Olefin Metathesis and Polymerization Catalysts Synthesis
Mechanism And Utilization

Olefin Metathesis and Polymerization Catalysts - Yavuz Imamogammalu 2012-12-06 Olefin metathesis reaction can be considered as one of the most successful organic reactions with many applications in the low molecular weight range and also in the polymer field. The use of catalysts with their selective and effective transformation properties in olefin metathesis I polymerization systems is a growing interest. There has been great effort and competition in developing active and commercially useful catalysts. The main aim of this ASI was to gather several research groups and also the people from industry, to present existing knowledge and latest results in the field. A wide range of topics through homogeneous and heterogeneous aspects have been considered. Attention has been drawn to the metal-carbene and metallocyclobutane complexes as active species, the initiation mechanisms, the stereochemistry and thermodynamics of these reactions. New catalytic systems for the metathesis of alkenes and alkynes and fot' ring opening polymerization I block copolymerization reactions have been introduced. Spectroscopic studies for the characteriZation of catalysts, simulation studies explaining the function of chain carrier species and polymer degradation have also been covered. A detailed industrial report concerning the patents and applications in olefin metathesis I cyc1001efin polymerization area, fabrication and derivation has been presented. This volume contains the main lectures and seminars given at the NATO Advanced Study Institute on " Olefin Metathesis and Polymerization Catalysts: Synthesis, Mechanism and Utilization", held at Akcay, Babkesir, Turkey between 10th and 22nd September 1989.

Olefin Metathesis and Metathesis Polymerization - K. J. Ivin 1997-01-07 This book is a follow-up to Ivins Olefin Metathesis, (Academic Press, 1983). Bringing the standard text in the field up to date, this Second Edition is a result of rapid growth in the field, sparked by the discovery of numerous well-defined metal carbene complexes that can act as very efficient initiators of all types of olefin metathesis reaction, including ring-closing metathesis of acyclic dienes, enynes, and dienynes; ring-opening metathesis polymerizatioro of cycloalkenes, acyclic diene metathesis polymerization; and polymerization of alkynes, as well as simple olefin metathesis. Olefin Metathesis and Metathesis Polymerization provides a broad, up-to-date account of the subject from its beginnings in 1957 to the latest applications in organic synthesis. The book follows the same format as the original, making it useful to teachers and to researchers, and will be of particular interest to those working in the fields of organic chemistry, polymer chemistry, organometallic chemistry, catalysis, materials science and chemical engineering. Discusses different classes of olefin metathesis and the choice of reaction conditions and catalyst Consider commercial processes with examples from existing and new technologies Provides a complete overview of the subject from its beginning to the present day

Metathesis Polymerization of Olefins and Polymerization of Alkynes - Yavuz Imamogammalu 2012-10-13 The first NATO Advanced Study Institute on Olefin Metathesis and Polymerization Catalysts was held on September 10-22, 1989 in Akcay, Turkey. Based on the fundamental research of RRSchrock, RGrubbs and K.B.Wagener in the field of ring opening metathesis polymerization (ROMP), acyclic diene metathesis (ADMET) and alkene polymerization, these areas gained growing interest within the last years. Therefore the second NATO-ASI held on metathesis reactions was on Ring Opening Metathesis Polymerization of Olefins and Polymerization of Alkynes on September 3-16, 1995 in Akcay, Turkey. The course joined inorganic, organic and polymer chemists to exchange their knowledge in this field. This volume contains the main and short lectures held in Akcay. To include ADMET reactions better into the title of this volume we changed it into: Metathesis Polymerization of Olefins and Alkyne Polymerization. This volume is addressed to research scientists, but also to those who start to work in the area of olefin metathesis and alkyn polymerization. The topics of the course were: mechanism of ROMP reactions/ new catalysts for ROMP/ new products by ROMP/ new catalysts for ADMET/ new products by ADMETI degradation of polymer by metathesis reactions/ alkyn polymerization and metathesis/ industrial application of metathesis reactions. The Advanced Study Institute was generously sponsored by the Scientific Affairs Division of NATO and the editor gratefully acknowledges this sponsorship. We also thank the Members of the Local Organizing Committee for their engagement on a successful NATO-ASI!

Olefin Metathesis and Polymerization Catalysts - Yavuz Imamogammalu 1990-11-30

Metathesis Polymerization of Olefins and Polymerization of Alkynes - Yavuz Imamogammalu 1998 This book contains contributions from inorganic, organic and polymer chemists, who join forces to report on the state of the art in ring opening metathesis polymerization, acyclic diene metathesis and alkyn polymerization. Topics covered are: mechanism of ROMP reactions, new catalysts for ROMP, new products by ROMP, new catalysts for ADMET, new products by ADMET, degradation of polymers by metathesis reactions, alkyn polymerization and metathesis, and industrial applications of metathesis reactions.

New and Future Developments in Catalysis - Hynek Balcar 2013-07-18

Catalytic Polymerization of Cycloolefins - V. Dragutan 2000-06-26 This book covers the most important topics concerning cationic Ziegler-Natta and ring-opening metathesis polymerization of cycloolefins. The work describes the major pathways that cycloolefins can follow under the action of specific catalytic systems, essentially vinyl and ring-opening polymerization, both reaction types allowing the manufacture of distinct products with wide applicability in modern technologies. The comprehensive data available on this subject are
logically and systematically selected and reviewed throughout 18 chapters, according to the basic catalytic processes involved, types of monomers and catalysts employed, reaction conditions and application fields. The modern trends in design of chiral metallocene catalysts, well-defined living metathesis catalysts, catalysts tolerant toward functionalities and water systems are highlighted. The book discusses in detail the relevant aspects of these processes including reaction thermodynamics, kinetics, mechanisms and stereochemistry and correlates the structure of produced polymers with their chemical and physical-mechanical properties. Related important topics include Ziegler-Natta polymerization of olefins and dienes, atom transfer radical polymerization of vinyl compounds, metathesis of olefins and acetylenes, acyclic diene metathesis reaction, carbonyl olefination reaction, metathesis polymerization of acetylenes, metathesis degradation of polymers and ring-opening polymerization of heterocycles. Special emphasis is laid upon the manufacture of commercial products, new polymers and copolymers of potential interest for industry and design and synthesis of specialty polymers with particular structures and architectures and desired properties. The book critically evaluates the most recent achievements reported in this field and outlines the modern trends on the research and application of the catalytic processes for cycloolefin polymerization. For the first time, comprehensive information about the published data on the subject up to now is provided for both academic and industrial researchers working in the areas of polymer chemistry, organic and organometallic chemistry, surface science and catalysis, petrochemistry and chemical engineering. This stimulating book offers an enlightening introduction and a quick documentation on the subject as well as a solid background in this field. Moreover, the work offers a wealth of useful information for specialists applying polymers in various scientific and industrial areas.

Part I, An Investigation of the Mechanism of the Olefin Metathesis Reaction Using a Heterogeneous Catalyst. Part II, Development of a Polymer-bound Catalyst for the Olefin Metathesis Reaction-Sandra Jean Swetnick 1979

Organometallic Reactions and Polymerization-Kohtarou Osaka 2014-07-15 This compilation provides advanced graduate students and researchers with a structured overview of olefin polymerization. Divided into eight chapters written by international experts, this book covers polymerization using various organotransition-metal catalysts, including early and late transition metal complexes, new trends in olefin oligomerization and related reactions. All authors address the historic and scientific backgrounds of the field as well as current research progress and potential for further research. The complete book is designed to present eight independent lectures and, because all authors are well versed in organometallic chemistry, each is based on a profound understanding of the reactions and structures of organotransition metal complexes. This book is an ideal accompaniment for researchers taking courses in olefin polymerization and also serves as a valuable resource for teachers and lecturers of chemistry when planning and researching material for advanced lecture courses.

Studies of the Mechanism of Alkyne Polymerization by an Olefin Metathesis Catalyst-Marijo Clark 1982


Green Metathesis Chemistry-Valerian Dragutan 2009-09-30 An outstanding international scientific event in the field of metathesis chemistry, the NATO ASI “Green Metathesis Chemistry: Great Challenges in Synthesis, Catalysis and Nanotechnology” has been recently organized in Bucharest, Romania (July 21- August 2, 2008). Numerous renowned scientists, young researchers and students, convened for two weeks to present and debate on the newest trends in alkene metathesis and identify future perspectives in this fascinating area of organic, organometallic, catalysis and polymer chemistry with foreseen important applications in materials science and technology. Following the fruitful practice of NATO Advanced Study Institutes, selected contributions covering plenary lectures, short communications and posters have been compiled in this special volume dedicated to this successful convention on green metathesis chemistry. General interest was primarily focused on relevant "green chemistry" features related to all types of metathesis reactions (RCM, CM, enyne metathesis, ADMET and ROMP). Diverse opportunities for green and sustainable technologies and industrial procedures based on metathesis have been identified. Largely exemplified was the utility of this broadly applicable strategy in organic synthesis, for accessing natural products and pharmaceuticals, and also its ability to fit in the manufacture of smart and nanostructured materials, self-assemblies with nanoscale morphologies, macromolecular engineering.

Handbook of Transition Metal Polymerization Catalysts-Ray Hoff 2018-05-08 Including recent advances and historically important catalysts, this book overviews methods for developing and applying polymerization catalysts - dealing with polymerization catalysts that afford commercially acceptable high yields of polymer with respect to catalyst mass or productivity. • Contains the valuable data needed to reproduce syntheses or use the catalyst for new applications • Offers a guide to the design and synthesis of catalysts, and their applications in synthesis of polymers • Includes the information essential for choosing the appropriate reactions to maximize yield of polymer synthesized • Presents new chapters on vanadium catalysts, Ziegler catalysts, laboratory homopolymerization, and copolymerization
Olefin Polymerization - Walter Kaminsky 2006-08-18 With an enormous velocity, olefin polymerization has expanded to one of the most significant fields in polymers since the first industrial use about 50 years ago. In 2005, 100 million tons of polyolefins were produced - the biggest part was catalyzed by metalloorganic compounds. The Hamburg Macromolecular Symposium 2005 with the title "Olefin Polymerization" involved topics such as new catalysts and cocatalysts, kinetics, mechanism and polymer reaction engineering, synthesis of special polymers, and characterization of polyolefins. The conference combined scientists from different disciplines to discuss latest research results of polymers and to offer each other the possibility of cooperation. This is reflected in this volume, which contains invited lectures and selected posters presented at the symposium.

Olefin Metathesis - Karol Grela 2014-04-11 This is a complete examination of the theory and methods of modern olefin metathesis, one of the most widely used chemical reactions in research and industry. Provides basic information for non-specialists, while also explaining the latest trends and advancements in the field. Discusses the various types of metathesis reactions, including CM, RCM, enyne metathesis, ROMP, and tandem processes, as well as their common applications. Outlines the tools of the trade—from the important classes of active metal complexes to optimal reaction conditions—and suggests practical solutions for common reaction problems. Includes tables with structures of commercial catalysts, and recommendations for commercial catalyst suppliers.

Metathesis Chemistry - Yavuz Imamoglu 2007-07-04 Discover why olefin metathesis has asserted itself as a powerful strategy for obtaining fine chemicals, biologically active compounds, architecturally complex assemblies, new materials, and functionalized polymers. This volume compiles all the latest trends in olefin metathesis. In particular, you'll learn how olefin metathesis has growing potential for the development of sustainable technologies with many possible industrial applications.

Fundamentals of Molecular Catalysis - 2003-04-02 Almost all contemporary organic synthesis involve transition metal complexes as catalysts or particular reagents. The aim of this book is to provide the reader with detailed accounts of elementary processes within molecular catalysis to allow its development and as an aid in designing novel catalytic systems. The book comprises authoritative reviews on elementary processes from experts working at the forefront of organometallic chemistry. This is the first book that focuses on elementary processes in transition metal complexes for understanding catalytic mechanisms. Provides detailed description of elementary processes involved in catalytic cycles by experts in the field. Provides an overview of the mechanisms of various homogeneous catalysts.

Metathesis in Natural Product Synthesis - Janine Cossy 2011-09-22 Emphasizing the impact of metathesis in natural product synthesis through the various types of key reactions, this is a comprehensive view of a hot topic. Written by top international authors, this ready reference is clearly structured and packed with important information, including representative experimental procedures for practical applications. A real must-have for anyone working in natural product synthesis.

Late Transition Metal Polymerization Catalysis - Bernhard Rieger 2006-03-06 At the start of the 1950s, Ziegler and Natta discovered that simple metalorganic catalysts are capable of transforming olefins into linear polymers with highly ordered structures. This pioneering discovery was recognized with a Nobel Prize in 1963. In the 80s and 90s, the development of molecular defined metallocones led to a renaissance for non-polar polyolefin materials. Designer catalysts allowed a greater precision in defining properties of the material. The past 10 years have seen the discovery of new catalysts based on late transition metals, which allow the combination of polar monomers with non-polar olefins and thus lead to innovative materials. Here, the world's leading authors from industry and academia describe the latest developments in this fascinating field for the first time in such comprehensive detail. In so doing, they introduce readers systematically to the basic principles and show how these new catalysts can effectively be used for polymerization reactions. This makes the book an ideal and indispensable reference for specialists, advanced students, and scientists of various disciplines dealing with research into catalysts and materials science.

Ring Opening Metathesis Polymerisation and Related Chemistry - Ezat Khosravi 2002-03-31 The book highlights the latest developments of new catalysts for stereoselective metathesis and catalysts with considerable functional group tolerance which have permitted the synthesis of novel materials. It also shows that these new catalysts in addition to Ring Opening Metathesis Polymerisation (ROMP), Acyclic Diene Metathesis (ADMET), and Cross metathesis (CM) are now powerful tools for Ring Closing Metathesis (RCM) which has found many applications in the synthesis of natural products.

Olefin Metathesis and Ring-opening Polymerization of Cyclo-olefins - Valerian Drăguțan 1985

Alkene Metathesis in Organic Synthesis - Alois Fuerstner 2003-07-01 Organometallic chemistry is a well established research area at the interface of organic and inorganic chemistry. In recent years this field has undergone a renaissance as our understanding of organometallic structure, properties and mechanism has opened the way for the design of organometallic compounds and reactions tailored to the needs of such diverse areas as medicine, biology, materials and polymer sciences and organic synthesis. For example, in the development of novel catalytic processes, organometallic chemistry is helping meet the challenge to society that the economic and environmental necessities of the future pose. As this field becomes increasingly interdisciplinary, we recognize the need for critical overviews of new developments that are of broad significance. This is our goal in starting this new series Topics in Organometallic Chemistry. The scope of coverage includes a broad range of topics of pure and applied or ganometallic chemistry, where new
breakthroughs are being achieved that are of significance to a larger scientific audience. Topics in Organometallic Chemistry differs from existing review series in that each volume is thematic, giving an overview of an area that has reached a stage of maturity such that coverage in a single review article is no longer possible. Furthermore, the treatment addresses a broad audience of researchers, who are not specialists in the field, starting at the graduate student level. Discussion of possible future research directions in the areas covered by the individual volumes is welcome.

**Novel Metathesis Chemistry: Well-Defined Initiator Systems for Specialty Chemical Synthesis, Tailored Polymers and Advanced Material Applications**-Y. Imamoglu 2012-12-06 A comprehensive discussion of the theory, practice and application of catalytically active transition metal species and their application in the production of specialist polymeric materials. The material is presented in a progressive manner, suitable for non-experts and those seeking an introduction to the field. The bibliographies supplied are complete and up to date, making the book an indispensable guide to the primary literature for the more theoretical background to the topics discussed. After a comprehensive discussion of initiating systems for specialty chemical synthesis the book goes on to deal with a wide range of topics in materials science, including: alkenamers, polyacetylenes, industrial applications and liquid rocket engine fuels.

**Applications in Design and Simulation of Sustainable Chemical Processes**-Alexandre C. Dimian 2019-08-08 Applications in Design and Simulation of Sustainable Chemical Processes addresses the challenging applications in designing eco-friendly but efficient chemical processes, including recent advances in chemistry and catalysis that rely on renewable raw materials. Grounded in the fundamental knowledge of chemistry, thermodynamics, chemical reaction engineering and unit operations, this book is an indispensable resource for developing and designing innovating chemical processes by employing computer simulations as an efficient conceptual tool. Targeted to graduate and post graduate students in chemical engineering, as well as to professionals, the book aims to advance their skills in process innovation and conceptual design. The work completes the book Integrated Design and Simulation of Chemical Processes by Elsevier (2014) authored by the same team. Includes comprehensive case studies of innovative processes based on renewable raw materials Outlines Process Systems Engineering approach with emphasis on systematic design methods Employs steady-state and dynamic process simulation as problem analysis and flowsheet creation tool Applies modern concepts, as process integration and intensification, for enhancing the sustainability

**Novel Catalysts for Olefin Metathesis**-Eyal Tzur 2010

**Olefin Metathesis**-Kenneth John Ivin 1983

**Homogeneous Catalysts**-John C. Chadwick 2011-06-09 This first book to illuminate this important aspect of chemical synthesis improves the lifetime of catalysts, thus reducing material and saving energy, costs and waste. The international panel of expert authors describes the studies that have been conducted concerning the way homogeneous catalysts decompose, and the differences between homogeneous and heterogeneous catalysts. The result is a ready reference for organic, catalytic, polymer and complex chemists, as well as those working in industry and with/on organometallics.

**Homopolymerization of Cyclic Olefins by a Molybdenum Olefin Metathesis Catalyst**-Jay A. Johnston 1991

**Ring Opening Metathesis Polymerisation and Related Chemistry**-Ezat Khosravi 2012-12-06 Since the last ASI in Turkey in Sept. 1995, the olefin metathesis has made remarkable strong developments with an incredible speed in various directions. New catalyst systems have been developed which have resulted in the synthesis of novel materials. Other fascinating developments have been the new catalysts for stereoselective metathesis and catalysts with considerable functional group tolerance. These new catalysts in addition to Ring Opening Metathesis Polymerisation (ROMP) and Acyclic Diene Metathesis (ADMET) are now powerful tools for Ring Closing Metathesis (RCM) and have found many applications in the synthesis of natural products. A lot of information has been established about all aspects of the olefin metathesis and there is a vast literature concerning the process, covering the initiators, mechanistic features and applications of this reaction in organic and polymer synthesis. The NATO ASI on rd th ROMP and Related Chemistry took place in Polanica-Zdroj, Poland during 3 to 15 Sept. 2000, to highlight the developments in this area and to discuss the prospects and visions for the year 2000 and beyond. The aims of the ASI were: to provide a platform for dissemination of knowledge; to promote communication between people who have a serious interest in this field of chemistry; to help establishing international scientific contacts and to provide an opportunity for the scientists with an appropriate scientific background to learn of recent developments in this field of science. There were 15 lecturers and 67 participants in this NATO ASI.

**Vanadium Catalysis**-Manas Sutraddhar 2020-11-11 Vanadium is one of the more abundant elements in the Earth’s crust and exhibits a wide range of oxidation states in its compounds making it potentially a more sustainable and more economical choice as a catalyst than the noble metals. A wide variety of reactions have been found to be catalysed by homogeneous, supported and heterogeneous vanadium complexes and the number of applications is growing fast. Bringing together the research on the catalytic uses of this element into one essential resource, including theoretical perspectives on proposed mechanisms for vanadium catalysis and an overview of its relevance in biological processes, this book is a useful reference for industrial and academic chemists alike.
The field of olefin metathesis has grown tremendously in recent decades. Elucidation of the mechanism and an improved understanding of the structure-activity relationship has enabled chemists to design catalysts which exhibit greater activity, stability, and selectivity. However, the economic feasibility of performing this reaction on the industrial scale is often restricted by the high cost of the catalysts in combination with modest turnover numbers (TON). The lifetime of an active catalyst species depends on the stability of intermediates in the catalytic cycle, and this ultimately determines the TON. Therefore, the various decomposition pathways leading to catalyst inactivation represents one of the greatest challenges still remaining in the field. The electron deficient Ru intermediates of the catalytic cycle are susceptible to decomposition through any reaction which provides the metal with additional electron density. The primary objective of this thesis project was to develop 2nd generation Hoveyda-Grubbs catalysts which contain an N-heterocyclic carbene (NHC) bearing hemilabile polyether arms in the ortho position of the aromatic rings. The purpose of incorporating these functional groups was to stabilize the fragile intermediates of the catalytic cycle via O – Ru coordination. The polyether arms have the potential to wrap around Ru via chelation and therefore provide electron density while simultaneously shielding the sterically wide open position trans to the NHC. The hypothesis was that stabilizing these intermediates would prolong the lifetime of the active catalyst, thus leading to increased TON and allowing for lowering loadings. A novel series of 5 catalysts bearing NHC ligands with hemilabile polyether arms were synthesized. The NHC ligands differed by the number of arms (1, 2, or 4) and the length of each arm (2 or 3 carbons between the ether oxygens). The structures of the catalysts and NHC ligand precursors were investigated by x-ray crystallography and NMR spectroscopy. The results of x-ray diffraction revealed that the 4-armed ligands adopt a propeller conformation, and their corresponding tetra-substituted catalysts displayed a single ortho O – Ru interaction in the solid state. This coordination forces the NHC to adopt a highly contorted conformation which is twisted far away from the default position seen for the unsubstituted commercial catalyst bearing an NHC with 2 mesitylene rings but no electron donor groups. NMR spectroscopy provided information about the conformation adopted in solution, and revealed that the NHC has restricted rotation once bound to Ru but does not display broken molecular symmetry. The combination of O – Ru coordination in the solid state but retention of symmetry in solution indicates that all of the available polyether arms take turns interacting with the metal faster than the NMR timescale. Catalyst decomposition studies were performed under normal metathesis conditions with a standard alkene substrate or by forming the inactive Fischer carbene by treating the catalyst with a vinyl ether. The purpose of intentional catalyst destruction was to generate an electron deficient Ru center which is stabilized by coordination with the polyether arms. These species are electronically and sterically more similar to the 14 electron active catalyst than the 16 electron pre-catalyst, and therefore provide greater insight into how the catalyst actually behaves in solution upon initiation. Only the decomposition products obtained from the 2C-2arm catalyst 15 displayed chelation in the solid state, while every other catalyst formed a non-chelated dimer upon decomposing. A variety of unexpected degradation products were observed by x-ray crystallography, and a potential mechanism was proposed for each decomposition pathway. The catalysts were screened for ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP) performance. Only the tetra-substituted catalysts exhibited a rate enhancement for RCM when compared with the commercial catalyst bearing 2 mesitylene rings. However, the TON did not differ significantly from the commercial catalyst, thus indicating that the electron deficient intermediates of the catalytic cycle are not stabilized by coordination with the polyether arms. All of the polyether-substituted catalysts were significantly inferior than the commercial catalyst at performing ROMP, exhibiting both decreased TON and slower kinetics. The information gathered from testing catalyst performance in combination with the structural data obtained by analyzing the catalysts and decomposition products via x-ray diffraction and NMR spectroscopy allowed for potential structure-activity relationships to be proposed. The insight into olefin metathesis catalyst structure and performance provided by the studies of this work may assist in future catalyst design.

Development of New Ruthenium Catalysts for Homogeneous and Heterogeneous Olefin-Metathesis- 2006 Different homogeneous ruthenium catalysts such as the Grubbs-Herrmann- (RuCl2(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolin-2-ylidene)(=CHPh)(PCy3)) and the Grubbs-Hoveyda-catalyst (RuCl2(=CH2(2-Pro-O-GH4)(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolin-2-ylidene)) were modified through chlorine exchange in reactivity and selectivity. The activity in olefin-metathesis could be improved. Exchange with CF3COOAg on the Hoveyda-Grubbs-catalyst provided the first time a catalyst active for the cycloalkyne polymerization. After further modifications of the catalyst, the polymerization could be performed in a living and controlled manner. Furthermore, the chlorine exchange was an attractive way of fixation of the catalyst to supports such as PS-DVP-CH2OH, ROMP-based monolithic supports and amphiphilic poly(2-oxazoline)n supports.

Catalytic Olefin Polymerization T. Keii 1990-09-12 Recent development of a new generation of Ziegler-Natta Catalysts using either magnesium dichloride as carrier or methylaluminoxane as cocatalyst has markedly stimulated the research activity in the field of olefin polymerization. These discoveries have not only yielded economical processes for polyolefin production but also opened the way to a new generation of novel polymers. Moreover, the nature of active species is being clarified well by the effort to simplify catalyst systems. The present volume includes 38 papers from the 31 lectures and 18 posters presented at the symposium on 'Recent Developments in Olefin Polymerization Catalysts', which covered the following topics: Overview of super-active homogeneous and heterogeneous catalysts, kinetic profile of olefin polymerization including copolymerization, characterization of catalysts and polymers, methods for the determination of active center concentration, role of Lewis bases on the catalysts isospecificity, polymerization mechanisms, and synthetic pathways for functionalized polyolefins. The contents are well balanced between fundamental research and application as well as between homogeneous and heterogeneous catalyst systems.

Polymeric Materials in Organic Synthesis and Catalysis- Michael R. Buchmeiser 2006-03-06 This is the first book to describe the synthesis and characterization of the materials used in polymer-supported synthesis. The authors cover not only the classical polymers and their use in homogenous, heterogeneous and micellar catalysis, but also such new developments as “enzyme-labile linkers”, illustrating how to simplify the purification process and avoid waste. The result is a wealth of useful information – for beginners and experts alike - in one handy reference, removing the need for difficult and time-consuming research among the literature.
Metal-catalysis in Industrial Organic Processes-Royal Society of Chemistry (Great Britain) 2008 Catalysis underpins most modern industrial organic processes. It has become an essential tool in creating a 'greener' chemical industry by replacing more traditional stoichiometric reactions, which have high energy consumption and high waste production, with mild processes which increasingly resemble Nature's enzymes. Metal-Catalysis in Industrial Organic Processes considers the major areas of the field and discusses the logic of using catalysis in industrial processes. This popular book, now available as softback, provides information on oxidation, hydrogenation, carbonylation, C-C bond formation, metathesis and polymerization processes, as well as on the mechanisms involved. In addition two appendices offer a concise treatment of homogeneous and heterogeneous catalysis. Numerous exercises referring to problems of catalytic processes, and research perspectives complete the book. This definitive reference source, written by practising experts in the field, provides detailed and up-to-date information on key aspects of metal catalysis.


Novel Olefin Metathesis Catalysts Bearing a Hemi-labile NHC Ligand-Nicolas Cena 2019 The field of olefin metathesis has grown appreciatively in recent decades. Elucidation of the mechanism and a deeper understanding of the key intermediates have enabled chemists to design catalysts, which exhibit greater activity, stability, and selectivity towards a variety of substrates. However, the economic impact of performing this reaction on the industrial scale is often governed by the high cost of the catalysts in comparison to modest turnover numbers (TON). The lifetime of an active catalyst species depends on the stability of intermediates in the catalytic cycle, and this ultimately determines the TON. One of the remaining goals in the field is to further stabilize the intermediates of the catalytic cycle in order to prolong the catalyst lifetimes and increase turnover numbers (TON). The ruthenium catalytic species cycle through several electron deficient intermediates, which lead towards decomposition pathways. These decomposition pathways are directed towards reactions that provide the metal with additional electron density. The primary focus of this thesis project was to develop a new generation of olefin metathesis catalysts employing a tridentate N-heterocyclic carbene (NHC) ligand bearing a hemi-labile pyridine arm in the ortho position of the aromatic ring. The rationale behind incorporating these functional groups was to stabilize the reactive intermediates of the catalytic cycle via electron donation from the ether O ≡ Ru and the pyridine N ≡ Ru. These ligands increase the likelihood of stabilization of the metal center by chelation of electron-donating substituents from the O and N, thus adding electron density back into the electron-deficient metal center. The ligand not only donates electron density back to the metal but also shields the sterically open position trans to the NHC. The hypothesis was that stabilizing these reactive intermediates would prolong the lifetime of the active catalyst and thus increase TON and allow for a much lower catalyst loading for industrial applications, thus vastly impacting the economical aspect of olefin metathesis processes. A novel set of two catalysts bearing tridentate NHC ligands with hemi-labile pyridine arms were synthesized. The ligands differed in one aromatic ring containing either a 2,6 disopropyl phenyl (DIPP) or mesityl (Mes) moiety. The result of the x-ray crystallographic analysis revealed the NHC ligand coordinated in the proposed tridentate meridional fashion around the central Ru atom. This coordination was proposed in order to affect a hinge-like mechanism in which the pyridine arm’s hemi-labile nature would be in close proximity to the electron deficient metal center, so that it could bind reversibly in order to satiate the metal's desire for electron density while still allowing reactivity upon dissociation. NMR spectroscopy revealed information about the proposed structure in solution and revealed that the ligand was bound in solution to the metal center in one orientation, owing to the coordination of the O and N to the metal center. Catalyst decomposition studies were performed using the methylidenic variant of the catalysts at elevated temperatures under inert conditions as well as under an atmosphere of ethylene gas. The purpose of intentionally decomposing the catalyst was to generate the electron deficient Ru center and probe the stabilizing effects of the pyridine arm coordination. These reactive intermediates are electronically and sterically more similar to the 14-electron active catalyst than the 16-electron pre-catalyst, giving insight into how the catalysts behave in solution upon metathesis active conditions. Decomposition products of the DIPP variant were analyzed by NMR and x-ray crystallography, giving insight into possible decomposition pathways for these novel catalysts. The catalysts were screened for metathesis activity in ring-closing metathesis (RCM) and ring opening metathesis polymerization (ROMP). Both showed noticeable differences from previous generations of Grubbs and Hoveyda-Grubbs catalysts in overall efficacy. The prolonged lifetimes of these new catalysts were competitive with commercially available catalysts in terms of lifetime and TON. Though slightly lower in TON, these catalysts lasted much longer in solution at elevated temperatures than their predecessors, thus indicating much more stabilized reactive intermediates. The data gathered from decomposition studies and metathesis activity along with NMR and x-ray crystallography allowed for potential structure-activity relationships and mechanistic pathways to be proposed. The insight into olefin metathesis catalyst structure, performance, and design provided by these studies may assist in future endeavors in the field of olefin metathesis catalyst design and employment.

Molybdenum Oxide & Mesoporous Silica Metathesis Catalysts-Pavel Topka 2013 Alkene metathesis attracted recently much attention, especially with the 2005 Nobel prize awarded for the development of the metathesis method in organic synthesis. Supported molybdenum oxide catalysts are widely used in industrial petrochemical processes, including metathesis (e.g. Phillips triolefin process, Shell higher olefin process). The present work discloses new type of metathesis catalysts based on molybdenum oxide supported on mesoporous silica. The key idea is to improve the activity of molybdenum oxide catalyst in this reaction utilizing high surface area and narrow pore size distribution of the support material. For the preparation of the catalysts, innovative and environmentally friendly thermal spreading method was employed. The thorough characterization of the catalysts by physicochemical techniques is described.
The analysis of activity/selectivity vs. composition/structure relationships should help shed some light on this new and exciting field of heterogeneous catalysis, and should be especially useful to professionals in metathesis chemistry, or anyone else who may be considering utilizing molybdenum oxide catalysts for another catalytic reaction.

Iron and Molybdenum Complexes Supported by Pincer Ligands—Steven Ryan Ruark 2016 Since its discovery in the mid 1950’s, olefin metathesis has become one of the most widely used chemical reactions. Olefin metathesis involves the breaking of carbon-carbon double bonds and the redistribution of the fragments to form new olefins by way of a metal alkylidene.6 It is used in industry to convert cheap plant oils into useful products such as alpha olefins, jet fuel and green diesel. The Elevance BioRefinery has the capacity to run this reaction and produce up to 400 million pounds of products per year. The most expensive part in this refinery process is the catalyst itself. The catalyst currently used is an alkylidene complex of ruthenium—an expensive and rare metal. This has led the Schrodung group to explore the possibility of developing catalytic complexes based on abundant and cheap metals such as iron or molybdenum.40,41 We first attempted to support iron with a tridentate pincer ligand, OiPrPONOP, however the ligand was not robust enough and more than one ligand was required to adequately protect the iron xv center. Ultimately, the ligand was reacted with Fe(PMe3)3 to make (OiPrPONOP)Fe(PMe3)2. This complex is very stable and unreactive, preventing its transformation into any catalytic species. We then turned our attention to a pincer OCO-NHC ligand. This ligand was able to stabilize an iron tricyclohexyphosphine complex, (OC-NHC)FePCy3, However, attempts to react this complex with diazo compounds to form an iron alkylidene (OCO-NHC)Fe=CHR were unsuccessful. Further studies focused on replacing the PCy3 ligand with pyridines, in an attempt to make the complex more labile. However, the resulting species proved much too sensitive to water and was difficult to isolate and characterize. Inspired by the research done by the Chirik group where they reduced several arylypyridinediimine (ArPDI) ironII complexes into a reduced N2-bridged complex. They reported the bound N2 molecules would readily exchange with 15N2 and ultimately they were able to form an iron alkylidene complex. However, the complex was not metathesis active.54,42 We successfully reduced MesPDIFeBr2 into the bis-N2 complex but the complex refused to react cleanly in attempts to make iron alkylidene species. We also explored the possibility of forming a molybdenum alkylidene supported by a tridentate iPrPONOP ligand. After successfully forming iPrPONOPMoCl3 we tried several strategies to form and isolate a molybdenum alkylidene. We attempted a similar reduction as the iron species trying to access a bis-N2 bridged molybdenum complex but the reaction resulted in decomposition of the complex. We then attempted ‘Schrock type’ chemistry by reacting the iPrPONOPMoCl3 complex with Grignard reagents.81 However, this strategy resulted in decomposition as well. We successfully performed ring opening metathesis polymerization (ROMP) of norbornene by adding Grignard reagents to several different tridentate supported MoCl3 precatalysts. Select polymers were then analyzed for cis content by 1 H NMR to probe for serioiregularity. The only precatalyst to have more than 50% cis content was the BinaphPONOPMoCl3 / methyl- and trimethylsilylmethyl-Grignard reagents but only when run at 25 °C. xvi We were able to perform ROMP of dicyclopentadiene (DCPD) with the molybdenum complex / Grignard reagents. However, while the fully polymerized product is extremely hard and transparent we could only achieve a soft nontransparent product, indicating incomplete polymerization.
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