## **Contents**

Preface xi

	Acknowledgments xv
1	Background and Overview 1
l.1	Introduction 1
1.2	Ionic Liquids 2
1.2.1	Acidic ILs 2
1.2.2	Basic ILs 6
1.2.3	Neutral ILs with HB Donor/Acceptor 12
1.2.4	Chiral ILs 14
1.3	Structure of This Book 15
	References 17
2	Ionic Liquid-Catalyzed Transformation of Carbon Dioxide to Chemicals
	Under Metal-free Conditions 23
2.1	Synthesis of Organic Carbonates 25
2.1.1	Synthesis of Symmetrically Linear Carbonates 25
2.1.2	Synthesis of Asymmetrically Linear Carbonates 28
2.1.3	Synthesis of Cyclic Carbonates 30
2.1.3.1	Cyclization of Epoxides with CO <sub>2</sub> 31
2.1.3.2	Cyclization of Propargylic Alcohols with CO <sub>2</sub> 46
2.2	Synthesis of N-containing Heterocycles 49
2.2.1	Synthesis of Quinazoline-2,4(1H, 3H)-Diones 50
2.2.2	Synthesis of 2-Oxazolidinones 52
2.2.3	Synthesis of Benzimidazolones 60
2.3	Reductive Transformation of CO <sub>2</sub> 60
2.3.1	Formylation of Amines with CO <sub>2</sub> and Hydrosilanes 60
2.3.2	Reductive Cyclization of X (NH, S)-o-substituted
	Anilines with CO <sub>2</sub> and Hydrosilanes 67
2.4	Synthesis of Other Compounds 67
2.5	Remarks and Perspectives 70
	References 71



	ā

3	Ionic Liquid-Mediated Reductive Transformation of Carbon Dioxide
	with Hydrogen 79
3.1	Direct Hydrogenation of CO <sub>2</sub> 80
3.1.1	CO <sub>2</sub> Hydrogenation to CO 80
3.1.2	CO <sub>2</sub> Hydrogenation to Formic Acid 81
3.1.3	CO <sub>2</sub> Hydrogenation to CH <sub>4</sub> 85
3.1.4	CO <sub>2</sub> Hydrogenation to C <sub>2+</sub> Hydrocarbons 86
3.2	N-formylation or N-methylation Reaction of Amines with CO <sub>2</sub> /H <sub>2</sub> 89
3.3	Hydroformylation of Olefin with CO <sub>2</sub> /H <sub>2</sub> 94
3.4	Hydromethylamination of Olefin with CO <sub>2</sub> /H <sub>2</sub> and Amines 97
3.5	Carbonylation of Alcohol/Ethers with CO <sub>2</sub> /H <sub>2</sub> 99
3.6	Remarks and Perspectives 102
	References 102
4	Electroreduction of Carbon Dioxide in Ionic Liquid-Based
•	Electrolytes 105
4.1	Fundamentals of CO <sub>2</sub> Electroreduction 107
4.1.1	Basic Principles of CO <sub>2</sub> Electroreduction 107
4.1.2	Reaction Pathways of CO <sub>2</sub> Electroreduction 108
4.2	IL-based Electrolytes for CO <sub>2</sub> Electroreduction 109
4.2.1	CO <sub>2</sub> Activation by IL-based Electrolytes 110
4.2.2	Influence of Chemical Structures of IL-based Electrolytes 111
4.2.2.1	Influence of Cation Structures 111
4.2.2.2	Influence of Anion Structures 113
4.2.2.3	Structural Influence of ILs for Homogeneous Electrocatalysts 115
4.2.3	Influence of Composition of the IL-based Electrolytes 117
4.3	Electroreduction of CO <sub>2</sub> to Various Chemicals in
	IL-based Electrolytes 121
4.3.1	Electroreduction of CO <sub>2</sub> to HCOOH 122
4.3.1.1	Ag-based Catalysts 122
	Bi-based Catalysts 124
4.3.1.3	In-based Catalysts 124
4.3.1.4	Pt-based Catalysts 124
	Sn-based Catalysts 124
	Cu-based Catalysts 124
	Mo-based Catalysts 125
4.3.1.8	
4.3.2	Electroreduction of CO <sub>2</sub> to CO 126
4.3.2.1	•
4.3.2.2	
4.3.2.3	
4.3.2.4	
4.3.2.5	Metal-free Catalysts 134
4.3.3	Electroreduction of CO <sub>2</sub> to CH <sub>3</sub> OH 134
4.3.4	Electroreduction of CO <sub>2</sub> to CH <sub>4</sub> 136

4.3.5	Electroreduction of $CO_2$ to $C_{2+}$ Compounds 137
4.4	Electrotransformation of CO <sub>2</sub> into Value-added Chemicals 140
4.4.1	Electrosynthesis of Carboxylic Acids 141
4.4.2	Electrosynthesis of Organic Carbonates with CO <sub>2</sub> 144
4.4.3	Electrosynthesis of Organic Carbamates from CO <sub>2</sub> and Amines 145
4.4.4	Electrosynthesis of Methylanilines from CO <sub>2</sub> 146
4.5	Remarks and Perspectives 147
	References 150
5	Ionic Liquid-Catalyzed Chemical Transformation of Lignocellulose 157
5.1	Ionic Liquid–Catalyzed Transformation of Cellulose and Its Derivatives 159
5.1.1	Hydrolysis of Cellulose to Reducing Sugars 159
5.1.2	Dehydration of Cellulose and Glucose to 5-Hydroxymethylfurfural 160
5.1.3	Dehydration of Cellulose and Glucose to Levulinic Acid 164
5.1.4	Oxidation of Cellulose to Formic Acid 167
5.1.5	Transesterification of Cellulose to Cellulose Esters 168
5.1.6	Pyrolysis of Cellulose to 5-Methylfurfural 169
5.2	Ionic Liquid-catalyzed Transformation of Hemicellulose and Xylose to Furfural 170
5.3	Ionic Liquid-Catalyzed Transformation of Lignin and Its Platforms 172
5.3.1	Direct Depolymerization of Lignin 173
5.3.2	Oxidative Depolymerization of Lignin and Its Derivatives 176
5.3.2.1	Oxidative Depolymerization of Lignin to Vanillin 176
5.3.2.2	Oxidative Depolymerization of Lignin and Derivatives to Aromatic
	Carboxylic Acids 178
5.3.2.3	
5.4	Remarks and Perspectives 184
	References 185
6	Ionic Liquid-Catalyzed Oxidation Reactions 189
6.1	Oxidation of Alcohols/Aldehydes 190
6.1.1	Oxidation of Primary Alcohols to Esters 190
6.1.2	Oxidation of Alcohols to Aldehydes or Ketones 193
6.2	Oxidation of Organic Sulfides and Oxidative Desulfurization 199
6.2.1	Oxidation of Organic Sulfides 199
6.2.2	Oxidative Desulfurization 205
6.2.2.1	Polyoxometalates-based IL Catalysts for Oxidative Desulfurization 206
6.2.2.2	Acidic Ionic Liquids for Oxidative Desulfurization 210
6.3	Oxidative Cyclization of Olefins and Allylic Alcohols 213
6.4	Oxidation of Amines 218
6.5	Baeyer-Villiger Oxidation 221
6.6	Oxidation of Other Compounds 224
6.6.1	Oxidation of Oxime 224
6.6.2	Oxidation of Toluene 224

6.6.3	Oxidation of Organic Halides 225
6.7	Remarks and Perspectives 225
	References 226
7	Ionic Liquid-Catalyzed Water-Involved Reactions 229
7.1	Dehydrative Esterification 229
7.1.1	Acidic Ionic Liquids 230
7.1.2	Basic Ionic Liquids 236
7.2	Dehydrative Etherification of Alcohols 237
7.3	Dehydration Alkenylation 243
7.4	Dehydrative Amidation 244
7.5	Ionic Liquid-catalyzed Hydration Reaction 249
7.5.1	Hydration of Alkynes 250
7.5.2	Hydration Reaction of Propargyl Alcohols 250
7.5.3	Hydration Reaction of Nitriles 254
7.5.4	Hydration of Epoxides 257
7.6	Hydrolysis of Esters/Ethers 260
7.6.1	Hydrolysis of Ester 260
7.6.2	Hydrolysis of Cyclic Carbonate 262
7.7	Remarks and Perspectives 264
	References 264
8	Ionic Liquid-Catalyzed Other Organic Reactions 269
8.1	Alkylation Reaction 269
8.1.1	Alkylation of Olefins 269
8.1.2	Friedel-Crafts Alkylation 271
8.1.2 8.2	Friedel-Crafts Alkylation 271 Michael Addition Reaction 274
	•
8.2	Michael Addition Reaction 274
8.2 8.2.1	Michael Addition Reaction 274 Aza-Michael Reaction 274
8.2 8.2.1 8.2.2	Michael Addition Reaction 274 Aza-Michael Reaction 274 Synthesis of Chiral Chemicals 277
8.2 8.2.1 8.2.2 8.3	Michael Addition Reaction 274 Aza-Michael Reaction 274 Synthesis of Chiral Chemicals 277 Diels-Alder Reactions 281
8.2 8.2.1 8.2.2 8.3 8.4	Michael Addition Reaction 274 Aza-Michael Reaction 274 Synthesis of Chiral Chemicals 277 Diels-Alder Reactions 281 Markovnikov Addition 284
8.2 8.2.1 8.2.2 8.3 8.4 8.5	Michael Addition Reaction 274 Aza-Michael Reaction 274 Synthesis of Chiral Chemicals 277 Diels-Alder Reactions 281 Markovnikov Addition 284 Knoevenagel Condensation 290
8.2 8.2.1 8.2.2 8.3 8.4 8.5 8.6	Michael Addition Reaction 274 Aza-Michael Reaction 274 Synthesis of Chiral Chemicals 277 Diels-Alder Reactions 281 Markovnikov Addition 284 Knoevenagel Condensation 290 Aldol Condensation Reaction 295
8.2 8.2.1 8.2.2 8.3 8.4 8.5 8.6 8.7	Michael Addition Reaction 274  Aza-Michael Reaction 274  Synthesis of Chiral Chemicals 277  Diels-Alder Reactions 281  Markovnikov Addition 284  Knoevenagel Condensation 290  Aldol Condensation Reaction 295  Ring-Closing C—O/C—O and C—O/O—H Bond Metathesis 298
8.2 8.2.1 8.2.2 8.3 8.4 8.5 8.6 8.7	Michael Addition Reaction 274  Aza-Michael Reaction 274  Synthesis of Chiral Chemicals 277  Diels-Alder Reactions 281  Markovnikov Addition 284  Knoevenagel Condensation 290  Aldol Condensation Reaction 295  Ring-Closing C—O/C—O and C—O/O—H Bond Metathesis 298  Ring-Closing Metathesis of Aliphatic Diethers 298
8.2 8.2.1 8.2.2 8.3 8.4 8.5 8.6 8.7 8.7.1 8.7.2	Michael Addition Reaction 274 Aza-Michael Reaction 274 Synthesis of Chiral Chemicals 277 Diels-Alder Reactions 281 Markovnikov Addition 284 Knoevenagel Condensation 290 Aldol Condensation Reaction 295 Ring-Closing C—O/C—O and C—O/O—H Bond Metathesis 298 Ring-Closing Metathesis of Aliphatic Diethers 298 Metathesis of Alkyloxy Alcohols 301
8.2 8.2.1 8.2.2 8.3 8.4 8.5 8.6 8.7 8.7.1 8.7.2	Michael Addition Reaction 274  Aza-Michael Reaction 274  Synthesis of Chiral Chemicals 277  Diels-Alder Reactions 281  Markovnikov Addition 284  Knoevenagel Condensation 290  Aldol Condensation Reaction 295  Ring-Closing C—O/C—O and C—O/O—H Bond Metathesis 298  Ring-Closing Metathesis of Aliphatic Diethers 298  Metathesis of Alkyloxy Alcohols 301  Remarks and Perspectives 303
8.2 8.2.1 8.2.2 8.3 8.4 8.5 8.6 8.7 8.7.1 8.7.2	Michael Addition Reaction 274  Aza-Michael Reaction 274  Synthesis of Chiral Chemicals 277  Diels-Alder Reactions 281  Markovnikov Addition 284  Knoevenagel Condensation 290  Aldol Condensation Reaction 295  Ring-Closing C—O/C—O and C—O/O—H Bond Metathesis 298  Ring-Closing Metathesis of Aliphatic Diethers 298  Metathesis of Alkyloxy Alcohols 301  Remarks and Perspectives 303
8.2 8.2.1 8.2.2 8.3 8.4 8.5 8.6 8.7 8.7.1 8.7.2 8.8	Michael Addition Reaction 274 Aza-Michael Reaction 274 Synthesis of Chiral Chemicals 277 Diels-Alder Reactions 281 Markovnikov Addition 284 Knoevenagel Condensation 290 Aldol Condensation Reaction 295 Ring-Closing C—O/C—O and C—O/O—H Bond Metathesis 298 Ring-Closing Metathesis of Aliphatic Diethers 298 Metathesis of Alkyloxy Alcohols 301 Remarks and Perspectives 303 References 303
8.2 8.2.1 8.2.2 8.3 8.4 8.5 8.6 8.7 8.7.1 8.7.2 8.8	Michael Addition Reaction 274 Aza-Michael Reaction 274 Synthesis of Chiral Chemicals 277 Diels-Alder Reactions 281 Markovnikov Addition 284 Knoevenagel Condensation 290 Aldol Condensation Reaction 295 Ring-Closing C—O/C—O and C—O/O—H Bond Metathesis 298 Ring-Closing Metathesis of Aliphatic Diethers 298 Metathesis of Alkyloxy Alcohols 301 Remarks and Perspectives 303 References 303  Ionic Liquid-Catalyzed Recycling of Spent Polymers 309
8.2 8.2.1 8.2.2 8.3 8.4 8.5 8.6 8.7 8.7.1 8.7.2 8.8	Michael Addition Reaction 274 Aza-Michael Reaction 274 Synthesis of Chiral Chemicals 277 Diels-Alder Reactions 281 Markovnikov Addition 284 Knoevenagel Condensation 290 Aldol Condensation Reaction 295 Ring-Closing C—O/C—O and C—O/O—H Bond Metathesis 298 Ring-Closing Metathesis of Aliphatic Diethers 298 Metathesis of Alkyloxy Alcohols 301 Remarks and Perspectives 303 References 303  lonic Liquid-Catalyzed Recycling of Spent Polymers 309 Degradation of Polyesters 310
8.2 8.2.1 8.2.2 8.3 8.4 8.5 8.6 8.7 8.7.1 8.7.2 8.8	Michael Addition Reaction 274 Aza-Michael Reaction 274 Synthesis of Chiral Chemicals 277 Diels-Alder Reactions 281 Markovnikov Addition 284 Knoevenagel Condensation 290 Aldol Condensation Reaction 295 Ring-Closing C—O/C—O and C—O/O—H Bond Metathesis 298 Ring-Closing Metathesis of Aliphatic Diethers 298 Metathesis of Alkyloxy Alcohols 301 Remarks and Perspectives 303 References 303  Ionic Liquid-Catalyzed Recycling of Spent Polymers 309 Degradation of Polyesters 310 Degradation of PET 310
8.2 8.2.1 8.2.2 8.3 8.4 8.5 8.6 8.7 8.7.1 8.7.2 8.8	Michael Addition Reaction 274 Aza-Michael Reaction 274 Synthesis of Chiral Chemicals 277 Diels-Alder Reactions 281 Markovnikov Addition 284 Knoevenagel Condensation 290 Aldol Condensation Reaction 295 Ring-Closing C—O/C—O and C—O/O—H Bond Metathesis 298 Ring-Closing Metathesis of Aliphatic Diethers 298 Metathesis of Alkyloxy Alcohols 301 Remarks and Perspectives 303 References 303  lonic Liquid-Catalyzed Recycling of Spent Polymers 309 Degradation of Polyesters 310 Degradation of PET 310 Hydrolysis of PET 311

9.1.2.1	Alcoholysis of PLA 324
9.1.2.2	Hydrolysis of PLA 327
9.1.2.3	Aminolysis of PLA 330
9.1.3	Degradation of PHB 332
9.1.3.1	Methanolysis of PHB 332
9.1.3.2	Decomposition of PHB 333
9.1.4	Degradation of PSS 334
9.1.5	Degradation of PC 336
9.1.5.1	Hydrolysis of PC 337
9.1.5.2	Alcoholysis of PC 338
9.1.5.3	Ammonolysis of PC 340
9.1.6	Methanolysis of PCL 342
9.1.7	General Approaches to Decompose Polyesters to Carboxylic Acids 343
9.2	Degradation of Polyamides 347
9.3	Upcycling of Polyolefins 348
9.4	Co-upcycling of Polyvinyl Chloride and Polyester 350
9.5	Remarks and Perspectives 351
	References 351

**Index** *357*