

Contents

Preface V

Contributors XXIII

Volume 1

- 1 **Introduction** 1
Boy Cornils, Wolfgang A. Herrmann, István T. Horváth, Walter Leitner, Stefan Mecking, Hélène Olivier-Bourbigou, and Dieter Vogt
- 2 **Aqueous-Phase Catalysis** 25
Boy Cornils and Wolfgang A. Herrmann
 - 2.1 Introduction 27
Boy Cornils
 - 2.2 State-of-the-Art 40
 - 2.2.1 Organic Chemistry in Water 40
André Lubineau, Jacques Augé, and Marie-Christine Scherrmann
 - 2.2.1.1 Introduction 40
 - 2.2.1.2 Origin of the Reactivity in Water 40
 - 2.2.1.3 Pericyclic Reactions 42
 - 2.2.1.4 Carbonyl Additions 43
 - 2.2.1.5 Radical Reactions 43
 - 2.2.2 Organometallic Chemistry of Water 46
Fritz E. Kühn and Wolfgang A. Herrmann
 - 2.2.2.1 Introduction 46
 - 2.2.2.2 Water as a Solvent and Ligand 46
 - 2.2.2.3 Organometallic Reactions of Water 48
 - 2.2.2.4 Water-Soluble Metal Complexes 51
 - 2.2.2.5 Perspectives 52

Multiphase Homogeneous Catalysis

Edited by Boy Cornils and Wolfgang A. Herrmann et al.

Copyright © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

ISBN: 3-527-30721-4

2.2.3	Catalysts for an Aqueous Biphasic Catalysis	55
2.2.3.1	Central Atoms	55
	<i>Ana M. Santos and Fritz E. Kühn</i>	
2.2.3.1.1	Introduction	55
2.2.3.1.2	Overview of the Metal Complexes Involved in Aqueous Catalysis	55
2.2.3.1.3	Complexes Containing an M–C Bond in Aqueous Catalysis	57
2.2.3.1.4	Mn, Tc, Re Complexes $\text{H}_3\text{C}-\text{MO}_3$ as an Example of Metal Variation in Potential Catalysts for Aqueous Systems	60
2.2.3.2	Ligands	66
2.2.3.2.1	Phosphorus-Containing Ligands	66
	<i>Othmar Stelzer (†), Stefan Rossenbach, Dietmar Hoff, Marcel Schreuder-Goedheijt, Paul C. J. Kamer, Joost N. H. Reek, and Piet W. N. M. van Leeuwen</i>	
2.2.3.2.2	Nitrogen- and Sulfur-Containing Water-Soluble Ligands	82
	<i>Philippe Kalck and Martine Urrutigoity</i>	
2.2.3.2.3	Other Concepts: Hydroxyphosphines	89
	<i>Mandy-Nicole Gensow and Armin Börner</i>	
2.2.3.3	Water-soluble Receptor as Mass Transfer Promoter	93
	<i>Eric Monflier</i>	
2.3	Homogeneous Catalysis in the Aqueous Phase as a Special Unit Operation	96
2.3.1	Fundamental Reaction Engineering of Aqueous Biphasic Catalysis	96
	<i>Zai-Sha Mao and Chao Yang</i>	
2.3.1.1	Introduction	96
2.3.1.2	Chemical Engineering Factors	98
2.3.1.3	Gas–Liquid–Liquid Three-Phase Hydroformylation	100
2.3.1.3.1	Effect of Agitation Speed	101
2.3.1.3.2	Orthogonal Experiment on Engineering Factors	102
2.3.1.3.3	Influence of Agitation Configuration	105
2.3.1.3.4	Emulsification of Reaction Mixture	107
2.3.1.3.5	Kinetics of Biphasic Hydroformylation	109
2.3.1.4	Mathematical Model for Biphasic Hydroformylation Reactor	110
2.3.1.5	Prospect of Reaction Engineering Study on Hydroformylation	111
2.3.2	Technical Solutions	114
	<i>Arno Behr and Joachim Seuster</i>	
2.3.2.1	Introduction	114
2.3.2.2	Technical Realization	114
2.3.2.2.1	Reaction and Product Separation	116
2.3.2.2.2	Reaction and Product Extraction	116
2.3.2.2.3	Reaction and Product Treatment	119

2.3.2.2.4	Reaction and Catalyst Separation	119
2.3.2.2.5	Reaction and Catalyst Extraction	120
2.3.2.2.6	Reaction and Catalyst Treatment	121
2.3.3	Membrane Techniques	122
	<i>José Sanchez Marcano</i>	
2.3.3.1	Membrane Separation Processes	122
2.3.3.2	The Coupling of a Membrane Separation Process with a Catalytic Reaction: the MR Concept	124
2.3.3.3	Application of the MR Concept to Homogeneous Catalytic Reactions (HCRs)	127
2.3.3.4	Conclusion	130
2.3.4	Micellar Systems	132
	<i>Günther Oehme</i>	
2.3.4.1	Introduction	132
2.3.4.2	Selected Reactions in Aqueous Micelles	133
2.3.4.3	Reactions in Reverse Micelles	135
2.3.4.4	Perspectives	135
2.3.5	Thermoregulated Phase-Transfer Catalysis	137
	<i>Zilin Jin and Yanhua Wang</i>	
2.3.5.1	Introduction	137
2.3.5.2	Thermoregulated Ligands and Thermoregulated Phase-Transfer Catalysis	137
2.3.5.3	Applications of Thermoregulated Phase-Transfer Catalysis	140
2.3.5.3.1	Hydroformylation of Higher Olefins	140
2.3.5.3.2	Selective Reduction of Nitroarenes	141
2.3.5.4	Conclusion	141
2.3.6	Environmental and Safety Aspects	143
	<i>Boy Cornils and Ernst Wiebus</i>	
2.4	Typical Reactions	148
2.4.1	Syntheses with Carbon Monoxide	148
2.4.1.1	Hydroformylation	148
2.4.1.1.1	Historical Development	148
	<i>Boy Cornils and Emile G. Kuntz</i>	
2.4.1.1.2	Kinetics	152
	<i>Raghunath V. Chaudhari</i>	
2.4.1.1.3	Conversion of Alkenes	164
	<i>Carl-Dieter Frohning, Christian W. Kohlpaintner, Helmut Bahrmann, Sandra Bogdanovic, Piet W. N. M. van Leeuwen, and Eric Monflier</i>	

2.4.1.2	Carbonylations	183
	<i>Matthias Beller and Jürgen G. E. Krauter</i>	
2.4.2	Hydrogenation and Hydrogenolysis	187
2.4.2.1	Hydrogenation	187
	<i>Ferenc Joó and Ágnes Kathó</i>	
2.4.2.1.1	Introduction	187
2.4.2.1.2	Catalysts and Mechanisms of Hydrogenation in Aqueous Solution	187
2.4.2.1.2	Hydrogenation of Alkenes, Alkynes, and Arenes	189
2.4.2.1.3	Hydrogenation of Compounds with C=O and C=N Bonds	191
2.4.2.1.4	Hydrogenolysis of C–O, C–N, C–S, and C–Halogen Bonds	193
2.4.2.1.5	Miscellaneous Hydrogenations	194
2.4.2.2	Hydrogenation, Hydrogenolysis, and Hydrodesulfurization of Thiophenes	196
	<i>Claudio Bianchini and Andrea Meli</i>	
2.4.2.2.1	Introduction	196
2.4.2.2.2	Hydrogenation Reactions	197
2.4.2.2.3	Hydrogenolysis/Desulfurization Reactions	199
2.4.2.2.4	Perspectives	201
2.4.3	Oxidations	202
2.4.3.1	Partial Oxidations	202
	<i>Roger A. Sheldon</i>	
2.4.3.1.1	Introduction	202
2.4.3.1.2	Water-Soluble Ligands	203
2.4.3.1.3	Concluding Remarks	206
2.4.3.2	Wacker-Type Oxidations	207
	<i>Eric Monflier</i>	
2.4.3.2.1	Co-Solvents or Solvents	208
2.4.3.2.2	Phase Transfer Catalysis	208
2.4.3.2.3	Microemulsion Systems	208
2.4.3.2.4	Immobilized Catalysts	208
2.4.3.2.5	Inverse Phase-Transfer Catalysis	209
2.4.3.2.6	Summary	209
2.4.3.3	Methyltrioxorhenium(VII) in Oxidation Catalysis	210
	<i>Fritz E. Kühn</i>	
2.4.3.3.1	Introduction	210
2.4.3.3.2	Synthesis of Methyltrioxorhenium(VII)	211
2.4.3.3.3	Behavior of Methyltrioxorhenium in Aqueous Solutions	211
2.4.3.3.4	Catalyst Formation and Catalytic Applications	212
2.4.3.3.5	Summary	215

2.4.4	Addition Reactions	217
2.4.4.1	Hydrocyanation	217
	<i>Henry E. Bryndza and John A. Harrelson Jr.</i>	
2.4.4.2	Hyrodimerization	221
	<i>Noriaki Yoshimura</i>	
2.4.4.3	Olefin Metathesis	225
	<i>Wolfgang A. Herrmann</i>	
2.4.4.3.1	Introduction	225
2.4.4.3.2	Ruthenium Catalysts	226
2.4.4.3.3	Rhenium Catalysts	228
2.4.4.3.4	Conclusion	229
2.4.4.4	Heck and Other C–C Coupling Reactions	230
	<i>Wolfgang A. Herrmann, Claus-Peter Reisinger, and Peter Härter</i>	
2.4.4.4.1	Introduction	230
2.4.4.4.2	Catalysts and Reaction Conditions	231
2.4.4.4.3	Olefination	231
2.4.4.4.4	Alkyne Coupling	233
2.4.4.4.5	Cross-Coupling Reactions	234
2.4.4.4.6	Conclusion	236
2.4.4.5	Aminations	238
	<i>Birgit Drießen-Hölscher (†)</i>	
2.4.4.5.1	Introduction	238
2.4.4.5.2	Hartwig–Buchwald Aminations	238
2.4.4.5.3	Telomerization to Yield Amines	240
2.4.4.5.4	Reductive Aminations/Hydroaminomethylations	242
2.4.4.5.5	Allylic Aminations	243
2.4.4.6	Alternating Copolymers from Alkenes and Carbon Monoxide	244
	<i>Eite Drent, Johannes A. M. van Broekhoven, and Peter H. M. Budzelaar</i>	
2.4.4.6.1	Introduction	244
2.4.4.6.2	Copolymerization of Ethylene and CO	245
2.4.4.6.3	Scope of Olefin/CO Copolymerization	252
2.4.4.6.4	Conclusions	253
2.4.5	Allylic Substitution Reactions	256
	<i>Denis Sinou</i>	
2.4.6	Asymmetric Synthesis	261
	<i>Denis Sinou</i>	
2.4.7	Biological Conversions	268
	<i>Peter J. Quinn</i>	
2.4.7.1	Introduction	268
2.4.7.2	Biochemical Substrates	269

2.4.7.3	Hydrogenation using Water-Soluble Catalysts	269
2.4.7.4	Hydrogenation of Biological Membranes	269
2.4.7.5	Conclusions	270
2.4.8	Other Examples	271
2.4.8.1	Lanthanides in Aqueous-Phase Catalysis	271
	<i>Shu Kobayashi</i>	
2.4.8.1.1	Introduction	271
2.4.8.1.2	Aldol Reactions	271
2.4.8.1.3	Mannich-Type Reactions	273
2.4.8.1.4	Diels–Alder Reactions	274
2.4.8.1.5	Micellar Systems	274
2.4.8.1.6	Asymmetric Catalysis in Aqueous Media	276
2.4.8.1.7	Conclusions	277
2.4.8.2	Dehalogenation	279
	<i>Mario Bressan</i>	
2.4.8.3	Various Other Reactions	283
	<i>Fritz E. Kühn, Ana M. Santos, and Wolfgang A. Herrmann</i>	
2.4.8.3.1	Isomerizations	283
2.4.8.3.2	Aldolizations	284
2.4.8.3.3	Hydroaminomethylation and Amination	285
2.4.8.3.4	Hydrosilylation Reactions	287
2.4.8.3.5	Thiolysis	287
2.4.8.3.6	Synthesis of Heterocycles	288
2.5	Commercial Applications	291
2.5.1	Oxo Synthesis (Hydroformylation)	291
	<i>Boy Cornils</i>	
2.5.2	Other Reactions	295
	<i>Boy Cornils</i>	
2.6	Supported Aqueous-Phase Catalysis as the Alternative Method	297
	<i>Henri Delmas, Ulises Jáuregui-Haza, and Anne-Marie Wilhelm</i>	
2.6.1	Introduction	297
2.6.2	SAPC: the Concept and Main Applications	297
2.6.3	The Supports and the Preparation of the SAP Catalysts	299
2.6.4	Main Factors Influencing the Efficiency of SAPC	299
2.6.5	Perspectives and Challenges	301
2.6.6	Conclusion	303

2.7	The Way Ahead: What Should be Done in the Future?	305
	<i>Boy Cornils and Wolfgang A. Herrmann</i>	
3	Organic–Organic Biphasic Catalysis	309
	<i>Dieter Vogt</i>	
3.1	Introduction	311
	<i>Dieter Vogt</i>	
3.2	State-of-the-Art and Typical Reactions	313
3.2.1	Organic–Organic Biphasic Catalysis on a Laboratory Scale	313
	<i>Dieter Vogt</i>	
3.2.1.1	Hydrogenation	313
3.2.1.2	Hydroformylation	315
3.2.1.3	Hydrogenolysis	317
3.2.1.4	Hydrosilylation	318
3.2.1.5	Oxidation	319
3.2.1.6	C–C Bond-Forming Reactions	321
3.2.1.6.1	Oxidative Coupling versus Hydroxylation	321
3.2.1.6.2	Heck Reaction	322
3.2.1.6.3	Suzuki Coupling	323
3.2.1.6.4	Alkylation of Hydroquinone with Isobutene	323
3.2.1.7	Isomerization	324
3.2.1.8	Hydration and Acetoxylation	325
3.2.2	Biphasic Catalysis on a Miniplant Scale	326
	<i>Arno Behr</i>	
3.2.3	Thermomorphic Solvent Systems	327
	<i>Arno Behr</i>	
3.3	Economical Applications (SHOP Process)	330
	<i>Dieter Vogt</i>	
3.3.1	Introduction	330
3.3.2	Process Description	331
3.4	Conclusions and Outlook	335
	<i>Dieter Vogt</i>	

4	Fluorous Catalysis	339
	<i>István T. Horváth</i>	
4.1	Introduction	341
	<i>István T. Horváth</i>	
4.2	State-of-the-Art and Typical Reactions	346
4.2.1	Carbon–Carbon Bond-Forming Reactions	346
	<i>Siegfried Schneider, Carl Christoph Tzschucke, and Willi Bannwarth</i>	
4.2.2	Hydroformylation and Hydrogenation Catalyzed by Perfluoroalkylated Phosphine–Metal Complexes	354
	<i>Eric G. Hope and Alison M. Stuart</i>	
4.2.2.1	Hydroformylation	354
4.2.2.2	Hydrogenation	359
4.2.3	Hydroformylation Catalyzed by Fluorous Triarylphosphite–Metal Complexes	362
	<i>Eric Monflier, André Mortreux, and Yves Castanet</i>	
4.2.4	Fluorous Nitrogen Ligands	368
4.2.4.1	For Oxidation Reactions	368
	<i>Gianluca Pozzi and Silvio Quici</i>	
4.2.4.2	Synthesis of Fluorous Nitrogen Ligands and Applications, Including Atom-Transfer Radical Reactions	375
	<i>Jean-Marc Vincent, Dominique Lastécouères, María Contel, Mariano Laguna, and Richard H. Fish</i>	
4.2.5	Enantioselective Catalysis	381
4.2.5.1	Under Biphasic Conditions	381
	<i>Denis Sinou</i>	
4.2.5.2	Under Non-biphasic Conditions	389
	<i>Seiji Takeuchi and Yutaka Nakamura</i>	
4.2.6	Liquid/Solid Catalyst-Recycling Method without Fluorous Solvents	394
	<i>Kazuaki Ishihara and Hisashi Yamamoto</i>	
4.3	Concluding Remarks	403
	<i>István T. Horváth</i>	

Volume 2

5	Catalysis in Nonaqueous Ionic Liquids (ILs)	405
	<i>Hélène Olivier-Bourbigou</i>	
5.1	General Introduction	407
	<i>Yves Chauvin</i>	
5.2	State-of-the-Art	413
5.2.1	Homogeneous Catalysis in Ionic Liquids	413
5.2.1.1	Ionic Liquids: Opportunities for Catalytic Reactions	413
	<i>Hélène Olivier-Bourbigou and Christophe Vallée</i>	
5.2.1.1.1	Introduction	413
5.2.1.1.2	Ionic Liquids: Non-Innocent Solvents	415
5.2.1.1.3	How to Choose Ionic Liquids	418
5.2.1.1.4	Advantages and Limitations of Using Ionic Liquids in Catalysis	420
5.2.1.1.5	Immobilization of the Metal Catalyst in the Solvent Phase	423
5.2.1.1.6	Separation of the Catalyst/Solvent from the Reaction Products	425
5.2.1.1.7	Ionic Liquids and scCO_2	426
5.2.1.1.8	Conclusion	428
5.2.1.2	Fundamentals	431
	<i>Tom Welton</i>	
5.2.1.2.1	Ionic Liquids: A New Class of Solvents	431
5.2.1.2.2	Physico-chemical Properties of ILs	432
5.2.1.2.3	Viscosities	439
5.2.1.2.4	Commonly Used ILs	441
5.2.1.2.5	Solubilities	441
5.2.1.2.6	Polarity	444
5.2.1.2.7	General Conclusions	452
5.2.1.3	Separation and Catalyst Recycling Techniques	455
	<i>Christian P. Mehnert</i>	
5.2.2	Selected Examples	468
5.2.2.1	Oligomerization	468
	<i>Hélène Olivier-Bourbigou</i>	
5.2.2.1.1	Introduction	468
5.2.2.1.2	Oligomerization in Chloroaluminate Ionic Liquids	469
5.2.2.1.3	Oligomerization in Non-chloroaluminate Ionic Liquids	474
5.2.2.1.4	Conclusion	476
5.2.2.2	Hydroformylation	477
	<i>Lionel Magna</i>	
5.2.2.2.1	Introduction	477

5.2.2.2.2	General Considerations for the Use of Ionic Liquids in Hydroformylation	479
5.2.2.2.3	Hydroformylation in Ionic Liquids	482
5.2.2.2.4	Conclusions	492
5.2.2.3	Hydrogenation	494
	<i>Paul J. Dyson and Dongbin Zhao</i>	
5.2.2.3.1	Introduction	494
5.2.2.3.2	Gas Solubilities in Molecular and Ionic Solvents	495
5.2.2.3.3	Detailed Examples	496
5.2.2.3.4	Concluding Remarks	508
5.2.2.4	Acidic Catalysis	511
	<i>Hélène Olivier-Bourbigou</i>	
5.2.2.4.1	Introduction	511
5.2.2.4.2	Use of Ionic Liquids in the Liquid Phase	511
5.2.2.4.3	Use of Ionic Liquids in the Solid Phase	517
5.2.2.4.4	Selected Applications	517
5.2.2.4.5	Conclusion	523
5.2.2.5	Biocatalysis	524
	<i>Jesper Brask, Christel T. Jørgensen, and Ole Kirk</i>	
5.2.2.5.1	Introduction	524
5.2.2.5.2	Ionic Liquids and Enzymes	525
5.2.2.5.3	Biocatalysis in Ionic Liquids	528
5.2.2.5.4	Opportunities and Potential Problem Areas	532
5.2.2.5.5	Conclusions and Perspectives	533
5.2.2.6	Liquid-phase HF Fluorination	535
	<i>Philippe Bonnet</i>	
5.2.2.6.1	Introduction	535
5.2.2.6.2	Context/Bibliographic Analysis	535
5.2.2.6.3	Super Acidic Ionic Liquids	536
5.2.2.6.4	Synthesis	537
5.2.2.6.5	Characterization of Superacidic Ionic Liquids Based on Sb	538
5.2.2.6.6	Activity/Catalysis	539
5.2.2.7	Application of Phosphonium Salts as Catalysts	542
	<i>James McNulty</i>	
5.3	Commercial Applications and Aspects	547
5.3.1	Difasol™ Process	547
	<i>Alain Forestière and Frédéric Favre</i>	
5.3.1.1	Introduction	547
5.3.1.2	One-Phase Butene Dimerization Process – Dimersol X™	548
5.3.1.2.1	The Reaction	548
5.3.1.2.2	The Process	550

5.3.1.2.3	Economics	551
5.3.1.3	Two Phase Butenes Dimerization Process – Difasol™	552
5.3.1.3.1	The Biphasic System	552
5.3.1.3.2	The Reaction	553
5.3.1.3.3	The Process	555
5.3.1.4	Outlook for Higher Olefin Dimerization	559
5.3.2	BASIL™ Process	560
	<i>Matthias Maase</i>	
5.3.2.1	Ionic Liquids in Industry	560
5.3.2.2	Solids and Suspensions	561
5.3.2.3	Acid Scavenging	562
5.3.2.4	Synthesis of Alkoxyphenylphosphines	563
5.3.2.5	Ionic Liquids (Dis)solve the Problem	564
5.3.2.6	Lesson Learned	565
5.3.2.7	BASIL™ is More than Just Acid Scavenging	566
5.3.3	Production (and Disposal) of ILs on a Large Scale	566
5.3.3.1	Industrial Aspects of Ionic Liquids	566
	<i>Markus Wagner and Marc Uerdingen</i>	
5.3.3.2	New Ionic Liquids with Stable Fluorinated Anions	568
	<i>Nikolai V. Ignatev and Urs Welz-Biermann</i>	
5.3.3.3	Industrial Synthesis of Phosphonium Ionic Liquids	570
	<i>Al Robertson</i>	
5.3.3.3.1	Introduction	570
5.3.3.3.2	Synthesis and Applications	571
5.3.3.3.3	Thermal Analysis	573
5.3.4	Industrial Production of Ionic Liquids	581
	<i>Christophe Vallée and Hélène Olivier-Bourbigou</i>	
5.3.4.1	Classical Methods for the Synthesis of Ionic Liquids	581
5.3.4.2	Purification and Analysis of Residual Impurities	583
5.3.4.3	Alternative Synthesis and Industrial Production	584
5.4	Preliminary (Eco-)Toxicological Risk Profiles of Ionic Liquids	588
	<i>Johannes Ranke, Frauke Stock, Reinhold Störmann, Kerstin Mölter, Jens Hoffmann, Bernd Ondruschka, and Bernd Jastorff</i>	
5.4.1	Background	588
5.4.1.1	Green and Sustainable Chemistry	588
5.4.1.2	Integrated and Sustainable Development of Products and Processes	589
5.4.2	Description of Selected Substances	590
5.4.2.1	General	590
5.4.2.2	The Test-Kits	593
5.4.2.3	Synthesis	593

5.4.3	First Results from Biological Testing	593
5.4.3.1	General	593
5.4.3.2	The Influence of Different Anions	595
5.4.3.3	The Influence of Varying Chain Lengths	596
5.4.4	Preliminary (Eco-)Toxicological Risk Profiles	596
5.4.4.1	General	596
5.4.4.2	Release R	598
5.4.4.3	Spatiotemporal Range S	598
5.4.4.4	Bioaccumulation B	598
5.4.4.5	Biological Activity A	599
5.4.4.6	Uncertainty	599
5.4.5	Outlook	599
5.5	Concluding Remarks and Outlook	601
	<i>Hélène Olivier-Bourbigou</i>	
6	Catalysis using Supercritical Solvents	605
	<i>Walter Leitner</i>	
6.1	Introduction	607
	<i>Aaron M. Scurto</i>	
6.1.1	Physico-Chemical Properties of Pure Supercritical Fluids	607
6.1.1.1	Thermodynamic Properties	608
6.1.1.1.1	Density	608
6.1.1.1.2	Joule–Thomson Coefficient	609
6.1.1.1.3	Heat Capacity	610
6.1.1.1.4	Dielectric Constant	611
6.1.1.2	Transport Properties	612
6.1.1.2.1	Diffusivity	612
6.1.1.2.2	Viscosity	613
6.1.1.2.3	Thermal Conductivity	613
6.1.2	Phase Behavior and Solubility in Supercritical Fluids	614
6.1.2.1	High-Pressure Phase Behavior of Mixtures	614
6.1.2.2	Phase Diagrams of Binary Mixtures: Liquids and Vapors	615
6.1.2.3	Phase Diagrams of Binary Mixtures: Solid–Fluid	617
6.1.2.4	Global Fluid Phase Behavior of Liquids and Gases	618
6.1.2.5	Global Phase Behavior with Solid and Fluid Phases	619
6.1.2.6	Multicomponent Phase Behavior	621
6.1.2.7	Examples of Combined Reaction/Phase Behavior Studies	622
6.1.3	Phase Behavior for Catalyst Immobilization	623
6.1.3.1	CO ₂ –Water	624
6.1.3.2	CO ₂ –Liquid Polymers	625
6.1.3.3	CO ₂ –Ionic Liquids	626
6.1.4	Conclusion	627

6.2	State-of-the-Art (Applications of SCFs in Areas other than Catalysis)	630
	<i>Nils Theyssen</i>	
6.2.1	Introduction	630
6.2.2	Extractions with Supercritical Fluids	630
6.2.2.1	Extraction of Caffeine	630
6.2.2.2	Other Extractions in the Food Industry	632
6.2.2.3	Extractions in the Pharmaceutical Industry	632
6.2.3	Impregnations with Supercritical Carbon Dioxide	633
6.2.3.1	Impregnation of Woods with Biocides	633
6.2.3.2	Textile Dyeing	633
6.2.3.3	Impregnation of Polymers with Drugs	634
6.2.4	Polymer Synthesis and Processing	634
6.2.4.1	Polymer Synthesis	634
6.2.4.2	Polymer Processing	635
6.2.5	Dry Cleaning with Compressed Carbon Dioxide	637
6.2.6	Utilisation in Semiconductor Processing and Cleaning	637
6.2.6.1	Photoresist Stripping	637
6.2.6.2	Chemical Fluid Deposition (CFD)	638
6.2.6.3	Drying	638
6.2.6.4	Snow Gun Cleaning	638
6.2.7	Formation of Fine Particles Using CO ₂	639
6.2.7.1	Rapid Expansions of Supercritical Solutions (RESS)	639
6.2.7.2	Gas Anti-Solvent Precipitation (GASP and Related Methods)	640
6.2.7.3	Particles from Gas-Saturated Solutions (PGSS)	640
6.2.8	CO ₂ as a Working Fluid for Heat Pump Systems	641
6.2.9	Conclusion	641
6.3	Homogeneous Catalysis in Supercritical Solvents as a Special Unit Operation	644
	<i>Charles M. Gordon and Walter Leitner</i>	
6.3.1	Introduction	644
6.3.2	Supercritical CO ₂ -Based Approaches to Catalyst Immobilization	646
6.3.2.1	General Considerations	646
6.3.2.2	Immobilization Methods Using CO ₂ Only	648
6.3.2.3	Solid-scCO ₂ Systems	651
6.3.2.4	Liquid-SCF Systems	652
6.3.2.4	Other Developments	656
6.3.3	Summary	657
6.4	Typical Reactions	659
6.4.1	Catalyst Immobilization using SCFs as the Only Mass-Separating Agent	659
	<i>Charles M. Gordon and Walter Leitner</i>	
6.4.1.1	Introduction	659

6.4.1.2	ScCO ₂ Insoluble Catalysts	661
6.4.1.3	ScCO ₂ -Soluble Catalysts	666
6.4.1.4	Conclusions	674
6.4.2	SCFs and Liquid Polymers	676
	<i>Philip G. Jessop</i>	
6.4.2.1	Introduction	676
6.4.2.2	CO ₂ -Insoluble Liquid Polymers	678
6.4.2.2.1	Physical Properties	678
6.4.2.2.2	Phase Behavior of CO ₂ /Liquid Polymer Mixtures	679
6.4.2.2.3	Physical Properties of CO ₂ -Expanded Liquid Polymers	681
6.4.2.3	Catalysis and Reactions in Liquid Polymer/scCO ₂ and Related Systems	682
6.4.2.4	Conclusions and Outlook	686
6.4.3	SCFs and Ionic Liquids	688
	<i>David J. Cole-Hamilton, Thulani E. Kunene, and Paul B. Webb</i>	
6.4.3.1	Introduction	688
6.4.3.2	Interaction of Supercritical Carbon Dioxide with Ionic Liquids	689
6.4.3.3	Extraction of Organic Compounds from Ionic Liquids using Supercritical Fluids	692
6.4.3.4	Solubility of Gases in Ionic Liquids	695
6.4.3.5	Continuous-Flow Homogeneous Catalysis using Supercritical Carbon Dioxide-Ionic Liquid Biphasic Systems	696
6.4.3.5.1	General Considerations and Background	696
6.4.3.5.2	Hydrogenation	698
6.4.3.5.3	Hydroformylation	700
6.4.3.5.4	Oxidation of Alkenes	703
6.4.3.5.5	Carbonate Formation	704
6.4.3.5.6	Alkene Coupling Reactions	705
6.4.3.5.7	Transesterification	707
6.4.3.6	Recent Developments	712
6.4.3.7	Outlook and Conclusions	713
6.4.4	SCFs and Water	716
	<i>Walter Leitner and Katja Burgemeister</i>	
6.4.4.1	Physico-chemical Properties of the scCO ₂ /H ₂ O System	716
6.4.4.2	Organic and Inorganic Synthesis in H ₂ O/CO ₂ Biphasic Systems	722
6.4.4.3	Catalysis in H ₂ O/CO ₂ Biphasic Systems	723
6.4.4.4	Catalysis in Inverted Biphasic Systems of Type scCO ₂ /H ₂ O	728
6.4.4.5	Outlook and Conclusion	731
6.5	Economics and Scale-Up	734
	<i>Peter Licence and Martyn Poliakoff</i>	
6.5.1	Introduction	734
6.5.2	Technical Issues	735

6.5.3	Economic Issues	737
6.5.4	The Commercial Scale-Up of the Hydrogenation of Isophorone	738
6.5.4.1	The Starting Point	738
6.5.4.2	The Strategy	739
6.5.4.3	Proof of Concept	739
6.5.4.4	Extending the Chemistry	740
6.5.4.5	Development of the Process	741
6.5.4.5.1	Choice of Catalyst	741
6.5.4.5.2	Reaction Optimization	742
6.5.4.5.3	Phase Behavior	742
6.5.4.6	The Plant	743
6.5.5	Conclusions	745
6.6	The Way Ahead: What Should be Done in the Future?	747
	<i>Walter Leitner</i>	
7	Soluble Polymer-Bound Catalysts	751
	<i>Stefan Mecking</i>	
7.1	Introduction	753
	<i>Stefan Mecking</i>	
7.1.1	General Background	753
7.1.2	Structure and Synthesis of Soluble Polymeric Supports	754
7.1.3	Binding of Catalytically Active Complexes	757
7.1.4	Metal Colloids	759
7.2	State-of-the-Art	763
	<i>Stefan Mecking</i>	
7.3	Homogeneous Catalysis with Soluble Polymer-Bound Catalysts as a Unit Operation	765
	<i>Stefan Mecking</i>	
7.3.1	Overview and General Considerations	765
7.3.2	Membrane Ultrafiltration Techniques	766
7.4	Typical Reactions	776
7.4.1	C–C Linkage Reactions by Formal Addition to Unsaturated Compounds	776
	<i>Christian Müller and Dieter Vogt</i>	
7.4.1.1	Introduction	776
7.4.1.2	Soluble Polymer- and Dendrimer-Bound Catalysts	776
7.4.1.3	Outlook	791

7.4.2	Coupling Reactions	793
	<i>Stefan Mecking and Ulf Schlotterbeck</i>	
7.4.2.1	Polymer-Bound Metal Complexes as Catalysts for C–C and C–N Coupling	793
7.4.2.2	C–C Coupling by Palladium Colloids	797
7.4.2.3	Homogeneous or Heterogeneous Catalysis in C–C Coupling by Palladium Colloids?	803
7.4.3	Oxidation Reactions	807
	<i>Ana M. Santos and Fritz E. Kühn</i>	
7.4.3.1	Introduction	807
7.4.3.2	Oxidation of Olefins	808
7.4.3.3	Oxidation of Alkanes	812
7.4.3.4	Wacker-Type Oxidation Reactions	812
7.4.3.5	Autoxidation of 2,6-Di- <i>tert</i> -butylphenol	813
7.4.3.6	Oxidative Decomposition of Polychlorophenols	815
7.4.4	Hydrogenation and Other Reduction Reactions	819
	<i>Lasse Greiner and Andreas Liese</i>	
7.4.4.1	Introduction	819
7.4.4.2	Borane Reduction	820
7.4.4.3	Molecular Hydrogen	823
7.4.4.4	Transfer Hydrogenation	831
7.4.4.5	Conclusion	832
7.5	Toward Economic Applications	835
	<i>Uwe Dingerdissen and Juan Almena</i>	
7.5.1	Introduction	835
7.5.2	Enantioselective Borane Reduction of Ketones	836
7.5.3	Asymmetric Transfer Hydrogenations	838
7.6	What Should be Done in the Future?	840
	<i>Stefan Mecking</i>	
8	Multiphase Processes as the Future of Homogeneous Catalysis	843
	<i>Boy Cornils and Wolfgang A. Herrmann</i>	
	Subject Index	853