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Catalytic Oxidation of Schiff Base metal Complexes: A Review

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ABSTRACT

Catalysis is an area of research which still continues to be a premier area of chemistry. It plays a key role in modern chemical technology. 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. However, it does have drawbacks it has limited stability in aqueous especially basic conditions, and it cannot easily be formed into membranes or into other forms which could be attached to novel reactors for use in intensive processing applications.

Keywords: Schiff base, Oxidation, Catalysis, Polymerization, Synthesis.

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INTRODUCTION

In 1864, German chemist Hugo Schiff developed a new class of organic compounds [1, 2,] these groups of compounds, imines, are often referred to as Schiff bases in his honour. The preparations of these compounds are simple and smart. They are prepared by condensing a carbonyl compound with an amine, generally in refluxing alcohol. The active and well-designed Schiff base ligands are considered as ‘‘privileged ligands’’ by Cozzi [3]. In fact, Schiff bases are able to stabilize many different metals in various oxidation states, controlling the performance of metals in a large variety of useful catalytic transformations. Several studies [4-7] showed that the presence of a lone pair of electrons in a sp^2 hybridised orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance. Ligands containing sp^2 hybridized nitrogen atoms, particularly those in which the N-atom is a part of the aromatic system, show very extensive coordination chemistry [8-10]. Because of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group, Schiff bases are considered as excellent chelating agents, [11-12] especially when a functional group like –OH or –SH is present close to the azomethine group so as to form a five or six membered chelate ring with the metal ion. Details regarding the preparation of Schiff bases and their metal complexes are spread out in the literature. The general scheme of formation of a Schiff base is given in Figure 1.

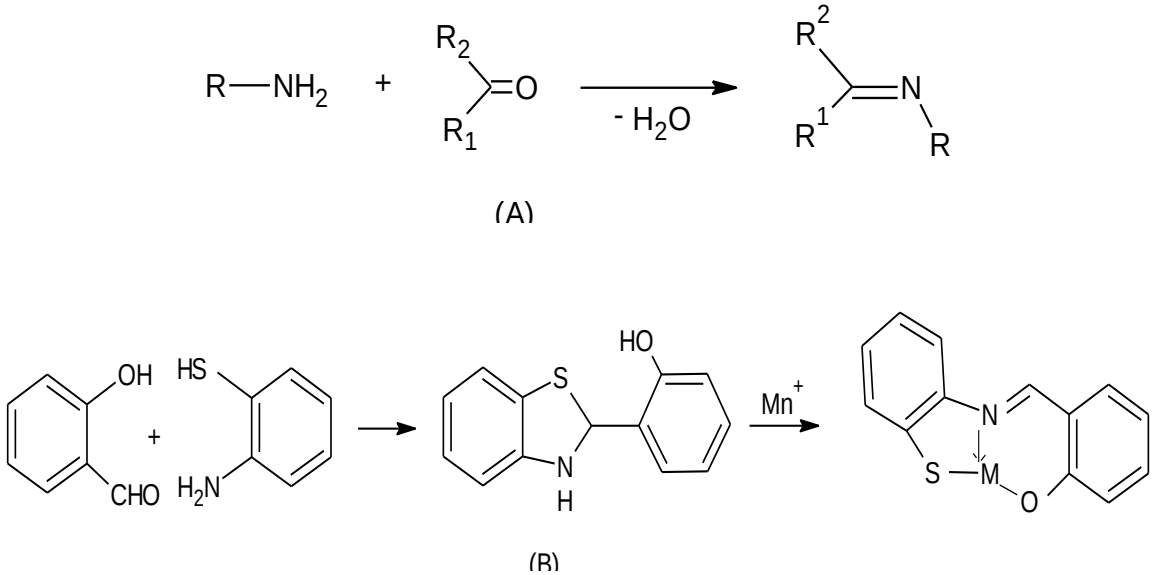


Figure 1: (A) Scheme for the synthesis of Schiff bases (B) Synthesis of benzothiazoline Schiff bases

Like aldehydes, the ketones are also able to form Schiff base ligands. However, Schiff base ligands with ketones are formed less readily than those with aldehydes. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizable [13]. In 1931, Dubsky and Sokol [14] isolated N-N'-bis (salicylidine ethylenediamino) copper (II) and nickel (II) complexes, which led to the formation of a new group of ligands called salen. The salen ligands are often the ligands of choice for several reasons. They are multidentate with four binding sites which form complexes with or without vacant sites for potential catalytic and enzymatic activity. Furthermore, substitution at the aromatic ring can modify the electronic and steric properties of the resulting complexes. In the review on metal complexesof Schiff bases by Holm *et al*., more than half of the referred complexes are derived from salicylaldehyde [6].

A large number of tetradentate Schiff base ligands are reported in literature. Majority of them are derived from salicylaldehyde and 1, 2-diamines (Figure 2). The ONNO donor Schiff bases form a family of compounds, salen or salophen, which possess a wide variety of applications [3]. Similarly there are a good number of reports on tridentate Schiff bases [15-18]. They may be of ONN, ONS, ONO, NNS or NNN donors. The tridentate ligands can tune the formation of complexesand these Schiff base complexes have found various applications in medicines such as antibacterial agents, local anaesthetics, antiviral agents and antispasmodics [19-20.]

Figure 2 Tetradentante Schiff base family (A) salen and (B) salophen

The ONS donor Schiff bases can show symbiosis [22]. The presence of soft sulphur atom softens the hardness of the oxygen atom, and this enables such ligands to form a large number of complexes with structural diversity. The basicity of the Schiff bases also plays a key role in the formation and stabilization of the complexes. The –OH or –SH groups present in the Schiff bases can induce tautomerism in the compound, which leads to complexes with different structures. A large number of salen complexes shows keto-enol tautomerism. Also the deprotonation of thiolic, alcoholic and phenolic groups are favoured due to the stabilization of various oxidation states of the central metal ion.

Catalytic applications of Schiff bases

In Schiff base metal complexes, the environment at the coordination center can be modified by attaching different substituents to the ligand and a useful range of steric and electronic properties essential for the fine-tuning of structure and reactivity can thus be provided [23-25]. The Schiff bases form metal complexes with p-block and d-block metals and these complexes have been known to act as highly efficient catalysts in various syntheses and other useful reactions [26-30]. Many Schiff base complexes of ruthenium and palladium are used as catalyst in the syntheses of quality polymers. Unique asymmetric catalysis of metal complexes of salen and the related Schiff-base ligands has been reviewed by Katsuki [31]. The review summarises the generation of *cis* metallo-salen and its related complexes, their structural features, and their application to asymmetric syntheses. Wang *et al*. in 1999 reported the effective oxidation of olefins using Mn (II) amino acid Schiff base complexes [32]. Gupta and Sutar reviewed the catalytic activities of transition metal complexes-both simple and polymer anchored. They have highlighted the potential of Schiff base complex as catalyst towards oxidations, hydrogenations, polymerizations, various coupling reactions and ring closures [33-34]. Heterogenization of homogeneous catalysts has recently attracted the attention of chemists due to better selectivity and recyclability of the catalysts. In recent years there is an exponential increase in the number of publications in catalysis by supported Schiff base complexes. However, homogeneous catalysis is more reactive and selective.

General reactions catalyzed by Schiff base metal complexes

Schiff base complexes have been used as catalysts in reduction of ketones to alcohols [35] and in the alkylation of allylic substrates [36.] Jacobsen *et al.* found that the enantioselective ring opening of large cycloalkanes are catalysed by chiral Schiff base complexes of cobalt (II) [37] and chromium (III) [38]. The reaction is found to be difficult to take place with routine reagents. Binaphthyl ligands are considered as versatile frameworks for chiral ligands in coordination and metallosupramolecular chemistry [39]. BINAP Schiff base complexes are found to catalyse many reactions [40]. Michael addition was easily carried out in presence of chiral salen Schiff base complexes and complexes of BINAP Schiff bases. Some of the chiral binaphthyl Schiff bases used by Zhou *et al.* are given in Figure 3.

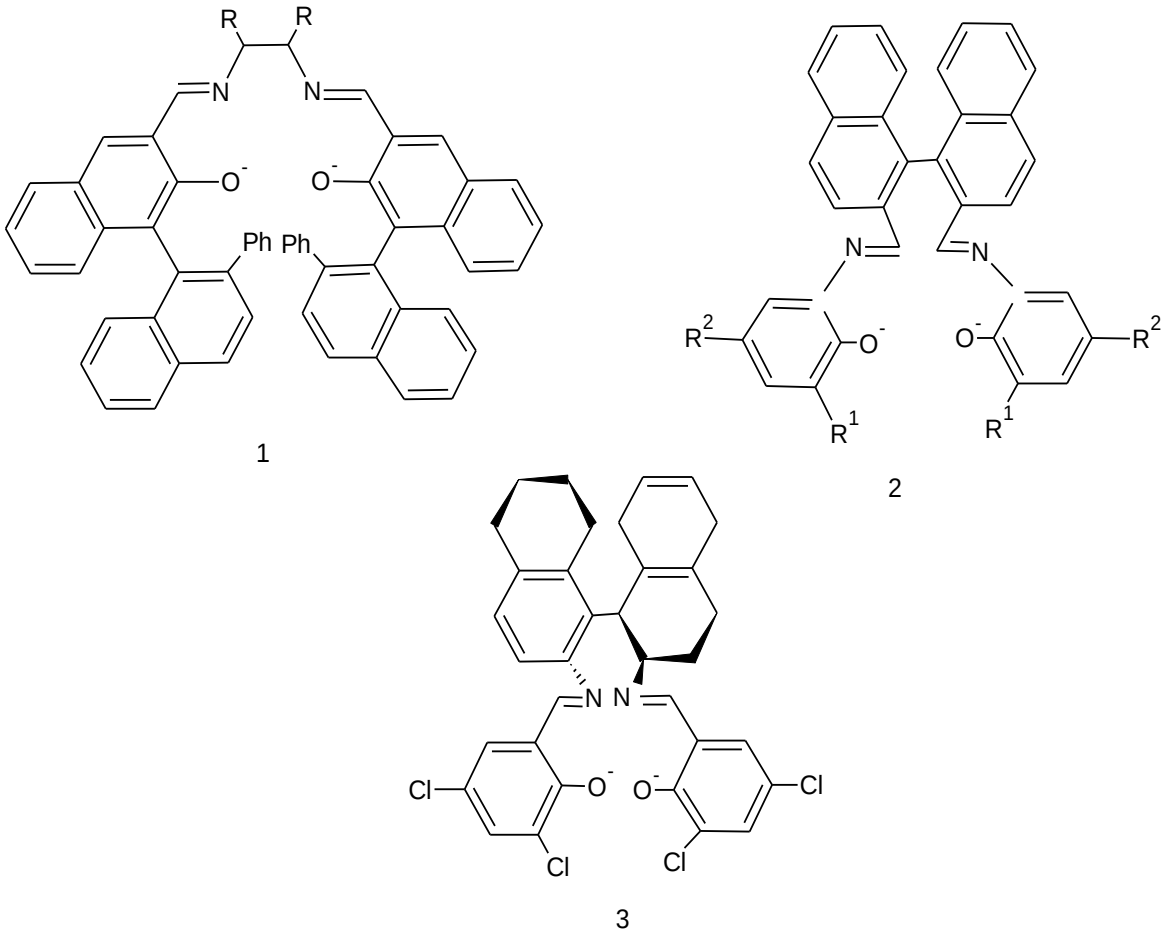
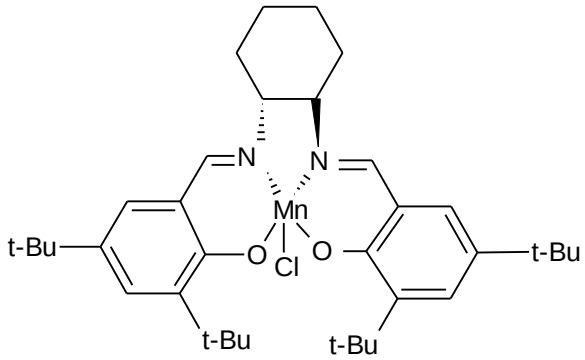


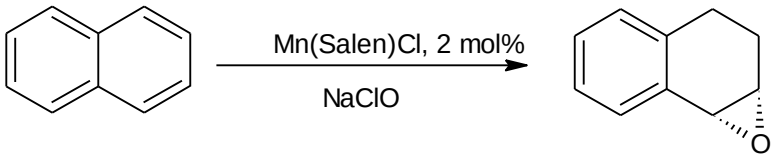
Figure 3 some commonly used binaphthyl Schiff bases [40]

Schiff base complexes showed catalytic activity in carbonylation of alcohols and alkenes at low pressure to produce aryl propionic acid and their esters [41], which are used as non-steroidal anti-inflammatory drugs. In addition to monometallic, the bimetallic Schiff base complexes also show catalytic activity in carbonylation reactions. The use of salen complexes as catalyst was first carried out in 1985 by Kochi and co-workers. Chiral manganese salen complexes were first developed by Jacobsen and Katsuki and are generally known as Jacobsen's Catalyst. Jacobsen's catalyst is (R,R)-N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamino manganese (III) chloride which is prepared by resolving 1,2-diamino cyclohexane as the appropriate tartrate, and reacting with 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde in the usual method of preparing salen-type ligands. Reaction with manganese (II) acetate in the presence of air gives the manganese (III) complex, which may be isolated as the chloro complex by addition of lithium chloride. These complexes are efficient catalyst towards epoxidation of *cis* olefins. One such complex used by them and the scheme of one of the reaction carried out using this catalyst are shown in Scheme and Figure 4A. It is generally agreed that the

Jacobsen's catalyst (Figure 4B) is oxidised to a reactive oxo-Mn (V) salen complex. The latter has not been isolated and characterised but related species withother metal centres are known. The Mn (salen) Cl is almost certainly planar; the oxospecies has been postulated as planar, bent and twisted (folded)



(A)



(B) 86%ee

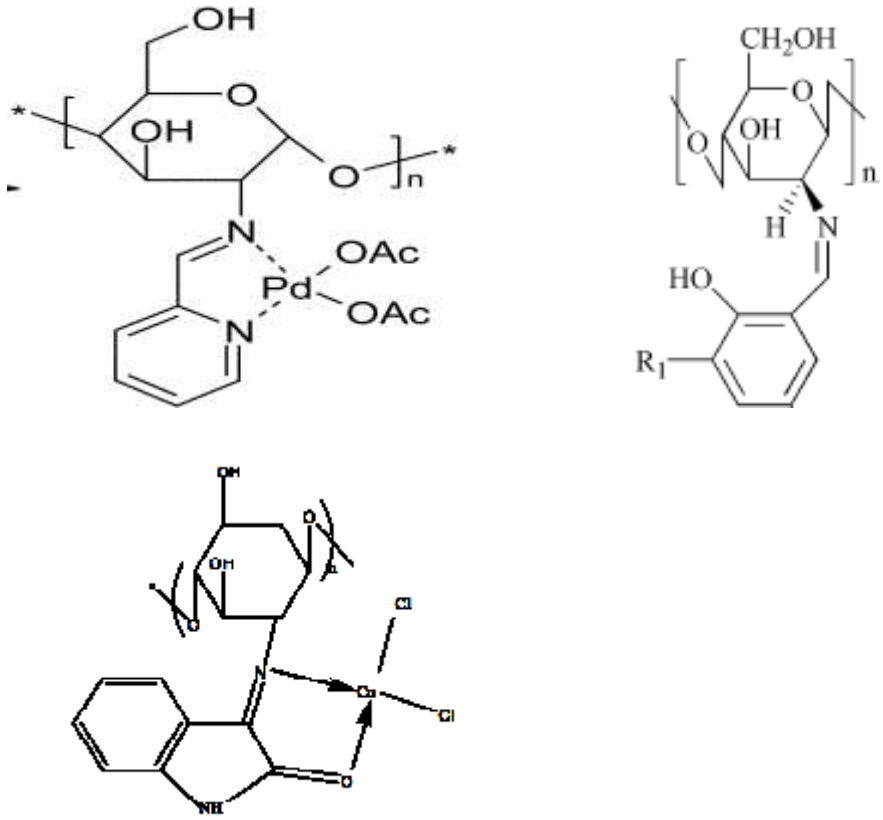
Figure4 (A) Structure of Jacobsens catalyst (B) Stereo-selective epoxidation catalyzed by Jacobsen catalyst [41]

Schiff base complexes are used as catalyst in Heck reaction [42]. Usually complexes of phosphene ligands are used to catalyse this reaction. But compared to phosphene, Schiff bases can easily be prepared. Palladium (II) complexes of sale Schiff base ligands showed high catalytic activity in Heck reaction than the commercially used phosphene complexes [43]. Arellano *et al.* [44] used the palladium (II) Schiff base complex of 2-*tert*-butyl-4-methyl-6{(*E*)-[(2*S*)-1-(1-arylmethyl) pyrrolidinyl] imino} methyl phenol as catalyst for Heck reaction. Legros and Bolm [45] reported the preparation of a tridentate Schiff base iron catalyst,prepared in situ from $Fe(acac)_3$, which is able to promote the enantioselective oxidation of sufide to sulfoxides. The iron (III) and cobalt (II) complexes of pyridine Schiff base ligands showed significant activity in the polymerization of ethylene. These complexeswere also used successfully for copolymerization of ethylene with 1-hexene [46].They have observed that the iron (III) Schiff base complexes showed higher yield and activity than the cobalt (II) complexes.

Canali and Sherrington reviewed the utilisation of homogeneous and supported metal salen complexes in asymmetric catalysis [47]. They have focused on the chiral salen ligands, and in particular on the use of their optically pure metal complexes as asymmetric catalysts. The activity of the chiral metallo porphyrins in the enantiomeric synthesis of aziridines and amides was moderate [48, 49] butthe activity was improved in the presence of manganese (III) complex of the chiral Schiff base, tetrabromo substituted salen [50]. The preparation of Schiff base ligands by condensation of readily available amines with aldehydes/ketones is much easier as compared to the lengthy steps involved in the synthesis of porphyrin ligands. The chiral complexes, *tert*-butyl glycinate-benzophenone nickel (II), diphenylmethylene imino palladium (II) and (1*R*, 2*R* or 1*S*,2*S*-[*N*,*N*ℓ-bis(2ℓ-hydroxybenzylidene)]-1,2-diaminocyclohexane copper (II), have increased enantioselectivity in alkylation of enolates [51-53]. The isomerization of norbornadiene to quadricyclane was significantly catalyzed using (9, 10-phenanthrenequinone di imine) rhodium complexes [54, 55.] These interconversions are useful for the storage of solar energy. The asymmetric reduction of dialkyl ketones to alcohols [56, 57] is very difficult to achieve, but Salen Schiff base complexes of transition metals have been found to be efficient catalysts in these reductions [58].The cobalt complexes with 3oxobutylideneaminato ligands were efficient catalysts for the enantioselective borohydride reduction of ketones, imines, and Į, unsaturated carbonyl compounds to afford the corresponding secondary alcohols [59]. Chiral Cr (salen) Cl complexes are used as catalyst in hetero-Diels-Alder reaction [60]. The product yield and enantioselectivity were influenced by the nature of catalysts. These studies reveal that Schiff base complexes are potential catalysts to influence the yield and selectivity in chemical transformations.

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 cyclopropanation of styrene. IR parrey et al. used Chitosan Schiff base metal complex of copper for oxidation of alcohols. Taren et al, and coworkers have used chitosan Schiff base of copper (1) 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.



Statures Showing Chitosan Schiff base metal complexes used as Catalysts

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 21st 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[62]. 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 [63]. 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 %) [63].The structure suggested for the polymeric iron (III) complex of the Schiff base, 4-(naphthalen-1-yliminomethyl)-phenol, is given in Figure 5.

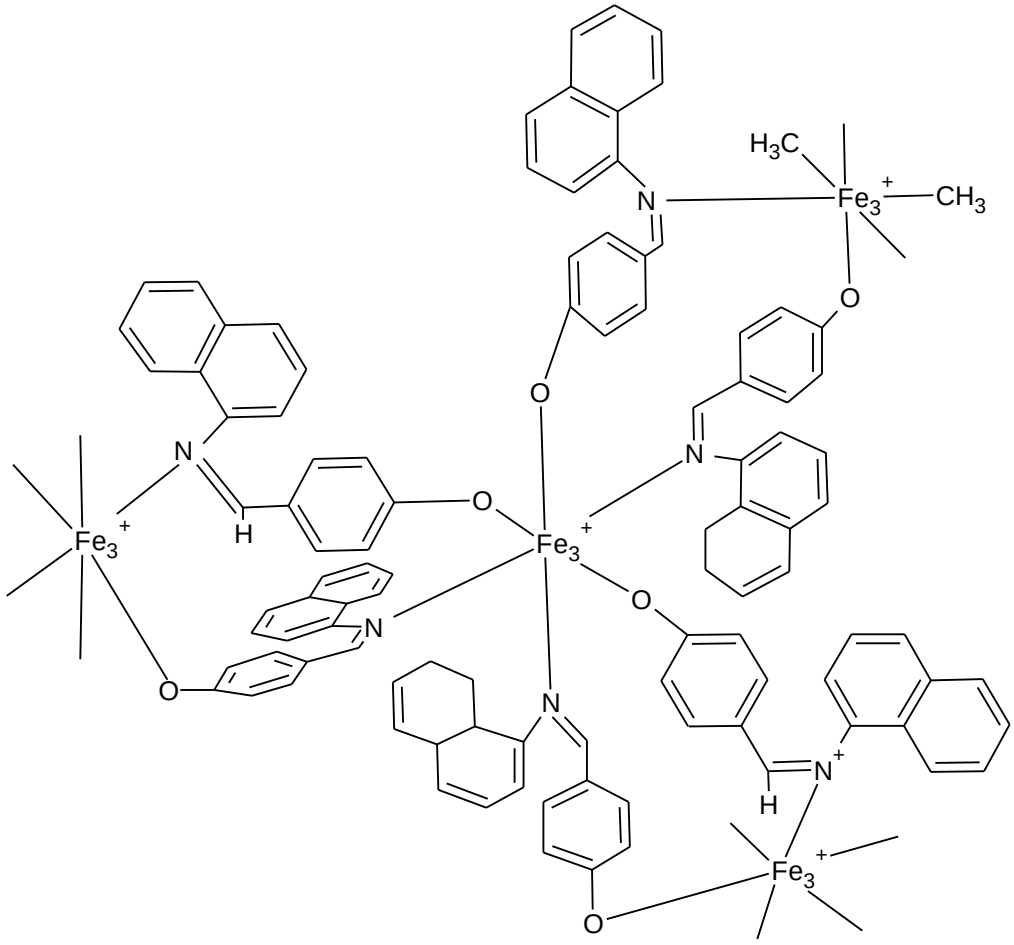


Figure 5 Structure of the polymeric Iron (III) complex [63]

Zhang *et al.* [64] 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 [65]. 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 depleter 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.

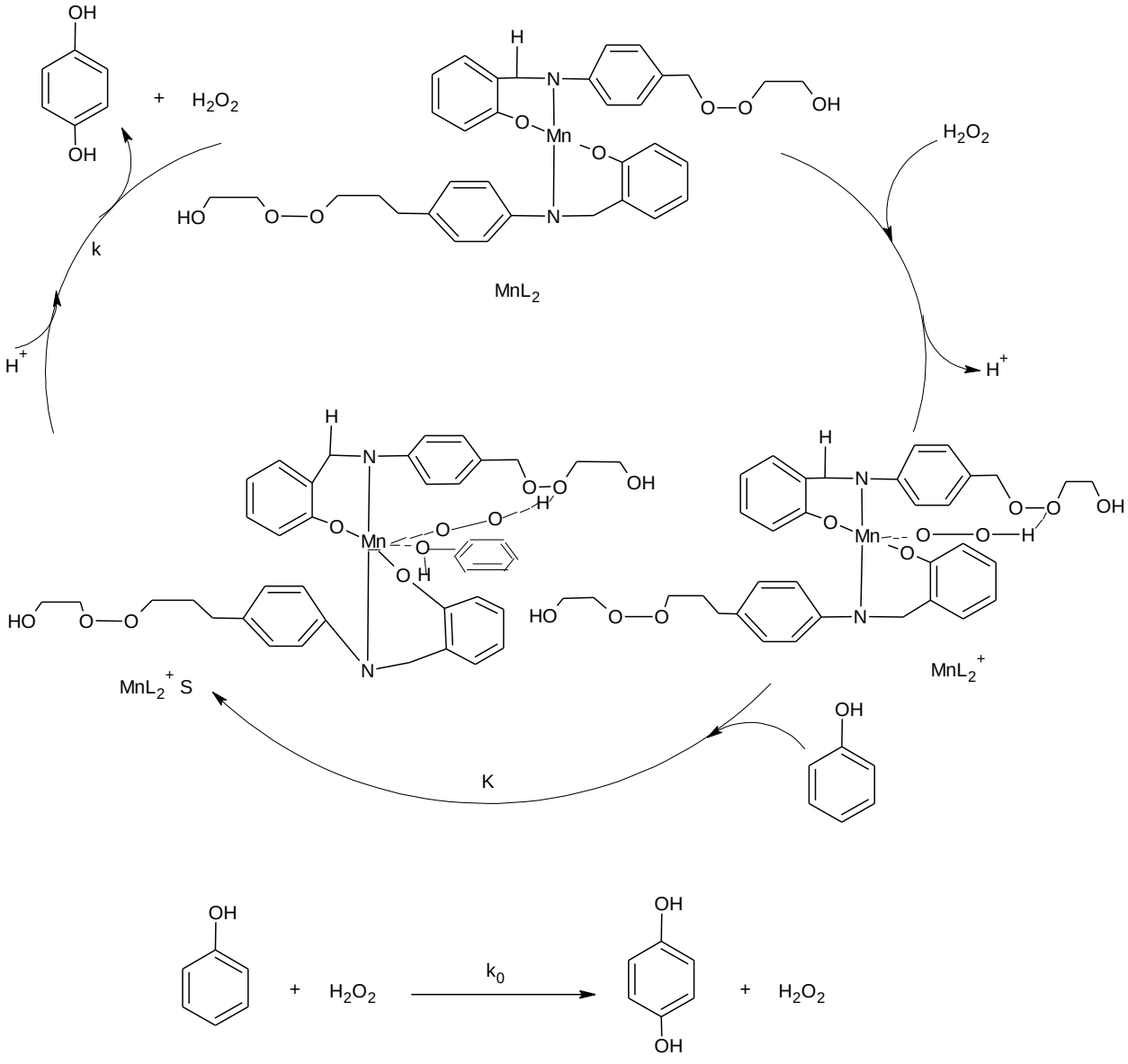


Figure 6 Mechanism of the oxidation of phenol catalyzed by the Schiff base complexes [64]

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 [67] 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 [68]. In 2009 Comba *et al.* [69] 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 7) for the reaction.

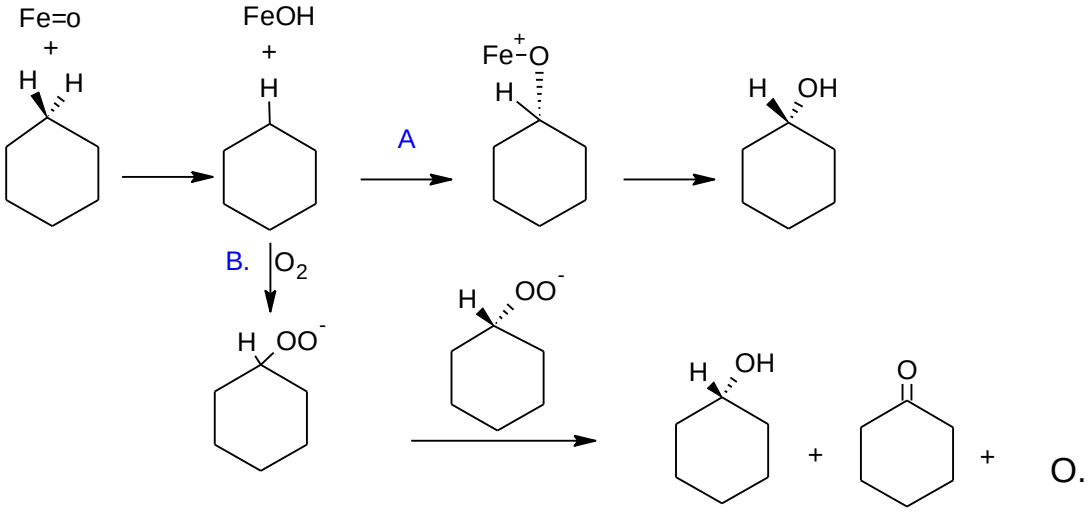


Figure 7: Anaerobic (A) and Aerobic (B) path way for the ferryl based oxidation of cyclohexane [69]

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 [70.] To reduce the harmness and cost of solvents, studies towards solvent free process have been carried out [71-74]. The copper (II) [75], manganese (II) [76] and ruthenium (II) [77] 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.* [78]. From an economic and environmental perspective, catalytic aerobic alcohol oxidation represents a promising protocol. [79-81].

Wang *et al.* [82] 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.* [83] and Ali *et al.* [84] 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.* [85] 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. Thus this reaction has both environmental and economical benefits in comparison with previously reported systems for benzyl alcohol oxidation.

CONCLUSION:

Schiff base complexes are found to catalyse a large number of organic transformations such as polymerization reaction, epoxidation, ring opening of epoxides, reductions, oxidations, alkylation, Michael addition, Heck reaction, annulation, carbonylation, benzoylation, cyclopropanation, Diels Alder reaction, aldol condensation etc. The oxidation of cyclohexane under mild condition is a topic of great interest. The reaction proceeds through the formation of peroxy intermediate. The cyclohexyl hydroperoxide is formed initially when hydrogen peroxide is used, which is later oxidised to cyclohexanol and cyclohexanone. The cobalt complexes with 3oxobutylideneaminato ligands were efficient

catalysts for the enantioselective borohydride reduction of ketones, imines, proceeds through the formation of the active species from hydrogen peroxide, OOH^{-}, which initially forms an intermediate with metal ion. The copper (II) manganese (II) and ruthenium (II) complexes are found to catalyze the selective oxidation of benzyl alcohol to benzaldehyde. Highly selective oxidation of benzylic alcohols to benzaldehyde using an active dinuclear manganese (IV) complex as catalyst and hydrogen peroxide or *tert*-butyl hydro peroxide as oxidant.

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