

Polarized $\text{Ni}^0\text{-Ni}^{\delta+}$ Catalysts Enable Asymmetric C–C Coupling for Long-Chain Hydrocarbons in Electrochemical CO_2 Reduction

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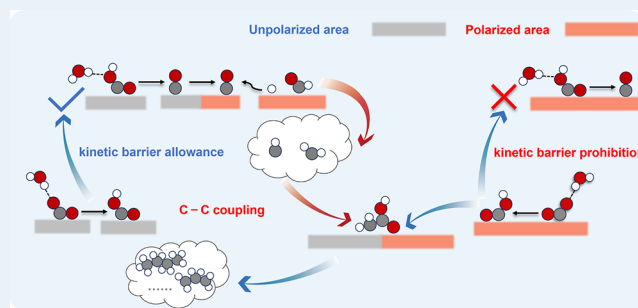
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ABSTRACT: The efficient electrochemical CO_2 reduction reaction (CO_2RR) to long-chain hydrocarbons (C_{3+}) still remains a formidable task even on the widely investigated copper-based catalysts. Recently, nickel-based catalysts have garnered wide attention for their promising ability to generate C_{3+} products. The design of $\text{Ni}^0\text{-Ni}^{\delta+}$ domains, analogous to the renowned $\text{Cu}^0\text{-Cu}^{\delta+}$ strategy, stands out as a hallmark approach, achieving substantial yields of $\text{C}_3\text{--C}_6$ compounds. However, theoretical understanding remains significantly limited. Here, we employ full-solvent *ab initio* molecular dynamics simulations with a slow-growth approach to investigate $\text{Ni}^0\text{-Ni}^{\delta+}$ -mediated C–C coupling at partially polarized nickel. In this system, the nonpolarized region is constantly covered by the generated *CO , while the polarized domain—through strategic modulation of Ni's d-band center—mitigates the poisoning effects of *CO_2 and *CO , thereby enhancing their activation. This facilitates C–C coupling primarily between *COOH and *CH_x ($x = 1, 2$), with significantly lower kinetic barriers compared to conventional *CO -involved pathways, laying the foundation for sustained carbon chain growth. Extending this concept to other metals ($M = \text{Fe, Rh, Pd, Co}$ and Ru) with similar adsorption characteristics akin to Ni further underscores the potential of $M^0\text{-}M^{\delta+}$ domains for CO_2 electroreduction. Our study elucidates the microscopic mechanisms by which polarization strategies promote the formation of long-chain products, providing an original perspective for designing CO_2 electroreduction catalysts.

KEYWORDS: CO_2 electrochemical reduction, asymmetric C–C coupling, long-chain hydrocarbons, nickel-based catalysts, *ab initio* molecular dynamics



INTRODUCTION

The electrochemical reduction of carbon dioxide (CO_2RR) into valuable multicarbon (C_{2+}) products offers a highly promising strategy for closing the carbon cycle while efficiently storing electricity generated from renewable energy sources.^{1–3} Copper is considered the only metal capable of reducing CO_2 to C_2 products, albeit with relatively low Faradaic efficiency in its pure metallic state.^{4–6} A major challenge, underscored by extensive experimental and theoretical studies, lies in the C–C coupling process, which is crucial for directing the formation of C_{2+} products, yet is hindered by slow kinetics under ambient conditions.^{7,8}

Among diverse strategies aimed at addressing this challenge, the construction of localized $\text{Cu}^0\text{-Cu}^{\delta+}$ environments through methods such as doping, morphology engineering, and molecular modification has emerged as one of the most effective approaches for promoting CO_2 reduction to multicarbon products on copper-based catalysts, garnering sustained interest and extensive research over the past decades.^{9–19} It is widely recognized that Cu^0 and $\text{Cu}^{\delta+}$ sites can increase *CO coverage and, owing to their distinct electron affinities, induce different activation states in neighboring *CO species.^{10,13}

This facilitates $\text{*CO}\text{-*CO}$ coupling or enables further reduction of *CO , promoting asymmetric C–C coupling modes, e.g., $\text{*CO}\text{-*COH}$ ^{9,11} or $\text{*CO}\text{-*CHO}$.²⁰ Through this strategy, the selectivity of C_2 products, including ethylene and ethanol, on copper-based catalysts has surpassed 80%.¹⁴ However, the efficient production of longer chain carbon products (C_{3+}) still remains a formidable task.

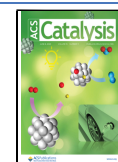
In recent years, Ni-based alloys and compounds have gained significant attention as highly promising CO_2RR systems due to their unparalleled potential for producing C_{3+} hydrocarbons.^{21–27} Intriguingly, the construction of $\text{Ni}^0\text{-Ni}^{\delta+}$ domain by oxygen doping in pure nickel has also been identified as an effective strategy to facilitate C–C coupling. This imparts the catalyst with a remarkable ability to produce $\text{C}_3\text{--C}_6$ products in substantial quantities, akin to the Fischer–

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Tropsch synthesis in thermochemical processes.²¹ Notably, researchers have observed that cofeeding CO₂ and CO as reactant gases yields a greater amount of multicarbon products compared to using either gas individually. This indicates that the carbon species participating in C–C coupling may originate from distinct stages—one prior to the formation of *CO and the other subsequent—marking a significant departure from the classical *CO dimerization mechanism.²¹ Despite the pioneering work, the limited research on the role of Ni⁰-Ni^{δ+} has so far fallen short of achieving the same level of mechanistic understanding as that of Cu-based counterparts. In particular, the detailed atomic reaction pathway and energetics, as well as the electronic structure origins of performance regulation, arise from the polarized regions. Additionally, solvent effects have a significant impact on the electrocatalytic reaction mechanisms.^{28–33} Yet, these issues remain largely unexplored and poorly understood. Taking them into account and elucidating a comprehensive picture for Ni⁰-Ni^{δ+}-mediated C–C coupling is significantly meaningful for opening a new way for efficient C₃₊ production.

In this work, we theoretically investigated the role of Ni⁰-Ni^{δ+} on C–C coupling at the partial polarized nickel using the full-solvent ab initio molecular dynamics (AIMD) simulations with a slow-growth approach.^{34,35} Our findings indicate that the downward shift of the polarized Ni d-band center effectively weakens the adsorption strength of the two critical intermediates, namely *CO₂ and *CO. As a direct outcome of this characteristic, *COOH forms more readily and remains stable in the polarized region. Furthermore, the mitigation of *CO poisoning allows for its further reduction within the polarized domain. After the hydrogenation of *CO to *CH_x (x = 1, 2), *COOH and *CH_x can readily combine, with a much lower activation energy than the traditional *CO involved C–C coupling. Considering that oxidation serves as a common method for lowering the d-band center of metals, we propose that constructing M⁰-M^{δ+} (M = Fe, Rh, Pd, Co, Ru) domains could also be promising catalyst systems for facilitating C–C coupling by mediating their adsorption strength of key intermediates. Collectively, we elucidate the microscopic mechanisms by which metal polarization, as a simple yet powerful approach, can regulate intermediate thermodynamics to promote the formation of long-chain carbon products in electrochemical CO₂ reduction.

RESULTS AND DISCUSSION

Catalyst Model Construction and Electronic Structure Analysis. Electrocatalysts derived from inorganic nickel oxygenates, exemplified by phosphate-derived nickel systems (denoted as PD-Ni), have demonstrated exceptional selectivity toward long-chain hydrocarbon production.²¹ Nevertheless, the fundamental mechanism governing the formation and evolution of active sites during catalytic operation remains a subject of ongoing debate.³⁶ To bridge this knowledge gap and establish a representative model system, we employ nickel phosphate (Ni₃(PO₄)₂) as a structural precursor to investigate the dynamic surface reconstruction processes under operational conditions. To accurately simulate the electrochemical environment, we systematically introduced 1–2 (K⁺ + e) ion pairs into the model system, thereby establishing a realistic representation of the electrode–electrolyte interface and solvent environment (Figure S1). Our analysis reveals that the introduction of (K⁺ + e) ion pairs significantly enhances the interfacial dynamical activity of phosphate (PO₄^{3–}) groups,

as evidenced by their increased positional fluctuations and altered bond-length distributions (Figures S2, S3). Furthermore, the enhanced interfacial dynamics of phosphate ions facilitate the leaching behavior of surface phosphate groups. As illustrated in Figure S4, the specific adsorption of (K⁺ + e) ions on phosphate significantly lowers the reaction energy barrier and promotes its adsorption at the interface. This indicates that cations induce the activation of the precursor and the leaching of phosphate groups, further triggering reconstruction of the catalyst precursor and is generally observed in the cathodic corrosion of other metals.^{37–39} This phenomenon is supported by experimental results, where the P/Ni ratio in PD-Ni samples gradually decreased by approximately 1 atom % during the reaction.²¹ Moreover, this suggests that phosphate groups may not participate in the formation of active sites under the final steady-state conditions. Another experimental observation is that Ni⁰ species gradually increase from 0% to 13%, while the remaining species consist of Ni^{δ+}.²¹ This indicates that, as phosphate groups leach out, the catalytic activity is primarily governed by the cooperative effect of the Ni⁰-Ni^{δ+} domain. To further explore its impact on the eCO₂RR catalytic mechanism, we will employ corresponding models for analysis.

Based on the aforementioned analysis, we employed *O species to construct the Ni⁰-Ni^{δ+} domain. As illustrated in Figure 1a, we systematically established a concentration gradient of *O coverage and ultimately identified 3/32 ML

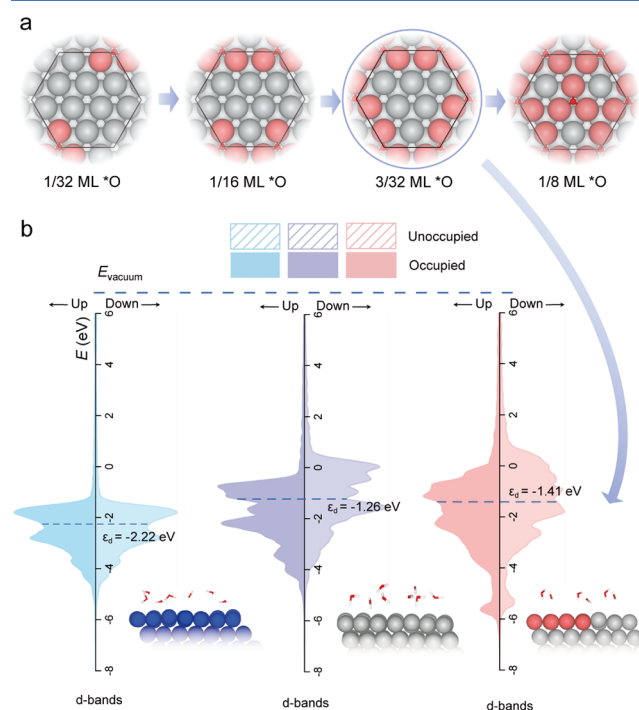


Figure 1. Electronic structure analysis of Cu (111), Ni (111), and Ni_{pol} (111): (a) Ni_{pol} (111) with four polarization degrees was constructed, and the surface oxygen atoms occupied 1/32, 1/16, 3/32, and 1/8 adsorption sites (ML *O), respectively (from left to right). Finally, Ni_{pol} with 3/32 ML *O was selected as the model to be studied, for its proper adsorption sites of both polarized and nonpolarized. (b) The blue, purple, and red DOS plots represent Cu, Ni, and Ni_{pol}, respectively. The structures in the bottom-right corner illustrate their slab with solvated configurations. Solvated configurations can be found in Figure S11. In the slab model, blue spheres represent Cu atoms, gray spheres represent Ni atoms, and red spheres represent Ni_{pol} atoms.

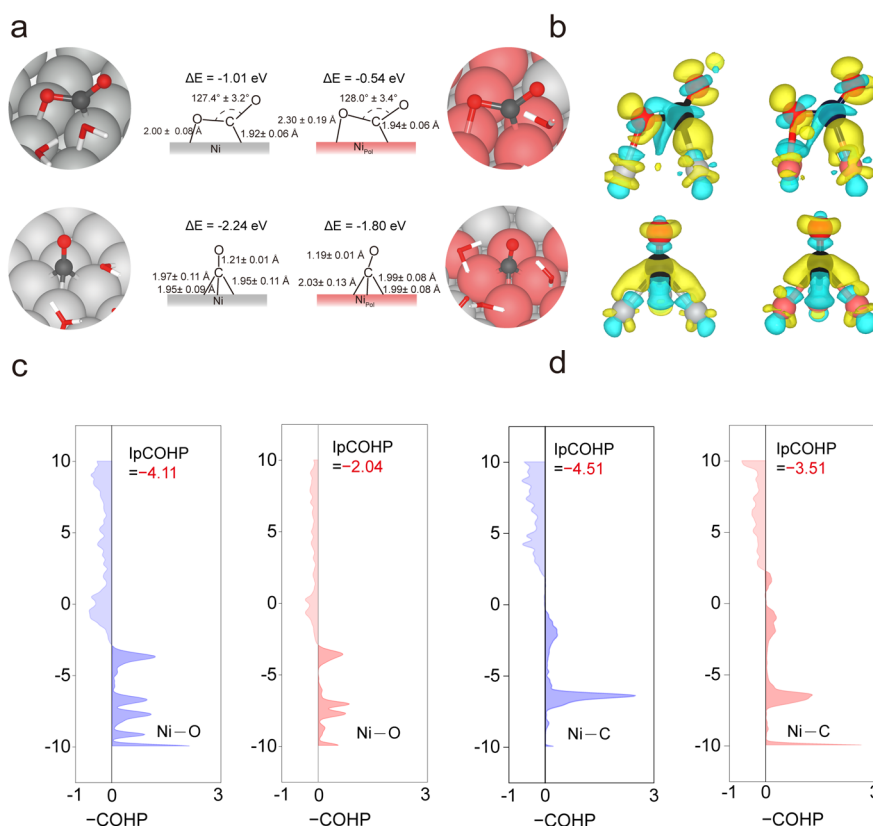


Figure 2. Comprehensive analysis of the CO_2 -to- CO conversion reaction mechanism: (a) CO_2 and CO adsorption configurations and corresponding adsorption energies on Ni and Ni_{pol} ; (b) Differential charge density isosurfaces for CO_2 and CO adsorption: yellow represents electron accumulation and cyan denotes electron depletion (Isovalue = $0.0067 \text{ e } \text{\AA}^{-3}$); (c) COHP analysis for Ni–O bonds between nickel atom from surface and oxygen atom from CO_2 ; (d) COHP analysis for Ni–C bonds between nickel atom from surface and carbon atom from CO ; in (c) and (d) purple represents metallic Ni, red represents Ni_{pol} .

O as the optimal model system. This selection was primarily based on the observation that both insufficient and excessive O coverage (e.g., $1/32$ ML and $1/8$ ML O , respectively) would result in inadequate $\text{Ni}^{\delta+}/\text{Ni}^0$ regions, thereby hindering the investigation of their influence on key reaction intermediates. The partially polarized Ni (111) (denoted as Ni_{pol}) was developed by introducing oxygen adsorb on surfaces. Considering the solvent environment (e.g., water) under real experimental conditions, O may convert into OH . Therefore, it is essential to systematically evaluate their impact on model construction. Then we calculate their adsorption energies on Ni(111) (Figure S5) and analyzing the free energy pathway for the O -to- OH -to- H_2O transition (Figure S6). The calculated Gibbs free energy changes for the $\text{O} \rightarrow \text{OH}$ and $\text{OH} \rightarrow \text{H}_2\text{O}$ transitions are -0.05 eV and -0.08 eV, respectively. The minimal energy differences indicate thermodynamically reversible interconversions and dynamic coexistence of O , OH . Subsequently, we investigate how these two species locally oxidize nickel atoms to a valence state of $+0.22 \text{ e}$ (O) and $+0.18 \text{ e}$ (OH), as confirmed by Bader charge analysis (Figures S7, S8). This slight charge difference suggests comparable electronic perturbation magnitudes between the two models with different adsorbed species. Therefore, we use models with O in Figure 1a to analyze the influence of the $\text{Ni}^0\text{--Ni}^{\delta+}$ domain on the eCO_2RR mechanism.

Based on above discussion, we then examined the d-band structures of Ni (111) and partially polarized Ni_{pol} (111) to gain a fundamental understanding of these materials from the perspective of electronic structure. The result of Cu (111) was

also presented as a comparison (Figure 1b, S9). By referencing the energy levels of the three systems, a direct comparison of their density of state (DOS) profiles reveals that the d-band center (ϵ_d) of Cu (-2.22 eV) is notably lower than that of Ni (-1.26 eV) relative to the Fermi level (Figure S10). Consequently, when adsorbates interact with Ni, the resulting antibonding orbitals originating from orbital splitting are more likely to occupy states above the Fermi level, leading to their stronger adsorption on Ni compared to Cu. Nevertheless, stronger adsorption does not always equate to better performance in catalysis, as dictated by the Sabatier principle.⁴⁰ In fact, Cu has emerged as a popular metal for CO_2 reduction precisely because its d-band center is well-positioned, resulting in moderate CO adsorption energy.⁴¹ In contrast, Ni is considered suffering from CO poisoning due to its excessively strong CO adsorption.^{42–44} Upon introducing oxygen into Ni, chemical bonds form between the Ni and oxygen atoms. Due to the high electronegativity of oxygen, electrons are drawn from Ni toward the oxygen atoms, which reduces the d-electron density of Ni, thus resulting a lower d-band center of polarized Ni (-1.41 eV). It can be anticipated that a weakened adsorption for intermediates during the CO_2 reduction will be achieved on Ni_{pol} , thereby alleviating the poisoning effect on pure Ni.

Effect of Polarization on the Reaction Mechanism.

The adsorption energies of the two key intermediates, CO_2 and CO , on Ni and Ni_{pol} were calculated by averaging over ten selected configurations from the AIMD trajectories (details in Figures S12, S13). On both surfaces, CO_2 exhibited a

bidentate adsorption mode on both surfaces, with one carbon and one oxygen atom binding to atop sites of the surface atoms. In contrast, $^*\text{CO}$ tended to adsorb at hollow sites. The adsorption energies of $^*\text{CO}_2$ and $^*\text{CO}$ on Ni were found to be -1.01 eV and -2.24 eV, respectively. Notably, we also calculated the adsorption energies of $^*\text{CO}_2$ and $^*\text{CO}$ on Ni in the absence of water environment, which were 0.96 and 0.15 eV higher than those in the presence of water (Figures S12 and S13). This highlights the importance of considering the solvation environment, especially for $^*\text{CO}_2$, which forms strong hydrogen bonds with the interfacial water (Figure S13).^{45,46} When $^*\text{CO}_2$ and $^*\text{CO}$ adsorb on Ni_{pol} , their adsorption energies become notably less negative (-0.54 eV for $^*\text{CO}_2$ and -1.80 eV for $^*\text{CO}$) in the solvation environment, accompanied by distinct changes in their adsorption configurations. Specifically, the Ni–O bonds between $^*\text{CO}_2$ and the interface lengthen, leading to reduced charge transfer between Ni and O (Figure 2b) and a significant decrease in the bond strength, as evidenced by the less negative IpCOHP (integrated crystal orbital Hamilton population) values (Figure 2c). For $^*\text{CO}$, the Ni–C bond also undergoes elongation (Figure 2a), leading to weakened bond strength (Figure 2b). The decreased charge accumulation on the carbon atom indicates reduced back-donation from the metal to the antibonding orbitals of $^*\text{CO}$ (Figure 2d), thereby shortening the C–O bond (Figure 2a). Collectively, the altered d-band electronic structure in the polarized region significantly impacts the adsorption behavior of $^*\text{CO}_2$ and $^*\text{CO}$.

Subsequently, we employed the slow-growth method to evaluate the kinetic barriers of the transformation of $^*\text{CO}_2$ into $^*\text{CO}$ (Figure 3). On the Ni_{pol} surface, the adsorption energy of

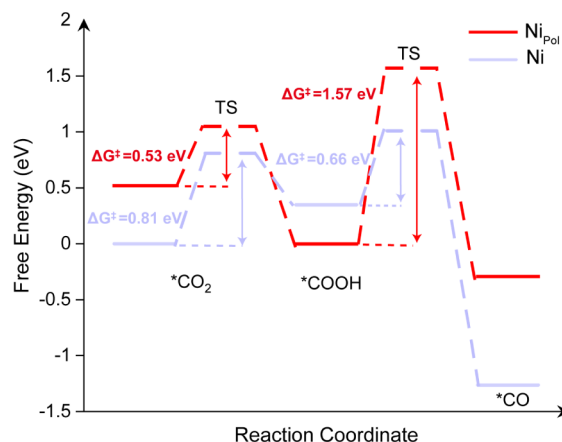


Figure 3. Free energy pathway diagram for $^*\text{CO}_2$ -to- $^*\text{COOH}$ -to- $^*\text{CO}$ conversion on Ni and Ni_{pol} . TS: transitional state.

$^*\text{CO}_2$ becomes less exergonic (while still remaining favorable), which substantially lowers the activation barrier (0.53 eV) for the conversion of $^*\text{CO}_2$ to the $^*\text{COOH}$ intermediate. Conversely, on pristine Ni, the excessively strong adsorption of $^*\text{CO}_2$ induces a degree of catalytic poisoning, resulting in a comparatively elevated activation energy of 0.81 eV. In the $^*\text{COOH}$ -to- $^*\text{CO}$ conversion process, however, the scenario is markedly different. The diminished adsorption strength of $^*\text{CO}$ on Ni_{pol} reduces the exothermicity of the $^*\text{COOH}$ -to- $^*\text{CO}$ transformation, thereby elevating the activation barrier to 1.57 eV. Conversely, on pristine Ni, the strongly exergonic $^*\text{CO}$ adsorption confers an inherent thermodynamic advantage

for $^*\text{COOH}$ hydrogenation, yielding a substantially lower barrier of 0.66 eV, further details are provided in Figures S15 and S16. This finding is consistent with the Brønsted–Evans–Polanyi (BEP) principle,⁴⁷ which posits a positive correlation between thermodynamic driving force and activation energy. As a result, the activated $^*\text{COOH}$ species tend to remain anchored at the interface on Ni_{pol} , whereas on pure Ni, $^*\text{COOH}$ is more inclined to undergo further reduction to $^*\text{CO}$.

The occurrence of C–C coupling requires the coadsorption of two carbon-containing species in a localized region. Experimental studies have shown that feeding CO_2 together with CO or HCHO yields significantly higher amounts of multicarbon products compared to using CO_2 or CO alone.²¹ This indicates that the species involved in C–C coupling are likely positioned such that one precedes $^*\text{CO}$ formation and the other follows it. In the region of polarized Ni, $^*\text{COOH}$ can remain adsorbed for extended periods due to the high energy barrier for its conversion to $^*\text{CO}$. We subsequently analyzed the energy required for further hydrogenation of $^*\text{CO}$ to explore the formation of another potential intermediate. In the CO_2RR process, $^*\text{CO}$ can undergo two potential hydrogenation pathways: one involves hydrogenation at the oxygen end to form $^*\text{COH}$,⁴⁸ and the other at the carbon end to form $^*\text{CHO}$.^{7,49,50} Both pathways can proceed via the Eley–Rideal (ER) or Langmuir–Hinshelwood (LH) mechanism.⁷ After a comprehensive evaluation of these possibilities, we found that only the hydrogenation of $^*\text{CO}$ to $^*\text{CHO}$ via the LH mechanism is energetically favorable in the Ni_{pol} region (0.82 eV, Figure 4). All other pathways, whether on Ni_{pol} or pristine Ni, exhibit high energy barriers or lack inflection points in the energy profile, indicating that these processes are unlikely to occur (Figure 4a, S17 and S18). It is evident, as illustrated in Figure 3, that the formation of $^*\text{CO}$ within the polarized Ni region is inherently challenging. Nonetheless, we discovered that $^*\text{CO}$ generated on the pristine Ni region can readily migrate to the polarized domain with a relatively low energy barrier (0.35 eV), revealing a synergistic interplay between the polarized and nonpolarized regions (Figure S19). Essentially, the pristine Ni region acts as a source for producing $^*\text{CO}$ necessary for subsequent transformations, while the polarized region, due to its attenuated adsorption strength and potentially lower activation barriers in accordance with the BEP relationship, facilitates the further hydrogenation of $^*\text{CO}$.

The hydrogenation step of $^*\text{CO}$ is widely regarded as the rate-determining step in the reduction of CO_2 to C_1 products.^{7,51} Once this barrier is overcome, the subsequent steps generally become energetically favorable, making them potential candidates for C–C coupling.⁵² To capture the overall energetic trends of C–C coupling, we evaluated the feasibility of coupling $^*\text{CO}$, $^*\text{CHO}$, $^*\text{CHOH}$, $^*\text{C}$, $^*\text{CH}$, $^*\text{CH}_2$ and $^*\text{CH}_3$ with $^*\text{CO}_2$, $^*\text{COOH}$ and $^*\text{CO}$ (Figure 5a and b), representing typical C–C coupling patterns.⁵³ All optimized structures, including the initial states and final states are presented in Figures S20 and S21. Notably, Due to the computational cost of AIMD simulations, we performed thermodynamic energy calculations based solely on structural optimization without considering solvent effects. It can be observed that among $^*\text{CO}_2$, $^*\text{COOH}$, and $^*\text{CO}$, the former two serve as more favorable building blocks for C–C coupling, exhibiting consistently lower reaction energies for the coupling process. In the case of species derived from the further reduction of $^*\text{CO}$, the thermodynamic feasibility of C–C

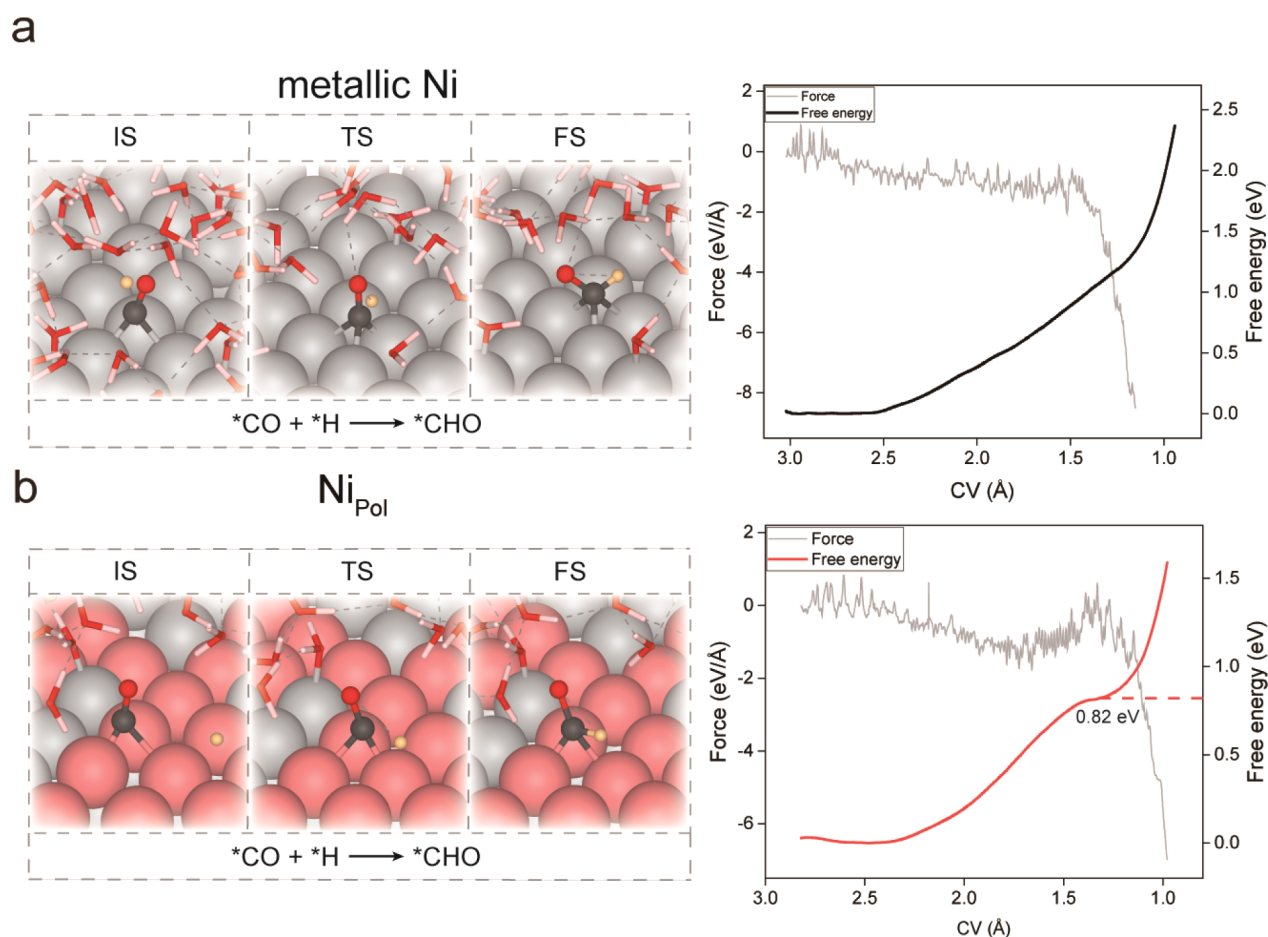


Figure 4. Energy barrier for $^*\text{CO}$ to $^*\text{CHO}$ conversion via Langmuir–Hinshelwood (LH) hydrogenation mechanism: (a) hydrogenation structures and energy profile on Ni (111); (b) hydrogenation structures and energy profile on Ni_{pol} (111).

coupling tends to improve with increasing reduction levels. This observation suggests that $^*\text{CO}$, contrary to conventional assumptions, may not be an optimal species for C–C coupling—a conclusion that can be rationalized from a chemical perspective.^{54,55} $^*\text{CO}$ possesses a highly stable electronic configuration and forms a robust bond with the Ni and Ni_{pol} surface, evidenced by its strongly negative adsorption energy (Figure 2a). In contrast, $^*\text{CO}_2$, due to its unoccupied antibonding orbitals and highly electronegative oxygen atoms, can undergo partial reduction at the interface to yield a more reactive species ($^*\text{CO}_2^-$), thereby significantly enhancing its catalytic reactivity.⁵⁶ Similarly, the antibonding orbitals of the carbonyl group in $^*\text{COOH}$, coupled with the electronegativity of the hydroxyl group, facilitate efficient electron acceptance during adsorption, promoting bond rearrangements and the formation of new C–C bonds. Interestingly, in the field of electrochemical C–N coupling toward urea using CO_2 and nitrogen oxides as reactants, $^*\text{CO}_2$ or $^*\text{COOH}$, rather than $^*\text{CO}$, has also been widely reported as the coupling species.^{33,57–59} Regarding the intermediates formed after the hydrogenation of $^*\text{CO}$, the weakening of the triple bond, followed by the complete dissociation of the oxygen, imparts a degree of radical character to the carbon species. This shift in electronic structure effectively reduces the energy barrier of C–C coupling, thereby facilitating the C–C coupling.

$\text{Ni}^0\text{-Ni}^{\delta+}$ Facilitates Asymmetric C–C Coupling. To validate the robustness of this conclusion, we employed the

slow-growth method with full solvent environment to calculate the kinetic barriers for several C–C coupling pathways, including $^*\text{CO}\text{-}^*\text{CO}$, $^*\text{CO}_2\text{-CH}_2$, $^*\text{COOH}\text{-}^*\text{CH}$, and $^*\text{COOH}\text{-CH}_2$. All figures and energy files can be found in Figures S22, S23. The results indicate that the dimerization of $^*\text{CO}$ is highly challenging both on Ni and Ni_{pol} surfaces, with activation energies exceeding 1.7 eV. In contrast, the coupling pathways involving $^*\text{COOH}$ and $^*\text{CO}_2$ exhibit significantly lower kinetic barriers, with the $^*\text{CO}_2\text{-CH}_2$ and $^*\text{COOH}\text{-CH}_2$ couplings showing activation barriers of 0.27 and 0.36 eV, respectively, suggesting a higher likelihood of occurrence under practical conditions. Interestingly, this conclusion holds true for Cu as well. Our calculations revealed that the kinetic barriers of coupling pathways involving $^*\text{COOH}$ and $^*\text{CO}_2$ on Cu are consistently lower than those of $^*\text{CO}\text{-}^*\text{CO}$ coupling. The work by Cheng et al. provides a more comprehensive analysis of the energy comparisons for C–C coupling involving $^*\text{CO}_2$ and $^*\text{CO}$ with other carbon species on Cu, demonstrating that $^*\text{CO}_2$ is a more favorable coupling species than $^*\text{CO}$.⁶⁰ This suggests that our analysis may possess a certain degree of general applicability. Another noteworthy point is that the energy barriers for C–C coupling on polarized Ni are consistently lower than those on pristine Ni. This decrease in barriers is likely attributed to the weakening of adsorption strength for carbon-containing species due to polarization, which in turn alleviates the poisoning effect. Additionally, we calculated the energy barriers for the conversion of $^*\text{CH}_2$ to $^*\text{CH}_3$. If $^*\text{CH}_3$ forms and subsequently

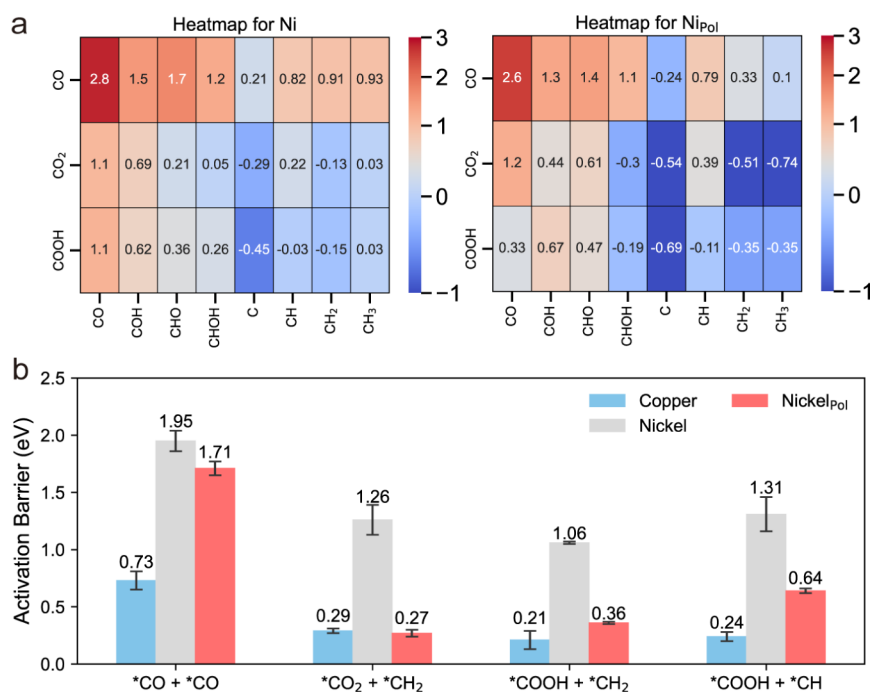


Figure 5. Thermodynamic and kinetic analysis of C–C coupling pathways: (a) Heatmap analysis of thermodynamic reaction energies for various C–C coupling patterns on Ni and Ni_{pol}. The thermodynamically favorable patterns ($\Delta E_{\text{free}} < 0$) are highlighted in blue, while the unfavorable patterns ($\Delta E_{\text{free}} > 0$) are highlighted in reddish-brown. (b) Kinetic energy barrier analysis of *CO+*CO, *CO₂+*CH₂, *COOH+*CH₂, *COOH+*CH on Cu, Ni, and Ni_{pol}. Ni_{pol} means C–C coupling process occurs on Ni⁰-Ni^{δ+} domain.

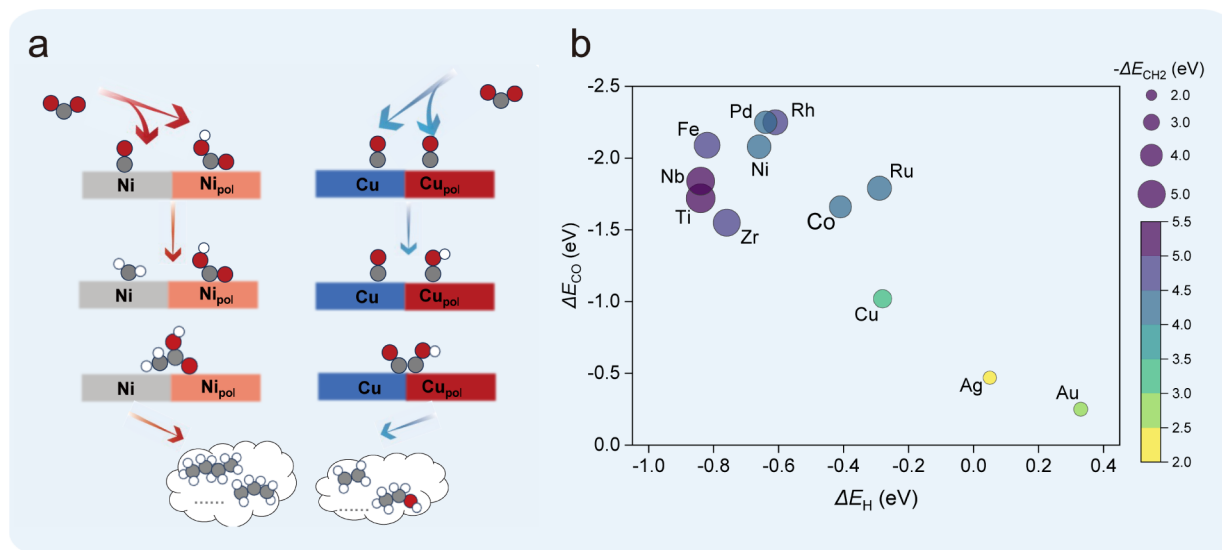


Figure 6. Scheme of (a) different mechanisms of C–C coupling for Ni⁰-Ni^{δ+} and Cu⁰-Cu^{δ+} regions; (b) Colormap plot for analyzing the potential of transition metal catalysts (Ti, Nb, Zr, Fe, Rh, Ni, Pd, Co, Ru, Cu, Ag, Au) for long-chain hydrocarbons synthesis, with the x-axis for *CO adsorption energy, y-axis for *H adsorption energy, and bubble size as well as its color for negative *CH₂ adsorption energy. More details are provided in Figures S25–27.

engages in C–C coupling, the growth of the carbon chain will terminate. Thus, to achieve the formation of long-chain hydrocarbons, it is crucial to inhibit the generation of *CH₃. We found that the energy barriers for this step are 0.66 eV on pristine Ni and 0.94 eV on Ni_{pol}, respectively (Figure S24). This energy barrier is sufficiently high to effectively prevent *CH₃ formation and thus serves as another key factor in enabling the experimental formation of even C₆ products.

A schematic diagram illustrating how Ni⁰-Ni^{δ+} facilitates C–C coupling is presented in Figure 6a. For comparison, the

general mechanism of Cu⁰-Cu^{δ+} promoting C–C coupling is also depicted. In the Ni system, the primary role of the polarized region is to weaken the adsorption of carbon-containing species, allowing *COOH to remain as a stable intermediate during the conversion of *CO₂ to *CO. Concurrently, *CO generated in the nonpolarized region can migrate to the polarized region, where it undergoes further reduction to *CH_x species, ultimately enabling an insertion-type C–C coupling process involving *CH_x. In the Cu system, due to the conversion of CO₂ to CO is a rapid process, the

primary role of the polarized region is to create a distinct $^*\text{CO}$ adsorption state with an electronic structure different from that of $^*\text{CO}$ in the nonpolarized region. This differentiation can enhance $^*\text{CO}$ – CO coupling or facilitate the reduction of $^*\text{CO}$ to $^*\text{COH}/^*\text{CHO}$, enabling subsequent $^*\text{CO}$ – $^*\text{COH}$ or $^*\text{CO}$ – $^*\text{CHO}$ coupling.^{10,11,13,18} The key distinction between the Ni and Cu systems lies in Ni's avoidance of reaction pathways that utilize $^*\text{CO}$ as the C–C coupling species, instead favoring $^*\text{CO}_2$ and/or $^*\text{COOH}$ based C–C coupling. This unique mechanism stems from the inherently strong adsorption of carbon-containing species on Ni. Polarization, such as through oxygen doping, raises the metal's oxidation state and shifts the d-band center away from the Fermi level. This effectively mitigates the poisoning effect of intermediates, preventing them from becoming trapped in thermodynamically stable states, such as $^*\text{CO}$ adsorption.

Extension of Mechanism to Other Transition Metals and Open Questions. Since elevating the oxidation state of metals through polarization to lower the d-band center represents a broadly applicable strategy, we were inspired to hypothesize that other metals with carbon-species affinities akin to Ni could also facilitate long-chain hydrocarbons via polarization. To identify potential candidates for long-chain hydrocarbons formation using this approach, we performed high-throughput calculations of the adsorption energies of key intermediates ($^*\text{CO}$, $^*\text{CH}_2$, $^*\text{H}$) across various metals ($M = \text{Ti, Nb, Zr, Fe, Rh, Ni, Pd, Co, Ru, Cu, Ag, Au}$). The calculation of $^*\text{CO}$ adsorption energy can be utilized to evaluate the affinity of different metal interfaces toward carbon oxides ($^*\text{CO}_2$, $^*\text{COOH}$ and $^*\text{CO}$), while strong $^*\text{CH}_2$ adsorption maximizes the possibility for the chain growth toward long-chain carbon products. We also calculated adsorption energies of $^*\text{H}$ to evaluate the potential for HER side reactions. To enhance screening efficiency, we performed only structural optimizations without employing molecular dynamics methods. The solvent environments were also not included since the adsorption energies of $^*\text{CO}$, $^*\text{CH}_2$, and $^*\text{H}$ are generally considered to be relatively unaffected by solvation effects. The results (Figure 6b) reveal that Ru, Rh, Fe, Co and Pd possess adsorption energies for key intermediates comparable to those of Ni, indicating their possibility for facilitating the formation of long-chain carbon product through polarization strategies. In contrast, Ti, Nb, and Zr exhibit excessively strong adsorption of carbon-containing species. Cu, with its moderate $^*\text{CO}$ adsorption strength, favors $^*\text{CO}$ – CO coupling, whereas Au and Ag, due to their weak $^*\text{CO}$ affinity, predominantly produce CO as the primary product. Notably, Co has recently been confirmed as capable of achieving long-chain carbon products in CO_2RR through the strategic construction of polarized-nonpolarized regions.⁶¹ Although similar evidence is so far lacking for Fe, Pd, Ru, and Rh, the demonstrated ability of Fe phosphides and Pd alloys to produce multicarbon products underscores their promising potential.^{62–65} Future work will involve constructing models with tunable polarization on various metals and applying machine learning to uncover universal relationships between polarization, d-band shifts, and the adsorption energies of key CO_2 reduction intermediates, aiming to build a more comprehensive mechanistic framework for long-chain product formation.

Based on the above findings, we propose that the $\text{Ni}^0\text{--Ni}^{\delta+}$ domain, by modulating the formation of various reaction intermediates, enables an asymmetric C–C coupling mecha-

nism that may also hold similar potential on other transition metals such as Fe, Pd, Ru, and Rh. It should be acknowledged that although we conducted an in-depth investigation into the thermodynamic and kinetic processes of the eCO_2RR on a nickel-based catalyst—leveraging AIMD and the slow-growth method in a solvent environment to systematically investigate the impact of metal polarization on the thermodynamic states of intermediates (an effect primarily governed by the intrinsic properties of the metal)—other factors influencing the reaction mechanism were not considered. For instance, factors such as potential and pH, which are relevant to the electrochemical environment, were not considered in this work. Despite the fact that polarization enables the feasibility of long-chain carbon products, the selectivity remains relatively low, with hydrogen gas often being the dominant product.^{21,61} This indicates that additional strategies need to be implemented to suppress the competing HER side reaction. Building on the polarization strategy, incorporating metals with low hydrogen affinity, such as Ga and Al, could be an effective approach. On Cu, the addition of Ga and Al has been demonstrated to successfully suppress HER and promote the formation of multicarbon products.^{66,67} On Ni, even the sole incorporation of Ga, without the construction of polarized regions, has been shown to yield multicarbon products.^{24,25} Additionally, electrolyte engineering to change interfacial environment presents another promising avenue for C–C coupling promotion.⁶⁸ This can be achieved by reducing water activity, introducing surface-modified molecules, or altering surface morphology.⁶⁹

CONCLUSIONS

In this study, we explored the influence of $\text{Ni}^0\text{--Ni}^{\delta+}$ on C–C coupling in partially polarized nickel through full-solvent ab initio molecular dynamics (AIMD) simulations combined with the slow-growth methodology. The results reveal that the d-band center shift in polarized Ni significantly diminish the poisonous effect of two key intermediates, namely $^*\text{CO}_2$ and $^*\text{CO}$, thereby enhancing their reactivity. As a direct result of this characteristic, $^*\text{COOH}$ is more easily formed and stays in the polarized region. Additionally, the $^*\text{CO}$ generated in the nonpolarized region can migrate to the polarized region, where it undergoes further hydrogenation to form $^*\text{CH}_x$ species. The $^*\text{COOH}$ and $^*\text{CH}_x$ species can efficiently combine, resembling the chain elongation process of Fischer–Tropsch synthesis, with a significantly lower activation energy compared to traditional $^*\text{CO}$ -mediated C–C coupling pathways. Given that oxidation is a general approach to lowering the d-band center of metals, we suggest that creating $\text{M}^0\text{--M}^{\delta+}$ domains may serve as an efficient strategy to enhance C–C coupling on Fe, Ru, Rh, Co, and Pd metals that exhibit similar adsorption characteristics of key species like Ni. In summary, we unveil the microscopic mechanisms through which metal polarization, as a straightforward yet potent strategy, modulates intermediate thermodynamics to drive the formation of long-chain carbon products in electrochemical CO_2 reduction.

METHODS

First, in model construction stage, the (001) facet of $\text{Ni}_3(\text{PO}_4)_2$ was employed, and 30 explicit water molecules were incorporated to establish the initial configuration for ab initio molecular dynamics (AIMD) simulations. Subsequently, a 20 ps molecular dynamics simulation was performed to

achieve system equilibration and the structural configurations, along with the temporal evolution of temperature and total energy fluctuations during the simulations, are comprehensively presented in Figure S1.

Then the Ni(111) surface, as a primary Miller index facet of polycrystalline nickel⁷⁰ and is notably selective in catalyzing long-chain hydrocarbon synthesis, particularly when alloyed or doped with other elements.^{22,71,72} In this article, we utilize the Ni(111) surface and partially polarized Ni(111) surface models to simulate metallic nickel and nickel-based catalysts polarized by highly electronegative species, such as oxygen. Additionally, we include a Cu(111) slab as a control to compare typical *CO-dominant reaction mechanisms.⁷³ All slabs were constructed using a four-layer 4×4 supercell with a vacuum region of approximately 15 Å along the *z*-axis to prevent interactions between periodic images. To simulate a fully solvated model, 30 water molecules were explicitly added above the Cu and (partially polarized) Ni surfaces, creating water layers with thickness of approximate 10 Å. Full-scale models of the three systems discussed are shown in Figures S9 and S11.

Density functional theory (DFT) calculations were carried out using the Vienna Ab initio Simulation Package (VASP)^{74,75} with the projector-augmented-wave (PAW) method.⁷⁶ To account for electron exchange-correlation interactions, we applied the Perdew–Burke–Ernzerhof (PBE) functional within the framework of the generalized gradient approximation (GGA).⁷⁷ Additionally, Grimme's D3 dispersion correction was included to account for van der Waals interactions.⁷⁸ The full solvated environment is simulated by AIMD simulations to model the dynamics of water molecules and the hydrogen bond network. The slow-growth method,^{34,35} applied with VASP, is employed to obtain the energy profile under explicit water conditions. The adsorption energies in solvent environment is obtained after performing self-consistent calculations on structures parallel-extracted from a 10 ps trajectory, where the adsorbate has been fully stabilized.

We conducted density of states (DOS) calculations and Bader charge analysis using the Device Studio integrated Projector Augmented-Wave method package (DS-PAW).⁷⁶ To further examine the bonding interactions between the adsorbate and the interface, we applied crystal orbital Hamiltonian population (COHP) calculations, providing a detailed evaluation of bond lengths within the interface structure.^{79,80} More details of our calculations can be found in the Supporting Information.

■ ASSOCIATED CONTENT

Data Availability Statement

Crucial model structure configurations and DFT-based calculation details are available at <https://github.com/dinghw49/ACS-Catalysis-Pol-Ni.git>

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.4c07353>.

Details of the computational models and equations used for AIMD simulations, all adsorbate configurations, free energy files for the eCO₂RR mechanism, the C–C coupling process on nickel-based catalysts, and adsorption energies for other transition metals are provided (PDF)

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Notes

The authors declare no competing financial interest.

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