Electrocatalytic Conversion of Biologically Produced Muconic Acid to a Bio-based Polymer Precursor

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Introduction

Coupling biocatalysis and chemical catalysis represents a promising approach to convert lignocellulosic feedstock into bio-based chemicals [1]. However, the amino acids found in the culture media and the biogenic impurities generated by the enzymes readily poison noble metal catalysts [2]. Substantial purification is currently required before the fermentation products can be further converted using chemical catalysts. Highly active and selective heterogeneous catalyst that can process fermentation broths directly, without extensive separation and purification, are highly desired.

Our group explored the electrocatalytic hydrogenation (ECH) of biologically-produced muconic acid to 3-hexenedioic acid (3-HDA), a bioadvantaged monomer similar to adipic acid. This approach offers key benefits compared to conventional catalytic hydrogenation [3]. For ECH, the hydrogen needed for the reaction is generated in situ from the aqueous electrolyte through the hydrogen evolution reaction. The reaction is performed at room temperature and atmospheric pressure, eliminating the need for an external hydrogen source. Most importantly, hydrogen generation and muconic acid hydrogenation are both catalyzed by the same Earth-abundant (non-noble) transition metal.

Materials and Methods

An engineered strain of *Saccharomyces cerevisiae* was used to convert glucose to muconic acid. ECH was then directly employed on a formic acid doped cell culture medium containing ammonium sulfate and amino acids, chemicals that would deactivate most catalysts. The reactions were carried out in a three-electrode electrochemical cell with lead, platinum, and Ag|AgCl as the working, counter, and reference electrodes, respectively. The lead electrocatalyst was held at a variety of potentials ranging from -0.8 V to -1.8 V to hydrogenate muconic acid to 3-HDA. Products were identified by ^{1}HNMR, mass spectroscopy, and were further quantified by UPLC-PDA-ELSD.

Results and Discussion

Lead was found to catalyze the hydrogenation of muconic acid to 3-HDA even in the presence of biogenic impurities. Minor differences in catalytic activity were observed for model solutions with and without contaminants, thus indicating that biogenic impurities had only little effect on the catalyst. Selectivity to 3-HDA remained high (~95%), under most reaction conditions and for the whole duration of the tests. Differences in rates were observed depending on the applied potential. The electrocatalyst held at -1.5 V converted approximately 97% of muconic acid within 2 hours when using a formic acid doped cell culture medium. Successive two-hour electrocatalytic batch reactions were performed in order to assess the stability of the catalyst (Figure 1). No sign of deactivation was observed after the 3rd run.

Significance

Electrocatalytic hydrogenation represents a green alternative to high pressure hydrogenation over noble metal catalysts. The reaction takes place in aqueous solvents under ambient conditions using Earth-abundant metal catalysts that are resistant to biogenic impurities. Hydrogen is produced in situ from the fermentation broth, directly at the surface of the hydrogenation catalyst. This technique could facilitate the integration of biocatalysis and chemical catalysis in the biorefinery by eliminating costly separation and purification steps. In this work, muconic acid produced by fermentation was selectively converted in a single step into 3-hexenedioic acid, a bioadvantaged substitute to adipic acid. The additional C=C functionality compared to adipic acid enables the synthesis of polymers with new properties.

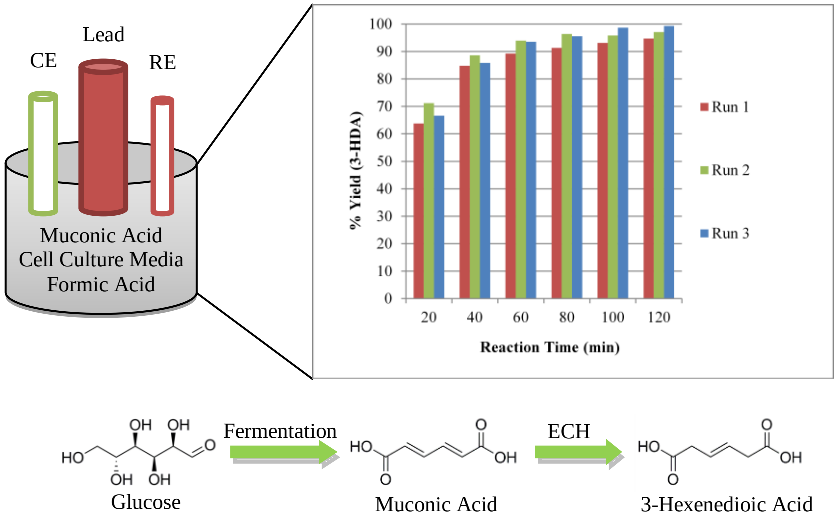

Figure 1. ECH of formic acid doped cell culture media using a three-electrode electrochemical cell at -1.5 V under ambient conditions. Recycling tests (runs 1-3) showed no deactivation.

References

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