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# Catalytic Oxidation of Phenols, Benzyl alcohols and Olefins using Schiff Base Metal Complexes- A review

**Fayaz Ahmad Bhat[1], Ghulam Mohammad Jan[1*], Haroon Rashid Boked[1]**

*1.Department of Chemistry, Govt. Degree College Boys, Anantnag Jammu & Kashmir (India)*

## ABSTRACT

There are a large number of important organic transformations such as oxidation, hydrogenation, hydroformylation, carbonylation, polymerization and various coupling reactions. The majority of these novel catalysts are based on silica, primarily since silica displays many advantageous properties excellent stability (chemical and thermal), high surface area, good accessibility, and organic groups can be robustly anchored to the surface, to provide catalytic centers. In this study we only discuss the catalytic application of schiff base metal complexes in the field of oxidation of phenol, benzyl alcohol, olefin etc

**Keywords:** High surface area, good accessibility, excellent stability, catalytic centers, benzyl alcohol, olefin

*Corresponding Author Email: gmjan64@gmail.com

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# INTRODUCTION

A large number of tetra dentate Schiff base ligands are reported in literature. Majority of them are derived from salicyl aldehyde and 1, 2-diamines. The ONNO donor Schiff bases form a family of compounds salen or salophen, which posses a wide variety of applications. Similarly there are a good number of reports on tridentate Schiffbases[1-3].

**Biopolymer (Chitosan) Schiff bases**

Chitosan is produced by the deacetylation of chitin, a major naturally occurring biopolymer, which is one of the key constituents of the shells of crustaceans, and is a by-product of the fishing industry. Chemical modification of chitosan. The applications of chitosan in catalyst are very important. Xia et al. have used Chitosan Schiff base of copper metal complex for cyclo propanation of styrene. IR parrey et al.[4-6] used Chitosan Schiff base metal complex of copper for oxidation of alcohols. Taren et al, and coworkers have used chitosan Schiff base of copper triflate complexes and used them in Huisgen cyclo addition reactions. Duncan et al synthesize the chitosan Schiff base of palladium metal complexes and used them in Suzuki Heck coupling reactions Figure 1

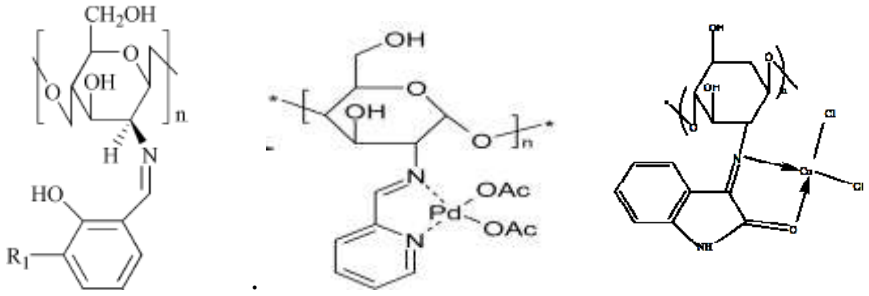


**Figure1: Showing the structures of Schiff base metal complexes derived from Chitosan**

**Hydroxylation of phenol**

The oxidation of phenol by hydrogen peroxide ($H_2O_2$) is a widely applied process in the chemical industry for the preparation of the dihydroxylated derivatives. This oxidation process is frequently reported as taking place through the decomposition of $H_2O_2$ with formation of an unstable electrophilic intermediate, which attacks the phenol nucleus to give a phenoxy ion. This ion can be considered as the precursor of the products usually formed in this process: hydroquinone, catechol and benzoquinone. Phenol and its derivatives are found in wastewaters including those from the oil refining, petrochemical, coke and coal gasification industries. Removal of phenol from such wastewaters is an important challenge for chemists. Diphenols, *i.e.*, catechol and hydroquinone, are considered as important chemicals in industrial

chemistry. Manufacture of diphenols through phenol hydroxylation with $H_2O_2$ as the oxidant has become one of the promising approaches in the 21$^{st}$ century, as the process demands for the simple techniques and produces little environmental pollution. A commercial catalytic process has been developed for hydroxylating phenol using hydrogen peroxide, which tends to produce mixtures containing a major fraction of catechol. A significant fraction of hydroquinone was also formed. The proportion of tarry by-products has been controlled by limiting the use of very low mole ratios of hydrogen peroxide to phenol; but, inevitably, this restricts the extent of conversion of the phenol and hence the space yield of the plant. The catalysts reported to be used in phenol hydroxylation to date are molecular sieves, heteropoly compounds of the Dawson structural type: molybdovanadophosphate and tungstovanadophophosphate, copper–aluminum hydrotalcite-like compounds and metal complexes. The catalysts mentioned above have some catalytic activity for phenol hydroxylation, but the reaction lacks industrial value because of their relatively low yield. Therefore, catalysts with high activity and high selectivity have become an important target in this field.

Many Schiff base complexes are used for catalytic phenol hydroxylation reaction. Copper (II) salicylaldimine complexes have been successfully employed in hydroxylation of phenol [61]. Van Wyk *et al.* reported the catalytic hydroxylationof phenol in aqueous media using cobalt (II) N-(aryl) salicylaldimine Schiff base complexes [7]. They reported catechol and hydroquinone as the products and at higher pH benzoquinone was also obtained. In 2001, Musie *et al.* reported a new method for phenol hydroxylation. They used supercritical carbon dioxide as the medium for reaction which is inert towards oxidation. Polymeric iron (III) Schiff base complexes catalyze hydroxylation of phenol. Due to the insolubility of the complex, the reaction is a heterogeneous catalytic reaction and catechol is obtained as the main product with good selectivity (78-85 %) [8,9].The structure suggested for the polymeric iron (III) complex of the Schiff base, 4-(naphthalen-1-yliminomethyl)-phenol, is given in Figure 2.

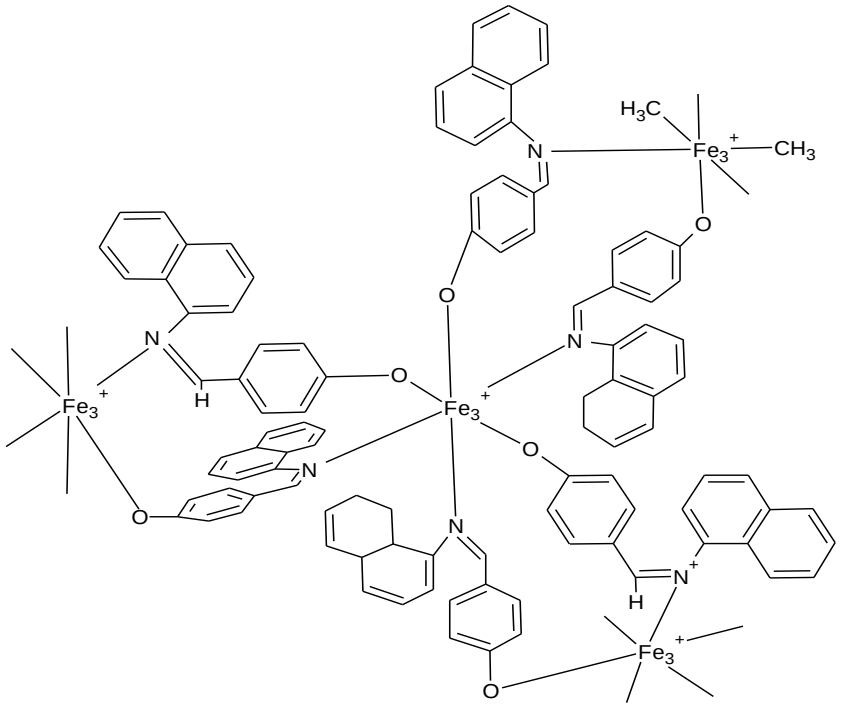


**Figure 2: Structure of the polymeric Iron (III) complex**

Zhang *et al.* [10] studied the hydrogen peroxide oxidation of phenol using a manganese (II) Schiff base complex as mimetic peroxidase and the mechanism suggested by them is given in Figure 6. The mechanism of phenol hydroxylation may follow an ionic pathway or free radical pathway. The reaction proceeds through the formation of the active species from hydrogen peroxide, $OOH^-$, which initially forms an intermediate with metal ion. In the next step a new intermediate, phenol-metal-OOH, is formed. This intermediate facilitates the attack of $OOH^-$ at the ortho and para position of the phenol to form catechol and hydroquinone.

**Oxidation of Cyclohexane**

The selective oxidation of saturated hydrocarbons is one of the most challenging and promising subjects in oxidation chemistry. Cycloalkanes are an important chemical class of hydrocarbons found in diesel, jet and gasoline fuels. The significant industrial production of cyclohexane derivatives $10^6$ton per year of cyclohexanone alone—has stimulated studies aiming to find milder, energy-saving conditions for the oxidation of cyclohexane. The system currently used makes use of soluble salts of cobalt and manganese as catalysts for the oxidation of cyclohexane by oxygen to cyclohexanol and cyclohexanone. Cyclohexanol and cyclohexanone are oxidized by nitric acid to give adipic acid (Figure 6). The oxidation of cyclohexanone by nitric acid leads to the generation of nitrogen dioxide, nitric oxide, and nitrous oxide. The first two gases can be recycled for the synthesis of nitric

acid. Nitrous oxide, however, is an ozone deplete and cannot be recycled. Indiscriminate nitrous oxide emission from this process is therefore the cause of considerable concern. Part of the cyclohexanone can also be converted to the corresponding oxime and then to caprolactam the monomer for nylon-6. Phthalic acids are one of the monomers for the manufacture of polyesters [11,12,13]. Figure 3.

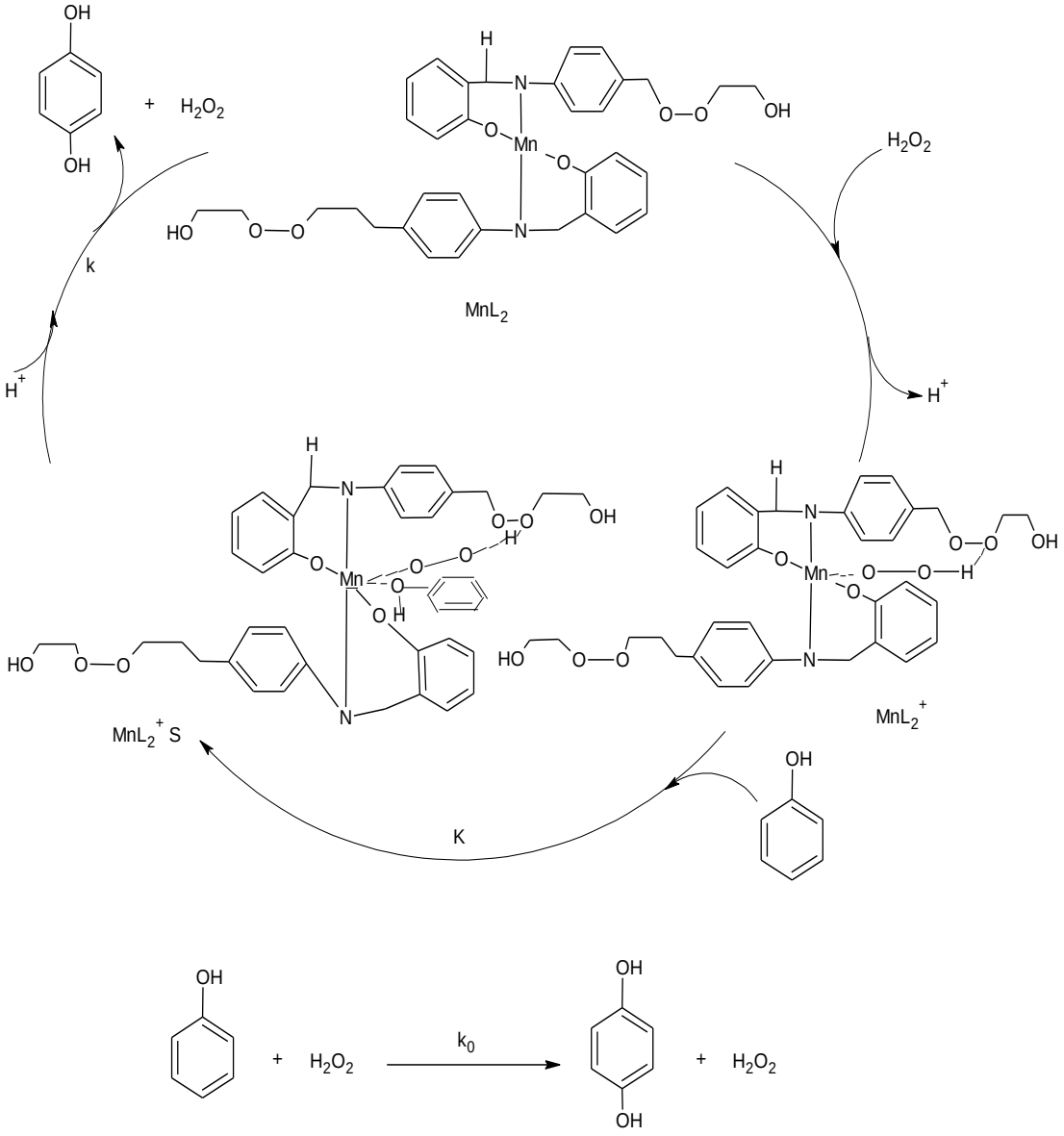


**Figure 3: Mechanism of the oxidation of phenol catalyzed by the Schiff base complexes**

The functionalization of unactivated C-H bonds of cyclohexane requires high pressure and temperature, and a number of catalysts have been developed. In this reaction, various oxidizing agents having active oxygen such as hydrogen peroxide, iodosobenzene, t-butyl peroxide and ozone have been used. Solvents (heptanol, 2-methylpropanal, acetaldehyde), and cocatalysts (such as acetic acid, chloroacetic acid, trifluoroacetic acid) have also been used for this reaction.

Imamoto et al. used porphyrin complexes as catalyst towards oxidation of cyclohexane [66]. Zhou *et al.* used transition metal complexes of deuteroporphyrins as catalyst. They proposed the reaction mechanism involving the intermediate formation of the μ– oxo dimer. In 2002, Rathnaswamy *et al.* used cobalt and manganese cluster compounds for the oxidation of cyclohexane [6] Supported metal complexes are also largely used for cyclohexane oxidation. The Co (II) complex of the Schiff base derived from di aldehyde starch (obtained by periodate oxidative cleavage of the $C_2$-$C_3$ bond in starch) and amino alcohol has been found to be an active and reusable catalyst for cyclohexane oxidation with oxygen. The reaction takes place in the absence of solvents or reducing agents and high turnover number of catalyst and high selectivity of the product could be obtained [14,15]. In 2009 Comba *et al.* [9] proposed a mechanism for the catalytic cyclohexane oxidation on the basis of labelling and computational studies. They have used high valent iron complexes and have proposed both aerobic and anaerobic mechanism (Figure 4) for the reaction

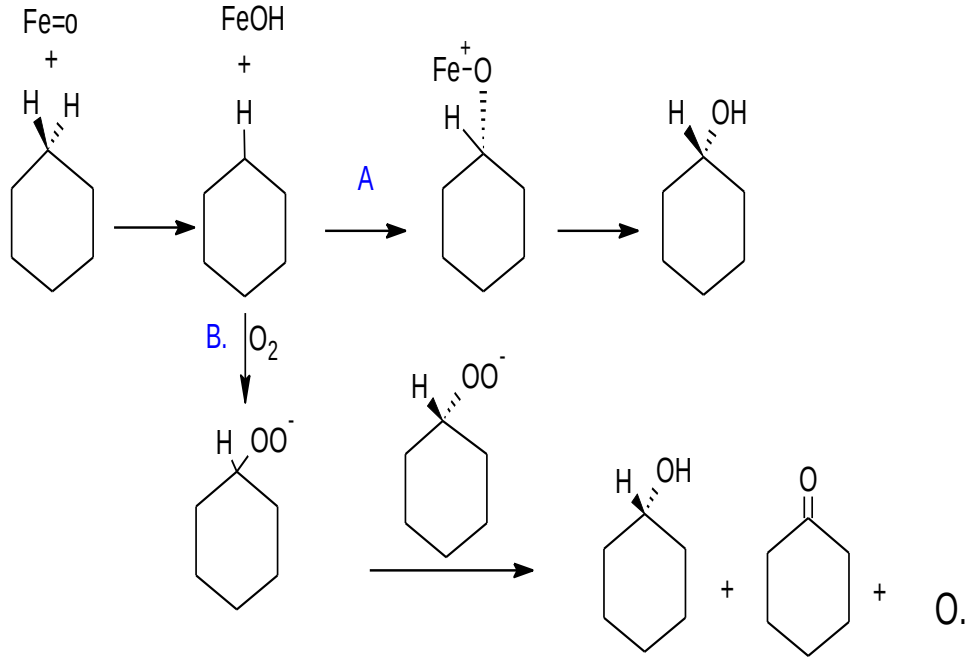


**Figure 4: Anaerobic (A) and Aerobic (B) path way for the ferryl based oxidation of cyclohexane**

**Catalytic Oxidation of benzyl alcohol:**

Traditionally, oxidation of benzyl alcohol to benzaldehyde is performed with stoichiometric amounts of chromium (VI) reagents. These oxidants are not only relatively expensive, but also they generate copious amounts of heavy-metal waste. Moreover, the reaction is often performed in environmentally undesirable solvents like chlorinated hydrocarbons. Hydrogen peroxide is

a clean oxidant compared to other oxidants [10.] To reduce the harmness and cost of solvents, studies towards solvent free process have been carried out The copper (II), manganese (II) and ruthenium (II) [16,17,18] complexes are found to catalyze the selective oxidation of benzyl alcohol to benzaldehyde. Highly selective oxidation of benzylic alcohols to benzaldehyde using active dinuclear manganese (IV) complex as catalyst and hydrogen peroxide or *tert*-butyl hydroperoxide as oxidant was reported by Feringa *et al.* [19]. From an economic and environmental perspective, catalytic aerobic alcohol oxidation represents a promising protocol.

Wang *et al.* [20] in 2007, reported the selective oxidation of benzyl alcohol to benzaldehyde using a supported Cr (salen) complex. The supported complexes show good conversion and selectivity. Kang *et al*. [21] and Ali *et al.* utilized the catalytic activity nanocubic zinc hexacyanoferrate for solvent-free oxidation of benzyl alcohol using $H_2O_2$ as oxidant. The reaction was carried under the optimum conditions of certain parameters such as benzyl alcohol to $H_2O_2$ molar ratio, the amount of catalyst, reaction time and temperature. Figiel *et al.* [22] reported the oxidation of benzyl alcohols to benzaldehydes by the TEMPO/$O_2$ system (TEMPO=*2,2,6,6*-tetra methyl piperidine-1-oxyl).They used copper (II) ethanolamine complexes and the reaction proceeds with a high efficiency (up to 99% yield of benzaldehyde with >99% selectivity) and without the need of any organic solvent, or of an ionic liquid. [23,24,25] Thus this reaction has both environmental and economical benefits in comparison with previously reported systems for benzyl alcohol oxidation [26,27]

## CONCLUSION

Schiff base metal complexes find versatile applications in the field of catalysis. The Schiff base metal complexes of Chitosan Schiff base metal complex of copper for oxidation of alcohols. The Schiff base metal complexes are used for the oxidations of phenols which can latter on used for the for the Manufacture of diphenols through phenol hydroxylation with $H_2O_2$ as the oxidant, The catalytic oxidation of cyclohexanol produces adapic acid which is used for the manufacture of various organic compounds and also used for the manufacture of nylon.

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