

Controlling Selectivity in Electrocatalysis by Ionic Liquids: Oxidation of 2,3-Butanediol on Pt(hkl) Electrodes Modified by [C₂C₁Im][OTf]

O. Brummel¹, J. Yang¹, T. Yang^{1,2}, E. Franz¹, X. Deng¹, L. Fromm³, N. Taccardi⁴, Z. Liu², A. Görling³, P. Wasserscheid^{4,5}, J. Libuda¹

¹Interface Research and Catalysis, Friedrich-Alexander-Universität (FAU) Erlangen-Nürnberg, Germany

²School of Physical Science and Technology, Shanghai Tech University, China

³Lehrstuhl für Theoretische Chemie, FAU Erlangen-Nürnberg, Germany

⁴Lehrstuhl für Chemische Reaktionstechnik, FAU Erlangen-Nürnberg, Germany

⁵Helmholtz-Institut Erlangen-Nürnberg for Renewable Energy, Germany

olaf.brummel@fau.de

In heterogeneous catalysis, ionic liquids (ILs) are used as chemical modifiers to control selectivity. In our work, we aim to apply the same concept to electrocatalytic systems.

As a model reaction, we studied the electrooxidation of 2,3-butanediol on the low-index Pt(111), Pt(100) and Pt(110) surfaces in an acidic environment. We modified the surfaces with the IL 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([C₂C₁Im][OTf]) dissolved in the aqueous electrolyte. The reaction mechanisms on the different surfaces were studied by electrochemical infrared reflection absorption spectroscopy (EC-IRRAS) in combination with density functional theory (DFT).

The oxidation of 2,3-butanediol is highly structure dependent. On Pt(111), the oxidation occurs in two steps, forming acetoin as an intermediate and diacetyl as the final product. On Pt(110), only the first oxidation step takes place, forming acetoin as the final product. No adsorbed CO_{ads} is formed during the reaction on either surface. On Pt(100), the final product is acetoin. However, adsorbed CO_{ads} is formed, which acts as a catalyst poison. On Pt(111), already low concentrations of IL (0.001 M) shift the selectivity towards acetoin from 19% to 56%.[1] We propose that the potential dependent co-adsorption of the [OTf]⁻ anion suppresses the adsorption of OH species required for oxidation in the potential region of the second oxidation step. On the Pt(100) surface, IL suppresses the formation of poisoning CO_{ads} while the surface remains active for the target reaction.[2] Our results demonstrate the potential of ILs to control selectivity in electrocatalytic reactions.

[1] T. Yang, J. Yang, X. Deng, E. Franz, L. Fromm, N. Taccardi, Z. Liu, A. Görling, P. Wasserscheid, O. Brummel, J. Libuda, *Angewandte Chemie International Edition*, **61**, e202202957 (2022).

[2] J. Yang, E. Franz, L. Fromm, N. Taccardi, A. Görling, P. Wasserscheid, O. Brummel, J. Libuda, **in preparation**.