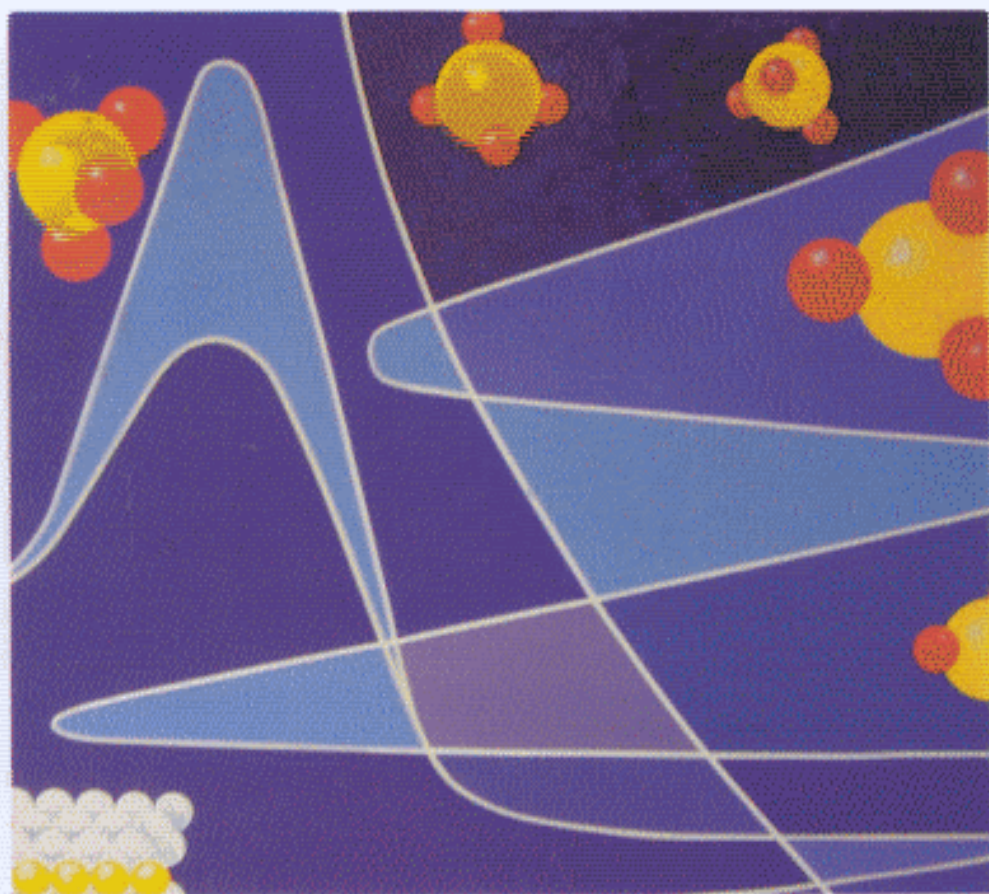


I. Chorkendorff, J. W. Niemantsverdriet

 WILEY-VCH

Concepts of Modern Catalysis and Kinetics



Contents

1	Introduction to Catalysis	1
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
2	Kinetics	23
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

3 Reaction Rate Theory 79

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 λ_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
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	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
6	Surface Reactivity	215
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 ₂ 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
7	Kinetics of Reactions on Surfaces	267
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
8	Heterogeneous Catalysis in Practice: Hydrogen	301
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 ₂	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
9	Oil Refining and Petrochemistry	349
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
10	Environmental Catalysis	377
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 _x 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
Questions and Exercises		401
Appendix A		443
Index		447