CO_2 reduction

https://doi.org/10.1038/s44286-023-00019-9

Beyond C–C coupling in CO_2 reduction

Yuting Xu & Fanglin Che

Directing CO_2 electroreduction toward a single C_2 product poses challenges because the reaction mechanism is unclear. Now, oxygen affinity is identified as a potential key descriptor to manipulate the selectivity of ethylene versus ethanol.

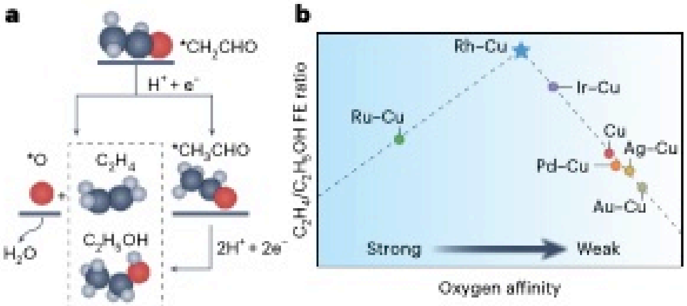

Fig. 1 | Oxygen affinity as a descriptor for ethylene versus ethanol selectivity. **a**, Schematic illustration of branching pathways to C_2H_4/C_2H_5OH from the *CH_2CHO intermediate as the selectivity-determining intermediate. **b**, A volcano-shaped correlation between experimentally measured C_2H_4/C_2H_5OH FE ratios and theoretically calculated relative adsorption energy of *O (referring to the pristine Cu as 0 eV). Figure adapted with permission from ref. 5, Springer Nature America, Inc.

Reducing carbon emissions by electrochemically converting CO_2 to a value-added product(s) supports the world's transition to clean energy[1]. Cu-based catalysts in electrochemical CO_2 reduction reactions (CO_2RR) have received the most attention because they are cost effective and can afford valuable multi-carbon products (C_2), such as ethylene (C_2H_4) and ethanol (C_2H_5OH), via C–C coupling[2]. However, the mechanism to control the post-C–C coupling pathway remains unclear, inhibiting the selectivity toward a specific C_2 product. Such challenges arise from the high computational costs associated with predicting the complex reaction networks of CO_2RR to a single C_2 product over structure-sensitive catalysts under electrochemical operating conditions[3], and the inability to probe the key C_2 intermediates during the post-C–C coupling steps using state-of-the-art operando technologies[4].

Now, writing in *Nature Chemical Engineering*, Shize Yang, Thomas Senftle, Jingjie Wu and colleagues introduce a generalizable concept — tuning oxygen affinity — to direct post-C–C coupling selectivity toward C_2H_4 or C_2H_5OH (ref. 5). To support this concept, the work closely integrates atomic-scale calculations with in situ experiments. For this work, the authors assume that the selectivity-determining step of post-C–C coupling is the C–O bond cleavage in the key selectivity-determining intermediate of *CH_2CHO (Fig. 1a). They then dope the noble-metal single site into Cu (that is, M–Cu, M = Rh, Ir, Ru, Pd, Au and Ag) to tune the favorability of the C–O bond scission in the selectivity-determining intermediate and manipulate the C_2 selectivity[6].

Compared with the pristine Cu, the stronger oxygen binding strength on the M–Cu (M = Rh, Ir and Ru) surface favors the cleavage of the C–O bond in the *CH_2CHO intermediate, producing C_2H_4 and leaving *O. When the *O binding strength is too strong, such as Ru–Cu, the high oxygen affinity leads to catalyst poisoning by *O. By contrast, the weaker oxygen binding strength on the M–Cu (M = Pd, Ag and Au) preserves the C–O bond in *CH_2CHO, preferentially forming C_2H_5OH. Thus, the oxygen affinity tunes the ratio of C_2H_4 to C_2H_5OH productivity. Taken together, the atomic simulation predicts that the Rh dopant presents the best selectivity of CO_2RR to C_2H_4.

The performance of a series of M–Cu catalysts for CO_2RR was evaluated in a flow cell. Experimental results agree with the theoretical prediction, revealing a volcano-like relationship between the C_2H_4/C_2H_5OH Faradaic efficiency (FE) ratios and the oxygen affinity across various M–Cu catalysts (Fig. 1b). The Rh–Cu catalyst exhibits the highest C_2H_4/C_2H_5OH FE ratio of approximately 4.50 at −0.66 V versus reversible hydrogen electrode (RHE) and maintains an C_2H_4 FE of approximately 61% for at least 35 h under a total current density of approximately 1 A cm^{-2}. Furthermore, through collectively promoting both initial and post-C–C coupling steps, a ZnO/Rh–Cu tandem electrode in a membrane electrode assembly (MEA) cell reaches a C_{2+} FE of 85.4% and C_2H_4 FE of 68.8% with a C_2H_4 partial current density of >1 A cm^{-2}. In situ Raman spectroscopy and ethylene oxide reduction reaction measurements validate that the oxygen affinity of M–Cu catalysts indeed modulates the adsorption of key selectivity-determining intermediates and *O intermediates, steering the reaction pathway to a specific C_2 product at the post-CO_2RR stages.

In recent years, many papers have been published on catalyst design for boosting C–C coupling to form C_{2+} products from CO_2RR. However, the post-C–C coupling process to tune a single C_2 product has remained relatively unexplored; this is what makes this approach so intriguing. The authors further envision that engineering oxygen affinity can benefit other reactions that involve the oxygen-bound intermediates, such as CO_2RR to formate and methanol, and ethylene oxide reduction to ethylene.

Despite the advances from this study and others in the field, there is still much to learn about CO_2RR. For example, it is not feasible to screen structure-sensitive catalysts in a vast chemical space for complex reaction networks, such as CO_2RR to C_{2+}, under real operating conditions using atomic-scale simulations (for example, considering electrolyte, solvation and applied potential). Physics-informed, interpretable machine learning opens a path toward developing new, disruptive computational technologies to accelerate and thoroughly explore large complex reaction networks over chemical spaces for an effective identification of promising material candidates[7]. In addition, understanding the transport processes coupled with chemical reaction kinetics is important for scaling up CO_2RR. Future investigations on multi-physics modeling combined with multi-scale simulations can guide the rational design of catalysts, reactors and operating conditions via potentially providing physically correct representations, such as product current densities at different cell voltages, local pH and CO_2/CO partial pressure[8]. Nevertheless, the work of Yang, Senftle, Wu and colleagues provides a general descriptor, oxygen affinity, to manipulate ethylene versus ethanol selectivity during the post-C–C coupling process in CO_2RR.

Yuting Xu & Fanglin Che
Department of Chemical Engineering, University of Massachusetts Lowell, Lowell, MA, USA.
e-mail: fanglin_che@uml.edu

References

1. Seh, Z. W. et al. *Science* **355**, eaad4998 (2017).
2. Kuhl, K. P., Cave, E. R., Abram, D. N. & Jaramillo, T. F. *Energy Environ. Sci.* **5**, 7050–7059 (2012).
3. Goodpaster, J. D., Bell, A. T. & Head-Gordon, M. *J. Phys. Chem. Lett.* **7**, 1471–1477 (2016).
4. Birdja, Y. Y. et al. *Nat. Energy* **4**, 732–745 (2019).
5. Li, Z. et al. *Nat. Chem. Eng.* https://doi.org/10.1038/s44286-023-00018-w (2024).
6. Calle-Vallejo, F. & Koper, M. T. M. *Angew. Chem. Int. Ed.* **52**, 7282–7285 (2013).
7. Mou, T. et al. *Nat. Catal.* **6**, 122–136 (2023).
8. Heenen, H. H. et al. *Energy Environ. Sci.* **15**, 3978–3990 (2022).

Competing interests

The authors declare no competing interests.