

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.

Israel E. Wachs, *Lehigh University*

JA033599M

10.1021/ja033599m

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.

Frieder Jäkle, *Rutgers University*

JA033623W

10.1021/ja033623w

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.

Victor S. Batista, *Yale University*

JA0336170

10.1021/ja0336170

@inproceedings{Davydov2003MolecularSO, title={Molecular Spectroscopy of Oxide Catalyst Surfaces}, author={A. A. Davydov and Norman Sheppard}, year={2003} }. A. A. Davydov, Norman Sheppard. Published 2003.Â 1. Theoretical fundamentals and experimental considerations of spectroscopic methods used in surface chemistry. Electronic spectroscopy (ES). Vibrational spectroscopy. Electron energy loss spectroscopy (EELS).

Molecular Spectroscopy of Oxide Catalyst Surfaces (A. Davydov). 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26
27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63. 64 65 66 67 68 69
70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106 107 108
109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126.

Interactions Molecular Spectroscopy and Molecular Structure: Commemorative Issue in Honor of Professor Austin J. Barnes on Occasion of his 75th Birthday Molecular Tools for Nucleic Acid Manipulation for Biological Intervention Molecule Adsorption and Desorption from and to Aqueous Media Molecules for Biotechnologies Multi-Functional Materials from Lignin and Nanocelluloses Multicomponent Reaction N-Heterocycles: Synthesis, Functionalization, Electrochemical, Spectroscopic Characterization and Mechanistic Investigation Named. These materials create novel synergies on the catalyst surface, which are not comprehensively understood due to complexity of the ternary system [22 , 23 , 24]. Possible mechanisms of numerous catalytic reactions, including the transformation of organic molecules over acidic catalysts via the carboionic mechanism, are discussed using the spectroscopic identifications of reaction intermediates. A comprehensive analysis of the literature on the interpretation of the spectra of surface compounds on oxides is presented. Buy Both and Save 25%! This item: Molecular Spectroscopy of Oxide Catalyst Surfaces. Handbook of Applied Surface and Colloid Chemistry, 2 Volume Set (Hardcover \$1,710.75). Cannot be combined with any other offers. Original Price:\$2,272.25. 2 The nature of oxide surface centers 2.1 Systems investigated 2.1.1 Solid structures 2.1.2 Surfaces 2.1.3 Active sites 2.2 Spectra of oxide surfaces 2.2.1 Vibrations of metal-oxygen bonds on oxide surfaces 2.2.2 Molecular forms of adsorbed oxygen 2.2.3 Surface hydroxyl groups 2.3 Determination of the nature of. The principles of the study of surface compounds and adsorbed molecules by molecular spectroscopy have been described in several books [18-35a]. Transition metal oxides are compounds composed of oxygen atoms bound to transition metals. They are commonly utilized for their catalytic activity and semiconductive properties. Transition metal oxides are also frequently used as pigments in paints and plastics, most notably titanium dioxide. Transition metal oxides have a wide variety of surface structures which affect the surface energy of these compounds and influence their chemical properties. The relative acidity and basicity of the atoms present

Electron spectroscopy of surfaces. Elemental and Chemical Analysis with X-ray Photoelectron Spectroscopy. Versuch Nr. n and m are integers and ϵ_p and ϵ_s are the energy of a bulk and a surface plasmon, respectively (Fig. 7). 2.3 Decay of a core hole. Thermal broadening by coupling with intra-molecular vibrations and phonons may be non-negligible in some cases. In addition, many-body effects, such as the excitation of electron-hole pairs close to the Fermi level in metals or shake-up satellites that cannot be resolved due to limited instrumental resolution, can cause additional asymmetric broadening with a tail on the low kinetic energy side of the photoemission peak. Different spectroscopy techniques combine to afford such objective. The composition of the surface Accepted 12 December 2011 species has been studied by Raman and UV-Vis spectroscopies, whereas it has been performed several Available online 9 February 2012 pyridine adsorption experiments to quantify the number of acid sites on the surface of catalysts. 1A) and Surface properties of the materials prepared were studied by with (Fig. In the lutetium is able to change the structure of the surface of the catalysts case of catalysts containing tellurium, the maximum number of as well as the adsorption properties, and, subsequently, the catalytic sites is detected for intermediate coverage (8 atoms/nm²), catalytic properties. Possible mechanisms of numerous catalytic reactions, including the transformation of organic molecules over acidic catalysts via the carboionic mechanism, are discussed using the spectroscopic identifications of reaction intermediates. A comprehensive analysis of the literature on the interpretation of the spectra of surface compounds on oxides is presented. Buy Both and Save 25%! This item: Molecular Spectroscopy of Oxide Catalyst Surfaces. Handbook of Applied Surface and Colloid Chemistry, 2 Volume Set (Hardcover \$1,710.75). Cannot be combined with any other offers. Original Price:\$2,272.25. Molecular spectroscopy relates to the interactions that occur between molecules and electromagnetic radiation. Electromagnetic radiation is a form of radiation in which the electric and magnetic fields simultaneously vary. One well known example of electromagnetic radiation is visible light. The initiation of the detection process involves radiation striking the surface of a photoactive surface and dislodging electrons. Electrons dislodged from this surface are accelerated toward the first dynode. In this case, the iron from the hemoglobin serves as the catalyst. Another important example of a chemiluminescent reaction involves the reaction of nitric oxide (NO) with ozone (O₃) to produce excited state nitrogen dioxide (NO₂^{*}) and oxygen gas.

Possible mechanisms of numerous catalytic reactions, including the transformation of organic molecules over acidic catalysts via the carboionic mechanism, are discussed using the spectroscopic identifications of reaction intermediates. A comprehensive analysis of the literature on the interpretation of the spectra of surface compounds on oxides is presented. Buy Both and Save 25%! This item: Molecular Spectroscopy of Oxide Catalyst Surfaces. Handbook of Applied Surface and Colloid Chemistry, 2 Volume Set (Hardcover \$1,710.75). Cannot be combined with any other offers. Original Price:\$2,272.25. The surface molecular structures of supported transition metal oxide layers on oxide supports are described in detail, focusing in particular on those vibrational modes that can be used for precise molecular structural determination. The structural response of such surface oxide species to environmental conditions (ambient, dehydrated, reduced, reaction conditions) is reviewed. Laser-Raman spectroscopy of the alumina-supported rhenium oxide metathesis catalyst showed that rhenium is present as a single species, consisting of tetrahedrally coordinated $\text{ReO}(-1)$ ions which are dynamically distorted by the carrier or surface hydroxyl ions. In situ IR, Raman, and UV-Vis DRS spectroscopy of supported vanadium oxide catalysts during methanol oxidation. Loyd J. Burcham The application of in situ Raman, IR, and UV-Vis DRS spectroscopies during steady-state methanol oxidation has demonstrated that the molecular structures of surface vanadium oxide species supported on metal oxides are very sensitive to the coordination and H-bonding effects of adsorbed methoxy surface species. Therefore, V^{5+} spectral signals are generally not representative of the percent vanadia reduction during the methanol oxidation redox cycle, although estimates made from the high temperature, low methoxy surface coverage IR spectra suggest that the catalyst surfaces remain mostly oxidized during steady-state methanol oxidation Wiley, 2003. - 691 p. - The book commences with an account of the basic theoretical principles and experimental techniques of the various molecular spectroscopic methods as applied to surfaces, namely the electronic (UV-Vis), vibrational (transmission IR, diffuse reflection, reflection-absorption IR and Raman), electron energy loss, inelastic electron tunneling, and inelastic neutron scattering spectroscopies. Special attention is devoted to in situ measurements where the oxide or catalyst sample is in contact with the adsorbate or reactant. According to Professor Misono: "A catalyst can be called catalytic converter only when it catalyses some reaction useful for practice and the society." He states that, "the progress of catalysts based on mixed and reducible oxides may be the key to the advancement of catalytic technologies" (Misono, 2005). Understanding the interaction mechanism of oxygen molecules with reducible oxide surfaces is crucial for understanding of oxide catalysts. The formed vacancies interact with O_2 molecules (see Figure 11), forming peroxo [MOOM] species on the surface, which are extremely reactive and strong oxidants (Paier et al., 2013).