

*I. Chorkendorff, J. W. Niemantsverdriet*

# Concepts of Modern Catalysis and Kinetics

Second, Revised and Enlarged Edition



WILEY-VCH Verlag GmbH & Co. KGaA

## Contents

### Preface XV

<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	15
1.4.1	The Many Length Scales of a “Catalyst”	15
1.4.2	Time Scales in Catalysis	17
1.5	The Scope of This Book	17
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	46
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	87
3.3.3	Total Partition Function of System	87
3.3.3.1	Translational Partition Function	88
3.3.3.2	Vibrational Partition Function	90
3.3.3.3	Rotational (and Nuclear) Partition Function	91
3.3.3.4	Electronic and Nuclear Partition Functions	92
3.4	Molecules in Equilibrium	93
3.5	Collision Theory	101
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	107
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	114
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 124
- 3.9 Summary 127
  
- 4 Catalyst Characterization 129**
  - 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
  
- 5 Solid Catalysts 167**
  - 5.1 Requirements of a Successful Catalyst 167
  - 5.2 Structure of Metals, Oxides and Sulfides and Their Surfaces 169
    - 5.2.1 Metal Structures 169
    - 5.2.2 Surface Crystallography of Metals 170
      - 5.2.2.1 Crystal Planes 170
      - 5.2.2.2 Adsorbate Sites 173
      - 5.2.2.3 The Two-dimensional Lattice 174
    - 5.2.3 Oxides and Sulfides 176
    - 5.2.4 Surface Free Energy 178
  - 5.3 Characteristics of Small Particles and Porous Material 180
    - 5.3.1 Wulff Construction 180
    - 5.3.2 Pore System 184
    - 5.3.3 Surface Area 185
  - 5.4 Catalyst Supports 190
    - 5.4.1 Silica 191
    - 5.4.2 Alumina 193
    - 5.4.3 Carbon 195
    - 5.4.4 Shaping of Catalyst Supports 195
  - 5.5 Preparation of Supported Catalysts 196
    - 5.5.1 Coprecipitation 197
    - 5.5.2 Impregnation, Adsorption and Ion-exchange 197
    - 5.5.3 Deposition Precipitation 199

5.6	Unsupported Catalysts	199
5.7	Zeolites	200
5.7.1	Structure of a Zeolite	201
5.7.2	Compensating Cations and Acidity	202
5.7.3	Applications of Zeolites	203
5.8	Catalyst Testing	204
5.8.1	Ten Commandments for Testing Catalysts	205
5.8.2	Activity Measurements	207
5.8.2.1	Transport Limitations and the Thiele Diffusion Modulus	207
5.8.2.2	Pore Diffusion	212
5.8.2.3	Consequences of Transport Limitations for Testing Catalysts	214
<b>6</b>	<b>Surface Reactivity</b>	<b>217</b>
6.1	Introduction	217
6.2	Physisorption	217
6.2.1	The Van der Waals Interaction	218
6.2.2	Including the Repulsive Part	219
6.3	Chemical Bonding	220
6.3.1	Bonding in Molecules	221
6.3.1.1	Diatomic Molecule	221
6.3.1.2	Homonuclear Diatomic Molecules	222
6.3.1.3	Heteronuclear System	223
6.3.2	The Solid Surface	226
6.3.2.1	Work Function	227
6.3.2.2	Free Electron Gas and the Jellium Model	228
6.3.2.3	Tight Binding Model	232
6.3.2.4	Simple Model of a Transition Metal	235
6.4	Chemisorption	237
6.4.1	Newns–Anderson Model	238
6.4.1.1	Case 1: Atom on a Metal of Constant Electron Density	241
6.4.1.2	Case 2: Atom on an sp Metal	242
6.4.1.3	Case 3: Atom on a Transition Metal	243
6.4.2	Summary of Newns–Anderson Approximation in Qualitative Terms	243
6.4.2.1	Adsorption on a Free-electron Metal	244
6.4.2.2	Atomic Adsorption on a Transition or d Metal	244
6.4.2.3	Adsorption of a Molecule on a Transition Metal	245
6.4.3	Electrostatic Effects in Atomic Adsorbates on Jellium	246
6.5	Important Trends in Surface Reactivity	248
6.5.1	Trend in Atomic Chemisorption Energies	249
6.5.2	Trends in Molecular Chemisorption	253
6.5.2.1	Effects of Stress and Strain on Chemisorption	255
6.5.3	Trends in Surface Reactivity	257
6.5.3.1	Physisorption, Chemisorption and Dissociation	257
6.5.3.2	Dissociative Adsorption: N <sub>2</sub> on Ruthenium Surfaces	258
6.5.3.3	Trends in Dissociative Adsorption	259

6.5.3.4	Transition States and the Effect of Coverage: Ethylene Hydrogenation	261
6.5.3.5	Sabatier's Principle	264
6.5.3.6	Opportunities for Tuning Surface Reactivity	265
6.5.4	Universality in Heterogeneous Catalysis	266
<b>7</b>	<b>Kinetics of Reactions on Surfaces</b>	<b>271</b>
7.1	Elementary Surface Reactions	271
7.1.1	Adsorption and Sticking	271
7.1.1.1	Determination of Sticking Coefficients	272
7.1.2	Desorption	278
7.1.2.1	Quantitative Interpretation of TPD Data	280
7.1.2.2	Compensation Effect in Temperature Programmed Desorption	282
7.1.3	Lateral Interactions in Surface Reactions	283
7.1.4	Dissociation Reactions on Surfaces	286
7.1.5	Intermediates in Surface Reactions	289
7.1.6	Association Reactions	290
7.2	Kinetic Parameters from Fitting Langmuir–Hinshelwood Models	292
7.3	Micro-kinetic Modeling	295
7.3.1	Reaction Scheme and Rate Expressions	295
7.3.2	Activation Energy and Reaction Orders	297
7.3.3	Ammonia Synthesis Catalyst under Working Conditions	301
<b>8</b>	<b>Heterogeneous Catalysis in Practice: Hydrogen</b>	<b>305</b>
8.1	Introduction	305
8.2	Steam Reforming Process	305
8.2.1	Basic Concepts of the Process	305
8.2.1	Mechanistic Details of Steam Reforming	308
8.2.3	Challenges in the Steam Reforming Process	309
8.2.4	The SPARG Process: Selective Poisoning by Sulfur	311
8.2.5	Gold–Nickel Alloy Catalysts for Steam Reforming	312
8.2.6	Direct Uses of Methane	313
8.2.6.1	Direct Methanol Formation	314
8.2.6.2	Catalytic Partial Oxidation of Methane	315
8.3	Reactions of Synthesis Gas	315
8.3.1	Methanol Synthesis	315
8.3.1.1	Basic Concepts of the Process	315
8.3.1.2	Methanol Directly Synthesized from CO and H <sub>2</sub>	323
8.3.2	Fischer–Tropsch Process	327
8.4	Water Gas Shift Reaction	330
8.5	Synthesis of Ammonia	331
8.5.1	History of Ammonia Synthesis	331
8.5.2	Ammonia Synthesis Plant	333
8.5.3	Operating the Reactor	335
8.5.4	Scientific Rationale for Improving Catalysts	337
8.6	Promoters and Inhibitors	339

8.7	The “Hydrogen Society”	343
8.7.1	The Need for Sustainable Energy	343
8.7.2	Sustainable Energy Sources	344
8.7.3	Hydrogen and Fuel Cells	346
8.7.3.1	The Proton Exchange Membrane Fuel Cell (PEMFC)	346
8.7.3.2	Solid Oxide Fuel Cell	349
8.7.3.3	Efficiency of Fuel Cells	350
8.7.3.4	Hydrogen Storage and Transportation	351
<b>9</b>	<b>Oil Refining and Petrochemistry</b>	<b>353</b>
9.1	Crude Oil	353
9.2	Hydrotreating	357
9.2.1	Heteroatoms and Undesired Compounds	357
9.2.2	Hydrotreating Catalysts	359
9.2.3	Hydrodesulfurization Reaction Mechanisms	361
9.3	Gasoline Production	364
9.3.1	Fluidized Catalytic Cracking	365
9.3.2	Reforming and Bifunctional Catalysis	368
9.3.3	Alkylation	372
9.4	Petrochemistry: Reactions of Small Olefins	374
9.4.1	Ethylene Epoxidation	374
9.4.2	Partial Oxidation and Ammoxidation of Propylene	376
9.4.3	Polymerization Catalysis	378
<b>10</b>	<b>Environmental Catalysis</b>	<b>381</b>
10.1	Introduction	381
10.2	Automotive Exhaust Catalysis	381
10.2.1	The Three-way Catalyst	383
10.2.1.1	Catalytic Converter	385
10.2.1.2	Demonstration Experiments	388
10.2.1.3	Catalyst Deactivation	388
10.2.2	Catalytic Reactions in the Three-way Catalyst: Mechanism and Kinetics	389
10.2.2.1	CO Oxidation Reaction	389
10.2.2.2	Is CO Oxidation a Structure-insensitive Reaction?	391
10.2.2.3	CO + NO Reaction	392
10.2.2.4	CO + NO Reaction at Higher Pressures	394
10.2.2.5	Reactions Involving Hydrocarbons	395
10.2.2.6	NO <sub>x</sub> Storage–Reduction Catalyst for Lean-burning Engines	395
10.2.3	Concluding Remarks on Automotive Catalysts	397
10.3	Air Pollution by Large Stationary Sources	397
10.3.1	Selective Catalytic Reduction: The SCR Process	397
10.3.1.1	Catalyst for the SCR Process	399
10.3.1.2	SCR Reaction Kinetics	401
10.3.2	SCR Process for Mobile Units	403

Questions and Exercises 405

Appendix A 447

Appendix B 448

Index 451