CHAPTER 1

Introduction

1.1 Preamble

Recent interest in the development of environmentally benign synthetic procedures that promote the use of active catalysts, having the advantages of recovery and recyclability, has evoked a renewed interest in generating polymer-supported metal catalysts for organic synthesis [1-3]. Moreover, design and synthesis of peroxidometal complexes have been the subject of intense research in recent decades mainly because of their role as potential catalysts in organic oxidations of industrial as well as biological significance [4-6]. The work presented in this thesis is focused on synthesis and characterization of new polymer immobilized peroxido derivatives of titanium and molybdenum and exploration of their catalytic activity in some fundamentally important organic oxidations. The primary goal of the work is to develop simple and environmentally safe, yet efficient and versatile homogeneous and heterogeneous catalysts which can facilitate the organic transformations under ecologically sustainable reaction conditions.

In this Chapter we present a concise review of the following interrelated areas relevant to the work embodied in the thesis.

(i) Immobilization of metal complexes on various types of polymer matrices and significance of such systems in catalysis.

(ii) Salient features of peroxido compounds of titanium and molybdenum.

(iii) Application of peroxido compounds of Ti(IV) and Mo(VI) in some selective organic oxidative transformations *viz*. sulfide oxidation, olefin epoxidation and oxidation of 5 -hydroxymethyl-2-furfural (HMF).

1.2 Polymer immobilized metal complexes –general aspects

It can be easily appreciated that attaching a metal complex or metal as part of a macromolecule can lead to the design and development of novel materials with unique physical and chemical properties [1-3,7,8]. As metals can adopt various oxidation states, co-ordination numbers and geometries, the presence of metals in the polymers usually provides access to versatile functional materials which seem to possess a wide range of applications in the field of advanced technology including catalysis, sensing, electrolysis, energy conversion and storage, electro-optical devices and biomedical applications [1-3,7-9].

In addition to carbon, there are five different elements normally found in the main polymeric network *viz.*, oxygen, nitrogen, sulfur, silicon and phosphorus [10]. Depending on the different combination of the elements, they can be subdivided into- (i) organic polymers which contain only carbon in the main chain (e.g. polyolefin, polystyrene), (ii) inorganic polymers which do not have any carbon in the chain (e.g. polysiloxanes, polysilanes), and (iii) semiorganic polymers which comprise at least one other element besides carbon (e.g. polyanilines, polyamides, polypyrrole) [10].

Diverse synthetic approaches to prepare polymer supported complexes in different combinations of metal complexes or metals with organic, inorganic and semi-organic macromolecules have been reported [10]. Moreover, a variety of terms for describing supporting processes have been proposed such as immobilization, anchoring, attachment or “heterogenization of homogeneous complexes” [11]. Based on the kind of interaction a metal complex or metal has with a macromolecule, Wöhrle *et al.* [10-12] classified metal containing macromolecules in the following ways:

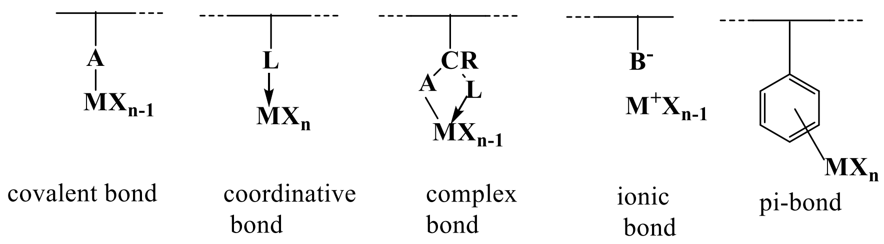
Macromolecular Metal Complexes (**Type I):** This class of compounds are formed when a metal complex or a metal ion is linked to a chain of a linear or cross-linked organic polymer *via* a covalent bond or coordinative (at the metal), a complex (at the ligand of a complex), an ionic, or a π-bond formed as illustrated in [**Fig 1.1 (a)]**.

Ligand Macromolecular Complexes (Type II): This type of complexes, in which the ligand of a metal complex is a part of a macromolecular chain or network [**Fig. 1.1(b)]**, are usually obtained either by direct synthesis from low molecular weight precursors or by metalation of preformed macromolecular ligand.

Metal Macromolecular Complexes (Type III): In such compounds, metals or metal complexes exist as part of a macromolecular chain or network [**Fig. 1.1(c**)]. This class includes co-ordination polymers, π-complexes in the main chain with a metal, cofacially stacked polymer metal complexes, polycatenanes, and dendrimers with metals. Usually the metal is attached with another element such as C, N, O, S *via* a covalent, a coordinate, an ionic, or a π-bond.

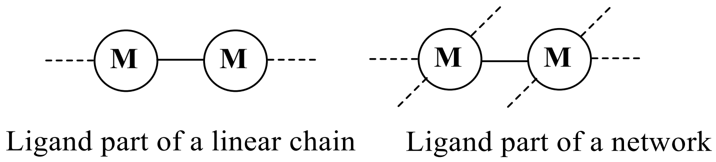
Macromolecule Incorporated Metal Complexes (**Type IV):** The physical inclusion and stabilization of metal clusters or metal complexes in macromolecular milieu [**Fig. 1.1(d**)] often provides an access to novel composite materials.

Type I: Binding of metals at a macromolecule



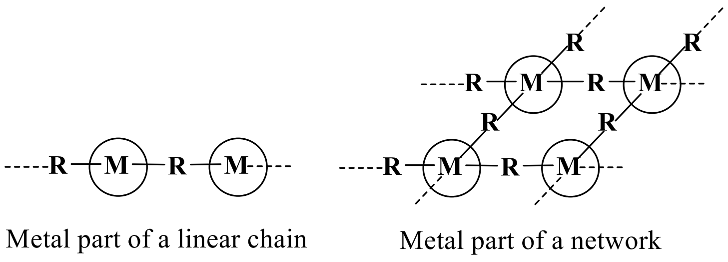
(a)

Type II: Ligand of metal complexes as part of a macromolecular chain



(b)

Type III: Metal complexes or metals as part of a linear or crosslinked macromolecule *via* the metal



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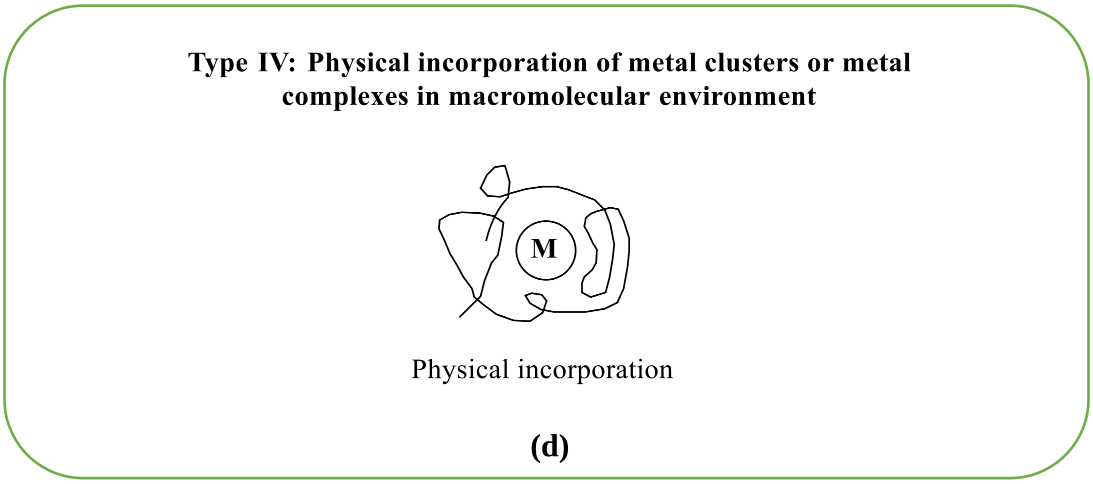


Fig. 1.1 Different approaches for the formation of metal containing polymers [10].

A variety of natural as well as synthetic polymeric materials have been employed as matrices to anchor metal complexes [1]. The active transition metal complex may be supported on insoluble or soluble polymeric supports with each type of the support being associated with some advantages as well as disadvantages [11]. In general, the macromolecular metal complexes with linear or branched organic polymers are soluble in organic solvents and their structures can be identified rather easily [13]. The bridged macromolecular metal complexes are less soluble and are more stable with less defined structures [13]. On the other hand, the complexes with intermolecular bridge bonds are difficult to characterize and are insoluble.

1.3 Catalytic application of polymer immobilized metal complexes

Immobilization of catalytically active transition metal complexes on a polymer support often confers catalytic activity to the polymer and generates a functional polymer. The resulting heterogenized catalysts offer the advantages of ease of separation and recovery of the catalyst by enhancing the catalyst stability within the polymer [11]. Apart from improving the overall productivity and cost effectiveness of the process, the catalyst recycling leads to minimizing the environmental impact of a chemical transformation, ultimately contributing to the sustainability of the process [14-17]. The so-called "heterogenized homogeneous catalysts" thus combine the desirable features of homogeneous, heterogeneous and enzymatic catalysis such as high activity, selectivity and stability which enhance their efficiencies [11].

The poly(styrene) based resins have greatly influenced the activity of supported catalysts as evident from several reviews on solid-supported catalyst and reagent chemistry [16,18-21]. Merrifield resin (**MR**) or chloromethylated polystyrene cross-linked with divinyl benzene (**Fig. 1.2**), invented by Merrifield in 1963 during his pioneering work on solid-peptide synthesis [22], is one of the most widely used functional resin for the synthesis of supported transition metal-based catalysts due to its ready availability, low cost, mechanical and chemical inertness as well as its ability to undergo facile functionalization [14,22-24]. Therefore, work has been focused on developing and screening **MR** supported complexes with new ligands for attachment of metals and on developing methods for increasing activity and selectivity of such catalysts [16,18-21]. Typical supports used 2% cross-linked (microporous or gel type resins) which require solvent swelling for reagents to access internal functional groups [16,25]. This requirement was overcome by the use of macroporous resins, which typically contain greater than 10-15% levels of the cross-linker. However, the macroporous systems sometimes suffer from poor loading capacity and brittleness along with difficulty in preparation. Such limitations could be minimized by modifying 1 or 2% cross-linked polystyrene resins with some suitable functionals [16].

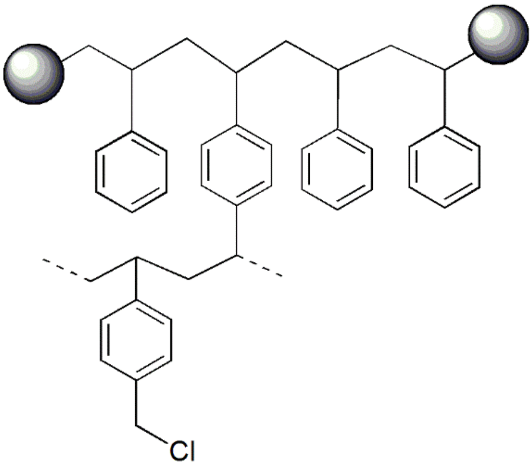
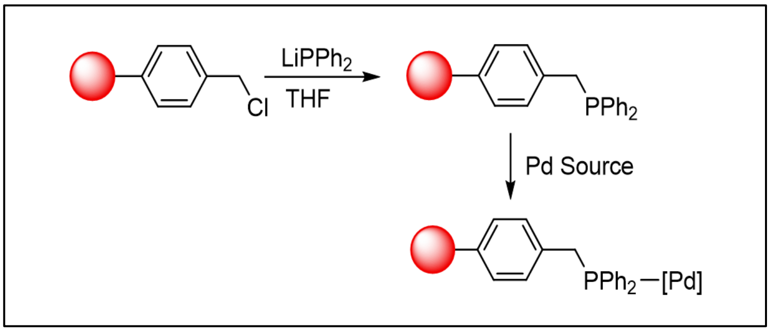


Fig. 1.2 Merrifield resin or Chloromethylated polystyrene cross-linked with divinylbenzene. The ball represents the backbone of polymer matrix [20].

The immobilization of homogeneous catalyst on the solid polymer can be obtained by three main methods [11,26]. These include: (a) entrapment, where a preformed catalyst is enveloped within a polystyrene network, (b) ion-pairing where cations or anions are bound to complementary resin sites, and (c) covalent binding. So far, last two methods are most commonly used due to their broad applicability, the fact that insignificant leaching is usually observed, and that stable, active catalysts and reagents are formed.

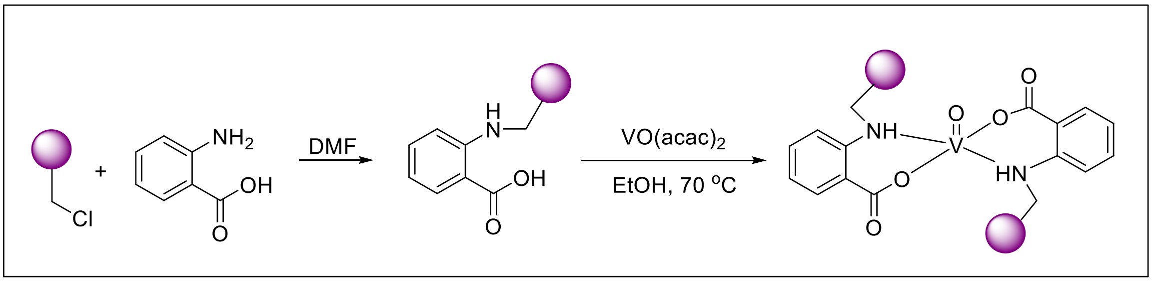
Jang and co-workers reported **MR** supported palladium as highly effective catalyst in the Suzuki coupling of a number of organoboranes with alkenyl bromides, iodobenzene, and aryl triflates (**Scheme 1.1**) [27]. Petit *et al.* reported the first example of an amino acid complex of Cu(II) bonded to cross-linked poly(styrene-divinylbenzene) resin, though the complexes were not examined for any catalytic activity [28]. Pd(II) and Ru(III) complexes anchored to a L-valine functionalized cross-linked poly(styrene-divinylbenzene) resin was synthesized by Valodkar and coworkers [29]. The catalytic activities of Pd(II) based complex was investigated for the hydrogenation of 1-octene, cyclohexene, acetophenone and nitrobenzene [29]. The catalyst was also found recyclable. On the other hand, Ru(III) based complex was obtained as an active catalyst in epoxidation of styrene, cyclooctene and cyclohexene in presence of tert-butyl hydroperoxide as the terminal oxidant [29]. Jun *et al.* has reported an *in situ* generated PS-supported rhodium complex as catalyst in the reaction of benzyl alcohols with terminal alkenes to give ketones [30].



Scheme 1.1 Synthesis of Merrifield resin supported palladium catalyst [16,31].

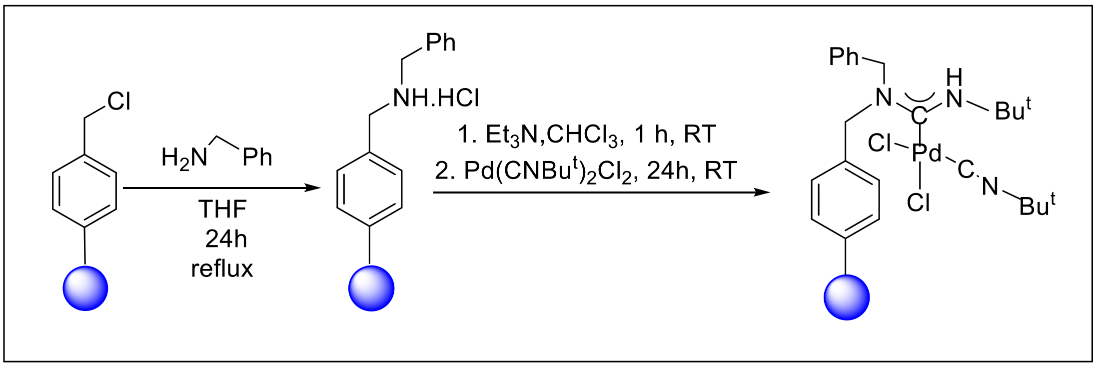
Miyaura *et al.* has shown another recoverable PS-bound palladium catalyst which was efficient in cross-coupling reactions and successfully extended the range of applicable substrates [31]. Significant improvement was also observed in turnover number of Heck reaction catalyzed by PS-supported 1,2-bis(diisopropylphosphino)-benzene Pd(II) complex over its solution analogue as well as Pd-$(OAc)_2$/PPh_3 [32]. Islam *et al.* in 2012, reported the anchoring of anthranilic acid with **MR** followed by the reaction with

$V^{IV}O(acac)_2$ (**Scheme 1.2**) [33]. The obtained heterogenized complex was reported to be active and a reusable catalyst for the oxidation of alkenes, sulfides and alcohols.



Scheme 1.2 Synthesis of polymer anchored VO(IV) complex [33].

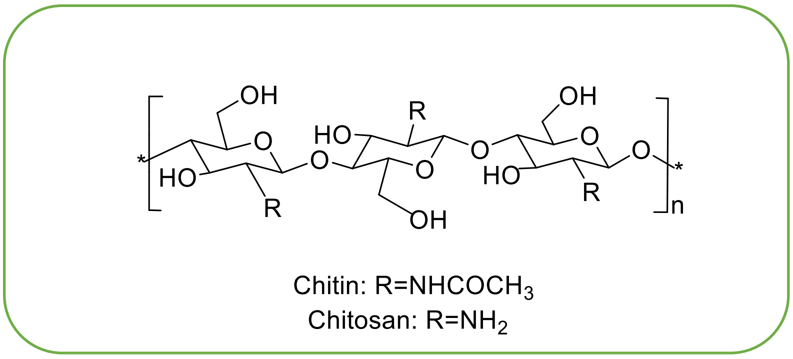
Very Recently, Balova *et al.* has reported the synthesis of amino-functionalized polystyrene-supported acyclic diaminocarbene palladium complexes (**Scheme 1.3**) and examined their catalytic activity in Sonogashira cross-coupling reaction [34]. Our group has previously reported the synthesis of a set of **MR** supported peroxidomolybdenum(VI) compounds which showed excellent activity, stability and selectivity for the oxidation of sulfides to the corresponding sulfoxides or sulfones by H_2O_2 at ambient temperature [23].



Scheme 1.3 Preparation of polystyrene-supported Pd complex NBn,NH-ADC-Pd(II) [33].

Apart from the polystyrene based polymers, various other polymers such as polyvinyls, polyacrylates, polyethers, poly(2-oxazoline), poly(ethylene glycol), silicon polymers and dendrimers are capable of undergoing a variety of chemical reactions and thus can be functionalized and have also been employed as polymeric support for various catalytic applications [1,11,12,14-18,26,35,36]. Some of the reported combinations of metal complexes with the available macroligands and their various catalytic applications, as summarized by Pomogailo [1], are listed in **Table 1.1**.

Biopolymers such as chitin and chitosan (**Fig. 1.3**), the most abundant naturally occurring polymers, ranked second after cellulose have been receiving considerable attention as macroligands for metal complex binding. These natural materials are expected to generate ecologically friendly systems which can meet the needs of new generation catalysts [37-41]. A number of favourable properties of these biopolymers such as high thermal stability, durability, facile functionalization of chitosan and its derivatives, insolubility in organic solvents etc, boost their applicability as promising solid support for immobilized complexes [37-45]. Chitosan is a partially deacetylated derivative of chitin and depending upon the requirement, it can be obtained with different molecular weights (60–375 kDa) and deacetylation degrees ranging from 50% to 99% [39]. Owing to the presence of active amino group along with the hydroxyl group in the polymer, it has the potential to bind with transition metals through chelation or ion exchange method facilitating chitosan metal complexes to be thermally stable and leaching resistant [45-51].



Chitin: R=$NHCOCH_3$
Chitosan: R=NH_2

Fig. 1.3 Molecular structure of chitin or chitosan [51].

Over the past few years there have been a large number of reports on application of chitosan metal complexes as heterogeneous catalysts in variety of organic transformations such as Bayer-Villiger oxidation, Heck reaction, Suzuki coupling reaction, C-N coupling reactions, formation of C-S bonds, hydrocarbon oxidation, catalytic hydrogenation, hydrogenolysis are some of the reactions where chitosan based metal complexes are used as catalyst [39,41-43].

Table 1.1 The summary of different combinations of metal complexes and macroligands, as well as catalyzed reactions most commonly used in practice [1]

Polymer support	Functional group	MX_n	Catalysed reaction
Phosphinated CSDVB	-PPh_2	$RhCl(PPh_3)$ $[CODRhCl]_2$ $Rh(CO)_2(PPh_3)_2$ $PdCl_2(PPh_3)$ $RhHCO(PPh_3)_3$ $[COdRhCl]_2$ $CoCl_2(PPh_3)$ $Mo(CO)_2(PPh)_2$ $Fe(CO)_4PPh_3$	Hydrogenation Hydroformylation Deuterium/hydrogen exchange Isomerisation Oligomerisation Cyclooligomerisation
CSDVB	Dipy Cp $NH_2CH_2CH_2NH_2$	$Pd(OCOCH_3)_2$ $CpTiCl_3$ $Pt(PhCN)_2Cl$	Hydrogenation
PA	-	Ni(napht)	PhA hydrogenation
PE-gr-P4VP	Py	$PdCl_2(PhCN_2)$	p-Nitrochlorobenzene hydrogenation
PMMA	-$COOCH_3$	Pd^0	Nitrocompound hydrogenation
PTFE	-	Au^0	Deuterium/hydrogen exchange
CSDVB	-NMe_2	MCl_2(Pt,Ru)	Hydrosilylation
PE-gr-PAAc	-COOH	Co(AcAc)	Cyclohexene oxidation
PAN	-C≡N	$M(AcAc)_2$(M= Mn,Co)	Ethyl benzeneIsoprpyl benzene oxidation
Polystyrene-co-divinyl-benzene-2-Me-5-VP)	N-	Cu^{2+}	
CSDVB		Co,Ni,VO, CO, Fe, Mn,phtalocyanines	Cyclohexene oxidation
PEG	-OCH_2CH_2-	MCl_2(M= Co, Mn, Cu) Co^{2+} ,Cu^{2+}	Teralin oxidation H_2O_2 oxidation
Poly(2-vinylpyridine-co-styrene)		Fe^{3+},Co^{2+},phthalocyanines	H_2O_2 oxidation
Phosphate cellulose	-PO_2OH	V^{5+},Mo^{5+}	Cyclohexene epoxidation
Chloromethylated CSDVB		Dithiocarbamate, Mo^{5+}	Olefin epoxidation
P4VP	-N	Cu^{2+}	Dialkylphenol oxidation

Continue...

Polyvinylamine	$-NH_2$	Co^{2+}, $Fe^{3+,}$ $Cu^{2+,}$phthalocyanines	Thiol oxidation
P4VP	-N	Cu^{2+}	Ascorbic acid oxidation
PMMA	C=O	$TiCl_4$,VCl_4	Ethylene polymerisation
PE-gr-PAAI	-OH	$Ti(OBu_4)_4$	Ethylene polymerisation
PE-gr-P4VP	-N -N	$TiCl_3$ $CoCl_2$	Stereospecific propylene polymerisation 1,4-cis-butadiene polymerisation
Copolymer of styrene and acrylic acid	-COOH	$Ni(napht)_2$	1,4-cis-butadiene polymerisation
PE-gr-PAAc	-COOH -COOH	$Ni(CH_3COO)_2$ $Ni^{2+,}$ V^{4+}	Ethylene polymerisation “Relay-race” ethylene copolymerisation
Triple copolymer of ethylene propylene and P4VP	-N	$CoCl_2$, $NiCl_2$	Butadiene di and oligomeerisation
PS	-	$AlCl_3$,$TiCl_4$	Styrene and ethyl styrene polymerisation
PE-grPAAI	-OH	$MoCl_5$,WCl_5,Cu^{2+}	PhA polymerisation
CSDVB-P4VP	-N	Cu^{2+}	Oxidative polycondensation of phenols
PE-gr-PAAc	-COOH	$Co(OCOCH_3)_2$	Phenol formaldehyde oligomers solidification
CSDVB	Cp	$CpCo(CO)_2$	Fischer-Tropsch synthesis
PEI	-NH	$RhCl_3$	Methanol carbonylation
PVAI	-OH	Cu^{2+}	2,4 dinitrophenyl acetate hydrolysis
CSDVB		$TiCl_4$	Etherification Alkylation, acetalisation
Copolymer of styrene and AAc	-COOH	Cp_2TiCl_2	Reduction of nitrogen to ammonia
Thioacetalderivatives of poly(4-amino-styrene)	$-CH_2$ $-NH_2$	$-Mo(NMe_2)_4$ -	Nitrogen reduction Photocatalytic hydrogen formation
PEI	-NH	Rh^{3+}	Formation of H_2 from H_2O
CSDVB	-	Mg,Mn,Fe,Ru,Pthalocyanines	Isomerisation of quadricycalne to norbornadiene
$Poly[Ru(DiPy)_3^{2+}$	-	-	Chemically modified electrodes
P4VP/Carbon	-N	Cu^{2+}	Electrochemical reduction of O_2 to H_2O
$Poly[Ru(Dipy)_3^{2+-}$4VP/Pt	-	-	Photodiodes (Chemically modified photoelectrods)

The first example of oxidation with chitosan based catalysts was reported by Pispisa and Chiessi applying immobilized iron(III) and Copper(II) complexes in alkaline solution [39,52]. The former catalyst facilitated the oxidation of catecholamines through intramolecular electron transfer within a binary adduct, whereas Cu(II) mediated the oxidation of adrenaline by molecular oxygen within a ternary precursor complex [39,52]. Huang and coworkers, reported oxidation of cyclohexene using Fe(III), Mn(III), and Co(II) tetraphenylporphyrin(TPP)-chitosan derivatives as catalyst [39,53]. The catalyst with Co(II) showed best activity and stability upto five runs. Another set of catalyst for the oxidation of ethylbenzene as well as cyclohexane was recently reported by the same group by immobilizing Fe(III) tetrakis(4-carboxyphenyl)porphyrin through covalent grafting on mesoporous and macroporous chitosans [39,54]. Two series of catalysts prepared by modifying chitosan with 1,2-diphenylethanedione [55] or isatin [56] followed by treatment with metal chlorides [M= Cu(II), Co(II), Ni(II)] (**Fig. 1.4**) were reported by Antony and co-workers. In most cases, the complexes afforded low yields in recycling attributed to poor chemical resistance and mechanical strength of chitosan [39]. Shaabani *et al.* have reported chitosan based cobalt by reducing the aqueous suspension of chitosan mixed with $CoCl_2$ with $NaBH_4$. The catalytic activity of the complex was studied in aerobic oxidation of benzylic carbon and also in benzylic alcohol oxidation. They observed product yield upto 90% in both cases [57].

A multi-functional ferric dimethyl dithiocarbamate chitosan-based magnetic catalyst capable of mediating selective oxidation of benzyl alcohols has recently been fabricated by the group of Baghban and Luque [58]. Oxidation of nitro- and chloro-benzyl alcohols, butan-2-ol, and octan-1-ol with 83–91% yield was achieved using a D-penicillamine modified chitosan supported Pd catalyst by Keshipour and coworkers [59].

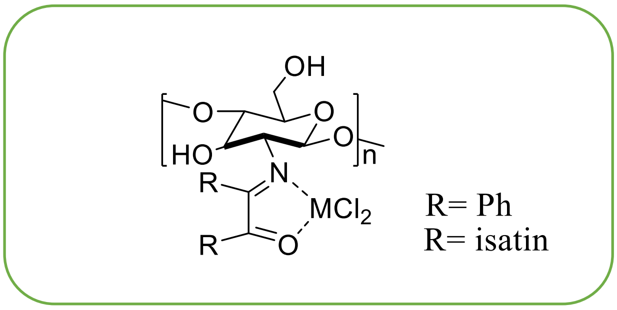


Fig. 1.4 Hydrocarbon oxidation catalysts reported by Antony *et al.* [55,56].

Metal catalysts supported on functionalized chitosan have been developed recently and used successfully as heterogeneous catalysts in selective oxidation of sulfides with 30% H_2O_2 [39]. Asymmetric oxidation of sulfides was reported with a new catalyst bearing a vanadium complex [60] synthesized by the treatment of silica-supported chitosan with substituted salicylaldehydes followed by immobilization of NH_4VO_3 in methanolic solution (**Fig. 1.5**). The Oxidations afforded sulfoxides with medium enantioselectivities and medium to high yields. The efficiency of the method was established by the synthesis of the marketed drug Nexium (the first proton-pump inhibitor, esomeprazole) with yield of 92% and enantiomeric excess of 68% [39]. Veisi and coworkers recently prepared $VO(acac)_2$ immobilized magnetic particles coated with a chitosan film [61] which was found to be active in selective oxidation of sulfides to sulfoxides with H_2O_2. A catalyst based on magnetite–chitosan core–shell-type nanocomposite with molybdenum–Schiff base has been reported very recently, in 2019 for selective epoxidation of olefin [62].

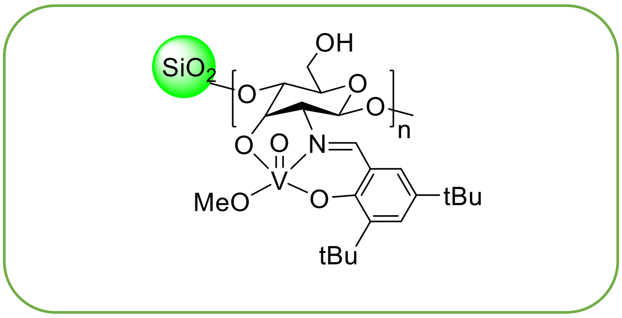


Fig. 1.5 Chitosan based metal catalyst reported by Shen *et al.* [60].

In this context, it is somewhat surprising that chitosan has rarely been used as support for immobilizing peroxidometal complexes. In fact, to our knowledge there have been only three reports so far, dealing with the application of peroxidometal derivatives supported on chitosan as oxidation catalyst [48,63,64]. For example, a chitosan supported protonated peroxidotungstate(pW) catalyst has been demonstrated previously to efficiently catalyze oxidation of a variety of organic substrates in acetonitrile [64].

1.4 Metal complexes immobilized on soluble polymers

The use of soluble polymers to recover catalysts and ligands in synthetic approaches to peptide and oligopeptide synthesis was developed decades back by Merrifield as well as Letsinger and Wagner in the 1960's [65,66]. However, their role in homogeneous catalysis remained relatively unexplored until the 1990s [67]. Recent upsurge in interest in the use of soluble polymers as tools in catalysis as observed by Bergbreiter *et al.* in a recent review, has mainly been triggered by the growing importance of green chemistry and sustainability in chemical processes, pervasiveness of homogeneous catalysts in synthesis, and availability of polymers with tailored specific properties [2].

Notwithstanding several advantages of insoluble supports, there are certain limitations involving these heterogeneous matrices such as, nonlinear kinetic behaviour, solvation issue, unequal access to the reaction, and difficulties in transferring chemical reactions to the solid phase in chemical synthesis [68]. In this regard, the unparalleled selectivity and excellent reactivity that many homogeneous catalysts offer usually cannot be accomplished in the corresponding heterogeneous systems [69]. The methodologies that utilize soluble polymer have the potential to combine the advantages of homogeneous solution chemistry such as high reactivity, lack of diffusion and ease of analysis with the easy separation property of solid phase method [70].

Several methods have been capitalized on the basis of the macromolecular properties of soluble support to attain product separation from the reaction mixture [68,70]. Solvent induced precipitation is one such method where homogeneous polymer solution is diluted by using proper solvent that induces precipitation of the support, followed by filtration to separate out the synthesized product [68,70]. Besides this technique, crystallization, centrifugation and dialysis are some methods that can also be applied to isolate the polymer from reaction mixtures. An additional advantage of using such polymer support is that monitoring of the chemical reaction occurred on such polymers can be possible by solution state spectroscopy [68,70].

Bayer and Schurig reported the first catalytic system in 1976 where a soluble polymer was used as an alternative to a cross-linked insoluble polymeric resin to support a chiral ligand [71]. A linear polystyrene-bound version of DIOP [4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxidolane] ligand was allowed to react with $HRh(CO)-(PPh_3)_3$, and the resulting polymer-bound Rh complex was used to hydroformylate styrene [71]. An important progress in soluble polymer support occurred with the report of Han and Janda on supported chiral catalysts for asymmetric dihydroxylation of olefins, in the year 1996 [72].

1.4.1 Water soluble polymers (WSP) as metal supports

The water soluble polymers are essentially polychelatogens with functional groups able to form co-ordinate bonds with metals [73]. Synthetic WSPs have been finding wide applications in diverse research arenas from drug delivery systems to the environmental use as heavy metal removers and, also in catalytic and separation processes [73-75]. They are often found to be nontoxic and biocompatible which contributed in their biomedical applications [74,75]. Co-ordination compounds of metal with soluble polymeric ligand provide impetus for designing biomimetic models since water being the natural solvent for biological macromolecules such as DNA and proteins [73,76].

Some examples of WSPs with various functional groups generally used as support for metal anchoring are listed in **Fig. 1.6**. The commonly occurring ligands in these systems include amines, carboxylic acids, amides, alcohols, amino acids, pyridines and thiourea [73,77]. In aqueous solution, they can undergo interaction with other high and low molecular weight species to form complexes. Polyvinyl alcohol, polyethylene glycol, polyacrylamide, poly(N-isopropylacrylamide), and polyvinylpyrrolidine are some common choices of synthetic water soluble polymers for metal anchoring [68,70,74,75].

Poly(ethylene glycol) (PEG) is the most popular choice among the soluble polymer supports for organic synthesis [78] . It is cheap, nontoxic and its properties can be tunable by altering the molecular weight [78,79]. By functionalizing with PEG, a catalyst could inherit several advantages including high water solubility and easy separation etc. [70,80]. Throughout the years, a variety of ligands have been used to functionalize PEG such as salen, phosphine, cinchona alkaloid, dipyridyl, tartarate ester, porphyrin and BINOL [68,70,72,81-88]. Liu *et al.* demonstrated the catalytic utility of poly(ethylene glycol) functionalized imidazolium salts-Pd in Suzuki reaction carried out in water, however the catalyst recovery was not achieved [89]. Wang *et al.* functionalized PEG-bridged dicationic ionic liquid with salicylaldoxime which could be used as ligand for Pd catalyzed Suzuki Miyaura reaction in water [90]. Hence, differently modified poly(ethylene glycol) has been used in various catalytic processes including C-C bond formation reaction [89,90], hydrogenation [81,82], epoxidation [68,88], Sharpless asymmetric dihydroxylation [83], Wacker oxidation [85,86], and also as phase transfer catalyst [70,91].

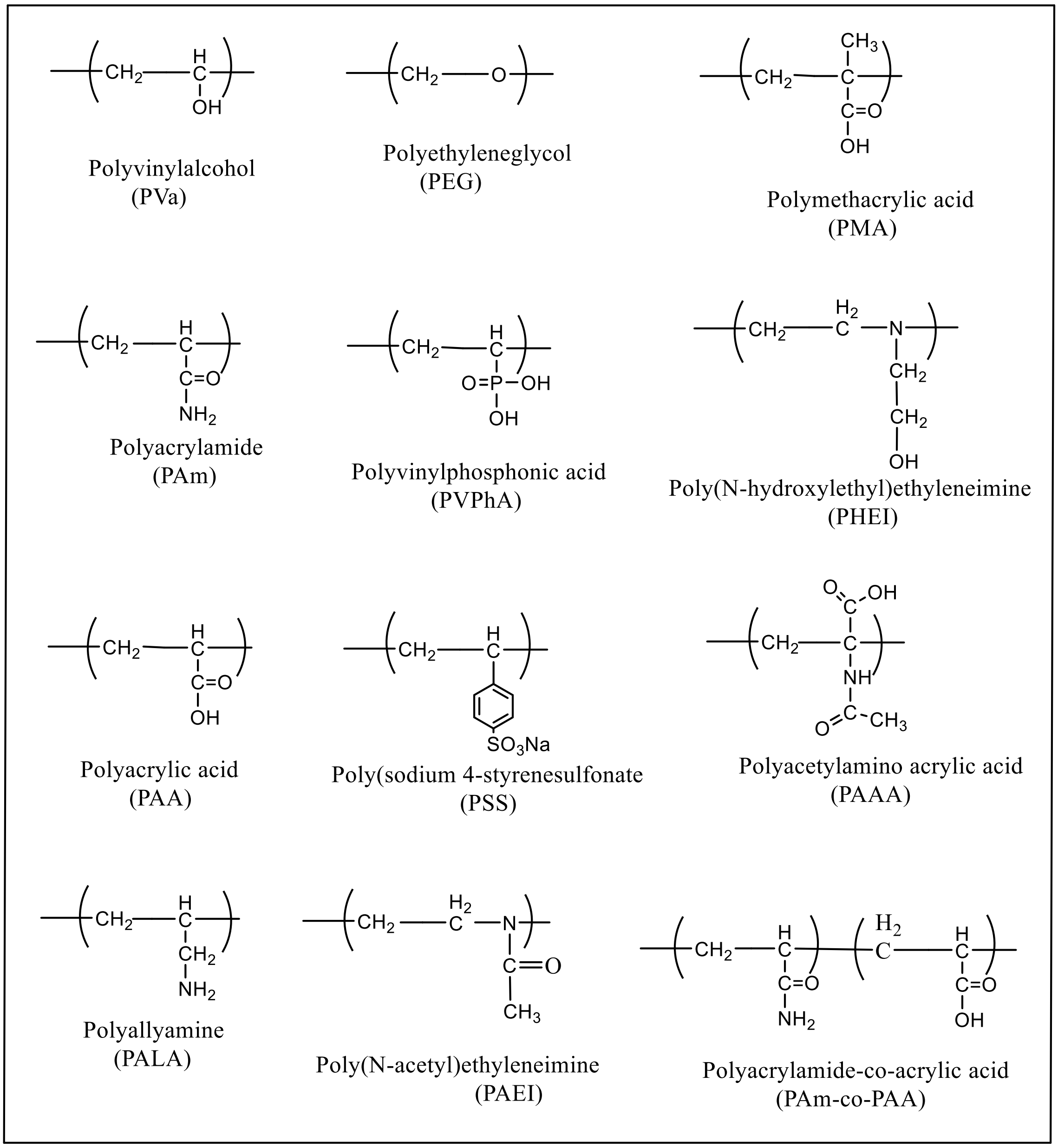


Fig. 1.6 Some water-soluble polymers used for metal ion interaction [68].

Various soluble polymers and their potential catalytic applications have been reviewed by Lu and Toy in 2009 [92]. Bayer and Schuman demonstrated the use of linear polymers, namely polyethyleneamine, polyacrylonitrile, poly(vinylpyrrolidine), and poly(ethylene diaminoacetic acid) as polychelatogen with Pt, Pd, Rh, and Ni and their efficiency as hydrogenation catalysts [93]. Polymeric N-(isopropylacrylamide) is an interesting thermoresponsive polymer [70]. Bergbreiter extensively studied the application of this polymer as support in organic synthesis [94]. Recently, Zhang *et al.* reported immobilization of a Mn-salen complex on this "smart" soluble polymer and studied their activity in the asymmetric epoxidation of olefin in water [95]. Xie *et al.* have successfully synthesized a pH responsive soluble polymer by copolymerization of dimethyl aminopropyl acrylamide and N-*p*-styrenesulfonyl-1,2-diphenylethylenediamine [96]. Ru complex with this pH responsive polymer was employed as an efficient catalyst of asymmetric transfer hydrogenation of a number of ketones [96].

In this context, it is relevant to highlight that, work from our laboratory on synthesis of a series of peroxido complexes of V(V) and Mo(VI) anchored to linear WSP matrices and investigation of their catalytic and biochemical properties, has established for the first time that it is possible to obtain stable, well-defined macromolecular peroxidometallates by incorporating metal peroxide species into suitable WSP matrices [13,23, 97-100].

1.5 Peroxido complexes of titanium and molybdenum- salient features and importance

One of the most important and fascinating domains of chemistry of metal ions of group 4-6, which has been garnering enormous contemporary interest, is their peroxido chemistry. Transition-metal peroxides correspond to a vital class of reactive intermediates in biological and synthetic catalytic oxidations as they can be obtained upon interaction of molecular oxygen, hydrogen peroxide, and inorganic or organic peroxides with metal salts or complexes [5,101]. One very remarkable reactivity feature of peroxido metal complexes is that they generally act as 1,3-dipolar reagents and can react with both electrophilic and nucleophilic substrates [102]. Thus, this class of compounds in general have received continued attention over past decades because of their key roles in biological processes and industrially important catalytic oxidations [4,5,101-112].

A peroxido (p) transition metal species, as rationalized by Vaska consists of a covalently bound dioxygen resembling O_2^{2-} in a peroxido configuration [113]. There are varieties of ways, ranging from symmetrical bidentate to a terminal monodentate mode as shown in **Fig. 1.7**, in which the electron rich peroxido group can be expected to co-ordinate to metals (M). Based on *ab initio* and semiempirical calculation, the bonding interaction between the metal ion and peroxido ligand has been described by Reynolds *et al.* as σ interaction between the d_{xy} orbital of metal and in-plane peroxido π* orbital [114].

Reynolds and Butler added a new dimension to this peroxido transition metal chemistry, who described the correlation between the physicochemical properties and reactivity of such systems [114]. According to the authors most reactive metal peroxido species exhibit λ_{max} values below 400 nm, stretching frequencies below 900 cm^{-1}, and ^{17}O chemical shifts below 600 nm.

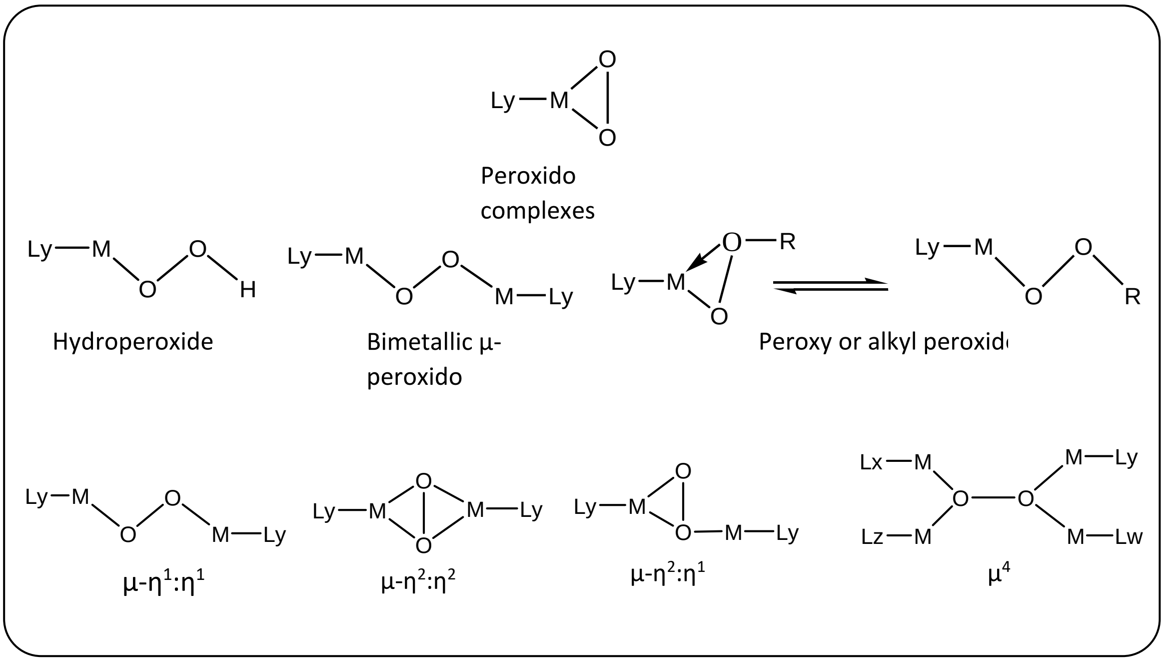
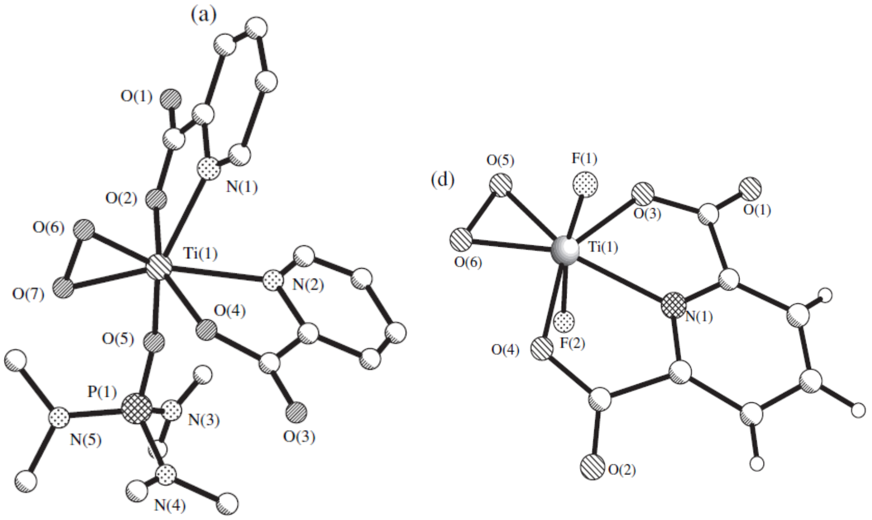


Fig. 1.7 Structural classification of metal-dioxygen complexes [5,113].

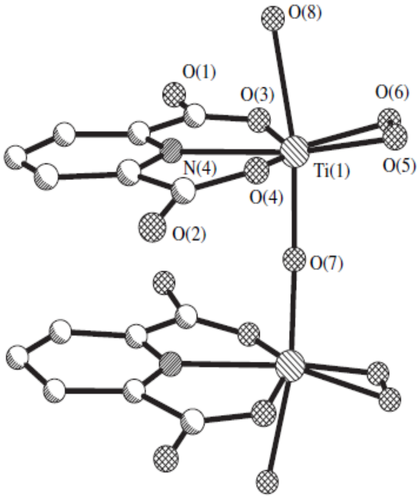
The η^2 –peroxido complexes are most common metal peroxides, particularly with respect to mono and diperoxido complexes. The most extensively studied group of peroxido transition metal complexes are those of V(V), Cr (VI), Ti(IV), Mo(VI) and W(VI) peroxidometallates [5]. There is a clear structural and isoelectric relationship between peroxido complexes of Group 4 and Group 6 metals, which makes it worthwhile and convenient to study some of their features in parallel. Both titanium and molybdenum are capable of forming various peroxido metal species in aqueous solution with the small variation of metal concentration, hydrogen peroxide amount, temperature or pH of the reaction medium [5,116-119]. Due to this, aqueous pTi as well as pMo chemistry seems rather complicated [5,116-119].

Titanium is capable of forming mainly monoperoxido complexes containing $M(O_2)$ fragment [120]. Mononuclear peroxidotitanium(Ti) complex with the pseudooctahedral coordination are highly stable and most of them show very low tendency towards the transfer of oxygen in reactions like epoxidation, sulfide oxidation or alcohol oxidation in comparison to the analogous molybdenum complexes under identical reaction conditions [120,121]. The mononuclear pTi complexes also exist in the pseudotetragonal-pyramidal coordination form (**Fig. 1.8**). This coordination mode is also observed in most of the transition metal complexes, especially, in peroxido complexes of molybdenum [120]. Binuclear complexes of pTi contain bridging oxido ligands that connect the metal atoms (**Fig. 1.9**).



(a) $[Ti(O_2)(\textit{Pic})_2(HMPT)]$ (b) $[Ti(O_2)(\textit{Dipic})F_2]^{2-}$

Fig. 1.8 Example of mononuclear peroxidotitanium complexes [119,121,122].

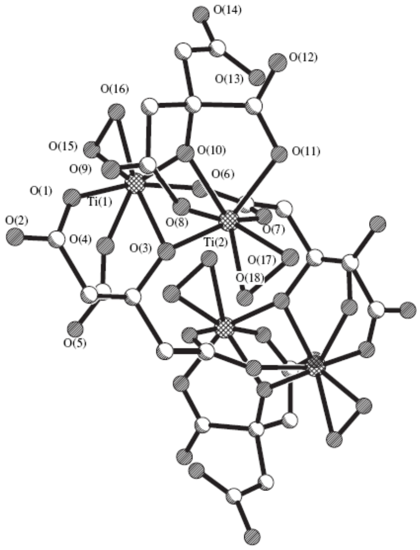


$[\{Ti(O_2)(Dipic)(H_2O)\}_2(\mu\text{-}O)]^{2-}$

Fig. 1.9 Example of binuclear peroxidotitaniumcomplex [119,123].

Schwarzenbach and his group, in 1970 reported first binuclear oxido-peroxido titanium complex with dipicolinic acid. The complex was crystalized in the form of potassium salt. The orange yellow crystal have $K_2[Ti_2O_5(H_3NC_7O_4)_2].5H_2O$ chemical composition [123]. Later on, variety of ligands were used and a number of binuclear pTi complexes have been developed [119]. Katsuki and coworkers have recently synthesized binuclear μ-Oxido-μ-η^2:η^2-Peroxidotitanium complex with salalen ligands and described as highly active catalyst in enantioselective epoxidation of unfunctionalized alkenes [124]. Besides this, peroxidotitanium can form complexes ranging from tetranuclear to polynuclear depending upon the pH and ligand type of the system [119]. In the tetranuclear pTi complexes reported by Kakihana and his group, two binuclear fragments are present which are interlinked through the bridging β-carboxylato group of one citrate ligand (**Fig. 1.10**) [125]. Crystal structures of both binuclear and tetranuclear peroxido titanium complexes display pseudooctahedral coordination mode [119].

Very recently, Jin and co-workers have reported synthesis and characterization of an icosanuclearperoxidotitanium complex, $K_{16}[Ti_{20}(\mu\text{-}O)_8(HO_2)_8(O_2)_{12}(R,R\text{-}tart)_{12}]\cdot 52H_2O$ chelated by tartrate [126]. The complex contains 20 peroxido group and three types of coordination modes (i) μ-η^1:η^2, (ii) μ-η^2:η^2, and (iii) η^2. Some examples of structurally characterized various types of pTi complexes are listed in **Table 1.2**.



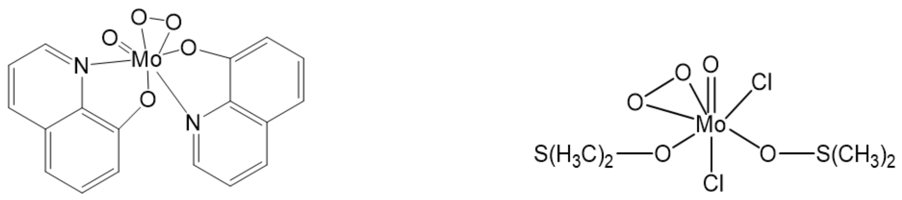
$[\{Ti(O_2)(\mu\text{-}\mathit{Cit})\}_4]^{8-}$

Fig. 1.10 Example of tetra nuclear peroxidotitanium complex [119,125].

Table 1.2 Some structurally characterized peroxidotitanium complexes, geometrical parameters in (Å)

Conpound	Ti-O(O_2)	O-O(O_2)	Ref
Mononuclear			
$[Ti(O_2)(Pic)_2(HMPT)]$	1.848(4)±0.006	1.419(6)	121
$K_2[Ti(O)_2(Dipic)F_2].H_2O$	1.854(5)±0.008	1.463(6)	122
Binuclear			
$K_2[\{Ti(O_2)(Dipic)(H_2O)\}_2(\mu\text{-}O)]. 3H_2O$	1.889(7)±0.017	1.45(1)	123
$Na_4[\{Ti(O_2)(Nta)\}_2(\mu\text{-}O)]. 11H_2O$	1.891(2)±0.002	1.469(3)	127
Tetranuclear			
$(NH_4)_8[\{Ti(O_2)(\mu\text{-}Cit)\}_4]. 8H_2O$	1.878(2)±0.021	1.464(2)± 0.001	125
Icosanuclear			
$K_{16}[Ti_{20}(\mu\text{-}O)_8(HO_2)_8(O_2)_{12}(R,R\text{-}tart)_{12}]\cdot 52H_2O$	1.88 (1)av	1.47(1)av	126

Molybdenum is capable of forming a variety of dioxygen complexes ranging from mono peroxido to tetra peroxido and mononuclear to polynuclear in different ligand environment [4,118,119,128]. Oxidoperoxido complexes of molybdenum of the type $MoO(O_2)L_4$ exhibit pentagonal-bipyramidal geometry similar to the diperoxido molybdenum species but with one of the peroxido group replaced by two equatorial ligands [4]. **Fig. 1.11** shows some examples of this type.



$MoO(O_2)$(8-quinolinate) [129]

$MoO(O_2)Cl_2$(dimethylsulfoxide)$_2$ [130]

Fig. 1.11 Example of monoperoxido molybdenum complexes [128,129,130].

Dioxidomonoperoxidomolybdenum(VI) complexes of the type $[Mo(O)_2(O_2)L]$, were also reported, where L = diethylene triamine, 2,2,2-triethylenetetraamine and 2,3,2-triethylenetetraamine [131]. In the existing literature, monoperoxido molybdenum derivatives are recognized as less stable than their diperoxido counterparts [128]. Therefore, in comparison to the monoperoxido complexes, large numbers of isolated and well characterized diperoxido molybdenum complexes are known. Diperoxidomolybdenum complexes of type $[MoO(O_2)_2L_{ax}L_{eq}]^{0/-1/-2}$, where metal atoms are hepta coordinated, exist in a pentagonal bipyramidal structure [4]. A large number of such complexes have been reported in which the oxido and one L ligand (or donor atom of a bidentate ligand) occupy axial positions, and the two η^2-peroxido groups and the remaining L are in the equatorial position. **Table 1.3** displays series of diperoxido molybdenum complexes of such types. The ligands L may also function as bridging groups in binuclear species. In 1969, Mimoun and his co-workers introduced an important class of Mo-peroxido complexes of the type $[MoO(O_2)_2L_n]$ (L = pyridine, hmpt, dmf, H_2O and so on; n =1,2) (**Fig. 1.12**) formed by the reaction MoO_3 and 30% H_2O_2 with organic bases [132].

Table 1.3 Structurally characterized oxidoperoxido complexes of molybdenum(VI),$[MoO(O_2)_2L_{ax}L_{eq}]^{n-}$ (n=0,1,2) [4]

L_{ax}	L_{eq}	n
H_2O	Hgly	0
H_2O	H_2O	0
H_2O	hmpt	0
H_2O	Hpro	0
½(bipy)	½(bipy)	0
½(tbbpy)	½(tbbpy)	0
Py	hmpt	0
F^-	F^-	2-
½(cit)	½(cit)	2-
½(pic[N])	½(pic[O])	1-

Subsequently, a large number of apparently similar complexes have been explored with different ligands, e.g. water, amides, amino acids, pyridine, pyridine-N-oxides, ureas, phosphoramides, arsine oxides and phosphine and bidentate 2,2'-bipyridine, 2,2'-bipyridine N,N'-dioxide, picolinate and its N-oxide, l,l0-phenanthroline, phenylenediamine and ethanolamine, octamethylpyrophosphoric triamide, (S)-dimethylactamide, etc [4]. In addition, to these mononuclear oxidodiperoxido complexes of molybdenum(VI), several binuclear pMo complexes with pseudotrigonal bipyramidal geometry have been reported and characterized [133]. Such complexes contain two

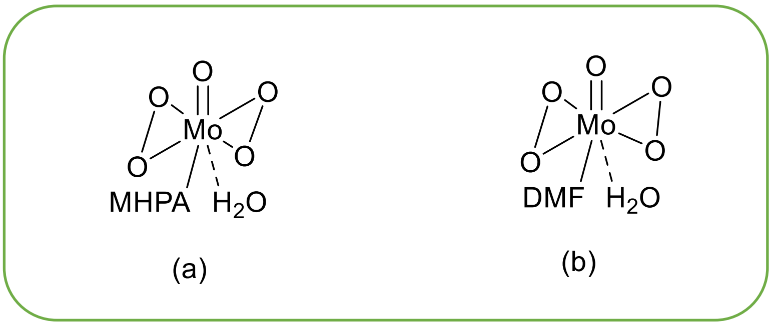


Fig. 1.12 Structures of Mimoun type complexes (a) $[MoO(O_2)_2(HMPA)(H_2O)]$ and(b) $[MoO(O_2)_2(DMF)(H_2O)]$[134].

$MoO(O_2)_2$ fragments which are joined together by a bridging ligand such as fluoro, oxido, hydroperoxido etc [134]. Also, isopolyperoxido and heteropolyperoxido complexes of molybdenum(VI) such as $A_4[Mo_3O_7(O_2)_4].2H_2O$ (A= K^+ and NH_4^+) with pseudotrigonal bipyramidal oxido diperoxido polyhedra are known [135,136].

Besides these oxidodiperoxido complexes, neutral non-oxido diperoxido molybdenum complexes of type $[MoL_2(O_2)_2]$, L=S-benzyldithiocarbazate(-) were reported [4]. The coordinated ligand is supposed to function in a bidentate (N,S) fashion. However, the complexes were found inactive towards alkenes [4].

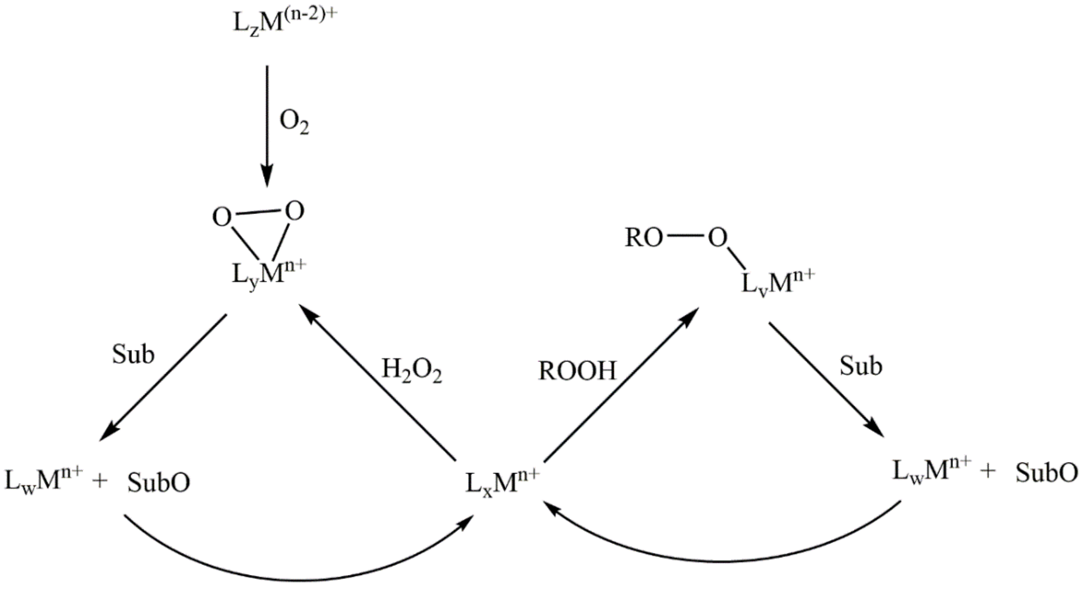
Till date, no structurally well characterized triperoxido complexes of molybdenum is known [4,128]. Tetraperoxidomolybdate anion, $[Mo(O_2)_4]^{2-}$ is formed in mildly alkaline solution (pH 7-9) by the addition of excess H_2O_2 to solutions of MoO_4^{2-} [4,137]. In 2007, Grzywa *et. al* have reported lithium tetraperoxidomolybdate(VI) tetrahydrate $Li_2[Mo(O_2)_4]$. $4H_2O$ as a new member of this group [128,138]. Listed in table 1.4 are examples of various types of structurally characterized **pMo** complexes with their geometrical parameters.

Table 1.4 Some structurally characterized peroxidomolybdenum complexes, geometrical parameters in (Å) [128]

Compound	Mo=O	Mo-O(O_2)	O-O	Ref
Monoperoxido				
$MoO(O_2)Cl_2(dmso)^a$	1.675	1.856, 1.913	1.324	130
Diperoxido				
Mononuclear				
$(NH_4)_2[MoO(O_2)_2(Ox)]^c$	1.671	1.919, 1.955	1.475	139
$MoO(O_2)_2(H_2O)OPMePh_2)$	1.671	1.909, 1.934 1.909, 1.938	1.450 1.461	140
Binuclear				
$[PPh_4]_2[(Me)(CH_2Cl)SiO_2\{Mo_2O_2(\mu-O_2)_2(O_2)_2\}]$	1.682	1.926, 1.926	1.469, 1.464	141
$K_2[Mo_2O_2(\mu-O)(O_2)_2(H_2O)_2].2H_2O$	1.688 1,911	1.943, 1.957 1.945, 1.967	1.477, 1,483 1.479, 1.482	142
Tetraperoxido				
$Li_2[Mo(O_2)_4]$. $4H_2O$	--	1.989, 1.955 1.971, 1.951 1.933, 1.931 1.977, 1.958	1.482 1.486 1.477 1.484	138

1.6 Catalytic application of pTi and pMo complexes in some important organic reactions

Recognition of catalytic activity of some of the group 4-6 transition metals in oxidation reactions with H_2O_2 dates back to the '30s of 20th century and mainly owes its origin to the work of Milas and co-workers [5,143-146]. Numerous interesting procedures were developed in this field during the subsequent decades and several of these have been used in industrial processes [5,147,148]. The accepted mechanism representing metal catalyzed oxidations with peroxides is depicted in **Scheme 1.4** [5]. It has already been established that peroxido metal complexes of the type shown in **Scheme 1.4** are much more reactive than that of the peroxide precursors *viz.*, hydrogen peroxide or alkylhydroperoxide [5]. This fundamental feature has been recognized as the direct link between the chemistry of peroxido metal complexes and metal catalyzed oxidations [5,113,144].

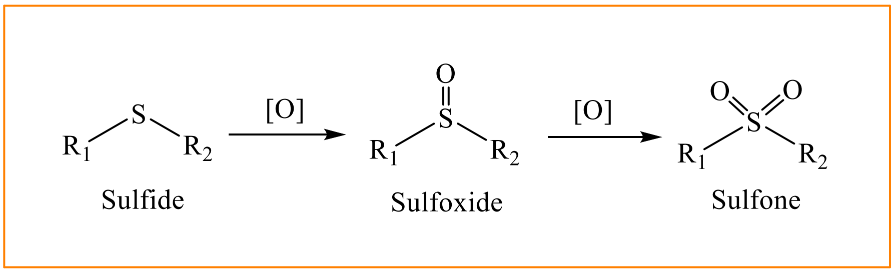


Scheme 1.4 Metal catalyzed oxidation with peroxides [5].

For achieving good performance of transition metal based catalysts the choice of metal is considered crucial. Both titanium and molybdenum are recognised as highly successful metals in the field of catalytic oxidations mainly owing to their rich coordination chemistry, labile nature in respect of ligand substitution, low cost, abundance and non-toxicity [4,5,128,149]. Over the past decades catalytic application of highly active Ti(IV) and Mo(VI) systems in variety of organic oxidations have been the subject of many reviews [5,6,128,149-151]. Without attempting to be exhaustive, we have endeavoured to highlight some of the key discoveries as well as recent developments in the field of **pTi** and **pMo** based catalysts, focusing on three fundamentally and industrially significant organic oxidations *viz,* selective oxidation of sulfides, epoxidation of alkenes and oxidation of 5-hydroxymethyl-2-furfural.

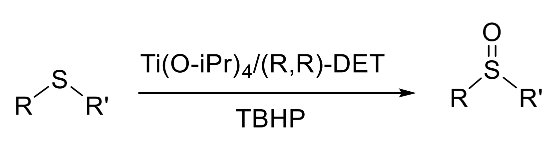
1.6.1 Sulfide oxidation

Selective oxidation of organic sulfur containing compounds to sulfoxides or sulfones (**Scheme 1.5**) is one of the pivotal reactions in organic synthesis, which holds immense interest from both chemical as well as biological perspectives [152-160]. Sulfoxides and sulfones serve as versatile synthetic precursors for production of a range of fine chemicals and biologically active molecules including pharmaceuticals, agrochemicals and chiral auxiliaries [155-160]. In addition, oxidative desulfurization of crude oil based on sulfide oxidation, is emerging as a sustainable alternative to the traditional catalytic hydrodesulfurization process [160-165].



Scheme 1.5 Oxidation of organic sulfur containing compounds to sulfoxides or sulfones.

The milestone work of Kagan [166] and Modena [167] in 1984, who discovered that titanium(IV) isopropoxide-diethyltartrate catalyst systems, also known as “modified Katsuki-Sharpless reagents”, are capable of the enantioselective oxidation of prochiral sulfides with alkyl hydroperoxides, provided the driving force for intensive research in this area (**Scheme 1.6**) [5].



Scheme 1.6 Enantioselective oxidation of prochiral sulfides with alkyl hydroperoxides by titanium(IV) isopropoxide-diethyltartrate.

The developed reaction protocol has since then been successfully applied in the large-scale synthesis of biologically active molecules of sulfoxide like RP 73163 (**Fig. 1.13**) [5,168].

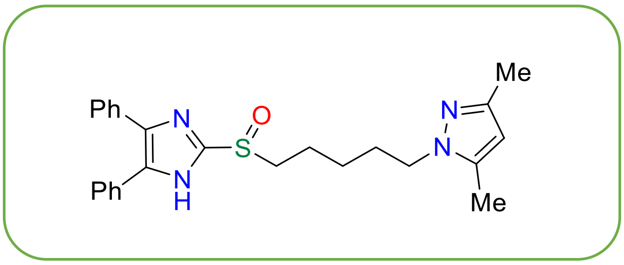
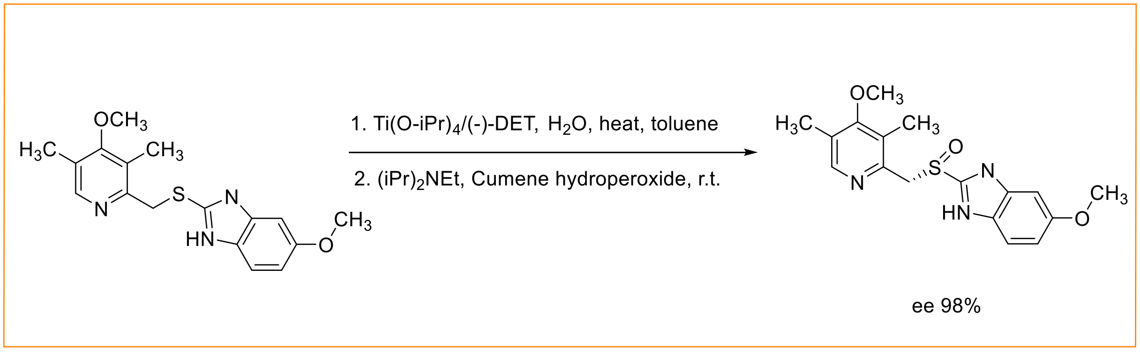


Fig. 1.13 Structure of RP 73163 [2,168].

Also, with a modification of traditional reagents by the addition of diisopropylethylamine (**Scheme 1.7**), this protocol was used in the synthesis of drug molecules like esomeprazole, medication used to reduce stomach acid [5,169]



Scheme 1.7 Synthesis of esomeprazole [5,169].

Uemura and his group, extended the sulfoxidation chemistry by combining Ti(IV)/TBHP with 1,1'-bi(2-naphthol) instead of diethyl tartrate (DET) [170,171]. This modification not only improved the enantioselective formation of sulfoxide but also promoted the kinetic resolution of the product. The main handicaps associated with majority of these systems are their low productivity, complexity of the systems and most importantly use of hazardous, corrosive, flammable and non-preferred oxidant i.e. alkyl hydroperoxides [5].

The first titanium-based catalysts for the sulfide oxidation reaction with aqueous H_2O_2 was reported by Pasini and his group in the year of 1986 [6,172]. They performed the oxidation reaction in aqueous methanol and dichloromethane using titanium salen catalysts and found catalytic efficiencies above 1000 turnovers (TNs). In 2001, Katsuki and his co-workers reported the ‘second generation’ di-μ-oxido titanium-salen complex as an efficient catalyst for the asymmetric oxidation of methyl phenyl sulfide (MPS) with UHP (urea hydroperoxide) or H_2O_2 in methanolic solution [173].

In recent years, various types of Ti based catalyst systems for selective oxidation of thioethers with H_2O_2 have been reported, bearing either Schiff bases or salan-type ligands [6] (**Fig. 1.14**). Using Ti(IV)–Amino triphenolate complexes as soluble catalyst Mba *et al.* has reported the oxidation of sulfide for the synthesis of sulfoxide as the major product in MeOH [174]. Reddy *et al.* developed a tetrameric titanium alkoxide/ionic liquid $[Ti_4[(OCH_2)_3CMe]_2(i\text{-}PrO)_{10}]$, as recyclable catalyst to obtain sulfone in a reaction carried out in MeOH under nitrogen atmosphere [175]. A Ti(IV)–Isopropoxide complex has also been reported as soluble catalyst for the production of sulfoxide using MeOH as solvent under N_2 atmosphere [176]. However, no reusability of the catalysts was reported by the authors. Titanium complexes of chiral amino alcohol derived Schiff bases as catalyst was used by the research group of Bera for the oxidation of sulfide to sulfoxide in dichloro methane at 0 ^{0}C for 10 h of reaction time [177]. Recently, Postigo *et al.* has reported cyclopentadienyl–silsesquioxane titanium complex $[Ti\{\eta^5\text{-}C_5H_4SiMe_2OPh_7Si_7O_{11}\text{-}\kappa_2O_2\}Cl]$, as a highly efficient catalyst for the selective oxidation of sulfide to sulfoxide and sulfone using MeOH as solvent [178].

In a recent work, Zhang and his group has used series of polymeric nanoparticles containing salen titanium(IV) complex as reusable catalyst for the synthesis of sulfoxide

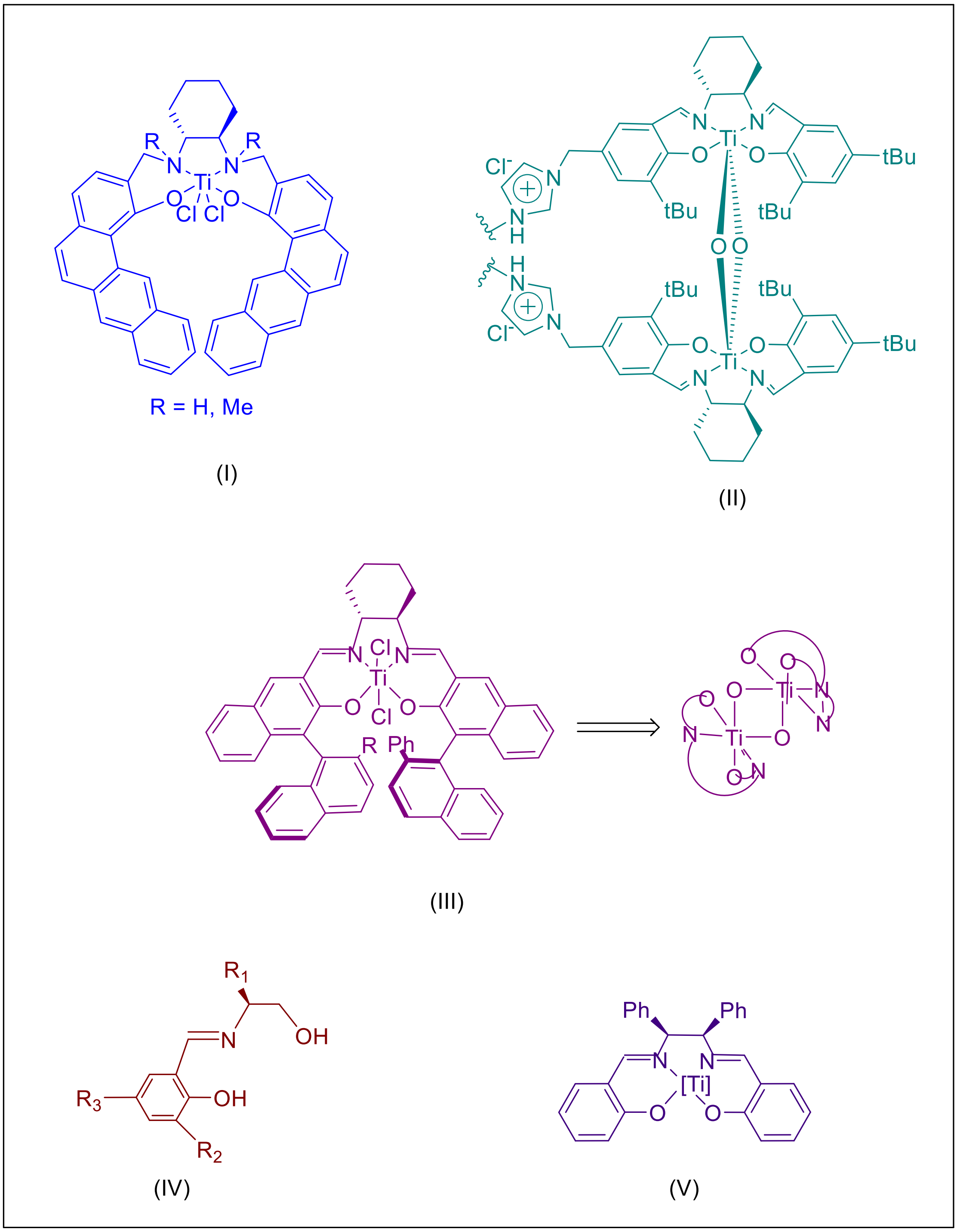


Fig. 1.14 Complexes and ligands used in titanium-catalyzed sulfoxidations with H_2O_2 [6]. Systems I [182], II[183], III [173], IV [184] and III [172].

as the major product in water as solvent [179]. A pair of titanium(IV)-oxido-clusters has been used as catalyst for the production of sulfoxide in MeOH as well as in water with high selectivity (<99%) by Wu *et al* [180]. Very recently, in 2018, Reviejo and his group has reported the oxidation reaction of sulfides to sulfoxides and sulfones selectively using

MeOH as solvent and chiral titanium(IV) complexes containing polydentate ligands based on α‑Pinene as catalysts [181]. The systems show 100% selectivity towards the formation of both sulfoxide and sulfone in the sulfoxidation reactions.

Significantly, majority of the Ti mediated sulfoxidation reactions have been achieved *via in situ* generated peroxidotitanium species employing Ti complexes as pre-catalysts or under "Ligand Assisted Catalysis" (LAC) [176,185]. On the other hand, reports on catalytic activity of well-defined pTi complexes in organic oxidation are relatively rare [186,187]. In a recent work, Zhou and coworkers reported an interesting wheel like icosanuclear peroxidotitanate, $K_{16}[Ti_{20}(\mu\text{-}O)_8(HO_2)_8(O_2)_{12}(R,R\text{-}tart)_{12}]\cdot52H_2O$, chelated by tartrate, as water soluble catalyst for the sulfide oxidation reaction in water using H_2O_2 as oxidant [126]. The selectivity for sulfoxide was found 88% for the complete conversion of sulfide, although the catalyst could not be recycled.

A significant contribution to the existing wealth of organic oxidants is the important class of molybdenum-peroxido complexes of the type, $[MoO(O_2)_2L_x]$, introduced by Mimoun *et al.* (**Fig. 1.12**) [132,188]. The Mimoun type complexes are highly soluble in both polar and nonpolar solvents. Thus the neutral compounds and appropriate salts of the monoanions have been widely used as both stoichiometric and catalytic oxidants in organic oxidations [4]. Epoxidation of alkene [189-192], oxidation of primary and secondary alcohols to aldehydes and ketones, respectively [193,194], oxidation of sulfides and sulfoxides to sulfoxides and sulfones [195-201], and oxidation of indoles [202], furans [203] and phenacetin [204] are few of the examples of stoichiometric oxygen transfer reactions by this class of compounds. It is notable that most of these investigation has been carried out with $[MoO(O_2)_2(hmpt)]$, however, other complexes are also effective [4]. Di Furia co-workers in 1985, introduced Mimoun type complexes $MoO(O_2)_2L$ [L =HMPT, L = HBPT as catalyst in the selective oxidation of sulfide (p-chlorophenyl methyl sulfide) to the corresponding sulfoxide [205]. The oxidation reaction was carried out in a two-phase system containing DCE and aqueous hydrogen peroxide. Furia *et al.* also reported oxido-diperoxido-molybdenum complexes, $[MoO(O_2)_2L]^-Bu_4N^+$ (L = $C_6H_4NCO_2^-$ or $C_5H_4N(O)CO_2^-$) as active catalysts and mentioned that quantitative yield of sulfone was obtained when applied as oxidant, for the stoichiometric oxidation of sulfoxide [192].

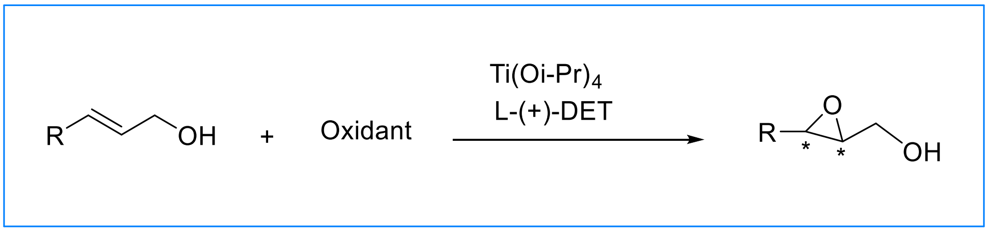
Cass *et al.* examined the use of Mimoun type complexes $MoO(O_2)_2(L)(H_2O)$, (L = pyridine N-oxide or pyrazole) to oxidize a wide variety of substituted sulfides and found that the procedure offers several major advantages such as control over the degree of oxidation of products [193], excellent chemoselectivity toward the sulfur group of substituted sulfides and sulfoxides [206]. Jacobson *et al.* synthesized and structurally characterized quite a few oxido-diperoxido-picolinato molybdenum complexes and used these in alcohol oxidation [207-209]. Bhattacharyya and co-workers [210,211] reported oxido-monoperoxido-molybdenum complexes of the type $[MoO(O_2)(QO)_2]$ as well as its diperoxido analogues $[MoO(O_2)_2.2QOH]$ and $[MoO(O_2)_2(QO)]^-$ using 8-quinolinolate (QO) anion as ancillary ligand [210]. The complexes act as efficient catalysts in the oxidation of alcohols and sulfides [210,212]. They have also reported a few oxido and oxidoperoxidomolybdate(VI) complexes coordinated with derivatives of hydroxamic acid which have high potential and selectivity as catalyst in the epoxidation of olefin [208].

The use of solid catalysts under heterogeneous conditions, which allows easy recovery of the catalyst are considered ideal for achieving the goals of green chemistry [213-215]. Accordingly, selective oxidation of sulfide has been carried out with a large number of supported reagents and catalysts [216-218]. Fuerte *et al.* reported dioxidomolybdenum(VI) complexes supported on USY-zeolite and mesoporous MCM-41 as recyclable heterogeneous catalysts [219], which selectively catalyzed the oxidation of sulfides to sulfoxides or sulfones. However, the catalysts lose their sulfoxide selectivity at higher conversion and overoxidation of sulfide to sulfone occurs. The important findings of a comparative study carried out by Gomez and co-workers with different oxidant and support to understand the role of support in selectivity of sulfoxidation [220], demonstrated that acid support (amberlyst) gave sulfoxide selectively, basic support (basic alumina) increased the proportion of sulfone formed [221]. Some of these systems however, are associated with the drawback of gradual leaching of the catalytic species during the repeated catalytic cycles. Very recently, in 2018, Rostamnia and Mohsenzad have shown oxidodiperoxido molybdenum complexes coordinated onto the ethylene diamine-decorated MIL-100(Cr) pore cage to synthesize a bifunctional $MoO(O_2)_2$@En/MIL-100(Cr) catalyst for H_2O_2 (30%) mediated selective oxidation of thioethers in water [222]. The catalyst was recyclable for 8 cycles under the standard reaction condition. Bagherzedah and in a recent review discussed application of oxidoperoxido Mo(VI) complexes as catalysts for a variety of organic oxidations [6].

1.6.2 Epoxidation reaction

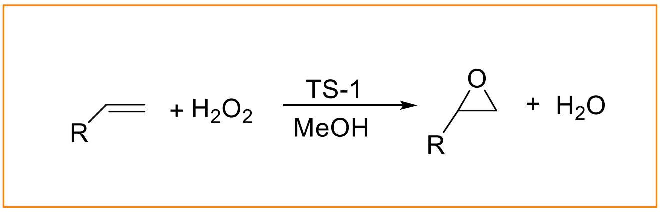
Development of efficient and environment-friendly catalytic systems for selective epoxidation of olefins has been an area of long standing interest from both academic as well as industrial standpoint [223-229]. Epoxides constitute an important class of reaction intermediates with vast application in synthesis of fine chemicals including industrial products such as pesticide, food additives, pharmaceuticals, photosensitive adhesives and coatings, flame retardants etc. [223-225]. Catalytic epoxidation of olefins is one of the main routes, for their production.

The pioneering work of Katsuki and Sharpless, who introduced asymmetric epoxidation of prochiral allylic alcohol by alkylhydroperoxides, catalyzed by titanium tetra-alkoxides equipped with chiral nonracemic tartrates is regarded as one of the most important milestones in the history of organic synthesis (**Scheme 1.8**) [5,230].



Scheme 1.8 Katsuki-Sharpless asymmetric epoxidation of allylic alcohols [5,230].

Since this development in 1980, Sharpless epoxidation has gained much attention and has been applied to the synthesis of many important chemical products and biologically active compounds [5,6]. Taramasso and Notari in 1981, added a new dimension to titanium catalyzed epoxidation reaction when they discovered Ti(IV)-silicalite (TS-1), a new synthetic zeolite of the ZSM family as an efficient catalyst for the epoxidation of unfunctionalized olefins, especially terminal ones in presence of H_2O_2 as oxidant (**Scheme 1.9**) [5,231]. However, the main drawback of this catalyst system is its small pore dimensions which makes it accessible to relatively small reactants only and limits the system to epoxidation of linear alkenes [5,229,232].



Scheme 1.9 Epoxidation of unfunctionalized short chain olefins by TS-1 in presence of H_2O_2 [5].

These observations triggered a spurt of research activity aimed at synthesizing amorphous titania-silica mixed oxides and titanium substituted molecular sieves with larger pores with comparable activity to TS-1 [5,229]. Katsuki *et al.*, in 2005, first introduced the application of titanium-based catalyst employing novel salalen ligands for asymmetric epoxidation of both non-conjugated and conjugated unfunctionalized olefins in presence of hydrogen peroxide [233]. High epoxide yields with enantioselectivity upto 99% were reported. However, sophisticated synthesis of the ligand salalen was a difficulty of this system. Thus in 2006, the same group synthesized a series of chiral salan ligands which were more easily accessible [6,234].

These findings inspired many researchers to investigate more synthetically accessible Ti-salan complexes as catalysts for asymmetric epoxidation reaction with H_2O_2 [6,229]. These developments have been comprehensively reviewed recently by Bryliakov [6]. Several Ti-substituted polyoxidometalates (POM) were also employed successfully as catalyst in epoxidation of olefins [235-237]. For instance, Mizuno *et al.* has synthesized Ti-substituted phosphotungstate, $TBA_6[(\gamma\text{-}PW_{10}O_{36})_2Ti_4(\mu\text{-}O)_2(\mu\text{-}OH)_4]$ (TBA = tetra-n-butylammonium) and applied it as a reusable catalyst for several oxidation reactions including epoxidation, sulfide oxidation, oxidative bromination with 30% H_2O_2 in acetonitrile [235]. Cummins *et al.* reported synthesis of tri- and tetrametaphosphate titanium(IV) oxido and peroxido complexes and studied their catalytic activies in various organic reactions including epoxidation of cyclohexene using hydrogen peroxide [236]. Very recently, in 2019, Guillemot and co-workers reported epoxidation of various olefins with H_2O_2 using Ti(IV) with the silanol-functionalized polyoxidotungstates in titanium(IV) complexes as homogeneous catalysts tetrahydrofuran [237]. Sawano and Yamamoto have synthesized binuclear titanium complex and applied as catalyst in enantioselective epoxidation of β,γ-unsaturated carboxylic acids with CHP [238].

Apart from Ti based catalysts, over the past decades, several highly active Mo(VI) alkene epoxidation catalysts have been developed and amongst these, Mimoun type oxido-bisperoxido molybdenum complexes stand out due to facile preparation, chemical simplicity and robustness [4,5,189-192]. Mimoun *et al.* reported for the first time, the synthesis and use of oxido-bisperoxido molybdenum(VI) complexes of the type, $[MoO(O_2)_2L_n]$ (n = 1–2; L =H_2O,DMF,HMPT and so on) as stoichiometric oxidizing reagent for the epoxidation of olefins [4,5,188,189]. Homogeneous molybdenum catalyzed epoxidations usually employ tert-butylhydroperoxides as oxidant [150]. The catalytic activity of oxido-bisperoxido molybdenum complexes of type $MoO(O_2)_2(OP(n\text{-}C_4H_9)_3)$ was reported in 1980, by Westland *et al*. in the epoxidation of cyclohexene by TBHP and in presence of benzene as solvent [6,239]. Until then, oxido-peroxido molybdenum complexes were considered as oxidizing reagents for the epoxidation of olefins [6].

Di Furia and Modena reported the use of Mimoun-type peroxido complexes as catalyst for the epoxidation of olefins with H_2O_2 under biphasic conditions [6,205]. The catalyst screening showed that the best conversions were obtained in acidic condition. Nevertheless, the epoxide selectivities tend to decrease with increase of H^+ ion concentration [6]. Thus although limited, a number of Mo(VI)-oxidoperoxido systems have been reported employing greener oxidant hydrogen peroxide [240], including the highly active $NaHCO_3$ co-catalyzed systems developed by Bhattacharyya *et al.* [208].

Although homogeneous peroxido molybdenum complexes exhibit excellent catalytic activity, but, the major difficulties associated with most of these systems are the tedious separation as well as contamination of the homogeneous catalyst with the final products [6,241]. In order to overcome these limitations many promising procedures have been developed for heterogenization of such systems [6,241]. For immobilization of peroxido molybdenum species, variety of solid supports have been employed such as mesoporous silica, zeolite, microporous polymer, nanoparticles etc. [6,241-245]. For instance, Thiel *et al*. prepared heterogeneous olefin epoxidation catalyst by immobilization of oxido-peroxido molybdenum complexes in mesoporous Si-MCM-41 and Al-MCM-41 functionalized with a bidentate 2- [3(5)-pyrazolyl] pyridine ligand. The synthesized systems showed best result in cyclooctene epoxidation with TBHP in chloroform [244,245].

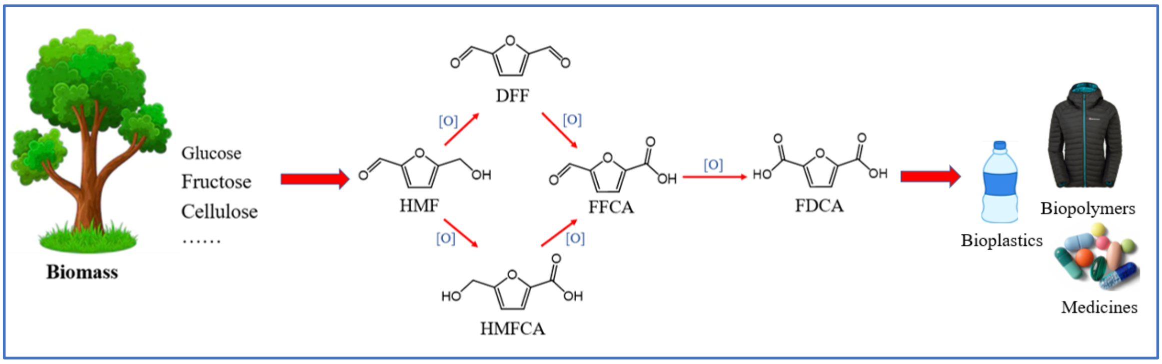
Polymer immobilized catalysts of the type, PS-[$MoO(O_2)_2(L)$] (L = 2-pybmz or 3-pybmz) were developed by immobilizing **pMo** moiety on polystyrene cross-linked with DVB functionalized with 5% divinylbenzene through the chelating ligands 2-pybmz and 3-pybmz [6,246]. However, these catalysts displayed poor activity and selectivity in styrene epoxidation with H_2O_2 in acetonitrile, although the activity could be improved using $NaHCO_3$ as a promoter. Mahjoub *et al.* reported the synthesis of polymeric oxidoperoxidomolybdenum(VI), [$MoO(O_2)_2$.4,4′-bipy$]_n$ and used the complex as catalyst in a heterogeneous system for the epoxidation of cyclohexene and cyclooctene in presence of H_2O_2 as an oxidant in CH_2Cl_2 [191]. The stability of the catalyst was determined upto five reaction cycles and observed a decrease in cyclohexene conversion starting from 95% to 65% in the fifth run [6]. Recently, a number of chelating functional Mo–based copolymers have been prepared and employed as catalysts in alkene epoxidation [6,244,245,247]. An efficient catalyst for alkene epoxidation with TBHP has been developed by Fan *et al*. using cross-linked porous copolymer to immobilize $MoO_2(acac)_2$ [248].

Zare *et al.* anchored Mo(VI)-oxidodiperoxido on the surface of magnetic nanoparticles to obtain an efficient magnetically recoverable heterogeneous catalyst [$MoO(O_2)_2$(phox)]/Fe_3O_4 which was used in alkene epoxidation with TBHP under solvent-free conditions [249]. The same group also reported recently a molybdenum(VI)-oxido-peroxido complex containing an oxazine ligand ($MoO(O_2)_2$(phox)) catalyst supported on chloro-functionalized SBA-15 as a heterogeneous catalyst in alkenes epoxidation, which showed good catalytic activity with TBHP as oxidant, without solvent [250]. Bezaatpour *et al.* in 2018, anchored an pMo- complex with Schiff base onto $MnFe_2O_4$ nanoparticles which was found to efficiently catalyze epoxidation of various olefins under solvent-free condition [251]. Using TBHP as oxidant, the catalyst showed excellent conversion (>99%) and complete selectivity. While in presence H_2O_2 only 5% product yield was observed.

1.6.3 Oxidation of 5-Hydroxymethyl-2-furfural (HMF)

Owing to the continuous consumption of non-renewable fossil resources such as oil and natural gas, in recent years, an enormous effort has been devoted to exploit and utilize abundant and renewable biomass resources for production of sustainable biofuels and generating bulk and fine chemicals [252-254]. 5-Hydroxymethyl-2-furfural (HMF), also called “the sleeping giant” in the field of biomass, is one of the most potential bioderived building blocks readily accessible from biobased carbohydrates [255-257].

There are myriads of reports available regarding the oxidation of HMF, the key platform molecule which serves as a bridge between biomass and chemicals, to a wide variety of value-added compounds like 2,5-diformylfuran (DFF), 2,5-furandicarboxylic acid (FDCA), 5-formyl-2-furancarboxylic acid (FFCA) or levulinic acid (LA) and 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) (**Scheme 1.10**) [258-266]. These valuable HMF derivatives can be applied as precursors for bioplastics [267-269], functional polymers [265,266,270], pharmaceutical intermediates [265,266,271], antifungal as well as antitumor agents [265,266,271], biofuel additives and macromolecules [262,265,266,272-276].



Scheme 1.10 Schematic representation of biomass conversion into value added chemicals to daily use products.

Selective oxidation of HMF has been performed under different conditions using both homogeneous and heterogeneous catalysts usually employing classical stoichiometric oxidants such as chromate, permanganate etc. [276-278]. Oxidation of HMF into FDCA has been accomplished by aerobic oxidation using inorganic material-supported Pt, Pd, Ru and Au nanoparticles as heterogeneous catalysts [265,266]. For example, Davis *et al.* reported that Pd/C and Pt/C catalysts promoted the aerobic oxidation of HMF under 690 kPaO_2 pressure [260]. However, many of these catalytic systems often suffer from lack of stability and reusability and high cost requiring high oxygen pressure [265,279].

Reports on molybdenum based catalytic systems in such oxidation reactions, although very limited, demonstrated that high catalytic activity with excellent selectivity towards the desired products using molecular oxygen in organic solvents could be achieved. For instance, in 2017, Zhao *el. al.* reported molybdenum incorporated nitrogen doped carbon (Mo-HNC) system as active catalyst for selective oxidation of HMF to DFF with dioxygen at 140 ^{0}C in DMSO [280]. A heterogeneous catalyst obtained by immobilizing molybdenum acetylacetonate complex on montmorillonite K-10 clay reported by Zhang *et al.* showed high catalytic activity for the oxidation of HMF to HMFCA with molecular oxygen in toluene [259]. Liu and co-workers reported Cs-exchanged molybdenum and vanadium containing heteropolyacid ($CsH_4PMo_{10}V_2O_{40}$) as catalyst for HMF oxidation to synthesize DFF in DMSO at 120 ^{0}C in presence of molecular oxygen [281]. We have so far come across only two reports on use of titanium based catalyst in HMF oxidation [282,283]. For instance, Gupta *et al.* reported titania nanoparticle embedded on sulfonated carbon (CSTi) as excellent catalyst for aqueous phase oxidation of HMF to DFF.

A survey of literature thus revealed that in majority of cases HMF oxidation has been performed under aerobic condition in presence of organic solvents, mainly DMSO [265,276,280]. Reports related to oxidation of HMF using H_2O_2 as an oxidant are still very limited. Moreover, there is also a paucity of information on application of discrete peroxidometal compounds as catalysts in the selective oxidation of HMF. Recently, Li and co-workers studied the HMF oxidation by quaternary ammonium octamolybdate and quaternary ammonium dectungstate in presence of H_2O_2 [284]. They reported *in situ* generated of peroxidometal complexes as the active species in the reaction (**Fig. 1.15**). The authors also observed that molybdenum-based catalyst exhibited high catalytic activity in the oxidation reaction [284]. We have however not come across a single report on oxidation of HMF using peroxidotitanium based system as catalyst.

From the foregoing discussion it is evident that, while there has been considerable advancement in the field of metal containing polymers, there appears to be very little application of polymer supported peroxidometal complexes in organic oxidations in general, despite the advantages associated with immobilization of active transition metal based catalysts on polymer supports. A great deal of effort is still required to develop macromolecular metal complexes as effective and safer synthetic catalyst for sustainable organic transformations. It is further evident from the relevant literature discussed above that most of the highly efficient homogeneous and heterogeneous Ti and Mo based catalytic oxidation procedures utilized alkyl peroxides, such as tert-butyl-hydroperoxide

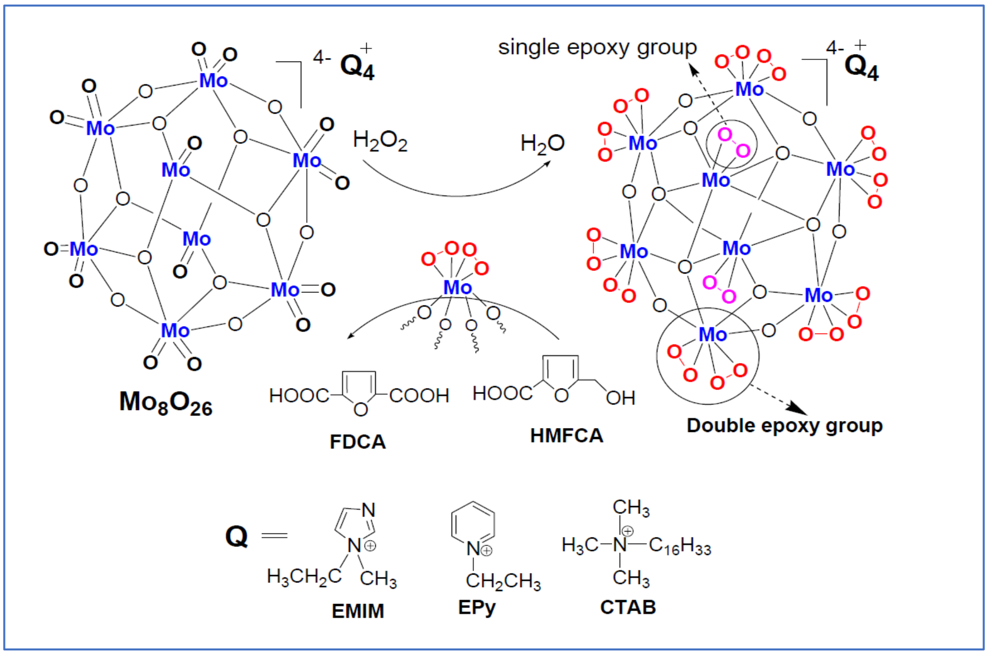


Fig. 1.15 Oxidation of HMF with ammonium octamolybdate in presence of H_2O_2 [284].

(TBHP) or cumene hydroperoxide (CHP) as oxidant along with chlorinated organic solvents. While these oxidants have good compatibility with organic substrates, they form toxic byproducts in stoichiometric amount [241].

Sustainability of a chemical transformation is mainly governed by the solvent, reagents and catalysts used [215,241,285,286]. There has been a lot of emphasis in recent years to find new and strategically important synthetic processes using greener ingredients and a robust and recyclable catalyst that provides higher atom utilization to minimize waste and pollution level [215,285,286]. From the sustainability point view, metal catalyzed organic oxidations using dilute H_2O_2 as terminal oxidant, have been gaining tremendous importance especially for large scale process [240,287-290]. Owing to its low cost, high atom efficiency, ease of handling and being ecologically benign, H_2O_2 has been considered as an industrially and environmentally important oxidant [287-290]. On the other hand, water has been recognized as the ultimate green natural solvent, being inexpensive, non-toxic, and readily available with great redox stability and heat capacity [291-300]. The use of water as reaction medium offers various advantages along with reduced environmental impact. In a recent review Kitanosono and co-workers, highlighted the utility of various supported catalysts in aqueous phase reactions [300].

It is pertinent to mention here that during the past decade, our group has reported synthesis and catalytic as well as biochemical activities of series of peroxido complexes of Group 5 and 6 transition metals immobilized on various polymeric supports [23,63,97,99,100,301,302]. Several of these systems demonstrated excellent stability, selectivity and efficiency in a variety of organic oxidations with H_2O_2 as terminal oxidant under environmentally benign conditions [23,63,99,301]. All of these supported catalysts were found to be recyclable and each of the procedures allowed the presence of water in the reaction system and also the use of H_2O_2 as oxidant.

In line with the scope highlighted above, in the present research programme, we have endeavoured to establish viable synthetic routes to new peroxidotitanium and peroxidomolybdenum complexes supported on soluble as well as insoluble polymer matrices. The work is mainly focused on pursuing the following goals: (i) to develop homogeneous and heterogeneous catalysts for organic oxidation which would be efficient, selective, robust and recyclable, and (ii) to establish catalytic protocols for facile organic oxidative transformations which would allow use of H_2O_2 as oxygen source and would be compatible with eco-friendly solvents such as H_2O, EtOH, MeOH, or can perform under solvent free conditions.

Chapters **3** to **6** of the thesis present interpretative accounts of the findings of our investigations on the aforementioned aspects of peroxidotitanium and peroxidomolybdenum chemistry. Each of these Chapters has been so designed as to make it a self-contained one with brief introduction, sections on experimental, results and discussion, and conclusion followed by relevant bibliography. Most of the new results have been either published or are under communication.

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