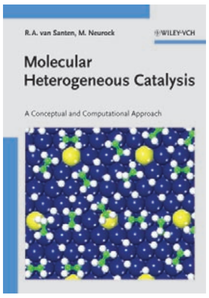
Molecular Heterogeneous Catalysis



A Conceptual and Computational Approach. Edited by *Rutger A. van Santen* and *Matthew Neurock*. Wiley-VCH, Weinheim 2006. 474 pp., softcover € 99.00.—ISBN 3-527-29662-X

This well-written and nicely illustrated book is a sort of compendium of contemporary heterogeneous catalysis. The volume, which consists of 474 pages, is divided into 10 chapters. The authors, Rutger Anthony van Santen and Matthew Neurock, of Eindhoven University of Technology and the University of Virginia, respectively, are both world leaders in catalysis research. Their book offers the viewpoint of a physical chemist, and articulates the opinion that, to fully understand catalytic phenomena, a detailed insight at the molecular level is required. Throughout the book, a reductionist approach is taken, and the chemistry is discussed in terms of elementary reaction and diffusion events at surfaces, although the emergence of kinetic phenomena are considered as resulting from complex interactive atomic and molecular networks. The material presented is up-to-date, and follows mainly from theoretical studies; key experimental results are described in this context. Classical heterogeneous catalysis is covered in detail at the molecular level, and the mechanistic principles of reactivity are compared with those of organometallic and enzymatic systems. The book also gives a solid account of biological systems, and deals specifically with theories about the emergence of protocellular life. Of particular interest is the discussion of chemo-evolutionary theory in relation to the design of a catalytically active protocell.

The book begins with an introductory chapter, which, after underlining the significance of catalysis in modern society, gives a brief overview of molecular heterogeneous catalysis and the theoretical methods used to study it, as well as an outline of the following chapters. The second chapter summarizes the principles of molecular heterogeneous catalysis. The chapter begins with a discussion of the principle of Sabatier, which is exemplified by the catalytic decomposition of N_2O over transition metals and zeolite catalysts. Some pertinent physical chemistry is then introduced, namely, transition-state theory and the Brönsted–Evans–Polanyi (BEP) relationship. The influence of the reaction environment is then addressed. The pressure–materials gap, that is, the frequently observed difference in catalytic activity between single-crystal surfaces under ultrahigh vacuum (UHV) and synthesized catalysts under normal operating conditions, is first examined by considering the methanation reaction and other examples. The effects of alloying and surface defects, such as steps and kinks, on reactivity are also explored in this subsection. In the following subsections, other key aspects of catalytic activity are tackled, for example, the importance of metal particle size is adequately treated by reference to the exciting field of gold catalysis, and the influence of the metal support is illustrated by considering the silver/alumina oxidative system. The chapter concludes with a discussion on stereoselectivity (both molecularly induced enantioselectivity on metal surfaces and stereochemistry in homogeneous systems), and the reconstruction of surfaces by strongly bound adsorbates.

Chapter 3 is more theoretical in nature, and gives a detailed account of contemporary ideas about chemical bonding and reactivity at surfaces. As a starting point, the basic quantum mechanics of chemical bonding in molecules is reiterated. Molecular F_2 and N_2 are used as examples to illustrate the ideas of bonding/antibonding orbitals and Pauli repulsion. An extended-Hückel (tight-binding) description of bonding in molecules is also given. The bonding interaction of molecules with transition-metal surfaces is then approached by considering the chemisorption of NH_3 and CO. Fundamental differences in the interactions of NH_3 and CO with transition metals are highlighted. Elegant molecular orbital diagrams, in conjunction with overlap population density of states (OPDOS) plots, are nicely applied to examine the bonding of CO at transition-metal surfaces. The language of donation and back-bonding, with respect to the interaction of CO with transition metals, is familiar from organometallic chemistry; indeed, the authors build upon the Blyholder model in their description of the bonding of CO at transition-metal surfaces. Finally, the bonding in transition-metal–carbonyl molecular complexes is discussed and compared with that of the interaction between transition-metal clusters and CO.

Atomic carbon and oxygen are used as examples to illustrate the bonding of adatoms at transition-metal surfaces; trends are compared and contrasted across rows and down columns in the Periodic Table. The elementary quantum mechanics of the chemisorption bond is then briefly discussed, from both a tight-binding and a molecular orbital perspective. The later part of the chapter deals with chemical reactivity at transition-metal surfaces, namely, the question of how the metal activates certain bonds within reacting adsorbates. The dissociative adsorption of CO and similar diatomic molecules is first explored; the nature of the respective transition states and the observed universal BEP relationship are discussed. This is followed by a brief exposition of carbon–carbon bond formation in the context of both homogeneous and heterogeneous catalytic systems, then the activation of CH_4, NH_3, and H_2O is examined and contrasted with that of π-bonded systems such as CO. Lastly, the cleavage or formation of C−C bonds is compared with CO oxidation, and the chapter concludes with a detailed look at the importance of intermolecular interactions between adsorbates and of the degree of surface coverage in catalytic processes.

The fourth chapter digresses from the chemistry of transition-metal surfaces, and presents a coherent exposé of zeolite catalysis. Particular attention is devoted to structure–activity relationships and the importance of the metal constituents. In the first section, the general structure of these microporous aluminosilicate compounds and the mechanism of their interaction with adsorbate molecules is discussed. Zeolites are known to act as both Brönsted acid and Lewis acid catalysts, and in addition exhibit redox behavior, depending on their composition. A detailed discussion is devoted to each type of catalysis. Brönsted acid catalysis is considered first, and is adequately illustrated by a number of examples, including the formation of propyl alkoxy from propene. Important factors in proton-activated catalysis are highlighted, such as the deprotonation energy of the zeolite, the stabilization of the carbocation intermediate by the negatively charged zeolite framework, and scaffolding effects. Lewis acid catalysis by zeolites occurs in the case of ion-exchanged Lewis acids such as Zn^{2+} derivatives; this behavior is nicely illustrated in the text by the hydrolysis of acetonitrile. The oxidation of alkenes by O_2 over $M_xAl_{(1-x)}PO_4$ systems (M = Co, Mn) is presented as the first example of redox catalysis. Further examples include the selective photocatalytic oxidation of alkenes, and the selective oxidation of benzene by N_2O over Fe systems. This chapter concludes with a discussion of the zeolite catalytic cycle, and aspects of catalytic selectivity and diffusion.

Chapter 5 builds upon the concepts outlined in the previous chapters regarding the reactivity of metals and zeolites to develop a fundamental understanding of the reactivity of metal oxides and sulfides. The chapter begins with an introduction to the electrostatic view of oxide and sulfide surfaces, and introduces Pauling's ideas on valency and excess ionic charge. These elementary bonding theories are then applied to consider the reactivity of hydroxylated Al_2O_3 and TiO_2 surfaces. This somewhat limited ionic model is developed further by considering covalent contributions. This is exemplified by an analysis of the bonding in RuO_2 and the interaction of CO with $RuO_2(110)$. The hybridization of atomic orbitals at surfaces is also discussed. The chapter then digresses to give a general discussion of Brönsted acidity, followed by a consideration of selective oxidation by oxide surfaces.

As pointed out by the authors, metal oxides are a diverse class of materials with varied properties. A number of case studies are discussed to highlight how certain properties of these systems influence their intrinsic reactivity. The oxidation of butane to maleic anhydride over vanadium pyrophosphate surfaces is first examined; it is pointed out that Lewis acidic vanadium sites and Brönsted acid sites on the surface phosphate groups both play a role in the overall activity and selectivity. Further examples given include the oxidation of methane over HPVMo Keggin structures and the reaction of NO with NH_3 over vanadium oxide. The concluding section of Chapter 5 deals with metal sulfide surfaces. By way of an example, the MoS_2 surface is discussed. Particular attention is drawn to the shape and electronic structure of molybdenum sulfide particles dispersed on inert supports. Lastly, the promotion of metal sulfide surfaces is addressed by discussing the hydrodesulfurization of thiophene over Co^{2+}-promoted MoS_2.

In physical organic chemistry, aqueous or polar solvents are known to influence certain reactions by stabilizing charge separation, and by facilitating proton and electron transfer. In Chapter 6, such solvent effects are discussed in relation to aqueous-phase heterogeneous catalysis. The effect of an applied potential in heterogeneous systems (electrocatalysis) is also discussed. After a short introduction, the chapter addresses the chemistry of water over transition-metal surfaces: the ensembles that water forms on transition metal surfaces and its activation are discussed. The topic of electrocatalysis in general is then considered, and a summary of the approximate methods used to model electrochemical systems is given. The first system discussed is the electrochemical activation of water. The structural and ionic changes undergone by water over Pd(111) and Cu(111), and their dependence on applied potential, are discussed.

In the latter half of the chapter, further examples of solution-phase and electrochemical catalytic systems are given. The synthesis of vinyl acetate by the acetoxylation of ethylene over Pd is one system considered. This example nicely illustrates how water promotes heterolytic cleavage of the acetic acid, which would otherwise undergo homolytic cleavage. It also shows how the aqueous layer formed at the Pd surface acts as a medium for the dissolution of Pd ions or reduced Pd clusters, which subsequently act as homogeneous catalysts. The oxidation of ammonia is given as a further example of an electrocatalytic system. This reaction highlights the effect of applied potential and the presence of water on both selectivity and catalytic activity. The oxidation of CO and reduction of NO are also given as examples of electrocatalytic systems. Electrochemical reduction of NO further illustrates the effect of applied potential on product selectivity. The oxidation of CO is an example of an electrochemical system that is affected by surface topology.

In Chapter 7 the focus shifts to catalysis in biological systems. This chapter deals with enzyme chemistry, and draws a number of parallels between biological and chemical catalysis. A brief introduction outlines the Michaelis–Menten expressions for enzyme kinetics, and provides an overview of enzyme structure–activity/selectivity relationships, including allosteric behavior. The induced-fit model in enzyme chemistry, which describes the mechanism of catalysis, is then elegantly demonstrated by discussing the phosphorylation of glucose by hexakinase. Enzyme catalysis is further illustrated by an account of the fascinating rotary action of ATP synthase, and a comparison between the hydrolysis of CO_2 by carbonic anhydrase and the hydrolysis of acetonitrile by Zn^{2+}-containing zeolites. Biomimicry, the design of compounds that mimic the catalytic action of enzymes, is introduced in the next section. This topic is illustrated by a number of examples, which include artificial chymotrypsin and an artificial organophosphorus hydrolyse. The latter part of the chapter deals with biological oxidation and reduction reactions. With regard to biological oxidation, both monooxygenases and dioxygenases are discussed. The hydroxylation of C–H bonds by the heme-containing enzyme cytochrome P450 is given as one example of biological oxidation. The catalytic cycle of the Mo-containing sulfite oxidase is also discussed. The chapter concludes with an account of biological reduction. The coenzymes NADPH and NADH are first discussed, both of which act by transferring a hydride ion to the substrate molecule that is to be reduced; the second hydrogen atom is subsequently added as a proton. Reduction is also discussed in terms of acid–base-type chemistry, which is induced by the electrostatic properties of the enzyme cavity. These types of processes are nicely illustrated by the chemistry of nitrogen fixation. Mechanistic aspects of nitrogenase, the enzyme that reduces molecular nitrogen, are discussed.

In Chapter 8 the phenomenon of self-organization in catalytic systems is addressed. The first topic to be approached is catalytic self-repair. This aspect of self-organization is first exemplified by the hydrodesulfurization of thiophene on a nickel–sulfur cluster; catalytic self-repair is further explored by a comparison of alkene epoxidation on titanium–silica gels and Ti-containing zeolites. The topic of synchronization of reaction centers is examined next. The example of CO oxidation on Pt(100) is given. This system nicely illustrates chemical synchronization: the adsorption of a critical amount of CO on stable Pt(100)hex (which cannot dissociate O_2) induces a reconstruction back to metastable Pt(100), which can do so. Thus, CO is oxidized and desorbs, which subsequently causes the Pt(100) to reconstruct to unreactive Pt(100)hex, thus terminating the reaction cycle. Some aspects of the physical chemistry of self-organization are dealt with next, followed by a discussion of immunoresponse and evolutionary catalysis, which begins with a description of the form and function of antibodies. Particular attention is paid to the so-called F_{ab} antigen-binding units and their interaction with antigen molecules. Some work on the use of antibodies as selective catalysts is discussed. This section concludes with a brief discussion of directed evolution in the production of novel enzymes. A fascinating account of the formation of siliceous silicalite, a zeolite, is presented in the following section. This compound beautifully exemplifies both evolutionary formation in its primary structure (Si_{33} clusters) and self-assembly in its secondary (nanoblocks) and higher structures. The concluding section of this chapter gives a brief exposition of evolutionary computer methods.

The book effectively ends with Chapter 9 (as Chapter 10 is a summary). Chapter 9 discusses the place of heterogeneous catalytic systems in the origin of life and biomineralization. This fascinating and informative account incorporates concepts from the previous chapters to highlight contemporary ideas in these topical areas of science. The chapter begins with an overview of our current understanding of the origin of protocellular systems. Important physical models are briefly discussed, and a distinction is made between the two chemical views, the "RNA world" model and the Oparin model. In the four sections that follow, theories about the generation of protocellular life are examined. The origin of chirality in biosystems is first considered, and theories of the amplification of enantiomeric excess are discussed. Artificial catalytic chemistry is explored in the following section, by reference to the graded autocatalysis replication domain (GARD) model and the lattice artificial chemistry model. Lastly, the conditions for the emergence of artificial life are explored through the application of computational models. This approach demonstrates the high dynamic complexity of a system close to phase transitions between periodic and chaotic behavior; such complexity is a necessity for life. The latter part of the chapter deals with the fundamental issue of biomineralization. The biosynthesis of cell walls of diatoms (single-cell algae) is discussed as an example of the biomineralization of porous silica structures. In the subsequent discussion, aspects of the chemistry that mimics biomineralization are highlighted. The chapter concludes with a summary, in which various aspects of this and earlier chapters are integrated to consider the goal of the formation of an evolutionary adaptive catalyst by self-assembly. The final chapter (10) gives a summary of important theoretical catalytic concepts used throughout the book.

This book provides a comprehensive overview of current ideas in the rapidly developing field of molecular heterogeneous catalysis. The subject matter, which includes bimetallic catalysts, metal oxide/sulfide catalysts, zeolites, and electrocatalysis in the context of fuel cells, covers highly topical aspects of heterogeneous catalysis, and should be of general interest to everyone with an interest in catalysis or surface chemistry. Results from a broad range of quantum-mechanical approaches, including Monte Carlo and molecular dynamics methods, are presented and discussed. A general conceptual approach to understanding catalysis is developed through the text, and detailed comparisons are made between heterogeneous and homogeneous/enzymatic systems. The chapters are written with clarity, and the concepts and models are illustrated well, with numerous unambiguous figures. There are a few typographical errors, but they in no way detract from the comprehension of the text or create any ambiguities. A useful in-depth account of the full range of different ab initio quantum-mechanical methods, including kinetic Monte Carlo and ab initio molecular dynamics procedures, is given in the appendix. Chapter 10 is also particularly helpful; here the catalytic principles highlighted within the book are summarized. The book would be especially suitable for graduate-level students and researchers working in heterogeneous catalysis, but anyone with an interest in molecular-level science would find this book appealing.

Paul Crawford, Peijun Hu
School of Chemistry and Chemical Engineering
The Queen's University of Belfast
Belfast (UK)

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