

Low-temperature selective conversion of biomass-derived compounds to fuels and chemicals

Investigators

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Abstract

In this 12 months project, we focused on studying electrocatalytic approaches for the conversion of biomass into useful fuels and chemicals. Specifically, we targeted the conversion of sorbitol, a polyol readily derived from cellulose and hemicellulose, to useful building blocks such as rare sugars and polymer starting materials. In this research, for the first time, we identified the steps required for the electrochemical oxidation of sorbitol in solution on platinum surfaces, thus establishing an area that has seen no or little contribution from past research. With the insights that we obtained, we are now ready to proceed to quantitatively produce chemicals from sorbitol with selectivity and rather large productivity, thus providing a promising pathway for the utilization of renewable electricity for the sustainable production of chemicals. Overall, this project is an important starting point towards decarbonization of chemical industry with consequences for reducing greenhouse gas emissions from the utilization of fossil fuels that could be replaced with the efficient use of biomass and renewable resources.

Introduction

While renewable electricity is expected to play a major role in a carbon-free future, it is much likely there will remain the demands for irreplaceable liquid fuels and platform chemicals that are currently entirely sourced from fossil fuels. Biomass represents an extremely valuable resource for these chemicals provided that it does not compete with food crops for land. However, catalytic upgrading of biomass-derived compounds is limited due to the intense energy involved in thermocatalytic reactions and the significant purification requirements after catalysis from their lack of product specificity. Therefore, finding alternative ways for biomass conversion that can achieve high selectivity with minimal energy input is crucial for the utilization of biomass-derived compounds at low or net-zero carbon emissions.

The aim of this project is to explore electrochemical methods (and, potentially, combined electro-thermochemical methods) for catalytic conversion of biomass-derived polyols (*e.g.* sorbitol). Efficient electrocatalytic systems coupled with renewable electricity will allow biomass conversion to be economically viable with a minimal carbon footprint. Polyols derived from lignocellulosic biomass are the starting substrates which can be converted to various useful chemical feedstocks, such as rare important monosaccharides (*e.g.* L-sorbose) and C₂-C₃ polyols (*e.g.* propylene glycol and ethylene glycol). Fundamental material/substrate interactions in an electrochemical environment have been explored using platinum-based electrocatalysts (polycrystalline bulk Pt and Pt nanoparticles). In-depth study reveals that the electrochemical interaction between the polyol and platinum surface is diverse and only at certain potential ranges the functional groups of polyols can be electrochemically activated. In addition, protocols for analyzing the possible reaction products by their separation in the liquid phase and detection by

Electrocatalytic approaches towards biomass utilization have the potential to be less energy-intensive by being conducted at room temperature in benign environmental conditions. In addition, it can be coupled to renewable sources of electricity, in contrast to the thermochemical plants which consumes a large amount of fuel just for chemical processing. However, very limited knowledge exists for the electrochemistry of C₅-C₆ polyols, in contrast to the vast amount of literature for more typical electrochemical reactions (*i.e.* water splitting, oxygen reduction, and CO₂ reduction), with only a few works using polycrystalline and single crystal platinum surfaces to observe charge transfer at the solid/electrolyte interface.[5,6] Moreover, the early works have focused on using these polar molecules as fuels for fuel cell devices, which tends to emphasize the availability of extracted charge instead of the chemical transformation that could result from the process. Therefore, the details of the molecular interactions and their correlation to the state of the catalyst surface are lacking which are critical to further developments in this field. Here, we develop fundamental understandings of Pt-based catalysts for the electrochemistry of lignocellulose-derived polyols. Further efforts have been made to demonstrate C₅-C₆ polyols electro-transformation at appreciable conversions (~10%) and to understand product selectivity governed by catalyst surfaces.

Results

Polycrystalline platinum was used as an electrode material to probe the basic interactions of polyols in an electrochemical environment. The choice of platinum as a catalyst material is based on several factors: 1) the need for an element to activate protons to oxidize (*i.e.* dehydrogenate) and cleave (*i.e.* hydrogenolysis) bonds and 2) the element's capability to remain catalytically active under a wide potential window in an aqueous environment, whereas other metals would become inactivated because of oxidation/water adsorption phenomena. While there may be several noble metals that satisfy the criteria, elements like base metals which readily surface oxidize are inactive for electrochemical charge transfer to these polyols, as evidenced from the experiments that we performed on ruthenium-based electrodes. Ruthenium electrodes only displayed their pseudocapacitive characteristics due to their surface hydroxide/oxide formation at a wide range of potential. In contrast, Pt-based electrodes exhibit rich interfacial chemistry associated with polyols as further discussed below.

The main approach taken under this work was to probe the electrochemical interactions of C₄-C₆ polyols such as erythritol, xylitol, and sorbitol, on Pt surfaces. Though C₄ polyol erythritol is not a biomass-derived compound, we expected a common rule of interaction for the C₄-C₆ polyols that we aimed to elucidate, since their functional units (*i.e.* CHOH and CH₂OH) are identical. The general set of rules gained will advance catalyst design and reaction engineering for electrochemical approaches to biomass valorization.

Voltammetric studies of C₄-C₆ polyols on platinum surfaces

The electrochemical interactions of C₄-C₆ polyols dispersed in acidic aqueous media were studied using polycrystalline Pt. Various modes of oxidative charge transfer reactions are observed over a wide potential range where the platinum surface itself exhibits unique surface chemistry in the aqueous phase (*e.g.* hydrogen underpotential deposition, surface oxygen adsorption). Most importantly, the voltammetric responses of

C₄-C₆ polyols exhibit high similarity where there should be common fundamental interactions at an electrified platinum surface. During the reverse sweep past the reduction of platinum oxides, an oxidation current is observed that lies in the similar region of the first oxidation peak. However, these oxidative responses tend to be mostly transient surface-limited processes. Furthermore, by probing the electrochemically accessible surface area of the platinum electrode at selected potentials under steady-state conditions, it was found that the polyols at potentials partially overlapping the hydrogen underpotential deposition region, the catalyst surface is bound by poisoning species that prohibit charge transfer and chemical transformation. Therefore, faradaic reactions for electroconversion of the polyols can only occur beyond certain potentials where surface blocking effects are avoided.

In the potential region where there is a continuous charge transfer process to the functional groups of polyols, a trend in catalytic activity is observed where the rate of charge being passed is the highest at the two ends. Therefore, the activity trend clearly indicates the necessity of exposed surface Pt atoms for charge transfer from these polyols and also explains the negligible activity of base metals like Ru from its tendency to completely passivate the surface with oxygen species under the potential window.

Analysis of reaction products in the aqueous phase

With the identification of a suitable range of potentials where the actual catalysis occurs on Pt, it becomes imperative to develop methods to detect the reaction products. The separation of small polar molecules in the aqueous phase is a nontrivial task which is also the primary reason why liquid phase conversion of biomass-derived compounds need to achieve high selectivity; otherwise, the energy and costs associated with product separation becomes prohibitive. While methods like nuclear magnetic resonance spectroscopy can be used for analysis without the need for product separation, the task of molecular identification/quantification still remains quite difficult due to the identical functional units (*i.e.* CHOH and CH₂OH) present in the reagents and products that result in similar chemical shifts difficult to deconvolve.

In collaboration with the catalysis center at Lawrence Berkeley National Laboratory (LBNL), we developed methods for the separation of possible products using high-pressure liquid chromatography coupled with mass spectrometry (HPLC-MS). By a suitable combination of the mobile phase which is usually a mix of polar and non-polar solvents (*e.g.* water and acetonitrile mix) and the stationary column phase, the specific one chosen to operate in HILIC (Hydrophilic Interaction Liquid Chromatography) mode, we were able to separate various monosaccharides that may result from the oxidation of hydroxide groups in sorbitol.

Conclusions

Overall, this work explores the basic electrochemical interactions of the biomass-derived polyols with Pt-based electrocatalysts that is the necessary starting point for advancing the field of biomass valorization using electrochemical methods. Combined with the efforts in product analysis, the structure-activity correlations are beginning to develop for the platinum electrodes that will provide much insight in ways to improve activity/selectivity for targeted products using the approach. The efforts described here

ultimately aims to utilize renewable sources of carbon for the production of fuels/chemicals by means of using renewable electricity at high energy efficiency. The proposed technology has the potential to minimize/replace the usage of traditional fossil fuels that are the material source of bulk chemicals and fuels used for the processing of those chemicals, curbing their foreseen usage inevitably linked to greenhouse gas emissions.

Publications and Presentations

The contents of this report are in preparation for a journal publication that will be submitted in the coming few weeks/months.

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