Co-electrolysis of CO_2 and formaldehyde to ethanol: An inspiring asymmetric C−C coupling pathway

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Summary

Selectively producing a target ethanol product is highly desired but challenging, especially when using CO_2 as a feedstock only. In this issue of *Chem Catalysis*, Han and coworkers describe a co-electrocatalytic conversion of CO_2 and formaldehyde toward ethanol, which expands the scopes of C−C coupling routes for CO_2 utilization.

The electrocatalytic refinery is an emerging route that promises to enable the transition of fuel and chemical production from fossil fuels to renewables. Especially, the electrochemical CO_2 reduction reaction (CO_2RR) to platform chemicals can potentially bring us a step closer to establishing a zero-emission carbon cycle when driven by renewable electricity.[1] Among the various products from CO_2RR, ethanol is an important transport fuel with a high energy density. However, the state-of-the-art electrocatalytic CO_2-to-ethanol conversion suffers from low selectivity, efficiency, and stability.[1]

Electrocatalytic CO_2 reduction to multi-carbon (C_{2+}) products must overcome the C−C coupling barrier, which is regarded as the rate determining step.[2-4] The C−C coupling proceeds via dimerization of adsorbed CO (*CO, the key intermediate) or coupling of *CO with its hydrogenated derivatives (e.g., *CHO and *COH).[4] Enhancing *CO binding energy or *CO coverage, two interdependent parameters, at the catalyst surface lowers the C−C coupling barrier and thus accelerating the C−C coupling kinetics. The higher *CO binding ability can be achieved by introducing low-coordinated active sites on catalyst surface. The *CO surface coverage can be experimentally improved by increasing local CO concentration at the catalyst-electrolyte interface. In addition, computational studies indicated that pathways toward ethylene and ethanol, the main C_2 products in CO_2RR, may share several common intermediates following C−C coupling.[2,3] While selective formation of ethanol is more challenging due to the energetically more favorable bifurcation toward ethylene on general Cu surfaces, including (100) and (111) facets.[2–4] Despite the open debate on the precise bifurcation(s), many strategies have been developed to manipulate the reaction pathways toward ethanol over ethylene, including alloying, tandem catalyst, and defect engineering,[4] all of which focus on the catalyst and interface design to steer the adsorption energy and configuration of key intermediates in CO_2 reduction.

Co-electrolysis of CO_2 and small molecules, such as nitrogen-containing NH_3, N_2, and nitrate, has gained significant interest in building C−N bonds. Although the mechanism is still under exploration, a variety of amines and amides (particularly urea), have been successfully synthesized by N-integrated CO_2 electroreduction.[5] Such co-reduction requires simultaneous activation of carbon and nitrogen precursors. Once activated species are stabilized, C−N coupling can be promoted by the nucleophilic attack of the nitrogenous reactant/intermediate on a carbon intermediate.[5] However, few studies have addressed the C−C coupling between CO_2 and another carbon precursor.

As a recent example, Han and coworkers, in this issue of *Chem Catalysis,* reported a novel route to produce ethanol through co-electrolysis of CO_2 and formaldehyde (FA) at ambient conditions.[6] By employing an iodine-modified Cu_2O (O-CuI) catalyst, they achieved 32.4% Faradaic efficiency of ethanol at a total current density of -8.8 mA cm^{-2} in the H-cell. In control experiments, the sole CO_2RR and FA reduction, produced no ethanol over the O-CuI catalyst, indicating the high electrocatalytic activity toward ethanol originated from the electrochemical C−C coupling between CO_2- and FA-derived intermediates. This coupling pathway was also validated by the observation of accelerated ethanol formation rate when CO and FA were co-fed. Furthermore, isotope-labeling results implied that CH_3- and $-CH_2-$ groups of ethanol evolved from FA and CO_2, respectively (**Scheme 1**). Combined *Operando* spectroscopy measurements and density functional theory (DFT) calculations suggested iodine doping and low-oxidized Cu species tailored electronic and geometric structures of catalyst, benefiting CO_2 activation, FA adsorption, and C−C bond formation. A reaction mechanism for ethanol formation was therefore proposed. Distinguishing from C−C coupling in sole CO_2RR, co-reduction of CO_2 and FA enables direct coupling of *CO with adsorbed FA (*HCHO). The formed $^*OCCH_2O$ then undergoes hydrogeneration and dehydration steps to form $^*OCCH_2$, which is further reduced to $^*OCCH_3$, and finally leads to ethanol (**Scheme 1**).

The authors not only realized CO_2 fixation and FA degradation simultaneously in a green way but also clearly showed the power of isotopic experiments, *operando* vibrational spectroscopy, and X-ray absorption and emission technologies in unraveling catalytic reaction mechanisms.[6] When further corroborated by advanced theoretical studies, they provide insight into the C−C coupling mechanism, which inspires people to expand reaction scopes involving CO_2 utilization.

From a more general perspective, combining CO_2 and FA is one prototypical example of C−C bond formation in a co-electrolysis system. Analogously, people can predict that co-reduction of CO_2 (or CO) with acetaldehyde may enhance propanol formation. Formate, another important CO_2 reduction intermediate, could participate in C−C coupling with acetaldehyde to form 1-butanol.[7] CO_2 upgrading with biomass derivatives is also an interesting electrochemical route. Moreover, one-pot synthesis of long-chain organic compounds (e.g., glucose) is another potential application by pairing CO_2 with appropriate carbon precursors. In terms of those more complex conversions, the desired catalysts must be capable of independently regulating the adsorption of distinct intermediates for each component reaction and accelerating the interaction between them for new bond formation.[8] Tandem catalysis through two distinct active sites should be highlighted as a promising strategy to facilitate such conversions.

In addition to novel reaction routes and catalysts, the reaction environment also plays a critical role in determining reactivity. Key factors, such as local pH, additives, and ion effects, have been well explored for CO_2RR, which provides universal guidance for new co-electrocatalytic routes.[9] When designing integrated electrocatalytic conversions, special attention should be paid to the stability of organic compounds in aqueous solutions. For example, severe hydrolysis and polymerization of aldehyde molecules in basic conditions will influence the target reaction rate, interfere with product analysis, and mislead mechanism understanding. Meanwhile, new testing setups are highly demanded but challenging to eliminate the mass transport limitation of organic molecules.

Finally, it is worth noting that introducing organic molecules into CO_2RR may be a powerful tool to probe key intermediates leading to the formation of specific C_{2+} products in CO_2RR. The previous study on the formation of acetamide from co-electrolysis of CO and NH_3 demonstrated that acetate production might undergo a pathway involving the nucleophilic attack of OH^- on the ketene-like intermediate (*CCO).[10] Substituting other carbon precursors for FA will offer opportunities to comprehend C−C coupling steps and bifurcation toward ethylene versus ethanol in CO_2RR. In summary, by taking co-electrolysis of CO_2 and FA as a showcase, Han and co-workers[6] have provided us with new inspiration for constructing C−C bonds and expanding the scopes of CO_2 utilization.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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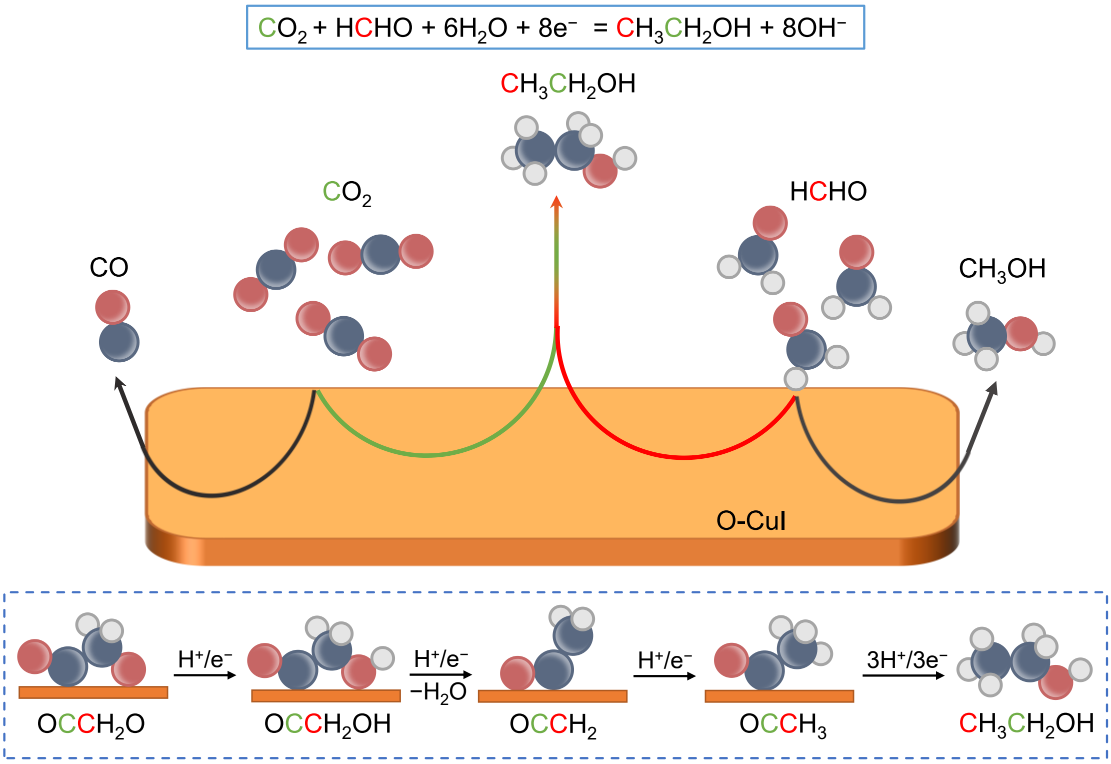

Scheme 1. Proposed mechanism of C−C coupling between CO_2 and FA to ethanol on O-CuI catalyst. Competitive reactions are CO_2 reduction to CO, FA reduction to methanol, and hydrogen evolution reaction (not shown here). The black, red and white spheres represent the C, O and H atoms, respectively.