

Dual-site catalysts featuring platinum-group-metal atoms on copper shapes boost hydrocarbon formations in electrocatalytic CO₂ reduction

Received: 28 July 2022

Accepted: 16 May 2023

Published online: 27 May 2023

 Check for updates

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Copper-based catalyst is uniquely positioned to catalyze the hydrocarbon formations through electrochemical CO₂ reduction. The catalyst design freedom is limited for alloying copper with H-affinitive elements represented by platinum group metals because the latter would easily drive the hydrogen evolution reaction to override CO₂ reduction. We report an adept design of anchoring atomically dispersed platinum group metal species on both polycrystalline and shape-controlled Cu catalysts, which now promote targeted CO₂ reduction reaction while frustrating the undesired hydrogen evolution reaction. Notably, alloys with similar metal formulations but comprising small platinum or palladium clusters would fail this objective. With an appreciable amount of CO-Pd₁ moieties on copper surfaces, facile CO' hydrogenation to CHO' or CO-CHO' coupling is now viable as one of the main pathways on Cu(111) or Cu(100) to selectively produce CH₄ or C₂H₄ through Pd-Cu dual-site pathways. The work broadens copper alloying choices for CO₂ reduction in aqueous phases.

Among the catalytic reactions that can hydrogenate CO₂ into energy-intensive hydrocarbon molecules (HCs), the electrocatalytic CO₂ reduction reaction (CO₂RR) featuring CO₂ hydrogenation without producing H₂ gas in any prior steps is of particular interest. While there are ample choices of elements to catalyze CO₂RR into CO and formate molecules¹, copper (Cu) is the demonstrated element that can effectively catalyze the HCs formation (especially C₂-) owing to its optimal binding energies for both hydrogen (ΔE_{H^*}) and carbonyl species (ΔE_{CO^*})^{2–4}, the ubiquitous intermediate during CO₂RR. Copper, therefore, serves as a unique catalytic metal to not only enable the circular

carbon economy on earth but to extend human life beyond earth's orbit through in situ utilization of the in-space CO₂ to make methane as fuel or ethylene as building block molecules.

Metal alloying is a broadly employed strategy to accelerate the CO₂RR while reasonably suppressing the competitive hydrogen evolution reaction (HER)^{5–7}. Metals such as Ag, Au, Pb, and Sn that are either in the same group or to the right of Cu in the periodic table have been extensively studied⁸. These metals, with a typical positive H' binding energy (>0.5 eV), are the well-accepted desired alloying choices with copper due to their unfavorable energetics toward the

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