Electrochemical synthesis of long-chain hydrocarbons and oxygenates using carbon dioxide and acetylene

- Time: 2026.03.24. (Tue) 16:00-17:15
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Speaker

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Abstract

The thermocatalytic Fischer-Tropsch (FT) synthesis can readily convert syngas (CO + H_2) into long-chain hydrocarbons. Herein, we share our works related to the development of catalysts and discovery of the mechanisms for the electroreduction of CO_2 to long-chain hydrocarbons. The catalysts that worked well are unexpectedly based on nickel and cobalt, rather than copper (which is generally known to reduce CO_2 to C_1-C_3 molecules). We first show, through experiments and theory, the reaction mechanism by which CO_2 is reduced to long-chain hydrocarbons on Ni-based catalysts. We then unravel ways to enhance the formation of branched hydrocarbons, which are highly prized for their superior fuel properties. Finally, we shall answer an old puzzle of why copper, which is the *de facto* used catalyst for converting CO_2 to multi-carbon products, has consistently fallen short in producing appreciable amounts of long-chain hydrocarbons. Essentially, nickel and copper catalysts behave differently at the molecular level: Nickel-based catalysts could promote the removal of oxygen from reaction intermediates and favour asymmetric coupling between *CO intermediates and unsaturated hydrocarbon species. This contrasts with copper-based catalysts, which tend to convert oxygen-containing intermediates into alcohols, which prevents the growth of longer hydrocarbon chains. These distinct properties mean that on Ni catalysts, the building blocks needed for longer and more complex hydrocarbons are more likely to form and link together, resulting in products that more closely resemble those made through the Fischer-Tropsch synthesis. We shall further reveal the role of organic solvents in regulating the extent of the hydrogen evolution reaction and CO_2 reduction.

1,3-butadiene is industrially produced as a by-product alongside ethylene from the energy-intensive thermal cracking of naphtha. We shall show that copper catalysts, after a modification with iodide anions, are efficacious for electro-converting acetylene to 1,3-butadiene at ambient temperature and pressure. 1,3-butadiene could be produced with a Faradaic efficiency of 93% at −0.85 V versus the Standard Hydrogen Electrode (SHE) and a partial current density of −75 mA cm^{-2} at −1.0 V versus SHE. The partial current density of 1,3-butadiene was at least 20 times higher than that reported in previous works. Characterisation of the catalyst using *in situ* spectroscopies and density functional theory calculations revealed that iodide promotes stable ensembles of neutral and partially oxidised Cu sites($Cu^{\delta+}$–Cu^0 sites), which enhance the C-C coupling of *C_2H_3 intermediates to form 1,3-butadiene. We shall also showcase strategies to couple acetylene into longer-chain hydrocarbons, which could potentially be used as aviation fuel.

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