

## Perspective

How to rationally design homogeneous catalysts for efficient CO<sub>2</sub> electroreduction?Hui Zhang,<sup>1</sup> Qinghua Liang,<sup>2,3,\*</sup> and Ke Xie<sup>4,\*</sup>

**Electrified converting CO<sub>2</sub> into valuable fuels and chemicals using a homogeneous electrochemical CO<sub>2</sub> reduction (CO<sub>2</sub>ER) approach simplifies the operation, providing a potential option for decoupling energy harvesting and renewable chemical production. These merits benefit the scenarios where decentralization and intermittent power are key factors. This perspective aims to provide an overview of recent progress in homogeneous CO<sub>2</sub>ER. We introduce firstly the fundamentals chemistry of the homogeneous CO<sub>2</sub>ER, followed by a summary of the crucial factors and the important criteria broadly employed for evaluating the performance. We then highlight the recent advances in the most widely explored transition-metal coordinate complexes for the C<sub>1</sub> and multicarbon (C<sub>2+</sub>) products from homogeneous CO<sub>2</sub>ER. Finally, we summarize the remaining challenges and opportunities for developing homogeneous electrocatalysts for efficient CO<sub>2</sub>ER. This perspective is expected to favor the rational design of efficient homogeneous electrocatalysts for selective CO<sub>2</sub>ER toward renewable fuels and feedstocks.**

## INTRODUCTION

During the past few decades, the huge energy demand and the rapid consumption of fossil fuels have caused increasing CO<sub>2</sub> emissions, leading to severe environmental impacts and the greenhouse effect. The issues of carbon emissions and global warming have received intensive attention from countries worldwide. Governments worldwide have made imperative and political commitments to achieve carbon neutrality. Notably, the Chinese government has released numerous implementations to realize carbon peaking in 2030 and carbon neutrality goals in 2060. Thus, peaking CO<sub>2</sub> emission presses for advanced CO<sub>2</sub> capture and transformation technologies. In accordance, developing efficient and durable strategies for the activation, selective conversion, and recovery of CO<sub>2</sub> has been receiving tremendous attention in the research community to realize the resource utilization of CO<sub>2</sub> toward a sustainable modern society.<sup>1,2</sup>

The efficient conversion of CO<sub>2</sub> into value-added chemicals through the reduction method has long been pursued as one of the most attractive and economical ways for the resource utilization of CO<sub>2</sub>. Generally, the chemical reduction of CO<sub>2</sub> molecules requires using catalysts for activation owing to their inert nature. In the last decades, many catalytic strategies, including chemical catalysis, photocatalysis, biomimetic catalysis, and electrocatalysis have been proposed for CO<sub>2</sub> reduction. Chemical catalysis is usually involved with the organic catalyzed reduction of CO<sub>2</sub> based on using the functional non-noble metal catalysts and the main group catalysts (e.g., frustrated Lewis pairs, carbene analogs, and so on).<sup>3–5</sup> The photocatalytic CO<sub>2</sub> reduction is often achieved using semiconductors-based photocatalysts such as metal oxides (e.g., TiO<sub>2</sub>, CeO<sub>2</sub>, and so on) and metal-organic frameworks.<sup>6–9</sup> As for biomimetic catalysis, metalloenzymes, and some natural products are explored to simulate the process for the biogeochemical cycles of CO<sub>2</sub>.<sup>10,11</sup> In particular, electrocatalytic CO<sub>2</sub> reduction, also termed CO<sub>2</sub> electroreduction (CO<sub>2</sub>ER), attracts increasing attention due to the sustainability and safety of electricity and numerous advantages such as mild reaction conditions, easy operability, and good tunability of reactivity and selectivity.<sup>12–14</sup> In addition, CO<sub>2</sub>ER is a promising approach to meet the prevailing trends in organic electrosynthesis, which has seen increasingly broad use in the synthetic community over the past several years.<sup>15–23</sup>

The CO<sub>2</sub>ER is usually carried out in the heterogeneous system and conducted in flow-cell setups to enable industrial-relevant productivity.<sup>24</sup> In the past decade, the flow-cell CO<sub>2</sub>ER devices of a gas-diffusion electrode (Figure 1A) were intensively studied majorly because they resemble industrial water electrolyzers.<sup>25</sup> The solid-state catalyst particles or thin film are loaded onto hydrophobic gas-diffusion layers, and the CO<sub>2</sub>ER occurs at the catalyst-electrolyte-CO<sub>2</sub> gas triple-phase boundary,<sup>26</sup> i.e., heterogeneous catalysis. As such, most of the studies on the heterogeneous CO<sub>2</sub>ER focus on developing highly active heterogeneous electrocatalysts and fabricating gas diffusion electrodes.<sup>27</sup> The gas diffusion electrode fabrication is complicated and costly, and its poor durability handicaps the industrial implementation of heterogeneous CO<sub>2</sub>ER. The gas diffusion layer may flood after 10–100 h of operation due to salt formation, electrowetting, or pressure

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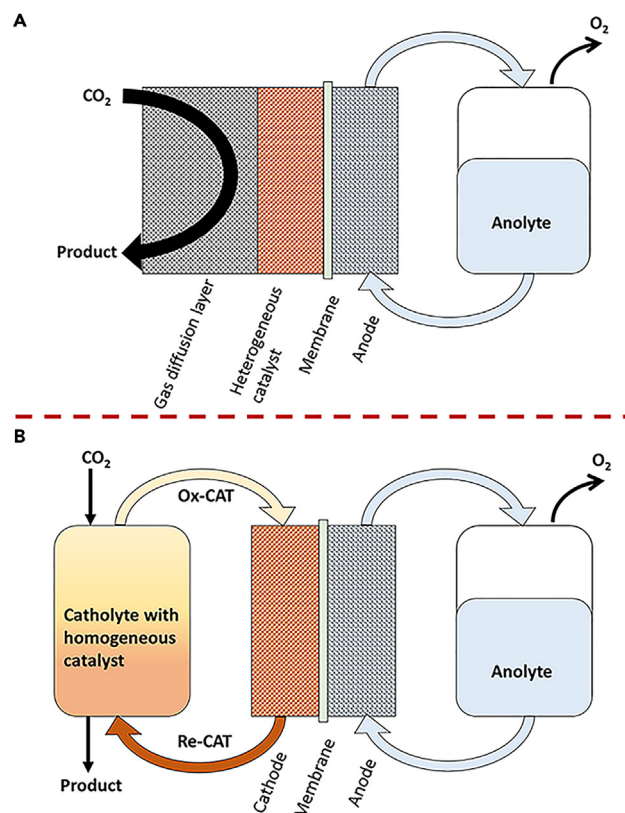
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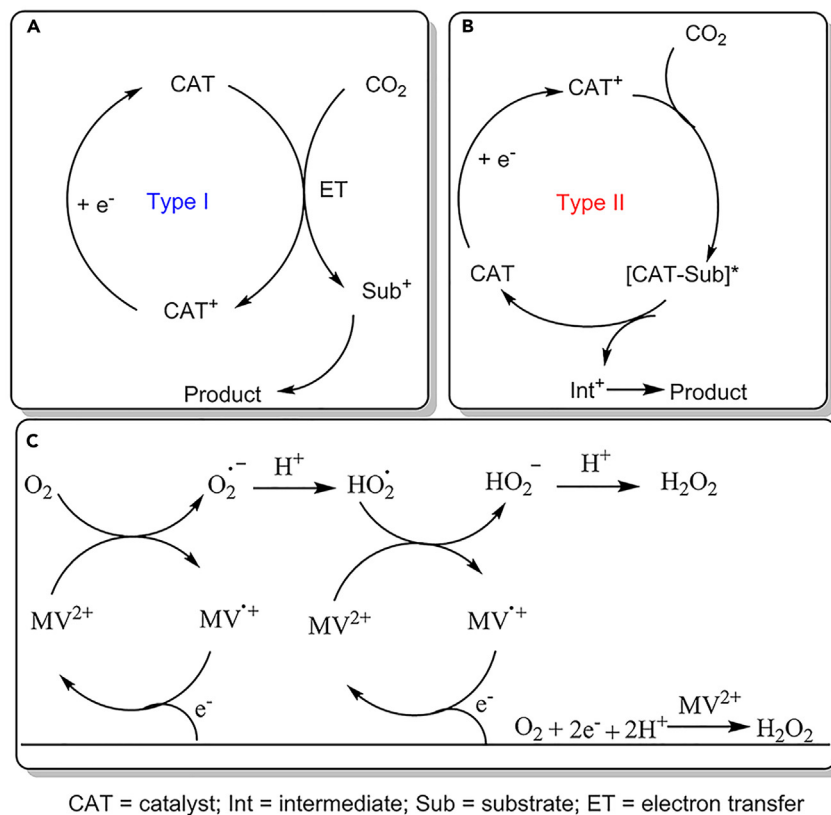
**Figure 1. The flow-cell CO<sub>2</sub>ER devices for heterogeneous and homogeneous catalysis**

The schematic illustration of heterogeneous catalyst (A) and homogeneous catalyst mediated (B) CO<sub>2</sub> reduction flow cells (Re stands for reduction, Ox stands for oxidation).

difference.<sup>28</sup> The heterogeneous catalyst deactivates due to chemical and mechanical instabilities. Power intermittent deteriorates the efficiency and durability problems. Low-temperature (<80°C) CO<sub>2</sub>ER-based energy storage for decentralized deployment lies in converting CO<sub>2</sub> to liquid fuel molecules, such as ethanol, methanol and propanol.<sup>29</sup> To date, Cu-based catalysts predominate the cathodic catalysts for such conversions. Typically, the selectivity of CO<sub>2</sub>ER in a specific device is determined by the operation current density, and the liquid product selectivity usually reaches the maximum at a narrow current density window (e.g., ± 50 mA/cm<sup>2</sup>).<sup>30,31</sup> The input power fluctuation can significantly alternate the selectivity of heterogeneous CO<sub>2</sub>ER devices and subsequently degrade their efficiency. In addition, the frequent on-off operation challenges Cu-based catalysts' robustness and the gas-diffusion electrode's stability.<sup>32</sup> Besides, replacing degraded catalysts requires the disassembly and reassembly of the electrolyzer, making the decentralized deployment of CO<sub>2</sub>ER devices challenging and incurring high electrolyzer maintenance costs.

The emerging homogeneous electrocatalytic system offers a potential solution to these challenges.<sup>33–36</sup> We illustrate a typical homogeneous electrocatalytic CO<sub>2</sub>ER in Figure 1B. A homogeneous electrocatalyst can usually move freely in the electrolyte. It is usually dissolved in the electrolyte, circulating between the electrode and the catholyte reservoir. The homogeneous electrocatalyst is electrochemically charged on the electrode and discharged in the reservoir through catalytic CO<sub>2</sub> reduction. The cathodic electrode can be inert, durable materials such as Ti and graphite foil. This installation thus removes the complicated cathodic electrode fabrication. The deactivated catalyst can be replenished by changing the catholyte. Therefore, homogeneous electrocatalytic CO<sub>2</sub>ER can potentially reduce the maintenance cost of CO<sub>2</sub>ER devices. Homogeneous CO<sub>2</sub>ER can decouple energy harvesting and consuming procedures,<sup>33–36</sup> enabling chemicals-in-demand operation, the optimization of each step independently and mitigating the impacts of intermittent power. For instance, we consider a homogeneous CO<sub>2</sub>ER device coupled with a solar farm. In the daytime, the device works as a flow battery with the redox mediates harvesting the energy from the photovoltaic cells. In the nighttime, the homogeneous CO<sub>2</sub>ER device works in a discharge mode, using the redox mediates to convert CO<sub>2</sub> to desired products under controlled and consistent conditions. Moreover, homogeneous CO<sub>2</sub>ER devices can use inert materials such as graphite, and the gas diffusion electrode configuration is unnecessary. These promote their robustness to the frequent on-off operation.

Generally, electrocatalysts play the most important critical roles in the overall electrochemical performance of homogeneous CO<sub>2</sub>ER. The homogeneous electrocatalysts can be roughly categorized into two types based on their different roles in the electron transfer steps. As shown in Figure 2, the Type I homogeneous electrocatalyst works as a redox mediator for shuttling electrons between the electrode and substrate, such as CO<sub>2</sub>. The electrocatalyst accelerates the redox reactions for homogeneous CO<sub>2</sub>ER that would otherwise be hindered by slow



**Figure 2. The generally proposed mechanisms for two types of homogeneous electrocatalysts for CO<sub>2</sub>ER and an example of type I electrocatalyst**  
(A) The Type I homogeneous electrocatalyst works as a redox mediator for shuttling electrons between the electrode surface and CO<sub>2</sub> substrate (the left one).  
(B) The type II homogeneous electrocatalyst not only serves as an electron shuttler but also produces new chemical bonds with the CO<sub>2</sub> substrates.  
(C) The MV<sup>2+</sup>/MV<sup>+</sup> couple serves as the electron shuttler in the oxygen electroreduction, the electrocatalyst does not form any chemical bonds, noncovalent bonds, or polymerized interactions with the O<sub>2</sub> substrate. Reproduced with permission from ref. <sup>37</sup> Copyright, American Chemical Society.

electron-transfer kinetics with electrode surfaces.<sup>38</sup> Since the type I electrocatalyst only serves as the electron shuttler, the electrocatalyst does not form chemical bonds, noncovalent bonds, or polymerized interactions with the CO<sub>2</sub> substrate. The type II homogeneous electrocatalyst serves as an electron shuttler to the CO<sub>2</sub> substrate and enables the formation of new chemical bonds, noncovalent bonds, or polymerized interactions with the CO<sub>2</sub> substrates. As such, the type II homogeneous electrocatalyst can improve both the reaction kinetics and chemical selectivity. Accordingly, type II electrocatalysts are more widely pursued.

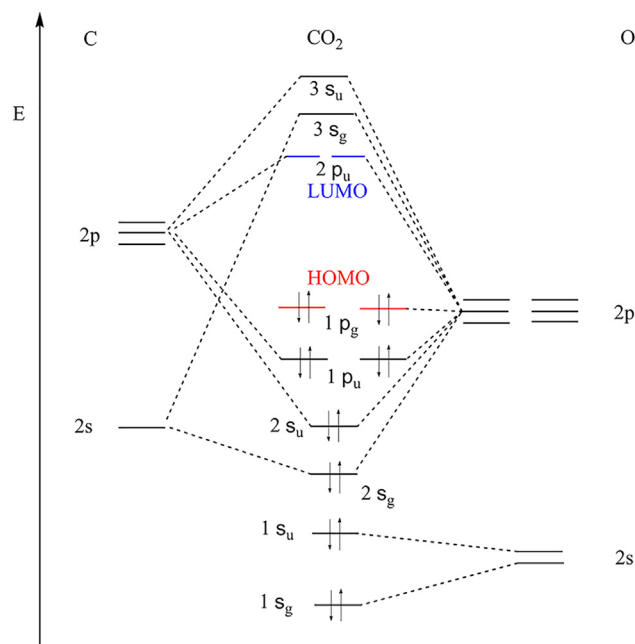
Few type I electrocatalysts has been reported since they generally show less activity than the type II electrocatalysts.<sup>37</sup> A typical example is that the MV<sup>2+</sup> (MV stands for methyl viologen) electrocatalysts was used for H<sub>2</sub>O<sub>2</sub> production from the O<sub>2</sub> electroreduction. The kinetic of catalytic process is similar to the homogeneous electron transfer of type I electrocatalyst. The rate constant of this rate-determining step is the type I electron transfer. The MV<sup>2+</sup>/MV<sup>+</sup> couple only serves as the electron shuttler.<sup>37</sup>

To date, many emerging electrocatalysts have been developed for homogeneous CO<sub>2</sub>ER.<sup>39–42</sup> To the best of our knowledge, although numerous reviews have discussed the recent advances in the design and development of electrocatalysts for heterogeneous CO<sub>2</sub>ER,<sup>43–46</sup> the current status and challenges for the rational design of electrocatalysts for homogeneous CO<sub>2</sub>ER are rarely discussed. To follow up on this field, here we provide this tutorial review for the rational design of efficient electrocatalysts for homogeneous CO<sub>2</sub>ER. We first present the fundamentals of homogeneous CO<sub>2</sub>ER, followed by a discussion of various critical influencing factors and criteria used to evaluate the performance of electrocatalysts for homogeneous CO<sub>2</sub>ER. We then highlight the most recent advances in the development of various efficient homogeneous electrocatalysts for selective CO<sub>2</sub>ER. Finally, we address the remained challenges and opportunities for future efforts in homogeneous CO<sub>2</sub>ER.

## FUNDAMENTALS OF HOMOGENEOUS CO<sub>2</sub>ER

### The molecular orbital of CO<sub>2</sub>

In general, the reduction of CO<sub>2</sub> occurs as a result of creating C–H and C–C bonds and cleaving C–O bonds. The molecular structure of CO<sub>2</sub> is linear with a very short and strong C–O distance of 1.16 Å. Although CO<sub>2</sub> shows nonpolar, it contains polar C–O bonds owing to the



**Figure 3. Molecular orbital diagram of CO<sub>2</sub>**

The highest occupied molecular orbital (HOMO) of  $1\pi_g$  orbitals is mainly ascribed to the terminal oxygen atoms. The empty antibonding  $2\pi_u$  orbitals of the lowest unoccupied molecular orbital (LUMO) are mostly contributed by the carbon atoms.

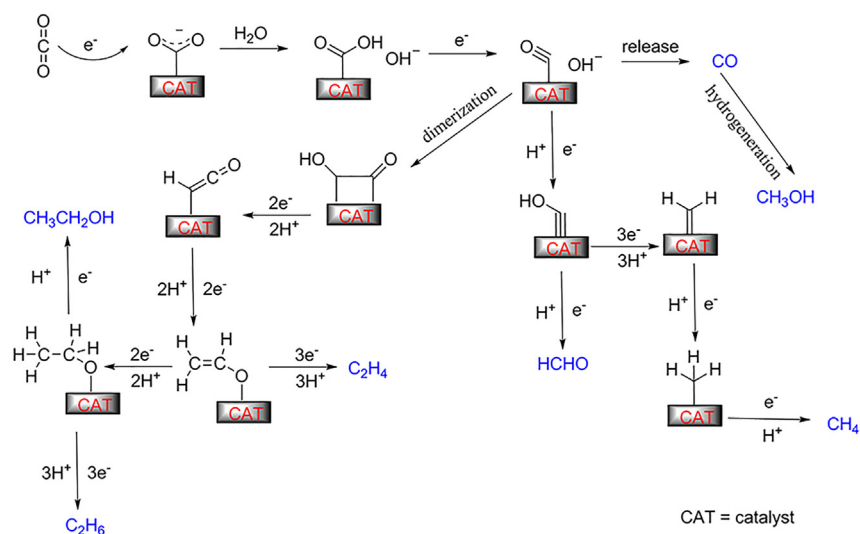
difference in electronegativity between C and O atoms. The intrinsic polarity of C–O gives rise to the susceptibility to nucleophilic attack on C and electrophilic attack on O atom. Generally, the reduction of CO<sub>2</sub> involves the activation of CO<sub>2</sub> through a decrease in the C–O bond.<sup>47</sup> This can be usually achieved by the use of functional catalysts owing to their inert nature.

The stability and chemical reactivity of a molecule is largely determined by the intrinsic molecular orbitals and bond energy. The molecular orbitals (Mos) for the energy diagram of CO<sub>2</sub> are illustrated in Figure 3. The doubly occupied nonbonding  $1\pi_g$  MOs mainly account for the HOMO (highest occupied molecular orbital). The  $1\pi_g$  MOs are principally contributed from the terminal oxygen atoms. The empty antibonding  $2\pi_u$  orbitals serving as the lowest unoccupied molecular orbital (LUMO) are mostly contributed by the carbon atom. In this regard, CO<sub>2</sub> can be considered an amphoteric molecule. Specifically, the oxygen atoms display a Lewis basic characteristic while the carbon atom behaves as a Lewis acid center. Since CO<sub>2</sub> has a slightly negative electron affinity ( $E_a$ ) of about  $-0.6$  eV<sup>48</sup> and a first ionization potential ( $I_p$ ) of about 13.8 eV,<sup>49</sup> CO<sub>2</sub> tends to accept electrons rather than donor electrons. The intrinsic reactivity of CO<sub>2</sub> molecules during reduction is thus usually dominated by the electrophilic character of the C atom rather than the weak nucleophilic properties of O atoms. When one LUMO orbital of CO<sub>2</sub> is filled by a transferred electron, the resultant lowest energy state could give rise to a bent geometry of the C–O bond. The C–O bond is thus simultaneously activated. Since one CO<sub>2</sub> molecule contains two  $2\pi_u$ , one  $3\sigma_u$ , and one  $3\sigma_g$  LUMO orbitals, one CO<sub>2</sub> molecule can accept up to 8 electrons. Accordingly, the reduction of one CO<sub>2</sub> molecule by a different number of electrons could result in different products. A complete reduction of one CO<sub>2</sub> molecule with a maximum of 8 electrons can give rise to the formation of CH<sub>4</sub>.

### Different reaction routes for homogeneous CO<sub>2</sub>ER

Different products such as CO, HCOOH, HCHO, and CH<sub>3</sub>CH<sub>2</sub>OH can be obtained from the homogeneous CO<sub>2</sub>ER through different reaction pathways. As illustrated in Figure 4, the products of homogeneous CO<sub>2</sub>ER depend highly on the type of homogeneous electrocatalysts and the experimental conditions. A multiple and cascaded electron transfer process could be also involved under certain conditions, giving rise to the formation of complex products. For example, a specific homogeneous electrocatalyst could enable the generation of CO<sub>2</sub><sup>•-</sup> intermediate through the transfer of one electron to CO<sub>2</sub>.<sup>51</sup> Accordingly, HCOOH can be produced if the radical is subsequently protonated. The HCOO<sup>-</sup> species can also be further reduced to generate HCHO and CH<sub>4</sub>.<sup>50</sup> In addition, CO can be produced from CO<sub>2</sub>ER after the reduction by two electrons. If the resultant CO cannot be activated by electrocatalysts, CO tends to be released for producing CH<sub>3</sub>OH through a hydrogenation process. Moreover, these intermediates can be further converted into alcohols or other hydrocarbons such as C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> through a dimerization pathway.<sup>50,52</sup> For heterogeneous CO<sub>2</sub>ER, the reaction path is a little different. Heterogeneous CO<sub>2</sub>ER usually involves the adsorption of CO<sub>2</sub> on the electrocatalyst surface, activation of the adsorbed CO<sub>2</sub> by the catalyst, and protonation of the activated CO<sub>2</sub>. While homogeneous CO<sub>2</sub>ER mainly involves the absorption of CO<sub>2</sub> in the electrolyte solvents and formation of an intermediate.

The homogeneous CO<sub>2</sub>ER has been reported to be accomplished through one-, two-, four-, six-, and eight-electron reduction pathways.<sup>53</sup> Accordingly, the main products such as CO, HCOOH/HCOO<sup>-</sup>, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>/C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, HCHO, and CH<sub>3</sub>OH can be obtained from homogeneous



**Figure 4. Schematic illustration of homogeneous CO<sub>2</sub>ER for various products enabled by type II electrocatalysts in aqueous electrolytes, the CAT stands for the homogeneous catalysts dissolved in the electrolyte solution**

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CO<sub>2</sub>ER.<sup>54</sup> Other products such as CH<sub>4</sub>, CH<sub>2</sub>CH<sub>2</sub>, and CH<sub>3</sub>CH<sub>2</sub>OH are rarely obtained as the main product but as the byproducts. Notably, the formation of different products from homogeneous CO<sub>2</sub>ER depends highly on the redox potentials. The standard redox potential for different products from homogeneous CO<sub>2</sub>ER is listed in Table 1. Generally, homogeneous CO<sub>2</sub>ER can proceed much more easily under acid conditions, as indicated by the lower required redox potential.<sup>55</sup> This could be owing to the higher energy barrier for CO<sub>2</sub> activation and more energy consumption in alkaline medium. For example, under alkaline conditions, more than 50% of the energy need to be used to recover CO<sub>2</sub> from CO<sub>3</sub><sup>2-</sup> during the homogeneous CO<sub>2</sub>ER.<sup>55</sup> As such, homogeneous CO<sub>2</sub>ER is intentionally carried out in acid electrolytes to improve overall energy efficiency.

### The main factors affecting homogeneous CO<sub>2</sub> electroreduction

Since the homogeneous CO<sub>2</sub>ER is a complicated process owing to many entangled steps during the electrochemical process, many factors can influence the product formation and the final electrocatalytic performance of an electrocatalyst. These factors include but are not limited to the types and concentrations of electrocatalysts, the electrolyte types, the electrolyte additives, and the external polarization potential. In this section, we briefly discuss how these factors impact the homogeneous CO<sub>2</sub>ER.

Generally, the influence of different factors can largely account for the affected corresponding steps in the CO<sub>2</sub>ER cycle. As shown in Figure 2, the types of homogeneous electrocatalysts can mainly impact the formation of [CAT-Sub]\* intermediates owing to the different intrinsic chemical structures and electrochemical kinetics. For example, using a dihydride complex (POCOP)Ir(H)<sub>2</sub> (POCOP stands for C<sub>6</sub>H<sub>4</sub>(OPPh<sub>2</sub>)<sub>2</sub>) as the electrocatalyst for CO<sub>2</sub>ER, the HCOOH was produced with a Faradaic efficiency of 93% at room temperature.<sup>56</sup> However, using homogeneous electrocatalysts based on the bipyridine (bpy) and terpyridine (tpy) complexes such as [Ru(tpy)(bpy)(MeCN)]<sup>2+</sup> enables CO production from CO<sub>2</sub>ER with a Faradaic efficiency of over 85%.<sup>57</sup> The reason for producing different products is mainly attributed to the formation of [CAT-Sub]\* with significantly different structures enabled by the different homogeneous electrocatalysts. The former Ir-based electrocatalyst gives rise to the [CAT-Sub]\* structure embedded with the formate, while the latter Ru-based electrocatalyst enables the formation of [CAT-Sub]\* composed of CO coordinate structure. It thus can be expected that the molecular structure of electrocatalysts plays a critical role in the selective homogeneous CO<sub>2</sub>ER.

Besides, the electrolyte components including the solvent and the additives can also impact the homogeneous CO<sub>2</sub>ER. Specifically, the formation process of the important intermediates (such as the Int\* in Figure 2) can be significantly influenced since the electrolyte has a great impact on the dissolved concentration of the CO<sub>2</sub> substrate and the stabilization of the transition states or intermediates. For instance, the solubility of CO<sub>2</sub> in the MeCN solution is 280 mM under 1.0 atm while this value is much lower in water (33 mM). The different concentrations of CO<sub>2</sub> in the electrolyte can significantly affect the reaction rate of CO<sub>2</sub>ER since the CO<sub>2</sub> substrate directly participates in the electrocatalytic reaction process.<sup>58</sup> Besides, the nature and the composition of the solvent matter a lot because the solvent can be also involved as the reactant during the CO<sub>2</sub>ER process. In particular, the protic solvents may be favorable for the formation of hydrogen bonds with the intermediates during homogeneous CO<sub>2</sub>ER. This can affect the electrocatalytic kinetics and product formation for homogeneous CO<sub>2</sub>ER. For instance, in the case of a primary amine-substituted Re(bpy)(CO)<sub>3</sub>Cl electrocatalyst (bpy = bipyridine, Re = Rhenium), the reduction potential for Re–Re dimerization intermediate is –2.11 V (vs. Fc<sup>+/0</sup>) when the CH<sub>3</sub>CN was used as the solvent for 0.1 M TBAPF<sub>6</sub> electrolyte

**Table 1. Half reactions of homogeneous CO<sub>2</sub>ER for different routes along with the corresponding standard redox potential (25°C, under 1 atm of gases, in an aqueous electrolyte)**

Reaction	$E^{\theta}/V$ (vs. SHE)
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{CO} + \text{H}_2\text{O}$	-0.530
$\text{CO}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{CO} + 2\text{OH}^-$	-1.347
$2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2\text{C}_2\text{O}_4$	-0.913
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{HCOOH}$	-0.610
$\text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{HCOO}^- + \text{OH}^-$	-1.491
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \longrightarrow \text{HCHO} + \text{H}_2\text{O}$	-0.480
$\text{CO}_2 + 3\text{H}_2\text{O} + 4\text{e}^- \longrightarrow \text{HCHO} + 4\text{OH}^-$	-1.311
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \longrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-0.380
$\text{CO}_2 + 5\text{H}_2\text{O} + 6\text{e}^- \longrightarrow \text{CH}_3\text{OH} + 6\text{OH}^-$	-1.225
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \longrightarrow \text{CH}_4 + \text{H}_2\text{O}$	-0.240
$\text{CO}_2 + 6\text{H}_2\text{O} + 8\text{e}^- \longrightarrow \text{CH}_4 + 8\text{OH}^-$	-1.072
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \longrightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$	-0.340
$2\text{CO}_2 + 8\text{H}_2\text{O} + 12\text{e}^- \longrightarrow \text{C}_2\text{H}_4 + 12\text{OH}^-$	-1.177
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \longrightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O}$	-0.330
$2\text{CO}_2 + 9\text{H}_2\text{O} + 12\text{e}^- \longrightarrow \text{C}_2\text{H}_5\text{OH} + 12\text{OH}^-$	-1.157
$2\text{CO}_2 + 14\text{H}^+ + 14\text{e}^- \longrightarrow \text{C}_2\text{H}_6 + 4\text{H}_2\text{O}$	-0.270
$3\text{CO}_2 + 18\text{H}^+ + 18\text{e}^- \longrightarrow \text{C}_3\text{H}_7\text{OH} + 5\text{H}_2\text{O}$	-0.320

(TBAPF<sub>6</sub> = tetrabutylammonium hexafluorophosphate). However, the intermediate structure of Re–Re dimerization cannot be produced when DMF (N, N-dimethylformamide) was explored as the electrolyte solvent.<sup>59</sup> Since CH<sub>3</sub>CN is a weakly acidic aprotic polar solvent, hydrogen bonds can hardly form. However, DMF is a basic aprotic polar solvent, enabling it to be a good hydrogen bond donor and acceptor. As such, although DMF can form hydrogen bonds with the Re(bpy)(CO)<sub>3</sub>Cl electrocatalyst, the formation of hydrogen-bonded dimers may be disrupted owing to the competition with intermolecular hydrogen bonds among DMF molecular.<sup>60</sup> This is not favorable for hydrogen bonding-facilitated Re–Re dimerization. Therefore, the electrolyte type can also give rise to a noticeable change in the product of the homogeneous CO<sub>2</sub>ER via mediating the intermediate formation.<sup>61</sup>

The functional additives are widely employed in advanced electrolytes to promote homogeneous CO<sub>2</sub>ER since the additive could mediate the structure of the intermediates and affect the electrocatalytic process. For instance, Maurice Brookhart and co-workers reported the use of CH<sub>3</sub>CN as the favorable additive in the electrolyte to promote the CO<sub>2</sub>ER when the (POCOP)Ir(OTf) (OTf stands for Trifluoromethanesulfonate) was used as the homogeneous electrocatalyst.<sup>56</sup> The CH<sub>3</sub>CN was revealed to be a key ancillary ligand that can play a critical role in alternating the formation of the intermediate by displacing formate from the insertion product to generate the bis-acetonitrile complex. This is important for the electrocatalytic cycling of HCOOH production from CO<sub>2</sub>ER.<sup>56</sup> The use of water (4.0%) as the additive in a DMF

electrolyte was also shown to promote the homogeneous CO<sub>2</sub>ER by an electrocatalyst based on the cobalt(II) complex with equatorial N<sub>4</sub> ligands because the replacement of axial ligand by water ligand results in the no longer interact with the latter intermediates.<sup>62</sup>

The magnitude of the external polarization potential also significantly affects the homogeneous CO<sub>2</sub>ER process since the charge accumulation on the electrocatalyst can largely impact the CAT<sup>+</sup> formation. Generally, the use of electrocatalysts allows homogeneous CO<sub>2</sub>ER to occur at much lower potentials lower than the redox potentials of the raw materials (CO<sub>2</sub>) under the same condition. The different strengths of external potential polarization can result in the formation of different reduced species of CO<sub>2</sub>ER by the homogeneous electrocatalyst. For instance, the CO<sub>2</sub> can be reduced to the radicals CO<sub>2</sub><sup>•-</sup> at a potential of -1.98 V when the DMF was used as the solvent. Such a radical cannot be activated subsequently by the electrocatalyst at such a potential. However, a further decrease in the polarization potential to -2.32 V can result in the CO<sub>2</sub>ER for HCOOH production with 68% FE.<sup>62</sup>

### Type of homogeneous electrocatalysts for CO<sub>2</sub>ER

The homogeneous electrocatalyst plays the most critical role in homogeneous CO<sub>2</sub>ER as the electrocatalyst can promote electron shuttling between the electrode and CO<sub>2</sub> for CO<sub>2</sub>ER.<sup>63</sup> To date, the reported types of homogeneous electrocatalysts for CO<sub>2</sub>ER can be broadly divided into metal-based organic compounds and non-metal organic complexes. Compared with metal-based organic compounds, the non-metal organic complexes are much less explored and are mainly based on ionic liquids composed of alkyl imidazole cations and alkyl amine cations.<sup>64</sup> The metal-organic compound-based electrocatalysts are usually coordinated compounds based on transition metals including Cr,<sup>65</sup> Re,<sup>66</sup> Fe,<sup>67</sup> Ru,<sup>44</sup> Ir,<sup>68,69</sup> and Ni.<sup>70</sup> The transition metals are mainly 3d-transition metals with variable valence. The ligands of the metal-coordinated compounds are usually nitrogen- or sulfur-containing compounds.<sup>65,67,71-74</sup> Generally, the lone pair electrons of nitrogen or sulfur ligand can donate electrons. This can stabilize the originally active transition metal complexes to some extent.<sup>75</sup> Furthermore, the homogeneous electrocatalysts can donate electrons under a certain voltage polarization,<sup>76</sup> causing the saturated transition metal complexes to lose their coordination ligands for providing active coordinating sites.<sup>77</sup> As can be seen from Figure 3, the non-bonding electrons are more likely to be localized in the 1π<sub>g</sub> orbital on the oxygen side. Thus, the electrons at the oxygen end of the CO<sub>2</sub> molecule tend to coordinate with the metal center that is not saturated with coordination.

When the transition metal-organic complex-based electrocatalysts are used for homogeneous CO<sub>2</sub>ER, the coordinated transition metal usually works as the active center for electrocatalysis. However, not all such transition metal-based coordinates are active for homogeneous CO<sub>2</sub>ER. We deem that the following characteristics can be favorable for being a good homogeneous electrocatalyst based on the transition-metal complexes: (1) showing high intrinsic activity for CO<sub>2</sub>ER; (2) working stably under normal electrolysis conditions (e.g., aqueous electrolytes, room temperature, etc.); (3) containing unsaturated coordination and valence electrons less than 18 electrons; (4) showing good stability under air and moisture environment; and (5) achieving stable electrochemical performance at a close thermodynamic potential of CO<sub>2</sub>ER reaction.

A metal-organic compound-based electrocatalyst for homogeneous CO<sub>2</sub>ER can be rationally designed and adjusted according to the desired electrocatalytic conditions and performance by choosing a suitable metal and tuning the ligand type.<sup>78-80</sup> In the recent two decades, tremendous progress has been made in the development of homogeneous electrocatalysts and optimizing the electrocatalytic performance as well as the mechanistic understanding.<sup>81-83</sup> As summarized in Table 2, we present some recently developed typical metal-organic compound-based electrocatalysts for homogeneous CO<sub>2</sub>ER. We can find that most of these metal-organic compound-based electrocatalysts show typical coordinated structures. The main products obtained from the homogeneous CO<sub>2</sub>ER are still the C1 compounds such as CO and HCOOH.

### KEY CRITERION FOR EVALUATING THE PERFORMANCE OF HOMOGENEOUS CO<sub>2</sub>ER

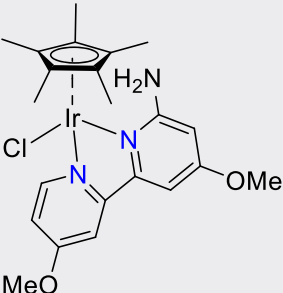
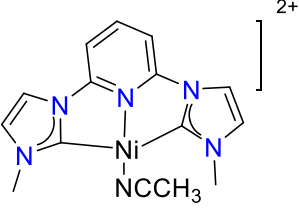
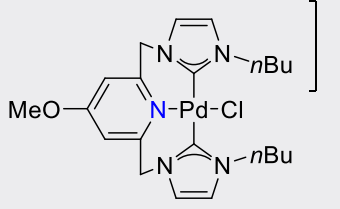
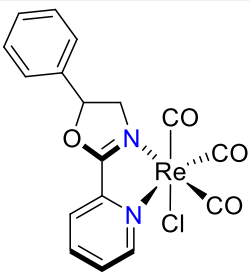
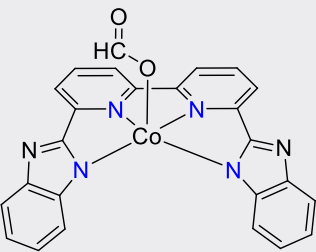
To better quantify and evaluate the electrochemical performance of an electrocatalyst for homogeneous CO<sub>2</sub>ER, some key criteria need to be established and obtained in experiments. Several important metrics have been explored to evaluate the activity and performance of a homogeneous electrocatalyst for CO<sub>2</sub>ER. As such, we here summarized these widely used metrics including the overpotential, current density, faradic efficiency (FE), turnover frequency (TOF), turnover number, and product yield in detail.

The overpotential refers to the potential difference (voltage) between the thermodynamically determined reduction potential of a half-reaction and the potential at which the electrochemical redox reaction is observed experimentally. This value also indicates that the CO<sub>2</sub>ER process (with electricity) requires how much electrical energy than the thermodynamic process (without electricity). The lost energy could be heat and other reactions. As such, the overpotential  $\eta$  is an important parameter to evaluate the catalytic activity of the electrocatalyst. The overpotential is usually measured experimentally by linear sweep voltammetry (LSV) and cyclic voltammetry (CV) tests. The overpotential  $\eta$  can be calculated by the following equation:

$$\eta = E_i - E_t$$

Where the  $E_t$  is the theoretical potential, and the  $E_i$  refers to the experimental potential in a CV measurement. When comparing the overpotentials of different catalysts in the same type of reaction, a specific current density needs to be specified (usually the current density is 10 mA cm<sup>-2</sup>). The overpotential thus is widely used to compare the intrinsic activity of an electrocatalyst. The lower the overpotential of the electrocatalyst, the generally higher the electrocatalytic activity for the target product. For instance, a homogeneous electrocatalyst Co(II) complex for CO<sub>2</sub>ER shows a good catalytic activity with an overpotential of 0.62 V for producing formic acid (at -2.07 V vs. Fc/Fc<sup>+</sup>). Without the electrocatalyst, a much larger overpotential of 0.87 V (at -2.32 V vs. Fc/Fc<sup>+</sup>) is required to proceed under the same condition.<sup>62</sup>

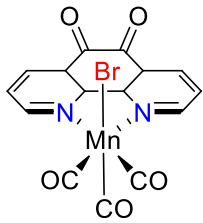
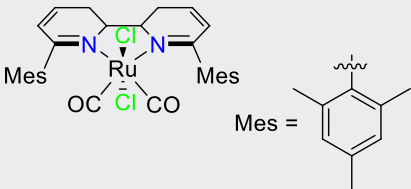
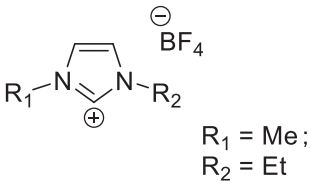
**Table 2. Typical electrocatalysts recently developed for homogeneous CO<sub>2</sub>ER**

Types	Molecular structure	Main product	Potential	Faradic efficiency	Reference
Ir-based complexes <sup>84</sup>		HCOO <sup>-</sup>	-1.80 V vs. (Ag/AgCl)	38%	Sypaseuth et al. <sup>84</sup>
Ni-based complexes <sup>85</sup>		CO	-1.77 V vs. (SHE)	34%	Sheng et al. <sup>85</sup>
Pd-based complex <sup>86</sup>		CO	-1.60 V vs. (Ag/AgNO <sub>3</sub> )	85%	Therrien and Wolf <sup>86</sup>
Re-based complex <sup>87</sup>		CO	-2.80 V vs. (Fc/Fc <sup>+</sup> )	30-55%	Nganga et al. <sup>87</sup>
Co-based complex <sup>62</sup>		HCOO <sup>-</sup>	-2.32 V vs. (Fc/Fc <sup>+</sup> )	68%	Tsubonouchi et al. <sup>62</sup>

(Continued on next page)



Table 2. Continued

Types	Molecular structure	Main product	Potential	Faradic efficiency	Reference
Mn-based complex <sup>88</sup>		CO	-2.24 V vs. (Fc/Fc <sup>+</sup> )	30-60%	Stanbury et al. <sup>88</sup>
Ru-based complex <sup>89</sup>		CO	-2.20 V vs. (Fc/Fc <sup>+</sup> )	95%	Machan et al. <sup>89</sup>
Non-metal ionic liquid complex <sup>90</sup>		C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	-2.60 V vs. (Fc/Fc <sup>+</sup> )	39.3%	Rosen et al. <sup>90</sup>

The main products, potential, and Faradic efficiency for the corresponding electrocatalyst are also listed.

The current density is normally referred to as the total amount of current flowing through one-unit value of the cross-sectional area, featuring the rate of the overall electrochemical reaction. The current density can be calculated as follows:

$$\text{Current density} = I \div S$$

Where the  $I$  stands for the whole current and the  $S$  is the area of the electrode. Generally, it is difficult to develop a highly active homogeneous electrocatalyst for CO<sub>2</sub>ER with high selectivity (high Faraday efficiency).<sup>91</sup> The origin of activity and selectivity of electrocatalysts can be understood by an interplay between ensemble (or geometrical) effects and ligand (or electronic) effects.<sup>91</sup> Under the same condition, a larger current density usually indicates the higher activity of the electrocatalysts. While the current density is widely used to compare the activity of an electrocatalyst, the intrinsic size and surface area of the electrode could also show an obvious impact on the current density for homogeneous CO<sub>2</sub>ER.<sup>92</sup>

The Faradic efficiency (FE) is another important criterion for evaluating the performance of an electrocatalyst. The FE for homogeneous CO<sub>2</sub>ER is usually defined as the ratio of the experimentally detected amount of objective products to the amount of theoretically generated products. The theoretical product production can be obtained by theoretical calculation, and the actual amount of product can be determined in practice. In a certain reaction period, the average Faraday rate can be calculated according to the following equation:

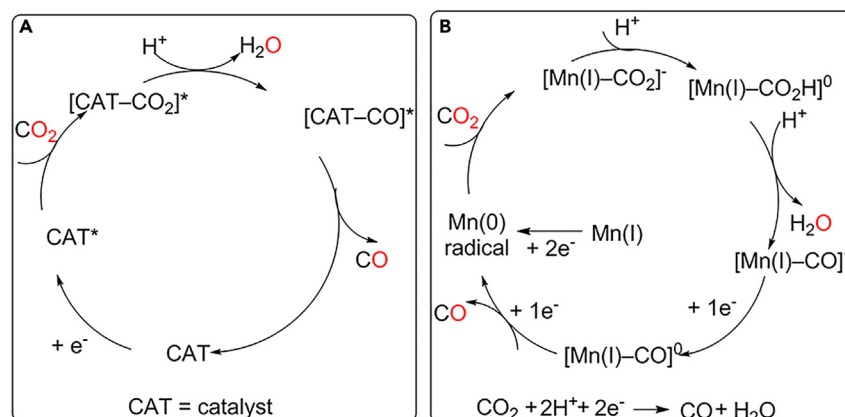
$$\text{FE} = Q_t \div Q_t$$

Where  $Q_t$  is the electron consumption for the corresponding product, and  $Q_t$  stands for the total electron consumption of the total products in this period. Because of the secondary reactions occurring during CO<sub>2</sub>ER, the FE is usually lower than 100%. Accordingly, the FE can be also used to describe electrocatalytic selectivity and energy efficiency.<sup>93</sup>

The turnover frequency (TOF) is widely a key parameter used to evaluate electrocatalytic efficiency. The TOF is derived from the turnover number, referring to the turnover per unit of time. It is defined as the number of catalytic reactions occurring on the active site per unit of time. The TOF can be calculated as follows:

$$\text{TOF} = I \div (\alpha \times N \times F)$$

Where the  $I(A)$  is the value of the catalytic current (directly given by the electrochemical workstation),  $\alpha$  is the number of transferred electrons corresponding to the half-reaction that generates a molecule of a target product or consumes a molecule of target reactant (the reaction equation Coefficient of electrons),  $N$  (mol) is the number of catalytically active sites,<sup>94</sup> and  $F$  (C/mol) is the Faraday constant.<sup>95</sup>



**Figure 5. Scheme for CO production from the homogeneous CO<sub>2</sub>ER**

(A) A general mechanism of CO production from homogeneous CO<sub>2</sub>ER.

(B) A specific example of CO production from CO<sub>2</sub>ER by Mn(I)-Tricarbonyl species. Reproduced with permission from ref. <sup>99</sup> Copyright, American Chemical Society.

The maximal turnover number of an electrocatalyst is the maximal number of substrate molecules converted into the product in a unit of time when the electrocatalyst is fully saturated with substrate.<sup>96</sup> This criterion can be also usually used to evaluate the stability of homogeneous electrocatalysts.<sup>97</sup> The TON can be calculated by the following equation:

$$\text{TON} = \text{TOF} \times t$$

Where *t* is the time (the period before the catalyst completely deactivates).

Another key criterion of the CO<sub>2</sub>ER process is the yield of the target product, and the overall cost of the process can make a big difference in industrial practice. Whether in an electrochemical process or a non-electrochemical process, the calculation of the product yield is all the same. The Yield can be calculated as follows.<sup>98</sup>

$$\text{Yield} = (n_a / n_e) \times 100\%$$

Where *n<sub>a</sub>* stands for the mole amount of the product yielded, and *n<sub>e</sub>* is the mole amount of the product expected.

## RECENT DEVELOPMENT OF ELECTROCATALYSTS FOR HOMOGENEOUS CO<sub>2</sub>ER

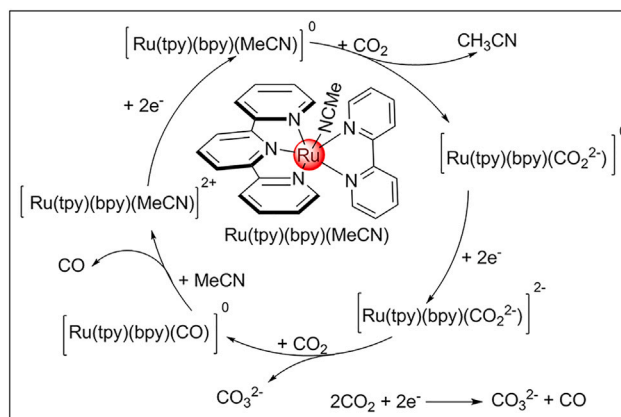
### Homogeneous CO<sub>2</sub>ER for C<sub>1</sub> products

Theoretically, a single CO<sub>2</sub> molecular can accept a different number of electrons to form C<sub>1</sub> products, including CO or HCOOH (2e<sup>-</sup>), HCHO (4e<sup>-</sup>), CH<sub>3</sub>OH (6e<sup>-</sup>), and CH<sub>4</sub> (8e<sup>-</sup>). However, the C<sub>1</sub> products from the homogeneous CO<sub>2</sub>ER are usually CO and HCOOH. In particular, CO is the most broadly reported C<sub>1</sub> product. Normally, a carbon dioxide-free radical (CO<sub>2</sub>·<sup>-</sup>) is produced when a single CO<sub>2</sub> molecule accepts an electron. Afterward, the CO<sub>2</sub>·<sup>-</sup> will combine with the homogeneous electrocatalyst to produce the C<sub>1</sub> product after reduction by two electrons. Although CO, HCOOH, and CH<sub>4</sub> have been reported as the C<sub>1</sub> product, producing CH<sub>4</sub> as the main product is still a challenging task for homogeneous CO<sub>2</sub>ER. So far, CH<sub>4</sub> is usually reported to be produced as a byproduct. As such, we focus on discussing the homogeneous CO<sub>2</sub>ER for producing CO and HCOOH.

#### The homogeneous CO<sub>2</sub>ER for producing CO

As shown in Figure 5A, the main process in homogeneous CO<sub>2</sub>ER to produce CO involves the following steps. The transient state CAT\* can be first obtained after the activation of the electrocatalyst. Afterward, [CAT-CO<sub>2</sub>]\* will be produced when the CO<sub>2</sub> interacts with the reduced CAT\*. The attack of a proton on the [CAT-CO<sub>2</sub>]\* gives rise to the release of an H<sub>2</sub>O molecular and the formation of [CAT-CO]\* intermediate. Finally, the CO can be released from the catalytic cycle.

As a typical example, Bocarsly and coworkers revealed the detailed mechanism of CO production through CO<sub>2</sub>ER by using the Mn(I)-Tricarbonyl species as the homogeneous electrocatalyst and the 0.1 M tetrabutylammonium perchlorate (Bu<sub>4</sub>NClO<sub>4</sub>) in CH<sub>3</sub>CN as the electrolyte.<sup>99</sup> The pathways of these carbonyl-metal complexes for the electroreduction of CO<sub>2</sub> to CO are illustrated in Figure 5B. Specifically, the Mn(I)-Tricarbonyl component of molecular electrocatalyst can get two electrons to produce the [Mn]<sup>-</sup> compound composed of the Mn (0) species. Then the CO<sub>2</sub> molecular can be inserted into the [Mn]<sup>-</sup> complex to form the [Mn-CO<sub>2</sub>]<sup>-</sup> intermediate with Mn (I) species. The following protonation of the [Mn-CO<sub>2</sub>]<sup>-</sup> gives rise to the formation of [Mn-CO<sub>2</sub>H]<sup>0</sup> complexes with Mn (I) species. Afterward, the [Mn-CO]<sup>+</sup> complexes were obtained without altering the valence of Mn (I) after the dehydration of [Mn-CO<sub>2</sub>H]<sup>0</sup>. Finally, the CO was obtained after getting two electrons. As such, the [Mn]<sup>-</sup> complex is produced again, enabling the electrocatalytic cycling process for homogeneous CO<sub>2</sub>ER.



**Figure 6. Scheme for CO production from the homogeneous CO<sub>2</sub>ER**

A specific example of CO production from CO<sub>2</sub>ER by [Ru(tpy)(bpy)(MeCN)]<sup>2+</sup> species. Reproduced with permission from ref. <sup>100</sup> Copyright, John Wiley and Sons.

Figure 6 shows an example of a Ru-based complex that catalyzes the reductive disproportionation of CO<sub>2</sub> to CO<sub>3</sub><sup>2-</sup> and CO through a new mechanistic pathway. The binding of CO<sub>2</sub> with the reduced Ru-based electrocatalyst is followed by catalytic turnover at the same potential. Electron transfer from the initially reduced tpy ligand to the coordinated CO<sub>2</sub> enables the subsequent electron uptake at the same potential, resulting in a lower of the reduction potentials and a decrease in the overpotential for catalysis from 0.87 V to 0.47 V<sup>100,101</sup>

#### The homogeneous CO<sub>2</sub>ER for producing HCOOH

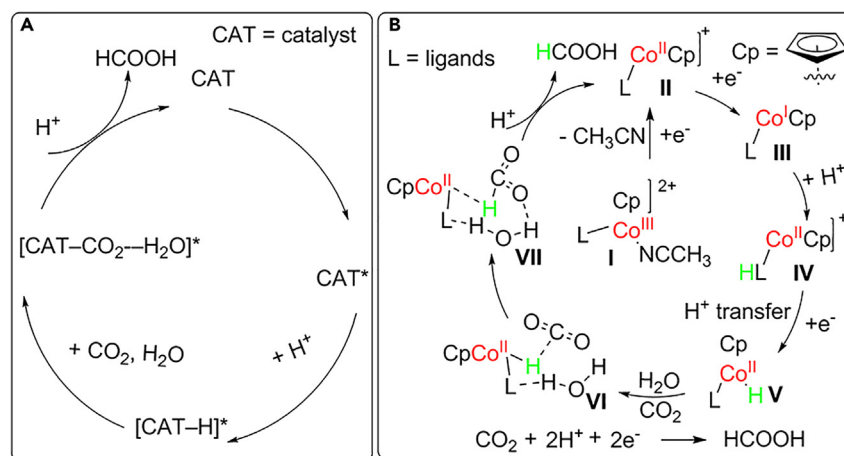
HCOOH is another main C<sub>1</sub> product obtained widely from homogeneous CO<sub>2</sub>ER. The main process for the homogeneous CO<sub>2</sub>ER into HCOOH involves the following steps. As shown in Figure 7A, CAT\* intermediate can be first produced from the reduction of electrocatalyst after the elimination of the ligand. Then the hydrogen coordination with the central metal of molecular electrocatalysts can give rise to the hydride species in the presence of H<sup>+</sup>. Afterward, CO<sub>2</sub> and H<sub>2</sub>O can simultaneously interact with the [CAT-H]\* species to produce the [CAT-CO<sub>2</sub>-H<sub>2</sub>O]\*. Due to the strong interaction of hydrogen bonds, the aggregation of [CAT-CO<sub>2</sub>-H<sub>2</sub>O]\* can occur as a result of producing an eight-ring intermediate. Finally, an acceptance of an H<sup>+</sup> can result in the release of HCOOH and the completion of the electrocatalytic cycling process.

For example, Vincent Artero and coworkers reported the highly efficient and selective cobalt-based electrocatalysts for HCOOH production from the homogeneous CO<sub>2</sub>ER.<sup>102</sup> These electrocatalysts exhibited impressive electrocatalytic performance with a low overpotential and fewer byproducts such as H<sub>2</sub> and CO.<sup>102</sup> The revealed electrocatalytic mechanism for the HCOOH formation is illustrated in Figure 7B. They carried out the homogeneous CO<sub>2</sub>ER with a glassy carbon electrode in 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> (DMF) electrolyte. The Co (III) species of the electrocatalyst (I) can be reduced into Co (II) species (II) after receiving one electron from the glassy electrode. After getting one more electron, the Co (I) species (III) was produced. The protonated Co (I) species (VI) can be further reduced to produce a Co (II)-hydride species (V) for chelating CO<sub>2</sub>. The resultant Co (II)-H intermediate (V) can be attacked by CO<sub>2</sub> and H<sub>2</sub>O for generating the [H<sub>2</sub>O-Co(II)-H-CO<sub>2</sub>] (VI) intermediates. The internal hydride transfer from Co(II)-H to CO<sub>2</sub> can give rise to the release of HCOOH, enabling the completion of the electrocatalytic cycles. Since the Co (III)-based electrocatalyst (I) is air-stable and can be easily handled, it shows great potential for future practical applications.

Meyer and coworkers reported Iridium dihydride complexes supported by PCP-type pincer ligands as the electrocatalyst in Figure 8. In acetonitrile/water mixtures, these complexes (POCOP)Ir(H)<sub>2</sub> become efficient and selective catalysts for the electrocatalytic reduction of CO<sub>2</sub> to formate.<sup>103</sup> Besides, another earth-abundant molecular electrocatalyst based on carbonyl cluster [Fe<sub>4</sub>N(CO)<sub>12</sub>]<sup>-</sup> was reported for CO<sub>2</sub>ER to produce HCOOH.<sup>104</sup> When a mixed solvent of MeCN and water (5%) was used, the HCOOH was obtained in a current density of 0.7 mA/cm<sup>2</sup> with an FE of 94%. One of the main processes for the homogeneous CO<sub>2</sub>ER to produce HCOOH by a carbonyl cluster [Fe<sub>4</sub>N(CO)<sub>12</sub>]<sup>-</sup> is the formation of a Fe-H-Fe intermediate. Then the internal hydride transfer to CO<sub>2</sub> can give rise to the release of HCOOH, similar to that for the above-mentioned Co (III) species.<sup>104</sup>

#### The homogeneous CO<sub>2</sub>ER for multicarbon (C<sub>2</sub>) products

The product with two carbon (C<sub>2</sub>) products can be also obtained from the homogeneous CO<sub>2</sub>ER. Among various C<sub>2+</sub> products, oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) is the most widely obtained and valuable since it is an important chemical for pharmaceutical, rare-earth extraction, and metal processing. Typically, the ionic liquid-based electrocatalysts for CO<sub>2</sub>ER generally involve the following process to produce H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. First, the aromatic ester anion functionalized ionic liquids can be reduced to produce the CAT\* intermediate containing active sites for CO<sub>2</sub><sup>-</sup> binding. The resultant CAT\* complex can further interact with CO<sub>2</sub> and H<sup>+</sup> to generate the [CAT-COOH]\* intermediate (Figure 9A). The H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> can be finally produced after a C-O bond breaking and dimerization of COO<sup>-</sup>.<sup>105</sup>



**Figure 7. Scheme for HCOOH production from homogeneous CO<sub>2</sub>ER**

(A) A general mechanism of HCOOH production from homogeneous CO<sub>2</sub>ER.

(B) A specific example of HCOOH production from CO<sub>2</sub>ER by a Co(III) species-based electrocatalyst. Reproduced with permission from ref. <sup>102</sup> Copyright, American Chemical Society.

For instance, Gennaro et al. reported the use of aromatic ester or aromatic nitrile-based electrocatalysts for efficient CO<sub>2</sub>ER into oxalate product of an FE over 99% by carrying out in the 0.1 M *n*-Bu<sub>4</sub>NClO<sub>4</sub>-DMF aprotic electrolyte.<sup>106</sup> However, the current density was only 1.6 mA cm<sup>-2</sup>. The oxalate formation rate was smaller than 30 μmol cm<sup>-2</sup> h<sup>-1</sup>. In another case, Zhang et al. developed aromatic ester anion functionalized ionic liquids as homogeneous electrocatalysts.<sup>105</sup> A high current density of 9.03 mA cm<sup>-2</sup> was obtained with an oxalic acid formation rate of 168.4 μmol cm<sup>-2</sup> h<sup>-1</sup>. As shown in Figure 9B, the proposed mechanism for high-efficiency CO<sub>2</sub>ER by the aromatic ester anion functionalized ionic liquids. Specifically, the ionic liquid with phenoxy and ester double active sites can effectively activate the stable linear CO<sub>2</sub> molecular into CO<sub>2</sub><sup>-</sup>. Besides, CO<sub>2</sub> can be activated to form a new C–O single bond with the O atom. The newly formed C–O bond can be successively broken as a result of generating the parent aromatic ester ionic liquid and –COOH intermediate. The resultant –COOH can be eventually dimerized to produce oxalic acid and complete the catalytic cycles.

### Homogeneous CO<sub>2</sub>ER for other C<sub>2+</sub> value-added products

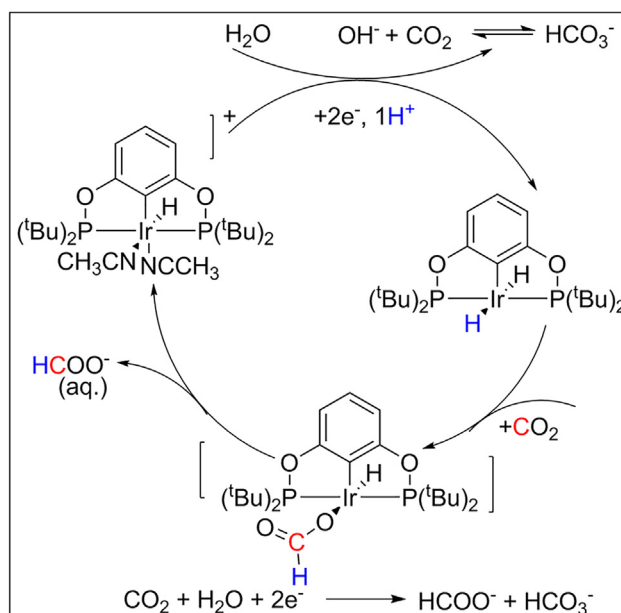
The above discussion mainly focuses on the C<sub>1</sub> and C<sub>2+</sub> products widely obtained from homogeneous CO<sub>2</sub>ER. Furthermore, other value-added products can be also obtained from the homogeneous CO<sub>2</sub>ER owing to the coupling of CO<sub>2</sub> molecules. For instance, CH<sub>3</sub>CH<sub>2</sub>OH is one of the most important chemical feedstocks and fuel for conventional combustion engines or fuel cells. CH<sub>3</sub>CH<sub>2</sub>OH can be also produced from homogeneous CO<sub>2</sub>ER through the following steps. One electron transfer to CO<sub>2</sub> can lead to the generation of CO<sub>2</sub><sup>-</sup> intermediate with the specific homogeneous electrocatalysts (CAT). The resultant [CAT–CO]<sup>\*</sup> intermediate can give rise to CO production. When the CO is not captured by the electrocatalyst, CH<sub>3</sub>OH can be produced through a hydrogenation process.<sup>52</sup>

For instance, Nakajima et al. reported the first catalytic formation of CH<sub>3</sub>COCH<sub>3</sub> by the double methylation of the carbonyl moiety with FE 16%. The reduction in the presence of Me<sub>4</sub>NBF<sub>4</sub> enables the formation of CH<sub>3</sub>COCH<sub>3</sub> in CH<sub>3</sub>CN/DMSO (1:1, v/v). The final product results from the reductive disproportionation of CO<sub>2</sub> followed by the subsequent carboxylation in the electrochemical CO<sub>2</sub> reduction.<sup>107</sup> As shown in Figure 10B, the proposed mechanism for the CH<sub>3</sub>COCH<sub>3</sub> formation. Specifically, the Ru(0) complex can effectively bind the CO<sub>2</sub> to form [Ru–CO<sub>2</sub>]<sup>0</sup>. Besides, [Ru–CO<sub>2</sub>]<sup>0</sup> can further promote the formation of the species of CO<sub>3</sub><sup>2-</sup> and [Ru–CO]<sup>2+</sup>. Through two electrons transfer, the [Ru–CO]<sup>0</sup> forms and the (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup> functions as the methylation agent of the carbonyl moiety. The reductive disproportionation of CO<sub>2</sub> can subsequently undergo a carboxylation in the electrochemical CO<sub>2</sub> reduction. This enables the formation of CH<sub>3</sub>COCH<sub>3</sub> product.

In addition, other C<sub>2+</sub> products such as hydrocarbons (C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>) are highly sought after as potential sustainable fuels, especially methane, and ethylene due to their high energy densities and extensive application. The formation of C<sub>2+</sub> products is usually produced through the transfer of two or more electrons to the [CAT–COOH]<sup>\*</sup> intermediates. The further dimerization of the [CAT–COOH]<sup>\*</sup> intermediates can give rise to the hydrocarbons such as C<sub>2</sub>H<sub>4</sub> (Cu porphyrin complex as electrocatalyst, faradic efficiency 44%, current density 8.4 mA/cm<sup>2</sup>) and C<sub>2</sub>H<sub>6</sub> (Cu nanowires as electrocatalyst, faradic efficiency 20.3%, current density 4–5 mA/cm<sup>2</sup>).<sup>50</sup> Although the above-mentioned value-added products have been reported from heterogeneous CO<sub>2</sub>ER methods, achieving high selectivity for value-added products is still challenging. The typical homogeneous CO<sub>2</sub>ER electrocatalysts are summarized in Table 3.

### Conclusions and perspectives

To conclude, we here present the fundamentals of homogeneous CO<sub>2</sub>ER and highlight the recent advances in the development of efficient homogeneous electrocatalysts. So far, the transition metal coordinate complexes and non-metal ionic liquids are the most widely explored

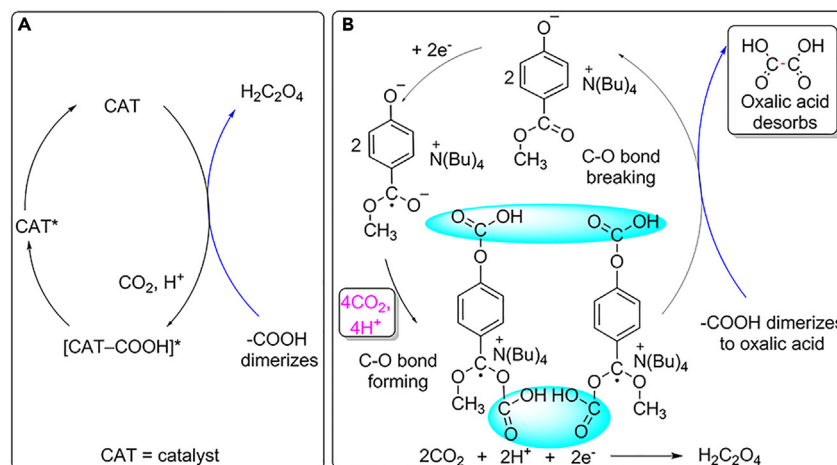


**Figure 8. Scheme for HCOOH production from homogeneous CO<sub>2</sub>ER**

A specific example of HCOOH production from CO<sub>2</sub>ER by a (POCOP)Ir(H)<sub>2</sub> electrocatalyst. Reproduced with permission from ref. <sup>103</sup> Copyright, American Chemical Society.

homogeneous electrocatalysts for CO<sub>2</sub>ER. Numerous factors can significantly influence the homogeneous CO<sub>2</sub>ER process and product formation. In particular, the type and concentration of a homogeneous electrocatalyst can affect the chemical structures and electrochemical kinetics of the [CAT-Sub]\* intermediates. The electrolytes can also impact the concentration of the dissolved CO<sub>2</sub> and the stabilization of the transition states or intermediates. The external polarization potential can largely impact the important intermediate CAT<sup>+</sup> formation by changing the charge accumulation on the electrocatalyst. The C1 compound such as the CO or HCOOH is generally the main product when using transition metal coordinates-based electrocatalysts while H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> is usually the main C<sub>2+</sub> product when using non-metal ionic liquids-based electrocatalysts. Although numerous homogeneous electrocatalysts have been developed for efficient CO<sub>2</sub>ER, the following challenges are expected to be addressed in future studies for promoting this promising sustainable technology.

- (1) The exact mechanism of homogeneous CO<sub>2</sub>ER for producing a specific product is still waiting to be explored in-depth. In particular, the capture and identification of some key intermediates are still challenging for both theoretical simulation and experiments owing to the complicated and interplayed multistep processes of homogeneous CO<sub>2</sub>ER. As such, more multiscale simulations and advanced Operando experimental techniques need to be further developed to reveal the exact mechanism in detail. While previous mechanistic studies through experiments largely relied entirely on electroanalytical techniques, more emerging advanced techniques such as spectro-electrochemistry (such as surface-enhanced infrared spectroscopy,<sup>108</sup> and surface-enhanced Raman scattering,<sup>109</sup> have been intensively used to probe the structure and composition of intermediates during CO<sub>2</sub>ER.<sup>110</sup> As for the theoretical study, the combined use of multiscale simulation including the density functional theory,<sup>111,112</sup> finite element simulations,<sup>113</sup> and machine learning<sup>114</sup> will be highly expected for future efforts to reveal the exact reaction mechanism at different scales. As such, it is practicable to rationally design efficient homogeneous electrocatalysts for selective CO<sub>2</sub>ER toward on-demand products.
- (2) The precise design and scalable preparation of efficient homogeneous electrocatalysts for the on-demand products from CO<sub>2</sub>ER are still challenging tasks. As discussed above, although many valuable products can be obtained from homogeneous CO<sub>2</sub>ER, these products are usually produced simultaneously with low selectivity. As such, tremendous efforts are expected to develop efficient electrocatalysts with high selectivity. This requires insightful knowledge of the mechanism for homogeneous CO<sub>2</sub>ER as well as the establishment of the exact structure-function relationship of homogeneous electrocatalysts. Although homogeneous CO<sub>2</sub>ER shows the advantages of controlling the reaction process by a rational design of the molecular structure of an electrocatalyst, efficient separation of electrocatalysts and various products from the homogeneous system also needs to be extensively explored. Accordingly, considerable efforts need to be paid to the predictive design of selective electrocatalysts that can be easily separated from the electrolyte for recycling use.<sup>115</sup>
- (3) The criterion for evaluating the specific electrochemical performance under the standard experimental operations are also needed to be strictly established and implemented for studying homogeneous CO<sub>2</sub>ER. Many factors like the nature of the electrocatalyst, the composition of the electrolyte, the size and hydrodynamics of the electrolytic cell, and the purity of the reagent, show an impact on the electrochemical performance of homogeneous electrocatalysts for CO<sub>2</sub>ER. Therefore, it is crucial to establish



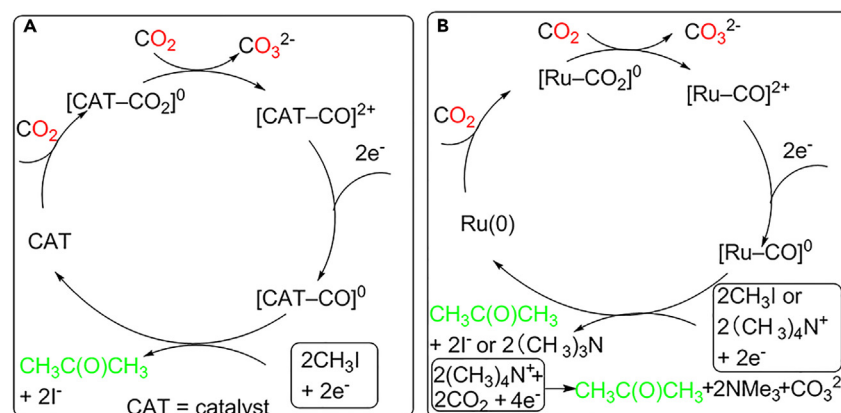
**Figure 9. Scheme for  $\text{H}_2\text{C}_2\text{O}_4$  (oxalic acid) production from homogeneous  $\text{CO}_2\text{ER}$**

(A) A general mechanism of  $\text{H}_2\text{C}_2\text{O}_4$  formation from homogeneous  $\text{CO}_2\text{ER}$ .

(B) A specific example of the  $\text{H}_2\text{C}_2\text{O}_4$  production from homogeneous  $\text{CO}_2\text{ER}$  by ionic liquids-based electrocatalysts. Reproduced with permission from ref. <sup>105</sup> Copyright, John Wiley and Sons.

standard experimental methods and protocols that can be explored to exactly evaluated the electrocatalytic performance of a homogeneous electrocatalyst. Designing and carrying out the benchmark electrocatalytic tests to exclusively study the influence of the electrocatalyst composition and structure will be preferred for future study. Before evaluating the electrocatalytic performance of new catalysts, using unified test devices and experimental conditions to assess the capability of conducting accurate and repeatable activity measurements is of great importance to compare the overall electrochemical performance. For example, thoroughly mixing the electrolyte to lessen the impact of mass transfer on the intrinsic activity can reduce the experimental error to some degree.<sup>116</sup> The activity and selectivity of the electrocatalysts should be also accurately determined without surface contamination. Therefore, future efforts are expected to develop better electrocatalytic systems and investigate the factors that can improve the accuracy of electrocatalytic activity evaluation parameters.

- (4) Last but not least, the scale-up for the preparation of electrocatalysts and scalable implementation of homogeneous  $\text{CO}_2\text{ER}$  is an also formidable task but highly desired for future industrial applications. The large-scale preparation of electrocatalysts with low-cost and high efficiency is essential for the scaling up of homogeneous  $\text{CO}_2\text{ER}$  for industrial applications in the future.<sup>117</sup> Although many studies have reported the preparation of efficient electrocatalysts on the lab scale,<sup>118</sup> more efforts are expected to develop large setups and automatic processes to achieve industrialized production.<sup>119</sup> Besides, it is necessary to improve the product selectivity of various homogeneous electrocatalysts by optimizing the experimental conditions. Another important but challenging aspect is scaling up the implementation of homogeneous  $\text{CO}_2\text{ER}$  for mass production because the multi-step product separation of homogeneous



**Figure 10. Scheme for  $\text{CH}_3\text{COCH}_3$  (acetone) production from homogeneous  $\text{CO}_2\text{ER}$**

(A) A general mechanism of  $\text{CH}_3\text{COCH}_3$  formation from homogeneous  $\text{CO}_2\text{ER}$ .

(B) A specific example of the  $\text{CH}_3\text{COCH}_3$  production from homogeneous  $\text{CO}_2\text{ER}$  by Ru-based electrocatalysts.<sup>107</sup> Reproduced with permission from ref. <sup>107</sup> Copyright, American Chemical Society.

**Table 3. The summarized typical homogeneous electrocatalysts for CO<sub>2</sub>ER**

Electrocatalyst	TOF	Main product	Potential	Electrolyte	Reference
Mn(I)-Tricarbonyl complex <sup>99</sup>	119 s <sup>-1</sup>	CO	-1.30 V vs. SCE	1.1 M Bu <sub>4</sub> NClO <sub>4</sub> (CH <sub>3</sub> CN)	Agarwal et al. <sup>99</sup>
[Ru(tpy)(bpy)(MeCN)] <sup>2+</sup> species <sup>100,101</sup>	Not mentioned	CO	-1.92 V vs. Fc <sup>+0</sup>	0.1 M Bu <sub>4</sub> NPF <sub>6</sub> (CH <sub>3</sub> CN)	Johnson et al., <sup>100</sup> Johnson et al. <sup>101</sup>
Co (III) species <sup>102</sup>	150 s <sup>-1</sup>	HCOOH	-2.15 V vs. Fc <sup>+0</sup>	1.1 M Bu <sub>4</sub> NBF <sub>4</sub> (DMF)	Roy et al. <sup>102</sup>
(POCOP)Ir(H) <sub>2</sub> complex <sup>103</sup>	Not mentioned	HCOO <sup>-</sup>	-1.2 V vs. NHE	5% H <sub>2</sub> O/THF	Kang et al. <sup>103</sup>
Ionic liquids species <sup>105</sup>	Not mentioned	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	-2.60 V vs. (Ag/AgNO <sub>3</sub> )	1.1 M Bu <sub>4</sub> NClO <sub>4</sub> (DMF)	Yang et al. <sup>105</sup>
Ru-based species <sup>107</sup>	Not mentioned	CH <sub>3</sub> C(O)CH <sub>3</sub>	-1.60 V vs. (Ag/AgNO <sub>3</sub> )	0.1 M Bu <sub>4</sub> NPF <sub>6</sub> (CH <sub>3</sub> CN)	Nakajima et al. <sup>107</sup>

electrocatalysis complicates the integration with electrolytic technologies. In this regard, more efforts will be needed to develop advanced systems capable of continuous production and separation for future industrial applications.<sup>120</sup>

In summary, the rational design of efficient electrocatalysts for homogeneous CO<sub>2</sub>ER is of significance to advance this exciting and burgeoning technology. The importance of the second coordination sphere has been increasingly recognized and has pushed ligand design in new directions. Metal–ligand cooperativity, ligand-based proton relays, and functional ionic groups that enhance catalysis through Coulombic interactions. These advancements have helped to establish new benchmarks and will continue to drive further progress.

With respect to the metal center, the focus has shifted from precious elements of the second and third d-block series, such as Ru, Pd, and Re, to more abundant 3d metals such as Mn, Fe, Co, and Ni. It has been demonstrated that these 3d metals can be highly competitive when appropriate ligands are used. The development of new ligands that are tailored to specific applications has opened up new possibilities for ligands that previously had not been considered for complexation with 3d metals.

The integration of computational methods and experimental approaches has allowed for a better understanding of reaction mechanisms and has facilitated the rational design of new catalysts. The future of coordination chemistry lies in the continued exploration of new ligands and metal centers, as well as in the development of more efficient and sustainable catalytic systems.

Although the study on homogeneous CO<sub>2</sub>ER is still much behind the research on heterogeneous CO<sub>2</sub>ER, significant advances will be expected over the coming years due to the above-mentioned numerous opportunities. We hope this perspective will provide favorable guidance for the research community in the rational design of more efficient homogeneous electrocatalysts for selective CO<sub>2</sub>ER in the future.

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## DECLARATION OF INTERESTS

The authors declare no competing interests.

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