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: singhsnittr15@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$_4^{2-}$. 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$_3$IrCl$_6$) 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 tetroxide cation; IrO$_4^{2+}$) 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$^2$s$^2$p$^5$s$^2$p$^3$d$^{10}$s$^2$4p$^4$4d$^{10}$5s$^2$5p$^5$5d$^5$6s$^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-I.
Group VIII

[0]4f^{14}5d^{6}s^{2}

Oxidation states

Oxidation states with example
-3 [Ir(CO)]^{3-}
-1 [Ir(CO)_{2}(PPh_{3})]^{-}
0 [Ir(CO)_{3}]^{2-}
+1 [Ir(CO)Cl(PPh_{3})_{2}]
+2 [IrCl_{4}]
+3 [IrCl_{5}]
+4 [IrO_{2}]
+5 [IrO_{3}]
+6 [IrO_{4}]
+7 [(n^{2}O_{2})IrO_{2}]^{+}
+8 [IrO_{3}]
+9 [IrO_{4}]^{+}

Discovered by Smithson Tennat in 1803.

Rh

Os 77Ir^{192,217}

Pt

Sn

1. Industrial
2. Medical
3. Catalysis

Period 6

Physical properties
Melting point 2719K
Boiling point 4403K

Isotopes
Natural isotopes and abundance (%)
77Ir^{191} 37.3 %
77Ir^{193} 62.7 %

Iridium (second densest element) is a very hard, brittle and silvery-white transition metal. It is known as the most corrosion resistant metal even at temperature as high as 2000°C

Due to its widest range of oxidation states (from -3 to +9) and its unique chemical and physical properties it shows wonderful catalytic properties.

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

- **Catalysis**
  - **Mode of Action:** Enhance the rate of reaction by opting lower activation energy pathway.

- **Fixation of atmospheric CO₂**
  - **Mode of Action:** By simple molecular arrangement on an iridium hydride catalyst, CO₂ can be transformed into HCOO (formate) a precursor of methanol.

- **Electrical and electrochemical use**
  - **Mode of Action:** Due to a wide range of oxidation state it is capable to form various alloys with other metals according to their redox potentials.

- **Anticancerous activity**
  - **Mode of Action:** [Due close structural and electronic similarities with Pt⁶⁺ cis-platin]

- **Energy Production**
  - **Mode of Action:** [Production of hydrogen as alternating source of renewable energy]

- **Scheme-2: Various applications of Iridium and its complexes**

**CATALYSIS BY IRIDIJUM**
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:

- **1,3-Dipolar Cycloaddition Reactions**
  - These are atom economic processes and are important for synthesis of heterocyclic compounds. Ir(III) plays a significant role in catalysis of 1,3-Dipolar cycloaddition reactions.

- **Allylic substitution reactions**
  - A number of nucleophile containing C, N & O reacts with allylic esters in the presence of iridium catalyst and forms branched allylic substitution products. Iridium-catalyzed asymmetric allylic substitution has become a valuable method to prepare products from the addition of nucleophiles at the more substituted carbon of an allyl unit.

- **Carbon-hydrogen bond functionalization**
  - It is also one of the most important process that holds enormous potential value in virtually every sphere of organic synthesis. First examples of oxidative addition of C–H bonds is shown by Iridium. This addition is key to iridium’s leading role in alkane dehydrogenation and related reactions. Catalysts based on iridium have also proven highly effective for valuable borylations of C–H bonds and, to a lesser extent, for C–Si coupling.

- **Hydrogenation**
  - It is the one of the most important method for reduction of C=C, C=N and C=O double bonds in organic synthesis. Iridium and its complexes play an important in organic synthesis through hydrogenation in presence/absence of selective ligands i.e. P, N&P and C&C.

- **Hydrogen transfer reactions**
  - It provides an alternative to direct hydrogenation for reduction of a wide range of substrates i.e. carbonyl compounds, imines, alkenes, arenes and CO₂ etc. Iridium complexes acts as one of most important catalyst for catalyzing hydrogen transfer reactions.

- **Carbon-carbon bond formation**
  - It is the key process in organic synthesis to synthesize the a large no of organic molecules. Iridium shows great efficiency to catalyze C-C bond formation via hydrogenation and hydrogen transfer reactions.

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

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.
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
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

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.