Contents

About the Editors XIII
List of Contributors XV

1 Zeolites in Catalysis 1
   Stephen H. Brown
   1.1 Introduction 1
   1.1.1 The Environmental Benefits of Zeolite-enabled Processes 2
   1.2 General Process Considerations 5
   1.3 Zeolite Fundamentals 6
   1.3.1 Other Properties 7
   1.3.2 Number of Acid Sites 8
   1.3.3 Acid Strength 8
   1.4 Reaction Mechanisms 8
   1.4.1 Hydrocarbon Cracking 8
   1.4.2 Oligomerization and Alkylation 12
   1.4.3 Isomerization 14
   1.4.4 Transalkylation of Aromatics 15
   1.4.5 Hydrogen Transfer or Conjunct Polymerization 18
   1.5 Mass Transport and Diffusion 21
   1.6 Zeolite Shape Selectivity 22
   1.6.1 Mass Transport Discrimination of Product Molecules 22
   1.6.2 Molecular Sieving 23
   1.6.3 Molecular Orientation 23
   1.6.4 Transition State Stabilization 25
   1.6.5 Organic Reaction Centers 26
   1.7 Counter Ion Mobility 29
   1.8 Conclusions 29
   References 29

2 Sol-Gel Sulfonic Acid Silicas as Catalysts 37
   Adam F. Lee and Karen Wilson
   2.1 Introduction 37
   2.2 Preparation of Meso-structured Silica Sulfonic Acid Catalysts 38
2.2.1 Templating Methods 38
2.2.1.1 Cationic/Anionic Templates 38
2.2.1.2 Neutral Templates 39
2.2.2 Organically Functionalized Silica 39
2.2.2.1 Characterization 40
2.2.2.2 Grafting Methods 42
2.2.2.3 Direct Preparation Methods 43
2.2.3 Acid Strength of Sulfonic Acid Catalysts 44
2.2.3.1 Phenyl- Versus Propylsulfonic Acids 45
2.2.4 Fine Tuning the Catalytic Activity of Sulfonic Acid Silicas 46
2.2.4.1 Cooperative Effects 46
2.2.4.2 Effect of Spectator Groups 48
2.3 Application in Organic Transformations 49
2.3.1 Condensation and Esterification 49
2.3.2 Electrophilic Aromatic Substitution 51
2.3.3 Miscellaneous Reactions 52
2.4 Conclusions and Future Prospects 53
References 55

3 Applications of Environmentally Friendly TiO₂ Photocatalysts in Green Chemistry: Environmental Purification and Clean Energy Production Under Solar Light Irradiation 59
Masaya Matsuoka and Masakazu Anpo

3.1 Introduction 59
3.2 Principles of Photocatalysis 61
3.3 Application of Photocatalysts in Green Chemistry: Solar Energy Conversion and Environmental Protection 62
3.3.1 Water Splitting to Produce Pure Hydrogen as Clean Fuel 62
3.3.2 Photocatalytic Reduction of CO₂ with H₂O (Artificial Photosynthesis) 64
3.3.3 Direct Photocatalytic Decomposition of NO into N₂ and O₂ 67
3.3.4 Application to the Purification of Air Polluted with Various Organic Compounds 70
3.3.5 Application to the Purification of Water Polluted with Toxic Compounds Such as Dioxins 71
3.3.6 Superhydrophilic Properties of TiO₂ Thin Films and Their Application in Self-cleaning Materials 72
3.4 Development of Visible Light-responsive TiO₂ Photocatalysts 73
3.4.1 Modification of the Electronic State of TiO₂ by Applying an Advanced Metal Ion Implantation Method 73
3.4.2 Design of Visible Light-responsive Ti/Zeolite Catalysts by Applying an Advanced Metal Ion Implantation Method 75
3.4.3 Preparation of Visible Light-responsive TiO₂ Thin-film Photocatalysts by an RF Magnetron Sputtering Deposition Method 76
4 Nanoparticles in Green Catalysis 81
   Mazaahir Kidwai
   4.1 Introduction 81
   4.2 Advanced Catalysis by Gold Nanoparticles 81
   4.3 Nickel Nanoparticles: a Versatile Green Catalyst 85
   4.4 Copper Nanoparticles: an Efficient Catalyst 87
   4.5 Bimetallic Nanoparticles in a Variety of Reactions 89
   References 91

5 'Heterogeneous Chemistry' 93
   Heiko Jacobsen
   5.1 Introduction 93
   5.2 'Heterogeneous Catalysis' 96
      5.2.1 An Exemplarily Reaction – Catalysts for Hydrogen Production
           from Biomass-Derived Hydrocarbons 97
      5.2.2 Transportation Fuels from Biomass – Catalytic Processing of
           Biomass-derived Reactants 100
      5.2.3 Diesel Fuels from Biomass – Heterogeneous Processes for
           Biodiesel Production 103
      5.2.4 Other Heterogeneous Aspects of Catalysis 106
         5.2.4.1 Solid and Solid Acid Catalysts 106
         5.2.4.2 Recycling Catalysts 107
         5.2.4.3 One-pot Catalysis 108
         5.2.4.4 Photocatalysis 108
      5.3 Solvents for Green Catalysis 108
      5.3.1 Heterogeneous Solvent Systems 109
      5.3.2 Solvent-free 'Heterogeneous Chemistry' 112
   5.4 Conclusion and Outlook 113
   References 114

6 Single-site Heterogeneous Catalysts via Surface-bound
   Organometallic and Inorganic Complexes 117
   Christophe Copéret
   6.1 Introduction 117
   6.2 Generalities 117
   6.3 Hydrogenation and Hydrosilylation 119
      6.3.1 Hydrogenation 119
      6.3.2 Hydrosilylation 123
   6.4 Metathesis and Homologation Processes of Alkenes 124
      6.4.1 Alkene Metathesis 124
         6.4.1.1 Silica-supported Catalysts 124
         6.4.1.2 Alumina-supported Catalysts 127
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.4.2 Other Alkene Homologation Processes</td>
<td>128</td>
</tr>
<tr>
<td>6.4.2.1 Direct Conversion of Ethene into Propene</td>
<td>128</td>
</tr>
<tr>
<td>6.4.2.2 Cyclization of Dienes</td>
<td>129</td>
</tr>
<tr>
<td>6.5 Metathesis, Dimerization, Trimerization and Other Reactions Involving Alkynes</td>
<td>129</td>
</tr>
<tr>
<td>6.5.1 Alkyne Metathesis</td>
<td>129</td>
</tr>
<tr>
<td>6.5.2 Dimerization and Trimerization of Alkynes</td>
<td>130</td>
</tr>
<tr>
<td>6.5.3 Hydroamination of Alkynes</td>
<td>131</td>
</tr>
<tr>
<td>6.6 Lewis Acid-catalyzed Reactions</td>
<td>131</td>
</tr>
<tr>
<td>6.6.1 Silica-supported Group 4 Metals</td>
<td>131</td>
</tr>
<tr>
<td>6.6.1.1 Reduction of Ketones Through Hydrogen Transfer</td>
<td>133</td>
</tr>
<tr>
<td>6.6.1.2 Transesterification of Esters</td>
<td>134</td>
</tr>
<tr>
<td>6.6.2 Silica-supported Group 3 Metals and Lanthanides</td>
<td>134</td>
</tr>
<tr>
<td>6.7 Oxidation</td>
<td>135</td>
</tr>
<tr>
<td>6.7.1 Single-site Titanium Species</td>
<td>135</td>
</tr>
<tr>
<td>6.7.2 Single-site Zirconium Species</td>
<td>137</td>
</tr>
<tr>
<td>6.7.3 Single-site Vanadium Species</td>
<td>137</td>
</tr>
<tr>
<td>6.7.4 Single-site Tantalum Species</td>
<td>137</td>
</tr>
<tr>
<td>6.7.5 Single-site Group 6 Species</td>
<td>138</td>
</tr>
<tr>
<td>6.7.6 Single-site Iron Species</td>
<td>139</td>
</tr>
<tr>
<td>6.7.7 Single-site Cobalt Species</td>
<td>141</td>
</tr>
<tr>
<td>6.8 Alkane Homologation</td>
<td>141</td>
</tr>
<tr>
<td>6.8.1 Alkane Hydrogenolysis</td>
<td>141</td>
</tr>
<tr>
<td>6.8.2 Alkane Metathesis</td>
<td>143</td>
</tr>
<tr>
<td>6.8.3 Alkane Cross-metathesis</td>
<td>146</td>
</tr>
<tr>
<td>References</td>
<td>146</td>
</tr>
</tbody>
</table>

7 Sustainable Heterogeneous Acid Catalysis by Heteropoly Acids 153

Ivan Kozhevnikov

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1 Introduction</td>
<td>153</td>
</tr>
<tr>
<td>7.2 Development of HPA Catalysts Possessing High Thermal Stability</td>
<td>156</td>
</tr>
<tr>
<td>7.3 Modification of HPA Catalysts to Enhance Coke Combustion</td>
<td>157</td>
</tr>
<tr>
<td>7.3.1 Propene Oligomerization</td>
<td>158</td>
</tr>
<tr>
<td>7.3.2 Friedel–Crafts Acylation</td>
<td>159</td>
</tr>
<tr>
<td>7.4 Inhibition of Coke Formation on HPA Catalysts</td>
<td>161</td>
</tr>
<tr>
<td>7.5 Reactions in Supercritical Fluids</td>
<td>163</td>
</tr>
<tr>
<td>7.6 Cascade Reactions Using Multifunctional HPA Catalysts</td>
<td>165</td>
</tr>
<tr>
<td>7.6.1 Synthesis of MIBK</td>
<td>166</td>
</tr>
<tr>
<td>7.6.2 Hydrogenolysis of Glycerol to Propanediol</td>
<td>167</td>
</tr>
<tr>
<td>7.6.3 Synthesis of Menthol from Citronellal</td>
<td>170</td>
</tr>
<tr>
<td>7.7 Conclusion</td>
<td>172</td>
</tr>
<tr>
<td>References</td>
<td>172</td>
</tr>
</tbody>
</table>
10.1.1 Renewable Energy 224
10.1.2 Hydrogen 225
10.1.3 Hydrogen from Ethanol Decomposition 226
10.1.4 Catalytic Oxidation 228
10.1.5 Steam Reforming 228
10.1.6 Dry Reforming 229
10.1.7 Water Gas Shift Reaction (WGSR) 229
10.1.8 Catalytic Reforming of Methane 230
10.1.9 Thermodynamics 230
10.2 Catalysis 231
10.2.1 The Noble Metals Pd and Rh 232
10.2.2 Structure and Properties of Cerium Dioxide 233
10.2.3 Noble Metal/Ceria Catalysts 235
10.2.4 Adsorption of Ethanol 236
10.2.5 Adsorption of Water 236
10.2.6 Adsorption of Carbon Oxides 237
10.2.7 Hydrides 237
10.3 Catalytic Decomposition of Ethanol 238
10.3.1 Ethanol on Metal Oxides 238
10.3.2 Ethanol on a Noble Metal/Ceria Surface 239
10.3.3 Catalytic Oxidation of Ethanol 242
10.3.4 Catalytic Reforming of Ethanol 243
10.4 Conclusions 244
References 245

11 High-Throughput Screening of Catalyst Libraries for Emissions Control 247

Stephen Cypes, Joel Cizeron, Alfred Hagemeyer, and Anthony Volpe

11.1 Introduction 247
11.1.1 Introduction to High-Throughput Heterogeneous Catalysis 247
11.1.2 The Hierarchical Workflow in Heterogeneous Catalysis 248
11.1.3 Applications to Green Chemistry 249
11.2 Experimental Techniques and Equipment 250
11.2.1 Overview of Hardware and Methodologies for Combinatorial Heterogeneous Catalysis 250
11.2.2 Experimental High-Throughput Workflow for Low-Temperature CO Oxidation and VOC Combustion 259
11.2.2.1 Primary Synthesis Methods 260
11.2.2.2 Secondary Synthesis Methods 260
11.2.2.3 IR Thermography Reactor 261
11.2.2.4 Multi-Channel Fixed-bed Reactor 263
11.2.3 Experimental High-Throughput Workflow for NOx Abatement 263
11.2.3.1 Primary Synthesis Methods 263
11.2.3.2 Primary Screening Methods 263
11.2.3.3 Data Analysis for NOx Abatement from SMS 264
11.3 Low-Temperature CO Oxidation and VOC Combustion 265
11.4 NO_x Abatement 273
11.5 Conclusion 277
11.5.1 Application of High-Throughput Screening to Emissions Control 277
11.5.2 Future Trends in Combinatorial Catalysis 278
References 278

12 Catalytic Conversion of High-Moisture Biomass to Synthetic Natural Gas in Supercritical Water 281
Frédéric Vogel
12.1 Introduction 281
12.1.1 Heterogeneous Catalysis in Hydrothermal Medium at the Origin of Life? 281
12.1.2 Biomethane – a Green and Sustainable Fuel 282
12.1.3 Energetic Potentials 283
12.1.4 Nutrient Cycles 284
12.2 Survey of Different Technologies for the Production of Methane from Carbonaceous Feedstocks 285
12.2.1 Anaerobic Digestion 285
12.2.2 Thermal Processes 286
12.3 Water as Solvent and Reactant 288
12.3.1 Solubility of Organic compounds and Gases 289
12.3.2 Solubility of Salts 290
12.4 The Role of Heterogeneous Catalysis 290
12.4.1 Experimental Methods 290
12.4.2 Thermodynamic Stability of Methane under Hydrothermal Conditions 291
12.4.3 Main Reactions of Biomass Gasification 293
12.4.4 Homogeneous, Non-catalyzed Pathways in Hot Compressed Water 294
12.4.5 Heterogeneously Catalyzed Pathways in Hot Compressed Water 297
12.4.6 Active Metals Suited to Hydrothermal Conditions 298
12.4.6.1 Methanation and Steam Reforming Catalysts 299
12.4.6.2 Nickel 302
12.4.6.3 Ruthenium 305
12.4.7 Catalyst Supports Suited to Hydrothermal Conditions 306
12.4.8 Deactivation Mechanisms in a Hydrothermal Environment 312
12.4.8.1 Coke Formation 312
12.4.8.2 Sintering 314
12.4.8.3 Poisoning 314
12.5 Continuous Catalytic Hydrothermal Process for the Production of Methane 315
12.5.1 Overview of Processes 315
12.5.2 PSI's Catalytic Hydrothermal Gasification Process 315
12.5.2.1 Continuous Salt Precipitation and Separation 316
12.5.2.2 Status 318
12.6 Summary and Conclusions 318
12.7 Outlook for Future Developments 319
12.7.1 A Self-sustaining Biomass Vision (SunCHem) 319
References 320

Index 325