

Contents

Preface — VII

1 Introduction and fundamental aspects — 1

- 1.1 General concepts of catalysis — 3
 - 1.1.1 Basics of thermodynamics and kinetics for chemical reactions — 3
 - 1.1.2 General principles of heterogeneous catalysis — 9
 - 1.1.3 Mechanisms and kinetics on catalyst surfaces — 11
 - 1.1.4 Characterisation of solid catalysts — 15
 - 1.1.5 Terms and definitions — 19
- 1.2 Catalyst preparation — 28
- 1.3 Chemical reactors for catalytic processes — 30
- 1.4 Outlook — 33
- References — 34

2 Heterogeneous hydrogenations — 37

- 2.1 Introduction — 37
- 2.2 Nickel catalysts — 43
 - 2.2.1 Hydrogenation of nitriles — 43
 - 2.2.2 Hydrogenation of carbonyl groups — 50
 - 2.2.3 Hydrogenation of other functional groups — 51
 - 2.2.4 Reduction of multiple functional groups in the same reaction — 54
- 2.3 Platinum Group Metal (PGM) based catalysts — 55
 - 2.3.1 Palladium catalysts — 58
 - 2.3.2 Platinum catalysts — 78
 - 2.3.3 Other PGM catalysts — 83
- 2.4 Other metal catalysts — 85
- 2.5 Summary — 86
- References — 86

3 Homogeneous hydrogenations — 91

- 3.1 Introduction — 91
- 3.2 Rh-catalysed hydrogenations — 92
 - 3.2.1 (S)-3-(3,4-dihydroxyphenyl)alanine, L-DOPA — 92
 - 3.2.2 Menthol (BASF Process) — 99
 - 3.2.3 Methylene succinamic acid — 102
 - 3.2.4 Aliskiren — 103
 - 3.2.5 Pregabalin — 107
 - 3.2.6 (+)-Biotin — 107
 - 3.2.7 Sitagliptin — 109
 - 3.2.8 Pantolactone — 111

3.3	Ru-catalysed hydrogenations — 112
3.3.1	Hydrogenation of allylic alcohols — 112
3.3.2	Pivotal glutarate intermediate for candoxatril — 114
3.3.3	Artemisinin — 115
3.3.4	Ketone reductions — 116
3.3.5	Dynamic kinetic resolution via asymmetric hydrogenation — 119
3.4	Ir-catalysed hydrogenation — 121
3.4.1	Hydrogenation of imines — 121
3.4.2	Hydrogenation of ketones with iridium catalysts — 124
3.4.3	Hydrogenation of unfunctionalised doubled bonds — 125
3.5	Asymmetric transfer hydrogenation of C=O and C=N — 128
3.5.1	Dorzolamide — 130
3.5.2	Styrene oxide — 131
3.5.3	(<i>R,R</i>)- <i>trans</i> -Actinol for zeaxanthin — 131
3.5.4	Almorexant — 132
	References — 133
4	Oxidations — 142
4.1	Introduction — 142
4.2	Oxidation of alcohols — 143
4.3	Oxidation of phenols and aromatic compounds — 144
4.4	Oxidation of various C–C bonds — 150
4.5	Oxidation for silane production — 162
	References — 164
5	Gas-phase reactions — 170
	References — 180
6	C–C-bond and C–N-bond forming reactions (metal-catalysed) — 184
6.1	Introduction and <i>Mizoroki–Heck</i> reactions — 184
6.2	Other palladium catalysed C–C bond forming reactions — 189
6.2.1	<i>Sonogashira–Hagihara</i> reaction — 189
6.2.2	<i>Suzuki–Miyaura</i> -coupling — 192
6.2.3	<i>Kumada–Corriu</i> coupling — 198
6.3	Carbonylation reactions — 199
6.4	Hydroformylation reactions — 201
6.5	SHOP process — 205
6.6	1,3-Diene functionalisation — 207
6.7	Telomerisation — 208
6.8	Metathesis — 217
6.9	Formation of C–N bonds (<i>Buchwald–Hartwig</i> coupling) — 222
	References — 226

7	Rearrangement reactions — 235
7.1	Introduction — 235
7.2	<i>Wagner–Meerwein</i> rearrangements — 235
7.3	<i>Beckmann</i> rearrangement — 237
7.4	[3,3]-Sigmatropic-type rearrangements — 237
7.5	The <i>Meyer–Schuster</i> , <i>Rupe–Kambli</i> and <i>Pauling</i> rearrangements — 246
7.6	Allylic rearrangements — 249
	References — 254
8	Acid–base-catalysed reactions — 257
8.1	Replacement of <i>Brønsted</i> acids — 257
8.2	Zeolite-based catalysis — 263
8.3	Heteropoly acids (HPAs) — 267
8.4	<i>Lewis</i> acids — 273
8.5	Base catalysis — 280
8.6	Ethynylation — 286
8.7	<i>Mannich</i> reactions — 288
	References — 289
9	Phase transfer catalysis (PTC) — 296
	References — 308
10	Biocatalysis — 311
10.1	Introduction to biocatalysis — 311
10.2	Industrial applications — 322
10.2.1	Sauerkraut and ethanol: applications with a long history — 322
10.2.2	Sugars and oligosaccharides — 325
10.2.3	Organic acids — 329
10.2.4	Amino acids — 335
10.2.5	Vitamins and carotenoids — 341
10.2.6	Active pharmaceutical ingredients — 353
10.2.7	Flavour compounds — 363
10.2.8	Pesticides — 365
10.2.9	Platform chemicals — 366
	References — 370
11	New trends — 378
	References — 383