Carbon Dioxide Reduction Mediated by Iron Catalysts: Mechanism and Intermediates That Guide Selectivity

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**ABSTRACT:** The reduction of carbon dioxide represents an ambitious target, with potential impact on several of the United Nations’ sustainable development goals including climate action, renewable energy, sustainable cities, and communities. This process shares a common issue with other redox reactions involved in energy-related schemes (i.e., proton reduction to hydrogen and water oxidation to oxygen), that is, the need for a catalyst in order to proceed at sustainable rates. Moreover, the reduction of CO₂ faces an additional selectivity complication, since several products can be formed, including carbon monoxide, formic acid/formate, methanol, and methane. In this Mini-Review, we will discuss iron-based molecular catalysts that catalyze the reduction of CO₂, focusing in particular on the selectivity of the processes, which is rationalized and guided on the basis of the reaction mechanism. Inspired by the active sites of carbon monoxide dehydrogenases, several synthetic systems have been proposed for the reduction of CO₂; these are discussed in terms of key intermediates such as iron hydrides or Fe-CO₂ adducts, where the ligand coordination motif, together with the presence of co-additives such as Brønsted acids, nucleophiles, or CO₂ trapping moieties, can guide the selectivity of the reaction. A mechanistic comparison is traced with heterogeneous iron single-atom catalysts. Perspectives on the use of molecular catalysts in devices for sustainable reduction of CO₂ are finally given.

**INTRODUCTION**

The utilization of carbon dioxide as a ubiquitous raw material in the synthesis of commodity chemicals and for the production of solar fuels is an ambitious target; an efficient and large-scale exploitation of CO₂ could also help in reducing its impact as a greenhouse gas in the atmosphere. A few industrial processes have been realized where CO₂ is incorporated in organic chemicals for the production of linear and cyclic carbonates or salicylic acid; conversely, processes leading to reduction of CO₂ are still not industrially developed. Issues associated with the reduction of CO₂ through electrochemical or photochemical processes are (i) the possibility of obtaining several products, such as carbon monoxide, formic acid or formate, methanol, and methane, which are discussed in this Mini-Review (eqs 1–5); potentials in aqueous medium are reported versus the normal hydrogen electrode, NHE; CO₂, CO, CH₄ are considered in the gaseous state, HCOOH, CH₃OH and H₂O in the liquid state, HCOO⁻ in aqueous solution; see ref 2 for an extensive discussion of CO₂ reduction products); (ii) the requirement to use a catalyst to overcome the kinetic barriers associated with the multi-electron/multiproton processes; and (iii) the competition of the hydrogen evolution reaction (eq 6) when proton donors are present in the reaction medium.

\[
\text{CO}_2 + 2\text{H}^+ + 2e^- \rightleftharpoons \text{HCOOH}
\]

\[
E(\text{CO}_2/\text{HCOOH}) = -0.25 \text{ V} - 0.0592 \times \text{pH vs NHE}
\]  

(2)

\[
\text{CO}_2 + \text{H}_2\text{O} + 2e^- \rightleftharpoons \text{HCOO}^- + \text{OH}^-
\]

\[
E(\text{CO}_2/\text{HCOO}^-) = -1.08 \text{ V} - 0.0592 \times \text{pH vs NHE}
\]

(3)

\[
\text{CO}_2 + 6\text{H}^+ + 6e^- \rightleftharpoons \text{CH}_3\text{OH}
\]

\[
E(\text{CO}_2/\text{CH}_3\text{OH}) = 0.02 \text{ V} - 0.0592 \times \text{pH vs NHE}
\]

(4)

\[
\text{CO}_2 + 8\text{H}^+ + 8e^- \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}
\]

\[
E(\text{CO}_2/\text{CH}_4) = 0.17 \text{ V} - 0.0592 \times \text{pH vs NHE}
\]

(5)

\[
2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2
\]

\[
E(\text{H}^+/\text{H}_2) = 0.00 \text{ V} - 0.0592 \times \text{pH vs NHE}
\]

(6)

\[
\text{CO}_2 + 2\text{H}^+ + 2e^- \rightleftharpoons \text{CO} + \text{H}_2\text{O}
\]

\[
E(\text{CO}_2/\text{CO}) = -0.11 \text{ V} - 0.0592 \times \text{pH vs NHE}
\]

(1)

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The binding of CO to the Ni$^{2+}$ center occurs, together with the Cred2 (Figure 1, clockwise cycle). Starting from the Cred1 state, produced CO being involved in the acetyl-CoA synthesis releases CO$_2$ and 2H$^+$, resulting in the formation of the Cred2 state; in this state Ni is formally zerovalent, taking into account the oxygen. These biological catalysts belong to the class of carbon monoxide dehydrogenases (CODHases).

CODHases can be divided into two main categories, based on the nature of their active sites: Mo,Cu-based cofactors are used by aerobic bacteria, while a Ni,Fe-based active site is present in both archaea and anaerobic bacteria. In particular, the latter is part of a [NiFe$_4$S$_4$]-cluster (cluster C), where the nickel center, three iron atoms, and four sulfur atoms are assembled in a distorted cubane; the last Fe(II) ion (ferrous metallic center) and the O atom to coordinate the Fe$^{2+}$. This particular coordination geometry promotes CO production and hinders HCOO$^-$ formation in the counter-clockwise, reverse cycle of CO$_2$ reduction.

### NATURAL SYSTEMS FOR REVERSIBLE CO OXIDATION: Ni,Fe-CLUSTER IN CODHases

Through evolution, Nature has developed an important class of metalloenzymes to catalyze the reversible oxidation of CO to CO$_2$, using H$_2$O present in the environment as the source of oxygen. These biological catalysts belong to the class of carbon monoxide dehydrogenases (CODHases). CODHases can be divided into two main categories, based on the nature of their active sites: Mo,Cu-based cofactors are used by aerobic bacteria, while a Ni,Fe-based active site is present in both archaea and anaerobic bacteria. In particular, the latter is part of a [NiFe$_4$S$_4$]-cluster (cluster C), where the nickel center, three iron atoms, and four sulfur atoms are assembled in a distorted cubane; the last Fe(II) ion (ferrous component II, FCI) is bound to a sulfur atom of the cubane and bears a hydroxide anion as an apical ligand, which is functional in the reactivity. Ni,Fe-based CODHases can be mono-, bi-, or even multifunctional. From a physiological perspective, while the former are able to catalyze only the CO oxidation, the latter are also capable of reducing CO$_2$ with the produced CO being involved in the acetyl-CoA synthesis taking place in a different subunit of the protein.

From a mechanistic perspective, the states involved in the reversible oxidation of CO are named C$_{\text{red1}}$, C$_{\text{red2}}$-CO$_2$, and C$_{\text{red2}}$CO$_2$ (Figure 1, clockwise cycle). Starting from the C$_{\text{red1}}$ state, the binding of CO to the Ni$^{2+}$ center occurs, together with the formation of a C–O bond between the carbon atom of CO and the oxygen of the OH group bound to FCI: this step results in the formation of the C$_{\text{red2}}$-CO$_2$ intermediate. As a matter of fact, in order to allow the formation of the new C–O bond, the coordination of CO to an equatorial position of Ni$^{2+}$ is required; however, it is still unclear if the appropriate position is taken from the very beginning of the coordination process or it is reached by a fast “flipping” from an apical position. This uncertainty is due to the intrinsic difficulty in characterizing the state with CO coordinated to the cofactor, caused by its high reactivity.

The second step is the reaction of C$_{\text{red2}}$-CO$_2$ with H$_2$O to release CO$_2$ and 2H$^+$, resulting in the formation of the C$_{\text{red2}}$ state; in this state Ni is formally zerovalent, taking into account the oxidation process that occurred in the previous step. The last process that closes the cycle is the two-electron (2e$^-$) oxidation of C$_{\text{red2}}$ to C$_{\text{red1}}$. A remarkable fact is that in this process the redox-active catalytic site is the Ni$^{2+/0}$ center, while the FCI acts as a Lewis acid and as a vessel for the hydroxido group.

Dobbeck and co-workers$^5$ were able to obtain the crystallographic structure of the C$_{\text{red1}}$ and C$_{\text{red2}}$ states of cluster C from *Carboxydothermus hydrogenoformans*, with 1.40 Å resolution. Both C$_{\text{red1}}$ and C$_{\text{red2}}$ states show identical coordination geometry for the metals and similar [NiFe$_4$S$_4$OH] structure: in these states, the Ni atom has a distorted T-shaped geometry with two sulfide ligands bound to the cluster and one thiol group from Cys$_{56}^\delta$; the Fe$^{2+}$ ions of the cubane are tetracoordinated, showing sulfide ligands from the cluster or amino acid backbone ligands (mainly Cys). FCI is tetracoordinated and is bound to an amino group from His$_{261}^\gamma$, a thiol group from Cys$_{295}^\alpha$, a sulfide ligand from the cluster, and a hydroxido ligand.

In addition, Dobbeck’s group also characterized the C$_{\text{red2}}$-CO$_2$ state by adding NaHCO$_3$ to the C$_{\text{red2}}$ state (moving therefore toward the opposite route with respect to the CO oxidation process, counter-clockwise direction in Figure 1)$^4$. The formal CO$_2$ coordination in C$_{\text{red2}}$ takes place at the Ni and FCI metallic centers, with CO$_2$ behaving as a $\mu$-2$\eta^2$ ligand, where the C atom is bound to the distorted square planar Ni center with a short distance of 1.8 Å and the O atom is coordinated to the FCI. The O–C–O angle decreases to 117$^\circ$ after coordination, while the C–O bond lengths increase to 1.30 and 1.32 Å; these features are consistent with the bond CO$_2$ being reduced by a 2e$^-$-backboning from the Ni center to the C-centered LUMO of CO$_2$. Therefore, in the C$_{\text{red2}}$-CO$_2$ state, Ni is formally recognized in the II oxidation state. The
partial negative charge present on the O atoms is stabilized via hydrogen-bonding interactions with the amino groups of His93 and Lys663.

The CODHases isolated from C. hydrogenoformans show a turnover frequency (TOF) of 31 000 s⁻¹ and a k_cat/K_M of 1.7 × 10⁹ M⁻¹ s⁻¹ for CO oxidation while working at 70 °C in buffered aqueous medium (pH = 8.0, 1 atm of CO) in the presence of dithioerythritol and of methyl viologen as a redox mediator. This result suggests that this system belongs to the class of the diffusion-limited perfect enzymes since its efficiency is only limited by the diffusion of CO in solution. When the reverse process is considered, namely CO₂ reduction to CO, CODHases isolated from Rhodospirillum rubrum show a TOF of 45 s⁻¹ and a k_cat/K_M of 2.5 × 10⁹ M⁻¹ s⁻¹ while working at 25 °C and pH = 7.5, still in the presence of methyl viologen mediator and of dithionite as a chemical reductant.8

The ability of CODHases to catalyze the CO₂ reduction to CO in the presence of chemical reductants, together with the observation that the E° of the 2e⁻ C_red1/C_red2 couple is ~530 mV vs NHE and close to the E° of the CO₂/CO couple at neutral pH, led Shin and co-workers6 to investigate Ni,Fe-CODH for the electrochemical reduction of CO₂ to CO. The study was conducted using a glassy carbon disk as working electrode, methyl viologen as redox mediator, CODHases from Moorella thermoacetica as electrocatalyst, and CO₂ as substrate in aqueous phosphate buffer at pH = 6.3 (Figure 2).

Comparing the cyclic voltammograms obtained in the presence and absence of CODHases, Shin’s group demonstrated the catalytic effect of the enzyme, as indicated by the formation of a catalytic current at potentials below ~0.4 V vs NHE, concomitant with the electrogeneration of C_red2 from C_red1 (Figure 2; C_red1 can be generated from an inactive state CInactive at applied potentials below ~200 mV vs NHE). A deeper insight into this process was achieved by carrying out a controlled potential electrolysis (CPE) experiment at ~0.57 V. According to the group’s conclusions, the process is highly selective toward CO since no byproduct was detected with GC nor LC. CODHases are among the most efficient electrocatalysts for CO₂ reduction since the process occurs with overpotential as low as 0.09 V with respect to the E° of CO₂/CO = −0.48 V at the same pH value (eq 1), and with a TOF of about 0.19 s⁻¹.

The elucidation of the structural features of the Ni,Fe site, together with the application of CODHases in artificial CO₂ electroreduction, prompted several research groups to design bioinspired synthetic catalysts for this transformation; some of them will be discussed in the next sections.

### Fe-HYDRIDE INTERMEDIATES IN THE REDUCTION OF CO₂ TO FORMATE

**Hydrides and Hydricity.** The reactivity of a metal hydride (M-H) is associated with its hydricity, defined as the ability of the species to transfer a hydride H⁻ and quantified as the free energy change ΔG_H⁻ (M-H) of the following reaction:9

\[
\text{M-H} \rightleftharpoons \text{M}^+ + \text{H}^-; \quad \Delta G_{\text{H}^-} \text{(M-H)}
\] (7)

In order to transfer the hydride to CO₂ and transform CO₂ into formate (eq 8), the thermodynamic requirement sets ΔG_{EQ8} < 0 (requirement 1); that is, ΔG_H⁻ (M-H) must be lower than the hydricity of formate, ΔG_H⁻ (HCOO⁻), eq 9.

\[
\begin{align*}
\text{M}^+ + \text{H}^- + \text{CO}_2 & \rightleftharpoons \text{M}^- + \text{HCOO}^-; \quad \Delta G_{\text{EQ8}} \\
\Delta G_{\text{EQ8}} &= \Delta G_{\text{H}^-} \text{(M-H)} - \Delta G_{\text{H}^-} \text{(HCOO}^-) \\
\text{HCOO}^- & \rightleftharpoons \text{CO}_2 + \text{H}^-; \quad \Delta G_{\text{H}^-} \text{(HCOO}^-) \\
\Delta G_{\text{H}^-} \text{(HCOO}^-) &= 44 \text{ kcal mol}^{-1} \text{ in CH}_3\text{CN}; \\
&= 24.1 \text{ kcal mol}^{-1} \text{ in water}
\end{align*}
\] (8)

Kubiak and co-workers demonstrated that the hydricity of M-H can be predicted on the basis of the potential of the metal ion redox couples, and is solvent dependent. As a second condition, it should be noted that an exoergonic character of eq 8 does not itself guarantee the selective reactivity of the metal hydride M-H toward CO₂, since a competitive reaction with protons to produce hydrogen can occur (eq 10, where BH is a proton donor present in solution, required in electrocatalytic CO₂ reduction routines).9

\[
\text{M-H} + \text{BH} \rightleftharpoons \text{M}^+ + \text{B}^- + \text{H}_2; \quad \Delta G_{\text{EQ10}}
\] (10)

Equation 10 can be considered as the sum of eq 7, eq 11, and eq 12:

\[
\text{H}^+ + \text{H}^- \rightleftharpoons \text{H}_2; \quad \Delta G_{\text{EQ11}}
\]

\[
\Delta G_{\text{EQ11}} = -76 \text{ kcal mol}^{-1} \text{ in CH}_3\text{CN}
\] (11)

\[
\text{BH} \rightleftharpoons \text{B}^- + \text{H}^+; \quad \Delta G_{\text{EQ12}}
\]

\[
\Delta G_{\text{EQ12}} = 2.303RT \times pK_{A}(\text{BH}/\text{B}^-)
\] (12)
The ideal situation occurs when M-H is sufficiently reactive toward CO₂ ($\Delta G_{EQ8} < 0$, i.e., hydricity of M-H lower than the hydricity of HCOO$^-$, see requirement 1 above) but not reactive toward BH (i.e., $\Delta G_{EQ10} > 0$). That is, $\Delta G_H$(M-H) $+ \Delta G_{EQ11} + \Delta G_{EQ12} > 0$, which, inserting the definition $\Delta G_{EQ12}$, results in $\Delta G_H$(M-H) $> -\Delta G_{EQ11} - 2.303RT \times pK_a$(BH/B$^-$) (requirement 2).

Combining then requirement 1 and requirement 2: $\Delta G_{EQ11} - 2.303RT \times pK_a$(BH/B$^-$) $< \Delta G_H$(M-H) $< \Delta G_H$(HCOO$^-$).

In CH$_3$CN, at 298 K and expressing the free energies $\Delta G_{EQ11}$ and $\Delta G_H$(HCOO$^-$) and $RT$ in kcal mol$^{-1}$, this results in $76 - 1.364 \times pK_a$(BH/B$^-$) < $\Delta G_H$(M-H) < $44$ kcal mol$^{-1}$ (in CH$_3$CN).

Therefore, this relationship sets the basis for the choice of a proton donor BH with a suitable range in order to direct the reactivity of M-H toward CO₂ reduction while avoiding H$_2$ evolution; the suitable range of $pK_a$(BH/B$^-$) has thus a lower limit of ca. 23.46, while the appropriate range depends on the hydricity of M-H. In particular, the lower the hydricity $\Delta G_H$(M-H), the higher the $pK_a$(BH/B$^-$) i.e., for very reactive M-H, very weak BH acids are required.

**Iron Carbonyl Clusters.** These considerations apply to the bioinspired, synthetic butterfly-like iron carbonyl clusters for CO₂ reduction to formate that have been reported by Berben and co-workers (Figure 3). The forerunner and the most active in the series$^{11}$ is [Fe$_4$N(CO)$_{12}$]$^2-$, hereafter abbreviated Fe$_2$N$^2-$; a key feature of this species is the possibility of it being electrochemically converted to the one- and two-electron-reduced species, Fe$_4$N$^{2+}$ ($-1.23$ V vs SCE) and Fe$_2$N$^{3+}$ ($-1.6$ V vs SCE), in acetonitrile as aprotic solvent.$^{10}$ These intermediates are clearly distinguishable spectroscopically, showing different ν$_{CO}$ stretching values in the range 1879–2018 cm$^{-1}$; a shift to lower wavenumbers upon reduction is consistent with the increase of electron density at the metal center, favoring the back-donation to π$^*$ orbitals of the CO and thus the weakening of the CO bond.

The presence of protons in the medium allows the formation of Fe$_4$N$^{2+}$ of a hydride species HFe$_4$N$^-$ as a key intermediate. This species was also structurally characterized, and the hydride was located between two iron centers by difference map.$^{12}$ In acetonitrile and in the presence of several Bronsted acids, HFe$_4$N$^-$ electrocatalytically evolves H$_2$. Cyclic voltammetry analysis revealed the accumulation of HFe$_4$N$^-$ when weak proton donors were employed, thus suggesting protonation of HFe$_4$N$^-$ as the rate-determining step, consistent with the higher reaction rate observed in the presence of stronger acids ($p$-toluenesulfoinic > chloroacetic > benzoic > butanoic). This evidence prompted Berben’s group to exploit the slow reactivity of HFe$_4$N$^-$ with “weak” butanoic acid, in order to direct it toward the reduction of CO₂.$^{10}$ Indeed, in the presence of CO₂, electrolysis gave formic acid as the main product; conversely, electrolysis in the presence of a stronger acid provided only H$_2$, even in the presence of CO₂ confirming that the H$_2$/HCOOH selectivity of the reaction could be directed by the strength of the proton donor.

The hydricity of HFe$_4$N$^-$ was calculated from a thermochemical analysis to be +49 kcal mol$^{-1}$ in acetonitrile and only 15.5 kcal mol$^{-1}$ in water, thus impacting on the $\Delta G$ of eq 8: $\Delta G_{EQ8}$ changes from +5 kcal mol$^{-1}$ in CH$_3$CN/water 95:5 (unfavorable hydride transfer from HFe$_4$N$^-$ to CO₂) to −8.6 kcal mol$^{-1}$ in water (favored hydride transfer from HFe$_4$N$^-$ to CO₂), thus predicting a more favorable driving force in aqueous medium. Indeed, in aqueous environment (pH range 5–13), the iron carbonyl cluster catalyzes CO₂ reduction to formate with a low overpotential (230–440 mV), a Faradaic yield (FY) up to 96%, and a TOF up to $3 \times 10^{-2}$ s$^{-1}$. Investigation of other iron carbonyl clusters led to less active and less selective processes, consistent with the thermochemical analysis predicting the hydricity of these species out of the optimal formate window.$^{11}$

**Figure 3.** Electrogeneration of Fe hydride HFe$_4$N$^-$ and its reactivity toward CO₂ or a Bronsted acid to generate formate or H$_2$, respectively. The 12 CO apical ligands of the Fe centers are omitted for clarity. Adapted with permission from ref 12. Copyright 2015 American Chemical Society.

**Figure 4.** Formation of hydride intermediate FeHP$^+_\text{a}$ and the competitive pathways of reactivity for the direct reduction of CO₂, leading to formate, or the reduction of the carbamate of diethylamine, leading to formation of methanol via an N,N-diethylformamide intermediate.
ences in transition-state structures, displaying a partial charge separation that can be likely solvated differently by the two media.

**Mononuclear Fe Complex with Tetradeutate Phosphine Ligand.** A recent example of an iron species operating through a hydride intermediate for the conversion of CO2 to formic acid was reported by Kang et al. (Figure 4).14 This deals with a mononuclear Fe(II) complex with a tetradentate tris[2-(diphenylphosphino)ethyl]phosphine ligand, FeP$_4^{2+}$, that upon a $2e^-$ reduction to Fe(0) at $E_{1/2} = -1.13$ V vs NHE in acetonitrile, in the presence of water, forms the Fe-hydride FeHP$_4^{+}$. This complex catalyzes the electrochemical reduction of CO2 to formate with a Faradaic yield in the range 90–98%, depending on the amount of water (up to 10%) and on the applied potential ($-1.0$ to $-1.6$ V vs NHE), with H$_2$ being observed as the byproduct. An interesting effect that led to a drastic change in product distribution was observed upon addition of diethylamine: in this case methanol was obtained under electrolysis at $-1.25$ V vs NHE with a FY of up to 68%. The formation of methanol was attributed to the reduction of the carbamate formed from reaction of CO2 with diethylamine, being competitive with the direct reduction of CO2 to formic acid (Figure 4): indeed, the highest selectivity for methanol was obtained when the excess of residual CO2 (i.e., the fraction that was not involved in carbamate formation) was removed from the solution. The authors identified N,N-diethylformamide as an intermediate product in methanol formation, since it initially accumulated during electrolysis, and was then consumed. Indeed, direct electrocatalytic reduction of N,N-diethylformamide led to methanol with a 90% Faradaic yield (Figure 4). Although several aspects of the mechanism still require further comprehension, the use of co-additives along with the catalyst to change the product selectivity and process efficiency is a most interesting topic that will likely be considered even more in future strategies for CO2 reduction.

### Fe-CO2 INTERMEDIATES IN MONONUCLEAR IRON CATALYSTS

**η^1-C Fe-CO2 Adducts.** In iron complexes for reduction of CO2, key intermediates are mononuclear η^1-C Fe-CO2 adducts, with CO2 binding to iron in low oxidation states, typically I or 0. In most of the cases, the reactivity of such intermediates is directed either toward the formation of an Fe-CO adduct, upon breaking of a C−O bond assisted by protons, or toward the formation of a formate-type adduct, upon protonation of the carbon (Figure 5). These two routes ultimately lead to the production of CO and formic acid, respectively. The selectivity of the process depends on the nature of the η^1-C Fe-CO2 intermediates, where the Fe−carbon bond is characterized by a significant electron density donation from the metal center to the π* orbitals of CO2. It is recognized that a high electron density of the iron center leads to a higher retrodonation, with the effect of increasing the electron density and the basicity of the carbon center. This ultimately favors protonation of carbon and the route toward formic acid.

**CO2 Reduction by Iron Porphyrins to CO.** Among mononuclear iron complexes, Fe porphyrins have been the most investigated class of catalysts for CO2 reduction.$^{15-17}$ Such catalysts display high reactivity and selectivity toward CO, and represent the forerunner category from both the application and the mechanistic knowledge standpoints. The catalytic mechanism proceeds through reaction between CO2...
and the Fe(0) active form of the catalyst: the resulting adduct is typically represented as an Fe(I)CO$_2$•$^-$ (Figure 5),$^{15-17}$ although the actual electron distribution is more properly depicted through the contribution of resonance formulas Fe(II)CO$_2$ and Fe(0)CO$_2$.

Spectroscopic investigation of iron tetraphenylporphyrin (Fe-TPP) intermediates with CO$_2$ was carried out by Mondal et al. under cryogenic conditions, upon a chemical reduction of the Fe-TPP catalyst. The authors isolated the Fe(I)CO$_2$•$^-$ adduct, which is then readily protonated by weakly protic solvents to form a long-lived Fe(I)C$\cdot$OOH species (Figure 5, see the CO route). In agreement with previous observations, this protonation step is believed not to be rate-determining: indeed, upon increasing the proton donor strength (i.e., using phenol), the Fe(I)CO$_2$•$^-$ complex was not detectable, since the Fe(0) intermediate is directly converted to the FeC$\cdot$OOH intermediate (dashed arrow in Figure 5).

Both Fe(I)CO$_2$•$^-$ and Fe(I)C$\cdot$OOH intermediates were identified by resonance Raman spectroscopy. The Fe(I)CO$_2$•$^-$ adduct displayed a signal in the low-frequency region at 590 cm$^{-1}$, attributed to stretching of the Fe–C bond, that shifts to 521 cm$^{-1}$ in Fe(I)C$\cdot$OOH upon protonation. The Fe(I)C$\cdot$OOH intermediate also displayed a FT-IR signal at 1573 cm$^{-1}$, attributed to the C–O stretching of the COOH moiety.$^{22}$ This represents a rare finding in terms of intermediate detection in the Fe(II) porphyrin carbonyl complex, between these catalytic systems and the biochemical routes of blood poisoning involving carbon monoxide coordination to oxygen-binding heme proteins.$^{27}$

As a final remark, it is worth highlighting the crucial, two-fold role of Brønsted acids in the Fe-porphyrin cycle: they are proton donors, i.e., co-substrates in the reaction, and co-catalysts. Indeed, as well as Lewis acids, they participate in a push–pull scheme in which the iron complex injects electron density into CO$_2$ by back-donation, while the co-catalyst interacts with the substrate through its oxygen atoms by electrostatics and/or hydrogen bonding. This provides a stabilizing effect on the Fe-CO$_2$ adduct and weakens the C–O bond after the first, protonation step. Outstanding catalytic performance could be achieved by installing such co-catalytic units into iron’s second coordination sphere. This strategy allows simultaneous activation of the CO$_2$ substrate, stabilization of key intermediates, and selectivity enhancement toward CO.$^{28-31}$

**CO$_2$ Reduction by Iron Porphyrins to Formate.** Recently, Margarit et al.$^{18}$ achieved switching the selectivity of Fe-TPP from CO toward formate (up to 68% FY with respect to Fe(II)).$^{23-25}$ The Fe(II)CO adduct formation is suggested by the appearance of new anodic peaks in the CV of CO$_2$-saturated solutions of Fe-porphyrin catalysts.$^{15-17}$ This complex is generated upon re-oxidation at $-1.6$ V vs SCE of a CO$_2$-saturated solution of Fe-TPP in dimethylformamide (DMF) after electrolysis at a potential value at which CO$_2$ is catalytically reduced ($-1.8$ V vs SCE).$^{23}$ Furthermore, spectroelectrochemistry (SEC) in the UV–visible range has provided evidence of such a Fe(II)CO intermediate, displaying a Soret band at 420 nm.$^{26}$ Incidentally, this last stage of the catalytic cycle is reminiscent of the well-known high affinity of heme complexes for CO. It is therefore possible to draw a parallel, based on the properties of the iron(II) porphyrin carbonyl complex, between these catalytic systems and the biochemical routes of blood poisoning involving carbon monoxide coordination to oxygen-binding heme proteins.$^{27}$
phenol proton donor) by employing tertiary amine co-
additives, acting as monodentate ligands to iron in the trans
position with respect to CO2 (Figure 5).7,18 This peculiarity is
justified by an enhanced Fe=CO2 electron density transfer
upon coordination of the amine, inducing an increase of the
basicity of the carbon atom of coordinated CO2 and thus
favoring the formic acid route (Figure 5). The back-bonding
ability of the iron center in heme systems is indeed promoted
by basic trans ancillary ligands; in this case a reactivity trend is
observed in the series quinuclidine > trimethylamine >
diisopropylmethylethylamine.18

The reported CO-to-HCOOH change of selectivity is
remarkable, since in this case no iron hydride intermediate is
involved toward the formation of formate, and thus the
possible competitive evolution of hydrogen is negligible.18 It
is worth highlighting that tertiary amines are often employed
in photocatalytic cycles for the reduction of CO2;32,33 the
evaluation of their effect on the selectivity of the process
in these systems should be thus considered.

**CO2 Reduction by Iron Porphyrins to Methane.** As
discussed above, the release of CO from iron porphyrins
involves a one-electron reduction of the Fe(II)CO adduct,
regenerating the Fe(I) resting state (Figure 5). Under
electrocatalytic conditions, the CO release is fast since it
occurs in the reaction—diffusion layer at the electrode, whose
potential during electrolysis favors the Fe(0) and Fe(I)
oxidation states. The fast release of CO by iron porphyrins
has been known to drive the reduction of CO2 to this 2e−/2H+
CO route for this class of catalysts.15−17 Conversely, when
CO2 reduction is conducted with photocatalytic systems, the
Fe(II)CO adduct may accumulate to a non-negligible extent,
since its further reduction requires a bimolecular reaction with
the reduced photosensitizer. Therefore, subsequent reactions
that involve participation of CO in the coordination sphere of
the iron catalyst may occur.

Indeed, two recent literature examples report that, under
optimized photocatalytic conditions, the complete 8e−/8H+
reduction of CO2 to CH4 can be achieved with a remarkable
selectivity of 14−15%,34,35 employing an iron catalyst bearing a
quaternary ammonium-functionalized porphyrin ligand. In the
first report, Ir(ppy)3 was used as photosensitizer,35 while in a
more recent work this role was played by a phenoazine
chromophore.35 These peculiar and novel examples highlight
how tuning of the system allows new catalytic routes to be
exploited by overcoming extrinsic mechanistic barriers.

**Non-heme Iron Mononuclear Complexes.** Non-heme
mononuclear iron complexes have been developed as another
class of catalysts for CO2 reduction, with mechanistic details
and principles being common to both categories (Figure 6).36−40
However, differently from the previously discussed iron
porphyrins, these systems share the common feature of
operating through a formal Fe(I) intermediate.

Three of these catalysts deal with iron complexes with N2O2
tetradentate ligands: 2,9-bis(2-hydroxyphenyl)-1,10-phen-
anthroline (H2dophen), 6,6′-di(3,5-di-tert-butyl-2-hydroxy-
benzene)-2,2′-bipyridine (H2dbppy), and N,N′-o-phenylenebis-
salicylimine) (H2salophen); the 2,2′:6,2′:6,2′-quater-
pyridine (qpy) and 2,13-dimethyl-3,6,9,12,18-
pentaaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene
(NS) provide instead nitrogen-based planar tetradentate and
pentadentate motifs, respectively.

Fe(dophen) catalyzes the reduction of CO2 through an
Fe(I) intermediate, generated in DMF or dimethyl sulfoxide at
$E = −2.0 \text{ V vs } \text{Fc}^+$/Fc, in the presence of proton donors;36 the
nature of these latter has an impact on the selectivity of the
process, where the main product is formate (FY up to 70%),
while CO, C2O4 2−, and H2 were also observed. This
observation was reasoned on the basis of two competitive
pathways, one involving a postulated Fe-hydride intermediate,
and the second one involving an η1−C Fe-CO2 adduct. The
former is responsible for formate and H2 evolution (see also
previous paragraph; in this case SEC-IR suggested the
involvement of an iron formato species, Fe-O(C(O)H, 1328
cm−1); the Fe-CO2 adduct is involved in CO and oxalate
formation. SEC-IR revealed also the accumulation of an
iron-carbonyl species (Fe-CO, 1934 and 1881 cm−1) before
evolution of CO (2140 cm−1).

A similar scenario involving two competitive pathways was
hypothesized for Fe(H2dbppy)37 which shows a higher
selectivity for formate (up to 68% FY at −2.5 V vs Fe+/Fc
with phenol proton donor, with ca. 1% FY for CO). Also in this
case the active Fe-hydrde intermediate was postulated to
form upon reduction of the Fe complex in the presence of
phenol; conversely, an Fe-CO2 intermediate was identified by a
feature at 1804 cm−1 in the SEC-IR, and was observed to
convert into an iron-carbonyl species (1847−1941 cm−1).
These, however, release CO very slowly, and therefore undergo
competitive catalyst degradation.

Formic acid is the main product observed also in the case of
Fe(NS), a reaction which, however, does not involve the
formation of an iron hydride. In this case, the reactivity occurs
at the Fe(I) state upon reaction with CO2, forming an Fe(III)-
CO2− adduct; the authors ascribed the favored selectivity
for formate to fast isomerization of the CO2 ligand into the
formate-type adduct, with respect to a slow C−O bond
 cleavage that would lead to the formation of CO.38 Carbon
monoxide was instead observed as the main product in the case
of the analogous Co complex, under both electrochemical and
photochemical conditions. Interestingly, this is one of few
cases in which iron and cobalt centers bearing the same organic
ligand both display CO2 reduction catalysis. This Fe/Co
similarity was observed also in the case of porphyrin
derivatives, and of salophen and qpy complexes discussed
below.

Fe(salophen) and Fe(qpy) are both active for catalytic CO
production in the presence of phenol as the proton donor with
a high initial selectivity (>99%), and involving Fe(I)
intermediates.39 In particular, Fe(salophen) evolves CO at
$E = −2.0 \text{ V vs } \text{Fc}^+$/Fc (FY up to 58%), while Fe(qpy) operates at
a less negative potential of $E = −1.58 \text{ V vs } \text{Fc}^+$/Fc (FY up to
48%). Both systems are, however, characterized by a limited
TON of ca. 3 in the case of Fe(salophen), while TON = 8 for
Fe(qpy). This limitation is again ascribable to competitive
degradation pathways that lead to electrodeposition of iron
nanoparticles at the working electrode. In the case of Fe(qpy),
the critical step is a further reduction of an Fe(I)CO
intermediate, active in the catalytic cycle, to a non-productive
Fe(0)CO (identified by a peak at 1854 cm−1 in SEC-IR), with
this latter being the one that undergoes demetalation and thus
inducing electrodeposition of metallic iron. Interestingly, the
durability of the Fe(qpy) catalyst is enhanced in photocatalytic
cycles for reduction of CO2 where the rate of the deleterious
Fe(1)CO → Fe(0)CO reduction is lowered since it is
controlled by diffusion processes; Fe(qpy) thus reaches
TON = 1880 with 97% catalytic selectivity with Ru(bpy)32+ as
sensitizer and triethanolamine as sacrificial electron donor.
It is worth highlighting that in all the cases reported in this section, with the exception of Fe(NS), an iron carbonyl complex (Fe-CO) is detected as an intermediate, generated upon C–O bond cleavage at the Fe-CO2 adduct (the C–O bond cleavage may be proton-assisted or, since instrumental features of the SEC-IR cell may limit the use of proton donors, can involve a second molecule of CO2).23 Iron carbonyl complexes have a vastly known and exploited chemistry, and the study of such intermediates by vibrational spectroscopy can indeed provide insights into the electronic environment of the catalytic active site. However, for the systems presented above, the experimentally observed Fe-CO adducts may represent turnover-limiting species, as observed for Fe(dophen) and Fe(tbbdbpy), or can be even responsible for catalyst decomposition (in the case of Fe(qpy), where the species observed by SEC-IR is an inert zerovalent iron carbonyl).

As a general principle in catalysis, observation of reaction intermediates should be met with caution. Their accumulation and spectroscopic characterization may in fact indicate a significant stability and inertness, suggesting that they could be possibly “out-of-the-cycle” intermediates. Furthermore, the iron carbonyl intermediates are a recurring motif in CO2 reduction catalysts, showing an intrinsic degree of preference of such systems for reaction pathways that eventually lead to C–O bond cleavage.

■ IRON SINGLE-ATOM HETEROGENEOUS CATALYSTS

The large-scale utilization of a CO2 reduction process requires the design of a device in which the catalysts can be ideally embedded in a low-cost, conductive material. Recently, several research groups have made efforts toward the design and preparation of iron single-atom catalysts, supported on nitrogen-doped carbon materials (Fe-N-C). This class of catalysts shows impressive analogies in terms of mechanism with coordination complexes discussed above.

Fe-N-C are prepared by pyrolysis of an iron precursor, together with a carbon source (typically a Zn-based zeolitic imidazolate framework, ZIF-8) and a nitrogen-containing organic ligand.41,42 In these Fe-N-C materials, the active sites are identified as FeN4 units,41 resembling the coordination motif of molecular porphyrins, and being indeed selective toward the electrochemical reduction of CO2 to CO in an aqueous environment (typically in bicarbonate electrolyte), while aggregated iron clusters or Fe-based nanoparticles favor the route toward hydrogen evolution.43 The activity of FeN4 sites was investigated theoretically, and a general operating mechanism involves (i) coordination of CO2 to iron together with the addition of one electron and one proton to form an Fe-COOH site, (ii) addition of a second electron and a second proton, associated with the release of a water molecule and formation of an Fe-CO intermediate, and finally (iii) desorption of CO from the Fe site (Figure 7).43,44 The activity for CO evolution is then determined by the Faradaic steps and by the adsorption energies of COOH and CO onto the Fe site.

In particular, the formation of the Fe-COOH adduct is predicted by simulations to be both the potential-liming step and the rate-limiting step when a low overpotential is applied.44 At intermediate overpotential, the rate-determining step involves the dissociative formation of H2O with the production of the Fe-CO intermediate (Figure 7); consistently, the TOF is correlated to the CO binding energy descriptor (i.e., the higher the driving force of this step, the higher the rate). At higher overpotentials, the rate-limiting step is CO desorption, and in this region the hydrogen evolution reaction becomes competitive.46 Interestingly, a strong binding of CO to the Fe site supports the partial formation of methane with this class of catalysts, since the bound CO can undergo the subsequent chemical steps necessary to arrive at CH4 (see also previous discussion dealing with formation of methane with iron porphyrins).46

Recently, a couple of examples were reported dealing with a rational optimization of Fe single sites for enhancing the selectivity for CO production, while lowering the overpotential.42,47 Zhang et al. selected a hemin ferric chloride as the iron source, thus providing a heme-like Fe(III) site bonded to the tetrapyrrole macrocycle, in combination with melamine as the nitrogen source. This resulted in the formation of FeN4 sites, with an additional pyrrolic nitrogen coordinated at the apical position of iron; this reduces the Fe-to-CO adsorption and boosting the selectivity, as predicted by DFT simulations.47

An even higher reactivity, with overpotential as low as 80 mV (in 0.5 M KHCO3 saturated with CO2), was observed for single-atom Fe(III)X4 sites, with X = C and N (average coordination numbers are 3.4 and 0.5 for N and C, respectively).42 In particular, the +3 oxidation state of iron was maintained along the catalysis, as revealed by operando X-ray absorption (XAS) spectroscopy; this feature was discussed to be crucial for the high reactivity, since Fe(III) guarantees faster CO2 adsorption and CO desorption with respect to conventional Fe(II) sites. Also in this case the rate-determining step was postulated to be the protonation of the adsorbed CO23 to form the Fe-COOH intermediate at low overpotential. Conversely, CO desorption becomes rate determining at higher overpotential, parallel to the formation of Fe(II) sites; in these conditions, the material loses stability, due to a decrease in coordination number of Fe from 4 to 3.42

■ CONCLUSIONS AND PERSPECTIVES

The reduction of CO2 has an intrinsic selectivity issue with respect to other reactions related to solar-to-fuel conversion.
(i.e., proton reduction to hydrogen or water oxidation to oxygen). Combining high reaction rates (i.e., current densities above $10^2\ mA\ cm^{-2}$ in the case of electrolyzers) with high selectivity for a single product remains a challenge. The heterogeneous single-atom catalysts seem indeed very promising toward this application, considering also their easier scalability, the Fe(III)X₄ catalyst developed by Hu et al. operates with a current density of 94 mA cm⁻² at 0.34 V overpotential, with >90% Faradaic yield for CO.⁴² On the other hand, although their synthetic and functionalization procedures are often challenging, molecularly defined catalysts can offer advantages over heterogeneous materials, and can help in their design.⁴⁷

The potential of molecular catalysts has been demonstrated by embedding cobalt phthalocyanine in a flow cell operating at >95% selectivity for CO at a current density of 150 mA cm⁻²;⁴⁸ this approach was recently extended to an iron porphyrin catalyst.⁴⁹ The role of molecular catalysts will be even more important in transformations where the selectivity target is more difficult to achieve, as in the case of highly reduced products of CO₂.

The control and orientation of selectivity are strictly connected to the comprehension of well-defined reaction mechanisms, as we have discussed in this Mini-Review for selected cases of iron coordination complexes. Formal electrokinetic analysis may be used to dissect the role of through-structure and through-space effects on each step of a catalytic mechanism. On the other hand, a complementary inorganic chemical approach based on experimental and computational techniques can be specifically devoted to clarifying the relationships binding together electronic and steric properties of the complexes, reactivity, and preferred reaction pathways. In this regard, theoretical calculations can be effectively integrated in the study of the catalytic mechanisms herein discussed. They provide fundamental quantitative and qualitative support to the interpretation of spectroscopic and electrochemical data, thus allowing a correct identification of the species involved and the determination of energetic profiles of possible reaction pathways. Furthermore, they can aid the study of catalytic systems involving second-sphere interactions, in which finely tuned catalyst–substrate adducts play a key role in justifying the superiority of such systems over simpler analogues.

These mutually integrating strategies make it possible not only to establish the role of key intermediates but also to steer their reactivity and enhance the selectivity of the overall process toward the desired reaction, while avoiding detrimental, turnover-limiting side reactions.

The ever-increasing corpus of design principles and investigation tools represents the key for a true, deep, rational implementation of the catalytic principles. This will eventually lead to the most effective, selective, and completely sustainable CO₂ reduction processes with the benefit of mechanistic knowledge and applications yet unreached.

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**Notes**

The authors declare no competing financial interest.

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Andrea Sartorel is an associate professor at the University of Padova and member of the Nano and Molecular Catalysis (NanoMolCat) Lab, based in the Department of Chemical Sciences. His research interests deal with electro- and photocatalysis for small molecule activation.

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**ABBREVIATIONS**

CODHases = carbon monoxide dehydrogenases; FY = Faradaic yield; SEC-IR = spectroelectrochemistry in the infrared region; TON = turnover number; TOF = turnover frequency; NHE = normal hydrogen electrode; Fe+/Fc = ferrocenium/ferroene

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