Electrochemical Activation of Catalysis: Promotion, Electrochemical Promotion, and Metal Support Interactions. By Costas Vayenas, Symeon Bebelis, Costas Pliangos, Susanne Brosda, and Demetrios Tsiplakides (University of Patras, Patras, Greece). Kluwer Academic/Plenum Publishers: New York. 2001. xxxii + 574 pp. $125.00. ISBN 0-306-46719-4.

This book covers electrochemical promotion or non-Faradaic electrochemical modification of catalytic activity (NEMCA). Vayenas coined the acronym in 1980 while studying ethylene epoxidation on a Ag catalyst film deposited on a ceramic oxide conductor. While co-feeding ethylene and oxygen over a Ag surface, Vayenas and co-workers were attempting to influence the rate and selectivity of ethylene epoxidation by electrochemically tuning the activity of oxygen via applied potential versus a counter electrode. The rate enhancement observed far exceeded the expectation. Since then, electrochemical promotion has been generalized to a wide variety of redox reactions and even to nonredox reactions such as olefin isomerization.

The book is divided into 12 chapters and 3 appendices. After a brief history and discussion of basic concepts in the first chapter, Chapter 2 presents a thorough “all you need to know about classical promoters in catalysis.” As NEMCA is a potentiostatic and/or galvanostatic takeoff of classical promotion, the third chapter discusses electrolytes and spillover. These first three chapters set the stage for the heart of the book, Chapters 4 and 5, the first of which covers the phenomenology of NEMCA, complete with case studies and experimental details. The apparent Faradaic efficiency, Λ, is introduced as $\Delta r/(I/2F)$, where Δr is the NEMCA-induced change in the rate of reaction of gaseous oxygen with CO over an anode surface in an oxide-conducting electrolyte system in a galvanostatic mode. This unconventional use of the term Faradaic efficiency evokes questions that, although fully addressed, could have been avoided by coining a different name for Λ. In any case, values of Λ exceeding 10^5 are spectacular and certainly warrant the attention that Vayenas has brought forth on the topic. Chapter 5 offers a fundamental discussion of electrochemical promotion employing an arsenal of techniques including electrochemical, surface science, and ab initio quantum mechanical calculations.

In Chapter 6, heuristic rules for classical and electrochemical promotion are backed up with rigorous models. I would recommend reading Chapter 7, which discusses the concept of the absolute potential, prior to Chapter 4. Chapters 8−10 cover electrochemical promotion classified by the electrolytes, O^{2-}, cationic conductors, and finally aqueous electrolytes and inorganic melts. Vayenas points out that in cases where classical promoters are sacrificial, electrochemical promotion can provide steady-state activity of promoters. Oxide conductors are a case in point. After an interesting discussion of the similarities between electrochemical promotion and metal−support interactions in Chapter 11, Chapter 12 discusses practical applications with some commercial applications.

Electrochemical promotion has been applied as a tool to optimize alkali promoter coverage on Ag epoxidation catalysts. Included among the reactor designs are induced bipolar designs that permit “wireless” NEMCA systems and systems based on operating PEM fuel cells. The appendices include information on (a) common questions and answers about NEMCA, (b) materials and instrumentation (including vendors), and (c) a thorough contact list of researchers in the field.

This book provides a thorough understanding of a field that has tremendous growth potential, particularly in the area of electrochemical promotion of nonredox systems as mentioned above. I highly recommend it.

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