CONTENTS

Preface xi

Acknowledgments xvii

Contributors xix

1. Perspectives and State of the Art in Producing Solar Fuels and Chemicals from CO_2 1
Gabriele Centi and Siglinda Perathoner

1.1 Introduction 1
1.1.1 GHG Impact Values of Pathways of CO_2 Chemical Recycling 3
1.1.2 CO_2 Recycling and Energy Vectors 7
1.2 Solar Fuels and Chemicals From CO_2 8
1.2.1 Routes for Converting CO_2 to Fuels 9
1.2.2 H_2 Production Using Renewable Energy 11
1.2.3 Converting CO_2 to Base Chemicals 12
1.2.4 Routes to Solar Fuels 14
1.3 Toward Artificial Leaves 16
1.3.1 PEC Cells for CO_2 Conversion 17
1.4 Conclusions 19
Acknowledgments 20
References 20

2. Transformation of Carbon Dioxide to Useable Products Through Free Radical-Induced Reactions 25
G. R. Dey

2.1 Introduction 25
2.1.1 Background 26
2.2 Chemical Reduction of CO_2 29
2.2.1 Photochemical Reduction of CO_2 29
2.2.2 Electrochemical Reduction of CO_2 38
2.3 Conclusions 46
Acknowledgments 46
References 46

3. Synthesis of Useful Compounds from CO_2 **51**
Boxun Hu and Steven L. Suib

3.1 Introduction 51
3.2 Photochemical Reduction 53
3.3 Electrochemical Reduction 55
3.4 Electrocatalytic Reduction 57
3.4.1 Transition Metal Nanoparticle Catalysts 58
3.4.2 Coordination Complexes 69
3.4.3 Enzymes 70
3.5 CO_2 Hydrogenation 71
3.5.1 Active Phases 71
3.5.2 Products of CO_2 Hydrogenation 74
3.5.3 Deactivation and Regeneration 77
3.5.4 Mechanisms of CO_2 Hydrogenation 79
3.6 CO_2 Reforming 84
3.7 Prospects in CO_2 Reduction 86
Acknowledgments 86
References 86

4. Hydrogenation of Carbon Dioxide to Liquid Fuels **99**
Muthu Kumaran Gnanamani, Gary Jacobs, Venkat Ramana Rao Pendyala, Wenping Ma, and Burtron H. Davis

4.1 Introduction 99
4.2 Methanation of Carbon Dioxide 100
4.3 Methanol and Higher Alcohol Synthesis by CO_2 Hydrogenation 102
4.4 Hydrocarbons Through Modified Fischer-Tropsch Synthesis 105
4.5 Conclusions 114
References 115

5. Direct Synthesis of Organic Carbonates from CO_2 and Alcohols Using Heterogeneous Oxide Catalysts **119**
Yoshinao Nakagawa, Masayoshi Honda, and Keiichi Tomishige

5.1 Introduction 120
5.2 Ceria-Based Catalysts 122
5.2.1 Choice of Ceria Catalysts in Direct DMC Synthesis 122
5.2.2 Performances of the Ceria Catalyst in DMC Synthesis 123
5.2.3 Direct Synthesis of Various Organic Carbonates from Alcohols and CO_2 Without Additives 125
5.2.4 Reaction Mechanism 125
5.2.5 Ceria-Zirconia Catalysts 128
5.2.6 Modification of Ceria-Based Catalysts 129

5.2.7 Use of Acetonitrile as a Dehydrating Agent for DMC Synthesis 129
5.2.8 Use of Acetonitrile as Dehydrating Agent for Synthesis of Various Carbonates 132
5.2.9 Use of Benzonitrile as Dehydrating Agent 133
5.2.10 Deactivation of the Ceria Catalyst in the Presence of Benzonitrile 135
5.2.11 Use of Other Dehydrating Agents 136
5.3 Zirconia-Based Catalysts 137
5.3.1 Structure and Catalytic Performance of Zirconia 137
5.3.2 Modification of Zirconia Catalysts 139
5.3.3 Reaction Mechanism over Zirconia-Based Catalysts 140
5.3.4 Combination of Dehydrating Agents with Zirconia-Based Catalysts 144
5.4 Other Metal Oxide Catalysts 145
5.5 Conclusions and Outlook 145
References 146

6. High-Solar-Efficiency Utilization of CO_2: the STEP (Solar Thermal Electrochemical Production) of Energetic Molecules 149
Stuart Licht

6.1 Introduction 149
6.2 Solar Thermal Electrochemical Production of Energetic Molecules: an Overview 151
6.2.1 STEP Theoretical Background 151
6.2.2 STEP Solar-to-Chemical Energy Conversion Efficiency 155
6.2.3 Identification of STEP Consistent Endothermic Processes 161
6.3 Demonstrated STEP Processes 165
6.3.1 STEP Hydrogen 165
6.3.2 STEP Carbon Capture 165
6.3.3 STEP Iron 170
6.3.4 STEP Chlorine and Magnesium Production (Chloride Electrolysis) 178
6.4 STEP Constraints 180
6.4.1 STEP Limiting Equations 180
6.4.2 Predicted STEP Efficiencies for Solar Splitting of CO_2 182
6.4.3 Scalability of STEP Processes 184
6.5 Conclusions 186
Acknowledgments 186
References 186

7. Electrocatalytic Reduction of CO_2 in Methanol Medium **191**
M. Murugananthan, S. Kaneco, H. Katsumata, T. Suzuki and M. Kumaravel

7.1 Introduction 191
7.2 Electrocatalytic Reduction of CO_2 in Methanol Medium 193
7.2.1 Effect of Electrolyte Containing Salt 200
7.2.2 Effect of Electrode Materials 204
7.2.3 Effect of Potential 208
7.3 Mechanisms of CO_2 Reduction in Nonaqueous Protic (CH_3OH) Medium 210
7.4 Conclusions 211
References 213

8. Synthetic Fuel Production from the Catalytic Thermochemical Conversion of Carbon Dioxide **215**
Navadol Laosiripojana, Kajornsak Faungnawakij, and Suttichai Assabumrungrat

8.1 Introduction 215
8.2 General Aspects of CO_2 Reforming 218
8.3 Catalyst Selection for CO_2 Reforming Reaction 221
8.3.1 Active Components 221
8.3.2 Support and Promoter 226
8.4 Reactor Technology for Dry Reforming 228
8.5 Conversion of Synthesis Gas to Synthetic Fuels 230
8.5.1 Gas-to-Liquid 231
8.5.2 Methanol and DME 234
8.6 Conclusions 239
Acknowledgments 240
References 240

9. Fuel Production from Photocatalytic Reduction of CO_2 with Water Using TiO_2-Based Nanocomposites **245**
Ying Li

9.1 Introduction 245
9.2 CO_2 Photoreduction: Principles and Challenges 246
9.3 TiO_2-Based Photocatalysts for CO_2 Photoreduction: Material Innovations 247
9.3.1 TiO_2 Nanoparticles and High-Surface-Area Support 247
9.3.2 Metal-Modified TiO_2 Photocatalysts 248
9.3.3 Metal-Modified TiO_2 Supported on Mesoporous SiO_2 249
9.3.4 Nonmetal-Doped TiO_2 Photocatalysts 251

9.4 Photocatalysis Experiments 254
9.5 CO_2 Photoreduction Activity 255
9.5.1 Cu/TiO_2-SiO_2 and $Ce-TiO_2$/SBA-15 Catalysts 255
9.5.2 Copper- and/or Iodine-Modified TiO_2 Catalysts 258
9.5.3 TiO_2 Polymorphs Engineered with Surface Defects 258
9.6 Reaction Mechanism and Factors Influencing Catalytic Activity 259
9.6.1 Effects of Cu and Iodine Modification on TiO_2 259
9.6.2 Effect of O_2 on CO_2 Photoreduction 261
9.6.3 In Situ DRIFTS Analysis on Surface Chemistry 261
9.7 Conclusions and Future Research Recommendations 265
References 265

10. Photocatalytic Reduction of CO_2 to Hydrocarbons Using Carbon-Based AgBr Nanocomposites Under Visible Light 269
Mudar Abou Asi, Chun He, Qiong Zhang, Zuocheng Xu, Jingling Yang, Linfei Zhu, Yanling Huang, Ya Xiong, and Dong Shu

10.1 Introduction 269
10.2 Mechanism of Photocatalytic Reduction for CO_2 270
10.3 Carbon Dioxide Reduction 271
10.4 AgBr Nanocomposites 274
10.4.1 Preparation of Catalyst 275
10.4.2 Characterization of Carbon-Based AgBr Photocatalysts 275
10.4.3 Photocatalytic Reduction Activity of Carbon-Based AgBr Nanocomposites 276
10.4.4 Stability of Carbon-Based AgBr Nanocomposites and Electron Transfer Mechanism 279
10.5 Conclusions 283
Acknowledgments 283
References 284

11. Use of Carbon Dioxide in Enhanced Oil Recovery and Carbon Capture and Sequestration 287
Suguru Uemura, Shohji Tsushima, and Shuichiro Hirai

11.1 Introduction 287
11.2 Enhanced Oil Recovery 288
11.2.1 Oil Production Stages 288
11.2.2 Physicochemical Mechanism of CO_2 EOR 290
11.2.3 Phase Equilibrium of CO_2 and Oil Binary Mixture 291
11.2.4 Minimum Miscibility Pressure 292
11.2.5 Implementation of EOR 293

11.3 Carbon Capture and Sequestration 294
11.3.1 Background and Basis of CCS 294
11.3.2 CCS with Micronized CO_2 295
11.3.3 Experimental CO_2 Micronization 295
11.3.4 Experimental Results 296
11.3.5 Droplet Diameter Distribution in the CO_2 Emulsion 297
11.4 Future Tasks 298
11.5 Summary 298
References 298

Index **301**