Green Chemistry & Technology Letters
Vol 2, No 4, December 2016, pg. 206-210
eISSN: 2455-3611, DoI: 10.18510/gctl.2016.247

IRIDIUM CHEMISTRY AND ITS CATALYTIC APPLICATIONS: A BRIEF REVIEW

SANTOSH BAHADUR SINGH
Department of Chemistry, National Institute of Technology Raipur, Raipur-492010, Chhattisgarh (India)
Corresponding author email id: singhsbnitrr15@gmail.com

Article History: Received on 05th March 2016, Revised on 17th September 2016, Published on 10th December 2016

Abstract

Iridium is very important element among the all transition metals with highest reported oxidation state i.e. +9 in gas phase existing species IrO_4^+. Instead of its less reactivity, it forms number of compounds having oxidation states between -3 to +9. It is second known densest element after osmium. Till now its toxicity and environmental impact is not much more reported and thus it may be use as green element in various fields of its application. Reason behinds it's less toxicity and environmental impact may be due to its less reactivity and solubility. Corrosion and heat resistant properties of Iridium makes it much more useful element for alloying purpose. Iridium is the member of platinum family and used as catalyst due to its variable oxidation states. Iridium(III) complexes show great catalytic activity in both the acidic and basic medium for various organic as well as inorganic chemical transformations. Catalyst may be defined as the substance which can increases the rate of reaction of a specific chemical reaction without changing its own composition. Iridium is only one reported catalyst which is able to capture the sunlight and convert it into the chemical energy. Thus, it may be used in artificial photosynthesis process to solve our future food problem. Instead of these advantage, Iridium chemistry and its catalytic activity is not much reviewed till date, therefore, present review includes a brief introduction about chemistry and catalytic application of Iridium, which proof itself a boon for beginners to start their research career in the field of Iridium chemistry.

Keywords: Iridium, Oxidation State, Catalysis, Photosynthesis, Alloys, Environmental Impact.

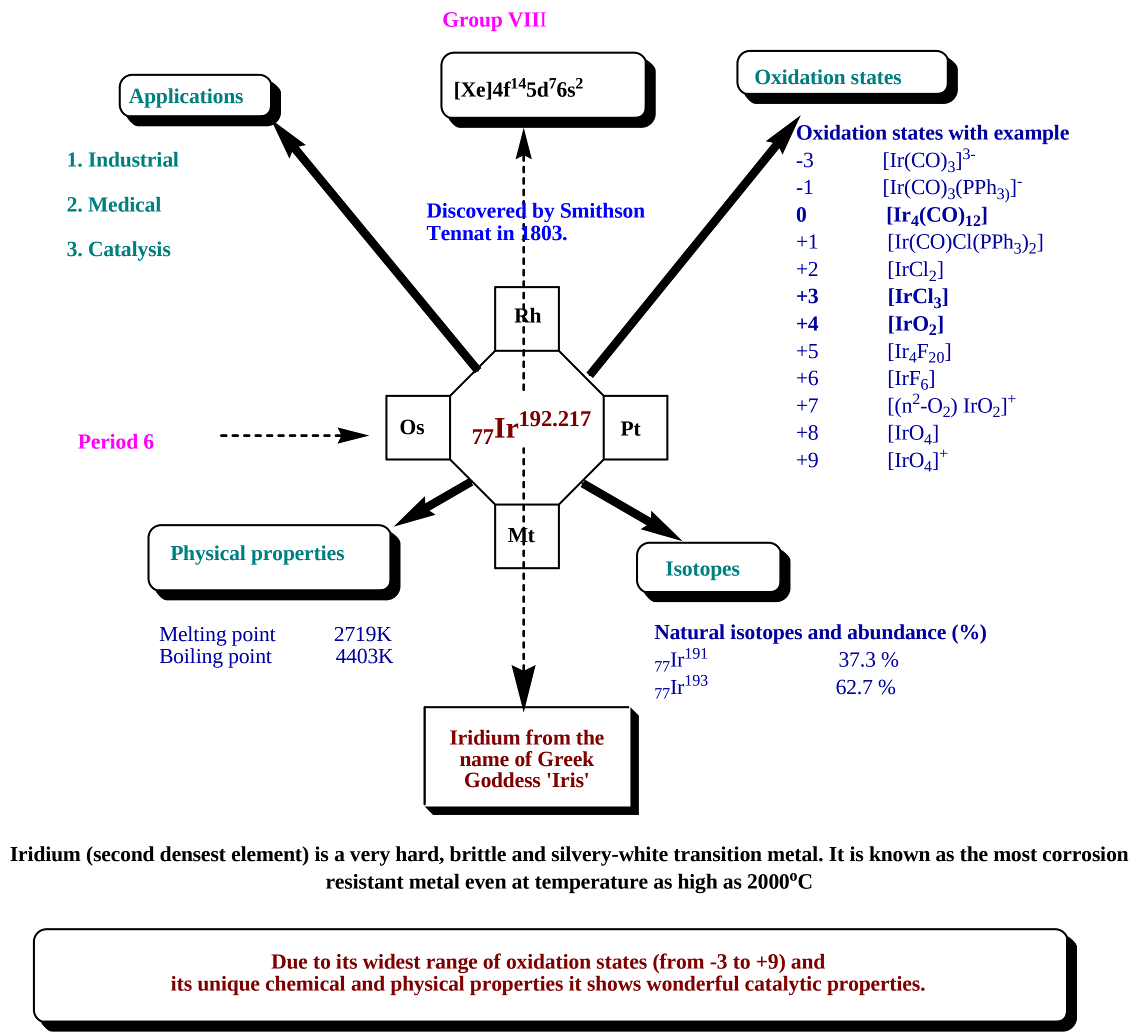
INTRODUCTION

Iridium (Ir) is one of most important rare element among nine rarest elements [i.e. Ruthenium (Ru), Rhodium (Rh), Palladium (Pd), Tellurium (Te), Rhenium (Re), Osmium (Os), Iridium (Ir), Platinum (Pt) and Gold (Au)] present in the Earth's crust. It usually occurs in nature as an uncombined element or in natural alloys, i.e. especially the osmium-iridium alloys, osmiridium (osmium rich) and iridosmium (iridium rich). Noble metals include the transition metals of Platinum family i.e. element of VIIIB groups namely Iron, Cobalt, Nickel, Ruthenium, Rhodium, Palladium, Osmium, Iridium and Platinum. Noble metals means less reactive elements, in fact, iridium is the most corrosion resistant metal known. Natural sources of Iridium are mainly found in Canada, South Africa, Russia and State of Alaska. Smithson Tennant (1761-1815) discovered the Iridium (in 1803), and named it Iridium (based on the name of Greek Goddess 'Iris', which symbol is a 'Rainbow'). Tennant choose this mainly due to various colours of Iridium compounds like Iridium potassium chloride (K_2IrCl_6) is dark red, Iridium tri-bromide ($IrBr_3$) is olive-green and Iridium tri-chloride ($IrCl_3$) is dark-green to blue-black [1]. Catalytic chemistry of Iridium started in 1960 by Lauri Vaska [2] [Vaska L (1968) Accounts Chem Res 1:335] with his studies on $IrCl(CO)(PPh_3)_2$ complex, later on it is known as "Vaska's complex. This was the first study that gives a major and different role to Iridium for Organometallic chemists to understand the oxidative addition, a fundamental step in homogeneous catalysis. Wang et al. (2014) reported an iridium containing compound (iridium tetraoxide cation; IrO_4^+) in gas phase [3]. This is highest experimentally known formal oxidation state of any chemical species till date. Present review mainly explores the basic chemistry of Iridium and its applications.

IRIDIUM CHEMISTRY

Iridium is one the most important element of the platinum group elements. It has an electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 5d^7 6s^2$. It has widest range of oxidation states i.e. -3 to +9 among the all transition metals. With this unique electronic configuration iridium shows various unique properties, that explores it broad area applications i.e. industrial, medical and catalysis [4,5,6,7]. Key process in photosynthesis is the photolysis of water means breaking of water molecules in hydrogen and oxygen [8,9]. Sheehan et al. (2015) reported the iridium as an effective molecular catalyst for water oxidation [10]. Thus, iridium becomes a most promising catalyst to solve food crisis (via catalyzing artificial photosynthesis) and energy problem (via production of hydrogen as alternating source of energy). A brief summary of iridium chemistry is shown below in diagrammatic scheme-1.

Green Chemistry & Technology Letters
Vol 2, No 4, December 2016, pg. 206-210
eISSN: 2455-3611, DoI: 10.18510/gctl.2016.247

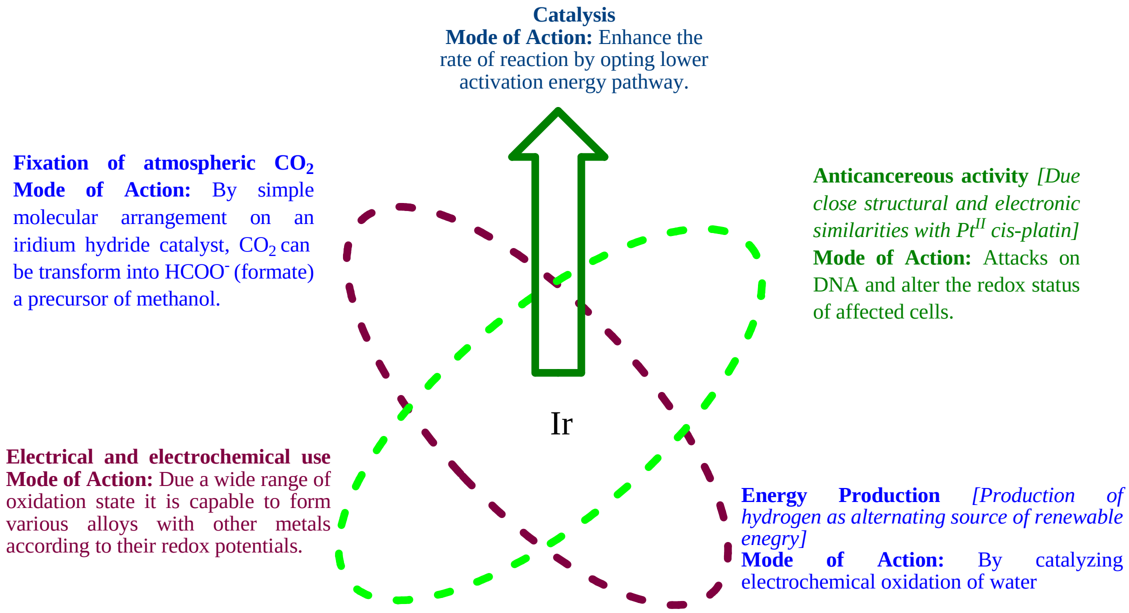


Scheme-1: A breif summary of Iridium Chemistry

APPLICATIONS OF IRIDIUM

Iridium and its complexes have wide range of application in various field of science. Catalysis is one most important application field of Iridium and its complexes i.e. catalyzed tritium labeling process for targeted drug design, catalyzed various organic reactions including hydrogenation, hydrogen-transfer reactions, functionalisation of C-H bonds, allylic substitution, 1,3-dipolar cycloadditions, catalyzed fine chemical synthesis, etc. Other applications of iridium and its complexes includes (i) used as anticancer agent, (ii) used in energy production, (iii) used in electrical and electrochemical processes and (iv) used for fixation of atmospheric carbon dioxide (CO_2) in useful products [5,6,10,11,12]. Scheme-2 includes brief information about various applications of iridium and iridium-based complexes.

Vol 2, No 4, December 2016, pg. 206-210
eISSN: 2455-3611, DoI: 10.18510/gctl.2016.247



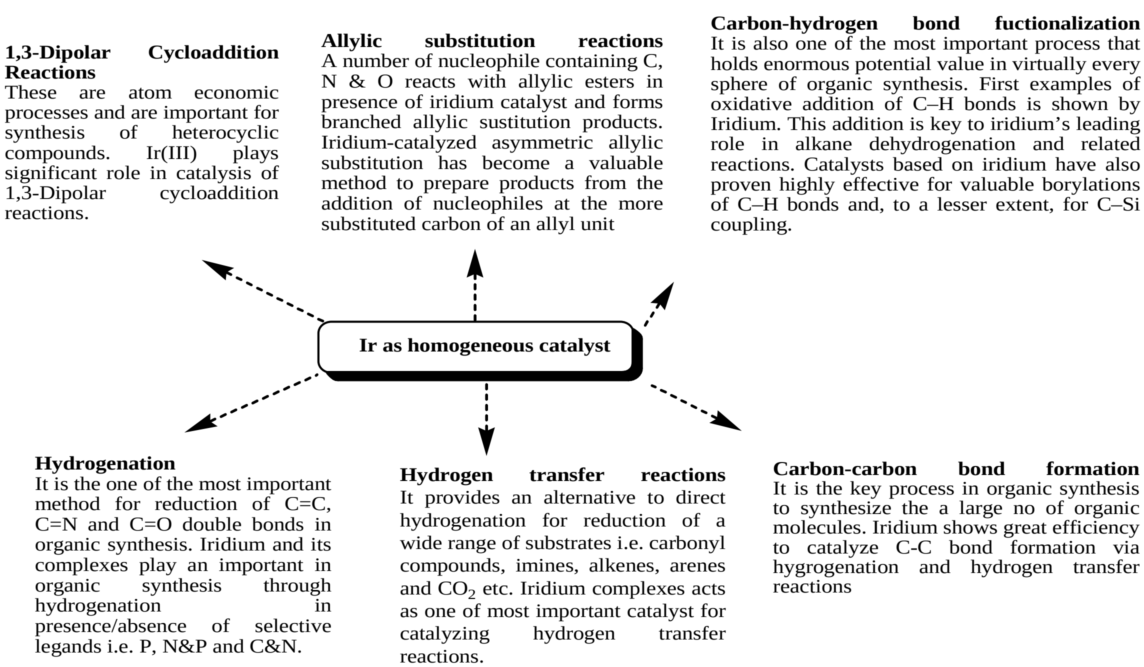
Scheme-2: Various applications of Iridium and its complexes

CATALYSIS BY IRIDIUM

Iridium has been reported as a versatile catalyst to catalyze various chemical reactions in both the acidic and basic medium [13,14]. Iridium and its complexes have been used as homogeneous catalyst, nano-catalyst and bio-catalyst.

Iridium as homogeneous catalyst

Iridium is a good homogeneous catalyst and has a wide range of applications [6,7] which is summarized in Scheme-3 given below:



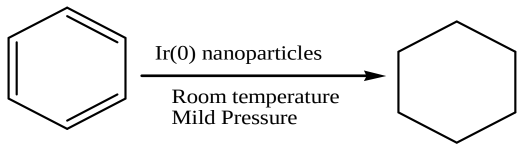
Scheme-3: Various fields of applications of Iridium as homogeneous catalyst

Green Chemistry & Technology Letters
Vol 2, No 4, December 2016, pg. 206-210
eISSN: 2455-3611, DoI: 10.18510/gctl.2016.247

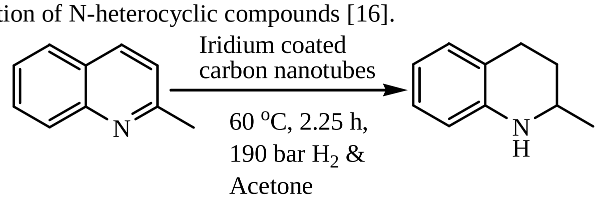
Iridium as nano-catalyst

Transition metal nanoparticles with controlled diameter, size, and shape show better efficiency of catalysis to catalyze various chemical reactions in comparison to bulk materials. Recent reporting on catalytic applications of iridium nanoparticles explores its important in the field of nanocatalysis [7].

Bayram et al. (2010) reported the complete hydrogenation of benzene at room temperature and mild pressure by using zero-valent iridium nanoparticles [15].



Rueping et al. (2011) reported the synthesis of stabilizer free iridium coated carbon nano-tubes (Ir@CNT) and their catalytic applications in hydrogenation of N-heterocyclic compounds [16].



Iridium as bio-catalyst

Catalytic activity of iridium and its complexes also makes them an attractive bio-catalyst which can catalyze some specific biological reactions [5,17,18]. Some of them illustrated below:

$$CH_2OHCH_2CH_2OH \xrightarrow[\text{Cp*Ir as hydride transfer catalyst}]{\text{Amination}} CH_2NH_2CH_2CH_2NH_2$$

1,3-Propanediol produced by *C.butyricum* grown on glycerol → 1,3-Propanediamine

$$NAD^+ \xrightarrow[\text{Ir}^{III}\text{ Cp* Complex}]{\text{Reduction with formate}} NADH$$

Environmental Impact of Iridium

There is no more reporting till date about any health benefits or risks associated with iridium and its complexes on human beings as well as on the environments.

CONCLUSION

Iridium and its complexes have a wide range catalytic activity to catalyze number of organic and inorganic transformations. It is most promising metal as bio-catalyst, catalyst for artificial photosynthesis and catalyst for water oxidation for hydrogen production in near future. Present review highlights the fundamentals of iridium chemistry and explores its applications in various dimensions and inspiring the further research to extend the iridium chemistry.

ACKNOWLEDGEMENT

I am very grateful to Professor Praveen Kumar Tandon, Department of Chemistry, University of Allahabad, Allahabad, who introduced me to chemical kinetics, catalysis and organic synthesis which I opted as my research fields. It was his valuable guidance and encouragement which inspired me and generated confidence in me right from the beginning of my research career to point at which I can write these lines. Further, I would like to express my sincere thanks to Professor (Mrs.) Fahmida Khan, Head, Department of Chemistry, National Institute of Technology Raipur, Raipur, for her moral support, inspiration and continuous blessing and providing departmental facilities.

Green Chemistry & Technology Letters
Vol 2, No 4, December 2016, pg. 206-210
eISSN: 2455-3611, DoI: 10.18510/gctl.2016.247

REFERENCES

1. Livingstone S. E., The chemistry of ruthenium, rhodium, palladium, osmium, iridium and platinum in comprehensive inorganic chemistry, 1975, Pergamon Press Ltd., Headington Hill Hall, Oxford, OX3 OBW, England
2. Vaska L., Reversible activation of covalent molecules by transition-metal complexes. The role of the covalent molecule, Accounts of Chemical Research 1(11), 1968, 335–344
3. Wang G.,Zhou M.,Goettel J.T.,Schrobilgen G.J.,Su J.,Li J., Schlöder T. and Riedel S., Identification of an iridium-containing compound with a formal oxidation state of IX, Nature 514, 2014, 475–477
4. Blaser H.-U., Application of iridium catalysts in the fine chemicals industry in Iridium Complexes in Organic Synthesis, Edited by Oro L.A. and Carmen Claver C., 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
5. Liu Z. and Sadler P.J., Organoiridium complexes: Anticancer agents and catalysts, Accounts of Chemical Research 47, 2014, 1174−1185
6. Andersson P.G., Iridium Catalysis in Topics in Organometallic Chemistry, 34, 2011, Springer Heidelberg Dordrecht London New York
7. Oro L.A. and Claver C., Iridium complexes in Organic Synthesis, 2009, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
8. Graetzel M., Artificial photosynthesis: water cleavage into hydrogen and oxygen by visible light, Accounts of Chemical Research 14(12), 1981, 376–384
9. Rüttinger W. and Dismukes G.C., Synthetic water-oxidation catalysts for artificial photosynthetic water oxidation, Chemical Reviews 97(1), 997, 1–24
10. Sheehan S.W., Thomsen J.M., Hintermair U., Crabtree R.H., Brudvig G.W. and Schmuttenmaer C.A., A molecular catalyst for water oxidation that binds to metal oxide surfaces, Nature Communications 2015, 6:6469, doi: 10.1038/ncomms7469
11. Garg K., Matsubara Y., Ertem M.Z., Andralojc A.L., Sato S., Szalda D.J., Muckerman J.T. and Fujita E., Striking differences in properties of geometric isomers of [Ir(tpy)(ppy)H] experimental and computational studies of their hydricities, interaction with CO2, and photochemistry, Angewandte Chemie International Edition, 54(47), 2015,14128-14132
12. D M., Glezakou V.A., Lebarbier V., Kovarik L., Wan H., Albrecht K.O., Gerber M., Rousseau R. and RA Dagle R.A., Highly active and stable MgAl2O4 supported Rh and Ir catalysts for methane steam reforming: A combined experimental and theoretical study, Journal of Catalysis 316, 2014, 11-23
13. Tandon P.K., Mehrotra A., Srivastava M. and Santosh B. Singh S.B., Iridium(III) catalyzed oxidation of iodide ions in aqueous acidic medium, Transition Metal Chemistry 32, 2007, 541-547
14. Tandon P.K. and Singh S.B., Hexacyanoferrate(III) oxidation of arsenic and its subsequent removal from the spent reaction mixture, Journal of Hazardous Materials 185, 2011, 930–937
15. Bayram E., Zahmakıran M., Ozkar S. and Richard G. Finke R.G., In situ formed “Weakly Ligated/Labile Ligand” iridium(0) nanoparticles and aggregates as catalysts for the complete hydrogenation of neat benzene at room temperature and mild pressures, Langmuir, 26(14), 2010, 12455–12464
16. Rueping M., Koenigs R.M., Borrmann R., Zoller J., Weirich T.E. and Mayer J., Size-selective, stabilizer-free, hydrogenolytic synthesis of iridium nanoparticles supported on carbon nanotubes, Chemistry of Materials 23, 2011, 2008–2010
17. Liu S., Rebros M., Stephens G. and Marr A.C., Adding value to renewables: A one pot process combining microbial cells and hydrogen transfer catalysis to utilise waste glycerol from biodiesel production, Chemical Communications 2009, 2308−2310
18. Canivet J., Süss-Fink G. and Štěpnička P., Water-soluble phenanthroline complexes of rhodium, iridium and ruthenium for the regeneration of NADH in the enzymatic reduction of ketones. European Journal of Inorganic Chemistry 2007, 4736−474

BIOGRAPHY:

Dr. Santosh Bahadur Singh received his D.Phil. Degree in 2010 at University of Allahabad, Allahabad, under the supervision of Professor Praveen K. Tandon. Subsequently he was a Research Associate of CSIR, New Delhi at University of Allahabad, Allahabad. From July 2015 to till date he is working as Faculty (Temp.) in Department of Chemistry, National Institute of Technology, Raipur (C.G.). He is a life member of Materials research society of India. His research interests are centered on the chemistry of surface in adsorption, nano-catalysis, chemical kinetics, water remediation and oxidative transformation of organic compounds.