO to migrate from the thermodynamically preferred Zn–3c–O bridge site to the Zn–Ni bridge site, where C binds to Ni and O coordinates to a Zn center. Subsequent CO formation therefore depends on this rearrangement.

R11: After CHO rearrangement, CO forms readily on Ni₁/ZnO. The C–H distance within the TS is 1.209 Å. On Pd₁/ZnO, the CO product binds to the Pd center through its C atom, and the C–H distance in the TS is 1.243 Å.

R12: The activation energies of R4, R9, R10, and R11 show that direct CO formation is favored on Pd₁/ZnO. The subsequent WGS step was therefore also considered, in agreement with earlier studies on Pt₁/ZnO as well as Au₁/ZnO [35]. This reaction is exothermic. The key TS bond lengths are 1.757 Å on Ni₁/ZnO and 1.774 Å on Pd₁/ZnO.

2.5. Kinetic Characteristics of the Individual Reaction Steps

The corresponding pre-exponential factors and rate constants obtained using transition state theory at 673 K are summarized in Table 3. For all elementary reactions with identified transition states on both catalysts, the pre-exponential factors lie in the range of 10¹²–10¹³ s^{−1}, consistent with the typical magnitude reported in previous kinetic studies of catalytic reforming [40,41].

Table 3. Pre-exponential factors (*A*, s^{−1}) and kinetic constants (*k*, s^{−1}) on Ni₁/ZnO and Pd₁/ZnO.

Elementary Reaction	Ni ₁ /ZnO		Pd ₁ /ZnO	
	<i>A</i>	<i>k</i>	<i>A</i>	<i>k</i>
R1: H ₂ O* → OH* + H*	8.284 × 10 ¹²	1.664 × 10 ⁸	7.947 × 10 ¹²	1.724 × 10 ¹⁰
R2: CH ₃ OH* → CH ₃ O* + H*	8.069 × 10 ¹²	3.001 × 10 ⁷	8.672 × 10 ¹²	4.623 × 10 ⁹
R3: CH ₃ O* → CH ₂ O* + H*	6.385 × 10 ¹²	1.869 × 10 ⁸	7.017 × 10 ¹²	8.204 × 10 ⁷
R4: CH ₂ O* + OH* → CH ₂ OOH*	2.038 × 10 ¹³	4.881 × 10 ⁶	1.467 × 10 ¹³	6.841 × 10 ³
R5: CH ₂ OOH* → CH ₂ OO* + H*	-	-	7.970 × 10 ¹²	7.295 × 10 ¹²
R6: CH ₂ OO* → bi-CHOO*	1.292 × 10 ¹³	1.515 × 10 ⁷	7.192 × 10 ¹²	6.417 × 10 ¹²
R7: bi-CHOO* → mono-CHOO*	9.845 × 10 ¹²	5.989 × 10 ⁶	1.044 × 10 ¹³	8.362 × 10 ⁶
R8: mono-CHOO* → CO ₂ * + H*	8.441 × 10 ¹²	1.060 × 10 ⁹	7.622 × 10 ¹²	7.230 × 10 ⁵
R9: CH ₂ O* → CHO* + H*	1.019 × 10 ¹³	3.984 × 10 ⁵	1.143 × 10 ¹³	2.051 × 10 ⁵
R10: CHO* rearrangement	9.214 × 10 ¹²	6.704 × 10 ⁰	8.735 × 10 ¹²	8.254 × 10 ³
R11: CHO* → CO* + H*	1.278 × 10 ¹³	7.886 × 10 ¹⁰	1.162 × 10 ¹³	1.052 × 10 ¹⁰
R12: CO* + OH* → CO ₂ * + H*	7.906 × 10 ¹²	9.580 × 10 ⁹	1.254 × 10 ¹³	5.787 × 10 ⁷

The asterisk (*) denotes a surface-adsorbed species.

The rate constants differ substantially between the two catalysts. Along the direct CO₂-forming pathway (R4 → R5 → R6 → R7 → R8), the key elementary steps proceed faster on Ni₁/ZnO than on Pd₁/ZnO. For R4, the rate constant calculated for Ni₁/ZnO is $4.881 \times 10^6 \text{ s}^{-1}$, nearly three orders of magnitude higher than $6.841 \times 10^3 \text{ s}^{-1}$ on Pd₁/ZnO.

For the competing CO-forming pathway (R10 → R11), the R10 rearrangement is the kinetic bottleneck. Repeated TS searches yielded a rate constant for this migration step on Ni₁/ZnO of only 6.704 s^{-1} , compared with $8.254 \times 10^3 \text{ s}^{-1}$ on Pd₁/ZnO. This kinetic contrast indicates that Ni₁/ZnO accelerates the direct CO₂-forming pathway and suppresses CO formation, resulting in higher CO₂ selectivity during MSR.

3. Discussion

3.1. Reaction Pathways and Product Selectivity on Ni₁/ZnO and Pd₁/ZnO

Figures 10 and 11 present the complete MSR energy profiles for Ni₁/ZnO and Pd₁/ZnO. The thermodynamically favored sequence on Ni₁/ZnO is CH₃OH → CH₃O → CH₂O → CH₂OOH → CH₂OO → bi-CHOO → mono-CHOO → CO₂. Coupling of CH₂O with surface OH to form CH₂OOH is the rate-determining step (RDS), with an activation barrier of 0.844 eV. Direct dehydrogenation of CH₂O to CHO forms a competing pathway with a higher barrier of 0.971 eV, while the subsequent geometric rearrangement of CHO requires 1.550 eV, which strongly limits CO formation. The dehydrogenation steps following CH₂OOH formation have moderate barriers of 0.5–0.8 eV and allow progression toward CO₂.

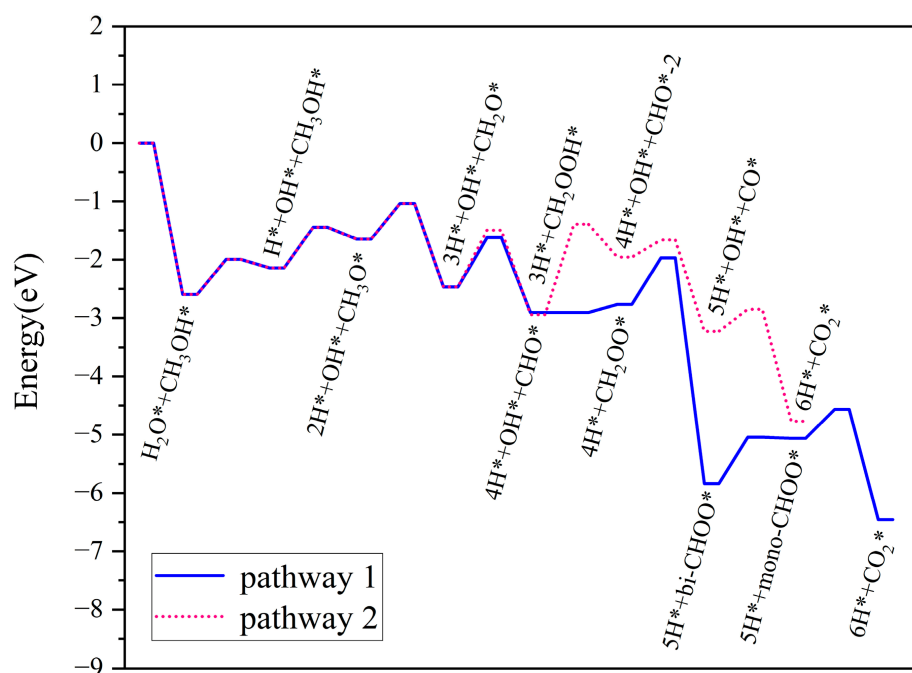


Figure 10. Relative-energy profile of all elementary steps on Ni₁/ZnO. The asterisk (*) denotes a surface-adsorbed species.

On Pd₁/ZnO, complete methanol dehydrogenation followed by the WGS process has a limiting barrier of 1.152 eV, and the highest barrier along the CH₂O + OH coupling pathway is 1.190 eV. The similar barriers make both routes kinetically accessible, with the CO-mediated dehydrogenation-WGS route slightly favored. The limiting barriers of both Pd₁/ZnO pathways exceed the RDS barrier of Ni₁/ZnO, indicating greater intrinsic activity of Ni₁/ZnO under the calculated conditions.

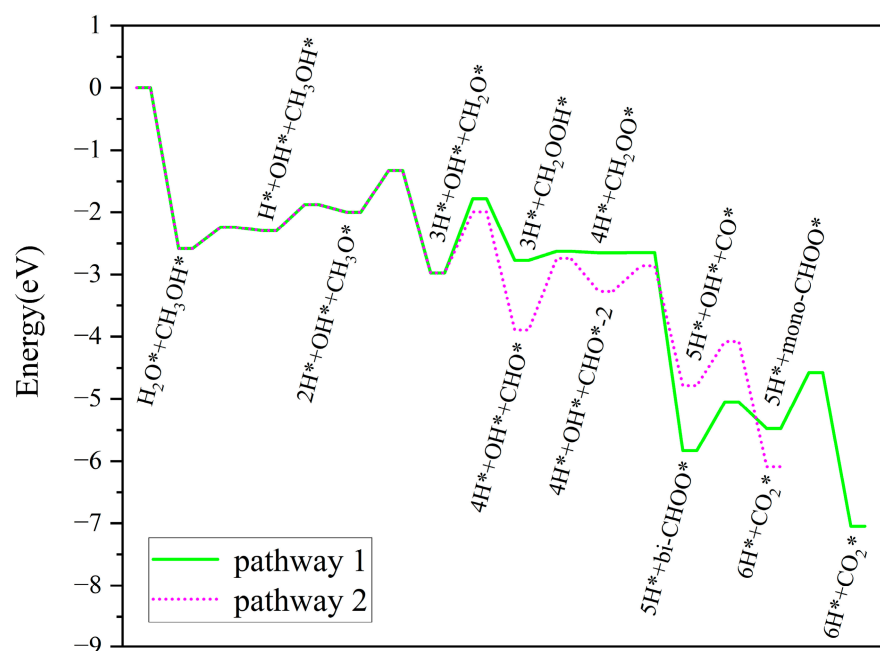


Figure 11. Relative-energy profile of all elementary steps on Pd₁/ZnO. The asterisk (*) denotes a surface-adsorbed species.

3.2. Origin of the Different Selectivity-Regulation Mechanisms

As shown in Section 3.1, Ni₁/ZnO produces CO₂ directly through the CH₂OOH intermediate during MSR, whereas the dominant route on Pd₁/ZnO proceeds through CO before CO₂ formation. Previous DFT studies of NiZn and PdZn intermetallic slabs proposed a simple selectivity rule based on formaldehyde adsorption strength [42]. On metallic alloy surfaces, weakly adsorbed CH₂O can more readily change its geometry and couple with dissociated surface OH, whereas strong formaldehyde binding restricts molecular distortion and suppresses CH₂OOH formation.

The relative CH₂O adsorption strengths on the single-atom catalysts follow the same order as those on the alloy slabs: Pd₁/ZnO binds formaldehyde more strongly than Ni₁/ZnO. The calculated adsorption energies equal −1.107 eV for Ni₁/ZnO and −1.664 eV for Pd₁/ZnO. Although formaldehyde adopts the same adsorption geometry on both single-atom catalysts, with the C atom bound to a surface 3c–O site, the C–3c–O bond lengths differ appreciably (1.465 Å on Ni₁/ZnO and 1.408 Å on Pd₁/ZnO). The shorter distance on Pd₁/ZnO suggests stronger orbital coupling between C and the lattice O atom.

Mayer bond orders calculated using Multiwfn (version 3.8) were used to quantify this interaction [43,44]. The C–3c–O bond order is 1.007 on Ni₁/ZnO and increases to 1.108 on Pd₁/ZnO. Figure 12 also shows the C– and 3c–O-resolved PDOS and the projected crystal orbital Hamilton populations (COHP) [45–47]. The orbital overlap between C and 3c–O is narrower and more localized on Ni₁/ZnO, consistent with weaker electronic coupling. The integrated COHP (ICOHP) values for the C–3c–O bond are −4.130 eV on Ni₁/ZnO and −4.630 eV on Pd₁/ZnO. Together, the geometric and electronic descriptors indicate a stronger and more rigid C–3c–O interaction on Pd₁/ZnO, which limits molecular rotation and tilting. Accordingly, CH₂OOH formation occurs more readily on Ni₁/ZnO.

Unlike conventional alloy catalysts, where the active sites consist of metal–metal bonds without the participation of lattice oxygen and selectivity is mainly regulated by tuning adsorption strength, the single-atom catalysts introduce an additional “geometric constraint” dimension—the C atom of CH₂O forms a C–3c–O bond with the surface lattice oxygen, serving as a conformational modulator. When this bond is weak, CH₂O retains

conformational freedom and can adjust its geometry to couple with OH, following the CO₂ pathway; when the bond is strong, the conformation of CH₂O is locked and it is forced to dehydrogenate to CO.

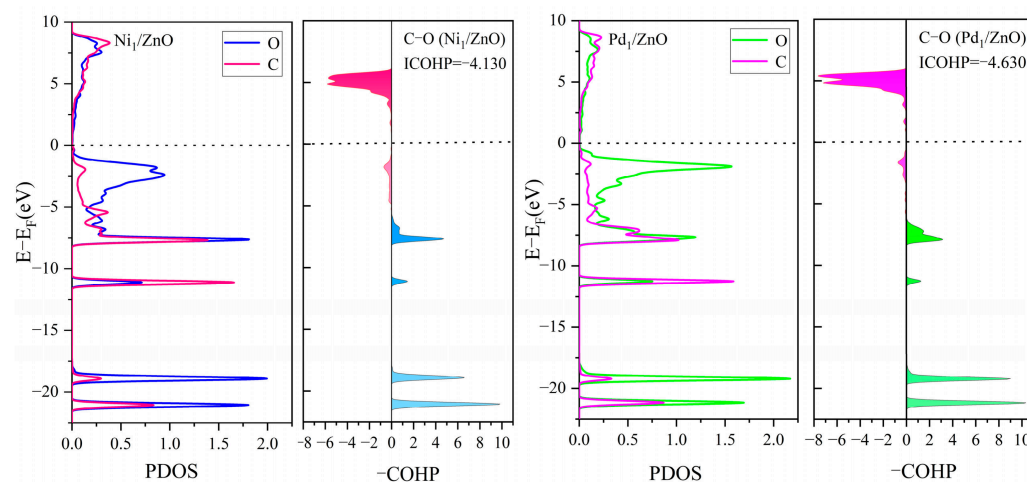


Figure 12. PDOS and $-COHP$ curves for CH₂O adsorption on Ni₁/ZnO and Pd₁/ZnO.

The influence of this geometric constraint becomes even more critical in the subsequent reaction steps. After CH₂O dehydrogenation to CHO, the CHO intermediate remains anchored to the lattice oxygen via its C atom, maintaining the C–3c–O bond constraint. This prevents CHO from directly dehydrogenating to CO; instead, it must first undergo a rearrangement step to release this geometric constraint. On Ni₁/ZnO, this rearrangement barrier is as high as 1.550 eV (R10), far exceeding the barrier for CH₂O + OH coupling (0.844 eV); thus, CO formation is kinetically suppressed. By contrast, on alloy surfaces, without the lattice oxygen anchor, CHO is adsorbed only through its O atom and experiences no such geometric constraint, so it can directly dehydrogenate to CO without a high-barrier rearrangement step. This dual regulation mechanism (electronic effect vs. geometric constraint) is a unique advantage of single-atom catalysts that distinguishes them from conventional alloys.

3.3. Comparison with the Single-Atom Doped ZnO Reference Catalyst

Here we compare the results with three reference systems: Pt₁/ZnO monoatomic catalyst reported by Gu et al. [35], and Pd₁/ZnO and Cu₁/ZnO catalysts studied by Qie et al. [36]. Gu et al. [35] reported that the MSR of Pt₁/ZnO was mainly completed by CO generation and subsequent WGS reaction. We re-evaluate its speed-limiting step (R12) with the same calculation setting, and get the energy barrier of 1.337 eV, which is higher than that of Ni₁/ZnO (0.844 eV) and Pd₁/ZnO (1.152 eV), indicating that the latter two have lower dynamic barriers.

Qie et al. [36] calculated Pd₁/ZnO by DFT-GGA, and proposed a single HCOO-mediated path with a decisive step energy barrier of 0.99 eV. However, our calculations show that there are two competing paths on Pd₁/ZnO, namely the direct CO₂ path and the CO-mediated path, and the latter was not considered in their work. At 673 K, the rate constants of these two paths are $8.254 \times 10^3 \text{ s}^{-1}$ (R10) and $6.841 \times 10^3 \text{ s}^{-1}$ (R4), respectively. These values are of the same order of magnitude, quantitatively confirming that both pathways are competitive and that the HCOO pathway is not exclusively dominant. In order to compare with the other system of Qie et al., we also calculated the energy barrier of methanol dehydrogenation step on Cu₁/ZnO, which was regarded as the decisive step. It was calculated that the energy barrier was 0.918 eV, higher than that of Ni₁/ZnO, indicating that the intrinsic activity of Ni₁/ZnO was better.

Table 4 compares the four catalysts quantitatively. The results show that Ni₁/ZnO not only has the lowest rate-limiting energy barrier but also follows the path of directly generating CO₂ and avoids the generation of CO, an advantage not shared by Pd₁/ZnO, Pt₁/ZnO or Cu₁/ZnO, making it a promising alternative for low-cost MSR catalysts.

Table 4. Comparison of RDS and corresponding activation barriers for MSR over Ni₁/ZnO, Pd₁/ZnO, Pt₁/ZnO, and Cu₁/ZnO.

Catalysts	Ni ₁ /ZnO	Pd ₁ /ZnO	Pt ₁ /ZnO	Cu ₁ /ZnO
RDS	R4	R10	R12	R2
<i>E_a</i> (eV)	0.844	1.152	1.337	0.918

4. Methods and Models

4.1. Computational Methods

All spin-polarized density functional theory calculations were performed using the Vienna ab initio simulation package (VASP 5.4.4, University of Vienna, Vienna, Austria) [48]. Exchange-correlation effects were described with the Perdew–Burke–Ernzerhof (PBE) functional [49], and projector augmented-wave (PAW) potentials represented electron–ion interactions [50]. The electronic-energy and force thresholds were set to 1×10^{-5} eV and 0.01 eV/Å, respectively. A plane-wave kinetic-energy cutoff of 400 eV was used. All geometry optimizations were performed without symmetry constraints (ISYM = 0) and with spin polarization included (ISPIN = 2). Dispersion interactions were included through the D3 correction (IVDW = 11) [51,52]. Brillouin-zone integration employed a $2 \times 2 \times 1$ Monkhorst–Pack k-point grid. For transition-state (TS) searches, the force threshold was set to 0.03 eV/Å. Initial minimum-energy paths were mapped with the climbing-image nudged elastic-band (CI-NEB) approach [53], and the TS geometries were refined with the dimer method where necessary [54,55]. Each optimized transition-state geometry was verified to contain exactly one characteristic imaginary vibrational mode corresponding to the reaction coordinate. Zero-point-energy (ZPE) contributions derived from vibrational analyses were applied to all reported energy values. The adsorption energy (*E_{ads}*), reaction energy (ΔE), and activation barrier (*E_a*) were calculated using the equations reported in previous work [56].

According to transition state theory [57], both the Arrhenius pre-exponential factor (*A*) and the rate constant (*k*) associated with each elementary step were calculated as follows:

$$A = \frac{k_B T}{h} \frac{Q^\ddagger}{Q} \quad (1)$$

$$k = A e^{\frac{-E_a}{k_B T}} \quad (2)$$

Here, *k_B* denotes the Boltzmann constant, *T* is the absolute temperature, and *h* represents the Planck constant. The symbols *Q[‡]* and *Q* denote the vibrational partition functions for the TS and initial configuration (IS). Consistent with experimental and theoretical studies of single-atom MSR catalysts [35,58], the reaction temperature was fixed at 673 K for the kinetic calculations.

4.2. Surface Models and Catalyst Stability

The bulk ZnO unit cell was first geometrically optimized, yielding lattice parameters of *a* = *b* = 3.274 Å and *c* = 5.281 Å, in good agreement with the experimental values of *a* = *b* = 3.250 Å and *c* = 5.207 Å [59]. A three-layer ZnO(10 $\bar{1}$ 0) slab with a (4 × 2) supercell was then constructed. A 15 Å vacuum region was introduced. To construct the single-atom

catalysts, one surface 3c-Zn atom was removed to create a Zn vacancy. An isolated Ni or Pd atom was embedded separately at the vacancy site, as illustrated in Figure 13. The corresponding binding energy (E_b) and metal cohesive energy (E_{coh}) were evaluated to examine the stability of the isolated metal atoms on ZnO. These quantities were defined as follows [60]:

$$E_b = E_{M/ZnO} - E_{ZnO-v} - E_{M-atom} \quad (3)$$

$$\Delta E_{coh} = E_{M-bulk/n} - E_{M-atom} \quad (4)$$

Here, $E_{M/ZnO}$, E_{ZnO-v} , and E_{M-atom} denote the total energies for the metal-doped ZnO system, the defective ZnO slab containing one Zn vacancy, and an isolated metal atom in vacuum, respectively. E_{M-bulk} gives the total energy of the bulk metallic phase, whereas n denotes the metal-atom count within the metallic unit cell.

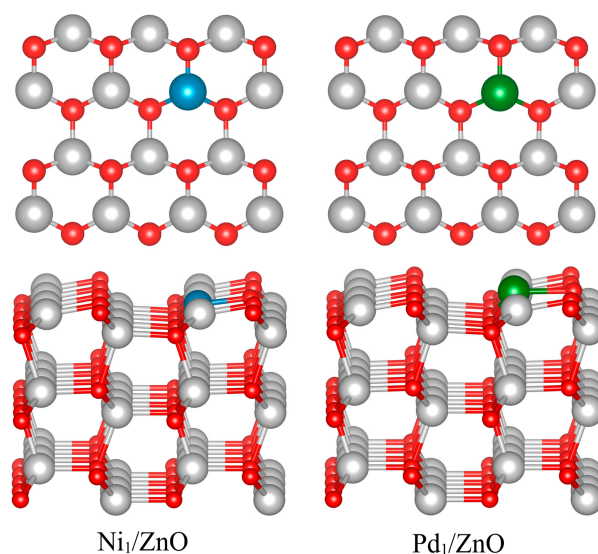


Figure 13. Structural models of the Ni_1/ZnO and Pd_1/ZnO catalysts. Color code: blue, Ni; green, Pd; gray, Zn; red, O.

When $E_b < \Delta E_{coh}$, attachment of the doped metal atom onto the defective ZnO support is stronger than metal–metal cohesion, indicating that isolated atoms are less likely to aggregate into clusters. The calculated binding energies for Ni and Pd were -7.548 and -5.100 eV, respectively. The cohesive energies of bulk Ni and Pd were -5.526 and -4.344 eV, respectively, and were less negative than the corresponding binding energies. These results indicate that both Ni and Pd can remain as isolated atoms on defective ZnO.

5. Conclusions

The MSR mechanisms over Ni_1/ZnO and Pd_1/ZnO atomically dispersed catalysts were compared systematically using DFT. The main findings are as follows:

(1) The stable adsorption configurations for the reactants and intermediates were located by systematic optimization. H_2O and CH_3OH both favor Zn-top sites and have similar adsorption energies on two catalysts. Most other intermediates bind more strongly on Pd_1/ZnO , consistent with the Pd d-state centroid lying closer to the Fermi level than the Ni d-state centroid.

(2) CH_2O controls product selectivity. In the most stable configuration, CH_2O binds through its C atom to a surface 3c–O site. The weaker C–3c–O interaction on Ni_1/ZnO provides CH_2O with greater conformational freedom, facilitates coupling with OH to form CH_2OOH , and favors the direct CO_2 -forming pathway.

(3) The two catalysts follow different dominant routes. Ni₁/ZnO predominantly follows the direct CO₂-forming pathway without a CO intermediate, and its RDS barrier is 0.844 eV. On Pd₁/ZnO, the CO-mediated and direct CO₂-forming pathways are similarly accessible, with limiting barriers of 1.152 and 1.190 eV, respectively. At 673 K, the rate constant for the CHO rearrangement that must occur before CO formation is only 6.704 s^{−1} on Ni₁/ZnO. The slow migration suppresses CO formation despite the relatively rapid subsequent CHO dehydrogenation step.

The adsorption thermodynamics, activation barriers, and rate constants collectively indicate that Ni₁/ZnO has higher intrinsic activity and CO₂ selectivity than the Pd₁/ZnO as well as Pt₁/ZnO and Cu₁/ZnO references considered here. This atomic-scale comparison provides a basis for the targeted development of high-performance atomically dispersed reforming catalysts.

Author Contributions: Conceptualization, methodology, formal analysis, data curation, writing—original draft preparation, visualization, R.W.; validation and investigation, R.W., Y.R., F.J., Y.L., W.L. and Q.D.; software, writing—review and editing, resources, supervision, J.J. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the Fundamental Research Program of Shanxi Province (202503021212289), the Research Start-up Funds of Shanxi College of Technology (2026BSL17), and Shanxi Undergraduate Innovation and Entrepreneurship Training Program (S202613534035).

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding authors.

Conflicts of Interest: The authors declare no conflicts of interest.

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