

Reaction Pathways for Electrochemical CO₂ Reduction into Ethanol

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Abstract

Electrochemical CO₂ reduction reaction (CO₂RR) offers a promising route to storing chemical energy and producing valuable chemicals, while also contributing to carbon cycle closure. Despite significant advances in electrocatalytic CO₂RR for multi-carbon products, challenges remain in optimizing catalysts for high selectivity and efficiency. Cu-based heterogeneous catalysts are among the most promising options; however, enhancing their catalytic efficiency and product selectivity remains complex due to several factors. One key challenge is that product selectivity heavily depends on the catalyst's surface morphology, which impacts both Faradaic efficiency and overpotential requirements for target product formation. Additionally, the reaction pathways and intermediates for multi-carbon products are not yet fully understood, complicating efforts to achieve consistent multi-carbon yields. Variability introduced by the electrolyte environment, applied potential, and operating conditions further impacts selectivity and efficiency. This review aims to address these challenges by exploring the interplay between the surface structure of Cu-based catalysts and system parameters that shape reaction pathways for ethanol formation. Notably, we explore alternative pathways beyond the conventional mechanisms involving CHO, COH, and CO dimers.

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1. Introduction

Using CO₂ as the raw material for generating fuels with high energy density would help to diminish our dependence on fossil fuels and provide a sustainable economic way to reduce the CO₂ level in the atmosphere.[1-3] Carbon dioxide conversion into useful chemicals is done by different methods such as reforming,[4, 5] biological,[6, 7] photochemical,[8, 9] organic synthesis,[10, 11] and electrochemical.[12-15] Electrochemical CO₂ reduction is attracting significant interest due to its ability to produce a wide range of valuable chemical feedstocks such as carbon monoxide, formic acid, methane, ethylene, methanol, ethanol, etc.[16-22] As CO₂ is a linear, stable molecule it is more difficult to break down, so its activation requires elevated temperature/pressure conditions or active reductants. Alternatively, CO₂ can be activated under ambient conditions with the assistance of a catalyst. The electrochemical reduction of CO₂ can be carried out in liquid, aqueous, or non-aqueous solvents. There are some main challenges associated with the process are, low absorption of CO₂ into the solution, hydrogen suppression reaction (HER), pH control issues, product separation issues, low energy efficiency due to higher overpotential, and low product selectivity.

The most common electrocatalysts used in CO₂ reduction reaction (CO₂RR) are heterogeneous catalysts,[23-26] homogeneous/molecular catalysts,[27, 28] and MOFs.[29, 30] Selective production of single-carbon (C₁) products, like carbon monoxide,[31-33] formic acid,[34-36] and methane[37, 38] via electrochemical CO₂RR have been achieved. Therefore, producing single-carbon (C₁) products via electrochemical CO₂RR is not very challenging compared to producing C₂₊ products. However, single-carbon products have a significantly lower energy density than multi-carbon products. Methanol is one of the promising C₁ products from electrochemical CO₂ reduction. Electrochemical conversion of CO₂ into methanol and formic acid has been achieved

with a good yield which makes this technique promising.[39-41] However, methanol is toxic in contrast with ethanol and not a promising fuel. The energy density of ethanol (8.0 kW h/kg) is higher than methanol (6.0 kW h/kg) in one process of complete oxidation.

There is a growing interest in producing multi-carbon (C_{2+}) products because of their higher added value. Nevertheless, selective production of C_{2+} is more challenging because of the complex mechanism, including many proton-coupled electron transfer (PCET) processes, and due to the limitations of effective electrocatalysts. Among C_{2+} species, ethanol (C_2H_5OH) is a highly valued product as an industrial feedstock, the largest additive to gasoline, and being relatively easy to store and transport (compared to gaseous products like ethylene and corrosive products like acetic acids). The electrochemical CO_2 reduction to ethanol requires 12 electrons ($2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$), with the equilibrium potential of 0.09 V vs. reversible hydrogen electrode (RHE). However, two main challenges must be overcome. They are a high onset potential of -1.0 V (or more negative) and low product selectivity.[14, 42] There are very few reported electrocatalysts for ethanol production with faradaic efficiency (FE) above 30%,[43-45] as competing double-carbon (C_2) products are also formed. [45-48] Thus, the industrial-scale electrochemical CO_2 reduction into ethanol is hindered by low energy efficiency and poor product selectivity.[25, 45, 49-51] To achieve the selective production of ethanol or other multi-carbon products efficiently, selective catalysts are essential.

Our interest in CO_2 reduction to ethanol is two-fold. First, it comes from our aim to develop tandem ethanol fuel cells, which features two cathodes: an oxygen reduction cathode, as in conventional fuel cells,[52] and a CO_2 reduction cathode. Unlike traditional ethanol fuel cells, the tandem design incorporates a second cathode to capture CO_2 released from the anode, convert it back to ethanol, and reuse it as fuel for the anode. The proposed tandem ethanol fuel cells have the

potential to significantly increase fuel efficiency while simultaneously reducing CO₂ emissions. Notably, rapid developments in CO₂ capture under various conditions[53] further improve the technical feasibility of tandem ethanol fuel cells. Second, CO₂ reduction to ethanol represents the reverse of the ethanol oxidation reaction (EOR). However, this area of chemical reaction space within CO₂RR remains largely unexplored. Our expertise in studying catalytic ethanol oxidation reaction[54-66] could provide valuable insight into discovering efficient pathways for the CO₂-to-CH₃CH₂OH conversion.

This review focuses on studies based on computational approaches for achieving efficient electrochemical CO₂RR to ethanol and other multi-carbon products, with an emphasis on Cu-based electrocatalysts. Achieving selectivity for multi-carbon products is challenging due to the potential dependence of the reactions, as well as the characteristics and surface morphology of the catalyst. Additionally, this review explores reaction pathways beyond those conventionally studied in the literature to expand the chemical reaction space for the efficient conversion of CO₂ to ethanol.

A fundamental understanding of the reaction intermediates and reaction pathways is essential in the rational design and further development of electrocatalysts for ethanol production. Due to the limitations of the experimental detection techniques, identifying possible reaction intermediates along the pathways to ethanol production is still challenging. So many experimental studies have been performed to determine the possible intermediates along the C₂ product formation on Cu surfaces.[67-70] Therefore, experimental studies combined with density functional theory (DFT) calculations were employed to support the proposed mechanism and possible intermediates. Computational studies have been widely used to provide detailed atomistic understandings along with the nature of the active site of used catalysts. The initial assessment of the Cu-based catalyst starts with predicting the adsorption energies of reaction intermediates and

constructing the free-energy diagrams.[49, 71, 72] Then thermodynamic analysis is performed to calculate the activation barriers of different elementary reactions in the proposed mechanism.[73, 74]

2. Heterogeneous catalysts

Electrochemical CO₂RR can be achieved via both homogeneous and heterogeneous catalysts. These two catalytic systems have different reaction mechanisms and experimental conditions. Homogeneous catalysts' performance[75] towards the electrochemical CO₂RR can be optimized by tuning the active sites in the metal centers. Homogeneous catalysts such as cyclam complexes [76, 77], pincer complexes [78, 79], and porphyrins [80, 81] have been tested as electrocatalysts for CO₂RR. But in large-scale applications, homogeneous catalyst recovery is more difficult than heterogeneous catalysts. To study the mechanistic pathways of CO₂RR, heterogeneous catalysts have many advantages over homogeneous catalysts as they can easily be recovered and have no need for separation from products. As copper is the only monometallic catalyst that facilitates the multi-carbon product formation, this review discusses only the progress of Cu-based electrocatalysts. More research efforts have been devoted to understanding the nature of the active sites and product selectivity on Cu catalysts.[82-86] To enhance the electrochemical CO₂ reduction process, it is important to investigate the geometry, morphology, and size of the catalyst particles.[87-103] Heterogeneous catalyst types have been mainly developed as nanomaterials,[104] oxide-derived metals,[105, 106] core-shell structures,[107] single-atom catalysts,[108-110] and nanoporous films.[111]

2.1 The C-C bond formation

Tuning electrocatalytic systems for CO₂RR into multi-carbon-containing products is much more attractive than C₁(single-carbon products).[112] Copper is the only reported metal for

catalyzing CO₂RR towards multi-carbon products which facilitates the C-C coupling.[13, 15, 113] The C-C bond formation is the more critical step in multi-carbon production which competes with the further hydrogenation of single-carbon products. At very high negative potentials, the hydrogen evolution reaction also occurs, which hinders C–C bond formation and reduces selectivity toward C₂₊ products. These activities in the electrochemical system further challenge the efficient reduction of CO₂ into desired multi-carbon products. Therefore, it is crucial to study the reaction mechanism of C–C coupling along with the optimal catalyst surface to achieve the efficient formation of multi-carbon products.

Based on both experimental and DFT calculations there are a few proposed pathways for C-C bond formation during the CO₂RR (Figure 1). The left route in Figure 1 indicated by the blue lines represents the mechanism proposed by Hori et al. toward the C₂H₄ formation.[114] Montoya et al. performed the first DFT studies of *CO dimerization to form *CO–*CO on Cu(111) and Cu(100) surfaces (Figure 1a top right branch).[74] Theoretical studies performed by Calle-Vallejo and his colleagues proposed that C-C coupling occurs via the pathway indicated in the red color route which suggested that *CO dimerization step coupled with an electron transfer ended up with the formation of *CO-COH.[115] However, there are still barriers preventing the use of Cu-based catalysts[71, 115] for CO₂RR into multi-carbon products as of higher overpotential requirement.

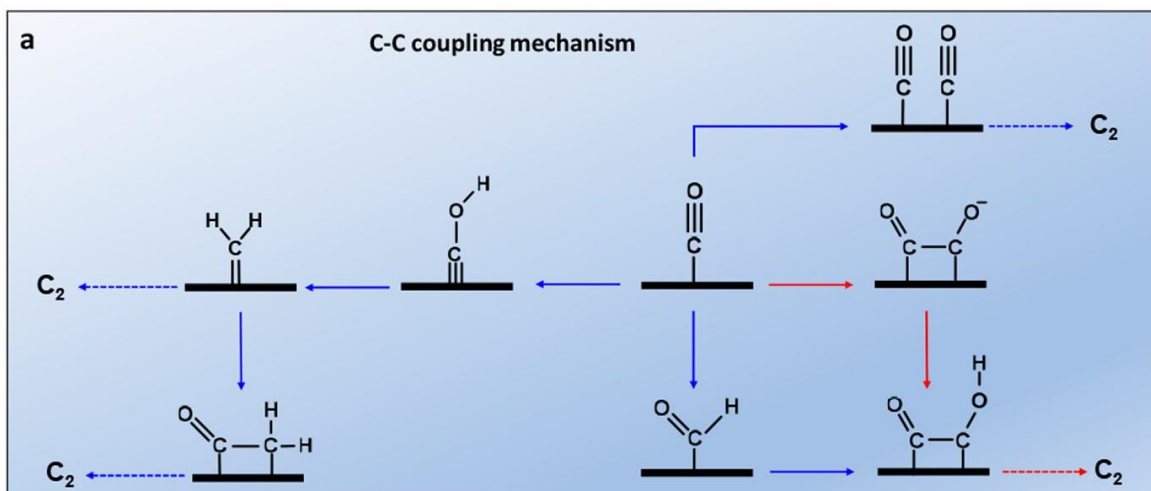


Figure 1. Proposed pathways for C-C bond formation. *CO on the Cu surface. Reproduced with permission. [116] Copyright 2019, JACS

Many researchers are working to address these challenges by developing novel Cu-based catalysts, as market interest largely focuses on reduced products with higher energy density. Therefore studying reaction mechanisms from CO₂ to main C₂ products, such as ethanol and ethylene has become concentrated in many experimental and theoretical studies.[117-120] Most studies have shown that rate-determining *CO dimerization as the critical C-C coupling step,[116, 119, 121] with the formation of enough *CO on the catalyst surface. Further, C-C coupling can occur via the reaction of *CO with *CHO or *COH as well. There are other possible pathways to form a C-C bond via the coupling of hydrogenated C₁ species.[74] Hence, understanding the reaction steps along with C-C coupling is essential for developing a selective and efficient catalyst for CO₂RR to ethanol. Various parameters, like crystal facet, applied potential, pH, electrolyte, and defective sites may affect the C-C coupling.

2.2 Catalyst facets

The morphology of the nanomaterial plays an important role in product selectivity which both experimental and theoretical studies have proved. Furthermore, the effect of catalyst facet on

CO₂RR has been extensively studied using theoretical simulations.[122, 123] Copper-based nanostructured catalysts[124-126] and oxide-derived (OD)[127, 128] electrodes have been shown the higher CO₂RR activity and selectivity in active sites with different coordination numbers. To promote CO₂RR products beyond the C₁, Cu catalysts should be modified with features including defects, different facets, low coordinated Cu sites, and surface roughness. For the formation of C₂⁺ products, the C–C coupling reaction is widely accepted to occur through *CO dimerization, followed by hydrogenation, as supported by many studies.[129-131] Theoretical studies conducted by Sandberg and his colleagues reported that the Cu(100) surface has the lowest energy barrier (0.45 eV), which is lower than that of the Cu(111) and Cu(211) surfaces.[132] As CO dimerization is an important step towards C₂ product formation, detailed understanding of CO adsorption[133-138] is useful to the design of catalysts.

Copper electrodes with different crystal facets exert different activity and selectivity, such as (111), (211), and (100) facets form different end products under similar electrochemical conditions.[125] Crystal facets of Cu(100), Cu(110), and Cu(111) have often shown different catalytic activities[139, 140] and illustrated effective catalytic activity towards CO₂RR, while Cu(100) has been reported as highly active for ethylene formation, and Cu(110) for acetate, ethanol, and acetaldehyde production, and Cu(111) for methane formation.[118] Further, it has been reported that Cu(100) facet prefers to the production of C₂H₄ over the formation of C₁ products.[115] Moreover, high-index surfaces also play a major role in product selectivity in CO₂RR. Highly stepped Cu(211) sites prefer CO₂ reduction into CH₄. [71] Wang and co-workers experimentally illustrated the significant enhancement of CO₂RR activity and C₂ product selectivity with stepped Cu(211) and Cu(200) facets.[141] A study based on micro-kinetic sites than Cu(100) and Cu(111).[142] Choi and co-workers reported a remarkably high faradaic

efficiency in the formation of C_2H_4 on Cu nanowires with rich surface steps.[143] The C-C coupling step should be promoted to enhance the Cu catalyst for higher selectivity and activity toward the C_{2+} product formation.[120, 142, 144] Ab initio molecular dynamics (AIMD) simulations also reported the high selectivity of C_{2+} products on high-index Cu facets, facilitating C-C coupling by lowering the C-C coupling barrier.[145] As shown in Figure 2 energy barriers for C-C coupling predominance on high-index Cu facets with less than 0.12 Ha (~ 3 eV). According to the energy barriers, the (911) facet has shown the best performance, followed by (511) and (711). The best formation efficiency of C_{2+} products on the Cu(911) facet is inconsistent with experimental results as well.[23] The impact of catalyst size and phase structure on the facet dependent is also interesting to investigate.[146-150]

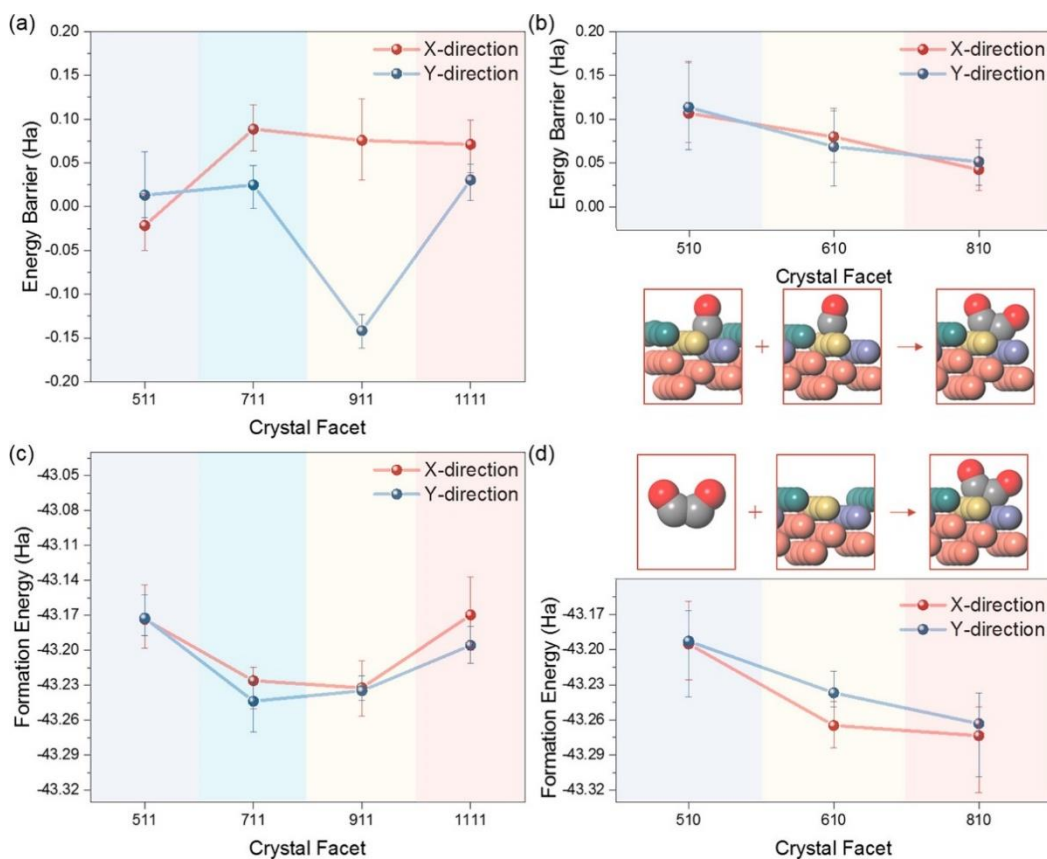


Figure 2. Energy barriers for CO dimerization into CO–CO structures on (a) Cu(S)-[$n(100) \times (111)$] and (b) Cu(S)-[$n(100) \times (110)$] along the x-direction and y-direction, respectively. The top inset shows the reaction process of CO dimerization. CO–CO formation energies on (c) Cu(S)-[$n(100) \times (111)$] and (d)

Cu(S)-[n(100) × (110)] along the x-direction and y-direction, respectively. The bottom inset shows the CO–CO adsorption process. Reproduced with permission.[145] Copyright 2022, J. Phys. Chem. Lett.

2.3 Oxide-derived Cu catalysts

Oxide-derived (OD) copper has shown a significant potential for forming value-added C₂₊ products during the CO₂ reduction process.[151] Partially oxidized Cu on the OD-Cu nanocatalyst could modify the electronic structure of the surface atoms and then promote the multi-carbon product formation by optimizing the binding energies of intermediates and the C-C coupling barrier.[127, 152] Both experimental and theoretical simulations have been conducted to investigate how the Cu⁺ state enhances the formation of multi-carbon products during the reaction. An experimental study conducted by Jang *et al.* reported that OD-Cu nanosheets, featuring a partially oxidized Cu surface, exhibit a 72% Faradaic efficiency with a higher current density for the formation of C₂₊ products.[153] OD-Cu nanowires fabricated with CuO_x sheath has also shown a significant Faradaic efficiency of 78% for C₂₊ products.[154]

Recently Chen *et al.* have presented experimental results on OD-Cu nanorod samples, demonstrating outstanding performance in the formation of C₂₊ products with 83.8% Faradaic efficiency and a current density of 341.5 mA cm⁻¹ at -0.9 V vs RHE.[155] Not only does the oxidation state promote the desired product, but the surface roughness of OD-Cu surfaces also enhances the catalytic activity of the electrocatalyst during the electrochemical CO₂RR.[143, 156] Furthermore, surface roughness, along with the generation of more defects on the catalytic surface can be attributed to the high yields of multi-carbon products during the electrochemical reduction of the oxidized Cu layer.[154] Therefore, studies on the effect of surface defects[157] and surface ligands[158-163] on the adsorption and catalytic activities as well as effective modulating oxidation states of catalysts via O species[164, 165] or alloying[166, 167] are critical for accurate prediction of efficient catalysts.

2.4 Applied potentials

Electrocatalysts play a major role in the product distribution of the CO₂RR and in determining the overpotential, which is closely related to the stability and binding affinity of the reaction intermediates to the catalyst surface. Despite the continuing expansion of research studies toward efficient electrocatalysts for CO₂RR, existing catalysts still operate at high overpotentials with low selectivity toward the desired products.[42, 168-171] Hence, a thorough understanding of the catalyst material, catalytic reaction pathway, and favorable intermediates is still a challenge in the field of CO₂RR into desired multi-carbon products.

Electrocatalytic CO₂RR is a very complex reaction that involves many reaction intermediates along with a series of proton coupled electron transfer (PCET) steps. CO₂RR starts with the adsorption of CO₂ to form *CO₂ (or *CO₂⁻) and then various reaction intermediates and products will be formed followed by proton and electron transfer.[142] This initial activation step requires an electrode potential of -1.9 V (vs RHE)[172] which makes the electrochemical CO₂ reduction process costly in terms of overpotential. Therefore, the catalyst should pre-activate the CO₂ in terms of reducing the overpotential. The equilibrium potentials for some of the main products in aqueous solutions are listed below:



By transferring a different number of electrons and protons to *CO₂, different products can be formed, such as CO, HCOOH, CH₃OH, CH₄, C₂H₅OH, and C₂H₄ shown in the above equations.[173] Very small differences between the thermodynamic potentials for CO₂ reduction products bring the challenge to selectively produce the desirable product. Hence the CO₂RR should be studied extensively by varying the applied potential to tune the product selectivity. It will be interesting to use the results of applied potential to design catalysts that have the built-in fields[174-178] to facilitate the reactions of interest.

Electrochemical CO₂RR on Cu(111) yields ethylene and methane at all applied potentials,[117, 118] while Cu(100) produces ethylene at low overpotentials and methane at high overpotentials.[117, 118, 179] Various DFT simulations have indicated that the *COCO dimer facilitates the C-C bond formation at low overpotentials, whereas the *CO and *CHO couples to form the C-C bond at high overpotentials.[73, 180-182] The C-C coupling step is crucial for the formation of multi-carbon products during the electrochemical CO₂ reduction. Therefore, it is essential to study the voltage dependence of this step. Goodpaster and his group conducted an intensive computational simulation to investigate this aspect via *CO dimerization on Cu(100) and Cu(111) surfaces at low overpotentials.[120] Furthermore, molecular dynamics (MD) simulations have also confirmed the voltage dependence of the C-C coupling steps on Cu(100) surfaces as mentioned above.[73] This simulation further reported that more negative potentials (than -0.85 V), it promotes the CH₄ formation than C-C coupling via *CHO intermediate.

2.5 Electrolytes

The efficiency and selectivity of the CO₂RR catalyst are influenced by the electrolyte's nature, primarily in terms of pH and the type of cation used in the system. The most used electrolytes in aqueous solutions are NaHCO₃, KHCO₃, and Na₂SO₄. The nature of alkali metal cations can

influence the efficiency of the metal catalyst and the selectivity of products in CO₂ reduction reactions.[183-186] The experimental studies have proven that increasing the cation size leads to higher product selectivity for multi-carbon products, higher current density, and lower overpotentials. During the electrochemical reaction pH is maintained at 7 to suppress the undesirable hydrogen evolution reaction (HER).

Resasco et al. performed DFT calculations and their results suggested that the size of the cation influences the stabilization of surface intermediates.[184] As the cation size increases, it enhances the stabilization of surface adsorbates. There are great needs of extensive studies on the effect of electrolytes through both DFT calculations and MD simulations[187-192] to fully understand CO₂RR.

3 Reduction mechanism for electrochemical CO₂RR to ethanol and other multi-carbon products

Electrochemical CO₂RR is a complex reaction that involves multiple proton and electron transfer steps along with different reaction intermediates and products. A detailed understanding of the reaction mechanism and the design of electrocatalysts with specific characteristics targeting desired products are essential to improve the efficiency of the electrochemical CO₂ reduction reaction. Copper is the only reported metal for catalyzing CO₂RR towards multi-carbon products. A fundamental understanding of the reaction intermediates and reaction pathways are essential in the rational design and further development of electrocatalysts for ethanol production. Due to the limitations of the experimental detection techniques, identifying possible reaction intermediates along the pathways to ethanol production is still challenging. These difficulties motivate people to computationally screen the reaction pathways of CO₂ reduction.

3.1 Computational methods

Simulations based on DFT studies have been extensively utilized to elucidate the underlying reaction mechanisms and the nature of active sites. The energetics associated with electrochemical CO₂ reduction reactions (CO₂RR) can be elucidated by incorporating solvent effects, primarily through two methods: implicit and explicit solvent models.[193-195] The computational hydrogen electrode (CHE) approach, suggested by Nørskov et al is convenient and useful in predicting catalytic activity and reaction mechanisms based on limiting potential which was suggested by.[196] Using this CHE model, we can generate the free energy landscape for the reaction mechanism at any applied potential, which involves multiple PCET steps, and then determine the potential determining step of the proposed reaction pathway.

The constant electrode potential (CEP) model enables improved simulation of the influence of applied potential on the electrode-electrolyte interface which addresses the drawback of the CHE model.[120] The limiting potential for each reaction pathway can be calculated using the CEP model hence offering the most feasible reaction mechanism. To identify promising catalysts for CO₂RR, kinetic models can be employed to calculate the reaction energies and activation barriers for the proposed reaction mechanisms. Machine learning methods are another approach to predict the reaction barriers.[197]

3.2 Mechanism of C-C coupling in CO₂RR

Activation of the CO₂ molecule is the initial step of electrochemical CO₂RR. CO₂ is a stable molecule with a higher negative potential, -1.9 V vs RHE.[172] In an aqueous medium, adsorbed CO₂ (*CO₂) either desorbs as formate ion after surface hydrogenation[198] or transforms to *CO and desorbs as gaseous CO. Further hydrogenation and reaction of *CO with other adsorbed

species can lead to the formation of hydrocarbons, alcohols, or other acids.[114, 179, 199-203] Hydrogenation of *CO via O-H can form *COH and via C-H can form *CHO. The formation pathway of *CHO on Cu(211) surface has been proposed by Peterson et al. based on the CHE model approach.[71]

The coexistence of both *COH and *CHO has been shown to depend on the coordination number of the active site of the Cu facet.[204] Schouten *et al.* conducted an experimental study to identify the C₁ and C₂ products. They reported that the formation pathways of ethylene and methane on Cu(111) share intermediates, including *CHO as the key intermediate.[118] Most of the computational studies have confirmed that initial protonation of *CO forms *CHO than *COH intermediate during the electrochemical CO₂RR on both Cu(100)[73, 119, 180, 205] and Cu(211)[71] surfaces, and *COH dominant on Cu(111).[206] Number of PCET steps determines the end products of electrochemical CO₂RR. In this process, the C-C coupling step plays the most important role in forming C₂₊ products. Overall, studies of reaction pathways suggest that the hydrogenation of *CO to form *CHO/*COH, which are key intermediates for single-carbon products, competes with the dimerization of adjacent *CO species to form multi-carbon products. Hence, another study performed by Schouten et al. proposed that dimerization of *CO occurs before the hydrogenation to form *CO-CO on certain Cu surfaces is the rate-determining step in multi-carbon product formation.[179]

Most of the theoretical studies reported that enhancing surface CO concentrations favors *CO dimerization to form C-C bond and it is the rate-determining step[207] and it is confirmed by some experimental analysis as well.[208, 209] When using catalyst surfaces encourages to enhance the *CO population than the reduced *CHO or *COH, dimerization is more likely to form C-C bond for multi-carbon products. The coupling between *CO and *COH has formed *COCO leading

to C₂ pathway on Cu(100) at 0V and its reaction barrier was lower than the dimerization.[210] The coupling between *CO and *CHO intermediates form *COCHO.[120, 181, 184, 211] However, the stability of those products depends on the catalytic system. In gas phase calculations, *COCOH was more stable than the *COCHO on Cu(100) surface.[115] When considering solvent effects on intermediates, these intermediates have exhibited different stabilities.[182, 212] Hence, a clear understanding of the C-C coupling step and key reaction intermediates, along with other system parameters, is essential for developing efficient electrocatalysts for the CO₂ reduction reaction into multi-carbon products.

3.3 Mechanism of C-C coupling in CO₂RR beyond CHO, COH, and CO species

Most of computational studies of CO₂RR to form C₂ species involving reaction pathways mentioned in the previous subsection as outlined by Kortlever, *et al.*[175] These reaction pathways represent a very limited chemical reaction space and can hinder our abilities to explore efficient catalysts. One of such an example is in the investigation of reaction mechanism for C₂₊ steam reforming. Most of computational studies focus on investigating the C-C bond cleavage along the pathways: C₂H₆ → ... → C₂H_x → CH_y + CH_z, namely the C-C bond cleavage at different degree of dehydrogenation. DFT studies on Ir(100) (see Table 1)[213] and on other metal catalysts[214] illustrate that the reaction barrier for C-C bond cleavage in C₂ steam reforming is above 1 eV regardless the catalysts. This is also the case for butane.[215, 216] However, when the DFT calculations include more chemical reaction space, better reaction pathways can be found (see Table 1) and the goal of C₂₊ steam reforming catalyst is shifted from C-C bond cleavage to the catalysts for better C-O coupling abilities. This is illustrated clearly in Figure 3. The addition of O species significantly changes reaction pathway.

Table 1. The activation barrier (E_a) and reaction energy (ΔE) of the C-C bond cleavage reactions of ethane on Ir(100) in the presence of O and OH species. Reproduced from Ref. [213].

Label	Reactant	$E_a/\Delta E$ (eV)	With O		With OH	
			Reactant	$E_a/\Delta E$ (eV)	Reactant	$E_a/\Delta E$ (eV)
Rx1	CH ₃ CH ₃	1.55/-0.22				
Rx2	CH ₃ CH ₂	1.19/-0.35	CH ₃ CH ₂ O ^b	1.37/-0.11	CH ₃ CH ₂ OH	2.31/-0.17
Rx3a	CH ₃ CH	0.97/-0.75	CH ₃ CHO ^b	0.80/-0.38	CH ₃ CHOH ^b	1.40/-0.16
Rx3b	CH ₂ CH ₂	1.36/-0.21	CH ₂ CH ₂ O ^b	1.13/-0.24	CH ₂ CH ₂ OH ^b	1.70/0.01
Rx4a	CH ₃ C	1.22/0.26	CH ₃ CO ^a	1.26/-0.06	CH ₃ COH ^b	1.87/-0.28
Rx4b	CH ₂ CH	1.49/-1.23	CH ₂ CHO ^a	0.91/-0.51	CH ₂ CHOH ^b	1.30/-0.15
			CHCH ₂ O	1.35/-0.08	CHCH ₂ OH	1.04/-0.62
Rx5a	CH ₂ C ^a	1.26/-0.40	CH ₂ CO ^a	0.52/-1.17	CH ₂ COH ^b	1.54/-0.44
			CCH ₂ O	1.18/-0.71	CCH ₂ OH	1.59/-0.56
Rx5b	CHCH	1.03/-0.71	CHCHO ^b	1.06/-0.30	CHCHOH ^b	1.13/-0.82
Rx6	CHC ^a	1.14/-0.54	CHCO ^a	0.30/-1.32	CHCOH ^b	1.04/-0.37
			CCHO ^b	0.88/-0.74	CCHOH	1.58/-0.99
Rx7	CC ^a	1.19/-1.45	CCO ^b	0.23/-1.16	CCOH ^b	0.95/-0.65

^aData was taken from ref.[60]; ^bData was taken from ref. [61].

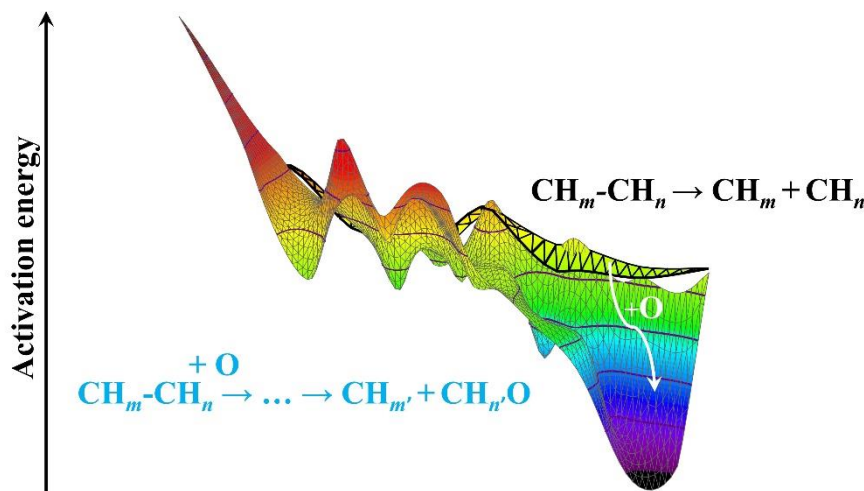


Figure 3. Activation energy surface in C₂ chemical reaction space. The black strip highlights are the activation energy barriers for reactions of CH_m-CH_n species only. Picture is taken from ref. [215].

In the case of CO₂RR, Table 2 lists several pathways based on the previous data on the studies of EOR. The results clearly demonstrate that Cu, particularly partially oxidized Cu (Cu₂O), outperforms other catalysts. Interestingly, very recent in-situ IR experiments by Zhan, *et al.* revealed [22] the possibility of new reaction pathways, further underscoring the importance of

exploring alternative feasible routes for effective CO₂-to-CH₃CH₂OH conversion. Therefore, investigations extending beyond the currently known chemical reaction space, while incorporating electrochemical environments, will significantly enhance the accuracy of CO₂RR mechanism predictions.

Table 2. Reaction barriers (ΔE_a) and reaction energy (ΔE) of C-C coupling on Cu(100), Cu₂O(111), and Ir(100).

Reaction	Cu(100) [58]		Cu ₂ O(111) [57]		Ir(100) [60]	
	ΔE_a (eV)	ΔE (eV)	ΔE_a (eV)	ΔE (eV)	ΔE_a (eV)	ΔE (eV)
CH ₃ +CO→CH ₃ CO	1.09	0.06	0.02	-1.22	1.32	0.06
CH ₂ +CO→CH ₂ CO	0.75	-0.27	0.49	-2.57	1.69	1.17
CH+CO→CHCO	0.89	-0.28	2.60	-0.83	1.62	1.32

4 Summary and perspectives

In the last two decades, people have devoted many studies, including theoretical and experimental to exploring the efficient catalysts for electrochemical CO₂RR into valuable products. The CO₂RR can easily produce C₁ products like methane, formate, methanol, and CO while multi-carbon products including C₂H₆, C₂H₄, C₂H₅OH, CH₃COOH, and C₃H₇OH make it more challenging to produce with desired yield and product selectivity. Multi-carbon product formation using electrochemical CO₂RR is still far away from industrial-level applications due to the low energy efficiency and low yield. Addressing these issues has become more complex due to the lack of a clear understanding of the reaction mechanisms and stable intermediates. Additionally, practical applications are significantly different from experimental and theoretical conditions, such as pH, applied potential, electrolyte, and catalyst morphology and composition. Bridging this gap is highly important for the rational design of efficient electrocatalysts. Carefully optimizing all the parameters toward the high faradaic efficiencies and current densities can lead to the formation of multi-carbon products with the desired selectivity.

To achieve efficient electrochemical CO₂ reduction to ethanol, novel catalyst designs are essential. The electronic structure of the catalyst can be modified by adjusting crystal facets and introducing defects with different active sites in nanocatalysts. In this regard, theoretical simulations can be designed to investigate the impact of crystal structure on intermediate stability through both thermodynamic and kinetic analyses. Currently, there is a shortage of theoretical studies addressing electrolyte-electrode interactions under applied potentials with along solvent models in the production of multi-carbon products via CO₂ reduction. Therefore, examining the effect of applied potentials on catalytic activity for multi-carbon products using a CEP model could provide valuable insights into changes in catalyst surfaces, selectivity determining intermediates, and the proposed reaction mechanisms. We believe that future studies should focus on various Cu-based nanocatalysts with surface modifications and explore chemical reaction space beyond the current areas, as well as consider solvent and applied potential effects, to establish detailed reaction pathways for electrochemical CO₂ reduction toward ethanol or other multi-carbon productions. Such research will support advancements in experimental trials and bring us closer to achieving successful CO₂ reduction to ethanol formation or any desired multi-carbon products.

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