Electrocatalytic Hydrodeoxygenation of Aldehydes in Pd@CNT-stabilized Pickering Emulsions.

Edwin Onoh, [1,2] Prof. Dr. Walter Leitner,[1,2] Dr. Nicolas Kaeffer [1], Dr. Alexis Bordet [1]

[1]Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany;
[2]Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany.

ABSTRACT

The global transition toward a sustainable chemical industry requires processes to shift from fossil to renewable carbon and energy sources. Many important platform molecules contain carbonyl functionalities such as aldehydes (e.g. furfural, HMF, vanillin, etc.), which need to be hydrodeoxgenated to produce bio-derived intermediates for the production of fuels and value-added chemicals.[1,2] High temperatures and pressures are typically needed for conventional thermal catalytic processes, and these harsh conditions can also promote side reactions such as polymerization and coke production, which can reduce yield and selectivity.[3]

With the ability to fine-tune electron transfer and redox transformations under moderate conditions without the need of stoichiometric oxidants or reductants, electrocatalysis and organic electrosynthesis have lately become attractive approaches.[4,5] One direct and atom-efficient method for removing oxygen from carbonyl substrates is electrochemical deoxygenation; yet, direct hydrodeoxygenation (HDO) of these substrates is still a major obstacle due the high bond dissociation energies (BDEs) of C−O and C=O bonds.[6]

Building on a concept recently established by our team,[7] this study investigates the electrocatalytic HDO (ECHDO) of aldehydes using a Pd@CNTs catalyst within a Pickering emulsion system. The unique properties of this Pickering emulsion system, such as enhanced mass transfer and optimized interactions between the catalyst, organic phase and electrolytes, provides a conducive environment for complex catalytic reactions

enabling effective dissociation of C−O and C=O bonds to tolyl products with higher selectivity and Faradaic efficiency than previously reported (Figure 1b). The hydrophilic carboxylated-CNTs stabilize the aqueous phase, while hydrophobic Pd NPs generate adsorbed hydrides (H_{ads}) at the interface and drive selective C–O bond cleavage in the organic phase (Figure 1a). This integrated catalytic–emulsion platform enables the selective hydrodeoxygenation of C=O bonds to alkanes, effectively overcoming the limitations of traditional hydrogenation pathways.

This method demonstrates a synergistic integration of electrocatalysis and emulsion chemistry for the sustainable upgrading of biomass-derived carbonyl compounds, advancing the frontier toward a green chemistry-energy nexus.

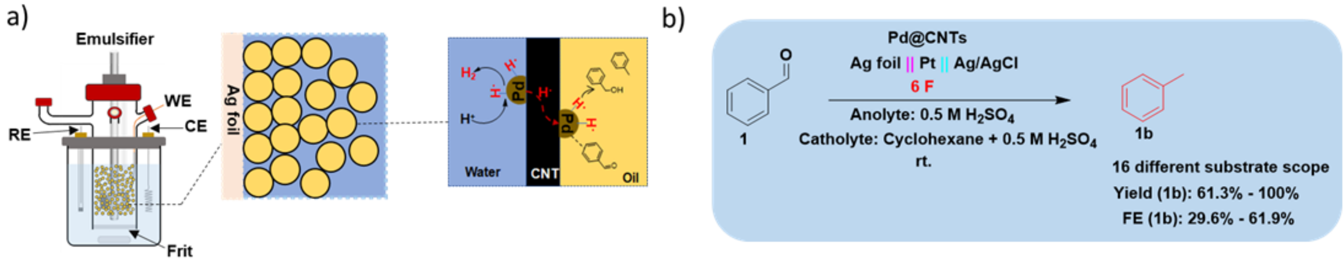

Figure 1: a) Pickering emulsion system, with CNT-stabilized oil-in-water emulsion on Ag electrode (WE: Working Electrode) enabling interfacial ECHDO of aromatics (where; CE: Counter Electrode, and RE: Reference Electrode). b) Optimized conditions for aldehyde ECHDO across substrates.

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