

## Contents

<b>Foreword</b>	V
<b>Preface</b>	XV
<b>About the editors</b>	XIX
<b>List of Contributors</b>	XXI

<b>1</b>	<b>Introduction</b>	1
	<i>Philip Jessop and Walter Leitner</i>	
1.1	What is a Supercritical Fluid (SCF)?	1
1.2	Practical Aspects of Reactions in Supercritical Fluids	4
1.3	The Motivation for Use of SCFs in Modern Chemical Synthesis	6
1.4	The History and Applications of SCFs	9
1.4.1	The Discovery of SCFs and Their Use as Solvents	9
1.4.2	Extraction and Chromatography in SCFs	14
1.4.3	The History of Chemical Reactions in SCFs	16
1.4.4	Industrial Use of SCFs as Reaction Media	20
	References	24
<b>2</b>	<b>High-pressure Methods and Equipment</b>	31
	<i>Nils Theyssen, Katherine Scovell, and Martyn Poliakoff</i>	
2.1	Introduction	31
2.2	Infrastructure for High-pressure Experiments	32
2.2.1	Location	32
2.2.2	Gas Supply, Compression, and Purification	33
2.3	High-pressure Reactors	34
2.3.1	Materials of Construction for High-pressure Reactors	34
2.3.1.1	Metal Components	34
2.3.1.2	Sealing Materials	35
2.3.2	Reactor Design	41
2.3.2.1	General Considerations	41
2.3.2.2	Pressure Vessels for Batch Processing	41
2.3.2.3	Continuous Flow Reactors	44
2.4	Auxiliary Equipment and Handling	45

2.4.1	Tubes and Fittings	45
2.4.2	Valves	47
2.4.3	Pressure Transmitter and Manometer	47
2.4.4	Reactor Heating and Temperature Control	48
2.4.5	Stirrer Types	51
2.4.6	Optical Windows	53
2.4.7	Pressure Safety Valves and Bursting Discs	53
2.4.8	Online Sampling	54
2.4.9	Inline Spectroscopic Measurements	56
2.4.10	Reactor Cleaning	57
2.4.10.1	Cleaning with Organic Solvents	57
2.4.10.2	Cleaning with Heated Solvents	58
2.4.10.3	Cleaning with Acids	58
2.4.10.4	Cleaning with a Combination of Organic Solvent and $\text{scCO}_2$	58
2.5	Dosage Under a High-pressure Regime	58
2.5.1	Dosage of Gases	58
2.5.1.1	Safety Warnings	58
2.5.1.2	Dosing in Batch Processes	60
2.5.1.3	Dosage for Continuous Flow Processes	61
2.5.2	Dosage of Liquids	62
2.5.3	Dosage of Solids	64
2.6	Further Regulations and Control in Flow Systems	64
2.6.1	Supply Pressure	64
2.6.2	Reactor Pressure	65
2.6.3	Flow and Total Volume Measurement of Depressurized Gas Streams	66
2.7	Evaporation and Condensation	66
2.7.1	Evaporation	66
2.7.2	Condensation	66
2.8	Complete Reactor Systems for Synthesis with SCFs	67
2.8.1	Standard Batch Reactor System	67
2.8.1.1	Essential equipment	67
2.8.1.2	Brief Description of Work Steps	67
2.8.2	Fully Automated System for Continuous Flow Operation	69
2.9	Conclusion	73
	References	73
<b>3</b>	<b>Basic Physical Properties, Phase Behavior and Solubility</b>	<b>77</b>
	<i>Neil R. Foster, Frank P. Lucien, and Raffaella Mammucari</i>	
3.1	Introduction	77
3.2	Basic Physical Properties of Supercritical Fluids	77
3.3	Phase Behavior in High-Pressure Systems	86
3.3.1	Types of Binary Phase Diagrams	86
3.3.2	Asymmetric Binary Mixtures	88
3.4	Factors Affecting Solubility in Supercritical Fluids	92

- 3.4.1 The Supercritical Solvent 92
- 3.4.2 Chemical Functionality of the Solute 94
- 3.4.3 Temperature and Pressure Effects 96
- References 97
  
- 4 **Expanded Liquid Phases in Catalysis: Gas-expanded Liquids and Liquid–Supercritical Fluid Biphasic Systems** 101  
*Ulrich Hintermair, Walter Leitner, and Philip Jessop*
- 4.1 A Practical Classification of Biphasic Systems Consisting of Liquids and Compressed Gases for Multiphase Catalysis 101
- 4.2 Physical Properties of Expanded Liquid Phases 106
  - 4.2.1 Volumetric Expansion 106
  - 4.2.2 Density 109
  - 4.2.3 Viscosity 110
  - 4.2.4 Melting Point 111
  - 4.2.5 Interfacial Tension 112
  - 4.2.6 Diffusivity 114
  - 4.2.7 Polarity 115
  - 4.2.8 Gas Solubility 118
- 4.3 Chemisorption of Gases in Liquids and their Use for Synthesis and Catalysis 120
  - 4.3.1 *In Situ* Generation of Acids and Temporary Protection Strategies 120
  - 4.3.2 Switchable Solvents and Catalyst Systems 124
  - 4.4 Using Gas-expanded Liquids for Catalysis 129
    - 4.4.1 Motivation and Potential Benefits 129
    - 4.4.2 Sequential Reaction–Separation Processes 130
      - 4.4.2.1 Tunable Precipitation and Crystallization 130
      - 4.4.2.2 Tunable Phase Separations 131
      - 4.4.2.3 Tunable Miscibility 134
    - 4.4.3 Hydrogenation Reactions 135
    - 4.4.4 Carbonylation Reactions 139
    - 4.4.5 Oxidation Reactions 143
    - 4.4.6 Miscellaneous 148
  - 4.5 Why Perform Liquid–SCF Biphasic Reactions? 150
    - 4.5.1 By Necessity (Unintentional Immiscibility) 151
    - 4.5.2 To Facilitate Post-Reaction Separation 152
    - 4.5.3 To Facilitate Product/Catalyst Separation in Continuous Flow Systems 154
    - 4.5.4 To Stabilize a Catalyst 155
    - 4.5.5 To Remove a Kinetic Product 156
    - 4.5.6 To Control the Concentration of Reagent or Product in the Reacting Phase 156
    - 4.5.7 To Permit Emulsion Polymerization 157
    - 4.5.8 To Create Templated Materials 158
  - 4.6 Biphasic Liquid–SCF Systems 159

- 4.6.1 Solvent Selection 159
- 4.6.2 Aqueous–SCF Biphasic Systems 159
- 4.6.3 Ionic Liquid–SCF Biphasic Systems 163
- 4.6.4 Polymer–SCF Biphasic Systems 167
- 4.6.5 Liquid Product–SCF Biphasic Systems 171
- 4.7 Biphasic Reactions in Emulsions 172
  - 4.7.1 Water-in-SCF Inverse Emulsions 172
  - 4.7.2 SCF-in-Water Emulsions 173
  - 4.7.3 Ionic Liquid-in-SCF Emulsions 173
  - 4.7.4 Applications of Emulsions 174
- References 175
  
- 5 Synthetic Organic Chemistry in Supercritical Fluids 189**  
*Christopher M. Rayner, Paul M. Rose, and Douglas C. Barnes*
- 5.1 Introduction 189
- 5.2 Hydrogenation in Supercritical Fluids 190
  - 5.2.1 Asymmetric Hydrogenation and Related Reactions 198
- 5.3 Hydroformylation and Related Reactions in Supercritical Fluids 202
- 5.4 Oxidation Reactions in Supercritical Fluids 205
- 5.5 Palladium-mediated Coupling Reactions in Supercritical Fluids 208
- 5.6 Miscellaneous Catalytic Reactions in Supercritical Fluids 214
  - 5.6.1 Metal-catalyzed Processes 214
  - 5.6.2 Base-catalyzed Processes 218
  - 5.6.3 Acid-Catalyzed Processes 219
- 5.7 Cycloaddition Reactions in Supercritical Fluids 221
- 5.8 Photochemical Reactions in Supercritical Fluids 224
- 5.9 Radical Reactions in Supercritical Fluids 228
- 5.10 Biotransformations in Supercritical Fluids 229
- 5.11 Conclusion 234
- References 235
  
- 6 Heterogeneous Catalysis 243**  
*Roger Gläser*
- 6.1 Introduction and Scope 243
- 6.2 General Aspects of Heterogeneous Catalysis in SCFs and GXLs 244
  - 6.2.1 Utilization of SCFs in Heterogeneous Catalysis 245
    - 6.2.1.1 General Considerations 245
    - 6.2.1.2 Rate Enhancement 247
    - 6.2.1.3 Selectivity Tuning 248
    - 6.2.1.4 Lifetime/Stability Enhancement 250
    - 6.2.1.5 Reactor and Process Design 251
  - 6.2.2 Utilization of GXLs in Heterogeneous Catalysis 251
- 6.3 Selected Examples of Heterogeneously Catalyzed Conversions in SCFs and GXLs 252
  - 6.3.1 Conversions in SCFs 252

- 6.3.1.1 Hydrogenations 256
- 6.3.1.2 Fischer–Tropsch Synthesis 260
- 6.3.1.3 Hydroformylations 262
- 6.3.1.4 Oxidations 263
- 6.3.1.5 Alkylations 266
- 6.3.1.6 Isomerizations 269
- 6.3.1.7 Miscellaneous 270
- 6.3.2 Conversions in GXLs 271
- 6.4 Outlook 273
- References 274
  
- 7 Enzymatic Catalysis 281**  
*Pedro Lozano, Teresa De Diego, and José L. Iborra*
- 7.1 Enzymes in Non-aqueous Environments 281
- 7.2 Supercritical Fluids for Enzyme Catalysis 283
- 7.3 Enzymatic Reactions in Supercritical Fluids 285
- 7.4 Reaction Parameters in Supercritical Biocatalysis 289
- 7.5 Stabilized Enzymes for Supercritical Biocatalysis 292
- 7.6 Enzymatic Catalysis in IL–scCO<sub>2</sub> Biphasic Systems 294
- 7.7 Future Trends 298
- References 298
  
- 8 Polymerization in Supercritical Carbon Dioxide 303**  
*Uwe Beginn*
- 8.1 General Aspects 303
- 8.1.1 Introduction and Scope 303
- 8.1.2 Supercritical Fluids 304
- 8.1.3 Solubility of Macromolecules in scCO<sub>2</sub> 306
- 8.1.4 Stabilizer Design for Dispersion Polymerizations 310
- 8.1.5 Limitations of Polymer Preparation in scCO<sub>2</sub> 314
- 8.2 Polymerization in scCO<sub>2</sub> 315
- 8.2.1 Radical Polymerization in scCO<sub>2</sub> 315
- 8.2.1.1 Side-chain Fluoropolymers 317
- 8.2.1.2 Fluoroolefin Polymers 319
- 8.2.1.3 Poly(Methyl Methacrylate) 326
- 8.2.1.4 Polystyrene 332
- 8.2.1.5 Other Vinyl Monomers 335
- 8.2.2 Metal-catalyzed Polymerizations 340
- 8.2.2.1 Polyolefins 340
- 8.2.2.2 Other Metal-catalyzed Polymerizations 342
- 8.2.3 Ionic Chain Polymerizations 346
- 8.2.3.1 Cationic Polymerizations 346
- 8.2.3.2 Coordinative Anionic Polymerization 348
- 8.3 Conclusion 352
- References 353

<b>9</b>	<b>Synthesis of Nanomaterials</b>	<b>369</b>
	<i>Zhimin Liu and Buxing Han</i>	
9.1	Introduction	369
9.2	Metal and Semiconductor Nanocrystals	369
9.2.1	Direct Synthesis of Nanocrystals in SCFs	369
9.2.1.1	Synthesis in $\text{scCO}_2$	370
9.2.1.2	Synthesis in Supercritical Organic Solvents	371
9.2.1.3	Synthesis in Supercritical Water ( $\text{scH}_2\text{O}$ )	373
9.2.2	Synthesis of Nanomaterials in SCF-based Microemulsions	374
9.2.2.1	Water-in-Supercritical Alkane Microemulsion	374
9.2.2.2	Water-in- $\text{scCO}_2$ Microemulsions	375
9.2.2.3	Recovery of Nanoparticles from Reverse Micelles Using $\text{scCO}_2$	377
9.3	Metal Oxide Nanoparticles	377
9.3.1	Supercritical Hydrothermal Synthesis	377
9.3.2	Direct Sol-Gel Synthesis in $\text{scCO}_2$	380
9.3.3	Synthesis Using Water-in- $\text{CO}_2$ Microemulsions	382
9.4	Carbon Nanomaterials	383
9.4.1	Carbon Nanotubes (CNTs)	383
9.4.2	Carbon Nanocages	385
9.5	Nanocomposites	385
9.5.1	Synthesis of Polymer-based Composites	386
9.5.2	Decoration of Nanoparticles on Carbon Nanotubes	388
9.5.3	Deposition of Nanoparticles on Porous Supports	391
9.5.4	Some Other Nanocomposites	393
9.6	Conclusion	393
	References	394
<b>10</b>	<b>Photochemical and Photo-induced Reactions in Supercritical Fluid Solvents</b>	<b>399</b>
	<i>James M. Tanko</i>	
10.1	Introduction	399
10.1.1	"Solvent" Properties of Supercritical Fluids	399
10.1.2	Scope of This Chapter	400
10.1.3	Experimental Considerations	400
10.2	Photochemical Reactions in Supercritical Fluid Solvents	403
10.2.1	Geometric Isomerization	403
10.2.2	Photodimerization	403
10.2.3	Carbonyl Photochemistry	405
10.2.4	Photosensitization and Photo-induced Electron Transfer	409
10.2.5	Photo-oxidation Reactions	410
10.3	Photo-initiated Radical Chain Reactions in Supercritical Fluid Solvents	410
10.3.1	Free Radical Brominations of Alkyl Aromatics in Supercritical Carbon Dioxide	410

- 10.3.2 Free Radical Chlorination of Alkanes in Supercritical Fluid Solvents 411
- 10.4 Conclusion 414
- References 415
  
- 11 Electrochemical Reactions 419**  
*Patricia Ann Mabrouk*
- 11.1 Introduction 419
- 11.2 Electrochemical Methods 419
- 11.3 Analytes 420
- 11.4 Electrolytes 421
- 11.5 Electrochemical Cell and Supercritical Fluid Delivery System 421
- 11.6 Electrodes 422
- 11.6.1 Working Electrode 422
- 11.6.2 Reference Electrode 422
- 11.7 Solvents 423
- 11.7.1 Supercritical Carbon Dioxide 424
- 11.7.1.1 Electrode Modification 425
- 11.7.1.2 Hydrophobic Electrolytes 426
- 11.7.1.3 Water-in-Carbon Dioxide Microemulsions 426
- 11.7.2 Hydrofluorocarbon Supercritical Solvents 426
- 11.8 Applications 429
- 11.8.1 Electrochemical Synthesis in Supercritical Solvents 429
- 11.8.2 Electrochemical Detection in Supercritical Solvents 429
- 11.9 Conclusion and Outlook 431
- References 431
  
- 12 Coupling Reactions and Separation in Tunable Fluids: Phase Transfer-Catalysis and Acid-catalyzed Reactions 435**  
*Pamela Pollet, Jason P. Hallett, Charles A. Eckert, and Charles L. Liotta*
- 12.1 Introduction 435
- 12.2 Phase Transfer Catalysis 435
- 12.2.1 Background 435
- 12.2.2 Phase Transfer Catalysis Quaternary Ammonium Salt-catalyzed Reactions 436
- 12.2.3 PTC Separation and Recycling Using CO<sub>2</sub> 437
- 12.3 Near-critical Water 438
- 12.3.1 Definition 438
- 12.3.2 Properties 439
- 12.3.3 Friedel–Crafts Chemistry in NCW 442
- 12.4 Alkylcarbonic Acids 448
- 12.4.1 Probing Alkylcarbonic Acids – Alkylcarbonic Acids with Diazodiphenylmethane (DDM) 448
- 12.4.2 Reactions Using Alkylcarbonic Acids 451
- 12.4.2.1 Ketal Formation 451

12.4.2.2	Formation of Diazonium Salts	452
12.5	Conclusion	453
	References	454
<b>13</b>	<b>Chemistry in Near- and Supercritical Water</b>	<b>457</b>
	<i>Andrea Kruse and G. Herbert Vogel</i>	
13.1	Introduction	457
13.2	Properties	457
13.3	Synthesis Reactions	459
13.3.1	Hydrations	460
13.3.2	Hydrolysis	460
13.3.2.1	Esters	460
13.3.2.2	Ethers	461
13.3.2.3	Amides	461
13.3.3	Dehydrations	461
13.3.4	Condensations	462
13.3.5	Diels–Alder Reactions	462
13.3.6	Rearrangements	463
13.3.7	Partial Oxidations	464
13.3.8	Reductions	464
13.3.9	Organometallic Reactions	465
13.4	Biomass Conversion	465
13.4.1	Platform Chemicals	465
13.4.1.1	Carbohydrates	465
13.4.1.2	Lignin	467
13.4.1.3	Proteins	467
13.4.2	Oil, Gases, Coke	468
13.5	Supercritical Water Oxidation (SCWO)	470
13.6	Inorganic Compounds in NSCW	471
13.6.1	Particle Formation	471
13.6.2	Corrosion	471
13.6.3	Unwanted Salt Precipitation and Salt Plugging	472
13.6.4	Poisoning of Heterogeneous Catalysts	472
13.7	Conclusion	472
13.8	Future Trends	473
	References	473
	<b>Index</b>	<b>477</b>