

Contents

Preface *xiii*

1 Strategies to Immobilized Catalysts: A Key Tool for Modern Chemistry 1

Oriana Piermatti, Raed Abu-Reziq, and Luigi Vaccaro

- 1.1 Introduction 1
- 1.2 Catalysis 3
- 1.3 Heterogenization of Homogeneous Catalysts 3
 - 1.3.1 Immobilization on Silica 4
 - 1.3.1.1 Covalent Binding 6
 - 1.3.1.2 Physical Entrapment 7
 - 1.3.1.3 Electrostatic Interactions 7
 - 1.3.1.4 Silica Microencapsulation 7
 - 1.3.2 Polymeric Supports 9
 - 1.3.2.1 Insoluble Polymers 10
 - 1.3.2.2 Soluble Polymers 10
 - 1.3.2.3 Polymeric Microcapsules 12
 - 1.3.3 Other Supports 13
 - 1.3.3.1 Metal–Organic Frameworks (MOFs) 13
 - 1.3.3.2 Periodic Mesoporous Organosilicas (PMOs) 14
 - 1.3.3.3 Magnetic Nanoparticles 14
 - 1.3.3.4 Membranes 14
- 1.4 Characterization of Heterogeneous Catalysts 15
- 1.5 Conclusions 16
- List of Abbreviations 16
- References 17

2 Catalysts Immobilized onto Polymers 23

Shinichi Itsuno and Naoki Haraguchi

- 2.1 Introduction 23
- 2.2 Organocatalyst Immobilized onto Polymers 24
 - 2.2.1 Polymer-Immobilized Cinchona Alkaloids 24
 - 2.2.2 Polymer-Immobilized Proline Derivatives 30
 - 2.2.3 Polymer-Immobilized Amino Acids 33
 - 2.2.4 Polymer-Immobilized Pyrrolidine Derivatives 35

2.2.5	Polymer-Immobilized Chiral Amines	39
2.2.6	Polymer-Immobilized MacMillan Catalysts	42
2.2.7	Polymer-Immobilized Thioureas and Ureas	50
2.2.8	Polymer-Immobilized Chiral Phosphoric Acids	53
2.2.9	Polymer-Immobilized Chiral <i>N</i> -Heterocyclic Carbenes	55
2.3	Metal Catalysts Immobilized onto Polymers	56
2.3.1	Al: Polymer-Immobilized Catechol–Al Catalyst	56
2.3.2	Au: Polymer-Immobilized Triazole–Gold Catalyst	56
2.3.3	Co: Polymer-Immobilized Co(III)–Salen Complex	57
2.3.4	Ir: Polymer-Immobilized Iridium Catalyst	58
2.3.5	Mo: Polymer-Immobilized Molybdenum Catalyst	60
2.3.6	Ni: Polymer-Immobilized Ni Catalyst	61
2.3.7	Pd: Polymer-Immobilized Pd Catalyst	62
2.3.8	Pt: Polymer-Immobilized Pt Nanoparticle	64
2.3.9	Rh: Polymer-Immobilized Rh Catalyst	65
2.3.10	Ru: Polymer-Immobilized Ru Catalyst	68
2.3.11	Ti: Polymer-Immobilized Ti Catalyst	69
2.3.12	Zn: Polymer-Immobilized Zn Catalyst	70
2.4	Outlook and Perspectives	71
2.5	List of Abbreviations	71
	References	72
3	Modified Nanocarbons as Catalysts in Organic Processes	77
	<i>Vincenzo Campisciano, Michelangelo Gruttadauria, and Francesco Giacalone</i>	
3.1	Introduction	77
3.2	Fullerene-Based Catalysts	78
3.2.1	Organocatalysis	78
3.2.2	Organometallic Catalysis	82
3.3	Carbon Nanotubes-Based Catalysts	87
3.3.1	Supramolecular Functionalization	88
3.3.2	Covalent Functionalization	92
3.3.2.1	Organocatalysis	92
3.3.2.2	Organometallic Catalysis	93
3.4	Graphene-Based Catalysts	99
3.4.1	Supramolecular Functionalization	100
3.4.2	Covalent Functionalization	102
3.4.2.1	Organocatalysis	102
3.4.2.2	Organometallic Catalysis	105
3.5	Outlook and Perspectives: Conclusions	109
	List of Abbreviations	110
	References	111
4	Stereoselective Synthesis by Catalysts Supported on Magnetic Nanoferrite	115
	<i>Alessandro Ponti, Anna M. Ferretti, and Giorgio Molteni</i>	
4.1	Introduction	115
4.2	Structure and Properties of the Nanocatalysts	117

4.2.1	Structure Types	118
4.2.1.1	MNP and Catalyst	118
4.2.1.2	Structure Type I	119
4.2.1.3	Structure Type II	121
4.2.1.4	Other Structure Types	122
4.2.2	A Few Points About Synthesis	123
4.2.3	Magnetic Recovery	126
4.2.4	Recycling	128
4.3	Characterization of the Nanocatalysts	129
4.3.1	Morphology and Crystal Structure	130
4.3.2	Magnetic Properties	131
4.3.3	Identification of the Supported Species	132
4.3.4	Catalyst Loading and Leaching	135
4.3.5	DLS and Z-potential	136
4.4	Stereoselective Reactions	137
4.4.1	Substitutions	138
4.4.2	Condensations	139
4.4.3	Additions	141
4.4.4	Hydrogenations and Reductions	146
4.4.5	Epoxidations and Oxidations	148
4.4.6	Carbon–Carbon Couplings	150
4.4.7	Kinetic Resolution of Racemic Mixtures	151
4.5	Conclusions	154
	References	154
5	Metal–Organic Frameworks as Catalysts	159
	<i>Pillaiyar Puthiaraj and Wha-Seung Ahn</i>	
5.1	Introduction	159
5.2	Open Metal Sites as Reaction Sites	159
5.3	Organic Linkers in the Frameworks as Reaction Sites	162
5.3.1	Single-Linker MOFs	163
5.3.2	Mixed Linker MOFs	164
5.4	Multifunctional MOFs for Catalysis	166
5.5	Post-synthetic Grafting of Active Guest Species Within MOFs	167
5.5.1	Grafting of Active Organic Species on Open Metal Sites	167
5.5.2	Grafting of Active Functional Groups on Organic Linkers	168
5.5.3	Grafting of Active Metal Complexes on Functionalized Organic Linkers	170
5.6	Encapsulation of Catalytically Active Guest Species Inside MOFs	173
5.6.1	Metal/Metal Oxide Nanoparticles on MOFs	173
5.6.2	Polyoxometalates (POMs)	175
5.6.3	Metalloporphyrins	176
5.7	MOF Membranes for Catalysis	177
5.8	Conclusions and Perspectives	182
	Acknowledgments	182
	References	183

6	Alternative Solvent Systems in Catalysis	187
	<i>Xavier Maset, Diego J. Ramón, and Gabriela Guillena</i>	
6.1	Introduction	187
6.2	Ionic Liquids as Solvents for Catalytic Organic Reactions	189
6.2.1	Transition-Metal Promoted Reaction in Ionic Liquids	189
6.2.2	Organocatalyzed Transformations Using Ionic Liquids	195
6.3	Deep Eutectic Solvents (DES) as Reaction Media in Catalysis	199
6.3.1	Non-innocent DES as Reaction Media	201
6.3.2	DES as Innocent Solvents for Recyclable Catalytic Transformations	205
6.3.2.1	Transition-Metal Catalyzed Processes	205
6.3.2.2	Organocatalyzed Reactions	207
6.4	Conclusion	211
	List of Abbreviations	211
	References	212
7	Immobilized Chiral Organocatalysts	217
	<i>Carles Rodríguez-Esrich</i>	
7.1	Introduction	217
7.2	Immobilized Chiral Aminocatalysts	219
7.2.1	Proline Derivatives	219
7.2.2	Diarylprolinol Derivatives	223
7.2.3	Imidazolidinones	227
7.2.4	Primary Amine Organocatalysts	230
7.2.5	Peptide Catalysts	233
7.3	Immobilized Chiral H-Bond Donors	235
7.3.1	Ureas and Thioureas	235
7.3.2	Squaramides	238
7.3.3	Amides and Sulfonamides	240
7.4	Immobilized Chiral Phosphoric Acids	241
7.5	Immobilized Lewis and Brønsted Base Organocatalysts	244
7.5.1	NHC Catalysts	245
7.5.2	Isothioureas	245
7.5.3	Amides as Lewis Bases	247
7.5.4	Brønsted Bases	247
7.6	Immobilized Phase Transfer Catalysts	249
7.7	Final Remarks and Future Perspectives	250
	References	251
8	Catalyst Recycling in Continuous Flow Reactors	257
	<i>Alessandro Mandoli</i>	
8.1	Introduction	257
8.2	Types of Catalytic Flow Reactors and Parameters for Assessing Their Performance	259
8.3	Soluble Catalytic Systems	260
8.3.1	Metal Catalysts	263
8.3.1.1	Organic Solvent Nanofiltration	263

8.3.1.2	Liquid–Liquid Biphase Media and Supercritical Fluids	269
8.3.1.3	SLP Systems	273
8.3.1.4	Other Approaches	276
8.3.2	Metal-Free Catalysts	276
8.4	Insoluble Catalytic Systems	277
8.4.1	Packed-bed CFRs	281
8.4.2	Monolithic CFRs	282
8.4.3	Wall-coated CFRs	284
8.4.4	Metal Catalysts	285
8.4.4.1	Reduction Reactions	285
8.4.4.2	Cross-Coupling Reactions	289
8.4.5	Metal-Free Catalysts	290
8.5	Conclusions	293
	List of Abbreviations	294
	References	295
9	Membrane Reactors	307
	<i>Parisa Biniiaz, Mohammad Amin Makarem, and Mohammad Reza Rahimpour</i>	
9.1	Introduction	307
9.2	Inert Membrane Reactor with Mobile Catalysts on the Reaction Side	308
9.2.1	Organic Solvent Nanofiltration	309
9.3	Catalytically Active Membrane Reactors	311
9.3.1	Hydrogenation Reactions	311
9.3.2	Carbon–Carbon (C–C) Cross-couplings	312
9.4	The Immobilized Catalyst in a Porous Membrane	313
9.5	Photocatalytic Organic Synthesis and Their Utilization in the Reduction of Organic Pollutant in Membrane Reactors	313
9.5.1	Photocatalytic Membrane Reactors	314
9.5.2	Membrane Reactors with Suspending Catalyst in the Reaction Mixture	314
9.6	The Applications of Membrane Reactors in the Biodiesel Transesterification	316
9.7	Conclusion and Future Trends	320
	List of Abbreviations	320
	References	321
10	Development of Polymer-Supported Transition-Metal Catalysts and Their Green Synthetic Applications	325
	<i>Takao Osako, Atsushi Ohtaka, and Yasuhiro Uozumi</i>	
10.1	Introduction	325
10.2	Polystyrene-Supported Transition-Metal Nanoparticle Catalysts	326
10.2.1	Background	326
10.2.2	Carbon–Carbon Coupling Reactions in Water Catalyzed by Linear-Polystyrene-Stabilized Palladium(II) Oxide or Palladium Nanoparticles	327
10.2.2.1	Suzuki Coupling Reaction	327

- 10.2.2.2 Hiyama Coupling Reaction 330
- 10.2.2.3 Ullmann Coupling Reaction 333
- 10.2.2.4 Heck Reaction 334
- 10.2.2.5 Copper-Free Sonogashira Coupling Reaction 335
- 10.2.2.6 One-Pot Synthesis of Dibenzyls and 3-Arylpropanoic Acids 337
- 10.2.3 Linear-Polystyrene-Stabilized Platinum Nanoparticles: Preparation and Evaluation of Their Catalytic Activity in Water 338
 - 10.2.3.1 Aerobic Oxidation of Alcohols 338
 - 10.2.3.2 Hydrogen-Transfer Reduction in the Presence of Polystyrene-Stabilized Platinum Nanoparticles 340
- 10.3 Polystyrene-Poly(ethylene glycol)-Supported Transition-Metal Catalysts 341
 - 10.3.1 Background 341
 - 10.3.2 Aqueous Aerobic Flow Oxidation of Alcohols by Amphiphilic Resin-Dispersed Particles of Platinum (ARP-Pt) 342
 - 10.3.3 Flow Hydrogenation of Olefins, Nitrobenzenes, and Aldehydes by Amphiphilic Resin-Dispersed Particles of Platinum (ARP-Pt) 349
 - 10.3.4 Flow Hydrogenation by Amphiphilic Resin-Dispersed Particles of Iron (ARP-Fe) [110] 352
 - 10.3.5 Aqueous Huisgen 1,3-Cycloaddition with an Amphiphilic Resin-Supported Triazine-Based Polyethyleneamine Dendrimer–Copper Catalyst 356
 - 10.3.6 Aqueous Asymmetric 1,4-Addition with an Amphiphilic Resin-Supported Chiral Diene–Rhodium Complex 359
- 10.4 Conclusion 363
 - List of Abbreviations 363
 - References 364
- 11 3D Printed Devices for Catalytic Systems 369**
Vittorio Saggiomo
 - 11.1 Introduction 369
 - 11.2 3D Printing 371
 - 11.2.1 Fuse Deposition Modeling (FDM) 373
 - 11.2.2 Millifluidic and Flow Reactors 374
 - 11.2.3 Catalysts Embedded Thermoplastics 376
 - 11.2.4 Resin Printers 382
 - 11.2.5 Robocasting (Direct Ink Writing) 388
 - 11.2.6 Powder Bed Fusion Printers 396
 - 11.3 Conclusion 399
 - 11.4 Outlook 402
 - List of Abbreviations 402
 - References 403
- 12 General Overview on Immobilization Techniques of Enzymes for Biocatalysis 409**
María Romero-Fernández and Francesca Paradisi
 - 12.1 Introduction 409

12.2	Physical Immobilization Methodologies	410
12.2.1	Entrapment	411
12.2.2	Encapsulation	411
12.3	Chemical Immobilization Methodologies	413
12.3.1	Non-covalent Bonding	413
12.3.1.1	Hydrophobic Adsorption	414
12.3.1.2	Ionic Exchange Adsorption	415
12.3.2	Covalent Bonding	418
12.4	Conclusion	426
	List of Abbreviations	426
	References	427
13	Immobilized Enzymes: Applications in Organic Synthesis	437
	<i>Hans-Jürgen Federsel, Jaan Pesti, and Matthew P. Thompson</i>	
13.1	Introduction: The Quest for Chemicals and the Role of Organic Synthesis	437
13.2	Enzymes as Enablers of Synthesis	441
13.3	Enzymes in Action: Immobilized Processes on Scale	444
13.4	Key Features of Systems Operating with Immobilized Enzymes	452
13.5	Future Perspectives: The Road Ahead	457
	List of Abbreviations	459
	References	460
	Index	465

