Towards understanding of CO₂ electroreduction to C₂⁺ products on copper-based catalysts

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Abstract
The electrochemical CO₂ reduction reaction (CO₂RR) has been regarded as a promising technique for converting CO₂ into high-value fuels and chemicals. Powered by renewable electricity, the CO₂RR provides a viable strategy to mitigate the CO₂ concentration in the atmosphere and close the anthropogenic carbon cycle. Recent studies exhibit that copper-based catalysts are capable of reducing CO₂ to C₂⁺ products, such as ethylene and ethanol, which are of higher value compared with C₁ products. The reaction process toward C₂⁺ products involves the formation of key intermediate *CO, the C–C bonding, and the post-C–C bonding to final products. This perspective is focusing on the mechanism leading to C₂⁺ products, examining the evidence from in situ/operando spectroscopy and density functional theory calculations. The effects of Cu facet and electrolyte on catalytic performance are reviewed. An in depth discussion of mechanistic aspects of Cu catalyst is presented, shedding light on the intrinsic features of catalyst and electrode-electrolyte interface, therefore moving towards an understanding of CO₂RR at the atomic level.

KEYWORDS
CO₂ electroreduction, copper-based catalysts, density functional theory, in situ spectroscopy

1 | INTRODUCTION

Since the industrial revolution, the CO₂ concentration in the atmosphere has risen rapidly to 412 ppm in 2020, which set a record high in more than 3 million years.¹ The main reason for the rising CO₂ concentration is the burning of fossil fuels which propels the development of civilization. However, the greenhouse effect from CO₂ is emerging as a lethal threat to humanity. Climate change due to the greenhouse effect leads to a doomsday apoplectic catastrophe such as rising sea levels and frequent dangerous weather events.²,³ The electrochemical CO₂ reduction reaction (CO₂RR) is a highly potential method to close the anthropogenic carbon cycle by utilizing CO₂ to produce useful chemicals and fuels, while electric energy could be generated from renewable...
sources such as solar and wind energy.\textsuperscript{4,5} On the other side, the astonishing progress of renewable energy also requires efficient techniques for energy storage. The energy stored in the form of chemical bonds is transportable, easy to be merged with the current industry, and safe.\textsuperscript{6,7} The C\textsubscript{1} products of CO\textsubscript{2}RR are CO and HCOOH, which are relatively easy to be generated in CO\textsubscript{2}RR, while the C\textsubscript{2+} products, such as oxygenates and hydrocarbons with high energy density, are more ideal for the practical mass application of CO\textsubscript{2}RR.\textsuperscript{8–10} The C\textsubscript{2+} products possess merits such as higher volumetric energy densities and the potential to build complex long-chain hydrocarbon chemicals. However, the production of C\textsubscript{2+} oxygenates and hydrocarbons (C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{5}OH, CH\textsubscript{3}COOH, etc.) involves C-C bonding with a high energy barrier to overcome.\textsuperscript{11} Compared with the C\textsubscript{1} products involving only oxygenation and hydrogenation, the inert C-C bonding is much more difficult to achieve.\textsuperscript{12–14} Therefore, C-C coupling requires high overpotential on the cathode catalyst. In the literature, the reported Faradaic efficiency (FE) for CO and HCOOH could reach \textasciitilde100\%, but the highest FE for C\textsubscript{2}H\textsubscript{4} is only around 60\%–70\%.\textsuperscript{15} The economic analysis indicates that the high reaction rate is crucial for the practical application of CO\textsubscript{2}RR, which requires a high current density of C\textsubscript{2+} products with satisfying stability. Moreover, the extra costs could be incurred from the separation of different products, liquid electrolytes, and unreacted CO\textsubscript{2}.\textsuperscript{16,17} Currently, the most commonly used catalysts for C\textsubscript{2+} products in CO\textsubscript{2}RR are copper-based materials.\textsuperscript{18–20} The performance of C-C coupling is especially sensitive to the interface of copper catalysts and electrolytes.\textsuperscript{21,22} Therefore, the improvement of reaction rate and energy efficiency for C\textsubscript{2+} products depends heavily on a deeper understanding of the C\textsubscript{2+} production mechanism.

In the literature, the mechanism of C\textsubscript{2+} product formation is widely investigated with density functional theoretical (DFT) calculations and in situ/operando spectroscopy characterizations. In situ/operando spectroscopy is utilized for the inspection of the presence and binding configurations of related intermediates,\textsuperscript{23,24} while DFT calculations are widely applied in investigating the binding energy of key intermediates, depicting the free energy profile, predicting, and explaining the activity and selectivity.\textsuperscript{6,25} Moreover, DFT calculations have evolved to understand the complexity of the operating conditions, such as solvent molecules and surface charge distributions.\textsuperscript{26–29} In this perspective, as shown in Figure 1, we focus on the studies with DFT calculations and in situ/operando spectroscopy characterizations in the C-C bonding mechanism, facet, and electrolyte effect, aiming at providing a brief account of C\textsubscript{2+} products formation on copper catalysts.

\section{REACTION MECHANISM TOWARDS C\textsubscript{2+} PRODUCTS}

\subsection{The production of *CO}

On a Cu-based catalyst, the CO\textsubscript{2} molecule is first reduced to *CO intermediate, and then *CO is reduced to *CHO, *COH, *COCO, *OCCHO, or *OCCHOH, of which the binding strength determines the final products.\textsuperscript{30,31} *CO is a key intermediate in C-C coupling reaction because *CO dimerization is generally believed to be the rate-determining step in CO\textsubscript{2}RR, which requires a high current density of C\textsubscript{2+} products with satisfying stability. Moreover, the extra costs could be incurred from the separation of different products, liquid electrolytes, and unreacted CO\textsubscript{2}.\textsuperscript{16,17} Currently, the most commonly used catalysts for C\textsubscript{2+} products in CO\textsubscript{2}RR are copper-based materials.\textsuperscript{18–20} The performance of C-C coupling is especially sensitive to the interface of copper catalysts and electrolytes.\textsuperscript{21,22} Therefore, the improvement of reaction rate and energy efficiency for C\textsubscript{2+} products depends heavily on a deeper understanding of the C\textsubscript{2+} production mechanism.

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\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{The outline of the review. There are three parts: The mechanism of C\textsubscript{2+} production; structure–activity relationships; and the design of catalysts assisted by theoretical calculations. We focus on the evidence and insights obtained from DFT calculations and in situ/operando spectroscopy. CO\textsubscript{2}RR, CO\textsubscript{2} reduction reaction; DFT, density functional theory.}
\end{figure}
been recognized that there are two possible C1 products, that is, CO and HCOOH from two-electron transfer of CO2 reduction. Concomitantly, hydrogen evolution reaction is competing with the CO2RR. The initial activation of the CO2 molecule could occur in two ways: proton–electron-coupled transfer (Equation 1) or electron-transfer-mediated CO2 binding step (Equation 2):

\[
\begin{align*}
* & + \text{CO2} + e^- + \text{H}^+ \rightarrow \text{COOH}, \quad (1) \\
* & + \text{CO2} + e^- \rightarrow \text{CO2}^-, \quad (2) \\
\text{COOH} & + e^- + \text{H}^+ \rightarrow \text{CO}. \quad (3)
\end{align*}
\]

On copper catalysts, the activation of CO2 is more likely to occur via Equation (1), while on the molecular catalyst, CO2− anionic adduct is adsorbed on the metal center. It should be noted that for some posttransition metals such as Pb and Sn, *OCOH formation is more favorable than *COOH, which indicates that Pb and Sn are more selective for formate. In the next step, *COOH intermediate is further reduced to *CO (Equation 3). The binding strength of *CO determines the subsequent pathway: *CO either is desorbed to form CO product or undergoes hydrogenation to *CHO or dimerization to *COCO, to form C2 or C3 products.

Moreover, one of the crucial features of high-performance copper catalysts is the high coverage of *CO. High concentration of CO facilitates C–C coupling reaction, thus enhancing C2+ production. An intensity ratio of Cu–CO stretching mode was reported to the restricted rotation of adsorbed CO in operando Raman experiment, which not only increased with the higher CO coverage but also followed the trend of C2+ production. The adsorption configurations of *CO is also a key point in C–C bond formation, which will be discussed in the part on facet effect.

### 2.2 The formation of the C–C bond

The most important step for C2 products is the C–C bond formation. As shown in Figure 2, there are several possible pathways: the *CO dimer could form directly, or *CO reacts simultaneously with H+ and e−, forming *HOCCO intermediate. Another competing pathway is *CO protonation to *CHO, which is selective to methane and glyoxal products. It is reported that on Cu(111) surface, CH4 is more favorable at high overpotential, while on Cu(100) surface, C2 products dominate over methane at low overpotential. The different selectivity of Cu(111) and Cu(100) is also related to the pH effects: Cu(111) pathway is pH dependent, while Cu(100) pathway is not, which indicates that CO dimerization is more dominant on Cu(100). However, at a very negative overpotential, CO dimerization is reportedly difficult. Instead, *CO is prone to (1) first reduce to *COH, and then form *HOCCO intermediate or (2) directly form *HOCCO with *CO and proton–electron-coupled transfer. The proton-coupled electron transfer is the rate-limiting step in this pathway, which indicates that it is pH sensitive.

The C–C bonding mechanism is one of the hottest debate fields in CO2RR research. Several alternative pathways were proposed to understand this demanding step. Earlier studies by Hori et al. proposed that *CH2 intermediate is generated from protonation of *COH.

![Figure 2](image-url) The pathways for C2+ products in CO2 reduction reaction.
For C–C bonding formation, two *CH₂ are dimerized or CO is inserted into *CH₂. However, this pathway is challenged by the fact that C₂H₆ is rarely observed on the copper catalyst. It is found that the charged water layer could stabilize the CO dimer, and without charged water layer, the CO dimer formation is energetically prohibited. Another possible C–C coupling pathway is proposed that negatively charged CO–CO⁻ species is formed during the dimerization process, and then protonated to form CO–COH. On the other hand, the C₃ products are reported to be generated from the insertion of CO to *C₂H₄, but details are still obscure.

Operando Fourier transform infrared spectroscopy (FTIR) has been used to provide useful information for C–C bond formation. FTIR reveals that two vibrational bands detected at 1191 and 1584 cm⁻¹ were ascribed to C–O–H and C–O stretching vibrations of a hydrogenated dimer intermediate *OCCHOH. An emerged peak at 2053 cm⁻¹ was observed in operando Raman spectra on Cu₂O catalyst, corresponding to confined *CO intermediate (Figure 3A). Cu₂−ₓS catalyst showed higher selectivity of C₂ products during CO₂RR, and C–H stretching mode of aldehydes (*CHO) was observed instead of C–O stretching mode of *CO with the...
operando Raman spectroscopy (Figure 3B). *CHO presumably coupled with *CO to form *COCHO, following the formation of C$_2$+ products. The in situ and operando spectroscopy studies overwhelmingly detect *CO and other protonated C–C intermediates such as *OCCOH, but *OCCO, if any, is much more difficult to be directly observed.

### 2.3 | The postcoupling reactions

For the post-C–C-coupling step, it is reported that protonation of *HOCCO intermediate leads to *CCO or *HOCCOH, which is further reduced to CH$_3$COOH and C$_2$H$_4$/CH$_3$CH$_2$OH, respectively. It could be seen that *HOCCO is the key intermediate of which protonation determines the selectivity towards ethylene/ethanol versus acetate. However, it is noted that the *CCO could also be reduced to ethylene via *HOCCH$_2$ intermediate. On the other hand, the bonding between *CHO and *CO generates *OCCHO, which is the precursor of glyoxal product. It should be pointed out that an alternative pathway proposed by the Sargent group argues that *HOCCH is the key intermediate instead of *HOCCO. *HOCCH is reduced to *CCH or *CHCHOH, which are the precursor of ethylene or alcohol, respectively. Meanwhile, with millisecond-resolved differential electrochemical mass spectrometry, the Strasser group detected and proposed that *CH$_3$ could serve as an unexpected intermediate shared for CH$_4$, CH$_3$CH$_2$OH, CH$_3$CHO, and CH$_3$COOH formation on (110) step sites adjacent to (100) terraces at higher overpotential, which shows that a much closer link between CH$_4$ and ethanol exists than previous thought.

### 3 | STRUCTURE–ACTIVITY RELATIONSHIP

#### 3.1 | The facet effects

The surface facet of copper catalyst exerts a significant influence on selectivity and activity. As mentioned above, Cu(100), Cu(111), and Cu(110) are all reported to be effective for CO$_2$RR, while Cu(100) is more commonly recognized as the active site for ethylene, and Cu(111) is inclined to produce methane, while acetate, ethanol, and acetaldehyde production are reported produced on Cu(110). On Cu(100), the CO–CO dimerization is more likely to occur, leading to ethylene production, while on Cu(111) and Cu(110), *COH intermediate was observed. However, it should be noted that in the CO$_2$RR experimental conditions, the copper catalyst exhibits complicated surface structures, where the facet index evolves and reconstructs all the time. For example, with the operando scanning tunneling microscopy, the polycrystalline Cu was observed to reconstruct from Cu(111) to Cu(100) in CO$_2$RR conditions.

Moreover, the surface steped sites (high indexed surfaces) are suggested to play an important role in the CO$_2$RR. Stepped sites have long been observed on the copper roughened surface. Cu(511) was shown to be generated in the electrolyte with surface *H species inducing the reconstruction and stabilizing stepped sites. High indexed surface/stipped sites are effective in adsorbing CO molecules and decreasing the energy barrier of the *CO + HCO* → OCCHO* step. With microkinetic modeling, it is found that CO$_2$RR exhibits a significantly higher current density on Cu(211) surface than Cu(111) and Cu(100). As shown in Figure 4A–C, Wang et al. found that the Cu(211), Cu(611) and pocket shape surfaces which represent the high-index facet are not sensitive in the formation of *HOCCOH. On the contrary, the C–O bond dissociation barrier is reduced on all high index surfaces, which indicates that *CCO formation is more favorable on high index surfaces. Considering that *HOCCOH is the key intermediate for C$_2$H$_4$ and *CCO for CH$_3$COOH, the high index surface is more selective for acetate, which agrees well with the experimental observation that Cu nanoparticles with a large edge-to-(100) ratio exhibit the highest acetic acid selectivity.

#### 3.2 | Grain boundaries

On the other hand, grain boundaries are also crucial active sites in CO$_2$RR. Kanan group first proposed that the high-density grain boundaries in the interconnected nanocrystallites derived from the constrained environment of Cu$_2$O lattice significantly enhance the CO electroreduction to C$_2$+ product. In a later study, using high-resolution transmission electron microscopy (TEM), Kanan and colleagues calculated the termination lengths on 200 copper nanoparticles by a conversion factor derived from simple geometrical models from two-dimensional (2D) images of TEM to 3D particle surface areas, and thus correlated CO electroreduction activity with the density of grain-boundary on the copper nanoparticle. Cu’(101) formed from lattice mismatch is reportedly favorable to adsorbed *CO with high coverage, which promotes oxygenate production. The complex lattice planes of Cu(111), (100), and (220) observed with spherical aberration-corrected TEM are stacked upon each other as premature crystalline with rich grain boundaries, which are attributed to the
kinetic-driven nucleation instead of Ostwald ripening. DFT calculations indicate that the boundary between (100) and (111) surface is selective for C₂H₄ production, via the route of proton-electron coupled *CO dimerization to *CO–COH. In a recent study, the oxide-derived copper with a well-controlled (100)/(111) interface shows higher activity for *CO adsorption and subsequent C–C bond formation compared to individual Cu(100) and Cu(111). It is noted that the highly esthetic copper structure was carefully dissected with 14 facets, and the C₂⁺ selectivity is correlated linearly with the length of the Cu(100)/Cu(111) interface, which is attributed to the lowered free energy barrier of *OCCO intermediate formation.

3.3 | CO adsorption configurations

The CO adsorption configuration is also one emerging and interesting topic for C₂⁺ formation. With multiscale simulations, Cheng et al. found that the surface under-coordinated square site substantially decreases the formation energy of *OCCOH. However, not all of the strong CO binding sites are active for C–C coupling reaction, and the best combination for C–C bond formation is one strong CO binding site and at least one under-coordinated neighboring square site (Figure 4D). Sargent group reported a volcano-curve relationship between the ethylene selectivity and the ratio of *CO with two adsorption configurations on Cu catalyst functionalized with organic molecules. In this study, they summarized the ratios between the intensities of atop bounded CO and bridge bounded CO using in situ Raman spectroscopy, they found that an appropriate amount of COatop and CObridge favored the ethylene production. In combination with DFT calculations, they calculated that a CO dimerization with atop:bridge site exhibits the lowest energy barrier, resulting in high C₂⁺ selectivity. Cuenya and colleagues demonstrated a potential-dependent intensity ratio of Cu–CO stretching mode to the restricted rotation of adsorbed CO in operando Raman experiment, which not only increased with the higher CO coverage but also followed the trend of C₂⁺ production. DFT calculations revealed that the participation of COatop played a key role in facilitating the CO–CO dimerization step. Our group introduced phosphorus into the lattice of cupric oxide (CuO) to synthesize Cu₂P₂O₇ with a high density of defects. The catalyst was electrochemically reconstructed under CO₂RR conditions, thus obtaining a highly porous Cu with a high electrochemically active surface area and abundant defects with low-coordinated sites. In situ Raman spectroscopy and DFT calculations suggest that the defects and low-coordinated sites from the reconstructed Cu₂P₂O₇ catalyst provide a suitable condition for bridge and atop adsorbed *CO, which was more favorable for C–C coupling.
3.4 | Anion effects

Ions in electrolytes, especially halogen, have been recognized as effective in improving the CO₂RR performance of the copper catalyst. It is reported that the ethane pathway is dominant over iodide-derived Cu foams.⁴⁸ The Fourier transformed extended X-ray fine structure spectra (EXAFS) presented a Cu-O bond length of 2.15 Å, which matches the bond length of adsorbed ethoxy intermediate (Cu–OCH₂CH₃). Further potential-dependent Raman spectra identified the symmetric –CH₂ and –CH₃ stretching located at 2890 and 2920 cm⁻¹. Such intermediate was involved in a selectivity-determining step that occurred later in ethane or ethanol production. Our group reported a CuI/Cu composite catalyst substantially improves the partial current density of C₂⁺ products, which was attributed to the residue iodine inducing a Cu⁰/Cu⁺ interface and improving the CO adsorption.⁶⁴ In addition, fluorine on the surface of copper catalyst was effective to assist the water activation and enhance the CO adsorption, and the authors proposed that the fluorine lowered the energy barrier of C–C coupling via two *CHO dimerization, and *CO hydrogenation to *CHO is the rate-determining step, which is arguably uncommon, and the in situ FTIR reveals that the band at 1754 cm⁻¹ is attributed to the *CHO species.⁶⁵

For the cations, the majority of studies are dealing with alkali metals, with the conclusion that Cs⁺ > K⁺ > Na⁺ > Li⁺.⁶⁶–⁷⁴ The researchers also checked the effect of cations and proposed that there are three different theories concerning the mechanism as reviewed by Waegelé et al.,⁷⁵ even though the general trend is similar. The first one proposed by Hori et al.⁷⁶,⁷⁷ argued that the potential was charged by cations in the electric double layer through specific adsorption. The cations are adsorbed near the surface via a noncovalent interaction to induce a high electric field in the outer Helmholtz plane. A continuum electrolyte model was presented by Ringe et al.⁷⁸ to show that weakly hydrated cations are more likely to concentrate at the outer Helmholtz plane, which lowers the activation energy of the overall reactions, leading to favorable interfacial energetics of the solution layer and stronger CO₂ adsorption. The second theory is that the cations buffer the interfacial pH, by stronger hydrolysis induced by the electrostatic field.⁷⁹ The surface-enhanced infrared (IR) spectroscopy was used to probe the pH at the gold electrode surface, and the ratio between the intensity of CO₂ and HCO₃⁻ band indicates that the larger cations could buffer the pH better than smaller ones.⁸⁰ The third theory suggests that the metal cations stabilize the intermediates by local electrostatic interactions within the electrical double layer.⁸¹ The stabilization effects are rationalized by DFT calculations, which indicates that the constrained minima hopping molecular dynamics in the interface between cation and electrode surface were improved by the solvated cations.⁸² Recently, Koper and colleagues presented a report showing that CO is only produced on gold, silver, or copper if a metal cation is added to the electrolyte.⁸³ With well-designed electrochemical experiments and ab-initio molecular dynamics simulations, the partially desolvated cations have arguably three promotional effects for CO₂ electroreduction: thermodynamics which stabilizes CO₂ adsorption, the changing of O–C–O bond angle, and the enhanced electron transfer from the surface to activated CO₂. An accurate understanding of the role of anion and water is still on the way, but more and more evidence indicates the crucial stabilizing effect of anion on CO₂.

3.5 | Copper chemical state

Most copper catalysts are prone to reconstruct under electroreduction conditions, leading to a significant change in valence state or morphology, especially Cu oxide or other derivatives.¹²,⁸⁴ Electronic structure (oxidation state) of Cu is usually analyzed by in situ X-ray absorption spectroscopy (XAS) and quasi in situ X-ray photoelectron spectroscopy (XPS).⁵⁵–⁸⁸ Oxidized copper species (CuOₓ) have been believed to facilitate the C–C coupling step due to a more stable binding and higher coverage of *CO.⁸⁹–⁹¹ In situ XAS at the Cu-L₂,3 edge and Cu-K edge by Cuena and colleagues indicated that a full or partial reduced Cu⁺ electrode makes dissociative CO₂ adsorption occur,⁹⁰,⁹¹ which is inhibited over the reduced Cu²⁺ because the formation of copper carbonates or the lack of conductivity at negative potentials.

Cu⁵⁺ species remaining on the surface have been suggested to be an active site in improving the selectivity towards C₂⁺ products; however, the chemical state evolved drastically during CO₂RR as Cu₂O reduction is highly favored compared to CO₂ electroreduction or water splitting.⁹³ Therefore, effective control of the chemical state and electronic structure is extensively studied, among them, devising the interfaces of copper and other oxides should be efficient for CO₂RR due to the modification of electronic structure or stabilization of Cu⁵⁺.⁹⁴–⁹⁷

Wen and colleagues demonstrated that the Cu⁵⁺ species was stabilized at the Cu/Cu₃S₄ interfaces obtained from the structural evolution of the S-HKUST-1.⁹⁵ They confirmed the formation of Cu⁰ species under CO₂RR conditions by observing the Cu–Cu peak in the operando
EXAFS spectra. Furthermore, they suggested an average oxidation state of Cu which is between 0 and +1 after 15 min reactions by comparing the Cu K-edge adsorption of S-HKUST-1 with Cu foil and Cu₂O. The energy barrier of *CO dimerization step at the Cu/Cu₂S interface was then proved to be lower than that over Cu(111).

By calculating the ratios of Cu states based on Cu/Cu₃P₂O₈ catalyst using linear combination fitting from in situ X-ray absorption near edge structure (XANES) spectra, Zheng and colleagues found a coexistence of metallic Cu and Cu₃P₂O₈ during CO₂RR, and the proportion of Cu²⁺ species maintains at 38%, leading to high C₂H₄ production. The analysis of wavelet-transform EXAFS further indicated the coexistence of Cu–O and Cu–Cu, and the experiment result was confirmed by DFT calculations that Cu₃P₂O₈/Cu(111) interface to stabilize the *OCCO intermediate and shifted the reaction towards C₂ products.

Wang and colleagues found an increase of Cu⁵⁺ species with the electronegativity of halogen in X–Cu catalysts (X=I, Br, Cl, F) by comparing the Cu K-edge adsorption with Cu and Cu₂O references (Figure 5A). The analysis of wavelet-transform EXAFS further indicated the coexistence of metallic Cu and Cu 3P2O8 during CO₂RR, and the proportion of Cu²⁺ species maintains at 38%, leading to high C₂H₄ production. The analysis of wavelet-transform EXAFS further indicated the coexistence of Cu–O and Cu–Cu, and the experiment result was confirmed by DFT calculations that Cu₃P₂O₈/Cu(111) interface to stabilize the *OCCO intermediate and shifted the reaction towards C₂ products.

DFT calculations further indicate that fluorine modification accelerated the *CO → *CHO step and then enhanced the coupling of *CHO, furthermore, an improved CO adsorption occurred on the increased Cu⁵⁺ sites, giving a highly active and selective catalyst for C₂⁺ formation in CO₂RR. Sargent and colleagues introduced Cu-SiOₓ step sites with enhanced CO coverage and lower formation energy of OCOH⁺ to promote C–C coupling toward ethylene production. The band at 530 cm⁻¹ from in situ Raman investigation confirmed a stable Cu–O–Si interaction. Further in situ XANES at the Cu K-edge revealed metallic Cu mainly existed in the Cu–SiOₓ catalyst.

The synergistic effect between Cu⁰ and Cu⁺ boosts the selectivity and efficiency of CO₂RR towards C₂⁺ products, which is proved by DFT calculations. Yu and colleagues performed linear-combination fitting of Cu K-edge XAS spectra to quantitative determined the retained Cu²⁺ in Cu₂O cavities during CO₂RR (Figure 5B,C). The stabilized Cu²⁺ species retained up to ∼32%, with ∼68% of Cu⁰, which led to the marked C₂⁺ selectivity. Strasser and colleagues found that the oxides in the surface layer stabilized on bulk Cu against reduction during CO₂RR, which resulted in a high...
ethanol in the simulation of IR absorption spectroscopy was studied by Katayama et al.,\textsuperscript{101} and the researchers pointed out that an implicit and explicit model of water could be very different in the shift of vibration frequency C–O bond. An implicit solvent model through a quantum-surface-dependent contribution and an explicit model with water molecules are included in the DFT calculations. It is shown that the C≡O bond stretching frequency in HCO$_3^-$ is 1355 cm$^{-1}$ in the implicit model, and the frequency shifts to 1376 cm$^{-1}$, which could be attributed to the water molecule in the first coordination shell. However, the C≡O stretching frequency in the *COOH is 1649 cm$^{-1}$, but shifts down to 1620 cm$^{-1}$. It could be seen that the implicit and explicit water model could produce positive or negative trends in a shift of frequency, which should be considered carefully in simulations.

4.2 Machine-learning assisted design of catalysts

Recently, the high-throughput computational screening of catalysts is proved to be an effective way to predict the performance of CO$_2$RR catalysts. However, the cost of time and money is huge for screening with DFT calculations, which involves potentially hundreds or even thousands of structures. The machine-learning assisted materials design uses DFT calculation results as training data and produces learned models for much larger data space. Chen et al.\textsuperscript{103} applied an extreme gradient boosting regression algorithm to predict CO adsorption energy on 1060 metal–graphene systems and predicted that Co-, Fe-, and Sc-supported on nitrogen or sulfur-doped graphene are active for CO$_2$ electroreduction. Zhong et al.\textsuperscript{104} uses a machine-learning accelerated workflow for screening copper–based intermetallic crystals with CO adsorption energy, and predicted that Cu–Al is a promising candidate material for CO$_2$ reduction to produce C$_2$H$_4$, which is successfully validated with experiments. A cyclical neural network framework was trained and refined by around 4000 DFT single-point simulations of the adsorption energy to correlate the E$_{CO}$ and E$_{HOCCO}$, and the (211) surface of nickel gallium bimetallic material was found to be active, while the crystal facets follow the step scaling relation.\textsuperscript{105} A regime combining multiple levels of theoretical computations with machine learning was developed to study the copper nanoparticle with large size of 10 nm, and *OCCOH intermediate was shown to be a more accurate descriptor for C$_2$+ selectivity than *CO.\textsuperscript{106} Guo and colleagues reported that the gradient boosting regression algorithm is verified as the most desirable model for investigating single-atom and dual-metal-sites catalysts for CO$_2$RR, and
Ag-MoPc is identified as the most active with a limiting potential of $-0.33\,\text{V}$.\cite{Wang2019} Wang and colleagues collected experimental data to build an additive library for electrochemical deposition of Cu catalysts and analyzed with random intersection tree machine-learning method, and then extracted recipe for the best copper catalyst for different products, which is verified by experiments.\cite{Wang2018} The combination of machine learning and advanced experimental techniques is promising in revealing the CO$_2$RR mechanism and designing novel catalysts.

5 | SUMMARY

The reaction roadmap of CO$_2$RR towards C$_{2+}$ products is reviewed and summarized above. In recent years, rapid progress has been witnessed in mechanistic studies with DFT calculations and in situ/operando spectroscopic characterization, which have already led to breakthroughs in the synthesis of high-performance copper catalysts. The energetic profile of the overall reaction pathway and evidence in FTIR spectroscopy of the key intermediates are laying a substantial foundation for development and research in reducing CO$_2$ to C$_{2+}$ products. However, it should be noted that the post-C–C-bonding steps are less investigated compared to the C–C bonding step. Considering that post-C–C bonding determines the selectivity among various C$_{2+}$ products, more efforts need to be devoted to understanding that. The crystalline facet of catalysts and electrolytes are imposing a significant influence on the catalytic performance through tuning CO adsorption configurations and therefore improving C–C coupling reaction barriers. The specifics in the in situ electrochemical environment, especially the copper chemical state and charge distribution in the electrolyte, have been discussed in detail in this perspective. The combination of theoretical calculations with experiments in the simulation of spectroscopy and machine-learning assisted design of catalysts is also included, which shed light on the mechanism and efficient catalysts. We hope the presented perspective help readers to better understand the CO$_2$RR at the atomic level, which benefits the development of theory for describing the CO$_2$RR towards C$_{2+}$ products, and more intrinsically active catalysts for a profitable practical system for CO$_2$ electrolysis in the future.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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