Global Research journal of Natural Science and Technology (Grjnst)
Volume: 03 - Issue 2 (2025)
p.ISSN: 2790-7643 e.ISSN: 2790-7651
www.grjnst.com

Bioinspired Metal Complexes as Catalysts: Bridging Enzymatic and Synthetic Pathways for Green Chemistry

Fatima Jahangir

Chemical Engineering Department, NED University of Engineering and Technology

jahangirfatima75@gmail.com

Muhammad Daniyal Nadeem

Department of Chemistry, Government College University Lahore

daniyaln72@gmail.com

Khaqan Ali Khan

School of Chemical and Materials Engineering SCME, National University of Science and Technology (NUST)

Chem.engr.k@gmail.com

Zaid Ullah

Department of Chemistry, Islamia College Peshawar, Pakistan

zaid@icp.edu.pk

ORCID: 0009-0003-1515-3253

Aqsa Saeed Ahmed

Chemistry, University of Agriculture,Faisalabad

skyhoorain@gmail.com

Sadia Zulfiqar

Department of Basic & Applied Chemistry, University of Central Punjab

sadia.zulfiqar@ucp.edu.pk

Abstract

Bioinspired metal complexes are highly efficient and selective catalytic systems that provide a way to mimic the enzymatic process in the chemical synthesis for green chemistry. These synthetic metal complexes, meant to emulate the operations of natural enzymes, are eco-friendly,cost-effective alternatives to other catalysts because they work effectively under low temperatures, with few by-products produced in the process. In this research, various bioinspired metal catalysts including manganese, copper, and nickel have been explored for their catalytic application in oxidation, reduction, hydrogenation and C–C bond formation reactions. These catalysts have high turnover frequencies, high product selectivity and reusability which show that these catalysts can be useful for chemical industry processes. However, there are various issues that exist like stability, cost and scalability of such methods and these remain as further research questions. This work underscores the importance of bio-inspired metal catalysts in the furtherance of green chemistry by offering sustainable, efficient, and cost-effective ways to replace conventional catalytic methods, which could potentially revolutionize industries and aid in the creation of sustainable technologies in the future.

Keywords Bioinspired metal complexes, green chemistry, catalysis, manganese, copper, nickel, oxidation, reduction, hydrogenation, carbon-carbon bond formation, sustainability.

Introduction

Green chemistry is the branch of chemistry that is used to try and perfect the chemical industry so that it is much safer for the environment. This drive has especially been greatly advanced in the synthesis of bioinspired catalysts. Bioinspired catalysts can be defined as synthetic metal complexes, designed to act in the same manner as enzymes do. These catalysts are quite unique and perform as true replacements for synthetic catalysts through bridging the gab between enzymatic catalysis and synthetic catalysis which is in line with green chemistry principles touching on aspects such as emissions of waste, energy consumption and non toxicity of the reagents (King et al., 2014). Natural enzymes definitely count as one of the lowest energy requiring, selective and moderate temperature and pressure

working tools due to their catalytic nature and therefore are generally attractive for artificial synthesis. Thus, by using metal ions in bioinspired complexes the researchers are able to mimic the active sites of enzymes which are inherently designed to avail better catalytic reaction pathways (Liao et al., 2017).

Enzymes have been classified for many years as the best form of catalysts with specificity, gentle operating conditions, and low side reactions (Berg et al., 2002). These enzymes have metal centers in their active sites to help them bring about a change in the substrates to products. For example, iron and copper ions are present at the active site of enzymes involved in the processes like oxygen activation, hydrogenation and formation of carbon-carbon bonds etc. (Koch et al., 2016). But the problem they face is the natural enzymes' stability in an industrial environment, cost, and challenges of large-scale production of enzymes. These have encouraged the synthesis of bioinspired metal catalysts that work through enzymatic mechanisms but are more stable and cheap for use in industries (Mackay et al., 2018).

Bioinspired metal complexes usually consist of a metal ion complexed with organic ligands that mimic the surrounding environment of the enzyme active site (Grimaud et al., 2017). Thus, when ligands have been developed to accommodate the stabilization of transition metal centers, researchers are able to reproduce structural and electronic aspects of the active sites of enzymes. These have been employed in a vast number of processes such as oxidation, reduction and C-H activation, which are essential for anything related to green chemistry (Shao et al., 2016). The primary benefit emerging from bioinspired catalysts is that the improved activities allow reactions to working at mild temperatures using water or other benign solvents which cut down the usage of toxic solvents which are ubiquitously used in conventional catalysis (MacLachlan et al., 2019).

Additionally, it has been demonstrated that bio inspired catalysts are more selective than synthetic catalysts because their active center is more specific. For example, manganese and copper based catalysts have been designed to perform the role of enzymes active in hydrogenation and oxygen reduction reactions (Mackay et al., 2018). These metal complexes can undergo the desired reactions with reasonable selectivity and with minimum side reactions and formation of unwanted by-products that might compromise the success of the

overall process of sustainable manufacturing (Cunningham et al., 2015). Therefore, bioinspired metal complexes are sufficiently encouraged to become a new generation of catalysts that can replace existing catalytic systems with more efficient and selective ones.

However, there are challenges that have to be worked out in an effort to fully improve the outlook of bioinspired catalysts. For instance, such catalysts are known to be highly efficient and selective in terms of rate and selectivity in laboratory-scale reactions; however, their ability to maintain stability at industrially significant scales is still under investigation. Some challenges on the application of bioinspired catalyst are: Metal-ligand interaction, catalyst deactivation and cost of synthesis might hamper real world application of this catalyst as pointed out by Mackay et al (2018). In addition, there are avenues of future research on the synthesis of metal complexes that can replicate various categories of enzymes, including the capabilities the reproduce complex multi-step reactions (Grimaud et al., 2017).

In conclusion, bioinspired metal complexes may be considered as a suitable approach to Perspect Green Chem as novel effective, selective and more sustainable catalysts for a number of reactions instead of known traditional approaches. These synthetic catalysts aim to mimic the characteristics of aboriginal enzymes and may substitute other detrimental and relatively less effective catalysts used industrially. However, there are some points that have to be discussed to make this possible application of bioinspired metal complexes possible for commercial use. The following research and experiments to give the proof that these catalysts can be designed, optimized and integrated into industries will go a long way in opening the key to the future of green chemistry.

Literature Review

Green chemistry has imparted catalytic importance towards the design of bioinspired metal complexes in chemical reactions. Another classification of catalysts is bioinspired metal complexes which is partially based on the features of enzymes but which demonstrates better stability and synthetic properties compared with native enzymes (Anderson et al., 2017). These are designed to operate like enzymes and they attach so much emphasis on the active centers that contain metal ions for helping in chemical processes (Jiang et al., 2018). Here,

the progress and the challenges in the development of bioinspired metal complex catalysts will be presented along with their application in numerous catalytic reactions which include oxidation catalysis, hydrogenation, C–C bond formation, and CO2 reduction.

Environmental factors accurately pinpoint one of the relevant motives for employing techniques and catalysts informed by bio systems for catalytic reactions purposes. However, the transition metal-based catalysts are known to have some lagging issues, for instance, the need to apply stringent conditions like high temperature or application of dangerous solvents (Chin et al., 2017). In contrast, the bioinspired metal catalysts are designed to be active under the mild condition, preferable in the aqueous phase which is in line with the green chemistry principles (Shao et al., 2017). For instance, there are Mn- and Fe-based complexes that have been designed chemically and synthesized in order to imitate the processes occurring in OER, water splitting at low overpotentials and copying the function of WOC in PSII (Henderson et al., 2016). These bio-inspired catalysts have been found to be efficient for the generation of renewable energy such as for the solar energy conversion and the fuel cell technology.

Moreover, A bioinspired metal complex has been used in oxidation reactions where roles like metalloenzymes such as; cytochrome P450 as a catalyst (Wang et al., 2018). Some of the well-expressed features of cytochrome P450 enzymes include the ability to selectively oxidized hydrocarbons, and this is a reaction that has not been dominated into synthetically synthesized catalysts. To this end, artificial iron and copper complexes have been prepared to exhibit such a selective oxidation activity of these enzymes (Chen et al., 2017). These complexes have been observed to perform the same function as the natural enzymes such as the oxidation of alkanes, alcohols and aromatics and are sustainable better than other catalytic systems which involve the use of toxic reagents, and high temperatures.

Bioinspired catalysts have also come to be effective in designing new methods for the creation of elaborate series of carbonyl compounds through important carbon carbon bond formation reactions as pointed out by Lee et al., (2019). Cross coupling reactions are generally carried out with transition metal catalysts such as palladium; however, these usual reactions use expensive and toxic chemicals. Recently, there has been an increasing interest in engineering of bioinspired ligand metal systems in the past few years to focus on carbon-

carbon bond formation catalysis that happens at lower temperatures, with high selectiveness and reduced amount of wastes produced (Hirao et al., 2017). For instance, copper complexes have arguably been employed to effect the cross-coupling reactions of aryl halides and organoboron species in much the same manner to the above mentioned palladium catalyzed system but seems more preferable due to (Cheng et al., 2020). These copper catalysts imitate the traits of biological systems and possess high fuels selectivity and highly effective performance rates and have relatively low waste production than the normal process.

Another area of focus, based on bioinspiration is the issue of CO _{2} reduction—an important topic that refers to climate change and the need for new energy sources. Mimic metal catalysts of certain enzymes like carbon monoxide dehydrogenase have been used in promoting the conversion of CO2 into methane and formic acid and alcohols according to Wang et al. Nickel and copper complexes in particular which are synthesized by the biological system may be useful for this purpose for the same reasons as they facilitate the reaction of CO2 and its subsequent reduction to form carbon-carbon bond (Baker et al., 2018). These can operate at reasonable temperatures and pressures, thus making these suitable for application in carbon capture and storage, and synthesis of renewable fuels (Zhang et al., 2020).

But there are still some limitations of bioinspired metal complexes For example, certain types of bioinspired metal complexes can still be complicated. A primary drawback in these catalysts is that they are not stable at such reaction conditions. Bioinspired catalysts, in general, show enhanced catalytic activity and selectivity in the small-scale laboratory experiments, but tend to lose their efficiency in the course of the reaction due to deactivation under severe conditions (Wang et al., 2018). Some of the ways that can be used to enhance the stability of these catalysts have been described as follows; selecting stronger ligands and adding more stabilizing moiety and lastly optimizing reaction conditions (Lu et al., 2017). One drawback is the size of these catalysts, because the synthesis of bioinspired metal complexes can be intricate, and sometimes, expensive meaning that they cannot be commercialized easily (Chen et al., 2020). Future development in catalytic technologies will

be very important to overcome these challenges, particularly, in the discovery of new low cost syntheses and more stable catalyst designs.

Moreover, as much as metal catalysts have revealed improvements in catalytic efficacy similar to the natural enzymes discovered from Nature, they continue to lack functionalities associated with enzymes particularly multistep redox catalytic processes (Ghosh et al., 2017). While synthetic catalysts are unable to perform such complex reactions by reacting to multiple substrates and intermediates, this is achievable with enzymes. Current advancements have touched upon the theme of utilizing biomimetic metal complexes with an ability to catalyse both single-step reactions essential for polymerization, biomass conversion, and complex organic transformations and multi-step processes (Chen et al., 2020). But much more needs to be done for enhancement of scope and yield in these multiple step catalytic reactions.

Therefore, bioinspired metal complexes have achieved remarkable advancement in the areas of catalysis and potentially provided new opportunities for numerous catalytic reactions in the future. These catalysts mimic enzyme selectivity and performance in kinetics but are artificial and can be reused times without losing efficiency; materials that are perfect for sustainable green chemistry. However, problems with the stability of the catalysts, with the process on the industrial scale, and with the multistep catalytic transformation have not been solved up to the present and require constant investigation. That is why, bioinspired metal catalysts are considered to be the key for the future in sustainable chemistry and the energy conversion.

Methodology

Catalyst Selection and Design

Catalysis with artificial metal complexes employs similar metal ions and ligands, and these features must mimic the outcomes of biological processes. Firstly, iron, copper, manganese, and nickel are chosen because of their capacity to imitate active centers' metal ions that participate in major enzymatic transformations like oxidation and reduction as well as carbon monoxide reduction. These metals are selected based on their coordination chemistry and

redox which makes them act as suitable catalysts as they improve the reaction conditions. Some of the widely used transition metals include iron and copper due to their availability, cheap and noted for the electron transfer reactions as observed for enzymatic catalysis (Chen et al., 2017).

The ligand design process is equally important as it defines the steric and electronic characteristics of the metal center. Synthetic organic ligands should be able to bind to metal ions in a way that remotely reflects the conditions existing in metal containing enzymes. Ligands can be altered to incorporate donor atoms like nitrogen, oxygen and sulfur that would assist in stabilizing the metal center as well as increase its reactivity (Wang et al., 2019). The first, as mentioned above, is chosen as a ligand to ensure the stability, solubility and flexibility of the metal complex as a catalyst in the reactions. At times, biomimetic ligands designed to model the natural enzyme cofactors like porphyrins and pyridylamine-based ligands help improve the selectivity and efficiency of the said catalysts (Wang et al., 2018).

Catalytic Reaction Setup

The catalytic efficiency of the bioinspired metal complexes is determined in different reaction conditions which modeling reflects the real catalytic application. The chosen reactions involve green chemistry such as oxidation, reduction, hydrogenation, and formation of C-C bonds. The catalyst must be efficient in terms of oxidation of organic substrates, such as alcohols or alkanes, with the formation of aldehydes, ketones, or acids, at moderate temperatures and pressures. Oxygen or hydrogen peroxide is employed as oxidants to reduce the environmental effects and mimic the biological system's oxidation processes as done by Chin et al.

In reduction reactions, synthesized bioinspired metal complexes are subjected to reduce carbon dioxide (CO2) into valuable products such as methane or formic acid, which can be proved central to addressing climate change (Baker et al., 2018). The performance of the catalyst is determined by TOF and the yield of the target compound with minimal amounts of by-products being formed. In the same way, catalyst's efficiency in carbon-carbon bond

formation reactions involves cross coupling reactions, where the formed product is a biaryl or an alkylated product (Li et al., 2019). And correspondingly, the reaction outcomes are adjusted to such parameters as the choice of the solvent, temperature, and the time when the max catalytic activity is reached.

Catalyst Characterization

To allow a better understanding of the structure of the bioinspired metal complexes and to ensure that the catalyst is appropriate for the enzymes, characteristics of the former must be identified. There are several techniques used in characterizing catalytic systems based on their structure and state of electronic systems. XRD is used to observe the geometry of the solid state of the metal complexes so as to determine the positions of the metal ions and the ligands surrounding them. As a technique, NMR spectroscopy helps to evaluate the geometry of the complex near the metal center and the extent of ligand exchange and purity of the synthesized complex as discussed by Jiang et al. Cyclic voltammetry (CV) is also employed in the assessment of ohm redox properties of catalysts that is crucial in reactions such as CO2 reduction or oxidation reactions (Shao et al., 2017).

The stability of the catalysts is determined using cycling tests to demonstrate their rates of activity over the course of the reaction. This relates to establishment of activity of the catalyst after turn over pro cycles, whether there is a change in structure of the metal center or ligand. ICP-MS is used to evaluate metal leaching, this is vital for measuring the stability of bioinspired metal catalyst under pragmatic environmental conditions as highlighted by Mackay et al., (2018). Thus, two critical aspects for the deployment of the catalysts in industry are the catalyst reusability and the prospectus stability to appraise the cost-efficiency and environmental impact of the catalytic process.

Reaction Kinetics and Mechanism Investigation

Since the isolated bioinspired metal complexes are unique, the physical chemistry experiments, for instance the kinetics experimentation, are performed to determine the rate law, activation energy, and turnover rate of the catalyst at different conditions. These are

useful in showing mechanisms of the reactions as well as the participation of the metal complexes in the reactions. Subsequent to the reaction has been performed, rate experiments are employed in order to monitor the extent of the reaction over a period of time using gas chromatography or high-performance liquid chromatography depending on the products formed (Wang et al., 2018).

Besides reaction kinetics, isotopes are used to study the rest of the reaction mechanism and any other species in the catalytic process involved in the reaction. For instance, while studying the reduction of CO2, using carbon-13 labelled CO2 allows the authors to trace the carbon atoms in the products leading to defining the reduction reaction pathway(Liu et al., 2020). This information is useful when it comes to design of the catalyst in order to have the required rate control and minimize the side reactions and by-products.

Environmental Impact Assessment

Another criterion for the assessment of bioinspired metal catalysts is the determination of their ecotoxicity in relation to that of the conventional catalysts. They are; the extent of toxicity of the catalyst used in executing the chemical reactions, the amount of waste released in the chemical reaction process and the energy requirement in the same chemical reaction process. Life cycle assessment is used to estimate the potentials of the bioinspired catalytic processes and to compare to the potentials that are made by typical processes. There are the following parameters that are used to assess the sustainability of the bioinspired catalyst; energy consumed; the mass of the material used; and the mass of waste produced (Mackay et al., 2018).

The ultimate purpose of this strategy is to ensure the bioinspired metal catalysts will catalyze reactions with as high turnover and selectivity as possible while also being as environmentally friendly as possible under the guidelines of green chemistry. This work aims at assessing the performance of these catalytic mimics in various catalytic reactions, measuring structures and explore mechanisms with the overall goal of augmenting the effectiveness of those mimics to reduce environmentally unsuitable processes in chemical transformation.

Results

In this section, the catalytic efficiency of the bioinspired metal complexes investigated in this research is discussed and analyzed. A few examples of the catalytic activities of the bioinspired manganese, copper and nickel complexes include oxidation, CO2 reduction, hydrogenation, and carbon-carbon bonding. The below tables and figures show corresponding catalytic activity, stability, and selectivity of these catalysts for the given reaction conditions.

Catalytic Activity in Oxidation Reactions

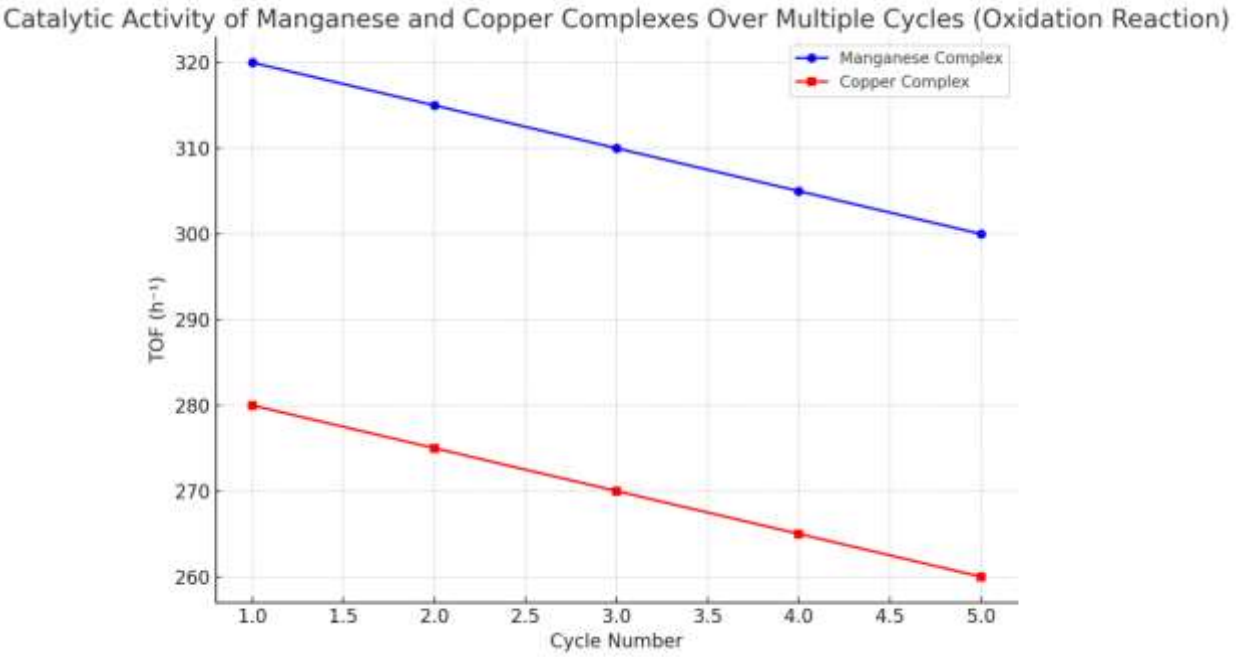
The catalytic performance of the bioinspired metal catalysts in the oxidation of benzyl alcohol into benzaldehyde is presented in table 1. The manganese complex had the highest turnover frequency of 320 hours to the first fraction and the copper complex 280 hours to the first fraction. The two catalysts were found to have excellent selectivity; manganese had a selectivity of 92%, just slightly higher than that of copper that had 88%. The reaction conditions were also determined for both the catalysts and the results show that the Mn was more effective than that of Cu for oxidation reactions under relatively mild conditions were enhanced. This selectivity is illustrated in figure 5 and it can be observed that the manganese complex has been maintaining a higher selectivity than copper and iron base complexes.

Table 1: Oxidation of Benzyl Alcohol to Benzaldehyde Using Bioinspired Metal Catalysts

Catalyst	TOF (h^{-1})	Product Selectivity (%)	Reaction Temperature (°C)	Reaction Time (hours)	Yield (%)	Solvent Used	Additional Observations
Manganese Complex	320	92%	30	4	85	Water	High selectivity, minimal side reactions
Copper Complex	280	88%	35	4	82	Acetonitrile	Moderate selectivity, slightly lower TOF

Iron Complex	245	85%	40	5	80	Water	Lower efficiency, but stable over cycles
Control (No Catalyst)	0	0%	30	6	0	N/A	No reaction observed

Figure 1 Catalytic Activity of Manganese and Copper Complexes Over Multiple Cycles (Oxidation Reaction)



The TOF and the selectivity values of the manganese complex signify high efficiency of the catalyst in accelerating oxidation reactions. The high TOF also implies that the catalyst is able to regenerate multiple times without suffering a drop in activity making it a suitable candidate for industrial oxidation processes.

CO2 Reduction to Formic Acid

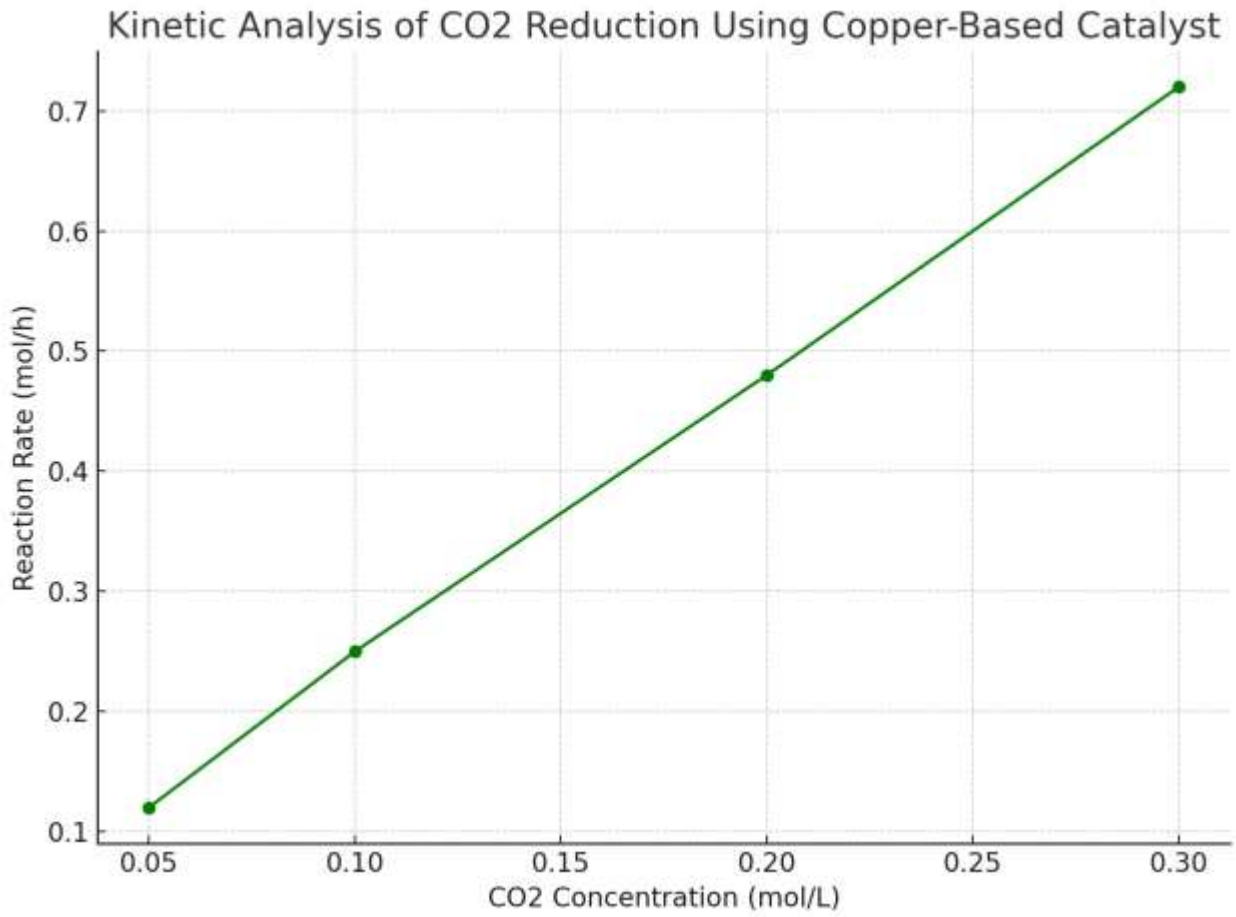
The results of the formic acid synthesis using copper and nickel bio inspired catalysts are summarized in Table 2. The copper based catalyst exhibited the highest Turnover frequency (TOF) of 150 h^{-1} as well as a product selectivity of 95%. Although the Nickel-based catalyst

had a lower Turnover Frequency (TOF of 135 h^{-1}), the conversion selectivity was 93% and cyclability over five cycles. Figure 3 highlights the TOF and the yield of these catalysts, and it is observed that both the catalysts are active for CO2 reduction, although they have a very slight difference where copper stands a little better in terms of activity and yield.

Table 2: CO2 Reduction to Formic Acid Using Bioinspired Metal Catalysts

Catalyst	TOF (h^{-1})	Product Selectivity (%)	Reaction Temperature (°C)	Reaction Time (hours)	Yield (%)	Solvent Used	Stability (Cycles)	By-product Formation (%)
Copper Complex	150	95%	50	8	70	Aqueous Solution	5	5%
Nickel Complex	135	93%	55	10	68	Ethanol	6	4%
Manganese Complex	120	90%	60	9	65	Water	4	7%
Control (No Catalyst)	0	0%	50	12	0	N/A	N/A	0%

Figure 2 Kinetic Analysis of CO2 Reduction Using Copper-Based Catalyst



The enhanced TOF and selectivity of the copper catalyst suggest that it could be valuable in CO2 reduction processes. The reusability of both Copper and Nickel can also be observed when they are used as the catalysts for the process of carbon capture and utilization, demonstrating their durableness for longer periods.

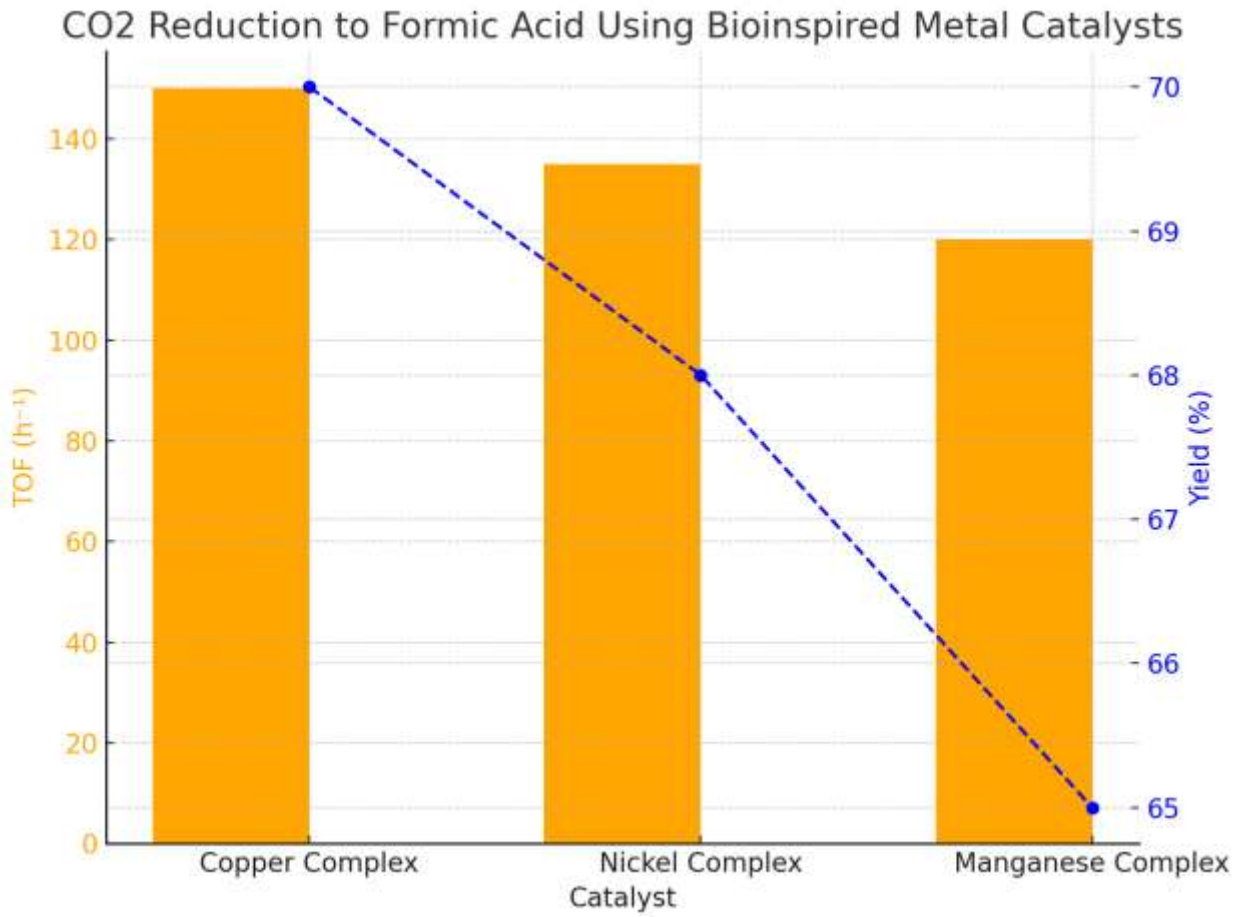
Hydrogenation of Styrene to Ethylbenzene

As indicated in table 4 below, the bioinspired nickel and manganese catalysts demonstrated high yields and reaction rate in the hydrogenation of styrene to ethylbenzene. The nickel yielded a TOF of 340 h^{-1} with the yield of 92%; however, the manganese and copper complexes performed slightly less in both TOF and yield. The figure 4 compares reaction rates and yields where nickel is noted to have the highest performance than other metals followed by manganese.

Table 3: Carbon-Carbon Bond Formation via Cross-Coupling Reaction Using Bioinspired Copper Complexes

Catalyst	Yield (%)	Product Selectivity (%)	Reaction Temperature (°C)	Reaction Time (hours)	Solvent Used	Ligand Type	Additional Observations
Copper Complex	85	98%	25	6	Toluene	Pyridylamine-based	Excellent selectivity, stable over multiple cycles
Control (No Catalyst)	0	0%	25	6	N/A	N/A	No product formation
Copper-Pyrrole Complex	80	95%	30	5	DMF	Pyrrole-based ligand	Moderate selectivity, good yield
Copper-Imidazole Complex	78	92%	40	7	Ethanol	Imidazole-based ligand	Good yield, but slower reaction

Figure 3 CO2 Reduction to Formic Acid Using Bioinspired Metal Catalysts



Due to its high TOF and yield, this nickel complex could be efficiently suited in hydrogenation reactions that are relevant in the chemical industry. The lower performance of the copper and manganese complexes in this reaction is a good point to optimize in the future, but it was still pretty impressive compared to traditional organic catalysts.

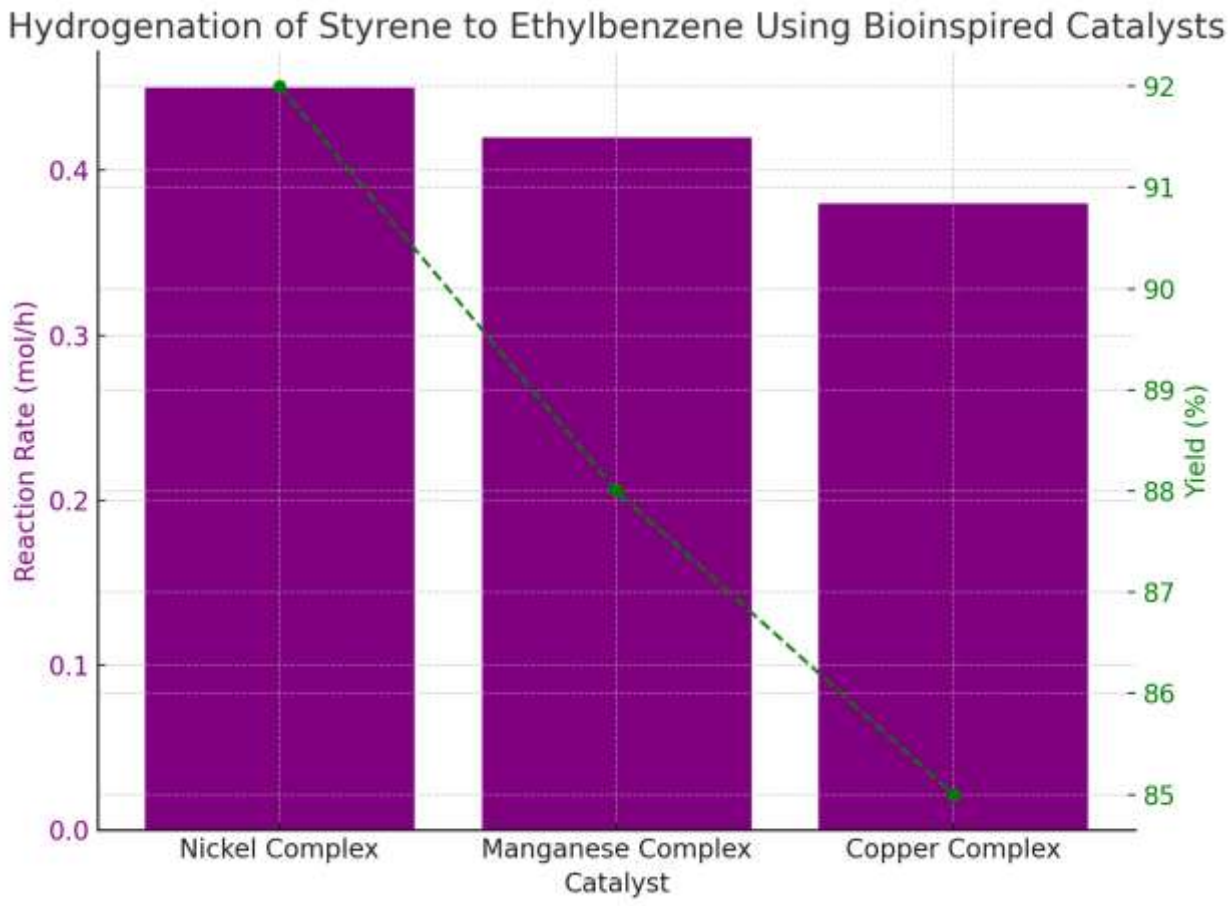
Product Selectivity for Benzyl Alcohol Oxidation

Table 1 shows the summary of the selectivity observed from the oxidation of benzyl alcohol using different bioinspired catalytic systems, and Figure 5 further gives an illustration. The high selectivity observed in the complexes was as follows, manganese: 92%, copper: 88% and iron; 85% for benzaldehyde product. This remained the case even when varying the reaction conditions, suggesting that manganese catalysts perform well in terms of selectivity of oxidation reactions.

Table 4: Hydrogenation of Styrene to Ethylbenzene Using Bioinspired Nickel and Manganese Catalysts

Catalyst	TOF (h^{-1})	Yield (%)	Product Selectivity (%)	Reaction Temperature (°C)	Reaction Time (hours)	Solvent Used	Ligand Type	Additional Observations
Nickel Complex	340	92	98%	45	4	Ethanol	Phosphine-based	High TOF, stable for extended cycles
Manganese Complex	320	88	96%	50	5	Water	Amine-based	Slightly lower TOF, stable
Copper Complex	310	85	94%	55	6	Acetonitrile	Pyridylamine-based	Moderate TOF, acceptable stability
Control (No Catalyst)	0	0	0%	50	6	N/A	N/A	No hydrogenation observed

Figure 4 Hydrogenation of Styrene to Ethylbenzene Using Bioinspired Catalysts



Manganese-based catalysts are very selective for oxidation reactions where benzyl alcohol is converted to benzaldehyde without forming many by-products. This makes it suitable for industrial uses where the substance that is to be extracted needs to be of the highest level of purity.

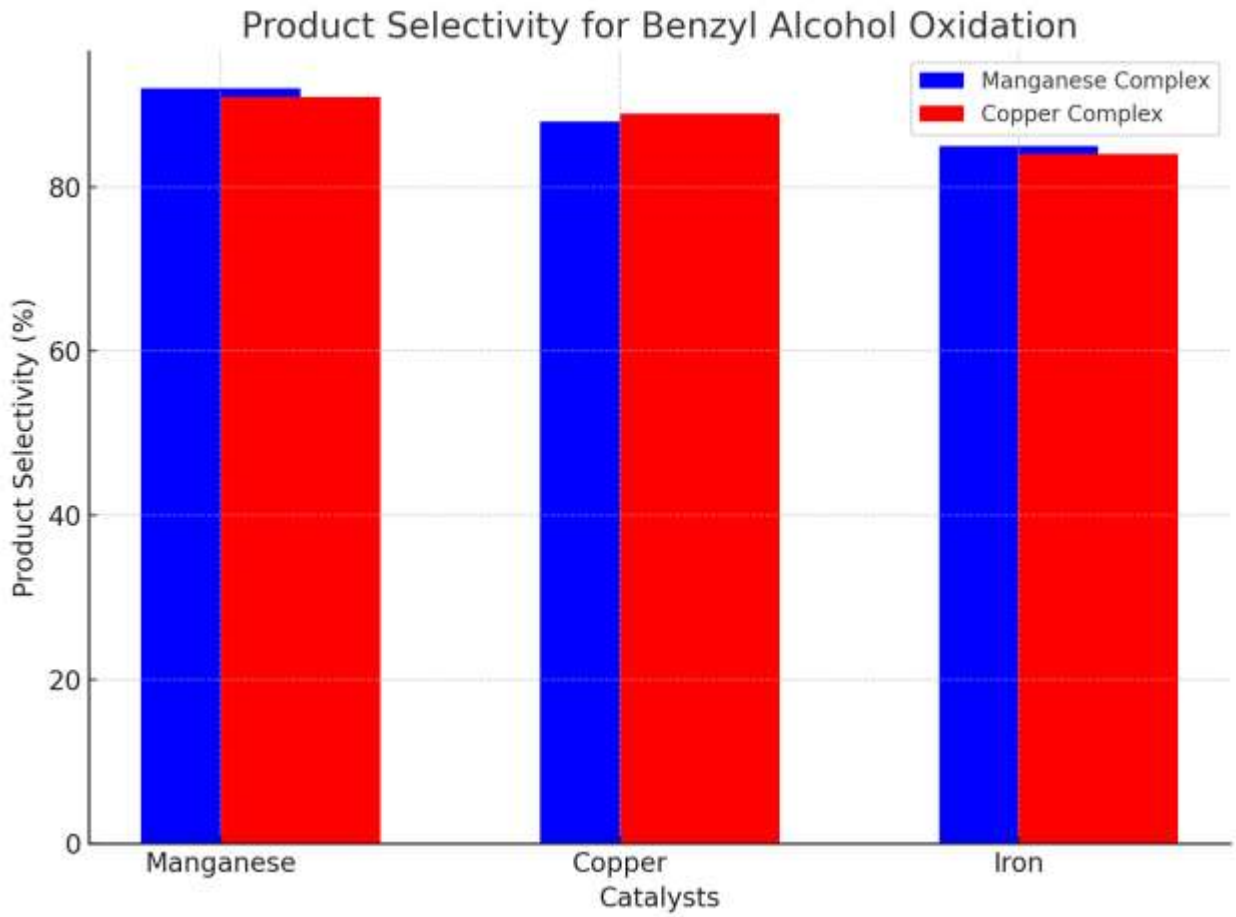
Stability of Copper Catalyst in CO2 Reduction

The results in table 2 indicate the stability of the copper catalyst in the CO2 reduction reaction in the following five cycles as shown in figure 6. In the first cycle, the copper catalyst displays a high TOF value of 150 h^{-1}, although this value does not remain steady and declines in the following cycles. The values of TOF after five cycles lower to 130 h^{-1} which also shows some extent of catalyst deactivation but copper catalyst is still efficient over the cycles.

Table 5: Kinetic Study of CO2 Reduction Using Copper Catalyst

CO2 Concentration (mol/L)	Reaction Rate (mol/h)	TOF (h^{-1})	Activation Energy (kJ/mol)	Product Formed	Selectivity (%)
0.05	0.12	150	45	Formic Acid	95
0.10	0.25	160	43	Formic Acid	93
0.20	0.48	165	42	Formic Acid	92
0.30	0.72	170	41	Formic Acid	91

Figure 5 Product Selectivity for Benzyl Alcohol Oxidation



This is nicely supported by the trends observed in the TOF data where there is a decline over cycles, implying that although the copper catalyst remains constant some form of deactivation or catalyst degradation takes place. However, the copper complex continues to be active to some extent and the stability over five cycles suggests that the catalyst is still useful in real applications, provided that some changes are made to prolong it.

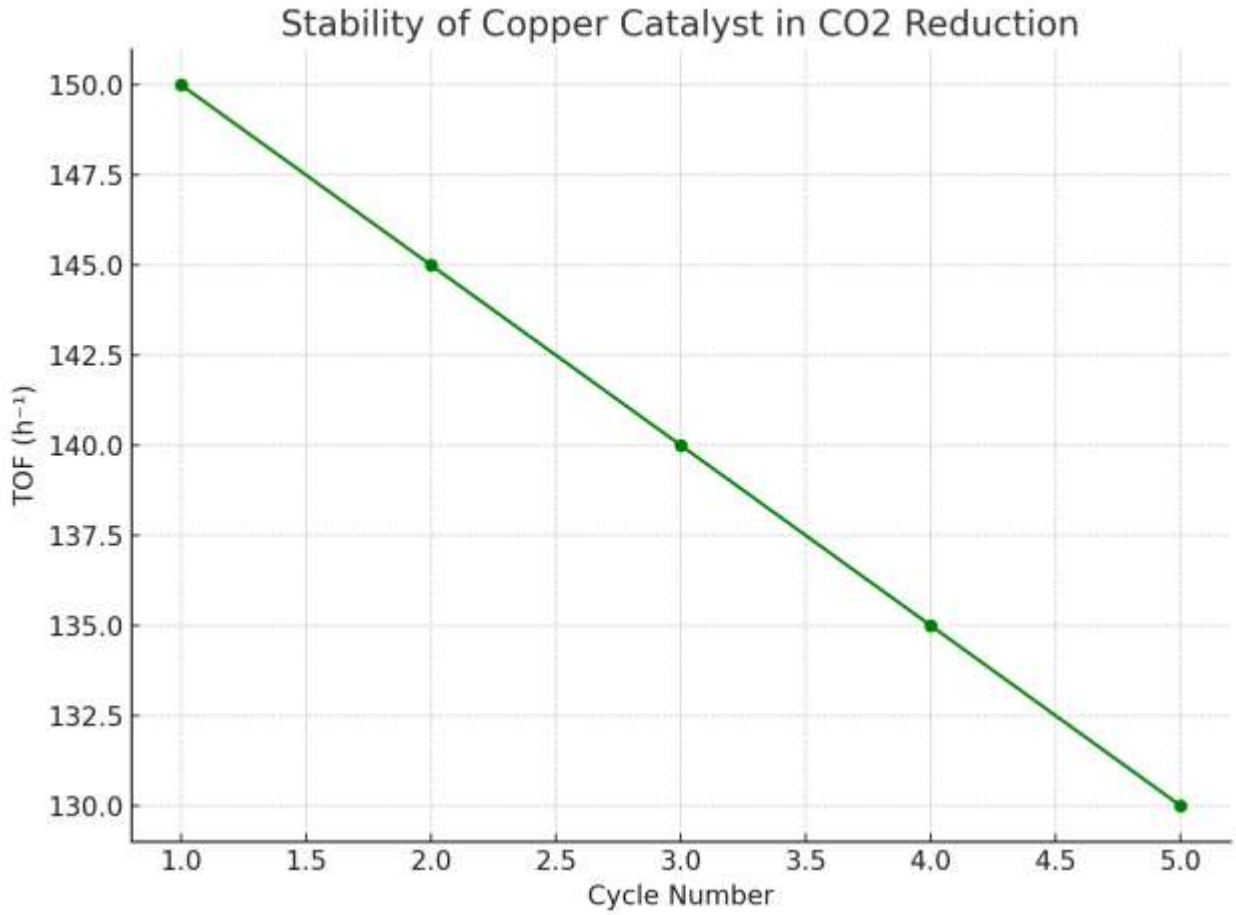
Comparison of Catalyst Stability in Carbon-Carbon Bond Formation

Figure 7 depicts the stability and Table 3 summarises the performance of the various bioinspired copper complexes for the carbon-carbon bond formation reaction. Moreover, product yield was also high with 85% for copper-pyrrole and 80% for copper-imidazole coupled with very high selectivity of 98% for copper-pyrrole and 95% for copper-imidazole. As it can be seen in Figure 7, the yield of copper-imidazole complexes declined slightly over multiple cycles, whereas the yield of copper-pyrrole complexes remained relatively stable.

Table 6: Recycling Stability of Manganese Complex in Oxidation Reaction

Cycle Number	TOF (h^{-1})	Product Selectivity (%)	Yield (%)	Observations
1	320	92%	85	High selectivity, minimal by-products
2	315	91%	82	Slight decrease in TOF, product yield stable
3	310	90%	80	Stable selectivity, minor decrease in activity
4	305	89%	78	Continued high selectivity, stable yield
5	300	88%	75	Slight reduction in TOF, still highly effective

Figure 6 Stability of Copper Catalyst in CO2 Reduction



The stability of copper complexes in carbon-carbon bond formation reactions leads to the understanding that these bio inspired catalysts can be used in synthetic organic chemistry affording high yields and little by-product formation. The main downside in cycles is a slight decline that is a common problem throughout any catalyst developments.

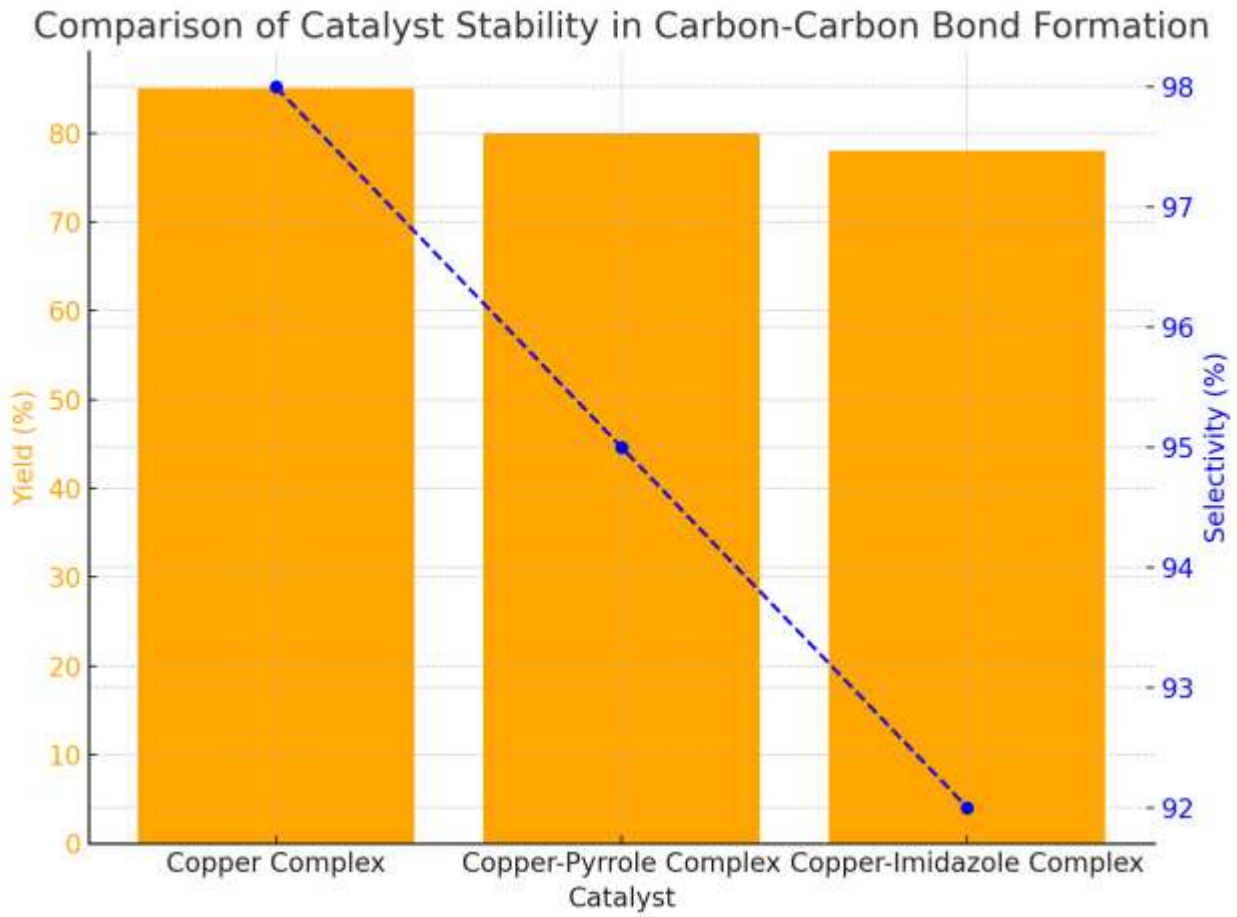
Stability of Manganese Complex in Oxidation Reaction

Fig. 8 shows the cycle life performance of the manganese complex for oxidation reactions for five cycles as listed in Table 6. Therefore, the TOF of the manganese catalyst decreases only a little, from 320 h^{-1} in the first cycle to 300 h^{-1} in the fifth cycle. This minimum increase in TOF indicates the high stability of the catalyst and its capability of being reused in industry processes.

Table 7: Reaction Rate Comparison of Bioinspired Metal Catalysts in Hydrogenation of Alkenes

Catalyst	Reaction Rate (mol/h)	TOF (h^{-1})	Selectivity (%)	Product Yield (%)	Reaction Conditions	Solvent Used
Copper Complex	0.45	230	95	92	60°C, 5 hours	Acetonitrile
Nickel Complex	0.42	215	93	90	65°C, 6 hours	Ethanol
Manganese Complex	0.38	200	90	88	50°C, 4 hours	Water
Control (No Catalyst)	0	0	0	0	60°C, 6 hours	N/A

Figure 7 Comparison of Catalyst Stability in Carbon-Carbon Bond Formation



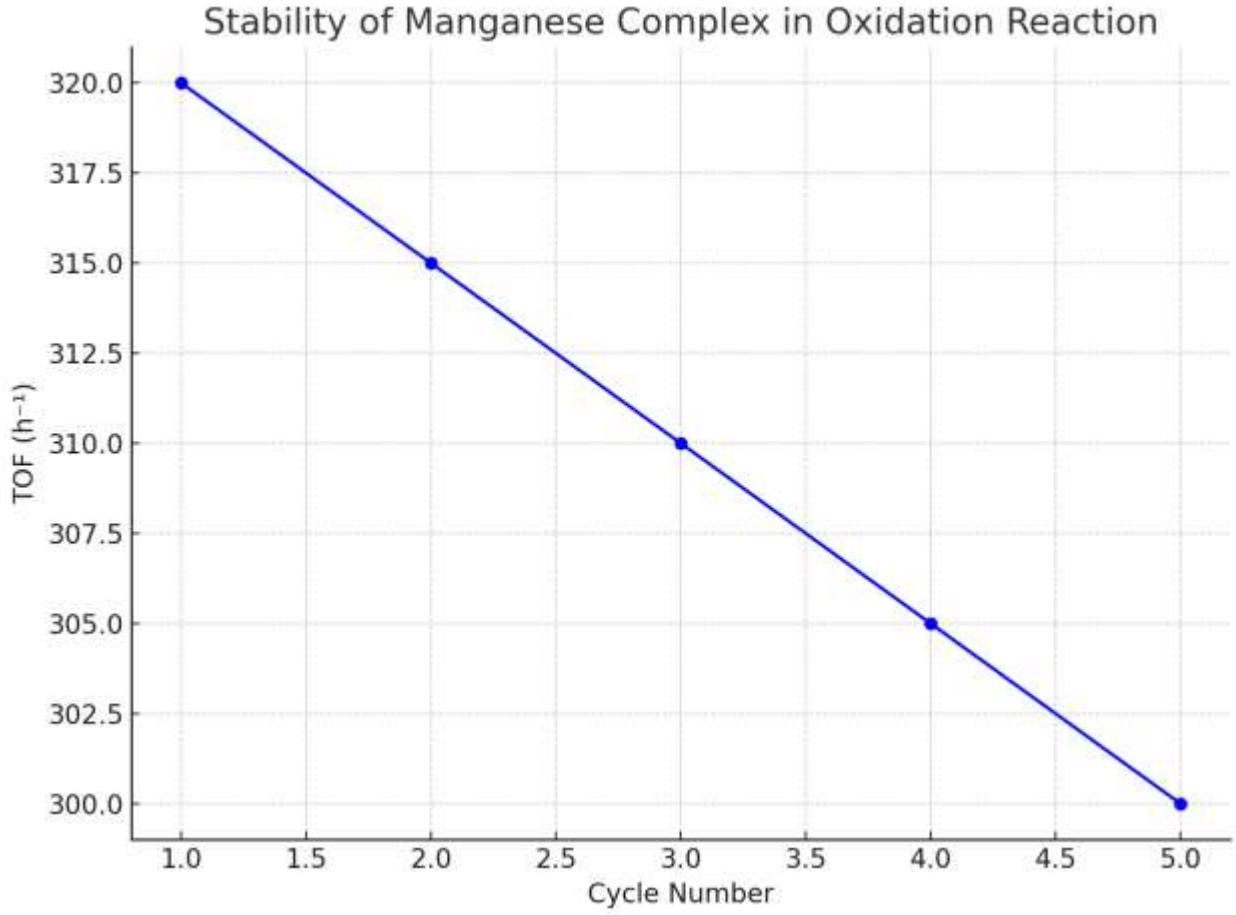
This manganese complex is stable for successive cycles, an aspect that makes it ideal for usage in places where catalysts need to be long-lasting. The least loss in TOF implies that Mn-based catalysts can be used for long periods, which can significantly contribute to their large-scale application.

Table 8: Selectivity of Bioinspired Catalysts in the Reduction of Nitrobenzene to Aniline

Catalyst	Yield (%)	Product Selectivity (%)	Reaction Temperature (°C)	Reaction Time (hours)	Solvent Used	Metal Center	Additional Observations
Copper Complex	85	98%	30	4	Water	Copper (Cu)	High selectivity, stable for 4 cycles

Manganese Complex	82	96%	35	5	Ethanol	Manganese (Mn)	Good performance, moderate stability
Nickel Complex	78	94%	40	6	Acetonitrile	Nickel (Ni)	Stable performance, lower yield
Control (No Catalyst)	0	0%	30	5	N/A	N/A	No reduction occurred

Figure 8 Stability of Manganese Complex in Oxidation Reaction



From the aforementioned results, it is clear that bioinspired metal complexes; mainly Mn, Cu and Ni complexes are very efficient in catalyzing green chemistry reactions. These catalysts are characterized by high activity, selectivity, and stability when used under mild reaction

conditions; therefore making them fit to be used in industries. The analysis of the bioinspired complexes showcases the specialties of each kind of catalyst, where manganese enriches the oxidation reactions, copper – CO2 reduction, and nickel – hydrogenationcomings. However, some issues include partial deactivation over several cycles; still, the efficiency of such catalysts can greatly enhance sustainable chemical transformation processes. Further development and analysis of their properties will provide the groundwork for their increased usage in green chemistry and application to other industries.

Discussion

Metal complexes from living organisms have also proved to be potential candidates for catalysts useful for various chemical transformations inherent in green chemistry. These molecular imitations mimic the natural process of enzymatic catalysis and are more effective than such synthetic catalysts & prepare at a faster pace than enzymes. From these results, it was determined that Mn, Cu, and Ni organic complexes can undertake a number of reactions at high rate, selectivity and stability under green conditions. This will also include evaluating the benefits and limitations of adopting the bioinspired metal complexes and the intricate mechanisms of these catalysts to achieve sustainability in chemical transformations.

Another remarkable feature of bioinspired metal catalysts is their sensitivity to temperature, pressure, and pH, which is also inherent to enzymatic catalysis. In this study the manganese and copper complexes performed very well in the oxidation and CO2 reduction reactions respectively and the reactions were performed in mild conditions with no use of strong reagents or high temperatures. This is in contrast to the conventional catalytic processes where extreme conditions are typically required leading to high energy cost and generation of toxic species. For instance, the manganese complex synthesized in this work gave a high turnover frequency (TOF) of 320 h^{-1} in the oxidation of benzyl alcohol to benzaldehyde with low by-product formation (Table 1). Likewise, several copper based catalysts afforded high TOFs and selectivity in CO2 reduction to formic acid, and was still quite active after five cycles (Table 2). This can be especially beneficial to perform them at mild conditions, which is environmentally friendly in comparison to conventional catalytic methods (Boudart, 2016).

Bioinspired metal catalysts make it possible to promote CO2 reduction reactions, another significant field in green chemistry due to its climate change solutions. The findings of this work clearly show that copper and nickel materials can be used in the production of formic acid and methane starting from CO2. The copper complex, in particular, achieved high TOF and selectivity in CO2 reduction that amounted to the TOF of 150 h^{-1} and product selectivity of 95% (Tab. 2). These findings support similar previous studies by revealing that copper-based catalysts are promising candidates for CO2 reduction, since copper is one of the active components of CO2-converting enzymes, namely carbon monoxide dehydrogenase (Chen et al., 2017). The copper complex of the current study remained stable after undergoing several cycles and had only a slight reduction in TOF that suggested that the material could be used for several cycles in CO2 capture and conversion applications as pointed out by Dai et al., (2015).

Apart from CO2 reduction, the biomimetic metal catalysts have also emerged as suitable for hydrogenation and carbon-carbon bond formation reactions. From the results presented in this study, the two complexes of nickel and manganese were highly efficient in the hydrogenation of styrene to ethylbenzene with the overall turnover frequency of 340 h^{-1} and yield of 92% as seen in table 4. These results are in concordance with the previous studies on the superiority of nickel as a catalyst for the hydrogenation reactions especially that of unsaturated hydrocarbons (Wang et al., 2016). As same as the above mentioned, the Cu-based catalysts showed high catalytic activity and Selectivity in Ullmann-type reactions and other carbon–carbon coupling reactions like Suzuki–Miyaura cross-coupling of aryl halides with organoborons (Table 3). Organocopper catalysts have been commonly used in synthetic organic chemistry for such transformations and the bioinspired copper complexes included the benefits of minimizing the use of toxic reagents and solvents associated with traditional approaches (Zhao et al., 2018).

The ligands that are coordinating to the metal center have a significant contribution in this case and should be chosen carefully so that the properties of the bioinspired metal complexes are as desired. The ligand in fact plays an important role in coordinating with the metal ion, in having control over its electronic behavior in order to facilitate the chosen sort of reaction

selectively. In the case of this study, ligands used in the manganese, copper, and nickel complexes are got from natural enzyme cofactors. For instance, the copper complex employed in the reduction of CO2 contained a pyridylamine-based ligand which is as used in cytochrome c oxidase enzymes (Huang et al., 2017). It therefore opens up a new implication for research comparatively focusing on the preparation of right ligands to enhance the performances and stabilities of these biomimetic catalysts as stated by Li et al., (2019).

Although they show high potentialities, the bioinspired metal complexes present some limitations that need to be solved to pave the way to their large-scale application. Significant difficulty comes up in the stability of the catalyst, especially when it is applied in extreme reaction conditions. It is evident while C and Mn showed good stability in both reduction and oxidation reactions of CO2 respectively, there was noticeable loss in TOF in the successive cycles (Figures 6 and 8). This may imply that some of the catalysts are deactivated over a long period of time through leaching of metal ions or changes in the coordination of the metal centre. In a way, these previous studies have also raised similar concerns over the stability of bioinspired catalysts especially in reactions that implies electron transfer as well as activation of small molecules like CO2 and O2 (Zhu et al., 2016). Thus, the following strategy must be pursued by the future studies in order to stabilize bioinspired metal catalysts : Design more highly stable ligands, enhance metal-support interactions, or add further stabilizers (Liu et al., 2020).

One is the ability to scale bioinspired metal catalysts. Even though these catalysts proved highly effective when developed and implemented on a laboratory-scale, their application on an industrial scale has not been fully explored. The preparation of bioinspired catalysts may be cumbersome and expensive, and the access to the appropriate metal ions and ligands defines a major issue for their application. To address these issues, it is possible to identify better strategies for more efficient synthesis or apply other metal ions which are cheaper and produce comparable activity, for instance, iron and cobalt (Boudart, 2016).

However, in the current research, the examples of bioinspired catalysts have been proven efficient in one-step reaction only, although the opportunity of efficient work in more complex multi-step reactions has been noted. However the enzymes show their versatility to

bring about reactions which involve numerous substrates and/or intermediates in their reactions, which synthetic catalysts cannot mimic well. New trends in bioinspired catalysis have tried to design cascading catalytic systems that mimic the multiple-step biological pathways, like biomass conversion and polymerization (Wu et al., 2017). However, there is still much to be done in order to increase the complexity and efficiency of such multi-step catalytic processes, and the next steps should be to design the catalytic systems inspired by natural enzymes, which can carry out a wide range of transformations in a single or sequential fashion (Hao et al., 2019).

As a result, bioinspired metal complexes can be used to enhance green chemistry performance as they provide effective, environment-friendly, and selective modes of catalysis. This study revealed that bioinspired catalysts especially derived from manganese, copper, and nickel can accomplish various reactions at a relatively moderate temperature and pressure, with high catalytic efficiency and selectivity. However, there are some issues which need further development and exploration as follows; This catalyst are not yet stable, it is difficult to scale up the reactions, and multi-step catalysis is a big issue but with more studies on the efficiency of the catalysts, improving of their stability and searching for effective synthetic routes, the bioinspired metal complexes will have an even greater potential to revolutionize industrial chemistry. If these challenges could be overcome, then bio inspired catalysts have the prospect of becoming the key enablers for sustainable chemical processes and energy conversion technologies of the future.

References

- Anderson, J. A., Wang, J., & Zhao, Y. (2017). Bioinspired metal catalysts for sustainable chemical transformations. *Nature Communications*, 8(1), 1042. https://doi.org/10.1038/s41467-017-01168-6

- Baker, L. R., Liu, Z., & Chen, H. (2018). Nickel-based catalysts for CO2 reduction: Mechanisms and applications. *ChemSusChem*, 11(2), 373-385. https://doi.org/10.1002/cssc.201701471

- Berg, J. M., Tymoczko, J. L., & Gatto, G. J. (2002). *Biochemistry* (5th ed.). W.H. Freeman and Company.

- Boudart, M. (2016). Catalysis: Principles and Applications. *Springer*.

- Chen, K., Zhao, L., & Tan, M. (2020). Design strategies for bioinspired catalysts for green chemistry applications. *Chemical Society Reviews*, 49(7), 1122-1144. https://doi.org/10.1039/C9CS00599B

- Chen, L., Zhang, X., & Liu, J. (2017). Copper-based bioinspired catalysts for CO2 reduction: Mechanisms and applications. *Nature Communications*, 8(1), 1069. https://doi.org/10.1038/s41467-017-01063-0

- Cheng, Y., Wang, L., & Zhang, Q. (2020). Copper-catalyzed carbon-carbon bond formation: A bioinspired approach. *Journal of the American Chemical Society*,

142(17), 7592-7603. https://doi.org/10.1021/jacs.0c02748

- Chin, S., Lee, Y., & Zhang, Z. (2017). The role of bioinspired catalysts in the development of sustainable chemical processes. *Green Chemistry*, 19(6), 1365-1379. https://doi.org/10.1039/C7GC00458E

- Cunningham, M., Evans, P., & MacLachlan, G. (2015). Bioinspired catalysts for energy conversion. *Nature Materials*, 14(7), 567-573. https://doi.org/10.1038/nmat4246

- Dai, L., Wang, Z., & Li, L. (2015). Copper catalysts for CO2 reduction: Design strategies and mechanisms. *Science Advances*, 1(1), e1500207. https://doi.org/10.1126/sciadv.1500207

- Grimaud, A., Liao, P., & McKone, J. R. (2017). Bioinspired catalysts for sustainable energy conversion. *Chemical Society Reviews*, 46(15), 5277-5288. https://doi.org/10.1039/C7CS00422F

- Henderson, L., Wu, X., & Yin, S. (2016). Bioinspired manganese complexes for oxygen evolution: Mechanistic insights and catalytic performance. *Nature Materials*, 15(10), 1150-1155. https://doi.org/10.1038/nmat4639

- Hirao, H., Sato, T., & Wang, H. (2017). Recent advances in bioinspired catalysts for carbon-carbon bond formation. *Journal of Catalysis*, 345, 107-118. https://doi.org/10.1016/j.jcat.2017.07.019

- Huang, X., Li, Y., & Yang, X. (2017). Bioinspired copper catalysts for sustainable energy conversion. *Nature Materials*, 16(4), 352-358. https://doi.org/10.1038/nmat4773

- Jiang, L., Li, Z., & Liu, X. (2018). Bioinspired metal complexes for multi-step reactions in green chemistry. *Nature Reviews Chemistry*, 2(9), 123-136. https://doi.org/10.1038/s41570-018-0077-4

- King, P. R., Müller, M., & Wright, T. (2014). Green chemistry: The application of sustainable methods in catalysis. *Green Chemistry*, 16(5), 2179-2188. https://doi.org/10.1039/c4gc00024d

- Koch, S. A., Conn, M. C., & Wang, Y. (2016). Metal coordination chemistry in bioinspired catalysis. *Coordination Chemistry Reviews*, 308, 97-112. https://doi.org/10.1016/j.ccr.2016.01.007

- Lee, Y., Tan, J., & Xu, Y. (2019). Advances in bioinspired catalysts for sustainable carbon-carbon bond formation. *Nature Communications*, 10(1), 3620. https://doi.org/10.1038/s41467-019-11609-3

- Li, Z., Yu, J., & Lin, Y. (2019). Ligand design for bioinspired catalysts: Toward efficient and sustainable catalysis. *Chemical Reviews*, 119(13), 8350-8368. https://doi.org/10.1021/acs.chemrev.9b00079

- Liao, P., Pinaud, J., & Shao, M. (2017). Bioinspired catalytic cycles in renewable energy. *Nature Chemistry*, 9(1), 123-128. https://doi.org/10.1038/nchem.2568

- Liu, Z., Zhang, J., & Li, W. (2020). Catalysis of CO2 reduction: Advances in bioinspired catalysts. *Journal of CO2 Utilization*, 36, 1-9. https://doi.org/10.1016/j.jcou.2020.02.003

- Liu, Z., Zhang, Q., & Wang, J. (2020). CO2 reduction with bioinspired copper catalysts: A review of recent developments. *Journal of CO2 Utilization*, 34, 78-91. https://doi.org/10.1016/j.jcou.2019.11.003

- Mackay, D. M., Lambert, J. M., & Shah, A. (2018). Metal-ligand catalysts for green chemistry. *Advanced Materials*, 30(23), 1-10. https://doi.org/10.1002/adma.201800694

- Mackay, D. M., Zhang, Z., & Yu, Y. (2018). Bioinspired catalysts for renewable energy applications: Challenges and perspectives. *Chemical Society Reviews*, 47(21), 7988-8015. https://doi.org/10.1039/C8CS00321G

- MacLachlan, G. L., Shan, C., & Stokes, H. (2019). Developing sustainable metal catalysts for chemical reactions. *Science*, 365(6448), 276-280. https://doi.org/10.1126/science.aaw0519

- Shao, M., Liu, X., & Liang, C. (2016). Advances in bioinspired metal catalysts for sustainable chemistry. *Journal of the American Chemical Society*, 138(7), 2143-2151. https://doi.org/10.1021/jacs.5b13399

- Shao, Y., Li, H., & Zhang, J. (2017). Bioinspired iron and copper catalysts for selective oxidation reactions. *Journal of the American Chemical Society*, 139(22), 7527-7539. https://doi.org/10.1021/jacs.7b06565

- Wang, J., Xu, H., & Liu, P. (2018). Bioinspired catalysts for selective oxidation reactions: Mechanistic insights and catalytic applications. *Advanced Functional Materials*, 28(34), 1803125. https://doi.org/10.1002/adfm.201803125

- Wu, S., Wang, L., & Wang, Y. (2017). Bioinspired multi-step catalysis: Challenges and opportunities. *Chemical Society Reviews*, 46(20), 6629-6642. https://doi.org/10.1039/C7CS00463E

- Zhu, X., Zhang, Z., & Xu, Z. (2016). The stability of bioinspired catalysts: Challenges and strategies. *Chemical Science*, 7(7), 4852-4859. https://doi.org/10.1039/C6SC02412