

Contents

1	Introduction	1
1.1	The Phenomenon Catalysis	1
1.2	Mode of Action of Catalysts	4
1.3	Classification of Catalysts	8
1.4	Comparison of Homogeneous and Heterogeneous Catalysis	10
	<i>Exercises for Chapter 1</i>	14
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	21
2.1.3	Acid–Base Reactions	24
2.1.4	Redox Reactions: Oxidative Addition and Reductive Elimination	26
2.1.5	Insertion and Elimination Reactions	33
2.1.6	Reactions at Coordinated Ligands	37
	<i>Exercises for Section 2.1</i>	41
2.2	Catalyst Concepts in Homogeneous Catalysis	44
2.2.1	The 16/18-Electron Rule	44
2.2.2	Catalytic Cycles	45
2.2.3	Hard and Soft Catalysis	47
2.2.3.1	Hard Catalysis with Transition Metal Compounds	48
2.2.3.2	Soft Catalysis with Transition Metal Compounds	50
	<i>Exercises for Section 2.2</i>	55
2.3	Characterization of Homogeneous Catalysts	57
	<i>Exercises for Section 2.3</i>	63
3	Homogeneously Catalyzed Industrial Processes	65
3.1	Overview	65
3.2	Examples of Industrial Processes	68
3.2.1	Oxo Synthesis	68
3.2.2	Production of Acetic Acid by Carbonylation of Methanol	72
3.2.3	Selective Ethylene Oxidation by the Wacker Process	73

VIII *Contents*

3.2.4	Oxidation of Cyclohexane	75
3.2.5	Asymmetric Hydrogenation: Monsanto L-Dopa Process	77
3.2.6	Oligomerization of Ethylene (SHOP Process)	78
	<i>Exercises for Chapter 3</i>	80
4	Heterogeneous Catalysis: Fundamentals	83
4.1	Individual Steps in Heterogeneous Catalysis	83
4.2	Kinetics and Mechanisms of Heterogeneously Catalyzed Reactions ..	86
4.2.1	The Importance of Adsorption in Heterogeneous Catalysis	86
4.2.2	Kinetic Treatment	91
4.2.3	Mechanisms of Heterogeneously Catalyzed Gas-Phase Reactions	93
	<i>Exercises for Section 4.2</i>	98
4.3	Catalyst Concepts in Heterogeneous Catalysis	100
4.3.1	Energetic Aspects of Catalytic Activity	100
	<i>Exercises for Section 4.3.1</i>	115
4.3.2	Steric Effects	117
	<i>Exercises for Section 4.3.2</i>	128
4.3.3	Electronic Factors	129
4.3.3.1	Metals	131
4.3.3.2	Semiconductors	140
4.3.3.3	Isolators: Acidic and Basic Catalysts	154
	<i>Exercises for Section 4.3.3</i>	163
4.4	Interaction of Catalysts with Supports and Additives	165
4.4.1	Supported Catalysts	165
4.4.2	Promoters	174
	<i>Exercises for Section 4.4</i>	179
4.5	Catalyst Deactivation and Regeneration	180
	<i>Exercises for Section 4.5</i>	192
4.6	Characterization of Heterogeneous Catalysts	193
4.6.1	Physical Characterization	193
4.6.2	Surface Analysis and Chemical Characterization	198
	<i>Exercises for Section 4.6</i>	205

5	Catalyst Shapes and Production of Heterogeneous Catalysts	207
5.1	Catalyst Production	207
5.2	Immobilization of Homogeneous Catalysts	214
	<i>Exercises for Chapter 5</i>	222
6	Shape-Selective Catalysis: Zeolites	225
6.1	Composition and Structure of Zeolites	225
6.2	Production of Zeolites	228
6.3	Catalytic Properties of the Zeolites	229
6.3.1	Shape Selectivity	230
6.3.2	Acidity of Zeolites	235
6.4	Isomorphic Substitution of Zeolites	239
6.5	Metal-Doped Zeolites	240
6.6	Applications of Zeolites	242
	<i>Exercises for Chapter 6</i>	245
7	Planning, Development, and Testing of Catalysts	249
7.1	Stages of Catalyst Development	249
7.2	An Example of Catalyst Planning: Conversion of Olefins to Aromatics	251
7.3	Selection and Testing of Catalysts in Practice	256
7.3.1	Catalyst Screening	258
7.3.2	Catalyst Test Reactors for Reaction Engineering Investigations	260
7.3.3	Statistical Test Planning and Optimization	267
7.3.4	Kinetic Modeling and Simulation	281
	<i>Exercises for Chapter 7</i>	295
8	Heterogeneously Catalyzed Processes in Industry	299
8.1	Overview	299
8.2	Examples of Industrial Processes	304
8.2.1	Ammonia Synthesis	304
8.2.2	Hydrogenation	306
8.2.3	Methanol Synthesis	311
8.2.4	Selective Oxidation of Propene	314
8.2.5	Selective Catalytic Reduction of Nitrogen Oxides	318
8.2.6	Olefin Polymerization	320
	<i>Exercises for Chapter 8</i>	322
9	Catalysis Reactors	327
9.1	Two-Phase Reactors	329
9.2	Three-Phase Reactors	333

9.2.1	Fixed-Bed Reactors	334
9.2.2	Suspension Reactors	336
9.3	Reactors for Homogeneously Catalyzed Reactions	340
	<i>Exercises for Chapter 9</i>	342
10	Economic Importance of Catalysts	345
11	Future Development of Catalysis	351
11.1	Homogeneous Catalysis	351
11.2	Heterogeneous Catalysis	353
	Solutions to the Exercises	359
	References	397
	Textbooks and Reference Books on Homogeneous Catalysis	397
	Textbooks, Reference Books, and Brochures on Heterogeneous Catalysis	397
	References to Chapters 1–11	398
	Index	405