

Single-Molecule Magnets and Related Phenomena. Structure and Bonding, 122. Edited by R. Winpenny (The University of Manchester, UK). Series Edited by D. M. P. Mingos. Springer: Berlin, Heidelberg, New York. 2006. xiv + 262 pp. \$239.00. ISBN 3-540-33239-1.

The *Structure and Bonding* series has recently focused on molecular and supramolecular species of interest for potential applications in materials. Thus it is no surprise that attention would eventually be drawn to the subject of single-molecule magnets (SMMs), discrete molecular species capable of retaining magnetization in the absence of a polarizing field. This book comprises six essays from leading European researchers in the field. The first three are exhaustive reviews of synthetic (Chapters 1 and 3) and spectroscopic (Chapter 2) investigations of SMMs. The fourth entry addresses efforts to prepare surfaces and solids decorated with SMMs, whereas the fifth presents the “related phenomena” of single-chain magnets, both their theoretical underpinnings and a description of the known examples. Finally, the book concludes with a new general theoretical treatment of superexchange.

In one sense, the book succeeds at presenting the diversity of approaches required and used to understand and exploit SMMs, be they chemical, physical, materials oriented, or theoretical. On the other hand, the book is dominated by the Mn₁₂ cluster, the first species characterized as a single-molecule magnet. This is hardly surprising, since the cluster also displays the highest reported reorientation barrier in an isolable species. The chapter on spectroscopy focuses only on Mn₁₂ and Fe₈, while the essay concerning incorporation of SMMs into new materials only uses examples in which Mn₁₂ is involved. Although it is important to compile these results, the field might be better served by focusing on the perplexing problem of synthesizing new molecules with substantially larger reorientation barriers.

The compilation of articles makes for a nonintegrated and somewhat incoherent presentation. For instance, the introductory remarks in several of the chapters gave the same information. Also, the uniformity of the structures/figures presented in Chapter 1 was not continued in subsequent entries, which is unfortunate since the structure of these species is so important to understanding their properties. Figure uniformity could have been very helpful for the reader to make new connections between structures. Finally, theoretical predictions and interpretations were scattered throughout the text; some coherence or at least productive cross-talk between authors would have been most helpful to the reader.

The references are exhaustive and adequately cover the field to the middle of 2005. For that reason alone it would be a good idea to have this book on hand in the laboratory. With the burgeoning interest in the field, however, it is clear that an update will be needed soon. Overall, this book is a good collection of the work that has been done in the field of SMMs. Some of the individual entries, especially the first review of the synthesis of SMMs and the essay concerning single-chain

magnets, will be especially useful to those who are relatively new to the field. Unfortunately, the whole is not greater than the sum of its parts.

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JA069806A

10.1021/ja069806a

Surface and Interfacial Organometallic Chemistry and Catalysis. Topics in Organometallic Chemistry, 16. Edited by Christophe Copéret (Laboratoire de Chimie Organometallique de Surface, Villeurbanne, France) and Bruno Chaudret (Laboratoire de Chimie de Coordination du CNRS, Toulouse, France). Springer: Berlin, Heidelberg, New York. 2005. x + 291 pp. \$259.00. ISBN 3-540-26496-5.

Surface and interfacial organometallic chemistry involves the study of catalytic events that take place between a gas or liquid reactant phase and an active surface. In this context, it is often practical and scientifically useful to draw clear analogies between relatively small, well-characterized homogeneous systems and the processes important in heterogeneous interactions, reactions, and catalysis. The complementary relationship between homogeneous systems and heterogeneous processes has been widely developed, and researchers in this field try to use well-defined model systems and detailed spectroscopic measurements to infer valuable mechanistic information about complex interfacial processes on high surface-area materials. The stated goal of this book, then, is “to show that molecular chemistry is also a tool for studying much larger systems, such as those involved in heterogeneous catalysis.”

This edition of *Topics in Organometallic Chemistry* is organized into eight chapters, including one from each of the co-editors of this volume and six solicited contributions. The style of the chapters varies from account-type reports focusing on the authors’ own work to more widely focused literature reviews. The individual chapters do well to span the discipline of surface-bound organometallic chemistry and synthesis of materials, given the stated goal of the editors. A cumulative author index of Volumes 1–16 in the series and a brief but useful subject index complete the book.

The opening two chapters are both concerned with industrially relevant heterogeneous catalytic processes. In the first, “Anatomy of Catalytic Centers in Phillips Ethylene Polymerization Catalyst”, Zecchina and co-workers review the recent progress made in elucidating the structure of the catalytic site for ethylene polymerization. This includes a well-organized discussion of the characterization of the catalyst in the resting state, proposed mechanisms, and homogeneous model systems. The thorough bibliography and discussion of unresolved topics in this research area will be useful to experienced researchers and newcomers alike. Chapter 2, “Single Site Catalyst for Partial Oxidation Reaction: TS-1 Case Study”, by Bordiga et al. outlines the

industrial applications of this titanium/zeolitic material for mild oxidation reactions using hydrogen peroxide as a cocatalyst. The chapter is largely focused on detailed characterization of the catalytic system in the absence and presence of ligands and aqueous hydrogen peroxide. Several physical and spectroscopic techniques are discussed in detail, including: XRD, UV-vis, IR, Raman, XANES, and EXAFS. This contribution highlights the recent use of physical techniques to gain detailed information regarding the catalyst in situations similar to operating conditions. The case-study format offers a convenient summary of some of the powerful tools available for the study of complex heterogeneous systems in the context of an industrially important process with many open mechanistic questions.

In the next four chapters, the topics of synthetic techniques, characterization, and catalytic activity of metal oxide materials and metal clusters are reviewed. Chapter 3, entitled "Tailored Oxide Materials via Thermolytic Molecular Precursor (TMP) Methods", is a contribution from Tilley and co-workers. They describe the development and utilization of the TMP method to create a wide variety of oxide materials from molecular precursors. This review and the references contained within provide an excellent overview of Tilley's pioneering work in this field along with the efforts of many others. For readers interested in this field, the chapter represents an expertly crafted and comprehensive description of the TMP method of materials synthesis. The theme of utilizing carefully designed model systems to study complex chemical processes is continued in the fourth chapter entitled "Spectroscopic Characterization of Organometallic Centers on Insulator Single Crystal Surfaces: From Metal Carbonyls to Ziegler-Natta Catalysts", where Risse and Freund review spectroscopic characterization of two such model systems. They discuss the use of techniques such as IR and EPR spectroscopy of well-defined models to glean detailed information about the mechanistic aspects of reactions on solid supports. In Chapter 5, "Analogy between Surface and Molecular Organometallic Chemistry", Copéret and co-workers begin with a concise introduction to the topic and go on to describe work in two areas of surface organometallic chemistry: using oxide supports and metal particles. This chapter is written in a manner that provides an approachable introduction to the current research at the boundary of the disciplines of homogeneous and heterogeneous organometallic chemistry and could quickly bring a reader up to speed on the important issues and recent accomplishments in this field. Chapter 6, "Oxide- and Zeolite-supported 'Molecular' Metal Clusters: Synthesis, Structure, Bonding, and Catalytic Properties" by Gates is a summary of supported metal clusters, and the parallels between their catalytic activity and that of bulk metal substrates are presented.

The final two chapters of this volume are both focused on the synthesis, characterization, and catalytic activity of metal nanoparticles and the structures formed thereof. In Chapter 7, "Synthesis and Surface Reactivity of Organometallic Nanoparticles", Chaudret provides a well-organized synopsis of recent work. Chapter 8 by Roucoux is entitled "Stabilized Noble Metal Nanoparticles: An Unavoidable Family of Catalysts for Arene Derivative Hydrogenation". These two chapters taken together represent the most contemporary topics addressed in this volume and provide an excellent conclusion with a tantalizing amount of insight into a promising new direction of surface organometallic chemistry. While these chapters are both account-style

contributions, a significant amount of commentary is provided to establish background and motivation.

Overall, the book fully accomplishes the editors' goal and as a whole makes a cogent argument in support of the importance of detailed model studies for understanding complex organometallic processes at heterogeneous interfaces. The book could have used a comprehensive introductory chapter or preface that more clearly emphasized the motivation behind the solicited contributions and presented a cohesive overview. Previous volumes of this series have been clearly aided by such a section (i.e., Volumes 2-4, 7, and 9). Chapter 5 could easily have been adapted for this purpose because it reiterates the thesis statement of the volume. I would suggest that the novice or educational reader begin here.

Scientists, upper-level graduate students, and post docs working in this field would greatly benefit by reading some or all of the excellent contributions that have been assembled in this volume. Although reasonably expensive for individual purchase, this 291-page book is highly recommended for purchase by academic and industrial libraries, especially as a component of the *Topics in Organometallic Chemistry* series. Additionally, the text is available on-line to subscribers.

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JA0697065

10.1021/ja0697065

Heterogeneous Enantioselective Hydrogenation: Theory and Practice. By Evgenii Klabunovskii (Russian Academy of Sciences, Moscow, Russia), Gerard V. Smith (Southern Illinois University, Carbondale, USA), and Ágnes Zsigmond (University of Szeged, Szeged, Hungary). From the Series: *Catalysis by Metal Complexes*, Volume 31. Series Edited by Brian James and Piet W. N. M. van Leeuwen. Springer: Dordrecht. 2006. xiv + 302 pp. \$175. ISBN 1-4020-4294-9.

This is a timely monograph because interest in heterogeneous enantioselective catalysis, which has been revived in the past two decades, is currently high. The intention of the authors was to review the development of the field and to give practical input for the utilization of the technology. The first three chapters are of a historical nature and cover in great detail early attempts at enantioselective catalysis using natural chiral materials, such as quartz, silk fibroins, or polysaccharides. This is the strongest section of the book, giving a very good impression of the problems associated with heterogeneous materials and the difficulties encountered with small effects, inadequate analytical methods, and irreproducible results due to the inability to characterize heterogeneous catalysts on a molecular basis. In the next chapter on nickel-based catalysts, the authors describe the development of the tartrate-modified Ni catalysts for the highly selective hydrogenation of β -functionalized ketones, one of the few synthetically useful systems for heterogeneous enantioselective catalysis. The review covers work carried out in the 1970s and 1980s quite comprehensively, although the most recent results in surface science and some of the newer and more detailed mechanistic ideas are not included. Chapter 5 reviews cinchona-modified Pt and Pd catalysts, which give very high enantioselectivities for α -functionalized ketones and

moderate-to-good results for selected activated C=C bonds, respectively. Again, with the exception of the latest work in surface science and the latest mechanistic discussions and theoretical calculations, most of the important contributions up to about 2004 have been included. These two chapters illustrate how much time and effort are involved to develop and understand enantioselective heterogeneous catalysts to the point where they truly become a useful synthetic technology. The last two chapters on electrochemical enantioselective reductions and on practical asymmetric catalysis—covering mostly homogeneous catalysts—do not have an obvious relation to the topic of this book or contribute much to our understanding of the topics at hand.

Overall, I have rather mixed impressions of this new monograph. On the positive side are the first three chapters and part of the fourth, which report on research where one of the senior authors has made many valuable contributions. The reader can find impressive insights and many helpful comments here, especially on the early ideas and mechanistic considerations. On the other hand, there are several negative aspects. As already pointed out, some of the most important recent results are not

included. The book is poorly edited, which makes it sometimes very awkward to read; it is often difficult to follow the thread of the discussion, even for somebody familiar with most of the literature. The book often oscillates between a systematic and a historical description, and there are frequent and sometimes rather long excursions away from the topic of a particular section. Finally, practical aspects such as the quality of reported procedures or the choice of catalysts are seldom commented on or assessed, which renders the book not very useful for readers looking for practical input.

In conclusion, one of the main goals of the book, the review of the development of enantioselective heterogeneous catalysis, has been reached, albeit in a sometimes rather unsystematic and not very concise way. The second claim, to give practical input for the application of such catalysts, has not really been fulfilled. I recommend the book to readers interested in the historical development of enantioselective catalysis.

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JA069831G

10.1021/ja069831g