

Mechanical Catalysis: Methods of Enzymatic, Homogeneous, and Heterogeneous Catalysis. By Gerhard F. Swiegers (Datatrace DNA Pty Ltd. and Division of Molecular Health Technologies, Melbourne, Australia). John Wiley & Sons, Inc.: Hoboken, NJ. 2008. xxx + 352 pp. \$100. ISBN 978-0-470-26202-3.

Numerous texts have been written on catalysis and reaction kinetics; however, Swiegers and coauthors of *Mechanical Catalysis* have added a new twist to the old story. The focus of this easily read reference text is on the underlying physical phenomena that determine the activity and selectivity of functionalized catalysts, especially enzymes and biomimetic ones. The traditional view of catalysis assumes that reactants diffuse to the catalyst site where they bind and are transformed and the products desorb to reveal an active catalyst site, which can repeat the process with fresh reactants. Depending on the nature of the catalytic process, any one of these energy-dependent steps could control or limit the overall rate of product formation. What is presented in this text is that certain reactions may instead be limited by time-dependent or mechanical processes, whose rates are negligibly affected by the energetics of any reactant, transition state, or product. Specifically, the catalyst undergoes a sequence of conformational changes that effectively move reactants through the reaction pathway toward product formation. However, the energy landscape for these transformations is relatively flat, which means that the overall reaction rate is limited by the speed of molecular rearrangements and the collision frequency of properly aligned species; therefore, these transformations are deemed time-dependent.

The idea of how reaction rates can become limited by both energy- and time-dependent processes is carefully laid out in the first six chapters of the book. Although these chapters suffer somewhat from some redundancy, they clearly define the nature of mechanical processes within catalytic systems and illustrate with creative examples how these processes, which have negligible energy barriers for their occurrence, exhibit a time-dependent behavior that is often synergistic in nature. For example, the author uses the analogy of a stacked array of dominos falling in an orderly fashion to illustrate the concept of a series of low energy transformations moving reactants toward products via a time-dependent process that is nearly independent of the temperature of the system. He proposes that this type of behavior is common to many enzymes and functionalized metal catalysts whose change in reaction rate does not correlate with temperature via traditional relationships, such as that of Arrhenius Law.

The latter half of the text begins with a detailed history of the kinetic models that have been used to explain the catalytic behavior of enzymes. This review is thorough but not long-winded and helps to provide a basis for the proposed model of mechanical catalysis. Using the foundations developed in earlier chapters, the author then illustrates how homogeneous, heterogeneous, and enzymatic catalysis can be explained by a single theory that assumes that reactions occur via a sequence of energy- and time-dependent processes. For most heterogeneous catalyzed reactions that are nondiffusion limited, the energetics

associated with key reaction steps dominate; whereas for many enzymatic processes, it is the orchestrated movement of reactants to the reaction site that determines the overall reaction rate. The final three chapters contain examples of nonenzymatic catalysts that exhibit time-dependent reaction behavior. In these chapters, the author also offers insights into molecular design features that could be incorporated into new catalysts that would take advantage of the synergistic conformational transitions observed with many enzymes.

In summary, this book is a useful addition to the library of any individual working with functionalized catalysts, especially those that may undergo conformational changes during the reaction process. This text is especially informative for those working with enzymes, biomimetic, and organometallic-based catalysts. It also unifies many of the kinetic models that have been put forth to describe heterogeneous, homogeneous, and enzymatic catalysis.

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Combinatorial Methods for Chemical and Biological Sensors. Edited by Radislav A. Potyrailo (General Electric Company, Niskayuna, NY, USA) and Vladimir M. Mirsky (Lausitz University of Applied Sciences, Senftenberg, Germany). From the series, *Integrated Analytical Systems*. Edited by Radislav A. Potyrailo. Springer Science + Business Media, LLC: New York. 2009. xx + 494 pp. \$99.00. ISBN 978-0-387-73712-6.

Combinatorial methods have recently risen to prominence in the field of materials science. Rapid parallel synthetic techniques have allowed researchers to explore larger parameter spaces with a level of detail that would have been inconceivable only a decade ago. Research on sensing materials has taken advantage of the opportunities offered by combinatorial synthesis, coupled with high-throughput screening of the newly prepared materials for activity, selectivity, and stability.

The present book gives a wide-ranging overview of the applications of combinatorial synthesis to the field of sensor development. Its scope is very broad, ranging from inorganic gas-sensing materials to biologically derived sensors based on the molecules of life. The chapters are organized into seven sections based on techniques for constructing the main sensors, e.g., self-assembled monolayers, biological receptors, and inorganic materials, with two more sections dedicated to introductory material and outlook. Individual chapters in each section were authored by authorities in the field, drawn from both academic and industrial environments. References to the original literature are consistently extensive and appropriate: the interested reader will have no difficulty in tracking down further material. Illustrations are plentiful and of generally good quality; color graphics were used very sparingly but effectively.

The material in this publication is presented in a very detailed and highly technical manner throughout, somewhat resembling

a collection of review articles. This is certainly no textbook but an interesting and insightful work nonetheless, aimed squarely at practicing scientists in the sensing community. Most chapters are captivating reads that provide ample food for thought and bring the reader up to speed with the latest advances in the field of combinatorial synthesis and high-throughput screening of sensing materials. Adequate space is given to the important subject of screening of the prepared materials: most contributors call attention to the fact that being able to screen the obtained sensors for activity, selectivity, and stability in a timely manner is just as important as the task of preparing them. The concept of a complete “combinatorial workflow”—combining synthesis and screening in an automated computer-controlled lab—is given due consideration by many of the authors and is a recurring topic in many chapters. However, we feel that it is a concept of such importance that a separate chapter might have been advantageously dedicated to its comprehensive treatment.

One of the messages that emerges from perusal of this treatise is the ever-present necessity for judicious experimental design. Even though scientists now have the possibility of generating a huge number of structures to test, the process of selection of the parameter space to be explored is still a major concern in the combinatorial community, and relevant examples of computational and statistical approaches to this problem are also presented. The outlook chapter concluding the book provides a bird’s eye view of the field, with emphasis on the practical challenges, e.g., instrument interoperability, data exchange formats, that still hamper the full development of combinatorial discovery methods.

As an aside, we realize that almost all the experimental techniques showcased in this book generate an unwieldy amount of experimental results. Treatment of data is a pivotal point in the design of combinatorial experiments and a common stumbling block for newcomers to the field. The authors of the

studies presented have routinely put to use powerful advanced statistical and chemometric techniques, whose application is generally described in great detail. Even though many excellent introductory textbooks on the subject matter of chemometrics have been published, the examples presented therein are often too simplified for a full understanding of the application of the methods to real data. We feel that, as an added bonus to its main content, this collection presents the reader with a wide array of complex practical examples from established practitioners in the field.

Most of the chapters focus mainly on the work of the authors themselves. Although this is conducive to detailed and clear explanations of the methods and results, a broader perspective would have greatly increased the utility of the book. Also, because many authors have contributed to this opus, some unevenness in the treatment of the subject matter is unavoidable and to be expected. Furthermore, considering that the contents are clearly aimed at an audience of experts in the sensing field, the two initial introductory chapters—especially the one on general concepts of chemical and biological sensing—are somewhat simplistic and could have been omitted without diminishing the value of the book.

In summary, this volume offers a carefully picked collection of relevant examples from the field of synthesis of combinatorial sensors. A reader interested in this field and already conversant in the science of sensors will find it a thought-provoking starting point for more in-depth literature research.

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