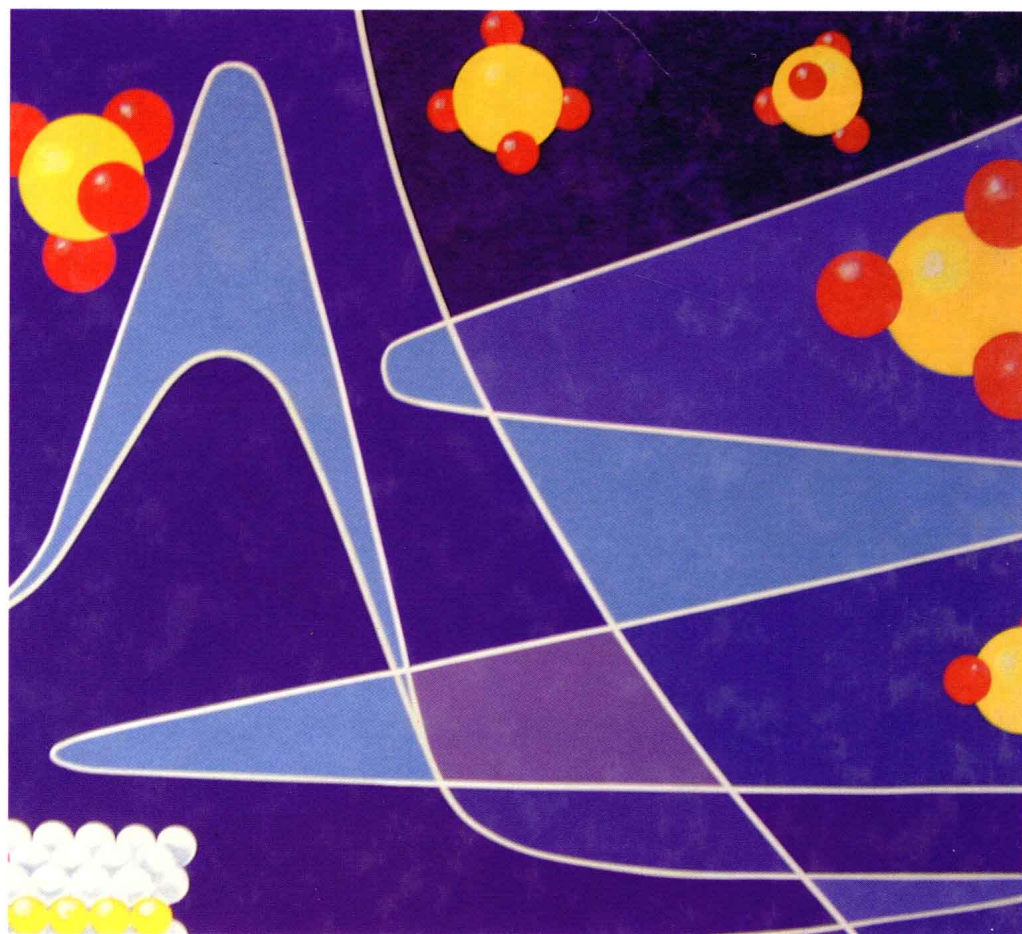


I. Chorkendorff, J. W. Niemantsverdriet

 WILEY-VCH

# Concepts of Modern Catalysis and Kinetics



*I. Chorkendorff, J. W. Niemantsverdriet*  
**Concepts of Modern Catalysis  
and Kinetics**

### ***Also of Interest:***

Niemantsverdriet, J. W.

#### **Spectroscopy in Catalysis**

##### **An Introduction**

Second, Completely Revised Edition

2000

3-527-30200-X

Hagen, J., Hawkins, S.

#### **Industrial Catalysis**

##### **A Practical Approach**

1999

ISBN 3-527-29528-3

Thomas, J. M., Thomas, W. J.

#### **Principles and Practice of Heterogeneous Catalysis**

1996

ISBN 3-527-29239-X

Green, M. M., Wittcoff, H.

#### **Organic Chemistry Principles and Industrial Practice**

2003

ISBN 3-527-30289-1

Wijngaarden, R. I., Westerterp, K. R., Kronberg, A.

#### **Industrial Catalysis**

##### **Optimizing Catalysts and Processes**

1998

ISBN 3-527-28581-4

**Prof. Dr. I. Chorkendorff**

Technical University of Denmark  
Interdisciplinary Research Center for Catalysis (ICAT)  
Building 312  
DK 2800 Lyngby  
Denmark

**Prof. Dr. J. W. Niemantsverdriet**

Eindhoven University of Technology  
Schuit Institute of Catalysis  
NL 5600 MB Eindhoven  
The Netherlands

**Cover illustration**

Artistic view of surface reaction and potential energy barriers. Painted by Ove Broo, reproduced with kind permission.

■ This book was carefully produced. Nevertheless, authors and publisher do not warrant the information contained therein to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

**Library of Congress Card No.:**

Applied for.

**British Library Cataloguing-in-Publication Data**

A catalogue record for this book is available from the British Library.

**Bibliographic information published by**

**Die Deutsche Bibliothek**

Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie, detailed bibliographic data is available in the Internet at <<http://dnb.ddb.de>>.

© 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

All rights reserved (including those of translation in other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publisher. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Printed in the Federal Republic of Germany  
Printed on acid-free paper.

**Composition** Kühn & Weyh, Freiburg

**Printing** Strauss Offsetdruck, Mörlenbach

**Bookbinding** Litges & Dopf Buchbinderei GmbH, Heppenheim

**ISBN** 3-527-30574-2

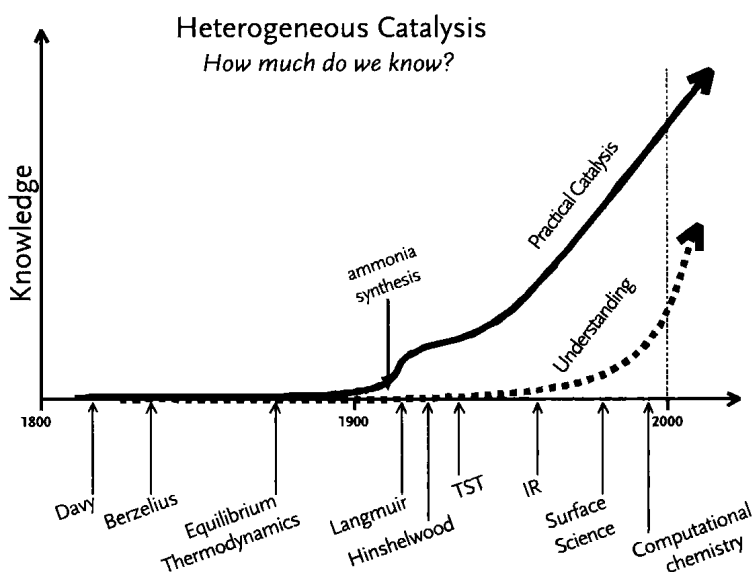
*To Ina and Camilla*

*To Marianne, Hanneke,  
Annemieke, Karin and Peter*

## Preface

### Catalysis: conceptually understood but far away from maturity

Catalysis as a phenomenon is becoming reasonably well understood on a conceptual level. Recognized as a phenomenon and utilized around 1816 by Davy in the mine safety lamp, and defined around 1835 by Berzelius, catalysis obtained an extensive empirical basis by the systematic experiments of Mittasch in the early 20<sup>th</sup> century. Studies of catalytic mechanisms became feasible when Langmuir – Hinshelwood kinetics became available in the mid 1920s. Since then, for many decades fundamental catalysis became more or less synonymous with kinetic analysis. The advent of spectroscopy, starting with infrared spectroscopy in the late 1950s, followed by a range of other techniques for catalyst characterization and investigation of surface species opened the opportunity to relate catalytic properties with composition and structure of materials. Surface science enabled one to resolve adsorption geometries and reactivity patterns in well-defined structures, culminating in scanning tunneling spectroscopy as the ultimate tool to resolve surface structure and adsorbed spe-



cies with atomic precision by the end of the 20<sup>th</sup> century. Techniques have become available to study catalysts under working conditions. Ever increasing computational power enables the calculation of adsorbate geometries, bond strengths and even reaction rates. Anno 2003, catalysis has developed into a scientific discipline with a firm conceptual basis. The relation between catalytic activity for a certain reaction and the composition, structure of a surface is in general qualitatively well understood, provided the surfaces are relatively simple and defined.

However, the prospect of designing a catalyst from first principles behind our desk is still far away. A number of reasons is responsible. Although we may be able to describe a catalytic reaction on a well-defined single crystal of a metal under well-defined and simplified conditions, this becomes tremendously more complicated when the same reaction runs over small catalyst particles on a support in a realistic reactor environment. The world of the ideal surface science laboratory and that of industrial practice are not only separated by the often cited pressure gap, but also by structural, and materials gaps. The complexity of small, supported crystallites that dynamically respond to every change in reaction environment is only beginning to be explored. Secondly, the way we describe the kinetics of catalytic reactions is, albeit greatly refined, still based on the adsorption isotherm of Langmuir (1915) and the kinetic formalism of Hinshelwood (1927), based on ideal surfaces with equivalent adsorption sites and adsorbate species that are randomly mixed and do not interact. This represents another gross over simplification, which has recently become recognized and is beginning to become addressed in terms of ensembles with reactivities many orders of magnitude more reactive than the planar surfaces.

This book intends to be an introduction to the fundamentals of heterogeneous catalysis, aiming to explain the phenomenon of catalysis on a conceptual level. Kinetics, being the tool to investigate and describe catalytic reactivity as it expresses itself in a reactor, plays an important role in this book. Also reaction rate theory, providing the formalism to relate reaction rates to molecular structure of reacting species is described extensively. Next we describe catalytic surfaces, as well as the tools to study them. With this knowledge we treat surface reactivity in greatly simplified molecular orbital theory, again with the aim to give a conceptual explanation of how a catalyst works and what are the trends when going from one surface/structure to another. The final chapters serve to illustrate catalysis in practice, to give the reader an impression of how catalysis is applied. We emphasize that the book is a textbook, written for students in chemistry, physics and chemical engineering who are interested in understanding the concepts. Many more important details are worthwhile knowing, but are beyond the scope of this book and will have to be found in specialist literature.

This book is based on courses, which the authors have taught at Lyngby and Eindhoven for many years. For example, Chapters 1–3 form the basis for a mandatory course “Kinetics and Catalysis” presented in the second year of the Bachelor’s curriculum at Eindhoven, while Chapters 4,5 and 8–10 formed the basis for an optional course Introduction to Catalysis. In Lyngby, Chapters 1–7 have been used for an optional course in “Chemical Reaction Kinetics and Catalysis” in the Master’s curriculum. At the end of the book we have added a list of questions for every chapter,

which students may use to test their knowledge. The exercises are mainly meant to enable students to acquire skills in kinetic modelling. Some of these exercises have been used in written examinations. We intend to make solutions available on our web sites ([www.icat.dtu.dk](http://www.icat.dtu.dk) and [www.catalysis.nl](http://www.catalysis.nl)).

The authors are indebted to many colleagues in the field of catalysis and surface science. We mention in particular Jens Nørskov and Rutger van Santen. Both made very substantial contributions to the theory of heterogeneous catalysis. We are very grateful for the many extensive and pleasant discussions we had with them. Also our contacts with industry have been most inspiring and indispensable. We mention in particular Haldor Topsøe A/S in Lyngby and the Shell Research and Technology Centre in Amsterdam. We also want to thank the numerous students who followed our courses in Lyngby and Eindhoven. They have taught us more than they perhaps realize. Finally we thank our families who patiently allowed us to spend a considerable amount of time on this book. We devote this book to them.

Lyngby/Eindhoven  
June 2003

*Ib Chorkendorff*  
*Hans Niemantsverdriet*



## Contents

<b>1</b>	<b>Introduction to Catalysis</b>	<b>1</b>
1.1	What is Catalysis?	2
1.2	Catalysts Can Be Atoms, Molecules, Enzymes and Solid Surfaces	4
1.2.1	Homogeneous Catalysis	4
1.2.2	Biocatalysis	5
1.2.3	Heterogeneous Catalysis	6
1.3	Why is Catalysis Important?	8
1.3.1	Catalysis and Green Chemistry	8
1.3.2	Atom Efficiency, <i>E</i> Factors and Environmental Friendliness	9
1.3.3	The Chemical Industry	11
1.4	Catalysis as a Multidisciplinary Science	16
1.4.1	The Many Length Scales of a “Catalyst”	16
1.4.2	Time Scales in Catalysis	17
1.5	The Scope of This Book	18
1.6	Catalysis in Journals	18
1.7	General References to Textbooks in Catalysis	21
<b>2</b>	<b>Kinetics</b>	<b>23</b>
2.1	Introduction	23
2.2	The Rate Equation and Power Rate Laws	25
2.3	Reactions and Thermodynamic Equilibrium	28
2.3.1	Example of Chemical Equilibrium: The Ammonia Synthesis	31
2.3.2	Chemical Equilibrium for a Non-ideal Gas	34
2.4	Temperature Dependence of the Rate	36
2.5	Integrated Rate Equations: Time Dependence of Concentrations in Reactions of Different Orders	38
2.6	Coupled Reactions in Flow Reactors: The Steady-state Approximation	41
2.7	Coupled Reactions in Batch Reactors	45
2.8	Catalytic Reactions	48
2.8.1	The Mean-field Approximation	52
2.9	Langmuir Adsorption Isotherms	53
2.9.1	Associative Adsorption	53
2.9.2	Dissociative Adsorption	55

2.9.3	Competitive Adsorption	55
2.10	Reaction Mechanisms	56
2.10.1	Langmuir–Hinshelwood or Eley–Rideal Mechanisms	56
2.10.2	Langmuir–Hinshelwood Kinetics	57
2.10.3	The Complete Solution	58
2.10.4	The Steady State Approximation	59
2.10.5	The Quasi-equilibrium Approximation	59
2.10.6	Steps with Similar Rates	61
2.10.7	Irreversible Step Approximation	61
2.10.8	The MARI Approximation	62
2.10.9	Nearly Empty Surface	62
2.10.10	Reaction Order	63
2.10.11	Apparent Activation Energy	65
2.11	Entropy, Entropy Production, Auto Catalysis and Oscillating Reactions	69
2.12	Kinetics of Enzyme-catalyzed Reactions	73
<b>3</b>	<b>Reaction Rate Theory</b>	<b>79</b>
3.1	Introduction	79
3.2	The Boltzmann Distribution and the Partition Function	80
3.3	Partition Functions of Atoms and Molecules	83
3.3.1	The Boltzmann Distribution	84
3.3.1.1	Justification for Equating $\lambda_2$ with $1/T$	86
3.3.2	Maxwell–Boltzmann Distribution of Velocities	86
3.3.3	Total Partition Function of System	87
3.3.3.1	Translational Partition Function	88
3.3.3.2	Vibrational Partition Function	89
3.3.3.3	Rotational (and Nuclear) Partition Function	90
3.3.3.4	Electronic and Nuclear Partition Functions	92
3.4	Molecules in Equilibrium	94
3.5	Collision Theory	100
3.5.1	Rate of Surface Collisions	103
3.5.2	Reaction Probability	104
3.5.3	Fundamental Objection Against Collision Theory	106
3.6	Activation of Reacting Molecules by Collisions: The Lindemann Theory	106
3.7	Transition State Theory	108
3.7.1	Thermodynamic Form of the Rate Transition State Expression	110
3.8	Transition State Theory of Surface Reactions	113
3.8.1	Adsorption of Atoms	113
3.8.1.1	Indirect Adsorption	114
3.8.1.2	Direct Adsorption	116
3.8.2	Adsorption of Molecules	119
3.8.2.1	Precursor-mediated or Indirect Adsorption	119

3.8.2.2	Direct Adsorption	120
3.8.3	Reaction Between Adsorbates	122
3.8.4	Desorption of Molecules	123
3.9	Summary	126
<b>4</b>	<b>Catalyst Characterization</b>	<b>129</b>
4.1	Introduction	129
4.2	X-Ray Diffraction (XRD)	131
4.3	X-ray Photoelectron Spectroscopy (XPS)	134
4.4	Extended X-Ray Absorption Fine Structure (EXAFS)	139
4.5	Electron Microscopy	143
4.6	Mössbauer Spectroscopy	147
4.7	Ion Spectroscopy: SIMS, LEIS, RBS	150
4.8	Temperature-programmed Reduction, Oxidation and Sulfidation	154
4.9	Infrared Spectroscopy	155
4.10	Surface Science Techniques	158
4.10.1	Low Energy Electron Diffraction (LEED)	158
4.10.2	Scanning Probe Microscopy	161
4.10.2.1	Scanning Tunneling Microscopy (STM)	161
4.10.2.2	The Atomic Force Microscope (AFM)	164
4.11	Concluding Remarks	166
<b>5</b>	<b>Solid Catalysts</b>	<b>167</b>
5.1	Requirements of a Successful Catalyst	167
5.2	Structure of Metals, Oxides and Sulfides and their Surfaces	168
5.2.1	Metal Structures	168
5.2.2	Surface Crystallography of Metals	168
5.2.2.1	Crystal Planes	169
5.2.2.2	Adsorbate Sites	171
5.2.2.3	The Two-dimensional Lattice	172
5.2.3	Oxides and Sulfides	174
5.2.4	Surface Free Energy	177
5.3	Characteristics of Small Particles and Porous Material	178
5.3.1	Wulff Construction	180
5.3.2	Pore System	182
5.3.3	Surface Area	183
5.4	Catalyst Supports	189
5.4.1	Silica	190
5.4.2	Alumina	192
5.4.3	Carbon	194
5.4.4	Shaping of Catalyst Supports	194
5.5	Preparation of Supported Catalysts	195
5.5.1	Coprecipitation	195
5.5.2	Impregnation, Adsorption and Ion-exchange	196
5.5.3	Deposition Precipitation	198

5.6	Unsupported Catalysts	198
5.7	Zeolites	199
5.7.1	Structure of a Zeolite	200
5.7.2	Compensating Cations and Acidity	201
5.7.3	Applications of Zeolites	202
5.8	Catalyst Testing	203
5.8.1	Ten Commandments for Testing Catalysts	204
5.8.2	Activity Measurements	206
5.8.2.1	Transport Limitations and the Thiele Diffusion Modulus	206
5.8.2.2	Pore Diffusion	211
5.8.2.3	Consequences of Transport Limitations for Testing Catalysts	213
<b>6</b>	<b>Surface Reactivity</b>	<b>215</b>
6.1	Introduction	215
6.2	Physisorption	215
6.2.1	The Van der Waals Interaction	216
6.2.2	Including the Repulsive Part	217
6.3	Chemical Bonding	218
6.3.1	Bonding in Molecules	219
6.3.1.1	Diatomic Molecule	219
6.3.1.2	Homonuclear Diatomic Molecules	220
6.3.1.3	Heteronuclear System	222
6.3.2	The Solid Surface	223
6.3.2.1	Work Function	225
6.3.2.2	Free Electron Gas and the Jellium Model	226
6.3.2.3	Tight Binding Model	229
6.3.2.4	Simple Model of a Transition Metal	233
6.4	Chemisorption	235
6.4.1	Newns–Anderson Model	236
6.4.1.1	Case 1: Atom on a Metal of Constant Electron Density	239
6.4.1.2	Case 2: Atom on an sp Metal	240
6.4.1.3	Case 3: Atom on a Transition Metal	241
6.4.2	Summary of Newns–Anderson Approximation in Qualitative Terms	242
6.4.2.1	Adsorption on a Free-electron Metal	242
6.4.2.2	Atomic Adsorption on a Transition or d Metal	242
6.4.2.3	Adsorption of a Molecule on a Transition Metal	243
6.4.3	Electrostatic Effects in Atomic Adsorbates on Jellium	244
6.5	Important Trends in Surface Reactivity	246
6.5.1	Trend in Atomic Chemisorption Energies	246
6.5.2	Trends in Molecular Chemisorption	250
6.5.2.1	Effects of Stress and Strain on Chemisorption	252
6.5.3	Trends in Surface Reactivity	254
6.5.3.1	Physisorption, Chemisorption and Dissociation	254
6.5.3.2	Dissociative Adsorption: N <sub>2</sub> on Ruthenium Surfaces	255
6.5.3.3	Trends in Dissociative Adsorption	256

6.5.3.4	Transition States and the Effect of Coverage: Ethylene Hydrogenation	258
6.5.3.5	Sabatier's Principle	261
6.5.3.6	Opportunities for Tuning Surface Reactivity	262
6.5.4	Universality in Heterogeneous Catalysis	263
<b>7</b>	<b>Kinetics of Reactions on Surfaces</b>	<b>267</b>
7.1	Elementary Surface Reactions	267
7.1.1	Adsorption and Sticking	267
7.1.1.1	Determination of Sticking Coefficients	268
7.1.2	Desorption	274
7.1.2.1	Quantitative Interpretation of TPD Data	276
7.1.2.2	Compensation Effect in Temperature Programmed Desorption	278
7.1.3	Lateral Interactions in Surface Reactions	279
7.1.4	Dissociation Reactions on Surfaces	282
7.1.5	Intermediates in Surface Reactions	285
7.1.6	Association Reactions	285
7.2	Kinetic Parameters from Fitting Langmuir–Hinshelwood Models	288
7.3	Micro-kinetic Modeling	290
7.3.1	Reaction Scheme and Rate Expressions	291
7.3.2	Activation Energy and Reaction Orders	293
7.3.3	Ammonia Synthesis Catalyst under Working Conditions	297
<b>8</b>	<b>Heterogeneous Catalysis in Practice: Hydrogen</b>	<b>301</b>
8.1	Introduction	301
8.2	Steam Reforming Process	301
8.2.1	Basic Concepts of the Process	301
8.2.1	Mechanistic Details of Steam Reforming	304
8.2.3	Challenges in the Steam Reforming Process	305
8.2.4	The SPARG Process: Selective Poisoning by Sulfur	307
8.2.5	Gold–Nickel Alloy Catalysts for Steam Reforming	308
8.2.6	Direct Uses of Methane	309
8.2.6.1	Direct Methanol Formation	310
8.2.6.2	Catalytic Partial Oxidation of Methane	311
8.3	Reactions of Synthesis Gas	311
8.3.1	Methanol Synthesis	311
8.3.1.1	Basic Concepts of the Process	311
8.3.1.2	Methanol Directly Synthesized from CO and H <sub>2</sub>	319
8.3.2	Fischer–Tropsch Process	323
8.4	Water Gas Shift Reaction	325
8.5	Synthesis of Ammonia	327
8.5.1	History of Ammonia Synthesis	327
8.5.2	Ammonia Synthesis Plant	329
8.5.3	Operating the Reactor	331
8.5.4	Scientific Rationale for Improving Catalysts	333

8.6	Promoters and Inhibitors	335
8.7	The “Hydrogen Society”	338
8.7.1	The Need for Sustainable Energy	338
8.7.2	Sustainable Energy Sources	340
8.7.3	Hydrogen and Fuel Cells	341
8.7.3.1	The Proton Exchange Membrane Fuel Cell (PEMFC)	342
8.7.3.2	Solid Oxide Fuel Cell	345
8.7.3.3	Efficiency of Fuel Cells	345
8.7.3.4	Hydrogen Storage and Transportation	347
<b>9</b>	<b>Oil Refining and Petrochemistry</b>	<b>349</b>
9.1	Crude Oil	349
9.2	Hydrotreating	353
9.2.1	Heteroatoms and Undesired Compounds	353
9.2.2	Hydrotreating Catalysts	355
9.2.3	Hydrosulfurization Reaction Mechanisms	357
9.3	Gasoline Production	360
9.3.1	Fluidized Catalytic Cracking	361
9.3.2	Reforming and Bifunctional Catalysis	364
9.3.3	Alkylation	368
9.4	Petrochemistry: Reactions of Small Olefins	370
9.4.1	Ethylene Epoxidation	370
9.4.2	Partial Oxidation and Ammoxidation of Propylene	372
9.4.3	Polymerization Catalysis	374
<b>10</b>	<b>Environmental Catalysis</b>	<b>377</b>
10.1	Introduction	377
10.2	Automotive Exhaust Catalysis	377
10.2.1	The Three-way Catalyst	379
10.2.1.1	Catalytic Converter	381
10.2.1.2	Demonstration Experiments	384
10.2.1.3	Catalyst Deactivation	384
10.2.2	Catalytic Reactions in the Three-way Catalyst: Mechanism and Kinetics	385
10.2.2.1	CO Oxidation Reaction	385
10.2.2.2	Is CO Oxidation a Structure-insensitive Reaction?	387
10.2.2.3	CO + NO Reaction	388
10.2.2.4	CO + NO Reaction at Higher Pressures	390
10.2.2.5	Reactions Involving Hydrocarbons	391
10.2.2.6	NO <sub>x</sub> Storage–Reduction Catalyst for Lean-burning Engines	391
10.2.3	Concluding Remarks on Automotive Catalysts	393
10.3	Air Pollution by Large Stationary Sources	393
10.3.1	Selective Catalytic Reduction: The SCR Process	393
10.3.3.1	Catalyst for the SCR Process	395

10.3.1.2	SCR Reaction Kinetics	396
10.3.2	SCR Process for Mobile Units	400

<b>Questions and Exercises</b>	<b>401</b>
--------------------------------	------------

<b>Appendix A</b>	<b>443</b>
-------------------	------------

<b>Index</b>	<b>447</b>
--------------	------------

## Introduction to Catalysis

Ask the average person in the street what a catalyst is, and he or she will probably tell you that a catalyst is what one has under the car to clean up the exhaust. Indeed, the automotive exhaust converter represents a very successful application of catalysis; it does a great job in removing most of the pollutants from the exhaust leaving the engines of cars. However, catalysis has a much wider scope of application than abating pollution.

### Catalysis in Industry

Catalysts are the workhorses of chemical transformations in the industry. Approximately 85–90 % of the products of chemical industry are made in catalytic processes. Catalysts are indispensable in

- Production of transportation fuels in one of the approximately 440 oil refineries all over the world
- Production of bulk and fine chemicals in all branches of chemical industry
- Prevention of pollution by avoiding formation of waste (unwanted byproducts)
- Abatement of pollution in end-of-pipe solutions (automotive and industrial exhaust)

A catalyst offers an alternative, energetically favorable mechanism to the non-catalytic reaction, thus enabling processes to be carried out under industrially feasible conditions of pressure and temperature.

For example, living matter relies on enzymes, which are the most specific catalysts one can think of. Also, the chemical industry cannot exist without catalysis, which is an indispensable tool in the production of bulk chemicals, fine chemicals and fuels.

For scientists and engineers catalysis is a tremendously challenging, highly multidisciplinary field. Let us first see what catalysis is, and then why it is so important for mankind.

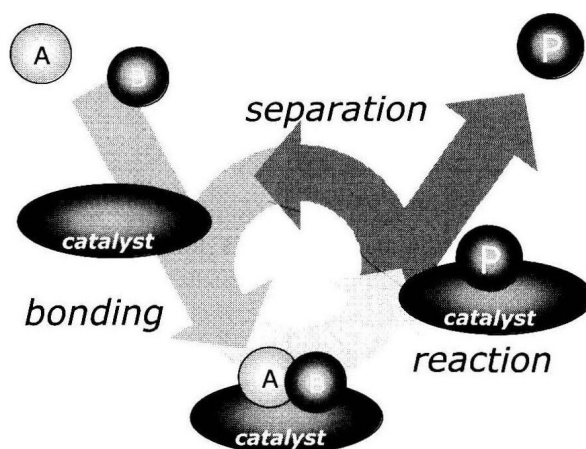


## 1.1

**What is Catalysis?**

A catalyst accelerates a chemical reaction. It does so by forming bonds with the reacting molecules, and by allowing these to react to a product, which detaches from the catalyst, and leaves it unaltered such that it is available for the next reaction. In fact, we can describe the catalytic reaction as a cyclic event in which the catalyst participates and is recovered in its original form at the end of the cycle.

Let us consider the catalytic reaction between two molecules A and B to give a product P, see Fig. 1.1. The cycle starts with the bonding of molecules A and B to the catalyst. A and B then react within this complex to give a product P, which is also bound to the catalyst. In the final step, P separates from the catalyst, thus leaving the reaction cycle in its original state.



**Figure 1.1.** Every catalytic reaction is a sequence of elementary steps, in which reactant molecules bind to the catalyst, where they react, after which the product detaches from the catalyst, liberating the latter for the next cycle.

To see how the catalyst accelerates the reaction, we need to look at the potential energy diagram in Fig. 1.2, which compares the non-catalytic and the catalytic reaction. For the non-catalytic reaction, the figure is simply the familiar way to visualize the Arrhenius equation: the reaction proceeds when A and B collide with sufficient energy to overcome the activation barrier in Fig. 1.2. The change in Gibbs free energy between the reactants,  $A + B$ , and the product P is  $\Delta G$ .

The catalytic reaction starts by bonding of the reactants A and B to the catalyst, in a spontaneous reaction. Hence, the formation of this complex is exothermic, and the free energy is lowered. There then follows the reaction between A and B while they are bound to the catalyst. This step is associated with an activation energy; however, it is significantly lower than that for the uncatalyzed reaction. Finally, the product P separates from the catalyst in an endothermic step.