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Highlight

Unlocking hydrogen transfer pathway in electrocatalytic CO_2 reduction: Paving the way for precise selectivity control

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As an efficient and sustainable alternative to traditional thermocatalytic hydrogenation in both petrochemical and fine chemical processes, electrochemical hydrogenation powered by renewable energy has attracted considerable attention [1]. Electrocatalytic CO_2 reduction reaction (CO_2RR) offers an appealing route for CO_2 resource utilization to produce high value-added chemicals or fuels. Specifically, the hydrogenation steps are deeply involved in the formation of multi-carbon (C_{2+}) oxygenate and hydrocarbon compounds [2]. The hydrogen transfer route in electrocatalytic CO_2RR relies on H_2O as the primary proton source. The hydrogenation pathways typically proceed via either direct proton transfer from H_2O (Eley–Rideal (ER) mechanism) or surface-adsorbed H from the electrochemical Volmer step (Langmuir–Hinshelwood (LH) mechanism) [3]. However, the electrochemical hydrogenation pathway which could largely affect the final reaction selectivity has not been understood thoroughly. In a recent work published in *Nature Chemistry*, Zhang et al. [3] unlocked the hydrogen transfer routes in electrochemical CO_2RR through isotopically labelling the H source-water. The roles of widely recognized ER and LH hydrogenation mechanisms in manipulating the product types were quantitatively decoupled. These findings open up many opportunities for electrocatalyst design to modulate hydrogenation pathway thus towards precise selectivity control.

The fundamental mechanism of electrocatalytic CO_2RR involves a sequence of physical and chemical processes, including CO_2 adsorption and activation, proton-coupled electron transfer (PCET), and the desorption of products at the active sites [4]. One of the primary challenges in CO_2RR lies in hydrogenation-stabilizing critical reaction intermediates and efficiently converting them into desired products with high activity and selectivity [5]. Obviously, due to the competitive hydrogen evolution reaction (HER), the prerequisite for CO_2RR selectivity is accelerating the *H generation but suppressing the binding between *H. The hydrogenation of C or O atoms in CO_2 is critical for its activation, with HCOO* and HOCO* intermediates branching the reaction towards C_1 or C_{2+} pathways [6]. The hydrogen-assisted C–C coupling mechanism has been proposed for C_{2+} generation, in which the hydrogenation of *CO to *CHO or COH* species on the Cu-based catalyst becomes the rate-determining step rather than C–C coupling process [7]. The derivatives of *CO successive hydrogenation, i.e., $*CH_2$ and $*CH_3$, have been identified as the key intermediates for C_2H_6 [8, 9]. Despite the same intermediate of $*C_2H_3O$, the product types can be switched between C_2H_4 and C_2H_5OH by steering the subsequent selective hydrogenation processes [10]. To enhance C_2H_5OH/C_2H_4 selectivity in Cu-based electrocatalysts, it is essential to promote surface-coupled/solvent hydrogenation while inhibiting solvent/surface-coupled hydrogenation. Therefore, elucidating the distinct contributions of the ER and LH mechanisms in hydrogenation pathways is crucial for guiding catalyst design to precisely control product selectivity.

The hydrogen transfer probabilities of the LH and ER mechanisms were experimentally evaluated with hydrogen and deuterium evolution reaction (HDER) and electrochemical acetylene reduction to ethylene experiments, respectively. The Cu electrode capable of generating C_{2+} species was used to analyze the hydrogen transfer effects on various products. The electrolytes containing H_2O-D_2O mixture varies the ratios of H_2O/D_2O with 100:0, 75:25, 50:50, 25:75 or 0:100. The H/D isotopic compositions in products were mainly determined by gas chromatography-mass spectrometry and ^1H nuclear magnetic resonance (NMR) spectroscopy. The classical collision model-derived sticking coefficient is fitted entirely with the HDER isotopic composition results and enables the quantitative evaluation of H/D transfer probability of the LH mechanism. A higher D_2O composition in H_2O-D_2O mixture results in a suppression in HDER. The kinetic isotope effect (KIE) value for acetylene reduction to ethylene is calculated to be 1.27, smaller than 2.35 for HDER, indicating that the D composition in the ethylene product increases with the D_2O content. The H/D transfer probability values for the ER mechanism was quantitatively described. Building upon these findings, the relative contributions of the LH and ER mechanisms to the hydrogenation pathway in CO_2RR were estimated by correlating the previously determined probabilities with the H/D isotopic compositions of the reaction products (Fig. 1(a)). The LH mechanism should dominate the formation of more than 85% of

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C–H bonds in C_2H_4, C_2H_5OH, and C_3H_8O. The formation of C–H bond ranging from 77% to 90% in acetate proceeds through ER mechanism. And then, comparative kinetic analysis indicated that the hydrogenation of the C and O atoms should proceed mainly via the LH and ER mechanisms, respectively, which is also in agreement with the isotopic labelling results (Fig. 1(b)). The experimental plot depicting the relationship between LH hydrogenation and Faraday efficiency (Fig. 1(c)) reveals that a decline in the LH hydrogenation ratio favors the formation of C_{2+} products. As the D_2O composition rises, a progressive shift from LH to ER hydrogenation becomes evident. For an identical H_2O/D_2O ratio in the electrolyte, the LH mechanism exhibits a higher probability of hydrogen transfer compared to the ER mechanism. This indicates that modulating the LH- to -ER hydrogenation ratio serves as a viable means to regulate the selectivity.

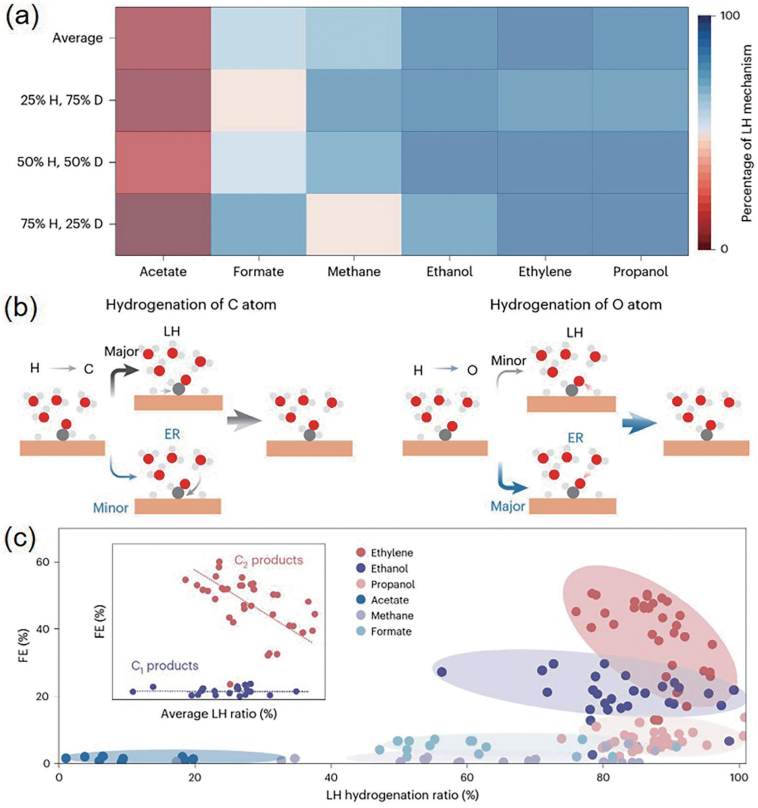

Figure 1 (a) The proportion of LH hydrogenation involved in the generation of each product under different ratios of H_2O/D_2O. (b) A diagram depicting the hydrogenation of C and O atoms by means of LH or ER mechanism. (c) The relationship between LH hydrogenation and Faraday efficiency. Reproduced with permission from Ref. [3], © Zhang, J. G. et al. under exclusive licence to Springer Nature Limited 2025.

Taken together, the in-depth computational and experimental analysis will motivate the rational design of electrocatalysts to manipulate hydrogen transfer route in electrochemical CO_2RR towards precise selectivity control. Bearing this in mind, we suggest that the strategies for modulating the CO_2/H_2O ratio and the activity of H_2O, such as catalyst structure/morphology, mass transfer, and electrolyte composition, will also affect the hydrogenation pathways through tuning the local supply of H source-H_2O.

Data availability

Not applicable.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Y. H. S. and H. R. Z.: Writing manuscript and data curation. W. L.: Polishing manuscript. H. Q. W.: Funding acquisition. All the authors have approved the final manuscript.

Use of AI statement

None.

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