Contents

Preface	XV	
List of Co	ntributors	XVII

Part I Radical Chain Aerobic Oxidation 1

1	Overview of Radical Chain Oxidation Chemistry 3
	Ive Hermans
1.1	Introduction 3
1.2	Chain Initiation 6
1.3	Chain Propagation 7
1.4	Formation of Ring-Opened By-Products in the Case of Cyclohexane Oxidation 11
1.5	Complications in the Case of Olefin Autoxidation 12
1.6	Summary and Conclusions 13
	References 14
2	Noncatalyzed Radical Chain Oxidation: Cumene Hydroperoxide 15 Manfred Weber, Jan-Bernd Grosse Daldrup, and Markus Weber
2.1	Introduction 15
2.2	Chemistry and Catalysis 15
2.2.1	Cumene Route to Phenol and Acetone: Chemistry Overview 16
2.2.2	Thermal Decomposition of Cumene Hydroperoxide 17
2.2.3	Oxidation of Cumene 19
2.3	Process Technology 21
2.3.1	Process Overview 21
2.3.2	Reactors for the Cumene Oxidation 22
2.3.3	Reactor Modeling 23
2.3.4	Process Safety Aspects 26
2.4	New Developments 27
2.4.1	Process Intensification by Modification of the Oxidation
	Reaction 27
2.4.2	Improvements of Reactor and Process Design 29
	References 30



٧١	Contents	
·	3	Cyclohexane Oxidation: History of Transition from Catalyzed to Noncatalyzed 33
	0.1	Johan Thomas Tinge
	3.1	Introduction 33
	3.2	Chemistry and Catalysis 34
	3.3	Process Technology 35
	3.3.1	The Traditional Catalyzed Cyclohexane Oxidation Process 35
	3.3.2	The Noncatalyzed DSM Oxanone® Cyclohexane Oxidation
		Process 37
	3.4	New Developments 38
		Epilogue 39
		References 39
	4	Chemistry and Mechanism of Oxidation of para-Xylene to Terephthalic
		Acid Using Co-Mn-Br Catalyst 41
		Victor A. Adamian and William H. Gong
	4.1	Introduction 41
	4.2	Chemistry and Catalysis 42
	4.2.1	Co-Br Catalysis 43
	4.2.2	Cobalt – Manganese – Bromide Catalysis (MC Oxidation): The Nature
		of Synergy between Co and Mn 48
	4.2.3	The Role and Nature of Bromine Species in MC Oxidation 50
	4.2.4	Nature of Cobalt(III) and Mn(III) Species 52
	4.2.5	Reactions of Cobalt(II) with Peroxy Radicals and the Effect of Solvent
		on Oxidation Rate 52
	4.2.6	Phenomenon of Manganese Precipitation 54
	4.2.7	Consolidated View of MC Oxidation Mechanism 54
	4.2.8	Oxidation By-products 56
	4.3	Process Technology 58
	4.3.1	Oxidation 58
	4.3.2	Purification 58
	4.4	New Developments 61
	4.4.1	Homogeneous Bromineless Catalysis 61
	4.4.2	Heterogeneous Bromineless Oxidation Catalysis 62
	4.4.3	Alternative Solvents 62
	4.5	Conclusions 62
		References 63
		Part II Cu-Catalyzed Aerobic Oxidation 67
	5	Cu-Catalyzed Aerobic Oxidation: Overview and New
		Developments 69
		Damian Hruszkewycz, Scott McCann, and Shannon Stahl
	5.1	Introduction 69
	5.2	Chemistry and Catalysis 70

5.2.1 5.2.2	Cu-Catalyzed Oxydecarboxylative Phenol Synthesis 70 Cu-Catalyzed Oxidative Carbonylation of Methanol for the Synthesis of Dimethyl Carbonate 72
5.3	Process Technology 74
5.3.1	Cu-Catalyzed Oxydecarboxylative Phenol Synthesis 74
5.3.2	Cu-Catalyzed Oxidative Carbonylation of Methanol for the Synthesis
	of Dimethyl Carbonate 75
5.4	New Developments: Pharmaceutical Applications of Cu-Catalyzed
	Aerobic Oxidation Reactions 76
	References 82
6	Copper-Catalyzed Aerobic Alcohol Oxidation 85
	Janelle E. Steves and Shannon S. Stahl
6.1	Introduction 85
6.2	Chemistry and Catalysis 86
6.3	Prospects for Scale-Up 91
6.4	Conclusions 93
	References 94
7	Phenol Oxidations 97
7.1	Polyphenylene Oxides by Oxidative Polymerization of Phenols 97
	Patrick Gamez
7.1.1	Introduction 97
7.1.2	Chemistry and Catalysis 99
7.1.3	Process Technology 102
7.1.4	New Developments 104
7.2	2,3,5-Trimethylhydroquinone as a Vitamin E Intermediate via
	Oxidation of Methyl-Substituted Phenols 106
	Jan Schütz and Thomas Netscher
	References 109
	Part III Pd-Catalyzed Aerobic Oxidation 113
8	Pd-Catalyzed Aerobic Oxidation Reactions: Industrial Applications
	and New Developments 115
	Dian Wang, Jonathan N. Jaworski, and Shannon S. Stahl
8.1	Introduction 115
8.2	Chemistry and Catalysis: Industrial Applications 117
8.2.1	Acetoxylation of Alkenes to Vinyl or Allyl Acetates 117
8.2.2	Oxidative Carbonylation of Alcohols to Carbonates, Oxalates,
	and Carbamates 118
8.2.3	Oxidative Coupling of Arenes to Biaryl Compounds 121
8.3	Chemistry and Catalysis: Applications of Potential Industrial
0 2 1	Interest 122
8.3.1	Oxidation of Alcohols to Aldehydes 122

VIII	Contents	
•	8.3.2	Oxidation of Arenes to Phenols and Phenyl Esters 123
	8.3.3	Benzylic Acetoxylation 125
	8.3.4	Arene Olefination (Oxidative Heck Reaction) 126
	8.4	Chemistry and Catalysis: New Developments and
		Opportunities 128
	8.4.1	Ligand-Modulated Aerobic Oxidation Catalysis 128
	8.4.2	Use of NO _x as Cocatalyst 130
	8.4.3	Methane Oxidation 132
	8.5	Conclusion 133
		References 133
	9	Acetaldehyde from Ethylene and Related Wacker-Type Reactions 139 Reinhard Jira
	9.1	Introduction 139
	9.2	Chemistry and Catalysis 140
	9.2.1	Oxidation of Olefinic Compounds to Carbonyl Compounds 140
	9.2.2	Kinetics and Mechanism 140
	9.2.3	Catalytic Oxidation of Ethylene 145
	9.2.3.1	Oxidation of Ethylene to Acetaldehyde in the Presence of
		CuCl ₂ 145
	9.2.3.2	Oxidation of Ethylene to 2-Chloroethanol 147
	9.3	Process Technology (Wacker Process) 148
	9.3.1	Single-Stage Acetaldehyde Process from Ethylene 148
	9.3.2	Two-Stage Acetaldehyde Process from Ethylene 149
	9.4	Other Developments 151
		References 155
		Further Reading 158
	10	1,4-Butanediol from 1,3-Butadiene 159
		Yusuke Izawa and Toshiharu Yokoyama
	10.1	Introduction 159
	10.2	Chemistry and Catalysis 160
	10.2.1	Short Overview of Non-butadiene-Based Routes to
		1,4-Butanediol <i>160</i>
	10.2.1.1	Acetylene-Based Reppe Process 160
	10.2.1.2	Butane-Based Process; Selective Oxidation of Butane to Maleic
		Anhydride 161
	10.2.1.3	Propylene-Based Process: Hydroformylation of Allyl Alcohol 161
	10.2.2	Butadiene-Based Routes to 1,4-Butanediol 162
	10.2.2.1	Oxyhalogenation of 1,3-Butadiene 162
	10.2.2.2	Oxidative Acetoxylation of 1,3-Butadiene 162
	10.3	Process Technology 164
	10.3.1	Mitsubishi Chemical's 1,4-Butanediol Manufacturing Process:
		First-Generation Process 165
	10.3.1.1	Oxidative Acetoxylation Step 165

	•
10.3.1.2	Hydrogenation Step 165
10.3.1.3	Hydrolysis Step 166
10.3.2	Mitsubishi Chemical's 1,4-Butanediol Manufacturing Process:
10.4	Second-Generation Process 167
10.4	New Developments 168
10.4.1	Improvement of the Current Process 168
10.4.2	Development of Alternative Processes 169
10.5	Summary and Conclusions 169 References 170
11	Mitsubishi Chemicals Liquid Phase Palladium-Catalyzed Oxidation
	Technology: Oxidation of Cyclohexene, Acrolein, and Methyl Acrylate
	to Useful Industrial Chemicals 173
	Yoshiyuki Tanaka, Jun P. Takahara, Tohru Setoyama, and Hans E. B. Lempers
11.1	Introduction 173
11.2	Chemistry and Catalysis 174
11.2.1	Aerobic Palladium-Catalyzed Oxidation of Cyclohexene to
	1,4-Dioxospiro-[4,5]-decane 174
11.2.1.1	Optimization of the Reaction Conditions 174
11.2.2	Aerobic Palladium-Catalyzed Oxidation of Other Types of
	Olefins 176
11.2.3	Aerobic Palladium-Catalyzed Oxidation of Acrolein to
	Malonaldehyde Bis-(1,3-dioxan-2-yl)-acetal Followed by
	Hydrolysis/Hydrogenation to 1,3-Propanediol 178
11.3	Prospects for Scale-Up 180
11.3.1	Aerobic Palladium-Catalyzed Oxidation of Methyl Acrylate (MA)
	to 3,3-Dimethoxy Methyl Propionate: Process Optimization and
	Scale-Up 180
11.3.2	Small-Scale Reaction Optimization 181
11.3.3	Large-Scale Methyl Acrylate Oxidation Reaction and Work-Up 184
11.3.4	Reaction Simulation Studies as Aid for Further Scale-Up 184
11.4	Conclusion 187
	References 187
12	Oxidative Carbonylation: Diphenyl Carbonate 189
10.1	Grigorii L. Soloveichik
12.1	Introduction 189
12.1.1	Diphenyl Carbonate in the Manufacturing of Polycarbonates 189
12.1.2	History of Direct Diphenyl Carbonate Process at GE 190
12.2	Chemistry and Catalysis 192
12.2.1	Mechanism of Oxidative Carbonylation of Phonol 192
12.2.2	Castalysts for Oxidative Carbonylation of Phenol 193
12.2.3	Cocatalysts for Oxidative Carbonylation of Phenol 196 Organic Cocatalysts 196
12.2.3.1	·
12.2.3.2	Inorganic Cocatalysts 196

x	Contents	
	12.2.4	Multicomponent Catalytic Packages 199
	12.2.5	Role of Bromide in Direct Synthesis of Diphenyl Carbonate 199
	12.3	Prospects for Scale-Up 201
	12.3.1	Catalyst Optimization 201
	12.3.2	Water Removal in Direct Diphenyl Carbonate Process 202
	12.3.3	Downstream Processing and Catalyst Recovery 203
	12.4	Conclusions and Outlook 203
		Acknowledgments 204
		References 205
	13	Aerobic Oxidative Esterification of Aldehydes with Alcohols: The Evolution from Pd-Pb Intermetallic Catalysts to Au-NiO _x Nanoparticle Catalysts for the Production of Methyl Methacrylate 209 Ken Suzuki and Setsuo Yamamatsu
	13.1	Introduction 209
	13.2	Chemistry and Catalysis 210
	13.2.1	Discovery of the Pd – Pb Catalyst 210
	13.2.2	Pd-Pb Intermetallic Compounds 210
	13.2.3	Mechanism 212
	13.2.4	The Role of Pb in the Pd – Pb Catalyst 213
	13.2.5	Industrial Catalyst 213
	13.3	Process Technology 214
	13.4	New Developments 215
	13.5	Conclusion and Outlook 217
		References 218
		Part IV Organocatalytic Aerobic Oxidation 219
	14	Quinones in Hydrogen Peroxide Synthesis and Catalytic Aerobic
		Oxidation Reactions 221
		Alison E. Wendlandt and Shannon S. Stahl
	14.1	Introduction 221
	14.2	Chemistry and Catalysis: Anthraquinone Oxidation (AO)
	1401	Process 223
	14.2.1	Autoxidation Process (Hydroquinone to Quinone) 223
	14.2.2	Hydrogenation Process (Quinone to Hydroquinone) 225
	14.3	Process Technology 227
	14.4	Future Developments: Selective Aerobic Oxidation Reactions
	1441	Catalyzed by Quinones 229 Aerobic DDQ-Catalyzed Reactions Using NO, Cocatalysts 229
	14.4.1 14.4.2	Aerobic DDQ-Catalyzed Reactions Using NO _x Cocatalysts 229 Aerobic Quinone-Catalyzed Reactions Using Other
	14.4.4	Cocatalysts 230
	14.4.3	CAO Mimics and Selective Oxidation of Amines 231
	17.7.0	References 234

NO _x Cocatalysts for Aerobic Oxidation Reactions: Application
to Alcohol Oxidation 239
Susan L. Zultanski and Shannon S. Stahl
Introduction 239
Chemistry and Catalysis 241
Aerobic Alcohol Oxidation with NO_x in the Absence of Other Redox
Cocatalysts 241
Aerobic Alcohol Oxidation with NO _x and Organic Nitroxyl
Cocatalysts 242
Prospects for Scale-Up 247
Conclusions 249
References 249
N-Hydroxyphthalimide (NHPI)-Organocatalyzed Aerobic Oxidations:
Advantages, Limits, and Industrial Perspectives 253
Lucio Melone and Carlo Punta
Introduction 253
Chemistry and Catalysis 254
Enthalpic Effect 256
Polar Effect 256
Entropic Effect 257
Process Technology 257
Oxidation of Adamantane to Adamantanols 257
Oxidation of Cyclohexane to Adipic Acid 258
Epoxidation of Olefins 259
Oxidation of Alkylaromatics to Corresponding
Hydroperoxides 260
New Developments 262
Acknowledgments 264
References 264
Carbon Materials as Nonmetal Catalysts for Aerobic Oxidations: The
Industrial Glyphosate Process and New Developments 267
Introduction 267
Mark Kuil and Annemarie E. W. Beers
Chemistry and Catalysis 268
Mark Kuil and Annemarie E. W. Beers
Process Technology 270
Mark Kuil and Annemarie E. W. Beers
Oxygen Pressure 271
Oxygen Flow 271
Activated Carbon Pore Size Distribution 271
Activated Carbon H ₂ O ₂ Time 271 Activated Carbon Nitrogen Content 272

XII	Contents	
	17.4	New Developments 274 Paul L. Alsters
	17.4.1	Aerobic Carbon Material Catalysis 275
	17.4.1.1	Oxygenations and Oxidative Cleavage Reactions 275
	17.4.1.2	Dehydrogenations and Dehydrogenative Coupling Reactions 279
	17.4.2	Aerobic Graphitic Carbon Nitride Catalysis 280
	17.4.2.1	Oxygenations and Oxidative Cleavage Reactions 280
	17.4.2.2	Dehydrogenations and Dehydrogenative Coupling Reactions 281
	17.5	Concluding Remarks 283
		References 283
		Part V Biocatalytic Aerobic Oxidation 289
	18	Enzyme Catalysis: Exploiting Biocatalysis and Aerobic Oxidations for High-Volume and High-Value Pharmaceutical Syntheses 291 Robert L. Osborne and Erika M. Milczek
	18.1	Introduction 291
	18.2	Chemistry and Catalysis 293
	18.2.1	Directed Evolution of BVMOs for the Manufacturing of
		Esomeprazole 295
	18.2.2	Directed Evolution and Incorporation of a Monoamine Oxidase for
		the Manufacturing of Boceprevir 298
	18.3	Process Technology 302
	18.4	New Developments 304
		References 306
		Part VI Oxidative Conversion of Renewable Feedstocks 311
	19	From Terephthalic Acid to 2,5-Furandicarboxylic Acid: An Industrial Perspective 313
		Jan C. van der Waal, Etienne Mazoyer, Hendrikus J. Baars,
		and Gert-Jan M. Gruter
	19.1	Introduction 313
	19.1.1	The Avantium YXY Technology to Produce PEF, a Novel Renewable
		Polymer 314
	19.2	Chemistry and Catalysis 314
	19.2.1	Production of 2,5-Furandicarboxylic Acid Using Heterogeneous
		Catalysts 316
	19.2.2	Production of 2,5-Furandicarboxylic Acid Using Homogeneous
		Catalysts 318
	19.3	Process Technology 320
	19.3.1	Process Economics and Engineering Challenges 320
	19.3.1.1	Gas Composition Control 322
	19.3.1.2	Temperature Control 323
	19.3.1.3	Oxygen Mass Transfer Limitations 324

19.3.1.4	Overall Safety Operation 324
19.4	New Developments 325
19.4.1	Outlook for Co/Mn/Br in the Air Oxidation of Biomass-Derived Molecules 325
19.5	Conclusion 327
	List of Abbreviations 327
	References 327
20	Azelaic Acid from Vegetable Feedstock via Oxidative Cleavage with
	Ozone or Oxygen 331
	Angela Köckritz
20.1	Introduction 331
20.1.1	Current Technical Process: Ozonolysis 332
20.1.1.1	Analytical Investigations of the Mechanism of Ozonolysis 336
20.2	Chemistry and Catalysis 336
20.2.1	Direct Aerobic Cleavage of the Double Bond of Oleic Acid or Methyl Oleate 336
20.2.2	Aerobic Oxidation Step within a Two-Stage Conversion of Oleic Acid or Methyl Oleate 337
20.2.3	Aerobic Oxidation Step within a Three-Stage Conversion of Oleic Acid or Methyl Oleate 339
20.2.4	Biocatalysis 339
20.2.4	Prospects for Scale-Up 341
20.4	Concluding Remarks and Perspectives 342
20.4.1	New Promising Developments 342
20.4.1	Summary 343
20.4.2	References 344
21	Oxidative Conversion of Renewable Feedstock: Carbohydrate
	Oxidation 349
	Cristina Della Pina, Ermelinda Falletta, and Michele Rossi
21.1	Introduction 349
21.2	Chemistry and Catalysis 351
21.2.1	Oxidation of Monosaccharides 354
21.2.2	Oxidation of Disaccharides 358
21.2.3	Polysaccharide Oxidation 361
21.3	Prospects for Scale-Up 362
21.3.1	Enzymatic Process versus Chemical Process: Glucose Oxidation as a
	Model Reaction 362
21.3.2	Enzymatic Oxidation: Industrial Process and Prospects 363
21.3.3	Chemical Oxidation: Industrial Process and Prospects 364
21.3.3.1	Metal Catalysts: Concepts Guiding Choice and Design 364
21.4	Concluding Remarks and Perspectives 366
	References 367