Transition Metal Complexes of Schiff Base Ligands as Efficient Catalysts for Epoxidation of Alkenes

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Abstract: Chiral Schiff base complexes are highly selective in reactions such as epoxidation of alkenes. Transition metal complexes of Schiff bases possess high catalytic activity in comparison to their unsupported analogues. In the present study catalytic activity of metal complexes of different types of Schiff bases for epoxidation of alkenes was analyzed in this review. The Schiff base complexes of manganese(II), iron(II), cobalt(II), nickel(II), Chromium(III) and other ions are used as catalysts in the epoxidation. The manganese(III) Schiff base complexes exhibited high catalytic activity in the epoxidation of alkenes both in homogeneous and heterogeneous conditions. Polymer-supported Schiff base complexes have demonstrated higher activity than unsupported Schiff base complexes of metal ions. The oxidation of styrene, indene, stilbene and its alkyl derivatives was catalyzed significantly by polymer-supported Schiff base complexes of different metal ions. The recyclability of polymer-supported Schiff base complexes is evaluated in this review.

Keywords: Schiff base complexes, epoxidation, catalyst, transition metal.

1. Introduction

Schiff base complexes have a high potential to act as versatile catalysts for organic synthesis resulting in a remarkable development in recent times. Several families of transition metal compounds are extensively used in a variety of chemical transformations such as hydration [1], hydrogenation [1], isomerization [2], decarbonylation [3], cyclopropanation [4], olefin metathesis [5], oxidation of hydrocarbon [6-12], epoxidation [13-16], nitro aldol reaction [17], Diels-Alder reaction [18], enol-ester synthesis [19] and other related catalytic process [1]. Schiff base metal complexes are important systems in asymmetric catalysis [20]. The versatility of the steric and electronic properties can be fine-tuned by choosing appropriate amine precursors and ring substituents. Metal complexes of Schiff bases derived from aromatic carbonyl compounds have received a great deal of attention in connection with studies on asymmetric catalysis and metalloprotein modeling [21-36]. Over the last few years, several reports have appeared on synthesis of Schiff base complexes and evaluation of their catalytic activities in epoxidation reaction [37-45] hence; the need of such review article highlighting the catalytic activity of Schiff base complexes was comprehended. In this review, the report on the Schiff base complexes in epoxidation reactions is presented for the period of 1980-2016.

Catalytic epoxidation of alkenes is a significant industrial reaction for the production of a wide variety of fine chemicals [46] derived directly from alkenes, a primary petrochemical source. Researchers worldwide investigated olefin epoxidation reactions that are catalyzed by a metal complex and this area is an important research topic in organic synthesis [47-52]. The last few decades witnessed the complexes of early transition metals such as rhenium [53], titanium [54, 55], manganese [56] and molybdenum [57-59] used as homogeneous catalysts in the alkene epoxidation.

In recent years, styrene oxide has been used as a preparatory material for epoxy resins, flavoring agents in food, tobacco, soap, cosmetic essences, perfumes, and pharmaceuticals [60, 61]. Catalytic pathways via the formation of high-valent metal-oxo intermediates involving some of the transition metal ions are well established [46]. Chiral salen Mn(III) complexes are found to be highly enantioselective for the asymmetric epoxidation of conjugated cis disubstituted and trisubstituted olefins [62-64]. Heterogeneous systems as compared to homogenous counterparts have the inherent advantages of easy separation, enhanced handling properties and higher stability; therefore, heterogenization of such complexes is widely considered [65-68]. As an application, Janssen et al [69] synthesized a dimeric form of Mn(III) salen ligand and retained metal complex in the cross-linked polymer membrane to use as a catalyst for epoxidation. Asymmetric epoxidation of alkenes is a powerful method for the synthesis of chiral intermediates in the pharmaceutical and agrochemical fields [70]. Among the most beneficial systems for the asymmetric epoxidation of non-functionalized olefins is the Jacobsen–Katsuki Salen(Mn)–catalyzed reaction [71, 72]. The (salen)Mn catalyst
system has been shown to be effective for the epoxidation of an impressive variety of unfunctionalized conjugated olefins [73]. Olefins could be effectively epoxidized by molecular oxygen, catalyzed by porous silica support metal Schiff base complexes [74].

2. Schiff base ligands

Schiff base ligands are formed by the condensation of aromatic or aliphatic primary amines with aldehydes. The resultant imines participate in binding with metal ions via nitrogen lone pair electrons [75, 76]. Like aldehydes, the ketones are also able to form Schiff base ligands, although Schiff base ligand with ketones are formed less readily than with aldehydes. The mono, di-, tri- and multi-dentate chelating Schiff base ligands are designed according to the binding environments of metal ions [77, 78].

2.1 Epoxidation

The epoxidation of hydrocarbons is an important reaction in chemical industry. Metal complex catalysis plays a significant role in the selective, partial oxidation of both saturated and unsaturated hydrocarbons into useful products.

![Scheme 1. Epoxidation reaction](image)

Epoxidation (Scheme 1) is an important reaction in organic synthesis because the formed epoxides are intermediates that can be converted to a variety of products. This reaction is widely used in asymmetric cases since it can lead to two chiral carbons in one step [79].

2.2 Schiff base catalyzed epoxidations

Matsumoto et al [80] developed another approach to Ti(salen) complexes: the transformation of Ti(salen) complexes 1 to the corresponding di-µ-oxo Ti(salen) complexes 2 via Meerwein–Ponndorf–Verley reduction (Scheme 2). In the above complex, salalen ligands adopted a cis β conformation. Ti(salen) complex 2 catalyzed various cyclic and acyclic conjugated olefins into corresponding epoxides with high to excellent enantioselectivity (Table 1, Scheme 3). Although the reaction mechanism is unclear, the peroxo titanium species activated by an intramolecular hydrogen bonding with the amino proton has been proposed to be the active species, on consideration of the difference in catalysis between Ti(salen) and Ti(salalen) complexes.

### Table 1. Asymmetric epoxidation of olefins catalyzed by Ti(salen) complex 2.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Product</th>
<th>yield (%)</th>
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<td>1&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>95</td>
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<td><img src="image" alt="image" /></td>
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<td>88</td>
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<tr>
<td>5&lt;sup&gt;b&lt;/sup&gt;</td>
<td><img src="image" alt="image" /></td>
<td>70</td>
<td>82</td>
</tr>
</tbody>
</table>

<sup>a</sup>AcOEt was used as the solvent.  
<sup>b</sup>3 mol% of 2 was used.

![Scheme 2. Synthesis of di-µ-oxo Ti(salalen) complex 2 via MPV reduction](image)
Soriente et al. [81] synthesized a new octahedral titanium complex bearing a bulky binaphthyl bridged Schiff base ligand. This complex has shown to be an effective catalyst for the epoxidation of allylic alcohols.

The vanadyl salen complexes (VOL$_x$; $x = 7$–18) were tested as catalysts (3, Fig. 1) for aerobic oxidation of hydrocarbons by Boghaei and Mohebi [82]. The unusual catalytic properties were observed with simple salen ligand systems. Under typical conditions, cyclohexene oxidized to mixture of cyclohexene oxide, 2-cyclohexene-1-ol and 2-cyclohexene-1-one in presence of major complexes. The vanadium catalyzed aerobic oxidation of cyclohexene proceeds with a moderate selectivity for epoxidations. (>50% for VOL$_x$; $x = 8, 16, 17$)

**Figure 1.** Structures of Vanadyl salen complexes 3

Chirally modified vanadium complexes [83] are used as catalysts in enantioselective epoxidations of allylic alcohols and asymmetric sulfide to sulfoxide oxidations. For both reactions various combinations of chiral ligands and vanadium sources were tested. Rayati et al. [84] have synthesized oxovanadium(IV) complexes (4, Fig. 2) of three N$_2$O$_2$ tetradentate Schiff base ligands (H$_2$L$^{1-3}$) by reaction of 1,2-propanediamine and appropriate aldehyde and ketone. These complexes are used as catalyst for the selective epoxidation of olefins. High selectivity of epoxidation for cyclooctene is observed from oxidation data. The catalytic activity increases as the number of electron donor groups increases and the catalytic selectivity is varied by changing the substituents on the ligands. The catalytic system described here is an efficient and inexpensive method for the oxidation of olefins with the advantages of high activity, selectivity, reusability and short reaction time. Rayati et al. [85-87] have also studied epoxidation of various alkenes using oxo-vanadium(IV), Dioxo-molybdenum(VI) Schiff bases complexes as catalysts.

Yaul et al. [88] synthesized vanadium complexes with quadridentate Schiff bases. The catalytic activity of these complexes was evaluated using H$_2$O$_2$ as oxidant for styrene oxidation. Bezaatapur et al. [89-90] synthesized Ni(II) and vanadyl Schiff base which showed good catalytic activity for the epoxidation of cyclooctene using TBHP as oxygen source in acetonitrile. Mandal et al. [91] synthesized homogeneous and heterogeneous mononuclear and dinuclear oxido vanadium Schiff base complexes which were found to be effective catalysts for epoxidation of styrene. Catalytic activity of the metal complexes was greatly influenced by the nature of the ligand and redox potential of the metal complexes. It was discovered that metal complexes with ligands having an electron pushing group or having higher conjugation show lesser catalytic activity then the unsubstituted or those having less conjugated ligand system.

Parida et al. [92] carried out covalent functionalization of vanadium Schiff base complex onto the CP-MCM-41. These catalysts showed pronounced efficiency with NaHCO$_3$ as co-catalyst and H$_2$O$_2$ as oxidant in a CH$_3$CN medium at room temperature. This method is green and economical from environment point of view. Zamanifar and Farzaneh [93] prepared vanadium complexes of N-salicyliden-L-histidine immobilized on Al-MCM-41 designated as VO(Sal-His)/Al-MCM-41 which were found to catalyze the epoxidation of trans-2-hexen-1-ol, cinnamyl alcohol and geraniol with TBHP.

Grivani et al. [94] synthesized oxovanadium(IV) Schiff base complex, V$^{1+}$OL$_2$ (Scheme 4), by the reaction of a bidentate Schiff base ligand L and VO(acac)$_2$. (L=N-salicylidin-2-chloroethylimine). The catalytic activity of the complex 5 was tested in the epoxidation of cyclooctene. The results showed that the complex 5 was highly active and selective catalyst in optimized conditions in the epoxidation of cyclooctene. The proposed mechanism for the epoxidation of alkenes by the oxovanadium complex VOL$_2$ in the presence of TBHP is shown in Scheme 5. Grivani et al. [95-97] have observed similar results in the case of vanadium complexes.
Jana Pisk et al [98] reported a series of dinuclear and mononuclear oxovanadium(V) complexes containing tridentate Schiff base ligands derived from pyridoxal and appropriate thiosemicarbazide or hydrazide. All vanadium complexes have been used as (pre) catalysts at 0.05% loading for epoxidation reactions of cis-cyclooctene under “green” reaction conditions.

Che and Huang [99] synthesized (R)-[Cr^{III}(L_4)Cl]-MCM-41(m) which are used for epoxidation of alkenes 6-9 (Scheme 6) is an unique example of heterogenized metal catalysts with chiral binaphthyl Schiff base ligands.

Chiral manganese(II) complexes [103] of 1,2-bis(salicylideneamino) cyclohexane entrapped in zeolite showed catalytic activity in the enatioselective epoxidation of alkenes. The manganese(II) complexes of bis(2-pyridinaldehyde) ethylenediamine, bis(2-pyridinaldehyde) propylene diamine ligands were used in epoxidation of olefins but epoxide selectivity was observed only in the presence of PhIO oxidant.

Skarzewski et al [104] carried out two-phase epoxidation of olefins with sodium hypochlorite, catalyzed by the salen-type Mn(III) complex 10, (Fig. 3) was examined in the presence of various additional ligands and 4-dodecyloxypyridine-1-oxide was found the most effective for epoxidation. Researchers [105, 106] studied similar epoxidations using Mn(III)-tridentate complexes as a catalyst.

Minutolo et al [107] studied polymer-supported manganese(III) salen complexes for heterogeneous asymmetric epoxidation of unfunctionalized alkenes.
in presence of mCPBA/NMO (65–72%). The polymer-supported chiral manganese(III) salen complexes [108] were used in the epoxidation of styrene derivatives in the presence of PhIO, which produced 16–46% ee. Li et al [109] Mono-Schiff base Mn(III) complexes with pendant aza-crown or morpholino substituents, and studied aerobic oxidation of p-xylene to p-toluic acid.

Seyedi et al [110] elaborated the effect of crown ether ring bonded to Mn(III) Schiff base catalysts on the efficiency of these catalysts for the epoxidation of cyclohexene and cyclooctene by KHSO4. The catalysts catalytic activity emerges completely when an aromatic nitrogen base such as pyridine as axial ligand and potassium nitrate when added to the reaction mixture. Thatte et al [111] prepared four unique, heterogeneous, chitosan-based Schiff base substituted with triazene, ethylene diamine and salicylaldehyde and their manganese, copper, cobalt and nickel complexes. Efficiency of these catalysts was tested with L-carvone, Limonene, cis-stilbene, trans-stilbene, α-terpenoene, α-methyl styrene.

Katia et al [112] synthesized new chiral Schiff base complexes obtained by condensation of 2,2′-diamino-1,1′-binaphthalene or 1,2-diaminocyclohexane and differently substituted salicylaldehydes (bearing tert-butyl, H, Cl, or Br). The manganese complexes containing the diiminobinaphthyl residue have been tested as catalysts for the epoxidation of a cis-disubstituted prochiral olefin, 1,2-dihydronaphthalene. In spite of a chiral manganese environment, the catalytic activity and enantioselectivity of these complexes were found to be lower as compared to those of their diiminocyclohexyl analogues. This low activity is probably due to extensive decomposition of the manganese binaphthyl based complexes under the oxidation reaction conditions. One possible explanation for the instability of these manganese complexes is the highly distorted geometry of the Salbinapht ligands which are highly compatible with tetrahedral rather than octahedral or square pyramidal coordination.

Che and co-workers [113-115] studied the epoxidation of 1,2-dihydronaphthalene 11, cis-β-methylstyrone 12, 4-chlorostyrene 13, styrene 14, 3-chlorostyrene 15, 3-nitrostyrene 16 and 4-methylstyrene 17 (Fig. 4) with PhIO by employing manganese catalysis formed in situ from Mn(OAc)3.xH2O with different ee values. (Scheme 7 Reaction 1-5). Che and co-workers [113-115] studied similar epoxidations using manganese, palladium and chromium complexes as a catalyst. Netalkar et al [116] prepared a series of aromatic spaced bipalladium center complexes from Schiff bases derived from 4,6-diacylresorcinol and 2,6-dialkyl substituted anilines. These complexes exhibited good catalytic activity for epoxidation of alkenes.

Figure 4. Structures of various alkenes used for epoxidation reaction by

Che and co-workers [113-115]

Manganese(II) Schiff base complexes [117] of 1,3-diamino-2-hydroxypropane with salicylaldehyde, 2-hydroxynaphthaldehyde or 2-hydroxycetophenone ligands were excellent catalysts in the epoxidation of olefins in the presence of PhIO as an oxidant. The extent of olefins epoxidation was dependent on OH substitution on Schiff base ligand. Sabater et al [4] used zeolite encapsulated chiral manganese(II) complexes of trans-(R,R‘)-1,2-(salicylidene amino) cyclohexane as active catalysts in the epoxidation of alkenes and highlighted the importance of chiral catalysts in the epoxidation of unfunctionalized alkenes.

Scheme 7. Epoxidation reactions studied by Che and co-workers [113-115]

Ogunwumi and Bein [118] synthesized intra-zeolite chiral salen complexes of manganese(III) which provided the benefit of shape selectivity of zeolites and stereo control of chiral manganese(III) complexes in the epoxidation of olefin. This intra zeolite combination showed high catalytic activity than the corresponding homogeneous conditions of these complexes. The activity of the catalysts in homogeneous conditions decreased due to the collapse of the mesoporous skeleton [119]. The
micelle templated silica (MTS)-supported complexes of manganese(III) were also used as catalysts. The 3-chloropropylsilane grafted MTS reacted with Salpr or ter-t-Salprpentadentate ligands [120] to produce suitable support for anchoring of Schiff base complexes (Scheme 8).

**Scheme 8.** Manganese(III) Salpr complex grafting on MTS materials

Diaz and Balkus [121] successfully prepared and characterized a series of MCM-41 grafted metal-amine complexes, including ligands based on ethylenediamine (M41ED), diethylenetriamine (M41DET), and ethylenediaminetricarboxylic acid (M41EDT). Ethylenediamine grafted to amorphous silica (SilED) was compared with the MCM-41 grafted metal complexes. Cobalt(II) complexes of M41ED and M41DET bind oxygen reversibly in contrast to the silica-supported complexes. The anchoring of chiral ligands on these surfaces produced chiral catalysts forenantioselective epoxidation of olefins.

Piaggio et al [122] showed that Mn-exchanged-Al-MCM-41 when modified by a chiral salen ligand can be an effective enantioselective heterogeneous epoxidation catalyst. The epoxidation of (Z) and (E)-stilbene was catalyzed using chiral (R,R')-(-)-N,N'-bis-(3,5-di-tert-butylsalicylidene) cyclohexane 1,2-diamine ligand modified and manganese exchanged Al-MCM-41 in the presence of PhIO as oxygen donor. The enantioselectivity of (Z)-stilbene to (E)-epoxide with heterogeneous catalyst was low (70% ee) in comparison to homogeneous catalyst (77% ee).

Tang et al [123] has synthesized a series of catalysts for epoxidation of styrene by immobilizing salicylaldimine transition metal complexes of copper, manganese and cobalt on mesoporous silica nanoparticles (MSNs) with diameters of 120–150 nm. These catalysts possess excellent catalytic efficiency in epoxidation of styrene in the presence of TBHP as oxidant. Styrene shows a high conversion (~99%) as well as epoxide selectivity (~80%) over Cu-MSN catalysts, and high conversion (~99%) and moderate epoxide selectivity (~65%) over Mn-MSN and Co-MSN catalysts. The catalytic activity of recycled catalyst is summarized in Table 2. The mesoporous silica nanoparticle-supported catalyst provides higher surface area of the support causes a higher concentration of catalytically active sites and thus show higher conversion. Results indicate that MSNs can serve as better catalyst supports. Massomeh Ghorbanloo [124-126] prepared silica gel-immobilized Mn(II) and Mo(VI) Schiff base complexes and studied its catalytic epoxidation of various alkenes.

Li et al [127] developed an innovative method to the epoxidation of cyclohexene under mild conditions using molecular oxygen as oxidant. The Mn(II) complexes of Schiff base ligands are supported on montmorillonite by ion exchange method. The montmorillonite catalysts performed high activity and epoxide selectivity for aerobic epoxidation of cyclohexene under Mukaiyama conditions.

<p>| Table 2. The catalytic activity of recycled catalysts |
|---------------------------------|--------|--------|</p>
<table>
<thead>
<tr>
<th>Run</th>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
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<tr>
<td>1</td>
<td>Cu-MSN</td>
<td>99</td>
<td>80</td>
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<tr>
<td>3</td>
<td>Mn-MSN</td>
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<td>64</td>
</tr>
</tbody>
</table>

The manganese(III) complexes [128] of N,N'-bis (salicylideneethylendiamine) catalyzed epoxidation of alkenes. These catalysts were used to study the formation of oxygen transfer agents [(salen)Mn=O]⁺ and [PhiO(salen)Mn–OMn(salen)OIPh]⁺, which were intermediates in the epoxidation of alkenes in the presence of PhIO. (Scheme 9)

Chiral manganese(III) salen complexes [129] in the presence of chiral additives were studied for epoxidation of 6-acetoamino-7-nitro-2,2-dimethyl chromene with moderate yield (5–65%) and 73% ee. The electrocatalytic activity and stability of differently substituted manganese Schiff base complexes, towards the oxidation by dioxygen of various substrates was analyzed by Mouret and Ourai [130]. Results obtained during the electrocatalytic epoxidation of cyclooctene have shown that Mn(III) complexes gave higher turnovers than the already described electrocatalytic system based on the unsubstituted Mn(III) Salen complex. The best results were obtained in the presence of 2-
methylimidazole (as the co-catalyst) and benzoic anhydride containing a small amount of benzoic acid as an activator.

\[
\text{Scheme 9. Mechanism of alkene epoxidation catalysed by chromium(III) and Manganese(III) salen complexes}
\]

Manganese salen complexes [131] have been investigated in alkene epoxidations with \(\text{H}_2\text{O}_2\), largely from the perspective of asymmetric catalysis. Katsuki [132] developed unfunctionalized Mn salen complex and obtained high ee (96%) but low yields (17%) in imidazole solution. Pietikainen [133] obtained higher yields and ee’s using carboxylates as additives. Jacobson et al [134] used another manganese(III) Schiff base complex in epoxidation of olefins in the presence of additives such as 4-phenylpyridine-N-oxide, N-methylmorpholine-N-oxide. Mansuy et al [135] developed a system to obtain high enantioselectivities (92%) and yields (86%) by adding ammonium acetate to Jacobsen’s catalysts. Durak et al [136] synthesized an unsymmetrical tetradentate Schiff base by the reaction of 3-methoxysalicylaldehyde, o-phenylenediamine, and salicylaldehyde. Its Co(II) and Mn(III) complexes were prepared and immobilized on 3-amino-propyltriethoxysilane functionalized silica gel. The immobilized materials were found to be efficient catalysts for epoxidation of styrene in the presence of TBHP in acetonitrile at 40°C.

Patel et al [137] successfully carried out epoxidation of alkene in the presence of calix[4]arene Schiff base Co(II) complexes as catalyst. A new Co(III) Schiff base complex was synthesized by Saha et al [138] which is capable of activating dioxygen in air to catalyze the epoxidation of various alkenes using isobutraldehyde as a co-reductant under homogeneous conditions. Among the series of Schiff base complexes 18-21 (Fig. 5) synthesized by Lu et al [139] Mn complex 18 resulting from \(\text{NN}^\prime\)-bis(2-hydroxy-1-naphthalidene) cyclohexanediamine ligand was considerably active for the catalytic epoxidation of styrene under mild conditions in which the highest yield of styrene oxide reached 91.2 mol%, notably higher than those achieved from simple manganese salt catalysts. Erdem and Guzel [140] also carried out similar epoxidation reactions.

Figure 5. Structures of salen-metal complexes 18-21

Polymer-supported manganese(II) salen complexes [141] were used as catalysts in the enantioselective epoxidation of 1,2-dihydronaphthalene, cis-\(\beta\)-methyl styrene and styrene. The heterogenized catalyst was more selective to form trans-epoxide with cis-\(\beta\)-methyl styrene. The supported salen complexes were produced by sequential treatment of polymer with 2,4,6-trihydroxy benzaldehyde and chiral trans-1,2-diamino cyclohexane and 3,5-di-tert-butyl salicylaldehyde and then manganese(II) ions were loaded.

Canali et al [142] has prepared polymer-supported salen ligand by polymerization of 4-(4-vinyl benzoxly) salicylaldehyde with styrene and vinyl benzene then reacting subsequently with 1,2-diaminocyclohexane. The prepared polymer-supported salen after reacting with manganese(II) was used as a catalyst in the asymmetric epoxidation of dihydroxy naphthalene and indene in the presence of \(\text{m}\)-chlorobenzoic acid as activator. The immobilized catalyst showed high chemical activity and modest enantioselectivity. Canali et al [143] also examined polymer-supported analogue of Jacobsen’s catalyst selectively as the homogeneous species. These catalysts were used in the epoxidation of 1,2-dihydronaphthalene, indene, 1-phenylcyclohex-1-ene and 1-phenyl-3,4-dihydronaphthalene using \(\text{m}\)-chloroperoxybenzoic acid as the oxidant and 4-methylmorpholine \(\text{N}\)-oxide as the co-oxidant but the catalysts show a very rapid fall in both activity and selectivity in the first and second cycles.

New unsymmetrical chiral salen complexes were synthesized by Kim and Shin [144] and the efficiency of Mn(III), Ti(IV), Co(II) and Co(III) type catalysts were examined in the enantioselective epoxidation of styrene and \(\alpha\)-methylstyrene. The unsymmetrical (salen) complexes showed
comparatively high enantioselectivity as compared to conventional symmetrical salen complexes, which were prepared mainly from salicylaldehyde and 2-formyl-4,6-di-tert-butylphenol derivatives. Several variables that affect the enantioselectivity in the epoxidation of unfunctionalized alkenes by amino acid based Schiff base complexes as catalysts were investigated by Kureshy et al [145]. Complexes 22-26 (Scheme 10) derived from L histidine are better catalysts than the other complexes synthesized by Kureshy et al [145]. On the basis of chemical yield and ee values, effectiveness of the solvents may be arranged in the following order, fluorobenzene > dichloromethane > acetonitrile which is in the reverse order of increasing polarity. As far as oxidant is concerned, only PhIO was able to perform epoxidation reaction. Other commonly used oxidants like H$_2$O$_2$, NaOCl, O$_3$ and mCPBA were either inactive or gave product other than epoxides.

![Scheme 10. Synthesis of the complexes 22-26](image)

Sivadasan and Sreekumar [146] synthesized cross linked polystyrene-supported Schiff’s base complexes of metal ions such as Fe(III), Co(II), Ni(II) and Cu(II). The catalytic activity of these metal complexes is studied in the epoxidation of cyclohexene and styrene. The reactions showed first order dependence on the concentration of both the substrates and the catalyst, Fe(III), Co(II) and Cu(II) complexes showed significant catalytic activity towards epoxidation of cyclohexene and styrene, but Ni(II) complex was found to be inactive. The metal complexes showed low catalytic activity at low crosslink density (2% and 5%) but 10% crosslink resins show higher activity. Erkenez and Tumer [147] prepared three polymer anchored Schiff base ligands from the reaction of 2,4-dihydroxybenzaldehyde with diamines in the ethanol solution. Cu(II), Co(II) and Ni(II) transition metal complexes of these Schiff bases showed low catalytic activity.

Thomas and Janla [148] used manganese(II) salen complexes on soluble and insoluble supports as catalysts in various asymmetric epoxidation reactions. Poly(ethylene glycol) monoethyl ether and non-cross linked polystyrene were used as soluble support, whereas Janda Jel and Merrifield resins were used as insoluble supports. These supports were linked to salen complexes through a glutarate spacer. The soluble supports were recovered by precipitation with suitable solvents, while insoluble catalysts were simply filtered from the reaction mixture. These catalysts were used in epoxidation of styrene, cis-β-methylstyrene and dihydronaphthalene.

Song and Roh [149] have developed a practical recycling procedure for Jacobsen’s chiral (salen) Mn(III) catalyst, using N,N’-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamine and manganese(III) chloride by use of ionic liquid 28 (Fig. 6). Results showed that the catalyst $(R,R)$ 27 in reaction medium containing ionic liquid 28 exhibited comparable enantioselectivity (96% ee for 2,2-dimethylchromene) in asymmetric epoxidation of alkenes as those obtained without ionic liquid and moreover, showed an increase in activity. At the end of reaction the immobilized catalyst in ionic liquid 28 could be easily recycled.

![Figure 6. Structures of Jacobsen’s chiral (salen) Mn(III) catalyst 27 and Ionic liquid 28](image)
donor imidazole increased the catalytic activity. These kinds of complexes are potentially important catalysts in quantitative cyclohexene oxidation or similar oxidation processes of hydrocarbons.

Star et al. [151] synthesized D-2,3-bis(arylideneamino)-1,4-butanediol derivatives 31-34 from 29 and 30 constituted a new class of salen based Schiff base ligands to form complexes with transition and heavy metal ions. The manganese(III) complexes (Scheme 12) 35-38 corresponding to Schiff base ligands 31-34 were used in asymmetric epoxidation of indene (Scheme 13).

Scheme 11. Synthesis of Schiff base manganese(II) complexes (Mn–L1-5)

Scheme 12. Synthesis of D-2,3-bis(arylideneamino)-1,4-butanediol derivatives (32-34) and of their manganese(III) complexes (35-38)

Scheme 13. The epoxidation of indene using the manganese(III) complexes of D-2,3-bis(di-t-butyl-salicylideneamino)-1,4-butanediol and dibenzyl ether

The ScCO2 manganese(II) salen complexes [152] were used as catalyst in the epoxidation of olefins using TBHP as terminal oxidant. Similarly, the substituted Mn[(5,5-NO2)salen] catalyst in CH3CN was used in the epoxidation of alkenes in the presence of PhIO as terminal oxidant resulted in corresponding epoxides and other products. Schuster et al. [153] synthesized immobilized sterically demanding complexes which were tested in the diastereoselective epoxidation of (-)-α-pinene in the liquid phase in an autoclave at room temperature and at elevated pressure using O2 as oxidant. Best results so far are 100% conversion, 96% epoxide chemoselectivity and 91% diastereomeric excess obtained in the presence of the entrapped [(R,R)-(N,N')-bis(3,5-di-tert-butyl salicylidene)-1,2-diphenylethylenediamino] cobalt(II) = Co(salen) complex (Fig. 7). Suggested mechanism of epoxidation is shown in Scheme 14.

Figure 7. Salen complexes derived from (R,R)-diphenylethylenediamine

Scheme 14. Mechanism of epoxidation suggested by Schuster et al. [90].

Kureshy et al. [154] synthesized dimeric Mn(III)-Schiff base complex 42 (Fig. 8) which successfully catalyzed the enantioselective epoxidation of the non-functionalized alkenes. Excellent ee of 100% was obtained in the epoxidation of nitro- and cyanochromene. The rate of reaction increased when ammonium acetate was used as co-catalyst. The activity of the recycled catalyst gradually decreased upon successive use,
possibly due to minor degradation during the reaction.

![Figure 8. Structure of dimeric Mn(III)-Schiff base complex 42](image)

Morries et al [155] described the use of supramolecular complexation to enhance (salen)Mn catalyst stability in the asymmetric epoxidation of unfunctionalized conjugated olefins namely styrene and 2,2-dimethylchromene as substrates (Scheme 15). (Salen)Mn(III) catalysts (43, Fig. 9) show increased turnover numbers in the catalytic asymmetric epoxidation of conjugated olefins upon addition of bulky Lewis acids such as zinc tetraphenylporphyrin (ZnTPP). It is observed that supramolecular complex formation enhanced the catalyst’s stability without compromising its enantioselectivity.

![Scheme 15. Asymmetric epoxidation of conjugated olefins](image)

Paulsamy et al [156] synthesized a series of new chiral binol based [1+1] macrocyclic Schiff bases and used it for the enantioselective epoxidation of unfunctionalized olefins that resulted high yields and good enantioselectivity.

Krishnan and Vencheshan [157] synthesized polymeric, polynuclear Schiff base Mn complexes, with repeating salen-like cores. Unfortunately they proved to be moderate catalysts for the epoxidation of simple alkenes and additives such as imidazole were required to achieve catalytic activity with H$_2$O$_2$. Das and Cheng [158] has synthesized a mononuclear complex of Mn(III) with a Schiff base ligand L $[L = N,N'$-ethylenbis(3-formyl-5-methylsalicylaldimine)]. A series of binuclear complexes, MnML'Cl$_2$ solvent $[M = Zn(II), Cu(II), Ni(II), Co(II), Fe(III),]$ and Mn(III); $x = 3$ or 4 depending on the oxidation state of M; L' is the aniline condensation product of L; y = 1, 2 or 3 and solvent = H$_2$O or CH$_3$OH have been prepared by the reaction of same mononuclear complex of Mn(III), aniline and M(II/III) chloride with a 1:3:1.2 molar ratio in methanolic media. The results of magnetic susceptibility measurements indicate that all the metal ions are in their high spin states. The catalytic properties have been investigated using PhIO as a terminal oxidant. The mononuclear Mn(III) complexes are more efficient epoxidation catalysts than the binuclear Mn(III) complexes. The reduced activities of the bimetallic complexes may be due to both the low rates of formation of a Mn(V)=O intermediate and the transfer of oxygen from this intermediate to the alkene.

Patel et al [159] have synthesized polymer-supported Mn(II) Schiff base complexes from cross linked chloromethylated poly(styrene-divinylbenzene) copolymer beads by sequential modification in to a Schiff base bearing ligand. These Schiff base bearing polymer on treatment with a solution of manganese salt gave the corresponding metal complexes. This Mn(II) complex bound to poly(styrene-divinylbenzene) copolymer catalyzed the epoxidation of norbornene and cis-cyclooctene in the presence of alkyl hydroperoxide under mild conditions. Kinetic experiments reveal that at elevated temperature the activity of the catalysts toward the epoxidation is enhanced. The catalysts can be recycled several times without any loss in selectivity. The mechanism of epoxidation is shown in Scheme 16.

![Figure 9. (Salen)Mn(III) catalysts 43](image)

![Scheme 16. Mechanism of olefin epoxidation](image)

Louloudi et al [160] prepared Schiff base ligands by template induced macrocyclization/condensation of diethylenetriamine (H$_2$NCH$_2$CH$_2$NHCH$_2$CH$_2$NH$_2$) with eitherpentane-2,4-dione or 1,3-diphenyl-propane-1,3-dione. The binuclear manganese complexes (47, Fig. 10) produced was moderately active in epoxidations, giving yields from 9% to
82% for isoprene and limonene in the presence of ammonium acetate. Researchers [161,162] synthesized phenoxy bridged dinuclear Mn(III) complex that acts as an efficient catalyst in the epoxidation of alkenes.

Costas et al [163] observed that a number of iron complexes have been applied as catalysts in alkene oxidations. The almost unexplored mechanism of the iron catalyzed olefin epoxidation with H_{2}O_{2}–acetic acid was studied by Mas-Balleste and Que [164]. In addition iron complexes such as novel tetra- [165] or pentadentated amino–pyridine ligands [166] N,N,O-ligands and (m-oxo)diiron complexes [167] are also used in epoxidation. Researchers have [168, 169] synthesized iron(III) complex and used as an alkene epoxidation catalyst. Researchers [170] have also synthesized Cobalt(II) Schiff base complex on multi-wall carbon nanotubes (MWCNTs) by covalently grafted method. The catalytic activity of the novel nanotubes based materials was tested in the epoxidation of cyclohexene. Kureshy et al [172] have presented the aerobic enantioselective epoxidation of 1-octene, 1-hexene, trans-4-octene and indene using Ni(II) symmetrical and non-symmetrical chiral Schiff base complexes in presence of molecular oxygen using isobutyraldehyde as sacrificial reductant. The catalyst 49, 51 and 52, 54 (Fig. 11) forms a conversion with 1-octene and trans-4-octene and catalyst 50 and 51 favor the formation of 1-hexene oxide in higher yield. The symmetric catalysts 49-51 gave the maximum enantioinduction with indene though the chemical conversions were low in comparison to the long chain olefins. As expected S form of the catalyst gave predominantly R form of the product.

Goldani et al [170] prepared a series of Fe(III) Schiff base complexes immobilized on MCM-41. The immobilized complexes proved to be effective catalysts and exhibited much higher catalytic performance than their homogeneous analogue. Among all the alkenes, those containing π-electron-withdrawing groups and trans-orientations exhibited lower tendency for oxidation.

Masoud et al [171] have also synthesized Nickel(II) and Manganese(III) metal complexes of Schiff bases such as N,N'-bis(2-hydroxyphenyl) ethylenediimine 55 and N-(2-hydroxyphenyl) acetyldiamine)-N-(2-hydroxyphenyl) acetamide 56 0.5 (Fig. 12) are prepared by Chatterjee et al [173] and Kureshy et al [174] in good yield by direct interaction of 2-aminophenol, glyoxal/methylacetatotate and NiCl_{2}. Catalytic ability of NiL complexes were examined and found that both the complexes can effectively catalyze the epoxidation of olefins namely cyclohexene, 1-hexene, cis- and trans-stilbenes, indene with NaOCl.

![Figure 10. Manganese-complexes synthesized by Louloudi et al [160]](image)

![Figure 11. Representative structures of the catalysts 49-54](image)
Bhunia and Koner [175] observed similar results by tethering nickel(II) Schiff base complex via post-synthesis modification of mesoporous silica, MCM-41. The Schiff base is derived from salicylaldehyde and 3-aminopropyltriethoxysilane (3-APTES). Immobilized nickel catalyst was found to be catalytically more active and selective as compared to the similar type of nickel(II) complex as well as Ni(NO$_3$)$_2$-6H$_2$O in homogeneous media. Mavrogiorgou et al [176, 177] developed a new functional catalytic material prepared via chemical modification of mesoporous silica SBA-15, MCM-41 or carbon nanomaterials CMK-3. All the catalysts were evaluated for alkene epoxidation with H$_2$O$_2$ as oxidant and CH$_3$COONH$_4$ as additive.

Jana et al [178] have anchored the copper(II) Schiff base complex immobilized into Si-MCM-41 (Scheme 17) matrix via covalent bond. The Cu-MCM-41 is porous but the mesoporous character of Si-MCM-41 was not retained after modification. The catalyst Cu-MCM-41 has shown excellent catalytic activities in epoxidation reaction toward various olefins including allylic alcohol. An unprecedented high conversion (97%) as well as selectivity of epoxide (89%) has been observed in styrene epoxidation. Notably, epoxidation of allylic alcohol showed considerably high turnover frequency (166 h$^{-1}$) in this study.

Three (II) Schiff base complexes, [Cu(L$^1$)(H$_2$O)](ClO$_4$), [Cu(L$^2$)]$^2+$ and [Cu(L$^3$)]$^2+$ have been synthesized by Adhikary et al. [46, 179] All of them are found to be catalytically active in industrially important epoxidation reactions in different solvent media under homogeneous conditions. The efficiency of the catalysts, in general, followed the order: acetonitrile > chloroform > dichloromethane > methanol. Ray et al [180] synthesized dicopper(II) complexes of tridentate pyrimidine derived Schiff base ligands which have presented excellent catalytic activities in epoxidation reactions towards various olefins. Shen et al [181] prepared a Copper(II) complex derived from the Schiff base ligand 2-hydroxy-5-methoxybenzaldehyde oxime (HL) and tested for its catalytic oxidation property. Abbasi et al [182] reported the results of solvent free epoxidation studies of cyclooctene to cycloocteneoxide using Cu(II) Schiff base complexes (Scheme 18). Higher catalytic activities, epoxide selectivity and lower reaction times were achieved.

**Scheme 17.**
(a) Modification of Si-MCM-41 Channel Wall: APTES/CHCl$_3$;
(b) Condensation with Salicylaldehyde in Methanol;
(c) Metal Complex Formation: Cu(NO$_3$)$_2$-3H$_2$O/MeOH

**Scheme 18.** Synthetic procedure for the preparation of ligands and complexes
Ethanol was used as solvent

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<th>Ligands and Complexes</th>
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<tr>
<td>H$_3$L$^5$, Cu$_3$(L$^3$)$_2$</td>
<td>H</td>
<td>OCH$_3$</td>
<td>H</td>
<td>H</td>
</tr>
</tbody>
</table>

Ambroziak et al [183] synthesized dioxomolybdenum(VI) complexes 57-62 of tetratentate Schiff base derivatives (Scheme 19) of trans-1,2-diaminocyclohexane were used for the epoxidation of cyclohexene and 1-octene. The best results were obtained for [trans-N,N'-bis-(4,6-dimethoxysalicylidene)-1,2-cyclohexanediaminato]dioxomolybdenum(VI) and [trans-N,N'-bis-(2-hydroxynaphthylidene)-1,2-cyclohexanediaminato]dioxomolybdenum. An increase in the reaction
temperature may lead to an increase in the yield of the epoxide.

Researchers [184, 185] synthesized cis-dioxo-Mo(VI) complexes (Scheme 20) containing simple ONO tridentate Schiff base ligands in the epoxidation of various olefins using TBHP with excellent chemo- and stereoselectivity.

Scheme 19. Synthesis of dioxomolybdenum(VI) complexes

Scheme 20. Epoxidation of olefins catalyzed by the MoO\(\text{VI}\) Schiff base complexes

Gao et al [186] prepared a new bidentate Schiff base dioxomolybdenum(VI) complex immobilized on chloromethlated cross linked polystyrene microspheres via two stepwise polymer reactions. The solid catalyst used in the epoxidation reaction of cyclohexene with TBHP exhibited high catalytic activity and excellent catalytic selectivity. Katkar et al [187] carried out green epoxidation of 1-hexene using [hydrazine-N-salicylidene-N'-salicyloyl-] cis-dioxomolybdenum(VI) and its zeolite-Y composite as catalyst in DMF in the presence of molecular oxygen as oxidant and in the temperature range 333–363 K. The ‘green’ factor of olefin oxidation catalysis using the Mo(VI) dioxo complex is its ability to use atmospheric oxygen which is non-hazardous and inexpensive and produces no harmful byproducts.

Sui et al [188] synthesized five kinds of dioxomolybdenum(VI) complexes with Schiff base ligands derived from (3-hydroxymethyl)amino methane (63 Fig. 13). These complexes show good catalytic activities and selectivity in the epoxidation of cyclohexene with TBHP, especially for complex [MoO\(\text{VI}\)(H\(\text{2}L\))(H\(\text{2O}\))], which could give a nearly 100% of epoxidation conversion and selectivity. The electron withdrawing group on the salicylidene ring of complex is advantageous over electron donating one on the effectiveness of a catalyst but disadvantageous on the redox stability of a complex.

Figure 13. Structure of tris(hydroxymethyl)amino methane 63

Grivani et al [189] produced polymer-bound molybdenum carbonyl Schiff base catalyst 64 as shown in Scheme 21. This supported catalyst shows high activity in epoxidation of various alkenes in the presence of TBHP. The supported molybdenum catalyst can be recovered and reused eight times without loss in its activity. Grivani and Akherati [190] have synthesized polymer-supported bis(2-hydroxylanyl) acetylacetonato Mo\(\text{VI}\) Schiff base complex which were used for selective in epoxidation of various alkenes.

Scheme 21. Preparation procedure of catalyst 64

Bagherzadeh et al [191, 192] synthesized Mo(VI) complexes of Schiff bases and used as catalyst for epoxidation of alkenes. Mirzaee et al [193] used boehmite nanoparticles (BNPs) grafted with 3-(trimethoxysilyl)propylamine (MSPA) to anchor Schiff base and to support two complexes of molybdenum and vanadium. Then, these supported catalysts were utilized in the epoxidation of various olefin substrates (Scheme 22 and 23).

Masoud and Mehdi [194] synthesized three dimeric cis-dioxomolybdenum(VI) complexes of Schiff bases. These bis-bidentate Schiff base ligands derived from aromatic nitrogen–nitrogen linkers (bis[(N,O-salicylidene)-4,4'-diaminodiphenyl] methane, H\(\text{2}L\); bis[(N,O-salicylidene)-4,4'-diazido-}

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Diaminodiphenyl ether, \( H_2L_2 \); bis\([(N,O-salicylidene)-4,4’-diaminodiphenyl] sulfone, \( H_2L_3 \) exhibit good catalytic activities and selectivity in the epoxidation of cyclohexene with TBHP forming six-coordinated cis-dioxo Mo(VI) complexes especially for complex \([MoO_2L_3]^2\)], which could give a nearly 88% of epoxidation conversion and 94% of selectivity. The electron withdrawing group on the aromatic nitrogen–nitrogen linkers of complex is advantageous over electron donating one on the effectiveness of a catalyst but disadvantageous on the redox stability of a complex. The addition of single wall carbon nanotubes (SWCNT) can enhance the activity of the Mo complexes and the selectivity toward epoxide.

\[\text{Scheme 22. Proposed mechanism for the epoxidation of olefin with TBHP catalyzed by Mo-IFBNPs}\]

Mohamed Shaker S. Adam [195] studied homogeneous oxidation processes of various aliphatic and cyclic alkenes using dioxomolybdenum(VI) and dioxouranium(VI) homobimetallic bis-ONO tridentate (2-hydroxy-1-benzylidene)malonyl-, succinyl-, and terephthalodihydrazone complexes. Mo(VI)O\(_2\) complexes were five times more selective than U(VI)O\(_2\) complexes.

\[\text{Scheme 23. Proposed mechanism for the epoxidation of olefin with TBHP catalyzed by V-IFBNPs}\]

M. Masteri-Farahani and S. Abednatanzi [196, 197] have prepared covalently attached molybdenum–Schiff base complex on the surface of MWCNTs as a new hybrid catalyst (Scheme 24). The prepared hybrid nanomaterial was found to be an efficient and stable heterogeneous catalyst in the selective epoxidation of olefins with TBHP and CHP as oxidants.

\[\text{Scheme 24. The sequence of events in the preparation of MoO}_2\text{(acac)sal-MWCNT’s nanomaterial}\]

Li et al [198] immobilized a series of tridentate Schiff base dioxomolybdenum(VI) complexes on to a promising organic–inorganic hybrid zirconium poly(styrene-phenylvinylphosphonate)-phosphate via covalent bond. The prepared heterogeneous catalysts are found to be highly reactive in the epoxidation of unfunctionalized olefins. Moreover, these catalysts are of higher stability and reusability in the oxidation reactions. Excellent enantiomeric excess was obtained for the epoxidation of \(\alpha\)-methylstyrene in this oxidant system. Similar dioxomolybdenum(VI) complexes [199-205] of Schiff bases is used as a catalyst for epoxidation of
various olefins. S. Ding and W. Li [206] synthesized tridentate Schiff base ligand and its dioxomolybdenum(VI) complexes. Molybdenum is octahedrally coordinated in the complexes. The complexes showed effective catalysis in oxidation of cyclohexene, vinylbenzene, 1-butylene, and 1-pentene, to their corresponding epoxides. Zeinab et al [207] prepared heterogeneous nanocatalyst via covalent anchoring of dioxomolybdenum(VI) Schiff base complex (Scheme 25) on core–shell structured Fe₃O₄@SiO₂. The synthesized hybrid material was an efficient nanocatalyst for selective oxidation of olefins to corresponding epoxides with TBHP in high yields and selectivity.

Scheme 25. Synthetic pathways for the synthesis of Fe₃O₄@SiO₂-NHAiMo nanocomposite

The electrocatalyst, ruthenium(III) Schiff base complex [Ru₃(Naphdien)Cl]Cl(Naphdien = bis(2-hydroxynaphthaldehyde)) to activate dioxygen for the epoxidation of olefins for the epoxidation of cyclohexene, vinylbenzene, and 1-pentene, to their corresponding epoxides. Zeinab et al. [207] prepared heterogeneous nanocatalyst via covalent anchoring of dioxomolybdenum(VI) Schiff base complex (Scheme 25) on core–shell structured Fe₃O₄@SiO₂. The synthesized hybrid material was an efficient nanocatalyst for selective oxidation of olefins to corresponding epoxides with TBHP in high yields and selectivity.

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Scheme 26. Electron reduction of Ru₃⁺-peroxo complex

Ali Ourari [209, 210] showed that the Ru(III)-species developed a particular reactivity towards molecular oxygen. It was revealed that the formation of byproducts such as μ-oxodimers is advantageously avoided with the Ru(III) complexes. De Sauza et al. [211] used ruthenium complexes of trans-[RuCl₂(bpydip)] and trans-[Ru(OH)₂(bpydip)][PF₆]₂ with tetradeinate Schiff base ligand N,N,N'-bis(7-methyl-2-pyridylmethylene)-1,3-diiminopropane as catalysts in the epoxidation of cyclohexene in the presence of PhIO. Amini et al. [212] synthesized an oxido-peroxido tungsten(VI) complex [WO₂L(CH₃OH)] using salicylidene benzoyl hydrazine as a tridentate ONO donor Schiff base (H₂L) (Scheme 27). The complex was used as a catalyst for epoxidation of olefins with high yield, turnover number, and selectivity. Rania et al. [213] carried out thermal reactions of Mo(CO)₆ and W(CO)₆ with the different Schiff bases the gave variety of carbonyl complexes. The two complexes were tested and found to have epoxidation activity toward olefins.

Scheme 27. Epoxidation of olefins and oxidation of sulfides in the presence of [WO₂L(CH₃OH)]

Sachse et al. [214] showed that mononuclear complexes of the type [ReOLCl₂(PPh₃)] or [NBu₄][ReOLCl₄] (Fig. 14), where L represents acetylacetonate derived β-ketoamine ligands, can be prepared in high yields. All compounds coordinate to the rhenium center with the oxygen atom of the ligands trans to the Re=O group and two chlorine atoms occupy trans positions to each other. Compound 65 proved to be a catalyst for the epoxidation of cis cyclooctene with TBHP at 50°C.

Figure 14. Mononuclear complexe 65 [ReOLCl₂(PPh₃)]

Bo Zhang et al [215] prepared Schiff base complexes of methyltrioxorhenium(VII) and applied them as catalysts for the epoxidation of cyclooctene in the ionic liquid with urea hydrogen peroxide as...
oxidant agent at room temperature. The results showed that the \((N\text{-salicylidene})\) aniline derived Schiff base complexes of methyltioxorhenium (MTO) exhibit higher catalytic activity and selectivity than di-nitrogen Schiff bases complexes of MTO. Gao et al \[216\] also synthesized several di-nitrogen Schiff bases through the condensation of 2-pyridinecarboxaldehyde with primary amines. The Schiff bases as ligands coordinated with methyltioxorhenium (MTO) smoothly to afford the correspondent complexes. Catalytic results indicated that the complexes as catalysts increased the selectivity of epoxides remarkably compared with MTO in the epoxidation. Grunwald et al \[217\] synthesized a series of Re(V) complexes bearing tridentate pyridazine-containing ligands. These oxo complexes were applied in the catalytic oxidation of cyclooctene with TBHP, yielding ~60% cyclooctene oxide after 24h.

Hailiang Su et al \[218\] Cobalt(II), iron(III) or oxovanadium(II) Schiff base metal complexes (Scheme 28) have been covalently grafted onto graphene oxide (GO) previously functionalized with 3-aminopropyltriethoxysilane. Potential catalytic behaviors were tested in the epoxidation of styrene, using air as the oxidant. Co-GO and Fe-GO showed high styrene conversion (90.8 versus 86.7\%) and epoxide selectivity (63.7 versus 51.4\%). VO-GO showed poor catalytic performance compared to Co-GO and Fe-GO.

Farzaneh et al \[219\] prepared magnetic nanoparticles (MNP\(\text{s}\)) by co-precipitation method. The MNPs was then coated by silica due to formation (SCMNP\(\text{s}\)) followed by modification with aminopropyltrimethoxysilane (AmpSCMNPs). Later, amino acid Schiff base ligands were prepared from salicylaldehyde and triptophane or histidine and immobilized on the surface of AmpSCMNPs through the formation of amide bonds. Finally, heterogenized vanadium nanocatalysts designated as VO(Sal-Trip)/AmpSCMNPs and VO(Sal-His)/AmpSCMNPs were prepared (Scheme 29). These catalysts were used for epoxidation of some allylic alcohols and alkenes. Epoxidation of geraniol, \(\text{trans-2-hexene-1-ol}, \text{1-octene-3-ol}, \text{trans-stilbene}, \text{norbornene and cyclooctene}\) with 100 \% selectivity is observed. High yields, clean reactions, ease of separation and recyclability of the solid catalyst are some advantages of this method.

Lu et al \[220\] prepared Co Schiff base functionalized MgAlLDH (layered double hydroxides) by a novel strategy, namely grafting silylated Co Schiff base on the exfoliated LDH nanosheets (Scheme 30). The hybrid prepared by this strategy exhibited a high catalytic activity in \(\text{H}_2\text{O}_2\) decomposition and styrene epoxidation with \(\text{O}_2\).
3. Conclusions and future outlook

Catalytic activity of Schiff base complexes showed significant variations with structure and type of Schiff base ligands have played a significant role in epoxidation of alkene to enhance product yield and selectivity. In the present review catalytic activity, selectivity and yield of various epoxide products have been shown. Clearly the oxidation of the carbon-carbon double bond to the corresponding epoxide compounds is a highly desirable and rewarding industrial process. Enantioselectivity in various reactions was controlled with metal complexes of chiral Schiff base ligands. The activity of Schiff base complexes of transition metals showed significant improvements on their immobilization on various supports. In addition to high catalytic activity of Schiff base complexes on various supports, the supported catalysts also showed efficient recovery and reuse in various reactions. Schiff base complexes of transition metal ions in supercritical carbon dioxide (ScCO₂) have further enlarged the range of substrates, which earlier were difficult to be oxidized in the presence of Schiff base complexes of metal ions alone or other catalysts. Various transition metal Schiff base complexes covalently grafted with functionalized SWCNT and GO showed high catalytic activity. The polarity of reaction media has also influenced the activity of Schiff base complexes of transition metal ions as observed in some reactions described in this review. These studies have clearly demonstrated that Schiff base complexes of transition metals are versatile, efficient and suitable to catalyze epoxidation reactions under mild experimental conditions. This work may broaden the application of salen complexes as new asymmetric catalysts. Although transition metal catalyzed allylic and benzylc oxidation have met with little success, the initial studies on this important chemical transformation are encouraging and it holds a promising future for its application in the industry. Finally, transition metal catalyzed oxidation of organic substrates with molecular oxygen is becoming an important and highly rewarding protocol for important feedstock for fine chemical industries.

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