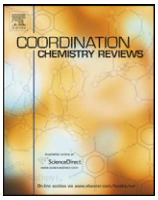
Coordination Chemistry Reviews 253 (2009) 1926–1946

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Polymer-supported Schiff base complexes in oxidation reactions

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Contents

ARTICLE INFO

Article history:
Received 12 November 2008
Accepted 24 March 2009
Available online 2 April 2009

Keywords:
Schiff base complexes
Polymer supports
Enantioselectivity
Catalysis
Transition metals

ABSTRACT

Polymer-supported Schiff base complexes of metal ions show high catalytic activity in comparison to their unsupported analogues. The catalytic activity of metal complexes of different types of Schiff base was analyzed and presented in this review. The manganese(III) Schiff base complexes exhibited high catalytic activity in the oxidation of alkenes and alkanes both in homogeneous and heterogeneous conditions. Similarly, the Schiff base complexes of iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) ions have been used as catalysts in the epoxidation of cyclohexene and oxidation of phenol. Polymer-supported iron(III) Schiff base complexes have demonstrated higher activity than unsupported and polymer-supported Schiff base complexes of other metal ions. Similarly, the polymer-supported salen complexes of ruthenium(III), iron(III) and Schiff base complexes of molybdenum carbonyls have been used successfully as catalysts in the oxidation of cyclo-octene. The oxidation of styrene, limonene, stilbene, benzene and its alkyl derivatives, adamantane, benzyl alcohol,

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0010-8545/$ – see front matter
doi:10.1016/j.ccr.2009.03.019

etc. was catalyzed significantly by polymer-supported Schiff base complexes of different metal ions. The recyclability of polymer-supported Schiff base complexes has also been evaluated and presented in this review. The thermal and moisture stability of polymer-supported Schiff base complexes is responsible for their high activities in reactions involving high temperatures.

Nomenclature

SLPC	solid supported liquid phase catalysts
PBC	polymer bound catalysts
TBHP	*tert*-butylhydroperoxide
PEG	poly ethylene glycol
CS	chitosan
ECH	epoxy cyclohexane
CH	cyclohexene
HPHZ	hydroxy acetophenone hydrazine
HPED	hydroxy acetophenone ethylenediamine
HPPn	hydroxy acetophenone 1,2-propylenediamine
UHP	urea-hydrogen peroxide
PAHs	polycyclic aromatic hydrocarbons
VOCs	volatile organic compounds
TEMPO	2,2,6,6,-tetramethylpiperidine-1-oxyl
m-CPBA	*meta*-chloroperoxybenzoic acid

1. Introduction

Polymer-supported Schiff base ligands are synthesized easily and loaded with different metal ions without any difficulty. The catalytic activities of polymer-supported Schiff base complexes are constant in the presence of moisture and during their applications in high temperature reactions. During the last few years, several reports on synthesis of polymer-supported Schiff base complexes and evaluation of their catalytic activities have appeared; hence, the need of such a review article highlighting the catalytic activity of polymer-supported Schiff base complexes was realized. In this review, the report on the polymer-supported Schiff base complexes in oxidation reactions have been presented for the period of 1996–2008.

Currently, many transition metal ions complexes have been identified as homogeneous catalysts for various reactions, which showed high homogeneity, reproducibility, selectivity, and high activity to catalyze reactions under mild conditions. Although the activities of these transition metal complexes in catalyzing various reactions have been explained at molecular level, these complexes are still associated with problems of corrosion, contamination of reaction products and difficulties in their separation. To overcome these difficulties, heterogeneous catalysts are developed, either by dispersing metal ions on porous solid supports, which are classified as solid supported liquid phase catalysts (SLPC) or chemical binding of metal ions on functionalized polymer supports, which are classified as polymer bound catalysts (PBC) [1–6]. The second method of synthesis of supported catalysts leads to simplification of reaction work-up and separation of supported species easily from reaction mixture by filtration.

Polymer supports are cross-linked resins with large surface area (macroporous or macroreticular resins) [7–14], which swell in reaction media to increase the activity of immobilized catalysts by providing sufficient interfacial interactions with the reactants. The functionalized porous cross-linked polymer beads have displayed significant influence on various reactions [15–18] and have been used as reagents [19–31], chelating agents for separation of metal ions and also as potential sorbents [32,33]. These novel polymer beads have been synthesized and modified using different methods for their applications in phase transfer catalysis [34–37]. However, polymer-supported catalysts suffered in their long-term applications in continuous and fixed bed reactors due to quantitative loss of metal ions from polymer-supported metal complexes. The loss in activity of polymer-supported catalysts is mainly due to the dissociation of metal ions from functionalized polymer beads under catalytic conditions. Therefore, the leaching of metal ions from supported catalyst is a serious problem and could be reduced either by increasing the amount of immobilized ligand on the polymer beads or by avoiding the use of coordinated solvents, or by using chelating ligands [2].

From a synthetic point of view, polystyrene is a popular support due to its cost effectiveness, ready availability, mechanical robustness, chemical inertness, and facile functionalization. In the polymer-supported catalyst, the polymer chain flexibility provides better microenvironment to the catalyst in comparison to silica, alumina and other supports used for immobilization of catalysts. Jacobsen and co-workers have used Co(salen) complexes on functionalized polystyrene in various reactions [38–44], which were effective and excellent catalysts in hydrolytic kinetics, resolution of racemic epoxides, and enantioselective parallel synthesis [45].

Transition metal complexes are effective and selective catalysts in a variety of organic reactions. Although these catalysts offered interesting results such as low influence of diffusion mechanisms on reaction performance, they become more useful if the separation process is tagged to recover them at the end of reaction especially for precious and strategic metal catalysts. However, the inclusion of separation process in some cases might be very difficult and challenging. The current developments in catalysis are mainly focused on immobilization of metal ions complexes either on inert materials, or on functionalized solid supports [46–49]. These heterogenized catalysts combine the advantages of homogeneous and heterogeneous catalysts and are capable of minimizing the drawbacks of both types of catalyst. They offered numerous advantages over solution phase catalysts such as, ease of separation from reaction mixture, significant reduction in problems of waste disposal, and re-use applications by recycling [50–52]. Early transition metal compounds (e.g., Mo, Ti, W, and V) in combination with hydrogen peroxide or alkylhydroperoxide are the most popular catalytic systems in the epoxidation of alkenes. In the industrial production of propylene oxide by Halcon process, the liquid phase epoxidation of propylene was carried out successfully using Mo(VI) catalyst in the presence of alkyl hydroperoxide. During the last decade, studies on the epoxidation of alkenes using heterogenized Mo(VI) catalysts have been carried out in the presence of *tert*-butylhydroperoxide (TBHP). Carreiro et al. used boronic acid group containing resins as a support for Mo(VI) catalyst in the epoxidation of alkenes by TBHP [53]. Sherrington group has developed a wide range of polymer-supported Mo(IV) catalysts for epoxidation of alkenes. Among these heterogenized Mo(IV) systems, the polybenzimidazole and polysiloxane-supported systems are stable and offered significant technological applications in catalysis [54,55].

Polymer-supported vanadium Schiff base complexes [56] have been considered as versatile catalytic reagents for a wide range of oxidation reactions like, oxidation of olefins and allylic alcohols [57–62], benzene/alkylaromatic compounds [61], sulfides [62–64] and alcohols [65–67]. In the presence of inexpensive oxidants such as O_2, H_2O_2 or hydroperoxides, catalysts work efficiently in homogeneous conditions [68].

Catalytic oxidation is an area of particular significance as most of the industrial oxidation reactions are accomplished in the presence of homogeneous catalysts [69]. The application of polymers as catalytic supports has gained significant attention because polymeric supports are inert, non-toxic, non-volatile, insoluble and recyclable [70]; hence, development of viable polymer-supported catalysts has gained a significant prominence in industrial and scientific research. The main drawback of supported catalysts is the leaching of metal ions from solid supports, which can be prevented by using suitable chelating ligands on solid supports. Polymer-supported ruthenium Schiff base complexes showed high catalytic activities in hydrogenation of olefins, oxidation of cyclohexane [71] and toluene [72–75].

Optically active sulfoxides are an important class of compounds and used as synthetic intermediates. The chiral auxiliaries have been used in asymmetric synthesis [76,77] and as bioactive ingredients in various pharmaceutical industries [78–80]. The asymmetric oxidation of sulfides is a convenient chemo and stereoselective route to synthesize the optically active sulfoxides. The polymer-supported vanadium chiral Schiff bases complexes derived from salicylaldehydes and optically active amino alcohols have catalyzed the enantioselective oxidation of sulfides to sulfoxides in the presence of hydrogen peroxide as an environmentally acceptable oxidant[62].

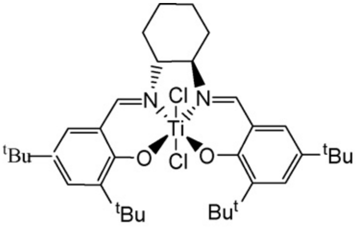
2. Polymer-supported catalysts

The polymer-supported catalytic system involves a robust polymer support and an active species immobilized either by forming chemical bonds or through physical interactions such as hydrogen bonding or donor–acceptor interactions. Polymer-supported catalysts are usually prepared using cross-linked polymer beads, which help in the easy separation of catalyst from reaction media without any significant loss in their activities. The polymer-supported catalysts are used in different forms such as: (a) polymer anchored metal complexes that coordinate with reactants, (b) colloidal catalysts dispersed in a swollen polymer network, and (c) enzymes supported on the polymers also fall in this category.

Environmentally friendly routes for various syntheses [81–85] have been explored using polymer-supported catalysts, which offered significant advantages over traditional routes of synthesis. The polymer-supported catalysts also help in minimizing the contamination of reaction products with toxic transition metal complexes and help in recycling of the catalysts [46,86–88].

Recently, low molecular weight polymer supports have been used for recycling [89–94] of catalysts and to catalyze reactions in homogeneous conditions [92–104]. In general, the reactivity and selectivity of supported catalysts is lower than unsupported analogues. In order to increase the accessibility of catalytic sites, a spacer between polymer support and catalyst was used [98,105–108]. The co-polymerization of metal containing monomers with styrene and divinylbenzene has also been used to prepare polymer-supported catalysts [109–111].

The soluble polymer-supported catalysts are recovered from reaction mixtures [89,112,113]. The titanium-salen complex **1** on PEG-support **2** is recycled five times without any significant loss in its activity and enantioselectivity [114].



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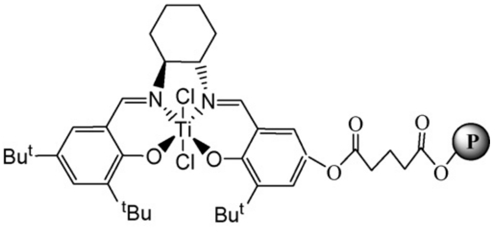

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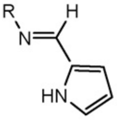
The application of soluble supports to anchor transition metal complexes has received considerable attention in recent years [101,115] because soluble polymer supports have ensured the phase homogeneity to catalyst and reactants, which is a significant advantage over insoluble, supports [116]. The recycling of catalyst from soluble supports is made by reducing the solubility, with poor solvents or by temperature variation [117] but recycled catalysts displayed reduced activity [113,118]. Although, dialysis methods have also been used [119,120] but to overcome the bulk application of solvent [121–123], a Soxhlet extraction method is currently used [124].

3. Polymer-supported Schiff base complexes in oxidation reactions

Oxidation is an important process in nature and industry, which is controlled by different types of catalyst. The oxidation includes different processes such as combustion, biological oxidation, corrosion and degradation of material. The transition metal catalyzed oxidation is important both in biological and industrial processes. In biological processes, metalloenzyme catalyzed reactions are essential for storage and transformation of energy. In industrial processes, the transition metal catalyzed reactions are important to produce oxygenated compounds [125]. The activity of polymer-supported Schiff base complexes of transition metal ions varies with the type of Schiff base ligands, coordination sites and metal ions used in their formation. The following Schiff base ligands **3**–**5** have been used frequently in the formation of metal complexes as catalysts [126].



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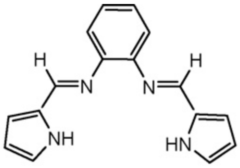

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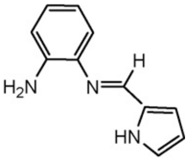

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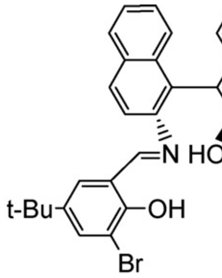
The binaphthyl chiral Schiff base ligands **6**–**8** were also found useful in various metal complex catalyzed reactions [126,127].



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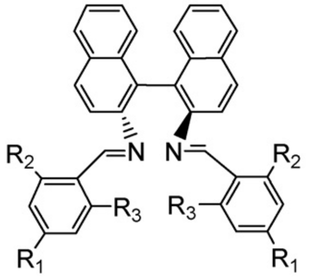

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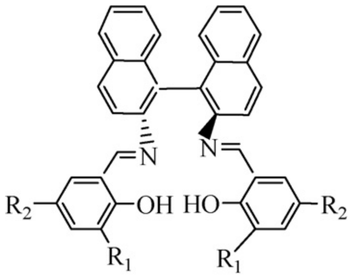

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These studies have clearly revealed that polymer-supported Schiff base complexes are potential catalysts to influence the yield and selectivity in chemical transformations; hence in this review, an attempt was made to critically analyze and discuss the role of polymer-supported Schiff base complexes of transition metal ions in oxidation reactions.

3.1. Alkenes oxidation

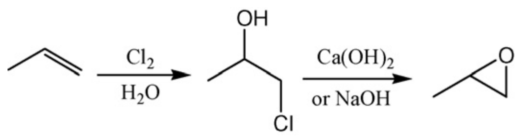
Epoxides, particularly ethylene and propene oxides, are key raw materials for the synthesis of a variety of chemicals such as, glycols, glycol ethers and alkanolamines and also act as building blocks in different polymers, such as, polyesters and polyurethanes.

The simplest epoxide, ethylene epoxide, was produced commercially by Union Carbide (1937), and Shell (1958) by vapor-phase oxidation of ethylene with air or oxygen using an alkali metal promoted supported silver catalyst. This method has replaced the practice of ethylene oxide production via chlorohydrin process. However, this silver catalyzed process is applicable to olefins without C–H allylic bonds, such as ethylene, 1,3-butadiene and styrene but other olefins, such as propene, have displayed low yields due to competitive oxidation of allylic C–H bonds [128]. The chlorohydrin route is traditionally used in the production of propene oxide (Scheme 1). But due to the application of expensive, toxic and corrosive chlorine, the process is being criticised by environmentalists.

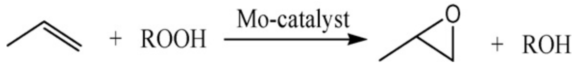
Therefore, epoxidation of olefins was carried out using hydrogen peroxide alone or with osmium tetraoxide, manganese dioxide, and tungsten and molybdenum oxides, although these systems were not commercially feasible. Hawkins (1937) first reported the metal-catalyzed epoxidation of cyclohexene using cumene hydroperoxide in the presence of V_2O_5, which produced 30% yield of cyclohexene oxide. Subsequently, Brill (1963) reported the use of *tert*-butyl hydroperoxide (TBHP) in the presence of hydrocarbon soluble acetyl acetonate complexes of molybdenum, vanadium and chromium as catalyst. The Shell (1974) and ARCO/Halcon (1979) are the most important industrial epoxidation processes, and are based on high valent transition metal ions as catalysts and carried out in the presence of alkyl hydroperoxides. The ARCO and Halcon formed a joint venture, the Oxirane Corporation for manufacturing the propylene epoxide using molybdenum(VI) as catalyst in the presence of organic hydroperoxides. Molybdenum catalysts are highly efficient and selective when used with TBHP or ethylbenzene hydroperoxide (Scheme 2) [129].

Currently, the world wide annual industrial production of propylene oxide is approximately 5 million tons by different processes [130]. Despite the widespread use of transition metal compounds as catalysts [131,132], the stoichiometric reactions are nevertheless commonly used for the oxidation of fine chemicals [133]. The most widely used epoxidation reagent is *meta*-chloroperoxybenzoic acid (*m*-CPBA) [134]. Attempts are being made to develop industrial epoxidation processes that can use hydrogen peroxide as oxidant though hydrogen peroxide is not a cost effective oxidant and difficult to recycle. However, environmentalists have encouraged the application of hydrogen peroxide as an oxidant as it produced eco-friendly by-products, such as water. Enichem developed an integrated process for a variety of liquid phase oxidation reactions, in which hydrogen peroxide is produced from water and methanol by the anthraquinone route and epoxidation is carried out without separating the hydrogen peroxide in the presence of titanium-substituted silicate (TS-1) as catalyst [130]. Degussa developed an industrial process using TS-1 catalyst and H_2O_2 as oxidant, but the process was used exclusively for the production of propylene oxide [134]. Currently, polymer-supported Schiff base complexes are promising catalysts in the oxidation of alkenes.

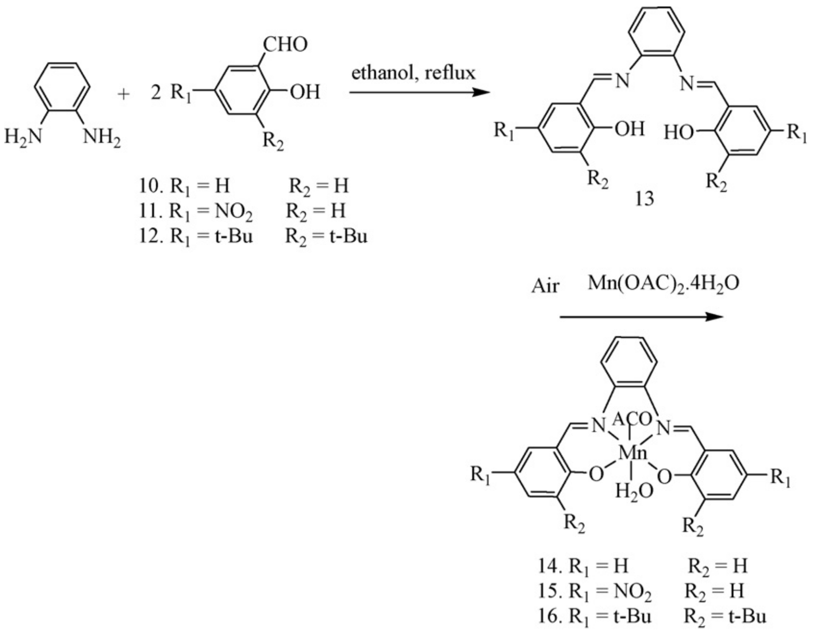
The need for optimal pure pharmaceuticals, herbicides and insecticides as well as perfumes had significantly influenced the development of enantioselective catalysts for epoxidation. In the production of pharmaceuticals and agrochemicals, the chiral epoxides are important intermediates and obtained from asymmetric epoxidation of olefins. The 2-(2,4-difluorophenyl)-epoxyallyalcohol was used as intermediate in the synthesis of triazol fungicide. Recently chirally modified lithium and magnesium *tert*-butyl peroxide have been used successfully in the epoxidation of electron deficient olefins, like chalcones, leading to yields of ca. 60% and ees of 90% [135]. The only system that affords high enantioselectivities is Jacobsen' catalyst **9**.



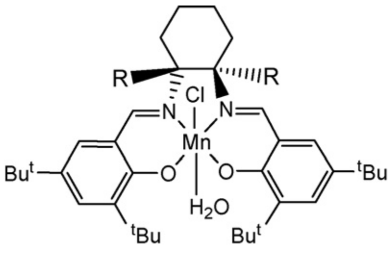
Scheme 1. The chlorohydrin route.



Scheme 2. ARCO and Halcon process [129].



Scheme 3. Procedure for synthesis of salophen Mn(III) complexes [183].



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3.1.1. Cyclohexene epoxidation

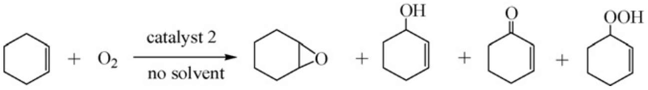
The field of catalysis by polymer-supported metal complexes in organic synthesis has become a subject of great interest ever since the use of a polymer-supported metal complex as catalyst by Lautsch et al. [136]. Cross-linked organic macromolecular species showed wide applications due to the ease with which the work-up of reaction mixture could be carried out and also due to their reusability [137]. Epoxidation of olefins in the presence of metal catalysts was widely investigated [138–150]. In particular, great effort was devoted to the oxidation of cyclohexene during the past few years [151–159]. Direct conversion of cyclohexene into adipic acid with H_2O_2 in the presence of polymer-supported $Na_2WO_4{\cdot}2H_2O$ was made by Sato et al. [160]. However, most processes reported suffer from relatively harsh conditions or poor conversions and selectivities. Awareness of environmental issues has proven a potent driving force in the development of environmentally friendly processes and technologies in chemical industry [161]. In this aspect, more efficient catalytic system in the oxidation of cyclohexene with molecular oxygen without using solvents or reducing agents is of current interests.

Manganese Schiff base complexes are active homogeneous catalysts in the epoxidation of olefins with various stoichiometric oxidants such as peroxides, NaOCl or PhIO. The chiral manganese Schiff base catalysts **9** developed by Jacobsen and co-workers are active and enantioselective epoxidation catalysts. Due to the inherent advantages of heterogeneous catalysts over homogeneous catalysts, much effort [162–164] was made to immobilize these homogeneous catalysts onto solid supports, such as polymers [165–171] and zeolites [172]. However, catalysts based on biopolymers have not received much attention. Chitosan, the most abundant natural amino polysaccharide, is produced by the deacetylation of chitin, which is one of the key constituents of crustaceans shells and is a by-product of the fishing industry. It readily forms films or fibres for various applications [171]. The ability to form films and fibres from chitosan in dilute acid, along with its inherent chirality, has made chitosan an excellent candidate to support various catalysts, and catalytic systems [173–179]. The functionalization of chitosan to provide co-ordination sites was carried out and metal ion anchored catalysts for oxidation reactions and Suzuki and Heck reactions were developed [180–182]. The results of cyclohexene oxidation (Scheme 4) catalyzed by salophen Mn(III) and CS-salophen Mn(III) complexes (Scheme 3) are listed in Table 1 [183] from which it is clear that CS-salophen Mn(III) complexes were more catalytic in the oxidation of cyclohexene and have high turnover numbers. The conversion of cyclohexene was higher with CS-**16** than CS-**14** and CS-**15** but CS-**14** displayed higher turnover numbers.

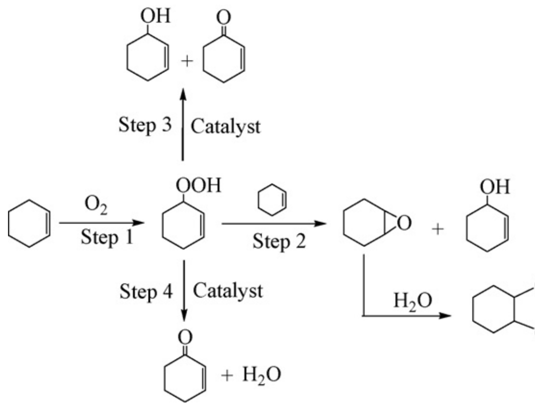
The distribution of oxidation products was different with these catalysts and CS-**14** shows high selectivity for 2-cyclohexene-1-one under the same conditions. A possible reason for the enhanced activity of these supported catalysts was due to the segregation of salophen Mn(III) complexes on the chitosan surface. Unsupported complexes can become inactive due to the formation of aggregates in the solution.

The selectivities of CS-salophen Mn(III) complexes for oxidation products of cyclohexene did not change significantly after four runs. However, the conversion of cyclohexene displayed a decreasing trend after four runs, which is mainly attributed to the loss of weakly bonded salophen Mn(III) complexes on CS [183] (Scheme 4).

The literature reports [184] indicated that the oxidation of cyclohexene with molecular oxygen initially forms 2-cyclohexene-1-hydroperoxide as displayed in Scheme 5 (Step 1). Since



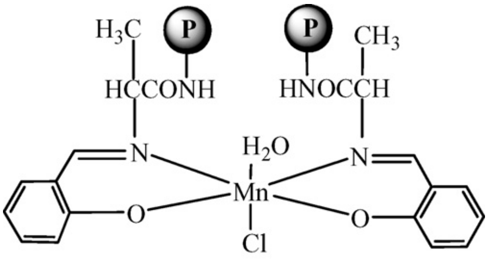
Scheme 4. Oxidation by-products of cyclohexene [183].



Scheme 5. Mechanism of oxidation of cyclohexene [183].

2-cyclohexene-1-hydroperoxide is not stable, it was converted to 2-cyclohexene-1-ol and 1,2-cyclohexenediol through Step 2. But in presence of catalyst, 2-cyclohexene-1-hydroperoxide was converted to 2-cyclohexene-1-ol and 2-cyclohexene-1-one through Step 3 and to 2-cyclohexene-1-one and water through Step 4. The conversion of cyclohexene is controlled by the rate of Step 1 in Scheme 5 and selectivity for cyclohexene oxide and 1,2-cyclohexanediol is controlled by the ratio of rate of Step 2 to the rates of Steps 3 and 4 [183].

The sol–gel technique is another way to heterogenize homogeneous metal complex catalysts. Generally, there are two principal methods for immobilizing metal complexes by this technique, i.e., either by directly physical doping [185,186] or functional modifications of ceramic matrix by co-polymerization with organometallic alkoxides [187]. The manganese-anchored catalyst **17** for epoxidation of cyclohexene was prepared by the functional modification of polymers [188].



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The amount of catalyst on the polymer support accelerated the rate of epoxidation of cyclohexene (Table 2). The conversion of cyclohexane increased to 97.3% and epoxide selectivity reached a maximum of 80.0%, when 0.18 g of catalyst was loaded. Upon increasing the catalyst loading beyond 0.18 g, the conversion increased slightly and selectivity for epoxide decreased.

These observations supported an idea that Schiff base complexes could be used to catalyze the aerobic oxidation of olefins to propenol derivatives in the absence of isobutyraldehyde [189], The catalyst heterogenized on the functionalized polymer is more active in the epoxidation of cyclohexene than physically encapsulated catalyst and homogeneous complexes [Table 3] as found with other systems [190]. The poor solubility of the metal complex in the solvent and its self-degradation was responsible for the low activity of the homogeneous catalyst. The site isolation effect and stability of homogeneous complexes on the polymer supports was also responsible for the high activity of the polymer-supported catalysts.

Table 1
Comparison of catalytic activities of CS-salophen Mn(III) complexes with unsupported salophen Mn(III) complexes [183].

Catalyst	Metal content (%)	Conversion[a] (%)	TON[b] ($\times 10^4$)	Epoxide selectivity[a] (%)			
				I	II	III	IV
CS-**14**	0.31	75.5	11.0	6.7	18.0	56.5	18.8
CS-**15**	0.59	67.0	5.1	10.7	18.6	36.9	33.8
CS-**16**	0.56	79.1	6.4	12.1	15.8	38.8	33.3
14[c]	14.89	83.6	0.2	5.2	23.5	61.3	10.0
15[d]	11.97	73.6	0.3	7.8	27.3	57.6	7.3
16[c]	9.26	82.3	0.4	6.1	25.4	59.3	9.2

Reaction conditions: catalyst, 2.4 mg; cyclohexene, 2.0 mL (19.7 mmol); temperature, 70 °C; time 12 h.

[a] Conversion and selectivity were determined by GC.

[b] Moles of substrate converted per mole of metal in the catalyst.

[c] Reaction in 5 mL CH_2Cl_2.

[d] Reaction in 5 mL CH_3CN.

Table 2
Epoxidation of cyclohexene by anchored catalyst [188].

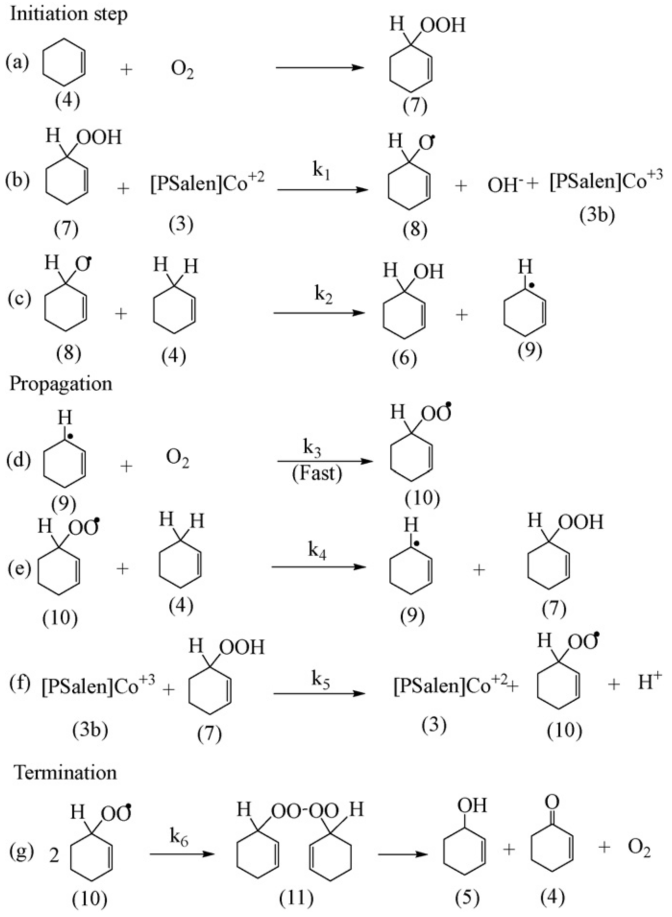
Effect	Time (h)	Temperature (°C)	Catalyst weight (g)	Conversion (%)	Epoxide selectivity (%)
Time	2	25	0.20	36.2	69.4
	4	25	0.20	58.0	72.2
	6	25	0.20	96.3	77.2
	8	25	0.20	98.2	76.6
Temperature	6	25	0.20	96.3	77.2
	6	35	0.20	98.1	79.3
	6	45	0.20	98.5	62.9
	6	55	0.20	97.7	60.7
Catalyst weight	6	35	0.15	90.7	73.5
	6	35	0.18	97.3	80.0
	6	35	0.20	98.1	79.3
	6	35	0.23	98.7	75.0

Reaction conditions: isobutyraldehyde:cyclohexene, 2:1; acetonitrile, 60 mL; cyclohexene, 2.5 mL; catalyst, 1.0×10^{-2} mmol.

Table 3
The catalytic activities of different catalysts [188].

Catalyst	Conversion (%)	Epoxide selectivity (%)
Homogeneous	89.3	73.2
Physically encapsulated	87.8	80.5
Anchored	99.6	88.2

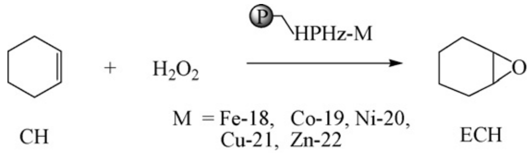
Reaction conditions: catalyst, 1.0×10^{-2} mmol; cyclohexene, 2.5 mL; isobutyraldehyde:cyclohexene, 2:1; acetonitrile, 60 mL; temperature, 60 °C, 6 h.



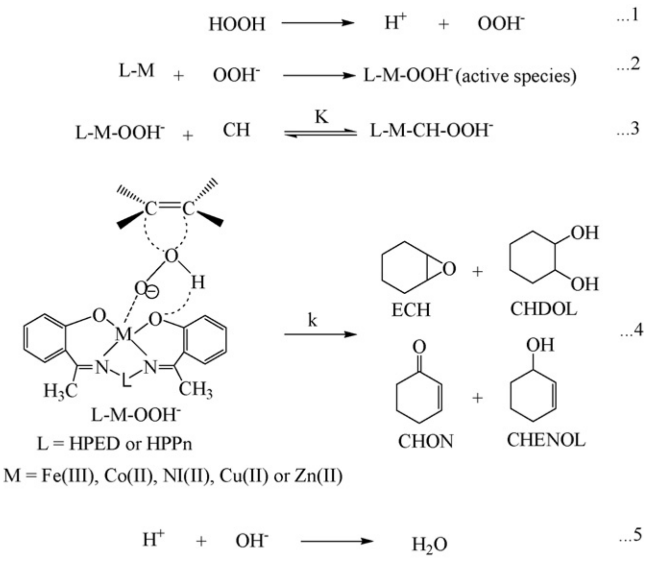
Scheme 6. Haber–Weiss radical-chain sequence mechanism for aerobic oxidation of cyclohexene catalyzed by P-SalenCo [193].

The conversion of cyclohexene and epoxide selectivity remained almost constant with the anchored catalyst after six runs but the physically anchored catalyst displayed poor recyclability [188]. The epoxidation of cyclohexene catalyzed by salen complexes with electronegative substituents demonstrated a radical-chain sequence mechanism (Scheme 6) [191,192]. The primary role of metal was to decompose hydroperoxide by alternate reduction and oxidation reactions [193].

The catalytic activity of unsupported and polymer-supported metal complexes of hydrazine Schiff base (Scheme 7) was evaluated by studying the epoxidation of cyclohexene in the presence of hydrogen peroxide as oxidant [194–196].



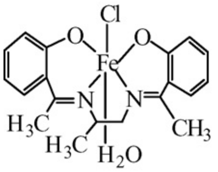
Scheme 7. Epoxiadation of cyclohexene with hydrazine Schiff base complexes [194–196].



Scheme 8. Mechanism of cyclohexene epoxidation [197,198].

The product formation in the epoxidation of cyclohexene was attributed to the enzymatic behavior [197,198] of metal complexes of Schiff bases (L-M), which produced an active species (M-L-OOH^-) by the interaction of hydrogen peroxide (Scheme 8). The peroxoanions (OOH^-) produced in Step 1 were linked with Schiff base complexes of iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) ions and produced active species through a fast Step 2. The subsequent interactions of active species with cyclohexene (CH) produced intermediates (M-L-CH-OOH^-) through a fast dynamic equilibrium (Step 3).

The rate of electron exchange in the intermediate and its decomposition through a slow reaction step (k) controlled the selective formation of epoxy cyclohexane (ECH) in the epoxidation of cyclohexene (Scheme 8).



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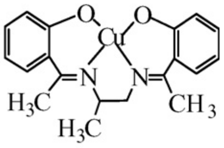

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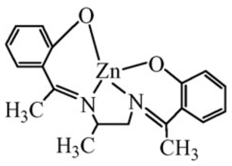

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The epoxidation of cyclohexene was more prominent with polymer-supported metal complexes in comparison to unsupported metal complexes different Schiff base (Table 4) [194–198]. The epoxidation of cyclohexene at 1:1:1 molar ratios of H_2O_2 to cyclohexene and supported catalyst was highest within a reaction time of 24 h in the presence of supported and unsupported Schiff base complexes (Table 4). However, the activity of unsupported Schiff base complexes of metal ions was low. The Schiff base complexes of iron(III) ions were more selective to produce epoxy cyclohexane than cobalt(II), nickel(II), copper(II) and zinc(II) ions.

Table 4
Oxidation of cyclohexene and selectivity for epoxy cyclohexane [194–198].

Metal complexes	Catalyst	Unsupported		Polymer supported	
		CH (wt%)	ECH (wt%)	CH (wt%)	ECH (wt%)
HPHZ-Fe	**18**	72.0	92.0	79.0	96.5
HPHZ-Co	**19**	56.0	88.0	66.2	94.2
HPHZ-Ni	**20**	68.0	92.0	74.7	95.9
HPHZ-Cu	**21**	54.5	89.0	43.4	88.8
HPHZ-Zn	**22**	47.8	82.0	36.3	86.1
HPPn-Fe	**23**	83.2	93.0	90.6	98.3
HPPn-Cu	**24**	54.2	91.8	69.7	93.0
HPPn-Zn	**25**	50.8	86.0	64.9	89.4

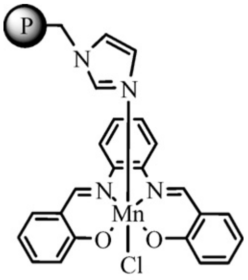
[H_2O_2]/[phenol]/[catalyst], 0.05 M; temperature, 70 °C; time, 24 h.

Table 5
Epoxidation of cyclohexene with $NaIO_4$ catalyzed by Mn(III)salophen and Mn(III)salophen-PSI [45].

Mn-catalyst	Conversion (%)[a]/time(h)	Epoxide yield (%)	Turnover frequency
Homogeneous	91/0.5	75	18.2
Heterogeneous	99/2.5	94	4.7

[a] GLC yield based on starting alkene.

The polymer-supported Mn(III)salophen complexes **26** oxidized cyclohexene in the presence of $NaIO_4$ and selectivity for epoxy cyclohexane was greater under heterogeneous conditions (Table 5) [45].



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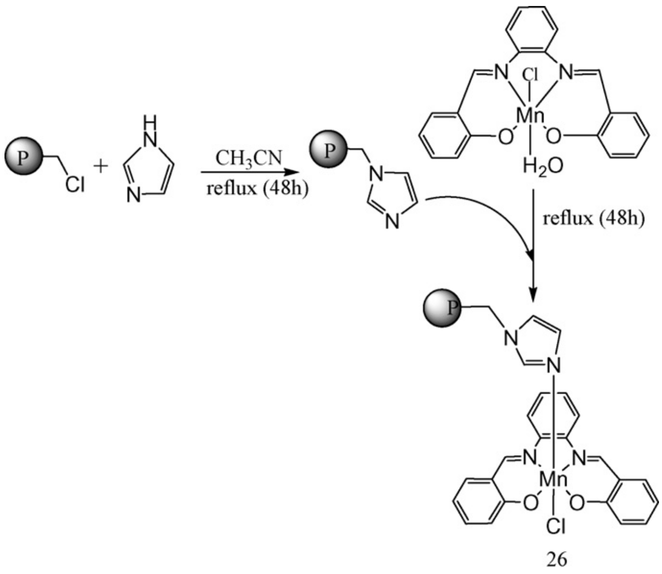
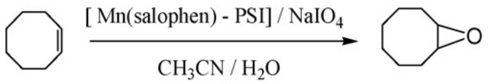
3.1.2. Cyclo-octene epoxidation

Manganese Schiff base complexes have been extensively used in homogeneous catalysis, mainly because of their high activity, selectivity and enantioselectivity [199–204]. The catalytic activity of manganese Schiff base complexes in homogeneous conditions usually decreases with time due to the oxidation of ligand or formation of dimeric oxo- and peroxo-bridged complexes. The heterogenization of these homogeneous catalysts on solid supports displayed high recyclability and stability [46,205,206]. The anchoring of manganese(III)–salen complexes on the polymer support lowered the local concentration of metal complexes, decreased the possibility of dimerization, and formation of undesired mono–oxo manganese(IV).

Schiff base complexes (salen or salophen) were immobilized on solid supports by different methods: (a) non-covalent immobilization on zeolites, clay or siloxane membranes [207–209]; (b) covalent grafting on inorganic supports such as silica or MCM-41 [210–214]; (c) co-polymerization of functionalized salen monomer to anchor on the polymer support; and (d) attaching or building-up a salen structure on a preformed polymer [90,215–218]. Polymers gained attention as supports as they are inert, non-toxic, non-volatile, insoluble and often recyclable. Imidazoles and pyridines ligands are anchored [219–220]. These nitrogen-based ligands displayed high catalytic efficiency in the epoxidation with single oxygen atom donors (Scheme 9) [45]. The polymer-supported catalyst, [Mn(salophen)Cl-PSI] **26**, showed high activity in the epoxidation of cyclo-octene in the presence of sodium periodate as oxidant at room temperature (Scheme 10) [45].



Scheme 9. Preparation of polymer-supported catalyst, Mn(III)salophen-PSI **26** [45].



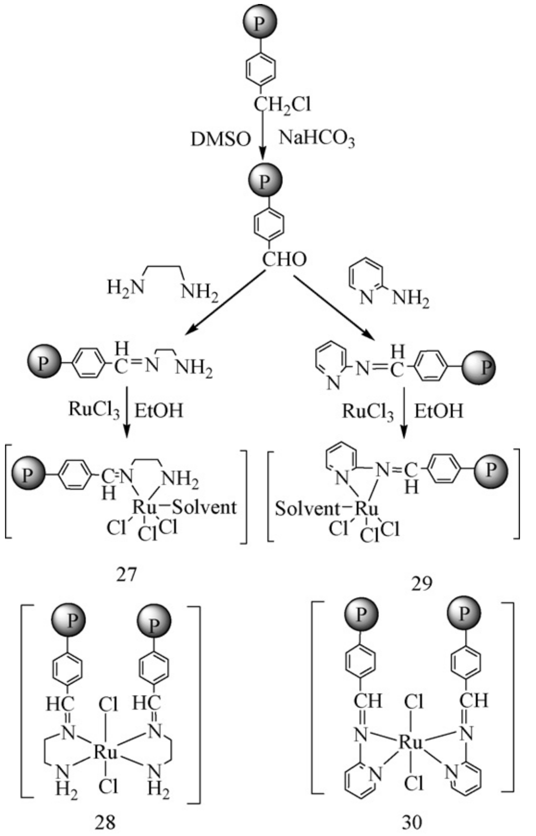
Scheme 10. Oxidation of cyclo-octene by polymer-supported Mn(III) Schiff base catalyst [45].

In the catalytic epoxidation of alkenes, the choice of oxygen donor and solvent is of crucial importance. In the heterogeneous Mn(III)salophen catalyzed epoxidation of cyclo-octene, the activity of different oxidants such as, NaOCl, $NaIO_4$, Bu_4NIO_4, H_2O_2, $KHSO_5$, *tert*-butylhydroperoxide, urea–H_2O_2 (UHP) was compared (Table 6) [45]. A small amount of cyclo-octene oxide was produced, when, NaOCl, H_2O_2, *tert*-butylhydroperoxide and urea–H_2O_2 (UHP) were used as a source of oxygen, either in acetonitrile or dichloromethane. The oxone ($KHSO_5$) in metalloporphyrin-catalyzed oxidation displayed various disadvantages such as: it needed buffering due to its acidity and some time it bleached the metal catalysts during oxidation reaction. Sodium periodate ($NaIO_4$) was also used as a source of oxygen donor, because: (i)

Table 6
Effect of oxidant and solvent on epoxidation of cyclo-octene catalyzed by Mn(III)salophen-PSI **26** at room temperature [45].[a].

Oxidant	Solvent	Epoxidation yield (%) after 2.5 h
$NaIO_4$	CH_3CN/H_2O	98
	CH_3COCH_3/H_2O	89
	CH_3OH/H_2O	58
	CH_3CH_2OH/H_2O	53
	$CHCl_3/H_2O$	33
	CH_2Cl_2/H_2O	21
	CCl_4/H_2O	15
Oxone ($KHSO_5$)	CH_3CN/H_2O	85
H_2O_2	CH_3CN	32
H_2O_2/urea	CH_3CN	16
NaOCl	CH_3CN	37
tert-BuOOH	CH_3CN	18
Bu_4NIO_4	CH_3CN	45

[a] Cyclo-octene, 0.50 mmol; oxidant, 1 mmol; catalyst, 0.04 mmol; CH_3CN, 5 mL; H_2O, 2.5 mL.

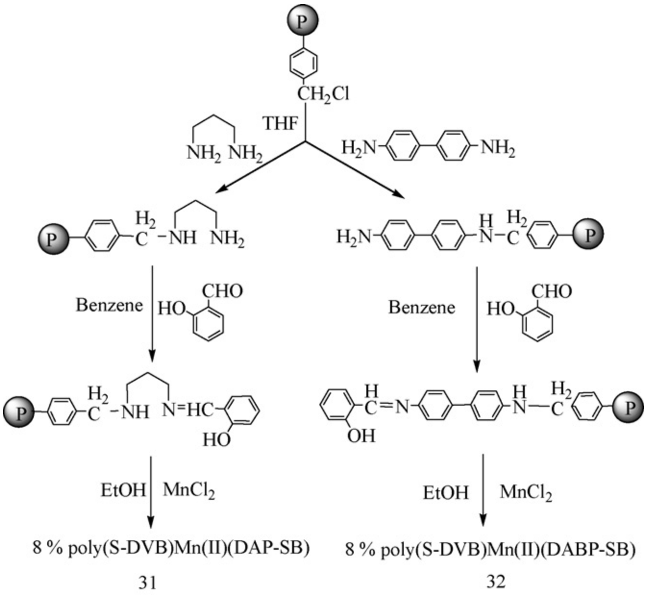


Scheme 11. Synthesis of poly(styrene-divinylbenzene) supported Schiff base complexes of Ru(III) **27**–**30** [221].

it is a strong oxidant; (ii) remains inert in the absence of catalyst; and (iii) is highly soluble in CH_3CN/H_2O.

The epoxidation of cyclo-octene was studied in the presence of various solvents at room temperature (Table 6). Among the mixtures of methanol, ethanol, acetone, and acetonitrile (single phase systems) chloroform, dichloromethane and carbon tetrachloride with water (two phase systems), the 2:1 mixture of acetonitrile/water was a suitable reaction medium because it produced a high yield of epoxide. The high catalytic activity in aqueous acetonitrile is attributed to the polarity of solvent, better swelling in polymer support and high solubility of $NaIO_4$ in the solvent [45]. Manganese Schiff base complexes on polystyrene-bound imidazole Schiff base ligand were able to enhance the activity of anchored manganese(III) ions [219,220].

The epoxidation of cis-cyclo-octene in the presence of Ru-catalysts **27**–**30** at ambient temperature and at 50 °C (Scheme 11) selectively produced cyclo-octene oxide in the presence of THBP oxidant [221].



Scheme 12. Synthesis of Mn(II) supported poly(styrene-divinylbenzene) Schiff base complexes **31** and **32** [165].

Table 8
Catalytic epoxidation of cis-cyclo-octene with supported Mn-catalysts [165].

Catalyst	Solvent	Temperature (°C)	Epoxide (%)
31	CH_2Cl_2	25	10.1
	CH_2Cl_2	40	13.9
	CH_3CN	25	3.2
	CH_3CN	50	4.6
32	CH_2Cl_2	25	9.4
	CH_2Cl_2	40	12.2
	CH_3CN	25	2.3
	CH_3CN	50	3.8

Reaction conditions: catalyst, 250 mg; TBHP, 2 mmol; solvent, 20 mL; 24 h.

The yields were substantially greater at 50 °C than at 26 °C and catalysts **29** and **30** produced high yields of reaction products (Table 7).

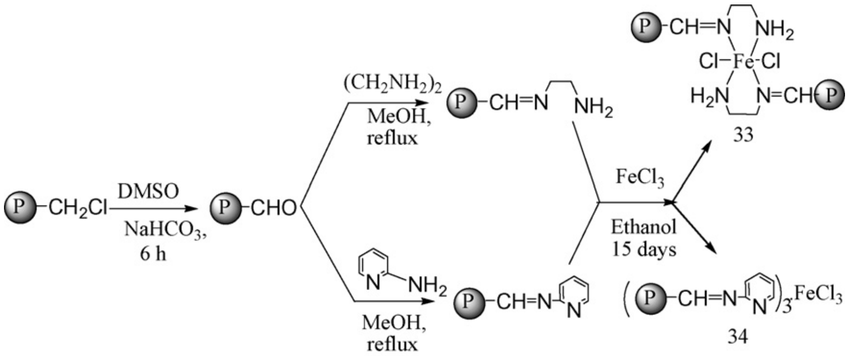
Mn(II)-**31** and Mn(II)-**32** complexes (Scheme 12) displayed catalytic activity in the epoxidation of electron rich olefins such as norbornene and cis-cyclo-octene [165]. The epoxidation of olefins increased slightly on increasing the temperature from 40 to 50 °C in the presence of TBHP oxidant (Table 8).

The catalytic activity of Mn(II) complexes was greater in methylene chloride than in acetonitrile. The polymeric Mn(II)-**31** displayed marginally better catalytic activity than Mn(II)-**32** catalyst [165]. The reaction rate of polymer bound catalysts was slower than their homogeneous analogues, attributed mainly to the slower

Table 7
Epoxidation of cis-cyclo-octene with polymer anchored Ru(III) catalysts [221].

Ru(III)-catalyst	Temperature	Cyclo-octene oxide (mmol)		Cyclo-octene conversion (%) (°C)	
		CH_3CN	CH_3OH	CH_3CN	CH_3OH
27	26	0.43	0.20	4.3	4.9
28	26	0.56	0.26	6.6	6.3
29	26	0.62	0.52	7.4	12.6
30	26	0.89	0.70	10.1	16.9
27	50	1.03	0.98	12.1	23.2
28	50	1.19	0.89	14.2	20.9
29	50	2.52	1.15	29.5	27.6
30	50	3.65	1.27	42.9	30.4

Conditions: catalysts **27**–**30**, 0.25 g; cis-cyclo-octene, 10 mmol; TBHP, 4 mmol; 24 h.



Scheme 13. Synthesis of poly(styrene-divinylbenzene) supported iron(III) Schiff base complexes **33** and **34** [224].

Table 9
Catalytic epoxidation of cis-cyclo-octene with supported Fe-catalysts [224].

Catalyst	Solvent	Temperature (°C)	Cyclo-octene oxide (%)
33	Acetonitrile	25	2.8
	Methanol	25	1.9
	Acetonitrile	50	10.4
	Methanol	50	7.4
34	Acetonitrile	25	2.5
	Methanol	25	2.6
	Acetonitrile	50	20.8
	Methanol	50	12.6

Reaction conditions: catalyst, 250 mg; alkene, 10 mmol; TBHP, 4.25 mmol; solvent, 20 mL; 24 h.

Table 10
Epoxidation of cis-cyclo-octene with TBHP catalyzed by polymer-supported molybdenum carbonyl Schiff base catalyst **37** [55].

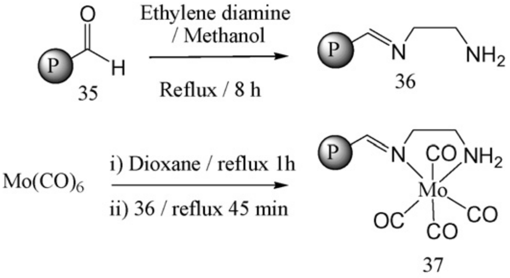
Solvents	Epoxide (%)
Me_2CO	–
THF	–
CH_3CN	1.5
$HCCl_3$	49
CCl_4	94

Reaction condition: cis-cyclo-octene, 0.5 mmol; TBHP, 1.5 mmol; catalyst, 0.01 mmol/Mo; solvent, 4 mL; 2.5 h.

rate of diffusion of olefinic substrates in the polymer matrix in which the active sites were placed [222].

The commonly used styrene-divinylbenzene polymer support has also been modified chemically into a ligand having a variety of coordination sites, such as diketones, dipyridylamine, diphosphine, glycine, and ethylenediamine. The salen type homogeneous complexes of transition metals, such as Ni(II), Mn(II) are known to be effective catalysts for epoxidation of olefins [223]. The iron(III) supported on functionalized polystyrene-Schiff base ligands was used as catalyst (Scheme 13) in the epoxidation of cis-cyclo-octene in the presence of *tert*-butylhydroperoxide as terminal oxidant at ambient temperature and at 50 °C, which indicated that the temperature has also played a significant role in controlling the rate of epoxidation (Table 9) [224].

The polymer-supported molybdenum carbonyl Schiff base catalyst **37** (Scheme 14) was also evaluated for their catalytic activity in the epoxidation of cis-cyclo-octene (Scheme 15) with TBHP in the presence of different solvents (CCl_4, THF, CH_3CN, and CH_3COCH_3) [55]. The activity of polymer-supported catalyst is high in CCl_4 (Table 10) in comparison to unsupported $Mo(CO)_6$ catalyst [225] in alkene epoxidation. The effect of other oxidants, such as $NaIO_4$ and H_2O_2 on epoxidation of cyclo-octene under various conditions was also investigated and no significant changes in the product's yield was noticed in the presence of catalyst **37**.



Scheme 14. Preparation procedures of catalyst **37** [55].

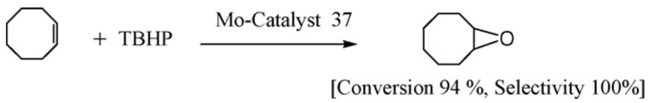
The polymer-supported catalyst has efficiently converted cis-cyclo-octene to corresponding epoxides with high selectivity in the presence of TBHP. The activity of catalyst remained constant even after recycling the catalyst for eight times.

3.1.3. Styrene oxidation

The polymer-supported ruthenium(III) Schiff base complexes **27**–**30** have been used as catalyst in the epoxidation of styrene in the presence of TBHP at ambient temperature and at 50 °C [221]. The styrene did not epoxidized in absence of catalyst or oxidant and in the presence of molecular oxygen. In these experimental conditions, the epoxidation of styrene in the presence of TBHP has resulted in cleavage of styrene, hence, in addition to styrene oxide; the secondary oxidation product benzaldehyde was also formed in substantial quantity [Table 11].

The epoxidation of styrene has also displayed significant variation on using methanol in place of acetonitrile. The epoxidation of styrene with polymer-supported catalyst has followed metal oxo based mechanism (Scheme 16) [221].

Vanadium Schiff base complexes have also been extensively used in homogeneous and heterogeneous catalysis, mainly because of their high activity, selectivity and enantioselectivity [62]. A decreasing trend with reaction time was observed in the catalytic activity of vanadium Schiff base complexes in homogeneous medium, due to ligand oxidation. Recently, the heterogenization of vanadium complexes on the polymer support was the subject of intensive research to produce stable and recyclable catalyst [62].



Scheme 15. Epoxidation of cis-cyclo-octene with TBHP catalyzed by polymer-supported molybdenum carbonyl Schiff base catalyst **37** [55].

Table 11
Oxidation of styrene with TBHP in presence of polymer Ru(III)-supported catalyst and CH_3CN Solvent [221].

Catalyst	Temperature (°C)	Styrene oxide (%)	Benzaldehyde (%)
27	26	4.8	4.9
28	26	1.3	6.6
29	26	1.7	7.5
30	26	0.74	5.7
27	50	17.2	81.6
28	50	11.8	84.5
29	50	26.0	73.5
30	50	26.7	73.8

Conditions: catalysts **27**–**30**, 0.25 g; styrene, 10 mmol; TBHP, 4 mmol; 24 h.

Table 12
Styrene epoxidation with polymer-supported Fe-catalysts [224].

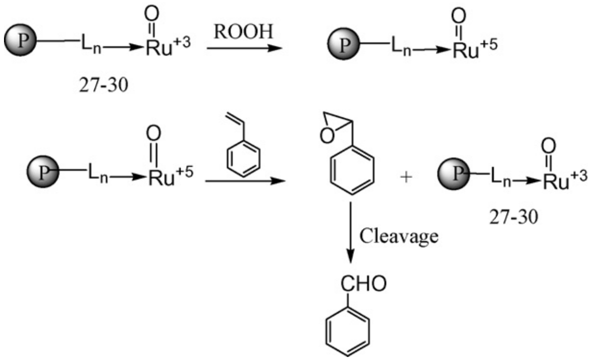
Catalyst	Solvent	Temperature (°C)	Styrene oxide (%)	Benzaldehyde (%)
33	Acetonitrile	25	1.7	8.0
	Methanol	25	1.0	7.2
	Acetonitrile	50	6.6	57.2
	Methanol	50	2.1	36.0
34	Acetonitrile	25	1.2	9.9
	Methanol	25	0.9	7.3
	Acetonitrile	50	7.2	64.3
	Methanol	50	3.4	48.8

Reaction conditions: catalyst, 250 mg; alkene, 10 mmol; TBHP, 4.25 mmol; solvent, 20 mL; 24 h.

Table 13
Epoxidation of limonene with $NaIO_4$ catalyzed by Mn(III)salophen and Mn(III)salophen-PSI [45].

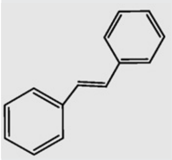
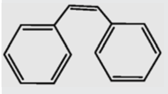
Mn-catalyst	Conversion (%)[a]/time (h)	Epoxide yield (%)	Turnover frequency
39	83/0.5	55 (1,2-epoxide)[b]	16.6
26	92/2.5	65 (1,2-epoxide)[b]	4.4

[a] GLC based on starting alkene.
[b] Both NMR and GLC approved the data.



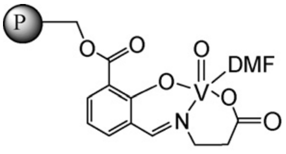
Scheme 16. Proposed mechanism of alkene epoxidation [221].

Table 15
Epoxidation of alkenes with TBHP catalyzed by polymer-supported molybdenum carbonyl Schiff base catalyst **37** [55].

Stilbene	Conversion (%)	Epoxide selectivity (%)	Time (h)
	100	100	5.0
	100	100 (77% cis and 23% trans)	5.0

Reaction conditions: alkene, 0.5 mmol; TBHP, 1.5 mmol; catalyst, 0.01 mmol/Mo; CCl_4, 4 mL.

The polymer-supported vanadium Schiff base complexes PS-[VO(fsal-β-ala)·DMF] **38** have been used as catalysts in the oxidation of styrene in the presence of hydrogen peroxide as oxidant and epoxidation of styrene increased to 72% at a 1:2.5 molar ratio of styrene to hydrogen peroxide [62,64].



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The polymer-supported iron(III) Schiff base complexes **33** and **34** were also used in the epoxidation of styrene in the presence of *tert*-butylhydroperoxide as terminal oxidant at ambient temperature [224].The epoxidation of styrene was highest at 50 °C and acetonitrile is a better solvent than methanol (Table 12).

The polymer-supported molybdenum carbonyl Schiff base catalyst **37** has also catalyzed the epoxidation of styrene in the presence of THBP oxidant [55].

3.1.4. *Limonene oxidation*

Limonene epoxide is a key raw material in the synthesis of pharmaceuticals, fragrances, perfumes and food additives [226]. Conventionally, it is manufactured by the oxidation of limonene with stoichiometric amount of peracids. As this process is not eco-friendly, attempts are in progress to develop suitable catalysts for this reaction [227–247]. The oxidation of limonene, in general, yields a variety of reaction products. If limonene is selectively oxidized at olefinic positions then epoxide is formed and oxidation at allylic position produces carveol and carvone. The polymer-supported Mn(salophen) catalyst **26** displayed 92% conversion of limonene with 65% yield of epoxide, whereas unsupported catalyst **39** provided 83% conversion of limonene with 55% yield of epoxide (Table 13) [45].

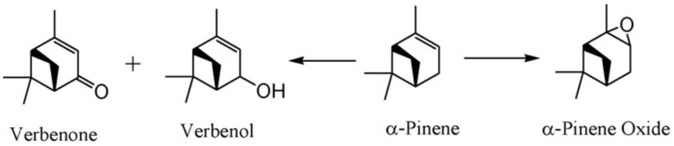
3.1.5. *Stilbene oxidation*

It is well known that the catalytic ability of manganese Schiff base complexes is improved by using a nitrogen base as co-catalyst [224,225]. The polystyrene-bound imidazole complexes of man-

Table 14
Epoxidation of stilbene with $NaIO_4$ catalyzed by Mn(III)salophen **39** and Mn(III)salophen-PSI **26** [45].

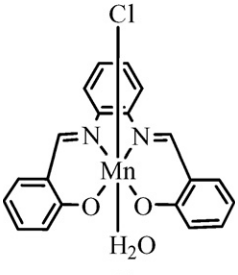
Mn-catalyst	Conversion (%)[a]/time (h)		Epoxide yield (%)		Turnover frequency	
	Cis	Trans	Cis	Trans	Cis	Trans
39	58/0.5	41/0.5	36	41	11.6	8.2
26	75/2.5	67/2.5	49	67	3.6	3.2

[a] GLC yields based on starting alkene.



Scheme 17. Oxidation products of pinene [55].

ganese have been used as catalyst in the epoxidation of stilbene at room temperature in CH_3CN/H_2O mixture [224,225] and epoxidation of trans-stilbene has taken place in a stereospecific manner. In contrast, the epoxidation of cis-stilbene displayed some loss of stereochemistry and afforded 36% cis- and 49% trans-stilbene oxides, respectively (Table 14). Apparently, the formation of thermodynamically more stable trans-stilbene oxide required a free rotation along C–C bond of alkene at some intermediate steps; such a rotation is expected to be more feasible using catalysts with less steric strain [45].



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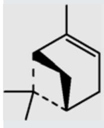
The supported molybdenum carbonyl Schiff base catalyst **37** is also reactive in the epoxidation of stilbene (Table 15). This catalyst has efficiently converted indene to its corresponding epoxides with high selectivity in the presence of TBHP [55].

3.1.6. *Pinene oxidation*

In the oxidation of α-pinene, the major product is α-pinene oxide (91%), and allylic oxidation products, verbenone and verbenol were produced as minor products (Scheme 17) (Table 16) [55].

The supported Mn(III)salophen **26** has also displayed catalytic activity in the epoxidation of pinenes (Table 17). The catalyst **26** efficiently converted pinenes to their corresponding epoxides (92%) with high selectivity in the presence of $NaIO_4$ [45] (Scheme 18).

Table 16
Epoxidation of alkenes with TBHP catalyzed by polymer-supported molybdenum carbonyl Schiff base catalyst **37** under reflux conditions [55].

Alkene	Conversion (%)	Epoxide selectivity (%)	Time (h)
	100	91 (7% verbenon, 2% verbenol)	2.0

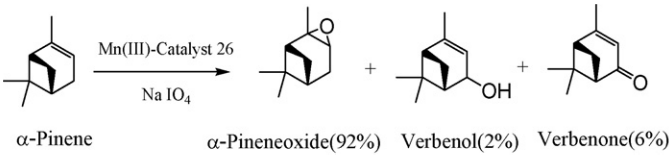
Reaction conditions: alkene, 0.5 mmol; TBHP, 1.5 mmol; catalyst, 0.01 mmol/Mo; CCl_4, 4 mL.

Table 17
Epoxidation of pinene with $NaIO_4$ catalyzed by Mn(III)salophen **39** and Mn(III)salophen-PSI **26** [45].

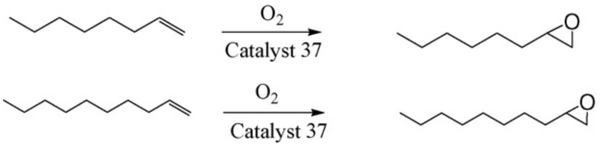
Mn-catalyst	Conversion (%)[a]/time (h)	Epoxide yield (%)	Turnover frequency
39	75[b]/0.5	66	15.0
26	100[b]/2.5	92	4.8

[a] GLC yields based on starting alkene.

[b] The by-products are 6% verbenone and 2% verbenol for heterogeneous system and 7% verbenone and 2% verbenol for homogeneous system.



Scheme 18. Epoxidation of pinene with polymer supported Mn(III)salophen **26** in presence of $NaIO_4$ [45].



Scheme 19. Aerobic oxidation of linear aliphatic olefins catalyzed by molybdenum carbonyl Schiff base catalyst [55].

3.1.7. *Linear alkene oxidation*

Linear olefins have been oxidized in the presence of Schiff base complexes but electron rich cyclic olefins are more active than electron-poor terminal olefins. This has clearly reflected the electrophilic nature of oxygen transfer from manganese-oxo intermediate to olefinic double bond. The linear alkenes such as 1-hexene and 1-dodecene are poorly oxidized with homogeneous Mn(salophen)Cl catalyst.

The polymer-supported catalytic system displayed good activity in the epoxidation of linear alkenes such as 1-hexene and 1-dodecene (Table 18) [45].

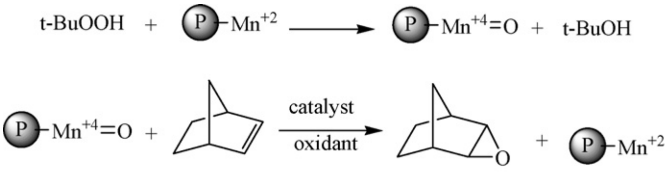
The supported molybdenum carbonyl Schiff base catalyst **37** also showed catalytic activities in the epoxidation of linear alkenes (Table 19). The catalyst has efficiently converted alkenes to their corresponding epoxides with high selectivity in the presence of TBHP (Scheme 19) [55].

The transfer of oxygen from manganese-oxo intermediate to olefinic double bond is electrophilic in nature; hence, cyclic olefins are more reactive for epoxidation than terminal olefins.

3.1.8. *Norbornene oxidation*

Mn(II) catalysts **31** and **32** (Scheme 12) also displayed activity in the epoxidation of electron rich olefins such as norbornene as is clear from the data summarized in Table 20 [165]. The epoxidation was poor at room temperature in the presence of TBHP but increased slightly at elevated temperature (40–50 °C) and in the presence of methylene chloride as a solvent. The catalytic activity of polymer-supported Mn(II)-**31** was marginally high than unbound catalyst Mn(II)-**32** (Fig. 1).

Two major mechanistic pathways for metal-catalyzed oxygen transfer are known, which involve either peroxometal or oxometal species as active intermediates. These mechanistic processes are normally observed in homogeneous catalysis but also applicable for polymer-supported metal complexes. The probable mechanism for polymer-supported Mn(II) catalysts is displayed in Scheme 20 [165].



Scheme 20. Mechanism of olefin epoxidation [165].

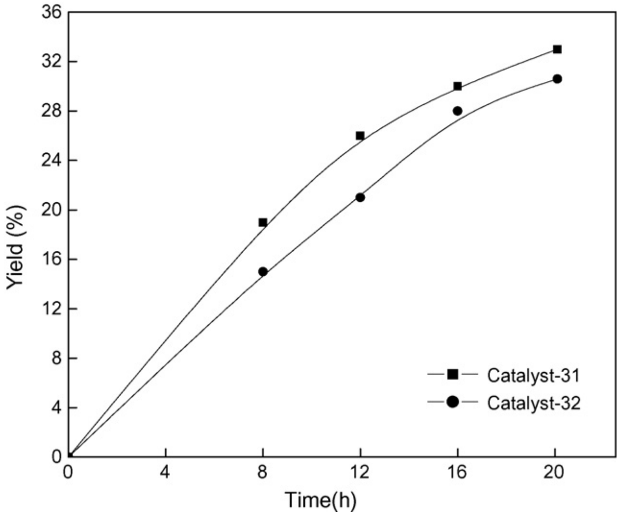


Fig. 1. Plot of conversion (%) vs. time for norbornene epoxidation using **31** and **32** catalysts [165].

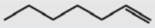
3.2. Cycloalkanes and benzenoids oxidation

The potential benefits of developing an armamentarium are to convert selectively the low cost readily available alkanes to more valuable unsaturated hydrocarbons and oxygenates such as alcohols, aldehydes, carboxylic acids and their derivatives. The first step in a 'default' mechanism for alkane oxidation is to create a reactive radical through homolytic cleavage of C–H bond but this homolytic cleavage of C–H bond is not achieved easily because C–H bonds are relatively strong [248]. In the metal oxide catalyzed oxidation of alkanes through Mars-van Krevelen mechanism, the surface metal-oxo sites are stabilized by strong M–O interactions; hence, it is also not effective to afford homolytic cleavage of C–H bonds of alkanes and to achieve adequate rate of oxidation of alkanes by rising temperatures in order of several hundred degrees C or more in the classic approach of heating the reactants. Therefore, the development of suitable catalyst mainly deals with homolytic cleavage of C–H bonds in the alkanes so that the chances for oxidation and product selectivity may improve. A semi-quantitative predictive scheme can be derived using a schematic reaction (Eq. (1)) for the oxidation of alkane (A), in which B is a desired oxidation product and C is resulted due to over oxidation. If species B contains weaker C–H bonds than A, then it will place severe constraints on the selectivity for B and in this situation B is achieved selectively by arresting reaction at low conversion.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad (1)$$

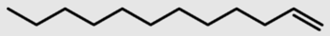
The heme-based cytochromes P450 and non-heme methane monooxygenases (MMO) are well-known enzymes that have been used in selective oxidation of one or more alkanes under ambient conditions. Furthermore, a large number of metal complexes of varying complexity, ranging from close structural analogues to enzymatic sites have been used as catalyst in selective oxidation of alkanes. The enzymatic analogues often termed 'biomimetic', and sometimes require molecular oxygen but frequently operative with more reactive oxidants, such as peroxides, hypochlorite, iodosylbenzene, amine N-oxides, etc. The iron complexes of perhalogenated porphyrin, octabromotetrakis (pentafluorophenyl) porphyrin have been used as active and selective catalysts for aerobic oxidation of isobutane to *t*-butanol [249,250].

Table 18
Epoxidation of alkenes with $NaIO_4$ catalyzed by Mn(III)salophen **39** and Mn(III)salophen-PSI **26** [45].

Alkene	Mn-catalyst	Conversion (%)[a]/time (h)	Epoxide yield (%)	Turnover frequency
	**39**	29/0.7	29	4.2
	26	81/2.5	81	3.9
	**39**	18/0.7	18	2.6
	26	59/2.5	59	2.8

[a] GLC yield based on starting alkene.

Table 19
Epoxidation of alkenes with TBHP catalyzed by polymer-supported molybdenum carbonyl Schiff base catalyst **37** [55].

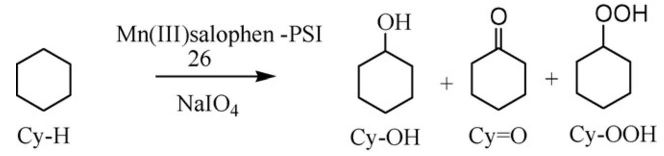
Alkene	Conversion (%)	Epoxide selectivity (%)	Time (h)
	94	100	4.0
	9	100	6.0

Conditions: alkene, 2 mL; catalyst, 1.0 mg; 100 °C; 12 h.

Table 20
Epoxidation of norbornene by **32** under different reaction conditions [165].

	Norbornene (mmol)	Catalyst weight (g)	Temperature (°C)	Epoxide (%)
Effect of temperature	5	0.25	25	29.4
	5	0.25	35	32.2
	5	0.25	40	37.7
Catalyst concentration effect	5	0.15	40	24.2
	5	0.25	40	37.7
	5	0.35	40	42.8
Substrate effect	5	0.25	40	37.7
	10	0.25	40	42.0
	15	0.25	40	45.2

Reaction conditions: CH_2Cl_2, 20 mL; TBHP, 2 mmol; 24 h.



Scheme 21. Oxidation of cyclohexane by polymer-supported Mn(III)salophen catalyst [45,253].

The selective transformation of low molecular weight alkanes into more valuable products was difficult due to their low intrinsic chemical reactivity but may be achieved by controlling the nature of active sites in catalysts, reactant composition, and reaction mechanism [251].

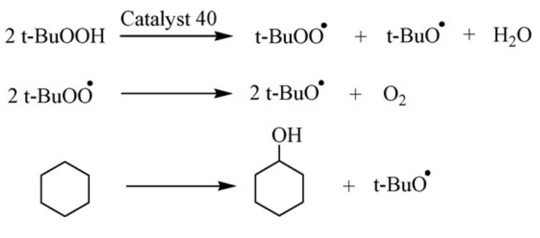
Transition metal complexes of Ti(IV), Mo(VI), Mn(III), Cr(VI) and Fe(III) with polymer-supported Schiff bases (N_2O_2 donor set) have been used as active catalysts in the oxidation of alkanes/alkenes in the presences of hydrogen peroxide, PhIO, *tert*-butyl hydroperoxide, NaOCl, etc., as oxidants but systematic studies on activities of polymer-supported analogues in the oxidation of alkenes are not reported abundantly [252].

3.2.1. Cyclohexane oxidation

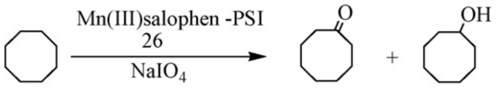
The oxidation of cyclohexane (Cy–H) to cyclohexanone (Cy=O) and cyclohexanol (Cy–OH) (Scheme 21) [45,253] under mild conditions is of academic and industrial significance because oxygenated intermediates are important for the production of nylon-6 and nylon-6,6 [254]. The demand of these oxidation products and increased environmental concerns has warranted the introduction of heterogeneous catalytic systems and environmentally benign oxidants such as molecular oxygen or hydrogen peroxide [255]. Although, great efforts have been made to improve the activity of various heterogeneous catalysts such as (Cr) MCM-41, TS-1, VPO, VMCM-41 and metal-containing AlPO redox molecular sieves [256–260] but unfortunately, the efficiency of these catalysts in the oxidation of cyclohexane is low in the presence of hydrogen peroxide as oxidant [261]. Recently the activity of a gold catalyst in the selective oxidation of cyclohexane has also been explored [262–266] particularly in the liquid phase oxidation of cyclohexane [267–270]. Unfortunately, in these investigations, the leaching of gold nanoparticles from solid support is a serious problem [271] and particles of gold become inactive at high temperatures [272].

Therefore, the traditional deposition–precipitation (DP) or co-precipitation (CP) methods of catalyst preparation failed to achieve active catalyst as observed in Co oxidation [273] but a polymer-supported cobalt catalyst was an ideal catalyst for oxidation of cyclohexane [274].

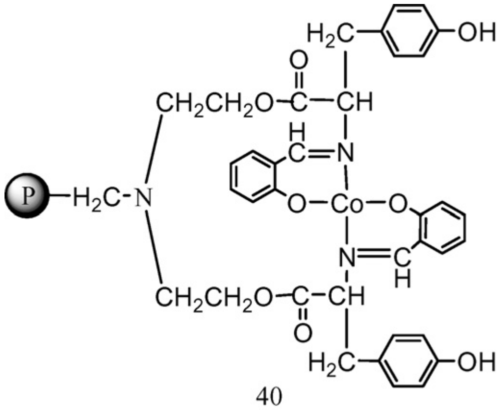
The polymer-supported cobalt complex **40** used in the oxidation of cyclohexane in the presence of molecular oxygen, in which a mixture of adipic acid, cyclohexanone, and cyclohexanol along with many other acids is obtained without leaching of cobalt ions from polymer support. In these studies, the effect of various metal salts is studied to control the yield and selectivity of adipic acid [2]. In the oxidation of cyclohexane using polymer-supported catalyst **40**, the yield of cyclohexanone and cyclohexanol was high without forming any acid [2].



Scheme 22. Proposed mechanism for oxidation of cyclohexane [2].



Scheme 23. Oxidation of cyclo-octane by metal Schiff base complexes [45,276].



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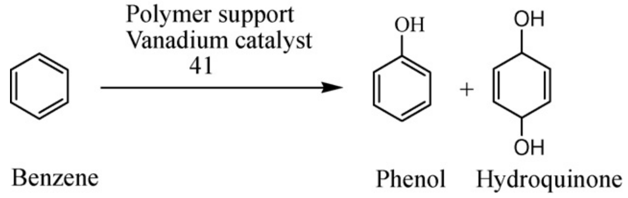
The conversion of cyclohexane increased with time but the selectivity to cyclohexanol displayed a decreasing trend. These observations were consistent with the proposed mechanism (Scheme 22) [2]. The conversion of cyclohexane and selectivity to cyclohexanone has increased on increasing the temperature. It is well recognized that the metal-catalyzed oxidation of olefins and or alkanes in the presence of alkyl hydroperoxides proceeds via two distinctly different mechanisms; one involving a high valent metal oxo/peroxo species or other involving free radical intermediates. In order to gain some insight into the nature of this reaction, a series of experiments were carried out using a free radical trap, 2,6-di-*tert*-butyl-4-methyl phenol (BHT) in the oxidation of cyclohexane using catalyst **40**. The addition of BHT has scavenged the peroxy free radicals and thus suppressed the reaction, which proceeded via free radical mechanism [275]. For the present catalytic system, the formation of products is explained considering the mechanism given in Scheme 22.

The polymer-supported Mn(salophen) displayed good regioselectivity in the oxidation of cyclohexane in the presence of NIO_4 oxidant [45]. In comparison to the unsupported catalyst, the polymer-supported catalyst yielded a high conversion of cyclohexane [Table 21] [45].

3.2.2. Cyclo-octane oxidation

Air oxidation of cyclo-octane to corresponding cycloketone and cycloalcohol (Scheme 23) [45,276] was catalyzed by both soluble and supported metalloporphyrines, metallophthalocyanines and metal Schiff base complexes, anchored on functionalized aminoalkylsilica gel, or polystyrene or montmorillonite K10, or encapsulated in zeolite NaX supercages [277–282].

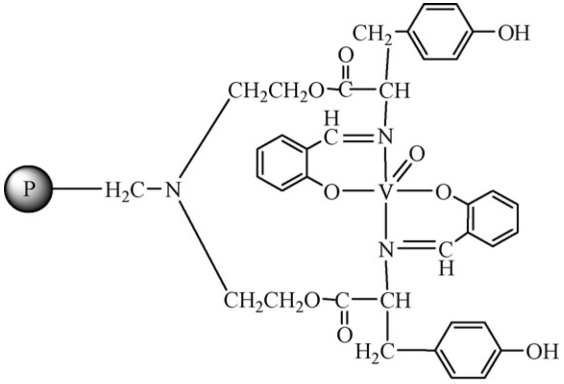
The direct oxidation of hydrocarbons is a typical reaction of cytochrome P-450 enzyme. The catalytic oxidation of alkanes with oxygen sources under mild conditions is especially a rewarding goal, since direct functionalization of inactivated C–H bonds in saturated hydrocarbons usually require high temperature and pressure. The polymer-supported Mn(salophen)Cl is an efficient catalyst for biomimetic oxidation of saturated hydrocarbons. The extent of oxidation to hydroxylation product is dependent on the nature of the alkanes [Table 22]. The supported Mn(III)salophen complex has given high yield [63%] of alcohols and ketones in comparison to unsupported Mn(III)salophen complex [38%] [45].



Scheme 24. Oxidation of benzene by polymer-supported vanadium catalyst [284].

3.2.3. *Benzene oxidation*

Direct oxidation of benzene to phenol is of great interest not only for its industrial importance, but also for its scientific point of view. The lack of studies on oxidation of benzene is largely due to the fact that activation of C–H bond in benzene is difficult due to its resonance stability; nonetheless, oxidation of benzene has produced phenols and benzoquinones [283]. The polymer-supported vanadium Schiff base complex **41** is an active catalyst in the oxidation of benzene and produced phenol as main product and hydroquinone (Scheme 24) as a side product. The selectivity for these products was 94% and 6%, respectively, within a reaction time of 2 h in the presence of H_2O_2 at 65 °C [284].



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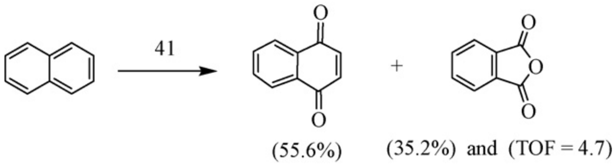
The homogeneous and supported Mn(salophen)Cl catalyst is also an efficient catalyst for biomimetic oxidation of ethyl and propyl benzene [45]. The catalyst displayed high activity in the oxidation of propyl benzene in comparison to ethyl benzene.

3.2.4. *Naphthalene oxidation*

Polycyclic aromatic hydrocarbons (PAHs) such as naphthalene, phenanthrene, and pyrene constitute a ubiquitous class of atmospheric pollutants released during the combustion of organic matter, such as diesel, gasoline, biomass, coal and wood [285–287]. Therefore, the release of PAHs to the atmosphere is widespread and takes place on a large scale, and these PAHs have been identified as serious material of health hazard and environmental pollutants. A range of technologies was developed for the abatement of volatile organic compounds (VOCs), like PAHs. The catalytic oxidation of PAHs to more environmentally benign CO_2 and H_2O appears to be one of the most cost effective methods to ensure their oxidation in comparison to thermal incineration. Relatively few studies on the catalytic oxidation of PAHs are available in the literature. The oxidation of naphthalene, and naphthalene-containing mixtures was attempted using metal oxide and metal-supported catalysts [288–295]. A review on these studies has revealed that polymer-supported Mn Schiff base complex is the best catalyst for the oxidation of naphthalene [296]. Polymer-supported VO^{2+} Schiff base complex displayed a 10.8% conversion of naphthalene (Scheme 25) with a turnover frequency of 4.7 in the presence of hydrogen peroxide [284].



Scheme 25. Oxidation of naphthalene by polymer support vanadium catalyst [284].

Table 23
Hydroxylation of tetrahydronaphthalene with $NaIO_4$ catalyzed by Mn(III)salophen and Mn(III)salophen-PSI [45].

Mn-catalyst	Conversion (%)[a]	Ketone (%)[a]	Turnover frequency
39	60[b]	51	8.6
26	93[b]	81	3.7

[a] GLC yield based on starting alkane.
[b] Only α-position was oxidized.

The polymer-supported Mn(salophen)Cl complex **39** is an efficient catalyst for biomimetic oxidation of tetrahydronaphthalene [Table 23]. The extent of conversion to ketonic products varied with the nature of the tetrahydronaphthalenes [45].

3.2.5. *Adamantane*

The activation of carbon–hydrogen bonds of an alkane is considerably more difficult due to its kinetic stability. The energy required to overcome the kinetic stability of alkanes leads to nonselective oxidation of the alkanes [297–299]. Adamantane was used as a model compound by numerous researchers to investigate C–H bond activation because substituted adamantane derivatives are used as precursors for photoresistants and medicines [300,301]. It is difficult to obtain tertiary mono- and di-oxygenated products of adamantane. Conventionally, 1-adamantanol and 1,3-adamantanediol are obtained by bromination of adamantane with molecular bromine, followed by hydrolysis of corresponding brominated derivatives, while 2-adamantanol is obtained by

Table 21
Hydroxylation of cyclohexane with $NaIO_4$ catalyzed by Mn(III)salophen **39** and Mn(III)salophen-PSI **26** [45].

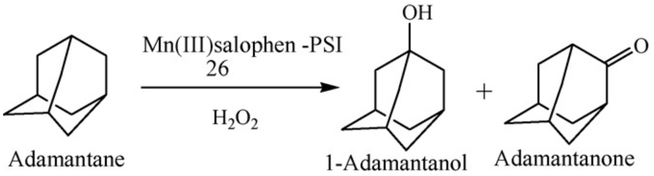
Mn-catalyst	Conversion (%)[a]	Ketone (%)[a]	Alcohol (%)[a]	Turnover frequency
39	16	13	3	2.3
26	36	30	6	1.4

[a] GLC yield based on starting alkane.

Table 22
Hydroxylation of cyclo-octane with $NaIO_4$ catalyzed by Mn(III)salophen and Mn(III)salophen-PSI [45].

Mn-catalyst	Conversion (%)[a]	Ketone (%)[a]	Alcohol (%)[a]	Turnover frequency
39	38/0.7	20	18	5.4
26	63/3.0	31	32	2.5

[a] GLC yield based on starting alkanes.



Scheme 26. Oxidation of adamantane by polymer-supported Mn(III)salophen catalyst [45].

the rearrangement of tertiary hydroxylated adamantanes using concentrated H_2SO_4. Due to the number of side products and application of harmful reagents, conventional techniques are not useful. Therefore, there is a challenge to develop an ecological and economical process in the oxidation of adamantane. In recent years, cleaner ones are replacing the conventional methods of oxidation and aerobic oxidation of alkanes to alcohol and carbonyl compounds has become important process [302]. The oxidation of adamantane by molecular oxygen using metal complexes or polyoxometalate as molecular catalysts is reported during last two decades. However, these catalysts are deactivated with time during reactions because of known conventional drawbacks associated with homogeneous catalytic systems [303–308]. The polymer-supported Mn(salophen)Cl is an efficient catalyst [Table 24] for biomimetic oxidation of adamantane (Scheme 26) and nature of adamantane has influenced the yield of oxidation products.

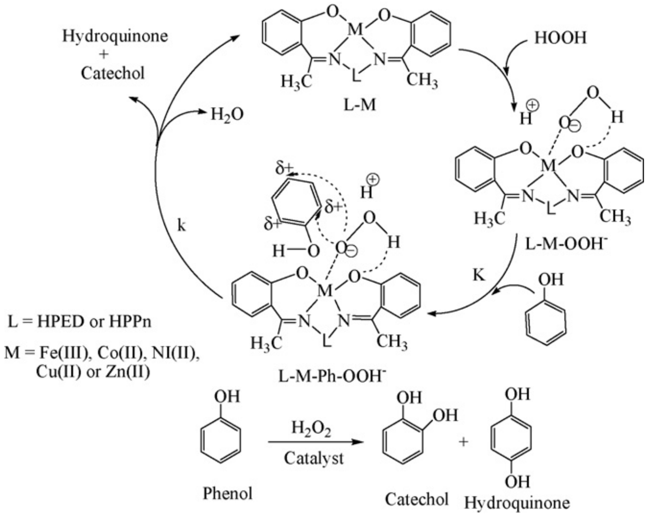
3.2.6. *Fluorene oxidation*

Fluorene is oxidized to corresponding ketone and alcohol in the presence of polymer-supported Mn(salophen)Cl catalyst (Scheme 27) [45]. The reactions might be proceeding via initial oxidation of benzylic position followed by cleavage, whereas, reaction products are obtained by the rearrangement of initially formed epoxides [309].

The supported Mn(salophen)Cl-PSI is an efficient catalyst for biomimetic oxidation of fluorenes [Table 25] [45]. The extent of oxidation to ketonic products is dependent on the nature of the substitution in the fluorenes.

3.3. *Alcohols oxidation*

The oxidation of alcohols is one of the most important transformations in organic chemistry. Early protocols for this transformation relied on the use of stoichiometric amount of oxidants such as chromium(VI) reagents [310]. The development of new environmentally friendly methods for the selective catalytic oxidation of alcohols to aldehydes and ketones is an important goal for chemical synthesis [68]. Various systems for catalytic oxidation of alcohols are reported, which involve transition metals as catalyst [311]. Of particular interest in the area of alcohol oxidation is the conversion of primary alcohols to aldehydes. This conversion is crucial for the synthesis of fine chemicals such as fragrances or food additives [68,312]. Systems involving nitroxyl radicals such as 2,2,6,6,-tetramethylpiperidine-1-oxyl (TEMPO) [313–315], have displayed great efficiency in selective oxidation of primary and secondary alcohols to corresponding aldehydes and ketones with high yields and selectivities. TEMPO was used in combination with a wide range of stoichiometric oxidants with sodium hypochlorite being arguably the most widely used oxidant [316–322].

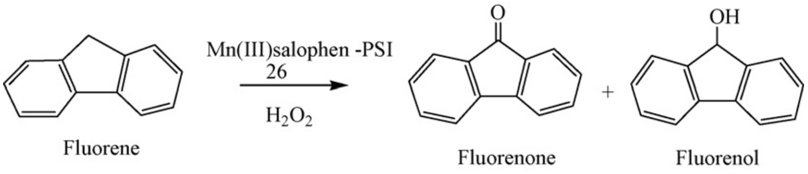


Scheme 28. Mechanism for phenol oxidation by polymer-supported catalyst [324,325].

3.3.1. *Phenol oxidation*

The supported catalysts were considered as versatile catalytic reagents for a wide range of oxidation reactions like, oxidation of olefins and allylic alcohols [57,58,60], benzene/alkylaromatic compounds [61], sulfides [62–64] and alcohols [65–67]. In the presence of inexpensive oxidant such as O_2, H_2O_2 or hydroperoxides, catalysts work satisfactorily in homogeneous conditions but recovery and recycling of the catalyst is difficult [1,323].

The catalytic activity of free and polymer-supported metal complexes was evaluated in the oxidation of phenol in the presence of hydrogen peroxide [194–196]. The selective oxidation of phenol to catechol and hydroquinone was attributed to the enzymatic behavior of metal complexes on polymer support



Scheme 27. Oxidation of fluorene by polymer-supported Mn(III)salophen catalyst [45].

Table 24
Hydroxylation of adamantane with $NaIO_4$ catalyzed by Mn(III)salophen and Mn(III)salophen-PSI [45].

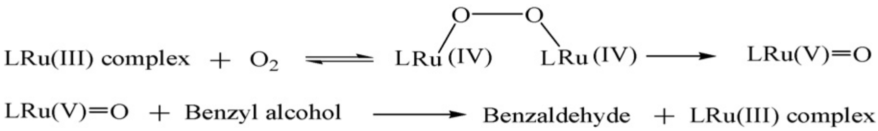
Mn-catalyst	Conversion (%)[a]	Ketone (%)[a]	Alcohol (%)[a]	Turnover frequency
39	48	36	12	6.9
26	83	35	48	3.3

[a] GLC yield based on starting alkane.

Table 25
Hydroxylation of fluorene with $NaIO_4$ catalyzed by Mn(III)salophen and Mn(III)salophen-PSI [45].

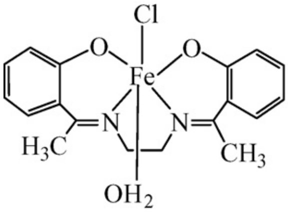
Mn-catalyst	Conversion (%)[a]	Ketone (%)[a]	Alcohol (%)[a]	Turnover frequency
39	39	39	–	5.6
26	79	35	44	3.1

[a] GLC yield based on starting alkane.



Scheme 29. Probable mechanism for oxidation of benzyl alcohol [71].

[Scheme 28] [194–198,324,325]. The fast intramolecular electron transfer process in the coordination spheres of the intermediate (L-M-Ph-OOH⁻) might be responsible for high conversion of phenol by polymer-supported Schiff base complexes than unsupported metal complexes. The coordination sphere of intermediates (L-M-Ph-OOH⁻) was also considered responsible for the selective oxidation of phenol to catechol and hydroquinone. The oxidation yield of phenol by polymer-supported metal complexes varied from 36.3% to 70%, whereas the oxidation yields of phenol with unsupported catalyst varied from 29.8% to 58.2% [Table 26] [324,325]. All the catalysts displayed optimum activity in the oxidation of phenol at molar ratios of 1:1:1 of H_2O_2 to phenol and supported catalyst.



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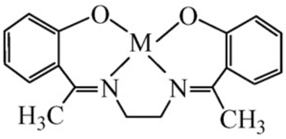
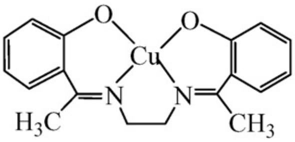


43. M = Co
44. M = Ni



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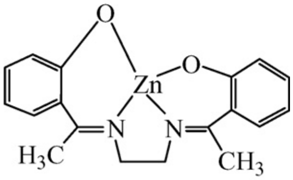

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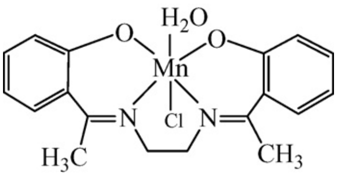
The selectivity for catechol and o-hydroquinone in the oxidation of phenol is also dependant on the molar ratio of hydrogen peroxide. The Schiff base complexes of iron(III) **18,23,42** were more selective for catechol than complexes of cobalt(II), **19**, **43** nickel(II), **20**, **44**,copper(II) and zinc(II) ions **22,25,46** [194–196,324,325].

3.3.2. *Benzyl alcohol oxidation*

The oxidation of alcohols is important in organic synthesis and in the development of industrial oxidation processes. The demand for eco-friendly chemical processes has encouraged the development of various clean reactions [326–336] and high yielding economical methods for the oxidation of alcohols [332]. Hydrogen peroxide is a useful oxidant in comparison to other oxidants [337]. To reduce the cost of the solvent from the reaction products some solvent free processes for oxidation reactions are reported [333–336]. Although, a variety of catalytic systems in the oxidation of alcohols by hydrogen peroxide are reported [68,338–342] but still there is ongoing interest to search new and efficient metal catalysts in the oxidation of alcohols [343–345]. The hydrogen peroxide oxidation of hydrocarbons catalyzed by Mn(IV) is reported widely [346,347] but Mn(III) Schiff base complex catalyzed oxidation has received less attention [348–354]. The selective oxidation of benzylic alcohols to corresponding ketones and carboxylic acids was catalyzed by Mn(III) Schiff base complex **47** in the presence of hydrogen peroxide under mild conditions [354].



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Recently, Sueto et al. [355] have reported the partial oxidation of benzyl alcohol to benzaldehyde using polymer-supported catalysts **48**.

Table 26
Oxidation of phenol and selectivity for catechol and hydroquinone [324,325].

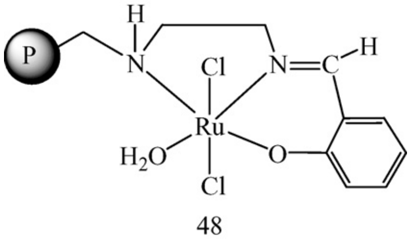
Metal complexes	Unsupported			Polymer supported		
	Phenol (wt%)	Catechol (wt%)	Hydroquinone (wt%)	Phenol (wt%)	Catechol (wt%)	Hydroquinone (wt%)
HPED-Fe **42**	58.2	70.0	30.0	70.0	80.0	20.0
HPED-Co **43**	50.4	65.0	35.0	62.0	76.0	24.0
HPED-Ni **44**	41.5	60.0	40.0	55.0	70.0	30.0
HPED-Cu **45**	36.6	60.0	40.0	49.0	49.0	51.0
HPED-Zn **46**	26.2	56.0	44.0	42.0	42.0	58.0
HPHZ-Fe **18**	56.0	86.0	14.0	61.4	90.5	9.5
HPHZ-Co **19**	42.0	76.0	24.0	49.0	88.9	11.1
HPHZ-Ni **20**	50.0	80.0	20.0	57.0	90.3	9.7
HPHZ-Cu **21**	38.2	82.0	18.0	43.4	88.8	11.2
HPHZ-Zn **22**	31.6	78.0	22.0	36.3	86.1	13.9
HPPn-Fe **23**	63.8	91.2	8.8	73.0	93.1	6.9
HPPn-Cu **24**	40.8	90.2	9.8	53.0	91.6	8.4
HPPn-Zn **25**	29.8	87.5	12.5	48.0	88.7	11.3

$[H_2O_2]$/[phenol]/[catalyst], 0.05 M; temperature, 70 °C; time, 24 h.

Table 27
Effect of concentration of substrate, catalyst and reaction temperature on oxidation of benzyl alcohol [71–73,356].

Temperature (°C)	[Ru] (mol L^{-1}) (×10^5)	[Benzyl alcohol] (mol L^{-1}) (×10^3)	Rate of reaction (mL min^{-1})	Order of reaction
35	7.12	4.83	0.35	0.58
35	7.12	9.66	0.50	
35	7.12	14.49	0.67	
35	7.12	19.32	0.80	
35	3.56	9.66	0.40	0.48
35	10.68	9.66	0.60	
35	14.24	9.66	0.70	
25	7.12	9.66	0.31	
30	7.12	9.66	0.40	
40	7.12	9.66	0.62	

Methanol, 20 mL; ΔE_a, 32.34 kJ mol^{-1}; ΔS, 40.44 eu; P, 1 atm.



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The influence of various parameters on the rate of oxidation of benzyl alcohol was studied as displayed in Table 27 [71–73,356].

The rate of oxidation of benzyl alcohol was increased on increasing the concentration of alcohol and catalyst and order of the reaction was half w.r.t. the concentration of alcohol and catalyst [Table 27]. The rate of oxidation of alcohol has also increased with reaction temperature with energy of activation of 32.34 kJ mol^{-1} [Table 27]. The supported catalyst displayed thermal stability and recyclability. On the basis of experimental results [71] and literature report [357], the following mechanism [Scheme 29] and reaction rate [Eq. (2)] are proposed for the oxidation of benzyl alcohol.

$$\text{Rate} = k\,[\text{catalyst}]\,[\text{benzyl alcohol}] \tag{2}$$

4. Concluding remarks

The polymer-supported Schiff base complexes of metal ions are highly active in various reactions. The discussion presented in the review has clearly demonstrated that an impressive progress is made in the area of polymer-supported catalysts in the oxidation of organic compounds. The methodologies described have clearly opened up new avenues for a major growth in the area of oxidation chemistry. The oxidation of alcohol reactions has made remarkable progress, while the oxidation of alkanes, benzylic substrates and alkenes was extensively explored. These reports demonstrated the potential of polymer-supported catalysts to facilitate the recyclability of the catalysts and to achieve high catalytic activity than unsupported analogues. In addition, the enantioselective oxidation of cyclohexene, cyclohexane, and styrene accomplished excellent enantioselectivity using polymer-supported catalysts. Efforts in this area should conclude in tackling the major issues pertaining to environmentally acceptable technologies for the future.

Acknowledgements

Authors are thankful to I.I.T. Roorkee for providing facilities to carry out these investigations. Financial assistance to Mr. Alekha Kumar Sutar from MHRD, New Delhi is thankfully acknowledged.

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