Modern Heterogeneous Catalysis
Modern Heterogeneous Catalysis

An Introduction

*Rutger A. van Santen*
To Edith
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Preface

The science of heterogeneous catalysis has flourished for over more than a century. Its processes have contributed significantly to our modern way of life by enabling the production of indispensable commodities such as fuel and fertilizer as well as materials with previously unknown properties such as the polymers.

Both serendipity and empirical chemical discovery have played a part in the development of many of the catalytic systems now used in large chemical processes. The early observations of catalysis and their scientific formulation by Ostwald, Sabatier, and Haber provided the insights and tools necessary for later developments in this field.

While the nineteenth century was the century characterized by categorizing scientific phenomena, the twentieth century can be seen as the century of developing the physical sciences at the molecular level. The formulation of a molecular theory and the development of predictive tools for heterogeneous catalysis has been a long and tortuous process that is now reaching a reasonable level of completion.

This book provides an introduction and overview of the molecular basis of heterogeneous catalysis. It took almost an entire century to arrive at this understanding because heterogeneous catalytic systems are extremely complex. The two main themes discussed in this text are the reaction mechanisms of the various currently known heterogeneous catalytic reactions and the relationship of catalytic reactivity to catalyst structure and composition.

The catalyst is, in itself, a complex material. It is usually a porous inorganic solid composed of various compounds that are often distributed as nano-sized particles over a heterogeneous surface. The catalytic reactions are also complex because they include many reaction steps that often compete. The reaction product is often a multicomponent mixture that requires the availability of advanced analytical tools for its characterization. The overall catalytic system is not easy to study because its performance often depends on reaction conditions and because catalytic activity may change over time. In addition, a catalyst may eventually deactivate during the reaction process.

Clearly, catalyst research requires an integration of many skills. Knowledge of applied inorganic chemistry is needed for the preparation of catalytic materials, training in spectroscopic measurement is essential for characterizing the catalyst as synthesized and at working conditions, and reactor engineering
skills are required for the proper measurement and interpretation of catalyst performance data.

The simulation of kinetics based on a mechanistic modeling of the reaction has always been an important tool in catalyst science. More recently, applied quantum-chemical calculations have been used as an aid in determining the mechanism of a particular reaction. These calculations have become relevant to heterogeneous catalysis only in the past decades with the development of computer hardware which is sufficiently powerful for calculating catalyst site models for a solid surface. Since the accurate calculation of elementary reaction rates is also now possible, detailed molecular information on many catalytic systems has become available. This information complements and enriches the chemical reactivity studies on well-defined scientific surface models, providing a powerful predictive tool for heterogeneous catalysis.

This detailed molecular information has enabled reinterpretation of many mechanistic questions that are fundamental to heterogeneous catalytic reactions. A correct mechanistic molecular model complemented by quantitative reactivity data is indispensable for predicting the activity and selectivity of a reaction catalyzed by a particular catalyst. This information can then be used to determine the optimum catalyst surface composition and structure for best catalytic performance. In this book, the concise and comprehensive descriptions of various catalytic systems and reactions can be considered as case studies that exemplify this approach.

One of the most important changes in theoretical chemistry has been in the development of quantitative methods to allow predictive catalysis. In the early nineties of the last century, theoretical concepts had already been formulated, but computational hardware was not yet available to allow their quantitative application to specific systems. Theoretical catalysis was mainly qualitative; conceptually useful but of limited direct practical use. At this time, the mechanism of catalytic reactions could be described in a kinetics context, but could only be applied using parametrized models. This changed dramatically when the necessary computer software and hardware became available for quantitative applications. This computational ability gave rise to the quantitative theories of catalyst activity based on both the molecular computational and spectroscopic data described in this book. The theoretical developments are based not only on chemical bonding data, but more importantly on information about elementary reaction transition states that is sufficiently accurate to allow discrimination between the different mechanisms that determine catalyst activity and selectivity.

In the experimental realm, contributions were largely due to the important advances in the development of sophisticated spectroscopic techniques, in the development of model catalytic systems, and in the discovery of practical catalysts that are atomistically well defined.
These developments are important because there is now quantitative molecular information that can be used to define a catalyst’s performance–structure relationship for most catalytic systems of interest. This relationship provides the scientific framework to the reaction mechanisms that are the main focus of the book.

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Acknowledgments

Writing this book has been both enjoyable and challenging. Over the past three decades I have co-authored several monographs on related topics with my colleagues and friends. The first book on theoretical heterogeneous catalysis was published in 1991, a second book on chemical kinetics and catalysis written with Hans Niemantsverdriet appeared in 1995, and the book “Molecular Heterogeneous Catalysis” that I wrote with Matthew Neurock was completed in 2006. These books document the gradual progress in our understanding of the molecular foundations of heterogeneous catalysis over the past 30 years. This book could not have been written without the experience of writing the previous books and the insights derived by communication with numerous contacts in the scientific community.

Since my first exposure to heterogeneous catalysis at Shell Research and later when I joined the faculty of Chemistry and Chemical Engineering of the Technical University Eindhoven, I have been fortunate to be surrounded by great colleagues and interested and sometimes excellent students and postdoctoral fellows. A scientific career also requires travel and the cultivation of contacts within the international scientific community. My communications with these numerous contacts (too many to mention here individually) have been instrumental in collecting the information and insights brought together in this book. An account of the importance of these contacts for my scientific work can be found in the book “40 Years Catalysis Research” which appeared on my 65th birthday. Here, I would like to mention a few notable colleagues from the past. Wolfgang Sachtler, who introduced me to heterogeneous catalysis at Shell, was also one of the early leaders of the “Dutch School of Catalysis.” One of its main research themes was the mechanism of heterogeneous catalytic reaction. The debates of that period provided the origin for many of the ideas on reaction mechanisms that I describe in this book. A second person I would like to mention is Vladimir Kazansky from Moscow, who visited our laboratories many times in the 1990s. Through him I became familiar with the Russian school of thinking, and I credit him with many of the insights on solid acid catalysis that are presented in this book.

The Laboratory of Inorganic Chemistry that I joined in 1988 had already been the leading academic center of molecular approach to heterogeneous catalysis for many years. This approach was started by George Schuit who occupied the first chair of this laboratory at the end of the 1950s. With Bruce Gates and James Katzer he co-authored the early textbook “Chemistry of Catalytic Processes”
that was published in 1979, and which I consulted frequently. It is interesting to compare the mechanistic discussions included in that earlier book with the discussions presented in the current book, which now contains a detailed molecular foundation for several of the early qualitative ideas.

Tonek Jansen and I joined the laboratory at around the same time, and together we started the computational catalysis program. He became the leading expert in microkinetics and kinetics Monte Carlo methods, and I am grateful for his help and inspirational ideas. The sections of this book dealing with electrocatalysis could not have been written without my acquaintance with Marc Koper, who joined our laboratory for a few years as a Royal Netherlands Academy of Arts and Sciences Fellow and taught us the molecular aspects of modern electrocatalysis.

I am very grateful for the hospitality of the Institute of Complex Molecular Sciences, and its director Bert Meijer, which gave me the opportunity to concentrate on the writing of this book for the past 3 years. I would also like to thank Emiel Hensen, my successor and currently head of the Laboratory of Inorganic Materials Chemistry. My communications with him and with faculty members, PhD students, and postdocs were invaluable and created an inspiring intellectual climate for writing. There are a few persons I would like to thank individually. The contributions of Ivo Filot to the microkinetics illustrations and results included in the book can be found in Chapters 3, 7, and 8. My work with Ionuth Tranca on chemical bonding contributed to most of Chapter 6 and important parts of Chapters 7 and 11. Over the years, I have enjoyed collaborative work with Evgeny Pidko, who helped me with sections on Brønsted and Lewis acid catalysis in Chapters 9 and 10. His student Chong Liu contributed the calculations on zeolitic protons. Discussions during many visits with Matthew Neurock continue until today. Matthew agreed to the use of many of the ideas that have their origin in our joint 2006 book, which are presented in this book within renovated context. I was fortunate to work with one of his students Craig Plaisance, a post-doctoral fellow at the TU/e, who contributed to the material discussed in Chapter 11, especially through our discussions that provided important insights on computational electrocatalysis.

Generous assistance is required to transform a book like this into a suitable format and to get the text and figures prepared and organized. I sincerely thank Floris Hieselaar, Tiana Plaisance, Freke Sens and Tom van den Berg for practical support in compiling the text properly, Koen Pieterse for producing some of the high quality figures and Bram Vermeer and Jeanne Daniele for editorial support.
Arrangement of This Book

This book consists of two parts. Part I is an introduction to the physical chemistry of heterogeneous catalysis. It aims to teach basic and well-established scientific theories to the student who is unfamiliar with heterogeneous catalysis. It starts with two chapters on the history of the discovery and development of catalytic systems, followed by an introduction to the chemistry and implementation of the major modern heterogeneous catalytic processes. Various classes of catalytic materials and the different types of known reactions are also described.

The following three chapters are essentially an introduction to the kinetics and reactivity of heterogeneous catalysis. The development of the chemical insights that form the basis of catalysis science is presented in a systematic way. The material is organized to provide an introduction to currently understood microkinetics and reactivity–structure relationships, and is illustrated by examples of recent theoretical applications to working catalyst systems and relevant experiments that reveal the molecular details of a working catalyst.

Part II of the book can be considered to be an advanced course of the molecular approach to heterogeneous catalysis. Four chapters deal with the mechanism of heterogeneous catalytic reactions on the molecular level from the perspective of a physical organic chemist. The chapters include the details of bond breaking, bond formation, and the skeletal organization of molecules. The complete spectrum of heterogeneous catalytic systems is covered. Relevant catalytic activity, spectroscopic data, and kinetics are discussed. Information on organometallic and coordination chemistry is also included, which is important in heterogeneous catalysis because elementary reactions occur in contact with an inorganic surface. These reactions also display unique aspects that relate to the chemistry of surfaces, requiring insights from inorganic chemistry.

The four mechanistic chapters of Part II are organized by the types of various catalytic systems: transition metal catalysts, solid acid catalysts, Lewis acidic catalysts, and reducible oxide catalysts and related inorganic materials such as the sulfides. Each chapter contains descriptions of the catalytic reactions, their mechanisms, and their relation to catalyst composition. The main heterogeneous catalytic reactions that are currently used or that appear to be promising candidates for further exploration are discussed. In addition, the physical chemistry and molecular basis of electrocatalytic hydrolysis are presented. Recent advances in this field have significantly contributed to our general understanding of heterogeneous catalytic reactivity. These descriptions
are based mainly on experimental and computational data providing detailed molecular information on the systems. The relationship between catalytic activity, selectivity, and catalyst stability with the structure and composition of the catalyst is essential to these discussions.

Because of the large variation in system types and reactions it is also important to present the general aspects that unify the different methods for reactant activation and the various reaction mechanisms. This information is provided in summary sections. In addition, sections are included to describe several reactions and systems such as enzymatic reactions that often share common features with the heterogeneous catalytic systems. These specialized sections feature the cross-referencing of descriptions of reactions on different systems to highlight their similarities.

The molecular basis for the reactivity of heterogeneous catalysts cannot be properly understood without a solid understanding of the surface chemical bond. The electronic structure of the catalyst surface determines the trends in chemical reactivity across different systems. For this reason, Part II of the book contains one chapter that provides an introduction to the quantum chemistry of chemical bonding in molecules and solids. The computational electronic structure and stability data that provide a basis for this chapter are now readily available from state-of-the-art density functional theory (DFT) calculations. These have become a useful tool to the chemist who wishes to analyze surface reactivity as a function of surface structure or composition. The following chapter contains a discussion of the surface chemical bonding on transition metals and the use of these theoretical concepts to analyze transition states of elementary reactions catalyzed by transition metal surfaces. The chemical bonding and reactivity concepts introduced in these two chapters are often referred to in the four later mechanistic chapters that focus more on the chemical aspects of catalysis.

This book has been designed to be accessible and interesting for students and researchers with very different backgrounds, from those who are new to the field to those with advanced research experience. Thus, the book is divided into two parts: an introductory part with basic information on heterogeneous catalysis and a more specialized part that covers the molecular aspects of catalyst reactivity. The book is tailored to suit both types of readers by presenting general information complemented by inserts. These inserts serve to include material that is useful, but not always of general interest or necessary in order to follow the main text. The inserts allow for the addition of relevant up-to-date information that is of more specific interest to the advanced reader, and they provide a rich source of illustrative material that can be used in lectures.
Catalysis is about reactivity, catalyst synthesis, and spectroscopy. This book focuses on reactivity and provides the reader with the tools to use computational and experimental data to select materials with the desired catalytic properties. While this text covers many topics (catalytic systems and their reactions, physical chemical processes, quantum-chemistry theory) that together present a complete picture of catalytic science, the topical sections have been written to be read independently so that the book is suitable for browsing. References are also provided to complementary materials concerning computational quantum-chemical methods and approaches as well as catalytic measurement and spectroscopic techniques.
Part I

Physical Chemistry and Kinetics
1

Heterogeneous Catalysis

1.1 What is Heterogeneous Catalysis?

The phenomenon of catalysis applies to a wide range of chemical reactions. By using a catalyst, chemical reactions that are non-selective can be made selective and those that require a high temperature can be conducted at a lower temperature (see Figure 1.1). In this and the next chapter, we will describe the discovery of this phenomenon in the nineteenth century, the understanding of catalysis that followed, and the main chemical industrial processes that developed in the twentieth century.

There are many chemical compounds that show catalytic action. In this book, we will mainly discuss heterogeneous catalysts. These are solid materials that are positioned in a reactor where they are exposed to reacting gasses or liquids. The reagents flow over the catalyst and are converted by it into products. These products and the unconverted reagents are continuously removed from the reactor, while the catalyst remains in the reactor and becomes exposed to fresh reactants. This continuous process operation is possible because the catalyst is in a separate phase.

We will focus primarily on inorganic materials, which were also the main focus of the early exploratory catalytic studies. When the molecular principles of heterogeneous catalyst activity were gradually understood, it became apparent that similarities exist between biochemical enzymatic processes and molecular organometallic catalysts. The knowledge of the molecular chemistry of the catalytic action of enzymes in biochemical systems as well as information about the action of molecular organic and metal–organic complexes has been of great importance to the further development of the molecular scientific basis of heterogeneous catalytic systems discussed later in this book.

Heterogeneous inorganic catalysts are often quite robust, which makes them especially useful for chemical reactions that operate under hostile conditions.

A specific advantage of the heterogeneous catalyst is that it can be used in a continuous process operation, instead of in a batch-type process where it must be separated in an individual step from the reaction product. Continuous process operation made the development of the large-scale chemical process industry possible once heterogeneous catalysis was discovered early in the previous
century. Heterogeneous catalysis has become basic to more than 80% of current bulk chemical processes used in the chemical and petrochemical industries [1].

The modern science of heterogeneous catalytic chemistry developed as the understanding of its chemical basis at a molecular level increased. The current understanding of the catalytic reaction mechanism at the physical and chemical levels and its relation to the structure and composition of heterogeneous catalysts is based to a large extent on the computational catalytic results obtained during the past decades. The ultimate aim of catalysis science is to predict the proper catalytic material for a given chemical conversion reaction. This is still far off due to the complexity of experimental catalytic systems, but the large body of empirical chemical information currently available about the reactivity of different catalytic materials is helpful. Computational methods provide tools for estimating the rate and selectivity of a catalytic reaction as a function of catalyst composition. In addition to spectroscopic characterization of a catalyst, this has become indispensable for research.

In this chapter, we will describe the discovery of the basic principles of heterogeneous catalysis. The next chapters will provide an introduction to current catalytic processes, followed by chapters on the principles of physical chemistry and inorganic chemistry of heterogeneous catalysis that are the basis of modern catalysis science.

The discovery of quantum mechanics provided the chemical sciences a predictive foundation, which led to the development of computational catalysis. Combined with the application of advanced spectroscopic techniques and advances in material synthesis, this discovery has provided the molecular foundation of heterogeneous catalysis that is the main topic of part II of this book.

1.2 Early Developments

In its infancy, the science of chemistry was highly exploratory and focused primarily on the categorization of chemical materials and their properties. Heterogeneous catalysis science started in that early period of modern chemistry, before the understanding of the molecular nature of matter. It has its origin in the early part of the nineteenth century, after the founding of modern chemistry by