

Progress and Perspective of Single-atom Catalysts for the Electrochemical CO₂ Reduction Reaction for Fuels and Chemicals

Benjamin Liu *

Department of Environmental Studies, Middlebury College, 005753, U.S

* Corresponding Author Email: benjaminl@middlebury.edu

Abstract. Electrochemical CO₂ Reduction Reaction (CO₂RR) presents a transformative approach for the sustainable synthesis of fuels and chemicals to address pressing environmental challenges. The efficiency and selectivity of the CO₂RR largely depend on the catalyst. Among which, Single-Atom Catalysts (SACs) have surfaced as a prominent design for this reaction, offering exceptional activity and selectivity. This paper delves into the progress and perspectives of SACs in CO₂RR, tracing their historical evolution, unique advantages, and underlying mechanisms. The superior atomic utilization, distinct electronic configurations, and enhanced product specificity of SACs over traditional catalysts have opened novel pathways for more efficient conversion of CO₂ to potent resources. However, challenges particularly concerning the stability, scalability, and product diversity of these catalysts constitutes as major impediments. Recent innovations, from advanced characterization techniques to novel synthesis methods, are spotlighted, showcasing the strides the scientific community has made. Looking forward, this paper underscores the potential of SACs in bridging sustainable energy sources with green chemical production and discuss prospective strategies to overcome existing limitations.

Keywords: Single atom-catalysts, CO₂ reduction reaction, reaction pathways, hydrogen evolution reaction, delocalization state-induced selectivity.

1. Introduction

The escalating levels of atmospheric carbon dioxide (CO₂) have become a focal concern in the contemporary global landscape. Overwhelming scientific evidence suggests that the sharp increase in anthropogenic CO₂ emissions is a major contributor to global climate change, manifesting in rising sea levels, more frequent extreme weather events, and disrupted ecological balances [1]. Electrochemical conversion of CO₂ into valuable chemical resources is not only considered as a promising technology to address this pressing environmental challenge, but also proves significance in generating versatile carbonaceous chemical/fuels to alleviate the pronounced deficits in fossil fuel reserves.

The CO₂RR process encompasses multiple proton and electron transfer steps that corresponds to conversion into different carbonaceous products (equations (1)-(4)). Thus, electrochemical reduction of CO₂ holds unique advantages compared to other existing methods of CO₂ reduction in terms of more free H sources, increased and manipulable selectivity, simple operation [2]. Effective and high-performing systems of CO₂RR are often evaluated on its stability, selectivity, current density, and the faraday efficiency (FE) of the reaction. Consequently, the selection of catalysts is crucial, given that the efficacy and scalability of CO₂RR are intrinsically linked to the type of catalyst utilized.



Traditional double-atom catalysts (DAC) and heterogeneous catalysts ranges from metals like silver or copper to metal compounds like nitrides, sulfides, and oxides has been used for CO₂RR. Although many efforts have been made to optimize the CO₂RR process, the efficacy of conversion of CO₂ remains subpar, characterized by suboptimal activity and poor product selectivity. Compromised activity sites due to bulky catalysts hinder the efficiency of conversion [3]. Therefore, seeking out versatile catalyst that could ensure stability and selectivity is crucial not only for the promotion of clean energy sources, but also for the development of a sustainable alternative energy source.

As Pt₁/FeO_x single-atom catalysts (SACs) got developed by Qiao et al., in 2011, the new approach to electrocatalyst fabrication has received growing attention [4]. At its core, an SAC features isolated metal atoms anchored firmly onto a substrate or support material. This design paradigm ensures maximal atomic utilization, leading to heightened efficiency, while the unique electronic configurations of these isolated atoms open the door to selectivity patterns previously unattainable with bulkier catalyst systems. The efficacy and adaptability of SACs are underpinned by several fundamental principles. Key among these is the idea that at the atomic scale, geometric and electronic heterogeneities typical of larger catalyst structures are absent. Consequently, SACs present a uniform, consistent reaction environment. Moreover, because every atom is a potential active site, the catalytic activity can, in principle, be maximized. Recently, utilizing SACs has ushered in a new era of advancements for field of electrochemical reactions.

Fig. 1 demonstrates a range of metal elements suitable for the construction of SACs along with their corresponding selectivity of products. The list mainly encompasses transition metals (Mo, Co, Ni, Cu, Zr...), noble metals (Ir, Pd, Ag...), and main group metals (In, Sn, Sb, Bi...) elements (Fig. 1) [5]. A majority of the documented SACs have shown yielding CO as the preferred product for the electrochemical conversion of CO₂, and this characteristic is particularly true for transition metal SACs. However, among transition metals, it has been documented that in Co, Cu, and Zn, and among main group metals Sn, and Sb-based SACs have demonstrated abilities to convert CO₂ to liquid products including formic acid (HCOOH) and methanol (CH₃OH). As Fig. 1 further shows, the same metal SAC could possess the ability to empower more than one product from CO₂RR. For example, Zn-SACs can reduce CO₂ to CO or CH₄, Sn- and Sb-SACs could reduce CO₂ to CO or HCOOH, while Cu-SACs, being one of the most versatile SACs, could yield products ranging from CO to HCOOH, CH₄, and other multi-carbon products. The precise determinants governing product selectivity in the CO₂RR process remain contentious. In pursuit of elucidating the role of SAC structures to the effects on activities inherent to the CO₂RR, and with a particular emphasis on advancing SACs exhibiting superior selectivity towards C₂⁺ products, more rigorous and systematic review of extant literature pertaining to SACs within the CO₂RR framework is imperative.

CO			HCOOH			CH ₃ OH		CH ₄		C ₂ ⁺			
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po

Figure 1. The reported elements in SACs for the electrochemical CO₂RR.
<https://pubs.rsc.org/en/content/articlelanding/2021/SC/D1SC01375K>

This paper aims to discuss reaction pathways of different metal-SACs in yielding different products in the process of CO₂RR, including insights into potential implications of the fuels/chemicals produced. Then, strategies to ameliorate the process of CO₂RR would be summarized, mentioning the suppression of H₂ products from hydrogen evolution reaction (HER) while bettering carbonaceous products' yield. Finally, recent advances and underlying challenges in the field would be outlined and future outlooks based on challenges and advancement are discussed.

2. CO₂RR Reaction Pathways for C₁ Products

2.1. Carbon Monoxide (CO)

As CO product is more favorable for most metal-SACs in the CO₂RR process, electrocatalytic conversion of CO₂ to CO represents one of the most foundational and studied transformations. SACs' application to this transformation allows for heightened efficiencies and a profound insight into the atomic-level reaction pathways. Common pathway of CO₂ reduction to CO is through ^{*}COOH intermediate. Potential reaction pathway for CO formation is shown in Fig. 2 [5]. The initial step in CO₂RR involves bond formation of CO₂ molecules with the surface of the catalyst. Regarding SACs, this adsorption often results in an activated CO^{•−} species. The activation usually involves the transfer of an electron from the SAC to the CO₂ molecule, weakening the C=O bond. The activated CO^{•−} can then undergo a proton-coupled electron transfer (PCET) to form a ^{*}COOH adsorbed intermediate. Given the unique atomic arrangement of SACs, the site where this ^{*}COOH binds is often isolated, ensuring that subsequent reactions proceed in a controlled and select manner. Afterwards the ^{*}COOH intermediate undergoes a C=O bond cleavage to release CO through another PCET step where another electron is transferred to the ^{*}COOH, followed by the release of a proton (H⁺). The precise energetics of this step, influenced by the SAC's nature, determines the efficiency and rate of CO production.

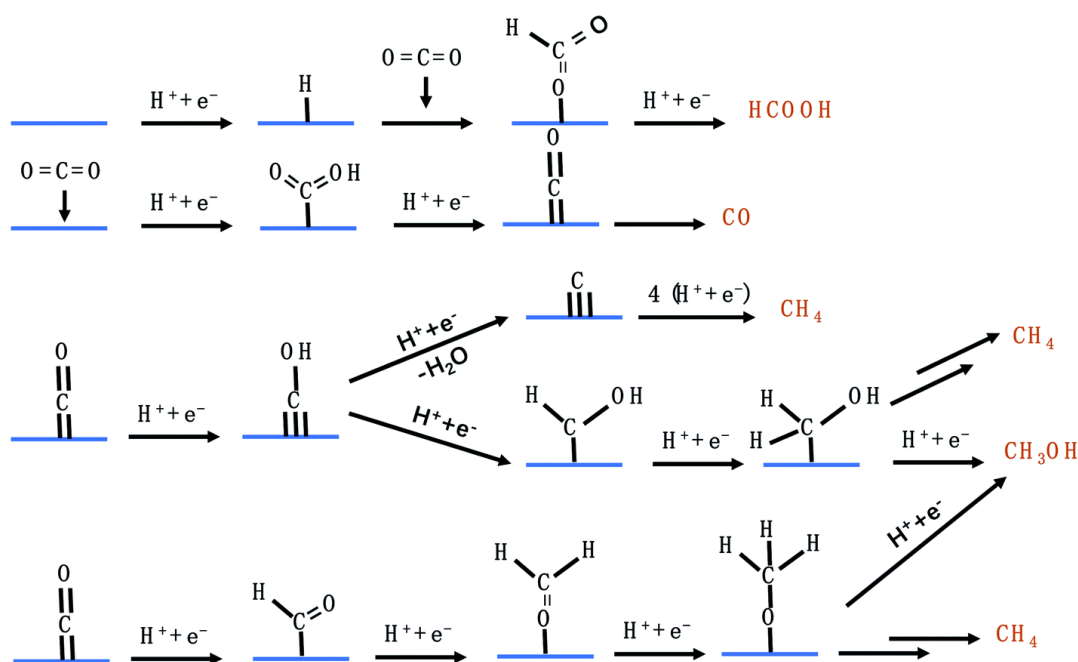


Figure 2. The possible CO₂RR pathways for C₁ products.

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Although most metal-based SACs can carry out CO₂RR to produce CO, nature of the metal atoms is one of the major factors influencing the mechanism. Different metal atoms in SACs can have distinct electronic properties and affinities for CO₂ and its intermediates. For instance, SACs with metals like Ag and Au often show high selectivity towards CO production. The support material on which SACs are anchored upon plays a paramount role in determining the overall catalytic behavior. Support materials provide not only the physical platform to stabilize the single atoms but also actively modulate their electronic environment, influencing both activity and selectivity [6]. The underlying substrate or support to which the individual atom is affixed can modulate its electronic configuration, subsequently impacting its catalytic characteristics. For instance, nitrogen-doped carbon supports might provide additional active sites or alter the electron density at the metal atom [7].

2.2. Formic Acid (HCOOH)

Formic acid is extensively used in agriculture as a preservative for silage and hay. In the leather industry, formic acid plays a pivotal role in the leather tanning process. Additionally, it's employed in the production of rubber and as a coagulating agent. Much like the path to CO, the first step involves bond formation with the surface of the catalyst. The unique atomic disposition of SACs encourages CO₂ to interact intimately with the metal atom, facilitating an electron transfer that weakens one of the C=O bonds, producing an activated CO₂⁻ species. Upon activation, the CO₂⁻ species undergoes a proton-coupled electron transfer, transforming it into an adsorbed HCOO⁻ (formate) intermediate. Finally, the adsorbed formate species undergoes another protonation, releasing HCOOH. The efficiency of this step is contingent on the SAC's nature and its interaction with formate, influencing how easily formate can be protonated and then desorb from the surface.

2.3. Methanol (CH₃OH) and Methane (CH₄)

Methanol production through the electrochemical reduction of CO₂ epitomizes a sustainable route to generate a versatile chemical feedstock and potential liquid fuel. Single-Atom Catalysts (SACs), given their distinct active sites and tunable properties, present an intriguing option for optimizing this conversion pathway. Through CO₂ activation process and PCET step mentioned above, CO⁻ intermediate can be formed. The produced CO gets adsorbed onto the SAC. Initially, CO undergoes hydrogenation to form HCO (formyl) species. This is then further hydrogenated to form an H₂CO (hydroxymethyl) species. Finally, the H₂CO undergoes a last hydrogenation step, culminating in methanol formation. The formed methanol, once synthesized on the catalyst's surface, desorbs, freeing up active sites for subsequent CO₂ reduction cycles. The binding affinity of CO to the SAC is essential, as a too-strong or too-weak bond can either hinder subsequent steps or lead to inadequate CO adsorption, respectively.

Proceeding the generation of methanol, the formyl species undergoes another hydrogenation step, accepting a proton and an electron to form a hydroxymethyl species. The hydroxymethyl species can further gain a proton and an electron, yielding a methyl species bound to the SAC. Last, the adsorbed methyl species undergoes a final hydrogenation, receiving a proton and an electron to form methane.

2.4. C₂ Products

Derivatives of CO₂RR of the C₂⁺ origins (ethylene, ethanol, and propanol) are of great significance due to their potential as fuel precursors and value-added chemicals. The electrocatalytic process involved in transformation of CO₂ into C₂⁺ compounds are a more intricate process than the reduction to C₁ products. The added complexity arises from the necessity for C-C bond formation. SACs with their atomically dispersed active sites disproportionately favor C₁ products. C-C coupling for C₂⁺ products require adjacent active sites which has been a persisting challenge for SAC CO₂RR since if metal catalytic atoms are too far apart, C-C coupling efficacy would be compromised, but if atoms are too close together, the bunching of atoms can result in lowered activity.

As with other CO₂RR pathways, the formation of C₂⁺ derivatives initiate with the activation of CO₂ after binding to the surface of the SAC. C₂⁺ products begin with the adsorption and activation of CO₂ on the SAC's surface. This leads to the formation of an activated CO₂⁻ species by facilitating an electron transfer that weakens one of the C=O bonds. The activated CO₂ can further reduce to a CO intermediate on the SAC's surface (Fig. 3a) [8]. This intermediate is a crucial species for C₂⁺ product formation. The central step for C₂⁺ product synthesis is the formation of a C-C bond. This typically involves the coupling of two CO intermediates or a CO intermediate with another activated CO₂ molecule. Depending on the catalyst and conditions, different pathways can dominate: (i) CO Dimerization: Two CO intermediates couple to form a C₂ dimer, which can subsequently be hydrogenated to form products like ethylene or further reduced to ethanol (Fig. 3b) [8]. (ii) CO + CO₂⁻ Coupling: A CO intermediate can couple with an activated CO₂⁻ species, leading to a C₂ intermediate. This can then undergo various reduction steps to yield C₂⁺ products (Fig. 3b) [8]. The

C₂ intermediates formed require further proton-coupled electron transfers to produce the final C₂⁺ products.

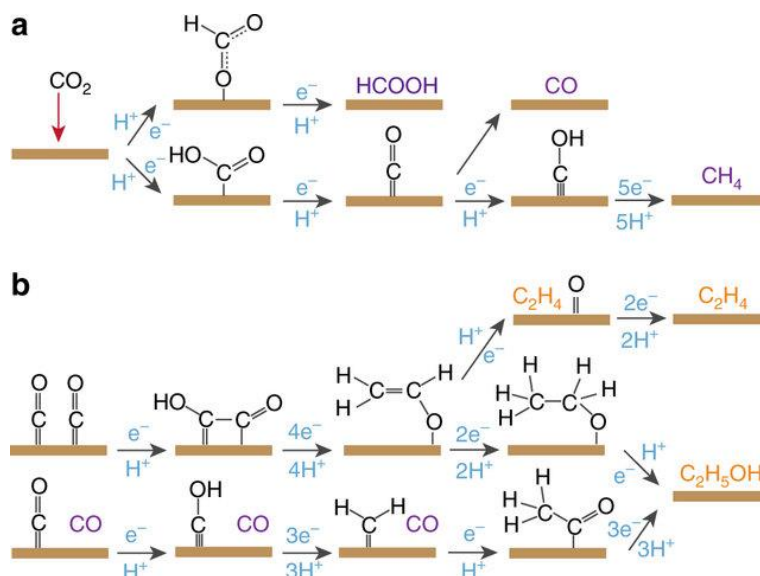


Figure 3. Potential CO₂RR pathways. (a) potential reaction pathways for C₁ and (b) potential reaction pathways for C₂ products. A free C₁ molecule is indicated in purple color and a free C₂ molecule is represented in the color orange. <https://www.nature.com/articles/s41467-018-03286-w>

3. Limitations and Ameliorations of SACs

3.1. Stability

Mechanical stability refers to the physical robustness and structural integrity of a material or catalyst under operational conditions. During the catalytic reaction, factors such as the elevated atom utilization rate, the augmentation of surface free energy, and the presence of a highly unsaturated coordination setting can enhance the mobility of individual atoms on the support surface [3]. As a result, individual atoms have the tendency to cluster together, in a process called sintering. Individual atoms or small clusters possess high surface energies due to unsaturated bonds. These unsaturated bonds make them energetically less stable compared to larger aggregates or bulk forms of the metal. Consequently, the system tends to move towards a state of reduced total surface energy, prompting these individual atoms or tiny clusters to coalesce into larger entities. Consequently, the catalyst suffers a reduction in active sites or even deactivation. Current measures to improve SAC stability focuses on support material choices. Enhancing the bond between the metal atom and its corresponding supporting substrate can markedly reduce the metal atom's mobility. Verlato et al. tested for ceria oxide to provide stronger anchoring points for single atoms [9]. Another strategy that can improve mechanical stability of SACs is by encapsulating or confining metal atoms within porous structures or matrices to spatially restrict the movement of these atoms. This spatial restriction not only curtails atom migration but also offers an additional barrier against external factors that might promote sintering. Metal-organic frameworks (MOFs) or zeolites, with their well-defined porosity, are excellent candidates for such encapsulation strategies [10].

Reduction in activity of catalysts often occur during long-term operation of catalytic processes. Contaminant binding to the active site, deposition of carbonaceous material, or oxidation or reduction that alter the active phase of the catalyst can result in deactivation. To improve stability of SACs for extensive CO₂RR, minimizing exposure to potential impurities is key. Implementing purification strategies or using high-purity reagents can ensure a consistent and clean reaction environment and maintaining a specific electrochemical potential, temperature conditions, and pH environment one can prevent the over-reduction of SACs and extending its optimal state. Further strategies include alloying and doping by introducing secondary metals or non-metal dopants. Hu et al. ran stability

tests over 120 hours for nickel-doped SACs and have demonstrated improved stability during CO₂RR due to a synergistic effect between the two metals [11].

3.2. Metal Loading Amount

A primary constraint in increasing metal loading for SACs is the potential loss of their single-atom character. As metal loading increases, the likelihood of atom aggregation and sintering becomes significant. This agglomeration results in the formation of metal nanoparticles rather than maintaining the desired single-atom dispersion. Such a transition can compromise the unique catalytic properties of SACs, making them behave more like traditional metal nanoparticle catalysts. Another limitation arises from the support material's capacity to anchor the metal atoms effectively. Beyond a certain metal loading threshold, the support might become saturated, leading to poor dispersion and increased agglomeration. One approach focuses on identifying and designing support materials with higher anchoring sites. Such materials can accommodate a higher concentration of metal atoms without promoting their aggregation. For instance, porous materials like Metal-Organic Frameworks (MOFs) or highly functionalized carbon supports can provide a dense array of anchoring points, enabling increased metal loading [10]. Other approaches include introduction of bimetallic SACs with a secondary metal, which either promotes the dispersion of the primary metal or acts as a spacer between primary metal atoms, can potentially increase overall metal loading. This bimetallic approach ensures that the primary metal atoms remain well-dispersed and retain their single-atom character. By similar logic, Kong et al. has modified active sites of Cu-SACs through cation polarization with NCN^{2-} . Consequently, through the construction of softer Cu sites on Cu_2NCN , not only can spacing between Cu metals be manipulated, but Kong et al. also managed to increase selectivity of C₂⁺ products by altering bond cleavage energies [12].

3.3. Faraday Efficiency (FE)

A key metric of SACs' performances in CO₂RR is the faraday efficiency (FE) which denotes the fraction of electron current that contributes to the desired reaction. SACs have demonstrated impressive capabilities in generating C₁ products. Given that CO is often an intermediate for other CO₂RR reactions, many SACs inherently favor CO production, achieving high FE. Bond strength between metal sites and CO serves as a pivotal factor to the selectivity of products. For instance, metal sites such as Cr, Fe, and Co exhibit a strong affinity to CO, leading to H₂ predominantly being produced. Conversely, Ni and Zn have a weaker bond with CO, making CO₂ more likely to be reduced to CO. Meanwhile, Sn and Bi, which also bind weakly to CO, primarily produce formate [3]. C₂ products on the other hand is more challenging than C₁ products due to the need for C-C coupling, a kinetically and mechanically difficult step. However, copper-based SACs have been found to effectively catalyze the production of C₂H₄ from CO₂ [13]. The single atomic sites allow for enhanced CO dimerization, which is a critical step for C₂ product formation, often leading to improved FE for C₂ products. The synergies between the metal atom and its supporting metal are vital for the optimization of FE. By selecting and modifying support materials judiciously, the electronic properties of the dispersed metal atoms can be improved. This approach is vital because optimizing binding energies for reaction intermediates can significantly enhance FE. Another crucial aspect is the initial activation of CO₂. Given that it's often a rate-limiting step, ensuring more CO₂ molecules are available near the active sites is paramount. Strategies that can activate or pre-concentrate CO₂ can swing the balance in favor of CO₂RR over competing reactions like hydrogen evolution reaction (HER). Bimetallic SACs, where a secondary metal is introduced, are also gaining traction. The cooperative effect between the two metals can be leveraged to improve FE. One metal might enhance the binding of intermediates, while the other can accelerate electron transfer [14]. The interaction between SACs and their supports can lead to charge transfer, altering the metal atom's electronic structure. This modification can, in turn, influence the catalyst's reactivity and selectivity. By pairing SACs with supports that induce the desired electronic effects, the reaction pathway to products with improved FE could be guided.

4. Conclusion

The urgent need for sustainable and eco-friendly solutions to combat rising CO₂ levels underscores the significance of the electrochemical CO₂ reduction reaction (CO₂RR). Within this domain, Single-Atom Catalysts (SACs) have emanated as a propitious frontier, combining the efficiency of atomic utilization with the potential for high selectivity and activity. This paper has delved into the mechanisms of SAC-mediated CO₂RR, shedding light on the intricate processes that lead to both C₁ and C₂⁺ products. The pivotal role of support materials, particularly nitrogen-doped carbons, in modulating catalytic behavior further highlights the multifaceted nature of these systems. While significant strides have been made in understanding the nuances of SACs in CO₂RR, challenges persist, particularly in improving stability, scalability, and broadening product selectivity. As the world grapples with the dual challenge of energy demand and environmental conservation, the pursuit of efficient CO₂RR using SACs offers a promising potential solution. The insights gleaned from research in this area not only propel the field of electrocatalysis forward but also inch us closer to a sustainable future where carbon dioxide, rather than being a problematic byproduct, becomes a valued feedstock for fuels and chemicals.

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