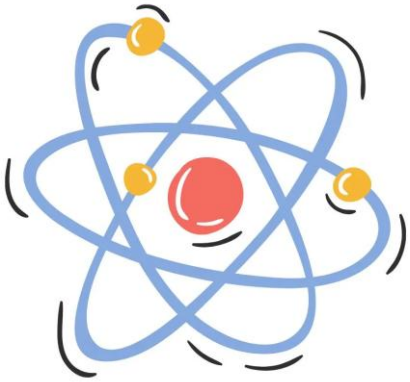

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Sonu Prasad, Jyoti Sharma, Gurdeep Sangwan, Avinash Rani

Department of Chemistry, MMEC, Maharishi Markandeshwar (Deemed to be University), Mullana- 133207(Ambala), India

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Sonu Prasad, Jyoti Sharma*, Gurdeep Sangwan, Avinash Rani
Department of Chemistry, MMEC, Maharishi Markandeshwar (Deemed to be University), Mullana- 133207(Ambala), India
Corresponding Author: E-mail: jsharma117@gmail.com

ABSTRACT: *A Schiff base metal complex has emerged as an effective catalyst in oxidation chemistry because of its remarkable structural diversity, tunable electronic stabilization properties, and ability to tolerate multiple oxidation states. This review examines the catalytic potential of Schiff base complexes derived from aldehydes and amines, coordinated with transition metal ions covering the 3d, 4d, and 5d series. Several green oxidants are mentioned, including hydrogen peroxide, tert-butyl hydroperoxide, and molecular oxygen, which are used to promote environmentally benign oxidation processes. In this paper, we discuss the mechanisms underlying these catalytic transformations, emphasizing how ligand architecture, metal centers, and reaction conditions affect catalysis efficiency and selectivity. In this study, we investigated how electronic and steric factors control the redox behavior of mono- and polynuclear complexes. Additionally, this review draws attention to recent developments in heterogeneous and recyclable Schiff metal complexes designed for sustainable oxidation methods. The discussion concludes with a discussion of the challenges and future perspectives associated with developing next-generation Schiff base catalysts that are able to enhance their activity, stability, and compliance with green chemistry requirements.*

Keyword: *Schiff base, Metal complexes, Green chemistry, Oxidation reactions, Sustainable catalysis.*

1. INTRODUCTION

Schiff bases with the general structure: $R^1R^2C=NR^3$ (R^3 = alkyl or aryl, but not hydrogen), are one of the sub-classes of imines. The name Schiff is derived from a German scientist, Hugo Schiff, who characterized the by-products of the reaction between primary amines and carbonyl compounds in 1864, giving rise to the moniker "Schiff's base" [1]. Pfeiffer began using them as ligands in the 1930s [2]. Spectroscopic methods such as ^{13}CNMR, ^{1}H-NMR, UV-Vis, and X-ray crystallography were used to confirm this phenomenon of tautomerism [3-4]. The studies have also found that in polar solvents, the keto form predominates while in nonpolar solvents, the enol form does [5]. Metal complexes are prepared when a metal ion coordinates with a Schiff base. This interaction leads to the establishment of a stable coordination complex, where the Schiff base functions as a ligand [6]. Schiff bases can form complexes with various metal ions, including transition metals like copper, nickel, iron, and cobalt as well as other metal ions such as zinc, silver, and mercury. The presence of another donor atom, such as SH or OH, near azomethine linkage makes the Schiff bases to form complexes with 4,5 or 6 membered rings of high stability [7][8]. These compounds are widely applied in a wide range of industries and applications, like food, agrochemical, dye, analytical chemistry, catalyst [9], energy storage, environmental [10], nanotechnology, bio-sensing, chemo-sensing, and biomedical applications: antiviral, antifungal, antibacterial and anticancer [11-13]. Schiff base metal complexes are showing excellent catalytic activity in several chemical transformations like polymerisations, coupling reactions, aldol condensation and oxidation reactions. These complexes

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can be easily modified to fine-tune their electronic and steric properties, allowing for the design of catalysts with specific reactivity and selectivity profiles [14]. With the ability to catalyze oxidation, reduction, hydrolysis, and carbon-carbon bond formation reactions, Schiff base metal complexes offer broad applicability in organic synthesis [15].

2. OXIDATION REACTIONS

Oxidation reactions are fundamental chemical processes that can be explained in a variety of ways, such as when an atom, ion, or molecule loses electrons, when oxygen is added to a substance, when hydrogen is removed from it, or when an element's oxidation number rises during a process. In this article, discussion is focus on chemical transformation happening by addition of oxygen form oxidizing agent with the help of Schiff base metal complexes. Different chemical substrate shown different oxidation activity with oxidizing agent as well as Schiff base metal complexes (as catalyst). This chemical transformation (oxidation) is affected by several chemical and physical parameters like reaction concentration, mole ratio of oxidizing reagent, mole ratio of catalyst, reaction temperature and pressure etc. As in literature several catalytic oxidations have been explained in research articles, review articles and several books. Among them some useful and informative summarization have been explained in this review article.

3. Oxidation of organic sulfide

The oxidation of organic sulfides to their corresponding sulfoxides and sulfones represents an important transformation in both synthetic and industrial chemistry. Sulfoxides and sulfones serve as key intermediates in the synthesis of pharmaceuticals, agrochemicals, and fine chemicals, as well as in materials and asymmetric synthesis. Traditional oxidation methods often employ stoichiometric oxidants such as peracids, chromium (VI) reagents, or permanganates, which are environmentally hazardous and generate large amounts of toxic waste.

In recent decades, Schiff base complexes of transition metals such as Mn, Fe, Co, Cu, Ni, and Zn have been explored as efficient catalysts for the selective oxidation of sulfides using environmentally benign oxidants like hydrogen peroxide (H_2O_2), tert-butyl hydroperoxide (TBHP), and molecular oxygen (O_2). Saeid Menati and colleagues [16] provided a detail of four Schiff base complexes synthesis (e.g. Pd_2LCl_4, Zinc $L(NO_3)_2$ complex, Nickel LCl_2 complex, and Cobalt $L(NO3)_2$). The ligand (L) was synthesized by reaction between amine (1,2-bis(2′-aminophenoxy)) and aldehyde (2-pyridinecarbaldehyde), followed by direct reaction with the respective metal salts to form the complexes. These complexes exhibited low solubility in both polar like water, methanol, ethanol, acetonitrile, dimethylformamide, dimethyl sulfoxide and non-polar solvents like chloroform, dichloromethane, and THF. To assess their catalytic efficacy in the oxidation of Thioanisole, they were employed as different kinds of catalysts (heterogeneous), with H_2O_2 serving as the oxidizing agent. Among the complexes, the palladium Schiff base complex (Pd_2LCl_4) demonstrated the highest catalytic activity and selectivity for sulfone production. Consequently, the Palladium (II) schiff base complex was utilized as a catalyst in acetonitrile to facilitate the oxidation of various sulfides into their respective sulfones with H_2O_2 serving as the oxidizing agent.

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S. Menati et al. [17] conducted a study in which a bidentate ON type ligand was synthesized through the reaction of Isopropyl amine and Salicylaldehyde. This ligand was then reacted with $VO(acac)_2$ in 2:1 ratio in the presence of triethylamine at room temperature, resulting in the formation of an VO (IV) complex (VOL_2). The selective oxidation of Thioanisole was used to evaluate the catalytic efficiency of VOL_2. This oxidation reaction was performed with the environmentally friendly oxidant H_2O_2 (35% aqueous solution), both in solvent-free conditions and in various organic solvents, including EtOH, $CHCl_3$, CH_2Cl_2, DMF, CH_3CN, and EtOAc. The results, summarized in **[Tables 1,2]** indicate that the choice of solvent and H_2O_2 concentration significantly influenced the selectivity toward sulfone or sulfoxide. The highest sulfone selectivity was observed under solvent-free conditions, with an increase in oxidant concentration up to 1.5 mmol further enhancing the yield.

Table 1: Selection of Solvent

Solvent	H_2O_2 (mmol)	Selectivity (%)
Neat	1.5	100
Ethanol	1.5	88
Dichloromethane	1.5	78
Acetonitrile	1.5	68
DMF	1.5	68
Ethyl acetate	1.5	28

Table 2: Selection of Quantity of H_2O_2 (without solvent)

Catalyst (mmol)	H_2O_2 (mmol)	Conversion(%)	Selectivity(%)
0.01	0.5	65	45
0.01	0.7	69	52
0.01	1	80	58
0.01	1.2	83	75
0.01	1.5	100	100
0.01	2	100	100

Ryuji Ando et al. [18] synthesized resin-based polymer-supported Schiff base metal complexes of oxovanadium (IV). The ligand **[Figure 1]** was prepared by reacting salicylaldehyde with 2-aminoethanol in dichloromethane, followed by complexation with $VO(acac)_2$. The resulting Schiff base metal complex was then isolated through crystallization using diethyl ether. Additionally, the researchers synthesized various other Schiff base metal complexes by modifying the amine and aldehyde components using the same chemical approach. A summary of the ligands produced is provided in **[Table 3].**

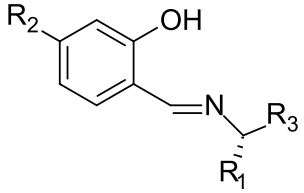

Figure 1: Schiff base ligand

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Table 3: List of Ligand and Respective Metal (V) Complex

Ligand				Respective V complex
	R-1	R-2	R-3	
L-1a	H	H	OH	**1-a**
L-2a	$CH_2–C_6H_5$	H	OH	**2-a**
L-3a		H	OH	**3-a**
L-4a	$CH_2–C_6H_5$	H	CO_2H	**4-a**
L-1b	H	OH	OH	**1-b**
L-2b	$CH_2–C_6H_5$	OH	OH	**2-b**
L-3b		OH	OH	**3-b**
L-4b	$CH_2–C_6H_5$	OH	OH	**4-b**

The catalytic behaviour of the polymer-based metal complexes of Schiff base was evaluated in the oxidation of sulfides, using methyl phenyl sulfide as the substrate. The conversion of methyl phenyl sulfide to its corresponding sulfoxide over time is summarized in **[Table 4].**

Table 4: Effect of Catalyst on Sulfide Oxidation

Catalyst	10 minutes	30 minutes	60 minutes	90 minutes
1-a	85	99	-	-
2-a	42	80	93	96
3-a	31	54	75	88
4-a	40	75	88	96
PSVC1	55	80	88	92
PSVC2	35	62	78	85
PSVC3	20	51	69	80
PSVC4	32	59	74	81

PSVC1= [mer-VO(salae)], PSVC2 = [mer-VO(salpheol)], PSVC3 = [mer-VO(salhisol)], PSVC4 [mer-VO(salphe)]
(mer = Merrifield resin)

They have also explained the advantage of polymer support Schiff base metal complexes for recyclability in multiple time use. By polymer support this homogeneous catalyst became heterogeneous and help to recycle of metal complexes in several run as given in below **[Table 5]**.

Table 5: Re-use of complexes

Catalyst	Trial-1	Trial-2	Trial-3
PSVC1	92	90	85
PSVC2	85	89	85
PSVC3	80	81	73
PSVC4	81	68	53

For oxidation of sulfide to sulfoxide, Schiff base metal complexes showing excellent activity with environment friendly oxidizing reaction i.e. hydrogen peroxide in very short time 60-120 minutes in neet without solvent. Some polymer-supported complexes achieved an 80–90% yield within 90 minutes, efficiently converting sulfide into the corresponding sulfoxide in the presence of peracid.

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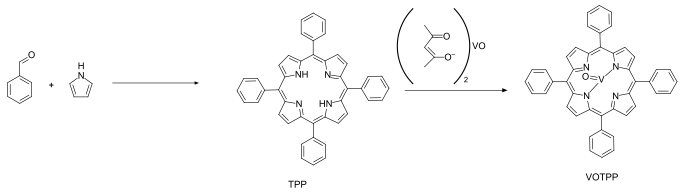
Several researchers [19–23] have investigated why Complex 3a, which was expected to have an imidazole nitrogen in the axial position, displayed the slowest reaction rate over the 90-minute period. The fastest oxidation rate was observed for PSVC1 and 1a, both of which lacked substituents. Regarding recyclability, PSVC1 and PSVC2 retained nearly the same activity after three cycles, whereas PSVC3 demonstrated moderate activity, and PSVC4 showed the lowest activity.

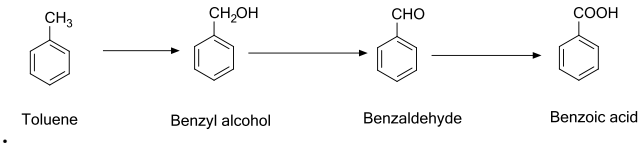
4. Oxidation of Toluene

The selective oxidation of toluene to value-added oxygenated products such as benzaldehyde, benzoic acid, and benzyl alcohol has attracted significant attention due to its industrial and environmental importance. Traditionally, toluene oxidation has been carried out using stoichiometric oxidants like chromates, permanganates, or nitric acid under harsh conditions, often leading to poor selectivity and the generation of large amounts of toxic waste. Therefore, the development of environmentally benign, efficient, and selective catalytic systems has become a key objective in green chemistry. The catalytic performance of Schiff base metal complexes in toluene oxidation largely depends on the nature of the central metal ion, the ligand framework, and the oxidant employed. Jia *et al* [24] have explained the aerobic oxidation of toluene to benzaldehyde, benzyl alcohol and benzoic acid in the presence of tetra phenyl porphyrin (TPP) metal complex of vanadyl acetyl acetonate [$VO(acac)_2$]. In this research, Schiff base was synthesized by benzaldehyde and pyrrole in o-xylene (solvent) via refluxing for 4 hrs **[Scheme-1]** [25]. Isolated crude Schiff base is crystallized in dichloromethane to get purple colour crystal as tetra phenyl porphyrin (TPP).



Scheme 1: Synthesis of Vanadium complex

Schiff base (TPP) reacts with vanadyl acetyl acetonate [VO(acac)2] in phenol after 9 hours of heating to create VOTPP [26]. For catalytic aerobic oxidation of toluene, 0.3 g VOTPP is used for 100 ml of toluene with 0.8 MPa oxygen gas pressure at 145°C and analyzed by HPLC (benzoic acid) and GC (benzaldehyde and benzyl alcohol) **[scheme 2].**



Scheme 2: Oxidation of Toluene to Benzyl alcohol, Benzaldehyde and Benzoic acid

The optimum conversion of the product is explained by series of experiments. The best condition for optimum conversion is 0.3 g VOTPP for 100 cm^3 of toluene at 145°C with oxygen gas pressure 0.8MPa for 4 hrs (**Scheme-2**). The benzoic acid selectivity under this condition is 86% with a toluene conversion 23%.

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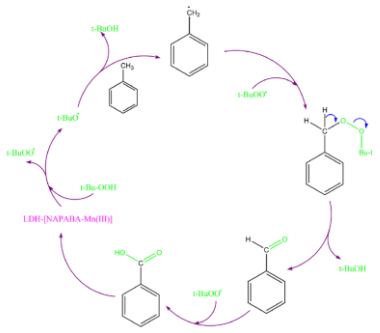
The catalytic oxidation of toluene in the presence of Schiff base metal complexes supported by layered double hydroxides has been investigated by Kirar et al [27]. The NAPABA-M complex is synthesized in-situ by adding metal salts, either ferric chloride or manganese acetate, to 20 mL of methanol and NaOH solution. The metal complex is separated after four hours of drying and filtering. Additionally, the ligands LDH.[NAPABA] and LDH.[$NH_2.C_6H_4COO$] [28–30] were synthesized using a 2-hydroxy-1-naphthaldehyde solution in methanol. The formation of imine bonds caused the solution to turn yellow. The mixture was then refluxed for three hours under continuous stirring in a nitrogen atmosphere. The resulting yellow solid was filtered, washed with methanol and acetonitrile, and dried overnight at 60°C. The heterogeneous catalysts LDH[NAPABAMn(Cl)] and LDH[NAPABAFe(Cl)] were prepared by refluxing a hot methanolic solution of the respective metal salts with LiCl. As shown in **[Scheme 3]**, the catalytic activity of NAPABA.M and LDH.[NAPABA.M**]** catalysts were evaluated using the oxidation of toluene with tert-butyl hydrogen peroxide (THP). The results, summarized in **Table 6**, demonstrate that toluene oxidation does not proceed in the absence of these catalysts.



Scheme 3: Plausible mechanism for oxidation of Toluene

The LDH[NAPABAM] complex functions as a heterogeneous catalyst, whereas NAPABAM is a homogeneous catalyst. Compared to its homogeneous counterpart, the heterogeneous LDH.[NAPABAM**]** catalyst demonstrates superior efficiency in the oxidation of toluene to benzaldehyde and benzoic acid. Additionally, key catalytic parameters such as turnover number (TON), % conversion, and % selectivity were calculated [31–32]. The LDH[NAPABAMn(Cl)] catalyst was selected as a model catalyst to investigate the effects of various factors including oxidant type, solvent choice, Tertiary butyl hydrogen peroxide (THP) concentration, catalyst concentration, and reaction temperature on optimizing toluene conversion and benzaldehyde selectivity **[Tables 6–9]**. To determine the optimal oxidant for toluene oxidation, the study evaluated H_2O_2, 70% THP, and 74% THP. No oxidation products were observed when H_2O_2 was used, as it rapidly decomposed due to its highly exothermic nature, and the presence of water hindered the reaction. However, when using 70% and 74% THP in toluene, conversion rates of 25.3% and 55.3%, respectively, were achieved [33]. The lower conversion rate with 70% THP indicated that 74% THP in toluene was the most effective oxidant for maximizing toluene conversion **[Table 8]**.

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Table 6: Effect of Catalysts on Toluene Oxidation to Benzaldehyde and Benzoic Acid

Catalyst	Conversion (%)	Selectivity (%)	
		Benzoic acid	Benzaldehyde
Without catalyst	–	–	–
LDH[NAPABAMn(Cl)] complex	55.3	13.9	86.1
NAPABAMn(Cl) complex	46.5	32.1	67.9
LDH[$NH_2C_6H_4COO$] complex	–	–	–
LDH[NAPABAFe(Cl)] complex	24.6	33.5	66.5
NAPABAFe(Cl) complex	38.4	30.2	69.8

Table 7: Optimization of type of oxidant for oxidation of Toluene.

Catalyst	Oxidizing reagent	Overall conversion (%)	Product selectivity (%)	
			Benzoic acid	Benzaldehyde
LDH[NAPABAFe(Cl)] complex	70% THP	24.6	33.5	66.5
LDH[NAPABAMn(Cl)] complex	70%THP	25.3	31.1	68.9
LDH[NAPABAM] complex	H2O2	Trace	Trace	Trace
LDH[NAPABAFe(Cl)] complex	70%THP	16.8	37.6	62.4
LDH[NAPABAMn(Cl)] complex	70%THP	55.3	13.9	86.1

THP = Tert-butyl hydrogen peroxide

Table 8: Oxidation of Toluene to Benzaldehyde and Benzoic Acid

Catalyst	Oxidizing reagent	Overall conversion (%)	Product selectivity (%)	
			Benzoic acid	Benzaldehyde
LDH[NAPABAM] complex	H2O2	Trace	Trace	Trace
LDH[NAPABAMn(Cl)] complex	70%THP	25.3	31.1	68.9
LDH[NAPABAFe(Cl)] complex	70%THP	16.8	37.6	62.4
LDH[NAPABAMn(Cl)] complex	74% THP	55.3	13.9	86.1
LDH[NAPABAFe(Cl)] complex	74% THP	24.6	33.5	66.5

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Table 9: Catalyst for Conversion and Selectivity of Benzaldehyde from Reported in Different Articles

Catalyst	Oxidant	Toluene conversion	Selectivity of BZ (%)	Ref.
Cu-MCM-22 complex	H_2O_2	9.3	71.1	[39]
MnCo-MOF-74 complex	THP	17.6	98.3	[35]
LDH-[NAPABA-Mn(Cl)] complex	THP	55.3	86.1	[27]
PhMnHMS complex	THP	12.6	11.9	[36]
CoMC complex	THP	9	92.4	[42]
LDH-[NAPABA-Fe(Cl)] complex	THP	24.6	66.5	[27]
Mn_3O_4	THP	45.2	3.4	[37]
Fe_2O_3/HZSM-5	THP	17.3	51.4	[38]
Co-SBA-15	THP	29.9	8.4	[41]
Cu/graphene	H_2O_2	11.5	66.5	[40]
MnOx/SBA-15	THP	24.7	8.3	[34]

For the oxidation of Toluene, Schiff base metal complexes showing excellent activity as catalyst, this review also showing effectiveness of Schiff base metal catalyst comparative traditional oxidizing catalyst as published earlier. This review has evaluate the different Schiff base metal complexes that are more stable, more active, and environmentally friendly heterogeneous catalysts for the solvent-free or with solvent for oxidation of toluene.

5. Oxidation of alkanes

The oxidation of alkanes represents one of the most challenging and important transformations in organic and industrial chemistry. Alkanes are chemically inert due to their strong C–H bonds and lack of functional groups, making their selective oxidation a key goal in both academic research and industrial applications. In this context, transition metal complexes of Schiff bases have attracted considerable attention as potential catalysts for alkane oxidation. Dmytro et al [43] have explained the oxidation of alkane with hydrogen peroxide in the presence of hetero metallic Schiff base metal complex of Co_4^{III} and Fe_2^{III} [**Scheme 4**]. The Schiff base was prepared by the reaction of salicylaldehyde and ethanolamine in dimethyl formamide (DMF) [44].

$$8H_2Sae + 2FeCl_2 + 4Co^0 + 3.5O_2 + 4Et_3N \longrightarrow [Co_4Fe_2OSae_8] + 6H_2O + 4Et_3N\cdot HCl$$

compound-1

Scheme 4: Synthesis of heterometallic Schiff base metal complex

They describe the mild catalytic oxidation of alkanes, highlighting the ability of heterometallic complex (compound-1) to facilitate to oxidize various alkanes with hydrogen peroxide (H_2O_2). The reaction proceeds effectively in an acetonitrile as reaction solvent, a small amount of nitric acid must be present in the reaction mixture. In the absence of key components such as the catalyst (compound-1), co-catalyst (nitric acid), or oxidant (hydrogen peroxide) no

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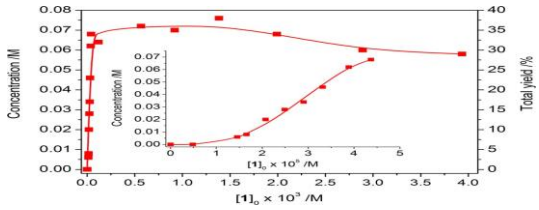
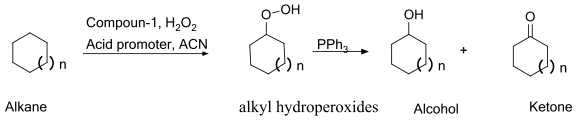


Figure 2: Effect of catalyst concentration on overall yield [43]

significant oxidation products were observed, apart from trace amounts. As illustrated in **[Scheme 5]**, the reaction pathway involves the formation of alkyl hydro peroxides, which subsequently undergo conversion into the corresponding oxidized products (like alcohols, aldehydes, and ketones).



Scheme 5: Oxidation of Cyclic Alkanes

Table 10: Conversion of Cyclic Alkane (Cy alkane)

Performed yield from Cy alkane, %							
Entry	**[Cy alkane], M**	***n*(H_2O_2)/*(Cy alkane)***	**[1] × 10^5, M**	**Ketonic product**	**Alcoholic product**	**Total conversion**	**TON**
1	0.2	5	14	6	32	38	543
2	0.2	5	14	20	11	31	443
3	0.2	5	3.9	2	29	31	1.60 × 10^3
4	0.2	5	3.9	20	7	26	1.34 × 10^3
5	0.6	1.67	4.4	3	23	26	3.57 × 10^3
6	0.6	1.67	4.4	15	9	23	3.20 × 10^3
7	0.8	1.25	4.4	1	15	16	2.83 × 10^3
8	0.37	2.7	11	3	18	21	722

Reaction conditions: Solvent (5 mL), H_2O_2 (30% aq. 1.0 M,), Cy alkane (0.2 M), HNO_3 (65% aq.0.04 M,), 5hrs, 20°C

For oxidation of cyclic alkane (cyclohexane) using hydrogen peroxide (H_2O_2) (30% aq.1.0 Mole,) catalyzed by catalyst (Compound-1), the reaction was carried out in the presence of HNO_3 (65% aq.0.04 Mole,) in ACN (Acetonitrile), with a total reaction volume of 5 mL, at room temperature for 5 hours. As illustrated in **[Figure 2],** they also evaluated the impact of catalyst concentration on the overall yield of oxidized products (cyclohexanol and cyclohexanone) which was analyse by GC following reduction with triphenyl phosphene (PPh_3).

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They also examine the influence of catalyst concentration on the total turnover number (TON), defined as the moles of catalyst with per mole of products. The experimental conditions remain identical to those outlined for **[Figure 3].**

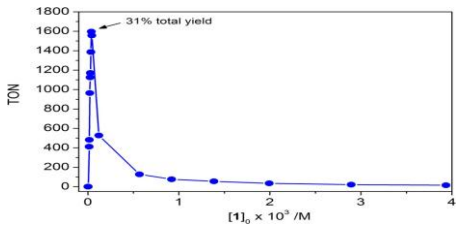

Figure 3: Effect Of Catalyst Concentration On TON [43]

The concentration of cyclohexane (CyH) influences both the total yield of cyclohexanone and cyclohexanol (represented in red) and the total turnover numbers (TONs) (represented in blue colour) in the oxidation of cyclic alkane (cyclohexane) using hydrogen peroxide (H_2O_2) (30% aqueous, 1.0 M). This reaction is catalyzed by catalyst (complex-1) (4.4×10^{-5} Mole) in acetonitrile at room temperature for 5 hours, in the presence of HNO_3 (65% aqueous, 0.04 M) as in **Figure 4**.

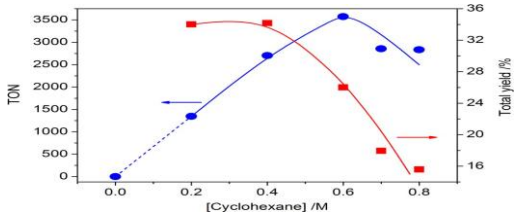

Figure 4: Effect Of Concentration Of Cyclohexane On Overall Yield And Ton[43]

The study highlights how a new Schiff base ligand (polydentate), salicylidene-2-ethanolamine, can be utilized in the "direct synthesis" method to form polynuclear heterometallic complexes with distinctive structures. It is suggested that this system of catalysis represents a new instance of homogeneous catalysis using a heterometallic coordination molecule. Furthermore, it is the first instance where catalytic activity is directly linked to a heterometallic species. The researchers propose that the high activity of the $[Co_2Fe(Sae)_4]^+$ complex may be attributed to the unique coordination environment of a tetra-coordinated Fe centre, as well as other elements like Fe-Co redox interactions and hydrogen-bonded support.

Ana Rosa Silva et al. [45] explained the catalytic oxidation of cyclohexane using a homogeneous catalyst composed of biomimetic Schiff base ligands with an N_2O_2 coordination sphere of first-row transition metals, including vanadyl (IV), Manganese (III), Iron (III), Cobalt (III), and Copper (II). The ligand is synthesized by refluxing alcoholic solutions of salicylaldehyde, or 2-pyridinecarboxaldehyde with cyclohexane diamine at a 2:1 molar ratio for one to two hours, following the method outlined by Holm et al [46]. The metal complexes of iron (III), manganese (III), vanadyl (IV), copper (II) and cobalt (III) were prepared using established literature methods [46, 47]. The synthesized metal complexes of Schiff base are shown in **Tables 11** and the structure of the metal complexes are represented by **Figure 5**.

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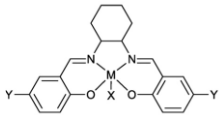


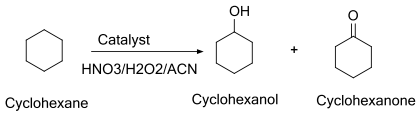
Where: Y= H/Br/CH_3, M=V/Mn/Fe/Co/Cu, X=O/Cl

Figure 5: Structure Of Metal Complexes Of Schiff Base

Table 11: Synthesized Schiff base metal complexes

Sr. No.	Metal salt	Ligand	Schiff base metal complexes
1	Vanadium oxide	Salhyd. (N,N-bis(salicylaldehyde)-cyclohexanodiimine)	[VO(Salhyd)]
2	Manganese chloride		[Mn(Salhyd)Cl]
3	Iron chloride		[Fe(Salhyd)Cl]
4	Iron chloride	Brsalhyd.(N,N-bis(5-bromosalicylaldehyde)-cyclohexanodiimine	[Fe(Brsalhyd)Cl]
5	Iron chloride	Mesalhyd.(N,N-bis(5-methylsalicylaldehyde)-cyclohexanodiimine)	[Fe(Mesalhyd)Cl]
6	Cobalt chloride	Salhyd (N,N-bis(salicylaldehyde)-cyclohexanodiimine)	[Co(Salhyd)Cl]
7	Copper chloride		[Cu(Salhyd)]
8	Iron chloride	Pyhyd.(N,N-bis(2-pyridinealdehyde)-cyclohexanodiimine)	[Fe(Pyhyd)Cl_2]

For the catalytic experiment, they were using 5.0 mmol of cyclohexane, 0.05 mmol of catalyst (homogeneous; 1 mole% with respect to cyclohexane), and 25 mmol of hydrogen peroxide, with 0.5 mmol of HNO_3 in 20 ml of ACN (Acetonitrile) as solvent at room temperature and under atmospheric pressure as shown in **[scheme 5].** They were using cyclohexane/catalyst/HNO_3/H_2O_2, in the ratio of 100/1/10/500 respectively [48]. Since nitric acid has been shown in the literature [49-51] to behave as a promoter for these kinds of reactions, it was employed as a co catalyst. They were quenching the hydrogen peroxide with PPh3 after the reaction completion as described by Shulpin et al [52, 53].



Scheme 5: Oxidation of Cyclohexane

The above catalyst (Table 11) are homogenous catalysts may present dismutase activity [49,54], the slow addition of hydrogen peroxide helps to avoid degradation of catalyst [55]. Oxidation of cyclohexane using acetonitrile as a solvent in excess hydrogen peroxide at ambient temperature. Use of acetonitrile for oxidation of alkane as a solvent are described in several literature [56-63]. Nitric acid use as co catalyst which is described as protomer for this type of oxidation. Most of the Schiff

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base metal complex as a catalyst, listed in **Table 12**, are used to oxidize cyclohexane to produce cyclohexanol and cyclohexanone as products.

Table 12: Conversion of Alkane to alcohol and carbonyl

S.No.	Schiff base metal complexes	Substrate	Co-catalyst/oxidant	OH and C=O ratio	Conversion (%)		Total conversion
					Carbonyl	Alcohol	
1	[Fe(Salhyd)Cl]	cyclohexane	Nitric acid /H_2O_2	0	14.9	0	14.9
2	[Fe(Salhyd)Cl]	cyclohexane	None/HP	2.8	1	2.7	3.7
3	[Mn(Salhyd)Cl]	cyclohexane	Nitric acid /H_2O_2	0	0	0	0
4	[VO(Salhyd)]	cyclohexane	Nitric acid /H_2O_2	3.6	4.6	16.9	21.5
5	[Fe(Salhyd)Cl]	cyclohexane	Nitric acid /H_2O_2	1.4	10.2	14.7	24.9
6	[Co (Salhyd)Cl]	cyclohexane	Nitric acid /H_2O_2	0	0	0	0
7	[Fe(Pyhyd)Cl_2]	cyclohexane	Nitric acid /H_2O_2	74.5	0.2	17.2	17.4
8	[Fe(Mesalhyd)Cl]	cyclohexane	Nitric acid /H_2O_2	3.4	10.5	35.3	45.8
9	[Fe(Salhyd)Cl]	cyclohexane	Nitric acid /H_2O_2	1.3	2.9	3.8	6.7
10	[Fe(Salhyd)Cl]	n-hexane	Nitric acid /H_2O_2	0.4	70.2	25.9	96.1
11	[Fe(Salhyd)Cl]	cyclohexane	HCl/ H_2O_2	0.5	0.2	0.1	0.3
12	[VO (acetylacetonate)$_2$]	cyclohexane	Nitric acid /H_2O_2	3.8	1.1	4.3	5.4
13	[Cu (Salhyd)]	cyclohexane	Nitric acid /H_2O_2	2.4	0.2	0.5	0.7
14	[Fe(Salhyd)Cl]	cyclohexane	Nitric acid /H_2O_2	0.5	4.2	2.3	6.5
15	[Fe (Brsalhyd)Cl]	cyclohexane	Nitric acid /H_2O_2	3.3	4.4	14.6	19
16	[Fe(Salhyd)Cl]	cyclohexane	Acetic acid/ H_2O_2	1.6	2.4	3.8	6.2
17	[Fe(Salhyd)Cl]	cyclooctane	Nitric acid /H_2O_2	0.7	34.6	25.8	60.3
18	[Fe(Pyhyd)Cl_2]	n-hexane	Nitric acid /H_2O_2	1.5	34.9	51.5	86.4

The [Fe(Salhyd)Cl] complex (entry 17) demonstrated the highest catalytic efficiency among the Schiff base metal complexes for oxidizing cyclohexane to cyclohexanol and cyclohexanone. However, consistent with previous literature reports on Manganese (II) and Cobalt (II) complexes with ligands (4N), the [Mn(Salhyd)Cl] (entry 3) and [Co (Salhyd)Cl] (entry 6) complexes exhibited no catalytic activity for this oxidation reaction [61]. At room temperature, Fe (III), Fe (II), VO (IV), and Cu (II) complexes efficiently catalyzed the selective oxidation of cyclohexane to cyclohexanol and cyclohexanone using less than 1 mol% catalyst,

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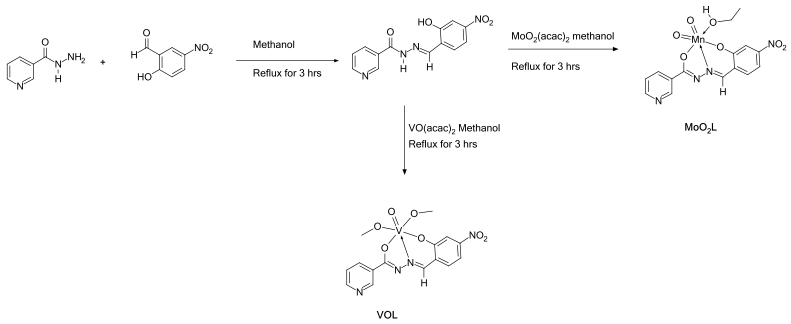
with excess hydrogen peroxide and nitric acid as co-catalysts. In contrast, the Schiff base complexes of Mn (III) and Co (III) produced almost no oxygenated compounds. Additionally, the [Fe(salhd)Cl] and [Fe(Pyhyd)Cl_2] catalyst demonstrated high efficiency in oxidizing cyclo-octane and n-hexane, a linear alkane, primarily yielding the corresponding ketones with a higher turnover number (TON) than observed for cyclohexane.

6. Benzylic alcohol Oxidation

The oxidation of alcohols to their corresponding carbonyl compounds is a fundamental transformation in organic chemistry and plays a pivotal role in both laboratory synthesis and industrial processes. Among various alcohols, **benzylic alcohols** are particularly important due to their prevalence as intermediates in the synthesis of fine chemicals, pharmaceuticals, fragrances, and agrochemicals. Among various alcohols, benzylic alcohols are particularly important due to their prevalence as intermediates in the synthesis of fine chemicals, pharmaceuticals, fragrances, and agrochemicals. Traditional oxidizing agents such as chromium (VI), manganese (VII), and permanganate reagents, though effective, often suffer from significant drawbacks including poor selectivity, harsh reaction conditions, high toxicity, and environmental pollution arising from heavy metal waste.

In recent years, catalytic oxidation using transition metal complexes has emerged as an environmentally benign and efficient alternative. Schiff base metal complexes have attracted considerable attention due to their versatile coordination chemistry, structural tunability, and ability to stabilize metal centres in multiple oxidation states. Hadi Kargar et al [64] explored the oxidation of benzylic alcohols using Schiff base metal complexes of oxovanadium (VO) and dioxo molybdenum (MoO_2) with urea hydrogen peroxide (UHP) in acetonitrile as solvent. The metal complexes were synthesized by reacting $VO(acac)_2$ and $MoO_2(acac)_2$ as metal oxide sources with an H_2L-type ligand in methanol under reflux conditions. As illustrated in **[scheme 6]**, the ligand H_2L was prepared by combining amine (nicotinic hydrazide) and aldehyde (5-nitrosalicylaldehyde) in an equimolar ratio in methanol.



Scheme 6: Synthesis of VO and MoO_2 metal complexes

The catalytic applications of dioxo molybdenum (MoO_2) and oxovanadium (VO) complexes have been widely use as catalyst in various oxidation reactions, that produces oxidation product, like, aldehydes and ketones from alcohols, sulfoxides from sulfides and epoxidation of alkenes, as reported in the literature [65–78]. Additionally, molybdenum (Mo) and vanadium (V) complexes have been employed as catalysts in numerous chemical transformations [79, 80]. Their study focuses on

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evaluating the catalytic efficiency of MoO_2L and VOL complexes for oxidation of benzylic alcohols. Urea hydrogen peroxide is utilized as the oxygen source for oxidation of other benzylic alcohol (4-chloro derivative) in different solvent, including alcohol, acetone, acetonitrile (ACN), dichloromethane, 1,2-dichloroethane, $CHCl_3$, and CCl_4, with 0.006 mmol of Mo or V complex. The summarized results are presented in **Table 13**.

Table 13: Impact Of The Solvent On Oxidation With Uhp, Which Is Accelerated By Vol And Moo_2l Complexes

Sr.No.	Solvent use	Impact of VOL complex on Yield %	Impact of MoO_2L complex on yield (%)
2	CH3CH2OH	50	35
3	$ClCH_2CH_2Cl$	30	20
4	CHCl3	30	20
5	CH COCH	80	50
6	CH2Cl2	0	0
7	CCl4	5	0

UHP was found to be the most efficient oxygen source among the screening oxidants, which comprised $NaIO_4$, H_2O_2, UHP, Bu_4NIO_4, and tert-BuOOH as shown in **Table 14**.

Table 14: Impact of oxidant on 4-chlorobenzyl alcohol oxidation mediated by MoO_2L and VOL complexes

Oxidant	Impact of VOL complex on Yield %	Impact of MoO_2L complex yield (%)
Without oxidant	0	0
Sodium periodate	15	20
Hydrogen peroxide	75	70
Urea hydrogen peroxide	90	88
Tetrabutylammonium periodate	5	0
tert-Butyl hydroperoxide	50	40

4-chlorobenzyl alcohol in acetonitrile with UHP has been oxidized under reflux temperature using different concentrations of the catalyst. Using 0.006 mmole of the VOL catalyst, it was discovered that the oxidation process took 10 minutes to finish and that increasing this amount had no discernible effect on the rate of reaction or yield. The ideal quantity of the catalyst (Mo complex) was the same in this reaction as in **Table 15**, except for a longer reaction time (2 hours).

Table 15: Influence of catalyst quantity (VOL and MoO2L complexes) on oxidation

Catalyst quantity (mmole)	VOL in 10 minutes Yield (%)	MoO_2L after 2h yield (%)
without catalyst	0	0
0.002	15	20
0.004	75	70
0.008	90	88

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The compounds' catalytic activity was further shown by oxidizing benzylic alcohols in acetonitrile with UHP. A high product yield and a quick reaction completion time are two advantages of the current strategy.

Al-Saeedi et al.[81] developed nanoscale Schiff base metal complexes using Cu and Ni and explored their catalytic performance in benzylic alcohol oxidation. These synthetic Schiff base ligands were derived from the condensation of 2-amino-3-hydroxypyridine with either 4-nitrobenzaldehyde or 3-methoxysalicylaldehyde. The resulting metal complexes from cupper and nickel metals (metal complexes: abpv.Cu, ahpnb.Cu, ahpv.Ni, and ahpnb.Ni) and were then converted into metal oxide nanoparticles (NiO and CuO) to facilitate the homogeneous oxidation of benzyl alcohols. Metal oxides have gained substantial attention due to their remarkable stability under extreme reaction conditions and their catalytic versatility in crucial chemical transformations [82–88]. However, a key challenge remains in designing nanotechnology-based metal complexes that not only endure harsh environments but also meet the required catalytic efficiency standards [89–92]. Other experimental parameters examined in the study included the influence of concentration, reaction temperature, and type of solvents for the benzyl alcohol (BzOH) oxidation. The results demonstrated that both the parent Schiff base metal complexes and their corresponding metal oxides (MO) exhibited high catalytic efficiency, achieving nearly 100% selectivity for the oxidation of benzyl alcohol to benzaldehyde (BzH) under moderate conditions **Table 16**.

Table 16: Benzyl Alcohol Oxidation By Using Metal Oxides And Schiff-Base Metal Complexes

Catalyst	Benzyl alcohol Conversion (%)	Product (Benzaldehyde) Selectivity (%)	Ref.
[1]ahpv.Cu	95	100	[81]
[1]ahpnb.Cu	94	100	[81]
[2]npisnph.Cu	79	100	[93]
[2]bsisnph.Cu	90	100	[93]
[1]Cu.O	96	100	[81]
[3]Cu.O	69	91	[82]

The impact of reaction temperature and time: The impact of reaction temperature for catalytic behaviour of the synthesized metal complexes (schiff base-M(II) (M = Cu and Ni) and metal oxides (MO) for the oxidation of benzyl alcohol was assessed and optimized across different reaction temperatures (60, 70, 80, and 90°C) and reaction times. Some other articles [94] also explain the impact of reaction temperature on oxidation of benzyl alcohol to corresponding aldehyde and acid.

Impact of the type of solvent: As demonstrated in previous studies, solvent properties significantly influence the catalytic oxidation of alcohols, affecting conversion yield as well as stereo- and chemo-selectivity [93–96]. They evaluate by using various solvents, including N,N′-dimethylformamide (DMF), acetonitrile (ACN), acetone, and dimethyl sulfoxide (DMSO). The results of these catalytic reactions, conducted under optimal conditions for each catalyst, are summarized in **Table 17**.

Table 17: Effect of solvent for oxidation of Benzyl alcohol

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Catalyst	Solvent	Temp. (°C)	Time (h)	Yield (%)				conversion (%)	Selectivity (%)
				BzH	BzA	Side Product	Unreacted		
ahpnv.Cu complex	Dimethyl formamide	70	2	33	0	0	67	33	100
	Acetone			7	7	0	86	14	50
	Dimethyl sulfoxide			95	0	0	5	95	100
	ACN			48	0	0	52	48	100
ahpnb.Cu complex	Dimethyl formamide	70	2	44	0	0	56	44	100
	Acetone			25	11	0	64	36	69
	Dimethyl sulfoxide			94	0	0	6	94	100
	ACN			46	0	0	54	46	100
ahpnv.Ni complex	Dimethyl formamide	70	1	15	0	0	85	15	100
	Acetone			5	4	3	88	12	42
	Dimethyl sulfoxide			55	0	0	45	55	100
	ACN			28	0	0	72	28	100
Copper oxide	Dimethyl formamide	70	2	61	0	0	39	61	100
	Acetone			18	11	4	67	33	54
	Dimethyl sulfoxide			98	0	0	2	98	100
	ACN			66	0	0	34	66	100
Nickel oxide	Dimethyl formamide	70	1	52	0	0	48	52	100
	Acetone			45	12	0	43	57	79
	Dimethyl sulfoxide			97	0	0	3	97	100
	ACN			84	0	0	16	84	100

Reaction condition: ahpv.Cu complex (0.03 mmol) catalyzed the oxidation of benzyl alcohol with aq. Hydrogen peroxide (3.00 mmol) [81]. (BzH) = benzaldehyde, BzA= benzoic acid

From the above data DMSO is the most effective solvent with all catalysts, facilitating a conversion 94.0–98.0% of benzyl alcohol to benzaldehyde, the data also suggest that solvent choice play significant impacts on catalytic activity. Among them, CuO showing highest conversion (98%) compared to its metal complex (ahpnb.Cu complex) exhibited the conversion (~94%) and selectivity (~100%) for benzyl alcohol oxidation in DMSO. Although NiO achieved a high benzaldehyde (BzH) yield of 92.0–97.0%, its while its Ni complex exhibited the lowest conversion (~55%). This suggests that Cu complexes of that schiff base are more effective catalysts than their Ni complex under these conditions.

Effect of concentration of catalyst: The concentration of catalyst plays an important role in the oxidation of alcohols like benzyl alcohol, significantly

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influencing reaction kinetics and by-product yields, particularly for benzaldehyde [97–102]. To investigate this effect, varying molar ratios (0.01 mmol, 0.02 mmol, 0.03 mmol, and 0.04 mmol) of the three Schiff base complexes (ahpv.Cu, ahpnb.Cu, and ahpv.Ni) and its corresponding metal oxides (CuO and NiO) were introduced into a benzyl alcohol solution in DMSO with aqueous H_2O_2. This allowed for a systematic evaluation of how catalyst concentration impacts oxidation efficiency. As previously reported [103], DMSO is the optimal solvent for the efficient catalytic oxidation of benzyl alcohol using the ahpv.Cu, ahpnb.Cu, and ahpv.Ni complexes, as well as CuO and NiO. Under reaction conditions of 70°C for two hours and a catalyst concentration ranging from 0.01 to 0.03 mmol, DMSO enabled the highest catalytic performance.

7. CONCLUSION AND PROSPECTS

In summary, this study stands out for its detailed examination of catalytic oxidation using Schiff base metal complexes, showcasing recent advancements and environmental advantages. It highlights the complexes' efficiency, selectivity, and versatility, especially having transition metals like zinc, copper, vanadium, and manganese. The study tackles issues such as catalyst deactivation and limited recyclability, suggesting solutions like immobilization on solid supports and hybrid catalytic systems. It offers in-depth insights into various oxidation processes, including the oxidation of organic sulfides, toluene, alkanes, and benzylic alcohols.

Looking ahead, future research should focus on optimizing reaction conditions and improving catalyst stability. Exploring new ligand designs and hybrid catalytic systems can further enhance performance. Understanding the mechanistic pathways and broadening the range of oxidation reactions facilitated by Schiff base metal complexes will be crucial. Additionally, developing more sustainable and environmentally friendly catalytic processes remains a priority. This review provides valuable direction for future research in sustainable oxidation technologies, with following outcomes.

1. **Focused Oxidation Analysis**: Concentrates on oxidation reactions, detailing catalytic efficiency, selectivity, and mechanisms of Schiff base metal complexes.
2. **Recent Innovations**: Highlights advancements like water-soluble ligands and green synthetic methods, not widely covered in other reviews.
3. **Environmental Benefits**: Emphasizes mild conditions and green oxidants, aligning with green chemistry principles.
4. **Mechanistic Insights**: Provides in-depth understanding of how these complexes stabilize intermediates and enable electron transfer.
5. **Diverse Oxidation Applications**: Covers a wide range of oxidation reactions, including organic sulfides, toluene, alkanes, and benzylic alcohols.

Overall, this review offers a focused, environmentally conscious, and detailed of the catalytic oxidation potential of Schiff base metal complexes, guiding future research in sustainable oxidation technologies.

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7. CONFLICT OF INTEREST:

The authors declare that there is no conflict of interests regarding the publication of this article.

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