# Contents

Preface to the Third Edition XV Abbreviations XVII

- 1 Introduction 1
- 1.1 The Phenomenon Catalysis 1
- 1.2 Mode of Action of Catalysts 2
- 1.2.1 Activity 4
- 1.2.1.1 Turnover Frequency TOF 6
- 1.2.1.2 Turnover Number TON 7
- 1.2.2 Selectivity 7
- 1.2.3 Stability 8
- 1.2.4 Mole Balance and Conversion 8
- 1.3 Classification of Catalysts 10
- 1.4 Comparison of Homogeneous and Heterogeneous Catalysis 11
  Exercises 14
  References 15

### 2 Homogeneous Catalysis with Transition Metal Catalysts 17

- 2.1 Key Reactions in Homogeneous Catalysis 18
- 2.1.1 Coordination and Exchange of Ligands 18
- 2.1.2 Complex Formation 20
- 2.1.3 Acid–Base Reactions 22
- 2.1.4 Redox Reactions: Oxidative Addition and Reductive Elimination 23
- 2.1.4.1 Oxidative Coupling and Reductive Cleavage 27
- 2.1.5 Insertion and Elimination Reactions 28
- 2.1.5.1  $\beta$ -Elimination 30
- 2.1.5.2  $\alpha$ -Elimination 30
- 2.1.6 Reactions at Coordinated Ligands 31
- 2.2 Catalyst Concepts in Homogeneous Catalysis 32
- 2.2.1 The 16/18-Electron Rule 32
- 2.2.2 Catalytic Cycles 34
- 2.3 Characterization of Homogeneous Catalysts 35
- 2.3.1 Infrared Spectroscopy 38

VII

VIII	Contents

2.3.2	NMR Spectroscopy 40
	Exercises 42
	References 45
3	Homogeneously Catalyzed Industrial Processes 47
3.1	Overview 47
3.2	Examples of Industrial Processes 48
3.2.1	Oxo Synthesis 50
3.2.2	Production of Acetic Acid by Carbonylation of Methanol 52
3.2.3	Selective Ethylene Oxidation by the Wacker Process 55
3.2.4	Oxidation of Cyclohexane 57
3.2.5	Suzuki Coupling 58
3.2.6	Oligomerization of Ethylene (SHOP Process) 59
3.2.7	Telomerization of Butadiene 61
3.2.8	Adipodinitrile 63
3.3	Asymmetric Catalysis 63
3.3.1	Introduction 63
3.3.2	Catalysts 64
3.3.3	Commercial Applications 65
3.3.3.1	Asymmetric Hydrogenation 65
3.3.3.2	Enantioselective Isomerization: L-Menthol 67
3.3.3.3	Asymmetric Epoxidation 68
3.4	Alkene Metathesis 69
3.4.1	Examples of Heterogeneous Catalysis 72
3.5	Recycling of Homogeneous Catalysts 73
3.5.1	Overview 73
3.5.1.1	Precipitation of the Catalyst or of the Product(s) 73
3.5.1.2	Thermal Separation 73
3.5.1.3	Membrane Separation 73
3.5.1.4	Adsorption 74
3.5.1.5	Phase Separation/Extraction 74
3.5.2	Reactions in Two-Phase Liquid – Liquid Systems 74
	Exercises 76
	References 78
4	Biocatalysis 81
4.1	Introduction 81
4.1.1	Active Sites 83
4.1.2	Coenzymes 84
4.2	Kinetics of Enzyme-Catalyzed Reactions 84
4.3	Industrial Processes with Biocatalysts 90
4.3.1	Acrylamide from Acrylonitrile 90
4.3.2	Aspartame Through Enzymatic Peptide Synthesis 91
4.3.3	L-Amino Acids by Aminoacylase Process 92
4.3.4	Pharmaceuticals 93

Contents IX

4.3.5	Herbicides 95
4.3.5.1	4-Hydroxyphenoxypropionic Acid as Herbicide
	Intermediate 96
	Exercises 97
	References 97
_	
5	Heterogeneous Catalysis: Fundamentals 99
5.1	Individual Steps in Heterogeneous Catalysis 99
5.2	Kinetics and Mechanisms of Heterogeneously Catalyzed
<b>F D 1</b>	Reactions 101 The lass outer as of A decumtion in Listens sources
5.2.1	Catalysis 102
5 7 7	Vinctic Treatment 106
5.2.2	Mashaniama of Hataragan acushy Catalward Cas Dhasa
5.2.5	Reactions 108
5221	Langmuir_Hinshelwood Mechanism (1921) 109
5232	Flev_Rideal Mechanism (1943) 111
53	Catalyst Concepts in Heterogeneous Catalysis 113
531	Energetic Aspects of Catalytic Activity 113
5.3.2	Steric Effects 124
5.3.3	Electronic Factors 134
5.3.3.1	Redox Catalysts 134
5.3.3.2	Acid/Base Catalysts (Ionic Catalysts) 135
5.3.3.3	Metals 136
5.3.3.4	Bimetallic Catalysts 140
5.3.3.5	Semiconductors 144
5.3.3.6	Insulators: Acidic and Basic Catalysts 157
5.4	Catalyst Performance 164
5.4.1	Factors Which Affect the Catalyst Performance 164
5.4.2	Supported Catalysts 166
5.4.3	Promoters 172
5.4.4	Inhibitors 176
5.5	Catalyst Deactivation 177
5.5.1	Catalyst Poisoning 179
5.5.2	Poisoning of Metals 179
5.5.3	Poisoning of Semiconductor Oxides 182
5.5.4	Poisoning of Solid Acids 182
5.5.5	Deposits on the Catalyst Surface 183
5.5.6	Thermal Processes and Sintering 185
5.5.7	Catalyst Losses via the Gas Phase 186
5.6	Regeneration and Recycling of Heterogeneous Catalysts 186
5.7	Characterization of Heterogeneous Catalysts 189
5.7.1	Physical Characterization 190
5.7.1.1	Temperature-Programmed Desorption 195

X Contents

5.7.2	Chemical Characterization and Surface Analysis 195
5.7.2.1	Temperature-Programmed Reaction Methods 196
5.7.2.2	Transmission Electron Microscopy 197
5.7.2.3	Low-Energy Electron Diffraction (LEED) 198
5.7.2.4	IR Spectroscopy 199
5.7.2.5	Electron Spectroscopy for Chemical Analysis (ESCA) 199
5.7.2.6	Auger Electron Spectroscopy (AES) 201
5.7.2.7	Ion Scattering Spectroscopy (ISS) 201
5.7.2.8	Secondary Ion Mass Spectrometry (SIMS) 202
	Exercises 203
	References 209
6	Catalyst Shapes and Production of Heterogeneous
	Catalysts 211
6.1	Introduction 211
6.2	Bulk Catalysts 212
6.2.1	Precipitation 212
6.2.2	Fusion and Alloy Leaching 214
6.2.3	Sol–Gel Synthesis 215
6.2.4	Flame Hydrolysis 217
6.2.5	Hydrothermal Synthesis 217
6.2.6	Heteropolyacids 219
6.3	Supported Catalysts 219
6.3.1	Impregnation 220
6.3.2	Coprecipitation 225
6.3.3	Adsorption/Ion-Exchange 226
6.3.3.1	Ion-Exchange Resins 227
6.3.4	Anchoring/Grafting 228
6.3.5	Monolithic Catalysts 229
6.4	Shaping of Catalysts and Catalyst Supports 230
6.5	Immobilization of Homogeneous Catalysts 232
6.5.1	Supported Solid-Phase Catalysts (SSPC) 234
6.5.2	Supported Liquid-Phase Catalysts (SLPC) 236
6.5.3	Encapsulation 236
	Exercises 237
	References 238
7	Shape-Selective Catalysis: Zeolites 239
7.1	Composition and Structure of Zeolites 239
7.2	Catalytic Properties of the Zeolites 242
7.2.1	Shape Selectivity 243
7.2.1.1	Reactant Selectivity 243
7.2.1.2	Product Selectivity 246
7.2.1.3	Restricted Transition State Selectivity 246
7.2.2	Acidity of Zeolites 247

Contents XI

- 7.3 Isomorphic Substitution of Zeolites 251
- 7.4 Metal-Doped Zeolites 252
- 7.5 Applications of Zeolites 255 Exercises 258 References 259

# 8 Heterogeneously Catalyzed Processes in Industry 261

- 8.1 Overview 261
- 8.1.1 Production of Inorganic Chemicals 261
- 8.1.2 Production of Organic Chemicals 261
- 8.1.3 Refinery Processes 262
- 8.1.4 Catalysts in Environmental Protection 264
- 8.2 Examples of Industrial Processes Bulk Chemicals 266
- 8.2.1 Ammonia Synthesis 266
- 8.2.2 Hydrogenation 268
- 8.2.3 Methanol Synthesis 270
- 8.2.4 Selective Oxidation of Propene 272
- 8.2.4.1 Oxidation of Propene with H<sub>2</sub>O<sub>2</sub> to Propylene Oxide 277
- 8.2.5 Selective Oxidation of Hydrocarbons 277
- 8.2.5.1 *n*-Butane to Maleic Anhydride 278
- 8.2.5.2 o-Xylene to Phthalic Anhydride 280
- 8.3 Fine Chemicals Manufacture 281
- 8.3.1 Fine Chemicals and Their Synthesis 281
- 8.3.2 Selected Examples of Industrial Processes 285
- 8.3.2.1 Hydrogenation 286
- 8.3.2.2 Oxidation 288
- 8.3.2.3 Catalytic C–C Linkage 290
- 8.3.2.4 Acid/Base Catalysis 292 Exercises 294 References 297
- 9 Refinery Processes and Petrochemistry 299
- 9.1 Hydrotreating 300
- 9.2 Catalytic Cracking 302
- 9.3 Hydrocracking 304
- 9.4 Catalytic Reforming 306
- 9.5 Alkylation 307
- 9.6 Hydroisomerization 308
- 9.7 Synthesis Gas and Hydrogen by Steam Reforming 310
- 9.8 Natural Gas Conversion to Fuels and Chemicals 312
- 9.9 Fischer–Tropsch Synthesis 313
- 9.10 Etherification Reactions 315
  - Exercises 316
    - References 317

XII Contents

10	Electrocatalytic Processes 319
10.1	Comparison Between Electrocatalysis and Heterogeneous
	Catalysis 319
10.2	Electroorganic Syntheses 319
10.2.1	Electrocatalytic Hydrogenation 320
10.2.2	Electrocatalytic Oxidation 322
10.2.3	Electrochemical Addition 323
10.3	Electrocatalysis in Fuel Cells 324
10.3.1	Basic Principles 324
10.3.2	Types of Fuel Cell and Catalyst 325
10.3.3	Important Reactions in Fuel Cell Technology 328
10.3.3.1	The Anodic Reaction 328
10.3.3.2	The Cathodic Reaction 329
10.3.3.3	Methanol Oxidation 331
	Exercises 332
	References 333
11	Environmental Catalysis and Green Chemistry 335
11.1	Automotive Exhaust Catalysis 335
11.2	$NO_x$ Removal Systems 338 Substitute Catalatia Dalaction of Nitranana Onidara 220
11.2.1	Selective Catalytic Reduction of Nitrogen Oxides 338
11.2.2	$NO_x$ Storage-Reduction Catalyst for Lean-Burning Engines 340
11.5	Catalytic Alterburning 541
11.4	Examples of Catalytical Processor 345
11. <del>1</del> .1 11 / 1 1	Aldol Condensation 345
11.4.1.2	Diels – Alder Reaction 346
11 4 1 3	Hydrogenation 347
11.4.1.4	Cyclization in Water 347
11.4.1.5	Use of Ionic Liquids 347
11.4.1.6	Green Solvents 349
	Exercises 350
	References 351
12	Phase-Transfer Catalysis 353
12.1	Definition 353
12.2	Catalysts for PTC 353
12.3	Mechanism and Benefits of PTC 354
12.4	PTC Reactions 355
12.5	Selected Industrial Processes with PTC 356
12.5.1	Continuous Dehydrohalogenation to Produce the Large-Scale
	Monomer Chloroprene 356
12.5.2	Polycarbonate Manufacture with Phosgene 356
12.5.3	Etherification (O-Alkylation) 357
12.5.4	Aldehydes by Oxidation of Alcohols with Hypochlorite 357

- 12.5.5 Carbonylation 357
- 12.5.6 2-Phenylbutyronitrile by Alkylation 358 Exercises 359 References 359

## 13 Catalytic Processes with Renewable Materials 361

- 13.1 Biofuels 361
- 13.2 Biorefinery 366
- 13.2.1 Lignocellulose Feedstock Biorefinery 368
- 13.3 Chemicals from Biomass 369
- 13.3.1 Chemicals from Biomass via Platform Molecules 369
- 13.3.1.1 Carbohydrates 369
- 13.3.1.2 Fats and Oils *373*
- 13.3.1.3 Terpenes 375
- 13.3.2 Direct Biomass Conversion to End-Products 376
  Exercises 378
  References 378

#### 14 Polymerization Catalysis 381

- 14.1 Introduction 381
- 14.2 Fundamentals of Catalytical Polymerization Processes 381
- 14.3 Coordination Polymerization 383
- 14.3.1 Ziegler–Natta Catalysts 383
- 14.3.1.1 Heterogeneous Ziegler-Natta Catalysts 384
- 14.3.1.2 Homogeneous Ziegler-Natta Catalysts 386
- 14.3.1.3 Metallocenes 386
- 14.3.1.4 Ring-Opening Metathetic Polymerization 388
- 14.4 Examples of Catalytical Polymerization Processes 389
- 14.4.1 Polyethylene Production 389
- 14.4.2 Polypropylene Production 391 Exercises 392 References 393
- 15 Planning, Development, and Testing of Catalysts 395
- 15.1 Stages of Catalyst Development 395
- 15.2 Development of a Catalytical Process: Hydrogenation of Benzene to Cyclohexane 398
- 15.3 Selection and Testing of Catalysts in Practice 401
- 15.3.1 Catalyst Screening 401
- 15.3.2 Catalyst Test Reactors and Kinetic Modeling 405
- 15.3.2.1 Differential Reactor 405
- 15.3.2.2 Differential Circulating Reactor 407
- 15.3.2.3 Integral reactor 411
- 15.3.3 Kinetic Modeling and Simulation 416
- 15.3.3.1 Hydrogenation of Benzaldehyde 416

XIV Contents

1		
15.3.3.2	Modeling of a Trickle Bed Reactor 420	
15.3.4	Catalyst Discovery via High-Throughput Experimentation	427
	Exercises 430	
	References 430	
16	Catalysis Reactors 433	
16.1	Plug Flow Reactor (PFR) 433	
16.2	Continuous Stirred-Tank Reactor (CSTR) 435	
16.3	Reactor Calculations 436	
16.4	Two-Phase Reactors 440	
16.4.1	Single-Bed Reactor 441	
16.4.2	Multibed Reactor 441	
16.4.3	Multitubular Reactors 442	
16.4.4	Shallow-Bed Reactors 442	
16.4.5	Fluidized-Bed Reactors 443	
16.5	Three-Phase Reactors 443	
16.5.1	Fixed-Bed Reactors 445	
16.5.2	Suspension Reactors 447	
16.6	Reactors for Homogeneously Catalyzed Reactions 451	
16.7	New Reactor Concepts 452	
16.7.1	Membrane Reactors 452	
16.7.2	Catalytic Reactive Distillation 453	
16.7.3	Catalytic Microreactors 454	
	Exercises 455	
	References 457	
17	Economic Importance of Catalysts 459	
	References 462	
18	Future Development of Catalysis 463	
18.1	Homogeneous Catalysis 463	
18.2	Heterogeneous Catalysis 465	
18.2.1	Use of Other Cheaper Raw Materials 467	
18.2.2	Catalysts for Energy Generation 468	
18.2.3	Better Strategies for Catalyst Development 469	
	References 472	
	Solutions to the Exercises 473	

Index 513