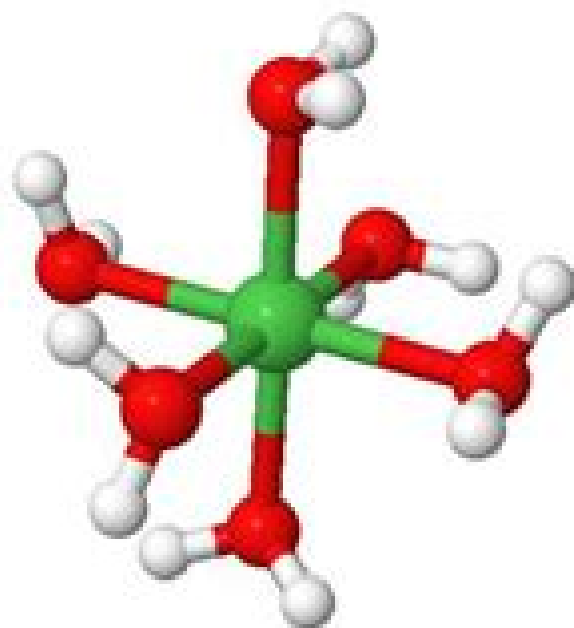
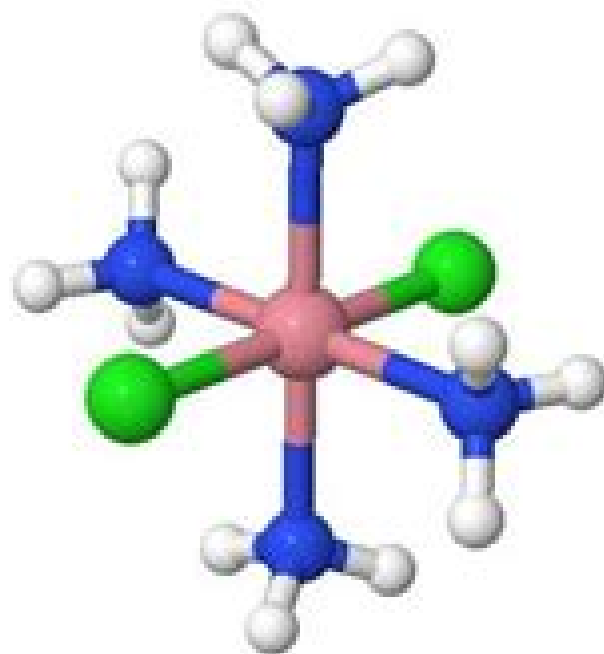


Examples of Metal Complexes



Six H₂O ligands bound
to a Ni²⁺ cation



Four NH₃ ligands and two Cl⁻
ligands bound to a Co³⁺ cation

<http://www.3dchem.com/3dinorgmolecule.asp?ID=490>

<http://www.3dchem.com/3dinorgmolecule.asp?ID=196>

Supported Metal Complexes

CH Cherryholmes



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.

Synthesis of Metal

not found in homogeneous catalysts Thus a new generation of catalysts was being developed *Synthesis of Metal Complexes Supported by Ferrocene-based Ligands for Tandem Catalysis and Applications Toward Liquid Cell Quantum Sensing* Yi Shen, 2023 Developing methodologies to synthesize high value products efficiently from simple substrates with control over the reactivity and selectivity is highly favored by the chemical industry Employing assisted tandem catalysis where serial reactions can be carried out in one pot to achieve streamlined complex syntheses significantly reduces the number of steps and waste Harnessing spatial and temporal control in catalysis enables approaches toward one pot transformations and allows the integration of several catalytic processes Ferrocene based ligand supported metal complexes represent a promising class of catalysts that can incorporate redox control over catalytic processes We have developed a redox controlled selective hydroamination reaction catalyzed by thiolfan Zr NEt₂ 2 thiolfan 1 1 bis 2 4 di tert butyl 6 thiophenoxy ferrocene In situ switching of the catalyst s state during the reaction enables selectivity toward different substrates Chapter 2 Incorporating the greenhouse gas CO₂ into N carboxyanhydrides NCAs followed by subsequent NCA utilization illustrates the possibility of integrating two synthetic steps in one vessel to afford a valuable material with possible CO₂ recycling To demonstrate the immense potential of integrating multi step transformations in one pot we developed a set of sustainable conditions for NCA synthesis Chapter 3 Moreover several metal catalysts supported by ferrocene based ligands were found to catalyze NCA polymerization in the presence of a co catalyst To establish an integrated system composed of two incompatible processes we aimed to compartmentalize the active reagents for each step The structure of the ferrocene based pro ligand was modified for surface anchoring Our efforts toward immobilizing ferrocene supported

metal catalysts onto conductive surfaces pave the way of achieving spatiotemporal control over the processes of NCA synthesis and polymerization Chapter 4 In addition to the redox switchable characteristic ferrocene based compounds provide a unique platform to support lanthanides and engender distinctive optical properties to them We synthesized and characterized a series of ytterbium complexes displaying an ultra narrow absorption in the ultraviolet visible UV Vis region The extraordinarily narrow linewidth observed for thiolfan YbCl THF thiolfan 1 1 bis 2 4 di tert butyl 6 thiomethylenephenoxy ferrocene allows us to investigate its applications toward magnetic field and liquid cell quantum sensing Chapter 5

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 Rh C₂H₄ 2 C₅H₇O₂ and a pre calcined magnesium oxide 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 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 MgO incorporating rhodium and osmium using Rh C₂H₄ 2 acac and Os₃ CO₁₂ 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 H₂ 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 MgO were synthesized on zeolite HY These catalysts were tested to determine structural and catalytic stability under hydrogen a reducing gas and CO a catalyst poison with the results showing that as compared to the complexes on zeolite HY MgO supported rhodium complexes form more uniform stable clusters under H₂ and develop unique catalytic properties selectivity for partial hydrogenation of dienes when exposed to CO Another zeolite KLTL was studied with supported platinum complexes synthesized from the salt precursor Pt NH₃ 4 NO₃ 2 This catalyst was oxidized at 633K to form supported single atom platinum complexes Both the as prepared Pt NH₃ 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 homogeneous 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/encat

Catalysis by Supported Complexes Y. I. Yermakov, B. N. Kuznetsov, V. A. Zakharov, 1981

Catalysis Joe W. Hightower, 1973

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 *Revue Roumaine de Chimie*, 2007

Metal-support Bonds in Supported Metal Catalysts, 1990 This research project now in its third year is an investigation of the synthesis structure and bonding of a family of metal complexes clusters and particles on the surfaces of high area metal oxide supports The focus is the structure of the metal support interface Surface species have been prepared by synthetic organometallic chemistry on the support surfaces The organometallic precursors are complexes of W Re Os Ir and Pt including W CO 6 HRe CO 5 Re₂ CO 10 H₃Re₃ CO 12 H₂O_s CO 4 Ir eta 3 C₃H₅ 3 and Pt eta 3 C₃H₅ 2 The supports are primarily MgO and gamma Al₂O₃ The surface species have been characterized by infrared and EXAFS spectroscopies among other techniques 7 refs 5 figs 4 tabs

Catalysis by Supported Complexes I. U. Ivanovich Ermakov, Boris Nikolaevich Kuznetsov, Vladimir A.

Zakharov, 1981 Adsorption of Transition Metal Complexes on Metal Oxide Supports Ahana Mukhopadhyay, 2018

Widespread industrial applications and large impact of supported late transition precious metal catalysts on the global economy serves as the prime motivation for the dedication of academic researchers towards focusing on the scalable and affordable design of efficient catalysts Catalyst design requires a fundamental understanding of how the different synthetic steps adsorption drying pretreatment etc influence the properties of the final catalyst Moreover in current times single atom catalysts represent an exciting new class of materials that have demonstrated high activity for chemical reactions relevant to energy production Among the various stages involved in catalyst synthesis the initial adsorption step between the support and the precursor is believed to be of most importance as this interaction influences the unit operations that follow and affects the final size distribution of the catalyst nanoparticles The ability of metal oxide supports to enhance the dispersion of the active metal on their surface and control their morphology and sintering kinetics is fundamentally related to the nature and strength of the metal support interaction which is determined at the time of adsorption at the solid liquid interface Documented studies on the importance of the adsorption step on the overall characteristics of the catalyst nanoparticle are limited in recent literature due to challenges associated with probing a buried solid liquid interface In this work we have examined the molecular level details of catalyst synthesis with substantial emphasis on the adsorption thermodynamics occurring at the solid liquid interface during the initial adsorption of transition metal complexes TMCs on metal oxide supports and its influence on nanoparticle size growth and stability Using a number of surface analytical tools we have probed at the interface during the adsorption process to quantify metal uptake and measure the kinetics and enthalpy of binding in order to identify the effect of different precursors and their ligand chemistry on the electrostatic driving force Isothermal Titration Calorimetry ITC is used to contact reducible and refractory supports like SiO₂ Al₂O₃ and CeO₂ with pH adjusted TMC solutions of Pt Pd Rh Ir and Ag at adjusted pH values providing a strong electrostatic driving force for adsorption and measure equilibrium binding constants stoichiometry and enthalpies of adsorption This study is unique in context that it truly

probes the interface during adsorption in situ of metal precursors on supports rather than as synthesized nanoparticles. The trends in the estimated thermodynamic parameters as a function of pH for both the cationic and anionic Pt complexes on silica and alumina respectively captures the effect of ligand speciation and complex solvation at acidic and basic solution conditions. Equilibrium adsorption isotherms from bench top bulk uptake studies aid in quantifying the amount of metal adsorbed on the support surface and by varying choice and weight loading of the precursors we are able to identify that chloride ligand speciation chemistry around main metal center and solvation strongly influenced metal uptake. Next we compared bulk and interfacial adsorption mechanisms through ex situ synthesis to determine how the particle size distribution and metal dispersion of the catalysts were influenced by the mode of adsorption. Thereafter we looked at cerium oxide which is an important support for transition metal catalysts due to its high oxygen storage capacity thus allowing it to successfully stabilize noble metals inhibit sintering and maintain small sized nanoparticles on its surface compared to other oxide supports. The thermodynamic adsorption parameters of a comprehensive list of late transition metal complexes in Group 9-11 on shape controlled faceted cerium oxide nano crystals demonstrated by ITC and DFT calculations showed a trend in the enthalpies of binding between support and metal precursors that correlates with the oxide formation tendency of the transition metal and the reducibility of the support. The ability of metals to form atomically dispersed metal nanoparticles on cerium oxide through formation of an M-O-Ce bond under strong oxidative conditions was examined using XPS and TEM. Several combinations of catalysts were synthesized using precursors having various ligand chemistries deposited on different facets of cerium oxide nano crystals and surface analytical tools were used to evaluate the optimal conditions for stable highly dispersed catalysts. From these design rules a series of ceria supported low weight loading single atom Pd catalysts were synthesized and examined for low temperature methane combustion that is highly in demand to reduce methane slip from lean burn natural gas vehicles. Here we probed into the effect of the transition from nano clusters to single atoms on the activity of the reaction. A possible mechanistic change in the Pd catalytic redox cycle is believed to enhance the catalytic turnover at low temperatures while maintaining reduced precious metal usage.

Index to Theses Accepted for Higher Degrees in the Universities of Great Britain and Ireland, 1968 **Theoretical Chemical Engineering Abstracts**

,1980 **Physics Briefs**, 1981-07 Chemical Abstracts, 2002 Late Transition-metal Complexes Supported by Pincer

Ligands Wilson D. Bailey, 2016. Late transition metal pincer complexes of primarily palladium II and platinum II have been investigated for their application as catalysts in partial oxidation reactions. The epoxidation of higher olefins using molecular oxygen as the oxidant has been targeted and the individual reaction steps needed to accomplish this overall transformation are described herein including 1) hydrogenolysis of a metal hydroxide M-OH species to yield a metal hydride M-H₂; 2) insertion of O₂ into the M-H bond to form a metal hydroperoxide M-OOH and 3) O atom transfer from the M-OOH to epoxides yielding a M-OH and completing the catalytic cycle. Previous results from our group on these individual transformations using tBuPCP

Pd and tBuPCO Pd fragments are also reviewed The requirements for O₂ insertion into PdII and PtII hydrides are discussed An array of cationic neutral and anionic Pd H and Pt H complexes supported by a tBuPNP backbone were synthesized and evaluated for O₂ insertion tBuPNP 2,6-bis(di-*t*-butylphosphinomethyl)pyridine Metal ligand cooperation was observed in the activation of H₂ to form neutral hydride complexes The effect of ligand protonation deprotonation on the trans influence experienced by the hydride ligand was investigated No reaction with O₂ was observed with the cationic hydrides while the neutral and anionic forms reacted with O₂ at the tBuPNP backbone The synthesis and characterization of mono and dinuclear Pd OH complexes supported by a PCNR pincer ligand PCNR 1,3-di-*tert*-butylphosphino methyl phenyl 1H-5-R pyrazole R = H, Me is presented When R = H ligand pyrazole rollover C-H activation was observed forming a mixed ligand PCNH Pd OH Pd PCC dinuclear structure This rollover was investigated using DFT computations The mono and dinuclear hydroxide species were evaluated for hydrogenolysis The dinuclear compounds PCNR Pd 2 OH OTf reacted under an H₂ atmosphere to yield the corresponding dinuclear hydrides PCNR Pd 2 H OTf A mechanistic study on the hydrogenolysis of the bridged hydroxide PCNMe Pd 2 OH OTf revealed first order kinetics in both Pd and H₂ Terminal hydrides were not detected and reduction of the mononuclear hydroxide complexes PCNR Pd OH to Pd⁰ was observed under H₂ The reduction was proposed to proceed through displacement of the pyrazole arm and was examined by DFT computations Lastly a new strategy to promote O atom transfer from M OOH to epoxides the final step in the targeted catalytic cycle is proposed Preliminary studies on NNNPyz NNNEt and NNMe ligated PdII and PtII are discussed NNNPyz 2,6-bis(5-*t*-butyl-1H-pyrazol-3-yl)pyridine NNNEt 2,5-*t*-butyl-1H-pyrazol-3-yl-6-diethylaminomethylpyridine NNMe 2,5-*t*-Bu-1H-pyrazol-3-yl-6-methylpyridine The NNNPyz ligand containing two acidic sites in proximity to the fourth site in the square plane was found to protonate M O₂ complexes chelate to the metal center and oxidize phosphine substrates Similar reactivity was observed with NNNEt and NNMe however hemilability of these ligands resulted in undesired coordination modes

Synthesis and Properties of Advanced Catalytic Materials Enrique Iglesia,1995 *Titles of Dissertations Approved for the Ph.D., M.Sc., M.Litt. Degrees* University of Cambridge Board of Graduate Studies,1978 **Indian Journal of Chemistry** ,2003

The Enigmatic Realm of **Supported Metal Complexes**: Unleashing the Language is Inner Magic

In a fast-paced digital era where connections and knowledge intertwine, the enigmatic realm of language reveals its inherent magic. Its capacity to stir emotions, ignite contemplation, and catalyze profound transformations is nothing lacking extraordinary. Within the captivating pages of **Supported Metal Complexes** a literary masterpiece penned by way of a renowned author, readers attempt a transformative journey, unlocking the secrets and untapped potential embedded within each word. In this evaluation, we shall explore the book is core themes, assess its distinct writing style, and delve into its lasting effect on the hearts and minds of people who partake in its reading experience.

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