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BOOK REVIEW

Experimental Methods in Catalytic Research. Edited by R. B. Anderson, Academic Press, Inc., New York and London, 1968. xii + 498 pp. Price $22.50/210s.

This book consists of a series of articles, in the main written by authorities in the fields, dealing with some of the principal physical methods used in catalysis. Despite the title, the book is concerned only with heterogeneous catalysis involving the solid state. The fields of homogeneous and liquid-phase catalysis are not considered. As such then, methods of investigating the solid state and gas- or vapor-solid interactions are discussed. In order to produce a volume of reasonable dimensions, the editor has obviously had to exercise some control of the breadth of topics discussed. Of the many techniques employed in heterogeneous catalysis, 13 frequently used techniques are reviewed. A number of the methods not discussed have recently been treated elsewhere.

According to the editor, the aim of the book is to describe various methods used in catalysis to physical chemists with no experience in the field of catalysis. The discussion of each method is to provide adequate theory and experimental background. The importance of a book in this area is readily appreciated when it is realized that many university Chemistry courses contain little treatment of catalysis and yet on the other hand, the majority of the chemical industry is dependent directly or indirectly on catalysis of some type. To the reviewer's knowledge, the only other recent treatments of the subject are "The Solid-Gas Interface" edited by E. A. Flood, various chapters in the Advances in Catalysis series and several monographs.

As is frequently the case with edited books, there is a wide variation in the standard of the contributions by the various authors especially in the distribution of the space between theory, experimental techniques, and applications. Thus, some authors consume most of their allotted space with theory, little or no discussion of experimental methods, and a brief discussion of applications to catalysis. The reverse is true of other chapters, while a number of chapters are very well balanced. On the whole, it seems that the authors have found considerable difficulty in describing their topics in the allotted space. In some chapters, the impression is given that the authors have been happy to discuss their specialty but that the relationship to and application in catalysis has been included as a bonus. Hence, the utility of this volume would be markedly increased by a greater emphasis of the role of the discussed experimental techniques in catalysis studies.

The editor states in his preface that the book is divided into four sections, namely (1) methods for determining the kinetics of catalytic reactions, (2) methods for elucidating catalyst structure, (3) methods for determining chemical and physical characteristics of surfaces and adsorbed species, and (4) methods involving magnetic properties of catalysts. The book can also be divided into two sections; namely, one dealing with methods suitable for elucidating fundamental aspects of catalysis, such as high vacuum techniques and field ion microscopy, and a second section concerning techniques for studying both fundamental and practical aspects of catalysis, such as surface area measurements and acidity measurements.

The opening chapter deals with the measurement of reaction kinetics in catalyzed reactions and presents a well-balanced discussion of various experimental techniques employed in catalysis and methods of treating the raw data. Clear discussions of the various types of reactor systems are given along with descriptions of the mechanical components of systems suitable for making kinetic measurements. The chapter is concluded by discussions of experimental techniques involved in catalyst preparation and refined kinetic studies involving the use of isotopes and poisoning techniques.

A reading of the chapter concerning surface area and pore structures of catalysts gives the impression that the author has attempted to cover much ground in a short space; the result is an encyclopedic review. The chapter contains numerous brief sentences and listings of equations, without critical evaluation or expository development, which might confuse the uninitiated reader. Numerous methods for determining surface areas and pore volume are covered, but due to the brief discussions, any reader desiring to familiarize himself with the method will be forced to look elsewhere. The studies by DeBoer *et al.* of the *t* curve techniques are not discussed. For a volume of this type, sections such as IX B to G

seem out of place, especially for a physical chemist with no background in catalysis. The space could have been used much more advantageously to discuss more important topics in greater detail. Molecular pore-sized materials, which are nowadays important from a theoretical and practical standpoint, are treated in nine lines and the important work of Dubinin is discussed simply by listing four of his publications.

An authoritative discussion of the use of surface potential measurements in catalysis follows. This chapter provides a good, well-balanced treatment of principles and experimental methods and concludes with a wide range of well-chosen specific catalytic applications. The presentation is well worth the attention of those interested in using such measurements.

The next three chapters discuss methods applicable to fundamental catalysis studies. The apparatus and experimental techniques used in low energy electron diffraction (LEED) studies are clearly presented so as to stimulate the reader. In contrast, the theory of the technique is treated in one and one-half pages. The chapter concludes with a brief description of applications to surface chemistry. The author appears to have overlooked many applications of LEED to surface-catalyzed reactions. Clear, well-balanced, and informative chapters dealing with field electron and field ion emission microscopy and methods involving chemisorption in ultrahigh vacuum systems (reactivity of evaporated metal films and flash desorption spectrometry) follow. These two chapters provide excellent basic discussions of the principles, theory, experimental techniques, and applications of the techniques.

The utility of electrical measurements in catalysis is introduced by a brief critical evaluation of theories and correlations of electronic properties of solids with catalysis. The areas of electrical conductivity, photoconductivity, thermal glow curves, Hall coefficient measurements, photoelectromagnetic effects, and thermoelectric effects are covered with strong emphasis on the actual measurement of the electronic effects. The reader is left with the problem of relating the measurements to conventional catalytic properties.

The chapter concerning spectra of adsorbed species contains an informative discussion of the theory of vibrational spectra and the interpretation of the spectra of adsorbed molecules, although the possibilities of studying and differentiating between physical adsorption, chemisorption, and hydrogen-bonding are not treated. The section dealing with experimental procedures presents a good treatment of cell designs and construction and of sample preparation for infrared, Raman, visible, and ultraviolet spectral studies. Requirements of spectrometers are dismissed. Thus, important problems encountered due to low transmissions of samples or due to emission of radiation by samples at elevated temperatures are not considered. The possibilities of interferometry and of observing spectra of adsorbed molecules under catalytic conditions, compared to simple gas (or vapor)-solid interactions, are not treated.

Numerous and widely varying methods which have been used to measure surface acidity, both directly and indirectly, are discussed. The treatment of the more common methods consists of well-balanced sections covering the background, experimental approach, and data interpretation. Unfortunately, many critical points and method limitations are omitted resulting in several potentially misleading discussions. Thus, no mention is made of the influence of the state of hydration or conditions of calcination of the catalyst on the acidity. Little attempt is made to distinguish between Lewis, Bronsted, and total acidity. Thus, in the section concerning nonaqueous titrations, it is not made clear that H_0 indicators measure both Lewis and Bronsted acidity whereas H_R indicators are alleged to measure only Bronsted acidity. Nor is it pointed out that indicator methods are limited in their application to crystalline catalysts, such as zeolites, due to steric restrictions. Again, although it is shown that ion-exchange techniques can be used to measure proton acidity (e.g., for silica-alumina), it is not pointed out that when other exchangeable cations are present (e.g., in synthetic zeolites) misleading results can be obtained. In other cases, uncertain observations are presented as established facts. Thus, in dealing with poisoning experiments, it is stated that "quinoline poisons one active site per molecule" without any qualifications. A number of techniques, whose relationship to catalyst acidity is rather vague, are included such as differential hydrogen analysis, competitive exchange reactions, and infrared spectra of hydroxyl groups. In summary, this chapter discusses most of the physical methods applicable to acidity measurements, but it requires reading with great discrimination.

The final two chapters concern the application of magnetic techniques to catalysis. The first chapter dealing with conventional magnetic methods provides a good introductory exposition of measurement principles and covers both classical and more recent experimental approaches. However, catalytic applications are few and brief. The advantages of the modern simple Faraday apparatus using a vacuum microbalance and suspension of catalyst materials into the magnetic

field and reaction zones could possibly have been more emphasized. The use of the magnetic method to follow *in situ* valence and coordination changes with temperature and treatments is not considered.

The phenomenological theory and the quantum treatment of electron spin resonance (ESR) are given a good exposition in the concluding chapter. However, any description of the rather complex equipment and techniques required to conduct the simplest experiments is almost completely omitted. For those not discouraged by the extensive theoretical treatment, the chapter concludes with a useful discussion of some of the more interesting and fruitful applications of ESR to catalysis.

There are numerous typographical errors in the text, tables, and indices (both subject and author), the most serious of these being the listing of the susceptibility of water as -0.271 instead of -0.721 in Table III, page 425, and an error in the values quoted for the nickel magnetization in Table IV, page 429. Several examples of incorrect and incomplete indexing were also noticed. Throughout the book, the term "molecular sieve" is loosely used to describe synthetic X and Y zeolites. The impression is also given that the volume was a long time in preparation. Thus, there are less than 25 references cited after 1965.

All in all, despite its shortcomings, this book fills a useful role in the chemical literature. It should be valuable to the physical chemist wishing to learn techniques used in catalysis and to catalyst and surface chemists wishing to broaden their scope into different areas.

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