

Electrocatalytic Hydrogenation of Furanic Compounds: From Mechanism Study to Paired Electrolyzer Design

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Electrocatalytic conversion of these furanic compounds is an emerging route for the sustainable production of valuable chemicals. I will present our recent mechanistic study of electrocatalytic hydrogenation (ECH) of furfural through a combination of voltammetry, preparative electrolysis, thiol-electrode modifications, and kinetic isotope studies. It is demonstrated that two distinct mechanisms are operable on metallic Cu electrodes in acidic electrolytes: ECH and direct electroreduction. The contributions of each mechanism to the observed product distribution are clarified by evaluating the requirement for direct chemical interactions with the electrode surface and the role of adsorbed hydrogen. Further analysis reveals that hydrogenation and hydrogenolysis products are generated by parallel ECH pathways. We further studied the mechanisms on the Pb electrodes, based on the potential regulated ECH and ER products. Isotopic incorporation studies and electrokinetics have confirmed ECH process to alcohol and alkyl product followed different pathways: alcohol was generated from Langmuir Hinshelwood step through surface-bound furfural and hydrogen, which is sensitive to surface structures. In contrast, alkyl product was formed through an Eley-Rideal step via surface-bound furfural and the inner-sphere protons. By modifying the electrode/electrolyte interface, we have elucidated H_2O and H_3O^+ matters in forming alcohol and alkyl products, respectively. Dynamic oscillation studies and electron paramagnetic resonance (EPR) finally confirmed that the alcohol and dimer products shared the same intermediate. The dimer was formed through the intermediate desorption from the surface to form radicals and the self-coupling of two radicals at the bulk electrolyte. Finally, we have demonstrated a flow cell with an oxide-derived Ag (OD-Ag) cathode and carbon felt anode for pairing electrocatalytic oxidation and reduction of HMF. The flow cell has a remarkably low cell voltage of ~ 2.0 V, which represents a more than fourfold increase in the energy efficiency at the 10 mA operation. A combined faradaic efficiency of 163% was obtained to BHMF and FDCA. Alternatively, the anodic hydrogen oxidation reaction on platinum further reduced the cell voltage to only ~ 0.85 V at 10 mA operation. These paired processes have shown potential for integrating renewable electricity and carbon for distributed chemical manufacturing in the future.