Understanding the Electrochemical Reduction and Coupling of Biomass Derived Carbonyl Species

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Thursday, March 18th at 8:00 pm

Biomass derived species offer a promising alternative to petroleum derived species for fuel and chemical production. However, such species are often low molecular weight and heavily oxygenated, and require reductive upgrading or coupling to form more valuable species. Electrochemistry offers a promising technology for biomass upgrading. Easily utilizing renewable energy sources, such as wind and solar power, electrochemical reduction uses an applied electrical potential to drive the reduction of biomass species. Despite these advantages, electrochemical biomass upgrading largely remains unviable due to poor catalysts and a lack of mechanistic understanding. This work seeks to advance electrochemical biomass upgrading by investigating the electrochemical reduction of carbonyl species.

First, the work investigates the reduction of benzaldehyde on Au, Cu, Pt and Pd electrodes. Reactivity tests show a coupling ability for Cu, but not the other metal catalysts. In situ spectroscopic experiments show ketyl radical species on Au and Cu, and benzaldehyde decomposition on Pt and Pd. Combined, the reactivity and spectroscopic experiments suggest that Cu coupling ability results from a more optimal ketyl radical stability compared to the other catalysts. Subsequently, the analysis is extended to the cross-coupling of different aldehydes, using a benzaldehyde-furfural model system. Effective cross-coupling of benzaldehyde and furfural is demonstrated on Cu and Pb electrodes. Catalyst influences coupling selectivity, with Cu favoring cross-coupling, while Pb favors furfural self-coupling. Comparison with a stochastic coupling model suggests the change in coupling selectivity results from greater over binding of benzaldehyde (relative to furfural) on Pb compared to Cu. A new parameter is developed to describe coupling stochasticity. Cyclic voltammetry and spectroscopic experiments further support binding energy differences as the likely cause for the different Pb and Cu coupling selectivities. The combined reactivity, cyclic voltammetry and spectroscopic data suggest aldehyde cross-coupling follows a two reactant Sabatier rule, with optimal cross-coupling for reactants with similar binding strengths. Finally, this work investigates the effect of structure on the reduction of aliphatic ketones. Reactivity tests show a decrease in reduction rate with size for linear ketones, with higher rates and the opposite trend for cyclic ketones. Activation parameter measurements suggest rate decreases result from smaller pre-exponential factors. Comparison with a kinetic model suggests that lower surface-carbonyl orbital overlap causes the decrease in pre-exponential factor for larger ketones, with hydraulic radius offering a good descriptor of ketone size. Further, activation energy measurements suggest similar intrinsic activation energies for all ketones, with observed activation energy size trends resulting from different adsorption energies.