## Contents

1

Preface XV List of Contributors XIX ۷

11

14

1.1	Introduction 1
1.1.1	Green versus Sustainable Chemistry 5
1.1.2	Sustainability through Chemistry and the F <sup>3</sup> -Factory 6
1.1.3	Role of Catalysis 8
1.1.4	Sustainable Industrial Chemistry 10
1.2	Principles of Green Chemistry, Sustainable Chemistry and Risk
1.2.1	Sustainable Risk: Reflections Arising from the Bhopal Accident
1.2.2	Risk Assessment and Sustainable versus Green Chemistry 20
1.2.3	Inherently Safer Process Design 21
1.2.4	On-Demand Synthesis and Process Minimization 23
1.2.5	Replacement of Hazardous Chemicals and Risk Reduction 26
1.2.6	Replacement of Hazardous Chemicals: the Case of DMC 26
1.2.7	Final Remarks on Sustainable Risk 35
1.3	Sustainable Chemical Production and REACH 36
1.3.1	How does REACH Works 38
1.3.2	REACH and Sustainable Industrial Chemistry 40
1.3.3	Safety and Sustainability of Chemicals 41
1.4	International Chemicals Policy and Sustainability 43
1.5	Sustainable Chemistry and Inherently Safer Design 47
1.6	A Vision and Roadmap for Sustainability Through Chemistry 56
1.6.1	Bio-Based Economy 59
1.6.2	Energy 62
1.6.3	Healthcare 63
1.6.4	Information and Communication Technologies 64
1.6.5	Nanotechnology 65
1.6.6	Sustainable Quality of Life 66
Sustainable Industrial Processes. Edited by F. Cavani, G. Centi, S. Perathoner, and F. Trifiró Copyright © 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 978-3-527-31552-9	

From Green to Sustainable Industrial Chemistry 1

Gabriele Centi and Siglinda Perathoner

VI Contents

1.6.7	Sustainable Product and Process Design 66
1.6.8	Transport 67
1.6.9	Risk Assessment and Management Strategies 68
1.7	Conclusions 69
	References 69
2	Methods and Tools of Sustainable Industrial Chemistry: Catalysis 73
	Gabriele Centi and Siglinda Perathoner
2.1	Introduction 73
2.2	Catalysis as Enabling Factor of Sustainable Chemical Production 74
2.3	Homogeneous Catalysis and the Role of Multiphase Operations 77
2.3.1	Multiphase Operations: General Aspects 79
2.3.2	Aqueous Biphase Operations 79
2.3.3	Organic Biphase Operations 84
2.3.4	Catalysts on Soluble Supports 87
2.3.5	Fluorous Liquids 88
2.3.6	Ionic Liquids 90
2.3.7	Supercritical Solvents 95
2.3.8	Supported Liquid Films 97
2.3.9	Conclusions on Multiphase Homogeneous Catalysis for
	Sustainable Processes 102
2.4	Bio- and Bioinspired-Catalysts 103
2.4.1	Industrial Uses of Biocatalysis 104
2.4.2	Advantages and Limits of Biocatalysis and Trends in Research 105
2.4.3	Biocatalysis for the Pharmaceutical Industry 107
2.4.4	Biocatalysis for Sustainable Chemical Production 108
2.4.5	Biocatalysis in Novel Polymers from Bio-Resources 112
2.4.6	Progresses in Biocatalysis 114
2.4.7	Biomimetic Catalysis 117
2.5	Solid Acids and Bases 120
2.5.1	Classes of Solid Acid/Base Catalysis 120
2.5.2	Alkylation with Solid Acid Catalysts 125
2.5.3	Synthesis of Cumene 130
2.5.4	Friedel–Crafts Acylation 132
2.5.5	Synthesis of Methylenedianiline 133
2.5.6	Synthesis of Caprolactam 135
2.5.7	Green Traffic Fuels 140
2.5.8	Solid Base Catalysts 144
2.5.8.1	Hydrotalcites 145
2.5.8.2	Other Solid Bases 154
2.6	Redox Catalysis 158
2.6.1	Hydrogenation 158
2.6.2	Asymmetric Hydrogenation 162

228

250

2.6.3 Selective Oxidation 167 2.6.3.1 Selective Oxidation: Liquid Phase 170 2.6.3.2 Selective Oxidation: Vapor Phase 171 Selective Oxidation: Examples of Directions to Improve 2.6.3.3 Sustainability 172 Cascade and Domino Catalytic Reactions 184 2.7 Multicomponent Catalytic Reactions 2.8 186 2.9 Organocatalysis 187 2.10 Conclusions 188 References 188 3 Methods and Tools of Sustainable Industrial Chemistry: Process Intensification 199 Gabriele Centi and Siglinda Perathoner 3.1 Introduction 199 3.1.1 Opportunities and Perspectives for a Sustainable Process Design 200 3.1.2 Process Intensification and Inherently Safer Processes 203 3.1.3 A Critical Toolbox for a Sustainable Industrial Chemistry 204 3.1.4 Fundaments of PI 210 3.1.5 Methodologies 213 3.1.5.1 Hybrid Unit Operations 213 3.1.5.2 New Operating Modes of Production 218 3.1.5.3 Microengineering and Microtechnology 225 3.1.6 Role for the Reduction of Emissions of Greenhouse Gases Alternative Sources and Forms of Energy for Process 3.2 Intensification 230 3.2.1 High-Gravity Fields 230 Electric Fields 232 3.2.2 3.2.3 Microwaves 232 Light 234 3.2.4 3.2.5 Acoustic Energy 237 Energy of Flow 242 3.2.6 3.3 Micro(structured)-Reactors 243 Microreactor Materials and Fabrication Methods 3.3.1 244 Microreactors for Catalytic Gas-Phase Reactions 245 3.3.2 Microreactors for Catalytic Multiphase Systems 3.3.3 246 3.3.4 Industrial Microreactors for Fine and Functional Chemistry 247 3.3.4.1 Phenyl Boronic Acid Synthesis (Clariant) 248 3.3.4.2 Azo Pigment Yellow 12 (Trust Chem/Hangzhou) 248 3.3.4.3 Hydrogen Peroxide Synthesis (UOP) 248 3.3.4.4 (S)-2-Acetyltetrahydrofuran Synthesis (SK Corporation/Daejeon) References 250

VIII Contents

4	Membrane Technologies at the Service of Sustainable Development
	Gilbert M. Rios. Marie-Pierre Belleville. Delnhine Paolucci-leaniean
	and losé Sanchez
4.1	Introduction 257
4.2	From Definitions to Function: A Few Fundamental Ideas 258
4.2.1	Membrane Operation 258
4.2.2	Overall Performance: A Balance Between Material and Fluid
	Limitations 259
4.2.3	Membrane Material as a "High Tech Product" Contacting Device 260
4.2.4	A Clear Distinction Between the "Function" and the "Material" 261
4.2.5	Enlarged Uses of Membrane Concepts 261
4.3	The Need for More Integrated Views on Materials and Process
	Conditions 262
4.3.1	When Dense or Microporous Materials Control the Overall Process
	Performance 262
4.3.2	Other Operations Using Meso- or Macroporous Membranes 264
4.3.3	Two Important Remarks 266
4.3.3.1	Nano- and Micro-Engineering for New Porous Thin Layers 266
4.3.3.2	Membrane Processes and Solid Bed Technologies:
	A Comparison 267
4.4	Use of Hybrid Processes and New Operating Modes:
	The Key to Many Problems 267
4.4.1	Nanofiltration-Coupled Catalysis 267
4.4.2	Supercritical Fluid-Assisted Membrane Separation and/or
	Reaction 269
4.4.3	Membrane-Assisted Fluidized Bed Reactors 270
4.4.4	Electrodialysis with A Non-stationary Field 271
4.5	Safe Management of Membrane Integration in Industrial Processes:
	A Huge Challenge 273
4.6	Conclusions 276
	References 277
F	Accounting for Chamical Sustainability 270
3	Accounting for Chemical Sustainability 279
<b>F</b> 1	Latroduction 270
5.1	Ecological Ecotorint 201
J.Z	Ecological Footprint 281
5.5 E 4	Ecological Indicators 200 Matrice for Environmental Analysis and Eco Efficiency 202
).4 E E	Sustainability Accounting 202
J.J 5 5 1	Sustainability Accounting 232
3.3.1 E C	System boundary 295 E Fostor and Atom Economy 206
J.U E ( 1	E-FACIOI AND ALOM ECONOMY 290
J.U.I	LIMILS TO THEIR USE 298 Applicability to Evaluating the Sustainability of Chamical Industrial
5.0.2	Processes 299

5.7	Energy Intensity 304
5.8	Environmental Impact Indicators 305
5.9	Sustainable Chemical Production Metrics 306
5.10	Life Cycle Tools 310
5.11	Conclusions 315
	References 316
6	Synthesis of Propene Oxide: A Successful Example of Sustainable
	Industrial Chemistry 319
	Fabrizio Cavani and Anne M. Gaffney
6.1	Introduction: Current Industrial Propene Oxide Production 319
6.1.1	CHPO (Chlorohydrin) Technology 321
6.1.2	PO/TBA Technology 321
6.1.3	PO/SM Technology 321
6.2	PO-only Routes: Several Approaches for Sustainable
	Alternatives 323
6.2.1	The First Industrial PO-Only Synthesis: the Sumitomo Process 325
6.2.2	HPPO Processes: HP Generation by Redox Cycles on
	Organic O Carriers 329
6.2.2.1	EniChem Approach: TS-1 Allows the Integration of HP and
	PO Synthesis 330
6.2.2.2	From the Dream Reaction to the Real Process: the Implemented
	HPPO Process 333
6.2.2.3	Other Integrated HPPO Processes 339
6.2.3	HPPO and In Situ HPPO Processes: HP Generation by Direct
	Oxidation of $H_2$ (DSHP) 341
6.2.3.1	Several Technologies for In Situ HPPO with TS-1-Supported
	Pd Catalysts 341
6.2.3.2	DSHP-HPPO Technology Developed by Degussa
	Evonik/Headwaters 344
6.2.4	An Alternative Approach: Gas-Phase Reaction Between Propene
	and HP Vapors 346
6.2.5	An Efficient Alternative Reductant for O <sub>2</sub> : Methanol 346
6.2.6	Potential Future Solutions for PO Synthesis: Direct Gas-Phase
	Oxidation of Propene with Oxygen (DOPO) 347
6.2.7	Potential Future Solutions for PO Synthesis: Gas-Phase
	Hydro-oxidation of Propene with Oxygen and Hydrogen (HOPO) 350
6.2.8	Alternatives for Gas-Phase PO Synthesis 356
6.2.8.1	Gas-Phase Oxidation with $N_2O$ 356
6.2.8.2	Gas-Phase Oxidation with $O_3$ 357
6.2.9	The Ultimate Challenge: Direct Oxidation of Propane to PO 358
6.3	Conclusions 358
	References 359

**X** Contents

7	Synthesis of Adipic Acid: On the Way to More Sustainable
	Froduction 307
71	Fubrizio Cuvuni una Siejuno Anni Introduction: The Adinic Acid Markot 267
7.1	Current Technologica for AA Dreduction 269
7.Z 7.2.1	Two Stop Transformation of Cyclobarana to AA, Ovidation of
/.2.1	Cyclohexane to Ol/One with Air 369
7.2.2	Alternatives for the Synthesis of Ol/One 372
7.2.3	Alternative Homogeneous Catalysts for Cyclohexane Oxidation to Ol/One 374
7.2.4	Two-Step Transformation of Cyclohexane to AA: Oxidation of
	Ol/One to AA with Nitric Acid 375
7.2.5	Environmental Issues in AA Production 378
7.2.6	Technologies for N <sub>2</sub> O Abatement 379
7.2.6.1	Catalytic Abatement 380
7.2.6.2	Thermal Abatement 382
7.2.7	N <sub>2</sub> O: From a Waste Compound to a Reactant for Downstream
	Applications 383
7.3	Alternatives for AA Production 385
7.3.1	Oxidation of KA Oil with Air 385
7.3.2	Direct Oxidation of Cyclohexane with Air 389
7.3.2.1	Homogeneous Autoxidation of Cyclohexane Catalyzed by Co, Mn
	or Cu 389
7.3.2.2	Heterogeneous Catalysis for Cyclohexane Oxidation to Either Ol/One
	or AA (Various Oxidants Included) 393
7.3.2.3	N-Hydroxyphthalimide as the Catalyst for the Oxidation of
	Cyclohexane to AA with Oxygen 395
7.3.3	Butadiene as the Starting Reagent 399
7.3.4	Dimerization of Methyl Acrylate 402
7.4	Emerging and Developing Technologies for AA Production 402
7.4.1	An Alternative Raw Material for AA Synthesis: Cyclohexene 402
7.4.1.1	Single-Step Oxidation of Cyclohexene to AA 403
7.4.1.2	Two-Step Oxidation of Cyclohexene to AA Via 1,2-Cyclohexandiol 406
7.4.1.3	Three-Step Oxidation of Cyclohexene to AA Via Epoxide 408
7.4.1.4	An Alternative Oxidant for Cyclohexene: Oxygen 409
7.4.2	The Greenest Way Ever: Two-Step Transformation of Glucose
	to AA 411
7.4.3	The Ultimate Challenge: Direct Oxidation of <i>n</i> -Hexane to AA 412
7.5	An Overview: Several Possible Green Routes to AA,
	Some Sustainable, Others Not 413
	References 414

8	Ecofining: New Process for Green Diesel Production from Vegetable Oil 427
	Franco Baldiraghi, Marco Di Stanislao, Giovanni Faraci, Carlo Perego, Terry Marker, Chris Gosling, Peter Kokayeff, Tom Kalnes, and Rich Marinangeli
8.1	Introduction 427
8.2	From Vegetable Oil to Green Diesel 428
8.3	UOP/Eni Ecofining Process 434
8.4	Life Cycle Assessment 435
8.5	Conclusion 437
	References 438
9	A New Process for the Production of Biodiesel by Transesterification of Vegetable Oils with Heterogeneous Catalysis 439 Edouard Freund
9.1	Introduction 439
9.2	Direct Use of Vegetable Oils 441
9.3	Methyl Ester Derived from Vegetable Oils 441
9.4	Homogeneous Process for the Production of Biodiesel 442
9.5	Improving the Transesterification Route: Esterfip-H 445
9.6	Future Improvements of the Process 447
9.6.1	Catalyst Improvement 447
9.6.2	Extension of the Process to other Feeds 447
9.6.3	Development of a Process for the Production of Ethyl Esters 447
9.7	Conclusion 448
	References 448
10	Highly Sour Gas Processing in a More Sustainable World 449 François Lallemand and Ari Minkkinen
10.1	Introduction 449
10.1.1	Background 450
10.2	Use of Activated MDEA for Acid Gas Removal 451
10.3	Process Performance Highlights 454
10.4	Case Study of the Use of Activated MDEA for Treatment of Very Sour Gas 454
10.5	Acid Gas Removal for Cycling and/or Disposal 456
10.6	Bulk H <sub>2</sub> S Removal for Disposal 458
10.7	SPREX Performance 459
10.8	Capital Cost and Energy Balance Comparison 460
10.9	Conclusions 461
	References 461

XII Contents

11	BioETBE: A New Component for Gasoline 463
11 1	Marco Di Girolamo and Domenico Sanfilippo
11.1	Introduction 463
11.2	High Quality Oxygenated as Gasoline Components 463
11.3	ETBE lechnology 466
11.3.1	EIBE Properties 466
11.3.2	ETBE Synthesis 467
11.3.3	ETBE Reactors 469
11.3.4	ETBE Process 472
	References 474
12	Olefin/Paraffin Alkylation: Evolution of a "Green" Technology 475
	Anne M. Gaffney and Philip J. Angevine
12.1	Introduction 475
12.2	Liquid Acid Catalysts 476
12.2.1	Reaction Mechanism 479
12.2.2	Operating Variables 481
12.2.3	Advantages Versus Disadvantages 484
12.3	Zeolite Catalysts 484
12.3.1	Zeolite Factors Impacting Alkylation Performance 485
12.3.2	Impact of Reaction Conditions for Zeolites 486
12.3.3	Overview of Zeolites in Alkylation 488
12.4	AlkyClean Alkylation Process: A True Solid Acid Catalyst (SAC)
	Process 488
12.4.1	Catalyst Selection and Development 489
12.4.2	Process Development Activities 489
12.4.3	Optimization of Process Conditions 492
12.4.4	Effect of Feedstock Variation 493
12.4.5	Effect of Impurities 494
12.4.6	Reactor System/Catalyst Regeneration 495
12.4.7	AlkyClean Process Demonstration Unit 496
12.4.8	Demo Unit Operation 497
12.4.9	Competitiveness versus Liquid Acid Technologies 501
12.4.10	Environmental, Cross-Media Effects 503
12.5	Conclusion 504
	References 504
13	Towards the Direct Oxidation of Benzene to Phenol 507
	Marco Ricci, Daniele Bianchi, and Rossella Bortolo
131	Introduction 507
13.2	Cumene Process 508
13.2	Alkylation 508
13.2.1	Oxidation and Concentration 510
13.4.4	Ondution and Concentration 510

- 13.2.3 Cleavage and Workup 511
- 13.2.4 Cumene Process: Final Considerations 512
- 13.3 Solutia Process 514
- 13.4 Direct Oxidation of Benzene to Phenol with Hydrogen Peroxide 516
- 13.4.1 Definition of the Problem and First Attempts 516
- 13.4.2 Homogeneous Catalysis by Iron Complexes: A Biphase Fenton Reagent 517
- 13.4.3 Heterogeneous Catalysis by Titanium Silicalite 519
- 13.5 Perspectives 525
- 13.6 Conclusions 525 References 526

## 14 Friedel–Crafts Acylation of Aromatic Ethers Using Zeolites 529

- Roland Jacquot and Philippe Marion
- 14.1 Introduction 529
- 14.2 Literature Background 530
- 14.3 Acylation of Anisole by Acetic Anhydride 530
- 14.3.1 Industrial Processes 531
- 14.4 Acylation of Veratrole by Acetic Anhydride Over HY Zeolite 533
- 14.5 Deactivation of the Catalysts 534
- 14.6 Benzoylation of Phenol Ether 536
- 14.7 Concluding Remarks 539 References 539

## **15 Green Sustainable Chemistry in the Production of Nicotinates** 541 *Roderick Chuck*

- 15.1 Requirements for Green Processes 541
- 15.2 Significance of Niacin 542
- 15.3 Green Principles in the Manufacture of Niacin 542
- 15.3.1 Choice of Feedstock 542
- 15.3.2 Reaction Paths for Producing Niacin 543
- 15.3.2.1 Liquid-Phase Oxidation of Nicotine with Permanganate, Chromic Acid, etc. 543
- 15.3.2.2 Liquid-Phase Oxidation of 3-Picoline with Permanganate, Chromic Acid or Nitric Acid 544
- 15.3.2.3 Liquid-Phase Oxidation of MEP with Nitric Acid 545
- 15.3.2.4 Direct Oxidation of 3-Picoline to Niacin 546
- 15.3.3 Choice of Catalyst (Efficiency, Separation, Recycling) 547
- 15.3.4 Down-Stream Processing/Unit Operations 547
- 15.3.5 Minimization of Pollutants and Waste Stream Volume 547
- 15.3.6 Recycling of Auxiliary, Side and Intermediate Products 548
- 15.4 Green Principles in Lonza's Niacinamide Process (5000 mtpa) 548

XIV Contents

16	Introducing Green Metrics Early in Process Development. Comparative Assessment of Alternative Industrial Routes to Elliott's Alcohol, A Key Intermediate in the Production of Resmethrins 551 Paolo Righi, Goffredo Rosini, and Valerio Borzatta
16.1	Introduction 551
16.2	Elliott's Alcohol 552
16.3	An Alternative Synthesis of Elliott's Alcohol 554
16.4	Comparative Assessment of the Two Alternative Routes to Elliott's Alcohol 555
16.4.1	Comparison of E-Factors 556
16.4.2	Comparison of Waste Environmental Impact 557
16.4.3	Comparison of Feedstock Environmental Impact 559
16.5	Driving the "Green" Improvement 561
16.6	Conclusions 561
	References 562
17	Basell Spherizone Technology 563
	Maurizio Dorini and Gabriele Mei
17.1	Introduction 563
17.2	Technology Evolution 563
17.3	Spherizone Technology 567
17.3.1	Process Description 568
17.3.2	Process Development and Scale Up 572
17.3.3	Modular Approach 574
17.4	Technology Comparison 575
17.5	Environmental Considerations 576 References 578

Index 579