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Review

Advancement in Polyaza Macrocyclic Complexes as Catalysts in CO₂ and O₂ Reduction For Renewable Energy Sources: A Review

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Abstract- In the past two decades, quest of finding sustainable and environment friendly energy sources has increased enormously. Fuel cell technology has seen exciting growth for the solution of requirement of sustainable energy. Fuel cells are based on electrochemical reactions to change chemical energy into electrical energy. For this, reduction of CO₂ and O₂ are two of the important reactions. Despite quite stable nature of CO₂, its reduction can be achieved effectively in presence of catalyst. Both the CO₂RR and ORR reactions yield useful byproducts like water, formic acid, formaldehyde, methanol etc. Earlier Pt based catalysts were in use for these conversions in fuel cells. In the recent years, polyaza macrocycle-based catalysts are being applied as these being cost effective. For both above-described purposes, polyazamacrocyclic complexes, like metalloporphyrin, phthalocyanine, have been proved to be very effective. This article is focused mainly on recent advancement in Tetra, Penta and Hexaazamacrocyclic complexes for CO₂ RR and ORR reactions.

Keywords- Fuel cell; Porphyrin; Polyazamacrocyclic complexes; Cyclic voltammetry; Photoreduction

1. INTRODUCTION

Coordination compounds with macrocyclic ligands have drawn a lot of interest because of their wild applications. Mimicking of naturally occurring macrocycles like porphyrin, corrin, cytochrome etc. have earned a lot of interest for a long time [1-3]. Macrocyclic ligands offer

unique features that's why interest in this field is growing all the time. We are living in a society where energy resources are matter of great concern. The natural resources of energy production are of traditional ways but we all are aware that these may end one day and while using these sources, environmental pollution is also a big problem [4]. For these reasons, scientists are continuously searching for alternative ways. In order to produce energy, one of the impressive options is fuel cells where energy is produced by reaction between a fuel (hydrogen, methane, carbon monoxide etc.) and an oxidizing agent like oxygen but the main problem in fuel cells is that Oxygen reduction reaction (ORR) at cathode is very slow to respond. Pt is well known efficient catalyst for speeding up the rection but it is very costly and available in less amount so, researchers have always been interested to prepare easily available and cheaper catalyst [5-7]. Among different type of macrocycles, transition metal based polyazamacrocyclic catalysts have been proved to be very efficient for ORR catalysis, therefore this is a continuously growing research field. After pyrolysis, porphyrin-based macrocycles have been investigated for use as catalyst and found to be very effective due to enhancement of surface area. The voltammetric study of polyazamacrocyclic complexes supports the effectiveness of these complexes. Also, the transition metal-based nanoparticles have been proved to be effective, as their electrochemical study showed [8-12]. Scientists have been particularly interested in polyaza macrocycles such as cyclam (Figure 1). Curtis created cycalm for the first time by combining ethylenediamine and acetone in the presence of Ni (II) or Cu(II). These macrocycles are called Curtis macrocycles. In radio immunotherapy, Cyclam and its derivatives with metal ion molecules are used as metal ion binding sites. The characteristics of cyclam derivatives are affected by substituting the ring, particularly nitrogen substitution. Metals have a square planer shape, which means they have more binding sites for redox processes. Cyclic voltammetric study of tetraazamacrocyclic complexes of Ni, Fe Co etc. reveals that these complexes have strong binding property with calf thymus DNA. Macrocyclic complex features are the result of an uncommon geometrical relationship [13-20].



Figure 1. Cyclam frame work

The rising level of CO_2 in the atmosphere contributed a lot into global warming and hence there is a lot of interest among scientists in recent years. Along with the ORR, the polyazamacrocycles have also been used for the reduction of CO_2 . CO_2 is reduced by single or multi electron pathways and converted into useful products like methanol, methane etc. This reduction of CO₂ is important in both ways as, reduction of CO₂ concentration and formation of fuel, both goals are achieved [21-24]. The methods for the reduction may be photocatalytic, electrochemical, catalytic hydrogenation etc. [25-27]. The use of sunlight to reduce CO₂ using H₂O is an innovative solution to address today's mounting environmental challenges. Fisher and Eisenberg were the first to show that various Co(III) and Ni(II) tetraazamacrocycle complexes (Figure 2) may reduce CO₂ to CO in CH₃CN/H₂O (v/v = 1/2) or H₂O alone [28]. Grant et al. have developed a homogeneous aqueous system for CO₂ photoreduction that uses Ni (II) and Co(II) Cyclam as the reduction catalyst. Nickel and cobalt transition metal complexes had been investigated as homogeneous and adsorbed heterogeneous catalysts for carbon dioxide electroreduction [29].



Figure 2. (a) Ni⁺²(cyclam) and (b) Co⁺²(substituted cyclam) complexes for homogenous catalysis of $CO_2 RR$

So, keeping the importance of these reduction reactions in potential field for renewable energy sources, this review has been taken into account for investigation of useful polyazamacrocyclic complexes as catalyst for affecting these reactions.

2. CATALYSIS OF CO₂ REDUCTION

Though CO₂ is a very stable molecule as expected from its bonding (C=O), however it can be reduced into various products. Electrochemical reduction in presence of a catalyst has been shown by various researchers which involve many pathways through 2-12 electron transfer or even more resulting in reduction of CO₂ into CO, HCHO, HCOOH, CH₄ and other hydrocarbon. This reduction is affected by nature of catalyst as well as experimental conditions. The conversion of carbon dioxide molecule to form different hydrocarbons is depicted in Figure 3.



Figure 3. Different pathways of reduction of CO₂

The carbon dioxide reduction catalysis has been reported by three major methods are discussed below:

2.1. Photochemical reduction

A well-known natural photoreduction of CO₂ into carbohydrates, known as 'Photosynthesis', occurs in all green plants. This significant process provides feeding to animals and human beings. It involves the direct use of sunlight to reduce CO₂ into other useful products (Figure 4). The process initiated by absorption of light energy by some pigment molecules, also referred as antenna pigments. This energy is then transferred to different molecules with simultaneous reduction of CO₂ into carbohydrate molecules [30-31]. Significance of the process has attracted the scientists all over the world to develop artificial ways to trap light energy for reduction of CO₂.

The concept is based on the efficient use of solar radiation to power an integrated photo redox cycle in which H₂O oxidation is combined with CO₂ reduction. The goal to reduce CO₂ emissions by photo reduction producing fuel like hydrocarbons as HCOOH, CO, CH₄, CH₃OH, syn gas mixtures (H₂/CO) [32-36].

In principle, two ways of artificial light harvesting have been developed:

(i) By Direct photocatalysis (by semiconductor) dispersed in aqueous solution. For direct photocatalysis, many advantages of TiO₂ based catalysts have been discovered, including the ability to function at low temperatures, low cost, and so on but their energy band gap is relatively higher. These were employed as pure and as silver based TiO₂ semiconductor. Polyazamacrocyclic complex of Ruthenium and Bipyridine [Ru (bpy) (CO)H]⁺ was studied as catalyst and photosensitizer. The TON frequency was recorded 125 h⁻. Ru and other 4d series metals with pyridine type ligands have been the choice for reduction of CO₂ due to their catalytic activities [37-41].



Figure 4. Diagrammatic representation of photoreduction of CO₂

(ii) Photovoltaic cells or solar cells are another and very efficient way for CO₂ reduction. Interest in this method is continuously increasing since last decade. Silicon based single or multi-junction cells are commonly used due to their cheap cost and reliability. But the multi-junction gallium-based cells have proved to be more efficient with higher power conversion efficiencies which is a numerical value of the ratio of incident photon energy and electrical energy. Photovoltaic cell is recently reported with gas diffusion electrode having 19.1% power conversion efficiencies for CO₂ reduction. Photovoltaic plus photo electrochemical (PV-PEC) combination were also used for better performance [42].

The main problem in the reduction of CO₂ is its poor activity. However, to prepare an efficient photocatalyst band plays important role. The photocatalyst should be thermally and chemically stable. It's worth noting that the semiconductors' shape, thickness, and exposed surface area are all elements that can alter light absorption by exposing active sites and so improve photocatalytic activity. The development of materials for increasing the efficiency of photovoltaic cells is also a field of interest [43-44].



Figure 5. Co(Cyclam)

Use of polyazamacrocyclic complexes as photocatalyst for CO₂ reduction is a promising field. Coordination complexes of Ru and Re for the purpose were synthesized and studied these

complexes were found to have sufficient selectivity for conversion of CO₂ into formic acid [45-46].

 $[Co(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetra-deca-4,11-diene)Cl_2]Cl$ (Figure 5) showed reactivity for the conversion of CO₂ to CO that is the similar activity shown by Co(cyclam). Many other poly azamacrocycles investigated and shown active for the purpose have been discussed in this review.

2.2. Electrochemical reduction

Another effective method is CO_2 reduction by electrochemical method. When CO_2 is reduced directly on an inert electrode, the very energetic CO_2 ⁻⁻ is produced. The standard potential of the pair CO_2/CO_2 ⁻⁻ in an aprotic solvent like DMF is certainly -1.97V against standard hydrogen electrode and 1.90V in the presence of water. In order to acquire the multiple products that can be derived from the electrochemical reduction of CO_2 at reduced energy expenditures, catalytic approaches were designed to avoid employing the CO_2 anion radical as an intermediate [47-49].

Oxalate, carbon monoxide and formate are created with a quantitative globally faradaic yield during electrolysis in DMF at the level of CO_2 reduction wave of cyclic voltammetry that is highly negative. Figure 6 depicts the chemical pathways that lead to these three molecules. They are the outcome of the CO_2 anion radical's homogeneous chemistry [50-54].



Figure 6. Routes of formation of different products in electrochemicalCO₂RR

The reduction of CO_2 by electrochemistry at the surface of several metal electrodes has been investigated. CO_2 reduction into methanol at the surface of copper oxide has a high yield, according to a study. Copper oxide is converted to metallic copper during the process [55].

Polyazamacrocyclic complexes have synthesized and investigated for CO₂ reduction via electrochemical routes. Although CO or Formate or both are commonly formed in this fashion, carbon dioxide electrochemical reduction catalysed by metal complexes has gotten a lot of attention in recent decades [56,57].

The reduction potential of CO_2^{-} is very negative. Polyazamacrocyclic complexes can act as electrocatalyst for the reduction. An investigation was made to check the ability of the complexes of the type shown in the Figure 7.



Figure 7. A type of Complex for CO₂ reduction into oxalate ion

The kinetic study of the complexes showed that complex catalyses the reduction of CO_2 into CO_2 ⁻ and then it dimerizes into oxalate ion.

2.3. Catalytic hydrogenation

Production of hydrocarbons from hydrogenation of CO₂ can be accomplished by different routes. The CO₂ hydrogenation method usually includes two parallel reactions: Reverse water–gas shift and methanol synthesis The hydrocarbons could be made directly from syngas (CO + H₂) using Fischer-Tropsch synthesis or indirectly using industrial methanol formation and then turning methanol to a number of different of hydrocarbons using the methanol-to-hydrocarbons process, which includes converting methanol to olefins, propene, and gasoline. Methanol and dimethyl ether have also been reported to produce aromatic or lower paraffin (LPG) hydrocarbons [58-60]. CO₂ as a substitute ingredient is thought to be an effective technique to use CO₂ in the methanol production process. In direct CO₂ hydrogenation, unlike methanol synthesis from syn gas, the generation of water vapour is unavoidable, which substantially slows the reaction and causes serious catalyst deactivation [61-63]. Figure 8 shows the different pathways for the production of hydrocarbons and methanol from hydrogenation of CO₂.



Figure 8. CO₂ reduction via catalytic hydrogenation

Many studies have been made for the production of novel and efficient catalyst for the catalytic hydrogenation of carbon dioxide into formate and also for the reversible reaction [64-68].

A lot of researchers have hydrogenated CO₂ at 200°C and 5.0 MPa in an organic solvent, an iridium complex containing a PNP pincer ligand displayed a massive turnover frequency of 150,000 h^{-1} and a notable turnover number of 3,500,000 [69].

Ruthenium complex coordinated by another pincer ligand showed the highest documented initial Turnover frequency was created at 120°C and 4.0 MPa of H₂/CO₂ (1,100,000 h⁻¹). However, several of these catalysts necessitate extreme temperatures, such as the addition of organic solvents and/ amine an amine. As a result, efforts were made to improve catalyst performance by utilising additives [70].

A complex of Iridium (shown in Figure 9) with cyclopentadienyl and 2,2'-bipyridine ligands and its hydroxy derivatives synthesized.



Figure 9. Iridium complexes with CP ligand a bipyridine

It was discovered that when the electron donating property of bipyridine grows, catalytic activity increases (from TOF 1h- to 650 h), and that when the hydroxyl ion is inserted at the fourth position, catalytic activity improves due to the strong electron donating nature of the group (Figure 9) [71].

It has been shown from the previous studies that polyazamacrocyclic complexes with transition metals can potentially be used as catalyst for catalytic hydrogenation of carbon dioxide.

2.4. CO₂ reduction reaction (CO₂ RR) by tetra azamacrocyclic complexes

Tetraazamacrocyclic complexes of transition metals had been investigated since very early as Fisher and Eisenberg investigated the electrochemical performance of cobalt(II) and nickel(II) macrocycles for CO₂ reduction in acetonitrile/water, giving CO and H₂. Sauvage and his colleagues investigated a Ni(II)-cyclam {cyclam ligand=1,4,8,11tetraazacyclotetradecane} complex and discovered good selectivity for CO₂ reduction at a mercury electrode when compared to H₂O reduction. The active catalyst was proposed to be an adsorbed [Ni (l) Li]⁺ species. The electro-reduction of CO₂ has also been demonstrated to be catalyzed by porphyrins and phthalocyanines. The nickel and cobalt macrocycles have also been utilized as catalysts in photo-assisted electro-reduction of CO₂ on semiconductor electrodes at significantly lower negative potentials [28,72-78]. The complex [Co (2,12dimethyl-3,7,11,17-tetraazabicyclo-[11.3.1]-heptadeca 1(17),2,11,13,15-pentaene)]⁺² reduce the CO₂ molecule. This complex was checked with two different visible-light sensitizers [Ru(2,2-bipyridine)₃] and [Ir(phenyl pyridine)₃]. The IR band for reduced state of the complex with Ru-photosensitizer obtained at 1670 cm⁻¹ attributed to COO⁻ ion [78]. Another tetradentate ligand containing N₂S₂ type moiety with Ni(II) also investigated with Ruphotosensitizer providing very high selectivity of CO (more than 99%) [80].

A number of novel mono-, di-, and tetrafluorinated cyclams (Figure 10) had been developed. The tetrafluorinated complex showed greater selectivity and efficiency at lower potential than compared to non-fluorinated cyclam. As the amount of fluorine atoms rises, the CO production drops [80]. N-Methyl substituted derivatives of cyclam were investigated for catalytic abilities and it was found that increasing the substitution the catalytic ability decreases. The tetra-methylated derivative's strong adsorption of the Ni⁺²compound made reduction to the catalytically active Ni(I) form challenging. When the Tetraazamacrocyclic ligand is entirely replaced by a methyl group, there is no CO₂ catalytic reduction [82].



Figure 10. (a) mono-fluoro (b) di-fluoro and (c), (d) tetra-fluoroderivatives of cyclam

A novel bifunctional super molecule (Figure 11e) was formed and catalytic properties were checked along with redox characteristics. Despite the supermolecule's reductive photocleavage, catalytic tests reveal that twice as much CO is created when compared to a multimolecular system containing $Ru[(bipyridiene)_3]^{+2}$, $Ni^{(II)}$ -cyclam and pyridinium salt. Other compounds of nickel substituted cyclam derivatives were also studied and found better CO₂ reduction ability than underivatized (Figure 11a,b,c,d) [83].



Figure 11. Ni substituted derivatives and Ru complex with Ni -cyclam for photo reduction of CO₂

The above discussion shows that tetraazamacrocyclic complexes have much potential to be used for reduction of CO₂. There is still work to do for better catalytic performance and new tetraazamacrocyclic can be formed for the same.

2.5. CO₂ RR by Pentaaza Macrocyclics complexes

Macrocyclic complexes containing 5 nitrogen atoms are also formed and studied for the purpose. Under argon and CO₂, cyclic voltammetry was utilized to describe 2 sets of binuclear macrocyclic Ni⁺² compound with varying chain lengths connecting the two macrocyclic rings.



Figure 12. Binuclear complexes of nickel with different bridging units

The first set included $[Ni_2 L^{2-6}]^{4+}$ binuclear complexes comprising macrocycles having 5 nitrogen with either p-xylyl linkage (L⁶) or (CH₂)_n bridges (n=2, 3, 4, 6). When the

electrochemical study was done in methyl cyanide/10% H₂O, it was found that the value E_p^c value of CO₂ reduction is near to -1.7V and catalytic currents was found to be half of the value found for mononuclear complex. The result can be explained on the basis of steric interaction of only one metal centre on the surface due to steric strain. As the length of bridging chain increases, the catalytic currents also increase marginally because the stereochemical restrictions were loosened a little (Figure 12 & 13) [84].



Figure 13. Ni complex with different bridging

2.6. CO₂ RR by hexaazamcrocyclic complexes

Hexaazamacrocyclic complexes are still waiting to be studied at large scale. Azamacrocycles, generated from bipyridine condensation have received little attention (Figure 14). The scarcity of knowledge on this topic appears to be linked to the low yield of these ligands when synthesized [85-87].

It's becoming more usual to use aza-macrocyclic compounds in the activation of smaller molecules like carbon dioxide. Complexes containing Zn, Ni, and bis-bipyridine hexa-aza-macrocycles easily co-ordinate as tetradentate complexes. Because in carbon dioxide, the free ligand has a low-intensity redox activity and metal center has the key role for the reduction of CO_2 by Ni⁺² compound [88].

Hexaazamacrocyclic complexes of Cu(II) and Ni(II) produced from 1,10-phenanthroline and study revealed that Cu(I) and Ni(I), both get stabilized at -0.80 and -0.85 respectively. It means that their reduction involves 1 e⁻ transfer which can reduce the CO₂ into CO₂⁻⁻[89].



Figure 14. Different hexaazamacrocyclic framework for CO₂ catalysis

The Lewis acidity of metal atom should be low to prevent the interaction of CO_2^{-} anion radical. This can be done by varying the groups attached in metal complexes.

3. CATALYSIS IN FUEL CELLS: OXYGEN REDUCTION REACTION (ORR)

ORR is based on naturally occurring phenomenon like porphyrin ring in haemoglobin capture the oxygen molecule at sixth position. So, efforts were made to mimic the porphyrin, phthalocyanines molecules etc. Transition metal based polyazamacrocyclic complexes were synthesized for the ORR and still studies are going on for better catalytic activity.

The complete electrochemical Oxygen Reduction Reaction is thought to include following net coupled proton and electron transfers (CPETs) to dioxygen at the cathode, however, the electroreduction of O₂ can take place in a variety of ways, including the following (Figure 15):

- 1. A reduction via four electrons to H_2O/OH .
- 2. A two-electron reduction to H_2O_2 .
- 3. Another pathway consisting a series of two- and four-electron reduction.
- 4. A parallel pathway involving 1–3 step

Other mechanisms, with the ones described above, may be used. Transition metal catalysts have been proven to decrease two electrons in less active metals like Au and Hg. Platinum, the most active catalyst, is expected to go through a four-electron reduction reaction. Many investigations were dedicated to discovering the rate determining step (RDS) and decoding the chain of electron and proton movements based on the above-mentioned possible approaches. Three steps impede the kinetics of this reaction in metal catalysts: (a) first electron transfer; (b) oxygen hydration; and (c) intermediate desorption.



Figure 15. Working of a fuel cell

Many studies have looked at the kinetics and determined the electron transfer step occurred initially should be the rate determining step [90-93].

Proton Exchange Membrane Fuel cells (PEMFCs) and Direct Methanol Fuel Cells (DMFCs) have been actively developed for application in cars, portable electronics and combined heat and power systems because these are simple, do not need higher temperature, start quickly and contain high power density [94].

3.1. ORR activity by Transition Metal Based Macrocyclic Complexes

Researchers found a succession of metal phthalocyanine macrocycles with diminishing catalytic activity toward the ORR in 1980s, in the order Fe > Co > Ni > Cu > Mn. Metal macrocyclic compounds with Fe or Co as the central atom have the highest catalytic activity for the ORR when compared to other non-precious metals. The catalytic activity of metals and ligands is determined by their interaction [95-96]. Transition metal macrocycles which were pyrolyzed and carbons based have a strong initial activity for oxygen reduction. However, capacity deterioration is still an issue with these catalysts. Electron spectroscopy for chemical analysis, electron energy loss spectroscopy and Mossbauer studies of cobalt-based macrocycles treated at high temperatures showed that link between metal and nitrogen was lost [97]. Along with the pyrolysis product, cobalt oxide is found [98-99].

In experimental and theoretical research, the action of manganese-based complexes in the ORR has already been documented, with Manganese bases phthalocyanine complexes having a stronger interaction with O₂ than iron based phthalocyanine and Cobalt based phthalocyanine complexes [100-102].

It depends on metal that how many numbers of electrons will get involved in the reduction of an oxygen molecule by phthalocyanine (Figure 16). For example, Co, Ni and Cu follow 2 electrons and generation of hydrogen peroxide occurs, on either hand the metals Mn and Fe reduce oxygen molecules via four electron pathways with the synthesis of H_2O_2 [103-105].



Figure 16. Metallphthallocyanine

3.2. ORR By Polyaazamacrocyclic ligands

Since 1964, when Jasinski discovered Cobalt phthalocyanines active for this purpose, the MN₄ macrocycles have been studied for ORR as an alternative for Pt electrocatalyst [106-109].

The density functional technique was used to measure the catalytic activity of many types of Mn-based Tetraazamacrocyclic complexes. The studied ligands (Figure 17) the most active was manganese-2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene, manganese-octamethyl porphyrin [110].

The coupling of 5,10,15,20-tetrakis (N-methylpyridinium-4-yl) porphyrinato cobalt with [NbMoO₆] nanosheets through a direct self-assembling approach, occurred to form a sandwich-like CoTMPyP/[NbMoO₆] NSs close-packed material. The electrode modified by CoTMPyP/[NbMoO₆] Nanosheets exhibited remarkable electrocatalytic property for oxygen reduction which was proved by the reduction peak voltage shifted from 0.681 to 0.235 V and reduction of oxygen into hydrogen peroxide occurred via a two-electron pathway [111].

The [Co^{II}(TAA)] complex (fig. 18) is more active than cobalt phthalocyanine complexes in the reduction of molecular oxygen (O₂), increasing the reduction of O₂ to H₂O₂ at 400 mV higher potentials. Fe⁺² and Ni⁺² polyazamacrocycles were synthesized and their cyclic voltammetric study revealed that metal had unusual oxidation state. Such compounds may contribute towards the ORR reduction [112-114].



Figure 17. Mn based tetraazamacrocycles

Substituted with hexamethyl for instance, macrocycles of tetraazaannulene (HMTAA). The electrocatalysts for ORR were hexamethyltetraazaannulene-14 (HMTAA-14) and hexamethyltetraazaannulene-16 (HMTAA-16) (Figure 18). According to the research, HMTAA-16 is a better catalyst. The increased catalytic activity is due to the increased macrocyclic ring conjugation as well as aromaticity. Catalytic activity is also influenced by the substituent on the macrocyclic framework [115].



Figure 18. Co-hexamethytetraazaanulene-14 and 16

4. CONCLUSIONS

The developments based on porphyrin and other naturally occurring important macrocycles have been proved to be very potent for catalysing the ORR and CO₂ RR reactions. Tetraaza, Pentaaza and Hexaazamacrocyclic macrocyclic complexes of transition metals have extreme potential to catalyse these reactions. Nickel, cobalt and iron like transition metals due to their different oxidation states, increase the properties of these complexes. Copper and zinc are also proved to be efficient and should be considered for more studies as these are involved in many enzymes responsible for catalysing biological processes. Better ring conjugation and aromaticity are other factors which are responsible

for increased catalytic properties. In future, the multimetallic polyazamacrocycles may also contribute for this, though difficulties in synthesis of complexes having more than one metal centre seek more involvement. Recently adequate amount of research has been done in the field of catalysis still there is scope for further work on polyazamacrocycles for finding better solution for catalysing these significant reactions.

Conflict of Interest

There is no conflict of interest.

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