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COMMENTARY

Isotopic labelling: A torch to explore the black box of CO_2 reduction mechanism

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Elucidating the mechanism of electrochemical or photochemical CO_2 reduction is essential for the rational design of efficient catalysts with high product selectivity. However, it is challenging to explore the hydrogen transfer route in electrochemical or photochemical CO_2 reduction via experimental methods. In *Nature Chemistry*, Zhang *et al.* recently employed H/D isotopic labelling to reveal the hydrogenation pathway in CO_2 reduction and estimated the extent to which pathway contributes to the CO_2 reduction products.

Converting CO_2 into fuels or value-added chemicals driven by renewable energy is a promising approach to mitigate the energy crisis and climate change.[1] However, the widespread application of electrochemical or photochemical CO_2 reduction (CO_2R) is limited by low energy efficiency, low activity and poor selectivity towards the desired products. The lack of exploration of the intrinsic mechanism causes a black box of the hydrogenation pathway in CO_2R. Recently in *Nature Chemistry*, Zhang *et al.* estimated the contribution of Langmuir-Hinshelwood (LH) pathway versus Eley-Rideal (ER) mechanism towards the hydrogenation of CO_2R by H/D isotopic labelling.[2] This discovery could promote a more in-depth understanding of hydrogen transfer pathways in electrochemical processes.

The mechanism of hydrogen evolution reaction (HER) is relatively well understood and can be experimentally evaluated using Tafel slope analysis. However, CO_2R is significantly more complex, involving numerous possible pathways and multiple hydrogenation steps. The hydrogenation of intermediates ($C_xH_yO_z$) in CO_2R can proceed through either ER mechanism or LH mechanism.[3] ER mechanism involves proton-coupled electron transfer (PCET) process, where solvent water serves as the direct H source ($*C_xH_yO_z + H_2O + e^- \rightarrow *C_xH_{y+1}O_z + OH^-$). By contrast, LH pathway involves a chemical

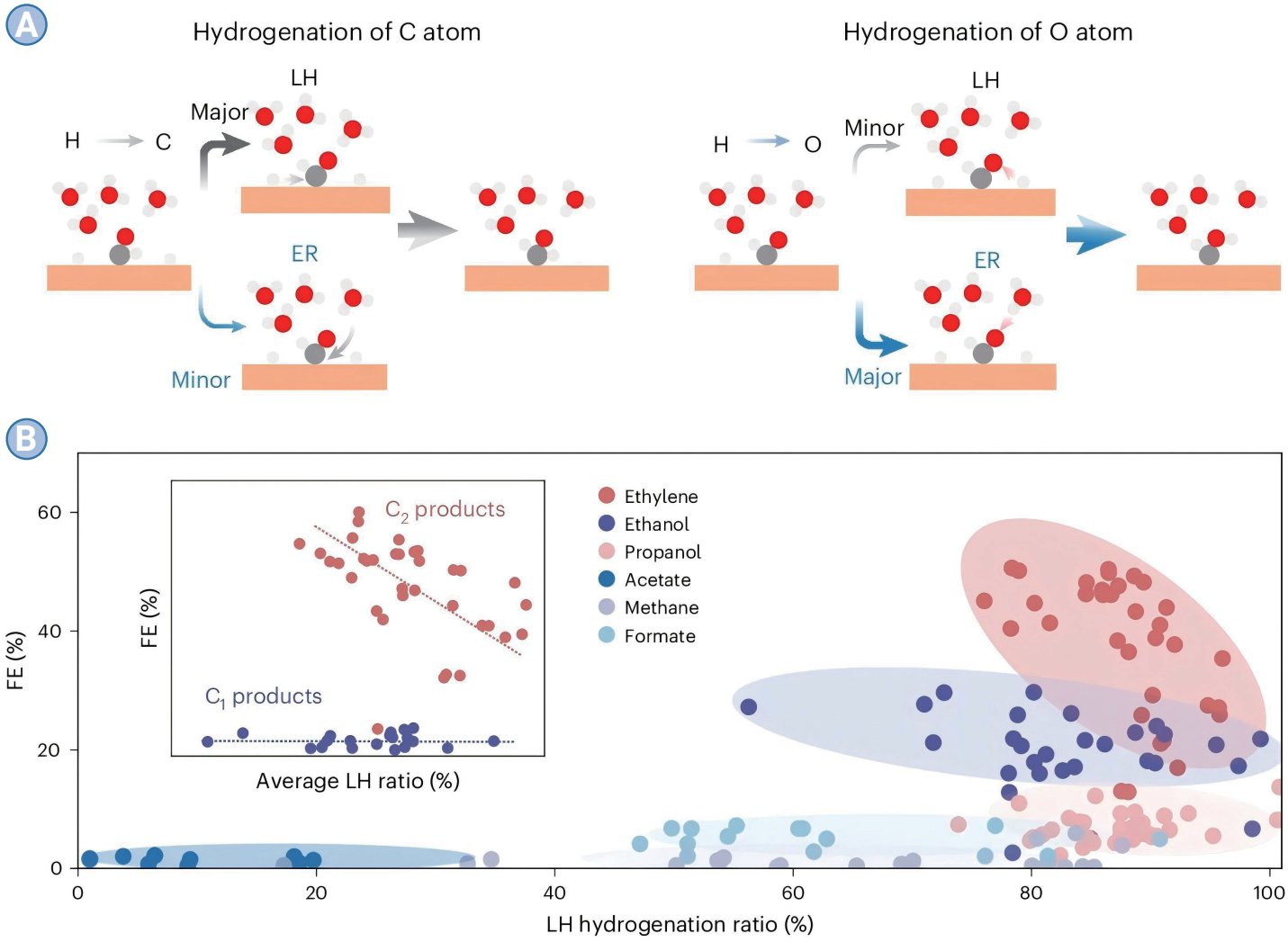

Figure 1. The hydrogenation process of electrochemical CO_2R on Cu (a) The illustration of the LH and ER hydrogenation mechanism on the C and O atoms, respectively. (b) Correlation between the LH hydrogenation ration and FE towards CO_2R products.

reaction between the intermediates and hydrogen atoms preferentially adsorbed on the catalyst surface ($*C_xH_yO_z + *H \rightarrow *C_xH_{y+1}O_z$). The surface-adsorbed *H is first generated from solvent water via Volmer step ($H_2O + e^- \rightarrow *H + OH^-$). However, the mechanism of hydrogenation via ER or LH pathway in CO_2R has been unclear. In previous computational studies even by the same group, competition conclusions were reported.[4] Additionally, due to the challenge of in situ spectroscopy in the kinetics of CO_2R, there is no experimental approach to elucidate the contribution of LH versus ER hydrogenation in CO_2R.

Zhang *et al.* employed H/D isotopic labelling combined with Cu-polytetrafluoroethylene (PTFE) gas diffusion electrodes to achieve dynamic tracking of surface-adsorbed hydrogen species (H*/D*), overcoming the limitations of traditional electrochemical characterization in capturing reaction intermediates. The H/D isotopic composition of products was analyzed using gas chromatography-mass spectrometry (GC-MS) and ^{1}H nuclear magnetic resonance (NMR) spectroscopy. They revealed the transfer probabilities of H versus D through a combination of kinetic isotope effect (KIE) and density functional theory (DFT) calculation. LH mechanism shows a much higher probability of H transfer. Its KIE is primarily determined by the variation of the surface H/D coverage, which is governed by the sticking coefficient in the Volmer step. By contrast, the H versus D transfer probability for ER mechanism is negligible. Hence, the relative contribution of each mechanism (LH versus ER) towards various CO_2R products can be systematically quantified through the distinct KIE values.

From the statistical results of the ratio between LH versus ER hydrogenation for each CO_2R product, the team found that C-H bonds tend to be formed via the LH mechanism, where 85.23%, 87.88%, and 87.59% of C-H bonds in ethylene, ethanol, and propanol, respectively, were formed via the LH mechanism. They further analyzed the hydrogenation of C and O atoms through either the LH or ER mechanism via computational simulations and found that the LH and ER mechanism controlled the hydrogenation of the C and O atoms, respectively (Figure 1A). Compared with the hydrogenation of near-surface C atom via LH mechanism, ER pathway would impose a considerable steric hindrance when hydrogen from solvent water targets the adjacent C atom. As for the hydrogenation of O atom, solvent water can easy access to the O atom via hydrogen bonds in ER mechanism, while surface *H must undertake a desorption step to come closer to the O atom in LH mechanism. It is worth noting that these simulation results are based on the carbon coordination configuration of the intermediates. As for oxygen coordination or mixed (carbon/oxygen) coordination, more extensive computational simulations are required. As shown in Fig. 1b, the researchers also observed that the Faradaic efficiency (FE) of the C_{2+} product would increase as the LH hydrogenation proportion decreased. In particular, it has variable effects on the formation of ethylene and ethanol, where the slope of ethylene shows a steeper function of the LH hydrogenation ratio than that of ethanol. This work significantly promotes the development of hydrogen transfer pathways in CO_2R. Regulating the ratio between the LH and ER pathways can be a promising approach to improve the selectivity of C_2 product desired in CO_2R.

Isotope labelling experiments are essential to accurately trace the products of CO_2R. Standard guidelines for isotope tracing experiments have been developed. However, the application of isotope labelling experiments to investigate the kinetic pathway in CO_2R remains considerably deficient. In situ spectroscopy presents significant challenges in obtaining high temporal resolution information of intermediates and pathways in CO_2R. First-principles calculations are most widely employed to explore the CO_2R pathway. However, current theoretical calculations suffer from the lack of sufficient experiment data. The pioneering work systematically investigated the hydrogenation process in electrochemical CO_2R and estimated the contribution of each mechanism (LH versus ER) towards the desired products via H/D isotopic labelling experiments. This will inspire further in-depth investigations of isotopic labelling and provide a powerful experimental tool for aiding in the elucidation of detailed reaction pathways.

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DECLARATION OF INTERESTS

The author declares no competing interests.