

Steven L. Suib  
Editor



# New and Future Developments in Catalysis

Hybrid Materials, Composites, and  
Organocatalysts

# NEW AND FUTURE DEVELOPMENTS IN CATALYSIS

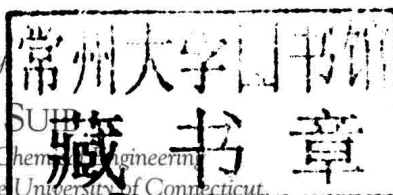
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HYBRID MATERIALS, COMPOSITES,  
AND ORGANOCATALYSTS

*Edited by*

STEVEN L. SUI

*Department of Chemistry and Chemical Engineering  
and Institute of Materials Science, The University of Connecticut  
Storrs, CT 06269-3060*



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# NEW AND FUTURE DEVELOPMENTS IN CATALYSIS

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# Introduction

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This book focuses on catalysts that have been developed as hybrid materials, composites, and organocatalysts. While research in these areas has been known for a while, the volume of research in these areas in recent years has skyrocketed. Reasons for these emerging areas of research are that simple catalytic systems are not often adequate to solve all of the required performance characteristics of a material as well as the ability of various phases to provide multiple functions and at times synergetic effects.

The development of supporting homogeneous catalysts on supports to make heterogeneous systems that have the inherent advantages of homogeneous systems like high activity and selectivity is making major leaps in recent years. Thermocatalytic steam cracking is an area where hybrid catalysts are being used for the selective production of hydrocarbons such as ethylene. Hybrid catalysts are also being developed for applications in olefin metathesis and polymerization reactions. Some specific reactions like spillover for oxygen and hydrogen are important in a variety of areas and hybrid materials are often the only way to go to produce excellent activity and stability. Immobilizing transition metal complexes on inorganic or hybrid matrices are summarized.

Catalytic processes that use hybrids, composites, and organocatalysts are discussed as a separate chapter for perspective. Organocatalysts involving hybrid gold materials are discussed. Encapsulated polyoxometalates are discussed. The ability to

support organocatalysts and their regeneration is another area being developed. Carbon-based catalysts are the focus of another chapter. Environmental concerns are important with these materials and the stable and active class of environmentally friendly aluminosilicate materials, zeolites, has seen considerable numbers of applications. These materials are often combined with other materials to improve mechanical strength and as such could be considered composites. Similar materials that are homogeneous such as the silsesquioxanes are also discussed in a separate chapter. Other composite materials produced by supporting noble metals on silica are also discussed.

While these three different systems appear to be markedly different, clearly there are similarities in the approaches that are being used to study hybrid, composite, and organocatalyst materials. Some of these authors are proposing various combinations of these three different materials in order to improve the rates of reaction and selectivities. Characterization of such complex systems is a major challenge and is touched upon by various authors.

## Acknowledgments

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# Contributors

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- Nabil Al-Yassir** King Fahd University for Petroleum and Minerals, Center of Research Excellence in Petroleum Refining and Petrochemicals, P.O. Box 5040, Dhahran 31261 Saudi Arabia
- Carmela Aprile** Unité de Chimie des Nanomatériaux, University of Namur (FUNDP), Rue de Bruxelles 61, 5000 Namur, Belgium
- Gerasimos S. Armatas** Department of Materials Science and Technology, University of Crete, Heraklion 71003, Greece
- Hynek Balcar** J. Heyrovský Institute of Physical Chemistry of the Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic
- Regina Buffon** Chemistry Institute, State University of Campinas, 13083-970 Campinas, SP, Brazil
- Sónia A.C. Carabineiro** LCM - Laboratory of Catalysis and Materials - Associate Laboratory LSRE/LCM, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
- J. Čejka** J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejškova 3, 182 23 Prague 8, Czech Republic
- Miguel Peixoto de Almeida** LCM-Laboratory of Catalysis and Materials - Associate Laboratory LSRE/LCM, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
- Kajornsak Faungnawakij** National Nanotechnology Center, National Science and Technology Development Agency, Patumthani, Thailand
- M. Ishaque Khan** Department of Biological and Chemical Sciences, Illinois Institute of Technology, Chicago, IL 60616, USA
- Jelena M. Jaksic** Institute of Chemical Engineering Sciences, ICEHT/FORTH, Patras, Greece
- Milan M. Jaksic** Institute of Chemical Engineering Sciences, ICEHT/FORTH, Patras, Greece
- Faculty of Agriculture, University of Belgrade, Belgrade, Serbia
- Venčeslav Kaučič** National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia
- Michael T. Keßler** Universität zu Köln, Institut für Anorganische Chemie, Köln, Germany
- Diamantoula Labou** Institute of Chemical Engineering Sciences, ICEHT/FORTH, Patras, Greece
- Frédéric Lefebvre** Université Lyon 1, CPE Lyon, CNRS, UMR C2P2, LCOMS, Bâtiment CPE Curien, 43 Boulevard du 11 Novembre 1918, F-69616 Villeurbanne, France
- Ping Liu** Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, USA
- Svetlana Mintova** Laboratoire Catalyse & Spectrochimie, ENSICAEN, Université de Caen - CNRS, 6 Boulevard du Maréchal Juin, 14050 Caen, France
- Abdualhafed Muntasar** Industrial Catalysis Laboratory, Department of Chemistry and Biochemistry, Concordia University, 7141 Sherbrooke, West, SP 201.12, Montreal, QC H4B 1R6, Canada
- Eng-Poh Ng** School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia



- Nataša Novak Tušar** National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia
- Georgios D. Papakonstantinou** Institute of Chemical Engineering Sciences, ICEHT/FORTH, Patras, Greece
- Paolo P. Pescarmona** Centre for Surface Chemistry and Catalysis, University of Leuven (KU Leuven), Kasteelpark Arenberg 23, 3001 Heverlee, Belgium
- Martin H.G. Precht** Universität zu Köln, Institut für Anorganische Chemie, Köln, Germany
- G. Rajesh Krishnan** Department of Applied Chemistry, Cochin University of Science and Technology, Cochin, Kerala, India
- M.C. Martínez-Román** Inorganic Chemistry Department, University of Alicante, Alicante, Spain
- Wieslaw J. Roth** J. Heyrovský Institute of Physical Chemistry of the Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic
- C. Salinas-Martínez de Lecea** Inorganic Chemistry Department, University of Alicante, Alicante, Spain
- Jackson D. Scholten** Universidade Federal do Rio Grande do Sul, Instituto de Química, Porto Alegre, Brazil
- M. Semler** Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030, 128 40 Prague 2, Czech Republic
- Angeliki Siokou** Institute of Chemical Engineering Sciences, ICEHT/FORTH, Patras, Greece
- K. Sreekumar** Department of Applied Chemistry, Cochin University of Science and Technology, Cochin, Kerala, India
- P. Štěpnička** Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030, 128 40 Prague 2, Czech Republic
- Kongkiat Suriye** SCG Chemicals Co., Ltd, Thailand
- Shanmugan Swaminathan** Centre for Surface Chemistry and Catalysis, University of Leuven (KU Leuven), Kasteelpark Arenberg 23, 3001 Heverlee, Belgium
- LaSalle Swenson** Department of Biological and Chemical Sciences, Illinois Institute of Technology, Chicago, IL 60616, USA
- Raymond Le Van Mao** Industrial Catalysis Laboratory, Department of Chemistry and Biochemistry, Concordia University, 7141 Sherbrooke West, SP 201.12, Montreal, QC H4B 1R6, Canada
- HaiTao Yan** Industrial Catalysis Laboratory, Department of Chemistry and Biochemistry, Concordia University, 7141 Sherbrooke West, SP 201.12, Montreal, QC H4B 1R6, Canada
- Nataša Zabukovec Logar** National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia
- Xiaoqin Zou** Laboratoire Catalyse & Spectrochimie, ENSICAEN, Université de Caen - CNRS, 6 Boulevard du Maréchal Juin, 14050 Caen, France

# Contents

---

## Introduction ix Contributors xi

### 1. Hybrid Catalysts for Olefin Metathesis and Related Polymerizations

HYNEK BALCAR AND WIESLAW J. ROTH

- 1.1 Introduction 1
- 1.2 Immobilization of Olefin Metathesis Catalysts on Solid Supports 2
- 1.3 Survey of Hybrid Catalysts for Olefin Metathesis 15
- 1.4 Application of Hybrid Catalysts in Metathesis Polymerization Reactions 21
- 1.5 Concluding Remarks and Future Prospects 23
- Acknowledgment 24
- References 24

### 2. Open-Framework Hybrid Materials and Composites from Polyoxometalates

M. ISHAQUE KHAN AND LASALLE SWENSON

- 2.1 Introduction 27
- 2.2 Polyoxometalates as Building Blocks for Making Extended Structures and Framework Materials 34
- 2.3 Polyoxometalates-Metal Organic Framework (POM-MOF) Composites 47
- Acknowledgments 49
- References 49

### 3. Heterogenization of Homogeneous Catalysts on Carbon Materials

M.C. ROMÁN-MARTÍNEZ AND C. SALINAS-MARTÍNEZ DE LECEA

- 3.1 Introduction 55
- 3.2 Strategies for the Heterogenization of Homogeneous Catalysts 57
- 3.3 Carbon Materials as Supports in Catalysis 61

- 3.4 Use of Activated Carbons as Support for Homogeneous Catalysts 63
- 3.5 Use of Carbon Nanotubes and Nanofibers as Support for Homogeneous Catalysts 70
- 3.6 Miscellaneous: Other Carbon Materials Used for the Immobilization of Homogeneous Catalysts 73
- 3.7 Conclusions 75
- Acknowledgments 75
- References 75

### 4. Current Catalytic Processes with Hybrid Materials and Composites for Heterogeneous Catalysis

KAJORNSAK FAUNGNAWAKIJ AND KONGKIAT SURIYE

- 4.1 Development Trend of Novel Catalyst for Commercial Processes 79
- 4.2 Current Catalytic Processes in Petrochemical and Energy Industries 81
- 4.3 Gap technology of Hybrid Catalysts 94
- 4.4 Perspective on the Way to Bridge the Gap from the Industrial Point of View 99
- References 103

### 5. Organogold Complexes—An Important Role in Homogenous Catalysis and a Golden Future as Heterogenized (Hybrid) Materials

MIGUEL PEIXOTO DE ALMEIDA AND SÓNIA A.C. CARABINEIRO

- 5.1 Introduction 105
- 5.2 A New Class of Hybrid Materials for Catalysis—Heterogenized Organogold Complexes 106
- 5.3 Conclusions 118
- References 119

## 6. Catalysis by Transition Metal Complexes Immobilized in Inorganic or Hybrid Matrices by the Sol-Gel Method

REGINA BUFFON

- 6.1 Introduction 123
- 6.2 The Sol-Gel Method [3–5] 124
- 6.3 Silica-Based Matrices 126
- 6.4 Commercial applications and perspectives 139
- References 141

## 7. Blending of Non-Petroleum Compounds with Current Hydrocarbon Feeds to Use in the Thermo-Catalytic Steam-Cracking Process for the Selective Production of Light Olefins

RAYMOND LE VAN MAO, HAITAO YAN, ABDUALHAFED MUNTASAR, AND NABIL AL-YASSIR

- Presentation 143
- 7.1 Current Technologies for the Production of Light Olefins 144
- 7.2 The Thermo-Catalytic Steam-Cracking (TCSC) Process. Hybrid Catalysts: the Concepts of Pore Continuum and Hydrogen Spillover 154
- 7.3 Technical Evolution of the TCSC Technology 159
- 7.4 Blending of Light Alcohols With Hydrocarbon Feeds (Naphthas and Gas Oils) Currently Used Cracking. Searching for Catalytic Compatibility of Mixed Feeds 161
- 7.5 Is Glycerol a Good Candidate for Blending With Petroleum Hydrocarbon Feeds? 163
- 7.6 Potential Blending Compounds 169
- 7.7 General Conclusion 169
- Acknowledgments 171
- References 171

## 8. Spillover Phenomena in Electrocatalysis for Oxygen and Hydrogen Electrode Reactions

JELENA M. JAKSIC, GEORGIOS D. PAPA KONSTANTINOY, DIAMANTOULA LABOU, ANGELIKI SIOKOU, AND MILAN M. JAKSIC

- 8.1 Introduction 175
- 8.2 Spillover Phenomena in Aqueous Media, Their Causes, Properties, Consequences, and Uses 190
- 8.3 Conclusions 209
- References 210

## 9. Synergistic Effect of Metal/Oxide Catalysts in the Water-Gas Shift Reactions: A Theory-Guided Rational Design of Better Catalysts

PING LIU

- 9.1 Introduction 213
- 9.2 Mechanism for the WGS Reaction 214
- 9.3 Rational Development of WGS Catalysts 215
- 9.4 Rational Catalyst Screening 236
- 9.5 Conclusion Remarks 237
- Acknowledgment 238
- References 238

## 10. Metal Catalysts Immobilized in Ionic Liquids: A Couple with Opportunities for Fine Chemicals Derived from Biomass

MICHAEL T. KEBLER, JACKSON D. SCHOLTEN, AND MARTIN H.G. PRECHTL

- 10.1 Introduction 243
- 10.2 Metal Salts as Catalysts for Biomass Transformation in ILs 245
- 10.3 Supported Metals Catalysts for Biomass Conversion in ILs 252
- 10.4 Metal Nanoparticles 254
- 10.5 Summary and Outlook 261
- References 262

## 11. Polyoxometalates Encapsulated in Inorganic Materials: Applications in Catalysis

FRÉDÉRIC LEFEBVRE

- 11.1 Introduction 265
- 11.2 Polyoxometalates Entrapped Within Silica 267
- 11.3 Polyoxometalates Entrapped Within Titania 269
- 11.4 Polyoxometalates Entrapped Within Zirconia 272
- 11.5 Polyoxometalates Entrapped Within Ta<sub>2</sub>O<sub>5</sub> 275
- 11.6 Polyoxometalates Entrapped Within Alumina 276
- 11.7 Polyoxometalates Entrapped Within Mesoporous Co<sub>3</sub>O<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub> 277
- 11.8 Polyoxometalates Entrapped Within Metallic Matrices 278

- 11.9 Polyoxometalates Encapsulated in Zeolites 279
- 11.10 Polyoxometalates Encapsulated in Metal Organic Frameworks (MOFs) 282
- 11.11 Conclusion 285
- References 286

## 12. Environmental Synthesis Concerns of Zeolites

ENG-POH NG, XIAOQIN ZOU, AND SVETLANA MINTOVA

- 12.1 Introduction 289
- 12.2 Environmental Synthesis Concerns 290
- 12.3 Conclusions and Prospective 306
- References 306

## 13. Heterogeneous Polyoxometalate-Containing Mesoporous Catalysts

GERASIMOS S. ARMATAS

- 13.1 Introduction 311
- 13.2 Heterogenization of Polyoxometalates 314
- 13.3 Conclusion 337
- Abbreviations 338
- Acknowledgments 339
- References 339

## 14. Supported and Reusable Organocatalysts

G. RAJESH KRISHNAN AND K. SREEKUMAR

- 14.1 Introduction 343
- 14.2 Inorganic Materials as Supports for Organocatalysts 344
- 14.3 Nanoparticle-Supported Organocatalysts 350
- 14.4 Polymer-Supported Organocatalysts 352
- 14.5 Conclusion 362
- References 363

## 15. Functionalized Porous Silicates as Catalysts for Water and Air Purification

NATAŠA NOVAK TUŠAR, VENČESLAV KAUČIČ, AND NATAŠA ZABUKOVEC LOGAR

- 15.1 Introduction 365
- 15.2 Synthesis of Functionalized Porous Silicates 369

- 15.3 Structure Characterization of Functionalized Porous Silicates 373
- 15.4 Case Studies of Environment Friendly Catalytic Applications Using Functionalized Porous Silicates 375
- 15.5 Conclusion 379
- Acknowledgment 379
- References 379

## 16. Silsesquioxanes and Their Use as Precursors for Catalysts and as Model Compounds

PAOLO P. PESCARMONA, CARMELA APRILE, AND SHANMUGAN SWAMINATHAN

- 16.1 Introduction 385
- 16.2 Synthesis of Oligomeric Silsesquioxanes 388
- 16.3 Characterization 395
- 16.4 Catalytic Applications 399
- 16.5 Conclusion and Perspectives 419
- References 419

## 17. Palladium Catalysts Deposited on Functionally Modified Siliceous Supports

P. ŠTĚPNIČKA, M. SEMLER, AND J. ČEJKA

- 17.1 Introduction 423
- 17.2 Simple and Branched Aliphatic Amine Groups 426
- 17.3 Heterocyclic Modifying Groups 433
- 17.4 Sulfur-Containing Modifying Groups 441
- 17.5 Phosphine Modifying Groups 444
- 17.6 Mixed-Donor Modifying Groups 451
- 17.7 Summary and Outlook 454
- Acknowledgment 454
- References 454

## Index 459



# Hybrid Catalysts for Olefin Metathesis and Related Polymerizations

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*Hynek Balcar and Wieslaw J. Roth*

J. Heyrovský Institute of Physical Chemistry of the Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic

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## 1.1 INTRODUCTION

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As a hybrid catalyst we shall understand in this chapter a combination of a transition metal organometallic catalyst with inorganic supporting material. The reason for supporting organometallic catalysts on suitable supports lies in the expectation of combining advantages of homogeneous and heterogeneous catalysis. Homogeneous organometallic catalysts usually exhibit high activity and especially high selectivity (including stereoselectivity), which in addition can be controlled by designed alterations in metal coordination sphere. On the other hand, heterogeneous catalysts have indisputable advantage despite their less controllable character: (i) their heterogeneity allows easy separation of catalyst from reaction mixtures (with possible catalyst recovering or even direct reusing) and (ii) these catalysts can be used in flow reaction systems.

The combination of the mentioned qualities is especially valuable when the transition metal catalysts are applied in fine chemical synthesis. In many cases, especially if the product is designed for medical, cosmetics, food processing, and similar applications, strict limits for the content of catalyst residues (especially transition metals) in products must be obeyed. Heterogeneous catalysts may directly afford a product with low metal content thus avoiding tedious and expensive purification procedures. In addition, the possibility of catalyst reuse is very important, because transition metal organometallic catalysts are usually quite expensive.

The immobilization of transition metal coordination and organometallic compounds on solid supports has attracted interests from the early 1970s [1–9]. Many hybrid catalysts were developed and tested for various chemical transformations such as hydrogenations,

hydroformylations, hydrosilylations, epoxidations, and C–C coupling reactions. Recently, the effort in this field has been stimulated in response to practical demands. Moreover, the advances in spectroscopic techniques (IR, Raman, solid-state NMR, XPS) allow nowadays detailed characterization of organometallic compounds on solid surfaces. The achievements in contemporary surface organometallic chemistry offer opportunities for deep understanding of processes on catalyst surface with relevance to the catalyst activity and selectivity [10,11].

Although insoluble organic polymers can be used as catalyst supports [12], the inorganic material such as silica, alumina, and similar oxides seems to be generally more advantageous because of (i) higher thermal stability and (ii) preservation of pore characteristics due to resistance to swelling by solvents. Modern inorganic supports such as zeolites, mesoporous molecular sieves, and mesoporous organized alumina possess additional outstanding properties—regular porosity and high surface area [13]. Several strategies have been developed for the immobilization of organometallic catalysts on these supports. With respect to the character of the bond between an organometallic compound and support they can be divided into the following categories: (i) immobilization by sorption (physi- and chemisorption), (ii) formation of a covalent bond between organometallic compounds and support surface atoms, (iii) immobilization via ionic interactions, and (iv) encapsulation of organometallic compounds inside the support cavities (ship in the bottle approach). To minimize transition metal leaching from the hybrid catalyst during catalytic reactions, strong bonds between organometallic compounds and the support are desirable. From this point of view immobilization via covalent bonding is preferred. However, as leaching depends on various reaction conditions (temperature, reaction medium, etc.) non-covalent interactions may give rise to a stable valuable hybrid catalyst in some cases.

Immobilization of an organometallic catalyst on the surface of a support may modify its catalytic activity and/or selectivity. First, attachment usually represents a perturbation in the metal coordination sphere. The accompanying electronic and steric changes may affect both the activity and selectivity (positively or negatively depending on the individual cases). Second, in contrast to homogeneous systems, diffusion phenomena may play an important role in the case of hybrid catalysts. Slow diffusion of substrate molecules to the catalytically active centers, and products in opposite direction, may seriously slow down the reaction rate in comparison with corresponding catalysts in the homogeneous phase. This decrease has been often observed and represents a main drawback of many hybrid catalysts designed up to now. Third, immobilization can also affect catalyst stability (both in positive and negative way). The positive effect of immobilization can be expected especially if the homogeneous catalyst is deactivated in a bimolecular process.

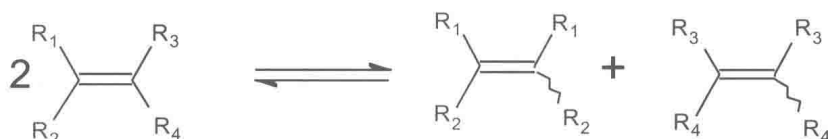
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## 1.2 IMMOBILIZATION OF OLEFIN METATHESIS CATALYSTS ON SOLID SUPPORTS

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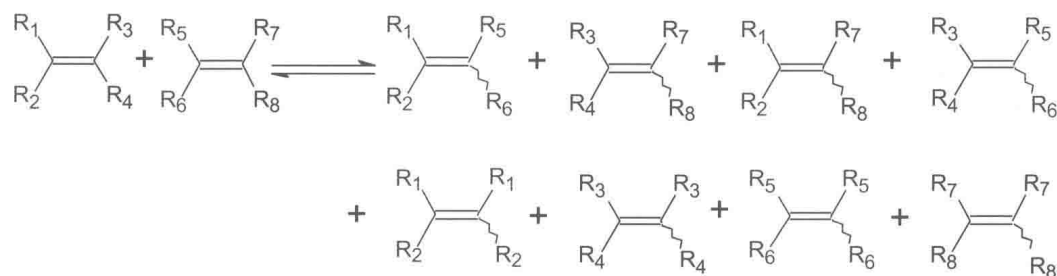
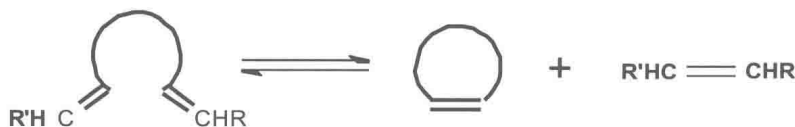
### 1.2.1 Olefin Metathesis

Olefin metathesis belongs to a few fundamentally novel organic reactions discovered in the last 50 years. Olefin metathesis entails splitting of a double bond between carbon atoms and exchanging of the formed alkylidene fragments as described in Scheme 1.1. Since its

SCHEME 1.1 Simple olefin metathesis.  $R_{1-4} = \text{H}$ , alkyl, aryl.

discovery, olefin metathesis has been widely investigated resulting in many applications in petrochemistry, polymer chemistry and synthesis of numerous drugs, natural products, and biologically active compounds [14–16]. The importance of olefin metathesis was underscored in 2005 by the Nobel Prize award to Yves Chauvin, Robert H. Grubbs, and Richard R. Schrock “for the development of the metathesis method in organic synthesis.”

In fact, olefin metathesis is a family of reactions connected by the same mechanism and principally the same catalysts (*vide infra*). In addition to the simple metathesis reaction of a single alkene (Scheme 1.1), this family includes cross metathesis (CM) of two different alkenes leading up to eight different products (Scheme 1.2), ring closing metathesis of dienes (RCM) leading to the formation of cycloalkene ring (Scheme 1.3), acyclic diene metathesis (ADMET) leading to oligomers and/or polymers (Scheme 1.4), and ring opening metathesis polymerization (ROMP) of cycloalkenes leading to high molecular weight polymers (Scheme 1.5). Moreover alkynes and enynes also undergo metathesis—alkyne metathesis of internal

SCHEME 1.2 Cross metathesis.  $R_{1-8} = \text{H}$ , alkyl, aryl.SCHEME 1.3 Ring closing metathesis of diene.  $R, R' = \text{H}$ , alkyl.SCHEME 1.4 Acyclic diene metathesis of  $\alpha,\omega$ -diene.





SCHEME 1.5 Ring opening metathesis polymerization of cycloalkene.

SCHEME 1.6 Alkyne metathesis,  $R_{1,2}$ =alkyl.SCHEME 1.7 Metathesis polymerization of 1-alkynes,  $R$ =alkyl, aryl.

SCHEME 1.8 Enyne metathesis.

alkynes (Scheme 1.6), metathesis polymerization of 1-alkynes (Scheme 1.7), and enyne metathesis (Scheme 1.8).

### 1.2.2 Homogeneous Catalysts for Olefin Metathesis

The olefin metathesis catalysts are based almost exclusively on W, Mo, Re, and Ru compounds. Initially, multicomponent homogeneous catalysts (e.g.,  $\text{WCl}_6 + \text{Me}_4\text{Sn}$ ) were used. The actual catalytic species were formed in the course of the reaction, however, the character of these catalytically active species was not known. In 1971 Hérisson and Chauvin [17] proposed the chain mechanism of olefin metathesis with metallocarbene complexes as the catalytic species and metallacyclobutane as an intermediate (Scheme 1.9). This mechanism was fully confirmed in subsequent years.

The discovery of the mechanism opened the way to a new generation of olefin metathesis catalysts—stable carbene complexes of W, Mo, and Ru. In 1976, Fisher carbenes,  $(\text{CO})_5\text{W}=\text{CPh}(\text{OMe})$  and  $(\text{CO})_5\text{W}=\text{CPh}_2$ , were used [18,19]. However, their activity was very limited. In late 1980s, Schrock et al. prepared high valent W and Mo carbenes (Figure 1.1),