

Molecular Spectroscopy of Oxide Catalyst Surfaces.

By Anatoli Davydov (University of Alberta and Syntroleum Corporation, Tulsa, OK). John Wiley & Sons, Inc.: Hoboken, NJ. 2003. xxii + 668 pp. \$265.00. ISBN 0-417-98731-X.

The surface chemistry of oxide surfaces has been receiving greater fundamental interest in recent years because of the expanding technological applications of oxide materials (e.g., photonics, electronics, adsorption and desorption phenomena, heterogeneous catalysis, etc.). In addition, the development of enhanced molecular spectroscopic instrumentation (IR, Raman, and ultraviolet–visible) is allowing the acquisition of more detailed molecular level information. The objective of this book is to provide a critical review of the literature on the interpretation of the molecular spectra of surface complexes on oxide catalytic surfaces, beginning with the groundbreaking work of half a century ago by Eischens and Pliskin [*Adv. Catal.* **1958**, 28, 1–56] and focusing primarily on the past three decades. As stated by the author, the impracticality of reviewing every single publication in the literature means that only key papers can be cited and discussed. Nevertheless, the book has almost 2000 highly relevant references, providing detailed titles from numerous international journals—Russian journals especially are cited extensively and are typically not as accessible to westerners. The intended audience of this book is specialists working in various areas of surface chemistry of oxide surfaces (surface science, surface materials science, surface physical chemistry, adsorption–desorption phenomena, and heterogeneous catalysis).

The author painstakingly and systematically reviews the literature of the coordination and oxidation states of various surface cations and oxygen anions (M^{n+} , $M^{n+}O^{2-}$, $M = O$, $M-O$, $M-OH$, defects, etc.) present on oxide surfaces as well as their chemical properties and surface Lewis and Bronsted acidic–basic sites. IR molecular spectroscopic measurements of simple probe molecules (NH_3 , pyridine, CO , CO_2 , H_2 , H_2O , NO , NO_2 , H_2S , and SO_2) are particularly emphasized. These portions of the book are extremely well organized and highly informative. The almost exclusive use of IR spectra from the author's own laboratory minimizes the variability in sample handling typically encountered in the literature. The important chemisorption of inorganic and organometallic complexes as well as simple acids and heteropolyoxo anion compounds on oxide supports (Al_2O_3 , SiO_2 , TiO_2 , etc.) and their surface modifying effects also receive much attention. Such fundamental information is critical to the synthesis of heterogeneous catalytic materials, conventional and advanced, as well as heterogenized homogeneous catalysts and anchored enzymes.

The largest portion of this book is devoted to the formation of surface complexes of organic molecules on oxide surfaces, which is of great interest to all researchers investigating oxide surfaces in reactive hydrocarbon environments (from ambient to high temperature heterogeneous catalytic reactions). The final portion of this book applies the above fundamental knowledge

and findings to the determination of the intermediates and mechanisms of surface reactions and the kinetics of various catalytic reactions that are known to occur on oxide surfaces. Unlike the outstanding previous sections on fundamentals of oxide surfaces, this applied section of the complex surface chemistry of oxide catalytic surfaces only focuses on specific molecule–oxide catalytic reaction systems and does not develop general molecular structure–reactivity/selectivity relationships that are critical for the design of advanced catalytic oxide materials.

This book is supposed to be on molecular spectroscopy; however, it almost exclusively focuses on IR, and very limited UV–vis and Raman data on the same systems are presented. This lack of corresponding complementary molecular spectroscopic measurements compromises the maximum impact of this book on describing the surface chemistry of oxide surfaces. UV–vis and Raman, unlike IR, are uniquely suited to provide the critical molecular structures and oxidation states of the active surface oxide sites. This is reflected in the final applied section where the establishment of molecular structure–reactivity/selectivity relationships is not fully developed.

The references unfortunately only cover the literature through about the mid-1990s and thus do not reflect the significant progress achieved in recent years in the application of molecular spectroscopy to elucidate the surface chemistry of oxide surfaces. Despite these limitations, this comprehensive book is truly indispensable as a reference text for researchers engaged in the surface chemistry of oxide surfaces.

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Macromolecules Containing Metal and Metal-Like Elements, Volume 1: A Half-Century of Metal- and Metalloid-Containing Polymers.

By Alaa S. Abd-El-Aziz (University of Winnipeg), Charles E. Carraher, Jr. (Florida Atlantic University), Charles U. Pittman, Jr. (Mississippi State University), John E. Sheats (Rider University), and Martel Zeldin (Hobart and William Smith Colleges). John Wiley & Sons, Inc.: Hoboken. 2003. x + 268 pp. \$125.00. ISBN 0-471-45832-5.

This book, the first volume of a new series on “Macromolecules Containing Metal and Metal-Like Elements”, provides a general overview of this emerging field of polymers. The scope is defined very broadly to include metals and metalloids, as well as materials that are metal-like with regard to at least one important physical characteristic. Although the first reports of such polymers date back to the 19th century, the development and commercialization of silicones in the 1950s represents the first major advance in this area. Over the past few decades, a renewed interest and strong research effort in the area of inorganic polymers has, for example, resulted in the discovery

of a room temperature synthesis for polyphosphazenes, the development of new routes to ferrocene polymers of high molecular weight, and the synthesis of soluble metal coordination polymers. Considering also the strong impact of metal- and metalloid-containing polymers on the field of materials chemistry with numerous applications, for instance, in device fabrication, in the medical sciences, and more recently in nanoscience, a comprehensive work that reviews these developments certainly is warranted.

The authors offer a historical perspective on the development of metal- and metalloid-containing polymers in the first chapter of the current volume. A concise classification according to structure and bonding and major synthetic methodologies is also given. Although historic developments are emphasized, more recent discoveries such as the ring-opening polymerization of metallocene-substituted phosphazenes and strained metallocenophanes, as well as the incorporation and attachment of metals to conjugated organic polymers, are discussed in detail. The following two chapters are devoted to metallocene-based polymers and to organometallic polymers with transition metal complexes that are π -coordinated to four-, five-, and six-membered rings within the polymer chain. Another chapter deals with transition metals within the backbone of polymers as encountered in acetylide and metallacyclopentadienyl polymers, for example. Metal coordination polymers are treated in Chapter 5 and are arranged according to the type of ligand employed, (i) Schiff base, (ii) porphyrin, (iii) phthalocyanine, and (iv) pyridine polymers. A final chapter on silicon-, germanium-, and tin-containing polymers completes the book.

The focus of the book is primarily on the synthesis and structures of the various types of metal- and metalloid-containing polymers. However, useful information on their properties and applications is also provided. While not all classes of polymers could receive equally detailed treatment because of the broad definition established by the authors, the book certainly lives up to its general objective of providing an extensive overview of their discovery and development. One of the nice features is the large number of references, many as recent as 2002, to the primary literature and to reviews on inorganic polymers that are included at the end of each chapter. In

addition, the "metals index" and the more general subject index are useful for finding information on specific polymers. Given the inclusion of many recent developments, the book will be of interest to polymer chemists and useful as a general reference. Practitioners in the field may also look forward to future volumes in this series covering specific topics within the scope of metal- and metalloid-containing polymers.

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Annual Review of Physical Chemistry, Vol. 54.

Edited by Stephen R. Leone, Paul Alivisatos (University of California, Berkeley), and Ann E. McDermott (Columbia University). Annual Reviews: Palo Alto, CA. 2003. xiv + 608 pp. \$75 Print Version for Individuals, \$165 Print Version for Institutions. ISBN 0-8243-1054-3.

In the spirit of this classic series, the 54th volume of the *Annual Review of Physical Chemistry* covers a remarkable range of current developments in molecular spectroscopy. The volume contains 18 individual chapters, which are not directly related, that include detailed studies of gas-phase chemical dynamics and reaction mechanisms as well as studies of nanocrystals, films, and biomaterials. The unifying theme is the review of rigorous and recent quantitative studies of chemical phenomena by eminent scientists. The volume could have benefited from reviews on recent advances in calculations of electronic structure as well as on theoretical studies based on mixed quantum-classical, semiclassical, and "on-the-fly" *ab initio* simulations of molecular dynamics. However, the volume continues the tradition of an excellent series of reviews with a significant number of recent references to important advances in chemical physics.

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This study demonstrates that molecular engineering of supported metal oxide catalysts is currently possible from molecular level information about the number of active surface sites and reactivity per site. Such fundamental information is currently obtainable from molecular spectroscopies such as Raman spectroscopy. The critical parameters that determine the view of Davydov A. A. (Anatoli Aleksandrovich) Molecular spectroscopy of oxide catalyst surfaces / Anatoli Davydov ; edited by N.T. Sheppard. p. cm. Includes bibliographical references and index. ISBN 0-471-98731-X (cloth : alk.paper) 1. Metallic oxides Surfaces Analysis. This present book is concerned with the even greater importance of molecular spectroscopic methods in developing similar understandings of the coordination chemistry of oxide surfaces where application of diffraction methods is much more difficult. The adsorption of molecules on the surfaces gives rise to ligands attached to free sites on the surface cations. Davydov A (2003) Molecular spectroscopy of oxide catalyst surfaces. Wiley, England CrossRef Google Scholar. 27. 1. Operando Molecular Spectroscopy and Catalysis Laboratory, Department of Chemical and Biomolecular Engineering Lehigh University Bethlehem USA. 2. Faculty of Chemical Engineering and Technology Cracow University of Technology Kraków Poland. About this article.