Contents

Preface XI List of Contributors XV

	The Complete of Board to Colorlary Law let be 6th
1	The Structure and Reactivity of Single and Multiple Sites on
	Heterogeneous and Homogeneous Catalysts: Analogies, Differences,
	and Challenges for Characterization Methods 1
1.1	Adriano Zecchina, Silvia Bordiga, and Elena Groppo
1.1	Introduction 1
1.2	Definition of Multiple- and Single-Site Centers in Homogeneous
	and Heterogeneous Catalysis 2
1.2.1	Single-Site Homogeneous Catalysts: Prototype Examples Taken
	from the Literature 2
1.2.2	Single-Site Heterogeneous Catalysts 5
1.2.2.1	TS-1 and the Shape Selectivity 5
1.2.2.2	H-ZSM-5: A Popular Example of Protonic Zeolite 7
1.2.2.3	The Ziegler–Natta Polymerization Catalyst 9
1.2.2.4	The Cr/SiO ₂ Phillips Catalyst for Ethylene
	Polymerization 10
1.2.3	Multiple-Site Heterogeneous Center 12
1.2.3.1	Surface Engineering and Selectivity in Heterogeneous
	Enantioselective Hydrogenation Catalysts 14
1.2.3.2	Is It Heterogeneous or Homogeneous? The Interplay between
	Homogeneous and Heterogeneous Catalysts 16
1.3	The Characterization Methods in Heterogeneous Catalysis
	(Including Operando Methods) 17
1.3.1	TS-1-(H ₂ O, H ₂ O ₂) Interaction: in situ
	XANES Experiments 18
1.3.2	H-ZSM5-Propene Interaction: An Example of Operando
	Experiment by Fast Scanning FTIR Spectroscopy 19

Phillips Catalyst: The Search of Precursors and Intermediates in

Ethylene Polymerization Reaction by Temperature- and

Time-Dependent FTIR Experiments 20

1.3.3

vi İ	Contents

۷۱	Contents	
•	1.4	Conclusions 24
		References 25
	2	Supported Nanoparticles and Selective Catalysis: A Surface Science
		Approach 29
		Wangqing Zhang, Da Wang, and Rui Yan
	2.1	General Introduction 29
	2.2	Synthesis of Supported Metal Nanoparticles:
	221	Size and Shape Control 30
	2.2.1 2.2.2	General Synthesis of Metal Nanoparticles 30 Synthetic Methodologies for Supported Metal Nanoparticles 31
	2.2.2.1	Metal Nanoparticles Stabilized by Polymeric Materials 31
	2.2.2.2	Metal Nanoparticles Supported on Carbon Nanotubes 44
	2.2.2.3	Metal Nanoparticles Supported on Metal Oxides 47
	2.2.2.4	Metal Nanoparticles in Mesoporous Silica 49
	2.3	Selective Catalysis of Supported Metal Nanoparticles 53
	2.3.1	Shape or Surface Structure Effect on Selective Hydrogenation
		of Cinnamaldehyde and Benzene 54
	2.3.2	Shape or Surface Structure Effect on the Selective Decomposition
		of Methanol 57
	2.3.3	Size Effect on the Selective Hydrogenation of 1,3-Butadiene
		and Pyrrole 59
	2.3.4	Support Effect on the Selective Catalysis 63
	2.4	Summary 66
		References 66
	3	When Does Catalysis with Transition Metal Complexes Turn into
		Catalysis by Nanoparticles? 73
		Johannes G. de Vries
	3.1	Introduction 73
	3.1.1	Homogeneous Catalysis 73
	3.1.2	Heterogeneous Metal Catalysis 74
	3.1.3	Catalysis with Soluble Metal Nanoparticles 75
	3.1.4	The Border between the Three Forms of Catalysis 76
	3.2	Nanoparticles vs. Homogeneous Catalysts in C–C
	3.2.1	Bond-Forming Reactions 77 The Heck–Mizoroki Reaction 77
	3.2.2	The Kumada–Corriu Reaction 85
	3.2.3	The Suzuki Reaction 87
	3.2.4	The Negishi Reaction 90
	3.2.5	The Sonogashira Reaction 90
	3.2.6	Allylic Alkylation 93
	3.3	Nanoparticles vs. Homogeneous Catalysts
		in Hydrogenation Reactions 94
	3.3.1	Hydrogenation of Arenes 94

3.3.2 3.4 3.5	Asymmetric Hydrogenation 97 Platinum-Catalyzed Hydrosilylation 97 Conclusions 98 References 100
4	Capsules and Cavitands: Synthetic Catalysts of Nanometric Dimension 105 Giuseppe Borsato, Julius Rebek Jr., and Alessandro Scarso
4.1	Introduction on Supramolecular Catalysis 105
4.1.1	Weak Intermolecular Forces 108
4.1.2	Compartmentalization and Catalysis 109
4.1.3	Cavitands and Self-Assembled Capsules as Synthetic Enzymes 112
4.2	Compartmentalization of Reactive Species in Synthetic Hosts as Supramolecular Catalysts 117
4.2.1	Cavitands and Capsules as Synthetic Enzymes 122
4.2.1.1	Reversible Reactions 122
4.2.2	Irreversible Reactions 129
4.2.2.1	Cavitand Catalysts 129
4.2.2.2	Self-Assembled Capsule Catalysts 140
4.3	Conclusions 163
4.4	Outlook 163
	Acknowledgments 164 References 165
5	Photocatalysts: Nanostructured Photocatalytic Materials for Solar Energy Conversion 169 Kazunari Domen
5.1	Principles of Overall Water Splitting Using Nanostructured Particulate Photocatalysts 169
5.1.1	Introduction to Photocatalytic Water Splitting 169
5.1.2	Energetics and Materials 170
5.1.3	Hydrogen and Oxygen Evolution Sites 171
5.2	Oxide Photocatalysts for Overall Water Splitting 172
5.2.1	Nanostructures of Particulate Photocatalysts 172
5.2.1.1	NiO/Ni/SrTiO ₃ 172
5.2.1.2	NiO/NaTaO ₃ :La 174
5.2.2	Photocatalysts with Ion-Exchangeable Layered Structures 175
5.2.2.1	NiK ₄ Nb ₆ O ₁₇ 175
5.2.2.2	$NiO/Ni/Rb_2La_2Ti_3O_{10}$ 178
5.3	Visible Light-Responsive Photocatalysts for Overall Water Splitting 181
5.3.1	(Oxy)nitrides and Oxysulfides as Photocatalysts 181
5.3.2	Overall Water Splitting on Oxynitride Photocatalysts Under Visible Light 185
5.3.3	Nanostructured Hydrogen Evolution Sites 188

/m	Contents	
1	5.4	Conclusions 189
		References 189
	6	Chiral Catalysts 193
		José M. Fraile, José I. García, and José A. Mayoral
	6.1	The Origin of Enantioselectivity in Catalytic Processes: the Nanoscale
		of Enantioselective Catalysis 193
	6.2	Parameters Affecting the Geometry of the Metal
		Environment 194
	6.2.1	The Modification of the Chiral Pocket 194
	6.2.2	Distal Modifications and Conformational Consequences 194
	6.2.3	Additional Ligands: Anions, Solvents, and Additives 194
	6.2.4	Parameters Beyond the Molecular Scale: Aggregates
		and Supported Catalysts 195
	6.3	Case of Study (1): Bis(oxazoline)-Cu Catalysts for
		Cyclopropanation 196
	6.3.1	The Mechanism of Chiral Induction 196
	6.3.2	The Importance of Symmetry: C ₁ versus C ₂ 198
	6.3.3	Distal Modifications: Substitution in the
		Methylene Bridge 200
	6.3.4	Effect of Anion 202
	6.3.5	Beyond the Coordination Sphere: Supports that Change the
		Dimensionality 204
	6.4	Case of Study (2): Catalysts for Diels-Alder Reactions 207
	6.4.1	Enantioselectivity in Diels-Alder Reactions 207
	6.4.2	Chiral Pocket in Box-Metal Complexes: Ligand, Metal, and
		Additives 207
	6.4.3	The Poorly Understood Effect of Surface 211
	6.4.4	Similar but not the Same: Control of Induction Sense with Different
		Lanthanides 212
	6.4.5	Chiral Relay Effects 215
	6.4.6	Subtle Changes in TADDOLate Geometry: Substitution and
		Immobilization 218
	6.5	Case of Study (3): Salen-Based Catalysts 222
	6.5.1	The Structural Variations of Salen Ligands and Complexes 222
	6.5.2	Effects of the Structural Variations in Epoxidation Reactions Catalyzed
		by Salen–Mn Complexes 222
	6.5.3	Control of the Sense of Asymmetric Induction in Salen–Ru
		Complexes 225

Case of Study (4): Multifunctional Catalysis 226

Intermolecular Homobimetallic Catalysis 227

Intermolecular Heterobimetallic Catalysis 227 Intramolecular Homobimetallic Catalysis

Intramolecular Heterobimetallic Catalysis 231

229

Cooperative Effects 226

6.6 6.6.1

6.6.2 6.6.3

6.6.4

6.6.5

6.7	Conclusions 232 References 233
7	Selective Catalysts for Petrochemical Industry 237
	Stian Svelle and Morten Bjørgen
7.1	Overview of Petrochemical Industry and Refinery Processes 237
7.1.1	Primary Raw Materials for the Petrochemical Industry 237
7.1.2	Processing of Petroleum and Natural Gas 238
7.2	Catalysis in the Petrochemical Industry 240
7.2.1	The Importance of Catalysis 240
7.2.2	Catalyst Selectivity 241
7.3	Microporous Materials and Shape Selectivity 244
7.3.1	Zeolites and Zeotypes 245
7.3.2	Catalytic Sites in Zeolites and Zeotypes 246
7.3.3	Zeolites in Petrochemistry and Refining 248
7.3.4	Zeolites as Shape-Selective Catalysts 248
7.4	Selected Examples of Shape-Selective Catalysis
	by Zeolites/Zeotypes 254
7.4.1	Industrial Relevance of the Conversion of Methanol
	to Hydrocarbons 254
7.4.2	Shape Selectivity in the Conversion of Methanol
	to Hydrocarbons 254
7.4.3	Industrial Relevance of Hydroconversion Reactions 258
7.4.4	Shape Selectivity in Hydrocracking 260
7.4.5	Industrial Relevance of Carbonylation Reactions 263
7.4.6	Shape Selectivity in Carbonylation 264
7.5	Summary and Outlook 265
	References 266
8	Crystal Engineering of Metal-Organic Frameworks
Ü	for Heterogeneous Catalysis 271
	Chuan-De Wu
8.1	Introduction 271
8.2	Volatile Molecules Coordinated Metal Nodes Acted as
	Catalytic Centers 272
8.3	Coordinatively Unsaturated Metal Nodes Acted as
	Catalytic Centers 275
8.4	Coordinatively Unsaturated Catalytic Metal Ions Exposed
	in the Pores of MOFs 285
8.5	Guest-Accessible Catalytically Functionalized Organic Sites
	in Porous MOF 288
8.6	Nanochannel-Promoted Polymerization of Organic Substrates
	in Porous MOFs 290
8.7	Homochiral MOFs Used as Enantioselective Catalysts 291
8.8	Conclusions and Outlook 295

(C
	l Content

Acknowledgments 296 References 296

Mechanism of Stereospecific Propene Polymerization Promoted by
Metallocene and Nonmetallocene Catalysts 299
Andrea Correa and Luigi Cavallo
Introduction 299
Mechanism of Polymerization 301
The Chain Growth Reaction 301
Regioselectivity of Propene Insertion 303
Elements of Chirality 306
Chiral-Site Stereocontrol: Isotactic Polypropylene by Primary
Propene Insertion 309
Well-Defined C ₂ -Symmetric Metallocene Catalysts 309
Well-Defined Bis(Phenoxy-Amine)-Based Octahedral Catalysts and
Poorly Defined Heterogeneous Ziegler–Natta Catalytic Systems 312
Chiral-Site Stereocontrol: Syndiotactic Polypropylene by Primary
Propene Insertion 313
Chain-End Stereocontrol: Syndiotactic Polypropylene by Secondary
Propene Insertion 314
Well-Defined Bis(Phenoxy-Imine)-Based Octahedral Catalysts 314
Poorly Defined V-Based Catalytic Systems 315
Conclusions 316
References 318

Index 323