## **Contents**

Preface XVAbout the Editors XVIIList of Contributors XIX

Part I	Microreactor Design, Fabrication and Assembly 1
1	Silicon and Glass Microreactors 3
	Roald M. Tiggelaar and J. G. E. (Han) Gardeniers
1.1	Introduction 3
1.2	Design and Fabrication of Microreactors for Heterogeneous Catalysis 4
1.2.1	Low-temperature Microreactors 5
1.2.2	High-temperature Microreactors 7
1.3	Design and Fabrication of Microreactors for High-pressure Applications 14
1.4	Microreactors for Liquid-phase Organic Chemistry and Biochemistry 15
1.4.1	Integrated Microfluidic Networks for High-throughput Experiments 15
1.4.2	Microreactors Employing Immobilized Molecular Catalysts 17
1.4.3	Enzymatic Microreactors 18
1.4.4	Synthesis of Bio-related Compounds: Peptides and Sugars 20
1.5	Conclusion 21
	References 21
2	Metallic, Steel, Ceramic and Plastic Microreactors 25
	Jürgen J. Brandner
2.1	Introduction 25
2.2	Manufacturing Techniques for Metals 26
2.2.1	Etching 26
2.2.2	Machining 28

Micro Process Engineering, Vol. 2: Devices, Reactions and Applications. Edited by V. Hessel, A. Renken, J.C. Schouten, and J.-I. Yoshida Copyright © 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 978-3-527-31550-5

Contents	
2.2.3	Generative Method: Selective Laser Melting 30
2.2.4	Metal Forming Techniques 31
2.2.5	Assembling and Bonding of Metal Microstructures 32
2.3	Ceramic and Glass Devices 33
2.3.1	Ceramic Devices 33
2.3.1.1	Joining and Sealing 35
2.3.2	Glass Devices 36
2.4	Polymer Microreactors 37
2.4.1	Bonding of Polymer Materials 39
2.5	Conclusion 39
_,,	References 40
Part II	Bulk and Fine Chemistry 45
1 411 11	bulk and the enemony 15
3	Liquid- and Liquid-Liquid-phase Reactions - Aliphatic Substitution
	Reactions 47
	Paul Watts and Charlotte Wiles
3.1	Nucleophilic Substitution at Saturated Carbon 47
3.2	Nucleophilic Substitution at Carbonyl Carbon 49
3.2.1	Amide Synthesis 49
3.2.2	Ester Synthesis 54
3.3	Conclusion 55
	References 55
4	Liquid- and Liquid-Liquid-phase Reactions - Aromatic Substitution
	Reactions 57
	Stefan Löbbecke
4.1	Electrophilic Aromatic Substitution 57
4.1.1	Friedel-Crafts Reactions 57
4.1.2	Nitrations 60
4.1.3	Brominations and Iodinations 66
4.1.4	Other Electrophilic Aromatic Substitutions 69
4.2	Nucleophilic Aromatic Substitution 73
4.3	Conclusion 77
	References 77
5	Liquid- and Liquid-Liquid-phase Reactions – Addition and
	Elimination 81
	Jun-ichi Yoshida and Aiichiro Nagaki
5.1	Addition Reactions 81
5.2	Elimination Reactions 89
5.3	Addition–Elimination Reactions 90
5.4	Conclusion 95

References 96

6	Liquid- and Liquid-Liquid-phase Reactions - Coupling Reactions 99  Ilhyong Ryu and Takahide Fukuyama
6.1	Metal-catalyzed Coupling 99
6.2	Reactions Using Organometallic Reagents 102
6.3	Photochemical Coupling 104
6.4	Conclusion 106
	References 106
7	Liquid- and Liquid-Liquid-phase Reactions – Oxidations and
	Reduction 109
7.1	Jun-ichi Yoshida and Aiichiro Nagaki
7.1	Oxidation 109
7.1.1	Chemical Oxidation 109
7.1.2	Electrochemical Oxidation 112
7.1.3	Biochemical Oxidation 118
7.1.4	Miscellaneous Oxidations 122
7.2	Reduction 123
7.3	Conclusion 124
	References 125
8	Gas-Liquid-phase Reactions: Substitution 131 Jun-ichi Yoshida and Aiichiro Nagaki
8.1	Fluorination 131
8.2	Chlorination 138
8.3	Nitration 139
8.4	Conclusion 139
	References 140
9	Gas-Liquid-phase Reactions: Addition 143
	Claude de Bellefon
9.1	Types of Reactors 143
9.2	Additions of $H_2$ , $O_2$ , $O_3$ and $CO/H_2$ Across $C=C$ 149
9.3	Other $H_2$ Additions Across C=O, C=N, C=C, Aromatic, Nitro and O=O
	Bonds 154
9.4	Miscellaneous Additions 161
9.5	Conclusion 162
	References 162
10	Gas-Liquid-phase Reactions: Reduction 167
	Harshal Surangalikar, Shaun McGovern, and Ronald S. Besser
10.1	Microreactor Configurations for Hydrogenation and Dehydrogenation
	Reactions 168
10.1.1	Glass/Quartz Microreactors 168
10.1.2	Metal/Alloy Microreactors 168
10.1.3	Silicon-based Microreactors 169

viii	Contents	
•	10.1.4	Ceramic Microreactors 170
	10.2	Catalysts 170
	10.3	Gas-phase Hydrogenation Reactions 170
	10.4	Multiphase Hydrogenation Reactions 176
	10.5	Conclusion 182
		References 182
	11	Gas-Liquid-phase Reactions: Miscellaneous Reactions 187 Ilhyong Ryu and Md Taifur Rahman
	11.1	Dehydration 187
	11.2	Phosgene Synthesis 188
	11.3	Fischer-Tropsch Synthesis 190
	11.4	Carbonylation 191
	11.5	Conclusion 195
		References 196
	Part III	Polymerization 197
	12	Free Radical Polymerization 199 Christophe Serra
	12.1	Introduction 199
	12.1.1	Mechanism 199

	References 170
Part III	Polymerization 197
12	Free Radical Polymerization 199
	Christophe Serra
12.1	Introduction 199
12.1.1	Mechanism 199
12.1.2	Main Features of FRP 201
12.1.3	Goodness of Mixing 202
12.2	Use of Microsystems in FRP 202
12.2.1	Advantages 202
12.2.2	Experimental Investigations of the Use of Microsystems in FRP 203
12.2.2.1	Micromixer-assisted Polymerization of Acrylate Resins 203
12.2.2.2	FRP in Microreactors 204
12.2.2.3	Numerical Simulations of Styrene FRP in Microsystems 209
12.3	Conclusion 211
	References 212
13	Living Radical Polymerization 213
	Thomas E. Enright
13.1	Living Polymerization 213
13.1.1	Free Radical Polymerization Mechanism 215
13.2	Living Radical Polymerization General Mechanisms 217
13.2.1	Dissociation–Combination 217
13.2.2	Atom Transfer 217
13.2.3	Degenerative Chain Transfer 218
13.3	Nitroxide-mediated Polymerization 218
13.4	Atom Transfer Radical Polymerization 219
13.5	Reversible Addition-Fragmentation Chain Transfer 220

13.6	NMP, ATRP and RAFT Summary 220
13.7	Living Radical Polymerization in Tubular Reactors 221
13.8	Living Radical Polymerization in Microreactors 221
13.9	Conclusion 223
	References 223
14	Cationic Polymerization 229
	Jun-ichi Yoshida and Aiichiro Nagaki
14.1	Introduction 229
14.1.1	Basic Principles of Cationic Polymerization 229
14.1.2	Controlled/Living Cationic Polymerization Based on Cation
	Stabilization 230
14.2	Cationic Polymerization Involving Carbocationic Intermediates Using
	Microflow Systems 231
14.2.1	Controlled/Living Cationic Polymerization Based on Cation Stabilization
	Using Microflow Systems 231
14.2.2	Controlled/Living Cationic Polymerization Without Stabilization of
	Carbocationic Intermediates Using Microflow Systems 232
14.2.2.1	Concept of Microflow System-controlled Polymerization Technology
	(MCPT) 232
14.2.2.2	"Cation Pool"-initiated Polymerization Using a Microflow System 233
14.2.2.3	Proton Acid-initiated Polymerization Using Microflow Systems 236
14.3	Ziegler-Natta Polymerization 241
14.4	Conclusion 241
1	References 242
15	Polycondensation 245
	Takeshi Honda and Hideaki Maeda
15.1	Introduction 245
15.2	Synthesis of Fine Solid Material in a Microreactor 246
15.2.1	Synthesis of Polymer Membranes 246
15.2.2	Syntheses of Various Solid Materials by Polycondensation 248
15.3	Solution-phase Polymerization Controlled in a Microreactor 249
15.3.1	Amino Acid Polymer Synthesis 249
15.3.2	Combinatorial and High-throughput Technologies in Microfluidic
	Polymerization 253
15.4	Conclusion 254
	References 255
Part IV	Functional Materials 257
16	Organic Particles and Pigments 259
	Hieng Kim
16.1	Introduction 259

Conte	ents

x

16.1.1	Definition of Microfluidics 259
16.1.1.1	Further Definitions 260
16.1.2	Historical Development of Pigments/ Colorants 260
16.1.3	Conventional Production Methods/Conventional Continuous Processes 261
16.2	Suitability of Microfluidic Devices for the Preparation of Organic Particles and Pigments 264
16.2.1	Mixing and Nucleation 264
16.3	Laboratory-Scale Preparation 265
16.3.1	Pigments, Colorants 265
16.3.2	Monomeric Dyes 266
16.3.3	Polymer-analogue Dyes 267
16.4	Technical-scale Production of Organic Particles and Pigments 268
16.4.1	Pigments, Colorants 268
16.5	Conclusion and Outlook 269
	References 270
17	Inorganic Particles 273
	Michael Köhler
17.1	Introduction 273
17.2	Dielectric Nanoparticles 274
17.3	Semiconductor Nanoparticles 275
17.4	Metal Nanoparticles 276
17.5	Transport Conditions in Nanoparticle Formation 284
17.6	Applications of Nanoparticles in Microreactors 285
17.7	Conclusion 286
	References 286
18	Polymer Particles 289
	Christophe Serra
18.1	Introduction 289
18.2	Most Common Microsystems 290
18.2.1	Emulsification Technique 290
18.2.2	Projection Photolithography Technique 291
18.3	Examples of Various Polymer Particles Produced with
	Microsystems 292
18.3.1	Terrace-like Microchannel Devices 292
18.3.2	T-junction Microchannel Devices 294
18.3.3	Flow Focusing Devices 298
18.3.4	Projection Photolithography Devices 307
18.4	Conclusion 310
	References 311

19	Microencapsulates, Proteins and Lipids/Vesicles 313 John van der Schaaf
19.1	Introduction 313
19.2	Production Methods 314
19.3	Conclusion 321
	References 321
20	Oil-in-Water and Water-in-Oil Emulsions 325
	Heike P. Schuchmann, Karsten Köhler, Freddy Aguilar, and Andreas Hensel
20.1	Emulsion Basics 325
20.1.1	Definitions, Major and Minor Ingredients 325
20.1.2	Emulsion Properties and Their Design 326
20.1.3	Principle of Emulsification 327
20.2	Emulsification Process Functions 327
20.2.1	Droplet Disruption Theory 327
20.2.2	Droplet Disruption in Turbulent and Laminar Flow 328
20.2.3	Droplet Formation and Detachment at Membrane Surfaces 330
20.3	Emulsification Processes 331
20.3.1	Conventional and Innovative Techniques 331
20.3.2	Microengineered Devices 332
20.3.2.1	High-pressure Homogenization Nozzles 332
20.3.2.2	Membranes, Microporous and Microchannel Systems 332
20.3.2.3	Microengineered Mixers (Micromixers) 335
20.3.2.4	Simultaneous Mixing and Homogenization (Microengineered
	SMH-Valve) 337
20.3.3	Emulsification in Microengineered Devices 339
20.4	Conclusion and Outlook 340
	References 341
21	<b>Double, Triple and Complex Multilayered Emulsions</b> 345 Takasi Nisisako
21.1	Introduction 345
21.2	Membrane Emulsification 347
21.3	Microchannel (MC) Emulsification 348
21.4	Two-dimensional Microfluidic Systems 350
21.5	Three-dimensional (3D) Coaxial Microcapillary Systems 352
21.6	Applications to Novel Materials 355
21.7	Conclusion 355
	References 355
22	Microreactor Applications in the Consumer Goods Industry 363 Patrick Löb, Volker Hessel, and Alberto Simoncelli
22.1	Introduction 363
22.2	General Aspects of Microreactor Applications for Emulsification
	Processes 364

XII	Contents	
	22.3	Comparison of Micromixers with Regard to Performance in Liquid– Liquid Dispersions 366
	22.4	Dispersion and Mixing of High-viscosity Liquids 368
	22.5	Cream Formation in Micromixers Targeting a Reduction in Emulsifiers and Preservatives 371
	22.6	Customer-based Production of Emulsions and More 372
	22.7	Vesicle Formation in Microfluidic Structures 376
	22.8	Liquid Detergent Production by Surfactant Dispersion 377
	22.9	Screening of Cream Formulations 380
	22.10	Microencapsulation Processes 381
	22.11	Alginate Gelation in Microfluidic Channels 383
	22.12	Production of Base Chemicals Exemplified by SO <sub>3</sub> and Detergent
		Production 384
	22.12.1	Introduction 385
	22.12.2	Sulfonation of Toluene with Gaseous Sulfur Trioxide in a Microreactor Setup 385
	22.12.3	One-pass Synthesis of Pure Sulfur Trioxide in Microreactors 387
	22.13	Homogenization of Dairy Products 389
	22.14	Outline of Additional and Potential Aspects of Microreactor Applications in the Consumer Goods Industry 390
	22.14.1	Microfluidic Devices in Chemical Sensing of Flavors and Fragrances 391
	22.14.2	Accessibility of New Materials Exemplified by the Controlled Synthesis of Polymer Particles 393
	22.14.3	Controlled Formation of Monodisperse Double Emulsions in a Microfluidic System 394
	22.15	Summary and Outlook 395
	22.13	References 399

23	Application and Operation of Microreactors for Fuel Conversion	405
	Peter Pfeifer, Katja Haas-Santo, and Oliver Görke	
23.1	Applications of Fuel Conversion 405	
23.1.1	Power Range 405	
23.1.2	Demands from Applications 406	
23.1.3	Fuels 407	
23.2	Operation of Microreactors for Fuel Conversion 407	
23.2.1	Routes for Fuel Conversion 407	
23.2.2	Gas Clean-up 409	
23.2.3	Heat Generation 410	
23.2.4	Development Stages 411	
23.2.5	Integrated Plant Concepts 411	
23.2.6	Examples of Different Approaches and Integration Levels 412	

23.2.7	Influences on Efficiency 417		
23.3	Conclusion and Outlook 418		
	References 419		
24	Steam Reforming 421		
	Gunther Kolb		
24.1	Introduction 421		
24.2	Reaction System 421		
24.3	Catalyst Coatings for Steam Reforming in Microchannels 422		
24.3.1	Catalyst Development and Characterization for Alcohol Steam		
	Reforming in Microchannels 422		
24.3.2	Development of Catalyst Coatings for Hydrocarbon Steam Reforming in Microchannels 425		
24.4	System Design and Integrated Microstructured Reactors 426		
24.4.1	Design Concepts of Microstructured Fuel Processors for Fuel Cells 426		
24.4.2	Reactors for Alcohol Steam Reforming 427		
24.4.2.1	Reactors for Methanol Steam Reforming in the Low and Sub-watt Power Range 428		
24.4.2.2	Alcohol Steam Reforming in Microstructured Plate Heat Exchangers 431		
24.4.2.3	Hydrocarbon Steam Reforming in Microstructured Plate Heat		
	Exchangers 435		
24.5	Conclusion 439		
	References 439		
25	Partial Oxidation 445		
	Peter Pfeifer		
25.1	Distinction Between Catalytic and Industrial Processes 446		
25.2	Catalysts 446		
25.2.1	Catalytically Active Species 447		
25.2.2	Catalytic Supports and Promoters 448		
25.3	Reactor Design and Results 450		
25.3.1	Packed Beds and Foams in Microstructures 451		
25.3.2	Catalytic Wall Reactors 453		
25.3.2.1	Microstructured Catalytically Active Materials 453		
25.3.2.2	Deposition of Catalytically Active Species on Microstructure Walls 455		
25.3.2.3	Deposition of Catalytically Active Species on Additional Catalyst		
	Supports 457		
25.4	Reactor Comparison 460		
25.5	Conclusion 462		
	References 463		
26	CO Clean-up: Water Gas Shift and Methanation Reactions 465		
	Andre C. van Veen, Yves Schuurman, and Claude Mirodatos		
26.1			
26.2	Background of the Two Reactions 465 Commercial and R&D Catalysts 468		

VIX	Contents

26.2.1	Temperature Range of Operation 468
26.2.2	Operational Limits 469
26.2.3	Non-pyrophoric Catalysts 469
26.2.4	Methanation Catalysts 470
26.3	Motivation for Microstructured Reactors 470
26.3.1	WGS Reaction 470
26.3.2	Methanation Reaction 470
26.4	Examples of Microstructured Reactor Developments 471
26.4.1	WGS Reaction 471
26.4.2	Methanation Reaction 475
26.5	Conclusion 476
20.3	References 476
	References 470
27	CO Clean-up: Preferential Oxidation 479
	Xun Ouyang and Ronald S. Besser
27.1	Introduction 479
27.2	PrOx Kinetics 480
27.3	PrOx in Microreactors 482
27.3.1	Microreactors as Tools for Catalyst and Kinetic Studies 482
27.3.1.1	Catalyzed Microstructured Reactors for PrOx Catalyst Screening 482
27.3.1.2	Silicon Microfabricated PrOx Reactor with Washcoated Microposts 484
27.3.1.3	Improved PrOx Performance Versus Monolith 484
27.3.1.4	PrOx Study with Grooved Stainless-steel Foils and Au-based
	Catalysts 485
27.3.2	PrOx in Integrated Fuel Processors 486
27.3.2.1	A 2.4 W <sub>e</sub> Micro Fuel Processor Based on Microchannels 486
27.3.2.2	Microchannel Reactors for a 100 W <sub>e</sub> Portable Fuel Processor 488
27.3.2.3	A 100 We Gasoline Fuel Processor Based on Foam Structure with
	Micropores 489
27.3.2.4	A 2 kW <sub>e</sub> Multistage PrOx Microchannel Reactor 490
27.4	A Detailed Example: A Thin-film Catalytic Microreactor as a Kinetic
	Tool 491
27.4.1	Experimental 492
27.4.2	Microkinetic Reaction Simulation 493
27.4.3	Quasi-3D Non-isothermal Reactor Model 495
27.5	Conclusion 499
	References 499

Index 503