

# The Electrochemical Nature of Non-Faradaic Catalysis at Interfaces

by

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Electric fields are known to play an important role in many catalytic transformations throughout chemistry and biology. In principle, oriented electric fields could also be used to control thermochemical catalysis at solid-liquid interfaces. Yet, the role of electrical polarization in non-faradaic heterogeneous catalysis remains poorly understood, primarily for two reasons.

First, it is difficult to monitor electrical polarization at interfaces that are not connected to macroscopic wires. Such “distributed” interfaces, which include solid catalysts (e.g., supported metal nanoparticles) distributed throughout packed-bed or stirred-tank reactors, underpin virtually all of heterogeneous catalysis. Second, mechanistic studies into the role of electric fields in heterogeneous catalysis have been hampered by the lack of a conceptual framework that rigorously captures the impact of electric fields on interfacial reaction kinetics in terms of experimentally measurable quantities. Yet, an experimentally accessible rate theory that rigorously captures electrostatic effects would enable deriving new molecular insight into the nature of interfacial reaction mechanisms from measurements of polarization-dependent reaction rates.

Herein, we tackle both challenges in turn. In the first part of this thesis (Chapters 2 and 3), we develop and apply electrochemical methods to study non-faradaic catalysis at distributed (i.e., dispersed in solution), supported catalysts. In Chapter 2, we show how equilibrated spontaneous ion and/or electron transfer reactions from redox active species in solution may be harnessed to electrochemically polarize distributed catalytic interfaces in a predictive and controllable fashion during catalysis. We apply these methods to Pt/C-catalyzed ethylene hydrogenation in aqueous and aprotic organic solutions, and discover that electrochemical polarization plays a key role in governing the rate of this non-polar, non-faradaic reaction across vastly disparate reaction media. In addition, in Chapter 3, we apply infrared and ambient-pressure X-ray photoelectron spectroscopies to demonstrate that spontaneous polarization prevails even for metal nanoparticles supported on a nonconductive oxide host. Although such materials preclude wired connections to control the degree of interfacial polarization, our studies demonstrate that nonconductive catalysts may be electrochemically polarized in a predictable way simply by varying the solution composition (e.g., pH).

In the second part of this thesis (Chapters 4 and 5), we investigate the molecular and thermodynamic origins of polarization effects in non-faradaic catalysis. In Chapter 4, we formally synthesize longstanding concepts across physical electrochemistry and chemical kinetics in order to clarify the role of electrostatics in catalysis at interfaces. Specifically, we recapitulate well-established concepts regarding the thermodynamics of adsorption at solid-liquid interfaces, and

apply these results within the framework of classical, non-ideal transition state theory to analyze polarization-dependent surface reaction kinetics. This analysis shows how the electric field-dependence of interfacial reaction kinetics arises from partial charge transfer to form surface intermediates and transition states (i.e., the electroadsorption valencies). This partial charge transfer endows non-faradaic elementary reactions with electrochemical character, and augments the integer charge equivalents transferred in faradaic elementary reactions.

In Chapter 5, we build upon the studies performed in Chapter 2 with experiments investigating the polarization-dependent reaction kinetics of Pt/C-catalyzed ethylene and *trans*-2-butene hydrogenation. Our observations are all consistent with a model in which polarization of the Pt surface away from the local potential of zero free charge induces polarization-driven adsorption of polar solvent or charged ions near the interface that competes with the olefin for available catalyst sites. In this model, olefin adsorption on the surface displaces polar solvent and charged ions from the interface, which is compensated in an obligatory fashion by spontaneous partial charge transfer from the solution. These results show that even non-faradaic elementary reactions involving negligibly polar species are electrochemical in nature because the surface reaction physically induces motion of polar or charged species near the interface during catalyst turnover.

Taken together, the results of this thesis reveal that non-faradaic elementary surface reactions are in fact electrochemical in nature. It is our hope that the approaches and framework advanced here will provide a useful roadmap for further experimental investigations into the electrochemical nature of reactions at interfaces.

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