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Mechanistic insights on CO_2 fixation via electrochemical and photocatalytic reduction

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The electrochemical and photochemical conversion of CO_2 into value-added chemicals and fuels has emerged as a sustainable approach to mitigate climate change and provide renewable energy carriers. Recent advances span heterogeneous and homogeneous catalysts, single- and dual-atom alloys, and MOF-derived materials, each offering unique opportunities to enhance activity, selectivity, and durability. Heterogenized molecular catalysts, such as $\text{Re}^{(I)}$, $\text{Mn}^{(I)}$, and $\text{Ru}^{(II)}$ complexes on TiO_2 , demonstrate site isolation that suppresses dimerization and side reactions, thereby improving product selectivity toward CO, formate, or syngas. Single-atom alloys (SAAs) and dual-atom catalysts (DACs) exploit synergistic electronic and geometric effects to tune the adsorption energies of key intermediates, enabling efficient formation of C_1 and C_{2+} products, including CH_4 , CH_3OH , and ethylene. MOF-derived electrocatalysts offer high surface areas, tunable pore environments, and adjustable active sites, promoting CO_2 adsorption, activation, and multielectron reduction. Photocatalytic systems benefit from optimized light absorption, efficient charge separation, and surface site engineering to drive selective CO_2 reduction under visible light. Integrating mechanistic insights with rational design principles, such as electronic structure modulation, heterogenization, and cooperative bimetallic interactions, provides a framework for developing next-generation CO_2 reduction catalysts with enhanced selectivity, turnover, and durability. This review highlights recent progress and mechanistic understanding.

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1. Introduction

The urgent need to transition from fossil fuels to renewable energy stems from escalating human-driven carbon dioxide



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levels in the atmosphere. To resolve this imbalance, surplus renewable electricity or direct solar energy can be harnessed to convert CO_2 into liquid fuels *via* electrolysis or photolysis.^{1–10} Photocatalytic CO_2 reduction pioneered through semiconductor-based systems uses sunlight to trigger reactions that transform CO_2 into fuels.^{11–15} Meanwhile, electrochemical methods leverage renewable electricity to convert captured CO_2 emissions into industrial feedstocks.^{16–18} Both pathways aim to close the carbon cycle by turning CO_2 into value-added products.^{19–22} Designing catalysts that drive the multi-proton, multi-electron reduction of CO_2 (CO_2RR) is crucial for transforming CO_2 into useful single-carbon compounds, such as formic acid, carbon monoxide, formaldehyde, methanol, and methane. A major obstacle lies in addressing the substantial energy hurdles tied to activating CO_2 , which must be lowered to allow the reaction to proceed efficiently at moderate voltages while maintaining precise control over the desired products.^{23–27}

The enthalpy of formation for carbon dioxide, a nonpolar molecule in which carbon exhibits a +4 oxidation state, is $-394.38 \text{ kJ mol}^{-1}$, reflecting its high thermodynamic stability. Capturing and converting CO_2 generally demands considerable energy input, often involving elevated pressures or catalytic assistance. Current CO_2 fixation strategies primarily include electrochemical,²⁸ thermochemical,^{29–31} photocatalytic^{32–34} and biological^{35–37} approaches. Among these, the thermochemical route typically involves high-temperature hydrogenation processes to enable the transformation and utilization of CO_2 *via* complex multistep reactions.³⁸ However, this method suffers from a low energy utilization rate and achieves a conversion efficiency of merely 0.7–0.8%.³⁹

Photocatalytic chemical fixation stands out due to its mild operating conditions, environmental compatibility, diverse product range, and high yields, making it a highly promising and ideal method.^{40–44} In 1979, Inoue and colleagues reported the use of semiconductor photocatalysts such as TiO_2 , ZnO , GaP , CdS and SiC suspended in CO_2 -saturated water, where CO_2 was successfully reduced under ambient conditions to produce hydrocarbons.⁴⁵ This pioneering work sparked widespread interest in photocatalytic CO_2 conversion. Utilizing solar energy and semiconductor photocatalysts, this approach enables the direct transformation of CO_2 into hydrocarbon fuels at room

temperature and atmospheric pressure. Given the abundance of raw materials and the sustainability of solar energy, this method is considered both environmentally benign and economically viable, offering a potential solution to both environmental pollution and energy shortages. Nevertheless, several challenges must be addressed for future industrial-scale application, particularly enhancing the efficiency of CO_2 fixation under natural sunlight and reducing the cost of photocatalysts and ligands.⁴⁶

In the electrochemical fixation of CO_2 , the primary pathway involves the electrochemical reduction of CO_2 , which predominantly yields short-chain carbon products. Due to the complex nature of this process, which involves multiple electron-transfer steps, a variety of short-chain reduction products are typically formed. However, achieving direct CO_2 reduction on the electrode surface requires the application of a substantial overpotential, which significantly lowers the overall energy utilization efficiency. Many catalysts built from transition metals, which can effectively bind and reduce CO_2 , become electron-rich when in their reduced state. While this property aids in CO_2 activation, it also enhances their tendency to promote the hydrogen evolution reaction (HER) (Fig. 1).^{47–49} Here, protons sourced from water required for CO_2 reduction compete with CO_2 molecules, diverting the reaction toward hydrogen gas production. Additionally, the inherent complexity of CO_2 reduction pathways often leads to a mix of possible outputs, further complicating efforts to steer the selectivity toward a single target product. For example, the complete reduction of CO_2 *via* an $8\text{H}^+/8\text{e}^-$ pathway yields CH_4 , while partial reductions produce intermediates such as CO or HCOOH ($2\text{H}^+/2\text{e}^-$), HCHO ($4\text{H}^+/4\text{e}^-$), or CH_3OH ($6\text{H}^+/6\text{e}^-$), alongside various C_2 and C_3 compounds (Scheme 1).^{50–62}

One-carbon-containing compounds are predominantly sourced from petrochemical feedstocks. It represents a vital economic resource, which motivates ongoing research into catalytic systems capable of converting CO_2 into C_1 -valuable products. Meanwhile, achieving selective CO_2 reduction remains a fundamental challenge. The viable CO_2RR must additionally withstand exposure to oxygen and common industrial byproducts such as sulfur and nitrogen oxides (SO_x or NO_x , respectively). This operational resilience is particularly essential for deploying CO_2 conversion technologies directly at heavy emission facilities which usually consume the fossil fuels. So, integrating such processes without costly CO_2 purification steps could significantly enhance feasibility.⁶³

The electronic structure of CO_2 frontier molecular orbitals serves as a critical guide for engineering effective metal-based catalysts to drive its reduction. This framework facilitates the optimization of the electronic properties of the catalytic metal center and its coordination geometry, thereby promoting CO_2 conversion. Specifically, a metal center with an oxidation state of +1 or 0 and d^8 electron configuration stabilized in a square-pyramidal ligand has been shown to exhibit high efficiency in interacting with and activating the CO_2 molecule (Fig. 2). This is achieved through synergistic orbital interactions. The filled d_{z^2} orbital engages in σ -bonding, while the $d_{x^2-y^2}$ orbitals enable π back-bonding, collectively weakening the $\text{C}=\text{O}$ bonds to drive reduction.^{63,64}



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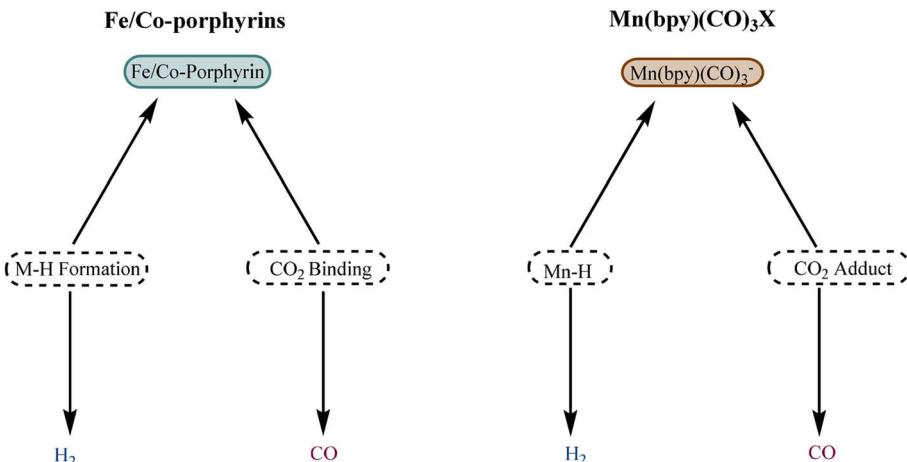


Fig. 1 CO₂ binding modulates the reaction pathways and facilitates the HER.

CO ₂ (aq) + e ⁻	→	CO [•] (aq)	E° = -1.90 V (1)
CO ₂ (g) + 2H ⁺ + 2e ⁻	→	CO(g) + 2H ₂ O	E° = -0.52 V (2)
CO ₂ (g) + 2H ⁺ + 2e ⁻	→	HCOOH(aq)	E° = -0.6 V (3)
CO ₂ (g) + 4H ⁺ + 4e ⁻	→	HCHO(g) + H ₂ O	E° = -0.48 V (4)
CO ₂ (g) + 6H ⁺ + 6e ⁻	→	CH ₃ OH(aq) + H ₂ O	E° = -0.38 V (5)
CO ₂ (g) + 8H ⁺ + 8e ⁻	→	CH ₄ (g) + 2H ₂ O	E° = -0.24 V (6)
2H ⁺ (aq) + 2e ⁻	→	H ₂ (g)	E° = 0 V (7)
O ₂ (g) + 4H ⁺ + 4e ⁻	→	2H ₂ O	E° = 0.82 V (8)

Scheme 1 Summary of half-cell reactions.

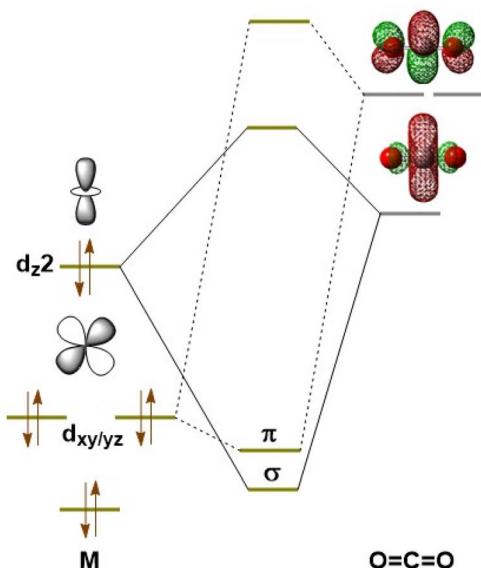


Fig. 2 Bonding between CO₂ and a d⁸ metallic orbital.

Researchers have successfully engineered a range of high-performance catalysts tailored for converting carbon dioxide efficiently and with precise control.^{65,66} Recent approaches

include incorporating functional groups that act as hydrogen bond donors, local proton donors, or positively charged moieties to boost the catalytic performance.^{67–74} The environment in the second sphere has led to a significantly higher rate of CO₂RR.^{75–78} Enhancing selectivity has been achieved by stabilizing reaction intermediates through hydrogen bonding and controlled proton transfer.^{75–77,79} Photocatalytic and electrocatalytic CO₂ reduction are two key methods for converting CO₂ into useful products. Photocatalysis harnesses solar energy, where semiconductors absorb light, generating electron–hole pairs that drive redox reactions on the surface. It operates under mild conditions but is limited by narrow light absorption, fast carrier recombination, and slow surface kinetics. Electrocatalysis uses an external electric field to drive CO₂ reduction at the cathode and oxidation at the anode, requiring conductive, corrosion-resistant materials with active sites. It offers faster rates and greater control. Photocatalytic systems need efficient light-transmitting reactors but face design trade-offs, while electrocatalytic systems depend on optimized electrodes, electrolytes, and membranes. Although photocatalysis has lower material costs, its low efficiency raises hydrogen production costs, whereas electrocatalysis, while efficient, requires affordable renewable electricity for sustainability.⁶¹

Reported review articles relatively tend to focus either on mechanistic details or specific factors affecting photocatalytic or electrochemical CO₂ reduction. Some reports highlight surface-science approaches such as MOF-based single-atom and dual-atom catalysts to improve C–C coupling and selectively produce valuable C₂₊ products *via* catalyst design, crystal surface control, and bimetallic systems. In contrast, this article delves into mechanistic insights of CO₂ photochemical and electrochemical reduction, emphasizing the electronic structure, spin states, and ligand design in directing product selectivity. It also presents molecular-level perspectives and introduces MIOM hybrid systems to address challenges related to efficiency and stability. Together, these studies demonstrate the importance of integrating a mechanistic understanding with advanced catalyst and system design to enable practical



CO₂ conversion technologies. This review specifically focuses on the fundamental mechanistic principles governing catalytic CO₂ reduction, examining how key intermediates are identified and characterized through spectroscopic and electrochemical techniques, revealing the influence of their electronic structures on the catalytic performance. The literature covered in this article spans published reports up to March 2025.

2. Electrochemical CO₂RR

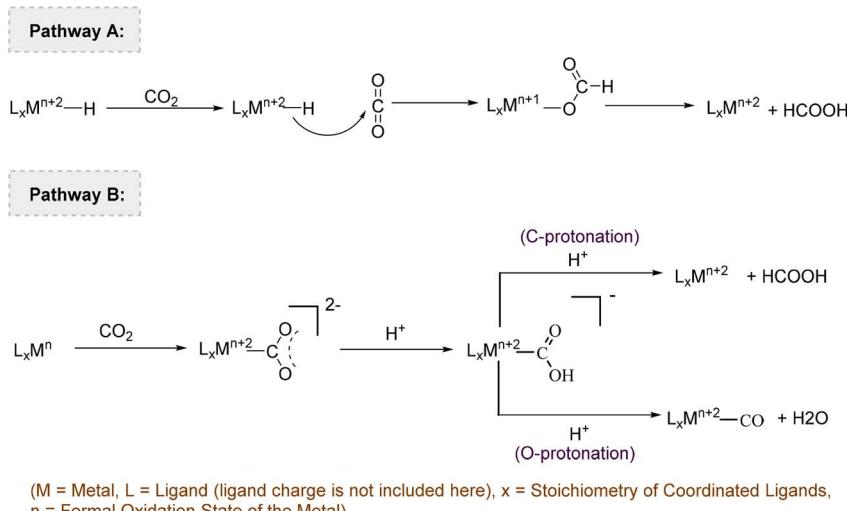
Carbon dioxide behaves as an amphoteric compound, with its carbon atom acting as a Lewis acid and its oxygen atoms functioning as Lewis bases. Its electron affinity is approximately -0.66 eV.⁸⁰⁻⁸⁴ With a first ionization potential around 13.8 eV, CO₂ is more inclined to accept electrons than to donate them. This characteristic plays a key role in CO₂RR, where the electrophilic carbon atom is more reactive than the mildly nucleophilic oxygen atoms. CO₂ reduction generally follows one of two primary pathways, one of which involves insertion into a metal-hydride bond (pathway A) or binding directly to the catalyst metal center (pathway B) (Scheme 2).

2.1. CO₂ binding

The first step in CO₂ activation typically involves a nucleophilic attack by an electron-rich metal center on the electrophilic carbon of the CO₂ molecule (Scheme 2; Pathway B). In the CO₂ molecule, the highest occupied molecular orbital (HOMO) is primarily localized on the more electronegative oxygen atoms. The lowest unoccupied molecular orbital (LUMO) is a C–O σ^* antibonding orbital with substantial electron density concentrated on the carbon atom. Additionally, the next set of unoccupied orbitals (LUMO+1) consists of degenerate C–O π^* orbitals both in plane and out of the plane (Fig. 1). To enable CO₂ reduction, electrons usually donated from the metal orbitals of the catalyst must fill the σ^* and π^* orbitals of the CO₂ molecule. Successful activation relies on the presence of

filled d_{z²} and d_{xz/yz} orbitals at the metal center that are well-suited to interact with the target CO₂ orbitals. Many complexes featuring a tetragonal ligand environment and d⁸ configuration (Co⁺, Fe⁰ and Ni²⁺) meet these criteria. Catalytic activity is also possible with species that have a half-filled d_{z²} orbital, including Co²⁺ and Fe⁺. Transition metal complexes from the second and third rows can exhibit similar behavior.^{64,85} The interactions between metal complexes and CO₂, along with their binding constants, can be evaluated using cyclic voltammetry. When CO₂ quickly associates with a metal center during its reduction, a noticeable shift in the faradaic signal is often observed. However, in some cases, no such shift is observed. This can occur if the reduced metal species either does not react with CO₂ within the timescale of the CV experiment, or if the CO₂ binding affinity is too weak to produce a detectable change.⁸⁶

Numerous M–CO₂ complexes have been documented in organometallic studies. Although these compounds may not directly participate in catalytic CO₂ reduction, they offer valuable insight into the spectroscopic characteristics typically associated with M–CO₂ bonding. M–CO₂ adducts are commonly analyzed using vibrational spectroscopy, as these species contain a prominent C=O chromophore that typically absorbs in the 1500–1800 cm⁻¹ range of the near-infrared spectrum.^{86–90} At -95 °C, these M–CO₂ complexes were formed through chemical methods by introducing CO₂ into a solution of Fe⁽⁰⁾ porphyrin. A transient intermediate was observed under these conditions, exhibiting a half-life of less than 30 seconds at -95 °C, as identified by resonance Raman spectroscopy (Fig. 3A).⁵⁰ The C–Fe stretching vibration and OCO bending mode appeared at 590 cm⁻¹ and 806 cm⁻¹, respectively. Both signals shifted to lower frequencies when ¹³C-labeled CO₂ was used. Notably, the δ_{OCO} bending frequency closely matches the values typically seen when CO₂ is coordinated to metal surfaces.⁹¹ Shifts were detected in the ν_4 and ν_2 bands of the porphyrin ligand, which are sensitive indicators of the metal oxidation and



Scheme 2 Proposed routes for CO₂ reduction reactions.



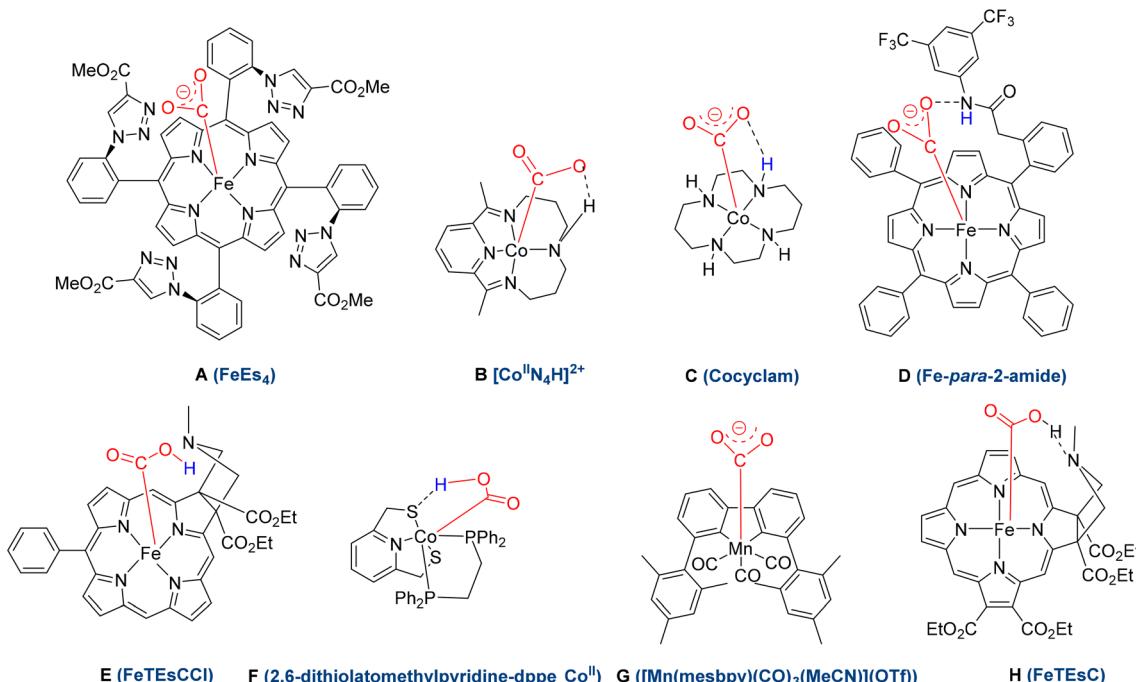


Fig. 3 Spectroscopically identified metal–COOH or metal–CO₂ intermediates participating in CO₂ reduction reactions.

spin states, confirming that CO₂ binding converted Fe⁽⁰⁾ to Fe^(II). This corresponds to a 2-electron reduction of CO₂, producing an electronic configuration of Fe^(II)–CO₂²⁻. A CoI–CO₂ intermediate has also been briefly detected during the photocatalytic reduction of CO₂ using a cobalt macrocycle, showing a CO stretching frequency at 1670 cm⁻¹ (Fig. 3B).⁹² In a separate study, a CoI–CO₂ adduct was identified through FTIR spectroscopy, with a CO₂ stretching frequency observed at 1544 cm⁻¹ (Fig. 3C).

X-ray absorption spectroscopy results provided confirmation that Co^(I) is oxidized to Co^(III) when CO₂ is bound. A notable shift of the absorption edge to higher energy in the CO₂-bound Co^(I) species pointed to the formation of a CO₂²⁻-bound Co^(III) species, which results from the transfer of 2e⁻ from the cobalt center to the coordinated carbon dioxide molecule.⁸⁶ CO₂ binding is enhanced when the extra negative charge is stabilized by a nearby Lewis acidic metal center, as well as through electrostatic interactions and hydrogen bonding.^{93,94} A recent study emphasized the importance of placing second-sphere donors. Positional isomers, *ortho* or *para* with pendant amide groups, are located either close to or farther from the active site. The study revealed that placing second-sphere donor groups at the *ortho* position, while maintaining a greater distance between the hydrogen bond donor and the metal center, markedly improves the rate of CO₂ reduction. This distal *ortho* arrangement allows the molecule to adopt a shape that promotes H-bonding and eases H⁺ transfer to the metal–CO₂ complex (Fig. 3D).⁹⁵ Recently, the Dey group reported an iron chlorin species featuring a pendant amine group in its secondary coordination sphere (Fig. 3H), which typically catalyzes CO₂ reduction to formic acid with low overpotential from its Fe^(I) state, which is also capable of driving CO₂ reduction

from its Fe⁽⁰⁾ state, producing methanol as the primary product with a faradaic efficiency of about 50%.⁹⁶ The Zhang group validated Dey's findings through computational studies. Their calculations are in good agreement with experimental observations that the formal Fe^(I)-porphyrin would directly bind with a CO₂ molecule to trigger a 2e⁻ reduction of CO₂. The unusual behavior could be ascribed to the significant hydrogen bonding and through-space electrostatic attractions between the cationic N–H terminal and the CO₂-adduct. The electronic structure of the formal Fe^(I)-porphyrin should be better demonstrated as Fe^(II)-Por⁻, which incorporates a ferrous center and a 1e⁻ reduced porphyrin ligand. The key Fe^(III)–COOH and Fe^(II)–COOH intermediates were investigated, which demonstrated that the cationic N–H would generate an H-bond with the O-terminal of the carbonyl of the COOH moiety. The significant H-bonds, as well as through-space electrostatic attraction, would facilitate the subsequent C-protonation to yield HCOOH. In addition, the cationic N–H terminal is found to hinder the dissociation of CO. The computational results adequately elucidate the origins of HCOOH selectivity over CO, and, more importantly, provide an insightful mechanistic understanding of the cooperative roles of second-sphere hydrogen bonding and cationic effects.⁹⁷

Enhanced electrochemical CO₂ reduction observed with iron porphyrins bearing H-bonding functionalities is attributed to the stabilization of the CO₂-bound intermediate through a combination of electrostatic interactions and H-bonding, as supported by DFT studies. When CO₂ binds to the reduced state, it forms an Mn²⁺–CO₂²⁻ intermediate. This species, due to its high basicity, is easily protonated by weak acids, leading to the formation of a metal carboxylate complex. The initial protonation step is particularly favorable, as the Mn²⁺–CO₂²⁻

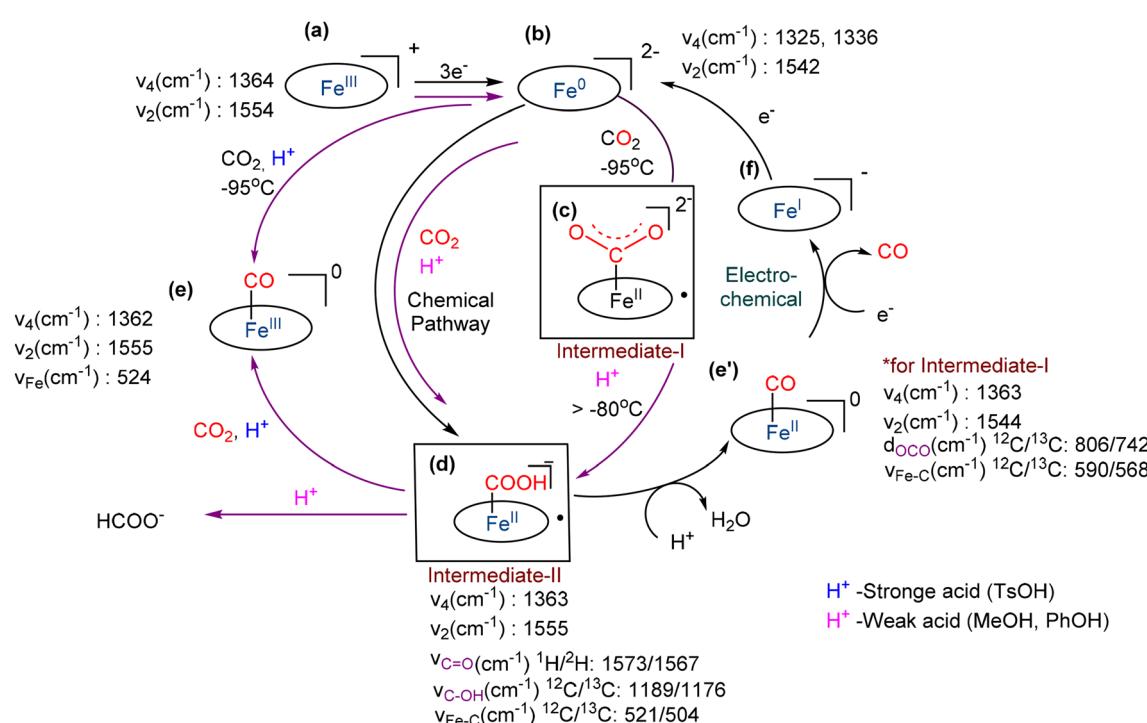


intermediate has a pK_a higher than that of methanol, making it highly susceptible to proton transfer. An example of this behavior is observed with the $\text{Fe}^{2+}\text{-CO}_2^{2-}$ complex. The enhanced rate of electrochemical CO_2 reduction observed with iron porphyrins that contain hydrogen-bonding groups is believed to stem from the stabilization of the CO_2 -bound intermediate. This stabilization arises through hydrogen bonding and electrostatic interactions, as suggested by DFT studies. When CO_2 binds to the reduced metal center (Mn), it forms a $\text{Mn}^{2+}\text{-CO}_2^{2-}$ complex. Due to the high basicity of this intermediate (with a pK_a higher than that of methanol), it readily undergoes protonation by weak acids, producing a metal-carboxylate species.

This initial protonation step is particularly favorable because of the strong basic character of the $\text{Mn}^{2+}\text{-CO}_2^{2-}$ species. For instance, in reactions where CO_2 is captured by an $\text{Fe}^{(0)}$ -porphyrin complex, an $\text{Fe}^{(II)}\text{-CO}_2^{2-}$ intermediate forms and is easily protonated by mild acids such as methanol or phenol. This yields an $\text{Fe}^{(II)}\text{-COOH}$ species which can be identified by characteristic vibrational markers, specifically the porphyrin ν_4 and ν_2 bands, which indicate a low-spin $\text{Fe}^{(II)}$ state. Additional spectroscopic signals include a C-OH stretch at 1189 cm^{-1} , a C=O stretch at 1573 cm^{-1} , and Fe-C stretch at 521 cm^{-1} . These assignments are confirmed through isotopic labeling with ^{13}C and ^2H . Among the steps in this CO_2 reduction process, the final protonation leading to carbon monoxide formation is the slowest under the studied conditions. The low-spin COOH-containing $\text{Fe}^{(II)}$ complex (Scheme 3d) undergoes C-hydroxyl bond breakage to generate the CO-bound $\text{Fe}^{(II)}$ species (Scheme 3e). A comparable process has been proposed for the electrochemical reduction of CO_2 using iron porphyrins. In this

pathway, the Fe-COOH intermediate is thought to undergo a concerted proton-electron transfer bond cleavage (CPETBC). This step involves proton transfer from a donor in the reaction medium, simultaneous electron transfer from the metal center, and cleavage of one of the C-O bonds. This CPETBC step is believed to be the rate-limiting stage in the overall homogeneous CO_2 electroreduction process (Scheme 3d to e').⁵⁰

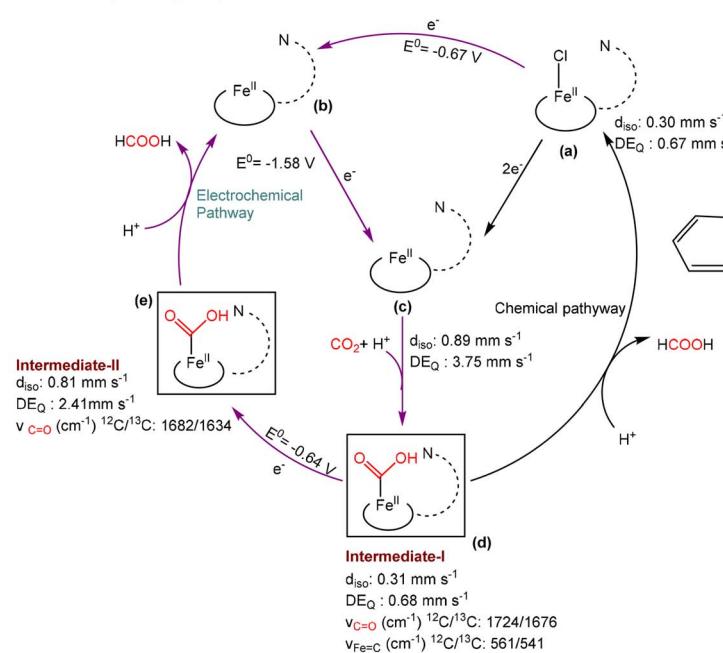
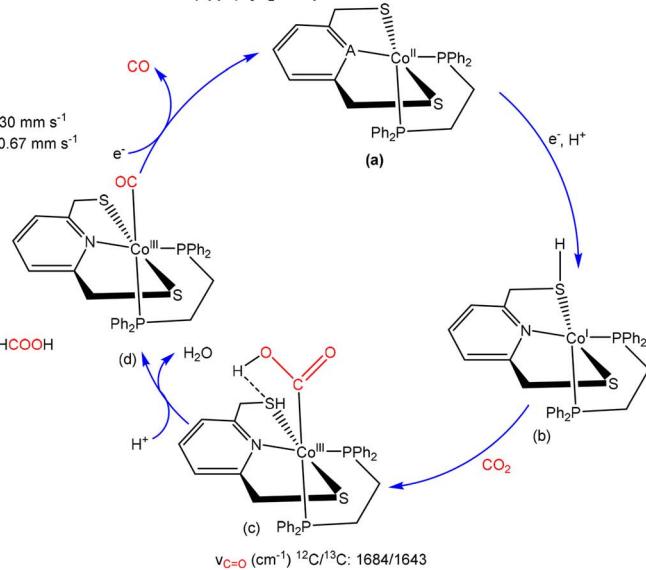
In the FeTEsCCl iron chlorin complex which contains a secondary H^+ transfer site (Scheme 4A(a)), CO_2 reduction and activation proceed from the $\text{Fe}^{(I)}$ oxidation state (Scheme 4A(c)), while the $\text{Fe}^{(0)}$ state is typically responsible for reactivity in iron porphyrin systems. Simultaneous binding of CO_2 and a proton to $\text{Fe}^{(I)}\text{TEsCl}$ leads to the formation of the COOH-containing $\text{Fe}^{(III)}$ intermediate (Int-I; Scheme 4A(d)). Mössbauer spectroscopy reveals that this species has $\Delta E_q = 0.68\text{ mm s}^{-1}$ and $\delta_{\text{iso}} = 0.31\text{ mm s}^{-1}$, closely matching the values for the initial $\text{Fe}^{(III)}\text{-Cl}$ complex ($\Delta E_q = 0.67\text{ mm s}^{-1}$, $\delta_{\text{iso}} = 0.30\text{ mm s}^{-1}$), which is consistent with a high-spin ferric state ($S = 5/2$). Vibrational spectroscopy identifies C=O and Fe-C stretching bands at 1724 cm^{-1} and 561 cm^{-1} , respectively, with ^{13}C labeling confirming these assignments. This COOH-containing $\text{Fe}^{(III)}$ intermediate is reduced by one electron either through chemical means or electrochemically at $E_0 = -0.64\text{ V vs. Fc}^{+/0}$ to produce the COOH-containing $\text{Fe}^{(II)}$ species (Int-II; Scheme 4A(e)). Mössbauer spectroscopy of the reduced complex shows $\Delta E_q = 2.41\text{ mm s}^{-1}$ and $\delta_{\text{iso}} = 0.81\text{ mm s}^{-1}$, which is consistent with a high-spin $\text{Fe}^{(II)}$ ground state ($S = 2$). The C=O stretching frequency shifts to 1682 cm^{-1} , which is lower than the 1724 cm^{-1} observed for the COOH-containing $\text{Fe}^{(III)}$ species. This suggests that the $\text{Fe}^{(II)}$ center donates more electron density into the CO π^* orbital. The $\text{Fe}^{(II)}$ species containing



Scheme 3 Mechanistic pathway for CO_2 reduction using the Fe-catalyzed porphyrins.



A. Fe-Chlorin (FeTEsCl) Complex

B. Co(dppe)PyS₂ ComplexScheme 4 Suggested catalytic pathway for CO_2 reduction.

a COOH group is also detected during *in situ* FTIR spectroelectrochemical experiments, suggesting that its decomposition represents the rate-determining step in the catalytic cycle (Scheme 4A(e)). Ultimately, cleavage of the Fe–C bond leads to the formation of formic acid⁵³ in the Co(dppe)PyS₂ species, which was modeled after the active part of the enzymes (Ni–CODH) (Scheme 4B(a)). The reduction of CO_2 is initiated with the protonation of the metal-bound thiolate, which occurs alongside the reduction of the cobalt center from Co^{II} to Co^{I} (Scheme 4B, step a to b). CO_2 then binds to the reduced Co^{I} center, forming a COOH-containing Co^{III} species (Scheme 4B(c)). This species shows a C=O stretching frequency at 1684 cm^{-1} which shifts to 1643 cm^{-1} when $^{13}\text{CO}_2$ is used, confirming the identity of the CO_2 -derived ligand. DFT calculations support this assignment and indicate that the electronic configuration corresponds to a low-spin ($S = 0$) COOH-containing Co^{III} intermediate. This intermediate eventually undergoes cleavage of the COH bond, releasing CO as the final product (Scheme 4B(d)).

2.2. Effect of hydrogen bonding

Recently, it has been investigated how internal and external Brønsted acids with varying $\text{p}K_a$ values influence catalytic performance. Interestingly, the most effective catalysts contained internal groups with relatively weak acidity. Overall, the optimization of CO_2 reduction by porphyrin-based catalysts involves careful consideration of solvent hydrogen bonding, the spatial arrangement of internal H-bond donors, and the interplay between the $\text{p}K_a$ values of both internal and external acid sources.^{98–101} Iron porphyrin complexes, including FePf (A), FeTDHPP (B), FeEs₄ (C), and Fe(^tBu)₄ (D), were studied to

investigate how second-sphere donors influence the kinetics of CO_2 reduction and hydrogen bonding. These complexes varied in the design of their distal framework or outer coordination environment. In FePf, the amide group serves as a relatively weak hydrogen bond donor (CON-H $\text{p}K_a = 22$ in CH_3CN) compared to the phenolic OH group in FeTDHPP, which has a higher $\text{p}K_a$ of 29.14 in CH_3CN , indicating stronger hydrogen bonding ability. The large pivaloyl group in FePf creates a hydrophobic setting around the active site. On the other hand, FeEs₄ features a hydrophilic environment near the catalytic center, resulting from the presence of four triazole units that help retain water molecules. The Fe(^tBu)₄ complex exhibits an amphiphilic local environment, characterized by hydrophilic triazole groups adjacent to the active site and a hydrophobic periphery formed by the *tert*-butyl ligands (Fig. 4).

Dey and coworkers performed a systematic study of the influence of electrostatic interactions and hydrogen-bonding substituents at the *ortho* position of the mesophenyl groups in an iron tetraphenylporphyrin, revealing that both play a significant role in enhancing the reduction selectivity of CO_2 . The effect of hydrogen bonding becomes stronger with increasing water concentration as water facilitates these interactions. In contrast, the impact of electrostatic interactions diminishes at higher water levels because solvation of the cationic groups alters the microsolvation environment around the active site, promoting proton reduction to H_2 over CO_2 reduction. These findings emphasize an important distinction between electrostatic interactions and hydrogen-bonding in controlling electrochemical CO_2 reduction selectivity depending on water content, highlighting the need to consider such factors when designing practical CO_2 reduction systems that use water as a sustainable proton source.¹⁰² Using phenol as the



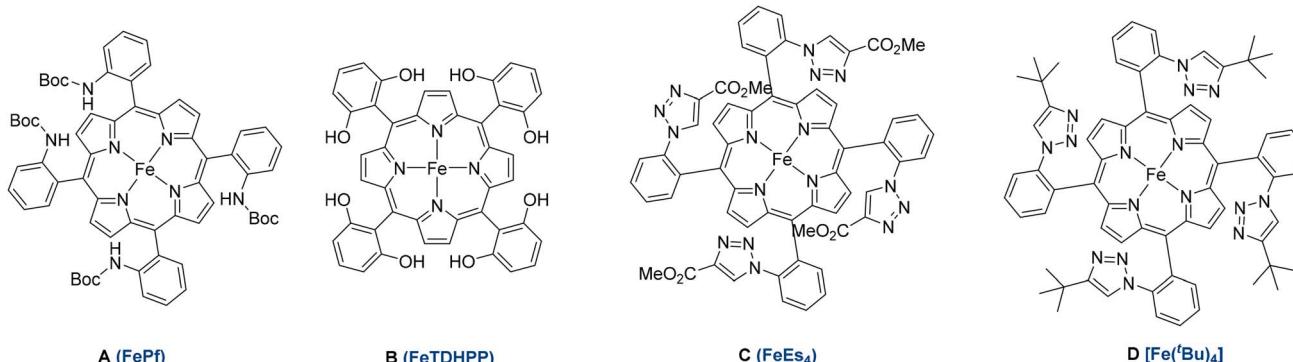


Fig. 4 Iron porphyrin complexes examined to evaluate the second-sphere interactions.

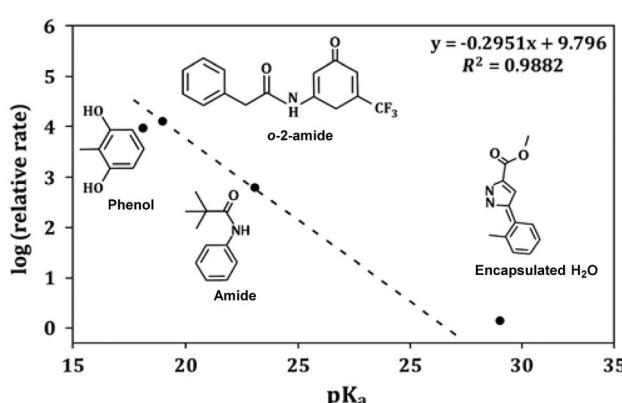
external H⁺ donor, the FePf demonstrated the fastest reaction rate attributed to the stabilization of the intermediate Fe^(II)-COO²⁻ by favorably aligned amide dipoles. Across these complexes, a fourfold dependence on the PhOH concentration was observed, and a clear relationship was established between the CO₂ reduction rates and the pK_a values of the H-bonding groups in various iron porphyrin systems; however, it might seem intuitive to attribute the improved CO₂ reduction rates mainly to hydrogen-bonding stabilization (Fig. 5).¹⁰³

The observed correlation was supported by DFT calculations, which suggested that electrostatic effects also play a key role by stabilizing the electron density transfer to the coordinated CO₂ during activation. This conclusion aligns with previous findings from the Savéant, Nippe, Aukauloo and Mayer groups, all of which reported increased catalytic activity upon incorporating cationic groups near the catalytic center (Fig. 6).^{68-71,104} In summary, amine, pyridine, imidazole, guanidine, phenol, amide, urea, thiourea, ester and ether groups have been utilized as the hydrogen-bond donor in the second coordination sphere of Fe, Re, Mn, Co and other transition-metal-based complexes. The hydrogen-bond interaction can assist catalyst molecules in adsorbing CO₂ and stabilizing the intermediates of the CO₂ reduction, thereby improving the catalytic activity and product selectivity of electrocatalytic CO₂RR. By adjusting the positioning accuracy and strength of the hydrogen-bond interaction

through appropriate structural modification in the second coordination sphere, transition-metal complexes show anticipated potential for homogeneous electrocatalytic CO₂ reduction (Scheme 5).⁹⁸ Furthermore, hydrogen-bond interaction and proton concentration may work together to regulate the reduction pathway, so they change the selectivity and catalytic activity of the product. For instance, the intermediate M-COOH is usually formed during the CO₂ reduction reaction and the protonation on the M-COOH could affect the type of reduction products. CO is formed after the protonation of the O-center, whereas HCOOH is released after the protonation of the C-center. The protonation process can be determined by the pK_a values of the C or O centers and the hydrogen-bond interaction, which also provides a new idea for regulating the types of CO₂ reduction products.¹⁰⁵⁻¹⁰⁷

2.3. Divergence point between CO and HCOOH formation

Spectroscopic evidence provides a basis for developing a molecular orbital diagram of the metal-COOH complex. The carboxylate HOMO originates from an sp² carbon and can form σ -type bonds with the metal d_{z²} orbital. Meanwhile, the carboxylate unoccupied LUMO is a C-O π^* orbital capable of accepting electron density from the metal-filled d_{xz} and d_{yz} orbitals via π back-donation (Fig. 7). The subsequent reactivity of this metal-carboxylate intermediate plays a crucial role in determining the selectivity of the two-electron, two-proton CO₂ reduction, directing the pathway toward either formic acid or carbon monoxide production. Protonation at the oxygen atom leads to CO release along with water elimination, whereas protonation at the carbon atom yields HCOOH. This selectivity can be influenced by tuning the pK_a values of the oxygen or carbon centers, which are governed by the nature of their bonding interactions. A strong C-Fe σ bond withdraws electron density from the carbon atom, thereby increasing the protonation susceptibility of the oxygen atom and facilitating C-O bond cleavage, which leads to CO formation. In contrast, a weaker C-Fe σ bond results in greater electron density on the carbon, favoring protonation at the carbon site and promoting the formation of formic acid. Additionally, significant d π to C=O π^* back-donation enhances electron density in the π^* orbital, primarily located on the oxygen atom, making it more

Fig. 5 Relative rate vs. pK_a.

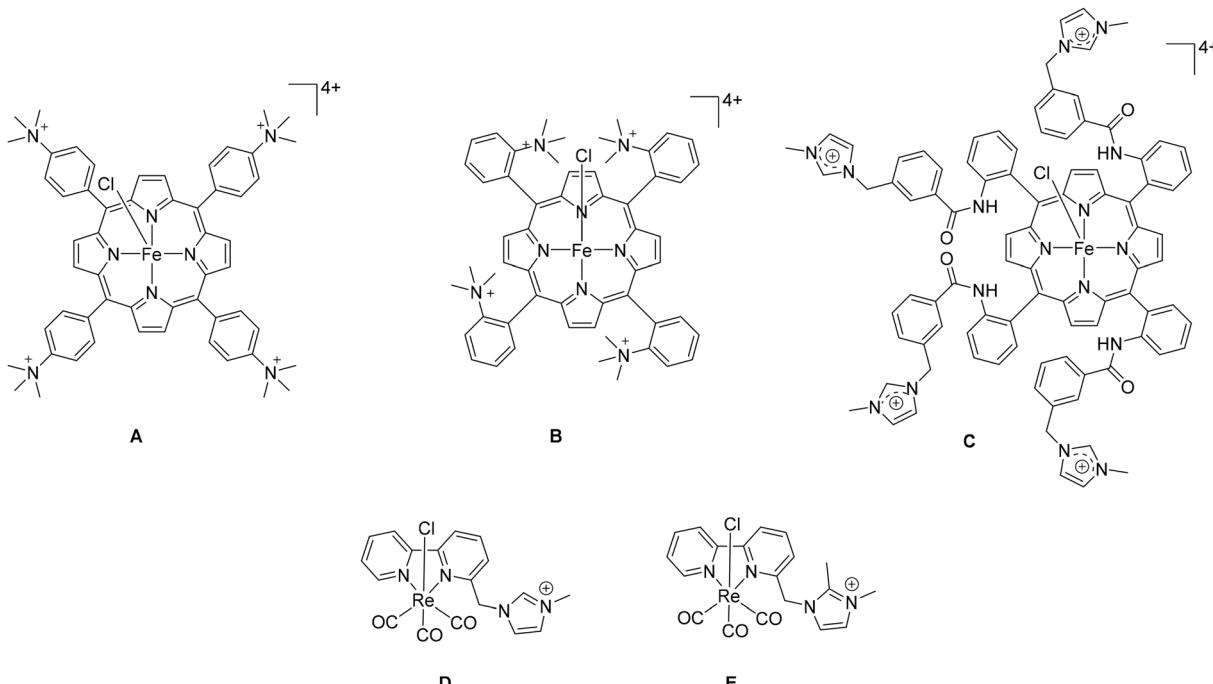
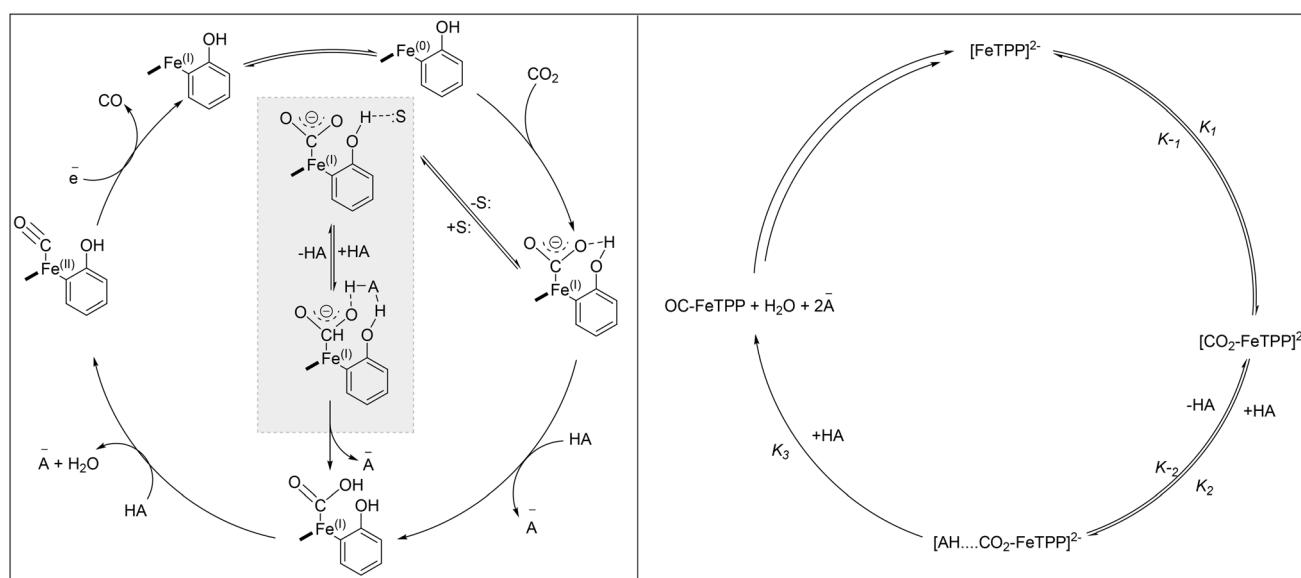


Fig. 6 Catalysts showing improved reaction rates when cationic groups are incorporated into the ligand framework.



Scheme 5 Iron porphyrin-mediated CO_2 reduction mechanism assisted by H-bonding.

prone to protonation and further encouraging cleavage of the C–O bond. However, C–M σ bonding typically plays a more dominant role in defining the C–M interaction, as evidenced by observations in Fe–O₂ complexes.⁷⁰ In the context of CO_2 reduction, the bonding interactions within the M–COOH intermediate are notably influenced by the effective nuclear charge (Z_{eff}), which itself is governed by the metal center spin state (Δ°). Low-spin configurations typically result in a greater population of d π orbitals, enhancing π back-donation to the

C=O π^* orbital. This increases the electron density on the oxygen atom, promoting protonation at the O-site and favoring C–O bond cleavage, ultimately leading to CO formation. Conversely, high-spin states which limit π back-donation tend to favor protonation at the carbon center, resulting in HCOOH production. These insights underscore the critical role of the spin state in dictating the product selectivity of the CO_2 reduction pathway.

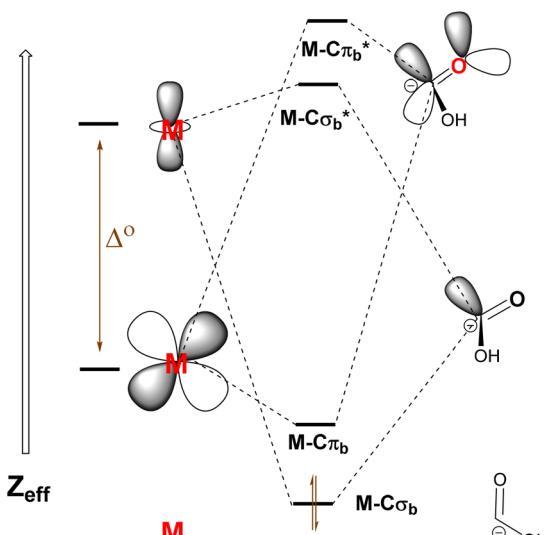


Fig. 7 Illustrative MO diagram of the M-COOH species depicting principal bonding interactions.

For the COOH-containing $\text{Co}^{(\text{III})}$ intermediate formed by the $\text{Co}(\text{dppe})\text{PyS}_2$ complex, the low-spin t_2^6 electronic configuration leads to a highly covalent $\text{Co}^{(\text{III})}$ –carbon bond. DFT studies also suggested that this strong covalent interaction effectively withdraws charge density from the carbon atom. As a result, the electron-deficient carbon enhances the electrophilicity of the oxygen site that favors its protonation. This pathway facilitates C–O bond cleavage and ultimately promotes the selective release of CO.¹⁰⁸ The impact of the spin state on the product selectivity is evident when comparing the COOH-bound $\text{Fe}^{(\text{II})}$ intermediates in iron chlorin and iron porphyrin complexes. For iron porphyrins such as FeEs_4 , resonance Raman studies confirm a low-spin $\text{Fe}^{(\text{II})}$ ground state, which aligns with the selective two-electron, two-proton electrochemical reduction of CO_2 to CO involving C–O bond cleavage through oxygen protonation. Conversely, the COOH-bound $\text{Fe}^{(\text{II})}$ intermediate from the iron chlorin complex (Fig. 3e) exhibits a high-spin configuration and exclusively produces HCOOH. While the presence of hydrogen-bonding groups or second-sphere proton-transfer influences the outcome, the spin state also plays a pivotal role when considered through the lens of molecular orbital theory. The low-spin metal carboxylic intermediates favor CO release, whereas the high-spin carboxylic intermediates species promote HCOOH formation.

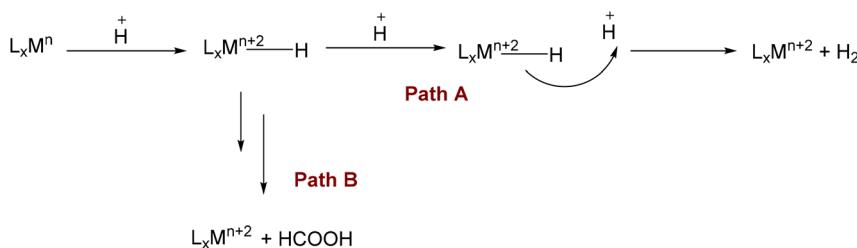
The recent finding that iron tetraphenylporphyrin produces HCOOH and not CO from CO_2 when an amine ligand binds opposite the CO_2 might be due to a change in spin state caused by the strong σ -donor ligand binding.¹⁰⁹ A distinctive pentadentate azamacrocyclic ligand framework exhibits a shift in product selectivity from CO to HCOOH when the metal center is changed from cobalt(II) to iron(II).¹¹⁰ CO_2 coordination to a formal $\text{Co}^{(0)}$ complex results in the formation of a putative COOH-bound $\text{Co}^{(\text{II})}$ intermediate. Conversely, when CO_2 interacts with a formal $\text{Fe}^{(\text{I})}$ species, it gives rise to a proposed COOH-bound $\text{Fe}^{(\text{III})}$ intermediate. In the case of cobalt, strong π back-

donation from the $\text{Co}^{(\text{II})}$ center into the π^* orbitals of CO_2 is believed to weaken the C–O bond, thereby favoring the generation of CO. On the other hand, weaker π back-bonding from the $\text{Fe}^{(\text{III})}$ center keeps the C–O bond strong and results in a low charge density on the oxygen atom. The Lou team performed kinetic and product determinations of the reaction of the simplest Criegee intermediate CH_2OO with HCHO by employing the highly flexible mid-infrared comb lasers and synchronized two-color time-resolved dual-comb spectroscopy. The bimolecular rate coefficients for the reaction $\text{CH}_2\text{OO} + \text{HCHO}$ were evaluated over the temperature range of 268.6 to 336.5 K at a total pressure of 6.4 to 56.0 torr.¹¹¹ Alternatively, the introduction of strategically positioned H^+ transfer sites has been demonstrated to enhance the selective reduction of CO_2 to CO in iron porphyrins, cobalt azacalix-pyridyl systems and metal bipyridine complexes (Fig. 3 and 4).^{64,103,112–114} While the exact role of spin state in determining selectivity in these systems still needs further investigation, it is probable that the strong equatorial ligand fields in porphyrin and azacalix-pyridyl complexes stabilize low-spin metal-COOH intermediates, leading to the selective formation of CO. In summary, factors such as spin state, back-bonding and the surrounding second-sphere environment can influence the pK_a values of the carbon and oxygen atoms in metal-COOH intermediates. Further investigation is required to identify which factors predominantly influence the structure of these intermediates and ultimately govern the selectivity of the two-electron, two-proton CO_2 reduction process. The key reaction intermediates for CO_2 conversion to CO and HCOOH are $^*\text{COOH}$ and $^*\text{OCHO}$, respectively, although the adsorption structure (e.g., monodentate, bidentate) has not been definitively determined. Furthermore, the competition between the CO and HCOOH pathways has generally been attributed to differences in the reaction energy barriers for forming $^*\text{COOH}$ and $^*\text{OCHO}$, with some studies suggesting that $^*\text{H}$ adsorption also plays a significant role. Beyond thermodynamic factors, recent research indicates that reaction kinetics are crucial in influencing product distribution. Moreover, an accurate description of the CO_2RR mechanism requires consideration not only of internal factors (e.g., binding energy, reorganization energy), but also external factors (e.g., pH, applied potential, and metal cations in the electrolyte). These mechanistic insights and recent studies on catalysts with tunable selectivity toward CO and HCOOH demonstrate how variations in the structure, oxidation state, composition, and coordination environment can direct a metal's selectivity between these two products.^{115–117}

2.4. Divergence between CO_2 reduction and hydrogen evolution

Metal centers capable of binding and reducing CO_2 are typically electron-rich, which often results in proton reduction competing with the CO_2RR . When protonation occurs at an metal center, it generates an $\text{M}^{n+2}–\text{H}$ intermediate that can react either with CO_2 or with protons (Scheme 6). The reaction with protons may proceed more readily, favoring hydrogen evolution as the primary outcome. In contrast, insertion of CO_2 into the



Scheme 6 Competing reactivity: CO_2 vs. proton reduction.

metal–hydride bond (pathway B) leads selectively to the formation of formic acid.^{118,119} The hydricity of the metal–hydride species is a key factor influencing both the thermodynamic and kinetic aspects of this competing process.^{120,121} The challenge of competing the HER can be addressed by strategies that enhance CO_2 coordination at the metal center, while steering protonation toward the ligand, thus avoiding protonation at the metal itself. This approach involves adjusting the metal electronic properties to lower its basicity and incorporating an electron-rich ligand framework. For example, in Ni-cyclam and Fe-chlorin complexes, CO_2 binds to the metal center in a formal +1 oxidation state rather than the zero-oxidation state. This oxidation state preference reduces the tendency for protonation at the metal, and thus lowers the chance of competing hydrogen evolution reaction.^{78,122} A Ni-CODH-inspired ligand featuring an electron-rich thiolate group can act as a preferred site for protonation, thereby inhibiting protonation at the metal center and enabling effective CO_2 coordination. This strategy has recently been demonstrated in two cobalt complexes (Fig. 3f).^{108,123} A positive shift in the metal center's reduction potential reduces the reaction overpotential. Additionally, these protonated moieties enhance the stability of the $\text{Mn}^{2+}-\text{CO}_2^{2-}$ intermediate by facilitating proton transfer, leading to the formation of the $\text{Mn}^{2+}-\text{CO}_2\text{H}$ species.¹²⁴

Another strategy utilizes the reductive disproportionation of CO_2 into CO and CO_3^{2-} , eliminating the need for a H^+ source and enabling selective CO production. This strategy has been successfully applied in various metal phosphine complexes, as well as in manganese–bipyridine systems (Fig. 3g).^{64,66,93,125} Moreover, in their earlier studies, the Yang group focused on how the hydricity of transition metal hydrides varies with solvent and how this influences the thermodynamics of CO_2 reduction to formate (HCO^{2-}). They also demonstrated how hydricity values can inform the design of catalysts for both the HER and CO_2 reduction (CO_2R), establishing a general framework for achieving selective formate production while minimizing undesired H_2 formation. By analyzing kinetic data from proposed catalytic cycles, they identified potential rate-limiting steps in both the HER and CO_2R pathways. To enhance the selectivity for CO_2 reduction, the group also pursued two catalyst design strategies aimed at kinetically suppressing HER: one leveraging electrostatic interaction through charged environments, and the other employing steric hindrance. These strategies, alongside thermodynamic considerations such as hydricity and the free energy profiles of catalytic steps, guided

the development of electrocatalysts capable of reversible CO_2 /formate conversion at low overpotentials. Furthermore, they explored the translation of CO_2 hydrogenation activity from homogeneous catalysis into the realm of electrocatalysis. All of the studied systems utilized classical metal hydrides, where both the electrons and proton reside on the metal center. However, generating hydrides strong enough for CO_2 reduction typically demands highly reducing potentials due to the intrinsic link between the reduction potential, hydricity, and pK_a . In contrast, the enzyme formate dehydrogenase (FDH) demonstrates a different mode of hydride delivery—bidirectional transfer, in which the proton and electrons are spatially separated. This bioinspired mechanism offers a compelling strategy for producing potent hydride donors under milder electrochemical conditions. It presents a new direction for catalyst design, suggesting that hydricity can serve as a powerful tool in addressing longstanding challenges and unlocking new possibilities in catalytic CO_2 conversion.^{126–130}

3. Photocatalytic CO_2RR

Photocatalytic CO_2 reduction methods are grouped as either heterogeneous or homogeneous processes. Heterogeneous approaches predominantly utilize solid photocatalysts like semiconductors or plasmonic metals. As depicted (Fig. 8a), the semiconductor-driven photocatalytic CO_2 reduction mechanism comprises at least three essential steps.^{124,131} Initially, absorption of light with photon energy matching or surpassing the semiconductor's bandgap excites electrons from the valence band maximum (VBM) to the conduction band minimum (CBM), generating holes at the VBM. Subsequently, these photo-generated charge carriers migrate to the catalyst surface, potentially mediated by a cocatalyst. Finally, adsorbed CO_2 undergoes reduction through interaction with the electrons, while adsorbed reductant molecules are oxidized by the holes. Ideally, CO_2 reduction occurs simultaneously with water oxidation or other beneficial oxidation reactions. Crucially, this process must meet two thermodynamic criteria: the reduction half-reaction's redox potential must be less negative (more positive) than the CBM potential, and the oxidation half-reaction's redox potential must be less positive (more negative) than the VBM potential. Scheme 1 lists common CO_2 reduction half-reactions and their apparent standard redox potentials at pH 7. Additionally, effective reaction kinetics necessitate the presence of catalytic sites capable of activating CO_2 molecules.



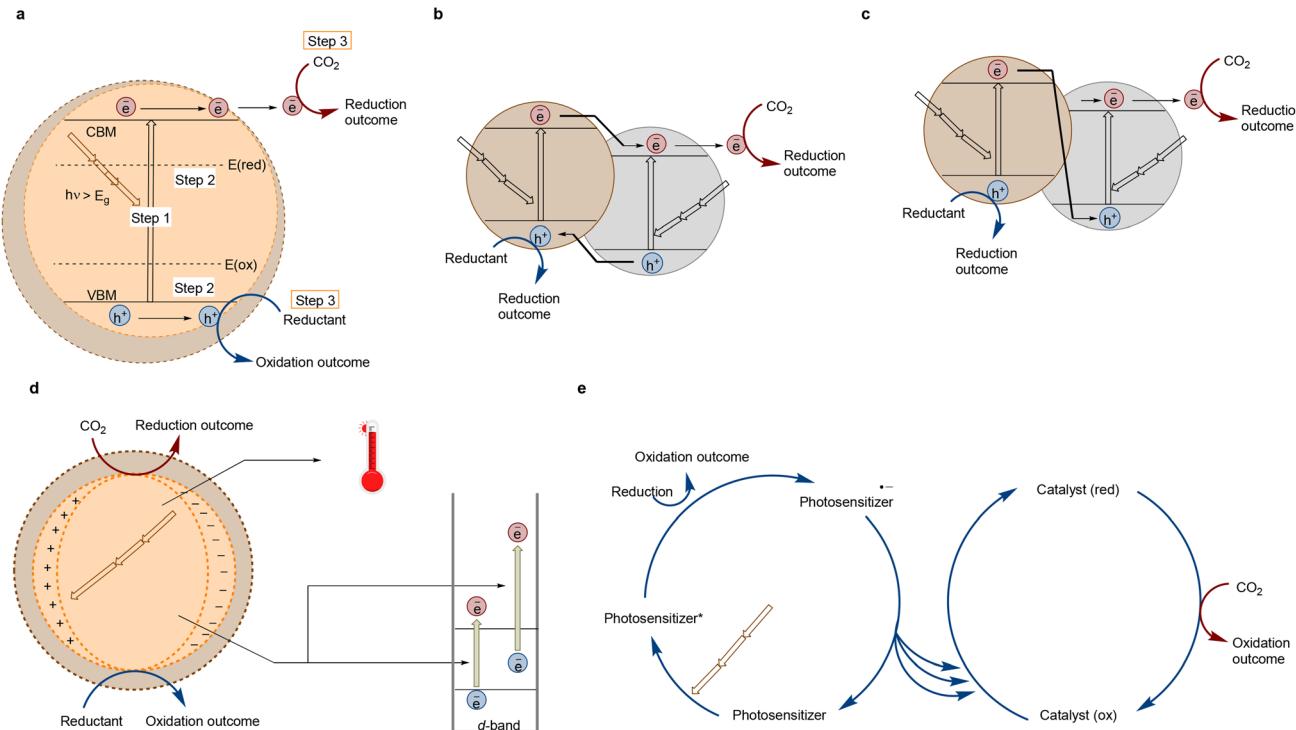


Fig. 8 Principles of photocatalytic CO_2 reduction.

Fabricating heterostructure catalysts that feature favorable band alignment is an effective strategy to achieve a broad spectral response and efficient charge separation.

Such catalysts are subdivided into p-n junction and Z-scheme configurations, according to their charge transfer pathways.¹³²⁻¹³⁶ Within a p-n junction heterostructure (Fig. 8b), photo-generated electrons transfer to the component possessing the more positive conduction band (CB) potential, while photo-generated holes migrate toward the component with the more negative valence band (VB) potential. In contrast, Z-scheme architectures (Fig. 8c) operate differently: electrons photo-generated in the component having the more positive CB potential transfer directly into the valence band of a second component with a more negative VB potential, or indirectly *via* conductive mediators or reversible redox shuttles. Furthermore, metals like gold, silver, copper, and bismuth can facilitate heterogeneous photocatalytic CO_2 reduction, an activity largely attributed to their localized surface plasmon resonance (Fig. 8d).¹³⁷⁻¹⁴⁰ Specifically, incident photons at the resonant frequency excite collective electron oscillations. This subsequently produces local heat and generates hot carriers *via* intraband (s-to-s) or interband (d-to-s) transitions under intense surface electric fields. Both the localized thermal energy and these hot carriers can drive CO_2 reduction.¹⁴¹⁻¹⁴³ The fundamental steps in homogeneous photocatalytic CO_2 reduction mirror those of semiconductor-based systems, but differ in employing a photosensitizer and molecular catalyst. As illustrated (Fig. 8e), light absorption first excites the photosensitizer, which is subsequently reductively quenched by a sacrificial electron donor, yielding its reduced form.¹⁴³

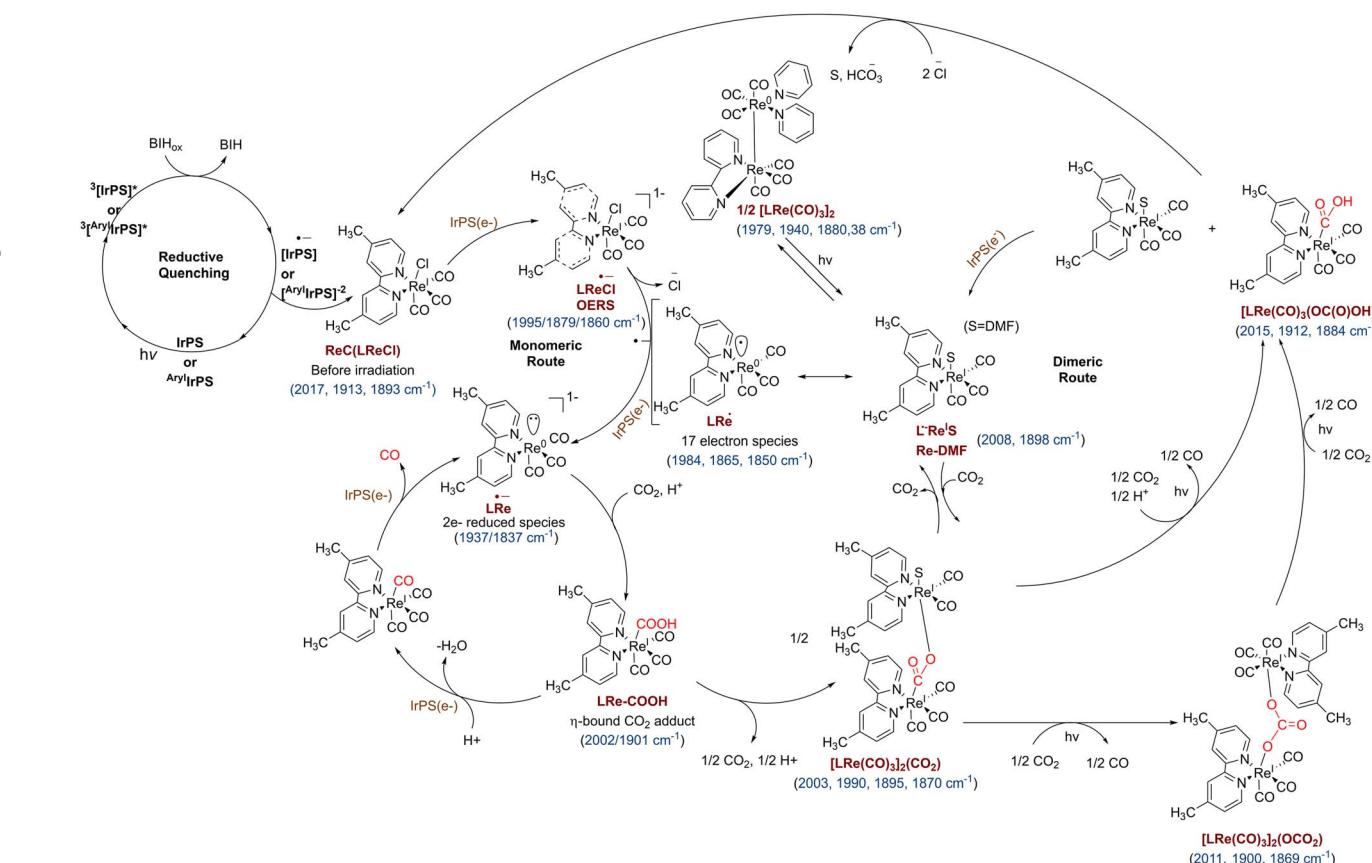
This reduced species then transfers electrons to the molecular catalyst, converting it from an oxidized to reduced state. Subsequently, the reduced catalyst donates electrons to CO_2 , driving its reduction. The alternative oxidative quenching pathway is less prevalent in CO_2 reduction systems.¹⁴⁴ Hybrid approaches also exist where molecular catalysts anchor to semiconductor surfaces *via* covalent or non-covalent bonds.¹⁴⁵ In these configurations, the semiconductor generates charge carriers upon illumination, while the tethered molecular catalyst functions as a cocatalyst, providing specialized sites for CO_2 activation and reduction.

3.1. Site-isolating molecular catalysts by TiO_2 heterogenization

Although the tricarbonyl $\text{Re}^{(\text{I})}$ complex, $(\text{bpy})\text{Re}^{(\text{I})}(\text{CO})_3\text{Cl}$, recognized for its near-perfect selectivity in catalyzing CO_2 reduction to CO (>99%), alternative dimeric catalytic routes have also been observed to yield CO , along with the partial conversion of CO_2 into bicarbonate (HCO_3^-).^{2,146-152} The formation of various binuclear intermediates during the catalytic process indicates that the reduced $\text{Re}^{(\text{I})}$ species undergo notable mutual interactions throughout the reaction (Scheme 7). Under these uncontrolled conditions, undesirable side reactions often take place in conventional $\text{Re}^{(\text{I})}$ -based catalysis, leading to structural degradation of the original catalyst and causing premature loss of catalytic activity.

Chemical fixation of the $\text{Re}^{(\text{I})}$ catalyst onto a TiO_2 semiconductor was found to induce site isolation. This promotes





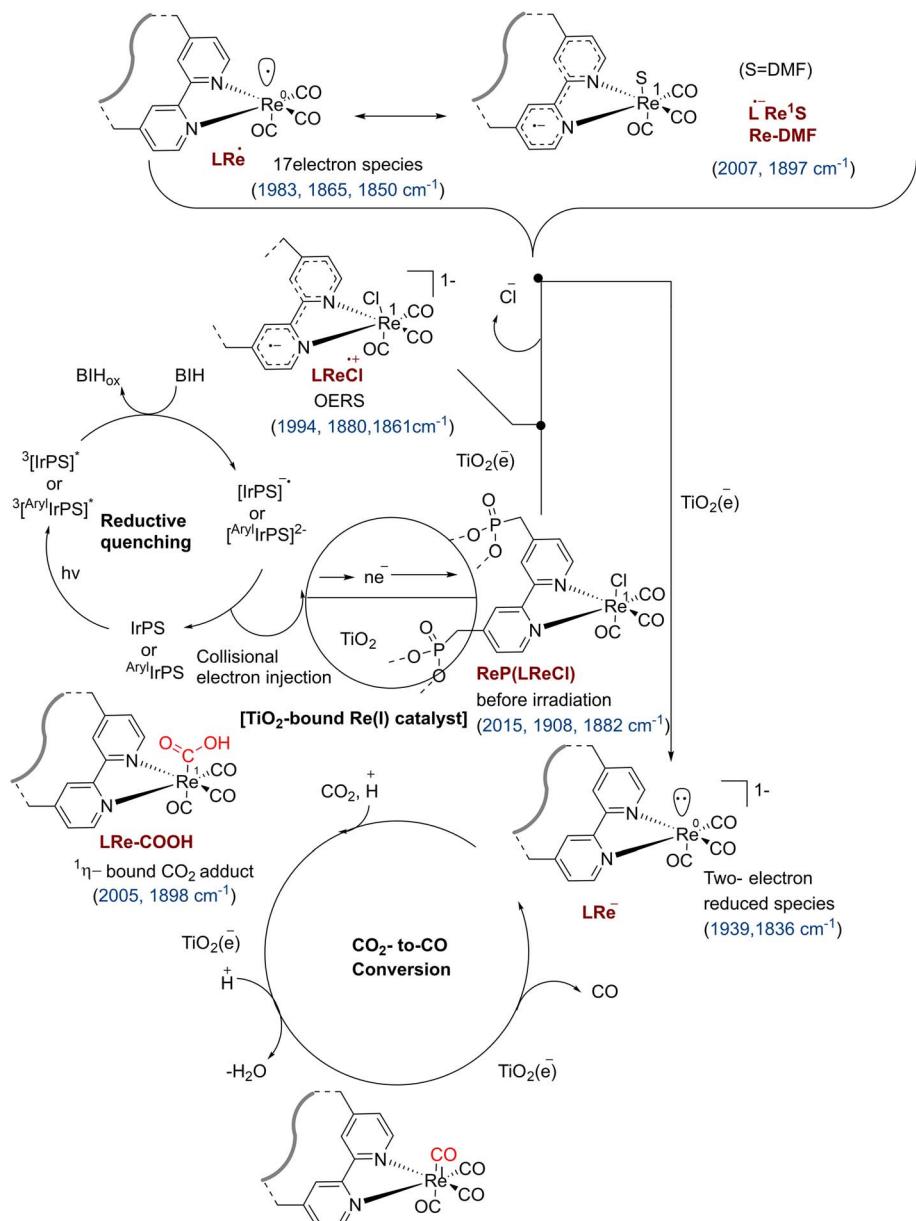
Scheme 7 Schematic of the monomeric and dimeric photochemical CO_2 reductions.

operation *via* the monomeric catalytic pathway, resulting in improved activity and durability (Scheme 8).¹⁵²

An *operando* FTIR spectrophotocatalytic comparison between the free Re^(I) catalyst and its TiO₂-anchored counterpart confirmed that TiO₂ immobilization significantly suppresses the formation of Re-Re dimeric intermediates, a key pathway associated with catalyst deactivation. Additionally, the *fac*-[(4,4'-Y₂-bpy)Mn^I(CO)₃Br] catalyst (MnP, Y = CH₂PO(OH)₂) was appended to the dye-sensitized TiO₂ platform employed for photochemical CO₂ reduction. The efficient visible-light sensitization of this platform allows the TiO₂ particles to function effectively as an electron supplier.¹⁵³ The Mn^(I)-based hybrid system (dye/TiO₂/MnP) demonstrated sustained photocatalytic performance, achieving high turnover numbers (TONs), along with outstanding selectivity for formate production over CO (Scheme 9). *In situ* FTIR spectrophotocatalytic analysis revealed that the catalytic mechanism (involving monomeric Mn-H or dimeric Mn-Mn intermediates) depends on Mn^(I) surface loading. Low Mn concentrations favor the monomeric Mn-H pathway producing formate (HCOO⁻), while high concentrations promote the dimeric Mn-Mn mechanism yielding CO. Specifically, under visible light with 0.1 M electron donor and 0.001 M LiClO₄, a hybrid catalyst with low MnP loading (0.1 μmol per 10 mg TiO₂) generated formate exclusively (>99% selectivity) with a turnover number (TON) of \sim 250 after 23 hours of irradiation.¹⁵³

These findings highlight that anchoring the molecular Mn^(I) catalyst onto the TiO₂ surface provides effective spatial separation, which minimizes the formation of dimeric intermediates and curbs side reactions arising from interactions between reactive Mn species. This spatial isolation significantly improves both the catalytic activity and product selectivity of the MnP-heterogenized MIOM system. Expanding this approach to a monobipyridyl Ru^(II) catalyst revealed distinct behavior. Unlike the highly selective CO/formate production typical of bipyridyl Re^(I) or Mn^(I) systems, the homogeneous (bpy) Ru^{II}(CO)₂X₂ complex (bpy = modified 2,2'-bipyridine; X = halide) mediates CO₂ reduction through an inherently more complex mechanism. Significant Ru^(I) dimerization occurs under catalytic conditions.^{125,143,144,154-157} Naturally, the tendency of Ru-Ru dimerization promotes significant self-polymerization, forming polymeric Ru^(II) chains $(-\text{L}(\text{CO})_2\text{Ru}-\text{Ru}(\text{CO})_2\text{L}-)^n$ which ultimately precipitate out as an inactive complex, causing premature loss of catalytic activity.^{158,159}

TiO₂ immobilization offers a viable strategy to improve the catalytic efficiency and durability of the bipyridyl Ru^(II) complex, as shown by these results.¹⁶⁰ Sequential *operando* FTIR and photophysical studies revealed that anchoring the molecular Ru^(II) catalyst, (4,4'-Y₂-bpy)Ru^{II}(CO)₂Cl₂ (RuP) (Y = CH₂PO(OH)₂), onto a TiO₂ semiconductor effectively stabilizes the key monomeric intermediate, (bpy)Ru(H)(CO)₂Cl (Ru-H). This heterogenization also significantly suppresses the formation of



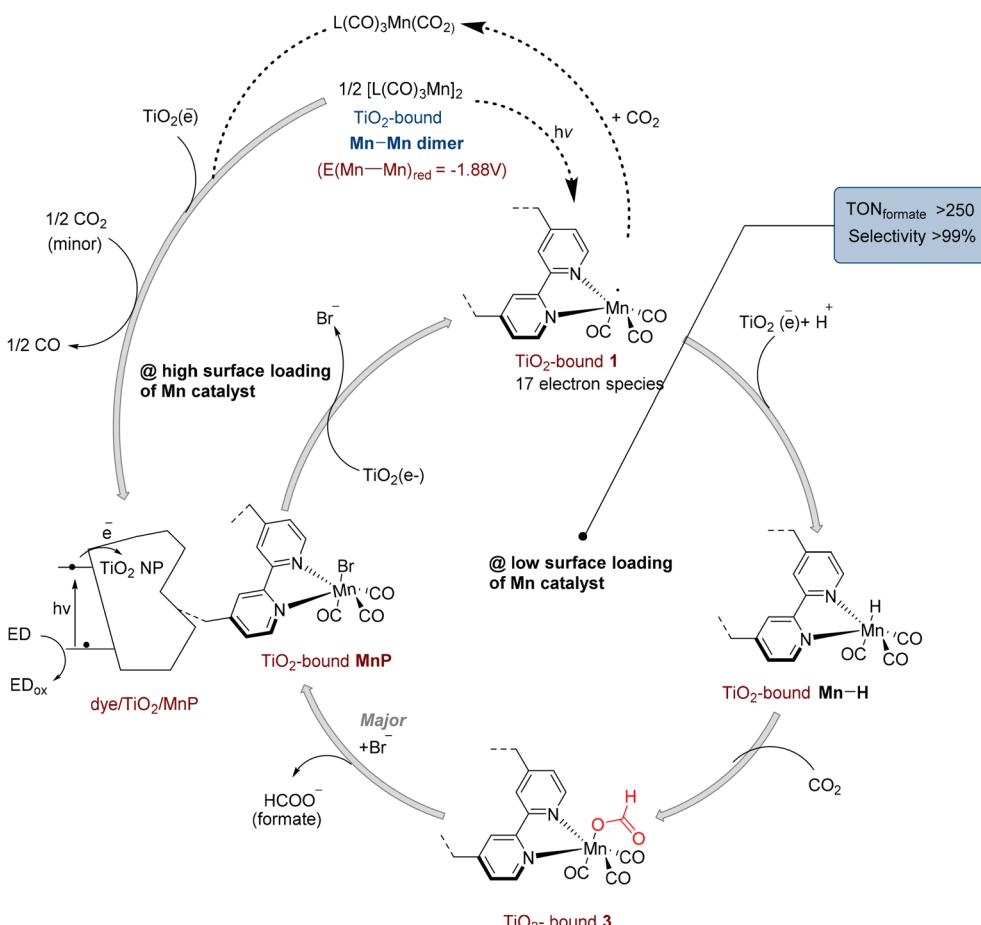
Scheme 8 Mechanistic pathways of the supported Re^(I) catalyst in photochemical CO₂ reduction by the mixed heterogeneous binary system.

the polymeric Ru^(II) species, a major degradation pathway observed in homogeneous photolysis with the molecular Ru^(II) catalyst. Consequently, selective promotion of the monomeric Ru^(II) pathway on TiO₂ significantly enhanced both photocatalytic activity and durability relative to the homogeneous IrPS + Ru(II) system. Under optimal conditions, the semi-heterogeneous IrPS + TiO₂/RuP strategy achieved maximum TONs exceeding 4816 (CO) and 2228 (formate) after 22 h of photolysis.

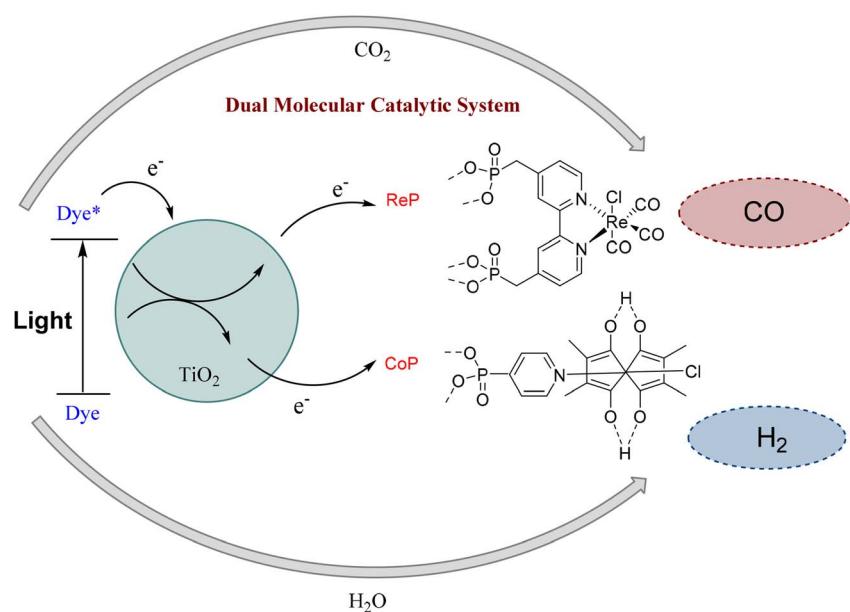
3.2. Tuning MIOM architectures for cooperative catalytic performance

The TiO_2 semiconductor serves as an effective scaffold for multifunctional hybrid systems, where multiple molecular catalysts operate simultaneously within a single MIOM platform. For

instance, syngas ($H_2 + CO$) a key feedstock for Fischer-Tropsch synthesis can be photochemically coproduced in a tunable manner using a dual-function MIOM system (dye/TiO₂/ReP:CoP). This system integrates the co-immobilized hydrogen evolution catalyst $[Co^{III}Cl(dimethylglyoximato)_2(pyridyl-4-phosphonic acid)]^-$ (CoP) and the CO₂-to-CO reduction catalyst $fac\text{-}[Re^I(4,4'\text{-bis}(dihydroxyphosphorylmethyl)-2,2'\text{-bipyridine})(CO)_3Cl]$ (ReP) on TiO₂ particles (Scheme 10). Photolysis experiments demonstrated tunable syngas H₂:CO ratios from 1:2 to 15:1 by adjusting the water content and ReP/CoP surface loadings. This offers a strategic framework for designing photochemical syngas systems with controlled H₂/CO composition.¹⁶¹ This finding offers valuable insight for guiding the design and development of next-generation photochemical syngas production systems capable of precisely controlling the H₂/CO ratio.



Scheme 9 Proposed MnP-concentration- and intermediate-dependent mechanistic pathways in photochemical CO_2 reduction by the ternary hybrid system.



Scheme 10 Multifunctional hybrid assembly: dye- TiO_2 -ReP:CoP.

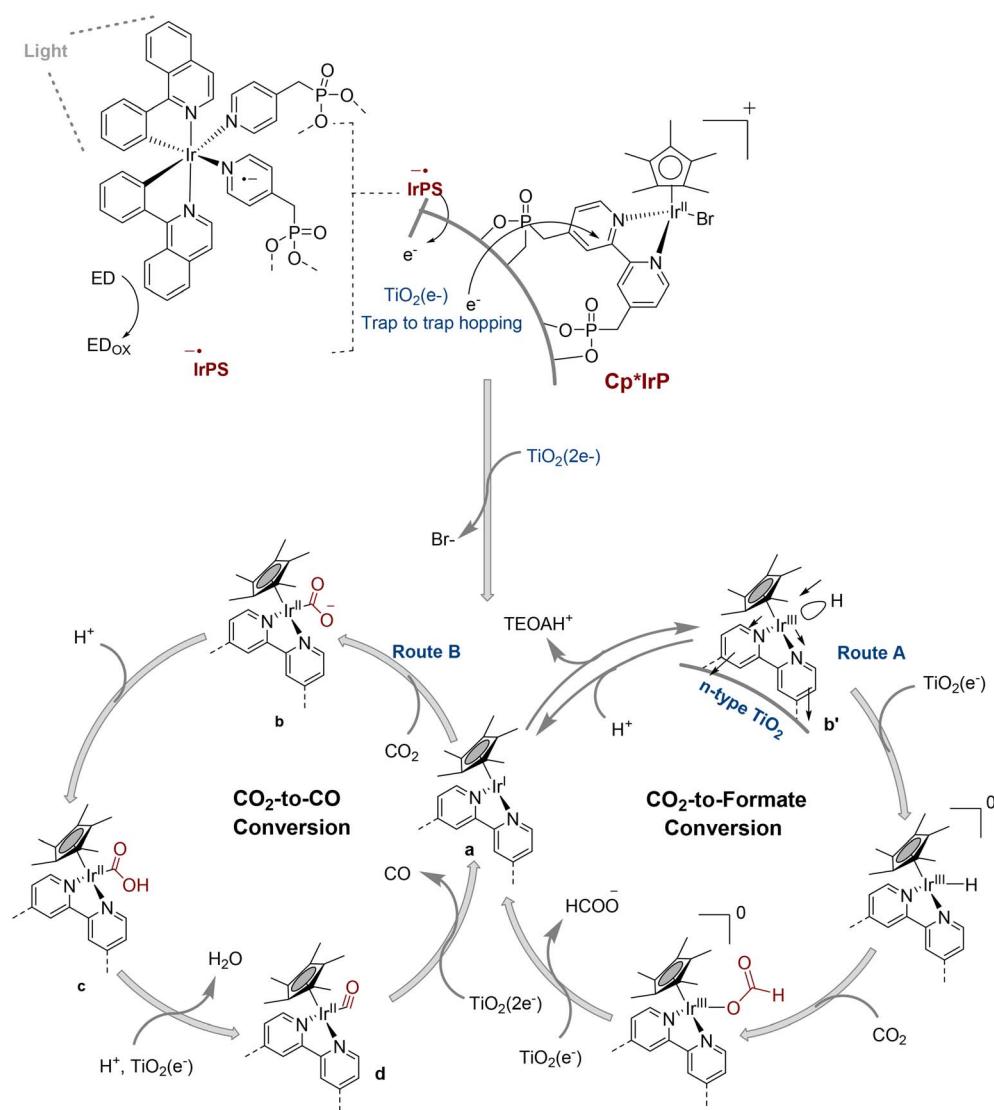
3.3. Mechanistic and electronic control of catalysts *via* TiO₂ heterogenization

Importantly, the n-type TiO₂ semiconductor modulates the electronic structure of chemisorbed metal complexes. The catalytic CO₂ reduction efficiencies of homogeneous [Cp*Ir^{III}(4,4'-Y₂-bpy)Cl]⁺ (Y = CH₂PO(OEt)₂; Cp*IrPE) and TiO₂-immobilized [Cp*Ir^{III}(4,4'-Y₂-bpy)Cl]⁺ (Y = CH₂PO(OH)₂; Cp*IrP) catalysts in IrPS-sensitized MIOM systems (homogeneous: IrPS + CpIrPE; heterogeneous: IrPS/TiO₂/CpIrP) (Scheme 11).¹⁶² The IrPS/TiO₂/CpIrP hybrid produces comparable quantities of formate and CO during photolysis, revealing that the TiO₂-immobilized CpIrP catalyst facilitates both CO₂-to-formate and CO₂-to-CO conversions. This contrasts with homogeneous solvated Cp*IrPE, which exclusively generates formate. Mechanistic studies combining photophysical and electrochemical analyses indicate that the electron-withdrawing effect of the TiO₂ support lowers the hydricity of the Ir^{III} hydride intermediate, promoting its deprotonation in the presence of the base additive TEOA. This conversion of [Cp*(bpy)Ir^{III}-H]⁺ and TEOA

to [Cp*(bpy)Ir(i)]⁰ and TEOA⁺ enables CO₂ reduction to CO through the formation of the η^1 -bound [Cp*(bpy)Ir^{III}(C(O)OH)]⁺ intermediate. In contrast, systems lacking TiO₂ anchoring mainly favor formate production. This mechanistic pathway is supported by both the observed TEOA-dependence of CO formation and UV-vis absorption data, which reveal a notable red shift (approximately 30 nm) in the MLCT (metal-to-ligand charge transfer) bands specifically from Ir^{III} d-orbitals to the bipyridine ligand when Cp*IrP is immobilized on n-type TiO₂ compared to its behavior on ZrO₂ or in DMF solution.

4. Single atom alloys for CO₂RR

Single-atom alloying (SAA) represents a powerful strategy to enhance the catalytic performance of metals in CO₂ reduction. By anchoring isolated metal atoms onto the surface of a host metal, SAA catalysts integrate the distinctive characteristics of both components, while preserving the advantages inherent to



Scheme 11 Photocatalytic pathways enabled by TiO₂ heterogenization of Cp*IrP in a three-component hybrid architecture.

single-atom catalysis.^{163,164} In SAA catalysts, the two metal elements can participate in distinct elementary steps of the catalytic process, thereby disrupting the scaling and Brønsted-Evans-Polanyi (BEP) relationships typical of single-metal catalysts and ultimately enhancing the overall reaction.^{165,166} Moreover, the geometric and electronic structures of the guest and host metals in SAA can be mutually tuned,¹⁶⁷ thereby modulating the adsorption strength of intermediates and altering the CO₂RR reaction pathway. Such adjustments ultimately enhance the intrinsic activity and selectivity of metal catalysts. For instance, dispersing single Sb atoms onto a Cu surface decreases the adsorption energy of CO by approximately 0.1 eV, while simultaneously increasing the faradaic efficiency for CO from 40% to nearly 90% at a constant current density of 400 mA cm⁻².¹⁶⁸ Among metal catalysts, Cu stands out for its unique selectivity in CO₂RR, as it can generate both C₁ and C₂₊ products such as CO, formate, ethylene, ethanol, and propanol.¹⁶⁹ Consequently, Cu-based SAA catalysts have been widely investigated to steer the activity and selectivity of CO₂RR toward the desired products.^{170,171}

Zhi *et al.*¹⁷² used DFT to study Cu(111)-supported single-atom alloy (M@Cu) catalysts for CO₂ electroreduction. They showed that the H and O affinities of the single-atom metal M effectively predict CO₂RR selectivity. As shown in Fig. 9A, Ag-, Zn-, In-, and Sn-doped M@Cu catalysts with weak M-H and M-O affinities mainly produce CO and HCOOH, whereas those with strong affinities favor CH₄ or CH₃OH formation.¹⁷³ Catalysts with strong M-H but weak M-O affinities are uniquely capable of generating C₂ products. This theoretical selectivity map is consistent with experimental observations; for instance, Cu-In and Cu-Sn alloy electrocatalysts have been shown to preferentially produce CO and HCO₂H.¹⁷⁴⁻¹⁷⁷ Cu-Pt nanocrystals with precisely controlled Cu/Pt ratios exhibited high faradaic efficiency toward CH₄.¹⁷⁸ Cu-Pd and Cu-Au alloy catalysts demonstrated high selectivity for C₂ products.¹⁷⁹⁻¹⁸¹ The CO₂RR selectivity of SAAs can be effectively described using the M-O and M-H affinities, which further show a correlation with the d-

band center of various SAAs (Fig. 9B). Lu *et al.* proposed a SAA catalyst, Co@Cu, capable of selective and efficient methanol production at low overpotential.¹⁸² On the Cu-Co interface, CO* is weakly adsorbed, facilitating its desorption and subsequent product formation. Additionally, the incorporation of Co single atoms modifies the electronic structure of Cu. Particularly, by tuning the d-band, CO₂ reduction to methanol is promoted. The narrowed Co d-band enhances bonding with key intermediates, eliminating the need for their migration and enabling selective and efficient methanol formation *via* the pathway: CO₂ → COOH* → CO* → COH* → CHO* → CH₂OH* → CH₃OH.

Although noble metals like gold and silver exhibit high selectivity for converting CO₂ to CO, Cu-based SAAs are often preferred. First, Cu-based catalysts bind *H relatively weakly (weaker than Pt or Pd), which suppresses the HER and enhances the CO₂RR selectivity. Second, the adsorption of key CO₂RR intermediates, such as *CO and *COOH, is moderate on Cu-based catalysts, which allows for efficient rapid *CO desorption and CO₂ activation. Additionally, Cu is more cost-effective than Au and Ag, making it particularly attractive for industrial applications.¹⁸³⁻¹⁸⁵ Besides CO, formate (HCOO⁻) and formic acid (HCO₂H) are important C₁ products of CO₂ electroreduction. However, Cu shows low selectivity for formic acid or formate, and the HER can compete within certain potential ranges. Consequently, steering Cu-based CO₂RR toward formate production remains a significant challenge.¹⁸⁶⁻¹⁸⁸ For instance, Zheng *et al.* reported a Pb SAA Cu catalyst (Pb₁Cu) designed for selective CO₂-to-formic acid conversion with record-high activity. The catalyst was synthesized *in situ* by reducing a Cu-Pb precursor under constant current. Electrochemical tests in a flow cell confirmed the catalyst's high selectivity and activity for formate production.¹⁸⁹ Methane is a primary component of natural gas which is the most reduced product of CO₂RR, requiring an eight-electron transfer. However, the poor selectivity and high overpotential of Cu catalysts for CO₂-to-CH₄ conversion limit their practical application. One effective strategy to enhance CH₄ selectivity on Cu is

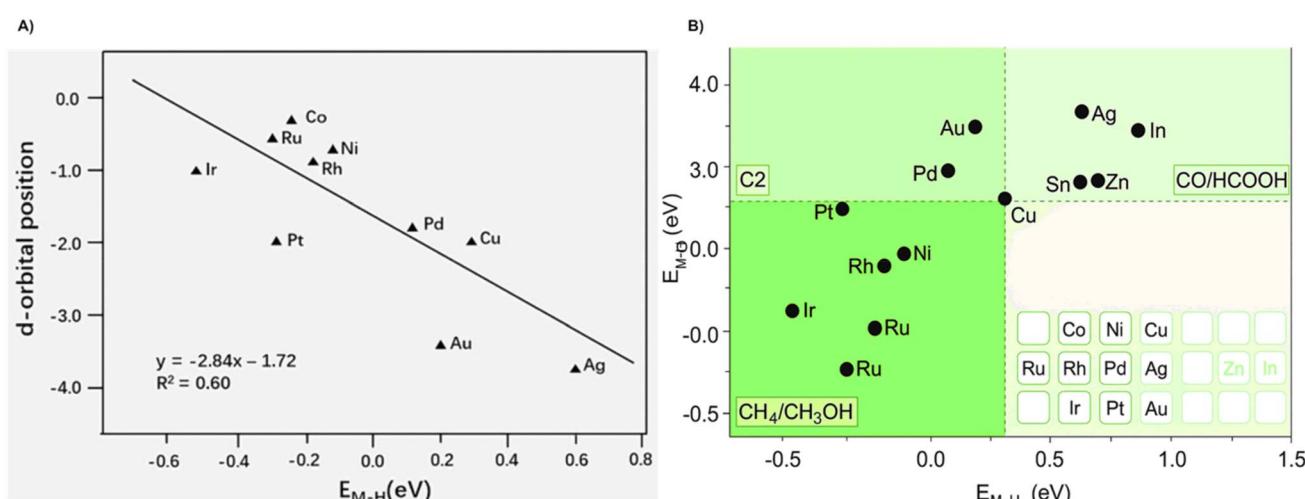


Fig. 9 (A) Classification of the products from M@Cu catalysts based on their affinities for M-H and M-O bonds; (B) correlation between the d-band center of the d-block metal and the M-H bond affinity in the M@Cu catalysts.



to suppress CO* desorption and promote its further protonation.¹⁷³ As the only metal capable of reducing CO₂ to multi-carbon products, Cu-based materials are being extensively studied for the selective production of C₂₊ compounds.^{190,191} C-C coupling is the key step in generating C₂₊ products during CO₂RR. For instance, Zhang *et al.* designed Cu-hosted SAAs with adjacent binary sites that facilitate asymmetric CO binding, thereby enhancing C-C coupling and promoting multicarbon product formation.¹⁹²

Apart from Cu, other metals are also important in CO₂RR. For instance, noble metals like Ag and Au display strong selectivity toward CO, and their catalytic efficiency can be greatly improved by incorporating single-atom alloying.¹⁹³⁻¹⁹⁷ Wang *et al.* investigated the surface reconstruction of Ag-supported Cu SAA catalysts during electrochemical CO₂ reduction.¹⁹⁸ Certain metals, including Bi-, Sn-, and Pb-based catalysts, are capable of catalyzing the electroreduction of CO₂ to formic acid or formate.¹⁹⁹

5. Dual-atom alloys for CO₂RR

In recent years, dual-atom catalysts (DACs), regarded as an important extension of single-atom catalysts (SACs), have attracted growing interest for CO₂ reduction reactions. These catalysts feature bimetallic active sites created by positioning a secondary metal center near the primary metal center.²⁰⁰ Compared with SACs, DACs not only retain the merits of single-atom catalysts, but also introduce additional functionalities. Their unique coordination environment offers a distinct advantage in regulating the adsorption and desorption behavior of reactants.²⁰¹ In addition, the interplay between the two metal atoms in DACs helps tune the electronic structure around the bimetallic active sites.²⁰² Third, the interaction between the two metal atoms in DACs gives rise to a synergistic effect,²⁰³ which not only enhances the overall catalytic performance, but also enables these catalysts to facilitate more complex chemical reactions.²⁰⁴ Beyond these advantages, DACs also display a spacing effect. When the two metal atoms are positioned in close proximity, their interaction disrupts the linear scaling relationship of intermediate adsorption energies and lowers the activation barrier, thereby markedly boosting the catalytic efficiency.²⁰⁵ Thanks to these advantages, DACs have found growing applications in CO₂ reduction. For instance, Zhao *et al.* reported a DAC (Fe₂NPC) constructed by anchoring Fe₂N₆ bimetallic sites onto nitrogen-doped porous carbon. This catalyst achieved a faradaic efficiency of 96.0% for CO, notably higher than the 83.5% obtained with the single-metal counterpart Fe₁NPC.²⁰⁶ The outstanding electrocatalytic activity of Fe₂NPC is attributed to its Fe-Fe dual active sites, which can simultaneously coordinate with the C and O atoms of CO₂, thereby promoting its activation. Similarly, Wang *et al.* synthesized both Co-based DACs and SACs for the photocatalytic reduction of CO₂ to CH₄, where the DACs exhibited superior selectivity toward CH₄ compared to their single-atom counterparts.²⁰⁷ Building on these advantages, DACs clearly hold great promise as highly effective catalysts for CO₂ reduction.

5.1. CO₂ adsorption

The CO₂ reduction reaction involves several fundamental stages, including CO₂ diffusion, adsorption, activation, intermediate generation, and final product desorption.²⁰⁸ The adsorption of CO₂ molecules on the catalyst surface represents a fundamental prerequisite for the initiation of CO₂RR. The strength and capacity of adsorption not only regulate the local concentration of reactants, but also modulate the binding configuration of CO₂, thereby influencing the activation pathway, turnover frequency, and ultimately the overall reaction kinetics and selectivity.²⁰⁹ Previous studies have shown that CO₂ may adsorb onto the catalyst surface either through physisorption in a linear configuration or *via* chemisorption as a partially charged CO₂^{δ+-} species through interactions with surface atoms.²¹⁰ During chemisorption, interactions between the catalyst surface atoms and the CO₂ molecule induce repulsion between the C and O atoms, leading to a bent molecular configuration.²¹¹ To date, four possible coordination modes of CO₂ molecules on catalyst surfaces have been proposed.^{212,213} The first proposed mode is a linear adsorption structure, in which the O atom acts as an electron acceptor and binds to the catalyst surface (Fig. 10a). The second is the C-coordination model, where the C atom interacts with the catalyst to form a monodentate carbonate species (Fig. 10b). The third is the O-coordination model, characterized by the interaction of both O atoms in the CO₂ molecule with the catalyst, leading to the formation of a bridged carbonate structure (Fig. 10c). The fourth is the C/O mixed-coordination model, in which both the C and O atoms simultaneously interact with the catalyst surface to generate a bidentate carbonate species (Fig. 10d). Unlike the linear CO₂ molecule, the chemisorbed CO₂^{δ+-} species adopts a bent configuration, which lowers the barrier for electron acceptance, since the energy level of its lowest unoccupied molecular orbital decreases upon bending.

5.2. CO₂ activation

The conversion of CO₂ is a highly complex process, involving multistep reaction pathways that generate a variety of intermediates and final products. As previously described, CO₂ molecules are first adsorbed onto the active sites of the catalyst. These adsorbed molecules are then activated *via* electron transfer and further protonated by nearby protons or proton-electron pairs, leading to the formation of various intermediates. The final products subsequently desorb from the active sites and diffuse away from the catalyst surface, either into the electrolyte or back into the bulk gas phase. A wide range of CO₂ reduction products can be obtained, including formate, CO, methanol, methane, ethylene, ethanol, and syngas.²¹⁴⁻²¹⁶ This diversity arises because different CO₂ adsorption configurations influence the reaction pathways, generating distinct intermediates and thereby affecting product selectivity. For instance, in the C-coordination model, when the C atom interacts with a Lewis base center on the catalyst to form a monodentate carbonate species, it promotes the formation of the carboxyl radical ('COOH).²¹⁷ However, when the two O atoms interact with the catalyst surface to form a bidentate carbonate species,



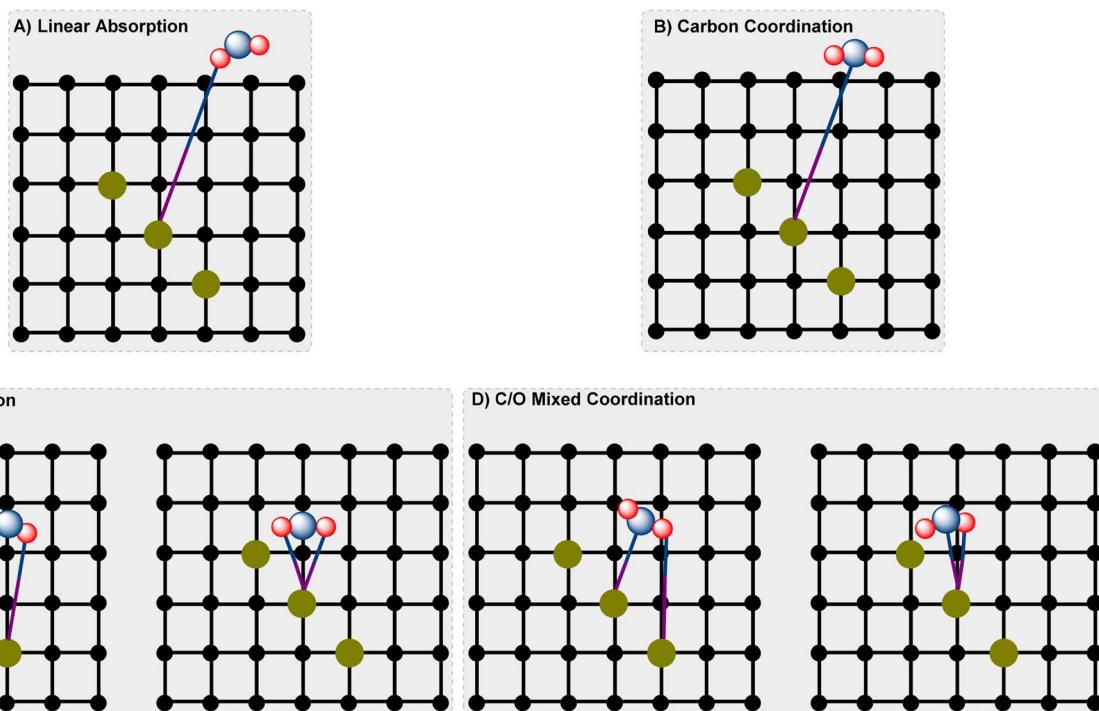


Fig. 10 Adsorption modes of CO_2 molecules on catalytic surfaces.

hydrogen atoms preferentially attach to the C atom of $\text{CO}_2^{\delta+}$, leading to the formation of a formate anion bound to the catalyst surface in a bidentate configuration.²¹⁸ In addition, from a thermodynamic perspective, CO_2 is relatively stable due to its linear structure and chemical inertness. The C=O bonds in CO_2 are particularly difficult to cleave, possessing a high dissociation energy of 750 kJ mol⁻¹.⁶⁶

6. MOF-derived CO_2 RR

Metal-organic frameworks (MOFs) represent a new class of crystalline porous materials formed by the coordination of inorganic nodes such as metal ions or clusters with organic linkers.^{6,219-221} Owing to the structural diversity and tunable composition of MOFs, pore sizes can be adjusted and a variety of catalytic sites can be introduced by manipulating the inorganic nodes and organic linkers. Their porous architecture and large surface areas facilitate improved CO_2 adsorption and efficient mass transport. In addition, the well-defined framework of MOFs provides a valuable platform for exploring the structure–property relationships and mechanistic studies. MOF-derived materials have emerged as versatile catalysts for both electrocatalytic and photocatalytic CO_2 reduction, building on Fischer's pioneering work with $\text{NH}_2\text{-MIL-125}$ -derived TiO_2 ,²²² while most reviews broadly cover MOFs, composites, and derived materials, and photocatalytic applications.²²³⁻²²⁹ Optimizing the morphology and electronic structure of MOF-derived catalysts for both electrocatalysis and photocatalysis can therefore unlock new strategies for enhanced CO_2 conversion.⁶

Due to its closed-shell electronic configuration, CO_2 is chemically inert and thermodynamically stable, with a bond

dissociation energy of 750 kJ mol⁻¹.^{230,231} Therefore, efficient electrocatalysts and photocatalysts are necessary to overcome these thermodynamic and kinetic barriers, and convert CO_2 into value-added products such as HCOOH , CO and CH_4 . MOF-derived materials, with their tunable structures, high surface areas, and adjustable catalytic sites, provide a promising platform to facilitate CO_2 activation and enhance the efficiency of both photocatalytic and electrocatalytic conversion processes.

In both photocatalytic and electrocatalytic CO_2 reduction reactions, CO_2 molecules are initially activated to form the $^*\text{CO}_2^-$ intermediate, requiring a negative reduction potential of -1.90 V *versus* the normal hydrogen electrode (NHE). The subsequent reduction of this intermediate, determined by the number of electrons transferred and protons added, leads to a variety of products, including two-electron reduction products such as CO and HCOOH , as well as multi-electron products like CH_4 , CH_3OH and $\text{C}_2\text{H}_5\text{OH}$.²³² In general, the $^*\text{CO}_2^-$ intermediate undergoes protonation to produce either the $^*\text{OCHO}$ or $^*\text{COOH}$ intermediate. The $^*\text{OCHO}$ intermediate can be further reduced to form formic acid, whereas $^*\text{COOH}$ proceeds to generate the $^*\text{CO}$ intermediate, which can then lead to C_1 products (HCHO , CH_4 , CH_3OH , CO) and C_{2+} products ($\text{C}_2\text{H}_5\text{OH}$, C_2H_4 , $\text{C}_3\text{H}_7\text{OH}$, $\text{CH}_3\text{CO}_2\text{H}$). Typically, C–C bond formation occurs more slowly than the hydrogen evolution reaction (HER), which results in lower selectivity toward C_{2+} products.²³³ Enhancing the conversion of the $^*\text{CO}$ intermediate into the desired C_{2+} products requires a sufficiently strong interaction between $^*\text{CO}$ and the catalytic site. However, excessively strong binding can lead to catalyst “poisoning,” as the desorption of $^*\text{CO}$ becomes difficult, ultimately reducing the overall catalytic



activity.^{223,233,234} The standard redox potentials for hydrogen evolution and CO₂ reduction to various products are comparable, which promotes the competing HER. In addition, the redox potentials among different CO₂ reduction products are similar, often resulting in the formation of mixed products and limiting selectivity toward a single desired product.²³² Consequently, minimizing side reactions and enhancing product selectivity are key factors to consider in the design of effective CO₂ reduction catalysts.

Electrocatalytic CO₂ reduction involves three main steps: (i) adsorption of CO₂ onto the catalyst surface, (ii) electron transfer and proton migration to the adsorbed CO₂, and (iii) structural rearrangement of intermediates, followed by desorption of the final products from the catalyst surface.⁶ Electrocatalytic CO₂ reduction typically requires a significant overpotential, the difference between the equilibrium potential and the applied

potential to enable CO₂ molecules to accept electrons and form the *CO₂⁻ intermediate. Depending on the type of electrocatalyst and experimental conditions, the reaction can follow multiple pathways, yielding a variety of reduction products (Fig. 11). Due to the similar reduction potentials of CO₂ products and the kinetically favorable HER, achieving high selectivity for a single product remains a major challenge. The rational design of catalyst morphologies can modulate key parameters, including exposed surface area, mass transport, and charge-transfer resistance, thereby enhancing the catalytic activity and steering product selectivity.^{235,236} By tuning the electronic structure of catalysts, the binding strength of the reaction intermediates can be adjusted, which in turn influences the reaction barriers and dictates the distribution of the reduction products.²³⁷

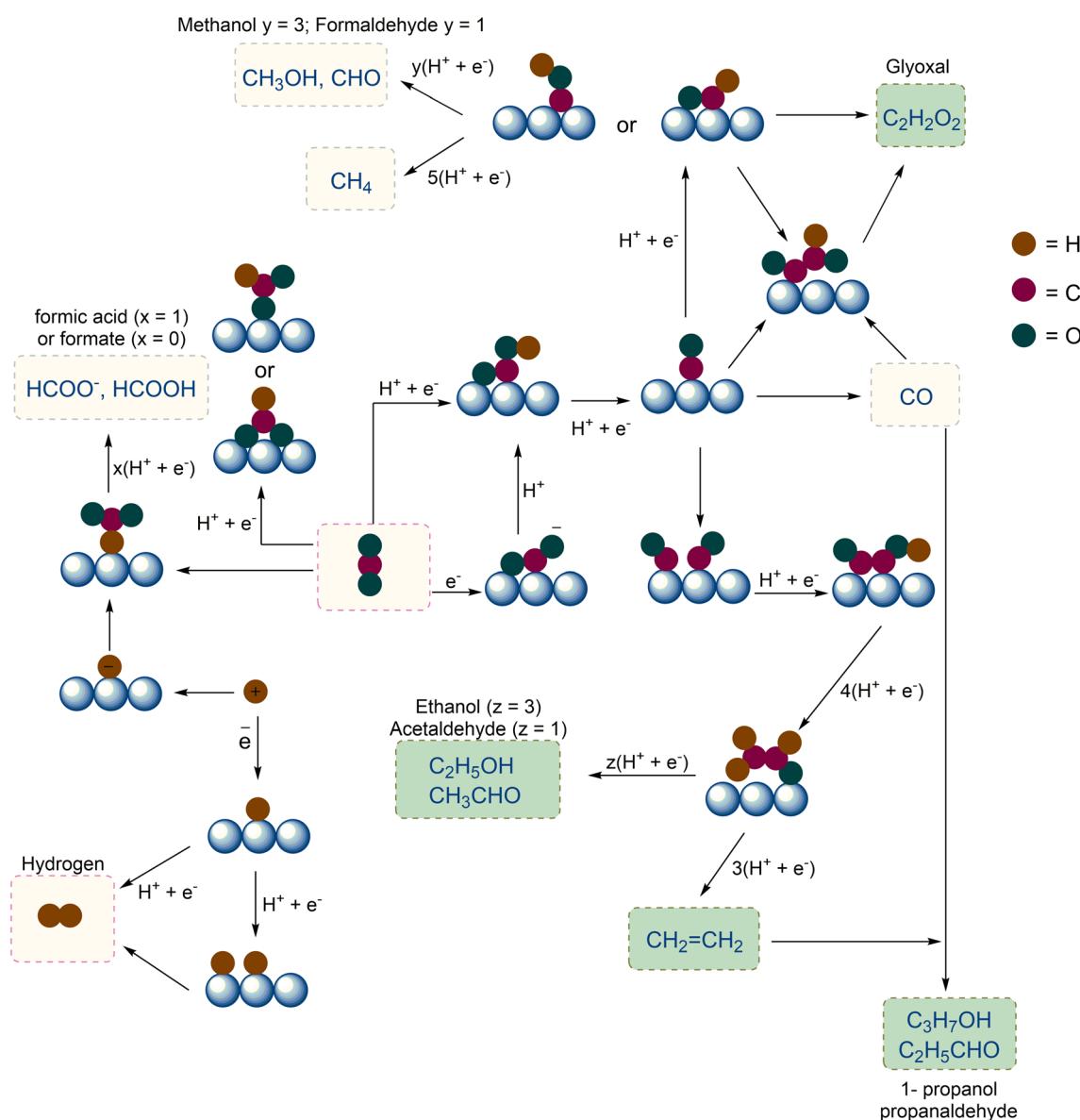


Fig. 11 Schematic reaction pathways for CO₂ reduction by MOF.



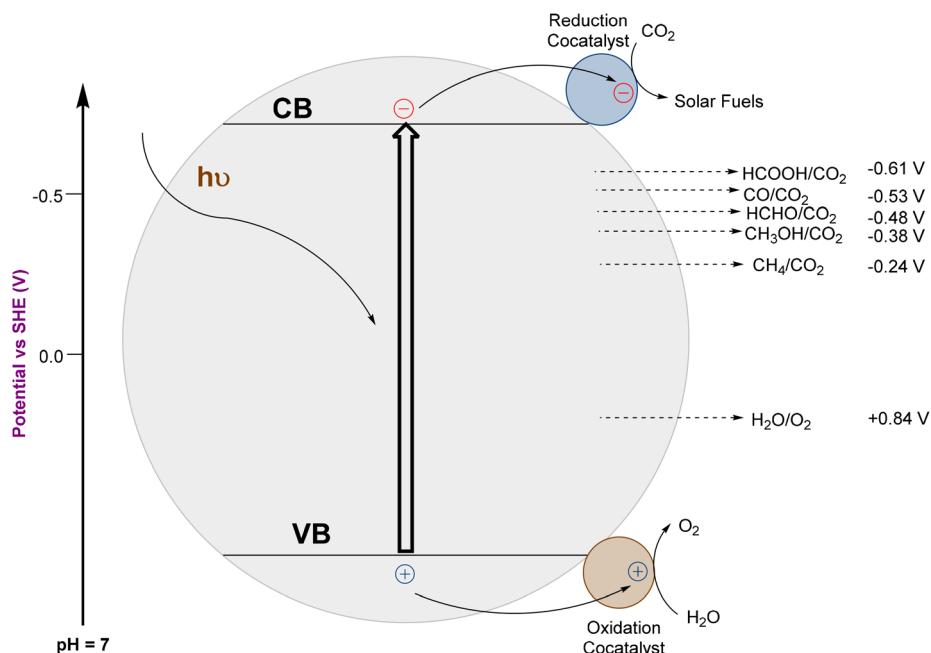


Fig. 12 Photocatalytic CO₂ reduction on a semiconductor photocatalyst.

In photocatalytic CO₂ reduction, the reaction is generally considered to proceed through three primary steps: (i) photo-excitation of the catalyst to generate electron–hole pairs ($e^- - h^+$), (ii) migration of the photogenerated electrons and holes to the catalyst surface, and (iii) reduction of CO₂ on the catalyst surface (Fig. 12).^{19,238} Unlike electrocatalysis, photocatalysis requires the conversion of light energy into excited electrons and holes to drive chemical reactions. Therefore, the ability of a photocatalyst to absorb light efficiently and separate charge carriers effectively is crucial. When the photocatalyst absorbs photons with energy equal to or greater than its bandgap, electrons are promoted from the valence band (VB) to the conduction band (CB), leaving holes in the VB and generating electron–hole pairs.⁶ The redox capabilities of photogenerated electrons and holes in photocatalysts are largely determined by the positions of the conduction band minimum (CBM) and valence band maximum (VBM), respectively. CO₂ reduction can proceed only when the CBM energy lies at a more negative potential than the redox potential of the CO₂RR.^{238,239} Similarly, VBM must be positioned at a more positive potential than the redox potential of the oxidation half-reaction; otherwise, sacrificial agents such as triethanolamine (TEOA), ascorbic acid, or lactic acid are required to serve as alternative electron donors. Careful design of the catalyst's morphology and electronic structure can significantly improve light absorption. In particular, tuning the catalyst's thickness and surface features influences the light penetration depth and scattering intensity, thereby enhancing the overall light-harvesting efficiency. Moreover, the electronic structure of a material directly affects its energy level distribution, enabling the absorption of longer-wavelength light and thereby enhancing the efficiency of light utilization.

The second step involves the separation of photogenerated electron–hole pairs and their migration to the catalyst surface. For effective CO₂ reduction, these charge carriers must have a sufficiently long lifetime to reach the active sites. However, this process is often hindered by the recombination of electrons and holes, which significantly reduces the utilization efficiency of the photogenerated charges.²⁴⁰ By tailoring the morphology and electronic structure of catalysts, the charge-transfer distance can be reduced and the lifetime of photogenerated carriers extended, thereby suppressing the recombination of electrons and holes.²⁴¹ To enhance the separation efficiency of charge carriers, strategies such as constructing heterojunctions and improving the crystallinity of the materials have been widely adopted.^{242,243} Similar to electrocatalysis, the surface redox reaction is a crucial step in photocatalysis. When photogenerated electrons reach the active sites, the adsorbed CO₂ molecules undergo reduction. Introducing CO₂ binding sites on the catalyst surface can enhance CO₂ enrichment and thereby improve catalytic performance. Additionally, tuning the coordination environment of active sites helps stabilize key intermediates and lowers the reaction barrier of the rate-determining step (RDS). To further enhance the surface reaction efficiency, strategies such as incorporating co-catalysts and creating surface defects are commonly employed.^{6,244,245}

7. Conclusion

The electrochemical and photocatalytic reduction of CO₂ represents a pivotal strategy for addressing rising carbon emissions, while generating value-added fuels and chemicals. Across homogeneous, heterogeneous, and hybrid platforms, recent advances underscore the importance of understanding



and controlling the fundamental steps of CO_2 activation, intermediate stabilization, and product selectivity. Key insights show that product selectivity is dictated by how catalysts stabilize CO_2 , hydride, and $^*\text{COOH}$ intermediates, and how effectively competing hydrogen evolution is suppressed. Photocatalytic systems complement electrocatalysis by coupling solar energy capture with catalytic turnover. Hybrid molecular-inorganic-organic assemblies, particularly TiO_2 -anchored complexes, illustrate how site isolation and semiconductor-molecule coupling suppress deactivation, reshape hydroicity, and even enable tunable syngas generation. At the materials frontier, single-atom and dual-atom alloys, alongside MOF-derived catalysts, are redefining heterogeneous CO_2RR . Single-atom alloys (SAAs) disrupt scaling relations by electronically coupling isolated guest atoms with host metals, offering precise control over $^*\text{CO}$ binding and C-C coupling pathways. Dual-atom catalysts (DACs) further introduce synergistic bimetallic effects, stabilizing bent $\text{CO}_2^{\delta-}$ intermediates and enabling complex multi-electron conversions with higher selectivity than SACs alone. Meanwhile, MOF-derived catalysts provide high surface area, tunable coordination environments, and structural porosity that enhance CO_2 adsorption and diffusion, enabling both C_1 and C_{2+} products. These platforms collectively illustrate how structural precision and compositional tuning can directly translate into reactivity and selectivity gains. Future progress will depend on uniting mechanistic insight, second-sphere tuning, and advanced material architectures to deliver efficient, durable, and practical CO_2 conversion technologies.

Data availability

Not applicable.

Conflicts of interest

There are no conflicts to declare.

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