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**C.G. Vayenas, S. Bebelis, C. Pliangos, S. Brosda, D. Tsiplakides:
Electrochemical activation of catalysis: promotion,
electrochemical promotion, and metal-support interaction**

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The electrochemical modification of catalytic activity is one of the most important developments in electrochemistry during the past 20 years. Today, more than 2000 papers have been published on this subject, many of them from the very active group of Costas G. Vayenas at the University of Patras in Greece and his co-workers.

The field of electrochemical activation of heterogeneous catalysis links two technologically important fields in physical chemistry: it combines electrochemistry and heterogeneous catalysis, both being mainly concerned with the chemistry at interfaces. Traditionally, the research in both fields is separated, and there are not many researchers with expertise in both of them. This is probably the main hindrance for an even broader acceptance of the results which are summarized in the present book. Still, many researchers in either electrochemistry or catalysis regard electrochemical activation as a mere curiosity or do not know it at all. The present book will definitely help to overcome these problems. It is written by some of the best experts in electrochemical activation and summarizes the current state of knowledge. More than 700 references make the book a valuable help in retrieving original work.

For those who are yet not familiar with electrochemical promotion in catalysis – what is it all about? The answer is quite simple from the experimental point of view: if a metal catalyst is deposited on the surface of an ion-conducting solid electrolyte, and if the catalyst film (electrode) is polarized electrochemically in a stan-

dard cell arrangement, then a pronounced increase of the catalytic activity has been observed in many cases. This phenomenon was shown for the first time more than 20 years ago by Vayenas and has meanwhile been investigated by a number of other research groups. From the theoretical point of view, the answer is less simple. It is now based on the idea that an outer electrochemical double layer is formed on the surface of the catalyst film, being composed of “backspillover” ions from the electrolyte support. This double layer of ions and their counter-charges in the metal modifies the work function of the catalyst very effectively. By varying the catalyst (electrode) potential, the double layer and the catalyst work function can be controlled electrochemically over a wide range.

However, let us consider the facts. The monograph includes 12 chapters and three appendices, of which the first three chapters give a brief but helpful introduction into the field in general (chapter 1; 14 pages), into promotion effects in heterogeneous catalysis (chapter 2; 76 pages) and into the basics of solid electrolytes and spillover at electrodes (chapter 3; 20 pages). The chapter on promotion in catalysis is definitely of great help to electrochemists, but the very short paragraph on solid electrolytes will not be of real use for specialists in catalysis who do not know much about solid state electrochemistry.

Chapter 4 introduces the essential aspects of electrochemical activation and presents some key definitions. The following three chapters represent the most important part of the book to those readers who are interested in the fundamental aspects. In chapter 5 the authors summarize the results from various experimental studies on the origin of electrochemical promotion, including XPS, UPS, STM, TPD and other techniques. It focuses on the proof of existence of an electrochemical double layer at the outer surface of the metal catalyst. Chapter 6 contains both empirical rules and theoretical models for

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a more detailed description and interpretation of electrochemical promotion, and thus for a better understanding of the relation between work function and surface kinetics. Chapter 7 contains a detailed analysis of the concept of an absolute electrode potential in relation to the idea of an effective double layer at metal/solid electrolyte interfaces and concludes the formal part of the book.

In the remaining five chapters the authors give a complete account of all electrochemical promotion studies so far. Definitely this part of the book will be of more interest to the scientist in industry than the first part. The majority of experiments have been performed with oxide supports (either ion-conducting like cubic-stabilized zirconia or mixed-conducting like TiO_2 , chapter 8), but alkali-conducting beta-alumina is also investigated intensively as an electrolyte material (chapter 9, cationic conductors). Interestingly, electrochemical promotion is also found in liquid electrolytes (chapter 10). Finally, chapters 11 and 12 point towards the future of research in the area of the book: In chapter 11 the authors discuss the close relation between electrochemically activated promotion with catalyst-support interaction and promotion effects in general. In chapter 12, one finds a critical analysis of possible industrial perspectives of electrochemical promotion. Any significant technical application will crucially depend on the ability to apply electric potentials to catalyst particles or films with sufficient surface area, i.e. the up-scaling problem has still to be solved.

The list of active groups in the field at the end of the book (appendix C) is unusual and will perhaps annoy those who are not in the list, but it helps in identifying major contributions. Appendix A (frequently asked questions about electrochemical promotion) supports the impression that the subject of the book is not yet accepted or at least understood everywhere and that it needs advertisement. Of course this is the case, since many electrochemists are not interested in catalysis and since many surface scientists regard electrochemistry with some scepticism.

Appendix B (materials and instrumentation) is meant as a help for the starter but also has a serious background. Not every laboratory has always been successful in reproducing, for example, the strong work function

changes on electrochemical polarization. The performance of a specific solid electrolyte/metal electrode depends obviously and crucially on the preparation of the sintered metal electrode (in particular in the case of platinum). The production of catalyst/electrolyte assemblies which show the 1:1 relation between electrode potential and work function is still an art and requires empirical experience. This is probably the most serious practical reason why electrochemical promotion has not been accepted immediately in past years.

Whether electrochemical promotion of heterogeneous catalysis will be of great technical relevance is still an open question. Owing to the work of Vayenas and his group there is growing interest in industry, but a number of practical problems have to be overcome, as pointed out in chapter 12. However, some promising developments have already been started.

The book is carefully written and contains only a small number of errors or inconsistencies, e.g. the symbol Φ_0 denotes the work function of an uncharged surface (according to the list of symbols) but throughout the book represents the work function of a clean uncovered surface.

The present book should be read by all scientists in the field of electrochemistry and heterogeneous catalysis, particular if they are working in applied science. The reader who is yet not familiar with the phenomenon and does not know Vayenas personally will probably be rather surprised by some unusual elements of the book. It took the main author 20 years to approach the current state of knowledge and to spread his ideas with enormous energy. Thus, one has to accept some self-appraisal as a by-product of great missionary spirit. The origin of electrochemical promotion is fundamental and the phenomenon itself leads to new concepts in solid state electrochemistry. The book is self-contained and its content can be understood without major difficulties by graduate students in chemistry. Students in chemical engineering might have some problems with the electrochemical aspects. Unfortunately, the length of the book (almost 600 pages!) precludes that it is read too easily. Nevertheless, the book should be on the shelves of any laboratory that is working either in solid state electrochemistry or heterogeneous catalysis.