

Catalysis  
by  
Metal  
Complexes

*Supported  
Metal  
Complexes*

*by F.R. Hartley*

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# Supported Metal Complexes

**R.M. Lambert, Gianfranco Pacchioni**

A red circular graphic with a gradient, appearing as a stylized arrow or a partial circle, located to the right of the authors' names.

## **Supported Metal Complexes:**

**Supported Metal Complexes** F.R. Hartley, 1985-11-30 It is now 35 years since the first patents in polymer supported metal complex catalysts were taken out In the early days ion exchange resins were used to support ionic metal complexes Soon covalent links were developed and after an initially slow start there was a period of explosive growth in the mid to late 1970s during which virtually every homogeneous metal complex catalyst ever reported was also studied bound to a support Both polymers and inorganic oxides were studied as supports although the great preponderance of workers studied polymeric supports and of these polystyrene was by far the commonest used This period served to show that by very careful design polymer supported metal complex catalysts could have specific advantages over homogeneous metal complex catalysts However the subject was a complicated one Merely immobilising a successful metal complex catalyst to a functionalised support rarely yielded other than an inferior version of the catalyst Amongst the many discouraging results of the 1970s there were more than enough results that were sufficiently encouraging to demonstrate that by careful design supported metal complex catalysts could be prepared in which both the metal complex and the support combined together to produce an active catalyst which due to the combination of support and complex had advantages of activity selectivity and specificity not found in homogeneous catalysts Thus a new generation of catalysts was being developed

**Supported Metal Complexes** F.R. Hartley, 2012-12-06 It is now 53 years since the first patents in polymer supported metal complex catalysts were taken out In the early days ion exchange resins were used to support ionic metal complexes Soon covalent links were developed and after an initially slow start there was a period of explosive growth in the mid to late 1970s during which virtually every homogeneous metal complex catalyst ever reported was also studied bound to a support Both polymers and inorganic oxides were studied as supports although the great preponderance of workers studied polymeric supports and of these polystyrene was by far the commonest used This period served to show that by very careful design polymer supported metal complex catalysts could have specific advantages over homogeneous metal complex catalysts However the subject was a complicated one Merely immobilising a successful metal complex catalyst to a functionalised support rarely yielded other than an inferior version of the catalyst Amongst the many discouraging results of the 1970s there were more than enough results that were sufficiently encouraging to demonstrate that by careful design supported metal complex catalysts could be prepared in which both the metal complex and the support combined together to produce an active catalyst which due to the combination of support and complex had advantages of activity selectivity and specificity not found in homogeneous catalysts Thus a new generation of catalysts was being developed

**Supported Metal Single Atom Catalysis** Philippe Serp, Doan Pham Minh, 2022-02-09 b Supported Metal Single Atom Catalysis Covers all key aspects of supported metal single atom catalysts an invaluable resource for academic researchers and industry professionals alike Single atom catalysis is one of the most innovative and dynamic research areas in catalysis science Supported metal catalysts

are used extensively across the chemical industry ranging from fine and bulk chemical production to petrochemicals Single atom catalysts SACs combine the advantages of both homogeneous and heterogeneous catalysts such as catalyst stability activity and high dispersion of the active phase Supported Metal Single Atom Catalysis provides an authoritative and up to date overview of the emerging field covering the synthesis preparation characterization modeling and applications of SACs This comprehensive volume introduces the basic principles of single atom catalysis describes metal oxide and carbon support materials for SAC preparation presents characterization techniques and theoretical calculations and discusses SACs in areas including selective hydrogenation oxidation reactions activation of small molecules C C bond formation and biomedical applications Highlights the activity selectivity and stability advantages of supported metal SACs compared to other heterogeneous catalysts Covers applications of SACs in thermal catalysis electrocatalysis and photocatalysis Includes chapters on single atom alloys and supported double and triple metal atom catalysts Discusses the prospects challenges and potential industrial applications of SACs Supported Metal Single Atom Catalysis is an indispensable reference for all those working in the fields of catalysis solid state chemistry materials science and spectroscopy including catalytic chemists organic chemists electrochemists theoretical chemists and industrial chemists

#### **Macromolecule-Metal Complexes**

Francesco Ciardelli, E. Tsuchida, Dieter Wöhrle, 2012-12-06 Macromolecule Metal Complexes gives the first concise overview on the topic both on fundamentals and new application areas Their synthesis kinetics and thermodynamics are detailed special properties such as gas transport charge transport catalysis and light induced processes are emphasized Furthermore the authors treat the actual working areas for new application methods Thus the book will be a very helpful tool for Polymer Scientists Materials Scientists Organic Chemists and Physical Chemists working in these fields

Catalysis by Polymer-Immobilized Metal Complexes Anatoly D. Pomogailo, 2020-08-18 Deals with a new and promising field developed during the last two decades on the boundary between homogeneous and heterogeneous catalysis This book presents general information on catalysis for a wide range of organic reactions e g hydrogenation and oxidation reactions and polymerization transformations Special attention is paid to electro and photochemical stimulation of catalytic processes in the presence of immobilized metal complexes Other topics covered are the quantitative data on the comparison of catalyses by mobile and immobilized metal complexes main factors affecting the activity of these catalytic systems and methods of optimizing their control and specific problems of catalysis by fixed complexes e g ligand exchange and electron transfer in metal polymer systems macromolecular effects and polyfunctional catalysis

#### **Metal-Metal Bonds and Clusters in Chemistry and**

**Catalysis** John P. Fackler Jr., 2013-11-22 This book contains a series of papers and abstracts from the 7th Industry University Cooperative Chemistry Program symposium held in the spring of 1989 at Texas A M University The symposium was larger than previous IUCCP symposia since it also celebrated the 25 years that had elapsed since the initial discovery by F A Cotton and his co workers of the existence of metal metal quadruple bonds Cotton s discovery demonstrated that multiple bonding in

inorganic systems is not governed by the same constraints observed in organic chemistry regarding s and p orbital involvement. The d orbitals are involved in the multiple bonding description. The quadruple bond involves considerable d orbital overlap between adjacent metal centers. Part I of this series of papers focuses upon the impact of this discovery and describes further contributions to the development of the field. Multiple metal metal bonding now is known to permeate broad areas of transition metal chemistry. The understanding of metal metal bonding that developed as a result of the discovery of multiple metal metal bonding awakened a new chemistry involving metal clusters. Clusters were defined by Cotton to be species containing metal metal bonding. Clusters in catalysis therefore seemed a logical grouping of papers in this symposium. Clusters play an every increasing role in the control of chemical reactions. Part II of this book describes some of the interesting new developments in this field. In Part III the papers examine the role clusters play in describing and understanding solid state materials.

**Nanostructured Materials**, 2001-12-18 This thematic volume of *Advances in Chemical Engineering* presents the latest advances in the exciting interdisciplinary field of nanostructured materials. Written by chemical engineers, chemists, physicists, materials scientists and bioengineers, this volume focuses on the molecular engineering of materials at the nanometer scale for unique size dependent properties. It describes a bottom up approach to designing nanostructured systems for a variety of chemical, physical and biological applications.

**Atomically-Precise Methods for Synthesis of Solid Catalysts** Sophie Hermans, Thierry Visart de Bocarme, 2014-10-31 There is much interest in preparing catalysts with specific structures for a desired catalytic activity. Although there has been a great amount of research into correlating particles sizes and microstructure to catalytic activity, knowledge about practical catalysts still remain ill defined. The current challenge is now to understand atomic control. *Atomically Precise Methods for Synthesis of Solid Catalysts* provides an overview of recent developments in heterogeneous catalysts preparation which aim at controlling the microstructure of such catalysts at the atomic scale. Each chapter provides a different synthetic approach to achieve atomic scale control along techniques to characterize the atomically precise solids. Topics covered include bimetallic supported catalysts from single source precursors, zeolite supported molecular metal complex catalyst, surface organometallic chemistry, atomic layer deposition and electron microscopy of catalysts. Edited by active researchers in the area, the book aims to bridge the gap between surface science and heterogeneous catalysis. The book is suitable for graduate students as well as researchers in academia or in industry from various disciplines including engineering, inorganic, organometallic chemistry, surface science and physical chemistry interested in catalyst design.

[Surface and Interfacial Organometallic Chemistry and Catalysis](#) C. Copéret, Bruno Chaudret, 2005-11-03 With contributions by numerous experts.

[Heterogeneous Catalysts for Clean Technology](#) Karen Wilson, Adam F. Lee, 2013-09-17 Reactive but not a reactant. Heterogeneous catalysts play an unseen role in many of today's processes and products. With the increasing emphasis on sustainability in both products and processes, this handbook is the first to combine the hot topics of heterogeneous catalysis and clean technology.

It focuses on the development of heterogeneous catalysts for use in clean chemical synthesis dealing with how modern spectroscopic techniques can aid the design of catalysts for use in liquid phase reactions their application in industrially important chemistries including selective oxidation hydrogenation solid acid and base catalyzed processes as well as the role of process intensification and use of renewable resources in improving the sustainability of chemical processes With its emphasis on applications this book is of high interest to those working in the industry Catalysis of Organic Reactions

Stephen R. Schmidt, 2006-12-07 Bringing together academic industrial and governmental researchers and developers *Catalysis of Organic Reactions* comprises 57 peer reviewed papers on the latest scientific developments in applied catalysis for organic reactions The volume describes the use of both heterogeneous and homogeneous catalyst systems and includes original research *Homogeneous Hydrogenation* P.A. Chaloner, M.A. Esteruelas, Ferenc Joó, L.A. Oro, 2013-11-11

Homogeneous hydrogenation is one of the most thoroughly studied fields of homogeneous catalysis The results of these studies have proved to be most important for an understanding of the underlying principles of the activation of small molecules by transition metal complexes During the past three decades homogeneous hydrogenation has found widespread application in organic chemistry including the production of important pharmaceuticals especially where a sophisticated degree of selectivity is required This volume presents a general account of the main principles and applications of homogeneous hydrogenation by transition metal complexes Special attention is devoted to the mechanisms by which these processes occur and the role of the recently discovered complexes of molecular hydrogen is described Sources of hydrogen other than H<sub>2</sub> are also considered transfer hydrogenation The latest achievements in highly stereoselective hydrogenations have made possible many new applications in organic synthesis These applications are documented by giving details of the reduction of important unsaturated substrates alkenes alkynes aldehydes and ketones nitrocompounds etc Hydrogenation in biphasic and phase transfer catalyzed systems is also described Finally a discussion of the biochemical routes of H<sub>2</sub> activation highlights the similarities and differences in performing hydrogenation in both natural and synthetic systems For researchers working in the fields of homogeneous catalysis especially in areas such as pharmaceuticals plastics and fine chemicals Preparation of Solid Catalysts Gerhard Ertl, Helmut Knözinger, Jens Weitkamp, 2008-08-29 Solid catalysts play a fundamental role in all areas between basic research and industrial applications This book offers a large amount of information about the preparation of solid catalysts All types of solid catalysts and all important aspects of their preparation are discussed The highly topical contributions are written by leading experts in disciplines ranging from solid state interface and solution chemistry to industrial engineering The straightforward presentation of the material and the comprehensive coverage make this book an essential and indispensable tool for every scientist and engineer working with solid catalysts

Arene Chemistry Jacques Mortier, 2015-12-14 Organized to enable students and synthetic chemists to understand and expand on aromatic reactions covered in foundation courses the book offers a thorough and accessible mechanistic

explanation of aromatic reactions involving arene compounds Surveys methods used for preparing arene compounds and their transformations Connects reactivity and methodology with mechanism Helps readers apply aromatic reactions in a practical context by designing syntheses Provides essential information about techniques used to determine reaction mechanisms

*X-Ray Absorption and X-Ray Emission Spectroscopy* Jeroen A. van Bokhoven, Carlo Lamberti, 2016-01-08 During the last two decades remarkable and often spectacular progress has been made in the methodological and instrumental aspects of x ray absorption and emission spectroscopy This progress includes considerable technological improvements in the design and production of detectors especially with the development and expansion of large scale synchrotron reactors All this has resulted in improved analytical performance and new applications as well as in the perspective of a dramatic enhancement in the potential of x ray based analysis techniques for the near future This comprehensive two volume treatise features articles that explain the phenomena and describe examples of X ray absorption and emission applications in several fields including chemistry biochemistry catalysis amorphous and liquid systems synchrotron radiation and surface phenomena Contributors explain the underlying theory how to set up X ray absorption experiments and how to analyze the details of the resulting spectra X Ray Absorption and X ray Emission Spectroscopy Theory and Applications Combines the theory instrumentation and applications of x ray absorption and emission spectroscopies which offer unique diagnostics to study almost any object in the Universe Is the go to reference book in the subject for all researchers across multi disciplines since intense beams from modern sources have revolutionized x ray science in recent years Is relevant to students postdocurates and researchers working on x rays and related synchrotron sources and applications in materials physics medicine environment geology and biomedical materials

**Chemisorption and Reactivity on Supported Clusters and Thin Films:** R.M. Lambert, Gianfranco Pacchioni, 2013-04-17 Heterogeneous catalysis provides the backbone of the world s chemical and oil industries The innate complexity of practical catalytic systems suggests that useful progress should be achievable by investigating key aspects of catalysis by experimental studies on idealised model systems Thin films and supported clusters are two promising types of model system that can be used for this purpose since they mimic important aspects of the properties of practical dispersed catalysts Similarly appropriate theoretical studies of chemisorption and surface reaction clusters or extended slab systems can provide valuable information on the factors that underlie bonding and catalytic activity This volume describes such experimental and theoretical approaches to the surface chemistry and catalytic behaviour of metals metal oxides and metal metal oxide systems An introduction to the principles and main themes of heterogeneous catalysis is followed by detailed accounts of the application of modern experimental and theoretical techniques to fundamental problems The application of advanced experimental methods is complemented by a full description of theoretical procedures including Hartree Fock density functional and similar techniques The relative merits of the various approaches are considered and directions for future progress are

indicated Supported Mono- and Bimetallic Complexes and Clusters Joseph David Kistler, 2014 Site isolated solid supported metal catalysts are important in industry and technology due to the cost efficiency to make and to recover and reuse them. These types of materials have catalytic properties similar to molecular complexes in solution while being easy to separate in heterogeneous catalytic reactions. The goal of this work was to synthesize supported metal complex catalysts while maintaining uniform catalytic sites. The syntheses were performed using precise glovebox and Schlenk techniques to achieve these highly uniform structures. These materials were then used to understand the relationship between structure of a catalytic site and the activity of the catalyst. This fundamental understanding of catalysts is important in advancing the field of catalysis. The structure of the catalysts were characterized using infrared IR, extended X-ray absorption fine structure EXAFS and X-ray absorption near edge structure XANES spectroscopies along with high angle annular dark field scanning transmission electron microscopy HAADF STEM with the HAADF STEM work carried out by colleagues in other research groups. The catalytic activity of the catalysts was examined with gas chromatography GC and mass spectrometry MS. The samples characterized in this work include complexes and clusters of second and third row transition metals supported on highly crystalline metal oxides. Specifically, there is a large focus in this work on supported rhodium complexes prepared from the organometallic precursor  $\text{Rh}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$  and a pre-calcined magnesium oxide  $\text{MgO}$ . This specific catalyst is important as not only is it active for olefin hydrogenation at mild temperatures but also there are reports of a unique surface mediated synthesis of uniform rhodium dimers which are ideal for catalytic comparison of structures with different nuclearities. Reactivities of the  $\text{MgO}$  supported rhodium complexes and dimers for carbon monoxide oxidation were investigated with the results showing the dimers were significantly more active for the reaction at 353 K. The stability of the dimers was tested in different reactive conditions with the results showing that under conditions with excess oxygen the dimers are less stable and less active than under conditions with excess carbon monoxide. A bimetallic catalyst was synthesized on  $\text{MgO}$  incorporating rhodium and osmium using  $\text{Rh}(\text{C}_2\text{H}_4)_2\text{acac}$  and  $\text{Os}_3\text{CO}_{12}$  as precursors. A unique synthesis method was developed to create a site isolated segregated bimetallic catalyst with the osmium and rhodium sites acting independently of each other for ethylene hydrogenation at 298 K. The metals remained structurally segregated and catalytically independent even following reduction in  $\text{H}_2$  at 393 K. Zeolites, another class of highly crystalline supports, were studied to gain information on the support effects in catalysts. The analogous rhodium complexes as were synthesized on the  $\text{MgO}$  were synthesized on zeolite HY. These catalysts were tested to determine structural and catalytic stability under hydrogen, a reducing gas, and  $\text{CO}$ , a catalyst poison, with the results showing that as compared to the complexes on zeolite HY,  $\text{MgO}$  supported rhodium complexes form more uniform stable clusters under  $\text{H}_2$  and develop unique catalytic properties, selectivity for partial hydrogenation of dienes when exposed to  $\text{CO}$ . Another zeolite, KLTL, was studied with supported platinum complexes synthesized from the salt precursor  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ . This catalyst was oxidized at 633 K to form



supported single atom platinum complexes Both the as prepared Pt NH<sub>3</sub> 4 and oxidized PtOx complexes were analyzed structurally and studied as catalysts for CO oxidation The oxidized platinum complexes proved to have significantly higher activity for CO oxidation at 423 K Furthermore HAADF STEM was used to directly identify the locations of the platinum atoms in the pores of the zeolite before and after oxidative treatment providing a method of ex situ tracking of supported metal atoms

**Comprehensive Coordination Chemistry II** J. A. McCleverty, T.J. Meyer, 2003-12-17 Comprehensive Coordination Chemistry II CCC II is the sequel to what has become a classic in the field Comprehensive Coordination Chemistry published in 1987 CCC II builds on the first and surveys new developments authoritatively in over 200 newly commissioned chapters with an emphasis on current trends in biology materials science and other areas of contemporary scientific interest

Encyclopedia of Catalysis István T. Horváth, 2003 Catalysis the speeding up of a chemical reaction by a substance which itself does not react is vital not only to the chemical process industry but also to life itself The six volume Encyclopedia of Catalysis is the definitive A to Z reference work covering the most significant aspects of homogenous heterogeneous asymmetric biomimetic and biological catalysis Available both on line and in print the state of the art Encyclopedia encompasses the principles of catalysis the scope of catalytic reactions the preparation characterization and use of catalysts including catalytic technology the modeling of catalytic processes and related reaction engineering techniques The logical organization of this seminal work renders the text easily accessible to both process personnel and those involved in basic and applied research and development For more information regarding the online edition please visit Wiley InterScience at [www.mrw.interscience.wiley.com/enccat](http://www.mrw.interscience.wiley.com/enccat)

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