

A Short Perspective on Electrochemical CO₂ Reduction to CO

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Abstract: This short review summarizes examples of many homogeneous non-noble catalysts for CO₂-to-CO reduction and compares their feasible mechanisms. The focus is to show that elucidating the electronic structure of the catalytic system likely provides better understanding of the reaction mechanism and product selectivity.

Keywords: Electrochemical CO₂ reduction · Non-noble metal catalysts



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Introduction

The past two decades have witnessed the increasing concentration of CO₂ in the atmosphere, in part due to human activities, to an all-time record value of 411 ppm in 2019.^[1] This is an urgent environmental issue that human beings are confronted with.^[2] To tackle this challenge, a series of measures have to be instituted for the sustainable development of industrialized societies.^[3] In addition to carbon capture and sequestration,^[4] which represents the most mature technology at our disposal thus far, a promising alternative solution is to use CO₂ as a feedstock for manufacturing value-added fine chemicals in place of hydrocarbons, considering the gradual scarcity of fossil fuel resources.^[5]

In this regard, a great deal of effort has been invested into electrocatalytic reduction of CO₂ to generate a range of C1 prod-

ucts, such as CO, HCOOH, HCHO, CH₃OH and CH₄.^[6–8] Not all reduction products can be directly used as biofuels, and some need further processing. For instance, in the presence of H₂, CO can be converted into different hydrocarbons *via* the well-known Fischer-Tropsch process.^[9] From a thermodynamic point of view, CO₂ is a stable molecule; hence, CO₂ functionalization inevitably needs considerable energy input. Furthermore, because one-electron reduction of CO₂ to CO₂^{•-} suffers from a formidable negative potential (−1.9 V vs NHE),^[10] facile CO₂ transformations are usually multiple-electron reduction processes, which are realized by coupling with additional electrophiles, typically H⁺, to stabilize electrons being transferred to CO₂. Kinetically, CO₂ is rather inert largely due to substantial geometric distortions accompanied by CO₂ reduction. CO₂ features an sp-hybridized central C atom that changes to sp₂-hybridization in all C1 products except CO. As elaborated below, key intermediates en route to CO also contain sp₂-hybridized C atoms. In fact, the prohibitively negative potential of the one-electron reduction of CO₂ is a manifestation, at least in part, of adjusting its linear geometry to an O-C-O angle of ~135° in CO₂^{•-}. Thus, CO₂ activation also requires appropriate catalysts.

Catalytic reactions are typically classified into two categories: heterogeneous and homogeneous. While less industrially relevant, homogeneous catalysis can allow detailed kinetic^[11] and spectroscopic investigations^[12] aimed at elucidating fundamental intricacies of the reaction mechanism. In contrast, heterogeneous catalytic processes often involve many catalytically irrelevant species, and/or often operate under more extreme temperature or pressure conditions, which largely hinder experimental mechanistic studies. Besides experimental work, mechanistic insights can be provided by theoretical computations. Recent developments, in particular the progress of low-computational cost methods both in terms of calculation time and accuracy,^[13,14] render quantum mechanics-based methods an invaluable tool to provide reliable energetics, interpret spectroscopic data, and ultimately aid in setting up structure and activity relationship.

The research field of CO₂ reduction is already more than thirty years old, and has been the subject of many studies. The purpose of this short review is to summarize the recent progress of electrocatalytic reduction of CO₂ to CO, which may serve as a starting point for a rational design of new generations of more efficient and environmentally benign catalysts.

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Non-noble Metal Catalysts for Electrochemical CO₂ to CO Reduction

Although some potent catalysts involving late transition metals, such as ruthenium,^[15] rhenium,^[16] osmium^[17] and palladium^[18] have been reported, most of the recent research efforts are directed towards the use of non-noble transition metal-based catalysts. One widely used approach is to design macrocyclic complexes with empty axial coordination sites. In this regard, the most representative examples are [Fe(TPP)] (TPP²⁻ = tetraphenylporphyrinate, **1** in Fig. 1) and its derivatives, which are among the most efficient catalysts for CO₂ reduction reported in the literature. For [Fe(TPP)], the catalytic reaction proceeds at potentials lower than -1.7 V vs. SCE with 100% Faradaic efficiency for CO generation,^[19] and was found to reach a tremendous turnover frequency (TOF) superior to 10⁷ h⁻¹ at a potential of -2.3 V. Nickel-cyclam^[20,21] (cyclam = 1,4,8,11-tetraazacyclotetradecane, **2** in Fig. 1) catalyzes CO₂ reduction to yield nearly exclusively CO at about -1.8 V vs SCE with a TOF of 324 000 h⁻¹. A macrocyclic cobalt complex (**3** in Fig. 1) reported by Chapovetsky *et al.* also exhibits high Faradaic efficiency of 98%,^[22] but works at very negative potentials (<-1.95 V)

with a TOF of 612 000 h⁻¹ recorded at a potential of -2.3 V. The catalytic reaction mediated by a cobalt-N₄H complex (N₄H = 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(7),2,11,13,15-pentaene) (**4** in Fig. 1) reported by Lacy *et al.* is operative at a potential of -1.7 V and has a total turnover number of 4.1 over 40 min (TOF 6.1 h⁻¹).^[23] A similar cobalt complex studied by Chen *et al.* (**5** in Fig. 1) is active at -1.5 V. The TOF was not calculated under electrocatalytic conditions, but under the photocatalytic conditions a TOF of 21.9 h⁻¹ was found.^[24]

Another successful family of catalysts are metal-pyridine complexes. Initially, Hawecker *et al.*^[16b] reported a rhenium complex, [Re(bpy)(CO)₃Cl] that catalyzes CO₂ reduction with 98% CO formation, but the reaction has a low TOF of 21.4 h⁻¹ at a potential of -1.5 V. Since then, intensive research has been carried out on [Re(bpy)(CO)₃Cl] to optimize its performance, most notably by tuning the bipyridine ligand.^[25] More recently, its manganese derivative [Mn^(mesbpy)(CO)₃(MeCN)]⁺ (mesbpy = 6,6'-dimesityl-bpy) (**7** in Fig. 1) was found to exhibit a very high catalytic activity.^[26,27] Cobalt-terpyridine complex (**8** in Fig. 1) has been shown to display activity for CO generation at a potential of -1.7 V, although

Fig. 1. Selected examples of catalysts for CO₂-to-CO reduction.

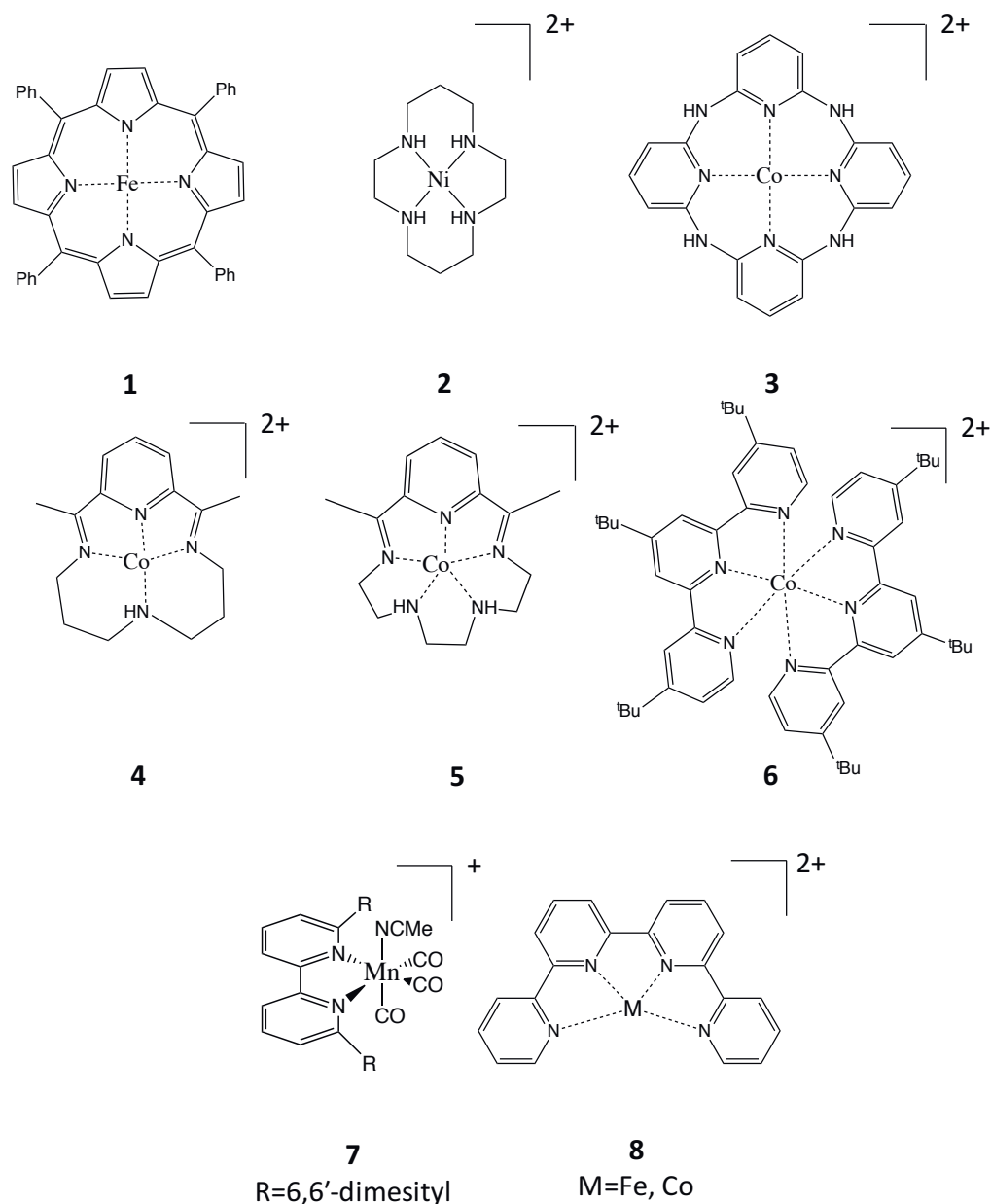


Table 1. Representative examples of homogeneous catalysts used for CO₂ electrocatalytic reduction to CO. The TOF is obtained by controlled potential electrolysis. Unless indicated otherwise, the Faradaic efficiency and operating potential correspond to the electrolysis at which the TOF was obtained, and the reference electrode is SCE.

Metal	Catalyst in Fig. 1	Operating potential	Faradaic efficiency for CO generation	TOF(h ⁻¹) (TON in brackets)
Fe	1	-2.3	100% (at -1.7 V)	>10 ⁷ [19b,c]
Fe	8	-1.4	72%	n.a. (19) ^[29b]
Ni	2	-1.8	90%	3.24 × 10 ⁵ [20]
Co	3	-2.3	98%	6.12 × 10 ⁵ [22]
Co	4	-1.7	45%	6.1 [23]
Co	5	-1.5	82%	n.a. ^[24]
Co	6	-1.7	37%	n.a. ^[28]
Co	8	-1.3	87%	n.a. (64) ^[29b]
Mn	7	-1.8	98%	1.7 × 10 ⁶ [26b]

the Faradaic efficiency is only 37%.^[28] Similarly, iron and cobalt quaterpyridine complexes (**8** in Fig. 1) catalyze the CO₂ transformation at -1.4 V and -1.3 V with Faradaic efficiencies of 72% and 87%, respectively.^[29]

Feasible Mechanisms for Electrochemical CO₂ to CO Reduction

In the literature, there are multiple reaction mechanisms proposed for electrochemical CO₂ reduction to generate CO. For mononuclear complexes, they can be categorized into five different types labelled as I, IIa, IIb, IIc and III in Fig. 2.

Type I entails the following sequence: (1) one-electron reduction of the catalyst, (2) formation of a η¹-CO₂ adduct with the metal center, M-CO₂, (3) protonation of the adduct to generate a metallacarboxylic acid intermediate M-C(O)OH, (4) proton-assisted cleavage of the C-O bond in M-C(O)OH to yield a metal-

carbonyl product, and (5) one-electron reduction of the catalytic system triggers CO dissociation of the metal center and restores the catalyst. Clearly, the driving force for the C-O bond breaking in step 4 originates from the formation of the O-H bond in H₂O. The reactions with cobalt macrocycle species **3**^[22] most likely follow the type I mechanism. The authors postulated this type of mechanism because the enhanced current in the presence of CO₂ is near the reversible wave of the molecular catalyst, suggesting that reduction of the catalyst must precede the formation of the adduct.

Different from I, in the type II mechanism, the metal-CO₂ adduct is formed in the first step. Subsequently, the electron reduction of M-CO₂ is coupled by proton transfer, and this process can proceed either in a step-wise fashion (IIa and IIb) or in a concerted manner (IIc), leading to the metallacarboxylic acid intermediate. Specifically, the electron transfer takes place first in the type IIa mechanism, which is followed by a proton transfer. By contrast, the type IIb mechanism features a reserved sequence of first protonation and then reduction. The following steps are the same as those in I. A range of catalysts follow the type II pathway, for example, nickel-cyclam. A DFT study compared pathways IIa, IIb and IIc and found IIc was the most probable one.^[30] Computational studies^[26] revealed that the 'reduction-first' pathway is the most plausible mechanism for the reactions catalyzed by the metal-bipyridine complexes operating at high potentials, which provides another example of the type IIb mechanism.^[26,31]

The type III mechanism involves first formation of the metal-CO₂ adduct after the reduction of the catalyst. Then the C-O bond scission takes place in M-CO₂, concurrently with transfer of two protons. Unlike I and II, the type III mechanism does not pass through the metallacarboxylic acid intermediate. To our knowledge, reactions invoking the type III mechanism are rare, and it is only proposed by Costentin *et al.* for [Fe(TPP)] on the basis of an experimental kinetic study.^[11]

Direct spectroscopic evidence of the existence of intermediates involved in any of these mechanisms remains limited. However, it is worthwhile to note that η¹-CO₂ adducts of zero-valent iron and cobalt have been detected by using transient infrared spectroscopy. These adducts decompose above 60 K, presumably suggesting their high reactivity.^[32] A cobalt(I) η¹-CO₂ adduct stabilized by the interaction with two K⁺ ions has been characterized by X-ray diffraction analysis,^[33] but this complex is too kinetically inert to yield CO. Recently, a kinetic and spectroscopic study provided

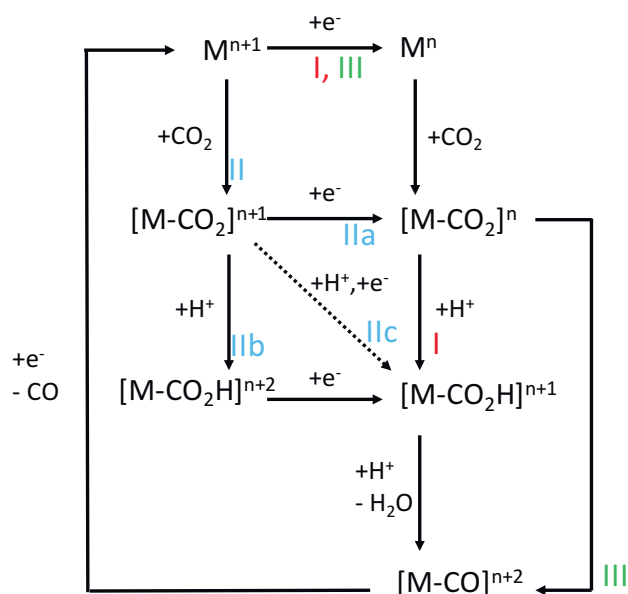


Fig. 2. The general mechanism of CO₂ reduction into carbon monoxide. The number n designates the charge of the molecular complex. The numbers I, IIa, IIb, IIc and III designate the mechanism types, as described in the text.

evidence of the existence of a Re-CO₂H carboxylate intermediate in the reaction with [Re(bpy)(CO)₃].^[34]

A better understanding of the electronic structure of the intermediates, which are often too unstable to be observed experimentally, is critical to identify the potential rate-determining states and provide insight into the catalytic mechanism. For that, DFT calculations are usually an invaluable tool. For instance, the Gibbs free energy change of the formation of the (cyclam)Ni-CO₂ adduct was computed to be as low as -1.7 kcal/mol.^[30] This is due to weak metal-CO₂ interactions and an unfavorable entropy contribution to a combination reaction. Keith *et al.* found that formation of adduct [Re(CO)₃(bpy)(CO₂)]⁻ was kinetically unfavorable unless in the presence of a stabilizing cation.^[31] In the case of [Co(N₄H)]⁺, the formation of the metal-CO₂ adduct was almost energetically neutral.^[35] For the C-O bond cleavage of [Ni(C(O)OH)(cyclam)]⁺, the barrier increases with the pK_a value of the acid and goes up to 21 kcal/mol in water. Similarly, for the Re system, the C-O scission needs to traverse a barrier of 24.4 kcal/mol with methanol as the proton donor. Those studies identify the formation of the CO₂ adduct and cleavage of the C-O bond as potential rate-determining steps, thus triggering new ideas for tuning the catalytic activities. For instance, to improve the catalytic performance of [Re(bpy)(CO)₃]⁻, the bipyridine ligand was modified in order to allow formation of an intramolecular H bond with the coordinated CO₂ ligand, thus stabilizing the η¹-CO₂ adduct.

Product Selectivity

The electrochemical CO₂ reduction always has to compete with hydrogen evolution and formic acid generation. Both pathways start with the protonation of the metal center to afford a metal-hydride species, which then acts as a hydride donor either to H⁺ (hydrogen evolution) or to CO₂ (formic acid generation).^[28,36] Therefore, the proton may compete with CO₂ to bind to the metal center. In the case of [Re(bpy)(CO)₃Cl], the formation of the metal-hydride (ΔG = -39.8 kcal/mol) was found to be highly favored thermodynamically over that of the metal-CO₂ adduct (ΔG = -10.5 kcal/mol). However, the former process requires a significant barrier (ΔG[‡] = 21.6 kcal/mol); in contrast, the latter has no barrier, indicating a kinetic origin to the product selectivity.^[31] Consistent with the theoretical predictions, it was shown that adding a local proton source to [Mn(bpy-R)(CO)₃Br] increases drastically the production of formic acid.^[27] This is likely due to the ease of formation of the metal-hydride species with the higher concentration in the vicinity.

Different from the aforementioned case involving metal-hydride species, starting from metal-CO₂ adducts, the reaction can also lead to formation of formic acid. DFT calculations^[30] have pointed out that the coordination mode of CO₂ to [Ni(cyclam)]⁺ dictates the final reaction outcome; generation of either formic acid or carbon monoxide depends on whether the coordination mode is η¹-OCO or η¹-CO₂ (Fig. 3). The driving force for the formation of the Ni-CO₂ adduct stems from the electron back donation of the metal center into the lowest unoccupied molecular orbital (LUMO) of CO₂. Addition of CO₂ to the Ni(I) center in a η¹-OCO mode was calculated to be thermodynamically uphill by 12.4 kcal/mol due to the large interelectronic repulsion between the oxygen of CO₂ and the low valent metal center. On the other hand, the η¹-CO₂ binding mode involves a partial electron transfer from the Ni d_{z²} orbital to the LUMO of CO₂, which is the in-plane π* orbital in nature and has much higher weight of the electrophilic carbon atom than those of the terminal O atoms. Hence, the favorite orbital overlap stabilizes the η¹-CO₂ rather than the η¹-OCO adduct, which selectively yields CO in the end.

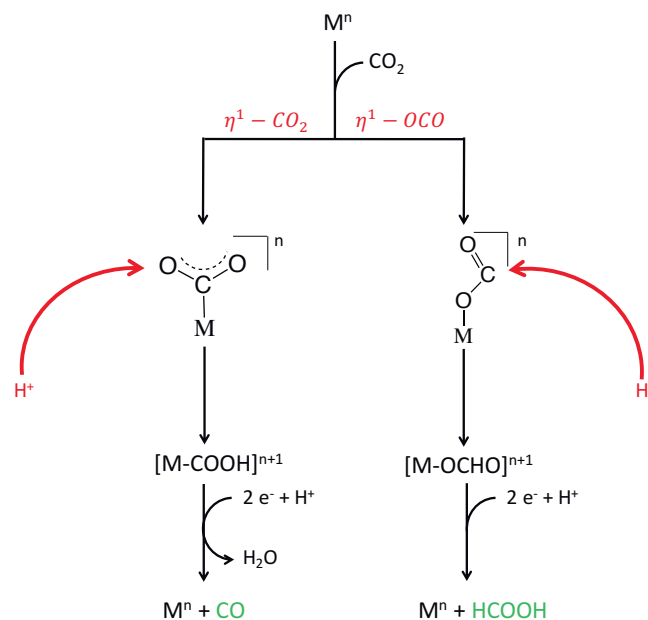


Fig. 3. Schematic representation of the η¹-OCO and η¹-CO₂ binding modes, leading to the formation of formic acid and carbon monoxide, respectively.

Conclusion

The present contribution summarizes representative examples of the vast majority of available homogeneous non-noble catalysts for the two-electron reduction of CO₂ to CO and compares their feasible mechanisms. Several examples are provided where theoretical chemistry was used as a tool to understand the reaction mechanism and product selectivity on the grounds of the electronic structure of the catalytic system. The underlying philosophy that we insist on is that thoroughly elucidating the electronic structure of a transition metal complex is the prerequisite for understanding its catalytic activity. In this regard, spectroscopic investigations on kinetically competent, unfortunately often fleeting, intermediates are highly valuable. In our opinion, the purpose of carrying out computational studies is not only to simply predict accurate reaction energies and barriers, but also to provide chemical understanding of the reaction mechanism. It should be noted that chemical insights can be used as a guide in designing new systems with tailored properties, but numbers alone can hardly do so.

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