

Handbook of Green Chemistry

Edited by Paul T. Anastas

 WILEY-VCH

Green Catalysis



Volume 2: Heterogeneous Catalysis

Volume Editor:
Robert H. Crabtree



Contents

About the Editors XIII

List of Contributors XV

1	Zeolites in Catalysis	1
	<i>Stephen H. Brown</i>	
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 Conjoint 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
	<i>Adam F. Lee and Karen Wilson</i>	
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
	<i>Masaya Matsuoka and Masakazu Anpo</i>	
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 CO ₂ with H ₂ O (Artificial Photosynthesis)	64
3.3.3	Direct Photocatalytic Decomposition of NO into N ₂ and O ₂	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 TiO ₂ Thin Films and Their Application in Self-cleaning Materials	72
3.4	Development of Visible Light-responsive TiO ₂ Photocatalysts	73
3.4.1	Modification of the Electronic State of TiO ₂ by Applying an Advanced Metal Ion Implantation Method	73
3.4.2	Design of Visible Light-responsive Ti/Zelite Catalysts by Applying an Advanced Metal Ion Implantation Method	75
3.4.3	Preparation of Visible Light-responsive TiO ₂ Thin-film Photocatalysts by an RF Magnetron Sputtering Deposition Method	76

3.5	Conclusion	79
	References	79
4	Nanoparticles in Green Catalysis	81
	<i>Mazaahir Kidwai</i>	
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	'Heterogreeneous Chemistry'	93
	<i>Heiko Jacobsen</i>	
5.1	Introduction	93
5.2	'Heterogreeneous 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 – Heterogreeneous Processes for Biodiesel Production	103
5.2.4	Other Heterogreeneous 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	Heterogreeneous Solvent Systems	109
5.3.2	Solvent-free 'Heterogreeneous Chemistry'	112
5.4	Conclusion and Outlook	113
	References	114
6	Single-site Heterogeneous Catalysts via Surface-bound Organometallic and Inorganic Complexes	117
	<i>Christophe Copéret</i>	
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

6.4.2	Other Alkene Homologation Processes	128
6.4.2.1	Direct Conversion of Ethene into Propene	128
6.4.2.2	Cyclization of Dienes	129
6.5	Metathesis, Dimerization, Trimerization and Other Reactions Involving Alkynes	129
6.5.1	Alkyne Metathesis	129
6.5.2	Dimerization and Trimerization of Alkynes	130
6.5.3	Hydroamination of Alkynes	131
6.6	Lewis Acid-catalyzed Reactions	131
6.6.1	Silica-supported Group 4 Metals	131
6.6.1.1	Reduction of Ketones Through Hydrogen Transfer	133
6.6.1.2	Transesterification of Esters	134
6.6.2	Silica-supported Group 3 Metals and Lanthanides	134
6.7	Oxidation	135
6.7.1	Single-site Titanium Species	135
6.7.2	Single-site Zirconium Species	137
6.7.3	Single-site Vanadium Species	137
6.7.4	Single-site Tantalum Species	137
6.7.5	Single-site Group 6 Species	138
6.7.6	Single-site Iron Species	139
6.7.7	Single-site Cobalt Species	141
6.8	Alkane Homologation	141
6.8.1	Alkane Hydrogenolysis	141
6.8.2	Alkane Metathesis	143
6.8.3	Alkane Cross-metathesis	146
	References	146

7 Sustainable Heterogeneous Acid Catalysis by Heteropoly Acids 153

Ivan Kozhevnikov

7.1	Introduction	153
7.2	Development of HPA Catalysts Possessing High Thermal Stability	156
7.3	Modification of HPA Catalysts to Enhance Coke Combustion	157
7.3.1	Propene Oligomerization	158
7.3.2	Friedel–Crafts Acylation	159
7.4	Inhibition of Coke Formation on HPA Catalysts	161
7.5	Reactions in Supercritical Fluids	163
7.6	Cascade Reactions Using Multifunctional HPA Catalysts	165
7.6.1	Synthesis of MIBK	166
7.6.2	Hydrogenolysis of Glycerol to Propanediol	167
7.6.3	Synthesis of Menthol from Citronellal	170
7.7	Conclusion	172
	References	172

8	The Kinetics of TiO_2-based Solar Cells Sensitized by Metal Complexes	175
	<i>Anthony G. Fitch, Don Walker, and Nathan S. Lewis</i>	
8.1	Introduction	175
8.2	History	176
8.3	DSSC Design	177
8.4	Function of the DSSC	178
8.5	Performance of a DSSC	179
8.6	Kinetics Processes	180
8.7	Charge Injection	181
8.8	Recombination to the Dye	184
8.9	Regeneration	187
8.10	Conclusion	190
	References	192
9	Automotive Emission Control: Past, Present and Future	197
	<i>Robert J. Farrauto and Jeffrey Hoke</i>	
9.1	Introduction	197
9.2	The First Oxidation Catalysts (1975–80)	198
9.2.1	Pollution Abatement Reactions for Gasoline-Fueled Engines	198
9.2.2	Catalyst Materials	199
9.2.3	Carriers	201
9.3	Three-Way Catalysis (1980–present)	202
9.3.1	Three-Way Catalysis	202
9.3.2	Oxygen or Lambda Sensor	203
9.3.3	Oxygen Storage Component	203
9.3.4	Further Improvements in TWC	204
9.4	Diesel Catalysis	206
9.4.1	Controlling Diesel Emissions	206
9.4.2	Diesel Emissions	207
9.4.3	Diesel Oxidation Catalysts (DOCs): the Past	208
9.5	Diesel Emission Control: the Future	210
9.5.1	Catalytic Solutions for the Existing Diesel IC Engine	210
9.5.2	The Homogeneous Charge Compression Ignition Engine (HCCI) and Advanced Engine Technology	213
9.6	Fuel Cells and the Hydrogen Economy for Transportation Applications: the Future	217
9.6.1	The Fuel Cell	217
9.6.2	Fuel Cells for Transportation	218
9.6.3	The Hydrogen Service Station	219
9.7	Conclusions	220
	References	220
10	Heterogeneous Catalysis for Hydrogen Production	223
	<i>Morgan S. Scott and Hicham Idriss</i>	
10.1	Introduction	223

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
	<i>Stephen Cypes, Joel Cizeron, Alfred Hagemeyer, and Anthony Volpe</i>	
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 NO _x 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 NO _x 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
	<i>Frédéric Vogel</i>	
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
--------------	------------