

REVIEW

Advances in the understanding of selective CO₂ reduction catalysis

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Abstract

The electrochemical synthesis for value-added chemicals and fuels via carbon dioxide reduction reaction (CO₂RR) offers an effective route to close the anthropogenic carbon cycle and store renewable energy. Currently, the copper-based catalyst is still the only choice for generating various CO₂RR species beyond two electron products. However, the wide range of CO₂RR products generated on copper leads to low selectivity, and their low concentrations in electrolytes pose great costs in the downstream purification process and significantly challenge the scalability of this technology. To make this technology economically viable, enhancing product selectivity is crucial. In this review, we identify the primary CO₂RR species and discuss the latest insights into the reaction mechanisms controlling CO₂RR selectivity. Then, we examined factors that affect CO₂RR selectivity. Emphasizing these factors in catalyst design, we highlight the importance of advanced technologies to expand our knowledge and prospects for the future of the CO₂RR.

KEYWORDS

copper surface, CO₂ reduction reaction, CO₂RR intermediates, electrocatalysts, selectivity

1 | INTRODUCTION

Excessive CO₂ emissions due to anthropogenic consumption of fossil fuels have led to an unprecedented CO₂ concentration level of 405 ppm in 2017.¹ This surge in CO₂ level has contributed to several global environmental issues, hampering the sustainable development of industrial activities. Besides, the energy fraction obtained from renewable sources (such as wind and solar) is only 30%,² which makes it difficult to replace the role of fossil fuels in the energy market. Electro-catalyzing CO₂ reduction reaction (CO₂RR) can convert renewable energy into chemical energy in the form of fuel and chemicals from

atmospheric CO₂ and water, which represent a visible avenue to close the anthropogenic carbon cycle.³ The commonly generated CO₂RR production on copper catalysts via multi-proton (H⁺)-coupling electron transferred steps (PCETs)⁴ includes a complexity in reaction pathways and a wide range of product distribution (Table 1) with various market values⁵ from single-carbon (C₁) products (e.g., formic acid [HCOOH: 0.74 USD/kg], carbon monoxide [CO: 0.06 USD/kg], methanol [CH₃OH: 0.58 USD/kg], and methane [CH₄: 0.18 USD/kg]) to high-value multi-carbon (C₂₊) products (e.g., ethylene [C₂H₄: 1.30 USD/kg], ethanol [C₂H₅OH: 1.00 USD/kg], and n-propanol [n-C₃H₇OH: 1.43 USD/kg]). It is crucial to accelerate CO₂RR

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TABLE 1 Standard electrode potentials of CO₂RR toward various products and the corresponding equilibrium potentials (E^0) versus reversible hydrogen electrode (RHE).^{7,8}

No.	Reactions	E^0 (V vs. RHE)
1	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{l})$	0.00
2	$2\text{H}_2\text{O} \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^-$	1.23
3	$\text{CO}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{l})$	-0.10
4	$\text{CO}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}(\text{l})$	-0.12
5	$\text{CO}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- \rightarrow (\text{CO}_2\text{H})_2(\text{s})$	-0.47
6	$\text{CO}_2(\text{g}) + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH}(\text{l}) + 2\text{H}_2\text{O}(\text{l})$	0.03
7	$\text{CO}_2(\text{g}) + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	0.17
8	$2\text{CO}_2(\text{g}) + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_3\text{COOH}(\text{l}) + 2\text{H}_2\text{O}(\text{l})$	0.11
9	$2\text{CO}_2(\text{g}) + 10\text{H}^+ + 10\text{e}^- \rightarrow \text{CH}_3\text{CHO}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$	0.06
10	$2\text{CO}_2(\text{g}) + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4(\text{g}) + 4\text{H}_2\text{O}(\text{l})$	0.08
11	$2\text{CO}_2(\text{g}) + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{H}_2\text{O}(\text{l})$	0.09
12	$2\text{CO}_2(\text{g}) + 14\text{H}^+ + 14\text{e}^- \rightarrow \text{C}_2\text{H}_6(\text{g}) + 4\text{H}_2\text{O}(\text{l})$	0.14
13	$3\text{CO}_2(\text{g}) + 18\text{H}^+ + 18\text{e}^- \rightarrow \text{n-C}_3\text{H}_7\text{OH}(\text{l}) + 2\text{H}_2\text{O}(\text{l})$	0.10

technologies toward selectively producing high-energy value-added products, especially multi-carbon species, enabling CO₂RR to become a more accessible alternative approach. High purity and concentration of products from CO₂RR electrolysis reduce the need for downstream purification, making it competitive with traditional chemical engineering industries.⁶ Improving the selectivity of CO₂RR products is also crucial from an industrial utilization standpoint.

So far, extensive experimental and theoretical studies have confirmed that typical methods of catalyst engineering, such as regulating composition,^{9,10} morphology,^{11,12} crystal phase,^{7,13} facet,^{14,15} and defect,¹⁶ are effective in tailoring the selectivity of Cu-based catalysts. Among these strategies, the design of CO₂RR catalysts toward reducing CO₂ at a low overpotential while maintaining high selectivity for the specific product remains challenging due to the complicated reaction process in CO₂RR.^{5,17–19} Besides the initial activation of CO₂ molecules,^{20,21} an advanced fundamental understanding of CO₂RR from the atomic interaction viewpoint (such as C-C coupling, C-O cleavage, or C-H hydrogenation) is significantly important to reveal the CO₂RR selectivity-determining step, such as the adsorption/desorption of key CO₂RR intermediates controlling the selectivity toward specific product.^{22–24}

Essentially, the C₂₊ production pathway primarily involves the formation and cleavage of C-C, C-O, and C-H bonds, which determines the selection of reduced carbon species. It should be noted that the preference for such bonds is highly sensitive to the local CO₂RR environment. Copper has been considered the sole metal catalyst capable of generating hydrocarbons and oxygenates in significant amounts, making it an ideal research platform for CO₂RR selectivity. Recently, the control in the formation/breakage of special bonds to enhance the CO₂RR selectivity has been widely accepted and applied to the regulation of Cu catalysts, such as reducing the energy barrier of C-C coupling to boost C₂₊ production,^{25–29} protecting C-O bonds in *CHCOH species to facilitate the generation of ethanol.²² As the needs for forming or breaking specific bonds are different during CO₂RR, consequently tailoring the catalytic environment to adapt to the formation of desired CO₂RR species is crucial, such as the catalytic sites,³⁰ electrode wettability,^{31–34} pH,^{34,35} local *CO concentration,^{36,37} even the optimizing reactors.^{38–41}

Although some theoretical, experimental work and review papers on the electrochemical CO₂RR have been published, most of them have focused on the design of catalysts^{10,13,16,42–45} or optimizing reaction environments^{46–48} to tailor the CO₂RR selectivity to a range of CO₂-reduction products. However, few of them focus on the CO₂RR selectivity from the theoretical viewpoints to unravel the relationship between the formation/breakage of special bonds and the generation of desired productions. This review mainly concentrated on the recent theoretical understanding of the CO₂RR selectivity of Cu-related catalysts. We first introduce the reaction mechanism of CO₂RR on typical Cu-based catalysts and discuss the bond formation/breakage to understand the selectivity. Meanwhile, we summarized the recent tailoring strategy and provided a theoretical insight into the underlying mechanisms. Finally, we provide some perspectives for future research in this research direction. We anticipate that this review on CO₂RR selectivity of Cu-related catalysts could inspire the development of high-selective catalysts for the practical applications of CO₂RR.

2 | THE CO₂RR MECHANISM

Numerous reports have shown the tendencies of CO₂RR behavior of various metal catalysts (Figure 1A).^{52,53} Transition metal before the IB group show relatively strong *CO adsorption (Figure 1B), even CO poisoning, significantly hindering the post-*CO behavior such as hydrogenation and C-C coupling. In contrast, these metal catalysts, such as Pt, exhibit moderate *H adsorption, which favors the hydrogen evolution reaction (HER) over

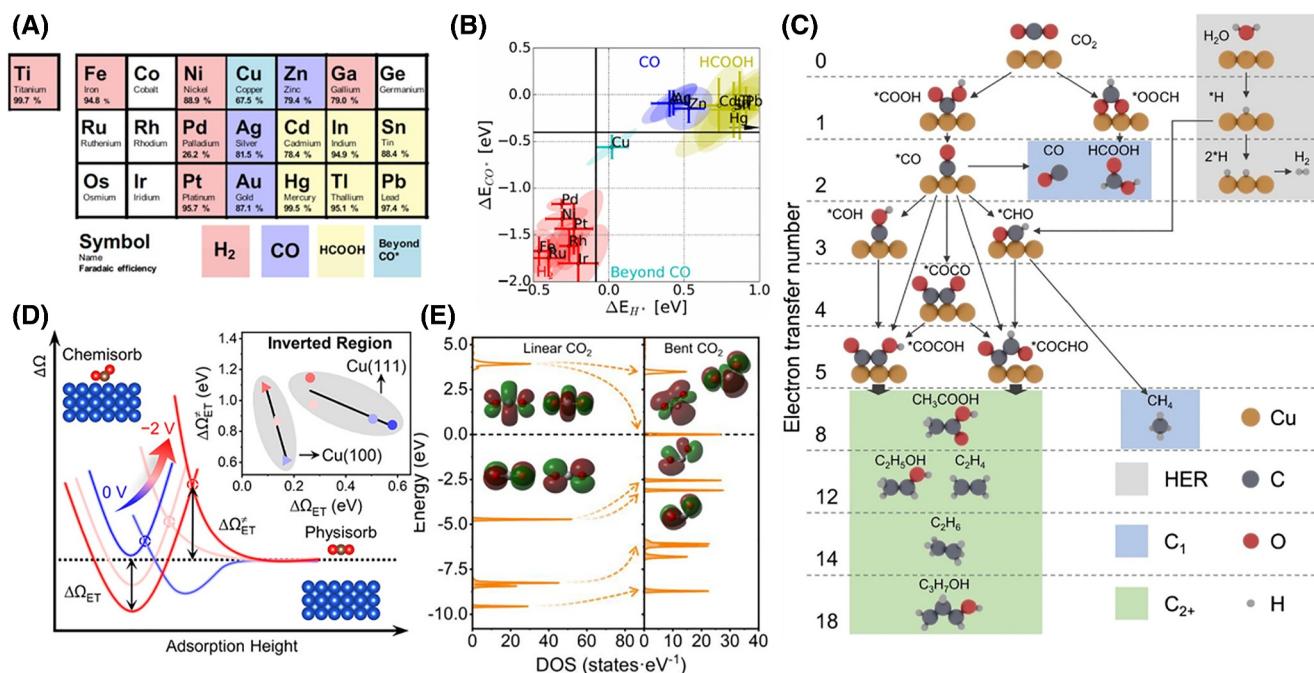


FIGURE 1 (A) Major product classification of metal catalysts for electroreduction of CO₂ from experiments by Hori⁴⁹ shown in a cropped periodic table with colors and major product FE. Four groups are identified: H₂ (red), formic acid (yellow), CO (blue), and CO* (cyan), which will be applied throughout the work. (B) The binding energies of the intermediate ΔE_{CO^*} and ΔE_{H^*} of various metal catalysts. Reproduced with permission from Ref. 4. Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (C) Possible reaction routes for the electrochemical CO₂RR toward multi-carbon products. Reproduced with permission from Ref. 50. Copyright 2022, Springer. (D) The potential energy curves of physisorption (linear CO₂) and chemisorption (bent CO₂) on Cu(100) at varying applied voltages. (E) The pDOSs of HOMOs and LUMOs of the linear and bent CO₂ molecule. With permission from Ref. 51. Copyright 2023, American Chemical Society. FE, faradaic efficiency; LUMO, lowest unoccupied molecular orbital.

CO₂RR. Additionally, Ag, Au, and Zn exhibited weakly bound CO species on surface, resulting in rapid *CO desorption while enabling *H adsorption to happen difficultly. As a result, these metals showed high selectivity toward CO. In comparison, main-group metals show a preference for *OCHO adsorption over *CO adsorption.⁵⁴ Furthermore, these metals exhibited weaker *H adsorption, and together with the *OCHO and *H adsorption behavior, higher selectivity for formic acid production can be achieved. Compared to other catalysts, copper uniquely catalyzes CO₂RR toward various multi-carbon or oxygenate products due to its unique *CO adsorption, which is neither strong enough to cause poisoning nor weak enough for rapid desorption. Additionally, highly active *H species allow for hydrogen attack on carbon/oxygen/hydrogen atoms, leading to complex products, including H₂, C₂H₄, and C₂H₅. The generation of multi-carbon (oxygenates and hydrocarbons [C₂₊]) products is highly desirable because of their higher energy density and wider applicability.⁵⁵ Consequently, copper and copper-related compounds have attracted significant attention. It is generally accepted that CO₂ reduction happens over metallic copper

regardless of various commonly used copper catalysts, such as cupric oxide^{56,57} and Metal-Organic Frameworks,^{58,59} since the CO₂RR working potential (<−0.8 V vs. reversible hydrogen electrode [RHE]) is more negative than that of cupric oxides (0.4 V vs. RHE).^{59,60}

On the copper surface, CO₂RR is typically a multi-electron transferred process, coupling with the sequent proton transfer on CO₂ molecules.^{56–58,61–63} The main CO₂-reduction steps can be divided into three steps: (1) chemical adsorption of CO₂ on an electrocatalyst; (2) with/without electron and/or proton transfer to cleave C–O bonds, form C–H bonds or form C–C bond; (3) rearrangement of configuration to desorb final products from the electrocatalyst surface and diffuse into the electrolyte.¹³ Owing to the complicated combination of CO₂ and water molecules, the CO₂RR process is highly complicated and shows multiple reaction steps with multi-electron/proton transfer via various reaction pathways (Figure 1C). These steps are highly related to the choice of catalysts and local catalytic environments. Clearly defining the relation between these bonds' formation/cleavage in key CO₂RR intermediate and CO₂RR selectivity is a challenging task. Therefore, the subsequent

section further discusses the mechanisms influencing CO₂RR selectivity from the perspective of bond changes.

The initial CO₂ activation step needs electron transfer to CO₂ molecules to *CO₂⁻ intermediates (Figure 1D), which happens at a highly negative redox potential (-1.9 V vs. normal hydrogen electrode). This leads to extremely high overpotential for CO₂RR. Generally, CO₂ activation needs to bind to the catalytic sites while capturing an electron. During this step, two types of CO₂-binding configuration are oxygen-bound and carbon-bound to the catalytic sites. On copper sites, the carbon-bound type CO₂ activation primarily proceeds with CO₂RR. As reported,^{20,21} when CO₂ absorbs onto the Cu surface, the CO₂ molecules must bend to lower the lowest unoccupied molecular orbital (LUMO) level, making the carbon atom more electrophilic. This allows the carbon atom to bind to the catalytic site and accept transferred electrons (Figure 1E). As the negative potential increases, the surface becomes more negatively charged, increasing the overlap between the d band of Cu atoms and the LUMOs of CO₂ molecules.^{20,51,64} After this step, hydrogenation simultaneously occurs on the oxygen atoms in *CO₂⁻ intermediates, which begins CO₂RR.

After the CO₂ activation, the subsequent proton-coupling electron transfer steps (PCETs) happen along the CO₂RR pathways. The CO₂RR reduction process is governed by a multi-step-based coordination chemistry comprising two, six, eight, and 12 electrons to form common products. Afterward, the CO₂RR process mainly involves the cleavage of the C-O bond or the formation of C-H bonds through PCETs and C-C bond formation via an electrochemical step. The former step was determined by the H-addition behavior. The first two hydrogenations usually lead to the removal of the first oxygen atoms in the form of the desorbed water molecule. It suggests the generation of *CO species, traditionally considered a pivotal intermediate, to diverge three different CO₂RR pathways, namely, *CO desorption, *CO hydrogenation to C₁ products, and *CO-*CO dimerization to C₂₊ products. In the latter two CO₂RR pathways, the C-O cleavage is significant to the selectivity of C₁ and C₂₊ products. In C₁ production, the C-O breakage through subsequent hydrogenation on oxygen atoms happens before desorption, showing the desorption of another water and a preference for methane.

On the contrary, the oxygen atom can be retained until carbon atoms bind to three hydrogen atoms, which subsequently generate methanol. More importantly, the C₂₊ products are also decided by whether the C-O cleavage. If the following step happens, the ethane can be determined after multiple hydrogenations until desorption. Nevertheless, ethanol products need to be concerned about how to protect the C-O bonds from

hydrogenation. It should be noted that acetic acid production not only preserves one of the C-O bonds in *COH-COH intermediate but also involves an additional chemical step of hydroxy addition to the same carbon atom, which presents more challenges. More importantly, the C₃₊ products must undergo two-step C-C coupling, showing a higher demand for *CO adsorption. To customize CO₂RR products on catalysts, the steps that need to be considered are different. During these explorations, the experimental and theoretical methodologies have been widely applied to provide atomistic insights into the bonds' behavior. There has been significant progress in theoretical understanding, and the reported selectivity has steadily improved to a new level.

3 | THE CO₂RR SELECTIVITY

3.1 | Competition between HER and CO₂RR

In the scenario of CO₂RR, the HER toward generating hydrogen molecules competes with CO₂RR due to similar reduction potentials (Table 1). HER is not tremendously desirable, which can significantly lower the Faraday efficiency of CO₂RR. Improving the selectivity of CO₂RR is very important in developing CO₂RR technology. On the catalytic surface, the adsorbed hydrogen can interact with the adsorbed one or hydrogen ion to generate H₂. Meanwhile, CO₂RR also needs such hydrogens for hydrogenation. However, the energy increase for H-H coupling is lower than that for CO₂RR. Besides, the HER is potential-dependent, while CO₂RR has several chemical steps, such as activating CO₂ molecules or C-C coupling, which is independent of potential. It suggests that the negatively charged surface has a great favor to prioritize HER. Meanwhile, the surface of catalysts generally shows relatively strong *H adsorption, while weak *CO₂ adsorption leads to high *H coverage and a small number of *CO₂ species. Such high *H coverage can make HER the dominant reaction. To overcome HER, suppressing *H adsorption while strengthening CO₂RR is a universal approach for highly selective CO₂RR (Figure 2A).

Optimizing catalysts or electrolytes can be visible for improving CO₂RR selectivity. In alkaline conditions, such as KOH solution,⁶⁸ the hydrogen can indirectly be obtained via water splitting, not directly through the adsorption of hydrogen ions, leading to more sluggish kinetics for HER. Meanwhile, the cation accumulated on the negatively charged surface also decreases the adsorbed *H due to the electrostatic repulsion. Meanwhile, alkali metal cations (e.g., K⁺), which have been reported

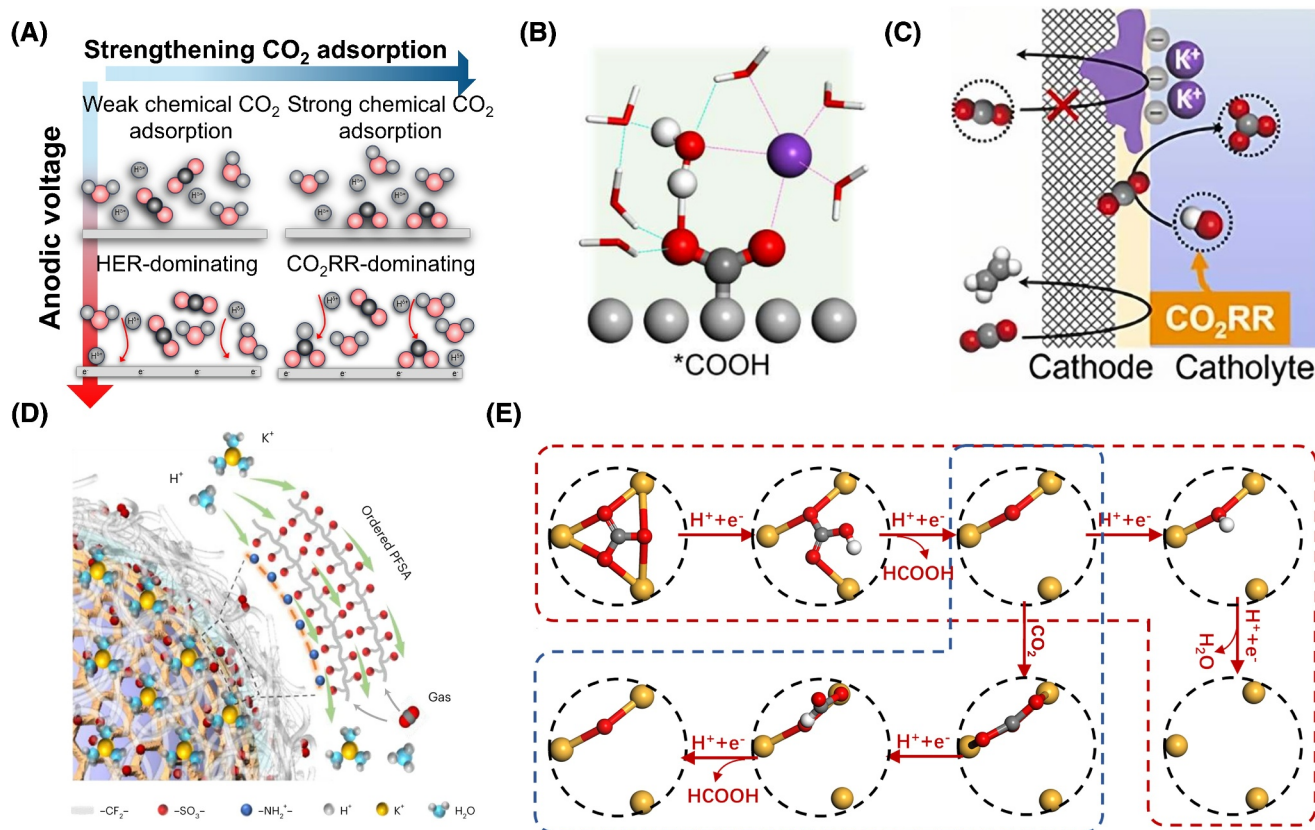


FIGURE 2 (A) Schematic diagram of weak and strong CO₂ adsorption determining the dominating reaction. (B) Local solvation structures of *COOH sampled from DFT-CES simulations. Reproduced with permission from Ref. 65. Copyright 2024, ChemRxiv. (C) Schematic representation of carbonate formation on the cathode composed of a catalyst layer (CL) and gas-diffusion layer (GDL) process in an MEA electrolyzer. Reproduced with permission from Ref. 66. Copyright 2023, Elsevier Ltd. (D) Schematic illustration of a functionalized COF particle for regulating ionomer structure and local ions and gas transport. Reproduced with permission from Ref. 35. Copyright 2023, Springer Nature. (E) Schematic diagram of the solid transformation-induced catalytic mechanism. White, gray, red, and orange spheres represent H, C, O, and Pb atoms, respectively. Reproduced with permission from Ref. 67. Copyright 2024, Springer Nature. COF, covalent organic frameworks; MEA, membrane electrode assembly.

to adjust local electric fields and stabilize reaction intermediates (Figure 2B), are indispensable in CO₂RR to compete with HER.^{69–71} Therefore, an alkaline environment can minimize the rate of competing HER. However, the presence of OH⁻ species can interact with CO₂ to form carbonate (carbonate crossover) (Figure 2C), which not only decreases single-pass CO₂ conversion^{72–74} but also leads to the precipitation of carbonate salt (e.g., K₂CO₃).⁷⁵ The precipitation can lower the durability of the CO₂RR system, especially the membrane electrode assembly system.⁶⁶ This phenomenon can be significantly reduced in acidic solutions, but CO₂RR must compete strongly with HER. Profiting from these understandings, the design of catalysts in acid electrolytes is vital to focus on enhancing CO₂ adsorption.⁷⁶ Huang et al.⁷⁷ reported a K⁺-assisted acidic CO₂RR strategy, in which the K⁺ reduces proton coverage and creates a local interaction to stabilize *OCHO interactions. Furthermore, they further achieved the C₂₊ production with a Faradaic efficiency

(FE) of $83.7 \pm 1.4\%$ and partial current density of $0.56 \pm 0.02 \text{ A cm}^{-2}$, single-pass carbon efficiency of 54.4%, and stable electrolysis of 30 h on reduced porous Cu nanosheet in acidic solution (pH < 1) via the accumulated species (e.g., K⁺ and OH⁻) on the Helmholtz plane.⁷⁸ Sinton et al. reported a heterogeneous catalyst adlayer to suppress HER by creating a local alkalinity and cation-enriched environment (Figure 2D), which exhibited CO₂RR toward C₂₊ with 75% FE at 200 mA cm⁻².³⁵ Conversely, we developed a new approach to stabilize CO₂ molecules via the lattice carbon activation mechanism (Figure 2E).⁶⁷ The recycled lead catalysts from lead-acid batteries can spontaneously capture CO₂ to form PbCO₃, showing strong CO₂ adsorption. The strong CO₂ adsorption guarantees CO₂RR over HER in an acid solution, which exhibited 93% FE, early 91% single-pass conversion efficiency at a current density of 600 mA cm⁻² and cell voltage of 2.2 V and durability of more than 5200 h.⁶⁷ Besides, Yeo and co-workers⁷⁹ also

found a similar mechanism in which CO_2RR happens toward formate from the reduction of $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$. This suggests that the alkali metal cations and the strong CO_2 adsorption ability of catalysis both provide opportunities to offer CO_2RR exceeding HER.

3.2 | The selectivity toward formic acid or CO

Under most conditions, copper preferentially binds to carbon-bound $^*\text{CO}_2$ rather than oxygen-bound $^*\text{CO}_2$,

resulting in post- $^*\text{CO}$ species being the primary products (Figure 3A).^{87–91} This selectivity arises from the differences in the first hydrogenated intermediates, namely $^*\text{COOH}$ for carbon-bound $^*\text{CO}_2$ and $^*\text{OCHO}$ for oxygen-bound $^*\text{CO}_2$. The $^*\text{COOH}$ species is an important intermediate for CO formation, while $^*\text{OCHO}$ species is likely the intermediate for formic acid formation. In terms of activity, the activity of CO_2 reduction toward formic acid is highly correlated with $^*\text{OCHO}$ adsorption, which is different from CO products that is highly related to $^*\text{COOH}$ adsorption. Therefore, the choice of catalysts significantly determined the selectivity within two-electron products. For example,

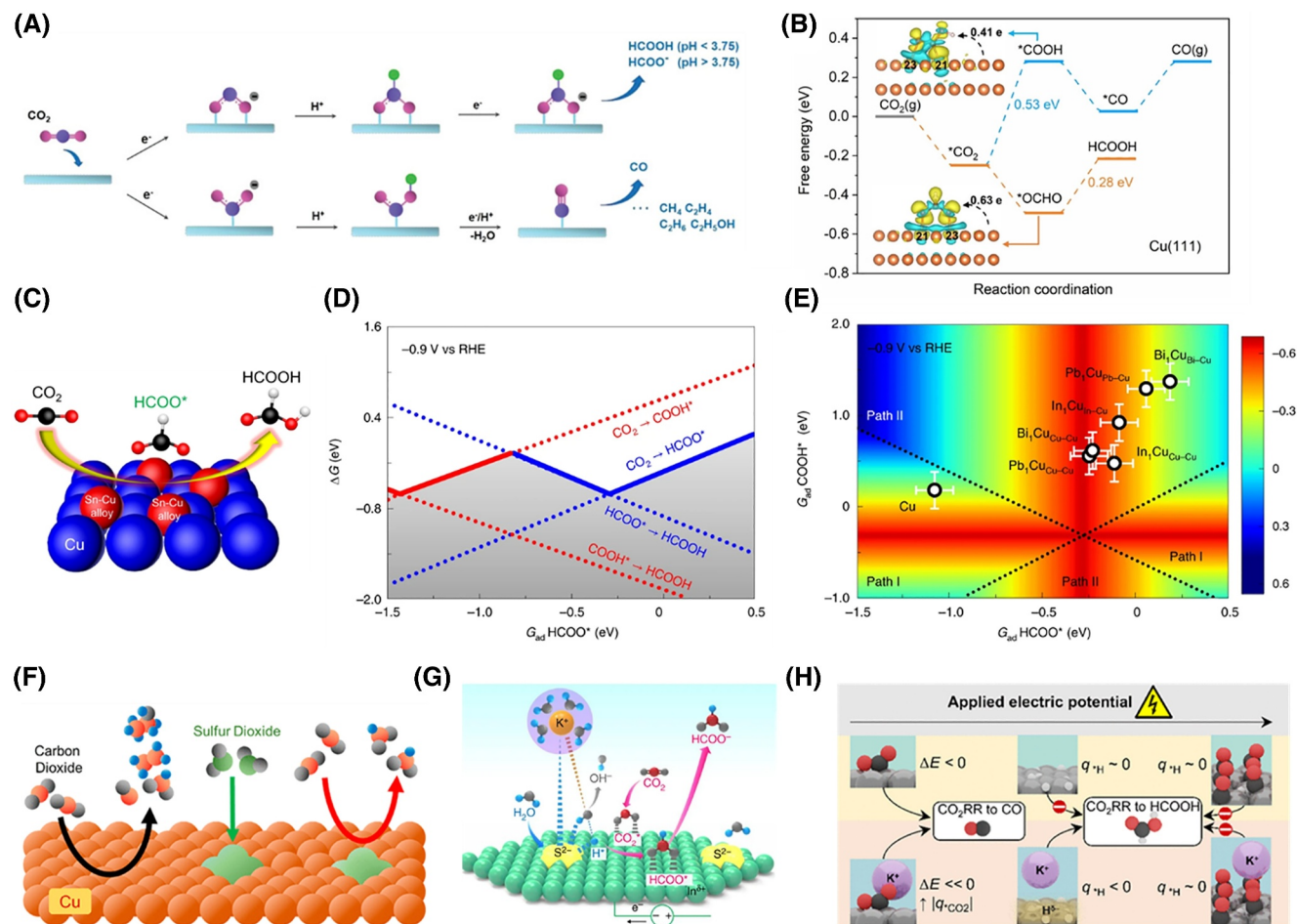


FIGURE 3 (A) Schematic diagram of $^*\text{CO}_2$ type determining CO_2RR products. Reproduced with permission from Ref. 80. Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (B) The free energy profile of CO_2RR toward CO or HCOOH. The inset is the charge difference density of $^*\text{COOH}$ and $^*\text{OCHO}$ adsorption on Cu(111). The number is the transferred electron from Cu(111) to adsorbates. Reproduced with permission from Ref. 81. Copyright 2023, Wiley-VCH GmbH. (C) Schematic diagram of introducing the main-group metal atom into Cu metal, which promotes the CO_2RR toward HCOOH. Reproduced with permission from Ref. 82. Copyright 2020, Elsevier B.V. and Science China Press. (D) The one-dimensional RPD for CO_2RR . The dotted lines represent the reaction-free energy of CO_2RR elemental steps. (E) The two-dimensional RPD for CO_2RR -producing formate based on two independent descriptors, the adsorption free energies of HCOO^* and COOH^* , on various surfaces considering different adsorption sites. Reproduced with permission from Ref. 83. Copyright 2021, Springer Nature. (F) Schematic diagram of SO_2 impurities induce CO_2RR toward HCOOH. Reproduced with permission from Ref. 84. Copyright 2019, American Chemical Society. (G) Schematic illustration of the role of S^{2-} in promoting water dissociation and H^+ formation for the reduction of CO_2 to formate. Reproduced with permission from Ref. 85. Copyright 2019, Springer Nature. (H) The illustration of a cation-induced electric field promotes CO_2RR toward CO or HCOOH at various electric potentials. Reproduced with permission from Ref. 86. Copyright 2023, American Chemical Society. RPD, reaction phase diagram.

the primary CO₂RR product of Bi is formic acid, while for Au and Ag, it is CO. Theoretical studies suggest that *COOH formation is challenging due to weak adsorption, whereas *OCHO encounters a sluggish desorption process because of strong adsorption (Figure 3B).⁸¹ Applying a negative potential can enhance *COOH adsorption, promoting CO₂RR toward *CO while further inhibiting *OCHO desorption.

It is effective for the tailoring of the adsorption of *COOH and *OCHO intermediates to control the selectivity, and many strategies have been developed for this purpose. Among them, alloying copper with other isolated metal atoms can modify the adsorption behavior, altering the preference for *COOH or *OCHO. For instance, incorporating main-group metal atoms like Sn,^{92,93} In,^{94,95} and Bi.⁹⁶ (Figure 3C) can enhance oxyphilic properties, favoring the *OCHO species. Zeng et al.⁸³ demonstrated that single-atom alloying on Cu(211) surface, especially Pb₁Cu, favored *OCHO path rather than the *COOH path (Figure 3D,E), resulting in the continuous production of pure formic acid (~96% FE) at 100 mA cm⁻² for over 180 h. Additionally, the introduction of non-metal species can weaken the adsorption strength, thereby promoting selectivity toward formic acid. Liu et al.⁸¹ reported that S-adsorbed metallic Cu, reconstructed from S-doped Cu₂O, exhibited a weakened adsorption due to S accumulation. This weakening adsorption led to formate becoming the dominant product while suppressing *COOH formation, achieving approximately 70% FE for formate.⁹⁷ Moreover, Jiao et al.⁸⁴ introduced SO₂ impurities in CO₂ flow, which were preferentially reduced, leaving S species on the surface. This shift led to enhanced selectivity toward formate and a reduction in multi-carbon products (Figure 3F,G). Similar observations were noted in our work.⁹⁸ Such effect can also be explored using phosphate additive,⁹⁹ thiocyanate ion (SCN⁻),¹⁰⁰ and pyridine.¹⁰¹ Koper and co-workers⁸⁶ further demonstrated that a cation-induced electric field (Figure 3H) could sustain HCOOH production at mild negative potentials. Conversely, high *CO coverage was observed at negative potentials, suggesting that *CO production is highly dependent on negative potential due to weak *COOH adsorption.

3.3 | The selectivity toward two or multi-electron species

The selectivity toward two-/multi-electron (>2e⁻) transferred products (Figure 4A). Among them, the two-electron products include HCOOH and CO, while multi-electron products are composed of CH₄, CH₃OH, and C₂₊ species.¹⁵ Beyond *OCHO species, which are key for formic acid production (Figure 4B),⁵⁴ *COOH and

subsequent *CO species are important intermediates for generating multi-electron species. The *CO adsorption determines whether CO will desorb as a CO₂RR product or undergo further hydrogenation to form multi-electron species (Figure 4C). With relatively strong *CO adsorption on Cu, once *CO is formed, it tends to undergo further hydrogenation or C-C coupling, which influences the selectivity toward various C₁ and C₂₊ products. For multi-electron (>2e⁻) products, the kinetics of CO₂RR becomes more sluggish due to the CO-CO coupling step becoming an additional limiting step besides the *COOH formation step (Figure 4D). Using density functional theory (DFT) calculations, Wang et al.¹⁰³ explore the rate-determining steps (RDSs) toward various multi-electron products, such as CO hydrogenation toward *CHO and *CO-*CO coupling toward C₂₊. Besides, the multi-electron products exhibit a complicated reaction mechanism and product selectivity.¹⁰⁶

Tailoring the distribution of the CO, C₁, and C₂₊ products has been extensively studied to enhance the CO₂RR selectivity. The *CO adsorption is the key to affecting the subsequent *CO behavior, including desorption, hydrogenation, and C-C coupling, all of which are directly related to the *CO adsorption energy. Using DFT calculations, coordination number (CN) can be applied to regulate *CO behavior (Figure 4E). As CN increases, *CO adsorption strengthens, and *CHO adsorption also increases (Figure 4F),^{107,108} which consequently leads to the increase in methane production.^{105,109} Lowering the *CO₂ coverage reduces the likelihood of C-C coupling, thereby favoring methane production in CO₂RR. Sargent et al.¹¹⁰ demonstrated that local CO₂ availability on a Cu catalyst can be modulated by adjusting CO₂ concentration in the gas stream, achieving a methane FE of 48 ± 2%. In this approach, low CO₂ coverage enables CO to interact with adjacent H atoms rather than nearby *CO, thus preventing C-C coupling. In another study,³⁶ Sargent also reduced *CO coverage by introducing Au, which weakened the *CO adsorption at adjacent Cu sites (Figure 4G). Besides, Koper and co-workers^{111,112} found that methane production is favored along a pH-dependent pathway at Cu(111) facets or steps while ethylene remains pH-independent on Cu(100). As the size of Cu nanoparticles increases, the ratio of Cu(100) to Cu(111) facets also rises, exposing more low-coordination number (CN) sites and shifting the reaction pathway from ethylene toward methane.¹¹³ Moreover, local environments play a crucial role in tuning selectivity between methane and ethylene. Hydrophobic surfaces reduce the water coverage on the surface, promoting the *CO protonation and further favoring methane generation.¹¹⁴ The chemical state is another significant factor affecting the interaction of *CO and catalytic sites.¹¹⁵ Low-coordination Cu⁰ sites tend to favor hydrogenation to CH₄,

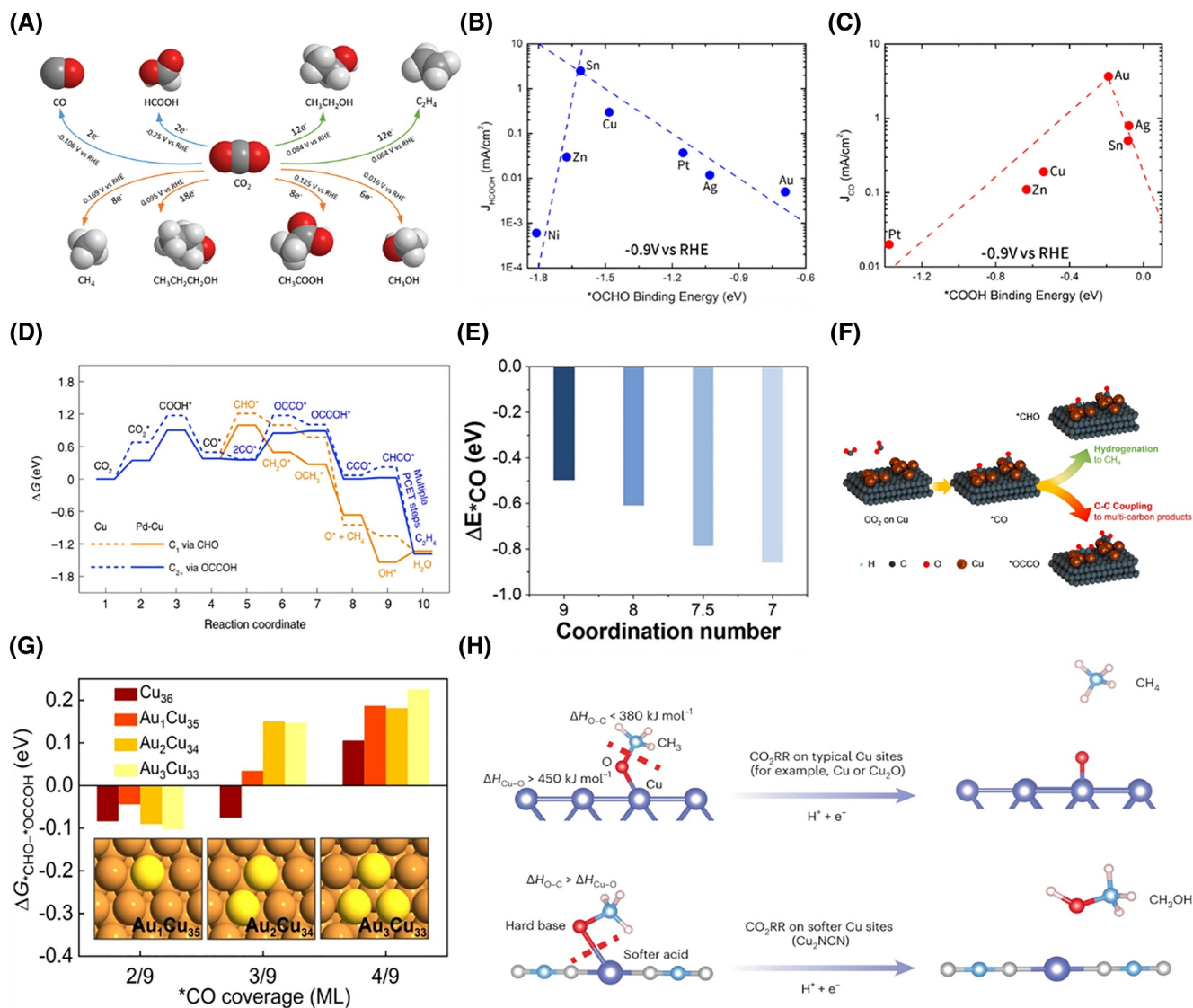


FIGURE 4 (A) Common electrochemical CO₂ reduction reaction products, number of electrons transferred, and reaction standard potentials. Reproduced with permission from Ref. 102. Copyright 2024, the Royal Society of Chemistry. (B) Volcano plot using *OCHO binding energy as a descriptor for HCOO⁻ partial current density at -0.9 V versus reversible hydrogen electrode (RHE). (C) Volcano plot using *COOH binding energy as a descriptor for CO partial current density at -0.9 V versus RHE. Reproduced with permission from Ref. 54. Copyright 2017, American Chemical Society. (D) Free energy diagram of CO₂RR via the CHO pathway toward C₁ products and the OCCOH pathway toward C₂₊ products. Reproduced with permission from Ref. 103. Copyright 2022, Springer Nature. (E) CO adsorption changes with the coordination number (CN) of the Cu sites. Reproduced with permission from Ref. 104. Copyright 2024, Wiley-VCH GmbH. (F) Schematic of key reaction pathways for CO₂RR: hydrogenation to *CHO for CH₄ production and C-C coupling to *OCCO leading to C₂ generation. Reproduced with permission from Ref. 105. Copyright 2021, Springer Nature. (G) Reaction free energy difference between *CO protonation and C-C coupling steps on Cu₃₆, Au₁Cu₃₅, Au₂Cu₃₄, and Au₃Cu₃₃ surfaces under varying *CO coverages. Reproduced with permission from Ref. 36. Copyright 2021, Springer Nature. (H) Comparison of Cu catalytic sites (e.g., Cu or Cu₂O) and Cu₂NCN, which displays various Cu-O bonds and leads to cleavage/retention of the O-C bond to release *CH₃ or *OCH₃ and then form CH₄ or CH₃OH, respectively. Reproduced with permission from Ref. 23. Copyright 2021, Springer Nature.

and local Cu⁰/Cu⁺ sites are more likely to facilitate coupling to form ethylene.¹¹⁶

In addition to the competition between methane and ethylene, the selectivity toward methane and methanol was primarily determined by the C-O bond breakage. After the first hydrogenation of *CO, the formyl (*CHO)

intermediate is reduced to formaldehyde (*CH₂O), followed by the formation of a methoxy species (*CH₃O). Whether methanol is produced or not depends on whether the C-O bonds in the *CH₃O intermediate are retained.¹¹⁷ The *CH₃O species is a crucial intermediate for controlling selectivity toward methane and methanol.

Gong et al.¹¹⁸ further introduced the oxyphilic La atom to strengthen metal-oxygen bonds, promoting C–O bond cleavage in $^*\text{CH}_3\text{O}$ intermediates and favoring CH_4 formation. On the other hand, Huang and co-workers²³ found that Cu_2NCN could significantly reduce the Cu–O interaction between $^*\text{OCH}_3$ and Cu site, thus shifting the pathway to release $^*\text{OCH}_3$ and form methanol, achieving the highest recorded CO_2 -to- CH_3OH selectivity (70%) and an impressive partial current density of -92.3 mA cm^{-2} (Figure 4H). Additionally, facilitating the desorption of $^*\text{CH}_3\text{O}$ by replacing TM–O bonds with H–O bonds can enhance CH_3OH selectivity. Yu et al.¹¹⁹ introduced an $^*\text{H}$ -rich surface to lower the hydrogenation barrier and the required potential, accelerating the $^*\text{CH}_3\text{O}$ hydrogenation for CH_3OH production. Therefore, retaining the C–O bond is crucial for improving methanol selectivity.

Besides optimizing copper for CO_2RR selectivity toward multi-carbon production,¹²⁰ the search for non-copper catalysts is also highly desirable and has garnered considerable attention.¹²¹ Koper et al.¹²² found that under high pressure, silver can catalyze CORR toward ethanol and propanol, demonstrating that high surface coverage is crucial for C_{2+} production on silver. This suggests that on the Ag surface, the weak $^*\text{CO}$ adsorption cannot retain sufficient surface $^*\text{CO}$ for effective C–C coupling. Besides, systems with strong adsorption, such as Ni, it is reported that altering their structure or compounds holds opportunities to facilitate CO_2RR toward multi-carbon species. Yeo and co-workers¹²³ found that an inorganic nickel oxygenates generate linear and branched C_3 to C_6 hydrocarbons with sustained Faradaic efficiencies of up to 6.5%. Meanwhile, NiGa ¹²⁴ and NiAl ¹²⁵ were also reported a poor CO_2RR selectivity toward hydrocarbons and alcohols. Recently, Asadi et al.¹²⁶ found that a 1-ethyl-3-methylimidazolium-functionalized Mo_3P nanoparticles has shown high selectivity toward C_{3+} species, showing the highly precise tuning of non-copper catalysts can be an accessible avenue for multi-carbon production. Therefore, compared to Cu, the tailoring of non-copper alters the local environment, which deviates from their bulk counterparts. Creating a local catalytic site with a CO binding affinity comparable to that of Cu can enable a balance where $^*\text{CO}$ adsorption is neither too weak, ensuring the retention of $^*\text{CO}$, nor too strong, preventing $^*\text{CO}$ poisoning. For instance, creating defects and low-coordinated sites allow Ag to strongly bind CO, facilitating its coupling with adjacent $^*\text{CO}$.¹²⁷ For transition metals preceding the Cu-related B group, the strong adsorption can be mitigated by converting them into metal compounds, such as carbides¹²⁸ or single-atom

catalysts,^{129,130} which reduces CO adsorption, enabling interaction with H or C atoms.

3.4 | The selectivity toward various C_2 species

The formation of C_2 species, such as ethylene and ethanol, during the CO_2 reduction on the copper surface happens within a complex reaction network.^{5,19,131,132} The great complexity is due to the competing process of bond formation or cleavage among C–C, C–H, and C–O bonds in CO_2RR . Besides, the C_2 species require a greater number of electrons ($>8e^-$) compared to the generation of formate, CO, or C_1 products, which present a significant challenge to the underlying mechanisms of C_2 species formation. Therefore, understanding the key species (e.g., $^*\text{CO}$) and steps are crucial for improving selectivity toward C_2 species.

Thus far, the C–C coupling has been widely recognized as the RDS for C_2 production from CO_2RR over Cu catalysts.¹⁰³ The specific mechanisms for C–C coupling are still under active discussion (Figure 5A).^{45,136} The classic C–C coupling configuration is $^*\text{CO}$ - CO species,¹³⁷ which has been commonly used to represent the initial step toward C_2 production.^{25,27,104,138} This is consistent with experimental findings. Starting from $^*\text{CO}$ coupling step, there are many strategies have been developed to tune the local environment around the catalytic site,¹³⁹ such as facet selection (Figure 5B),^{27,52} coverage effect (Figure 5C),³⁷ pH change,^{89,134} surface modification,^{24,25,103,140–143} interfacing on Cu surface,^{28,135,144} all of which can lower the energy barrier for C–C coupling.

Additional C–C coupling mechanisms have been proposed to enable CO_2RR to follow new C_2 pathways with a lower energy increase,^{145,146} including $^*\text{COH}$ - $^*\text{CO}$, $^*\text{CO}$ - $^*\text{CHO}$, $^*\text{CHO}$ - $^*\text{CHO}$, $^*\text{COH}$ - $^*\text{COH}$, and $^*\text{COH}$ - $^*\text{CHO}$. Compared to $^*\text{CO}$, which can desorb at any time, the first hydrogenated $^*\text{CO}$ species can show longer standing time and higher activity for interacting with surrounding $^*\text{COH}$ / $^*\text{CHO}$ / $^*\text{CO}$. The formation of heterogeneous carbonaceous species (e.g., $^*\text{CO}$ and $^*\text{CHO}$) for C–C coupling is highly dependent on the structure of the copper surface.¹⁴⁷ Generally, the surface species can tune the surface state, which affects the $^*\text{CO}$ behavior. The greater the variation in the local copper environment,¹⁴⁵ the higher the likelihood of observing different $^*\text{CO}$ states and C–C binding configurations. Introducing fluoride ions (F^-) can weaken $^*\text{H}$ binding for $^*\text{CO}$ hydrogenation, further inducing $^*\text{CHO}$ - $^*\text{CHO}$ coupling for lower energy input in C_{2+} production.⁸⁸ Additionally, adjacent atomic sites can provide an abundant source of

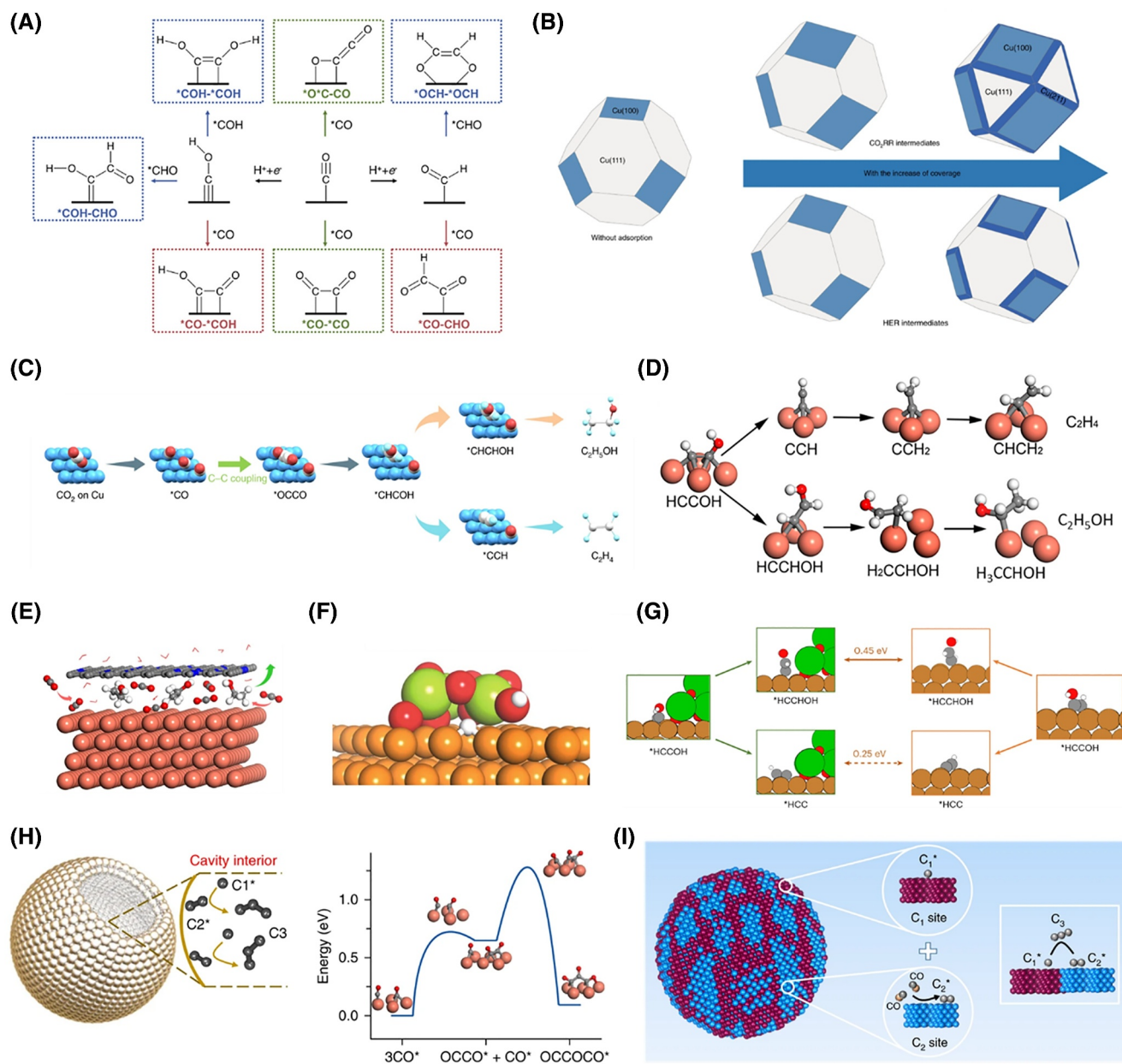


FIGURE 5 (A) Possible reaction pathways considered for C-C coupling in electrochemical CO₂RR toward C₂₊ products on Cu(111). Reproduced with permission from Ref. 133. Copyright 2022, the PNAS. (B) Wulff construction clusters of copper without and with adsorption of CO₂RR and hydrogen evolution reaction (HER) intermediates. Reproduced with permission from Ref. 27. Copyright 2020, Springer Nature. (C) Key reaction pathways for CO₂RR to ethanol and ethylene illustrated using two CO^* for C-C coupling in the presence of one additional CO^* . Blue, copper; gray, carbon; red, oxygen; light blue, hydrogen. Reproduced with permission from Ref. 37. Copyright 2019, Springer Nature. (D) Reaction paths for ethylene versus ethanol on a Cu(111) surface. Reproduced with permission from Ref. 22. Copyright 2019, American Chemical Society. (E) Illustration of CO₂ intercalation at the N-C/Cu interface and the production of ethanol. Reproduced with permission from Ref. 28. Copyright 2020, Springer Nature. (F) Surface configurations of CeO₂/Cu with adsorbed hydrogen from water dissolution on CeO₂. Reproduced with permission from Ref. 134. Copyright 2019, Springer Nature. (G) Configurations of HCCOH^* on BaO(111)/Cu(111) (left) and Cu(111) (right) in the different reaction path. The adsorption energy of HCCOH^* on BaO(111)/Cu(111) is 0.45 eV lower than on Cu(111), whereas the adsorption energy of HCC^* is lower by 0.25 eV. Reproduced with permission from Ref. 135. Copyright 2022, Springer Nature. (H) Catalysts with highly mixed nanofragments of the Cu (200) and Cu(111) facets may bring the optimal C₁ and C₂ sites into physical proximity, contributing with one another to the coupling of C₁-C₂ and then the coupling into C₃ products. Reproduced with permission from Ref. 26. Copyright 2019, Springer Nature. (I) The schematic shows that the cavity confinement effect promotes C₂ species binding and further conversion to C₃. The right represents the surface species and energy profile of the C₃ formation intermediate. Reproduced with permission from Ref. 29. Copyright 2018, Springer Nature.

hydrogen from H_2O dissociation, facilitating C-C coupling through $^*\text{CHO}$ dimerization.^{148,149}

After the C-C coupling step, the subsequent CO_2RR step can spontaneously occur at CO_2RR potential. The three main products, including ethylene, ethanol, and acetic acid, are significantly sensitive to the change in the surface of catalysts. This offers an opportunity to tailor the product distribution. Like methanol production, the retention of C-O bond in C_2 intermediate is also important to ethanol production. In Sargent's work,²² an asymmetrical Cu-Ag site was developed, allowing one carbon atom of $^*\text{CHCOH}$ species to be adsorbed on Cu sites. In these Cu-Ag sites, the weakly bound Ag site causes the $^*\text{COH}$ moieties in $^*\text{CHCOH}$ species to be positioned farther from the surface, preventing their reduction and allowing the $^*\text{COH}$ moieties to be retained for ethanol formation. In contrast, the Ag site weakly interacts with other carbon atoms (Figure 5D). This asymmetrical adsorption configuration helps protect C-O moieties by keeping them far from the surface and making them difficult to reduce.¹⁵⁰ Subsequently, hydrogenation can occur on the carbon atoms in the $^*\text{CHCOH}$ intermediate until $\text{CH}_3\text{CH}_2\text{OH}$ desorbs. On the contrary, if both carbon atoms in $^*\text{CHCOH}$ species bind to sites, both exhibit a huge possibility of being reduced to CH_2CH_2 via hydrogenation. Half-Cu(0) and half-Cu(I) sites can also show a similar asymmetrical role in ethanol production.^{151,152} Besides, it also provides a useful avenue for suppressing the deoxygenation of $^*\text{CHCOH}$ to retain C-O bonds (Figure 5E), which can promote ethanol production, such as coating Cu catalysts with nitrogen-doped carbon.²⁸ Meanwhile, introducing metal oxides (MOs) on the surface can favor hydroxy-containing C_2 intermediate over hydrocarbon intermediate (Figure 5F), promoting ethanol production.^{134,135} From atomistic viewpoints, the MOs can stabilize the OH-C bonds, which is highly correlated with the selectivity for alcohol over hydrocarbons (Figure 5G). In comparison, strong Si-O interactions can capture the OH from C_2 intermediate, benefiting the deoxygenation of C_2 intermediate and enhancing the ethylene selectivity.¹⁴⁴ Strong TM-O (e.g., Cu-O) interaction also enables oxygen atoms of $^*\text{CH}_2\text{CHO}$ species to stay at the unsaturated Cu_2O site and release CH_2CH_2 .¹⁵³ Introducing a suite of transition metal adatoms with strong adsorption can improve $^*\text{H}$ adsorption,¹⁴⁰ hindering the hydrogenation process in $^*\text{CHCOH}$ intermediates. The difference in the need for adsorbed $^*\text{H}$ is present between CH_2CH_2 and $\text{CH}_3\text{CH}_2\text{OH}$, meaning tuning adsorbed $^*\text{H}$ via wettability can steer the selectivity.¹⁵⁴ Meanwhile, when adatom serves as an active site, the interaction between sites and oxygenated species controls the favorability of C-O bond scission. The optimal Rh dopant in the Cu surface can

show the optimal oxygen binding strength to retain the C-O bonds in $^*\text{CH}_3\text{CHO}$ intermediates to two-step hydrogenation for ethanol production.¹⁵⁵ The more difficult hydrogenation can favor the retention of oxygen atoms until the formation of ethanol. Moreover, a high concentration of local $^*\text{CO}$ can facilitate the upright standing of $^*\text{CHCOH}$ due to the adsorbate-adsorbate interaction, which benefits the $^*\text{CHCHOH}$ formation.^{24,37,156} Besides, a high fraction of Cu(100) compared to Cu(111) displayed a preference for C_2H_4 production, rather than $\text{C}_2\text{H}_5\text{OH}$. It mainly originated from the fact that the strong adsorption induces the generation of $^*\text{CCH}$ rather than $^*\text{CHCHOH}$, which has a strong interaction with the catalytic site and the key intermediate toward C_2H_4 .^{27,157}

Different from ethylene and ethanol, acetic acid production is likely to be more complicated, involving C-C coupling and the addition of OH moieties on one carbon in related CO_2RR intermediates.¹⁵⁸ According to Goddard and Feng Jiao's work,¹⁸ the $^*\text{CCO}$ intermediates are formed from $^*\text{COHCOH}$, which is also an intermediate for ethylene and ethanol. Moreover, the step that determines acetic acid happens before the step regarding the ethylene and ethanol selectivity. However, in most cases, the FEs of acetic acid are significantly lower than that of ethylene and ethanol. It should be noted that CORR usually produces acetic acid with high selectivity.^{26,87,159-163} Little work has been reported on CO_2RR toward acetic acid.¹⁶¹ Understanding the underlying mechanism of the selectivity toward acetic acid remains challenging. To date, three possible mechanisms have been proposed and discussed,¹⁶⁴ in which key steps are the step of $^*\text{CCO}$ formation, $^*\text{CH}_2\text{-CO}$ coupling, and $^*\text{OCH}_2\text{CO}$ generation, respectively. All these potential pathways undergo the same step of OH addition to form a COOH functional group in related intermediates. Therefore, more theoretical and experimental findings are desired to explore the mechanisms.

3.5 | The selectivity toward C_{3+} species

In comparison to various C_2 species, the primary C_{3+} species is n-propanol.¹⁶⁵ n-propanol production needs two-step C-C coupling, showing a higher activation energy barrier than one-step C-C coupling in C_2 species. Therefore, a crucial step in generating C_3 species is the coupling between C_1 and C_2 species. It demands sufficient $^*\text{CO}$ coverage for CO-CO coupling and adequate stabilization of $^*\text{C}_2$ intermediates to couple to the next $^*\text{CO}$. Sargent et al.²⁹ developed a reactive nanocavity that can promote C_3 formation via the nanoconfinement of C_2 and C_1 intermediates (Figure 5H). The finite-element method simulations validated the potential for the

retention and binding of C_2 intermediates as a function of cavity structure, showing a morphology-driven shift in selectivity from C_2 to C_3 products. In supersaturated conditions,¹⁶⁶ dispersed Ag atoms in CuAg weaken the adsorption of intermediates in the middle position of the alkyl chain and strengthen the C–O bonds, favoring 2-propanol over 1-propanol (Figure 5I). Besides, highly fragmented copper provided a strong binding to C_1 and C_2 species, promoting further coupling of these intermediates into n-propanol.²⁶ Besides the tailoring of morphology, introducing strongly adsorbed adatoms can be another approach to strengthen the adsorption ability of catalysts for n-propanol formation. Jun Li et al.¹⁶⁷ found that copper adparticles increase $^*CO$ adsorption and further stabilize two-carbon intermediates, facilitating the two-step coupling between adsorbed $^*CO$ and two-carbon intermediates. Such strategies were also applied to the introduction of adatoms on copper surfaces.^{168–170} Besides, Bo Zhang et al.¹⁷¹ found that Pb-doped Cu catalysts with numerous atomic Pb-concentrated grain boundaries show abundant low coordination sites with a stronger CO adsorption for a higher surface CO coverage. Such Pb–Cu catalysts show a CO-to-n-propanol FE of about 47% with partial current above 300 mA (5 cm^2 electrode) for 100-h operation. Zheng et al.¹⁷² reported a double sulfur vacancy formed on hexagonal copper sulfide for stabilizing both $^*CO$ and $^*OCCO$ dimer and further CO– $^*OCCO$ coupling to form C_3 species, displaying a FE toward n-propanol of $15.4 \pm 1\%$.

4 | CONCLUSIONS AND PERSPECTIVES

Overall, in this review, we point out the CO_2RR process toward various products in a real complex reaction network, in which the steps of C–C coupling, C–H formation, and C–O cleavage are intersectional in CO_2RR . It is helpful to disentangle the key steps and intermediates for selectively improving the production of various products. Further investigations into CO_2RR mechanisms, such as the rate-determining and selectivity-determining steps, are required. The fundamental knowledge that can be obtained from the existing systems can be used to guide the design of advanced catalysts with high selectivity. Besides, most of the current studies focused on improving the selectivity toward single products, especially C_2 species, on copper catalysts. Additional work on other non-copper catalysts in the form of single-atom catalysts, alloys, and meal compounds should be further explored and developed for high selectivity.

4.1 | In situ characteristics

To untangle the CO_2RR selectivity and underlying mechanism, it is urgently necessary to develop the operando and in situ characterization techniques since we have learned that insights from the information about the structure or reaction process from those characterization techniques do help the rational design of advanced catalysts and electrolyte to improve the selectivity.^{173–175} For example, we identified the negative correlation between ethylene production and the low CN.¹⁰⁴ based on an operando X-ray absorption fine structure study. Followed by a work about the local CO concentration on the surface, correlating the CO coverage and the selectivity toward ethylene products need in situ technologies to track the surface species in CO_2RR conditions, such as in situ Raman.^{24,37} Furthermore, structural and electronic information, such as the chemical state of adatom and coronation number, is important in building the relationship between structure and selectivity. This is particularly important in CO_2RR systems,^{36,103,159,167–169} where adatoms tailor the C_{2+} selectivity. Besides, the role in the reconstruction of copper catalysts during CO_2RR should be further discussed, and we need more detailed information to deepen the understanding of the facet-determining selectivity,^{26,176} such as Cu(111) favors C_2H_4 while Cu(111) prefers CH_4 .¹¹² These important advances in understanding clearly show the crucial role of in situ and operando techniques in electro-catalyzing CO_2RR studies.

4.2 | Advanced theoretical technique

Efficient selectivity and production rates from CO_2RR can be achieved by rationally designing catalysts and electrolytes. Before these, advanced theoretical techniques and understanding are urgently needed,¹⁷⁷ Such as the role of cation (e.g., K^+)^{68,71} and anion (e.g., F^-)⁸⁸ in tuning the shift of CO_2RR production toward various products.^{178–180} Besides, many essential phenomena are difficult to observe clearly from experiments, such as CO_2 activation and adsorption,^{51,181} pH effects,^{70,182} charge transfer,¹⁸³ and C–C coupling¹⁸⁴ is essential to consolidating our theoretical framework. This advanced understanding is highly dependent on using advanced theoretical techniques, such as ab initio molecular dynamics simulations and microkinetics. Using these theoretical methodologies, we can observe some phenomena that are difficult to detect in characterization and electrochemical techniques.

4.3 | Precious atomic control

To improve the CO₂RR selectivity, besides characterization and theoretical understanding, the advanced synthesis of catalysts is also desirable. Traditionally, pure catalysts exhibited high products distribution with low selectivity. Most advanced catalysts can be gained through the tailoring of copper catalysts,¹⁸⁵ such as introducing adatom,^{103,135,144,169} two-dimensional/highly fragmented copper,^{26,89,106,167} and tandem catalysts.^{37,156} These designs highly demand precious atomic control in the synthesis of catalysts. The advanced synthesis of catalysts can provide clear research subjects, which can be effectively characterized for modeling and simulating CO₂RR toward specific products using first-principles density functional calculations. The design of advanced catalysts with high selectivity can be rapidly developed. Furthermore, the exploration of CO₂RR selectivity can effectively proceed. A fundamental premise of this research workflow is the precious atomic control in catalysts' synthesis.

4.4 | Discovery of novel CO₂RR catalysts

Although a significant amount of research has been dedicated to the design of CO₂RR catalysts, achieving industrial-level C₁ and C₂ selectivity and partial current density on copper has been possible. However, the long-term durability of CO₂RR catalysts remains limited to hundreds of hours, particularly with inferior stability under high current density, posing a significant challenge for practical application.⁶⁷ Furthermore, higher selectivity and activity are required to improve the economic profile and reduce final costs associated with post-purification and voltage loss. Moreover, using a pure CO₂ source, which comes from reactive capture or sequential capture and conversion for CO₂RR, incurs significant operating costs and limits the practicality of the process.¹⁸⁶ On the other hand, feeding CO₂RR with direct CO₂ sources, such as industrial CO₂ point sources and flue gas, can significantly reduce the operating cost. However, impurities in flue gas, such as SO₂ and NO_x, present substantial challenges for CO₂RR operation. Therefore, designing CO₂RR catalysts with high resistance to these impurities is crucial to ensuring the effectiveness of the process. On the other hand, high selectivity is commonly achieved in alkaline CO₂RR; however, due to carbonate crossover, this results in low carbon utilization.^{72,79} Additionally, long-term operation can lead to salt precipitation, which is another factor affecting the stability of the CO₂RR system. On the con-

trary, acidic CO₂RR can avoid this issue but HER strongly competes with CO₂RR. Designing effective CO₂RR catalysts to exceed HER is crucial to further improve CO₂RR application.⁶⁶ Besides, C₃₊ products from CO₂RR can endow higher energy density and larger economic value. Enhancing the production of C₃₊ species from CO₂RR can make CO₂RR operations more profitable. However, C₃₊ production involves two or more C-C coupling steps, making the CO₂RR process more sluggish compared to C₂ production. This presents a significant challenge in the design of CO₂RR catalysts.

Therefore, serious efforts have already been made to understand the CO₂RR selectivity; more works will be made in the years to come to develop further characterization, theoretical technique, and synthesis comparable with an aqueous environment under CO₂RR conditions. With a synergistic combination of these tools, it may be possible to explore CO₂RR selectivity and mechanisms, including key intermediates, and to elucidate the CO₂RR reaction pathways. A closer interaction between experimental, characterized, and theoretical groups in this field is encouraged to address the complex CO₂RR design altogether. Furthermore, it summarizes recent knowledge about CO₂RR selectivity and will provide predictive guidance to experimenters for optimizing catalysts.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no datasets were generated or analyzed during the current study.

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