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CO₂ ELECTROCATALYSIS

Co-feeding copper catalysts couples carbon

The mechanistic electrochemical mass spectrometry study of ethylene production on Cu-based nanocatalysts under CO₂/CO co-feeds indicates the existence of separate, reactant specific surface adsorption sites for CO₂ and CO, which guided the design of a multicomponent CO₂RR electrocatalyst.

Much of modern society's fuels, materials, and chemicals are built from the combustion products of fossil fuels. This carbon-intensive process results in an over-reliance on petroleum, coupled with untenable greenhouse gas emissions that worsen anthropogenic climate change. However, the same CO₂ gas streams that are emitted as waste could instead be recycled as value-added fuels and chemical precursors. If such a process could be powered with renewable electricity, it would yield a valuable method to close the carbon cycle while offering chemical avenues of renewable electricity storage.¹ Central to this technology is a catalyst, frequently nanomaterial-based, which can channel this electricity into a chemical transformation of CO₂.² Taking inspiration from the mixed nature of typical industrial waste streams, Wang *et al.* co-feed their copper nanoparticle catalysts with both carbon monoxide and carbon dioxide to improve the rate of ethylene production. By studying the product stream using isotope labeling experiments under operation, the authors derive important mechanistic insights into the formation of multi-carbon product like ethylene under co-fed conditions, informing future nanocatalyst design.

Despite much progress in the conversion of aqueous CO₂ to single-carbon products such as carbon monoxide and formate, understanding the conditions in which C-C bonds can be favorably created to make more valuable multicarbon (C₂₊) products has been a key gating obstacle to the further development of this technology. With copper as the only heterogeneous catalyst material known to favor C₂₊ formation, much effort has gone into understanding how C-C bonds form on a copper surface under various conditions.³ In addition to the direct conversion of CO₂, works are

increasingly investigating the reduction of CO to multicarbon products, given its proposed role as an intermediate to C₂₊ formation.⁴ The co-feeding of CO and CO₂ as investigated by Wang *et al.* appears counter-productive at first glance, as the presence of one would lower the local concentration of the other by necessity, resulting in possible competition between the two reactants.

Wang *et al.* discovered that under a variety of co-feeding CO:CO₂ ratios, the copper oxide based nanoparticle catalyst has increased production rate of ethylene compared to either pure CO₂ feeds or pure CO feeds, once the electrochemical potential becomes sufficiently negative. To understand the mechanistic origins of this enhanced ethylene production, the authors developed a method to measure the products in real-time by *operando* differential electrochemical mass spectrometry (DEMS). By using mixed feeds with different isotopic labels, ¹³CO and ¹²CO₂, the authors are able to probe the mass fragments of the resulting C₂H₄ and trace back from which gas each carbon is derived. They find that in the conditions in which C₂H₄ production is enhanced under co-feed vs. pure feed, a plurality of the produced C₂H₄ is derived from “cross-coupled” ¹³CO-¹²CO₂ (Fig. 1a). In other words, adding gaseous CO into the feed at sufficiently negative potentials provides a significant source of carbon for coupling distinct from CO₂-derived carbon, potentially due to the replenishment of depleted carbon intermediates at such potentials. Furthermore, their results imply the presence of non-competing surface sites for CO and CO₂ adsorption on their catalyst. Using these insights, they show how a nanocatalyst system can be designed to take advantage of increased local CO partial pressure by using a proximal co-catalyst to generate CO to feed the copper catalyst’s ethylene production (Fig. 1b).

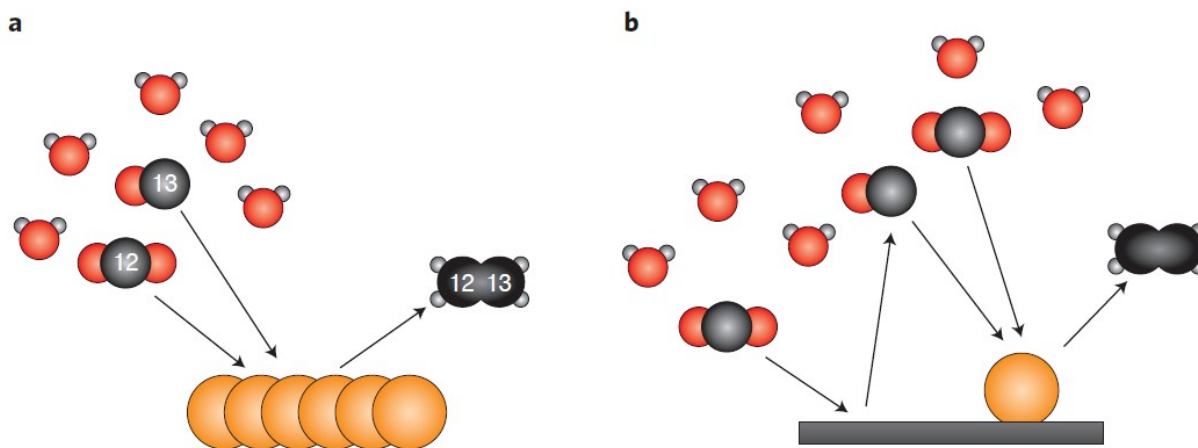


Figure 1. Cross-coupling of CO and CO₂-derived species to result in increased C₂H₄ yields in co-feed conditions on copper oxide derived

nanoparticle catalysts. (a) Isotopic labeling in combination with operando DEMS in co-feed conditions shows a plurality of cross-coupled C₂H₄ from ¹³CO and ¹²CO₂ sources. (b) A sequential bifunctional catalyst is designed using a non-metallic component to reduce CO₂ to CO, creating a co-feed condition for downstream copper oxide nanoparticles to form C₂H₄.

Wang *et al.*'s work essentially joins two emerging directions in the field of CO₂ catalysis. First, the use of isotopic labeling is being used to gain valuable mechanistic insight in addition to being a control experiment. As affirmed with other recent work, isotopic labeling of mixed feeds is beginning to unravel the subtle and exquisite complexity involved even in forming "simple" multi-carbon molecules such as ethylene on copper surfaces.⁵ Secondly, the design of "sequential" nanocatalysts for higher-order product formation, in which CO is first generated and then surmised to be further reduced by a second site, is being explored as a strategy to enhance production rates.^{6,7} In addition to these concepts, the demonstration of isotopically-labeled *operando* DEMS as a time-resolved mechanistic probe offers the field a real-time window into the formation of value-added multicarbon products, a useful contribution to the comprehensive understanding of CO₂ electroconversion.

Much work remains to be done in CO₂ electrocatalysis, especially towards multicarbon products. Overpotentials must be reduced considerably to increase energy efficiency, and the fundamental mechanistic pathways towards different multicarbon products (*e.g.* ethylene vs. ethanol or other oxygenates) has yet to be elucidated. From a materials standpoint, a clear picture of the surface sites that promote C-C coupling reactions, as hinted by this work and previous works, remains elusive. However, the prospect of effectively using co-fed CO/CO₂ systems vs. pure feed CO₂ or CO opens up new opportunities to explore these questions. For example, in recent years, substantial progress in increasing bulk production rates in a gas diffusion environment has steadily pushed CO₂ electroreduction closer to industrial relevance.⁸ Since the application of gas diffusion environments is also being demonstrated for pure CO feeds,⁴ one wonders how mixed feed CO/CO₂ systems may respond when translated to this technology. The future design of nanoscale catalysts, with well-defined and well-controlled structural and compositional features that take advantage of these various catalytic paradigms, will continue to push CO₂ electrocatalysis towards fruition.

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References

1. Chu, S., Cui, Y. & Liu, N. *Nat. Mater.* **16**, 16–22 (2017).
2. Ross, M. B. *et al.* *Nat. Catal.* **2**, 648–658 (2019).
3. Nitopi, S. *et al.* *Chem. Rev.* **119**, 7610–7672 (2019).
4. Jouny, M., Luc, W. & Jiao, F. *Nat. Catal.* **1**, 748–755 (2018).
5. Lum, Y. & Ager, J. W. *Nat. Catal.* **2**, 86–93 (2019).
6. Lum, Y. & Ager, J. W. *Energy Environ. Sci.* **11**, 2935–2944 (2018).
7. Huang, J., Mensi, M., Oveisi, E., Mantella, V. & Buonsanti, R. *J. Am. Chem. Soc.* **141**, 2490–2499 (2019).
8. Dinh, C.-T. *et al.* *Science* **360**, 783–787 (2018).