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Book Review

Mechanisms in Homogeneous Catalysis: A Spectroscopic Approach Edited by Brian Heaton (University of Liverpool). Wiley-VCH GmbH & Co. KGaA: Weiheim. 2005. xvi + 388 pp. $180.00. ISBN 3-527-31025-8

Robert H. Morris

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Electrochemistry of Immobilized Particles and Droplets. By Fritz Scholz, Uwe Schröder (Universität Greifswald, Germany), and Rubin Gulaboski (Universidade do Porto, Portugal). Springer: Berlin, Heidelberg, New York. 2005. xiv + 290 pp. $129.00. ISBN 3-540-22005-4.

This is a highly specialized book that attempts to provide a unifying framework for the treatment of the electrochemistry of immobilized particles and immobilized droplets on electrode surfaces. Although the material covered is interesting, much of the attention was focused on electroanalysis, an area in which the main author, Scholz, is indisputably an expert. This reviewer particularly enjoyed the vastly qualitative information obtained from art specimens, although it is doubtful that electrochemical techniques could compete with more modern methods of analysis such as X-ray photoelectron spectroscopy or atomic absorption. Because of the overemphasis on electroanalysis, other topics that would normally fall squarely under the title of the book were not given the prominence they deserve. Notably limited was the discussion of immobilized particles in fuel cells (e.g., Pt nanoparticles supported on high area carbon) and lithium ion battery electrodes (e.g., micrometer-size carbon and transition metal oxide particles mixed with carbon and a binder), which in the opinion of this reviewer represent perhaps the most important examples of genuine immobilized particles in electrochemical technology today. As noted by the authors, the complexities associated with the presence of "reactive" three-boundary phase interfaces do pose serious challenges toward the quantitative interpretation of electrochemical data, including volume changes and moving boundaries. Further complexities are derived from the dependence of the particle shape and the area of contact with the current collector on the temporal behavior of the profiles of relevant species. In fact, solutions to such systems can only be obtained through numerical simulations, with only a few notable exceptions. The authors should have stressed that, in many instances, it is not necessary to perform experiments employing immobilized particles (or droplets) to extract meaningful data regarding such aspects as solid-state transport and electron and ion transfer rates at interfaces, should that be the desired aim of the studies. In fact, as only too briefly touched upon by the authors, experiments involving thin layers of electroactive materials (e.g., Prussian blue and its derivatives) can provide exceedingly valuable information regarding some of these issues without the complexities associated with three-phase boundaries. Also disappointing was the brief and largely incomplete summary review of in situ techniques applicable to immobilized particles, which ignored the great progress achieved using synchrotron radiation methods including EXAFS, NEXAFS, and diffraction.

In stark contrast to the direct technological relevance of immobilized solid particles, there are very few technical systems that involve electroactive immobilized droplets. One notable exception would be the ingenious use of rotating microdroplets by Gratzl at Case Western Reserve University (Cserey, A.; Gratzl, M. Rotating Sample System: An Equivalent of a Rotating Electrode for Microliter Samples. *Anal. Chem.* **1997**, *69*, 3687−3692). Nevertheless, despite its shortcomings, this book should provide those interested in the area with enough background information to become acquainted with major developments in the subject matter.

Daniel A. Scherson, *Case Western Reserve University*

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Mechanisms in Homogeneous Catalysis: A Spectroscopic Approach. Edited by Brian Heaton (University of Liverpool). Wiley-VCH GmbH & Co. KGaA: Weiheim. 2005. xvi + 388 pp. $180.00. ISBN 3-527-31025-8

A great challenge in determining the mechanism of a homogeneous catalytic reaction is to observe directly the intermediates within the catalytic cycle. Attempts using conventional spectroscopic methods often fail so that only the resting states of the catalyst are detected. These are the high concentration species. Catalysts of industrial importance are present at only the part-per-million level; thus very sensitive methods are needed to detect the active species in very low concentration. This book is devoted to the investigation of several catalytic systems of industrial interest by in situ IR and NMR methods, including rhodium-catalyzed hydroformylation of olefins, rhodium- and iridium-catalyzed carbonylation of methanol and methyl acetate, palladium-catalyzed alkene/CO copolymerization, metallocene-catalyzed olefin polymerization, and rhodium-catalyzed hydrogenation of chiral enamides. The authors, all recognized authorities in their respective areas, describe the ingenious methods that are employed to study these reactions, most under high pressures of gases, and the successful identification of active species. The text provides a valuable collection of actual NMR and IR spectra and important references to the literature up to early 2004.

There are two introductory chapters by Pregosin and coworkers and Laurenczy and Helm, respectively, on the implementation and application of NMR, especially high-pressure techniques, to study the mechanisms of homogeneous catalysts. The first chapter presents lots of clearly labeled 1D, 2D, and VT spectra of metal-containing species probed via ^{1}H, ^{11}B,^{13}C, ^{19}F, ^{31}P, ^{59}Co, and ^{103}Rh nuclei. This chapter provides brief coverage of a wide range of catalytic processes, including asymmetric hydrogenation, 1,4 addition of boronic acid to an unsaturated ketone, metallocene polymerization, the Heck and Stille reactions, the methoxycarbonylation of ethane, the cycloisomerization of diallyl malonate, the amination of aryl halides and hydroformylation, and a brief description of the useful pulse gradient spin−echo method for studying the sizes of molecules and ion pair aggregates in solution. The second chapter concisely covers the design of high-pressure NMR probes.

Unsigned book reviews are by the Book Review Editor.

Two chapters introduce the implementation and application of high pressure IR. Haynes reviews various cell designs and their applications in methanol carbonylation and hydroformylation and reactions relevant to these processes. Garland writes an outstanding chapter on how to extract the maximum amount of information mathematically and algorithmically from a sequence of spectra that track the progress of a reaction. The powerful method of band-target entropy minimization is introduced and demonstrated to pick out the tiny signals of an important rhodium acyl intermediate from numerous more intense peaks of other carbonyls under conditions of hydroformylation.

The three detailed chapters on the carbonylation of methanol and methyl acetate by Morris, the hydroformylation of olefins by van Leeuwen and co-workers, and alkene/CO copolymerization by Bianchini and Meli are all of high standard. These groups all utilize high-pressure NMR and IR spectra for their respective contributions. The editor could have required more organization of the various discussions of rhodium-catalyzed hydroformylation that appear in several chapters so that there was a more unified description of the possible mechanisms.

The last two chapters cover aspects of two very large topics: the polymerization of olefins catalyzed by metallocene catalysts and the asymmetric hydrogenation of enamides catalyzed by rhodium diphosphine complexes. Bochmann does an admirable job at summarizing the important information that NMR spectra can provide in understanding the types of group 3 and 4 metal structures present during polymerization as well as ion pairing and polymer microstructure. Giernoth writes a short, interesting detective story on the use of *para*-hydrogen-induced polarization to solve the crime of the missing rhodium dihydride in hydrogenations. A suspect is caught in the end, although the ChemDraw diagram of the suspect has flaws that make it resemble an M. C. Escher drawing.

This book will educate those interested in homogeneous catalysis. It has more detail than needed for a specialized course at the graduate level but is certainly a useful reference for those working in the field.

Robert H. Morris, *University of Toronto*

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Advanced Biomaterials for Medical Applications. Edited by David W. Thomas (Cardiff University, UK). Kluwer Academic Publishers: Dordrecht. 2004. xii + 200 pp. $88.00. ISBN 1-4020-2906-3.

This book was developed from a NATO Advanced Research Workshop entitled “Macromolecular Approaches to Advanced Biomaterials Engineering Systems” held in Sofia, Bulgaria in November 2003. It comprises 14 chapters on a range of topics from the design of polymers for medical applications to nonviral gene delivery systems to the development of porous scaffolds for wound healing. There is no index.

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Handbook of Hydroxyacetophenones: Preparation and Physical Properties. Enlarged Second Edition, Volumes 1–2. By Robert Martin (Institut Curie, Paris, France). Springer: Dordrecht. 2005. xiv + 554 pp (Volume 1) and xvi + 556 pp (Volume 2). $650.00 (Set). ISBN 1-4020-2290-5 (Set).

This edition updates the first, published in 1997, and covers approximately 3000 hydroxyacetophenones, including all the ketones appearing in the original edition as well as an additional 1500 others. Each entry provides the different protocols of synthesis for the compound at hand, its main physicochemical properties, and references of spectroscopic data. Volume 1 covers “Monoketones Unsubstituted on the Acetyl Groups”, whereas Volume 2 covers “Monoketones Substituted on the Acetyl Groups”. Ketones may be looked up using the “Molecular Formula Index”, the table of “Chemical Abstracts Registry Numbers”, or the “Usual Names Index”. The book also includes an extensive list of references as well as a list of common abbreviations.

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