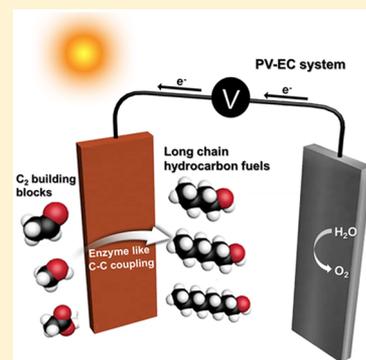


Current Status and Bioinspired Perspective of Electrochemical Conversion of CO₂ to a Long-Chain Hydrocarbon

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ABSTRACT: Electrocatalytic conversion of CO₂ into a long-chain hydrocarbon represents an important research direction in adding value to CO₂-based chemicals and realizing its practical application. Long-chain hydrocarbons may change the current fossil fuel-based industry in that those chemicals have a similar energy density as gasoline, high compatibility with the current infrastructure, and low hydroscopicity for pipeline distribution. However, most of the electrocatalysts produce C₁, C₂, and C₃ chemicals, and methods for producing long-chain hydrocarbons are not available thus far. Interestingly, nature utilizes many enzymes to generate long-chain hydrocarbons using C₂ building blocks and suggests key mechanisms, inspiring new perspective in the design of electrocatalysts. In this Perspective, we present case studies to demonstrate how CO₂ and its reductive derivatives interact with the electrode surface during C–C bond formation and introduce how these issues are addressed in biological systems. We end this Perspective by outlining possible strategies to translate the natural mechanism into a heterogeneous electrode.



The current energy crisis caused by the depletion of fossil fuels has brought about the need to develop alternative energy sources.¹ In addition, the indiscrete use of fossil fuels has accelerated global climate change owing to the increase in greenhouse gas emissions.² The current statistics reveal that the carbon dioxide level will increase up to 800 ppm during this century and potentially up to 2000 ppm by 2300,³ which will lead to not only a dramatic temperature increase but also ocean acidification.⁴ One of the methods to resolve this problem is use of solar energy as an alternative to fossil fuel. Solar light-driven fuel generation technology is highly beneficial because of its clean nature.⁵ Additionally, this method can mitigate the current energy imbalance observed in specific regions because solar light can be harvested all over the world.

One of the methods to resolve problems with fossil fuels is to use solar energy as an alternative. This method can also mitigate the current energy imbalance observed in specific regions because solar light can be harvested all over the world.

Figure 1 shows the schematic of a photovoltaic-electrolysis cell (PV-EC) system converting solar energy into fuel. Unlike a photoelectrochemical cell (PEC) in which the light absorber and fuel-generating interfaces are integrated in a single electrode, a PV-EC system has separate photovoltaic and electrolysis cells, thus allowing for further optimization. However, for the industrialization of solar-to-fuel conversion systems, the

production of high-quality liquid products from the cathodic CO₂ reduction reaction along with rapid oxidation of water at the anode is the most essential requirement. Long-chain hydrocarbons are more advantageous transportation fuels than short-chain hydrocarbons. For instance, *n*-butanol exhibits nearly 30% higher volumetric energy density (26.9 MJ L⁻¹) than ethanol (21.4 MJ L⁻¹) and methanol (15.9 MJ L⁻¹).⁶ Such a high volumetric energy density makes the driving range of a vehicle comparable to that of a vehicle running on petroleum-derived gasoline. In addition, long-chain hydrocarbon fuels are less volatile and can easily be stored in fuel tanks.^{6,7} Moreover, the long hydrophobic carbon chain in these hydrocarbons makes them less hydroscopic, thereby making them compatible with the existing fuel infrastructure.⁸ Therefore, the production of long-chain hydrocarbon fuels with high selectivity is expected to reduce the fuel generation price to less than the market price.

However, in aqueous systems, C–C bond formation competes with the H–H and C–H bond formation, making it difficult to produce long-chain hydrocarbons. Room temperature C–C coupling energetics have been intensively studied theoretically on Cu surfaces to check the feasibility of the C–C coupling reaction under various conditions such as different intermediate types,^{10–12} surrounding environments,^{13–15} and electrode facets.⁹ Figure 1 shows the calculated free energies for C–C, H–H, and C–H bond formation and the corresponding activation energies in *CO dimerization and *CHO- and *COH-mediated pathways. Compared to C–C bonds, H–H and C–H bonds have stronger bond energies of 104.2 and 99 kcal/mol, respectively,^{16,17} and require lower energies for their formation.⁹

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In addition, the hydrogenation of adsorbed C₁ intermediates is kinetically much easier than the formation of C–C bonds and limits the rate and selectivity of long-chain hydrocarbon production.^{10,18} Due to these factors, C–C bond formation acts as a rate-determining step (RDS) in the formation of long-chain hydrocarbons. Indeed, the maximum Faradaic efficiency for the formation of even the simplest C₂ product, ethylene, was reported to be 60%,¹⁹ while that of propanol (C₃ product) is limited to 11%.^{20,21} Although intense research efforts have been devoted to develop active catalysts to lower the kinetic barrier of C–C bond formation, no fundamental breakthrough has been achieved thus far.

In order to realize the aforementioned solar-to-fuel conversion system, the C–C coupling reaction mechanism should be carefully investigated with comprehensive understanding. In this Perspective, we will first discuss various naturally existing enzymes. Surprisingly, a biological complex, coenzyme A (CoA), can efficiently generate long-chain hydrocarbons by C–C coupling. Thus, it is imperative to understand the mechanism by which these natural enzymes aid the formation of long-chain hydrocarbons. This article covers the mechanistic investigation of the formation of long-chain hydrocarbons by the aforementioned enzymes with a focus on recent advances in this field. Starting with recently reported CO₂ reduction catalysts and the mechanism underlying the formation of long-chain hydrocarbons, recent studies focusing on the C–C coupling reaction of natural enzymes, and recent discoveries in the field of

molecular complexes and hybrid inorganic nanomaterials and chemical production of liquid fuels will be discussed.

Let us first take a look at the C–C coupling reaction reported with synthetic catalysts. Because of the selectivity issue, mechanistic investigations for the C–C coupling reaction have been confined to only a few metal electrodes.²² Previous studies have demonstrated that Cu electrodes inherently possess the ability to produce more reduced hydrocarbon products such as methane (CH₄), ethylene (C₂H₄), ethanol (C₂H₅OH), and *n*-propanol (C₃H₇OH).²³ This unique feature of the Cu surface can be explained in terms of the binding energy of adsorbed CO (*CO), which is the key intermediate for the formation of long-chain hydrocarbons. Cu is the only pure metal positioned around the top of the volcano-type relation and satisfies the Sabatier principle.²⁴ The moderate affinity of the Cu surface for *CO enables the stabilization of *CO as a precursor for further reduction reactions. Figure 2 depicts proposed reaction pathways for the electrochemical conversion of CO₂ to C₁ or C₂ products on a Cu surface. CO dimerization has been suggested to be the key step for C–C coupling at low overpotentials. Calle-Vallejo et al. proposed that the CO dimerization starts with electron transfer to form the *C₂O₂[−] intermediate, which is later protonated to *CO–COH.¹⁰ The decoupling of proton and electron transfer is supported by the pH-dependent behavior of C₂H₄ formation on Cu(100) surfaces on the RHE scale.^{25,26} Recently, Montoya and co-workers also found that the CO dimer configuration, in which both carbon atoms are bound to the surface, can be stabilized by a charged water layer on both Cu(111) and Cu(100).¹⁴ In contrast, at high overpotentials and turnover rates, the hydrogenation of *CO is kinetically facile compared to the C–C coupling in *CO. The *CO first undergoes hydrogenation to formyl (*CHO) or hydroxymethylidene (*COH) species as a rate-limiting step, which leads to methane as a major product and methanol as a minor product.^{11,27} The electrokinetic studies of CO reduction support that the RDS proceeds with a concerted proton–electron transfer from pH-independent behavior on the RHE scale.^{25,26} At high overpotentials, C–C coupling is likely to occur between the intermediates produced from hydrogenated *CHO or *COH rather than *CO. Montoya and co-workers calculated the kinetic barriers for C–C bond formation between the adsorbates derived from *CO on a Cu(211) surface.¹³ The results showed

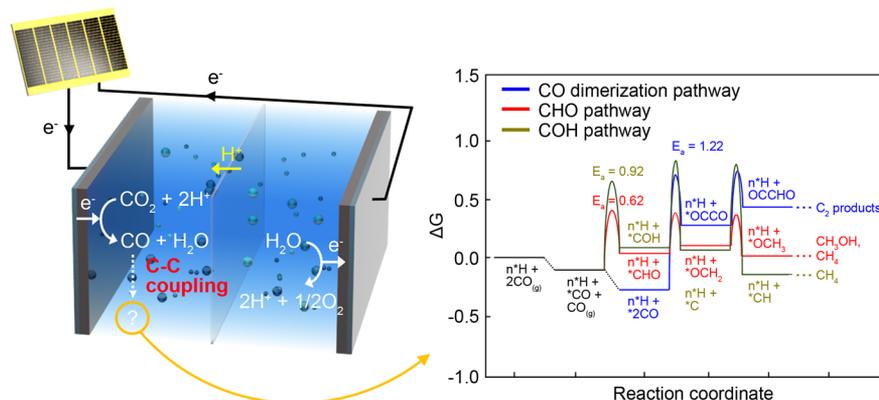


Figure 1. Schematic illustration of a PV-EC system for solar-to-fuel conversion. The PV-EC system is composed of photovoltaic and electrolysis cells, in which the cathodic reaction brings about electroconversion of CO₂ to long-chain hydrocarbon fuels, while the anodic reaction is associated with water oxidation. The right panel shows the free energy diagram for the formation of CH₄, CH₃OH, and C₂ products from CO_(g) and adsorbed hydrogen (*H) on Cu(100). For each reaction step, the activation barriers (E_a) are depicted by parabolic curves. The free energy and activation barrier values were obtained from previous studies.⁵

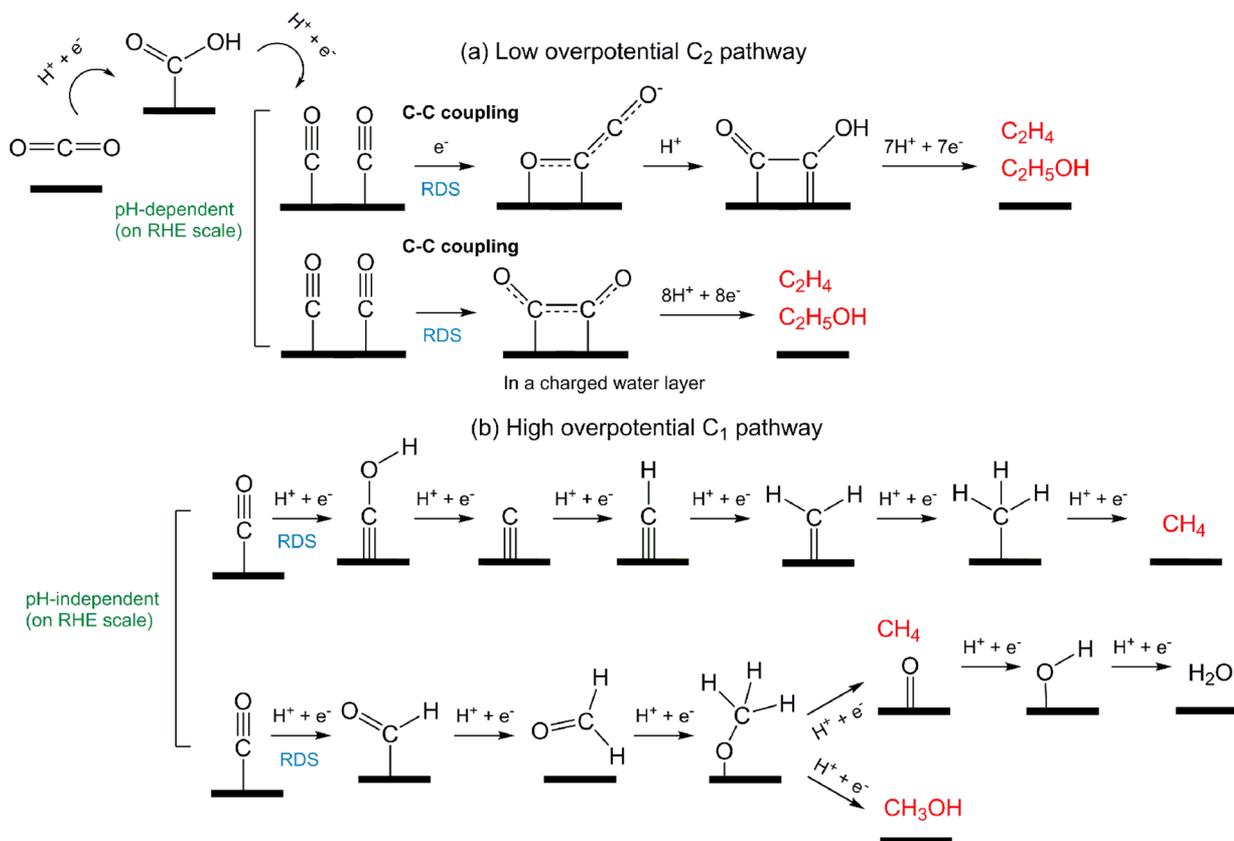


Figure 2. Proposed reaction pathways for the electrochemical reduction of CO₂ to C₁–C₂ products on the Cu surface. (a) Pathways to produce C₂H₄ and C₂H₅OH at low potentials (around –0.4 V vs RHE) on Cu(100). (b) Pathways to form CH₄ and CH₃OH at high potentials (more negative than –0.8 V vs RHE) on both Cu(100) and Cu(111). The reactants and intermediates are denoted by black text, while the products are denoted by red text. The RDS starts from CO. The H⁺ and e[–] with black arrows represent a concerted proton–electron transfer, which is based on the pH-independent onset potential on the RHE scale. CO dimerization involves a one or no electron transfer in the RDS.

that the direct dimerization of *CO is the most difficult process from a kinetic point of view. As the extent of hydrogenation is increased, the kinetic barrier is decreased.

Empirically, highly selective C–C coupling to produce liquid carbon fuels has been realized through electrochemical reduction of CO in a basic solution. Kanan et al. have shown that the oxide-derived Cu electrodes can produce ethanol, acetate, and *n*-propanol with a faradaic efficiency of 57% at –0.3 V vs RHE in a CO-saturated 0.1 M KOH solution.²⁸ Earlier studies by Hori et al. also exhibited that CO reduction on a Cu electrode can promote the formation of C₂H₄, C₂H₅OH, and C₃H₇OH over CH₄ at less negative overpotentials in high-pH solutions.²⁹ This corresponds to the low-overpotential C–C coupling pathways (*CO dimerization).⁹ In addition, Bertheussen and co-workers empirically proposed acetaldehyde (CH₃CHO) as the key intermediate for the formation of C₂H₅OH in the electroreduction of CO on oxide-derived Cu electrodes, and this was confirmed by the direct reduction of acetaldehyde.³⁰ The reaction started with *CO dimerization followed by hydrogenation and proceeded via the following pathway: *OCCHO → *OCHCHO → *OCHCHOH → *OCHCH → *OCHCH₂ → CH₃CHO_(aq) on a Cu(211) surface. Therefore, *CO dimerization is the most efficient pathway known to date to produce long-chain carbon fuels.

C–C coupling can be also found in reduced dinuclear metal complexes. Dinuclear copper(I) complex is the only catalyst capable of converting CO₂ to oxalate electrochemically in an acetonitrile solution at readily accessible potentials (0 V vs

***CO dimerization is the most efficient pathway known to date to produce long-chain carbon fuels.**

NHE).^{31,32} In principle, the electrochemical or chemical reduction of a dinuclear Cu(II) complex leads to the formation of a Cu(I) complex, which can produce an oxalate-bridged Cu(II) dimer in the presence of CO₂. Upon treatment with dilute acid or lithium perchlorate, the coordinated oxalate is detached from the coordination sphere and regenerates the starting Cu(II) complex. In addition, Saouma and co-workers developed a reactive Fe(I) complex supported by tris(phosphino)borate ligands, [PhBP₃^{CH₂Cy}]Fe(I), that also exhibit coupling of CO₂ in tetrahydrofuran (THF).³³ Reductive coupling of CO₂ to oxalate is catalyzed by an electronically saturated iron complex formed by the coordination of two THF solvent ligands and CO₂ to the Fe(I) center. In the coordinated complex, the unpaired electron was delocalized from the Fe center to the coordinated CO₂ ligand (Fe(II)–CO₂^{•–} species). Similarly, Horn and co-workers found that the dinuclear Ni(I) complex carries out a reductive coupling of CO₂ to produce an oxalate-bridged dinickel(II) complex.³⁴ To close the synthetic cycle, KC₈ was employed as a reducing agent in a N₂ atmosphere and the original Ni(I) complex was obtained. These previous studies suggest that C–C coupling in a dinuclear complex is promoted by the

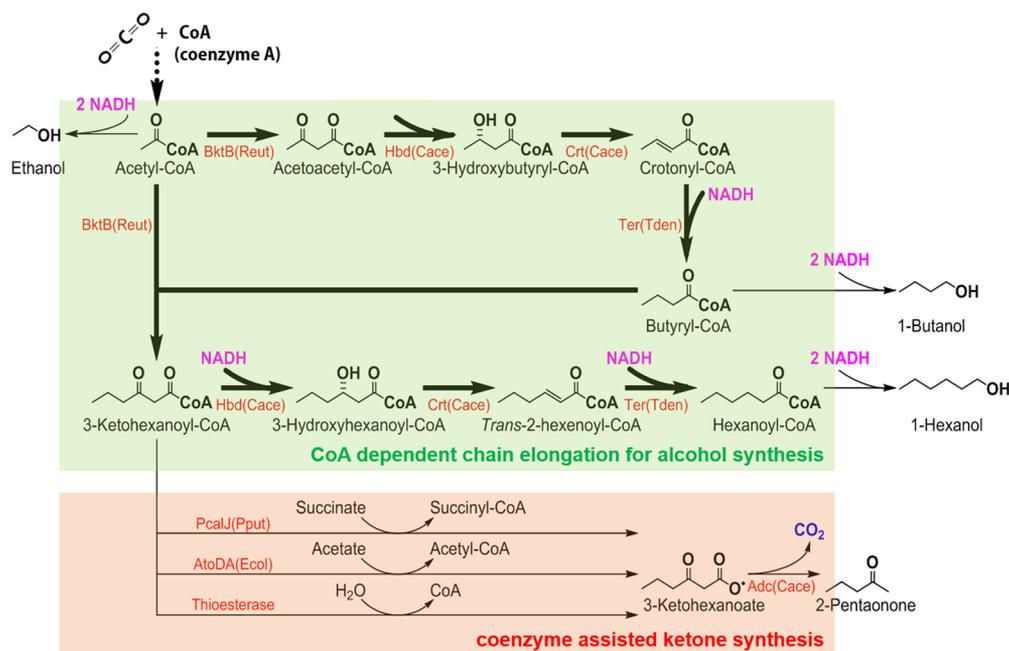


Figure 3. Schematic illustration of the biological synthesis of long-chain liquid fuels. Enzymatic fixation of CO₂ and its carbonyl condensation reaction to produce C₄ products. The CoA-dependent pathways are indicated by green boxes, while the coenzyme-assisted ketoester (such as 2-pentaonone) production is depicted by the red box. (BktB, β -keto-thiolase; Hbd, hydroxybutyryl-CoA dehydrogenase; Crt, crotonase; Ter, *trans*-22-enoyl-CoA reductase; PcaJ, 3-oxoadipate CoA-succinyl transferase; AtoDA, acetate CoA-transferase. Reut, *Ralstonia eutropha*; Cace, *Clostridium acetobutylicum*; Tden, *Treponema denticola*; Pput, *Pseudomonas putida*; Ecol, *Escherichia coli*).

interaction between the electronically saturated coordinated CO₂^{•-} anions.

The electrochemical reduction of CO₂ has been challenging, despite the development of many catalysts over the past few years. The challenges include the low activity, product selectivity, and stability of the catalysts, which make them unsuitable for practical applications. In addition, these catalysts seem to produce mostly C₁ and C₂ products. Although the use of preproduced CO instead of CO₂ yields C₃ products, long-chain products cannot be achieved. This implies that most of the artificial electrocatalysts are not suitable for C–C coupling. Therefore, extensive work is required to develop new catalysts capable of overcoming these challenges to produce long-chain hydrocarbon fuels.

Interestingly, nature has addressed these issues with its own active catalytic complexes. Living systems are characterized by remarkable molecular functions, which can be redesigned for *in vivo* synthesis of long-chain hydrocarbon fuels such as *n*-hexanol, *n*-octanol, and even some polymeric compounds. Because these reactions include efficient CO₂ fixation and its subsequent coupling, deep insight into the underlying biochemical principles can inspire us to develop synthetic catalysts capable of producing the desired value-added fuels with high selectivity and quantitative yields. Compared to the *in vivo* fuel production methods using enzymes and metabolites, in which the highly reversible nature of each component needs to be managed, synthetic catalysts are more adaptive to the sequestration process, and thus, the turnover rate of the catalytic system can be easily optimized. Combining these two approaches paves a new path to the utilization of CO₂, which is highly abundant in nature and inexpensive, and to realization of cost-effective carbon cycling. In this context, from now on, we will discuss the biological pathways and their possible

applications in developing synthetic catalysts for the production of long-chain hydrocarbon fuels.

CoA and its thioester derivative, acetyl-coenzyme A (acetyl-CoA), are reported to participate in over 100 different reactions in intermediary metabolism of microorganisms.³⁵ One of the most important metabolic reactions they are involved in is the C–C coupling of short-chain carbon building blocks, for example, the alcohol–acetyl transferase reaction to produce various acetate esters. These acetate ester intermediates are then reduced to produce long-chain liquid fuels. Indeed, various *Clostridium* species can produce *n*-butanol (C₄) biochemically, where *n*-butanol is assembled from the direct condensation of two acetyl monomers (C₂) and their subsequent reduction reactions.³⁶ The early stages of the CoA involved in the C–C coupling pathway of acetyl groups to *n*-butanol are shown in Figure 3. The acetyl groups are attached to CoA, and continuous formation of disulfide bridges between the two acetyl-CoA species brings the acetyl groups adjacent to each other, thus triggering the Claisen condensation reaction to produce a butyl group. The butyryl-CoA is then reduced to *n*-butanol with the help of butyryl-CoA dehydrogenase (Bcd), the electron transferring proteins A and B (EtfAB), and the bifunctional aldehyde alcohol dehydrogenase (AdhE2). However, these reactions are reversible and hence proceed only up to the equilibrium point. Therefore, many efforts have been made to enhance the yield of *n*-butanol through genetic engineering of key enzymes by taking into account the directionality of the reaction. Thus far, a highest *n*-butanol yield of 88% with a high flux production and an effective titer of up to 30 g/L of *n*-butanol in *E. coli* has been achieved by Shen et al. by using *trans*-enoyl-CoA reductase (Ter), which causes irreversible reduction of butyryl-CoA.³⁷

Interestingly, this approach can also be applied to synthesize even longer chain hydrocarbon fuels, and Figure 3 shows the extended CoA-dependent pathways for producing C₅, C₆, and

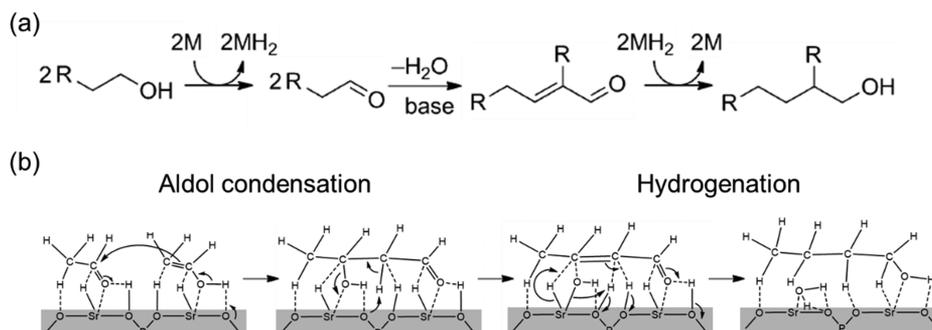


Figure 4. Artificial modification of biological C–C bond formation reactions. (a) Schematic of the Guerbet reaction. (b) Reaction mechanism for the formation of *n*-butanol from ethanol over Sr-HAP catalysts.⁴³

C₈ species from acetyl groups. Dekishima et al. reported that the carbon chain can be elongated from butyryl-CoA (C₄) to hexanoyl-CoA (C₆) by utilizing the β -ketothiolase (BktB) enzyme.³⁸ The BktB enzyme induces C–C bond formation between the β -site of butyl groups and the carbonyl site of acetyl groups to yield 3-ketohexanoyl-CoA, which is the precursor for *n*-hexanol, and suppresses the formation of isomers such as 2-ethyl butanol or 3-ethyl butanol. Similarly, the same β -site-directed Claisen condensation between two butyl-CoAs is reported to produce 1-octanol.³⁹ More interestingly, the reaction scheme is similar to that of a polymerization process and can be applied for synthesizing polyhydroxyalkanoate, which is a representative biodegradable plastic. Sinsky et al. demonstrated the sequential chain addition of butyryl-CoA to yield C₈, C₁₂, and C_{4*n*} species as the reaction products using *phbC* gene expressed *E. coli*.⁴⁰ This discussion highlights that unlike the electrochemical approach, which involves the formation of long-chain hydrocarbon fuels by sequential chain addition from C₁ to C₂ to C₃ and so on, biological systems can effectively realize the long-chain liquid fuel formation pathways by direct coupling of short-chain carbon building blocks.

Inspired by these C₂ condensation reactions found in living systems, researchers have attempted the synthesis of C₄ products from ethanol (C₂ product) using molecular catalysts and thermally activated process. In general, the catalytic reactions for the conversion of these alcoholic substrates are surprisingly rare. One ideal example is the Guerbet reaction, a method that enables facile C–C bond formation with normally unreactive alcohols.⁴¹ In a typical catalytic reaction, as shown in Figure 4a, an alcohol is dehydrogenated to form an aldehyde, which then undergoes Aldol condensation followed by rehydrogenation to produce a long-chain alcohol. This condensation and reduction process is very similar to the CoA-dependent C–C coupling pathway in which both reactions are mediated by a nucleophilic molecular substrate. However, unlike Claisen condensation in the CoA-dependent pathway, this coupling reaction leaves the OH[–] group during the reaction. Hence, the reaction kinetics in this case highly depends on the pH and temperature. Thus, both the selectivity and conversion yield are severely limited by the experimental conditions. Some progress was made in the pioneering studies by Ishii and co-workers with a homogeneous iridium catalyst, [Ir(cod)(acac)] (acac = acetylacetonate, cod = 1,5-cyclooctadiene),⁴² where the basic iridium center acts as an active site stabilized by phosphine ligand. In this study, they reported *n*-butanol selectivity of up to 67% at 12% conversion. More recently, Dowson et al. reported that the Ru- and phosphine-based molecular catalysts oxygenate the ethanol and produce *n*-butanol with 94% selectivity at over 20% conversion.⁷

In addition to the Guerbet reaction on molecular catalysts, a condensation reaction between the two alcohols has also been demonstrated on heterogeneous catalysts by thermally activated processes. Similar to the molecular catalyst, heterogeneous substrates also necessitate highly basic active sites.⁴⁴ Recently, the Ca-rich hydroxyl apatite (Ca-HAP) has been reported to be a potential platform for the thermally driven selective conversion of ethanol to *n*-butanol. In such catalytic systems, the catalytic activity and selectivity of Ca-HAP catalysts are affected by the Ca/P molar ratios of the catalysts, and the Ca-HAP catalysts with higher Ca/P molar ratios exhibit high catalytic activity and *n*-butanol selectivity.⁴⁵ Ogo et al. suggested that the surface basicity is directly related to the conversion efficiency of ethanol and demonstrated that by substituting Ca with Sr, which has higher basicity, a coupling reaction can be made to proceed even at temperatures lower than 180 °C.⁴³ According to the time-dependent product analysis, they proposed that the oxygen atom of ethanol is likely to be attached on the basic sites, that is, O–Ca–O or O–Sr–O, and transformed to acetaldehyde in the same manner as that observed when molecular catalysts are used. The aldehyde adsorbates produce crotoaldehyde by Aldol condensation and then reduce to *n*-butanol. Taken together, controlling acid–base properties of materials and their activities in the individual reaction steps are the key parameters in C₂ chemical-mediated long-chain hydrocarbon synthesis.

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However, both the molecular catalysts and heterogeneous substrates in thermally activated processes require stepwise oxidation and rehydrogenation of the intermediates, which increase the activation energy and limit the kinetics. Hence, realizing their practical applications seems distant at the moment. The realization of these reactions in electrochemical systems may provide a new breakthrough in the field because the resulting systems will be capable of using water as a proton source, producing value-added chemicals at ambient conditions, and being easily combined with renewable energy sources. Interestingly, some ketone and aldehyde compounds, which can serve as building blocks for the synthesis of long-chain

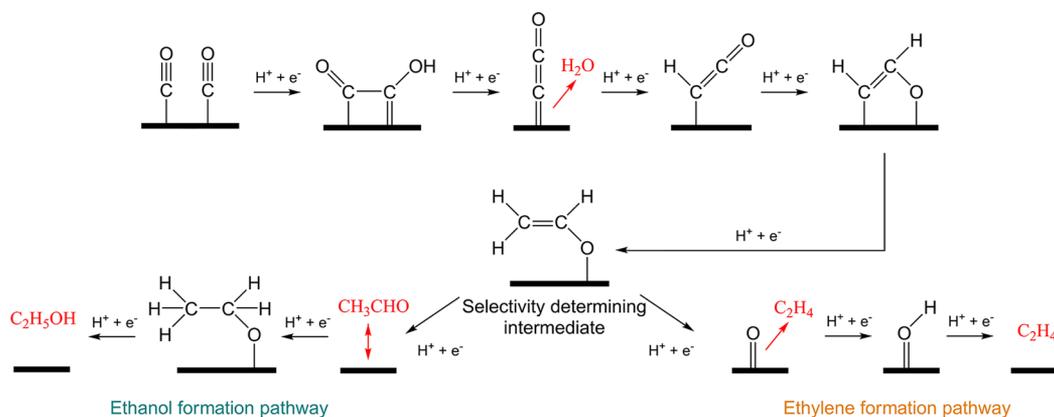


Figure 5. Mechanism for the electrochemical reduction of CO to produce C₂ species on Cu(100). The pathways for the production of acetaldehyde, ethanol, and ethylene are identical up to the formation CH₂CHO*, which is the SDI.^{10,47} Protonation of the SDI on β-C leads to the formation of acetaldehyde and ethanol (cyan), whereas protonation on α-C leads to the formation of ethylene and water (orange). Protonation of the SDI on Cu(100) is inclined toward the ethylene pathway.

hydrocarbon fuels, have also been proposed as the reaction intermediates in the electrochemical CO₂ reduction reaction. Jaramillo et al. empirically observed the formation of acetaldehyde, propionaldehyde, hydroxyacetone, and so on.⁴⁶ All of these compounds possess carbonyl groups and enol tautomers. Here, the enol tautomer can act as a nucleophile, making new C–C bonds between the C₂ building blocks. Bertheussen and co-workers also proved that acetaldehyde merges during the electrochemical CO conversion and acts as a key intermediate for the fluent production of ethanol.²⁵ They also assumed the possible condensation of acetaldehyde; however, any related C₄ compound was not observed. One possible explanation is that the enol tautomer is thermodynamically unstable in aqueous solutions and, thereby, the compound desorbs from the electrode and quickly converts to its stable keto form. In the same context, Koper et al. theoretically suggested the mechanism for the generation of acetaldehyde from *CO adsorbents and its further reduction to ethanol or ethylene.⁴⁷ As shown in Figure 5, the product of the fifth proton–electron transfer from CO is ethenol, the enol tautomer of acetaldehyde, and acts as a selectivity-determining intermediate (SDI) for ethanol and ethylene, depending on which part of the intermediate is detached from the electrode. Considering that Cu has moderate binding affinity for oxygen²⁴ and that the C–C coupling reactions are generally affected by the surface coverage of intermediates,^{9,47} it is speculated that the currently used Cu-based electrode is not suitable to hold the enol tautomer of acetaldehyde.

If we can precisely manipulate the adsorption energy and the surface coverage of the intermediates on the substrate, the coupling reaction of carbonyl compounds can be realized on heterogeneous electrodes similar to the biological systems. One possible strategy is to incorporate metal atoms with higher oxygen affinity for the Cu substrate.⁴⁸ As demonstrated by the previous works using tandem catalysts,^{49,50} by activating CO₂ and stabilizing the carbonyl compounds, a reaction similar to the acetyl-CoA enzyme can be obtained. However, these approaches may produce other effects such as a change in the binding modes of the reaction intermediates and electronic structure of the catalytic substrates. Kim and co-workers reported that varying the composition in Au–Cu nanocrystals leads to a d-band shift and observed additional stabilization of the COOH intermediate because of having the Cu atom adjacent to a Au–C primary bond, where it can form another bond with the oxygen

end of COOH.⁵¹ In addition, an element with high oxygen affinity can also change the potential-determining step such as the clearing of OH* from those sites.²⁴ Because all of these features directly affect the product selectivity, a balance must be obtained.

In this Perspective, recent developments in CO₂ conversion have been made, focusing on the strategies to take scientific lessons from nature. In living systems, acetyl groups attached on CoA enzymes act as short-chain carbon building blocks to producing long-chain hydrocarbons. Numerous artificial catalysts inspired from nature have been developed. Previously suggested Guerbet reaction and thermally activated Aldol condensation are interesting approaches to make C₄ products from C₂ chemicals such as ethanol, which are relatively abundant. However, their high activation energy and limited yields are major hindrances in the formation of C₄ products. Hence, a more systematic approach is required. The electrocatalytic conversion of CO₂ is a possible solution to this problem. Moreover, the electrocatalytic conversion systems can be operated under ambient conditions with renewable energy sources. Although the electrochemical synthesis of C₄ products by utilizing C₂ intermediates has not been demonstrated yet, recent studies suggest that by precisely controlling the oxygen affinity of electrodes, the electrochemical synthesis of C₄ products can be realized. The ultimate production of long-chain hydrocarbon fuels from abundant and inexpensive CO₂ by electrochemical reduction will provide a new approach to reduce the carbon footprint and close the carbon cycle.

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Notes

The authors declare no competing financial interest.

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