

Contents

List of Contributors XVII

Preface XXI

Part I Basic Concepts 1

1	Catalysis in Perspective: Historic Review 3
	<i>Rutger van Santen</i>
1.1	History of Catalysis Science 3
1.1.1	General Introduction 3
1.1.2	Heterogeneous Catalysis: the Relationship between a Catalyst's Performance and its Composition and Structure 4
1.1.3	Homogeneous and Enzyme Catalysis 8
1.1.4	Important Scientific Discoveries 9
1.2	The Development of Catalytic Processes: History and Future 11
1.3	Fundamental Catalysis in Practice 13
1.4	Catalyst Selection 13
1.5	Reactor Choice 16
1.6	Process Choice 17
	References 19
	Further Reading 19
2	Kinetics of Heterogeneous Catalytic Reactions 20
	<i>Rutger van Santen</i>
2.1	Physical chemical principles 20
2.1.1	The Catalytic Cycle 20
2.2	The Lock and Key Model, the Role of Adsorption Entropy 27
2.3	Equivalence of Electrocatalysis and Chemocatalysis 30
2.4	Microkinetics; the Rate-Determining Step 32
2.5	Elementary Rate Constant Expressions for Surface Reactions 34
2.6	The Pressure Gap 36
2.6.1	Surface Reconstruction 37
2.6.2	Altered Surface Reactivity 38
2.7	The Materials Gap 39

2.7.1	Structure Sensitivity	39
2.7.2	Catalyst Activation or Deactivation	40
2.7.3	Inhomogeneous Site Distribution	40
2.8	Coupling of Catalytic Reaction and Inorganic Solid Chemistry	42
2.9	<i>In situ</i> Generation of Organo-Catalyst	42
2.10	The Compensation Effect	44
	References	46
3	Kinetics in Homogeneous Catalysis	48
	<i>Detlef Heller</i>	
3.1	Principles of a Catalyst and Kinetic Description	48
3.2	Catalyst Activity	54
3.3	Catalyst Activation and Deactivation	58
3.3.1	Induction Periods as Catalyst Activation	59
3.3.2	Catalyst Deactivation due to Formation of Non-Reactive Complexes	61
3.3.3	Catalyst Deactivation due to Formation of Multinuclear Complexes	61
3.3.4	Catalyst Deactivation due to Irreversible Reactions	63
	References	64
4	Catalytic Reaction Engineering Principles	67
	<i>Albert Renken and Lioubov Kiwi-Minsker</i>	
4.1	Preface	67
4.2	Formal Kinetics of Catalytic Reactions	68
4.2.1	General Definitions	69
4.2.2	Heterogeneous Catalytic Reactions	70
4.2.3	The Langmuir Adsorption Isotherms	72
4.2.4	Reaction Mechanisms	73
4.2.4.1	Langmuir–Hinshelwood Model	74
4.2.4.2	The Quasi-Surface Equilibrium Approximation	75
4.2.4.3	The Masi Approximation	75
4.2.4.4	Bimolecular Catalytic Reactions	76
4.3	Mass and Heat Transfer Effects	77
4.3.1	Introduction	77
4.3.2	External Mass and Heat Transfer	78
4.3.2.1	Isothermal Pellet	78
4.3.2.2	Non-Isothermal Pellet	84
4.3.3	Internal Mass and Heat Transfer	85
4.3.3.1	Isothermal Pellet	87
4.3.3.2	Non-Isothermal Pellet	94
4.3.4	Combination of External and Internal Transfer Resistances	96
4.3.4.1	Internal and External Mass Transport in Isothermal Pellets	96
4.3.4.2	Implication of Mass Transfer on the Temperature Dependence	98
4.3.4.3	External and Internal Temperature Gradient	100

4.3.5	Criteria for the Estimation of Transport Effects	101
4.4	Homogenous Catalysis in Biphasic Fluid/Fluid Systems	103
	References	108

Part II The Chemistry of Catalytic Reactivity 111

5	Heterogeneous Catalysis	113
	<i>Rutger van Santen</i>	
5.1	General Introduction	113
5.2	Transition Metal Catalysis	114
5.2.1	Ammonia Synthesis	114
5.2.1.1	The Mechanism of the Reaction	114
5.2.1.2	Structure Sensitivity, Composition Dependence	114
5.2.2	Methane Reforming	120
5.2.2.1	The Mechanism of the Reaction	120
5.2.2.2	Structure Sensitivity and Composition Dependence	120
5.2.3	Hydrogenation, Dehydrogenation, and C–C Bond Cleavage	126
5.2.3.1	Mechanism of Hydrogenation and Dehydrogenation	126
5.2.3.2	Kinetics of Olefin Hydrogenation	126
5.2.3.3	The Mechanism of Ethane Hydrogenolysis	127
5.3	Solid Acids and Bases	132
5.3.1	Introduction	132
5.3.2	Proton Activation by Zeolites	135
5.3.3	General Mechanistic Considerations	139
5.3.3.1	Direct Alkane Activation	139
5.3.3.2	Hydride Transfer	141
5.3.3.3	Isomerization Catalysis	141
5.4	Reducible Oxides	143
5.4.1	Comparison of the Relative Stabilities of Some Oxides	143
5.4.2	Structure Sensitivity	145
5.4.3	Mechanism of Important Oxidation Reactions	148
5.4.3.1	The Selective Oxidation of Propylene	148
5.4.3.2	Propane Oxidation	150
	References	150
6	Homogeneous Catalysis	152
	<i>Matthias Beller, Serafino Gladiali, and Detlef Heller</i>	
6.1	General Features	152
6.1.1	Acid and Base Catalysis	155
6.1.2	Nucleophilic and Electrophilic Catalysis	157
6.1.3	Transition Metal-Centered Homogeneous Catalysis	159
	References	169

7	Biocatalysis	171
	<i>Uwe Bornscheuer</i>	
7.1	Introduction	171
7.1.1	Choice of Reaction Strategy: Kinetic Resolution or Asymmetric Synthesis	174
7.1.2	Choice of Reaction Systems	175
7.2	Examples	176
7.2.1	Oxidoreductases (EC 1)	176
7.2.1.1	Dehydrogenases (EC 1.1.1.-, EC 1.2.1.-, EC 1.4.1.-)	176
7.2.1.2	Oxygenases	178
7.2.2	Hydrolases (EC 3.1)	182
7.2.2.1	Lipases (EC 3.1.1.3) and Esterases (EC 3.1.1.1)	182
7.2.2.2	Peptidases, Acylases, and Amidases	185
7.2.2.3	Nitrilases (EC 3.5.5.1) and Nitrile Hydratases (EC 4.2.1.84)	186
7.2.2.4	Hydantoinases (EC 3.5.2.-)	187
7.2.3	Lyases (EC 4)	188
7.2.3.1	Hydroxynitrile Lyases (EC 4.1.2.-)	188
7.2.3.2	Aldolases (EC 4.1.2.-; 4.1.3.-)	190
7.2.4	Transaminases	193
7.3	Summary/Conclusions	194
	References	194
8	Electrocatalysis	201
	<i>Timo Jacob</i>	
8.1	Introduction	201
8.2	Theory	203
8.2.1	Electrochemical Potentials	203
8.2.2	Electric Double Layer	204
8.3	Application to the Oxygen Reduction Reaction (ORR) on Pt(111)	207
8.4	Summary	212
	References	213
9	Heterogeneous Photocatalysis	216
	<i>Guido Mul</i>	
9.1	Introduction	216
9.1.1	What Is Photocatalysis?	216
9.1.2	What Is the Principle of Photocatalysis?	217
9.2	Applications of Photocatalysis	219
9.3	Case Studies	220
9.3.1	Water Purification: the Quest for the Structure–Activity Relationship of TiO ₂	220
9.3.2	Energy Conversion: Advanced Materials to Go Thermodynamically Uphill!	222
9.3.2.1	Design of Crystalline Catalysts	222
9.3.2.2	The Quest for Visible Light-Sensitive Systems	223

9.3.2.3	Supported Chromophores	223
9.3.3	Photocatalysis in Practice: Some Reactor Considerations	225
9.3.3.1	Microreactors	227
9.4	Concluding Remarks	228
	References	228

Part III Industrial Catalytic Conversions 231

10	Carbonylation Reactions	233
-----------	--------------------------------	-----

Matthias Beller

10.1	General Aspects	233
10.2	Hydroformylation	234
10.3	Other Carbonylations of Olefins and Alkynes	238
10.4	Carbonylations of Alcohols and Aryl Halides	244
	References	246

11	Biocatalytic Processes	250
-----------	-------------------------------	-----

Uwe Bornscheuer

11.1	Introduction	250
11.1.1	How to Choose the Best Route?	250
11.2	Examples	253
11.2.1	General Applications	253
11.3	Case Study: Synthesis of Lipitor Building Blocks	257
11.4	Conclusions	259
	References	259

12	Polymerization	261
-----------	-----------------------	-----

Vincenzo Busico

12.1	Introduction	261
12.2	Polyolefins in Brief	262
12.3	Olefin Polymerization Catalysts	264
12.3.1	The Catalytic Species: Structure and Reactivity	264
12.3.2	Polymerization Kinetics: Active, 'Dormant' and 'Triggered' (?) Sites	269
12.4	Olefin Polymerization Process Technology	273
12.4.1	Heterogeneous Catalysis	273
12.4.2	Homogeneous Catalysis	278
12.5	The Latest Breakthroughs	280
	References	285

13	Ammonia Synthesis	289
-----------	--------------------------	-----

Jens Rostrup-Nielsen

13.1	Ammonia Plant	289
13.2	Synthesis	291
13.2.1	Technology Development	291

13.2.2	The Catalysis	292
13.2.3	Process Optimization	295
13.3	Steam Reforming	295
13.3.1	Technology	295
13.3.2	The Catalysis	296
13.3.3	Secondary Phenomena	297
13.4	Conclusions	299
	Abbreviations	299
	References	299
14	Fischer–Tropsch Synthesis in a Modern Perspective	301
	<i>Hans Schulz</i>	
14.1	Introduction	301
14.2	Stoichiometry and Thermodynamic Aspects	304
14.2.1	Stoichiometry	304
14.2.1.1	Thermodynamic Aspects	305
14.2.1.2	Rate Equations and Operation Ranges	306
14.2.1.3	Operating Ranges (Pichler)	306
14.3	Processes and Product Composition	308
14.3.1	Commercial FT-Synthesis	308
14.3.1.1	Low-Temperature Synthesis	309
14.3.1.2	Slurry Reactors	310
14.3.1.3	High-Temperature Fischer–Tropsch Synthesis	310
14.3.1.4	Synthesis Gas	311
14.4	Catalysts, General	311
14.4.1	Cobalt	312
14.4.2	Iron	312
14.5	Reaction Fundamentals	313
14.5.1	Ideal Polymerization Model	313
14.5.1.1	Chain Growth	314
14.5.1.2	Alternative Reactions on Growth Site	315
14.5.1.3	Branching	315
14.5.1.4	Alcohols in FT-Synthesis	316
14.5.1.5	Desorption (Olefins/Paraffins)	316
14.5.1.6	Catalyst Formation <i>in situ</i>	319
14.6	Concluding Remarks	323
	References	323
15	Zeolite Catalysis	325
	<i>Rutger van Santen</i>	
15.1	Introduction	325
15.2	The Hydrocracking Reaction; Acid Catalysis	325
15.2.1	The Dependence of Cracking Selectivity and Activity on Hydrocarbon Chain Length	326

15.2.2	Symmetric versus Asymmetric Cracking Patterns. Stereoselectivity, Pore Size, and Topology Dependence	328
15.3	Lewis Acid–Lewis Base Catalysis; Hydrocarbon Activation	332
15.4	Selective Oxidation; Redox Catalysis	333
15.4.1	The Reactivity of Extra-Framework Single-Site versus Two-Center Fe Oxygens	334
15.5	Framework-Substituted Redox Ions	335
15.5.1	Ti-Catalyzed Epoxidation	335
15.5.2	Thomas Chemistry; Redox Cations in the AlPO ₄ Framework	339
	References	339
16	Catalytic Selective Oxidation – Fundamentals, Consolidated Technologies, and Directions for Innovation	341
	<i>Fabrizio Cavani</i>	
16.1	Catalytic Selective Oxidation: Main Features	341
16.2	Catalytic Selective Oxidation: What Makes the Development of an Industrial Process More Challenging (and Troublesome) than Other Reactions	353
16.3	Catalytic Selective Oxidation: the Forefront in the Continuous Development of More-Sustainable Industrial Technologies	355
16.4	The Main Issue in Catalytic Oxidation: the Control of Selectivity	356
16.5	Dream Reactions in Catalytic Selective Oxidation: a Few Examples (Some Sustainable, Some Not Sustainable)	359
16.6	A New Golden Age for Catalytic Selective Oxidation?	361
16.7	Conclusions: Several Opportunities for More Sustainable Oxidation Processes	363
	References	363
17	High-Temperature Catalysis: Role of Heterogeneous, Homogeneous, and Radical Chemistry	365
	<i>Olaf Deutschmann</i>	
17.1	Introduction	365
17.2	Fundamentals	366
17.2.1	Heterogeneous Reaction Mechanisms	367
17.2.2	Homogeneous Reactions	369
17.2.3	Coupling of Chemistry with Mass and Heat Transport	369
17.2.4	Monolithic Catalysts	370
17.2.5	Experimental Evaluation of Models Describing Radical Interactions	371
17.2.6	Mathematical Optimization of Reactor Conditions and Catalyst Loading	372
17.3	Applications	372
17.3.1	Turbulent Flow through Channels with Radical Interactions	372
17.3.2	Synthesis Gas from Natural Gas by High-Temperature Catalysis	373

17.3.3	Olefin Production by High-Temperature Oxidative Dehydrogenation of Alkanes	373
17.3.3.1	Formulation of an Optimal Control Problem	375
17.4	Hydrogen Production from Logistic Fuels by High-Temperature Catalysis	378
17.5	High-Temperature Catalysis in Solid Oxide Fuel Cells	380
	References	385
18	Hydrodesulfurization	390
	<i>Roel Prins</i>	
18.1	Introduction	390
18.2	Hydrodesulfurization	391
18.3	The C-X Bond-Breaking Mechanism	393
18.4	Structure of the Sulfidic Catalyst	393
18.4.1	Structure of Mo	393
18.4.2	Structure of the Promoter	394
18.4.3	DFT Calculations	395
18.5	Hydrodenitrogenation	397
18.6	Determination of Surface Sites	398
	References	398
	Part IV Catalyst Synthesis and Materials	399
19	Molecularly Defined Systems in Heterogeneous Catalysis	401
	<i>Fernando Rascón and Christophe Copéret</i>	
19.1	Introduction	401
19.2	Single Sites: On the Border between Homogeneous and Heterogeneous Catalysis	402
19.2.1	Taking Homogeneous Catalysis to the Heterogeneous Phase via a Molecular Approach: the Case of Single-Site Alkene Metathesis Catalysts	404
19.2.2	Bridging the Gap with Classical Heterogeneous Systems by a Molecular Approach: the Case of $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ vs $\text{MeReO}_3/\text{Al}_2\text{O}_3$	408
19.2.3	Toward New Reactivity: the Case of Supported Transition-Metal Hydrides	410
19.2.4	Beyond a Molecular Viewpoint: a Closer Look at the Role of the Surfaces	413
19.3	Conclusion and Perspectives	415
	References	415
20	Preparation of Supported Catalysts	420
	<i>Krijn P. de Jong</i>	
20.1	Introduction	420
20.2	Support Surface Chemistry	422

20.3	Ion Adsorption	423
20.4	Impregnation and Drying	425
20.5	Deposition Precipitation	427
20.6	Thermal Treatment	428
	References	429
21	Porous Materials as Catalysts and Catalyst Supports	431
	<i>Petra de Jongh</i>	
21.1	General Characteristics	431
21.2	Sol-gel and Fumed Silica	433
21.3	Alumina and Other Oxides	436
21.4	Carbon Materials	438
21.5	Zeolites	440
21.6	Ordered Mesoporous Materials	442
21.7	Metal-Organic Frameworks	442
21.8	Shaping	443
	References	444
22	Development of Catalytic Materials	445
	<i>Manfred Baerns</i>	
22.1	Introduction	445
22.2	Fundamental Aspects	446
22.3	Micro-Kinetics and Solid-State Properties as a Knowledge Source in Catalyst Development	448
22.3.1	Reaction Mechanism and Kinetics of the Catalytic OCM Reaction	448
22.3.2	Surface Oxygen Species in Methane Conversion	449
22.3.3	Kinetic Analysis	450
22.3.4	Physico-Chemical Properties of Catalytic Solid Materials for the OCM Reaction	451
22.3.5	Structural Defects	451
22.3.6	Surface Acidity and Basicity	452
22.3.7	Redox Properties, Electronic Conductivity, and Ion Conductivity	452
22.3.8	Supported Catalysts	453
22.3.9	Conclusions	453
22.4	Combinatorial Approaches and High-Throughput Technologies in the Development of Solid Catalysts	453
22.4.1	Combinatorial Design of Catalytic Materials for Optimal Catalytic Performance	453
22.4.2	High-Throughput Technologies for Preparation and Testing of Large Numbers of Catalytic Materials	456
22.4.2.1	Preparation of Catalytic Materials	457
22.4.2.2	Testing and Screening of Catalytic Materials	457
22.4.3	Data Analysis	458
	References	459

	Part V Characterization Methods	463
23	<i>In-situ Techniques for Homogeneous Catalysis</i>	465
	<i>Detlef Selent and Detlef Heller</i>	
23.1	Introduction	465
23.2	<i>In-situ Techniques for Homogeneous Catalysis</i>	466
23.3	Gas Consumption and Gas Formation	467
23.4	NMR Spectroscopy	470
23.5	IR-Spectroscopy	481
23.6	UV/Vis Spectroscopy	486
23.7	Summary	490
	References	490
24	<i>In-situ Characterization of Heterogeneous Catalysts</i>	493
	<i>Bert Weckhuysen</i>	
24.1	Introduction	493
24.2	Some History, Recent Developments, and Applications	495
24.3	<i>In situ</i> Characterization of a Reactor Loaded with a Catalytic Solid	497
24.3.1	A Reactor Loaded with a Catalytic Solid Probed by One Characterization Method	497
24.3.2	A Reactor Loaded with a Catalytic Solid Probed by Multiple Characterization Methods	499
24.4	<i>In situ</i> Characterization at a Single Catalyst Particle Level	501
24.4.1	<i>In situ</i> Micro-Spectroscopy of a Catalytic Solid	501
24.4.2	Single-Molecule <i>in-situ</i> Spectroscopy of a Catalytic Solid	504
24.4.3	<i>In-situ</i> Nano-Spectroscopy of a Catalytic Solid	509
24.5	Concluding Remarks	511
	Acknowledgments	511
	References	511
25	<i>Adsorption Methods for Characterization of Porous Materials</i>	514
	<i>Evgeny Pidko and Emiel Hensen</i>	
25.1	Introduction	514
25.2	Physical Adsorption	514
25.3	Classification of Porous Materials	517
25.4	Adsorption Isotherms	517
25.5	The Application of Adsorption Methods	518
25.6	Theoretical Description of Adsorption	519
25.6.1	Langmuir Isotherm	519
25.6.2	BET Theory	521
25.6.3	Standard Isotherms and the t-Method	522
25.7	Characterization of Microporous Materials	524
25.7.1	Dubinin–Radushkevich and Dubinin–Astakhov Methods	524
25.7.2	Horvath–Kawazoe (HK) Equation	525

25.8	Characterization of Mesoporous Materials	527
25.8.1	The Kelvin equation	528
25.8.2	BJH Method	529
25.8.3	Nonlocal Density Functional Theory (NL-DFT)	530
25.9	Mercury Porosimetry	533
25.10	Xenon Porosimetry	533
	References	534
26	A Critical Review of Some “Classical” Guidelines for Catalyst Testing	536
	<i>Frits Dautzenberg</i>	
26.1	Introduction	536
26.2	Encouraging Effectiveness	536
26.3	Ensuring Efficiency	537
26.3.1	Apply Effective Experimental Strategies	538
26.3.2	Collect Meaningful Data	540
26.3.3	Select the Most Appropriate Laboratory Reactor	543
26.3.4	Establish Ideal Flow Pattern	545
26.3.5	Ensure Isothermal Conditions	546
26.3.6	Diagnose and Minimize Effects of Transport	549
26.3.7	Assess Catalyst Stability Early	551
26.4	Concluding Remarks	552
	Appendix A: Three-Phase Trickle-Bed Reactors	552
	List of Symbols and Abbreviations	558
	References	559
Part VI Catalytic Reactor Engineering 561		
27	Catalytic Reactor Engineering	563
	<i>Albert Renken and Madhvanand N. Kashid</i>	
27.1	Introduction	563
27.2	Types of Catalytic Reactors	564
27.2.1	Single-Phase Reactors	564
27.2.1.1	Stirred-Tank Reactor	564
27.2.1.2	Tubular Reactors	567
27.2.2	Fluid–Solid Reactors	568
27.2.2.1	Fixed-bed Reactors	568
27.2.2.2	Fluidized-bed Reactors	569
27.2.3	Fluid–Fluid Reactors	571
27.2.3.1	Liquid–Liquid–Gas System	573
27.2.4	Three-Phase Gas–Liquid–Solid Systems	573
27.2.4.1	Fixed-Bed Reactors	574
27.2.4.2	Slurry–Suspension Reactors	574
27.2.4.3	Structured Catalysts for Multiphase Reactions	575
27.3	Ideal Reactor Modeling/Heat Management	575

27.3.1	Mass and Energy Balances	576
27.3.2	Batchwise-Operated Stirred-Tank Reactors	578
27.3.3	Continuously Operated Ideal Stirred Tank Reactors	580
27.3.4	Ideal Plug Flow Reactor	581
27.4	Residence Time Distribution	587
27.4.1	Experimental Determination of the Residence Time Distribution	589
27.4.1.1	Step Function	589
27.4.1.2	The Pulse Function	590
27.4.2	RTD for Ideal Reactors	591
27.4.2.1	Ideal Plug Flow Reactor	591
27.4.2.2	Ideal Continuously-Operated Stirred Tank Reactor	591
27.4.2.3	Cascade of Ideally Stirred Tanks	592
27.4.2.4	Laminar Flow Reactor	593
27.4.3	RTD Models for Real Reactors	595
27.4.3.1	Dispersion Model	595
27.4.3.2	Cell Model	596
27.4.4	Estimation of the Residence Time Distribution in Tubular Reactors	597
27.4.5	Influence of RTD on Performance of Real Reactors	599
27.5	Microreaction Engineering	602
27.5.1	General Criteria for Reactor Selection	602
27.5.2	Types of Microstructured Reactors	604
27.5.2.1	Single-Phase MSR	604
27.5.2.2	Fluid–Solid MSR	607
27.5.3	Fluid–Fluid MSR	610
27.5.3.1	Gas–Liquid Systems	611
27.5.3.2	Liquid–Liquid Systems	613
27.5.3.3	Three-Phase Reactors	616
27.5.4	Heat Management in Microstructured Reactors	622
	References	625

Index 629